The 8th International Conference on Modification, Degradation and Stabilization of Polymers

BOOK OF ABSTRACTS

August 31st – September 4th
Portorož, Slovenia
2014
CIP - Kataložni zapis o publikaciji
Narodna in univerzitetna knjižnica, Ljubljana

678.7(082)

INTERNATIONAL Conference on Modification, Degradation and Stabilization of Polymers (8; 2014 ; Portorož)

ISBN 978-961-281-511-0


275059968

* Abstracts are printed without corrections
Welcome from Organizing Committee

WELCOME TO MoDeSt 2014, WELCOME TO PORTOROŽ!

Dear participants and accompanying guests, welcome to MoDeSt 2014, welcome to Slovenia!

MoDeSt 2014 is the eighth of the consecutive conferences organized every second year and dedicated to modification, degradation and stabilization of polymers, and to other polymer related topics.

Without biopolymers there would be no life, as we know it, and without synthetic polymers there would be no standard of living, as we know it. This is why topics addressed at MoDeSt Conferences are instrumental for the mankind and world economy, now and in time to come.

Therefore, I am proposing to utilize the friendly environment of this conference to initiate discussions for establishing a joint EU program and/or platform within HORIZON 2020, dedicated to strategically important questions related to sustainability, functionality and durability of bio-, and synthetic-polymers.

Enjoy the scientific program, enjoy meeting friends and colleagues, and last but not least, enjoy Portorož!

Welcome!

Igor Emri
MoDeSt 2014 local organizing committee
Message from the President of MoDeSt Society

Dear Participants and Friends!

As the President of the MoDeSt Society, I would like to personally welcome you all to the 8th biennial MoDeSt Conference held in the lovely town of Portoroz.

This Conference, follows on the successes of earlier MoDeSt meetings: Prague (2012), Athens (2010), Liege (2008), San Sebastian (2006), Lyon (2004), Budapest (2002) and Palermo (2000), and offers a great opportunity and a unique platform for networking and for learning about the latest advances and developments in the field, and to encourage open and unscripted discussions on all aspects of Polymer Modification, Degradation, Stabilisation and related areas in an informal friendly atmosphere.

The MoDeSt Society, which coordinates and organises scientific activities in this field across Europe, offers also an opportunity for young scientists to actively participate in these conferences by presenting their Doctoral research findings and follow up discussions. To this end, the Society has awarded, for this 8th Conference, a number of competitive bursaries to doctoral students to enable them to attend and to present their work. There is also a poster competition with prizes awarded to the best posters presented by doctoral students.

The 8th MoDeSt Conference has a well-structured scientific programme with a large number of presentations dealing with the latest scientific advances and developments given by experts in the field; including a wide range of areas related to modification, degradation and stabilisation of polymers and related areas including fire retardancy, polymers and the environment, bio-related polymers, polymer blends and composites, polymer coatings and optoelectronic materials. The Programme provides therefor ample opportunities for all participants to discuss, exchange and to sharing their ideas, and to identify and highlight emerging and future areas of research, as well as, initiating Europe-wide research collaborations.

Finally, and on behalf of the Board of the MoDeSt Society, I would like to express my sincere gratitude to the local organising committee for all the hard work that they have put in to make this meeting a great success, and to thank all the participants and wish you all a very fruitful scientific week and to have an enjoyable time in Portoroz.

Sahar Al-Malaika
President of the MoDeSt Society
Contents

Welcome from Organizing Committee ................................................................. 2
Message from the President of MoDeSt society.................................................. 3
Contents .................................................................................................................. 4
Committees ............................................................................................................ 5
General information ............................................................................................... 6
Program .................................................................................................................. 8
List of oral presentations ....................................................................................... 15
List of poster presentations ................................................................................... 22
Invited lectures ..................................................................................................... 27
Oral lectures ........................................................................................................... 35
Poster session ....................................................................................................... 115
Author Index .......................................................................................................... 184
Notes ....................................................................................................................... 189
Committees

**International Advisory board:**
Prof. dr. Sahar Al-Malaika (MoDeSt society)
Prof. dr. Norman Billingham (MoDeSt society)
Prof. dr. Jean-Luc Gardette (MoDeSt society)
Prof. dr. Franco La Mantia (MoDeSt society)
Dr. Pieter Gijsman (MoDeSt Society)
Prof. dr. Regina Jeziórska (MoDeSt Society)
Dr. Mathias Celina
Prof. dr. Igor Emri
Prof. dr. Rostislav Simonyants
Prof. dr. Alberto D’Amore
Prof. dr. Crispulo Gallegos
Prof. dr. Boris Gusev
Dr. Anatolii Vasilyev
Prof. dr. Bakitzhan Zhumagulov
Prof. dr. Ahad Janahmadov

**Local organizing committee:**
Prof. dr. Igor Emri
Prof. dr. Rostislav Simonyants
Prof. dr. Arkady Voloshin
Dr. Anatoly Nikonov
Joamin González-Gutiérrez
Marko Bek
Pavel Oblak
Alexandra Aulova
Alenka Rogelj
Alen Oseli
Jure Kobal
General information

**Name:** The 8th International Conference on Modification Stabilization and Degradation of Polymers

**Organized by:**
- **Center for Experimental Mechanics** - Faculty of Mechanical Engineering, University of Ljubljana, Pot za Brdom 104, Ljubljana 1000, Slovenia
- **Institute for Sustainable Innovative Technologies** - Pot za Brdom 104, Ljubljana 1000, Slovenia
- **Slovenian Society of Rheology** – Cesta na Brdo 85, 1000 Ljubljana, Slovenia

Under umbrella of MoDeSt society.

**MoDeSt Society**

The MoDeSt Society was founded in 1999. The objective of the society is to promote scientific understanding and technical innovation in the modification, degradation and stabilization of polymers, however without excluding all other aspects of polymer science and technology. It dynamically consists of a valuable forum for world wide community of polymer engineers and scientists, stimulating common projects and justifying state-of-the-art knowledge.


**MoDeSt conference scope**

The conference aim is to provide a forum for polymer scientists and engineers to present and share the state-of-the-art knowledge on polymer modification, degradation and stabilization and related areas.

**Conference topics**

- Polymer degradation and stabilization (including fire retardancy and art conservation)
- Polymers and environment (recycling, reuse, biodegradation, bio-based polymers)
- Polymer modification, blends, composites and nanostructured polymers
- Polymers for innovative technical and medical applications (including polymer coatings and optoelectronic materials)
- Degradation and protection of wood products

**Venue**

The 8th MoDeSt conference will take place in Grand Hotel Bernardin & Congress center Bernardin, Portorož from August 31 to September 4, 2014.
Sponsors
Chemass d.o.o., Merilni sistemi, Slovenia
Anton Paar, GmbH, Slovenian representative
TECOS - Slovenian Tool and Die Development Centre, Slovenia

Oral presentations
- Each presentation has 20 min time slot (15 min presentation + 5 min discussion), Plenary lecture – 40 min, Keynote lecture – 30 min;
- presentations should be loaded one day in advance to the computer available for this and checked (videos, animations, content, etc.). For presentations to be held on Monday files might be uploaded during registration on Sunday (15:00 - 18:00) or on Monday morning (8:00 - 9:00);
- presentations should be compatible with Microsoft Office 2007.

Posters
- format of the poster is B1 size: 707 × 1000 mm;
- posters will be available for review during 1 and 2 of September;
- posters should be collected during registration on Sunday (15:00 - 18:00) or on Monday morning (8:00 - 9:00). Presenter should put the poster on the stand with the corresponding number (received via mail).

Social events
During the conference following social events are planned:

<table>
<thead>
<tr>
<th>Event</th>
<th>Day</th>
<th>Time</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Welcome reception</td>
<td>Sunday, 31.08</td>
<td>19.00 – 21.00</td>
<td>Welcome cocktail and buffe for all arrived participants</td>
</tr>
<tr>
<td>Opening ceremony</td>
<td>Monday, 1.09</td>
<td>9.00 – 9.20</td>
<td>Welcome words from President of MoDeSt society prof. Sahar Al-Malaika and Head of Organizing Committee prof. Igor Emri</td>
</tr>
<tr>
<td>General Assembly of the MoDeSt society members</td>
<td>Tuesday, 2.09</td>
<td>17.40 – 19.00</td>
<td>Meeting of the MoDeSt society members and Board</td>
</tr>
<tr>
<td>Gala dinner</td>
<td>Tuesday, 2.09</td>
<td>20.00 – 22.00</td>
<td>Gala dinner, accompanied with entertainment program</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Announcement of poster contest winners</td>
</tr>
<tr>
<td>Excursion</td>
<td>Wednesday, 3.09</td>
<td>15.00 – 19.00</td>
<td>Organized excursion to Postojna Cave</td>
</tr>
<tr>
<td>Closing ceremony</td>
<td>Thursday, 4.09</td>
<td>13.00 – 14.30</td>
<td>Closing lunch</td>
</tr>
</tbody>
</table>
# Program

## 31st of August, Sunday
- **15.00-18.00**  
  Registration

- **19.00-21.00**  
  Welcome reception

## 1st of September, Monday

### 8.00 - 9.00
- Registartion

### 9.00 - 9.20
- Opening ceremony

### 9.20 - 10.00
- **Chair: Sahar Al-Malaika**

### 10.00 - 10.10
- **Chair: Andrzej Dworak**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.10 - 10.20</td>
<td>Ewa Kicko-Walczak</td>
<td>Flame retardants nano-composites - synergy effect of combining conventional antipirenes with nanofillers on the level of flammability of thermoset resins</td>
</tr>
<tr>
<td>10.20 - 10.30</td>
<td>Hanna Maria</td>
<td>Effect of nanoclay in natural rubber-nitrile rubber blends and its effect on morphological and physicomechanical properties</td>
</tr>
<tr>
<td>10.30 - 10.40</td>
<td>Jingbo Wang</td>
<td>Melamine/phenol derivatives: synthesis and potential application as antioxidants in polypropylene</td>
</tr>
<tr>
<td>10.40 - 10.50</td>
<td>Beata Kaczmarek</td>
<td>The influence of UV-irradiation on mechanical properties of chitosan cross-linked by tannic acid</td>
</tr>
<tr>
<td>11.00 - 11.10</td>
<td>Hajme Ohtani</td>
<td>On-line UV irradiation pyrolysis-GC/MS system for rapid evaluation of photo, thermal and oxidative degradation of polymeric materials</td>
</tr>
<tr>
<td>11.10 - 11.20</td>
<td>Cristian-Dragos Varganici</td>
<td>Characterization of thermally, thermally and photo-oxidatively degraded LDPE</td>
</tr>
<tr>
<td>11.20 - 11.30</td>
<td>Hanna Maria</td>
<td>Effect of nanoclay in natural rubber-nitrile rubber blends and its effect on morphological and physicomechanical properties</td>
</tr>
<tr>
<td>11.30 - 11.40</td>
<td>Beata Kaczmarek</td>
<td>The influence of UV-irradiation on mechanical properties of chitosan cross-linked by tannic acid</td>
</tr>
<tr>
<td>11.40 - 11.50</td>
<td>Dan Rosu</td>
<td>Accelerated photoaging of dyed textiles</td>
</tr>
<tr>
<td>11.50 - 12.00</td>
<td>Emmanuel Richaud</td>
<td>Understanding of carbonyls products formation during polydicyclopentadiene oxidation based on kinetic approach</td>
</tr>
<tr>
<td>12.00 - 12.10</td>
<td>Victor Rollon-Garrido</td>
<td>Characterization of thermally, thermally and photo-oxidatively degraded LDPE</td>
</tr>
<tr>
<td>12.10 - 12.20</td>
<td>Erik Duemichen</td>
<td>Investigation of the influence of metal oxide particles on the thermal degradation mechanism of polyamid 66 and polybutylene terephthalate</td>
</tr>
</tbody>
</table>

### 12.00 - 13.50
- **Lunch**
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
</tr>
</thead>
</table>
| 13.50 - 14.20| Chair: Mathew Celina  
KL1: Alberto D’Amore  
Instability of polymer glasses |
| 14.20 - 14.30| Technical break                                                                             |
| 14.30 - 14.40| 62. Stephane Bruzaud  
Polyhydroxyalkanoates-based blends: an efficient way to modulate functional properties of materials |
| 14.40 - 14.50| 63. Mario Stein  
Degradation of organic radioactive waste and impact of released gas on repository safety |
| 14.50 - 15.00| 64. Boris Eyheraguibel  
Impact of environmental conditions on oxobiodegradable polymers decomposition |
| 15.00 - 15.10| 34. Julie Courtat  
Chemical modification of spherical fillers by phosphorous to improve the flame retardancy of polypropylene |
| 15.10 - 15.20| 35. Jihane Sahyoun  
Synthesis of fire retarded PA66-PA6 copolymers by association of sol-gel chemistry and reactive extrusion |
| 15.20 - 15.30| 36. Manfred Bohn  
Kinetic modelling of stabilizer consumption and molar mass degradation in NC-based materials |
| 15.30 - 16.10| Coffee break + Poster session                                                                |
| 16.10 - 16.20| 65. Serena Coiai  
Functionalized poly(butylene succinate) by nitroxide radical coupling |
| 16.20 - 16.30| 66. Irena Vukovic-Kwiatkowska  
Packaging materials of new generation based on PLA modified with polyacrylates |
| 16.30 - 16.40| 37. Ulrike Braun  
Sulphur containing additives for polystyrene: influencing the decomposition behaviour in the condensed phase |
| 16.40 - 16.50| 38. Anil Naik  
Melamine integrated metal phosphates in the flame retardancy of polyamide-66 |
| 16.50 - 17.00| 67. Morgan Deroine  
Accelerated ageing and lifetime prediction of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) immersed in distilled water |
| 17.00 - 17.10| 39. Koen Adema  
Depth-resolved characterization of chemical composition and light absorption in a weathered polyester-urethane clearcoat |
| 17.10 - 17.20| 68. Kahina Iggui  
Biodegradation of PHBV nanobiocomposites films: effect of the clays |
| 17.20 - 17.30| 40. Agnieszka Bereska  
Synthesis and application of organophosphorus flame retardants |
| 17.30 - 17.40| 69. Henrik Petersen  
Development of environmentally friendly plasticized PVC by means of nanotechnology |
| 17.40 - 17.50| 41. Renaud Dupretz  
Fire retardancy of a new polypropylene-grafted starch |
<p>| 17.50 - 19.00| Coffee break + Poster session                                                                |</p>
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
</tr>
</thead>
</table>
| 9.00 - 9.30  | KL2: Philip Evans  
Wood photostabilization and protection: divergent pathways and future prospects |
| 9.30 - 9.40  | Technical break                             |
| 9.40 - 9.50  | Chair: Philip Evans  
74. Holger Militz  
Reactive resins for wood modification |
| 9.50 - 10.00 | Chair: Jan Pilar                            |
| 10.00 - 10.10| 42. Mathew Celina  
Oxygen diffusion through polymer at elevated temperature |
| 10.10 - 10.20| 75. Lone Ross Gobakken  
Deterioration of wood by mould and blue stain fungi |
| 10.20 - 10.30| 43. Tetiana Salivon  
Thermo-oxidative degradation of XPE and PVC used in electrical insulation |
| 10.30 - 10.40| 76. Andreja Kutnar  
End of life scenarios and environmental impacts of wood products |
| 10.40 - 10.50| 78. Marko Petrič  
Wood coatings made of liquefied wood and some other lignocellulosic materials |
| 10.50 - 11.00| Coffee break + Poster session               |
| 11.00 - 11.40| Chair: Andreja Kutnar  
70. Beata Szołnoki  
Synthesis and characterization of epoxy resins derived from d-glucose |
| 11.40 - 11.50| 45. Emilie Courvoisier  
Kinetic analysis of the thermal degradation of PEEK |
| 11.50 - 12.00| 46. Xavier Colin  
A general kinetic model for the photothermal oxidation of polypropylene |
| 12.00 - 12.10| 71. Marta-Małgorzata Targosz  
Aerosols emitted in post-crash fires from structural composite materials |
| 12.10 - 12.20| 48. Qing Lin  
Investigation of thermal stability and flammability of PMMA composites by combination of APP with ZrO₂, sepiolite or MMT |
| 12.20 - 12.30| 72. Alojz Anžlovar  
Fast preparation of nanocrystalline cellulose by microwave-assisted hydrolysis |
| 12.30 - 12.40| 49. Aleksandra Sut  
Synergy in flame retardant polymers: solid-state NMR identifying the chemistry behind it |
| 12.40 - 12.50| 73. Stamatina Vouyiouka  
Mechanical recycling of poly(butylene succinate) through the remelting-restabilization technique |
| 12.50 - 13.00| 47. Katalin Bocz  
Oriented polymer fibres for improving the flame retardant efficiency of intumescent additive systems |
<p>| 13.00 - 13.10| Lunch                                        |
| 13.10 - 13.20|                                             |
| 13.20 - 14.40|                                             |</p>
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Speakers</th>
<th>Topics</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.40 - 15.10</td>
<td><strong>KL3: Pieter Gijsman</strong> The (unexpected) role of water in the thermo-and photo-oxidative degradation of polyamide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.10 - 15.20</td>
<td><strong>Technical break</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.20 - 15.30</td>
<td><strong>Chair: Mathew Celina</strong> 7. Ewa Wierzbicka The role of block thermoplastic rubber of diynene-isoprene-styrene type functionalized by a boron compound as compatibilizer to polystyrene/polypropylene blends</td>
<td>50. Nadka Dintcheva Thermo stable polymer-layered silicate nanocomposites through intercalation of novel organo-modifier</td>
<td></td>
</tr>
<tr>
<td>15.40 - 15.50</td>
<td>9. Laida Cano Nanostructured and toughened thermosetting systems modified with PEO-b-PPO-b-PEO triblock copolymers</td>
<td>52. Lata Soccalingame Influence of artificial UV weathering on the reprocessing of wood flour reinforced polypropylene</td>
<td></td>
</tr>
<tr>
<td>15.50 - 16.00</td>
<td>10. Irati Barandiaran Generation of nanocomposites based on block copolymer and Fe$_2$O$_3$ nanoparticles modified by grafting to method with PMMA-b-PLC copolymer</td>
<td>53. Ghania Ounoughene Fate of Halloysite nanotubes (HNTs) when incinerating PA6/HNTs composites</td>
<td></td>
</tr>
<tr>
<td>16.00 - 16.10</td>
<td>11. Demet Kaya Effect of PH on volume phase transition for (acrylamide-co-acrylic acid) composite hydrogel by using fluorescence technique</td>
<td>27. Pavel Oblak Processability and mechanical properties of extensively recycled HDPE</td>
<td></td>
</tr>
<tr>
<td>16.10 - 16.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.20 - 16.30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.30 - 16.40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.40 - 16.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.50 - 17.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.00 - 17.40</td>
<td><strong>Coffee break + Poster session</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.40 - 19.00</td>
<td></td>
<td></td>
<td>General assembly for MoDeSt society members</td>
</tr>
<tr>
<td>19.00 - 20.00</td>
<td></td>
<td></td>
<td>Gala dinner</td>
</tr>
<tr>
<td>20.00 - 22.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>Session</td>
<td>Speaker(s)</td>
<td>Title</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------------------</td>
<td>-----------------------------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>9.00 - 9.40</td>
<td>PL2: Matija Strlič</td>
<td>Chair: Igor Emri</td>
<td>Thermoresponsive polymer surfaces for cell sheet culture and harvesting</td>
</tr>
<tr>
<td>9.40 - 10.10</td>
<td>KL4: Andrzej Dworak</td>
<td>Chair: Francesco La-Mantia</td>
<td>Lifetime prediction of materials of historic value</td>
</tr>
<tr>
<td>10.10 - 10.40</td>
<td>Coffee break</td>
<td>Chair: Crispulo Gallegos</td>
<td></td>
</tr>
<tr>
<td>11.00 - 11.10</td>
<td>16. Jiaohong Zhao</td>
<td>82. Agnes Rivaton</td>
<td>Investigation of thermo-oxidative aging behavior of NBR in oils</td>
</tr>
<tr>
<td>11.20 - 11.30</td>
<td>18. Manuel Oliveira</td>
<td>Unravelling the photodegradation mechanisms of a low bandgap polymer by combining experimental and modeling approaches</td>
<td></td>
</tr>
<tr>
<td>11.30 - 11.40</td>
<td>Lunch</td>
<td>84. Boris Gorelik</td>
<td>Synthesis of functional block copolymers by controled radical polymerization</td>
</tr>
<tr>
<td>12.00 - 12.10</td>
<td></td>
<td>85. Anthony Chapel</td>
<td>Photo-stabilization of highly filled thermostet composites</td>
</tr>
<tr>
<td>12.10 - 12.20</td>
<td></td>
<td></td>
<td>Luminiscent composite phosphors/polymer: impact of red phosphor (Y₃BO₃:Eu³⁺) on EVA properties and photoageing</td>
</tr>
<tr>
<td>12.20 - 13.40</td>
<td></td>
<td>Chair: Jean-Luc Gardette</td>
<td></td>
</tr>
<tr>
<td>13.40 - 13.50</td>
<td></td>
<td>85. Anthony Chapel</td>
<td></td>
</tr>
<tr>
<td>13.50 - 14.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.00 - 14.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.10 - 14.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.20 - 14.40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.00 - 19.00</td>
<td></td>
<td>85. Anthony Chapel</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Wednesday, Afternoon**

**3rd of September, Wednesday**

Chair: Igor Emri

**PL2: Matija Strlič**
Thermoresponsive polymer surfaces for cell sheet culture and harvesting

**KL4: Andrzej Dworak**
Lifetime prediction of materials of historic value

**Chair: Francesco La-Mantia**

**12. Magdalena Perchacz**
Organic/inorganic hybrid materials based on epoxy matrix

**13. Octavie Okamba Diogo**
Correlation between macromolecular and mechanical properties changes during polyamide-11 oxidation

**16. Jiaohong Zhao**
Investigation of thermo-oxidative aging behavior of NBR in oils

**17. Rui Yang**
Investigation of natural aging behavior of PP/CaCO₃ composites

**18. Manuel Oliveira**
Synthesis of functional block copolymers by controled radical polymerization

**Chair: Crispulo Gallegos**

**79. James Lewicki**
Smart silicone composites. The synthesis, characterization and application of well-defined hierarchical PDMS/inorganic composites with novel physical properties

**80. Regina Jeziorska**
Polyolefines with antimicrobial activity

**81. Annegret Jentsch**
Influence of typical stabilizers on the aging behavior of EVA foils for PV applications during artificial UV-weathering

**82. Agnes Rivaton**
Is there any possible conjugated polymer for efficient solar cells?

**83. Isabel Fraga**
Unravelling the photodegradation mechanisms of a low bandgap polymer by combining experimental and modeling approaches

**Chair: Jean-Luc Gardette**

**84. Boris Gorelik**
Photo-stabilization of highly filled thermostet composites

**85. Anthony Chapel**
Luminiscent composite phosphors/polymer: impact of red phosphor (Y₃BO₃:Eu³⁺) on EVA properties and photoageing

**Excursion**
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Presenter(s)</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.00 - 9.30</td>
<td><strong>Chair: Manfred Wagner</strong></td>
<td><strong>KL5: Sandrine Therias</strong></td>
<td>Latest Advances in the Photodegradation of Nanocomposites</td>
</tr>
<tr>
<td>9.30 - 9.40</td>
<td></td>
<td></td>
<td>Technical break</td>
</tr>
<tr>
<td>9.40 - 9.50</td>
<td>Chair: Alojz Anžlovar</td>
<td>19. Hesham Moustafa</td>
<td>Study the effect of maleic anhydride as compatibilizing agent on filler-rubber interaction, rheological, mechanical and swelling properties of NR/clay platelet NC</td>
</tr>
<tr>
<td>9.50 - 10.00</td>
<td></td>
<td>20. Ievgeniia Topolniak</td>
<td>Influence of zeolite particles loading on the morphology and photostability of ethylene vinyl alcohol copolymer (evoh) nanocomposite</td>
</tr>
<tr>
<td>10.00 - 10.10</td>
<td></td>
<td>21. Bartlomej Bereska</td>
<td>Novel self-lubricating epoxy composites comprising hyperbranched cross-linking agents</td>
</tr>
<tr>
<td>10.10 - 10.20</td>
<td></td>
<td>54. Alexis Colin</td>
<td>Thermo-oxidation of an acrylic-silicone coating: degradation mechanism related to material properties evolution</td>
</tr>
<tr>
<td>10.20 - 10.30</td>
<td></td>
<td>55. Laurent Chazeau</td>
<td>Rupture properties of gamma irradiated EPDMs with different chemical compositions</td>
</tr>
<tr>
<td>10.30 - 10.40</td>
<td></td>
<td>26. Mogon Patel</td>
<td>Accelerated thermal ageing and mechanical stress-strain responses of foamed polysiloxanes</td>
</tr>
<tr>
<td>10.40 - 11.10</td>
<td></td>
<td></td>
<td>Coffee break</td>
</tr>
<tr>
<td>11.10 - 11.20</td>
<td>Chair: Regina Jeziorska</td>
<td>22. Mirela Zaltariov</td>
<td>Nanostructures self-assembled through non-covalent bonding of metal complexes with ligands containing siloxane or silane fragments</td>
</tr>
<tr>
<td>11.20 - 11.30</td>
<td></td>
<td>23. Béla Pukánszky</td>
<td>Interactions, structure and properties in ionomer/lignosulfonate blends</td>
</tr>
<tr>
<td>11.30 - 11.40</td>
<td></td>
<td>24. Sergii Ponyrko</td>
<td>Epoxy-silica nanocomposite by nanoaqueous sol-gel process</td>
</tr>
<tr>
<td>11.40 - 11.50</td>
<td></td>
<td>25. Roberto Benavides</td>
<td>Electron beam Irradiation of PVC formulations added with transfer agents</td>
</tr>
<tr>
<td>11.50 - 12.00</td>
<td></td>
<td>57. Camille Rouillon</td>
<td>Pigmented polypropylene photo-ageing: an AFM study</td>
</tr>
<tr>
<td>12.00 - 12.10</td>
<td></td>
<td>58. Baltus Bonse</td>
<td>Organic and inorganic pigments in polypropylene: mechanical and flame retardant properties</td>
</tr>
<tr>
<td>12.10 - 12.20</td>
<td></td>
<td>60. Bettina Dittrich</td>
<td>Graphene - promising nanofiller and adjuvant for flame retarded polymer composites</td>
</tr>
<tr>
<td>12.20 - 12.30</td>
<td></td>
<td>61. Florian Cavodeau</td>
<td>Influence of the mechanical properties of fillers on the breakdown of barrier layer in EVA/ATH composites</td>
</tr>
<tr>
<td>12.30 - 13.00</td>
<td></td>
<td></td>
<td>Lunch + Closing ceremony</td>
</tr>
<tr>
<td>13.00 - 14.30</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Legend:

- social events
- lunches
- coffee breaks
- technical breaks
- Plenary lecture
- Keynote lecture
- Polymer modification, blends, composites and nanostructured polymers
- Polymer degradation and stabilization (including fire retardancy and art conservation)
- Polymers for innovative technical and medical applications (including polymer coatings and optoelectronic materials)
- Degradation and protection of wood products
- Polymers and environment (recycling, reuse, biodegradation, bio-based polymers)
List of oral presentations

<table>
<thead>
<tr>
<th>Page</th>
<th>#</th>
<th>Presentor</th>
<th>Title</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>INVITED LECTURES</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>KL6</td>
<td>Emo Chiellini</td>
<td>BIODEGRADABLE POLYMERIC MATERIALS AND PLASTICS FROM RENEWABLE SOURCES &amp; FOSSIL FUEL FEEDSTOCK: PROS &amp; CONS</td>
<td>Italy</td>
</tr>
<tr>
<td>29</td>
<td>KL1</td>
<td>Alberto D’Amore</td>
<td>INSTABILITY OF POLYMER GLASSES</td>
<td>Italy</td>
</tr>
<tr>
<td>32</td>
<td>KL4</td>
<td>Andrzej Dworak</td>
<td>THERMORESPONSIVE POLYMER SURFACES FOR CELL SHEET CULTURE AND HARVESTING</td>
<td>Poland</td>
</tr>
<tr>
<td>30</td>
<td>KL2</td>
<td>Philip Evans</td>
<td>WOOD PHOTOSTABILIZATION &amp; PROTECTION: DIVERGENT EVOLUTION &amp; FUTURE PROSPECTS</td>
<td>Canada</td>
</tr>
<tr>
<td>27</td>
<td>PL1</td>
<td>Crispulo Gallegos</td>
<td>PROTEIN-BASED BIOPLASTICS: AN OVERVIEW</td>
<td>Germany</td>
</tr>
<tr>
<td>31</td>
<td>KL3</td>
<td>Pieter Gijsman</td>
<td>THE UNEXPECTED IMPORTANCE OF HUMIDITY ON THE THERMO- AND PHOTO-OXIDATIVE DEGRADATION OF POLYAMIDES</td>
<td>Netherlands</td>
</tr>
<tr>
<td>28</td>
<td>PL2</td>
<td>Matija Strlič</td>
<td>LIFETIME PREDICTION OF MATERIALS OF HISTORIC VALUE</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>33</td>
<td>KL5</td>
<td>Sandrine Thérias</td>
<td>LATEST ADVANCES IN THE PHOTODEGRADATION OF NANOCOMPOSITES</td>
<td>France</td>
</tr>
<tr>
<td></td>
<td>POLYMER MODIFICATION, BLENDS, COMPOSITES AND NANOSTRUCTURED POLYMERS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>10</td>
<td>Irati Barandiari</td>
<td>GENERATION OF NANOCOMPOSITES BASED ON BLOCK COPOLYMER AND FE2O3 NANOPARTICLES MODIFIED BY GRAFTING TO METHOD WITH PMMA-B-PCL COPOLYMER</td>
<td>Spain</td>
</tr>
<tr>
<td>56</td>
<td>25</td>
<td>Roberto Benavides</td>
<td>ELECTRON BEAM IRRADIATION OF PVC FORMULATIONS ADDED WITH TRANSFER AGENTS</td>
<td>Mexico</td>
</tr>
<tr>
<td>52</td>
<td>21</td>
<td>Bartolomiej Bereska</td>
<td>NOVEL SELF-LUBRICATING EPOXY COPOSITES COMPRISING HYPERBRANCHED CROSS-LINKING AGENTS</td>
<td>Poland</td>
</tr>
<tr>
<td>41</td>
<td>9</td>
<td>Laida Cano</td>
<td>NANOSTRUCTURED AND TOUGHENED THERMOSETTING SYSTEMS MODIFIED WITH PEO-B-PPO-B-PEO TRIBLOCK COPOLYMER</td>
<td>Spain</td>
</tr>
<tr>
<td>Page</td>
<td>#</td>
<td>Presentor</td>
<td>Title</td>
<td>Country</td>
</tr>
<tr>
<td>------</td>
<td>----</td>
<td>----------------</td>
<td>----------------------------------------------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>38</td>
<td>6</td>
<td>Beata Kaczmarek</td>
<td>THE INFLUENCE OF UV-IRRADIATION ON MECHANICAL PROPERTIES OF CHITOSAN CROSS-LINKED BY TANNIC ACID</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>11</td>
<td>Demet Kaya</td>
<td>EFFECT OF pH ON VOLUME PHASE TRANSITION FOR (ACRYLAMIDE-CO-ACRYLIC ACID) COMPOSITE HYDROGEL USING BY FLUORESCENCE TECHNIQUE</td>
<td>Turkey</td>
</tr>
<tr>
<td>35</td>
<td>3</td>
<td>Ewa Kicko-Walczak</td>
<td>FLAME RETARDANTS NANOCOMPOSITES-SYNERGY EFFECT OF COMBINING CONVENTIONAL ANTPIRENES WITH NANOFILLERS ON THE LEVEL OF FLAMMABILITY OF THERMOSET RESINS</td>
<td>Poland</td>
</tr>
<tr>
<td>37</td>
<td>5</td>
<td>Hanna Maria</td>
<td>EFFECT OF NANOCLAY IN NATURAL RUBBER-NITRILE RUBBER BLENDS AND ITS EFFECT ON MORPHOLOGICAL, AND PHYSICOMECHANICAL PROPERTIES</td>
<td>India</td>
</tr>
<tr>
<td>50</td>
<td>19</td>
<td>Hesham Moustafa</td>
<td>STUDY THE EFFECT OF MALEIC ANHYDRIDE AS COMPATABILIZING AGENT ON FILLER-RUBBER INTERACTION, RHEOLOGICAL, MECHANICAL AND SWELLING PROPERTIES OF NR/CLAY PLATELET NANOCOMPOSITES</td>
<td>Egypt</td>
</tr>
<tr>
<td>45</td>
<td>13</td>
<td>Octavie Diogo</td>
<td>CORRELATION BETWEEN MACROMOLECULAR AND MECHANICAL PROPERTIES CHANGES DURING POLYAMIDE 11 OXIDATION</td>
<td>France</td>
</tr>
<tr>
<td>49</td>
<td>18</td>
<td>Manuel Oliveira</td>
<td>SYNTHESIS OF FUNCTIONAL BLOCK COPOLYMERS BY CONTROLLED RADICAL POLYMERIZATION</td>
<td>Portugal</td>
</tr>
<tr>
<td>44</td>
<td>12</td>
<td>Magdalena Perchacz</td>
<td>ORGANIC/INORGANIC HYBRID MATERIALS BASED ON EPOXY MATRIX</td>
<td>Czech Republic</td>
</tr>
<tr>
<td>40</td>
<td>8</td>
<td>Jan Pilař</td>
<td>HETEROGENEITY OF ACCELERATED PHOTOOXIDATION IN COMMODITY POLYMERS STABILIZED BY HAS: ESRI, IR, AND MICROHARDNESS STUDY.</td>
<td>Czech Republic</td>
</tr>
<tr>
<td>55</td>
<td>24</td>
<td>Sergii Ponyrko</td>
<td>EPOXY-SILICA NANOCOMPOSITE BY NONAQUEOUS SOL-GEL PROCESS</td>
<td>Czech Republic</td>
</tr>
<tr>
<td>54</td>
<td>23</td>
<td>Béla Pukánszky</td>
<td>INTERACTIONS, STRUCTURE AND PROPERTIES IN IONOMER/LIGNOSULFONATE BLENDS</td>
<td>Hungary</td>
</tr>
<tr>
<td>36</td>
<td>4</td>
<td>Intan Tawakkal</td>
<td>DEVELOPMENT OF POLY(LACTIC ACID) COMPOSITES REINFORCED WITH NATURAL FIBRES</td>
<td>Australia</td>
</tr>
<tr>
<td>51</td>
<td>20</td>
<td>Ievgenii Topolniak</td>
<td>INFLUENCE OF ZEOLITE PARTICLES LOADING ON THE MORPHOLOGY AND PHOTOSTABILITY OF ETHYLENE VINYL</td>
<td>France</td>
</tr>
<tr>
<td>Page</td>
<td>#</td>
<td>Presentor</td>
<td>Title</td>
<td>Country</td>
</tr>
<tr>
<td>------</td>
<td>---</td>
<td>--------------</td>
<td>------------------------------------------------------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>46</td>
<td>15</td>
<td>Jingbo Wang</td>
<td>ALCOHOL COPOLYMER (EVOH) NANOCOMPOSITE</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>7</td>
<td>Ewa Wierzbicka</td>
<td>MELAMINE/PHENOL DERIVATIVES: SYNTHESIS AND POTENTIAL APPLICATION AS ANTIOXIDANTS IN POLYPROPYLENE</td>
<td>Austria</td>
</tr>
<tr>
<td>48</td>
<td>17</td>
<td>Rui Yang</td>
<td>THE ROLE OF BLOCK THERMOPLASTIC RUBBER OF STYRENE-ISOPRENE-STYRENE TYPE FUNCTIONALIZED BY A BORON COMPOUND AS COMPATIBILIZER TO POLYSTYRENE/POLYPROPYLENE BLENDS</td>
<td>Poland</td>
</tr>
<tr>
<td>47</td>
<td>16</td>
<td>Jiaohong Zhao</td>
<td>INVESTIGATION OF NATURAL AGING BEHAVIOR OF PP/CACO3 COMPOSITES[1]</td>
<td>China</td>
</tr>
<tr>
<td>53</td>
<td>22</td>
<td>Mirela Zaltariov</td>
<td>NANOSTRUCTURES SELF-ASSEMBLED THROUGH NON-COVALENT BONDING OF METAL COMPLEXES WITH LIGANDS CONTAINING SILOXANE OR SILANE FRAGMENTS</td>
<td>Romania</td>
</tr>
<tr>
<td>70</td>
<td>39</td>
<td>Koen Adema</td>
<td>INVESTIGATION OF THERMO-OXIDATIVE AGING BEHAVIOR OF NBR IN OILS</td>
<td>China</td>
</tr>
<tr>
<td>71</td>
<td>40</td>
<td>Agnieszka Bereska</td>
<td>DEPTH-RESOLVED CHARACTERISATION OF CHEMICAL COMPOSITION AND LIGHT ABSORPTION IN A WEATHERED POLYESTER-URETHANE CLEARCOAT</td>
<td>Netherlands</td>
</tr>
<tr>
<td>78</td>
<td>47</td>
<td>Katalin Bocz</td>
<td>SYNTHESIS AND APPLICATION OF ORGANOPHOSPHORUS FLAME RETARDANTS</td>
<td>Poland</td>
</tr>
<tr>
<td>67</td>
<td>36</td>
<td>Manfred Bohn</td>
<td>ORIENTED POLYMER FIBRES FOR IMPROVING THE FLAME RETARDANT EFFICIENCY OF INTUMESCENT ADDITIVE SYSTEMS</td>
<td>Hungary</td>
</tr>
<tr>
<td>89</td>
<td>58</td>
<td>Baltus Bonse</td>
<td>KINETIC MODELLING OF STABILIZER CONSUMPTION AND MOLAR MASS DEGRADATION IN NC-BASED MATERIALS</td>
<td>Germany</td>
</tr>
<tr>
<td>68</td>
<td>37</td>
<td>Ulrike Braun</td>
<td>ORGANIC AND INORGANIC PIGMENTS IN POLYPROPYLENE: MECHANICAL AND FLAME RETARDANT PROPERTIES</td>
<td>Brazil</td>
</tr>
</tbody>
</table>

**POLYMER DEGRADATION AND STABILIZATION (INCLUDING FIRE RETARDANCY AND ART CONSERVATION)**

<table>
<thead>
<tr>
<th>Page</th>
<th>#</th>
<th>Presentor</th>
<th>Title</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>39</td>
<td>Koen Adema</td>
<td>DEPTH-RESOLVED CHARACTERISATION OF CHEMICAL COMPOSITION AND LIGHT ABSORPTION IN A WEATHERED POLYESTER-URETHANE CLEARCOAT</td>
<td>Netherlands</td>
</tr>
<tr>
<td>71</td>
<td>40</td>
<td>Agnieszka Bereska</td>
<td>SYNTHESIS AND APPLICATION OF ORGANOPHOSPHORUS FLAME RETARDANTS</td>
<td>Poland</td>
</tr>
<tr>
<td>78</td>
<td>47</td>
<td>Katalin Bocz</td>
<td>ORIENTED POLYMER FIBRES FOR IMPROVING THE FLAME RETARDANT EFFICIENCY OF INTUMESCENT ADDITIVE SYSTEMS</td>
<td>Hungary</td>
</tr>
<tr>
<td>67</td>
<td>36</td>
<td>Manfred Bohn</td>
<td>KINETIC MODELLING OF STABILIZER CONSUMPTION AND MOLAR MASS DEGRADATION IN NC-BASED MATERIALS</td>
<td>Germany</td>
</tr>
<tr>
<td>89</td>
<td>58</td>
<td>Baltus Bonse</td>
<td>ORGANIC AND INORGANIC PIGMENTS IN POLYPROPYLENE: MECHANICAL AND FLAME RETARDANT PROPERTIES</td>
<td>Brazil</td>
</tr>
<tr>
<td>67</td>
<td>36</td>
<td>Manfred Bohn</td>
<td>KINETIC MODELLING OF STABILIZER CONSUMPTION AND MOLAR MASS DEGRADATION IN NC-BASED MATERIALS</td>
<td>Germany</td>
</tr>
<tr>
<td>89</td>
<td>58</td>
<td>Baltus Bonse</td>
<td>ORGANIC AND INORGANIC PIGMENTS IN POLYPROPYLENE: MECHANICAL AND FLAME RETARDANT PROPERTIES</td>
<td>Brazil</td>
</tr>
<tr>
<td>68</td>
<td>37</td>
<td>Ulrike Braun</td>
<td>SULPHUR CONTAINING ADDITIVES FOR POLYSTYRENE: INFLUENCING THE DECOMPOSITION BEHAVIOUR IN THE CONDENSED PHASE</td>
<td>Germany</td>
</tr>
<tr>
<td>Page</td>
<td>#</td>
<td>Presentor</td>
<td>Title</td>
<td>Country</td>
</tr>
<tr>
<td>------</td>
<td>----</td>
<td>----------------</td>
<td>----------------------------------------------------------------------</td>
<td>---------</td>
</tr>
<tr>
<td>91</td>
<td>61</td>
<td>Florian Cavodeau</td>
<td>INFLUENCE OF THE MECHANICAL PROPERTIES OF FILLERS ON THE BREAKDOWN OF BARRIER LAYER IN EVA/ATH COMPOSITES</td>
<td>France</td>
</tr>
<tr>
<td>73</td>
<td>42</td>
<td>Mathew Celina</td>
<td>OXYGEN DIFFUSION THROUGH POLYMERS AT ELEVATED TEMPERATURE</td>
<td>USA</td>
</tr>
<tr>
<td>86</td>
<td>55</td>
<td>Laurent Chazeau</td>
<td>RUPTURE PROPERTIES OF GAMMA IRRADIATED EPDMs WITH DIFFERENT CHEMICAL COMPOSITIONS</td>
<td>France</td>
</tr>
<tr>
<td>77</td>
<td>46</td>
<td>Xavier Colin</td>
<td>A GENERAL KINETIC MODEL FOR THE PHOTOTHERMAL OXIDATION OF POLYPROPYLENE</td>
<td>France</td>
</tr>
<tr>
<td>85</td>
<td>54</td>
<td>Alexis Colin</td>
<td>THERMO-OXIDATION OF AN ACRYLIC-SILICONE COATING: DEGRADATION MECHANISM RELATED TO MATERIAL PROPERTIES EVOLUTION</td>
<td>France</td>
</tr>
<tr>
<td>65</td>
<td>34</td>
<td>Julie Courtat</td>
<td>CHEMICAL MODIFICATION OF SPHERICAL FILLERS BY PHOSPHOROUS TO IMPROVE THE FLAME RETARDANCY OF POLYPROPYLENE</td>
<td>France</td>
</tr>
<tr>
<td>76</td>
<td>45</td>
<td>Emilie Courvoisier</td>
<td>KINETIC ANALYSIS OF THE THERMAL DEGRADATION OF PEEK</td>
<td>France</td>
</tr>
<tr>
<td>81</td>
<td>50</td>
<td>Nadka Dintcheva</td>
<td>THERMALLY-STABLE POLYMER-LAYERED SILICATE NANOCOMPOSITES THROUGH INTERCALATION OF NOVEL ORGANO-MODIFIER</td>
<td>Italy</td>
</tr>
<tr>
<td>90</td>
<td>60</td>
<td>Bettina Dittrich</td>
<td>GRAPHENE – PROMISING NANOFILLER AND ADJUVANT FOR FLAME RETARDED POLYMER COMPOSITES</td>
<td>Germany</td>
</tr>
<tr>
<td>64</td>
<td>33</td>
<td>Erik Duemichen</td>
<td>INVESTIGATION OF THE INFLUENCE OF METAL OXIDE PARTICLES ON THE THERMAL DEGRADATION MECHANISM OF POLYAMIDE 66 AND POLYBUTYLENE TEREPTHALATE</td>
<td>Germany</td>
</tr>
<tr>
<td>72</td>
<td>41</td>
<td>Renaud Dupretz</td>
<td>FIRE RETARDANCY OF A NEW POLYPROPYLENE-GRAFTED STARCH</td>
<td>France</td>
</tr>
<tr>
<td>79</td>
<td>48</td>
<td>Qing Lin</td>
<td>INVESTIGATION OF THERMAL STABILITY AND FLAMMABILITY OF PMMA COMPOSITES BY COMBINATION OF APP WITH ZRO2, SEPIOLITE OR MMT</td>
<td>France</td>
</tr>
<tr>
<td>75</td>
<td>44</td>
<td>Hesam Makki</td>
<td>A MULTI-SCALE SIMULATION APPROACH TO STUDY THE</td>
<td>Netherlands</td>
</tr>
<tr>
<td>Page</td>
<td>#</td>
<td>Presentor</td>
<td>Title</td>
<td>Country</td>
</tr>
<tr>
<td>------</td>
<td>----</td>
<td>----------------</td>
<td>----------------------------------------------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>69</td>
<td>38</td>
<td>Anil Naik</td>
<td>WEATHERING OF POLYESTER-URETHANE COATINGS</td>
<td>France</td>
</tr>
<tr>
<td>58</td>
<td>27</td>
<td>Pavel Oblak</td>
<td>PROCESSABILITY AND MECHANICAL PROPERTIES OF EXTENSIVELY RECYCLED HDPE</td>
<td>Slovenia</td>
</tr>
<tr>
<td>87</td>
<td>56</td>
<td>Hajime Ohtani</td>
<td>ON-LINE UV IRRADIATION PYROLYSIS-GC/MS SYSTEM FOR RAPID EVALUATION OF PHOTO, THERMAL AND OXIDATIVE DEGRADATION OF POLYMERIC MATERIALS</td>
<td>Japan</td>
</tr>
<tr>
<td>84</td>
<td>53</td>
<td>Ghania Ounoughene</td>
<td>FATE OF HALLOYSITE NANOTUBES (HNTs) WHEN INCINERATING PA6/HNTS NANOCOMPOSITE</td>
<td>France</td>
</tr>
<tr>
<td>57</td>
<td>26</td>
<td>Mogon Patel</td>
<td>ACCELERATED THERMAL AGEING AND MECHANICAL STRESS STRAIN RESPONSES OF FOAMED POLYSILOXANES</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>62</td>
<td>31</td>
<td>Emmanuel Richaud</td>
<td>UNDERSTANDING OF CARBONYLS PRODUCTS FORMATION DURING POLYDICYCLOPENTADIENE OXIDATION BASED ON KINETIC APPROACH.</td>
<td>France</td>
</tr>
<tr>
<td>59</td>
<td>28</td>
<td>Viktor Rolon-Garrido</td>
<td>CHARACTERIZATION OF THERMALLY, THERMO- AND PHOTO-OXIDATIVELY DEGRADED LDPE</td>
<td>Germany</td>
</tr>
<tr>
<td>61</td>
<td>30</td>
<td>Dan Rosu</td>
<td>ACCELERATED PHOTOAGING OF DYED TEXTILES</td>
<td>Romania</td>
</tr>
<tr>
<td>88</td>
<td>57</td>
<td>Camille Rouillon</td>
<td>SYNTHESIS OF FIRE RETARDED PA66-PA6 COPOLYMERS BY ASSOCIATION OF SOL-GEL CHEMISTRY AND REACTIVE EXTRUSION</td>
<td>France</td>
</tr>
<tr>
<td>66</td>
<td>35</td>
<td>Jihane Sahyoun</td>
<td>THERMO-OXIDATIVE DEGRADATION OF XPE AND PVC USED IN ELECTRICAL INSULATION</td>
<td>France</td>
</tr>
<tr>
<td>74</td>
<td>43</td>
<td>Tetiana Salivon</td>
<td>ON THE THERMAL STABILITY OF POLY(VINYL ALCOHOL) AND CELLULOSE BASED CRYOGELS</td>
<td>France</td>
</tr>
<tr>
<td>83</td>
<td>52</td>
<td>Lata Soccaligame</td>
<td>INFLUENCE OF ARTIFICIAL UV WEATHERING ON THE REPROCESSING OF WOOD FLOUR REINFORCED POLYPROPYLENE</td>
<td>France</td>
</tr>
<tr>
<td>80</td>
<td>49</td>
<td>Aleksandra Sut</td>
<td>SYNERGY IN FLAME RETARDANT POLYMERS: SOLID-STATE NMR IDENTIFYING THE CHEMISTRY BEHIND IT</td>
<td>Germany</td>
</tr>
<tr>
<td>60</td>
<td>29</td>
<td>Cristian–Dragos Varganici</td>
<td>UNDERSTANDING OF CARBONYLS PRODUCTS FORMATION DURING POLYDICYCLOPENTADIENE OXIDATION BASED ON KINETIC APPROACH.</td>
<td>Romania</td>
</tr>
<tr>
<td>Page</td>
<td>#</td>
<td>Presentor</td>
<td>Title</td>
<td>Country</td>
</tr>
<tr>
<td>------</td>
<td>---</td>
<td>------------------</td>
<td>----------------------------------------------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>82</td>
<td>51</td>
<td>Amandine Viretto</td>
<td>PCFC-FTIR COUPLING: A NEW TOOL TO STUDY THE COMBUSTION</td>
<td>France</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>POLYMERS AND ENVIRONMENT (RECYCLING, REUSE, BIODEGRADATION, BIO-BASED POLYMERS)</strong></td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>72</td>
<td>Alojz Anžlovar</td>
<td>FAST PREPARATION OF NANOCRYSTALLINE CELLULOSE BY MICROWAVE-ASSISTED HYDROLYSIS</td>
<td>Slovenia</td>
</tr>
<tr>
<td>92</td>
<td>62</td>
<td>Stephane Bruzaud</td>
<td>POLYHYDROXYALKANOATES-BASED BLENDS: AN EFFICIENT WAY TO MODULATE FUNCTIONAL PROPERTIES OF MATERIALS</td>
<td>France</td>
</tr>
<tr>
<td>95</td>
<td>65</td>
<td>Serena Coiai</td>
<td>FUNCTIONALIZED POLY(BUTYLENE SUCCINATE) BY NITROXIDE RADICAL COUPLING</td>
<td>Italy</td>
</tr>
<tr>
<td>97</td>
<td>67</td>
<td>Morgan Deroiné</td>
<td>ACCELERATED AGEING AND LIFETIME PREDICTION OF POLY(3-HYDROXYBUTYRATE-CO-3-HYDROXYVALERATE) IMMERSED IN DISTILLED WATER</td>
<td>France</td>
</tr>
<tr>
<td>94</td>
<td>64</td>
<td>Boris Eyheraguibel</td>
<td>IMPACT OF ENVIRONMENTAL CONDITIONS ON OXOBIODEGRADABLE POLYMERS DECOMPOSITION</td>
<td>France</td>
</tr>
<tr>
<td>98</td>
<td>68</td>
<td>Kahina Iggui</td>
<td>BIODEGRADATION OF PHBV NANOBIOCOMPOSITES FILMS: EFFECT OF THE CLAYS.</td>
<td>France</td>
</tr>
<tr>
<td>99</td>
<td>69</td>
<td>Henrik Petersen</td>
<td>DEVELOPMENT OF ENVIRONMENTALLY FRIENDLY PLASTICIZED PVC BY MEANS OF NANOTECHNOLOGY</td>
<td>Sweden</td>
</tr>
<tr>
<td>93</td>
<td>63</td>
<td>Mario Stein</td>
<td>DEGRADATION OF ORGANIC RADIOACTIVE WASTE AND IMPACT OF RELEASED GAS ON REPOSITORY SAFETY</td>
<td>Switzerland</td>
</tr>
<tr>
<td>100</td>
<td>70</td>
<td>Beáta Szolnoki</td>
<td>SYNTHESIS AND CHARACTERIZATION OF EPOXY RESINS DERIVED FROM D-GLUCOSE</td>
<td>Hungary</td>
</tr>
<tr>
<td>101</td>
<td>71</td>
<td>Marta-Malgorzata Targosz</td>
<td>AEROSOLS EMITTED IN POST-CRASH FIRES FROM STRUCTURAL COMPOSITE MATERIALS</td>
<td>France</td>
</tr>
<tr>
<td>103</td>
<td>73</td>
<td>Stamatina Vouyiouka</td>
<td>MECHANICAL RECYCLING OF POLY(BUTYLENE SUCCINATE) THROUGH THE REMELTING-RESTABILIZATION TECHNIQUE</td>
<td>Greece</td>
</tr>
<tr>
<td>96</td>
<td>66</td>
<td>Irena Vuković-Kwiatkowska</td>
<td>PACKAGING MATERIALS OF NEW GENERATION BASED ON PLA MODIFIED WITH POLYACRYLATES</td>
<td>Poland</td>
</tr>
</tbody>
</table>

<p>|                  | 105 | Lone Ross Gobakken | DETERIORATION OF WOOD BY MOULD AND BLUE STAIN FUNGI | Norway    |</p>
<table>
<thead>
<tr>
<th>Page</th>
<th>#</th>
<th>Presentor</th>
<th>Title</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>106</td>
<td>76</td>
<td>Andreja Kutnar</td>
<td>END OF LIFE SCENARIOS AND ENVIRONMENTAL IMPACTS OF WOOD PRODUCTS</td>
<td>Slovenia</td>
</tr>
<tr>
<td>104</td>
<td>74</td>
<td>Holger Militz</td>
<td>REACTIVE RESINS FOR WOOD MODIFICATION</td>
<td>Germany</td>
</tr>
<tr>
<td>107</td>
<td>78</td>
<td>Marko Petrič</td>
<td>WOOD COATINGS MADE OF LIQUEFIED WOOD AND SOME OTHER LIGNOCELLULOSIC MATERIALS</td>
<td>Slovenia</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>POLYMERS FOR INNOVATIVE TECHNICAL AND MEDICAL APPLICATIONS (INCLUDING POLYMER COATINGS AND OPTOELECTRONIC MATERIALS)</strong></td>
<td></td>
</tr>
<tr>
<td>114</td>
<td>85</td>
<td>Anthony Chapel</td>
<td>LUMINESCENT COMPOSITE PHOSPHORS/POLYMER: IMPACT OF RED PHOSPHOR (Υ3BO6:EU3+) ON EVA PROPERTIES AND PHOTOAGEING</td>
<td>Chapel</td>
</tr>
<tr>
<td>112</td>
<td>83</td>
<td>Isabel Dominguez</td>
<td>UNRAVELLING THE PHOTODEGRADATION MECHANISMS OF A LOW BANDGAP POLYMER BY COMBINING EXPERIMENTAL AND MODELLING APPROACHES</td>
<td>France</td>
</tr>
<tr>
<td>113</td>
<td>84</td>
<td>Boris Gorelik</td>
<td>PHOTO-STABILIZATION OF HIGHLY FILLED THERMOSET COMPOSITES</td>
<td>Israel</td>
</tr>
<tr>
<td>110</td>
<td>81</td>
<td>Annegret Jentsch</td>
<td>INFLUENCE OF TYPICAL STABILIZERS ON THE AGING BEHAVIOR OF EVA FOILS FOR PV APPLICATIONS DURING ARTIFICIAL UV-WEATHERING</td>
<td>France</td>
</tr>
<tr>
<td>109</td>
<td>80</td>
<td>Regina Jeziórska</td>
<td>POLYOLEFINES WITH ANTIMICROBIAL ACTIVITY</td>
<td>Poland</td>
</tr>
<tr>
<td>108</td>
<td>79</td>
<td>James Lewicki</td>
<td>SMART SILICONE COMPOSITES. THE SYNTHESIS, CHARACTERIZATION AND APPLICATION OF WELL-DEFINED, HIERARCHICAL PDMS/INORGANIC COMPOSITES WITH NOVEL PHYSICAL PROPERTIES</td>
<td>USA</td>
</tr>
<tr>
<td>111</td>
<td>82</td>
<td>Agnes Rivaton</td>
<td>IS THERE ANY PHOTOSTABLE CONJUGATED POLYMER FOR EFFICIENT SOLAR CELLS ?</td>
<td>France</td>
</tr>
<tr>
<td>Page</td>
<td>#</td>
<td>Presentor</td>
<td>Title</td>
<td>Country</td>
</tr>
<tr>
<td>------</td>
<td>----</td>
<td>-----------</td>
<td>----------------------------------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>119</td>
<td>P6</td>
<td>Paulo</td>
<td>INFLUENCE OF FIBER-LIKE NANOFILERS ON THE RHEOLOGICAL PROPERTIES OF POLYPROPYLENE</td>
<td>Brazil</td>
</tr>
<tr>
<td>129</td>
<td>P17</td>
<td>Rosella</td>
<td>NATURAL ANTI-OXIDANTS IMMOBILIZED ONTO CARBON NANOTUBES FOR THERMO-OXIDATION RESISTANT POLYMER-BASED NANOCOMPOSITES</td>
<td>Italy</td>
</tr>
<tr>
<td>130</td>
<td>P18</td>
<td>Rosella</td>
<td>PHOTO- AND THERMO-OXIDATIVE RESISTANCE OF NOVEL NANOCOMPOSITES BASED ON CNT-POSS HYBRID NANOFILERS</td>
<td>Italy</td>
</tr>
<tr>
<td>120</td>
<td>P8</td>
<td>Kamila</td>
<td>INFLUENCE OF TEMPERATURE, IRRADIATION, EXPOSURE MEDIA AND PRESSURE ON THE ACCELERATED OXIDATION OF POLYPROPYLENE IN AN AUTOCLAVE</td>
<td>Germany</td>
</tr>
<tr>
<td>141</td>
<td>P30</td>
<td>Roberto</td>
<td>MODIFICATIONS INDUCED BY SULPHONATION REACTIONS OF PARTIALLY CROSSLINKED PS-AA COPOLYMERS</td>
<td>Mexico</td>
</tr>
<tr>
<td>142</td>
<td>P31</td>
<td>Roberto</td>
<td>CHANGES IN SULPHONATED POLYSTYRENE-ACRYLIC ACID COPOLYMERS ADDED WITH AG AND AU NANOPARTICLES FOR THEIR USE AS MEMBRANES IN FUEL CELLS</td>
<td>Mexico</td>
</tr>
<tr>
<td>136</td>
<td>P25</td>
<td>Hynek</td>
<td>IONIC LIQUIDS AS COMPATIBILIZERS FOR EPOXY-THERMOPLASTIC BLENDS AND COMPOSITES</td>
<td>Czech Republic</td>
</tr>
<tr>
<td>139</td>
<td>P28</td>
<td>Silvia</td>
<td>MODIFICATION OF THERMOPLASTIC STARCH WITH MALEIC ANHYDRIDE OR SEBATIC ACID, BY REACTIVE EXTRUSION, FOR COMPATIBILIZING TPS/PBAT BLENDS</td>
<td>Brazil</td>
</tr>
<tr>
<td>140</td>
<td>P29</td>
<td>Silvia</td>
<td>MODIFICATION OF POLY(ACID LACTIC) WITH MALEIC ANHYDRIDE, BY REACTIVE EXTRUSION, FOR COMPATIBILIZING PLA/PBAT BLENDS</td>
<td>Brazil</td>
</tr>
<tr>
<td>116</td>
<td>P2</td>
<td>Haibo</td>
<td>NITRATION OF CYCLIC LADDER POLYPHENYLSILSESQUIOXANE</td>
<td>China</td>
</tr>
<tr>
<td>125</td>
<td>P13</td>
<td>Caroline</td>
<td>EFFECTS OF NOVEL CLASS II HYDROPHOBINS ON ENZYMATIC HYDROLYSIS OF POLYETHYLENE TEREPTHALATE</td>
<td>Austria</td>
</tr>
<tr>
<td>Page</td>
<td>Code</td>
<td>Last Name</td>
<td>First Name</td>
<td>Title</td>
</tr>
<tr>
<td>------</td>
<td>------</td>
<td>------------------</td>
<td>------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>135</td>
<td>P24</td>
<td>György</td>
<td>Kasza</td>
<td>SYNTHESIS OF HYPERBRANCHED POLYGLYCEROL BASED MACROMOLECULAR ANTIOXIDANTS</td>
</tr>
<tr>
<td>133</td>
<td>P22</td>
<td>Jana</td>
<td>Kredatusová</td>
<td>NEW STABILIZATION SYSTEMS FOR UHMWPE TESTED IN BIO-ANALOGOUS CONDITIONS</td>
</tr>
<tr>
<td>121</td>
<td>P9</td>
<td>Francesco Paulo</td>
<td>La Mantia</td>
<td>EFFECT OF THE COMPATIBILIZATION ON THE PHOTOOXIDATION OF A PA6/LDPE BLEND AND THEIR CLAY NANOCOMPOSITES</td>
</tr>
<tr>
<td>118</td>
<td>P4</td>
<td>Izabella</td>
<td>Legocka</td>
<td>COMPATIBILIZING EFFECTS OF TRIBLOCK COPOLYMER STYRENE/ISOPRENE/STYRENE IN LOW DENSITY POLYETHYLENE/POLYSTYRENE BLENDS</td>
</tr>
<tr>
<td>126</td>
<td>P14</td>
<td>Andrea</td>
<td>Maio</td>
<td>IMPROVED STABILITY OF GRAPHENE OXIDE-SILICA NANOHYBRIDS AND RELATED POLYMER-BASED NANOCOMPOSITES</td>
</tr>
<tr>
<td>127</td>
<td>P15</td>
<td>Andrea</td>
<td>Maio</td>
<td>CORRELATION BETWEEN THE CHEMICAL-PHYSICAL PROPERTIES OF CNT AND MACROSCOPIC PROPERTIES OF RELATED NANOCOMPOSITES: A STATISTICAL APPROACH</td>
</tr>
<tr>
<td>128</td>
<td>P16</td>
<td>Andrea</td>
<td>Maio</td>
<td>PHOTO-OXIDATION OF PA6/GRAHENE OXIDE FILMS</td>
</tr>
<tr>
<td>131</td>
<td>P19</td>
<td>Elisabetta</td>
<td>Morici</td>
<td>ADVANCED NANOFILLERS FOR POLYMERS: ANTIOXIDANTS IMMOBILIZED IN LAYERED CLAYS</td>
</tr>
<tr>
<td>115</td>
<td>P1</td>
<td>Maria</td>
<td>Mucha</td>
<td>COMPARISON OF PHOTOCHEMICAL AND THERMAL DEGRADATION OF POLYLACTIC ACID DOPED BY NANO SILVER</td>
</tr>
<tr>
<td>134</td>
<td>P23</td>
<td>Attila</td>
<td>Nádor</td>
<td>SYNTHESIS OF BRANCHED POLY(ETHYLENEIMINE) BASED MACROMOLECULAR STABILIZERS</td>
</tr>
<tr>
<td>137</td>
<td>P26</td>
<td>Monica</td>
<td>Nemţanu</td>
<td>STARCH MODIFICATION BY ELECTRON BEAM PROCESSING FOR USE IN THE WASTEWATER TREATMENT</td>
</tr>
<tr>
<td>124</td>
<td>P12</td>
<td>Andreas</td>
<td>Ortner</td>
<td>LACCASE FUNCTIONALIZATION OF FLAX AND COCONUT FIBRES</td>
</tr>
<tr>
<td>143</td>
<td>P32</td>
<td>Zsofia</td>
<td>Osvath</td>
<td>SMART HYBRID TEMPERATURE RESPONSIVE GELS AND POTENTIAL APPLICATION POSSIBILITIES</td>
</tr>
<tr>
<td>144</td>
<td>P33</td>
<td>Carlos</td>
<td>Scuracchio</td>
<td>DYNAMIC MECHANICAL PROPERTIES OF BLENDS GTR DEVULCANIZED BY MICROWAVES/HDPE</td>
</tr>
<tr>
<td>145</td>
<td>P34</td>
<td>Carlos</td>
<td>Scuracchio</td>
<td>RHEOLOGICAL PROPERTIES OF BLENDS GTR DEVULCANIZED BY MICROWAVES/HDPE</td>
</tr>
<tr>
<td>Paper No.</td>
<td>Session No.</td>
<td>Author(s)</td>
<td>Title</td>
<td>Country</td>
</tr>
<tr>
<td>-----------</td>
<td>-------------</td>
<td>-----------</td>
<td>-------</td>
<td>---------</td>
</tr>
<tr>
<td>138</td>
<td>P27</td>
<td>Gregor Tegl</td>
<td>IMPACT OF RECOMBINANT MYRIOCOCCUM THERMOPHILUM CELLOBIOSE DEHYDROGENASE FOR THE APPLICATION IN BLEACHING PROCESSES</td>
<td>Austria</td>
</tr>
<tr>
<td>123</td>
<td>P11</td>
<td>Krystyna Twarowska-Schmidt</td>
<td>MODIFICATION OF PLA FIBRES IN THE COURSE OF MELT-SPINNING</td>
<td>Poland</td>
</tr>
<tr>
<td>132</td>
<td>P20</td>
<td>Sarah Van Mierloo</td>
<td>STABILIZATION OF LOW TALCUM FILLED PP IMPACT COPOLYMERS</td>
<td>Netherlands</td>
</tr>
<tr>
<td>122</td>
<td>P10</td>
<td>Angelica Vlad</td>
<td>FUNCTIONAL AND FLEXIBLE NANOSTRUCTURED COORDINATION POLYMERS</td>
<td>Romania</td>
</tr>
<tr>
<td>117</td>
<td>P3</td>
<td>Chuen-kai Wang</td>
<td>ULTRADRAWING PROPERTIES OF ULTRAHIGH MOLECULAR WEIGHT POLYETHYLENES / FUNCTIONALIZED ACTIVATED NANO-CARBON AS-PREPARED FIBERS</td>
<td>Taiwan</td>
</tr>
</tbody>
</table>

**POLYMER DEGRADATION AND STABILIZATION (INCLUDING FIRE RETARDANCY AND ART CONSERVATION)**

<table>
<thead>
<tr>
<th>Paper No.</th>
<th>Session No.</th>
<th>Author(s)</th>
<th>Title</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>164</td>
<td>P56</td>
<td>Alexandra Aulova</td>
<td>PROCESSABILITY AND TIME-DEPENDENT PROPERTIES OF MECHANICALLY RECYCLED LDPE</td>
<td>Slovenia</td>
</tr>
<tr>
<td>150</td>
<td>P40</td>
<td>Mohamed Baba</td>
<td>THE INFLUENCE OF CRYSTALLINITY ON THE PHOTOOXIDATION OF SEMI-CRYSTALLINE POLYMERS</td>
<td>France</td>
</tr>
<tr>
<td>163</td>
<td>P55</td>
<td>Marko Bek</td>
<td>COMBINED EFFECT OF TEMPERATURE AND PRESSURE ON THERMO-MECHANICAL PROPERTIES OF THERMAL INSULATION MATERIAL (POLYAMIDE) FOR OFFSHORE OIL EXPLOITATION</td>
<td>Slovenia</td>
</tr>
<tr>
<td>165</td>
<td>P57</td>
<td>Gabriela Botelho</td>
<td>REPROCESSING OF POLY(LACTIC ACID): EFFECT ON PROPERTIES</td>
<td>Portugal</td>
</tr>
<tr>
<td>160</td>
<td>P52</td>
<td>Mirela Brașoveanu</td>
<td>DEGRADATION OF NATURAL POLYMERS BY ELECTRON BEAM IRRADIATION</td>
<td>Romania</td>
</tr>
<tr>
<td>161</td>
<td>P53</td>
<td>Pierre-Olivier Bussière</td>
<td>PHOTODEGRADATION OF CELLULOID USED IN MUSEUM ARTIFACTS</td>
<td>France</td>
</tr>
<tr>
<td>151</td>
<td>P41</td>
<td>Sandra Andrea Cruz</td>
<td>STABILIZATION OF POLYPROPYLENE-MONTMORILLONITE NANOCOMPOSITES WITH A METAL DEACTIVATOR</td>
<td>Brazil</td>
</tr>
<tr>
<td>156</td>
<td>P48</td>
<td>Nadka Dintcheva</td>
<td>PHOTO-OXIDATION BEHAVIOUR OF POLYSTYRENE-BLOCK-POLYBUTADIENE-BLOCK-POLYSTYRENE/CNTS NANOCOMPOSITES</td>
<td>Italy</td>
</tr>
<tr>
<td>149</td>
<td>P39</td>
<td>Esteve Ernault</td>
<td>INFLUENCE OF HARDENER ON KINETIC OXIDATION OF EPOXY NETWORKS</td>
<td>France</td>
</tr>
<tr>
<td>158</td>
<td>P50</td>
<td>Ryszard Gąsiorowski</td>
<td>INFLUENCE OF VINYL POLISILOXANES ON FLAMMABILITY AND BIODETERIORATION OF COMPOSITES FILLED WITH NATURAL FIBRES</td>
<td>Poland</td>
</tr>
<tr>
<td>Paper</td>
<td>Authors</td>
<td>Title</td>
<td>Country</td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>---------</td>
<td>-------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>P38</td>
<td>Karolina Haernvall</td>
<td>NEW ASPECTS OF ENZYME BASED DEGRADATION OF SYNTHETIC POLYESTERS</td>
<td>Austria</td>
<td></td>
</tr>
<tr>
<td>P45</td>
<td>Virginie Imholz</td>
<td>INFLUENCE OF MOLECULAR MOTIONS IN POLY(DICYCLOPENDATIENE) OXIDATION</td>
<td>France</td>
<td></td>
</tr>
<tr>
<td>P42</td>
<td>Francesco Paulo La Mantia</td>
<td>PHOTOOXIDATION AND STABILIZATION OF A SOLAR CELL ENCAPSULATING CROSSLINKED EVA</td>
<td>Italy</td>
<td></td>
</tr>
<tr>
<td>P36</td>
<td>Ziqian Li</td>
<td>STUDY OF THE SYNERGISTIC EFFECT OF ODPSS AND DOPO ON FLAME RETARDED EPOXY RESINS</td>
<td>China</td>
<td></td>
</tr>
<tr>
<td>P49</td>
<td>Elisabetta Morici</td>
<td>PHOTO-OXIDATION BEHAVIOUR AND MORPHOLOGY OF ZINC OXIDE-POSS POLYSTYRENE BASED NANOCOMPOSITES</td>
<td>Italy</td>
<td></td>
</tr>
<tr>
<td>P46</td>
<td>Stefan Oprea</td>
<td>BEHAVIOR OF POLYURETHANE ACRYLATES WITH CRUDE AND MODIFIED SOYBEAN OIL BLENDS ON THE SOIL-BURIAL BIODEGRADATION PROCESS</td>
<td>Romania</td>
<td></td>
</tr>
<tr>
<td>P47</td>
<td>Stefan Oprea</td>
<td>SYNTHESIS, PROPERTIES AND BEHAVIOR WHEN SUBJECTED TO FUNGAL DEGRADATION OF SILVER SULFADIAZINE-BASED POLYURETHANE ELASTOMERS</td>
<td>Romania</td>
<td></td>
</tr>
<tr>
<td>P54</td>
<td>Marzena Półka</td>
<td>HEAT RELEASE RATE FROM THE EPIDIAN 5 RESIN UNMODIFIED AND MODIFIED BY FIRE RETARDANTS</td>
<td>Poland</td>
<td></td>
</tr>
<tr>
<td>P51</td>
<td>Maite Rico</td>
<td>FLAME RETARDANCY AND THERMAL PROPERTIES OF A HYBRID COMPOSITE, POSS/IPP. EFFECT OF A COUPLING AGENT</td>
<td>Spain</td>
<td></td>
</tr>
<tr>
<td>P37</td>
<td>Liliana Rosu</td>
<td>ON THE PHOTODEGRADATION OF POLY(VINYL ALCOHOL) AND CELLULOSE BASED CRYOGELS</td>
<td>Romania</td>
<td></td>
</tr>
</tbody>
</table>

**POLYMERS AND ENVIRONMENT (RECYCLING, REUSE, BIODEGRADATION, BIO-BASED POLYMERS)**

<table>
<thead>
<tr>
<th>Paper</th>
<th>Authors</th>
<th>Title</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>P63</td>
<td>Sandra Andrea Cruz</td>
<td>HOLLOW FIBER LIQUID-PHASE MICROEXTRACTION AND SOLID-PHASE MICROEXTRACTION ANALYSIS FOR EVALUATION OF DECONTAMINATION EFFICIENCY IN RECYCLED PET</td>
<td>Brazil</td>
</tr>
<tr>
<td>P59</td>
<td>Gabriela Dziworska</td>
<td>POLYMER MATERIALS AND COMPOSITES PREPARED FROM PLANT BIOMASS</td>
<td>Poland</td>
</tr>
<tr>
<td>P61</td>
<td>Justyna Kozłowska</td>
<td>MODIFICATION OF THIN KERATIN FILMS BY THE ADDITION OF FISH COLLAGEN</td>
<td>Poland</td>
</tr>
<tr>
<td>Page</td>
<td>ID</td>
<td>Authors</td>
<td>Title</td>
</tr>
<tr>
<td>------</td>
<td>----</td>
<td>--------------------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>170</td>
<td>P62</td>
<td>Justyna Kozłowska</td>
<td>MODIFICATION OF THE METHOD OF COLLAGEN EXTRACTION FROM FISH TISSUES</td>
</tr>
<tr>
<td>166</td>
<td>P58</td>
<td>Elena Marlica</td>
<td>CURING REACTIONS OF EPOXIDIZED METHYL ESTERS OF CORN OIL AND THERMAL CHARACTERIZATION OF THE OBTAINED CROSSLINKED PRODUCTS</td>
</tr>
<tr>
<td>172</td>
<td>P65</td>
<td>Malgorzata Michniewicz</td>
<td>LIFE CYCLE ASSESSMENT OF INNOVATIVE FIBROUS PRODUCTS MANUFACTURED ON THE BASE OF POLI-(LACTIC ACID) PLA</td>
</tr>
<tr>
<td>168</td>
<td>P60</td>
<td>Manuel Oliveira</td>
<td>DEVELOPMENT OF ECO-FRIENDLY POLYMERIC MATERIALS FOR AGRICULTURE APPLICATIONS</td>
</tr>
<tr>
<td>174</td>
<td>P67</td>
<td>Györgyi Szarka</td>
<td>THERMAL BEHAVIOR AND STABILITY OF BLENDS OF POLY(LACTIC ACID) WITH PVC THERMOOXIDIZED UNDER MILD CONDITIONS</td>
</tr>
<tr>
<td>173</td>
<td>P66</td>
<td>Stamatina Vouyiouka</td>
<td>STUDY OF SIGNIFICANT PARAMETERS OF AUREUSIDIN ENCAPSULATION IN PLA NANOPARTICLES</td>
</tr>
</tbody>
</table>

**DEGRADATION AND PROTECTION OF WOOD PRODUCTS**

<table>
<thead>
<tr>
<th>Page</th>
<th>ID</th>
<th>Authors</th>
<th>Title</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>176</td>
<td>P69</td>
<td>Ruxanda Bodîrlău</td>
<td>STARCH/WOOD BIO-BASED POLYMER SYSTEMS - STRUCTURE AND THERMAL PROPERTIES</td>
<td>Romania</td>
</tr>
<tr>
<td>177</td>
<td>P70</td>
<td>Zvonimir Katančić</td>
<td>INTUMESCEINCE IN FIRE RETARDANCY OF WOOD-HDPE/PVC COMPOSITES</td>
<td>Croatia</td>
</tr>
<tr>
<td>175</td>
<td>P68</td>
<td>Carmen-Alice Teacă</td>
<td>INVESTIGATION OF STRUCTURAL CHANGES OCCURRED IN WOOD DUE TO CHEMICAL TREATMENT</td>
<td>Romania</td>
</tr>
</tbody>
</table>

**POLYMERS FOR INNOVATIVE TECHNICAL AND MEDICAL APPLICATIONS (INCLUDING POLYMER COATINGS AND OPTOELECTRONIC MATERIALS)**

<table>
<thead>
<tr>
<th>Page</th>
<th>ID</th>
<th>Authors</th>
<th>Title</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>179</td>
<td>P72</td>
<td>Gabriela Botelho</td>
<td>MODIFICATION OF POLY(VINYLDENE FLUORIDE-TRIFUOROETHYLENE) MEMBRANES FOR DRUG RELEASE</td>
<td>Portugal</td>
</tr>
<tr>
<td>183</td>
<td>P77</td>
<td>Ilaria Domenichelli</td>
<td>LIGHT RESPONSIVE FUNCTIONAL POLYLEFINS</td>
<td>Italy</td>
</tr>
<tr>
<td>181</td>
<td>P74</td>
<td>Andrzej Dworak</td>
<td>N,N'-DIMETHYLAMINOETHYL METACRYLATE STAR POLYMERS AS NON-VIRAL VECTORS</td>
<td>Poland</td>
</tr>
<tr>
<td>182</td>
<td>P75</td>
<td>Andrzej Dworak</td>
<td>RESISTING OF FIBRINOGEN ADSORPTION BY THE POLYETHER-BASED SURFACES</td>
<td>Poland</td>
</tr>
<tr>
<td>180</td>
<td>P73</td>
<td>Aurélien Tournebize</td>
<td>IS IT POSSIBLE TO IMPROVE THE MORPHOLOGY AND THE PHOTOSTABILITY OF P3HT:PCBM BY USING ADDITIVES?</td>
<td>Germany</td>
</tr>
<tr>
<td>178</td>
<td>P71</td>
<td>Miroslava Trchova</td>
<td>THE STABILITY OF CONDUCTIVITY OF REPROTONATED POLYANILINES AT ELEVATED TEMPERATURE</td>
<td>Czech Republic</td>
</tr>
</tbody>
</table>
PL1

PROTEIN-BASED BIOPLASTICS: AN OVERVIEW

Inmaculada Martínez¹, Pedro Partal¹, Críspulo Gallegos¹,²

Departamento de Ingeniería Química. Universidad de Huelva. Campus de “El Carmen”. 21071 Huelva, Spain; e-mail: cgallego@uhu.es
Fresenius Kabi Deutschland GmbH. Frankfurter Landstrasse 160. 61352 Bad Homburg. Germany

Keywords: Protein, Bioplastic, Rheology, Viscoelasticity, Processing, Water absorption, Controlled-release

Biopolymer materials derived from renewable agricultural resources have received increasing interest in the last decade. The main renewable sources of biopolymers are proteins, polysaccharides and lipids. The formation of protein–based materials and their final characteristics and properties depend on protein structure and structural heterogeneity, heat sensitivity, and hydrophilic/hydrophobic characteristics.

Processing of films, coatings or other protein-based materials requires three main steps: breaking of intermolecular bonds that stabilize polymers in their native forms by using chemical or physical rupturing agents; arranging and orienting mobile polymer chains in the desired shape; and, finally, allowing the formation of new intermolecular bonds and interactions to stabilize the three-dimensional network. A way of processing protein-based biomaterials is the mechanical method, or thermoplastic processing, which consists of mixing proteins and plasticizer to obtain a dough-like material, and, finally, a thermal and moulding process, which shapes the materials and gives them suitable mechanical properties to be used as substitutive materials of synthetic polymers in certain applications. In this sense, bioplastics applications include matrices for enzyme immobilization, matrices for controlled-release of active-agents, etc.

This presentation intends to give a general overview of the influence of bioplastic processing on their thermo-mechanical and release/swelling properties. With this aim, results from oscillatory shear, dynamic mechanical thermal analysis, modulated differential scanning calorimetry, thermogravimetric analysis, active components releasing rate and water absorption tests carried out on different bioplastic samples will be presented.

For example, the use of albumen or rice protein allows reducing both protein concentration and bioplastic thermosetting temperature, leading to linear viscoelastic moduli values similar to those of synthetic polymers such as LDPE and HDPE. On the other hand, lower water absorption and active-agent release rates are obtained by submitting the biomaterials to more severe thermo-mechanical treatments.

References

LIFETIME PREDICTION OF MATERIAL OF HISTORIC VALUE

Matija Strlic
Centre for Sustainable Heritage, University College London
m.strlic@ucl.ac.uk

Studies of degradation of historic polymeric materials rely on a thorough understanding of the chemistry of interactions between the environment and the materials, as is the case of any polymer. However, such studies often pose research questions, which are not in the remit of natural sciences, such as when in the future could unacceptable damage be tolerated, and what makes such damage unacceptable. This makes research of polymers of historic value particularly interdisciplinary.

Looking at a well-known historic material, paper degrades predominantly hydrolytically if the material is acidic, while oxidation dominates at pH>7. The rate of degradation can be expressed as loss of molecular weight over time, and depends on water content in paper, its acidity, and temperature. A function has recently been developed [1] based on data from more than 80 degradation experiments using real and model papers. This now allows us to conveniently map the dependence of degradation rates on storage temperature and humidity, the starting degree of polymerisation (DP) and pH of the material.

However, for lifetime prediction, experiments involving users of historic paper were necessary in order to decide what constitutes unacceptable damage. The decrease of DP with time is not an issue in itself; however, wear and tear due to use accumulates faster if the DP of paper is lower and the material more brittle. Therefore, a wear-and-tear function was developed to describe how quickly material breaks during use as it is this type of damage that is considered unacceptable to users.

Putting research into degradation of materials into context, such studies provide a possible long-term planning horizon, definition of fitness-for-purpose of materials, and enable us to use models of chemical and physical degradation to explore how expected lifetimes depend on environmental parameters and material properties. In turn, this provides guidance on how to optimise conditions of storage or display accordingly.

References
Polymer glasses show continuous densification until the equilibrium is reached. However, the achievement of equilibrium, 30°C below Tg, can take a century and 50°C below Tg the age of the universe is an insufficient length of time. Nonetheless, depending on the relative timescale, the mechanical properties of polymer-based structures show dramatic changes, below Tg. In this talk we first illustrate theoretically the way the correlation between properties change and densification can be achieved, then the reliability of the approach is verified with a series of experimental evidences. The approach helps also quantifying the residual stresses accumulation, a rather involved and underestimate phenomenon. Residual stresses can be the source of crack initiation in composite structures and may induce warping and, at nanoscale, may explain the anomalous behavior of thin polymeric films, namely the negative coefficients of thermal expansion and the dramatic variation of the glass transition temperature, Tg.
WOO D PHOTOSTABILIZATION & PROTECTION: DIVERGENT EVOLUTION & FUTURE PROSPECTS

Philip D. Evans, Stephan Vollmer, Vicente Hernandez

University of British Columbia, Centre for Advanced Wood Processing, 2900-2424 Main Mall, Vancouver, BC, V6T 1Z4, Canada: phil.evans@ubc.ca

Keywords: wood, photostabilization, weathering, additives, chemical modification, fungi

The additives that are effective at protecting synthetic polymers from photodegradation are far less effective at protecting wood from photodegradation. Wood is also degraded much more severely by water than most synthetic polymers and is also rapidly colonized and disfigured by black melanized fungi. In response to this situation, researchers in the field of wood photoprotection have explored a range of techniques for protecting wood from weathering that are seldom employed by those working in the much larger field of polymer photodegradation and protection (Evans et al. 2013, Vollmer and Evans 2013). These techniques are the focus of this paper. We describe how chemical modification of the molecular structure of wood is a more effective way of protecting wood from photodegradation than the use of additives such as UV absorbers (UVA), hindered amine light stabilizers (HALS) and micronized and nano-reflectors (Table 1).

Table 1. Properties and physical changes of chemically modified or treated yellow cedar veneers exposed to natural weathering for 35 days in Vancouver, Canada

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Veneer properties and physical changes</th>
<th>Weight losses (%)</th>
<th>Tensile strength (N/mm²)</th>
<th>Erosion (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UVA/HALS</td>
<td></td>
<td>18.9</td>
<td>7.3</td>
<td>18.5</td>
</tr>
<tr>
<td>Benzoyl chloride</td>
<td></td>
<td>2.2</td>
<td>7.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Viny benzoate</td>
<td></td>
<td>7.0</td>
<td>6.7</td>
<td>7.7</td>
</tr>
<tr>
<td>Untreated</td>
<td></td>
<td>20.7</td>
<td>4.6</td>
<td>38.6</td>
</tr>
</tbody>
</table>

Chemical modification and also hydrophobic additives (waxes and oils) can restrict the degradation of wood by water (checking and erosion), but they are less effective at preventing the colonization of wood surfaces by melanized fungi. These micro-organisms are also difficult to control with the biocides that are currently available. Hence, the development of new approaches to controlling the microbial disfigurement of wood surfaces is assuming greater importance. We also focus on this issue and describe a promising approach to controlling melanized fungi that does not rely on the use of conventional biocides. We conclude by discussing the prospects for developing photostable wood-based materials that can match the performance of synthetic polymers.

References


THE UNEXPECTED IMPORTANCE OF HUMIDITY ON THE THERMO- AND PHOTO-OXIDATIVE DEGRADATION OF POLYAMIDES

Pieter Gijsman

DSM Ahead TP, P.O. Box 6160 MD Geleen, The Netherlands, pieter.gijsman@dsm.com

Keywords: oxygen uptake, hydrolysis, weathering

It is well known that due to reactions with oxygen from the environment polymers degrade. However, as polyamides can hydrolyse besides oxygen, water can have an influence on their degradation too\textsuperscript{1,2,3}. The role of water in the thermo- and photo-oxidative degradation was determined, by performing degradation experiments in dry and humid atmospheres. It will be shown that increasing the relative humidity lead to a considerable acceleration of

![Fig. 1. Change in solution viscosity of PA6 films (50µm) due to 405 hours ageing in oxygen (O2) and nitrogen (N2) at 100% RH (in duplicate) (1)](image1)

the degradation rate of PA6 in an oxygen containing atmosphere. At temperatures between 50 and 90°C, the degradation in a humidified air environment is much faster than in an inert humidified environment (Fig. 1). Using oxygen uptake experiments it will be shown that this faster degradation is due to a higher oxidation rate of PA6 in a humid environment. Thus, water increase the degradation rate not by inducing hydrolysis of the polymer chain, but by increasing the oxidation rate as a result of an increase in oxygen permeability and chain mobility.

![Fig. 2. Discolouration (whitening) of glass fiber reinforced PA6 during accelerated weathering in dry (Arizona simulating) and wet (Florida simulating) conditions.](image2)

In the case of weathering the role of water is a different one. In this case it is not related to increasing the photo-oxidation rate. There is hardly any influence of humidity on the photo-oxidation rate of unfilled polyamides as determined with IR and UV spectroscopy. However, for glass fiber reinforced polyamides a large difference in discoloration during accelerated weathering with and without a rain cycle was observed (Fig. 2). It will be shown that in this case the role of water can be ascribed to washing away products that are formed by photo-oxidation, which leads to cracks that cause whitening of the polymer.

References

THERMORESPONSIVE POLYMER SURFACES FOR CELL SHEET CULTURE AND HARVESTING

A. Dworak, A. Utrata-Wesołek, N. Oleszko, W. Wałach, D. Szweda, M. Bochenek, B. Trzebicka

Centre of Polymer and Carbon Materials, Polish Academy of Sciences, M. Curie-Skłodowskiej 34, 41-819 Zabrze, Poland; adworak@cmpw-pan.edu.pl

Keywords: thermoresponsive surfaces, surface modification, cell sheet engineering

The temperature-responsive (thermoresponsive) polymers on the surface for cell sheet engineering have gained a considerable interest in recent years as an innovative approach to tissue regeneration based on “cell sheet technology”\(^1\). The idea of this technology assumes culturing of cells in a form of monolayers/sheets on surfaces covered with a thermosensitive polymer and their detachment by cooling the system below the phase transition temperature of the polymer. Until now, although large group of thermosensitive synthetic polymers has been developed, only poly(N-isopropylacrylamide) (PNIPAM) and its copolymers with oligoethylene glycol methacrylates were used for preparation of polymer layer efficient in cell sheet engineering\(^3\).

In this work we report the use of polymer surfaces, based on polyoxazolines and polyacrylates, for growth and controlled detachment of skin cell sheets\(^4,5\). To control the structure of polymer, controlled or living polymerizations have been applied. The thermosensitive polymers were covalently attached to modified glass or silica surface. For that purpose chemical and photochemical reactions as well as “grafting to” and “grafting from” methods were applied. The surface properties were investigated using FT IR, AFM, contact angle and ellipsometry. The thickness of the obtained polymer layers ranged between 5 ÷ 20 nm. The increase of environment temperature above the phase transition temperature of polymer-coated surfaces changed of surface thickness and philicity indicating the thermoresponsive character of obtained layers. The obtained surfaces were evaluated for the growth and harvesting of human cells. Proper choice of the polymer brushes structure makes detachment of genetically unchanged cell sheets possible by simple change of temperature, still within physiological limits. These results open a route to therapeutic applications.

This work was supported by the National Centre for Research and Development, project POLYCELL PBS1/B9/10/2012.

References

KL5

LATEST ADVANCES IN THE PHOTODEGRADATION OF NANOCOMPOSITES

Sandrine Thérias

1. Clermont Université, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, Equipe Photochimie, BP 10448, F-63000 Clermont-Ferrand, FRANCE
2. CNRS, UMR 6296, ICCF, Equipe Photochimie, BP 80026, F-63171 Aubière, FRANCE
(sandrine.therias@univ-bpclermont.fr)

Keywords: nanocomposites, photodegradation,

Finely dispersing particles in polymer matrices allow properties such as stiffness and mechanical behavior of the composite materials to be improved. Depending on the structure of the added filler, other properties can also be enhanced, such as fire resistance, gas barrier properties, thermal properties and electrical conductivity.

A tremendous literature devoted to nanocomposite materials is related to synthesis, processing and characterization of nanocomposites. Among all the papers related to nanocomposites, only few of them (less than 100) focused on photodegradation and tried to answer the question of the photooxidation. In this field of polymer nanocomposites photooxidation, the most studied nanocomposites were polymer-clay nanocomposites, mainly based on polyolefins such as PP or PE. Recently, research arose focusing on the photodegradation of nanocomposites based on other kinds of nanofillers, such as phosphors or zeolites.

Phosphor particles display an emission in the visible domain upon a UV excitation, and the luminescent polymer/phosphor nanocomposites nanocomposites can be used for eco-energetic lighting devices such as LEDs or as multifunctional coatings for organic solar cells. Considering these domains of application, this makes the photostability of the materials an important issue that merits some further consideration.

Zeolites as nanofillers are expected to improve the water barrier properties of the materials which makes polymer/zeolite nanocomposites good candidates for encapsulation of organic solar cells, The photostability of the materials and the durability of the barrier properties is then challenging for developing new applications in this domain.

It is now well admitted that in many cases, nanoparticles are likely to negatively impact the durability of the nanocomposite materials under UV-light exposure. However, the impact of nanofillers depends on the functionality of the nanoparticles and no general rules can be drawn dealing with the photostability of the nanocomposites. In this presentation, recent advances in this field will be presented.
BIODEGRADABLE POLYMERIC MATERIALS AND PLASTICS FROM RENEWABLE SOURCES & FOSSIL FUEL FEEDSTOCK: PROS & CONS

E. Chiellini

Laboratory of Bioactive Polymeric Materials for Biomedical and Environmental Applications (BIOLab), Department of Chemistry and Industrial Chemistry, University of Pisa, via Vecchia Livornese 1291, 56010 San Piero a Grado (Pi), Italy
emo.chiellini@dcci.unipi.it

Keywords: degradability, biodegradability, plastics, oxo-biodegradability

At world wide scale, the increase of human population and the connected economic growth have led to an increase in the demand for food and feed and consequently for consumable goods such as commodities based on polymeric materials convertible to plastic items by means of different processing techniques implying, among the others, bubble and casting extrusion, compression and injection molding and thermoforming.

The different plastic items during their service life are exposed to a variety of mechanical, physical and chemical weathering processes and at the end of their service life can be released in the environment in a controlled and very often in an uncontrolled manner.

In the latter case the plastic waste from conventional commodities may accumulate in the different environmental compartments and may compromise the viability of organisms at all trophic levels.

At the light of the fact that about of 80% of plastic commodities, that are holding a 40-45% share of the overall plastic consumption, is consisting of full carbon backbone polymeric materials (PE, PP, PS), in order to moderate the environmental burden bound to their recalcitrance to biodegradation in a reasonable time frame, there are two basic options to take into accounts:

i) Complete banning of plastic commodities from the market with catastrophic effects on various productive scenarios;

ii) Reengineering of full carbon backbone polymeric materials aimed at promoting their oxidation, followed by degradation to oxidized fragments vulnerable to microorganisms ubiquitous in different environmental compartments.

The last option should not interfere with the other management opportunities of plastic waste implying their recovery via mechanical recycling or incineration with energy recovery. A front of the discussed issues, the present contribution is aimed at highlighting the pros & cons of the strategies that have been adopted in order to mitigate the environmental burden of plastic waste.
FLAME RETARDANTS NANO COMPOSITES-SYNERGY EFFECT OF COMBINING CONVENTIONAL ANTPIRENES WITH NANOFILLERS ON THE LEVEL OF FLAMMABILITY OF THERMOSET RESINS

Ewa Kicko –Walczak, Grażyna Rymarz

Institute for Engineering of Polymers Materials and Dyes, Sklodowskiej-Curie55/87-100 Toruń
Plant and Polymers Department-Gliwice;POLAND
(e-mail: e.kicko-walczak@impib.pl)

Keywords: Fire retardants(FR), halogen-free FR additives, flammability of thermoset resins, test methods

The consumption of thermoset resins as a building polymers is approximately over one million tone word wide. The thermoset resins are proven construction materials for the technical and highly demanding applications of the transportation, electrical and building part industry. Heat stability, high thermal, low shrinkage, excellent mechanical properties are typical for their type of polymers. Above applications in addition to the mechanical properties also requires a good flame retardants of the materials.

This paper presents positive effect of reduced flammability of thermoset resins (usaturated polyester and epoxy resins) thanks to the use of nanocomposites containing multi-ingredient halogen-free flame retardants which combine conventional phosphorus/nitrogen modifiers interacting with nanofillers (organomodified montmorillonite, expandable graphite, nanosilica).

The flame retardancy and thermal stabilization of modified polymers has been investigated by Limiting Oxygen Index (LOI), by thermogravimetric analysis (TG); (TG-FTIR, TG-MS) and by using Cone Calorimeter (CC) method. The fine-plates, phase morphology of nanocomposites was assessed by scanning electron microscopy (SEM). A synergy effect was observed between conventional modifiers and nanofillers. We confirm that nanocomposites formation is an important concept for the flame retardants industry to enhance easily the FR properties of the products. Laminates made of modified and crosslinked polyester/epoxy resins meet requirements concerning heat, thermal stability and LOI over 28-34 % flammability, reduced 30-50% HRR and THR by CC method. No adverse impact of modification was ascertained on basic strength properties of final products.

References:
DEVELOPMENT OF POLY(LACTIC ACID) COMPOSITES REINFORCED WITH NATURAL FIBRES

Intan S. M. A. Tawakkal1, Marlene J. Cran2*, and Stephen W. Bigger1

1 College of Engineering and Science, Victoria University, PO Box 14428, Melbourne, 8001, Australia, bintimohamed.intansyafinaz@live.vu.edu.au, stephen.bigger@vu.edu.au

2 Institute for Sustainability and Innovation, Victoria University, PO Box 14428, Melbourne, 8001, Australia, marlene.cran@vu.edu.au

Keywords: composites, poly(lactic acid), natural fibre, active packaging

Over the past few decades, the sustainability of synthetic materials derived from petroleum-based sources has been widely scrutinised. As a result, industry and researchers are focusing on more environmentally-friendly alternatives. Biopolymers offer one such alternative and are described as materials derived from natural sources that have eco-friendly attributes, are technically and economically feasible, and minimise environmental impacts at their end-of-life. Biopolymers derived from starches include polyesters such as polylactic acid (PLA) and other polysaccharides and these have been widely used in packaging applications [1]. In many cases, the initial costs associated with new technologies to produce biopolymers that rival synthetically derived materials are typically high so new techniques must be employed to reduce costs without compromising material properties. The combination of natural fibres or biofillers with PLA is receiving considerable academic and commercial attention mainly for the purpose of creating materials that potentially have lower environmental impacts as well as lower production costs. In addition, PLA also provides an excellent matrix for incorporating naturally sourced additives such as antimicrobial agents in order to prolong the shelf life of packaged food products [2]. This work explores the mechanical, thermal and morphological properties of PLA composites incorporated with treated or untreated kenaf fibres together with the addition of thymol, an essential oil extract that is also a well established natural antimicrobial agent [3]. Composites of PLA incorporated with 30% w/w kenaf fibre and 10% w/w thymol were prepared and compared with control systems containing either no kenaf or no thymol. The composites containing treated fibres had significantly higher tensile strength than composites prepared with untreated fibres. Micrograph images of the fracture surface revealed better adhesion between the treated fibres and the matrix was achieved resulting in improved reinforcement of the composite. For composites containing thymol, lower tensile strength than those without thymol was observed suggesting a possible plasticizing effect of the additive. Thermal analysis by differential scanning calorimetry showed similar trends for composites with treated and untreated fibres with decreases in the glass transition temperature, melting temperature and melting enthalpy with the addition of thymol.

References


EFFECT OF NANOCLAY IN NATURAL RUBBER-NITRILE RUBBER BLENDS AND ITS EFFECT ON MORPHOLOGICAL, AND PHYSICOMECHANICAL PROPERTIES

Hanna. J. Maria¹, Sabu Thomas¹²

¹ School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills, Kottayam, Kerala, India Institution, address, hannavidhu@gmail.com
² International and Inter University Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Priyadarshini Hills, Kottayam, Kerala, India Institution, address, e-mail

Keywords: Nitrile rubber, Natural Rubber, Imiiscible, compatibilization

Nanocomposites based on polymer blends are one of the key areas of research now, due to their wide range applicability. The presence of OMt (organically modified clay) in complementing the properties of Natural rubber and / Nitrile rubber in their immiscible blends system was studied. Natural rubber / Nitrile rubber / Organoclay (NR/NBR/OMt) composites were prepared through melt compounding in a conventional two roll mill. The weight ratio of NR to NBR and the filler loading of organoclay (OMt) was varied. The morphological, and mechanical properties were studied inorder to explain the effect of nanoclay as compatibilizer. The morphological developments of the nanocomposites were analyzed through scanning electron microscopy as well as transmission electron microscopy. This revealed that the organic modification influenced the migration of OMt. The blend composition also affected the morphological evolution. The 50/50 blend composition had a higher increase in the total surface area exposed by the dispersed phase per unit volumetric space of the blend. The decrease in domain size of the dispersed phase was also found to be higher for this composition. Analysis of tensile properties showed its dependence on OMt localization and blend composition. Composite with 1 wt % OMt content showed slight improvement in tensile strength and elongation at break. This paper demonstrates the significance of the clay localization, organic modification and blend composition on the properties of the NR/NBR blends and the resultant properties.
THE INFLUENCE OF UV-IRRADIATION ON MECHANICAL PROPERTIES OF CHITOSAN CROSS-LINKED BY TANNIC ACID

Alina Sionkowska, Beata Kaczmarek, Maria Gnatowska

Department of Biomaterials and Cosmetics, Faculty of Chemistry, Nicolaus Copernicus University, Gagarin 7, 87-100 Torun, Poland

Key words: chitosan, tannic acid, cross-linking, mechanical properties, UV-irradiation

Properties of materials can be modified by cross-linking methods, physical or chemical ones [1-3]. Tannic acid is a natural compound, which can be used as chemical cross-linking agent [4]. It is non-toxic compound and can be used in biomaterials science [5].

Chitosan was used as a 1% solution in 0.5 M acetic acid. Tannic acid was added in different amounts – 2, 5, 10 and 20 wt% based on chitosan. Chitosan films were obtained by solvent evaporation from chitosan solution. Samples were irradiated by UVC light (254 nm) for 2, 4, 6 and 18 h.

FTIR analysis for chitosan (CTS) with and without addition of tannic acid (TA) before and after exposure on UV light was made. Mechanical properties were measured for chitosan films before and after UV-irradiation. Table 1 shows differences in mechanical properties of chitosan films after exposure to UV-irradiation.

Table 1. Mechanical properties of chitosan samples before and after 4h exposure to UV-irradiation.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Time of UV-irradiation</th>
<th>0 h</th>
<th>4 h</th>
<th>0 h</th>
<th>4 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTS</td>
<td>1.75±0.14</td>
<td>70.79±0.69</td>
<td>2.63±0.14</td>
<td>65.34±0.49</td>
<td></td>
</tr>
<tr>
<td>CTS_2%TA</td>
<td>2.05±0.15</td>
<td>79.28±0.53</td>
<td>1.54±0.11</td>
<td>72.66±0.63</td>
<td></td>
</tr>
<tr>
<td>CTS_5%TA</td>
<td>2.47±0.12</td>
<td>91.97±0.62</td>
<td>1.57±0.13</td>
<td>78.86±0.67</td>
<td></td>
</tr>
<tr>
<td>CTS_10%TA</td>
<td>2.82±0.13</td>
<td>93.91±0.58</td>
<td>1.62±0.09</td>
<td>88.97±0.59</td>
<td></td>
</tr>
<tr>
<td>CTS_20%TA</td>
<td>2.86±0.15</td>
<td>97.09±0.53</td>
<td>2.45±0.15</td>
<td>74.75±0.60</td>
<td></td>
</tr>
</tbody>
</table>

Degradation of chitosan, also with addition of tannic acid, can be observed on the base of FTIR spectra. Mechanical properties of chitosan films were changed after exposure to UV-irradiation. Young Modulus and ultimate tensile strength increased for chitosan films after UV-irradiation. Tannic acid used as a cross-linking agent led to modification of mechanical properties of chitosan films. The alterations of mechanical properties of chitosan films depend on the amount of cross-linking agent added to chitosan.

References
THE ROLE OF BLOCK THERMOPLASTIC RUBBER OF STYRENE-ISOPRENE-STYRENE TYPE FUNCTIONALIZED BY A BORON COMPOUND AS COMPATIBILIZER TO POLYSTYRENE/POLYPROPYLENE BLENDS

Ewa Wierzbicka, Izabella Legocka

Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland
(ewa.wierzbicka@ichp.pl, www.ichp.pl)

Keywords: chemical modification, compatibilization, polymer blends, mechanical and rheological properties

Physical mixing of polymers of various chemical structures and differing in their properties gives an opportunity to obtain totally new polymer materials which often have very unique parameters. It must be emphasized, that a wide variety of polymers with different chemical properties, such as polyolefin’s and polystyrene, are immiscible and any efforts to blend them lead to materials with weak interfacial adhesion and thus, poor mechanical performances [1-2].

The morphology, mechanical and rheological properties of a polypropylene/polystyrene 25/75 (PP/PS) blend have been determined after compatibilization with styrene/isoprene/styrene block copolymer (SIS) modified by 9-borabicyclo[3.3.1]nonane (9-BBN). The compatibilizer was synthesized by mixing SIS and 9-BBN at high temperature in the presence of initiator. The polymer compositions containing 2 or 6 % mass. of compatibilizer were prepared by using co-rotating twin-screw extruder. Mechanical properties have been investigated by tensile, flexural and impact strength testing.

PP/PS blends without compatibilizer exhibit poor mechanical properties due to the weak interaction between polyolefin and polystyrene. A substantial increase of their mechanical properties is achieved with the use of the SIS/9-BBN as a modifier. Scanning electron microscopy (SEM) results indicate a better interfacial adhesion for blends containing compatibilizer. The shape of the rheological curve of blends and very good mechanical properties of PP/PS blends with miscibility modifier prove the strengthening of this product.

References


HETEROGENEITY OF ACCELERATED PHOTOOXIDATION IN COMMODITY POLYMERS STABILIZED BY HAS: ESRI, IR, AND MICROHARDNESS STUDY

J. Pilař

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, v.v.i., 162 06 Prague 6, Czech Republic.

Keywords: commodity polymers, hindered amine stabilizers, heterogeneity of photooxidation, electron spin resonance imaging, microhardness, oxidation products, crystallinity

At the beginning of photooxidation process activation of chromophoric initiation centers present in polymer matrix by incident radiation in the range of actinic part of UV solar radiation results in generation of polymer alkyl radicals \( P^\bullet \). Local concentration of generated polymer alkyl radicals \( P^\bullet \) depends among others on the intensity of incident radiation penetrating into location of the centers, i.e. on the diffuse transmission of incident radiation through the polymer matrix. Oxidation of the primarily created polymer alkyl radicals \( P^\bullet \) is followed by consecutive formation of oxygen centered peroxyls \( POO^\bullet \) and hydroperoxides \( POOH \) involved in the oxidation chain mechanism. Hindered Amine Stabilizers (HAS) interfered in the first step with \( POOH \). Hydroxylamine species \( \text{>NOH} \) and \( \text{>NOCH}_3 \) formed are involved in the chain-breaking process by scavenging peroxyls \( POO^\bullet \). It has been accepted that formation of HAS-derived nitroxides \( \text{>NO}^\bullet \) in this step is indicative for the active participation of HAS in the stabilization process.

Thick polymer plaques made of commodity polymers (polypropylene, polyethylene, polystyrene and poly(ethylene-co-norbornene) stabilized with secondary, tertiary or NOR HAS were exposed to accelerated aging in a Weather-Ometer (WOM). Nitroxide concentration profiles along direction of the incident radiation (perpendicular to the surface of the plaques) determined by electron spin resonance imaging technique, indicate spatial heterogeneity of the photooxidation process inside the plaques. Dependence of the nitroxide concentration in a particular volume of the exposed plaque on the WOM exposure time was found to be determined by competition between generation and regeneration of the nitroxides on one side and their consumption in the process of quenching polymer alkyl radicals or at transformation into inactive products on the second side. Spatial heterogeneity of the photooxidation process was found to depend strongly on both polymer and stabilizing system.

Heterogeneity of photooxidation process in stabilized semicrystalline polymers PE and PP was confirmed by profiles of oxidation products, crystallinity and microhardness inside the plaques gained using independent microscopic-scale methods (infrared microscopy (IR) and microhardness (MH)) and by SEM micrographs.

Support by the Grant Agency of the Czech Republic project #202/09/2078 is acknowledged.

References:

NANOSTRUCTURED AND TOUGHENED THERMOSETTING SYSTEMS MODIFIED WITH PEO-B-PPO-B-PEO TRIBLOCK COPOLYMER

Laida Cano¹, Daniel H. Builes², Agnieszka Tercjak¹

¹ Group 'Materials + Technologies'. Dpto. Ingeniería Química y M. Ambiente. Escuela Politécnica/Eskola Politeknikoa. Universidad del País Vasco/Euskar Herriko Unibertsitatea (UPV/EHU), Pza. Europa 1, 20018 Donostia-San Sebastián, Spain, laida.cano@ehu.es, agnieszka.tercjaks@ehu.es.

² Department of Innovation, Andercol S.A., Autopista Norte 95-84, Medellín, Colombia, daniel.builes@andercol.com.co.

Keywords: thermosetting polymers, epoxy resin, block copolymers, PEO-b-PPO-b-PEO, AFM, TEM, mechanical properties, toughness.

Epoxy resins are one of the most widely employed thermosetting polymers due to their good mechanical and thermal properties, high chemical and corrosion resistance and low shrinkage during curing. However, their main drawback is their low toughness. The modification with block copolymers can reach an improvement in toughness as well as a microphase-separated morphology. This is why in this work the poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) (EPE) triblock copolymer was employed as modifier of a DGEBA based epoxy matrix with the aim to obtain nanostructured thermoset systems with improved mechanical properties. Different contents of a triblock copolymer up to 50 wt % were added to the matrix in order to study the influence of the content of block copolymer on the morphology and mechanical properties of the epoxy system. DSC results proved the partial miscibility of EPE triblock copolymer in the epoxy resin. The morphologies studied by AFM and TEM showed clear nanostructuration up to 25 wt % EPE content. As a result of the interactions between PEO block and epoxy resin, this block is miscible with epoxy resin and consequently PPO appeared as a microseparated phase. The addition of 5 and 15 wt % of EPE block copolymer led to a considerable improvement in the toughness (KIC) of the materials. UV-vis measurements mainly indicated a decrease in the transmittance with the increase of EPE block copolymer content.

Fig. 1. AFM phase images (1 µm x 1 µm) of a) neat epoxy, b) 5 wt % EPE/epoxy and c) 25 wt % EPE/epoxy systems.

Acknowledgements

Financial support from the Spanish Ministry of Economy and Competitiveness (MAT2012-31675) is acknowledged. L.C. thanks the Basque Government for the PhD Fellowship (PRE_2013_2_418).

References

GENERATION OF NANOCOMPOSITES BASED ON BLOCK COPOLYMER AND Fe₂O₃ NANOPARTICLES MODIFIED BY GRAFTING TO METHOD WITH PMMA-B-PCL COPOLYMER

Irati Barandiaran¹, Ariel Cappelletti², Miriam Strumia², Galder Kortaberria¹

¹ “Materials + Technologies” Group, Basque Country University, Plaza Europa 1, 20018 Donostia, Spain
² Facultad de Ciencias Químicas, Universidad de Córdoba, Haya de la Torre Esq. Medina Allende 5000, Córdoba, Argentina
irati.barandiaran@ehu.es

Keywords: Block copolymer, Fe₂O₃ magnetic nanoparticle

Nanocomposites based on block copolymer matrix and inorganic nanoparticles have received special interest in the last years [1,2]. The interest in block copolymers is principally based on its ability to self-assembly generating different nanostructures. In this way, block copolymers have been used for different applications such as microelectronics, biomedical, surfactant, nanowires and magnetic storage media. Magnetic nanoparticles have received special attention due to their properties and potential applications in many diverse fields. When dispersing nanoparticles into a copolymer matrix an important issue is their dispersion and selective placement into desired domains. In order to overcome this problem a common practice is their surface functionalization in order to increase compatibility with matrix.

The aim of this work was to disperse Fe₂O₃ magnetic nanoparticles into a PS-b-PCL block copolymer. To increase compatibility with one of the blocks of the copolymer, nanoparticles were modified by grafting a PMMA-b-PCL block copolymer to their surface. The success of modification was corroborated by means of FTIR, TGA and TEM analysis. Once nanoparticles were modified they were dispersed into a PS-b-PCL block copolymer. The effect of nanoparticle addition on the morphology of self-assembled copolymer was analyzed by AFM. It was demonstrated that nanoparticle dispersion has been improved when compared to unmodified one, being selectively located at the interfaces between both domains, without altering nanostructuring and crystallinity of block copolymer matrix.

Fig. 1. AFM phase image (3x3 μm) of PS-b-PCL block copolymer with 5 % of: a) unmodified Fe₂O₃ nanoparticles and b) surface modified ones

References
EFFECT OF PH ON VOLUME PHASE TRANSITION FOR (ACRYLAMIDE-CO-ACRYLIC ACID) COMPOSITE HYDROGEL USING BY FLUORESCENCE TECHNIQUE

Demet Kaya Aktaş1, Gürer Zeren1 and Aybars Akakıncı1

1 Istanbul Technical University, Department of Physics, Maslak 34469 Istanbul - Turkey
demet@itu.edu.tr

Keywords: Composite hydrogel, Swelling, pH, Fluorescence

Hydrogels can be defined as three-dimensional networks of polymers which can swell several hundred times in relation to their dry network mass when in contact with water or aqueous solutions [1]. Hydrogel properties depend strongly on their degree of crosslinking, the chemical composition of the polymer chains, as well as chemical and physical properties of the surrounding materials they are exposed to which vary the interactions between the network and surrounding liquids. Especially, on the basis of their dramatic swelling and shrinking behaviours, pH-sensitive hydrogels are being utilized for new potential applications [2]. In this work, we studied the effect of pH on the swelling of poly(acrylamide-co-acrylic acid) (P(AAm-co-AAc)) composite gels using by Steady-state fluorescence (SSF) technique. Disc shaped composite gels were prepared by free-radical crosslinking copolymerization of P(AAm-co-AAc). N, N'- methylenebis (acrylamide) (BIS) and ammonium persulfate (APS) were used as crosslinker and initiator, respectively. Pyranine 4 was introduced as a fluorescence probe. P(AAm-co-AAc) composite gels were dried before being used for swelling experiments. The fluorescence intensity measurements were carried out using the Model LS-50 spectrometer of Perkin-Elmer. All measurements were made at vertical position and slit widths were kept at 5 nm. Disc-shaped gel samples were placed on the walls of 1x1 quartz cells filled with different pH solutions for the swelling experiments. Fluorescence intensity of pyranine 4 was monitored during in situ swelling processes of composite gels. Emission and scattered intensity of P(AAm-co-AAc) composite gel samples were monitored during the swelling processes in different pH solutions. It can be seen that as the water uptake is increased, fluorescence intensity, Iem decreased and the scattered light intensity, Isc increased. Since the increase in Isc corresponds to increase in turbidity of the swelling gel, then we have defined corrected fluorescence intensity, “I” as Iem/Isc. It was observed that fluorescence intensity values decreased as swelling progressed. Li-Tanaka equation [3] was used to determine the swelling time constants, ς and cooperative diffusion coefficients, Dc for the swelling processes. Results were shown that swelling time constants, ς decreased and diffusion coefficients, D increased as the pH values increased.

In conclusion these results have shown that the direct fluorescence method can be used for real-time monitoring of P(AAm-co-AAc) composite hydrogel swelling process. In this method in situ fluorescence experiments are easy to perform and provide us with quite sensitive results to measure the swelling parameters.

References

ORGANIC/INORGANIC HYBRID MATERIALS BASED ON EPOXY MATRIX

Perchacz M.¹, Beneš H., Donato K.R.²

¹Department of Polymer Processing, Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Heyrovsky sq. 2, 162 06 Prague 6, Czech Republic, (perchacz@imc.cas.cz)
²Laboratory of Technological Processes and Catalysis, Institute of Chemistry, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, Porto Alegre-RS, Brazil

Keywords: epoxy; organic-inorganic hybrid, ionic liquids; sol-gel; graphene

In this study, we reported the preparation of hybrid organic/inorganic materials based on epoxy matrix. The inorganic structures were created via sol-gel process of (3-glycidoxypropyl)trimethoxysilane (GPS). Their final shape and condensation degree was directed by a choice of suitable catalytic agent. Two conventional catalysts – tin- (DBTDL) and amine-based (DABCO) – were compared with novel, imidazolium-based ionic liquids (ILs). The influence of catalyst on morphology of formed nano-objects (cycles, cages and ladders) was evaluated by means of NMR in solid state, DLS, MALDI-TOF MS, FT-IR, SEC and Raman spectroscopy.

The role of the chosen ILs as coupling agents between silica and graphene fillers was also studied in order to prepare the final organic-inorganic hybrid materials. The impact of the type of inorganic precursor and interphase interactions on final thermo-mechanical properties of O/I hybrids was determined by a set of methods including: DMTA and tensile tests, scattering methods (SAXS, WAXS), morphology evaluation (TEM, SEM) and TGA. The completely cured hybrid materials showed an improvement in rubbery modulus, toughness as well as thermal stability. At the same time the glass transition temperature remained nearly unchanged. Furthermore, the procedures enabled to prepare fully transparent bulk (massive) hybrid materials.

Acknowledgement

Financial support of the Grant Agency of the Czech Republic (project 14-05146S) is gratefully appreciated by the authors.

References


CORRELATION BETWEEN MACROMOLECULAR AND MECHANICAL PROPERTIES CHANGES DURING POLYAMIDE 11 OXIDATION

Octavie Okamba Diogo¹², Emmanuel Richaud¹, François Fernagut², Jean Guilment², Bruno Fayolle¹ and Jacques Verdu¹

¹ Arts et Métiers ParisTech, PIMM, UMR 8006 (CNRS), 151 Boulevard de l’Hôpital, 75013 Paris, France, octavie.okamba-diogo@ensam.eu

² ARKEMA, CERDATO, LEM, Route du Rilsan, 27470 Serquigny, France

Keywords: polyamide, oxidation, embrittlement, chain scission, chemicrystallization

Oxidation is responsible for the degeneration of aliphatic polyamide use properties due to their sensitivity to the presence of oxygen when exposed to moderate and high temperatures. Chain scission mechanisms occur in the amorphous phase via radical chain reactions [1] implying the reduction of molar mass and in the end, lead to embrittlement.

The present work is a study of embrittlement induced by thermal oxidation for polyamide 11 (PA11) with different initial molar mass. The test samples were films (about 70 µm thick to avoid DLO) aged under air at 110 °C. Size exclusion chromatography (SEC) and DSC measurements reveal random chain scission and chemicrystallization processes [2]. A correlation between strain at break measured at 23 °C and molar mass is assessed without initial molar mass dependency (Fig. 1). Furthermore, we will investigate the influence of tensile testing temperature on the critical molar mass (M’c) controlling the ductile-brittle transition.

Fig. 3. Strain at break (%) measured at 23 °C as a function of molar mass for PA11 films (70 µm thick) with different initial molar mass (Mn0) during air aging at 110 °C.

References


MELAMINE/PHENOL DERIVATIVES: SYNTHESIS AND POTENTIAL APPLICATION AS ANTIOXIDANTS IN POLYPROPYLINE

Jingbo Wang, Helmut Puchinger, Markus Gahleitner, Petar Doshev

Borealis Polyolefine GmbH, St. Peterstr. 25, 4021 Linz, Austria; jingbo.wang@borealisgroup.com

Keywords: Polypropylene, stabilization, antioxidant, melamine

While polyolefins are generally prone to oxidative degradation, this is even more critical for polypropylene (PP) due to its chain structure. At application temperatures and, even more so, during processing, the molecular weight will be reduced, causing a deterioration of the mechanical properties. In order to limit these phenomena, antioxidants are used in all commercial PP formulations. Various chemistries have been developed over time, among which hindered phenolic antioxidants (e.g. (Pentaerythrityl-tetrakis(3'-3',5'-di-tert.butyl-4-hydroxytoluyl)-propionate commercially available as Irganox® 1010 from BASF AG) are frequently used due to their combination of efficiency and cost. People are searching for new chemistry (meaning new molecules) or for new synergisms between existing compounds, in order to further improve the performance and / or reduce the cost.

Fig. 1. Chemical structure of investigated melamine/phenol derivatives.

Fig. 2. Chemical structure of investigated melamine/phenol derivatives.

In the current research a serious of new hindered phenol compounds carried by a triazine core were prepared in lab scale; the structures derived from internal work on melamine chemistry are shown in Figure 1. The performance of these compounds as an antioxidant of polypropylene was evaluated at a test concentration of 500 ppm with multiple extrusions at 250°C for processing stability and oven aging tests at 150°C for long-term stability. The melt flow rate (MFR) change and the discoloration of the materials as measured by yellowness index (YI) was checked after each extrusion. As summarized in Figure 2, the new compounds can be used as antioxidants for both processing and long-term stability in PP. The performance strongly depends on the chemical structure.
INVESTIGATION OF THERMO-OXIDATIVE AGING BEHAVIOR OF NBR IN OILS

Jiaohong Zhao\textsuperscript{1}, Rui Yang\textsuperscript{2,1}, Rossana Iervolino\textsuperscript{3}, Stellario Barbera\textsuperscript{4}

1 Institute of Polymer Science and Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China. Email: happyzjh123@126.com
2 Institute of Polymer Science and Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China. Email: yangr@mail.tsinghua.edu.cn
3 Engineering and Research Center, SKF B. V., Kelvinbaan 16, 3439 MT Nieuwegein, the Netherlands. Email: Rossana.Iervolino@skf.com
4 Engineering and Research Center, SKF B. V., Kelvinbaan 16, 3439 MT Nieuwegein, the Netherlands. Email: stellario.barbera@skf.com

Keywords: thermo-oxidative aging, NBR, oils, additives

NBR is widely used in automotive and petroleum industries due to its high abrasion and oil resistances. It inevitably contacts oils when it is used as seals. On one hand, oils might extract oil-soluble additives in NBR, e.g., antioxidants and plasticizers. On the other hand, some additives in oils such as extreme pressure additives might accelerate deterioration of the seals. In this article, the thermo-oxidative aging of NBR immersed in different kinds of oils was studied. The recovery from bending test showed that the samples aged in different oils had similar behavior. For the chemical changes, the samples aged in base oil are the most stable when compared with those aged in air and in full oil (the formulation of which is the base oil together with some extreme pressure additives). The oxidative reaction and crosslinking degree of samples in base oil are the lowest. The base oil serves as a good barrier and prevents oxidative reaction from going in depth. While for the samples aged in full oil, they get higher oxidative degree than that in base oil, and the crosslinking degree of them are also higher. For additives in full oil, some of them can easily be absorbed on samples and then diffused into the interior, especially for that contains N element. Some other additives can be oxidized and deposited on NBR.

References:


\textsuperscript{1} Corresponding author. Tel: +86-10-62782345. Fax: +86-10-62782345
INVESTIGATION OF NATURAL AGING BEHAVIOR OF PP/CACO\textsubscript{3} COMPOSITES\textsuperscript{*}

Jiaohong Zhao\textsuperscript{1}, Rui Yang\textsuperscript{2}, Jian Yu\textsuperscript{3}

1 Institute of Polymer Science and Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China. Email: happyzjh123@126.com
2 Institute of Polymer Science and Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China. Email: yangr@mail.tsinghua.edu.cn
3 Institute of Polymer Science and Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China. Email: yuj@tsinghua.edu.cn

Keywords: PP/CaCO\textsubscript{3}, composites, natural aging

Polypropylene (PP)/CaCO\textsubscript{3} composite is widely used in industry and daily life. The addition of CaCO\textsubscript{3} could improve the mechanical strength of PP greatly, but bring negative effect to the stability of PP. This article mainly focuses on the natural aging of PP/CaCO\textsubscript{3} composites and illuminates how fillers accelerate the aging of PP. During aging, the carbonyl indices of PP/CaCO\textsubscript{3} composites increased faster than that of pure PP as expected, and the volatile aging products were detected. The PP/nano-CaCO\textsubscript{3} composite had higher oxidation rate than the PP/micron-CaCO\textsubscript{3} composite. With CaCO\textsubscript{3} particles treated with different coupling agents, the composites showed different oxidation rates but their aging mechanism was the same. The coupling agents and CaCO\textsubscript{3} showed synergistic effect on natural aging of PP. The results demonstrated that the interfacial area of PP and CaCO\textsubscript{3} particles, together with the surface chemicals of the latter, accounted for the accelerated degradation of PP. Meanwhile, unlike commonly observed results that the tensile strength of polymer materials decreased monotonously during aging, the tensile strength of PP/CaCO\textsubscript{3} composites increased in the beginning unexpectedly and then decreased in the later stage. A vague interface of PP and CaCO\textsubscript{3} could be observed, but the carbonyl index did not increase obviously. A surface expanding experiment was designed to demonstrate that the aging of composites began from the interface, and interactions/reactions generated between PP and CaCO\textsubscript{3} particles during aging.

References:


\textsuperscript{*} Project 21274078 financially supported by NSFC.

\textsuperscript{2}Corresponding author. Tel: +86-10-62782345. Fax: +86-10-62782345
SYNTHESIS OF FUNCTIONAL BLOCK COPOLYMERS BY CONTROLED RADICAL POLYMERIZATION

M. Oliveira¹, Ana S. Abreu², P. Rodrigues¹, G. Botelho², A.V. Machado¹

1 Institute of Polymers and Composites/I3N, University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal, moliveira@dep.uminho.pt, anasofiaabreu@dep.uminho.pt, avm@dep.uminho.pt

2 Center of Chemistry, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal, gbotelho@quimica.uminho.pt

Keywords: Block copolymer, RAFT

The interest in new materials with specific properties able to respond to an external solicitation has been growing. These materials can be developed by designing block copolymer with “smart” molecular architectures capable to carry out a variety of functions. Comprising, at least, two chemically different polymer segments, block copolymer combine the properties of the both original polymers, offering the possibility to tailoring the physico-chemical and thermo-mechanical properties to obtain new engineering materials [1].

Controlled radical polymerization (CRP) techniques have been widely used for the preparation of several block polymers with controlled molecular weight, narrow polydispersity and well-defined architecture (e.g. block, gradient and graft copolymers and stars), namely the reversible addition fragmentation chain transfer (RAFT) polymerization. RAFT polymerization is arguably a versatile method due to its compatibility with a wide range of functional monomers and reaction media along with its relative ease of use.

This research work focuses on the synthesis and characterization of styrene and 4-vinylbenzoic acid copolymer (PS-b-P4VBA) by RAFT polymerization. NMR-¹H and gel permeation chromatography (GPC) evidenced that a block-copolymer was successfully synthesized.

Fig. 1. a) NMR-¹H spectrum of block-copolymer; b) molecular weight distribution of the synthesized PS MACRO RAFT and PS-b-P4VBA copolymer.

References

STUDY THE EFFECT OF MALEIC ANHYDRIDE AS COMPATIBILIZING AGENT ON FILLER-RUBBER INTERACTION, RHEOLOGICAL, MECHANICAL AND SWELLING PROPERTIES OF NR/CLAY PLATELET NANOCOMPOSITES

H. Moustafa¹, N. A. Darwish¹, F. M. Helaly²

¹National Institute of Standards (NIS), Tersa Street, El Haram, El-Giza, P.O Box 136, Giza 12211, Egypt, hesham.moustafa21@gmail.com, nadarwish@yahoo.com
²Polymers & Pigments Department, National Research Center, Dokki, Giza, Egypt, f_m_helaly@hotmail.com

Keywords: Modified clays (CEC); maleic anhydride; bound rubber content; rheological data

Natural rubber SMR20 was compounded with three levels of modified clays, 1 CEC, 2 CEC, and 4 CEC at 5 phr filler content in terms of improving its properties [1]. The essence of this work was to study the effect of maleic anhydride (MA) used as compatibilizing agent on the filler-rubber interaction (bound rubber content), rheological, mechanical, and swelling properties. The results showed that, bound rubber content of uncurative MA samples increases with increasing the modification degree of clay as compared to those without MA. This implies that filler-rubber interactions were achieved in the presence of MA because of chemical and physical bond formations. The rheological data in terms of curing time, $T_{90}$ and maximum torque, $M_{\text{max}}$ were determined and it was found that there is a long delayed onset of curing for approximately 7 min and a decrease of torque in the presence of MA as compared to that of samples in absence of MA. The tensile tests of curative samples NR/1CEC, NR/2CEC, and NR/4CEC without MA showed higher tensile values, 15.70, 15.63 and 10.96 MPa, respectively at 5 phr filler loading as compared to that of neat NR, or samples with MA. Previous work [2] reported that NR-LMR20 filled by 60 phr carbon black filler content exhibited comparable tensile values. The retardation in the curing time and the decrease in the tensile values may be due to the reaction between the accelerator (MBT) and MA which caused a suppression of the cross-linking formations within polymer chains [3]. Furthermore, the swelling measurements for curative samples with/and without MA were carried out in toluene. The results showed that samples without MA improved the swelling behavior rather than those with MA. This result is in agreement with the mechanical data discussed above.

References


INFLUENCE OF ZEOLITE PARTICLES LOADING ON THE MORPHOLOGY AND PHOTOStABILITY OF ETHYLENE VINYL ALCOHOL COPOLYMER (EVOH) NANOCOMPOSITE

Ievgeniia Topolniak1,2, Jean-Luc Gardette1,2, Sandrine Thérias1,2

1. Clermont Université, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, Equipe Photochimie, BP 10448, F-63000 Clermont-Ferrand, FRANCE
2. CNRS, UMR 6296, ICCF, Equipe Photochimie, BP 80026, F-63171 Aubière, FRANCE

Keywords: nanocomposites, photodegradation, photostability, zeolite

Nanostructured materials have been in the focus of growing research interest since decades due to their barrier property improvement comparing to the pristine polymer based materials. The present work is focused on the development and studies of new polymer nanocomposite materials based on ethylene-vinyl alcohol copolymer (EVOH), which is good candidate for packaging purposes [1]. Zeolite nanoparticles were used as filler in order to develop materials for encapsulation of photovoltaic devices. Zeolites were chosen due to their high and adjustable absorption capacity which makes them suitable to use as water scavenger for electronics in order to decrease the effect of humidity on the device performance.

The aim of this work is to optimise the nanocomposite film processing and to study the effect of zeolite particles loading on EVOH based material morphology and photostability. Two L-type zeolites of nano- and micro-scale sizes were used as fillers. The nanocomposites with 5, 10 and 20% particle additions were processed either by solution casting or by melt mixing in twin-screw extruder (TSE). Transmission and scanning electron microscopy carried out on EVOH/composites showed a homogenous distribution of the particles for the samples obtained by solution casting (Fig. 1).

Fig. 1. TEM images of EVOH/20wt% zeolite nanocomposites

The photochemical behaviour of EVOH/zeolite nanocomposites and the impact of the fillers were studied by FTIR and UV-Visible spectroscopies. It was found that zeolite loading doesn’t change the main mechanism of polymer photodegradation. However, zeolites show a prodegradant effect on EVOH photooxidation. It was found out that correlation between the nanoparticles content and the increasing of the photo-oxidation rate is linear and may be mainly caused by metal impurities present in the zeolite powders. Additionally, the characterisation of zeolite particles by TEM, FTIR and UV-Visible spectroscopies will be examined in terms of their influence on EVOH nanocomposites properties.

Acknowledgements

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2011 under grant agreement ESTABLIS no. 290022).

References

NOVEL SELF-LUBRICATING EPOXY COMPOSITES COMPRISING HYPERBRANCHED CROSS-LINKING AGENTS

Bartłomiej Bereska\textsuperscript{1,2}, Jolanta Iłowska\textsuperscript{1}, Krystyna Czaja\textsuperscript{2}, Jolanta Drabik\textsuperscript{3}, Agnieszka Bereska\textsuperscript{1,2}

1 Institute of Heavy Organic Synthesis “Blachownia”, Energetyków 9, Kędzierzyn-Koźle 47-225, bereska.b@icso.com.pl
2 Opole University, Faculty of Chemistry, Oleska 48, Opole 45-052
3 Institute for Sustainable Technologies – National Research Institute, K. Pułaskiego 6/10, Radom 26-600

Keywords: composites, epoxy resins, hyperbranched cross-linkers

Epoxy resins due to their excellent mechanical and dielectric properties along with relatively low shrinkage, high resistance to elevated temperatures and chemical media are widely used in various applications including coatings, adhesives, electronics or structural engineering. Such huge versatility of epoxy resins comes from their feasibility to undergo numerous modifications either by non-reactive fillers but also by huge array of cross-linking agents. In recent years some efforts have been undertaken to increase the flexibility of cured epoxy resins by incorporation of highly branched polymeric structures into the network [1, 2]. Hyperbranched polymers (HBPs), often referred to as starburst polymers, cascade polymers or dendrimers can be regarded as a new class of efficient polymer modifiers of thermosetting materials, including epoxy resins. Due to some advantageous properties of dendronized polymers, i.e. high degree of branching what makes them much less viscous in comparison to their linear analogues with the same equivalent molecular weight and high concentration of terminating functional groups available for the reaction with epoxy systems, this class of compounds may be an appealing class of novel curing agents.

We developed a new class of self-lubricating epoxy composites, comprising both, hyperbranched polyamines as a cross-linking agents and also complex grease [3, 4] acting as an inherent lubricant. The field of application of these new materials can be found in marine industry, forestry as well as in food industry where high risk of environment or food contamination exists. New composites exhibit great mechanical and tribological properties what makes them an excellent choice for such applications as substitute for bears or any moving elements made of steel, where severe conditions are present - high temperature, humidity and dust – and constant lubrication is needed.

Bartłomiej Bereska is a recipient of a Ph.D. scholarship under a project funded by the European Social Fund.

References
NANOSTRUCTURES SELF-ASSEMBLED THROUGH NON-COVALENT BONDING OF METAL COMPLEXES WITH LIGANDS CONTAINING SILOXANE OR SILANE FRAGMENTS

Mirela-Fernanda Zaltariov\textsuperscript{1}, Maria Cazacu\textsuperscript{1}, Angelica Vlad\textsuperscript{1}

\textsuperscript{1}``Petru Poni'' Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, 700487 Iasi, Romania

Keywords: nanostructures, hydrogen bonds, AFM, TEM, self-assembly

Our current research interest is the synthesis of new ligands containing siloxane or silane units in structure and their using in build-up metal complexes. Thus, a series of silicon-containing amine and carboxylic acids were prepared, full characterized and reacted, often in presence of pyridyl derivatives, as co-ligands with different metal salts or clusters. Either small molecules or coordination polymers were obtained which, in solid state self-assemble in structures with different functionalities through non-covalent bonds (hydrogen bonds, π-π stacking, etc.) as was proved by X-ray single crystal diffraction and spectral analysis (Fig. 1).

Fig. 1. Illustrative 2D structures obtained.

Fig. 2. (1) AFM images of manganese-containing coordination polymer (a)-phase contrast image, (b)-topographic image 2D, (c)- topographic image 2D, (2) TEM image of manganese-containing coordination polymer.

In general, these are porous being suitable for gas sorption and storage as was verified by registering the sorption isotherms. The presence in structure of the flexible bridge (i.e., siloxane) confer them adaptability to the guest molecules. The presence of metal centers (Mn, Co or Cu) confers many properties of interest such as magnetism, catalytic or/and biological activity, etc. proved by adequate measurements. Co-existence in structure of the highly hydrophobe dimethylsiloxane or dimethylsilane units and polar metal-organic fragments confer somewhat amphiphile character to the compounds which are self-assembling both in solution and in film as was emphasized by surface tension and AFM, TEM (Fig. 2) measurements, respectively. This ability is of interest for their potential application to orient other chemical species, such as biomolecules, or in catalysis [1].

Acknowledgments:

This work was supported by a grant of the Ministry of National Education, CNCS – UEFISCDI, project number PN-II-ID-PCE-2012-4-0261 (Contract 53/02.09.2013).

References

INTERACTIONS, STRUCTURE AND PROPERTIES IN Ionomer/Lignosulfonate Blends

G. Szabó,1,2, D. Kun,1,2, Zs. Horváth1,2, B. Pukánszky1,2

1 Laboratory of Plastics and Rubber Technology, Budapest University of Technology and Economics, H-1521 Budapest, Pf. 91, Hungary, bpukanszky@mail.bme.hu
2 Institute of Materials and Environmental Chemistry, Research Center for Natural Sciences, HAS, 1519 Budapest, P.O. Box 286., Hungary

Keywords: lignin, ionomer, polymer blends, structure, interfacial interactions, reinforcement

The interest in using natural resources increased considerably in recent years also in the plastics industry. Wood and lignocellulose fibers are used extensively as reinforcements in a wide variety of polymers. Lignin is also a good candidate for combining it with polymers. Lignin is produced as a byproduct in the paper and bioethanol industry; using it in value added applications would be beneficial for the industry. However, lignin is a very polar material with a large number of functional groups, thus its molecules interact with each other very strongly. The polymer cannot be melted, fused or dissolved in most solvents and it is not miscible with commodity polymers. Although several attempts have been made to blend lignin with various polymers, the properties of the blends deteriorated in most cases and especially in polyolefins. The goal of our work was to prepare polymer blends with ionomers and study interfacial interactions, structure and properties of the blends.

Two lignosulfonates produced by Burgo Cartiere SpA, Italy, with sodium (Bretax SRO2) and calcium (Bretax CRO2) counterions and three Surlyn ethylene-acrylic acid-acrylate copolymers produced by DuPont, USA, were used for the preparation of the blends. The components were homogenized in an internal mixer at 190 °C and then compression molded into 1 mm thick plates at the same temperature. Structure was characterized by SEM, while mechanical properties by tensile testing. Micromechanical deformation processes were followed by acoustic emission measurements. The originally very large particles (72 and 82 µm, respectively) of lignin broke down to very small droplets (0.35-0.85 µm) during mixing indicating strong interactions between the two components. The stiffness of the blends increased considerably with increasing lignin content, while strength varied in a wide range among the polymers, but depended only relatively slightly on the amount of lignin. The type of the lignin did not seem to influence properties, but reinforcement was inversely proportional to the ion content of the ionomer. Further study and analysis are needed to determine all correlations among the molecular characteristics of the polymer and lignin, the dispersed structure of the polymer and the properties of the blends.

Fig. 1 Effect of the ion concentration of the polymer on reinforcement in ionomer/lignin blends
EPOXY-SILICA NANOCOMPOSITE BY NONAQUEOUS SOL-GEL PROCESS

Sergii Ponyrko, Libor Matějka

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovského sq. 2, 162 06 Prague 6, Czech Republic

Keywords: Epoxy-silica hybrid, nonaqueous sole-gel process, gelation

Organic-inorganic nanocomposites have drawn a considerable attention in polymer science in last decades. Epoxy resin diglycidyl ether of bisphenol A (DGEBA) was cured with different amines including oligomeric diamines (Jeffamines), aromatic diamine dianinodiphenylmethane (DDM) and cycloaliphatic 3,3'-dimethyl-4,4'-diaminocyclohexylmethane (Laromin C260). Silica was generated in situ from the most common alkoxysilane precursor, TEOS or TMOS by using BF3MEA as an initiator. Nonaqueous solvent-free sol-gel reactions are relatively slow under these conditions thus making possible to control the silica structure evolution and to prevent a phase separation that often occurs during the fast classical “aqueous” sol-gel process [1].

The coupling agent GTMS was used to strengthen an interphase interaction by covalent bonding with an epoxy matrix. The most efficient reinforcement of the epoxy network is achieved by the combination of both TMOS and GTMS alkoxysilanes, showing synergy effects.

The structure, morphology, chemorheology, mechanical properties and thermal stability were followed by NMR, TEM, DMA and TGA.

Acknowledgement

The authors thank the Grant Agency of the Czech Republic, Project Nr. P108/12/1459 for financial support of this work.

References

ELECTRON BEAM IRRADIATION OF PVC FORMULATIONS ADDED WITH TRANSFER AGENTS

R. Benavides¹, C. García-Castañeda¹, G. Neira¹, R.M. Uribe², C. Kotzian³

¹Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna, Saltillo, Coahuila, México. roberto.benavides@ciqa.edu.mx
²Kent State University, Program en Electron Beam Technology, P.O. Box 5109, Kent, OH, USA
³Hospital Universitario, U.A.de C., Fco. I. Madero 1291, Saltillo, Coahuila, México

Keywords: PS-AA copolymers, DVB, TMPTMA

Introduction. PVC treated with ionizing radiation has a very low crosslinking yield, such that a crosslinking agent is needed. During irradiation the crosslinking monomer also suffers homopolymerization, reducing PVC crosslinking density [1]. Transfer agents are known to have control of growing chains and expected to influence crosslinking mechanism.

Experimental. An industrial PVC K=72 was used to prepare typical plasticized formulations. The polyfunctional TMPTMA was used as crosslinking agent, and lead or a synergistic mixture of Ca/Zn stereates (2/1 % w) as stabilizers; all industrial grade. Three transfer agents were added: mercaptoethanol (ME), dodecylmercaptide (DDM) and bencyl-triphenyl-phosphonium chloride (CBF). Other components of formulation were also industrial grade.

Samples were mixed in a roller mill at 150ºC, and the final samples prepared in a hot press to have 2 mm thickness. The electron beam treatment was carried out in a Dynamitron of 4.85 MeV and a K=27 kGy/(ft/min)/mA to provide a dose of 75 kGy. Characterization of irradiated samples consisted in gel percentage, spectroscopic studies with FTIR, mechanical tests using DMA, HCl evolution and Activation energy (Ea) to degradation by TGA. Flory-Rehner equation was used to calculate crosslinking density when a sample was kept under THF during 48 h and then dried during 24 h at 50ºC for obtaining soak and dried weights.

Results. Gel percentage is considerably high for irradiated material and FTIR indicate the presence of peroxide and carbonyl groups in a smaller amount to unirradiated samples, suggesting the use of such species during crosslinking. Elastic and viscous modulii are enhanced after irradiation, as measured by DMA, suggesting high tenacity, especially for the DDM agent and very similar among lead and Ca/Zn stabilized formulations.

HCl evolution showed a reduction in induction time (Ti) but activation energy (Ea) calculated using arrhenius showed an enhanced value after irradiation. Finally, crosslinking density increases for Ca/Zn formulations, except for the CBF agent, while this effect is not observed for the lead stabilized materials, as seen in Table 1.

Table 1. Crosslinking density and molecular weight between crosslinks (M’c)

<table>
<thead>
<tr>
<th>Formulations</th>
<th>% Gel</th>
<th>Crosslinking Density (mol/m³)</th>
<th>M’c (Kg/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca/Zn</td>
<td>42</td>
<td>39.81</td>
<td>32.9</td>
</tr>
<tr>
<td>Ca/Zn-ME</td>
<td>35</td>
<td>41.37</td>
<td>31.7</td>
</tr>
<tr>
<td>Ca/Zn-DDM</td>
<td>37</td>
<td>41.33</td>
<td>31.7</td>
</tr>
<tr>
<td>Ca/Zn-CBF</td>
<td>38</td>
<td>37.24</td>
<td>35.2</td>
</tr>
<tr>
<td>Pb</td>
<td>40</td>
<td>44.12</td>
<td>29.7</td>
</tr>
<tr>
<td>Pb-ME</td>
<td>35</td>
<td>43.09</td>
<td>30.4</td>
</tr>
<tr>
<td>Pb-DDM</td>
<td>37</td>
<td>42.76</td>
<td>30.6</td>
</tr>
<tr>
<td>Pb-CBF</td>
<td>29</td>
<td>39.37</td>
<td>33.3</td>
</tr>
</tbody>
</table>

References
ACCELERATED THERMAL AGEING AND MECHANICAL STRESS STRAIN RESPONSES OF FOAMED POLYSILOXANES

Mogon Patel, Anna Walmsley, Terrence Smith, Mat Robinson

Keywords: Ageing, Polysiloxanes, Mechanical, Stabilisation.

The experimental strategy and initial results from accelerated thermal ageing and mechanical testing trials on foamed polysiloxane materials (see Fig 1) will be reported and discussed in this presentation. In particular, an understanding of changes in mechanical responses and load retention properties with age is required to support engineering (FEA) codes which provide indicators of the wider impact of polymer degradation to the performance of the assembly.

These materials typically suffer from compression set and loss of load retention properties (see Fig 2) which is highlighted by a gradual shift in the stress/strain profiles along the strain axis with a corresponding reduction in the preload at a given strain. Potential strategies to stabilise the material to limit degradation will be detailed.

![Fig. 1. X-ray computer tomography image of RTV 5370 foamed polysiloxanes.](image1.jpg)

![Fig. 2: Changes in foam mechanical response with age evidence showing the deterioration in the stress required to compress the material to ~50% of initial thickness. The lines refer to age (in yr) of 0, 0.4, 0.8, 1.2, 1.6 and are represented by black, orange, green, blue, pink and light green. The arrow and box represent the specification limits.](image2.jpg)
PROCESSABILITY AND MECHANICAL PROPERTIES OF EXTENSIVELY RECYCLED HDPE

Pavel Oblak, Joamin González-Gutiérrez, Barbara Zupančič and Igor Emri

University of Ljubljana, Faculty of Mechanical Engineering, Center for Experimental Mechanics, Pot za Brdom 104, Ljubljana, SI-1125, Slovenia, cem@fs.uni-lj.si

Keywords: HDPE, mechanical recycling, processability, mechanical properties

Plastics production has continuously grown over the past decades what consequently reflects in the problem of post-consumer waste disposed into landfills, which represents long-term environmental issue. One of the most widely used solutions for waist treatment is recycling. Among several recycling methods, mechanical recycling represents one of the most common recycling procedures. During mechanical recycling material is ground down and physically reprocessed, therefore it is exposed to mechanical and thermal degradation as well as oxidation [1]. Eventually material properties do not remain the same and this represents the issue which should be considered when designing the technology and applications of the products made of recycled material. In this context, the current study deals with the investigation of the effect of extensive mechanical recycling on processability and mechanical properties of high density polyethylene (HDPE), as it is one of the most widely used plastics.

For the purpose of our research, extensive mechanical recycling of HDPE was simulated with the extrusion process, thus the material was exposed to 100 consecutive extrusion cycles. Recycled materials extruded in 1st, 2nd, 5th, 10th and every next 10th extrusion cycle (20th, 30th... 90th and 100th) as well as the non-recycled HDPE were taken to prepare the samples for further characterization with the process of gravimetrical casting [2].

Processability of virgin HDPE and its recyclates was studied during extrusion by recording the processing conditions, i.e., melt pressure and extrusion torque, while after preparation of the recyclates, we performed melt flow index measurements (MFI), small amplitude oscillatory shear tests (rheological properties), and DSC measurements of thermal properties. Further, mechanical properties in solid state were characterized in terms of hardness and modulus measured with nanoindentation, and finally, shear creep compliance was measured to characterize the materials’ time-dependence properties in solid state.

Rheological results and MFI measurements indicate significant structural changes in the material that occurred during the first 30 extrusion cycles. Those changes affect material processability which is as well supported by the recorded processing pressure and torque. On the other hand, processing did not significantly affect the thermal properties. Results on hardness and modulus show deterioration of the material mechanical properties through the process of repeating recycling. Similarly, shear creep compliance measurements shown an unfavorable effect of mechanical recycling on the time-dependent mechanical properties, particularly after the 30th extrusion cycle.

In general, it can be concluded that mechanical recycling affects HDPE processability and its mechanical properties. Therefore, these changes needs to be taken into account when designing the products made of recycled HDPE and selecting its production technologies.

References

CHARACTERIZATION OF THERMALLY, THERMO- AND PHOTO-OXIDATIVELY DEGRADED LDPE

Víctor H. Rolón-Garrido¹, Manfred H. Wagner²

Chair of Polymer Engineering/Polymer Physics, Berlin Institute of Technology (TU Berlin), Fasanenstrasse 90, D-10623 Berlin, Germany. victor.h.rolongarrido@tu-berlin.de¹, manfred.wagner@tu-berlin.de²

Keywords: thermal, thermo-oxidative, photo-oxidative degradation, MSF model, rheology

Low density polyethylene (LDPE) was thermally [1], thermo- [1,2] and photo-oxidatively [3,4] degraded (Td, TOd and POd, respectively) and mainly characterized in shear and uniaxial extensional flows. FTIR spectroscopy, GPC and the solvent extraction method were also selectively used. Linear viscoelasticity seems to be marginally affected in Td and TOd in contrast to POd. The enhanced strain-hardening observed in uniaxial experiments presents a clear evidence for long chain branching formation in the case of Td and TOd and also crosslinking in POd (Fig. 1). Details will be given about the structural modification in the different type of degradations, quantifying the non-linear data with the MSF model.

Fig. 1. Difference between the reference sample (fulfilled squares) and the 75min thermo-oxidative (empty circles) and 1 week photo-oxidative (empty triangles) degraded samples for elongational rates between 0.05 and 8 s⁻¹. Lines correspond to the linear viscoelastic start-up.

References


ON THE THERMAL STABILITY OF POLY(VINYL ALCOHOL) AND CELLULOSE BASED CRYOGENS

Cristian–Dragos Varganici, Dan Rosu, Oana Maria Mocanu (Paduraru), Liliana Rosu

Centre of Advanced Research in Bionanoconjugates and Biopolymers, “Petru Poni” Institute of, Macromolecular Chemistry, 41A Gr. Ghica-Voda Alley, 700487 Iasi, Romania, varganici.cristian@imcpp.ro

Keywords: cryogels, thermogravimetric analysis, thermokinetics, evolved gas analysis

The thermal behavior of some cellulose and poly(vinyl alcohol) based cryogels was studied by simultaneous dynamic thermogravimetry and differential scanning calorimetry in nitrogen atmosphere, up to 600°C. The isoconversional differential kinetic method of Friedman [1] and the integral one of Flynn–Wall–Ozawa [2,3] were applied to determine the global kinetic parameters values by recording thermograms at four different heating rates. The activation energy values increased with the conversion degree for all samples, suggesting a complex mechanism of thermal decomposition. Non-linear multivariate regression method was used to find the forms of the kinetic models which best fitted the thermogravimetric data and to determine the individual kinetic parameters for each stage of thermal decomposition of all studied structures. An n-th order kinetic model best described the thermal decomposition of pure PVA and cryogels, whilst the n-th order and expanded Prout-Tompkins models better described the former and latter thermal decomposition stage of pure cellulose. A coupling to a quadrupole mass spectrometer and a Fourier transform infrared spectrophotometer were applied for the evolved gases analysis. A vast number of gaseous products were identified during the thermal degradation of cryogels such as carbon dioxide, water, carbonyl and olefin structures.

Acknowledgement

Authors acknowledge the financial support of a grant of the Romanian National Authority for Scientific Research, CNCS–UEFISCDI, project number PN-II-ID-PCE-2011-3-0187.

References


ACCELERATED PHOTOAGING OF DYED TEXTILES

Dan Rosu, Cristian–Dragos Varganici, Liliana Rosu

Centre of Advanced Research in Bionanoconjugates and Biopolymers, “Petru Poni” Institute of, Macromolecular Chemistry, 41A Gr. Ghica-Voda Alley, 700487 Iasi, Romania, drosu@imcpp.ro

Keywords: cellulose fabrics, azo-triazine dyes, color modifications, photochemical stability

The structural and color modifications of cellulosic textile materials painted with four different azo-triazine dyes (Reactive Yellow 143, Reactive Orange 13, Reactive Red 183 and Reactive Red 2) were studied during 100 h UV irradiation time and at an irradiation dose up to 35000 kJ m\(^{-2}\). Structural changes during irradiation were compared by applying FTIR and UV-VIS techniques. Insignificant modification of the lightness factor (L*) values of the fabrics painted with RR-2 and RR-183 was observed. Fabrics dyed with RY-143 and RO-13 showed a darkening tendency during irradiation. This was due to accumulation of blue and green chromophores during irradiation because of photooxidation reactions on the cellulose substrate. Structural changes of dyes during irradiation led to a simultaneous hypochrome and bathochrome displacement of the absorption FTIR maxima, leading to coloring of the samples in complementary colors (blue and green). These observations were supported by changes in visible absorption spectra as a result of irradiation. A photodegradation mechanism of RY-143 was proposed, due to the other dyes structures similar photochemical behavior. UV exposure led to the partial detachment of the dyes and glucose units from the textile surfaces and dye photodegradation by C–N bond scission with destruction of azo groups and aromatic rings [1,2].

Acknowledgement

Authors acknowledge the financial support of a grant of the Romanian National Authority for Scientific Research, CNCS–UEFISCDI, project number PN-II-ID-PCE-2011-3-0187.

References


UNDERSTANDING OF CARBONYLS PRODUCTS FORMATION DURING POLYDICYCLOPENTADIENE OXIDATION BASED ON KINETIC APPROACH

Emmanuel Richaud1, Pierre Yves Le Gac2, Jacques Verdu1

1 Arts et Métiers ParisTech, CNRS, PIMM UMR 8006, 75013 PARIS, FRANCE, emmanuel.richaud@ensam.eu, jacques.verdu@ensam.eu
2 IFREMER (French Ocean Research Institute), Centre de Brest, Marine Structures Group, F-29280 PLOUZANÉ, FRANCE, pierre.yves.le.gac@ifremer.fr

Keywords: Carbonyl build up, chemical derivatization, poly(dicyclopentadiene), thermal oxidation, kinetic modeling

Polydicyclopentadiene (pDCPD) is a tridimensional hydrocarbon polymer with a high Tg (i.e. 160°C) obtained from Ring Opening Metathesis followed by a curing step. During oxidation, studied at temperature from 30 to 120°C, carbonyl build up was monitored by FTIR and NH3 treatment [1] was used in order to identify oxidation products. It was shown that both carboxylic acids and ketones are formed during pDCPD oxidation, moreover it appears that concentration ratio of carboxylic acids over ketones is higher at 30°C than at 120°C which is unexpected since carboxylic acids result from the transformation of unstable aldehydes.

A kinetic model of oxidation has been set up based on hydroperoxide titration using DSC, iodometry and SO2 treatments [2] in order to explain this unexpected behavior. This model shows that activation energy is higher for termination than for initiation which is a clear novelty compared to previous results obtained on model liquid systems or hydrocarbon polymers aged at rubbery state [3]. This behavior could be explained by the fact that oxidation occurred below Tg i.e. in a domain of low mobility where peroxo radical bimolecular combinations are diffusion controlled. Furthermore, this kinetic model has been used to explain the unexpected evolution of carbonyl products with ageing temperature and so led to a better understanding of oxidation processes in pDCPD.

References


Dóra Tátraaljai¹,², Tünde Janecska³, Péter Suba³, Enikő Földes¹,², Béla Pukánszky¹,²

¹Laboratory of Plastics and Rubber Technology, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521 Budapest, P.O. Box 91, Hungary, tatraaljai@mail.bme.hu, BPukanszky@mail.bme.hu
²Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1519 Budapest, P.O. Box 286, Hungary, foldes.eniko@ttk.mta.hu
³Tisza Chemical Group Public Limited Company (TVK), H-3581 Tiszaujváros, P.O. Box 20, Hungary, tjanecska@tvk.hu, subap@tvk.hu

Polyethylene is one of the commodity plastics applied in large quantities for its several advantageous properties (low density, transparency, water-resistance, innocuousness for human health, recyclability, and low-cost). However, the polymer has to be protected from damaging chemical reactions during processing which lead to undesired property changes. The degradation is caused by the combined effect of heat, shear and small amounts of oxygen present in the processing machine, and is initiated by the weak sites (unsaturated groups, branching points) of polyethylene. These reactions can be inhibited by the use of antioxidants. Results of our earlier research revealed that the characteristics of the polymer powder determined by the polymerization conditions, processing parameters, as well as the type and amount of antioxidants influence together the chemical reactions taking place during processing. The aim of the present work was to explore the defining characteristics of the nascent polyethylene powder which affect the properties of the polymer product processed without and with stabilizers. We studied the effect of the catalyst residues, the low molecular mass fraction, the particle size distribution of polymer powder, and the characteristics of the particles of different sizes on processing stability and the properties of product.

The results showed that although catalyst residues affect the properties of the polymer product, the amount of the low molecular mass (low polymer, LP) fraction has the most significant effect on the characteristics investigated. The concentration of unsaturated groups – which are initiating sites for degradation – is large in the low polymer fraction; consequently the number of unsaturated groups in the polymer powder increases with increasing LP content. This results in a reduced stability of the polymer and larger antioxidant consumption during processing. Most of the characteristics of polyethylene change with particle size. Molecules with smaller molecular masses dominate in small particles. These molecules contain larger number of functional groups (methyl, vinyl, vinylidene) and more catalyst residues. The chemical structure and rheological properties of the polymer processed without and with stabilizer, as well as the strength of films produced from them are controlled mainly by the characteristics of the polymer powder; processing conditions have less significant effect. The composition of the stabilizer package influences the reactions of vinyl groups, as well as the discoloration and the residual thermo-oxidative stability of the polymer.
INVESTIGATION OF THE INFLUENCE OF METAL OXIDE PARTICLES ON THE THERMAL DEGRADATION MECHANISM OF POLYAMIDE 66 AND POLYBUTYLENE TEREPTHALATE

E. Duemichen1, U. Braun1, H. Sturm1, R. Senz2, R. Kraemer3, P. Deglmann3

1 BAM Federal Institute of Material Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany, erik.duemichen@bam.de
2 Beuth University of Applied Sciences, Luxemburger Straße 10, 13353 Berlin, Germany
3 BASF SE, 67056 Ludwigshafen, Germany

Keywords: PA 66, PBT, metal oxides particles, degradation, solid phase extraction

Polyamide 66 (PA 66) and polybutylene terephthalate (PBT) are two common thermoplastic polymer systems which are used for a wide range of applications in household as well as in the automotive industry and elsewhere [1]. In the past there were only a few investigations on the influence of metals as well as their oxides or salts on the thermal degradation mechanism of thermoplastics [2-6]. Our focus is on the thermal degradation mechanism and how it is being influenced by metal oxide particles with a high surface area. Among these are Fe2O3 and two modifications of alumina (γ- and η-Alumina). Alumina is often used as carrier for other transition metals in catalytic chemistry because of its high surface [7-10]. Therefore we investigated alumina doped with CuO and Fe2O3.

For investigating the thermal degradation mechanism common analyzing techniques like DSC and thermogravimetry coupled with Fourier transformed infra red spectroscopy (TGA-FTIR) or mass spectrometry (TGA-MS) were used. These methods are only suitable to detect the main degradation products and small molecules like NH3, H2O, CO, CO2, cyclopentanone etc. For both methods it comes to an overlay of spectra of all components in the gaseous mixtures of degradation products which reach the analyzer at the same time. Therefore an exact qualification via comparison with reference spectra is difficult to achieve. A chromatographic system is needed to separate the decomposition products. A new analytic technique was developed with a solid phase extraction (SPE) coupled to the TGA. The volatile decomposition products were trapped on stirring bars coated with an adsorption material (Twister) like polydimethylsiloxane (PDMS). Afterwards these Twisters were analyzed by thermal desorption gas chromatography mass spectrometry (TDS-GC-MS). Thus, it is possible to separate the compounds and qualify the exact structure over reference spectra from MS data bases. This method has a very high sensitivity and only small amounts of polymer are needed.

Significant differences between the doped polymers could be determined. Especially doping with Fe2O3 leads to strong differences in the decomposition. All dopings lead to an increased release of CO2 and NH3 in the TGA-FTIR. Derived from that, the dopings lead to an increase of decarboxylation and deamination. With the gaseous stirring bar sorptive extraction new decomposition products could be found.

References

CHEMICAL MODIFICATION OF SPHERICAL FILLERS BY PHOSPHOROUS TO IMPROVE THE FLAME RETARDANCY OF POLYPROPYLENE

J. Courtat¹, V. Bounor-Legaré¹, R. Sonnier², P. Cassagnau¹, L. Ferry²

¹Université Lyon 1, Ingénierie des Matériaux Polymères, IMP@Lyon1, UMR CNRS 5223, Bât. EPU Lyon 1, 15 Bd. A. Latarjet, 69622 Villeurbanne Cedex, France.
julie.courtat@gmail.com, veronique.bounor-legare@univ-lyon1.fr, philippe.cassagnau@univ-lyon1.fr
²Centre de Recherche C2MA, Ecole des Mines d’Alès, 6 Avenue de Clavières, F-30319 Alès Cedex, France.
rodolphe.sonnier@mines-ales.fr, laurent.ferry@mines-ales.fr

Keywords: spherical filler, surface modification, PP, dispersion, rheology, flame retardancy

Surface modification of various spherical mineral fillers by phosphorous agents (Tm and Zm) was carried out with the aim to use these particles (10wt%) as flame retardant additive in polypropylene (PP). Indeed, phosphorous agents are good alternative to replace halogen-containing flame retardant widely used in PP [1]. Thermal and flammability properties of PP/modified fillers (PP-Tm-10%, PP-Zm-10%) was studied using TGA and PCFC and compared to those conferred by spherical pure fillers (PP-T-10%, PP-Z-10%). The combustion properties of the composites were estimated using cone calorimeter.

Fig. 1 shows that the untreated fillers induce the most significant reduction of peak of Heat Release Rate while the surface modification by phosphorous agents does not lead to the expected effect on the fire behavior of PP composite. The origin of this phenomenon was deeply studied and was related to the difference of morphology and rheological behavior between the several PP composites [2, 3].

References
SYNTHESIS OF FIRE RETARDED PA66-PA6 COPOLYMERS BY ASSOCIATION OF SOL-GEL CHEMISTRY AND REACTIVE EXTRUSION

J. Sahyoun1, V. Bounor-Legaré1, P. Cassagnau1, R. Sonnier2, L. Ferry2

1 Université de Lyon, Université Lyon 1, Ingénierie des Matériaux Polymères, IMP@Lyon1, UMR CNRS 5223, Bât EPU Lyon 1, 15 Bd A. Latarjet, 69622 Villeurbanne Cedex, France.
jihane.sahyoun@yahoo.com, veronique.bounor-legare@univ-lyon1.fr, philippe.cassagnau@univ-lyon1.fr

2 Centre de Recherche C2MA, Ecole des Mines d'Alès, 6 Avenue de Clavières, F-30319, Alès Cedex, France, rodolphe.sonnier@mines-ales.fr, Laurent.Ferry@mines-ales.fr

Keywords: PA66, sol-gel, reactive extrusion, flame retardancy, thermal degradation.

Flame retardants are classically added to the polymer matrix as additives and/or fillers. Few years ago, a new approach was developed as an alternative to this path of dispersion [1, 2, 3], and lately for improving the flame retardancy of thermoplastic polymers (PA6) [4]. The syntheses are based on hydrolysis-condensation reactions of alkoxysilanes precursors during extrusion process without adding solvents e.g. Fig. 1. This work aims to show that in situ generation of functionalized inorganic fillers during melt extrusion can be successfully exploited for enhancing the fire retardancy of a PA66 copolymer.

![Fig. 1: Synthesis of silico-functionalized fillers in molten PA66 copolymers](image)

Morphological and chemical characterization revealed the formation of these ‘hybrids’. The thermal degradation and major decomposition products were studied using TGA and TGA coupled with FTIR. Pyrolysis Combustion Flow Calorimeter and cone calorimeter were used to investigate the fire behavior. The use of organophosphorous silica precursor results in a decrease about 57% and 17% in the peak of heat release rate and total heat release respectively. The residue rate was also increased about 8% due to the char formation.

References


KINETIC MODELLING OF STABILIZER CONSUMPTION AND MOLAR MASS DEGRADATION IN NC-BASED MATERIALS

Manfred A. Bohn
Fraunhofer Institut für Chemische Technologie (ICT)
Postfach 1240, D-76318 Pfinztal, Germany, Manfred.Bohn@ict.fraunhofer.de

Keywords: nitrocellulose; degradation of nitrocellulose; molar mass degradation; stabilizer consumption; reaction kinetic description; bimolecular stabilizer reaction;

It seems that nitrocellulose (NC) will continue to survive as energetic polymeric binder and in the civilian market. With nitrocellulose stabilizers must be used to prevent it against the autocatalytic decomposition. However, the slow intrinsic decomposition cannot be prevented and therefore a slow degradation happens always, which leads to stabilizer consumption and the splitting of the NC chains. The last effect means molar mass degradation of NC. Both phenomena are irresolvable coupled. In splitting off the \( \bullet \text{NO}_2 \) radical from the nitrate ester groups R-CO-NO\(_2\) the remaining radical function written as R-C-O• stabilizes itself by molecular rearrangement of the anhydroglucopyranose ring and by splitting-off stable small molecular species. This means molar mass degradation happens by destruction of chain units and not be mere bond splitting between chain units, which is in accordance with the observed mass loss with NC.

Several kinetic descriptions of stabilizer consumption are available [1], which have proven to be acceptable applicable, but mostly in demanding a simplified model base. In other words the stabilization reaction is still a not easy to handle one in reaction kinetic terms. But a reasonable solution can be achieved by starting with the basic reaction scheme Eq.(1), which shows that the stabilization reaction is a bimolecular one.

\[
\begin{align*}
\text{NC} & \xrightarrow{k_{\text{NC}}} \text{P} + \text{NC} - \text{residue} \\
\text{S} + \text{P} & \xrightarrow{k_{\text{S}}} \text{S} - \text{P}
\end{align*}
\]

The elaboration of this relatively simple reaction scheme ends up in an equation for the bimolecular stabilizer reaction, whereby the preceeding production of P (means NO\(_2\)) from NC is included, because the concentration of P is not constant with time. The model contains therefore both reaction rate constants of the above reaction scheme, which is a general and necessary condition for correct modelling of stabilizer consumption.

Molar mass decrease of NC caused by random chain scission is describable with models based on the averaged characterizing parameters of the molar mass distribution (MMD) functions. The correct distribution function in terms of reaction kinetics is the one which counts the numbers (or mols) of polymers in the molar mass fraction and the number averaged mean molar mass \( \text{Mn} \) is the correct quantity. Based on this quantity models of random chain scission and random chain scission with chain recombination are discussed including several special cases: change of molar mass of chain element unit and the order of the reaction of chain element decomposition from zero to second order.

References

SULPHUR CONTAINING ADDITIVES FOR POLYSTYRENE: INFLUENCING THE DECOMPOSITION BEHAVIOUR IN THE CONDENSED PHASE

U. Braun 1, P. Eisentraut 1, S. Fuchs 2, P. Deglmann 2

1 BAM Federal Institute for Materials Research and Testing Unter den Eichen 87, 12200 Berlin, Germany, ulrike.braun@bam.de
2 BASF SE, GMV/F – B001, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany

Keywords: Polystyrene, sulphur, triphenylphosphate, TGA-FTIR, decomposition mechanism

It is documented in literature that a mixture of elemental sulphur and phosphorus compounds, e.g. aryl phosphates, imparts flame retardancy to polystyrene (PS) materials [1-2]. Recent research has shown that also organic sulphur compounds can play a similar synergistic role as elemental sulphur [3]. Although the role of phosphorous compounds as flame retardants is most probable flame poisoning (PS, independent of its additivation, burns without leaving residue), the synergistic mode of action of sulphur compounds as well as their interaction with the polymer matrix and/or PS decomposition intermediates is much less clear. Therefore, the scope of this work is the analysis of the thermal decomposition of this sulphur and/or phosphorous containing PS materials compared to the pure polymer.

The thermal decomposition behaviour of polystyrene (PS), containing various sulphur and triphenyl phosphate (TPP) was investigated, using thermogravimetry, coupled with Fourier transform infrared spectroscopy (TGA-FTIR). It was found that the additives influence the decomposition process of the polymer in condensed phase, resulting in a decreased styrene monomer formation and increased styrene oligomer derivatives. Via reference measurements with binary mixtures it was found that the presence of sulphur additives influences the radicalic decomposition process of PS.

References
MELAMINE INTEGRATED METAL PHOSPHATES IN THE FLAME RETARDANCY OF POLYAMIDE-66

Anil D. Naik,1 Gaëlle Fontaine,1 Fabienne Samyn,1 Xavier Delva,2 Jérémie Louisy,2 Séverine Bellayer,1 Yann Bourgeois,2 and Serge Bourbigot1

1ISP/UMET – UMR/CNRS 8207, Ecole Nationale Supérieure de Chimie de Lille (ENSCL), Avenue Dimitri Mendeleïev – Bât. C7a, BP 90108, 59652 Villeneuve d’Ascq Cedex, France.
2Floridienne Chimie, 12 Quai des Usines, 7800 Ath, Belgium.
Email: adnaiklin@gmail.com

Keywords: Flame retardancy, Polyamide-66, Melamine poly(aluminum phosphate), Safire®200

Polyamides comprise the largest family of engineering polymers in consumer market with wide range of applications. But its technical utility is restricted due to its inherent flammability [1]. Recently [2] an integrated multicomponent molecule, Melamine-poly(aluminum phosphate) (Safire®200), was developed and along with aluminium phosphinate it is found to act synergistically in the flame retardancy of glass fiber reinforced polyamide-66 [2,3]. We have prepared and characterised novel formulations and we have studied their properties. Performance tests like UL-94, glow-wire tests, and cone calorimetry were carried out. Formulations containing 15% of additives loading are found to achieve V0 rating according to UL-94. There is considerable reduction (up to 80%) in the peak of heat release rate (pHRR) obtained from cone calorimetry with significant intumescence behavior. A multimodal action is assumed from multi-component Safire®200 in the reinforcement of polyamide-66 and a detailed investigation is undertaken to elucidate their mode of action. The strategy was to characterize different chemical species generated at different stages of their decomposition under a fire scenario following HRR curve. The species generated in the condensed phase were studied by spectroscopy (FTIR, solid state NMR), X-ray powder diffraction and microscopy (SEM, EPMA, optical microscope). TGA coupled FTIR, and pyrolysis gas chromatography mass spectrometry (Py/GC/MS) were utilized to investigate chemical species released in the gas phase. Flame retardancy mechanism is investigated based on the identification of the chemical species in both gas and condensed phases. Their contributing role in flame retardancy is understood and it will be presented in the talk.

References

DEPTH-RESOLVED CHARACTERISATION OF CHEMICAL COMPOSITION AND LIGHT ABSORPTION IN A WEATHERED POLYESTER-URETHANE CLEARCOAT

K.N.S. Adema¹, H. Makki, E.A.J.F. Peters, J. Laven, L.G.J. van der Ven, R.A.T.M. van Benthem, G. de With

¹ Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, Den Dolech
E-mail: k.n.s.adema@tue.nl

Keywords: photodegradation, polyester-urethane coatings, FTIR spectroscopy, UV-VIS spectroscopy

Polyester-based resins are good candidates for outdoor coating applications because they combine good mechanical properties with good stability against weathering. The latter is particularly true for resins based on isophthalic acid (IPA) [1-3]. Despite the practical relevance of these materials, they are not very often selected as the topic of weathering studies, due to their complicated photo-oxidation chemistry and the long exposure times required. In this study, we expose coatings based on poly(neopentylisophthalate), cross-linked to a polyester-urethane, in artificial weathering equipment and follow the changes in chemical composition and light absorption by FTIR and UV-VIS spectroscopy, respectively. Because coatings often degrade in a spatially inhomogeneous fashion (especially in the depth dimension), both analyses are tuned as to provide depth-dependent information. For the FTIR analysis, a depth-resolved measurement method is employed by combining FTIR-ATR microscopy with a depth gradient that is introduced in the coating after degradation (see Fig. 1.). For the UV-VIS analysis, samples with varied coating thicknesses are characterised in a transmission measurement and analysed with a newly developed model that allows for interpretation of the light absorption at different coating depths. The results of the FTIR and the UV-VIS measurements are interpreted and related in the context of photodegradation. It should be emphasised that the analysis methods developed in this work can be applied more generally in weathering studies on polymer coatings.

Fig. 1. Schematic of the sample preparation procedure prior to FTIR-ATR microscopy. A depth gradient x(z) allows for determining an FTIR-ATR line scan (red arrows) at different coating depths.

References


SYNTHESIS AND APPLICATION OF ORGANOPHOSPHORUS FLAME RETARDANTS

A. Bereska¹, P. Kafarski ², B. Bereska¹, B. Tkacz¹

1 Institute of Heavy Organic Synthesis “Blachownia”, Kędzierzyn-Koźle, Opole University, Opole, Poland, bereska.a@icso.com.pl
2 Wrocław University of Technology, Wrocław, Poland, pawel.kafarski@pwr.wroc.pl

Keywords: flame retardants, epoxy resins, phosphates

Epoxy resins, due to their unique properties, constitute one of the most versatile group of polymers. However, like large majority of polymers, this kind of material suffers from poor fire resistance [1,2]. Transportation (automotive, trains, military and commercial aircrafts), electrical and electronics (printed writing boards, semiconductors, encapsulation), constructions and furnishing elements are the main fields where fire retardancy of epoxy resins is required. Because investigations on thermal degradation are crucial for understanding flame retardancy mechanism and further designing of new materials, the influence of two novel phosphate flame retardant mixtures of bisphenol A alkylphenyl phosphates on fire retardancy and thermal stability of epoxy resin at different incorporation levels were studied. Organophosphorus compounds are believed to remove flammable particles, reduce the energy of the flame in the gas phase and form a protective carbonaceous layer on the surface of the polymer [3]. Thus, combustion behavior, decomposition pathway, thermal and thermooxidative degradation properties of the epoxy resin containing phosphate flame retardants were assayed by limiting oxygen index, vertical burning test (UL-94) and cone calorimeter tests, thermogravimetric analysis and thermogravimetry coupled with Fourier transform infrared spectroscopy. The application of both phosphate mixtures amounting 20 % in epoxy resin resulted in satisfied oxygen index (30-33 %) and UL94 V2. The peak of heat release, determining fire propagation, was strongly reduced by about 50%. Both, condensed and gaseous phase action of flame retardants is proposed to be the flame retardancy mechanism of used phosphates in epoxy resin.

References:

**FIRE RETARDANCY OF A NEW POLYPOLYPROPYLENE-GRAFTED STARCH**

R. Dupretz\(^1\), G. Fontaine\(^1\), S. Bourbigot\(^1\)

1 ENSCL, UMET R2Fire UMR CNRS 8207, Cité Scientifique - Bât C7 - BP 90108
59652 Villeneuve d'Ascq Cedex – France

*Keywords: Gaialene, biobased, intumescence, polymer, fire retardancy*

Reaction to fire of several intumescent Gaialene (Gaialene is a polypropylene-grafted starch) was investigated by mass loss cone calorimeter (MLC). After screening different intumescent ingredients, formulations exhibiting the most promising results were optimized by a design of experiments using MLC, UL-94, and limiting oxygen index (LOI) tests as response. It is shown that the conventional ammonium polyphosphate (APP) used alone at 30 wt% loading provides the best results: 60% reduction of the peak of heat release rate, high LOI (30 vol% O\(_2\)) and UL-94 V0 ranking at 1.6 mm (V2 at 0.8 mm) [1].

Mechanisms of fire retardancy were then investigated by thermogravimetric analysis coupled with Fourier transform infrared gas phase analysis, by pyrolysis/gas chromatography/mass spectroscopy, by rheology, and by solid-state nuclear magnetic resonance (Figure 1). It was shown that phosphoric acid released upon fire acts in solid phase by catalyzing the degradation of starch, enhancing the development of an intumescent shield protecting the polymer [2]. A complete mechanism of action will be discussed in the talk.

![Figure 1](image)

**Fig. 1:** a: MAS CP/DD \(^{13}\)C NMR spectra of non-treated and heat-treated G, b: general hexose structure

**References**


OXYGEN DIFFUSION THROUGH POLYMERS AT ELEVATED TEMPERATURE

M. Celina, A. Quintana, N. Giron

Sandia National Laboratories, Materials Characterization and Performance Dept. 1819, Albuquerque, NM 87185, USA

Keywords: Oxidative polymer degradation, oxygen transport, materials characterization

Thermal performance of polymers and degradation under oxidative conditions depends on oxygen permeation. Prediction of spatially dependent polymer degradation with DLO models or related degradation mechanistic kinetic models for lifetime extrapolations, require input of oxygen diffusivity, solubility, or overall permeability at elevated temperature. Unfortunately, such data are not always available and basic physical transport measurements can be convoluted by ‘reactive chemistry’ loss of oxygen. Often estimations are made from indirect measurements or theoretical approaches. This presentation will focus on the optimization of experimental approaches and data extraction, which can now be applied to characterize thin films of low permeable polymers. Checks and corrections for oxidative chemistry during the experiment can be accommodated. The $O_2$ permeation features of a few epoxy thermo-set materials, Kapton, and polypropylene between 25 and 140°C were investigated with time-dependent flux measurements and are being compared to offer data, which so far have not been available in the literature. Interestingly, the glass transition of Epon 828/D230 epoxy at ~95°C has a significant effect on the permeability, but not the diffusion constant in an Arrhenius plot.

Fig. 1: $O_2$ permeability and diffusivity for a polyether amine cured epoxy system.

Acknowledgments

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under Contract DE-AC04-94AL85000.

Submitted for oral presentation at the MODEST Potoroz meeting, Aug. 31 – Sept. 4 2014.
THERMO-OXIDATIVE DEGRADATION OF XPE AND PVC USED IN ELECTRICAL INSULATION

Tetiana Salivon¹,², Xavier Colin¹, Johann Grandvuillemin²

1 Laboratory PIMM, ARTS ET METIERS ParisTech, 151 Boulevard de l’Hôpital, 75013 Paris, France,
tetiana.salivon@ensam.eu, xavier.colin@ensam.eu
2 PSA Peugeot Citroën, Electrical Electronics Design Department, Technical Center of Vélizy-Villacoublay,
Route de Gisy – 78140 Vélizy-Villacoublay, France, tetiana.salivon@mpsa.com,
johann.grandvuillemin@mpsa.com

Keywords: Electric cable insulation, PVC, XPE, Thermo-oxidative degradation, Dielectric properties

Polymers are widely used as insulating materials due to their excellent dielectric and mechanical properties, and their relatively low cost. PVC and XPE are one of the most used materials for this application in automotive industry. Insulating materials undergo heating by Joule effect while cable is in operation. The temperature factor accelerates the oxidative degradation and causes the premature loss of their use properties.

PVC and XPE insulators under study have been especially developed for the automotive industry. PVC is plasticized by phthalate and filled by carbon black and talc. XPE is obtained by electron beam irradiation of a low-density PE of 8% crystalline ratio, stabilized by Irganox 1010 and filled by chalk and magnesium hydroxide. Both insulating materials have been cut into slices of some hundreds of micrometers before physico-chemical analysis.

Several analytical techniques have been used to monitor the polymer degradation at both the molecular and macromolecular scales: Stabilizer depletion (i.e. diffusion, evaporation and chemical consumption) by OIT measurement and FTIR spectroscopy in XPE; Plasticizer depletion (i.e. diffusion and evaporation) by ATG, FTIR spectroscopy and DSC in PVC; Formation of oxidation products by FTIR spectroscopy in both polymers; Chains scissions and crosslinking by rheometry in PVC and swelling in an adequate solvent in XPE. The consequences of these modifications on the macroscopic behavior have been evaluated by dynamic dielectric spectrometry (measurement of dielectric constant and loss angle) and uniaxial tensile testing (elongation and strain at break).

After having discussed the main experimental results, we will strive to build fundamental structure/property relationships for well understanding and predicting the macroscopic behavior at long term of both insulating materials. In particular, the changes in dielectric properties will be connected to the modification of side functional groups, i.e. of polymer polarity [1]. In contrast, the changes in mechanical properties will be related to the decrease in average molecular mass (for linear PVC) or concentration of elastically active chains (XPE network) due to oxidative chain scissions [2].

References


A MULTI-SCALE SIMULATION APPROACH TO STUDY THE WEATHERING OF POLYESTER-URETHANE COATINGS


Laboratory of Materials and Interface Chemistry
Eindhoven University of Technology, Eindhoven, The Netherlands
e-mail : h.makki@tue.nl

Chemical degradation of polymer coatings via a photo-oxidative pathway, that is photodegradation, results in physical changes which eventually lead to failure of the material. Photodegradation processes of polymer coatings involve different cooperative events; absorption of photons, diffusion of oxygen and water, chain scission, cross-linking, etc. Despite considerable research effort, a complete explanation of all the effects that play a role in this process has not been achieved yet. Extensive experimental studies have been conducted in order to elucidate the mechanisms of photo-oxidation of several coatings. Most of these studies indicate a huge variety of chemical reactions which strongly depend on many different parameters such as the presence of oxygen and water, the wavelength of the radiation, the internal and external stresses in the material.

Using a multi-scale simulation, we study the changes in chemical, physical and mechanical properties of a model polyester-urethane coating during degradation. This simulation consists of different methods in order to cover a wide range of the time and length scales involved in changing properties due to photodegradation. A coarse-grained molecular simulation has been used to build up the initial network structure of the material. By coupling a kinetic Monte Carlo simulation to a Dissipative Particle Dynamics method, a novel simulation approach has been developed that makes it possible to take into account chemical and physical pathways of the photo-degradation process. In the end, several Molecular Dynamics simulations have been performed in order to compute number of thermo-mechanical properties of the material during the photo-degradation process.
KINETIC ANALYSIS OF THE THERMAL DEGRADATION OF PEEK

E. Courvoisier, X. Colin

Arts et Métiers ParisTech, PIMM, 151 boulevard de l’Hôpital, 75013 Paris, France

Keywords: PEEK, thermal ageing, chain scissions, crosslinking, thermal properties

Poly(ether ether ketone) (PEEK) is an aromatic semi-crystalline thermoplastic displaying high thermo-mechanical performances (e.g. Tg ≈ 150°C and Tm ≈ 340°C) and chemical resistance to common solvents such as acetone, toluene, ethyl acetate, etc. That is the reason why this polymer is now considered as matrix of carbon fibers reinforced composite materials for various applications.

Thermal degradation of PEEK has been investigated by several authors at high temperature essentially in melt state [1] [2] [3] [4], but rarely in rubbery state [4] [5] and never in glassy state. Its structural modifications have been evidenced at different scales by a limited number of analytical techniques, in particular: chemical composition by FTIR spectrometry, macromolecular architecture by GPC and rheometry, and crystalline morphology by DSC. In the 320-440°C temperature range, it was evidenced that the partial instability of PEEK results in the rupture of ether and carbonyl linkages thus giving macro-radicals. The coupling of these radicals leads to a predominant crosslinking process both in nitrogen and air, thus modifying the macromolecular architecture and crystalline morphology of PEEK.

The objective of the present communication is to investigate the thermal degradation kinetics of PEEK from liquid (T ≈ 440°C) to glassy state (T < 150°C), in order to respond to frequently asked questions: Does the thermal degradation kinetics of PEEK obey a relatively simple law (e.g. Arrhenius law) throughout the temperature range under study? Should we expect discontinuities in the corresponding Arrhenius graph due to the presence of two physical transitions (Tg and Tm)? Are these discontinuities of the first or second order? Indeed, it is suspected that both transitions (mainly Tg) affect the molecular mobility in amorphous phase and thus, induce a sudden change in the reaction rates involving low concentrations of reactive species (in particular, termination rates of macro-radicals).

Two grades of PEEK with different molecular masses have been supplied as pellets. Films of about 50 µm thick were processed by compression molding at 370°C under 10 MPa during 4 min. Their thermal degradation has been monitored by three complementary analytical techniques (i.e. FTIR spectrophotometry, rheometry and DSC) after exposure between 120 and 320°C under 0 and 10 MPa of oxygen pressure. Two ageing indicators — induction time ti and maximal degradation rate rm — have been determined for each physico-chemical quantity under study and plotted in Arrhenius graphs to be compared to a compilation of literature data. A kinetic model will be proposed to predict these changes of ti and rm in function of temperature and oxygen partial pressure, and answer the above questions. This model will be derived from a radical chain reaction and coupled with well-known structure/Tg and Tm relationships established by Flory in the 1950s [6] [7], to access the thermal properties.

References

A GENERAL KINETIC MODEL FOR THE PHOTOTHERMAL OXIDATION OF POLYPROPYLENE

A. François-Heude\textsuperscript{1,2}, E. Richaud\textsuperscript{1}, E. Desnoux\textsuperscript{2}, X. Colin\textsuperscript{1}

1 PIMM, Arts et Métiers ParisTech, 151 boulevard de l’Hôpital, 75 013, Paris, France
2 DETC-A, Renault, 1 rue du Golf, 78 288, Guyancourt, France

Keywords: Polypropylene; Photothermal oxidation; Kinetic modeling; Photochemistry

A general kinetic model for the photothermal oxidation of polypropylene has been derived from the basic auto-oxidation mechanistic scheme in which the main sources of radicals are the thermolysis and photolysis of the most unstable species, i.e. hydroperoxides:

\begin{align*}
\text{Thermolysis} & \quad \delta \text{POOH} \rightarrow \alpha \text{P}^\bullet + \beta \text{PO}_2^\bullet \quad (k_1) \\
\text{Photolysis} & \quad \text{POOH} + h\nu \rightarrow 2\text{P}^\bullet \quad (k_i = \Phi \cdot J_{\text{POOH}})
\end{align*}

where \(\alpha\), \(\beta\) and \(\delta\) are stoichiometric coefficients accounting for the reaction molecularity, and \(J_{\text{POOH}}\) corresponds to the UV-light energy absorbed by the photosensitive species, whose calculation procedure has been given elsewhere \cite{1} according to the quantum theory.

The validity of this model will be checked for a wide range of temperatures and UV-light sources (Fig. 1). It will be shown that it gives access to the global changes in concentration of: (i) primary (hydroperoxides) and secondary (carbonyls) oxidation products, (ii) double bonds, (iii) chains scissions and crosslink nodes, but also in weight and number average molecular masses. These results are in full agreement with the photolysis results reported by Carlsson and Wiles in the 70’s in reference papers \cite{2, 3}. However, the model seems to be only valid for UV-light energies equivalent to about 10 suns as upper boundary, which could be due to multiphotonic excitations or chromophores photosensitization (i.e. termolecular photo-physical reactions), both enhanced at high irradiances.

Fig. 1: Simulation of iPP photothermal oxidation in Weather’OMeter at 64°C (a and b) and SEPAP 12-24 at 60°C (c and d). Symbols: experimental data: ◆ hydroperoxides, ■ carbonyl products, ▲ weight and ● number average molecular masses. Lines: kinetic modeling.

References

\cite{2} Carlsson DJ, Wiles DM. Macromolecules, 2, 1969, pp. 587-97 and 597-606;
47

ORIENTED POLYMER FIBRES FOR IMPROVING THE FLAME RETARDANT EFFICIENCY OF INTUMESCENT ADDITIVE SYSTEMS

Katalin Bocz¹, Dániel Vadas¹, Ákos Kmetty²,³, Tamás Bárány²,³, György Marosi¹

1 Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary, kbocz@mail.bme.hu
2 Department of Polymer Engineering, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary
3 MTA–BME Research Group for Composite Science and Technology, Műegyetem rkp. 3., H-1111 Budapest, Hungary

Keywords: self-reinforced PP composites, flame retardancy, intumescence, orientation

Recently, significantly enhanced flame retardant efficiency of common ammonium polyphosphate based intumescent system was found in self-reinforced polypropylene (PP) composites [1]. In this study, the observed novel flame retardant synergism evinced between intumescent additive system and highly oriented polymer fibres [2] has been investigated both in PP fabric reinforced, film-stacked composite sheets and in short-fibre reinforced, injection moulded all-PP composites.

After comprehensive mechanical characterization (tensile tests, impact tests and DMA analyses), the ignitability and combustion behaviour of the two types of flame retarded self-reinforced composites were monitored. The results were compared to simple melt compounded flame retardant compounds of identical low (up to 15 wt%) additive contents. SEM and EDS analyses supported the different intumescent mechanism of each kind of samples to be understood, while the structure and character of the (after combustion) obtained charred residues were examined by compression tests. Considering the results of all the applied testing methods, the complex picture of the mechanism behind the enhanced flame retardant efficiency in self-reinforced composites could be clarified. The observed outstanding efficiency is explained by the beneficial physical cooperation between the intumescent, i.e. expanding structure, and the shrinking of fibres. Such system, exposed to heat, forms charred surface layer of special, compact structure resulting in effective fire extinction.

It was concluded that the embedding of additive-free, highly stretched (oriented) fibres into the polymer matrix can basically change the burning behaviour (ignitability, char forming process, migration effects, etc.) of a flame retarded polymer system. It is prospected that high amount of flame retardant additives could be spared this way, and by this means a more cost-effective flame retardancy of polymers can be realized in the near future.

References

INVESTIGATION OF THERMAL STABILITY AND FLAMMABILITY OF PMMA COMPOSITES BY COMBINATION OF APP WITH ZRO$_2$, SEPIOLITE OR MMT

Q. Lin $^{a, *}$, H. Vahabi $^a$, C. Vagner $^{a,b}$, M. Cochez $^a$, M. Ferriol $^a$

$^a$ University of Lorraine, LMOPS E.A. 4423, Metz, F-57070, France
$^b$ University of Aix-Marseille, Laboratory MADIREL UMR 7246, Avenue Escadrille Normandie-Niemen F-13397 Marseille, France
$^{*}$ E-mail: qing.lin@univ-lorraine.fr

Keyword: flame retardancy, thermal stability, Poly(methyl methacrylate)

Poly(methyl methacrylate) (PMMA) as one of the most important thermoplastics is used in a wide variety of applications due to its interesting properties such as transparency, resistance to scratch and hardness. Unfortunately, PMMA is highly flammable [1], and its flame retardancy becomes a challenge. The fire resistance of PMMA could be improved by incorporating various flame retardants, such as inorganic compounds [2], phosphorus-containing molecules [3] or their combination [4].

In this research, three kinds of inorganic particles were chosen: ZrO$_2$ (spherical morphology), sepiolite (fibrillar morphology) and MMT (layered morphology) were combined with ammonium polyphosphate (APP). Formulations were as follows: PMMA/15%APP/10X (X = ZrO$_2$, sepiolite or MMT). The mixture of APP/X was blended with PMMA pellets in an internal mixer at 220°C during 10 minutes. The blends were then ground and pressed under 60 bars at 240°C to obtain the specimens in form of square sheets which have been characterized.

The thermal degradation and flammability behavior of PMMA composites were characterized using thermogravimetric analysis (TGA), pyrolysis combustion flow calorimetry (PCFC), cone calorimetry and also limiting oxygen index measurements (LOI). Morphology state was investigated with scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results showed that the combination of APP and oxide particles led to a significant improvement of the fire behavior and thermal properties of PMMA and that the three oxides used in the system behaved as synergistic agents. The influence of morphology was also investigated. The residues after combustion in cone calorimeter were analyzed by XRD, chemical interactions between APP and oxide particles were identified which implied the formation of a protective layer during the combustion.

References
SYNERGY IN FLAME RETARDANT POLYMERS: SOLID-STATE NMR IDENTIFYING THE CHEMISTRY BEHIND IT

A. Sut\textsuperscript{1}, S. Greiser\textsuperscript{2}, C. Jäger\textsuperscript{2}, B. Schartel\textsuperscript{1*}

\textsuperscript{1} BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany
\textsuperscript{2} BAM Federal Institute for Materials Research and Testing, Richard-Willstätter-Str. 11, 12489 Berlin, Germany
* Corresponding author. E-mail address: Bernhard.Schartel@bam.de

Keywords: solid-state NMR, flame retardancy, synergy, aluminium diethylphosphinat, zinc borate, magnesium hydroxide

Flame protection is a key issue in many industrial applications and flame retardant polymers are highly desired. Distinct approaches to reduce the fire risk of polymers are used. One way is the use of synergy in multicomponent systems. To optimize the composition of such flame retardant systems it is essential to understand the fire retardancy mechanism in the condensed phase.

In this work, for the analysis of the solid residues, different spectroscopic methods are used, with the main focus on the solid-state NMR. The structural changes in the condensed phase of two systems based on thermoplastic elastomer (copolymer Styrene-Ethylene-Butadiene-Styrene, SEBS) were investigated: SEBS-Aluminium diethylphosphinate (AlPi)/Magnesium hydroxide (Mg(OH)\textsubscript{2}) and SEBS/AlPi/Zinc Borate (ZB)/Poly(phenylene oxide) (PPO). \(^{13}\text{C}, {^{27}\text{Al}, {^{11}\text{B} and {^{31}\text{P}}}}\) NMR experiments using direct excitation with single pulse and \(^1\text{H}-{^{31}\text{P}}\) cross-polarization (CP) were carried out as well as double resonance techniques. It was concluded that for the system SEBS/AlPi/Mg(OH)\textsubscript{2} the formation of magnesium phosphates during the pyrolysis occurs, while for the system SEBS/AlPi/ZB/PPO zinc phosphates and borophosphate were found. Thus, the chemistry of the examined systems, which is standing behind the synergistic phenomenon, was characterized.
THERMALLY-STABLE POLYMER-LAYERED SILICATE NANOCOMPOSITES THROUGH INTERCALATION OF NOVEL ORGANO-MODIFIER

Nadka Tz. Dintcheva¹,², Sahar Al-Malaika², Elisabetta Morici³

¹DICAM, Università di Palermo, 90128 Palermo, IT, nadka.dintcheva@unipa.it; ²PPP Research Unit, School of Engineering and Applied Science, Aston University, Aston Triangle, Birmingham, B4 7ET, UK, s.al-malaika@aston.ac.uk; ³DICGIM, Università di Palermo, 90128 Palermo, IT, elisabetta.morici@unipa.it

**Keywords:** Styrene-Butadiene block copolymer, stabilization, carbon nanotubes

The primary interest in the clay-reinforced polymer nanocomposites (PNCs) is related to the reinforcement aspects but other important matters include their flammability resistance, mechanical performance, electrical/electronic properties, barrier properties, polymer blend compatibilisation. To achieve PNCs with good performances, the silicate platelets must be well dispersed and delaminated in the polymeric matrix. Despite the proven above mentioned benefits of polymer nanocomposite, they are used today only in niche industrial applications because of a difficult oxidation stability than the neat matrix [1-2].

In this work novel organo-modifier formulation through innovative chemical approach is proposed and used to produce PNCs with in-build lifetime stability and performance properties. The innovative chemical approach consists in grafting of reactive anti-oxidant molecules (AO), as hindered phenols, on the ammonium salt (OM) in order to formulate the novel organo-modifier ((AO)OM). Then thermally stable organo-modified montmorillonite, through ions exchanging with unmodified MMt, are formulated. Accurate characterization of the innovative clay is performed through spectroscopy and x-ray diffraction and its thermo-oxidative resistance is compared to those of the commercial unmodified and organo-modified clays. Obtained results suggest that the presence of hindered phenol molecules does not hinder the intercalation of the OM between the silicate layers.

The nanocomposites having novel organo-modified clay undergoes lower thermo-degradation at high temperature, typical in processing of the polymeric matrices, than that the nanocomposites with commercial clays. Although, novel organo-modifier is subjected to Hoffman elimination, its main advantageous is the possibility to release low molecular weight species having stabilizing functionalities. Besides, these anti-oxidant functionalities act locally in the interface between the inorganic clay platelets and polymeric matrix, that appears to be the critical area for beginning of the degradation process.

Finally, this work has two main aims: first, the introduction of the novel organo-modifier for natural montmorillonite containing anti-oxidant functionalities and second, to propose an innovative methodology for the stabilization of the nanocomposites in the interface between the matrix and the filler particles.

**Acknowledgment**

This work is financially supported by EU under Marie Curie Action–PEOPLE 2011–IEF, Project: NANOSTAB-GB 300302.

**References**

PCFC-FTIR COUPLING: A NEW TOOL TO STUDY THE COMBUSTION

A. Viretto, R. Sonnier, L. Dumazert, C. Longuet & L. Ferry

1 C2MA Material Center, Ecole des Mines d’Alès – 6 avenue de Clavières 30319 Alès (France) – amandine.viretto@mines-ales.fr

Keywords: Pyrolysis combustion flow calorimetry, Fourier transform infrared spectroscopy, Combustion efficiency, Flame retardants (phosphorus and halogenated compounds)

When an organic material is exposed to an intense source of heat, it undergoes heating up to a temperature high enough to break covalent bonds. This phenomenon is called pyrolysis. The release of fuel gases from the pyrolysis accelerates until ignition corresponding to the beginning of combustion. The combustion may be complete or partial, depending on the temperature, the excess of oxygen, the nature of the fuel gases, and also the presence of flame retardants (the decrease in combustion efficiency is the main mode-of-action of halogenated compounds).

The pyrolysis combustion flow calorimetry (PCFC) is used to assess the flammability of small samples 2-3mg [1]. The sample is heated under nitrogen flow at 1K/s typically up to 750°C. The released pyrolytic gases are extracted to the combustor where they are burnt. Pyrolysis and combustion are well separated and the parameters such as temperature and oxygen content could be controlled in the combustor. The heat release is calculated via an oxygen analyzer according to Huggett’s relation [2], (1kg of oxygen consumed releases 13.1MJ of heat). Compared with other conventional techniques for studying the fire reaction of materials such as cone calorimeter (uncontrolled combustion) or TGA (pyrolysis without combustion), the PCFC enables to separate and to control the different phenomena, pyrolysis as well as combustion. The nature of the fuel gases has been identified as a major factor in the study of the fire reaction. Therefore, the PCFC was instrumented with a FTIR spectrometer that allows us following the evolution of released gases during pyrolysis and undergoing combustion (complete or partial) [3] as shown in Fig. 2.

Fig. 2. PCFC-FTIR coupling

References


INFLUENCE OF ARTIFICIAL UV WEATHERING ON THE REPROCESSING OF WOOD FLOUR REINFORCED POLYPROPYLENE

L. Soccalingame¹, D. Perrin¹, J-C. Benezet¹, S. Mani², F. Coiffier², A. Bergeret¹

¹ C2MA, Ecole des Mines d’Alès, 6 Avenue de Clavières, 30319 Alès Cedex, France. Anne.Bergeret@mines-ales.fr
² PEP, Pôle Européen de Plasturgie, Rue Pierre et Marie Curie, 01100 Bellignat, France.

Keywords: Reprocessing, UV weathering, polypropylene, wood filler

The use of natural filler reinforced composites is growing since a few years. Assessing their recycling capability by taking into account their ageing during service life can be considered as a challenging economic and scientific goal [1]. Just a few papers evaluate the reprocessing behaviour of neat polyolefins [2, 3], but none deals with the influence of the presence of natural fillers on this reprocessing. As a consequence, this study aims to simulate a recycling process after a photochemical degradation inherent to a product service life in the case of spruce wood flour (WF) reinforced polypropylene (PP). After an artificial UV weathering (xenon arc UV and water spray cycles), WF/PP composites are grinded and processed by injection moulding to obtain new samples. Flexural and impact tests permit to assess mechanical properties. DSC tests lead to a better understanding of the microstructure evolution. The goal is to determine the influence of UV ageing on the recyclability of wood flour reinforced PP and understand the physical and chemical mechanisms induced by the reprocessing after ageing. Moreover, the impact of wood flour on these mechanisms is assessed.

Figure 1 presents unnotched Charpy test results at the different stages. One can see a very large decrease of the impact resistance due to the PP photodegradation. After one processing cycle after ageing, a noteworthy increase is observed. It can be explained by a chain branching phenomenon during the process, which is really benefic to recover a part of the initial strength of the material. This tendency is less pronounced with high wood flour content. The results are really promising and should incentive to develop recycling for this type of materials.

![Figure 1](image_url)

**Fig. 1.** Impact resistance at initial state, after ageing and after ageing and reprocessing of neat PP and PP composites

References


BEHAVIOR AND FATE OF HALLOYSITE NANOTUBES (HNTs) WHEN INCINERATING PA6/HNTs NANOComposite

G. Ounoughene1,2,3, O. Le Bihan4, C. Chivas-Joly5, C. Motzkus5, C. Longuet2, B. Debray4, A. Joubert1, L. Le Coq1, J-M. Lopez-Cuesta2

1 LUNAM, Ecole des Mines de Nantes, GEPEA, CNRS, UMR 6144, 4 rue Alfred Kastler, 44307 Nantes Cedex 03, France
2 C2MA, Ecole des Mines d’Alès, 6 Avenue de Clavières, 30319 Alès Cedex, France
3 ADEME, 20 avenue du Grésillé, 49004 Angers Cedex 01, France
4 INERIS, Parc Technologique Alata, 60550 Verneuil-en-Halatte, France
5 LNE, 29 Avenue Roger Hennequin, 78197 Trappes Cedex, France

Ghania.Ounoughene@mines-ales.fr

Keywords: combustion, incineration, nanocomposite, HNTs, PA6, aerosol

Since the end of the nineties, nanoclays based nanocomposites have been widely studied and produced. Such trendy materials are expected to end up in waste disposal plants. Recently, various studies have focused on the potential risks related to the particulate emissions of polymer nanocomposites during their combustion [1, 2, 3]. The aim of our work is to investigate the behavior of some polymer nanocomposites during their incineration. This study focuses on PA6/HNTs nanocomposites (nylon 6 incorporating halloysite nanotubes). Incineration tests have been performed at lab-scale using a peculiar tubular furnace modified in order to control the key incineration parameters within both the combustion and post-combustion zones [4]. The combustion residues and the combustion aerosol (particle matter and gas phase) collected downstream the incinerator furnace have been characterized using various techniques devoted to the analysis of aerosols. Time tracking for gas concentration and particle number concentration reveals a two steps char formation during the combustion. HNTs have been found both in aerosol and residues. As shown in Fig.1., some remains intact, while others seem to have undergone thermal modification consequently to the combustion parameters.

Authors thank: TREDI - Séché Environnement and Mines-ParisTech for their collaboration and ADEME for the financial support.

Fig. 1. MET Image of combustion residues with intact HNTs and polycrystalline aggregates of HNTs

References
THERMO-OXIDATION OF AN ACRYLIC-SILICONE COATING: DEGRADATION MECHANISM RELATED TO MATERIAL PROPERTIES EVOLUTION

A. Colin1,2,4, M. Baba1,3, P.-O. Bussière2,3, E. Cavaletti4, F. Nizeyimana4, S. Thérias1,2

1 Clermont Université, UBP, ICCF, Equipe Photochimie, BP 10448, F-63000 Clermont-Ferrand, alexis.colin@univ-bpclermont.fr
2 CNRS, UMR 6296, ICCF, Equipe Photochimie, BP 80026, F-63171 Aubière
3 Clermont Université, ENSCCF, Equipe Photochimie, BP 10448, F-63000 Clermont-Ferrand
4 AREVA TN, 1 rue des hérons, F-78180 Montigny-le-Bretonneux

Keywords: thermo-oxidation, acrylic, silicone, coating, yellowing, crazing.

Silicone acrylic-urethane / amino-silane coating can be considered as promising candidates among other systems to be used as topcoat in high temperature engineering applications. In these conditions, the functional properties can be affected. It is well known that the loss of functional properties is usually related to a modification of the chemical structure.

The main objectives of this study were to identify the main criteria of degradation, establish a mechanism of degradation and then correlate the kinetics of chemical structure modifications with the changes of the functional properties. For this purpose, the thermo-oxidative aging of the topcoat has been studied from molecular to macroscopic scale. Chemical modification have been studied by FTIR, coupling with chemical treatments and SPME/GC-MS. Architectural and aspect properties modifications were monitored by DMTA, Vickers micro-hardness, glossmetry and spectrocolorimetry.

![Infrared spectrum](image)

**Fig. 3.** Thermal aging at 160°C (a) Infrared spectrum of the topcoat with different exposure time, zoom on the region 1900-1500 cm\(^{-1}\). (b) Illustration of yellowing and crazing phenomenon.

The results reported in Fig. 1. (a) show that degradation leads to anhydride, acetylene and amide oxidation products. These degradation products are associated to the release of numerous volatile compounds such as lactones or cyclic polysiloxane. All these phenomena generate a strong yellowing, an increase of thermo-mechanical properties and finally to crazing phenomena (Fig. 1. (b)).

**References**


RUPTURE PROPERTIES OF GAMMA IRRADIATED EPDMS WITH DIFFERENT CHEMICAL COMPOSITIONS

A. De Almeida¹, L. Chazeau¹, G. Vigier¹, G. Marque², Y. Goutille³

1 Laboratoire MATEIS, Bâtiment Blaise Pascal, INSA-Lyon, 20 Avenue Albert Einstein, F-69621 Villeurbanne Cedex, France
2 EDF - R&D, Site des Renardieres, Avenue des Renardières – Ecuelles, F-77818 Moret-sur-Loing Cedex, France
3 NEXANS Research Center, 29 Rue du Pré Gaudry, 69353 Lyon Cedex 07 Lyon Cedex 07, France

Keywords: gamma irradiation, EPDM, mechanical properties, microstructure

Different Ethylene Propylene Diene Monomer have been characterized then aged by γ-irradiation in oxygen atmosphere. For each chemical composition, the degradation kinetics (cross-linking and chain scissions) have been estimated thanks to statistical models, and experimental data such as modulus, swelling ratio and sol fraction [1]. The microstructural evolution of these elastomer networks being characterised, we have tried to relate it to the one of the mechanical properties, at large deformation up to rupture.

We have first studied these properties at 80°C to avoid the influence of the crystallites which are present at ambient temperature in one of the tested EPDM. It appeared that parameters such as the density of chemical crosslinks, the density of trapped entanglements, and finally all the parameters which are an average value over the whole sample, are not the only ones to control the rupture properties. Indeed, the difference between our different irradiated EPDMs, and the thermoporosimetry data which inform on crosslinking heterogeneities, suggest that the latter have a very important influence. In particular, the heterogeneities can control the crack initiation in the materials. Hence, tests on Single Edge Notched samples have also been performed to avoid the influence of the macrodefects possibly created by these heterogeneities. As expected, it was found that the tearing energy deduced from these tests is not correlated to the rupture energy of sample tested without a notch. Nevertheless, the Lake and Thomas model, accounting for the estimated length of the active chains in the elastomer network, enables to describe the evolution of the tearing energy with the irradiation dose. In addition, in the semicrystalline state (ambient temperature), the EPDMs have systematically better rupture properties, as classically found. With the known evolution of the amorphous phase during irradiation, the radiation induced modification of the crystallinity enables the rupture properties of these materials. At last, it was found that the rupture properties of irradiated amorphous EPDMs are much better at 25°C than at higher temperature, at least for the first irradiation doses. Different hypothesis are proposed concerning this astonishing result.

References

ON-LINE UV IRRADIATION PYROLYSIS-GC/MS SYSTEM FOR RAPID EVALUATION OF PHOTO, THERMAL AND OXIDATIVE DEGRADATION OF POLYMERIC MATERIALS

Hajime Ohtani¹, Akihiko Hoska² and Chuichi Watanabe²

1 Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan, ohtani.hajime@nitech.ac.jp
2 Frontier Laboratories Ltd., 1-8-14 Saikon, Koriyama 963-8862, Japan

Keywords: UV irradiation, Pyrolysis-GC/MS, Photo degradation, Thermal degradation, Oxidative Degradation, Weatherability test, Evolved gas analysis, Polymer degradation

On-line ultraviolet (UV) irradiation pyrolysis(Py)-GC/MS system incorporating a micro-UV irradiator using a xenon lamp has been developed based on the microfurnace Py-GC/MS system. Fig. 1 shows the schematic diagram of the UV/Py-GC/MS system. A small amount of sample in a sample cup is irradiated by the UV light through an optical fiber under air or other various gas flow including humidified conditions at a preset temperature. This method allows a rapid on-line analysis of volatile products released from a polymer sample during UV irradiation under photo, thermal and oxidative conditions. In addition, the residual polymeric materials after UV irradiation can be also characterized by using various analytical pyrolysis techniques in terms of polymer deterioration. Moreover, the obtained results for the polymer degradation evaluated by this method have been proved to be well correlated with those by the conventional weatherability test methods for polymeric materials even in a much shorter period of time. In this presentation, evaluations for degradations of various polymeric materials by this technique are demonstrated

![Fig. 1. Schematic diagram of the UV/Py-GC/MS system.](image)

(a) Whole view of the system. (b) Expanded view of the sample cup region of the system.

References
PIGMENTED POLYPROPYLENE PHOTO-AGEING: AN AFM STUDY

Camille Rouillon\textsuperscript{1,2,3}, Jean-Luc Gardette\textsuperscript{1,2}, Pierre-Olivier Bussière\textsuperscript{1,4*}, Eric Desnoux\textsuperscript{3} and Sandrine Thérias\textsuperscript{1,2}

\textsuperscript{1} Institut de Chimie de Clermont-Ferrand, Equipe Photochimie, BP 10448, F-63000 Clermont-Ferrand, \texttt{camille.rouillon@univ-bpclermont.fr}
\textsuperscript{2} CNRS, UMR 6296, ICCF, Equipe Photochimie, BP 80026, F-63171 Aubière
\textsuperscript{3} RENAULT, DE-TC Ingénierie des Matériaux – Caractérisation des Matériaux, F-78284 Guyancourt
\textsuperscript{4} Ecole Nationale Supérieure de Chimie Institut de Chimie de Clermont-Ferrand, Equipe Photochimie, BP 10448, F-63000 Clermont-Ferrand

Keywords: Polypropylene, Photo-ageing, AFM, crystallization, pigments

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{DMTA.png}
\caption{DMTA thermograms of polypropylene at different irradiation times (left), AFM image phase of pigmented polypropylene before and after nano-indentation testing}
\end{figure}

This study aims at describing crystallization of polypropylene resulting from photo-oxidation. Atomic Force Microscopy was used as a tool to monitor degradation at the polymer surface such as topographic modifications and nanomechanical properties [1]. The shift of the melting temperature, determined by AFM Nanoscale Thermal Analysis and Dynamic Mechanical Thermal Analysis was linked to the size of crystallites and correlated to the changes of micro-hardness.

This investigation allowed the formation of cracks at the surface of polypropylene to be explained. This resulted in a dramatic loss of gloss after few hours of irradiation. The effect of organic pigments on the ageing behaviour of polypropylene will also be detailed.

References

ORGANIC AND INORGANIC PIGMENTS IN POLYPROPYLENE: MECHANICAL AND FLAME RETARDANT PROPERTIES

Baltus C. Bonse\(^1\), Rafael S. Cardoso\(^2\), Ana C. B. Ferreira\(^2\), Juliano M. Barbosa\(^3\)

\(^1\)Centro Universitário da FEI, São Bernardo do Campo SP Brazil, prebbonse@fei.edu.br
\(^2\)Faculdade SENAI de Tecnologia Ambiental, São Bernardo do Campo SP Brazil
\(^3\)Cromex S/A, São Paulo SP Brazil

Keywords: pigment, flame retardant, polypropylene impact copolymer

An assessment was made of the effect of blue pigments phthalocyanine (organic) and cobalt titanate (inorganic) on mechanical, thermal and flame retardant properties of PP impact copolymer containing phosphorus flame retardant. Pigments, organic and inorganic, may act synergistically or antagonistically with flame retardants [1]. Three PP color concentrates containing TiO\(_2\), PE wax and calcium stearate were prepared in a co-rotating twin-screw extruder: 10wt\% phthalocyanine, 10wt\% cobalt titanate, and 40wt\% cobalt titanate (to match the 10wt\% phthalocyanine color intensity). The same extruder was used to prepare 23 and 25wt\% flame retardant PP compounds, pigment-free and compounded with 10wt\% of each color concentrate, totaling eight compounds. Injection molded specimens were subjected to Izod notched impact, tensile and UL94 flammability testing. DSC analysis was also performed.

DSC results showed that both flame retardant and pigment affected thermal transitions and melt enthalpy of the PP copolymer compounds. The phthalocyanine compounds showed values close to neat PP copolymer, while compounds with flame retardant and cobalt titanate lower values, suggesting changes in molecular organization of PP.

Changes in values of all tensile properties were observed, but lesser impact was seen in tensile strength of the compounds compared to neat PP. The phthalocyanine compounds showed notably lower strain at break values, likely due to decrease in molecular mobility caused by this pigment, which also resulted in higher tensile modulus values in relation to neat PP. Impact strength values were also lower for the phthalocyanine compounds. Organic phthalocyanine increased burning time of the PP flame retardant compounds, whereas inorganic cobalt titanate practically did not affect combustibility.

References

GRAPHENE – PROMISING NANOFILLER AND ADJUVANT FOR FLAME RETARDED POLYMER COMPOSITES

Bettina Dittrich¹, Bernhard Schartel*, Karen-Alessa Wartig², Daniel Hofmann², Rolf Mühlaupt²

¹ BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany, *bernhard.schartel@bam.de
² Freiburg Materials Research Center and Institute for Macromolecular Chemistry, Albert-Ludwigs-University of Freiburg, Stefan-Meier-Str. 31, 79104 Freiburg, Germany

Keywords: Graphene, Flame Retardancy, Nanocomposites

The self-produced carbon nanoparticle graphene, consisting of four to seven single graphene layers, was investigated with respect to its flame retardancy in different fire scenarios in nanocomposites of polypropylene (PP), flame retarded PP and polybutylene terephthalate. To identify the flame retardancy potential, graphene was used as single additive filler and as adjuvant in established flame retardant systems. As additive filler, graphene was compared to commercially available carbon particles with varying morphology (spheres, tubes, platelets and thin layers) and ranked within this group of filler particles. Variation of the fillers’ concentration in the nanocomposites revealed structure-property relationships and concentration dependency at the same time. Among the tested carbon particles, graphene showed the best dispersion in the polymer matrix, led to the formation of an interconnected particle network at the lowest concentration and changed dramatically the flow characteristics of the polymer melt, the pyrolysis, the nanocomposites’ reaction to small flame and burning behavior under forced flaming conditions by heat shielding [1-3]. As adjuvant, graphene was combined with a phosphorus-containing, with an intumescent and with a metal hydroxide flame retardant system respectively. The effectivity of graphene as flame retardant adjuvant depended strongly on the modes of action of the used systems [4]. The results are basis to deduce guidelines for further optimization of graphene based flame retardancy.

References


INFLUENCE OF THE MECHANICAL PROPERTIES OF FILLERS ON THE BREAKDOWN OF BARRIER LAYER IN EVA/ATH COMPOSITES

Florian Cavodeau¹, Rodolphe Sonnier¹, Belkacem Otazaghine¹, José-Marie Lopez-Cuesta¹, Christelle Delaite²

1 Centre des Matériaux des Mines d’Alès (C²MA), 6 Avenue de Clavières, 30319 Alès Cedex, France
2 Laboratoire de Photochimie et d’Ingénierie Macromoléculaire (LPIM), Rue Alfred Werner, 68093 Mulhouse Cedex, France
florian.cavodeau@mines-ales.fr

Keywords: Flame retardancy, Oedometric compression, Barrier effect, Aluminium hydroxide, EVA

EVA is a commodity polymer particularly used in wire and cable industry. EVA is flame retarded by incorporating high amounts of hydrated fillers like aluminium trihydroxide (ATH) [1]. The formation of a mineral layer at the sample surface during cone calorimeter test insulates thermally the underlying material and reduces the heat release rate. The breakdown of this layer is often observed at the end of the test, leading to a second peak of HRR (Fig. 1). To improve the flame retardancy of EVA, it is important to understand how this breakdown occurs.

In this study, pure filler powders (constituted of various ATH and combinations of ATH and other mineral fillers [2]) and residues after cone calorimeter test were characterized using oedometric compression tests [3]. A good correlation between the slopes of oedometric compression has evidenced that the mechanical properties of the residues depend on those of the filler powders [4].

Moreover, the appearance and the intensity of the second pHRR in cone calorimeter test are directly linked to the slope of oedometric compression. These results would allow predicting the breakdown of the mineral layer from the mechanical properties of filler powders. The ultimate objective is to prevent this breakdown by choosing the suitable fillers.

Fig. 1: HRR curves in cone calorimeter (Black frame shows the second peak of HRR studied in this work)

Fig. 2: Delay in second pHRR vs slope of oedometric compression

References
POLYHYDROXYALKANOATES-BASED BLENDS: AN EFFICIENT WAY TO MODULATE FUNCTIONAL PROPERTIES OF MATERIALS

Idris Zembouai1,2, Stéphane Bruzaud1, Mustapha Kaci2, Yves Grohens1

1 Université de Bretagne-Sud, Laboratoire d’Ingénierie des Matériaux de Bretagne, 56321 Lorient, France. E-mail: stephane.bruzaud@univ-ubs.fr
2 Université Abderrahmane Mira, Laboratoire des Matériaux Polymères Avancés, 06000 Bejaia, Algeria.

Keywords: Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), polylactide, blends.

Many methods have been developed to increase the properties of biopolymers [1], such as random and block copolymerization, chemical modification or incorporation of numerous fillers, which modulate both the biodegradation rate and the mechanical properties of the final products. Polymer blends have attracted more attention in the last decades, since physical blending is another effective and simple way to prepare biodegradable composites with different morphologies and physical characteristics. Thus, one of the methods to improve the physical and mechanical properties of PHA is to blend PHA with other polymers, including biopolymers and conventional petroleum-based polymers [2].

In this work, blends of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and polylactide (PLA) with different PHBV/PLA weight ratios (100/0, 75/25, 50/50, 25/75, 0/100) were prepared by melt compounding [3]. The study showed through scanning electron microscopy that blends of PHBV/PLA are not miscible. Water and oxygen barrier properties of PHBV/PLA blends are significantly improved with increasing the PHBV content in the blend. Further, morphological analyzes indicated that increasing the PHBV content in the polymer blends results in increasing the PLA crystallinity due to the finely dispersed PHBV crystals acting as a filler and a nucleating agent for PLA.

Their mutual contributions in terms of thermal stability, flammability resistance and mechanical properties were also investigated [4]. To improve the miscibility between the two components of the blend, low amount of compatibilizing agent (5 wt.%), obtained by grafting maleic anhydride onto PHBV, was used [5]. When compared with the uncompatibilized blends, the compatibilizer presence induces a greater interfacial adhesion. The effect of Cloisite 30B (C30B) on the blend morphology and the blend properties was also investigated. The morphology of the different blends as well as the evolution of their material properties were discussed in terms of the nanoclay and compatibilizing agent contents. A synergistic effect of compatibilizer and C30B was highlighted leading to an improved miscibility of the two blend components.

References
DEGRADATION OF ORGANIC RADIOACTIVE WASTE AND IMPACT OF RELEASED GAS ON REPOSITORY SAFETY

Mario Stein

National Cooperative for the Disposal of Radioactive Materials (Nagra), Hardstrasse 73, 5430 Wettingen/Switzerland, mario.stein@nagra.ch

Keywords: biodegradation, polymers, gas production

Radioactive waste has to be disposed of in such a way as to ensure the long-term protection of mankind and environment [1]. To ensure this, it has to be isolated from the human environment until its activity has decayed to negligible levels. A geological disposal is regarded as the only method meeting the requirements of long-term safety [2], and is the designated concept in the Nuclear Energy Act of Switzerland [3].

For the purpose of a clear illustration of impacts and improvements on repository safety, factors of uncertainty have to be recognized. Gas generating materials are perceived as a major uncertainty. Hence, relevant processes that contribute to the production of gases must be understood. Different strategies for the investigation of gas generation from the degradation of organic radioactive waste will be presented.

References

IMPACT OF ENVIRONMENTAL CONDITIONS ON OXOBIODEGRADABLE POLYMERS DECOMPOSITION

B. Eyheraguibel¹, M. Sancelme¹, S. Fontanella², S. Bonhomme², M. Traikia¹, D. Fromageot², J. Lemaire², G. Samuel³, J. Lacoste ¹², A.M. Delort ¹

1 Institut de Chimie de Clermont-Ferrand, 24 avenue des Landais 63171 AUBIERE Cedex France, boris.eyheraguibel@univ-bpclermontferrand.fr
2 Centre National d’Evaluation de Photoprotection, 24 avenue des Landais 63171 AUBIERE Cedex, France.
3 Ribeyron SA, ZI les taillats, BP18 43600 Sainte Sigolene, France.

Keywords: oxobiodegradable polymers, biodegradation, Phanerocaete chrysosporium, Rhodococcus rhodochrous

Oxobiodegradable polymers were developed to improve disposal of plastic waste and limit their impact on the environment. Under abiotic stresses, the molecules are oxidized and break down into small fragments that can be biodegradable. To assess the oxobiodegradability of polymer materials, a standard test method was developed using an oxidation pre-treatment and the inoculation with a pure microorganism strain [1]. This test showed that under controlled conditions, oxidized fragments of polyethylene [2] and polypropylene [3] films containing pro-oxidant additives become readily biodegradable. Under environmental conditions, a large number of microorganisms can use a wide range of substrate as nutrients. This complex system can trigger co-metabolic biodegradation of contaminant or competition for substrate that can impact the rate of polymer degradation. To improve the standard test method and bring it closer to environmental conditions, the influence of different source of microorganisms and nutrients on the rate of polymer degradation was assessed. The biodegradability of high-density polyethylene films (HDPE), containing pro-oxidant additives (manganese + iron salts) was studied using the standard test method [1]. Photo and thermal oxidation pre-treatment, corresponding to about three years of outdoor weathering, was monitored by FTIR measurements. The oxidized samples were then inoculated with identified microbial strains in a controlled mineral medium containing the polymer as sole carbon source and incubated up to 180 days. The metabolic activity of the microorganisms was determined by measuring the adenosine triphosphate (ATP) and the adenosine diphosphate (ADP) content. This sensitive and quantitative measurement reflects the energetic metabolism state of the cells and indicates if microorganisms use polymer fragments as a substrate. A bacterium strain (Rhodochoccus rhodochrous ATCC 29672) producing bio-surfactant and a fungal strain (Phanerocaete chrysosporium ATCC 34541) producing exoenzymes (peroxidases) were grown separately and in co-cultivation to detect synergistic or antagonistic activities that can modulate the efficiency of biodegradation. The results show that the two strains incubated with oxidized polymer present a higher ATP content and a better energetic state than the control cultures that did not contain any polymer. It suggested that the cells were able to grow and to maintain their energetic status over months by using oxidized fragments as substrate. Their co-cultivation promotes the growth of the fungal strain at the expense of the bacterial one indicating a competition for the nutrients. The use of glucose, as an additional carbon source, enhances the initial growth of the two strains, but does not induce co-metabolism to accelerate biodegradation. These results provide a better understanding on the processes occurring between abiotic degradation and biodegradation of polymers. They will be completed by the study of other strains and substrates and use to improve standard test method to assess the biodegradability of oxobiodegradable material.

References

FUNCTIONALIZED POLY(BUTYLENE SUCCINATE) BY NITROXIDE RADICAL COUPLING

Serena Coiai,1 Francesca Cucogna,2 Chengcheng Yang,1 Ilaria Domenichelli, Calogero Pinzino,1 Paola Rizzarelli,2 Sabrina Carroccio,2 Cristian Gambarotti,3 Nadka Tz. Dintcheva,4 Giovanni Filippone,5 Elisa Passaglia1

1 Istituto di Chimica dei Composti Organo Metallici (ICCOM), Consiglio Nazionale delle Ricerche, UOS Pisa, Via G. Moruzzi 1, 56124 Pisa, Italy, serena.coiai@pi.iccom.cnr.it
2 Istituto di Chimica e Tecnologia dei Polimeri (ICTP), Consiglio Nazionale delle Ricerche, UOS Catania, Via P. Gaifami 18, 95126 Catania, Italy
3 Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milano, Italy
4 Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali, Università di Palermo, Viale delle Scienze, Ed. 6, 90128 Palermo, Italy
5 Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II, Piazzale V. Tecchio 80, 80125 Napoli, Italy

Keywords: radical functionalization, functional nitroxides, fluorescence

In recent years there has been a growing interest in developing sustainable alternatives to oil-based plastics. In particular, biodegradable aliphatic polyesters, such as poly(lactic acid) (PLA) and poly(butylene succinate) (PBS), are becoming increasingly important due to their valuable properties including thermoplastic processability and thermo-mechanical properties. Nonetheless, these materials present several drawbacks, such as the lack of reactive functionalities that are limiting their applications, versatility and successful use as commodity plastics. In this work it was investigated for the first time a new method of preparation of functionalized PBS by a post-polymerization approach based on the radical coupling between PBS macroradicals and TEMPO derivatives carrying different functionalities. Our method turned out to be successful in promoting grafting by limiting the radical-induced crosslinking/branching of the polymer substrate (Fig. 1). In particular, two different series of functionalized PBS samples were obtained by grafting the 4-benzoxyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (BzO-TEMPO), and the pro-fluorescent 4-(1-naphtoate)-2,2,6,6-tetramethylpiperidine-1-oxyl (NfO-TEMPO). The grafting was clearly evidenced by MALDI-TOF MS, UV-Vis and \(^1\)H-NMR spectroscopy from which it was estimated the functionalization degree. Moreover, by electron paramagnetic resonance (EPR) experiments it was determined the grafting site. Finally, the exploitation of a pro-fluorescent nitroxide to form functionalized PBS samples represents a significant step toward the unambiguous demonstration of the radical grafting on this type of polymers, proving also the possibility of tailoring a well-defined fluorescently labeled biodegradable polyester via a feasible process.

Fig. 1 A versatile route to introduce functional groups on PBS by selecting from a range of functional TEMPO derivatives thus providing polymer tailoring, polymer functionalization and molecular weight preservation

Acknowledgments. This work is financially supported by the Italian Ministry of University and Research (MIUR) under the program FIRB 2010 – Futuro in Ricerca (Project cod: RBFR10DCS7).
PACKAGING MATERIALS OF NEW GENERATION BASED ON PLA MODIFIED WITH POLYACRYLATES

Irena Vuković-Kwiatkowska, Halina Kaczmarek, Janusz Dzwonkowski

1 Nicolaus Copernicus University, Gagarin str.7 Toruń irenvuk@doktorant.umk.pl
2 Nicolaus Copernicus University, Gagarin str.7 Toruń, Poland halina@chem.uni.torun.pl
3 Institute of Polymer Materials Engineering and Dyes, IMPiB, Sklodowska-Curie str. 55, Toruń, Poland j.dzwonkowski@impib.pl

Keywords: Poly (lactic acid), polyacrylates, monomer dipentaerythritol pentaacrylate DPEPA, photocrosslinking, Intepenetrating Polymer Network, gas barrier properties, water vapor permeability, photostability, packaging films

Poly (lactic acid) is worldwide well known polymer, called green material because of its origin (renewable resources) and biodegradability. About 90 % of PLA is obtained by fermentation of hydrocarbons from agriculture (corn, sugar cane, potatoes, sugar beets, biomass waste).

Poly (lactic acid) has poor resistance to permeation of gases, relatively weak photo and thermal stability. In our work, we modified the barrier properties, improved photostability and thermal resistance. Composites of poly(lactic acid) (PLA) and acrylate monomer (DPEPA) were prepared in different composition by photochemical reaction. We tested mechanical properties, permeability to water vapor and carbon dioxide through the composite films. Their resistance to ultraviolet radiation used in the sterilization process and resistant to artificial sunlight exposure was also studied. The samples were conditioned at -18°C and the influence of refrigeration on the properties was tested.

We found that such modification of PLA with formation of Interpenetrating Polymer Network using photopolymerisation improves barrier and mechanical properties of the composites with respect to the pure PLA, as well as their photochemical stability and resistance to low temperatures, which makes possible to use these composites in the food packaging production. We also tested our films in use, including fresh food packaging and storing in low temperature.

Fig.1. PLA structure

Fig.2. Monomer structure

References
ACCELERATED AGEING AND LIFETIME PREDICTION OF POLY(3-HYDROXYBUTYRATE-CO-3-HYDROXYVALERATE) IMMERSED IN DISTILLED WATER

Morgan Deroiné123, Antoine Le Duigou1, Yves-Marie Corre1, Pierre-Yves Le Gac2, Peter Davies2, Guy César3, Stéphane Bruzaud1

1 Université de Bretagne-Sud, EA 4250, LIMATB, 56100 Lorient, France, morgan.deroine@univ-ubs.fr
2 IFREMER, Marine Structure Groups, BP 70, 29280 Plouzané, France, e-mail
3 SERPBIO, 56100 Lorient, France

Keywords: PHBV, accelerated ageing, hydrothermal degradation, lifetime prediction

Plastic materials are used in many areas, especially in the packaging industry. They have many advantages like light weight, low cost and formability. They are also the cause of current environmental concerns [1]. Indeed, plastics are mainly based on non-renewable resources and their lifetimes, after typical use, are much extended, implying high volumes of waste. A large amount of waste is found in the nature and can pollute the world’s oceans.

In recent years, new bio-based biodegradable polymers as polyhydroxyalkanoates (PHA) have received considerable attention as an alternative to conventional petro-based plastics. Even if degradation mechanisms of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) which is the most promising PHA [2] are well-known [3], the lifetime of PHBV is not clearly established. Polymer ageing in water is a slow process and accelerated ageing tests in the laboratory are required [4]. Water ageing is commonly accelerated according to the time-temperature correspondence principle and Arrhenius extrapolation is one way to predict the value of a given functional parameter for a specific temperature and longer times. The aim of this study is to predict PHBV lifetime immersed in seawater. As seawater is a complex medium which can generate chemical, physical or biological degradation mechanisms, the present study emphasizes only chemical degradation, based on the hydrolysis mechanism of PHBV.

Accelerated ageing has been performed in distilled water baths at different temperatures: 25, 30, 40 and 50°C. The water uptake, the mechanical properties evolution and the molecular weight changes were studied and the relation between all these parameters was analysed. Then, the lifetime estimation of PHBV samples immersed in distilled water was performed in the case of temperate water temperature and the validity of this approach is discussed.

First, the water uptake within PHBV in distilled water is temperature dependant and DVS results show a typical Fickian behaviour. Moreover, a linear relation appears between ln D and the inverse of temperature, governed by an activation energy. Then, despite the high crystallinity of PHBV, chain scission degradation which is activated by the temperature occurs mainly due to the hydrolysis of ester functions. The loss of linearity between mechanical properties and molecular weight reveals that a threshold exists above which PHBV mechanical properties are not altered. Finally, according to a specific end-of-life criterion and considering only the water effect, the lifetime of PHBV at seawater average temperature can be predicted.

References
BIODEGRADATION OF PHBV NANOBIOCOMPOSITES FILMS: EFFECT OF THE CLAYS

Kahina Iggui1,2, Nicolas Le Moigne2, Mustapha Kaci1, Jean-Regis Degorce-Dumas2, Anne Bergeret2

1 Laboratoire des Matériaux Polymères Avancés, Faculté de Technologie, Université Abderrahmane Mira, Bejai-06000, Algérie. Kacimu@yahoo.fr ; iguikahina@yahoo.fr
2 Centre des Matériaux des Mines d’Alès (C2MA), Ecole des Mines d’Alès, 6 avenue de Clavières, 30319 Alès Cedex, France. Anne.Bergeret@mines-ales.fr; Nicolas.Le-Moigne@mines-ales.fr

Keywords: poly (hydroxybutyrate-co-hydroxyvalerate) (PHBV), clay, nanobiocomposites, biodegradation, compost.

In the last years, the renewable biobased polymers and composite materials have received a great attention and became the subject of intense research activity. Their current advanced development is aimed to preserve the environment and to improve the management of natural resources from cradle to grave. Poly (hydroxybutyrate-co-hydroxyvalerate) (PHBV) is a promising biobased and biodegradable polyester produced from a variety of bacteria as intracellular carbon and energy reserves [1]. Nevertheless, its slow crystallisation kinetics, and its poor thermal stability make it difficult to process [2] and limit up to now its large commercial implementation. As a consequence, several studies aimed at better controlling PHBV properties by the dispersion of nanoparticles such as organomodified montmorillonite (MMT) [3]. In this study, we investigate the effect of the clays on the biodegradation kinetics of PHBV/MMT nanobiocomposites films. The films were prepared by cast extrusion using a masterbatch approach to prevent thermal degradation. The morphology, i.e. clays dispersion and crystalline structure, and thermo-mechanical properties of the resulting nanostructured films are analysed and discussed considering the clay content. The biodegradation of the films was studied both in aqueous and accelerated composting conditions. The biodegradation kinetics and the effect of the clays are investigated by the coupled study of the aspect (weight and surface) and the structure of the films (molecular weight, crystallinity) as well as biological analyses (biological oxygen demand DBO, pH). A significant decrease of the biodegradation kinetics was observed for the PHBV/MMT films opening up interesting questions about the future of these materials at the end of life.

References
DEVELOPMENT OF ENVIRONMENTALLY FRIENDLY PLASTICIZED PVC BY MEANS OF NANOTECHNOLOGY

Henrik Petersen, Ignacy Jakubowicz, Nazdaneh Yarahmadi and Jonas Enebro

SP Technical Research Institute of Sweden
Chemistry, Materials and Surfaces, Box 857, SE-50115, Borås, Sweden
henrik.petersen@sp.se

Keywords: PVC, nanoclay, organo-modification, nanocomposite, morphology

Polyvinyl chloride (PVC) is used in a wide range of industrial areas. Manufacturing of PVC products requires use of additives, such as plasticizers, heat stabilizers and flame retardants. The main goal in this project is to develop a plasticized PVC nanocomposite with improved barrier properties, and thereby reduce possible migration of additives. This can be achieved by incorporation of a nanoclay consisting of very thin plate-shaped particles with high aspect ratio. Besides reducing permeation there are also many examples in literature proposing that nanoclays have flame retardant qualities, such as reducing the peak heat release rate (PHRR) \[1\].

One major challenge for producing PVC/clay nanocomposites is the organo-modification of natural Montmorillonite (MMT) clay to make it suitable for incorporation in plasticized PVC. Commercially available organoclays (OMMT) are usually modified by exchanging existing cations with quaternary ammonium cations (“quats”). However, when quats degrade during melt processing, they promote dehydrochlorination of PVC \[2\] and for this reason it is necessary to find an alternative organo-modifier. In an earlier project \[3\] the idea of using chelating agents as organic modifiers (OM) was presented as a feasible path to modify clay tailored for use in PVC to produce nanocomposites. In the current study we took advantage of Hansen Solubility Parameters (HSP) to predict the miscibility between potential organomodifiers and PVC. In a series of systematic experiments using three very different solvents viz. water, ethanol and THF and three different types of clay viz. Na⁺MMT, PGV-MMT and Ca**MMT we investigated the importance of various parameters on the process of clay intercalation. The effects from each combination were evaluated using X-ray diffraction (XRD) and thermo-gravimetry (TGA).

In the second part of the study the OMMT was melt processed with PVC in order to produce nanocomposites. The focus was to identify factors that influence the final result, both regarding organo-modification of clay and the melt processing parameters. High resolution scanning electron microscope (HR-SEM) was applied to analyze the clay morphology as well as clay dispersion and compatibility with the polymer matrix. Furthermore, tensile testing, cone calorimetry and gas permeability was applied for evaluation of the clay impact on the material properties of the produced PVC nanocomposites.

References
SYNTHESIS AND CHARACTERIZATION OF EPOXY RESINS DERIVED FROM D-GLUCOSE

Beáta Szolnoki¹, Zsolt Rapi¹, Dániel Budai¹, Péter Niedermann², Péter Bakó¹, Andrea Toldy², Brigitta Bodzay¹, György Marosi¹

¹ Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, H-1111, Budapest, Műegyetem rkp. 3., bszolnoki@mail.bme.hu
² Department of Polymer Engineering, Budapest University of Technology and Economics, H-1111, Budapest, Műegyetem rkp. 3.

Keywords: bioepoxy, D-glucose, synthesis, thermal stability, flame retardancy, mechanical evaluation

Preparation of renewable and/or biodegradable polymers applicable as structural materials became increasingly important recently. Sugar is a renewable resource that has the potential to be used as an alternative to petroleum-based polymers. Carbohydrate-derived monomers are particularly appropriate for polycondensation due to their highly reactive hydroxyl groups [1]. Monosaccharides, especially glucose, are inexpensive and suitable starting materials for the synthesis of bio-based epoxy components.

In this work, several bioepoxy components, starting from D-glucose, have been synthesized. As preliminary tests, the curing properties were determined in DSC, as well as the glass transition temperature, and also the thermal stability were evaluated. The best results were reached in the case of the glucofuranoside-based trifunctional epoxy component (GFTE).

As the aim of the present research was to find a suitable alternative for the petroleum-based high-tech epoxies, also the flame retardant and mechanical performance of the synthesized GFTE was evaluated, applying both amine- and anhydride type hardener. For flame retardancy, two different phosphorus-containing additive-type FRs were applied (ammonium polyphosphate, APP and resorcinol-bis(diphenylphosphate), RDP) alone and combined, with increasing P-content.

Based on the tensile and three-point bending tests, the moduli of the GFTE-based formulations are similar to that of the reference DGEBA, in some cases even higher values were reached. When applied in composite formulations, the tensile and flexural strengths of the synthesized resin are also comparable to the reference values, while the glass transition temperature was even higher with the application of the aromatic amine-type hardener.

Regarding the flame retardancy, a synergistic effect was found in the case of the mixed formulations: when APP and RDP were applied together, V-0 rating was reached at lower P-content, than in the case of “pure” FR formulations.

References

AEROSOLS EMITTED IN POST-CRASH FIRES FROM STRUCTURAL COMPOSITE MATERIALS

M.Targosz1, C. Chivas-Joly1, C. Motzkus1, F. Gaie-Levrel1, S. Le Nevé2, J. Gutierrez3, J.-M. Lopez-Cuesta4

1 Laboratoire national de métrologie et d’essais (LNE), 29, av. Roger Hennequin, 78197 Trappes, France
martalaboratoirenationaldemetroteoieetdessais@lne.fr
2 DGA-Aeronautical Systems, 47 rue Saint-Jean, 31130 Balma, France
3 DCNS Research, Indret, 44620 La Montagne, France
4 Ecole des Mines d’Alès (C2MA), 6 Avenue de Clavières, 30319 Alès Cedex, France
martalaboratoirenationaldemetroteoieetdessais@lne.fr

Keywords: aerosol measurements, cone calorimeter, fibres emission, smoke release

Introduction. The use of composite materials for aeronautical and naval applications becomes widespread nowadays. Composites have the potential to reduce the mass of vehicles and to contribute to the improvement of other characteristics like mechanical strength and stiffness. However, one of the main problems of using composites is their fire behavior. At higher temperatures, the organic matrix decomposes with gaseous species and aerosols release, which toxicity aspects are still poorly known. For that reason, the assessment of potential health and environmental impacts caused by the dispersion of degradation products from aeronautical materials in a post-crash fire is essential.

This research project intends to understand and characterize the production of aerosols and gases from the combustion of composite materials as well as to model their dispersion into the atmosphere, based on experimental and numerical results.

Experimental setup was composed of a cone calorimeter coupled with hot and cold stage dilutors and aerosol instruments, such as Dekati Low Pressure Impactor, Aerodynamic Particle Sizer, Condensation Particle Counter, Fast Aerosol Mobility Size Spectrometer and Scanning Mobility Particle Sizer. The influence of polymer matrices, fibers and carbon nanotubes involvement, as well as the presence of glass reinforcement on the number and mass concentrations of particles, and size distribution was studied in real time, in range of 2 nm – 2 µm.

Results. The fire behavior of various structural aircraft and naval composites under defined fire conditions of 75 kW/m² (cone calorimeter) and 180 kW/m² (FAA Burnthroug test) was studied. Materials were characterized by the shortest burnthrough time, the highest level of damages, the highest yield of smoke release and the presence of volatile soot and fibers. As an example, the results in term of particle number generated during combustion of epoxy resin based two composites are shown in Fig.1.

Conclusions. Particles generation from combustion of structural composites depends on the nature of organic matrix, presence or not of carbon fibers or carbon nanotubes and also on the orientation of fibers reinforcement.

Fig.1. Number concentration of particles for epoxy resin based composites, MAT4 and MAT5.

References
FAST PREPARATION OF NANOCRYSTALLINE CELLULOSE BY MICROWAVE-ASSISTED HYDROLYSIS

Alojz Anžlovar¹, Tomaž Kos¹, Matjaž Kunaver¹, Miroslav Huskić¹, Ema Žagar¹

¹National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia, E-mail: alojz.anzlovar@ki.si

Keywords: Nanocrystalline cellulose, Microcrystalline cellulose, Microwave-assisted hydrolysis, XRD diffraction, Dynamic light-scattering (DLS), Scanning transmission electron microscopy (STEM)

Nanocrystalline cellulose (NCC), obtained from abundant cellulose sources, has been recognized as a promising class of biobased nanomaterials. We present the procedure for fast and controlled preparation of NCC from commercially available microcrystalline cellulose (MCC) using microwave heating (Fig. 1a). We studied the influence of concentration of sulfuric acid and hydrolysis temperature on average NCC particle size and yield. By varying the sulfuric acid concentration and hydrolysis temperature an average NCC particle size between 126 nm and 1310 nm with corresponding yields between 16 % and 82 %, respectively, were obtained in a very short reaction time of 10 min. Additional advantage of the described procedure is its high reproducibility and ability to fine-tune the NCC particle size by adjusting the reaction conditions, i.e., the sulfuric acid concentration and/or reaction temperature. The NCC particle size and morphology were studied by dynamic light scattering - DLS and by scanning transmission electron microscopy while the crystallinity of NCC was confirmed by XRD diffraction. The minimal concentration of sulphuric acid and temperature to obtain cellulose nanocrystals are 60 % and 70 °C, respectively. In this case, the smallest NCC nanoparticles (360 nm) with the highest yield (38 %) were prepared (Fig. 1b).

Fig. 1. a) Schematic presentation of the NCC preparation procedure (left) and suspensions of NCC with concentration of 0.1 wt% prepared in microwave reactor (right), and b) STEM micrograph of NCC: magnification - 50000x

---

The 8th International Conference on Modification, Degradation and Stabilization of Polymers
MECHANICAL RECYCLING OF POLY(BUTYLENE SUCCINATE) THROUGH THE REMELTING-RESTABILIZATION TECHNIQUE

I. Georgousopoulou¹, S. Vouyiouka¹, C. Papaspyrides¹, P. Dole², C. Joly³

¹ Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Zografou Campus 15780, Athens, Greece
² CTCPA Centre Technique de la Conservation des Produits Agricoles, BOURG-EN-BRESSE, France
³ BIODYMIA IUT Lyon 1-EMA 3733, Universite Lyon 1- ISARA Lyon, Alimentec

Keywords: remelting-restabilization, degradation mechanism, poly(butylene succinate)

Poly(butylene succinate) (PBS) comprises one of the most promising biodegradable polymers, potentially being fully derived from renewable resources through fermentation processes. In literature, there are extensive studies concerning the enzymatic and biological degradation of PBS [1-2], but only a few regarding reprocessing [3-4]. In particular, to the best of our knowledge, no study has been published on the thermomechanical degradation of PBS in order to evaluate a proper restabilization system for closed-loop recycling.

The aim of the current work was first to examine the reprocessing effect upon the structure of PBS via subjecting the polymer to successive extrusion cycles, similarly to previous studies on polyolefins [5-6]. Accordingly, it was found that PBS degrades via a branching mechanism, which was accompanied by a severe decrease of the melt flow index (MFI), an increase of the weight-average molecular weight and of the polydispersity index and by a slight increase in the carboxyl end group concentration.

Following, two antioxidants (Irgafos® 168 and Irganox® 1010) were examined for secure PBS reprocessing. The addition of the selected additive systems resulted in stabilizing the material, while PBS formulation with 0.10 % Irganox® 1010 was considered the most efficient in terms of low additive concentration and stabilization performance. Finally, vigorous study on the thermal properties of non-stabilized and stabilized and materials was also performed.

![Fig. 1. Effects of multiple extrusions on the melt flow index (MFI) of 0.10 wt%](image)

Acknowledgments

This work has been supported by the EC within the 7th framework programme under grant agreement 289196 (Development of active, intelligent and sustainable food Packaging using PolybutyleneSUCCInate-SUCCHIPACK).

References

REACTIVE RESINS FOR WOOD MODIFICATION

Holger Militz

Wood Biology and Wood Products, Georg-August-Universität Göttingen, Büsgenweg 4, 37077 Göttingen, Germany: hmilitz@gwdg.de

Keywords: wood, modification, reactive resins, phenol, melamine, DMDHEU

Wood is the World’s the most important renewable building material. Beside its many advantageous properties, wood is relatively susceptible to degradation processes caused by natural weathering and by microorganisms and insects. By modifying the wood cell wall’s polymers with reactive chemicals, important wood properties can be improved (Hill 2006, Militz et al. 2012, Trinh et al. 2012). Some of the modification techniques, like acetylation with anhydrides, furfurylation with furfuryl alcohol and silanisation with silanes or siloxanes, were introduced into the wood industry during the last decade. Other processes are still under development. In this presentation, our work on wood modification processes using reactive resins will be reviewed. The main focus will be on biological and technological properties of solid wood, modified with formaldehyde-based resins, mainly on basis of phenol, melamine and DMDHEU (dimethylolhydroxyethylenurea).

References


DETERIORATION OF WOOD BY MOULD AND BLUE STAIN FUNGI

Lone Ross Gobakken
Norwegian Forest and Landscape Institute, 1431 Ås, Norway,
lone.ross.gobakken@skogoglandskap.no

Keywords: blue stain fungi, mould, outdoor exposure, service life, weathering, wood

Mould and blue stain fungi are able to colonise and grow on a broad range of surfaces and materials, including plastics, coatings, paper etc, but wood, in particular, is quickly colonized by such fungi. Growth of mould and blue stain on wood exposed outdoors in building applications is undesirable as it leads to increased maintenance and reduces the length of time that wood retains its pleasant appearance. On the other hand, rapid colonisation and colour change of unpainted wooden cladding is often anticipated and is used as a design element. Moulds at the surface of coated and uncoated wood produce powdery and/or spotty patterns. The colours of moulds may range from lighter shades of green and yellow to black. The mould fungi referred to as blue stain in service, mildew and discolouring fungi have mainly dark-coloured hyphae and spores. The predominant factors required for mould growth are: free water, moderate temperatures, a substrate with nutrients for the fungi, and oxygen [1]. Surface moulds do not degrade the wood since they are not capable of utilising cellulose, lignin, or hemicelluloses as nutrients. Moulds will, however, make use of non-polymeric materials in the wood, such as freely available carbohydrates, simple sugars and starch [2]. On a paint film moulds will generally metabolise organic food sources like starches, sugars, proteins and some oils found in paints, and more specifically surface moulds can feed on bacteria, pollen and other contaminants on the surface of the paint film [3]. Components present in the wood may also diffuse into the paint film and provide a source of nutrients for surface moulds [4]. Studies have shown that deterioration of wood by mould and blue stain is related to a number of factors, which I will review, including wood species and wood properties, the treatment of the wood (use of preservatives, modification systems or surface treatment), wood product and building design, the maintenance regime and climatic factors [5-8].

References

END OF LIFE SCENARIOS AND ENVIRONMENTAL IMPACTS OF WOOD PRODUCTS

Andreja Kutnar 1,2

1 University of Primorska, Andrej Marušič Institute, Muzejski trg 2, SI-6000 Koper, andreja.kutnar@upr.si
2 University of Primorska, Faculty of Mathematics, Natural Sciences and Information Technologies, Glagoljaška 8, SI-6000 Koper, andreja.kutnar@upr.si

Keywords: durability, LCA, sustainability, up-cycling, wood

Sustainability is increasingly becoming a key consideration of building practitioners, policy makers, and industry alike. The goals of sustainable development are ‘increasing economic efficiency, protecting, and restoring ecological systems and improving human well-being, or a combination of the three’. Wood as one of the most important renewable materials exhibits superior properties compared to many other materials, helped in part by its ability to sequester carbon. However, as a biological material, wood can suffer from physico-chemical and biological degradation. Generally preservative and/or modification treatments have proven to be quite effective in providing long term durability in the end use applications of wood. Therefore recycling/disposal at the end of service life has not been a significant and immediate concern. However, the diversity of wood uses and potential for development of alternative specialty products with shorter life cycles can be anticipated to bring more emphasis on the life cycle of products, including recycling and disposal options at the end of the service life.

In sustainable design, “durability” is increasingly being included on priority lists under the assumption that designing for longevity is an environmental imperative. However, this is unsupported in the absence of life cycle assessment and accurate lifespan predictions. In the worst case, designing for longevity can lead to design choices that are well-intentioned but, in fact, yield poor environmental results. Rather than attempt to predict the future and design permanent structures with an infinite lifespan, design for easy adaptation and material recovery should be acknowledged.

In this presentation wood as building material is discussed in relation to the environmental benefits of using wood products. Different environmental impacts, including sequestered carbon, wood products with different ‘end of life’ scenarios and susceptibility to degradation are compared.
WOOD COATINGS MADE OF LIQUEFIED WOOD AND SOME OTHER LIGNOCELLULOSIC MATERIALS

Marko Petrič¹, Borut Kričej², Matjaž Pavlič³, Pavel Pori⁴, Arnaud Maxime Cheumani Yona⁵

¹ University of Ljubljana, Biotechnical Faculty, Jamnikarjeva 101, 1000 Ljubljana, Slovenia, marko.petric@bf.uni-lj.si
² University of Ljubljana, Biotechnical Faculty, Jamnikarjeva 101, 1000 Ljubljana, Slovenia, borut.kricej@bf.uni-lj.si
³ University of Ljubljana, Biotechnical Faculty, Jamnikarjeva 101, 1000 Ljubljana, Slovenia, matjaz.pavlic@bf.uni-lj.si
⁴ Chemcolor Sevnica d.o.o., Dolnje Brezovo 35, 8290 Sevnica, Slovenia, pavli.pori@gmail.com
⁵ University of Ljubljana, Biotechnical Faculty, Jamnikarjeva 101, 1000 Ljubljana, Slovenia AND Iltra d.o.o., Celovška cesta 268, 1000 Ljubljana, acheumani@yahoo.fr

Keywords: liquefaction, liquefied wood, surface coating, polyurethane

Solvolytic liquefaction of various bio-resources, including wood and other lignocellulosics, is an attractive possibility for the production of bio-based sustainable materials. The process leads to depolymerisation of cellulose, hemicelluloses and lignin, and the solubilised fragments of polymers can serve as precursors for preparation of new bio-based resins. These can be applied as binders in wood surface coatings. This paper is a resume of our several year investigations of possible applications of liquefied wood, bark, cork and some other lignocellulosics for preparation of bio-based wood coatings. Some selected examples prove that wood coatings can be made of liquefied lignocellulosic biomass by its self-crosslinking[1], or in combination with appropriate curing agents, to produce polyurethane[2] or amine-formaldehyde resin based wood surface finishes. It was also succeeded to convert the aesthetically unpleasant dark brown colour of liquefied biomass and of liquefied based wood coatings into a more acceptable light one[3]. Further on, it was shown that liquefaction and preparation of liquefied based wood coatings may represent an alternative way of managing post-consumed contaminated wood, containing remains of copper, chromium and boron (CCB) based wood preservatives[2]. Characterisation of the novel bio-based surface finishes by standard and other methods has shown that some have very similar characteristics to those of commercial wood coatings based on resins produced from oil refinery derivatives. Finally, future perspectives in the fields of preparation of liquefied wood based coatings and their potential commercialisation are critically discussed.

References

SMART SILICONE COMPOSITES. THE SYNTHESIS, CHARACTERIZATION AND APPLICATION OF WELL-DEFINED, HIERARCHICAL PDMS/INORGANIC COMPOSITES WITH NOVEL PHYSICAL PROPERTIES

James P. Lewicki¹, Marcus A. Worsley¹, Theodore F. Baumann¹, Eric Duoss¹, & Robert S. Maxwell¹

1 Lawrence Livermore National Laboratory, 7000 East Ave. Livermore, CA.
Corresponding author email: lewicki1@llnl.gov

Polysiloxanes are a uniquely versatile family of inorganic polymeric materials which can be utilized to design a vast range of complex and hierarchal 3-dimensional, flexible network architectures. At LLNL we have been making extensive use of this diverse polysiloxane network chemistry to design and synthesize some truly novel composite materials - with the potential for applications ranging from; flexible ultra-low ‘k’ dielectric coatings, negative temperature coefficient electronic switching materials, flexible electromagnetic shielding layers, highly thermally resistant coatings and patterned media capable of large-scale isotropic dimensional change. Here we present a review of some of our recent efforts in this exciting and technologically relevant area of advanced polymeric materials science. The results of the synthesis and characterization (via a range of analytical methodologies including solid state NMR, degradative thermal analysis and broadband dielectric spectroscopy) of unique polysiloxane/carbon aerogel/carbon nanotube architecture will be presented. This system is the only known example of a polymeric ‘inverse’ PTC switching material which is both reversible and highly thermally stable. We will also present an overview of our ‘materials by design’ approach for the formation of 3-dimensional polysiloxane based structures of sub-micron pattern resolution which can be triggered to undergo large-scale (fully reversible) isotropic changes in volume in response to external stimuli.

Fig. 4. Left: A siloxane layer embossed with a 3D-micron layer pattern capable of isotropic dimensional change. Center: Dielectric spectroscopy analysis of a hierarchical siloxane-carbon aerogel hybrid showing energy absorption in the microwave region. Right: Hysteresis free switching of a negative temperature coefficient polysiloxane composite.

Emphasis will be given to the relationship between the underlying (dynamic) network structure and the macro-scale physical properties of complex polysiloxane composites. And to the importance of combining a range of interrogative analytical methodologies with a ground up synthetic approach, in order to build well-defined & well understood materials at all size scales.

Acknowledgement

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.
POLYOLEFINES WITH ANTIMICROBIAL ACTIVITY

Regina Jeziórska¹, Maria Zielecka¹, Agnieszka Szadkowska¹, Beata Gutarowska²

¹Department of Polymer Technology and Processing, Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland
²Technical University of Lodz, Wolczanska 171/173, 90-924 Lodz, Poland
* Corresponding author: tel/fax: +48 22 568 21 84, e-mail: regina.jeziorska-dn@ichp.pl

In this work, the effects of the nanosilica containing immobilized nanosilver (SiO₂-Ag) or nanocopper (SiO₂-Cu) [1–3] as well as maleic anhydride or glycidyl methacrylate grafted polyolefines [4, 5] on the phase behavior, microstructure and mechanical properties of polyolefines were studied using scanning (SEM) and transmission electron microscopy (TEM), differential scanning calorimetry (DSC), thermogravimetry (TGA) and dynamic-mechanical analysis (DMTA). Furthermore, the ability of spherical silica containing immobilized nanosilver or nanocopper to give antimicrobial activity to polyolefines was also investigated. All materials were compounded in a co-rotating twin-screw extruder and then injection molded. Maleated polyolefines improve compatibility between the polyolefine matrix and silica due to the more uniform dispersion of the silica nanoparticles as well as better mechanical properties. The thermal stability of the composites was significantly better compared to the neat polymer. Moreover, the improvement in stiffness was observed. DMTA measurements confirmed these observations, showing an enhancement of the storage modulus in the presence of nanosilica. Moreover, higher silica contents resulted in higher storage modulus, proving that the material became stiffer. Improved resistance to microorganisms (E. coli, S. aureus, S. typhimurium, L. motocytogenes, B. subtilis and P. fluorescens) of the polyolefines containing SiO₂-Ag or SiO₂-Cu was also observed whereas pure polyolefines did not show this activity.

Acknowledgements

This work has been financially supported by project No UDA-POIG.01.03.01-00-073/08-00 co-financed by EU (European Regional Development Fund).

References

INFLUENCE OF TYPICAL STABILIZERS ON THE AGING BEHAVIOR OF EVA FOILS FOR PV APPLICATIONS DURING ARTIFICIAL UV-WEATHERING

Annegret Jentsch¹,², Klaus-Jochen Eichhorn³, Brigitte Voit²,³

1 BOSCH Solar CISTech GmbH, Münstersche Straße 24, 14772 Brandenburg a. d. Havel, Germany, annegret.jentsch@bosch.com
2 Organic Chemistry of Polymers, Technische Universität Dresden, 01062 Dresden, Germany
3 Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany, kjeich@ipfdd.de, voit@ipfdd.de

Keywords: EVA, stabilizer, UV degradation

Ethylene vinylacetate (EVA) is the most common used embedding material in crystalline photovoltaic. It is responsible for fixing module components and saving cells against mechanical and environmental stresses like temperature, humidity and (UV) radiation.

Adhesion loss, so-called delamination, and yellowing being reasons for efficiency drop are the consequence of EVA aging during weathering. To improve long-term stability stabilizers are added, even if it is not yet clear whether they have an impact on failure mechanisms. Therefore we investigated the effect of typical additives focusing on UV-absorbers on EVA degradation during UV exposure.

Test specimens with different EVA foils containing variable additive mixtures were exposed to artificial UV irradiation. Peel test, IR-spectroscopy, transmission and color measurements are performed to observe property changes.

As a result delayed EVA degradation could be observed depending on stabilizers added. Otherwise some of these additive mixtures were found to be the course of delamination and yellowing. Possible degradation mechanisms causing the observed effects are discussed.
IS THERE ANY PHOTOSTABLE CONJUGATED POLYMER FOR EFFICIENT SOLAR CELLS?

Agnès Rivaton\textsuperscript{1,2}, Aurélien Tournebize\textsuperscript{1,2}, Jean-Luc Gardette\textsuperscript{1,2}, Christine Taviot-Gueho\textsuperscript{3,4}, Didier Bégué\textsuperscript{5}, Marc-Alexandre Arnaud\textsuperscript{5}, Christine Dagron-Lartigau\textsuperscript{5}, Hussein Medlej\textsuperscript{6}, Roger C. Hiorns\textsuperscript{6}, Serge Beaupré\textsuperscript{7}, Mario Leclerc\textsuperscript{7}

1 CNRS, UMR 6296, ICCF, Equipe Photochimie, BP 80026, F-63171 Aubière, France.
2 Clermont Université, Université Blaise Pascal, ICCF, Equipe Photochimie, BP 10448, F-63000 Clermont-Ferrand, France.
3 CNRS, UMR 6296, ICCF, Equipe Matériaux Inorganiques, BP 80026, F-63171 Aubière, France.
4 Clermont Université, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, Equipe Matériaux Inorganiques, BP 10448, F-63000 Clermont-Ferrand, France.
5 Institut des Sciences Analytiques et de Physico-Chimie pour l’Environnement et les Matériaux, CNRS, UMR 5254, Equipe de Chimie Physique, 64053, Pau Cedex 9, France.
6 Institut des Sciences Analytiques et de Physico-Chimie pour l’Environnement et les Matériaux (IPREM), CNRS, UMR 5254, Equipe de Physico-Chimie des Polymères, 64053, Pau Cedex 9, France.
7 Canada Research Chair on Electroactive and Photoactive Polymers, Département de Chimie, Université Laval, Quebec City, QC G1V 0A6, Canada.

Keywords: Low band gap polymers, computational study, photooxidation, organic photovoltaics, photochemical stability, degradation, morphology.

The preservation of organic polymer solar cell (PSC) performances over time is a significant concern for their commercial development. One PSC degradation pathway is due to inherently photo-unstable conjugated polymers which are incorporated into devices and bear continuousillumination in the presence of atmospheric oxygen that may diffuse across the encapsulation in the whole device. This paper reports on the unexpected photostability of a low band gap polymer, namely poly[[benzo[1,2-b:4,5-b’]dithiophene]-alt-(thieno[3,4-c]pyrrole-4,6-dione)] (PBDTTPD), which was designed for efficient bulk heterojunction PSCs. We have implemented an approach based on joint computational study and spectroscopies to explain the high resistance of PBDTTPD towards photooxidation. It is shown that alkoxy side-chains on benzo[1,2-b:4,5-b’]dithiophene (BDT) moieties, by reducing radical formation, mitigate the photodegradation of the whole polymer. Additionally, PBCTTPD favors well-organized structures, which inhibit the propagation of the chain oxidation process. The first main highlight of this study is that the structure-photostability relationship of conjugated polymers can be dependent on both the molecular structure of the polymer and the morphology of the deposits. The second highlight is that the choice of solubilizing side chains is a critical factor in the design of stable conjugated polymers for efficient PSCs.
UNRAVELLING THE PHOTODEGRADATION MECHANISMS OF A LOW BANDGAP POLYMER BY COMBINING EXPERIMENTAL AND MODELLING APPROACHES

Isabel Fraga Dominguez¹², Paul D. Topham³, Pierre-Olivier Bussière⁴, Didier Bégué⁵, Agnès Rivaton¹²

¹ CNRS, UMR 6296, ICCF, Equipe Photochimie, BP 80026, F-63171 Aubière, France.
² Clermont Université, Université Blaise Pascal, ICCF, Equipe Photochimie, BP 10448, F-63000 Clermont-Ferrand, France.
³ Chemical Engineering and Applied Chemistry, Aston University, Birmingham, B4 7ET, United Kingdom.
⁴ Clermont Université, Ecole Nationale Supérieure de Chimie, ICCF, Equipe Photochimie, BP 10448, F-63000 Clermont-Ferrand, France.
⁵ Université de Pau et des Pays de l’Adour, IPREM, UMR 5254, Equipe de Chimie Physique, F-64053, Pau, France.

Keywords: organic solar cells; low bandgap polymers; photooxidation; degradation mechanisms; modelling

During the last decade, much effort has been made to improve the efficiencies of organic photovoltaics. With this aim, new conjugated polymers with bandgaps below 1.5 eV (low bandgap polymers) have been synthesised, reaching efficiencies that nowadays overpass 10% [1]. However, the lifetime of organic photovoltaic devices is still insufficient to allow them to enter the market. In fact, one of the major problems is the stability of these polymers against external stress factors, such as UV-visible light, oxygen, or heat [2]. This study reports on the elucidation of the photodegradation mechanisms occurring in low bandgap polymer, Si-PCPDTBT, (poly[2,6-(4,4-bis(2-ethylhexyl)dithieno[3,2-b:2′,3′-d]silole)-alt-4,7-(2,1,3-benzothiadiazole)]) under different accelerated ageing conditions. To this end, thin films of neat polymer were deposited on transparent substrates, aged and monitored using a range of complementary analytical techniques. Combining these experimental results with theoretical calculations based on quantum chemistry has allowed the photodegradation mechanisms to be elucidated. Additionally, the relative photostability of Si-PCPDTBT and other state-of-the art polymers, such as P3HT or PCPDTBT, is explained in terms of their structural features.

References


Acknowledgements

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2011 under grant agreement ESTABLIS no. 290022).
PHOTO-STABILIZATION OF HIGHLY FILLED THERMOSET COMPOSITES

Boris Gorelik, Oleg Berezin, Anna Drabkin, Moshe Voskoboinik

MOBIChem Scientific Engineering Ltd. Hartum St. 19, Har Hotzvim 91451, Jerusalem Israel, email: borisg@mobichem-sci.com

Keywords: Epoxy Resins, Unsaturated Polyesters, HALS, Composites, Photo-Stabilization

Highly filled thermoset composites (HFTC) based on Epoxy resins (ER), Unsaturated Polyester Resins (UPR), Acrylic Resins (AR) are widely used in production of Engineered Stones, Cultured Onyx, Artificial Marble, etc. Concentration of fillers (Quartz, Al(OH)₃, glass, TiO₂, etc.) in above products varied from 75% w/w to 90% w/w. Long term application of thermoset composites in outdoor conditions results in discoloration and loss of tensile properties. Attempts of increasing light fastness of HFTC by introduction of different UV absorbers did not lead to positive effect because photo-degradation is concentrated in the surface layer of 10-20 microns. That low thickness is not sufficient to provide screen effect by UV-absorbers. Application of Hindered Amine Light Stabilizers (HALS) proved to be also challenging. Common HALS are substituted amines and are able to participate in different reactions of thermosets curing to effect parameters of curing (gel time, maximal curing temperature, curing time, etc.) and tensile properties of cured HFTS (e.g. by influence on cross-linking density). Consumption of HALS in curing reactions substantially decreases their activity as scavengers of during photo-aging of thermosets. In our work we studied reactions of curing of thermosets in the presence of secondary, tertiary HALS and NOR type HALS. Thermosets can be divided into cured by radical mechanism (UPR and Acrylic Resins), by nucleophilic reactions (ER cured by amine hardeners) or by cationic polymerization (ER curing by anhydrides). In case of UPR and Acrylic Resins all types of HALS showed retarding effect on curing rate because of reactions with radicals responsible for curing process. DSC simulation of curing process showed lower values of heat of curing compared to samples free of HALS. NOR HALSs have stronger retarding effect compared to other HALSs used. Optimal concentration ratios were found between HALS and peroxide initiators to provide optimal curing procedure and appropriate photo-protection of UPR and Acrylic HFTC. Curing of ER by amines follows nucleophilic reaction with epoxy groups. NOR HALS proved to be inactive in these reactions and left in cured matrix to provide photo-stabilization. Secondary and tertiary types of HALS participate in curing reactions. We found pairs of ER and amine hardeners efficiently excluding that HALS from curing process, thus left as photo-stabilizers. Anhydrides used for ER curing reacts with secondary and tertiary HALS. So that HALS can't be used for photo-stabilization of Anhydride cured ER. NOR type HALSs behavior depends on types of accelerators used for cationic polymerization and types of ER used (e.g. bisphenol-A based or based on aliphatic epoxies). Optimal systems were found in terms of high photo-stabilizing effect of NOR HALS.
LUMINESCENT COMPOSITE PHOSPHORS/POLYMER: IMPACT OF RED PHOSPHOR (Y_3BO_6:Eu^{3+}) ON EVA PROPERTIES AND PHOTOAGEING

Anthony Chapel^{1,2}, Geneviève Chadeyron^{2,3}, Rachid Mahiou^{1,2}, Sandrine Thérias^{1,2}

1 Clermont Université, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand, France
2 CNRS, UMR 6296, ICCF, BP 80026, F-63171 Aubière, France
3 Clermont Université, Ecole Nationale Supérieure de Chimie de Clermont-Ferrand, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand, France

Anthony.chapel@univ-bpclermont.fr

Keywords: Composite, phosphor, ageing, EVA, LEDs.

Eco-energetic lightning is one of the greatest challenges of our society. For the coming years, most of white light emitting devices will be based on light emitting diodes (LEDs) combined with suitable phosphors. The LEDs technology is considered to be eco-friendly since it prevents the use of mercury like in fluorescent lamps and it consumes much less energy in comparison with incandescent lamps. Up to now, the common approach for producing white emitting LEDs has consisted in combining a blue LED (λ_{em} = 465 nm) with a yellow phosphor (e.g. YAG:Ce). However a new strategy based on near UV LED is being investigated. Indeed, the combination of near UV LED with these phosphor (red, blue and green) is expected to enable a better control over IRC and color temperature. In most case to be associated with LED, these phosphors must be incorporated in a polymer matrix resulting in luminescent composites. Nowadays, the photostability is a keypoint for LEDs marketing in order to develop a complete product sheet characterizing devices durability.

The aim of this work is to determine the impact of an efficient red phosphor under UV LED excitation (Y_3BO_6:Eu^{3+}) on the photostability of a model polymer such as EVA (33wt% vinyl acetate) [1]. The optical properties of Y_3BO_6:Eu^{3+} were studied before and after incorporation in the EVA matrix. Furthermore, the influence of the EVA degradation on luminescent properties of the composite was investigated. In the same time, the impact of Y_3BO_6:Eu^{3+} on the evolution of principal characteristic of EVA upon irradiation was determined.

The phosphor was synthesized using the Pechini method. This luminescent powder was then mixed with an EVA solution. Composite film were cast using a doctor blade and sample were irradiated in a SEAPAP 12/24 device. Thermomechanic and structural properties of the composite were measured by the mean of FTIR, DMTA, DSC, SEC and SAXS. Complete optical characterisation of composite was done: emission, excitation spectra, luminescent quantum yield, trichromatic coordinates and fluorescence lifetime were analysed.

Fig. 5: Y_3BO_6:Eu^{3+} powder (a) and EVA/Y_3BO_6:Eu^{3+} composite film (b) under UV light

References

COMPARISON OF PHOTOCHEMICAL AND THERMAL DEGRADATION OF POLY(LACTIC ACID) DOPED BY NANOSILVER

Maria Mucha¹*, Sylwia Białas¹

¹Faculty of Process and Environmental Engineering, Łódź University of Technology, Wólczańska 15 street, 90-924 Łódź, Poland
* corresponding author, e-mail: muchama@wipos.p.lodz.pl

Keywords: Poly(lactic acid), nanosilver particles, nanocomposite, photodegradation, thermal degradation

Nanoparticles can be incorporated into polymer as nano-additives for both the purposes, i.e. degradation and stabilization of polymers. The study of degradation and stabilization of polymer-nanocomposites is an extremely important area from the scientific and industrial point of view and a better understanding of degradation mechanism of these materials will ensure the long service life of the product.

A comparison of thermal and photochemical degradation of poly(lactic acid) thin film materials (10μm) containing nanosilver are studied by Fourier Transform Infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC) and viscometry. Rates of thermal and photochemical degradation are determined by measuring the relative changes of absorbance (At/A0) of selected bands in PLA spectra. Comparison of the effect of both degradation on PLA structure showed, that nanosilver act as a stabilizer for photodegradation at 254nm. As oppose, thermal degradation at 80°C indicate, that nanosilver accelerates PLA degradation at higher temperature. Glass transition and crystallization/melting processes of degraded samples were also compared.. Main alteration was observed in PLA melting process caused by different effect of heat and UV-radiation on macromolecular order.

The modification of PLA by nanosilver allows to obtain the environmentally friendly, biodegradable material with end-use properties such as anti-UV and antibacterial effects.

References:
NITRATION OF CYCLIC LADDER POLYPHENYL SILSESQUIOXANE

Haibo Fan¹, Rongjie Yang²

¹ Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, Beijing 100081, P. R. China, bitfanhaibo@163.com
² Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, Beijing 100081, P. R. China, yrj@bit.edu.cn

Keywords: Polyphenylsilsesquioxane, Nitration, Cyclic Ladder

A well-defined cyclic ladder polyphenylsilsesquioxane (CL-PPSQ) was prepared in our previous studies. The chemical structure of CL-PPSQ is shown in Scheme 1. In this research, the CL-PPSQ nitration derivative was prepared which was in order to enhance the compatibility of the polysilsesquioxane in polymers.

![Chemical structure of CL-PPSQ](image)

It’s believed that fuming nitric acid is an effective nitrating reagent, which is used to prepare polyhedral oligomeric octa(nitraphenyl)silsesquioxane widely [1,2]. Nitro groups could be linked with phenyl groups in CL-PPSQ using the fuming nitric acid. However, the $M_n$ of NO$_2$-PPSQ was sharply dropped by 50% compared with that of CL-PPSQ even though the HNO$_3$ concentration was reduced to 84.5%.

In order to protect the cyclic ladder structure of PPSQ, other nitrating methods were experimented. It is founded that the nitrating reagents of H$_2$SO$_4$/HNO$_3$ and H$_2$SO$_4$/KNO$_3$ could nitrate CL-PPSQ, but they break the cyclic structure also like fuming HNO$_3$. The nitrating reagents of HNO$_3$/KNO$_3$, CH$_3$COOH/KNO$_3$ and HNO$_3$/CH$_3$COOH had no nitration effect on CL-PPSQ. At last, NO$_2$-CL-PPSQ was prepared using HNO$_3$/(CH$_3$O)$_2$O, while the cyclic structure of PPSQ was remained.

References


ULTRADRAWING PROPERTIES OF ULTRAHIGH MOLECULAR WEIGHT POLYETHYLENES / FUNCTIONALIZED ACTIVATED NANO-CARBON AS-PREPARED FIBERS

Jen-taut Yeh¹-³, Chuen-kai Wang³, Chih-chen Tsai³, Wen Yu⁴ and Yi Ding¹

¹ Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials
Ministry of Education, Key Laboratory for the Green Preparation and Application of Functional Materials, Faculty of Materials Science and Engineering, Hubei University, Wuhan, China
E-mail: yjeh@mail.ntust.edu.tw
² Department of Materials Engineering, Kun Shan University, Tainan, Taiwan
³ Graduate School of Material Science and Engineering
National Taiwan University of Science and Technology, Taipei, Taiwan
⁴ College of Chemistry and Chemical Engineering, Wuhan Textile University, Wuhan, China

Keywords: ultradrawing, activated nano-carbon, ultrahigh molecular weight polyethylene.

Systemic investigation of the influence of the activated nano-carbon (ANC) and functionalized activated nano-carbon (FANC) contents on the ultradrawing properties of ultrahigh molecular weight polyethylene / ANC (UHMWPE/ANC, F₁₀₀ANC₀.₁) and UHMWPE / FANC (F₁₀₀FANCᵐₓ₀.₀₇₅) as-prepared fibers are reported. In a way similar to those found for the orientation factor values, the achievable draw ratios (D₉₀) of the F₁₀₀ANC₀.₁ and F₁₀₀FANCᵐₓ₀.₀₇₅) as-prepared fibers approached a maximum value as their ANC and/or FANC contents reached their corresponding optimum values at 0.1 and 0.075 phr, respectively. The maximal D₉₀ values obtained for F₁₀₀FANCᵐₓ₀.₀₇₅ as-prepared fiber specimens prepared at varying PE₈-MAH / acid treated ANC weight ratios were significantly higher that of the F₁₀₀ANC₀.₁ as-prepared fiber specimen prepared at the optimum plain ANC content. In which, the maximum D₉₀ value obtained for F₁₀₀FANCᵐₓ₀.₀₇₅ as-prepared fiber specimen prepared at the optimal FANC content are significantly higher than those of the corresponding F₁₀₀FANCᵐₓ₀.₀₇₅ as-prepared fiber specimens with FANC modified with weight ratios of PE₈-MAH to acid treated ANC other than 12.5. It is worth to note that, the specific strength of F₁₀₀FANCᵐₓ₀.₀₇₅ drawn fiber specimen reached around 95 g/d, which was 200% more than that of the F₁₀₀ drawn fiber specimen prepared without addition of ANC and/or FANC. It is worth noting that the specific strength obtained for F₁₀₀FANCᵐₓ₀.₀₇₅ drawn fiber specimen are about 50% more than the specific strength of the best prepared UHMWPE / functionalized carbon nano-tube drawn fiber specimen prepared in our previous investigation. Tensile property analysis further suggested that excellent orientation and tensile properties of the drawn F₁₀₀ANC₀.₁ and F₁₀₀FANCᵐₓ₀.₀₇₅ fibers can be obtained by ultradrawing the fibers prepared at their optimum ANC and/or FANC contents. To understand the interesting orientation, ultradrawing and tensile properties of F₁₀₀ANC₀.₁ and F₁₀₀FANCᵐₓ₀.₀₇₅ fiber specimens, FTIR, specific surface area, and SEM morphology analysis of the ANC and FANC were performed in this study.
COMPATIBILIZING EFFECTS OF TRIBLOCK COPOLYMER STYRENE/ISOPRENE/STYRENE IN LOW DENSITY POLYETHYLENE/POLYSTYRENE BLENDS

Ewa Wierzbicka, Izabella Legocka

Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland
(ewa.wierzbicka@ichp.pl, www.ichp.pl)

Keywords: chemical modification, compatibilization, polymer blends, mechanical and rheological properties

As a rule the conversion of the immiscible blend into a useful polymeric product with the desired properties requires some modification of the interface. The application of compatibilizer is, among a series of well-known methods, aimed at improving the intermiscibility of thermodynamically immiscible polymer blends. Of course, a compatibilizer has to be compatible or miscible with both phases [1-2].

SEM microphotographs of cryogenically fractured surfaces of LDPE/PS (25/75) blends without and with compatibilizer are made. For blends without SIS/9-BBN modifier, particles of PS and the holes left by them during the fracturing can be observed. The facture is clearly inter-particle and the border is distinct. In contrast, the blends with compatibilizer exhibit a comparatively better interfacial adhesion. The heterogeneous structure with good disperse of one polymer in to the other can be observed. For that reason, we could notice better mechanical properties of LDPE/PS blends in comparison to the same blends without the compatibilizer. The shape of the rheological curve of polymer blends proves that the plasticized effect of compatibilizer in LDPE/PS blends was confirmed. As a consequence, the increase in flexural strength and elongation at break were observed. On the other hand, the decrease in Young modulus, which is a stiffness coefficient, was observed and the tensile strength stayed on the same level as in case of unmodified LDPE/PS blends.

References:
INFLUENCE OF FIBER-LIKE NANOFILERS ON THE RHEOLOGICAL PROPERTIES OF POLYPROPYLENE

Paulo H. L. Aguiar¹, Marcio Yee², Sandra A. Cruz³

¹ Programa de Pós-Graduação em Nanociências e Materiais Avançados, Universidade Federal do ABC, Santo André, SP, Brasil. e-mail: paulo.lopes@ufabc.edu.br
² Departamento de Ciências do Mar – Universidade Federal de São Paulo – DCMAR, Santos, SP, Brasil. e-mail: marcioyee@hotmail.com
³ Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas – Universidade Federal do ABC – CEC/UFABC, Santo André, SP, Brasil. e-mail: sandra.cruz@ufabc.edu.br

Keywords: nanocomposites, polymers, sepiolite, polypropylene

Sepiolite (SEP), a fibrous shaped mineral, has recently gained increasing attention as nanofiller reinforcement [1,2]. One of the few aspects discussed in scientific literature of polypropylene-sepiolite nanocomposites is the influence the SEP on polymeric melt rheological behavior. The nanocomposites PP/SEP were prepared by melt process in a twin-screw corotating extruder and after that, injected molding. Dynamic frequency sweep tests were performed using a controlled stress rheometer (MCR 501 - Anton Paar) under dry nitrogen atmosphere at 200°C. A plate–plate configuration was used with a gap size of 1.0 mm and a plate diameter of 25 mm. The measurements were carried out in the linear viscoelastic regime decreasing the frequency from 300 to 0.01 rad/s. In the lower frequency region (Fig. 1-a), a slight increase in complex viscosity can be observed for the samples containing SEP (with 2.5 and 5%) compared to pure PP. In higher frequency regions, the complex viscosity is the same, independent of the clay content. It can also be seen that, at lower frequency regions, (G') values are slightly higher (with 2.5 and 5% of SEP) than pure PP, once the mobility and relaxation of polymer chains would be retarded by the needle-like nanoclay.

Fig. 1. Complex viscosity (a) and storage modulus (b) as a function of the frequency for PP-SEP with 1, 2.5, and 5% w/w samples.

References
INFLUENCE OF TEMPERATURE, IRRADIATION, EXPOSURE MEDIA AND PRESSURE ON THE ACCELERATED OXIDATION OF POLYPROPYLENE IN AN AUTOCLAVE

K. Bajer, U. Braun

BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin,
kamila.bajer@bam.de

Keywords: Autoclave Test, Polypropylene, Accelerated Oxidation, Temperature, Pressure

The aim of this work is to investigate and compare four different factors, temperature, irradiation, exposure media and pressure, on the oxidation and aging behaviour of polypropylene (PP) bulk samples in the autoclave test. The aging of polypropylene, in this case syringe material, was accelerated under different conditions. The samples were aged at 75°, 80° and 85°C under pure oxygen and at 75°C under ultra-pure water at 50 bar. Further samples treated with 15 kGy (e-beam) were aged at 75°C under pure oxygen at 10, 30 and 50 bar. The different courses of aging were evaluated and compared. Weight, geometry and tensile test were used to assess the changes in technical properties; and DSC, FTIR and TDS-GC-MS to improve the physico-chemical understanding of the aging processes.

The investigations show that all factors tested influence oxidation/aging behaviour. Dry or wet exposure has no effect on aging during the induction time. But after the point of maximum service time the degradation process of polymer changes significantly in the presence of water (Fig. 1). The increase of temperature and pressure decrease the maximum service time; however a temperature higher than 80°C changes the relative ratio of surface and bulk oxidation. The pretreatment with irradiation decrease the maximum service time further (Fig. 1), because the irradiation damages the antioxidant in part. By this the mobility of antioxidant fragments changes a diffusion effects influence the relative ration of bulk and surface oxidation.

Fig. 1. Residual tensile strength after exposure at 75°C and 50 bar of the untreated samples under different exposure media (pure oxygen and ultra-pure water) and of the 15kGy samples under pure oxygen (fit curves added for visual clarity)
EFFECT OF THE COMPATIBILIZATION ON THE PHOTOOXIDATION OF A PA6/LDPE BLEND AND THEIR CLAY NANOCOMPOSITES

M.C. Mistretta¹, P. Fontana¹, M. Morreale², M. Ceraulo¹, F.P. La Mantia¹

1 Department of Civil, Environmental, Aerospace, Materials Engineering, University of Palermo, Viale delle Scienze Ed.6, Palermo, Italy, mariachiara.mistretta@unipa.it
2 Faculty of Engineering and Architecture, Kore University of Enna, Cittadella Universitaria, Enna, Italy

Keywords: Photooxidation, Compatibilization, Blends

Photooxidation of polymer blends shows very interesting features because of the possible interactions between the two phases and between the radicals coming from the two components during UV irradiation [1]. On the other hand, nanocomposites with organomodified clays show, in turn, a photooxidation behaviour depending on the presence of the nanofiller and on the possible interaction between the polymer matrix and the degradation product of the clay [2]. Furthermore, both blends and nanocomposites need the presence of a third component as compatibilizing agent between the different phases. In this work, we investigated the effect of two functionalized polymers used to compatibilize both a PE/PA blend and a nanocomposite prepared by adding an organomodified clay to this blend.

Fig. 1. Elongation at break as a function of UV irradiation time for blends(a) and their nanocomposite(b)

The dimensionless elongation at break as a function of the exposure time clearly suggests that the presence of the compatibilizer slows down the photooxidation kinetics of the uncompatibilized blend, while no significant effect is observed in the nanocomposites. This last feature could be attributed to a strong pro-oxidative effect of the iron present in the clay, while the protective effect in the blend could be interpreted in term of a better morphology achieved. Indeed the compatibilization gives rise to a better adhesion between the phases, with lesser defects and then with a lower oxygen permeability.

References


P10

FUNCTIONAL AND FLEXIBLE NANOSTRUCTURED COORDINATION POLYMERS

Angelica Vlad*, Mirela F. Zaltariov, Maria Cazacu

“Petru Poni” Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, 700487 Iasi, Romania,
e-mail: avlad@icmpp.ro

Keywords: self-assembly, nanostructures, siloxane moieties, AFM images

Coordination polymers have attracted considerable interest because they combine many of the attractive features of conventional polymers with properties that result from the metal-mediated self-assembly process. These materials have found a large number of applications in many fields, such as adsorption, separation and purification, and catalysis.

Our aim was to develop new functional materials using simple molecules having both organic and siloxanic moieties and to control their build-up by self-assembly in the presence of metal (Co and Zn) ions [1,2]. The subsequent adding of the supramolecular assemblies to the metal ions solutions leads to a complete reorganization of the organic phases, as single crystals X-ray diffraction revealed. The co-existence of the hydrophobic dimethylsiloxane sequence and more polar metal-coordinated by carboxylate and pyridyl or imidazol fragments gives an amphiphilic character to the formed compounds that leads to the structuration in solution and in film. The morphology of film investigated by AFM reveals formation of the columnar aggregates having the size of 100-200 nm order (the figure below).

Thermal behaviour, moisture and gas (nitrogen and hydrogen) sorption were investigated. Magnetic susceptibility was determined for paramagnetic Co(II)-containing polyorganometalosiloxane. The dielectric response and ac conductivity were investigated by dielectric spectroscopy at different temperatures and frequencies [1,2].

Acknowledgments:

This work was supported by a grant of the Ministry of National Education, CNCS – UEFISCDI, project number PN-II-ID-PCE-2012-4-0261. The authors also express sincere thanks to Prof. Sergiu Shova for X-ray diffraction analysis data and to Dr. Iuliana Stoica for AFM images.

References:

MODIFICATION OF PLA FIBRES IN THE COURSE OF MELT-SPINNING

Krystyna Twarowska-Schmidt, Grzegorz Maciejewski, Dorota Kaźmierczak

Institute of Biopolymers and Chemical Fibres, M. Sklodowskiej-Curie 19/27, 90-570 Lodz, Poland, e-mail: syntetyk@ibwch.lodz.pl

Keywords: poly(lactic acid) fibres, melt spinning, antimicrobial fibres, profiled cross section, bicomponent fibres

Special fibers fit to satisfy various demands can be prepared either by an adequate modification of the used fibre-grade polymers or by the selection of specific fibre-forming parameters. Thermoplastic fibre-grade polymers are modified in two ways: (a) by chemical modification of the polymer or (b) by admixing special additives to the spinning dope. Some specific fibre properties result from the modification of the fibre cross-section, exemplified by profile or hollow fibres. The technique of spinning bi-component fibres offers another chance of preparing special fibres. Such modifications are since long applied in IBWCh for modeling fibres in the course of spinning.

In the presented work, shown are results of investigations related to the modification of properties of fibers from poly(lactic acid) (PLA) which count to the newest generation of textile raw materials. Alike other synthetic fibers, the biodegradable PLA fibers can be used in the manufacture of textiles like underwear, clothing, sanitary- and medical disposals, geotextiles and technical textile like agro-novowens, fishing nets and ropes.

The fibers were formed from PLA type 6201 D, supplied by NatureWorks LLC. The experimental IBWCh line was used for the purpose. It is a two-step process comprising separate spinning and drawing. Various PLA fibers were prepared: with improved elasticity, antibacterial, with profiled cross-section, bi-component fibers: of the S/S type, self-crimping split fibers and of the C/C type from PLA and PP.

Acknowledgements

The research was made within the project “Biodegradable fibrous materials”, POIG.01.03.01-00-007/08, co-sponsored from EU funds in the frame of the European Fund of Regional Development – Operative Programme Innovative Economy
P12

LACCASE FUNCTIONALIZATION OF FLAX AND COCONUT FIBRES

Andreas Ortner1, Caroline Gamerith1, Enrique Herrero Acero1, Tayuki Kudanga2, Iwona Kaluzna3, Stefaan de Wildeman3,4, Gibson S. Nyanhongo5, Georg M. Guebitz1,5

1 Austrian Centre of Industrial Biotechnology, Konrad Lorenz Strasse 20, 3430, Tulln, Austria; E-mails: enrique.herreroacero@acib.at; caroline.gamerith@acib.at; georg.guebitz@acib.at
2 Institute for Biomedical and Microbial Biotechnology, Biocatalysis and Technical Biology Research Group, Cape Peninsula University of Technology, PO Box 1906, Bellville, 7535, South Africa; E-mail: kudangat@cup.ac.za
3 DSM Innovative Synthesis B.V., Urmonderbaan 22, 6167 RD Geleen, P.O., 6160 MD Geleen, The Netherland; E-mail: iwona.kaluzna@dsm.com, Stefaan.Wildeman-De@dsm
4 Aachen-Maastricht Institute for Biobased Materials, Maastricht University, PO Box 616, 6200 MD Maastricht, The Netherlands; E-mail: s.dewildeman@maastrichtuniversity.nl
5 Institute for Environmental Biotechnology, University of Natural Resources and Applied Life Sciences, Vienna, Konrad Lorenz Strasse 20, 3430, Tulln, Austria; E-mail: g.nyanhongo@boku.ac.at, guebitz@boku.ac.at

Corresponding author: andreas.ortner@acib.at

Keywords: Laccase, flax, coconut, dimer fatty amine

Natural fibres as reinforcing components in composite materials have gained considerable attention. Despite the numerous advantages like low cost, low density, high specific properties and biodegradability, typically they show poor compatibility with the polymer matrix. Laccase mediated grafting of phenols has been commonly used to upgrade the properties of lignocellulose [1, 2]. For examples it is possible to bring antibacterial properties to cellulose fibres [3], or increase the pulp strength and swelling properties [4].

In this study we were able to prove the attachment of different types of functional phenolic molecules onto fibres by using a laccase from Trametes hirsuta as a biocatalyst. XPS analysis indicated almost 5% incorporation of these molecules in flax, however, grafting was not that effective on coconut fibres. To broaden the activation scope, mediators, which act as electron shuttles between the laccase and the substrate, were used allowing grafting of hydrophobic molecules like dimer fatty amines. Different mediators like HBT, TEMPO and ABTS were tested, being TEMPO the most effective achieving an increase of the aliphatic groups grafted by 10% according to XPS analysis.

References

P13

EFFECTS OF NOVEL CLASS II HYDROPHOBINS ON ENZYMATIC HYDROLYSIS OF POLYETHYLENE TEREPTHALATE

Caroline Gamerith1, Enrique Herrero Acero1, Andreas Ortner1,2, Agnieszka Przylucka1, Irina S. Druzhinina1,3, Christian P. Kubicek1,3, Georg M. Guebitz1,2

1 Austrian Centre of Industrial Biotechnology, Konrad Lorenz Straße 20, 3430 Tulln, Austria, caroline.gamerith@acib.at
2 Institute of Environmental biotechnology, University of Natural Resources and Life Sciences, Konrad Lorenz Straße 20, 3430 Tulln, Austria
3 Institute of Chemical Engineering, University of Technology, Gumpendorferstraße 1a, 1060 Vienna, Austria

Keywords: poly(ethylene)terephthalate, hydrophobin, cutinase

Poly(ethylene terephthalate) (PET) is one of the most widely used synthetic polymers worldwide. Despite its many outstanding properties, PET has a very hydrophobic character, which makes its processability very challenging. A wide variety of enzymes have been described to be able to hydrolyse PET [1, 2]. Mild hydrolysis of the upper most layer of the polymer or extensive hydrolysis to the monomers are two approaches that can be used to functionalize or recycle PET in a highly selective and environmentally friendly way.

Among the different enzymes able to hydrolyse PET, cutinases have been described to be the most efficient, however, the fact that PET is a non-natural, hydrophobic substrate the hydrolysis-rates are rather low. Hydrophobins (Hfbs) are small cysteine-rich proteins expressed by filamentous fungi that form amphipathic monolayers on hydrophobic/hydrophilic interfaces and are supposed to stimulate the hydrolysis rate of PET. In nature they occur on the outer surfaces of cell walls of hyphae and conidia where they play a major role for interactions between the fungus and the environment. The effect of class II Hfbs fused to glutathione S-transferase (GST) on PET hydrolysis by H. insolens was investigated, showing a stimulation of the polymer hydrolysis [3]. The soluble release products of PET hydrolysis namely terephthalic acid (TA), mono-(2-hydroxyethyl) terephthalate (MHET), and bis-(2-hydroxyethyl) terephthalate (BHET) were measured by HPLC with a UV detector.

Acknowledgments

This work has been supported by the Federal Ministry of Science, Research and Economy (BMWFW), the Federal Ministry of Traffic, Innovation and Technology (bmvit), the Styrian Business Promotion Agency SFG, the Standortagentur Tirol and ZIT - Technology Agency of the City of Vienna through the COMET-Funding Program managed by the Austrian Research Promotion Agency FFG.

References

IMPROVED STABILITY OF GRAPHENE OXIDE-SILICA NANOHYBRIDS AND RELATED POLYMER-BASED NANOCOMPOSITES

A. Maio1, R. Scaffaro1, R. Khatibi1, S.P. Agnello2, A. Piazza2, L. Botta1, Gianpiero Buscarino2

1 DICAM, University of Palermo, V.le Scienze, ed. 6, Palermo. andrea.maio@unipa.it
2 STEBICEF, University of Palermo, V.le Scienze, ed. 6, Palermo.

Keywords: graphene oxide, nanosilica, nanohybrids, thermal treatment, melt processing.

Although its promising properties make the graphene oxide (GO) very interesting as filler for polymer matrices, some problems related to its thermal stability in the region which ranges from 80 to 200 °C, are crucial for the possibility to melt process GO together with practically all the polymers [1,2]. Moreover, above 100 °C GO lamellae were found to become stacked. In this work, two different ways to preserve the GO structure and ensure its dispersion within different polymer matrices have been investigated and schematized in Fig. 1. Exfoliation plays a key-role in the achievement of good mechanical properties since it preserves the GO from both stacking phenomena. The capability of silica to exfoliate the GO lamellae is confirmed by SEM analysis and probably this feature leads to the achievement of a better morphology in terms of exfoliation/intercalation thus resulting in a better load transfer. Moreover, the presence of silica results in an increased thermal stability of the GO, as confirmed by Raman analysis and TGA. The nanocomposites prepared by incorporating GO-silica nanohybrids within PA6, EVA and PC showed mechanical properties higher than those directly melt mixed with GO. Furthermore, the GO-silica-polymer nanocomposites were found to have mechanical performance similar or better than GO-polymer prepared via solvent casting.

Fig. 1. Schematization of the process.

References


CORRELATION BETWEEN THE CHEMICAL-PHYSICAL PROPERTIES OF CNT AND MACROSCOPIC PROPERTIES OF RELATED NANOCOMPOSITES: A STATISTICAL APPROACH

A. Maio¹, L. Botta¹, R. Scaffaro¹

¹ Department of Civil, Environmental, Aerospace, Materials Engineering, University of Palermo, V.le delle Scienze, Ed. 6, 90128 Palermo, Italy, roberto.scaffaro@unipa.it

Keywords: CNTs, PC, nanocomposites, statistical analysis, full factorial design, DMTA

In the frame of this work, two different samples of CNTs, namely CNT 1 and CNT 2, were synthesized [1] with different degree of purity and aspect ratio and used as fillers either without any treatment or after a plasma-oxidation, to prepare polycarbonate (PC)-based nanocomposites by melt mixing. The influence of plasma treatment, filler content and type of CNTs on the mechanical, dynamic-mechanical, and electrical properties of the materials was assessed by a two level full factorial design. The morphological analysis carried out by SEM and TEM evidenced the formation of a nanohybrid structure when oxidized CNTs were used as filler. Generally speaking, CNT 2 showed the best dispersion and the strongest adhesion to the matrix. As regards the effect of the functionalization, it was evident that a stronger interfacial adhesion and a better dispersion were achieved after fillers plasma-treatment. The statistical approach pointed out that functionalization and typology of the CNTs played a crucial role on the properties of the nanocomposites rather than filler content. The main effect of these 3 variables on the storage modulus at 50 °C carried out by DMTA (a) and on the electrical conductivity (b) of the nanocomposites is reported in Fig. 1.

![Fig. 1. Main effect of content, plasma functionalization and typology of CNT on the dynamic-mechanical (a) and electrical properties (b) of PC-based nanocomposites.](image)

References

Graphene oxide (GrO) was synthesized with Marcano’s method [1] and added at 0.5 and 1 wt% loading content to a polyamide 6 (PA6). In particular, three different techniques have been used for the preparation of the nanocomposites: (i) melt blending in a batch mixer, (ii) solvent casting in formic acid, (iii) preparation of a masterbatch by solvent casting and further melt processing. The films (80 μm) were photo-oxidized in a QU-V chamber up to about 100 hours. The effect of filler content and preparation technique on the photo-stability of the nanocomposites has been followed by monitoring the change of the mechanical and spectroscopic properties undergone upon artificial exposure to UV-B light. The elongation at break is an excellent parameter to establish the photo-oxidation resistance of polymer materials as it is very sensitive to the molecular and morphological changes undergone by the polymer during irradiation [2]. Indeed, these changes strongly affect the values of the elongation at break. The dimensionless elongation at break as a function of the exposure time of nanocomposite films is reported in Fig. 1. The results clearly show that adding GrO determines a strong increase of the photo-stability of the PA6 in almost all the cases. Moreover, it is possible to notice a strong interaction between filler content and preparation technique adopted. The materials prepared according to (i) take advantage by higher level of filler loading, while undergo a rapid degradation after 48 h when loaded with 0.5 wt% of GrO. Those prepared according to (ii) are more resistant and their dimensionless EB plots, not influenced by GrO content, are steady within the temporal range investigated. The photo-oxidation behaviour of the materials prepared according to (iii) was halfway between (i) and (ii) at lower loading and was found to be closer to that of the PA6 when GrO is loaded at wt1%, thus confirming a worsening of the photo-resistance upon increasing filler content.

Fig. 1. Normalized elongation at break vs photo-oxidation time of the nanocomposites investigated.

References


NATURAL ANTI-OXIDANTS IMMOBILIZED ONTO CARBON NANOTUBES FOR THERMO-OXIDATION RESISTANT POLYMER-BASED NANOCOMPOSITES

Rossella Arrigo¹, Nadka Tz. Dintcheva¹, Cristian Gambarotti², Monica Guenzi², Sabrina Carroccio³, Francesca Cicogna⁴, Giovanni Filippone⁵

¹DICAM, University of Palermo, 90128 Palermo, IT, rossella.arrigo@unipa.it, nadka.dintcheva@unipa.it;  
²Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milano, IT, cristian.gambarotti@polimi.it, monica.guenzi@polimi.it;  
³CNR - ICTP UOS Catania, Via P. Gaifami 18, 95126 Catania, IT, sabrinacarola.carroccio@cnr.it;  
⁴CNR - ICCOM UOS Pisa, Area della Ricerca, Via G. Moruzzi 1, 56124 Pisa, IT, francesca.cicogna@pi.iccom.cnr.it;  
⁵Università di Napoli Federico II, Piazzale V. Tecchio 80, 80125 Napoli, IT, giovanni.filippone@unina.it

Keywords: Carbon nanotubes, α-Tocopherol, Quercetin, UHMWPE, Stabilization.

The use of natural antioxidants is an attractive way to formulate nanocomposites with extended durability and with potential applications in bio-medical field. In this work, Vitamin E (VE) in the form of α-tocopherol and Quercetin (Q) were physically immobilized onto multi-walled carbon nanotubes bearing covalently-linked long-chain alkyl ester groups (CNTs) and the resulting hybrids CNTs-VE and CNTs-Q were used to formulate thermo-oxidation stable ultra high molecular weight polyethylene based nanocomposites. The thermo-oxidation of the nanocomposites was performed at 120°C in air oven. The samples were then subjected to FTIR analyses at different annealing times. In Figure 1, the trends of carbonyl and hydroxyl indices for all the investigated systems are reported as a function of the thermo-oxidation times. It is evident that the degradation process is slower for the nanocomposites containing VE and Q molecules. As known, the VE and Q molecules are both known to be effective in the protection of the polymeric matrices against thermo-oxidation, but their the excellent obtained stabilizing actions attained in our samples are definitely much higher than what commonly reported in literature. Such an unexpected finding could be explained considering some specific interactions between the used natural anti-oxidants and the carbon atoms of the outer surface of the CNTs. Such interactions could give rise to the formation, upon thermal treatment, of several intermediate anti-oxidant radicals, which induce the formation of CNT surface defects. In this way, some carbon atoms change their hybridization from sp² to sp³, achieving radical scavenging properties.

Fig. 1. Carbonyl (a) and Hydroxyl (b) Indices for neat UHMWPE and complex nanocomposites systems as a function of the thermo-oxidation times.

Acknowledgment:

This work is financially supported by MIUR-Italy, FIRB2010 – Project: GREENER (cod: RBFR10DCS7).
PHOTO- AND THERMO- OXIDATIVE RESISTANCE OF NOVEL NANO COMPOSITES BASED ON CNT-POSS HYBRID NANO FILLERS

Rossella Arrigo ¹, Nadka Tz. Dintcheva ¹, Vitangelo Pampalone ¹, Cristian Gambarotti ², Monica Guenzi ²

¹DICAM, University of Palermo, 90128 Palermo, IT, rossella.arrigo@unipa.it, nadka.dintcheva@unipa.it; ²Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milano, IT, cristian.gambarotti@polimi.it, monica.guenzi@polimi.it

Keywords: Carbon nanotubes, POSS molecules, UHMWPE, photo- and thermo-oxidation.

The formulation of innovative nanofillers containing nanoparticles having different chemical nature and physical properties can be considered as an attractive way to obtain hybrid multi-functional nanostructures. In this work, POSS molecules (Three Silanol Phenyl POSS; TSPH) has been successfully grafted onto the outer surface of CNTs bearing long alkyl-chains functionalities and the obtained hybrid nanoparticles have been used for the formulation of Ultra High Molecular Weight PolyEthylene (UHMWPE) based nanocomposites. The rheological, morphological and thermo-mechanical analysis has been accurately performed (not reported here) and the obtained results suggest a well pronounced beneficial effect of POSS molecules grafted onto CNTs on the dispersion and morphology of the nanocomposites. Besides, the photo- and thermo-oxidation of the nanocomposites was performed and the samples were then subjected to FTIR analyses at different aging/annealing times. In Figure 1, the trends of carbonyl indices for all the investigated systems are reported as a function of the (a) photo- and (b) thermo-oxidation times. The adding of CNTs slow down both photo- and thermo-degradation phenomena due to the well known radical scavenging action of CNTs. Similarly, the POSS molecules are able to protect the polymer matrix against degradation, acting as H donor and/or UV absorber. CNTs-POSS/UHMWPE nanocomposites show excellent photo- and thermo-oxidative resistance because the hybrid nanoparticles are very effective in the protection of the polymeric matrix, offering a stabilizing action which is absolutely much higher than those showed by CNTs and POSS molecules, added one by one. Such this unexpected finding could be explained considering some synergistic action between the electronic system of CNTs and the inorganic framework of POSS molecules.

Fig. 1. Carbonyl Index for neat UHMWPE and complex nanocomposites systems as a function of the photo-oxidation (a) and thermo-oxidation (b) times.

Acknowledgment:

This work is financially supported by MIUR-Italy, FIRB2010 – Project: GREENER (cod: RBFR10DCS7).
ADVANCED NANOFILLERS FOR POLYMERS: ANTIOXIDANTS IMMOBILIZED IN LAYERED CLAYS

Elisabetta Morici¹, Nadka Tz. Dintcheva²,³, Sahar Al-Malaika³, Lucia Pérez Amaro⁴, Elisa Passaglia⁴

¹DICGIM, Università di Palermo, 90128 Palermo, IT, elisabetta.morici@unipa.it; ²DICAM, Università di Palermo, 90128 Palermo, IT, nadka.dintcheva@unipa.it; ³PPP Research Unit, School of Engineering and Applied Science, Aston University, Aston Triangle, Birmingham, B4 7ET, UK, s.al-malaika@aston.ac.uk; ⁴CNR - ICCOM UOS Pisa, Via G. Moruzzi 1, 56124 Pisa, IT, passaglia@pi.iccom.cnr.it.

Keywords: Stabilization, Antioxidant, Clay, Polymeric nanocomposite

The use of natural clays as nanofillers for polymer matrices is attractive because of low cost, improvement of mechanical and barrier properties, inflammability, and eco-compatibility. The problems are related to their tendency to accelerate the photo- and thermo-oxidative degradation, above all in organo-modifier presence. In order to increase durability, the traditional approach is the incorporation within the polymeric matrices of stabilizing additives. To be effective, additives have to be well dispersed and to remain physically in the polymer matrix but, usually, they have a limited compatibility i.e. poor dispersion, and tendency to migrate or volatilize during processing. To solve this matter, a possible approach is the immobilization of stabilizer molecules. In this work reactive antioxidant molecules (r-AO), as hindered phenols, are performed by hydrolysis reaction of commercial Ciba® Irganox® 1076 and, through ion exchange, are directly intercalated in anionic clays (layered double hydroxides, LDH). Moreover the r-AOs are grafted on the ammonium salt and, then, through ions exchanging with cationic clay (montmorillonite MMT), thermally stable organo-modified montmorillonite is formulated. The novel nanofillers are exploited to produce, by melt mixing, biopolymer-based nanocomposites using poly lactid-acid (PLA), polyamide11 (PA11) and polybutylene succinate (PBS) as matrices. The morphology after processing of all nanocomposites is investigated through XRD, SEM and TEM observations. The results show that the clay layers are uniformly dispersed in the polymer matrix, and exfoliated structures are obtained. Moreover, to investigate the thermo-degradation of the nanocomposites during processing, rheological analysis is performed and the findings suggest a beneficial effect of the presence of antioxidant molecules. The thermo-oxidation resistance of nanocomposites is evaluated through the exposure of thin films at high temperature (below T_melt) in air oven and then FT-IR spectra, at different exposure times, are collected. FT-IR spectroscopy and calorimetric analyses show that all nanocomposites exhibit high thermo-oxidative resistance, with increased induction time of the degradation phenomena. Therefore, the intercalation or immobilization of active antioxidant compounds in natural layered clay enhance the thermo-oxidative stability of the nanocomposites. The reasons could be different: the good dispersion of the stabilizer; the release of anti-oxidant as byproducts coming from decomposition of ammonium ion (Hoffmann elimination reaction); the stabilizing action exercised locally at the interface between the inorganic clay and the organic polymer macromolecules i.e. where the degradation process begins. Moreover it cannot be excluded that the clay platelets could prevent the migration or volatilization of the antioxidant molecules during processing.

Acknowledgment:

This work is financially supported by Marie Curie Action–PEOPLE 2011–IEF, Project: NANOSTAB-GB 300302.
P20

STABILIZATION OF LOW TALCUM FILLED PP IMPACT COPOLYMERS

Sarah Van Mierloo ¹, Marc Herklots ²

¹,² SABIC Technology Center, SABIC, Geleen, The Netherlands

Keywords: Talcum, long term heat stability, processing stability, OIT-DSC, TGA, chemiluminescence

Talcum is widely used to enhance the stiffness of polypropylene. Talcum is a layered magnesium silicate consisting of sheets of magnesium in octahedral coordination. The layered sheets are held together by weak van der Waals forces. The crystal presents basal hydrophobic surfaces with Si–O–Si groups, as well as lateral surfaces with Si–OH groups and residual magnesium cations. Depending on the source, talcum often contains traces of dolomite, chlorite, magnesite, Fe₂O₃ and graphite. The nature and level of the impurities determine the final color and the surface characteristics of the talcum. Although the mineral is often considered as chemically inert, it contains certain reactive groups on its surface and it is generally known that talcum can interact and react with additives like for example stabilizers.

Based on reviewed literature¹–⁴, the presence of talcum can have an adverse effect on processing, long term heat and light stability of polyolefins. The influence of addition of 20-40 wt% talcum on the thermal and photochemical stability has been extensively investigated. On the contrary, the influence of talcum on stability was not particularly studied for lower talcum content (3-5 wt%).

This study concentrates on heat and processing stability of up to 5 wt% talcum filled polypropylene and especially on the influence of stabilizer-talcum interactions. Talcum types with different surface treatment were examined. Investigated stabilizers were amongst others tetrakis[methylene-3(3',5'-di-t-butyl-4-hydroxyphenyl)propionate]methane (BASF: Irganox 1010) and tris[2,4-di-t-butylphenyl]phosphite (BASF: Irgafos 168).

Oven ageing, repeated extrusion, DSC and chemiluminescence were used for studying thermal stability of the talcum filled polypropylene. Also various analytical techniques such as TGA and TGA-TD-GC-MS have been used to study talcum-antioxidant interactions and appeared to be very useful as a screening tool for revealing possible talcum-antioxidant interactions.

References
P22

NEW STABILIZATION SYSTEMS FOR UHMWPE TESTED IN BIO-ANALOGOUS CONDITIONS

J. Kredatusová, H. Beneš, M. Nevoralová, M. Šlouf, Z. Kruliš, D. Michálková, M. Brunclíková

1 Institute of Macromolecular Chemistry AS CR, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic, kredatusova@imc.cas.cz

Keywords: accelerated ageing, polyethylene, stabilization

For many years, ultra-high molecular weight polyethylene (UHMWPE, $M_w \approx 2 - 6 \times 10^6$ g/mol) has been successfully used in total joint replacement (TJR). Nevertheless, a relatively high abrasive wear of UHMWPE can cause serious problems leading to failure of the TJR [1]. To improve its wear resistance as well as its oxidation stability, UHMWPE is cross-linked by gamma irradiation and stabilized with $\alpha$-tocopherol [2]. However, during the gamma irradiation $\alpha$-tocopherol reacts with formed radicals and is partially consumed, resulted in a reduced efficiency of irradiation [3]. This problem can be solved by using a different class of stabilizers – hindered amine light stabilizers (HALS) which do not show these negative attributes of $\alpha$-tocopherol [4].

The aim of this work was to compare the effect of $\alpha$-tocopherol, HALS stabilizers and their mixtures and to find a suitable stabilization system for UHMWPE components of TJR with a longer lifetime. Their effects on the cross-linking of UHMWPE by irradiation and on the oxidation stability and changes in wear resistance of UHMWPE during an accelerated ageing were evaluated.

The accelerated ageing was performed either in water bath of $H_2O_2$ (0.1 M) or in water saturated with oxygen (5 atm). The aged samples were extracted in xylene and their swelling ratio and cross-linking density were determined. The degree of oxidative degradation of the samples was assessed using IR spectroscopy – oxidation index, differential scanning calorimetry – crystallinity, and by mechanical testing. Due to exceptional properties of UHMWPE some measurements could not be accurately evaluated, therefore, three model polyethylenes (HDPE) with lower molecular weight – $M_w \approx 5 \times 10^4$ – $1 \times 10^6$ g/mol were used for these measurements.

Acknowledgement

The research was financially supported by the Technology Agency of the Czech Republic (grant No. TA01011406).

References

SYNTHESIS OF BRANCHED POLY(ETHYLENEIMINE) BASED MACROMOLECULAR STABILIZERS

Attila Nádor, György Kasza, Györgyi Szarka, Béla Iván

Polymer Chemistry Group, Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1117 Budapest, Magyar tudósok krt. 2, nador.attila@ttk.mta.hu

Keywords: stabilizer, functionalization

Nowadays significant problem is that the widely used low molecular weight additives of food packaging materials and agricultural foils (e.g., antioxidants, stabilizers) can migrate to the surface and then contaminate the food and the environment. A solution is to develop macromolecular additives, wherein the higher molecular weight inhibits the migration in the plastic films.

We tried to develop a new poly(ethyleneimine) (PEI) based macromolecular stabilizer (Figure 1). We used a BHT analogue, the 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoic acid as stabilizer. We also investigated to link three different chain lengths of alkyl-carboxylic acids (butyric acid, lauric acid and stearic acid) as compatibilisers simultaneously with different ratios of the antioxidant to improve miscibility with polymers. The functionalizations were carried out with the amidation reaction using DCC and HOBt in DMF at room temperature. The functionalized macromolecules were characterized via NMR and UV/VIS spectroscopies and GPC chromatography.

Our results show that the functionalization reactions were successfull and the ratio of antioxidant and compatibilizer in the produced macrostabilizer can be influenced easily by the feed ratio of the reactants.

Acknowledgement

The authors would thank the European Regional Development Fund through the Hungary-Slovakia Cross Border Cooperation Programme 2007-2013 (HUSK/1101/1.2.1/0209) for their support of this research.
SYNTHESIS OF HYPERBRANCHED POLYGLYCEROL BASED MACROMOLECULAR ANTIOXIDANTS

György Kasza, Attila Nádor, Györgyi Szarka, Béla Iván

Polymer Chemistry Group, Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1117 Budapest, Magyar tudósok krt. 2, kasza.gyorgy@ttk.mta.hu

Keywords: stabilizer, functionalization, polyglycerol

Significant amount of additives (e.g., antioxidants, stabilizers) are used in food packaging materials and agricultural foils. Most commonly used additives are low molecular weight which can migrate easily to the surface therefore leaching into the environment is a main problem.

We tried to develop a new hyperbranched polyglycerol (HbPG) based macromolecular stabilizer (Fig 1.). The hyperbranched polyglycerol is a polyether polyol which has proved biocompatible properties. We functionalized it by a BHT analogue, the 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoic acid as antioxidant. We investigated different esterification methods for functionalization of hydroxyl groups of HbPG by the BHT analogue and our result clearly indicates that the Steglich esterification method was most effective. We also investigated to improve miscibility with the foil’s polymers by using compatibilizer agents such as butyric acid, lauric acid and stearic acid. The functionalized macromolecules were characterized by GPC chromatography and $^1$H-NMR and the antioxidant capacities were measured by UV/VIS spectroscopy. The antioxidative properties of produced macromolecular antioxidants were demonstrated by thermal oxidative degradation tests of PVC.

Fig. 1. Schematic structure of HbPG based macromolecular antioxidant

We successfully synthesized macromolecular antioxidant with hyperbranched polyglycerol core with different ratio of antioxidant and compatibilizer.

Acknowledgement

The authors would thank the European Regional Development Fund through the Hungary-Slovakia Cross Border Cooperation Programme 2007-2013 (HUSK/1101/1.2.1/0209) for their support of this research.
P25

IONIC LIQUIDS AS COMPATIBILIZERS FOR EPOXY-THERMOPLASTIC BLENDS AND COMPOSITES

H. Beneš¹, S. Livi², M. Perchacz¹, V. Štengl³

¹ Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Heyrovsky sq. 2, 162 06 Prague 6, Czech Republic, benesh@imc.cas.cz
² Ingénierie des Matériaux Polyémers, INSA Lyon, UMR CRNS 5223, Université de Lyon, 17 Avenue Jean Capelle, F-69621 Villeurbanne Cedex, France
³ Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, v.v.i., 250 68 Husinec-Rez, Czech Republic

Keywords: epoxy, polyethersulfone, ionic liquids, graphene

Highly-functionalized epoxy resins and aromatic diamine hardeners are the most popular in commercial epoxide systems exhibiting high Tg, which are commonly used in aerospace, railway and automotive industry for structural fibre-reinforced composites. Nevertheless, these materials are usually brittle with poor fracture toughness. Therefore, addition of glassy thermoplastics exhibiting high Tg (such as polyethersulfone, PES [1], etc.) and acting as toughener is often demanded. The morphology of created blends consisting of thermoplastic-rich particles dispersed in the continuous epoxy matrix can contribute to toughening [2]. In order to obtain homogeneously distributed thermoplastic domains in the surrounding matrix, a suitable compatibilizer can be advantageously added.

In the present work, the effects of different ionic liquids (ILs) on morphologies of epoxy-PES blends as well as epoxy-PES-graphene composites were evaluated by means of SEM, TEM, AFM, DMA, mechanical testing and surface tension measurements. It was found that the role of ILs in the final material was highly dependent on IL structure and interactions with surrounding environment (epoxy matrix, PES nodules or graphene filler). In consequence, the ILs acted as compatibilizers, which decrease the epoxy-PES interfacial energy, or as coupling agents, which improve adhesion between the graphene filler and the epoxy matrix.

Acknowledgment

Financial support of the Grant Agency of the Czech Republic (project 14-05146S) is gratefully appreciated by the authors.

References


P26

STARCH MODIFICATION BY ELECTRON BEAM PROCESSING FOR USE IN THE WASTEWATER TREATMENT

Mirela Brașoveanu¹, Monica R. Nemțanu¹, Liliana Flore², Veronica Anca²

1 National Institute for Lasers, Plasma and Radiation Physics, Electron Accelerators Laboratory, 409 Atomiștilor St., PO Box MG-36, 077125, Bucharest-Magurele, Romania, mirela.brasoveanu@inflpr.ro, monica.nemtanu@inflpr.ro
2 SC ICA Research & Development SRL (ICA R&D), 202 Splaiul Independenței, Etj. 4, Sector 6, Bucharest, Romania

Keywords: starch, irradiation, grafting, flocculation performance

Modification of natural polymers for applications in wastewater treatment is a continuous concern of researchers and technologists in close relation to advantages they provide as related to classical polymeric flocculants. The main methods to synthesize grafted polysaccharides involve the use of a chemical free radical initiator (conventional method), ionizing radiation (gamma and X rays, electron beam), ultraviolet or microwave radiation. Although the most used ionizing radiation is gamma radiation, electron beams are preferred for easy and secure handling lately. Thus, in order to develop a new starch-based flocculant material, graft copolymerization of acrylamide onto starch induced by electron beam processing as the free radical initiator and no additional chemicals was investigated in this work. The grafting parameters such as monomer conversion and grafting ratio were evaluated. The graft copolymers were characterized by intrinsic viscosity, elemental analysis, infrared spectroscopy and scanning electron microscopy in correlation with monomer-to-starch ratio and irradiation dose. Flocculation performances of the grafted copolymers were evaluated by combining with classical electrolytes in order to remove the organic load of wastewater collected from a meat products processing plant. The results proved that the grafting occurred in each particular case, and the level of grafting was obviously influenced by the monomer-to-starch ratio and less by irradiation dose in the range of doses investigated herein. The flocculation study revealed that all synthesized graft copolymers were efficient for properties like total suspended solids and chemical oxygen demand. Instead, the desired reduction of fatty matter in suspension depended on copolymers dosage as well as their monomer-to-starch ratio and irradiation dose.

Acknowledgements:

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI–UEFISCDI, project number 64/2012.
IMPACT OF RECOMBINANT MYRIOCOCCUM THERMOPHILUM CELLOBIOSE DEHYDROGENASE FOR THE APPLICATION IN BLEACHING PROCESSES

Gregor Tegl1, Daniela Huber1, Annemarie Flitsch2, Christoph Sygmund3, Roland Ludwig3, Gibson S. Nyanhongo1, Georg M. Guebitz1,4

1 BOKU – University of Natural Resources and Life Sciences, Institute for Environmental Biotechnology, Konrad Lorenz Straße 20, 3430 Tulln an der Donau, Austria
2 Graz University of Technology, Institute of Environmental Biotechnology, Petersgasse 12/1, A-8010 Graz, Austria
3 BOKU – University of Natural Resources and Life Sciences, Department of Food Sciences and Technology, Vienna Institute of Biotechnology, Muthgasse 18, 1190 Vienna, Austria
4 Austrian Center of Industrial Biotechnology, Petersgasse 14, 8010 Graz, Austria

Keywords: oxidoreductase, hydrogen peroxide, cellulose oligomers

The oxidoreductase cellobiose dehydrogenase (CDH) is an extracellular flavocytochrome produced by wood degrading fungi. Furthermore, CDH can oxidize cellobiose and cello-oligomers by using a wide range of electron acceptors like quinones, phenoxyradicals, etc. [1,2]. Many industrial interesting cello-oligomers like maltose, lactose, celloextrins etc. can be reduced or oxidized by CDH and are also employed in biosensors [3,4].

In this study, the ability of a recombinant M. thermophilum cellobiose dehydrogenase (MtCDH) to be used as a bleaching agent based of its ability to produce hydrogen peroxide was investigated. MtCDH was therefore incubated with different cellulose oligomers and the oxidation of the substrates was monitored by using FTIR, HPLC-MS and determination of the resulting hydrogen peroxide. For the first time, in vitro HPLC-MS studies showed that MtCDH oxidized cellulose oligomers on the C-1 on glucose moiety at the reducing ends. This fact is an agreement for current mechanism for other CDHs [2]. The ability of CDH to oxidize structurally different cellulose oligomers makes it interesting for in situ bleaching systems.

References

MODIFICATION OF THERMOPLASTIC STARCH WITH MALEIC ANHYDRIDE OR SEBACIC ACID, BY REACTIVE EXTRUSION, FOR COMPATIBILIZING TPS/PBAT BLENDS

Stella Risso¹, Pablo Andres Riveros Muñoz ¹, Alex Sandro Babetto¹, Ana Cristina Sousa², Alessandra Almeida Lucas¹, Sílvia Helena Prado Bettini¹

1 Federal University of São Carlos, Rod. Washington Luiz, km 235, São Carlos. São Paulo. - Brazil, silvia.bettini@ufscar.br
2 Universidade Federal do Triângulo Mineiro - Minas Gerais - Brazil

Keywords: thermoplastic starch (TPS), reactive extrusion, maleic anhydride, TPS/PBAT blends

Modifications of thermoplastic starch (TPS) with maleic anhydride (MTPS) and sebacic acid (STPS) were conducted by reactive extrusion to improve compatibilization of TPS/PBAT blends (50/50). TPS was prepared by mixture of cassava starch (67 %), glycerol (23 %) and water (10%). TPS modifications were conducted in a twin screw extruder. MTPS and STPS were then melt-blended with PBAT in a subsequent extrusion process. Effects of starch modification onto TPS/PBAT blends were analyzed by mechanical properties and morphological analyses. The morphological properties were assessed by scanning electron microscopy (SEM). The results obtained from the morphological analysis (Figure 1) showed higher phase dispersion of the starch on PBAT, when the TPS was reacted with maleic anhydride (esterification agent). However, the micrographs suggest that sebacic acid does not react with TPS, due, probably, its higher aliphatic chain, which may be exuded from the TPS. The mechanical properties of TPS/PBAT and MTPS/PBAT blends presented similar tensile strength, despite the greater dispersed phase distribution of the blend containing MTPS. These results were attributed to starch degradation during the reactive extrusion and the presence of unreacted maleic anhydride, which formed lamellae in the blends, acting as stress concentrator in the blend.

![Fig. 1: SEM micrographs of (A) TPS/PBAT 1000x, (B) STPS/PBAT 1000x, (C) MTPS/PBAT 1000x and (D) MTPS/PBAT 5000x.](image)

Table 1: Mechanical properties of blends.

<table>
<thead>
<tr>
<th></th>
<th>Yield Tension</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBAT</td>
<td>8.6 ± 0.6</td>
<td>20.2</td>
<td>299 ± 44.6</td>
</tr>
<tr>
<td>TPS/PBAT</td>
<td>6.1 ± 0.9</td>
<td>7.8</td>
<td>320 ± 26.3</td>
</tr>
<tr>
<td>MTPS/PBAT</td>
<td>6.0 ± 1.4</td>
<td>6.0</td>
<td>311 ± 14.2</td>
</tr>
<tr>
<td>STPS/PBAT</td>
<td>4.4 ± 0.3</td>
<td>4.4</td>
<td>27 ± 13.0</td>
</tr>
</tbody>
</table>
MODIFICATION OF POLY(ACID LACTIC) WITH MALEIC ANHYDRIDE, BY REACTIVE EXTRUSION, FOR COMPATIBILIZING PLA/PBAT BLENDS

Talita Rocha Rigolin, Pablo Andres Riveros Muñoz, Sílvia Helena Prado Bettini

Federal University of São Carlos, Rod. Washington Luiz, km 235, São Carlos. São Paulo. - Brazil, talita.rigolin@gmail.com

Keywords: poly(acid lactic), reactive extrusion, maleic anhydride, PLA/PBAT blends

Melt blending of poly(acid lactic) (PLA) and poly(butylene adipate-co-terephthalate) (PBAT) was investigated. In order to improve the interfacial adhesion during the melt blending, PLA was modified with maleic anhydride (MA) in the presence of dicumyl peroxide (DCP) and the study of reaction routes was performed. All reactions were carried out in the molten state in a corotating intermeshing twin-screw extruder. The amount of MA and DCP (2 phr and 1 phr, respectively) and the polymers ratio (PLA/PBAT – 70/30) were both maintained constant.Compatibilization of the blend was performed by two ways, one using in situ PLA/PBAT modification and the other using a pre-modified PLA (PLA-g-MA). A blend without MA (PLA/PBAT) was used as reference. The modified PLA was characterized by size exclusion chromatography (SEC). Additional analysis by scanning electron microscopy (SEM) were performed for the blends. During the PLA modification, with MA, was observed a reduction of 45% in Mn. The blends presented similar mechanical behavior, however, when the data are inputted additivity rule equation, a synergic effect is observed for PLA-g-MA/PBAT. Morphological analysis, performed by SEM, shows a better adhesion phase when the blend is produced using PLA-g-MA, in according with the observed mechanical behavior.

Table 1: Properties of PLA, PBAT and blends.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Tensile Strength MPa</th>
<th>Tensile Modulus GPa</th>
<th>Tensile Strength* MPa</th>
<th>Tensile Modulus* GPa</th>
<th>Mn kg/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>64,79 ± 0,33</td>
<td>3,22 ± 0,02</td>
<td>-</td>
<td>-</td>
<td>131</td>
</tr>
<tr>
<td>PLA-g-MA</td>
<td>51,67 ± 1,64</td>
<td>3,09 ± 0,08</td>
<td>-</td>
<td>-</td>
<td>82</td>
</tr>
<tr>
<td>PBAT</td>
<td>9,60 ± 0,08</td>
<td>0,07 ± 0,001</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PLA/PBAT</td>
<td>40,96 ± 0,82</td>
<td>2,02 ± 0,03</td>
<td>48,23</td>
<td>2,28</td>
<td>-</td>
</tr>
<tr>
<td>PLA-g-MA/PBAT</td>
<td>44,22 ± 0,97</td>
<td>2,18 ± 0,04</td>
<td>39,05</td>
<td>2,18</td>
<td>-</td>
</tr>
<tr>
<td>PLA/PBAT in situ</td>
<td>42,45 ± 0,55</td>
<td>2,12 ± 0,02</td>
<td>48,23</td>
<td>2,28</td>
<td>-</td>
</tr>
</tbody>
</table>

*Calculated by additivity rule equation
P30

MODIFICATIONS INDUCED BY SULPHONATION REACTIONS OF PARTIALLY CROSSLINKED PS-AA COPOLYMERS

L. Melo¹, R. Benavides¹, G. Martínez¹, S. Torres¹, M.M.S. Paula², L. Da Silva²

¹Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna 140, Saltillo, Coah., México. 25294, roberto.benavides@ciqa.edu.mx
²Laboratório de Síntese de Complexos Multifuncionais - LASICOM – Universidade do Extremo Sul Catarinense, Criciúma, Brasil. Luciano.silva@unesc.net

Keywords: PS-AA copolymers, DVB, TMPTMA

Sulphonation reactions are very important to incorporate sulphonylic groups into aromatic polymer structures; however, the sulphonating agent is not the only variable to take into account, the chemical structure of the material to be sulphonated is critical as well.

A random copolymer of poly(styrene-acrylic acid) (PS-AA) was synthesized in solution by radical polymerization and partially crosslinked with divinyl benzene (DVB) or trimethylolpropane trimethacrylate (TMPTMA) to improve mechanical resistance. The copolymer was sulphonated at 40°C with sulphuric acid (H₂SO₄) or acetyl sulphate (CH₃COOSO₄H) and 20% mol of theoretical rings. Sulphonating times of 2, 10 and 30 min were used. Materials were characterized by infrared spectroscopy (FTIR), insoluble material percentage by soxhlet extraction and molar mass by gel permeation chromatography (GPC).

FTIR indicate the presence of sulphonylic groups bound into the copolymer matrix and some changes in specific bands. Gel percentage and molecular weight increase when H₂SO₄ was used as the sulphonation agent, while when CH₃COOSO₄H was used both properties decreased. These effects are more noticeable when TMPTMA is used as crosslinking agent, comparing with DVB (Fig. 1).

![Fig.1. GPC of PSAA crosslinked with DVB and TMPTMA and sulphonated with H2SO4 and AS.](image)

Chemical structure of DVB is chemically more stable than TMPTMA in the acidic environment during sulphonation reaction. This can be explained considering that the TMPTMA is a crosslinking agent containing ester bonds that can be modified in an acidic media, as with CH₃COOSO₄H [1]. On the other hand, during use of H₂SO₄, insoluble material and Mw increase, probably due to the increment of the previously existing crosslinks through sulphone groups between aromatic rings [2], as is widely reported in the literature.

References


CHANGES IN SULPHONATED POLY(STYRENE-ACRYLIC ACID) COPOLYMERS ADDED WITH AG AND AU NANOPARTICLES FOR THEIR USE AS MEMBRANES IN FUEL CELLS

J. Ortiz¹, R. Benavides¹, G. Méndez¹, M.S. Paula², L. Da Silva²

¹Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna 140, Saltillo, Coah., México. 25294, roberto.benavides@ciqa.edu.mx
²Laboratório de Síntese de Complexos Multifuncionais - LASICOM – Universidade do Extremo Sul Catarinense, Criciúma, Brasil. Luciano.silva@unesc.net

Keywords: PS-AA copolymers, TMPTMA, Fuel Cell

Common fuel cells, specifically PEMFC, use an polymeric electrolyte as membrane. The most popular commercialized are the polyfluorosulfonic acid membranes, highly expensive as well. An economic option is the use of low cost hydrocarbonated membranes, which in turn can be modified through sulphonation to increase ionic properties [1].

A random copolymer of poly(styrene-acrylic acid) (PSAA) was synthesized in mass by radical polymerization and partially crosslinked with trimethylolpropane trimethacrylate (TMPTMA) to improve mechanical resistance. The PS-AA copolymer was then sulphonated (PSAAS) at 40ºC with sulphuric acid (H2SO4) at 100% mol of theoretical benzene rings, during 2 hours of Sulphonation time. Nanoparticles of gold (Au) and silver (Ag) were also synthesized by reduction of their corresponding salts: Chloroauric acid (HAuCl4) and silver nitrate (AgNO3). Both nanoparticles were incorporated in solution (8 ml) to PSAAS, dissolved in tetrahydrofuran (THF) at a concentration of 1 g/ml. The materials were characterized by infrared spectroscopy (FTIR), gel permeation chromatography (GPC) and thermal analysis. The latter by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanic analysis (DMA).

FTIR (Figure 1) indicate the presence of sulphonic groups, in 3100 to 3250 cm⁻¹ indicating the incorporation of the sulphonic group into the copolymer matrix. The molecular weight of the copolymer decreased from 258,345 g/mol to 87,575 g/mol when H2SO4 was used to sulphonate it, suggesting a decomposition process. Thermal properties like glass transition (Tg) and decomposition temperature have similar values before and after sulphonation; similarly before and after the incorporation of nanoparticles into the materials. The results indicate that sulphonation and addition of Au and Ag nanoparticles to PSAAS does not induce important changes in the physico-mechanical properties of the membrane and will make them available to be used as a PEM in fuel cells.

![Fig. 1. FTIR of PSAA and sulphonated PSAA](image-url)

References

SMART HYBRID TEMPERATURE RESPONSIVE GELS AND POTENTIAL APPLICATION POSSIBILITIES

Zsófia Osváth1,2, Kristóf Bányai1, Tamás Tóth1,2, Béla Iván1,2

1 Polymer Chemistry Group, Hungarian Academy of Sciences, Research Centre for Natural Sciences, Magyar tudósok boulevard 2, 1117 Budapest, Hungary, osvath.zsofia@ttk.mta.hu
2 Department of Organic Chemistry, Eötvös Loránd University, Pázmány Péter walkway 1/A, 1117 Budapest, Hungary

Keywords: smart gels, temperature responsive, agricultural applications

Nowadays the drought is a worldwide agricultural problem. Some polymer gel systems are able to absorb water as well, which properties can provide a solution to the long-term water storage.

In our research novel non-toxic high absorbent gels were intended to create. N-isopropylacrylamide or N,N-diethylacrylamide were copolymerized with 3-trimethoxysilylpropyl methacrylate and then prepared hybrid gels by sol-gel method.

The precursor PNIPAAm or PDEAAm containing hybrid polymer structure were analyzed by nuclear magnetic resonance spectroscopy (NMR) and the thermoreversible phase transition was studied by visible spectroscopy (VIS). The final gels swelling kinetics were studied in water at different temperatures. Our results showed that the swelling capacity depends on the number of crosslinking, but every sample were well to swell under a lower critical solution temperature (LCST). Above this temperature the gels were lost hold of easily the water, which is preferably in agriculture. The process is always reversible.

Acknowledgement

The authors would thank the European Regional Development Fund through the Hungary-Slovakia Cross Border Cooperation Programme 2007-2013 (HUSK/1101/1.2.1/0209) for their support of this research.

Fig. 1. Synthesis scheme of smart hybrid gel systems
DYNAMIC MECHANICAL PROPERTIES OF BLENDS GTR DEVULCANIZED BY MICROWAVES/HDPE

Fabiula Danielli Bastos de Sousa1,2*, Carlos Henrique Scuracchio1, Guo-Hua Hu2 and Sandrine Hoppe2

1 Cento de Engenharia, Modelagem e Ciências Sociais Aplicadas, Universidade Federal do ABC, Santo André - São Paulo - Brazil
2 CNRS, Laboratoire Réactions et Génie des Procédés, LRGP, Nancy, France
fabiuladesousa@gmail.com

Keywords: GTR, recycling, devulcanization, HDPE, polymer blends.

Ground tire rubber (GTR) was devulcanized in a system composed by a conventional microwave oven adapted with a motorized stirring system with speed control by 5.5 minutes. Devulcanized GTR was processed with HDPE in a twin screw extruder to produce a dynamically vulcanized blend, and some important parameters of the process like speed of the screw, number of feeders, residence time and shear rate were varied. These parameters were carefully analyzed with the blend containing 40 wt% of HDPE and 60 wt% of GTR5.5, using different screw speeds: 100, 150, 200, 250 and 300 rpm, and different number of feeders. When the blends were produced with only one feeder, the both phases, thermoplastic and devulcanized rubber, were added together, and for the blends produced with two feeders, the HDPE phase was added in the first feeder and the GTR phase was added in the second one (Figure 1). The influence of these processing parameters was evaluated in terms of the viscoelastic properties.

![Graph showing Tan δ of the blends produced in twin screw extruder with different speeds and number of feeders.](image)

**Fig. 1.** Tan δ of the blends produced in twin screw extruder with different speeds and number of feeders. The insert shows an amplification of the rubber Tg region. The blends produced in the extruder with one feeder have in the nomenclature the screw speed (in rpm) used during the processing, and the blends produced in the extruder with two feeders have the number 2 after the screw speed.

The results showed the immiscible character of blends. Regarding the values of glass transitions of the elastomeric phase, no significant changes were observed among the different blends. The different parameters adopted during processing of the blends changed the crystallinity of the HDPE phase, as well as degradation of the same phase was observed in the blends produced with higher speeds.
RHEOLOGICAL PROPERTIES OF BLENDS GTR DEVULCANIZED BY MICROWAVES/HDPE

Fabiula Danielli Bastos de Sousa1,2*, Carlos Henrique Scuracchio1, Guo-Hua Hu2 and Sandrine Hoppe2

1 Cenfo de Engenharia, Modelagem e Ciências Sociais Aplicadas, Universidade Federal do ABC, Santo André - São Paulo - Brazil
2 CNRS, Laboratoire Réactions et Génie des Procédés, LRGP, Nancy, France
fabuladesousa@gmail.com

Keywords: GTR, recycling, devulcanization, HDPE, polymer blends.

Ground tire rubber (GTR) was devulcanized in a system composed by a conventional microwave oven adapted with a motorized stirring system with speed control by 5.5 minutes. Devulcanized GTR was processed with HDPE in a twin screw extruder to produce a dynamically vulcanized blend, and some important parameters of the process like speed of the screw, number of feeders, residence time and shear rate were varied. These parameters were carefully analyzed with the blend containing 40 wt% of HDPE and 60 wt% of GTR5.5, using different screw speeds: 100, 150, 200, 250 and 300 rpm, and different number of feeders. When the blends were produced with only one feeder, the both phases, thermoplastic and devulcanized rubber, were added together, and for the blends produced with two feeders, the HDPE phase was added in the first feeder and the GTR phase was added in the second one (Figure 1). The influence of these processing parameters was evaluated in terms of the small amplitude oscillatory shear properties, The results are shown in Figure 1.

![Graph showing the evolution of G' and η* of the blends.](image)

**Fig. 1.** Evolution of G’ and η* of the blends. The blends produced in the extruder with one feeder have in the nomenclature the screw speed (in rpm) used during the processing, and the blends produced in the extruder with two feeders have the number 2 after the screw speed.

The results presented two distinct groups: one group of blends with higher G’ and complex viscosity, and another group with smaller values of these properties. In the first group are the blends produced in the extruder containing only one feeder, while the second group are those produced in the extruder with two feeders. The residence time of the rubber phase inside the extruder is important due to its cross-link density.
STUDY OF THE SYNERGISTIC EFFECT OF ODPSS AND DOPO ON FLAME RETARDED EPOXY RESINS

Li, Ziqian¹, Yang, Rongjie²

¹ Beijing Institute of Technology, 5 South Zhongguancun Street, liziqian@bit.edu.cn
² Beijing Institute of Technology, 5 South Zhongguancun Street, yrj@bit.edu.cn, Corresponding author

Keywords: polyhedral oligomeric silsesquioxane; diphenyl sulfonyl; Epoxy resin; Flame retardancy; DOPO

A novel flame retardant additive, polyhedral oligomeric octa(diphenyl sulfonyl) silsesquioxane (ODPSS) has been used to retard combustion of an epoxy resin (EP) of DGEBA (diglycidyl ether of bisphenol A) with curing agent 4,4’-diaminodiphenylsulphone (DDS). A series of flame-retarded EP was prepared with ODPSS and DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) loaded. The flame retardant properties of the EP were characterized by the LOI, UL-94 and cone calorimeter test. The EP loading with 2.5 wt.% ODPSS/2.5 wt.% DOPO showed a longer TTI, lower value of p-HRR and higher flammability rating than that loading with 5 wt.% DOPO. The char residue of these EP composites after the cone calorimeter tests were investigated by FTIR and XPS. The thermal stability and pyrolytic gases of the EP composites were detected by TGA-FTIR in air atmosphere. The results indicated that the mixture of ODPSS and DOPO has a remarkable synergistic effect on retarding flame of the EP composites.

Fig. 1. Morphology of chars from EP, EP/5%ODPSS, EP/5%DOPO and EP/2.5%OPS/2.5%DOPO after the cone calorimeter test
ON THE PHOTODEGRADATION OF POLY(VINYL ALCOHOL) AND CELLULOSE BASED CRYOGELS

Liliana Rosu, Cristian–Dragos Varganici, Oana Maria Mocanu (Paduraru), Elena Marlica

Centre of Advanced Research in Bionanoconjugates and Biopolymers, “Petru Poni” Institute of, Macromolecular Chemistry, 41A Gr. Ghica-Voda Alley, 700487 Iasi, Romania, lrosu@imcpp.ro

Keywords: cryogels, thermogravimetric analysis, thermokinetics, evolved gas analysis

Three cryogels based on poly(vinyl alcohol) and cellulose [1,2] were studied by means of surface properties modifications during exposure to several doses of UV irradiation. Significant color changes were observed during photoirradiation. Structures exhibited a fading tendency with increase in irradiation dose, due to lightness factor and chromatic coefficients values increase. The cryogels accumulated instable red chromophores and showed a yellowing tendency. Structural modifications were monitored by FTIR technique. No new structural entities were formed during the cryogels photodecomposition, only depolymerization phenomena occurred. Formed hydroperoxides acted as important initiating sites. The cryogels photochemically decomposed in a four stage mechanism through macromolecular chain scissions and decarbonylation and photooxidation with carbonyl groups formation. It was found that poly(vinyl alcohol) acted as UV stabilizer for the cellulose fibers up to a concentration of 70% [3].

Acknowledgement

Authors acknowledge the financial support of a grant of the Romanian National Authority for Scientific Research, CNCS–UEFISCDI, project number PN-II-ID-PCE-2011-3-0187.

References


NEW ASPECTS OF ENZYME BASED DEGRADATION OF SYNTHETIC POLYESTERS

Veronika Perz 1, Doris Ribitsch 1, Karolina Härnvall 1, Julian Ihssen 2, Carsten Sinkel 3, Ulf Küper 3, Melanie Bonnekessel 3, Georg M. Guebitz 1,4

1 ACIB GmbH, Petersgasse 14, 8010 Graz, Austria, Email veronika.perz@acib.at
2 Laboratory for Biomaterials, Empa, Swiss Federal Laboratories for Biomaterials Science and Technology, Lerchenfeldstrasse, 5, CH-9014 St. Gallen, Switzerland
3 BASF SE, Carl-Bosch-Straße 38, 67056 Ludwigshafen, Germany
4 Institute of Environmental Biotechnology, IFA Tulln, University of Natural Resources and Life Sciences, Vienna, Konrad Lorenz Str. 20, 3430 Tulln, Austria

Keywords: Aliphatic-aromatic polyesters, Enzymatic hydrolysis, Biodegradability, Cutinase

One of the primary goals of polymer development was to design materials of high stability and durability. Today, these features lead to major environmental problems. That is why society is confronted with the need to reduce packaging waste as well as to find and enhance polyesters that are biodegradable and show required material properties. Several studies have clearly demonstrated the biodegradability of the aliphatic-aromatic copolyester PBAT (poly(butylene adipate-co-butylene terephthalate)). Nevertheless, there exists hardly any information about the enzymes that play the major role during PBAT hydrolysis.

In this research study, enzymatic degradation pattern of different hydrolases was tested on polymeric and oligomeric PBAT model substrates. The substrate specificities of a bacterial cutinase from Thermobifida cellulosilytica (Thc_Cut1), a fungal cutinase from Humicula insolens (HiC) and a polyhydroxyalkanoate depolymerase (ePhaZmcl) from Pseudomonas fluorescens was evaluated. The degradation process was followed over time and hydrolysis products were analyzed and quantified via HPLC-MS. The difference between the temperature where the degradation takes place and the melting temperature ($T_m$) of the polymer was reported to be a crucial factor for enzymatic hydrolysis [1,2]. Consequently a TG-DSC analysis was performed for PBAT and all tested model substrates and $T_m$ values were taken into account during the evaluation of the degradation results. It is notable that the enzymes show a distinct mechanism for the model substrates and for PBAT.

References


INFLUENCE OF HARDENER ON KINETIC OXIDATION OF EPOXY NETWORKS

Estève Ernaulet\textsuperscript{1,a}, Emmanuel Richaud\textsuperscript{1,b}, Bruno Fayolle\textsuperscript{1,c}

1 Arts et Métiers ParisTech, Process and Engineering in Mechanics and Materials (PIMM) laboratory, 151 boulevard de l’Hôpital 75013 Paris - France.
\textsuperscript{a.} esteve.ernault@ensam.eu \textsuperscript{b.} emmanuel.richaud@ensam.eu \textsuperscript{c.} bruno.fayolle@ensam.eu

Keywords: epoxy, oxidation, kinetics, FTIR, glass transition, weight change evolution

Since epoxy resins are used in many industrial applications, the lifetime assessment of these polymers is crucial. Actually, exposure in air can lead to epoxy oxidation which induces physical and mechanical properties modifications. Although oxidation of epoxy has been investigated in numerous studies in the literature \[1\], the epoxy family covers many molecular architectures depending on the type of hardener for instance. Knowing that the choice of hardener can have a strong influence on the network glass transition temperature, we will focus on oxidation kinetic of different epoxy systems in the same ageing conditions.

In this work, the thermo-oxidation of thin films (thickness equal or lower than 100 µm) of two epoxy resins is studied. Systems considered are based on Bisphenol A epichlorhydrine (DGEBA) and hardeners are diethylene glycol bis 3-aminopropyl ether (figure 1a.) leading to Tg \(\sim 72.1^\circ C\) and an anhydride leading to Tg \(\sim 185.1^\circ C\). Films are exposed in air at 110°C, 130°C and 150°C.

The formation of oxidation products is evidenced by infra-red spectroscopy (FTIR), (amide absorbance at 1650 cm\(^{-1}\)) \[2\]. In addition, weight, density and glass transition temperature (differential scanning calorimetry) measurements are performed to follow macromolecular modifications (chain scission or crosslinking). At the three temperatures under study, it is shown that low Tg resins degrades faster than high Tg one which is discussed regarding the existing literature on polymer degradation.

Fig. 6: Chemical structure of a) diethylene glycol bis 3-aminopropyl ether and b) anhydride.

References

\[1\] Celina MC et al., A perspective on the inherent oxidation sensitivity of epoxy materials, Polymer, Elsevier, 54(13), 2013, pp3290-3296.

THE INFLUENCE OF CRYSTALLINITY ON THE PHOTOOXIDATION OF SEMI-CRYSTALLINE POLYMERS

Mohamedou Ould Isselmou 1,3, Pierre-Olivier Bussière 2,3, Jean-Luc Gardette 1,3, Sandrine Thérias 1,3 and Mohamed Baba 1,3

1 Clermont Université, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand mohamed.baba@univ-bpclermont.fr
2 Clermont Université, ENSCCF, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand
3 CNRS, UMR 6296, ICCF, BP 80026, F-63171 Aubière

Keywords: PLA, Crystallinity, PhotoDSC, DSC, IRTF

This work studies the impact of crystallinity on the photooxidation of semi-crystalline polymers. The study was performed for two semi-crystalline polymers, polylactide (PLA) and poly(ethyleneterephthalate) (PET). Cold crystallization was used to prepare samples with different degrees of crystallinity (6 to 62 %). The degree of crystallinity was adjusted using the furnace of a differential scanning calorimeter (DSC). Photochemical aging was conducted in a SEPAP 12/24 device and also using a PhotoDSC. The oxidation of the samples was measured by infrared spectroscopy. It was shown that the crystallinity strongly affected the photochemical oxidation. The extent of oxidation was found to dramatically increase for decreasing levels of crystallinity. A clear correlation was found between the oxidation rate on the one hand and the crystallinity on the other. This effect was attributed to the very weak oxygen permeability of the crystalline parts, which decreases the total volume available for oxidation to occur.

Fig. 1. Photo-oxidation of PLA samples at four time points (0, 5, 30 and 60 hours). The temperature axis corresponds to the end heating temperature, which determines the degree of crystallinity.

References


STABILIZATION OF POLYPROPYLENE-MONTMORILLONITE NANOCOMPOSITES WITH A METAL DEACTIVATOR

Lays Batista Fitaroni¹, Sandra Andrea Cruz¹, Walter Ruggeri Waldman²

¹ Universidade Federal do ABC, Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas, Rua Santa Adélia, 166, Bairro Bangu, Santo André, São Paulo - Brasil - CEP: 09210-170, sandra.cruz@ufabc.edu.br
² Universidade Federal de São Carlos, Departamento de Física, Química e Matemática, Rodovia João Leme dos Santos, Km 110, Bairro do Itinga, Sorocaba, São Paulo - Brasil - CEP: 18052-780, walter@ufscar.br

Keywords: stabilization; nanocomposites; metal deactivator

The polymeric material thermo-oxidative stability reinforced with mineral fillers, such as clay, can be lower than the pristine polymer. This is due to mineral fillers present metal ions in its composition, such as manganese, aluminum and iron, and also by the presence of others contaminants, which affect the polymer stability. The addition of stabilizers is necessary in some cases to prevent the degradation process and to give a longer shelf life to the material [1]. In this study, different concentrations of a metal deactivator were used to analyze the effect of this additive on the polymeric nanocomposites stabilization. The thermo-oxidative stability of polypropylene/montmorillonite nanocomposites (PP/PP-g-MA/OMMT) with metal deactivator in their formulation were studied by Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Oxidative Induction Time (OIT) measurements. The results showed that adding the additive resulted in a positive effect, increasing the stability and retarding the degradation reactions of the materials (Fig. 1).

Fig. 1. (a) TGA in oxidative atmosphere, (b) DSC and (c) OIT curves for nanocomposites: PP/PP-g-MA/OMMT (PP:5:5) and nanocomposites with different concentrations of metal deactivator (PP:5:5:0.3, PP:5:5:0.5, PP:5:5:0.7).

Nanocomposites containing stabilizer showed a very high resistance to oxidation and a significant improvement in its stability with increasing concentration of the additive used.

References
PHOTOXIDATION AND STABILIZATION OF A SOLAR CELL ENCAPSULATING CROSSLINKED EVA

M. Ceraulo, M.C. Mistretta, F.P. La Mantia

Department of Civil, Environmental, Aerospace and Materials Engineering, University of Palermo, Viale delle Scienze Ed. 6, Palermo, Italy, manuela.ceraulo@unipa.it

Keywords: Photooxidation, crosslinked EVA, stabilization

Crosslinked EVA is one of the best materials as encapsulant in the fabrication of encapsulating material for solar cell module. The main challenge for this material is the photo-oxidative resistance. This material should resist for very long periods in order to ensure a good efficiency of the photovoltaic solar cell. Indeed, not only the mechanical resistance should be retained, but also the yellowing and/or EVA browning should avoid because this changes the light transmission and then the efficiency of the photovoltaic cell.

In this work EVA and cross-linked EVA has been stabilized with a stabilizing system made by UV quenchers and HALS. The curing has been carried out by compression moulding at 180°C for 15 minutes under a pressure of about 80 Kg/cm². The irradiation has been carried out on a QUV equipped with UVB lamps with a solar cycle of 8 hours at the temperature of 55°C and a condensation cycle of 4 hours at the temperature of 40°C.

Fig. 1. Elongation at break as a function of the UV irradiation time for all the investigated samples

The elongation at break-exposure time curves indicates that at long irradiation time the cured EVA (about 92% of crosslinked material) shows a slight better photostability with respect to the flexible EVA; the presence of the stabilizing system strongly improves the resistance to the UV irradiation for both materials. However, this improvement seems more efficient for the cured EVA.

References
INFLUENCE OF MOLECULAR MOTIONS IN POLY(DICYCLOPENTADIENE) OXIDATION

Virginie Imholz\textsuperscript{1}, Pierre Yves Le Gac\textsuperscript{2}, Emmanuel Richaud\textsuperscript{1}, Jacques Verdu\textsuperscript{1}

\textsuperscript{1}Arts et Métiers ParisTech, CNRS, PIMM UMR 8006, 75013 PARIS, FRANCE, virginie.imholz@ensam.eu, emmanuel.richaud@ensam.eu, jacques.verdu@ensam.eu
\textsuperscript{2}IFREMER (French Ocean Research Institute), Centre de Brest, Marine Structures Group, F-29280 PLOUZANÉ, FRANCE, pierre.yves.le.gac@ifremer.fr

Keywords: poly(dicyclopentadiene), thermal oxidation, TGA, molecular mobility

In a recent paper, the pDCPD was shown to display a relatively high sensitivity to thermal ageing even in its glassy state. This was highlighted by the comparisons with polybutadiene and polyisoprene, having a significantly higher concentration in double bonds but oxidizing slower. This was tentatively ascribed to the control of termination process by the low segmental mobility. In this paper we will consider:

- the nature of the inhibited process: termination between two $P^\circ$, or two $POO^\circ$ or else,
- the influence of segmental motions on terminations when passing over T\textsubscript{g}.

We have thus investigated the degradation in the temperature range around T\textsubscript{g} by using in situ techniques: mass uptake by TGA, oxidation induced heat release by DSC under oxygen. Figure 1 shows that the level of the plateau ($\Delta m/m_0$) of oxidation monitored by decreases above T\textsubscript{g} without displaying any evidence of volatile compounds release. The hypothesis of supplementary reactions activated above T\textsubscript{g} is thus confirmed.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{TGA curves at several temperatures under 100\% O\textsubscript{2}.}
\end{figure}

References

BEHAVIOR OF POLYURETHANE ACRYLATES WITH CRUDE AND MODIFIED
SOYBEAN OIL BLENDS ON THE SOIL-BURIAL BIODEGRADATION PROCESS

Stefan Oprea 1*, Joga Aurora 2, Stanciu Aurelian 1, Oprea Veronica 3, Potolinca Otilia Violeta 1

1 “Petru Poni” Institute of Macromolecular Chemistry Aleea Ghica Voda No.41-A, Iasi, Romania, e-mail: stefop@icmpp.ro
2 National Institute for Research and Development in Electrical Engineering ICPE-CA, Splaiul Unirii 313, Bucharest, Romania
3 Faculty of Bioengineering, “Gr. T. Popa” University of Medicine and Pharmacy, Iasi, Romania

Synthetic urethane and natural curable acrylate oligomer blends with a relatively high content of crude and modified (acrylated epoxidized) soybean oil in their matrix composition were subjected to biodegradation by soil burial under natural conditions (for a period of 12 months). The presence of soybean oil components in the polymer blends had an enhancing effect on the biodegradation rate. The loss in the physical properties indicates a complete polymer biodegradation due the presence of relatively high amounts of soybean oil in the polymer structure. FT-IR spectra show changes occurring in the chemical structure of polyurethane acrylates/soybean oil blends, especially changes concerning the ester and urethane bonds in the main chains which were enabled by the action of bacteria, fungi and other microorganisms. This work shows that a high content of either crude or modified soybean oil in the structure of the matrix of crosslinked polyurethane acrylates contributes to achieving a complete biodegradation by soil burial in environment conditions. These polyurethane materials were selected for study as all ready being environmentally degradable and eco-compatible polymeric materials, and were evaluated in view of their ultimate stage of life service.

Acknowledgement

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI-UEFISCDI, project number 178/2012 (BIOCOMRAN).
SYNTHESIS, PROPERTIES AND BEHAVIOR WHEN SUBJECT TO FUNGAL DEGRADATION OF SILVER SULFAZIDINE-BASED POLYURETHANE ELASTOMERS

Stefan Oprea1*, Petronela Gradinariu2, Bica Zorlescu3, Veronica Oprea4

1 “Petru Poni” Institute of Macromolecular Chemistry Aleea Gr. Ghica Voda No.41-A, Iasi, Romania, e-mail: stefop@icmpp.ro
2 Biological Research Institute, Str. Lascar Catargi, No 47, Iasi Romania
3 National Institute for Research and Development in Electrical Engineering ICPE-CA, Splaiul Unirii 313, Bucharest, Romania
4 Faculty of Bioengineering, “Gr. T. Popa” University of Medicine and Pharmacy, Iasi, Romania

Silver sulfadiazine based-polyurethane elastomers have been synthesized by chain extending polyether-urethane prepolymer with silver sulfadiazine. The polyurethane elastomers were varied in term of stoichiometric ratios and crosslinker nature. The changes that occurred in the hard segment structure - generated by chemical crosslinking with different crosslinkers - lead to polymeric films with improved physico-mechanical properties. Both the linear and crosslinked polyurethane elastomers which included silver sulfadiazine into their main chain suffered reduced biodegradation under the action of Fusarium graminearum fungus. The introduction of silver sulfadiazine moieties into the main chain of the polyurethane urea ensures a constant inhibitive quality against degradation, without losing the concentration by diffusion. This study demonstrated that the use of biological active compounds in the backbone of the polymer chains generates materials that are resistant to fungi while maintaining good mechanical properties.

Acknowledgement

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI-UEFISCDI, project number 178/2012 (BIOCOMRAN).
PHOTO-OXIDATION BEHAVIOUR OF POLYSTYRENE-BLOCK-POLYBUTADIENE-BLOCK-POLYSTYRENE/CNTS NANOCOMPOSITES

Nadka Tz. Dintcheva, Rossella Arrigo, Francesco Catalanotto

Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali, Università di Palermo, 90128 Palermo, IT, nadka.dintcheva@unipa.it, rossella.arrigo@unipa.it

Keywords: Styrene-Butadiene block copolymer, stabilization, carbon nanotubes

Nanocomposites based on polystyrene-block-polybutadiene-block-polystyrene (SBS) and CNTs without and with COOH functionalities have been prepared and their rheological, morphological and mechanical analysis have been accurately performed. Special attention has been focused on the photo-oxidation behavior of all nanocomposites. In particular, the effect of the CNTs on the degradation phenomena has been evaluated monitoring the growth of carbonyl and hydroxyl species and disappearance of double bonds by means of FTIR analysis. The oxidation phenomena in neat SBS begins since the early stages of the photo-oxidation and after 24h, the calculated carbonyl and hydroxyl indices remain almost unchanged. This finding can be explained considering the competition between the two different phenomena, i.e. oxidative reactions and crosslinking reactions, which occurs mainly in the polybutadiene phase [1]. The CNTs presence in the nanocomposites, instead, hinders the crosslinking reaction in the rubber phase, as probed by DMTA and rheological analysis. Moreover, to evaluate the macroscopic effect of the photo-degradation on the mechanical performances, the elongation at break (EB) as a function of the exposure time has been recorded, see Fig. 1. The results shows that CNTs are able to slow down photo-oxidation phenomena because of their ability to act as radical scavenger, maintaining the values of the elongation at break of the nanocomposites significantly higher than those of the neat SBS. Finally, the nanocomposites containing COOH functionalized CNTs show better performance, that is because the functionalization leads to the formation of more surface defects onto CNTs and this increases their radical scavenging activity.

![Fig. 1. Dimensionless EB as a function of photo-oxidation time for neat SBS and nanocomposites](image)

References

PHOTO-OXIDATION BEHAVIOUR AND MORPHOLOGY OF ZINC OXIDE-POSS POLYSTYRENE BASED NANOCOMPOSITES

Elisabetta Morici¹, Nadka Tzankova Dintcheva², Rossella Arrigo², Francesco Paolo La Mantia²

¹ Dipartimento di Ingegneria Chimica, Gestionale, Informatica, Meccanica, Università di Palermo, 90128 Palermo, IT, elisabetta.morici@unipa.it
² Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali, Università di Palermo, 90128 Palermo.

Keywords: Stabilization, Polystyrenic nanocomposite, POSS, Zinc oxide, Dispersion.

POSS are an innovative class of organosilicon compounds suitable for formulation of advanced organic-inorganic hybrid materials. Nanocomposites based POSS found application mostly in high-temperature resistance and fire-resistance materials. Few studies investigate the dispersant ability of POSS molecules. In particular silanol POSS, having three reactive groups, can create a stable system with the solid particle to disperse even at high temperatures. Among inorganic nanoparticle to disperse, nano-ZnO is specifically interesting because of intensive ultraviolet and infrared absorption, chemical stability, antibacterial and bactericide function, etc [1]. In this study polystyrene/zinc oxide and polystyrene/zinc oxide/POSS nanocomposite were prepared by melt mixing. The POSS dispersant ability was assessed by morphological, rheological, thermal mechanical analyses. POSS molecules improve the dispersion of the nanoparticles overcoming the problem related to weak interaction between non-polar PS chain and polar ZnO nanoparticles. The photo-ageing behaviour of all investigate nanocomposites was monitored, as a function of the exposure time, by FT-IR. ZnO nanoparticles absorb UV light at wavelengths under 400 nm and improve the photo-oxidation resistance of the PS based nanocomposites. However the ZnO adding, results in a reduction of the optical transparency in the visible region respect to the neat PS film. The POSS loading do not affect the excellent photo-oxidative resistance showed by ZnO filled PS nanocomposites (Fig.1) and leads to obtain nanocomposites with a lower amount of hydroxyl product and films with good optical transparency.

Fig. 1. Variations of the carbonyl and hydroxyl bands areas vs photo-oxidation time for PS and PS based nanocomposites.

References

INFLUENCE OF VINYL POLISILOXANES ON FLAMMABILITY AND BIODETERIORATION OF COMPOSITES FILLED WITH NATURAL FIBRES

R. Gąsiorowski¹, S. Rojewski¹, J. Walentowska¹, J. Foksowicz-Flaczyk¹, D. Wesołek¹, H. Maciejewski², K. Bujnowicz¹, R. Wójcik¹

1 Institute of Natural Fibres & Medicinal Plants, ul. Wojska Polskiego 71B, Poznan, Poland, ryszard.gasiorowski@iwnirz.pl
2 Adam Mickiewicz University Foundation - Poznan Science and Technology Park, Ul. Rubiez 46, Poznan, Poland

Keywords: silanization, natural fibres, composites, flammability, biodeterioration

Polymer materials are an integral part of our everyday life. Better awareness and willingness to care for the environment makes people more often to turn to natural materials. Products manufactured from pure polymers are frequently replaced by those made from composites filled with natural raw materials. One of the fillers currently used are natural fibers which, in order to improve the properties of the finished products, are subjected to various kinds of modifications.

Aim of the study is to investigate effect of vinyl polisiloxanes on flammability and biodeterioration of composites filled with modified natural fibres. Composites will be prepared by introducing silanized natural fibres into polyethylene matrix. For modification will be used silanes with various chain length and number of vinyl groups. As the result known will be influence of modifier structure on properties of fibres and composites filled with them.

Flammability of prepared samples of fibres and composites will be tested according to ASTM D7309-07a 2009: Determining flammability characteristics of plastics and other solid materials using pyrolysis combustion flow calorimeter. Defined will be changes in heat release rate against temperature and time.

Microbial research will be conducted on composites with a polymeric matrix made of polyethylene, and reinforced with flax fibres. Their susceptibility to biodeterioration and microbial resistance to action of mould fungi mixture, e.g. to Chaetomium globosum, Aspergillus niger, Paecilomyces variotii, Penicillium funiculosum, Aureobasidium pullulans will be tested in according to EN ISO 846 Standard. Microbial activity evaluation will be made by determining the degree of mould fungi growth and their impact on the mass and mechanical properties of the tested polymer composites.

The studies are carried out within the Silantex Project - New silicone finishing agents for fibers and natural fabrics, financed by the National Research and Development Centre for Applied Research Program, 2012-2015.
FLAME RETARDANCY AND THERMAL PROPERTIES OF A HYBRID COMPOSITE, POSS/IPP. EFFECT OF A COUPLING AGENT

R. Bouza, L. Barral, B. Montero, M. Rico, C. Ramírez

Grupo de Polímeros, Departamento de Física, E.U. Politécnica, Universidade da Coruña (UDC), Campus de Ferrol, 15405 Ferrol, Spain. labpolim@udc.es

Keywords: polyhedral oligomeric silsesquioxane (POSS), flame retardancy, crystallization

The development of hybrid polymer-inorganic nanocomposites with new properties has been steady interest in research. One of the topics that is increasingly popular is the possibility of preparing hybrids nanocomposites using polyhedral oligomeric silsesquioxanes (POSS). POSS are true hybrid inorganic/organic composites that possess an inner inorganic silicon and oxygen core (SiO$_{1.5}$)$_n$ and external organic substituents that can feature a range of functional groups. Incorporating POSS cages into polymeric materials improves polymer properties, increasing the used temperature, oxidative resistance and surface hardening, as well as reducing the flammability and improving the heat behaviour.

In this work a semicrystalline thermoplastic, an isotactic polypropylene, iPP, was used as polymeric matrix; and a polyhedral oligomeric silsesquioxane was used as modifier, the aminopropylisobutyl POSS. Moreover the use of a coupling agent that optimizes the interface between the matrix and POSS was investigated, the maleic anhydride polypropylene (MAPP). The main purpose of this study is to discuss the influence of POSS on properties and behaviour of isotactic polypropylene both with and without coupling agent.

The crystallization, thermomechanical properties and degradation were examined by means of differential scanning calorimetry, dynamic mechanical analysis, thermogravimetry and X-ray diffraction. Scanning electronic microscopy was used to study the morphology and fire testing was done to measure the limiting oxygen index parameter, LOI.

Acknowledgements

Financial support provided by Xunta de Galicia Govern-FEDER, Program of Consolidation and Structuring Competitive Research Units, CN 2011/008.

References


DEGRADATION OF NATURAL POLYMERS BY ELECTRON BEAM IRRADIATION

Monica R. Nemţanu, Mirela Braşoveanu

National Institute for Lasers, Plasma and Radiation Physics, Electron Accelerators Laboratory, 409 Atomiştilor St., PO Box MG-36, 077125, Bucharest-Magurele, Romania, monica.nemtanu@inflpr.ro, mirela.brasoveanu@inflpr.ro

Keywords: amylose, amylopectin, ionizing radiation, molecular weight, kinetics

Degradation of natural polymers like alginate, chitosan, starch, carrageenan, glucomannans [1-5] by ionizing radiation (gamma rays and electron beam) was widely investigated lately. Most of such investigations have been carried out in aqueous solution since the effects can be spectacular due to action of very reactive chemical species resulted from water radiolysis as indirect effect of radiation energy on polymer aqueous solution. Instead irradiation of solid polysaccharides leads to free radicals generated by excitation and ionization of the molecules as a result of the direct interaction between the radiation and initial macromolecule. In this work degradation of amylose and amylopectin exposed in solid state to accelerated electron beam in the range of 10 – 50 kGy is presented. Effects of irradiation on polymers were investigated by gel permeation chromatography, Fourier transform infrared spectroscopy and scanning electron microscopy. In order to evaluate quantitatively the radiation degradation in amylose (linear polymer), radiation-chemical yield of degradation, degradation rate constant and half value dose of the number-average molecular weight and weight-average molecular weight were determined. The results proved that electron beam degradation of investigated polymers is based on a complex mechanism of the radical-induced scission of the glycosidic bonds, which leads to the reduction of their molecular weight and formation of different lower molecular weight radiolytic products.

Acknowledgements:

This work was supported by project Nucleu (2014) and IIN (Electron Accelerators Laboratory of the National Institute for Lasers, Plasma and Radiation Physics).

References


PHOTODEGRADATION OF CELLULOID USED IN MUSEUM ARTIFACTS

P.-O. Bussière\textsuperscript{1,2}, J.-L. Gardette\textsuperscript{1,3} and S. Thérias\textsuperscript{1,3}

1 Clermont Université, Université Blaise Pascal, BP 10448, F-63000 Clermont-Ferrand, France
2 Clermont Université, ENSCCF, Laboratoire de Photochimie Moléculaire et Macromoléculaire, BP 10448, F-63000 Clermont-Ferrand
3 CNRS, UMR 6505, Laboratoire de Photochimie Moléculaire et Macromoléculaire, F-63177 Aubière,

Keywords: Celluloid, photooxidation, Atomic Force Microscopy

The consequences of the photodegradation of Celluloid on the modification of the material properties have been analysed. Various techniques were used to follow the accelerated degradation provoked by exposure to light ($\lambda > 300$ nm). The objective was to relate the modification of the properties at various levels of investigation, from the molecular properties towards the degradation of the macroscopic properties.

The modification of the chemical structure was followed by infrared and UV-visible spectroscopic analyses. Gloss and color measurements were performed, as well as characterization of surface mechanical properties by microhardness. We realised also roughness and stiffness measurements by Atomic Force Microscopy (AFM) completed by thermal studies using DSC and Vita devices.

\textbf{Fig. 7}. Force-displacement curves of celluloid before and after 50h of irradiation time

The results show that the loss of gloss and the decrease of the mechanical properties is a result of a combination of the progressive loss of plasticizer and chain-scission reactions. These developments were explained in light of the modifications of the chemical structure. Quantitative cross-correlations of the degradation chemistry with performance-critical physical properties were established.
HEAT RELEASE RATE FROM THE EPIDIAN 5 RESIN UNMODIFIED AND MODIFIED BY FIRE RETARDANTS

Marzena Półka, Aneta Łukaszek-Chmielewska

Main School of Fire Service, Warsaw; e-mail: marzena.polka@gmail.com (correspondence address: 01-629 Warszawa, ul. Słwickiego 52/54)

The present study is an attempt at the determination of the influence of flame retardants, such as aluminium hydroxide - Apyral, oligomeric methyl etylophosphate - Fyrol PNX, organically modified montmorillonite - Nanobent ® ZW1 (MM), melamine polyphosphate - Melapur 200 (PM) and their mixed compositions on the flammability parameters of the cured epoxy resin Epidian 5. Experimental test was made using a cone calorimeter at heat flux 30 kW/m², and comprised the determination such parameters, as: rate of heat (HRR) and smoke release rate, materials inflammability and the toxicity of volatile phase of modified and unmodified epoxide samples under decomposition conditions. Studies have shown that introduced flame retardants favourably influenced the flame retardancy of epoxy material as evidenced by lower values of the heat and smoke release rate as compared to unmodified resin Epidian5. The lowest values of $HRR_{max}$ and $HRR_{av}$ have been obtained for samples with 5% of MM by weight + 5% PM by weight and modified samples 5% of PM by weight.

Conclusions from concluded research

- The introduction of fire retardants to the Epidian 5 resin has enhanced the safety of all the obtained epoxy materials with respect to the fire hazard, which may be proven by lower values of the heat and smoke release rate.
- The values of the rate of heat and smoke released by the tested epoxy materials depend on the heat flux falling on the sample, as well as the type of introduced combustion inhibitors.
- The most effective tested composition for the analysed resin was the concurrent introduction of 5% MM and 5% PM, for which the smallest value of $HRR_{max}$ has been ascertained. This parameter determined the rate at which a fire spreads and the survival time of humans.
- The average heat release rates of all epoxy materials modified by flame retardants were lower than the $HRR_{av}$ value of unmodified Ep 5 epoxy.
- All the introduced anti-pyrenes have contributed to reducing the amount of released smoke as compared to unmodified material. This allows the presumption that the introduced flame retardants would to a lesser degree hinder the execution of effective rescue actions and that they should not cause an impairment in the visibility during a fire as compared to Ep 5.
- The majority of the introduced combustion inhibitors led to shortening the times until ignition as compared to unmodified Ep 5 resin, with the exception of the sample of Ep 5 + 5% MM. This allows the presumption that the action of the introduced anti-pyrenes took place in the solid phase and did not inhibit the ignition moment of the flammable gaseous phase. This may be proven by higher values of sample remnants after thermal decomposition and combustion as compared to the Epidian 5 resin unmodified by fire retardants.

Acknowledgements

The paper was carried out under project by MNiSW no S/E-422/23/14-12-11

References

COMBINED EFFECT OF TEMPERATURE AND PRESSURE ON THERMO-MECHANICAL PROPERTIES OF THERMAL INSULATION MATERIAL (POLYAMIDE) FOR OFFSHORE OIL EXPLOITATION

Marko Bek¹, Alen Oseli², Ted Prodan³, Bojan Starman⁴, Igor Emri⁵, Boris Štok⁶

¹ Gorenje gospodinjski apatati d.d., Velenj, Slovenia, marko.bek@fs.uni-lj.si
² Institute for Sustainable Innovative Technologies-iSIT, Ljubljana, alen.oseli@isit.si
³ Faculty of Mechanical Engineering, University of Ljubljana, ted.prodan@fs.uni-lj.si
⁴ Faculty of Mechanical Engineering, University of Ljubljana, bojan.starman@fs.uni-lj.si
⁵ Faculty of Mechanical Engineering, University of Ljubljana, igor.emri@fs.uni-lj.si
⁶ Faculty of Mechanical Engineering, University of Ljubljana, boris.stok@fs.uni-lj.si

Keywords: oil exploitation, off-shore, passive thermal insulation, polymers, mechanical properties, temperature effect, pressure effect, polyamide

Polymers are commonly used as passive thermal insulation materials in offshore oil excavation technologies [1]. Since oil reserves are becoming rare at conventional water depths, ultra deep water (3000 m and beyond) is the next frontier in oil excavation industry. At this depths polymers are exposed to sever environmental conditions, namely pressures beyond 300 bar and temperature gradients of more than 100°C (between inner and outer surface of insulation wall), which profoundly affect their thermo-mechanical properties.

In this paper we report on thermo-mechanical behavior of Polyamide (PA), which is commonly used insulating material in offshore oil exploration technologies [2]. Material was exposed to pressure of 300 bar and temperatures of 4°C and 120°C, simulating environmental and working conditions at depths of 3000 m. We have analyzed how thermo-mechanical properties of the material, i.e. coefficient of volumetric thermal expansion and shear relaxation modulus may change with environmental conditions. The experimental results show that shear relaxation modulus may change by orders of magnitude whereas the change of coefficient of volumetric thermal expansion is almost negligible. Moreover, results were used in finite element analysis, simulating pipe-insulation system at given conditions, showing evolved stress-strain field which may lead to crack formation on inner surface of insulation.

This research confirm that understanding the combined effect of temperature and pressure on thermo-mechanical properties of polymeric insulation materials is of key importance in order to predict long-term behavior of polymeric insulation, which presents sustainable and safe offshore oil exploitation.

References


PROCESSABILITY AND TIME-DEPENDENT PROPERTIES OF MECHANICALLY RECYCLED LDPE

Huiying Jin¹, Pavel Oblak¹, Joamin González-Gutiérrez¹, Alexandra Aulova¹, Barbara Zupančič and Igor Emri²

Center for Experimental Mechanics, Faculty for Mechanical Engineering, University of Ljubljana, Ljubljana 1000, Aškerčeva 6, alexandra.aulova@fs.inu-lj.si

Keywords: LDPE, low density polyethylene, mechanical recycling, processability, extrusion

Low density polyethylene (LDPE) is a widely used polymer for variety of applications in our everyday life including plastic bags, food packaging films and laboratory equipment, etc. Since LDPE takes a great sector of production market (17.5% of European plastic demand in 2012, [1]) it requires recycling in order to fulfill European strategy to minimize landfill disposal of plastics [2]. The most widely used technique is mechanical recycling [3], but it may cause changes in mechanical properties and processability of the material due to degradation from heat, mechanical stress, oxidation and ultraviolet radiation during reprocessing and lifetime [4].

This paper investigates the effect of recycling on LDPE processability and durability during the process of 100(!) simulated recycling. In particular we have analyzed viscosity and thermal properties, and time-dependent shear creep behavior, respectively. Material was exposed to one hundred of extrusion cycles and properties were analyzed at every cycle during the first ten recycling and then after at every 10th cycle.

Thermo-mechanical and thermo-oxidative degradation usually cause chain scission and crosslinking in LDPE but there is a higher tendency to crosslink [5], which leads to a decreased chain mobility and an increase in viscosity.

DSC measurements did not detect significant difference in melting and crystallization temperatures but showed a decrease in degree of crystallinity starting at the 50th extrusion. Analysis of creep measurements showed a pronounced increase of creep compliance after 40th extrusion, which is directly related to the decrease in degree in crystallinity observed by DSC. It can be concluded that LDPE could be extruded for up to 40 time without significant deviations in its processability and long-term mechanical properties [6].

References


REPROCESSING OF POLY(LACTIC ACID): EFFECT ON PROPERTIES

G. Botelho¹, E. Santos¹, A. Araújo², A. V. Machado², G. J. M. Fechine³

¹ Chemistry Department, University of Minho, Braga Portugal, gbotelho@quimica.uminho.pt
² IPC-Institute for Polymers and Composites/I3N, University of Minho, Guimarães, Portugal
³ Graphene and Nano-Materials Research Center, Mackenzie Presbyterian University, São Paulo, Brasil

Keywords: polylactic acid; reprocessing; thermal degradation; properties

Poly(lactic acid) (PLA) is a biodegradable aliphatic thermoplastic polyester well known for being a promising alternative to petroleum-based materials since it can be produced from renewable resources. Although this polymer has good properties when compared to other biodegradable polymers, it presents some limitations like poor thermal, mechanical resistance and gas barrier [1, 2].

An important issue that should be taken into consideration is the viability of reprocessing and its effect on properties. Therefore, the aim of this work was to investigate PLA reprocessing and the influence of the addition of a primary and secondary stabilizers. The processing experiments, without and with stabilizers, were performed under constant processing conditions in a batch mixer (Haake Rheodrive 5000), at 190 °C and a rotor speed of 100 rpm. The collected samples were characterized by ¹H-NMR spectroscopy, size exclusion chromatography (GPC) and thermal analysis. The proton area ratio (CH₃/CH), which lightly decrease with degradation indicating that chain scission has occurred [3]. This ratio has a theoretical value of 3 and it must remain constant if degradation takes place upon ester linkage degradation, hydrolysis or radical degradation, or decrease if pyrolytic elimination (which is responsible for the transformation of CH-CH₃ into CH=CH₂). The other techniques corroborate with these results and allow to conclude that the addition of stabilizers avoids chain scission during processing.

Acknowledgements

The authors acknowledge the n-SteP Project, reference NORTE-07-0124-FEDER-000039, supported by the Programa Operacional Regional do Norte (ON.2) and FAPESP (Brazilian Research Foundation).

References

CURING REACTIONS OF EPOXIDIZED METHYL ESTERS OF CORN OIL AND THERMAL CHARACTERIZATION OF THE OBTAINED CROSSLINKED PRODUCTS

Fanica Mustata, Elena Marlica, Nita Tudorachi, Ioan Bicu, Cristian-Dragos Varganici

Centre of Advanced Research in Bionanoconjugates and Biopolymers, “Petru Poni” Institute of, Macromolecular Chemistry, 41A Gr. Ghica-Voda Alley, 700487 Iasi, Romania, emarlica@imcpp.ro

Keywords: methyl esters, epoxidation thermogravimetric analysis, thermokinetics, evolved gas analysis

In the last decade vegetable oils as renewable raw materials became a promising regenerable feedstock. By transesterification of such oils with methanol in presence of catalyst, methyl esters were obtained. These esters can be converted by various chemical reactions into monomers used in polymer synthesis. In the present study, corn oil methyl ester is epoxidized in the presence of acid catalyst and solvent with a mixture of H$_2$O$_2$ / acetic acid solutions and converted into an epoxy monomer with an epoxy equivalent weight of 0.0041 eq•g$^{-1}$. By crosslinking with the Diels-Alder adduct of rosin acids, these monomers are transformed into polymers. The kinetic analysis of the cure process and thermal characterization of crosslinked products was carried out using non-isothermal differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The non-isothermal scans were obtained at multiple heating rates under nitrogen and processed with Netzsch Thermokinetics software. Depending on the chemical structure of cured agent, the crosslinking and thermal decomposition reactions occurred in three steps. Starting from the chemical structure of the evolved gases obtained during the thermal decomposition and identified with the FTIR and MS techniques, a schematic mechanism for the thermal degradation process was proposed.

Acknowledgement

Authors acknowledge the financial support of a grant of the Romanian National Authority for Scientific Research, CNCS–UEFISCDI, project number PN-II-ID-PCE-2011-3-0187.
POLYMER MATERIALS AND COMPOSITES PREPARED FROM PLANT BIOMASS

Gabriela Dziworska, Andrzej Okruszek
Faculty of Biotechnology and Food Sciences, Lodz University of Technology
Stefanowskiego 4/10, 90-924 Lodz, Poland
gabriela.dziworska@p.lodz.pl

Various kinds of plant biomass are employed for the preparation of biodegradable fibrous polymer materials and composites by biotechnological methods, involving enzymatic or microbial processes. The major intermediates in the preparation of final products are cellulose nanofibres, tactical polylactide and biodegradable aliphatic-aromatic copolymesters.

For the preparation of cellulose nanofibres, a cellulose rich plant biomass is being utilized, including grass and straw of various cereals or other agriculture useful plants, as well as waste fibres from textile industry (cotton, linen). The biomass is first pretreated with physical and/or chemical methods including boiling, steam-explosion or treatment with appropriate chemicals. Multienzyme complex obtained from Aspergillus niger mould serves as the main enzymatic tool.

Saccharification of other kinds of biomass (potatoes, cereal grains or beet pulp) with Aspergillus niger preparations leads to simple sugars which are being subjected to the fermentation yielding L-lactic acid. The fermentation microorganisms (bacteria) are selected by classical microbiology methods from the environment. L-Lactic acid, after its dimerization to L,L-lactide is chemically polymerized to give tactical polylactide, a substrate for many fibrous materials and thermoforming.

The third path involves utilization of various oil-plant biomass, which on sequential treatment with lipase preparations obtained from Mucor circinelloides and Mucor racemosus moulds (transesterification) and appropriate chemical reactions (cycloaddition) are transformed into dimer esters with fatty acid residues. These will be copolymerized with appropriate reagents to produce new biodegradable aliphatic-aromatic copolymesters. The polyesters will be utilized for preparation of fibrous polymers and composites.

The fibrous materials and composites prepared on the basis of abovementioned intermediates will be further utilized for obtaining new functional textiles and nonwovens with potential sanitary or technical applications, such as sweat-absorbing textile inserts, sanitary textiles, filtration materials, geotextiles and agrotexites. The processes of ageing and controlled biodegradation of prepared materials will be studied, as well as the conditions of their recycling and possible use of degradation products in agriculture.

The poster presents information about the research project “Utilization of biomass for the preparation of environmentally friendly polymer materials” which is being realized within the time frame 2010-2015 by the Consortium composed of nine research groups from Poland.

Acknowledgements

The Project (POIG 01.01.02-10-123/09) is partially financed by the European Union within the European Regional Development Fund
The management of solid waste is a growing concern in many countries. In the 90s, organizations, such as APC (American Plastics Council) had invested more than $1 billion to support increased recycling and educate communities [1]. Particular acute, the disposal of agricultural plastic wastes has become more and more severe. In 2007 was estimate between 2–3 million tons of plastics used each year in agricultural applications, the today’s plasticulture (use of plastics in agriculture) results in increased yields, earlier harvests, less reliance on herbicides and pesticides, better protection of food products and more efficient water conservation [2]. As result, the accumulation of agricultural plastic waste is a fact due to collection, clearing and disposal problems. For this reason, biodegradable polymers arose as solution to this global problem.

Our research focus on the study of poly(lactic acid) (PLA) and thermoplastic starch (TPS) as biodegradable materials for horticulture pots and agriculture mulch’s, respectively. Regarding horticulture pots, PLA was mixed with different amounts of wood fibers, coffee grounds, foaming agent and fertilizer. Similarly, agriculture mulch’s were prepared by addition of different fertilizers to TPS. Besides to fulfil the mechanical and biodegradation requirements (Figure 1), the developed composites contain fertilizer to support the plants growth.

**Fig. 1.** a) flexural properties of PLA and prepared composites; b) molecular weight distribution of initial and degraded samples after 12 weeks in compost.

**References**


MODIFICATION OF THIN KERATIN FILMS BY THE ADDITION OF FISH COLLAGEN

J. Kozłowska, A. Sionkowska, M. Skorupska

Faculty of Chemistry, Nicolaus Copernicus University, Toruń, Poland
justynak@chem.umk.pl

Keywords: keratin, fish collagen, biomaterials

Keratins are a family of protein that constitute hair, wool and feather and are characterized by high cysteine content. Keratin-based materials are promising candidates to application in biomedical fields, due to their biodegradability and biocompatibility [1].

Collagen is the main protein of connective tissue and the main component of the skin. It is considered as one of the most useful natural biomaterials. The interests of collagen in medicine still rise [2]. There are different sources of collagen. Collagen isolated from tissues of marine is a good alternative to bovine collagen because it is more safe - free from pathogenic prions [3].

The aim of this work was to study the properties of keratin films in the presence of small amount of collagen (5, 10 and 20%). The surface properties of keratin/collagen materials were compared with the surface properties of keratin films to determine the influence of addition of collagen on these properties.

In this study keratin was obtained in our laboratory from chicken feather. Acid-solubilized collagen was extracted from the skin of Brama australis (fish which lives in tropical and subtropical climate). Polymeric blends were prepared by mixing suitable volumes of chitosan and keratin aqueous solutions and polymeric films were obtained by casting the solutions onto glass plates.

The surface properties of keratin, collagen and keratin/collagen blended films have been studied by contact angle measurements, which allow to calculate the surface free energy. Contact angles of two liquids: diiodomethane and glycerol on studied films were measured at constant temperature using goniometer equipped with a system of drop shape analysis (DSA 10 produced by Krüss, Germany).

Acknowledgments

Financial support from the National Science Centre (NCN, Poland) Grant No UMO-2012/05/N/ST8/02283 is gratefully acknowledged.

References


MODIFICATION OF THE METHOD OF COLLAGEN EXTRACTION FROM FISH TISSUES

J. Kozłowska, A. Sionkowska, K. Piechowicz

Faculty of Chemistry, Nicolaus Copernicus University, Toruń, Poland
justynak@chem.umk.pl

**Keywords: fish collagen, fish scales, extraction of collagen, biomaterials**

Collagen isolated from different tissues is a very attractive source for biomaterial production. Mammalian tissues, especially bovine or porcine skin and bovine or equine Achilles tendons, have been used as a base source of this protein. However collagen products of bovine origin have been shown to be contaminated with some diseases [1]. Recently, increasing interest in search a new and safe sources of collagen was observed. Type I collagen has been also extracted from skin, bone, fins and scales of fresh water and marine fishes [1, 2]. Fish scales are composed of collagen fibrils type I covered with calcium salts (16–59% mineral content in weight) [3].

The aim of this study was to extract, characterize and comparison of acid soluble collagen (ASC) and pepsin soluble collagen (PSC) from scale of *Esox Lucius*.

In our previous study we extracted the acid soluble collagen from *Esox Lucius* scales [4, 5]. Undissolved matter from acid soluble collagen extraction was further extracted in 0.5 M acetic acid containing 1% pepsin. The yield of ASC and PSC was appraised and both collagens were subjected to analyses. In the present study, we investigated the denaturation temperature and mechanical properties of ASC and PSC. The sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) analysis was performed to assess the molecular weight of both collagens.

**Acknowledgments**

Financial support from the National Science Centre (NCN, Poland) Grant No UMO-2012/05/N/ST8/02283 is gratefully acknowledged.

**References**


HOLLOW FIBER LIQUID-PHASE MICROEXTRACTION AND SOLID-PHASE MICROEXTRACTION ANALYSIS FOR EVALUATION OF DECONTAMINATION EFFICIENCY IN RECYCLED PET

É. Oliveira¹, S. Cruz¹, Y. Echegoyen², C. Nerín²

1 Federal University of ABC, Santo André, Brazil, sandra.cruz@ufabc.edu.br
2 I3A, University of Zaragoza, Zaragoza, Spain, cnerin@unizar.es

Keywords: PET recycled, food packaging, decontamination efficiency recycling

The increasing consumption of plastics, especially PET for use in food packaging, has been causing environmental impacts. In view of this scenario, research involving recycled PET for food contact materials has been developed with the purpose of increasing the time of this product in the commercial chain [1]. However, the use of recycled polymers in contact with food must comply with certain requirements according to legislation [2]. For example, the recycled material must not contain toxic substances that can migrate from the packaging into food (order of lower ppb) and affect the consumers’ health. The guidelines published by Food and Drug Administration (FDA) establish that the concentration of surrogates in food should be lower than 0.010 mg.kg⁻¹ [3]. This value requires a very sensitive procedure for controlling the safety in use of recycled material. Thus, various technologies have been studied to allow the use of recycled polymers for food contact [3,4]. Furthermore, sophisticated analytical procedures have been proposed to determine different types of packaging migrants at trace concentration levels. Without a doubt, the sample treatment techniques, mainly those concerning extraction and pre-concentration of the sample are the bottleneck. Among the more used techniques for this purpose the Solid-Phase Microextraction (SPME) [5] and more recently the Hollow Fiber Liquid-Phase Microextraction (HF-LPME) techniques have been used [6]. In this study, recycled PET resin was contaminated with a series of surrogates using a FDA protocol [2] to simulate the worst case of misuse of PET packaging. Then, the samples were extruded and re-polymerized. In order to determine the decontamination efficiency of the recycling process in the PET material, migration analysis were performed using different food simulants. After migration tests the contaminants were pre-concentrated from the aqueous phases using SPME and HF-LPME techniques and quantification was performed by gas chromatography with different detectors. The results obtained are shown and discussed.

References
LIFE CYCLE ASSESSMENT OF INNOVATIVE FIBROUS PRODUCTS MANUFACTURED ON THE BASE OF POLI-(LACTIC ACID) PLA

Malgorzata Michniewicz¹, Michal Janiga¹, Hanna Zakowska², Konrad Nowakowski², Izabella Krucinska³, Danuta Ciechanska¹, Agnieszka Komisarczyk³

¹ Institute of Biopolymers and Chemical Fibres, Lodz, Poland
² COBRO – Packaging Research Institute, Warsaw, Poland
³ Lodz University of Technology, Poland

Key words: bio-based polymers; sustainable development; LCA, biodegradable, fibrous products.

In the last years tendencies of replacing the traditional petroleum-based plastics through polymer materials of new generation, determined as biopolymers are being observed. In the scope of the synthesis of polymers from renewable raw materials technological results of the polylactide and poly(lactic acid) production from lactic acid as the substratum are the most advanced. These polymers are being obtained in the biotechnological process on the way of the fermentation of sugars to lactic acid, of conversion to cyclical lactide dimer and then of polymerization to PLA. PLA is the polymer of the future, the bio-based material susceptible to the biodegradation, having great applying potential, particularly for manufacturing disposable products or the products with the short life time.

In the Biogratex project a series of innovative products was worked out on the basis of bio-based polymers, including PLA. The selected products were rated and compared with conventional products, taking into consideration widely understood environmental issues, using the life cycle assessments (LCA) as the research tool.

Examinations of products by using the LCA method consist in inventory of environment loads in established stages of their life cycle (borders of the system). Thanks to that, showing the full image and the assessment of influences of the examined product on individual elements of the environment are available. The knowledge on this topic permits to make the choices more profitable for the environment – rational resources management in harmony with the principle of sustainable development is enabled. Knowing the levels of environmental influences makes it possible to describe the strategy of reducing them. In this way LCA can be rated among aiding decisions tools and to be taken both in the area of designing new products / technology as well as the development of already existing technology.

In this work the results of LCA study for selected PLA based, fibrous products, developed in the project, and LCA results for conventional products made of plastics were presented and compared. The processes and environmental impact categories which have the dominating shares in the environmental loads were showed.

Acknowledgment:

The study was executed in the frame of BIOGRATEX project funded from European Fund of the Regional Development in the frame of Innovative Economy Operational Programme (IE OP) 2007-2013, project No POIG.01.03.01-00-007/08.
STUDY OF SIGNIFICANT PARAMETERS OF AUREUSIDIN ENCAPSULATION IN PLA NANOPARTICLES

M. Roussaki¹, A. Gaitanarou¹, S. Vouyiouka², C. Papaspyrides², A. Detsi¹

¹ Laboratory of Organic Chemistry, School of Chemical Engineering, National Technical University of Athens, Athens, Greece
² Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Zografou Campus 15780, Athens, Greece

Keywords: Encapsulation, nanoparticles, polymers, PLA, aureusidin

Biodegradable polymers are considered as the ‘green’ eco-friendly materials used in encapsulation of active molecules in nanoparticles, due to their biocompatibility and non-toxic properties. Among all biopolymers, poly(lactic acid) (PLA) is extensively used as a delivery vehicle for various pharmaceutical agents due to its early use and approval as a compatible biomaterial in humans.

In the present work, a technique for encapsulation of a naturally-occurring flavonoid, i.e. aureusidin, in PLA nanoparticles was developed. Aureusidin (Fig.1) is a naturally-occurring aurone biosynthesized in plant tissues from 2',3,4,4',6'-pentahydroxy-chalcone by the key enzyme aureusidin synthase, possessing important antioxidant activity with however low aqueous solubility and can cause some toxic effects [1].

Encapsulation of aureusidin in biodegradable PLA nanoparticles was formulated by emulsification-solvent evaporation technique, while the molecular weight of the synthesized PLA polymers was investigated as a parameter which may affect the formed nanoparticles.

The PLA nanoparticles were characterised for their size and their loading efficiency. The obtained results were promising, suggesting that the particular polymer-technique system is a valid choice for aureusidin encapsulation.

References
THERMAL BEHAVIOR AND STABILITY OF BLENDS OF POLY(LACTIC ACID) WITH PVC THERMOOXIDIZED UNDER MILD CONDITIONS

Györgyi Szarka, Béla Iván, Attila Domján

1Polymer Chemistry Group, Institute of Material and Environmental Sciences, Research Centre for Natural Sciences, Hungarian Academy of Sciences,
2NMR Research Group, Institute of Organic Sciences, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1117 Budapest, Magyar tudósok körútja 2, Hungary, szarka.gyorgyi@ttk.mta.hu

Keywords: PVC, PLA, thermooxidation, blend, thermal stability, environmental friendly

Poly(lactic acid) (PLA) is a well-known bio-friendly and biodegradable polymer. It is increasingly used in several areas, including food packaging as well. Unfortunately, its brittleness limits its use. Our work deals with polymer blends of PLA and preoxidized poly(vinyl chloride) (PVC), another packaging material. This way, not only the reuse of the partially degraded PVC can be solved, but the brittleness of the PLA may be improved as well, and at the end a new product can be earned.

Systematic investigations were carried out in order to reveal the degradation processes during processing of PVC. It was found that under mild circumstances oxidation and chain scission with relatively high rate take place. Not only the PVC but the degradation of the plasticizer also occurred. It was also proved with DSC that the products of this process are connected to the PVC chain and act as inner plasticizer.

The recycling ability of the thermooxidatively pretreated PVC was attempted by making polymer blends with poly(lactic acid), a biodegradable polymer. It was found that thermooxidized PVCs are miscible with poly(lactic acid) in a wide range of composition. This may create unique opportunities for manufacturing of new kinds of blends made from waste PVC and the bio-friendly and biodegradable poly(lactic acid).

Acknowledgement

Supporting this work by the European Regional Development Fund through the Hungary-Slovakia Cross-Border Cooperation Programme 2007-2013 (HUSK/1101/1.2.1/0209) and the technical assistance in the GPC analysis by Mr. Tamás Ignáth and in the DSC measurements by Ms. Judit Szauer are gratefully acknowledged.

References


INVESTIGATION OF STRUCTURAL CHANGES OCCURRED IN WOOD DUE TO CHEMICAL TREATMENT

Carmen-Alice Teacă¹, Ruxanda Bodîrlău¹, Dan Roșu², Liliana Roșu²

1 “Petru Poni” Institute of Macromolecular Chemistry, Natural Polymers Department, 41 A Gr. Ghica-Voda Alley, Iasi, RO-700487, Romania; E-mail: cateaca@icmpp.ro

2 “Petru Poni” Institute of Macromolecular Chemistry, Center of Advanced Research in Bionanoconjugates and Biopolymers, 41 A Gr. Ghica-Voda Alley, Iasi, RO-700487, Romania

Keywords: wood, chemical modification, epoxy functionalized soybean oil, FTIR spectroscopy, X-ray diffraction, TG-DTG analysis

Wood is a complex multi-component polymeric material system containing two major components: carbohydrates (65–75%), and lignin (18–35%) [1]. Wood deterioration occurs in the presence of environmental factors, namely ultraviolet and visible light, humidity, and pollutants, with the cleavage of C-H, C-O, and C-C bonds [2-4]. Different treatments (chemical, thermal) can be effective methods to improve wood resistance to environmental degradation processes. In the present work, softwood specimens as discs (ϕ=15–40 mm, thickness 1.5–2.0 mm) were treated with succinic anhydride (SA) in dimethylformamide (DMF) as solvent, with different concentration values (reaction time 1h and 90°C). Modified wood samples were further treated with epoxy functionalized soybean oil (ESO) in the presence of triethylamine (TEA), as catalyst (reaction time 1h and 100°C). Weight percent gain (WPG) values for non-treated and treated wood samples were evaluated. Structural changes were evidenced by FTIR spectroscopy and X-ray diffraction methods. Investigation of thermal properties was also performed, thermal stability of the treated wood samples decreasing by chemical modification. Wood resistance to moisture was improved through chemical treatment. Both treatments can be effective for improving wood properties under accelerated degradation conditions (humidity, polychromic light action).

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS-UEFISCDI - Project number PN-II-ID-PCE-2011-3-0187.

References


STARCH/WOOD BIO-BASED POLYMER SYSTEMS - STRUCTURE AND THERMAL PROPERTIES

Ruxanda Bodîrlău¹, Carmen-Alice Teacă¹, Dan Roșu², Liliana Roșu², Cristian-Dragoș Varganici²

¹ “Petru Poni” Institute of Macromolecular Chemistry, Natural Polymers Department, 41 A Gr. Ghica-Voda Alley, Iasi, RO-700487, Romania, E-mail: boruxan@icmpp.ro
² “Petru Poni” Institute of Macromolecular Chemistry, Center of Advanced Research in Bionanoconjugates and Biopolymers, 41 A Gr. Ghica-Voda Alley, Iasi, RO-700487, Romania

Keywords: wood, cellulose, lignin, thermoplastic starch, biocomposite

The use of lignocellulose fillers obtained from renewable resources as a reinforcing phase in polymer matrix composites provides positive environmental benefits with respect to ultimate disposability and raw material use [1-4]. In the present work, thermoplastic corn starch and blends of starch and wood particles/wood polymers were used as matrix materials, solution-cast films being obtained by the casting method. Fillers including wood sawdust, cellulose and lignin separated from wood through standard methods were subsequently added within thermoplastic starch matrix in order to obtain filler loading of 20 wt % based on the amount of corn starch. Biopolymer film samples with a thickness of around 0.25 mm were investigated through Fourier Transform infrared spectroscopy, and X-ray diffraction analyses, water sorption tests, and scanning electron microscopy method. Simultaneous thermal analysis was further used for thermal stability investigation in order to evaluate the influence of the biopolymer filler upon starch based matrix thermal properties.

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS-UEFISCDI - Project number PN-II-ID-PCE-2011-3-0187.

References

INTUMESCENCE IN FIRE RETARDANCY OF WOOD-HDPE/PVC COMPOSITES

Zvonimir Katanić¹, Ljerka Kratofil Krehula², Anita Ptiček Siročić³, Zlata Hrnjak-Murgić⁴

¹ Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, Hr-10000, Zagreb, katancic@fkit.hr
² Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, Hr-10000, Zagreb, krehula@fkit.hr
³ Faculty of Geotechnical Engineering, University of Zagreb, Hallerova aleja 7, HR-42000 Varaždin, anitaps@gfv.hr
⁴ Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, Hr-10000, Zagreb, zhrnjak@fkit.hr

Keywords: flammability, intumescence, polyethylene, wood-plastic composites

The production of wood-plastic composites (WPCs) in the thermoplastic industry has gained much acceptance in recent years and is expected to keep growing. The main application area of wood-plastic composites is in the building and automotive industries, but they are also applied for packaging, for the preparation of various household articles with increasing usage in interior as office appliances and furniture [1]. Therefore fire retardancy of the WPCs is important key point because modern safety demands require fire resistant materials. The goal of this research was to investigate effect of intumescent [2] ammonium polyphosphate/pentaerythritol (APP/PER) system on fire retardancy and thermal stability of wood-plastic composites based on HDPE/PVC blend. Fumed silica nanoparticles were added to some samples to examine possible further improvement of fire and thermal. Thermal stability was characterized by thermogravimetric analysis (TGA) while fire performance was evaluated by UL-94 test. Tensile properties were also measured to determine effect of fillers loadings on mechanical properties of WPCs. TGA results showed that there is no significant improvement of degradation temperatures, but char yield increased for 50 % in samples that contained PER. It was found that with addition of APP alone it is not possible to achieve any classification in UL-94 test while APP/PER samples self-extinguished in less than 5 seconds without burning drops thus obtaining highest V-0 rating in UL-94 test. No improvement of thermal and fire properties was noticed in samples containing silica nanoparticles and at the same time those samples had degraded mechanical properties.

References

THE STABILITY OF CONDUCTIVITY OF REPROTONATED POLYANILINES AT ELEVATED TEMPERATURE

Miroslava Trchová¹, Jan Prokeš², Jaroslav Stejskal¹

¹ Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic, trchova@imc.cas.cz, stejskal@imc.cas.cz
² Charles University in Prague, Faculty of Mathematics and Physics, 180 00 Prague 8, Czech Republic, jprokes@semi.mff.cuni.cz

Keywords: Conducting polymer; Conductivity; Hydrogen bonding; Polyaniline; Thermal stability

Reprotonation of polyaniline base with various acids opens a way to conducting materials widely differing in physical properties (Fig.1). The thermal stability of the resulting polyaniline salts was tested by measurements of the conductivity at 125 °C for up to 500 h. Polyaniline sulfate was the most stable and its resistivity increased only by 3.6 times after that time. The stability differed considerably depending on the acid used for reprotonation [1]. The room-temperature conductivity of polyaniline salt is determined by the strength of the acid and its ionic bond with the imine nitrogen in polyaniline. The thermal stability of conductivity, however, is controlled by the ability of the acid to constitute hydrogen bonds with the secondary amine nitrogens in polyaniline. For that reason, oxygen-containing counter-ions, such as sulfates or sulfonates, produce more stable salts with polyaniline, compared with polyaniline protonated with, e.g., hydrochloric acid. The presence of hydroxyl group in the counter-ions also enhances the thermal stability of the polyaniline salt [2]. These conclusions are supported by the analysis of FTIR spectra.

Fig. 1. Conducting polyaniline salt is deprotonated in alkaline media to a polyaniline base. The base can be again reprotonated with acids (HA) to corresponding salts.

References

MODIFICATION OF POLY(VINYLIDENE FLUORIDE-TRIFUOROETHYLENE) MEMBRANES FOR DRUG RELEASE

H. Salazar\textsuperscript{1,2}, A.C. Lima\textsuperscript{1}, A.C. Lopes\textsuperscript{1}, G. Botelho\textsuperscript{2}, S. Lanceros-Mendez\textsuperscript{1}

\textsuperscript{1}Centro/Departamento de Física, Universidade do Minho, 4710-057, Braga, Portugal
\textsuperscript{2}Centro/Departamento de Química, Universidade do Minho, 4710-057, Braga, Portugal

Keywords: PVDF, drug delivery, ibuprofen

Polymer/zeolite membranes are raising increasing interest due to the cross-coupling of filler and polymer matrix properties. Their application areas are expanding from the traditional uses as adsorbents and catalysis to novel ones, including the biomedical and biological fields [1]. In this context, poly(vinylidene fluoride-trifluoroethylene)/zeolite porous membranes are a promising system for the development of drug delivery systems, since it combines the selective absorption of zeolites with the tailored polymer microstructure and phase, its biocompatibility and chemical stability [2,3].

This investigation reports on a drug release system based on macroporous P(VDF-TrFE)/NaY membranes, with 0, 4, 16 and 32 %wt NaY filler content, produced by isothermal crystallization from dimethylformamide. The morphological, thermal and mechanical properties of the composite membranes are also discussed.

The membranes show an interconnected spherical pore architecture with the zeolite fillers decorating the polymer pore surface. A sublimation process was used for the encapsulation of ibuprofen (IBU) in the membrane pores and its release was evaluated by chromatographic and spectroscopic techniques after the immersion of P(VDF-TrFE)/NaY+IBU in a PBS solution.

It was observed that the zeolite content has a strong influence on the amount of IBU absorbed by the membrane, as well as on its release rate, allowing tailoring membrane uptake and release performance. In this way, it was proved the suitability of the system for the development of biocompatible and nonbiodegradable drug release membranes.

Acknowledgements

The authors acknowledge the n-STeP Project, reference NORTE-07-0124-FEDER-000039, supported by the Programa Operacional Regional do Norte (ON.2)

References


IS IT POSSIBLE TO IMPROVE THE MORPHOLOGY AND THE PHOTOSTABILITY OF P3HT:PCBM BY USING ADDITIVES?

Aurélien Tournebize, Agnès Rivaton, Heiko Peisert and Thomas Chassé

1 Institut für Physikalische und Theoretische Chemie (IPTC), Auf der Morgenstelle 18, Tübingen, Germany, aurelien.tournebize@uni-tuebingen.de, heiko.peisert@uni-tuebingen.de, thomas.chasse@uni-tuebingen.de
2 Institut de Chimie de Clermont-Ferrand (ICCF) UMR 6296, Université Blaise Pascal, 24 avenue des Landais, BP 80026, 63171 AUBIERE Cedex, France, agnes.rivaton@univ-bpclermont.fr

Keywords: Organic solar cells, photostability, conjugated polymer, processing additives.

Processing additives for improved the morphology of the bulk heterojunction (BHJ) materials used in organic solar cells (OSCs) is now very popular. However the use of high boiling point additives leads the formation of residues which decrease the reproducibility of the device performances and the BHJ morphological stability. It has been demonstrated that these residues are hardly removable without impacting the BHJ morphology. The performance racing of OSCs is not useful if the stability and especially the photostability is not studied in parallel. How these residues impact the polymer blend photostability is still unknown but is crucial for all the organic photovoltaic (OPV) community and is a key factor for a promising industrial future.

Herein, we have investigated the impact of diiodooctane (DIO) and octanedithiol (ODT) residues which are the two most used additives on the state of the art active layer P3HT:PCBM photostability. Our work revealed the acceleration of the polymer and fullerene photodegradation by the presence of DIO or ODT residues when a top layer is deposited with complex and different mechanisms of degradation. In this context, the use of hindered amine light stabilizers (HALS) has been explored as new additives for improved both morphology and stability of polymer blend materials. The results show first that HALSs are able to tune the morphology as well as DIO or ODT, and different impact on the P3HT:PCBM have been identified depending of chemical structure of the HALS.

Our work clearly shows that processing additives play an important role on the polymer blend photostability and thus opening up future investigations on the use of morphological improver but also photo stabilizer additives.

Acknowledgements

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2011 under grant agreement ESTABLIS no. 290022).

References


**N,N'-DIMETHYLAMINOETHYL METACRYLATE STAR POLYMERS AS NON-VIRAL VECTORS**

A. Dworak, B. Mendrek, A. Kowalczuk, B. Trzebicka

Centre of Polymer and Carbon Materials, Polish Academy of Sciences, M. Curie-Skłodowskiej 34, 41-819 Zabrze, Poland; adworak@cmpw-pan.edu.pl

**Keywords:** star polymers, gene therapy, N,N'-dimethylaminoethyl methacrylate

The design of effective systems for protection of the genetic material from degradation and for transferring of nucleic acid to a specific target is an important task in gene transfection studies. The recent progress in stars synthesis and characterization [1, 2] opened the route for creating star-based vectors [3, 4]. The data obtained up to now for non-viral vectors based upon polycationic star polymers are rather rough and require deeper analysis.

Star polymers with N,N'-dimethylaminoethyl methacrylate (DMAEMA) arms (DP from 14 to 98) and hyperbranched poly(arylene oxindole) core were synthesized using atom transfer radical polymerization (Fig.1) and used for delivery of nucleic acid. The star are pH and thermoresponsive. The sizes of the stars were investigated by dynamic light scattering as a function of pH and temperature. The values of hydrodynamic radii revealed that in aqueous solution small aggregates are present, while in the organic solvent isolated star macromolecules in the size of 7 to 14.5 nm were observed. The star polymers complex luciferase encoding plasmid DNA into particles with the size up to 400 nm dependent on the molar ratio of nitrogen groups of polycation to phosphate groups of DNA (N/P ratio). Zeta potential of obtained star/DNA complexes is positive, what facilities their cellular uptake. The length of star arms determined the transfection efficiency of obtained polyplexes.

![hyperbranched poly(arylene oxindole) with 28 initiating groups](image)

**Fig. 1.** Synthesis of the PDMAEMA stars

**Acknowledgements**

This work was supported by the Polish National Science Centre contract No. DEC-2011/01/B/ST5/05982.

**References**

RESISTING OF FIBRINOGEN ADSORPTION BY THE POLYETHER-BASED SURFACES

A. Dworak, A. Utrata-Wesołek, W. Wałach

Centre of Polymer and Carbon Materials, Polish Academy of Sciences, M. Curie-Skłodowskiej 34, 41-819 Zabrze, Poland; adworak@cmpw-pan.edu.pl

Keywords: antifouling surfaces, protein adsorption, polyglycidol surface

Medical implants, regardless of their composition, become coated with a layer of proteins within a few seconds of contact with physiological fluids and tissues. This harmful process deteriorates the function of medical devices. The host defence mechanism is activated, which results in inflammation, infection, thrombosis, fibrosis or allergy. Therefore, materials with antifouling properties have been the subject of much interest within the last few years1-3. For that purpose among other dextran, polyoxazolines or polyzwitterions have been used, but most frequently poly(ethylene glycol)-based surfaces (with different polymer length, topology or grafting density) have been extensively studied4. The close structural similarity of polyglycidol (PG) to poly(ethylene glycol) renders the polymer predetermined for biological applications. This polymer is biocompatible and non-cytotoxic. It possesses free hydroxyl groups that are available for further functionalization. In this work we report the synthesis and characterization of polyglycidol-based surfaces and their application in the adsorption of fibrinogen. The polyglycidol coated-surfaces were obtained via the “grafting to” and “grafting from” technique. Hydrophilic surfaces (water contact angle = from 62° to 39°) with different polymer structure and thickness ranged between 2 to 130 nm were obtained (Fig. 1).

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Polyglycidol coating" /></td>
<td><img src="image2.png" alt="Linear polyglycidol" /></td>
<td><img src="image3.png" alt="Branch polyglycidol" /></td>
</tr>
</tbody>
</table>

Fig. 1: Different chain topology of polymers of glycidol on the surface: A) and B) linear polyglycidol grafted to the surface, C) branched polyglycidol grafted from the surface

It was established that the polyglycidol-coated surfaces limited the fibrinogen adsorption in comparison with bare silica supports. The ability to prevent the fibrinogen adsorption depends on the molar mass of the polymer, polymer layer thickness and structure.

Acknowledgements

This work was supported by the National Science Centre, grant no. UMO-2011/01/B/ST5/05279.

References

LIGHT RESPONSIVE FUNCTIONAL POLYOLEFINS

Ilaria Domenichelli, Francesca Cicogna, Serena Coiai, Marco Lessi, Fabio Bellina, Elisa Passaglia

1 Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy
2 CNR-ICCOM UOS Pisa, Via Moruzzi 1, 56121 Pisa, Italy
3 Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126 Pisa, Italy

Keywords: azobenzene, light-responsive polymers, TEMPO-derivatives

Azobenzene and its derivatives are interesting molecules because of their ability to switch from more stable trans isomer to less stable cis form by using opportune wavelength light irradiation. This rapid and reversible photoisomerization can cause changes to the optical, geometric, mechanical and chemical properties of materials where these chromophores are incorporated. The grafting of azobenzene derivatives to polymers can provide functional materials which can for example undergo light-induced shape changes giving rise to non-linear optical devices and reversible memory storage systems [1]. With the aim of obtaining polymeric materials able to respond to light stimuli high density polyethylene (HDPE) was functionalized with 4-(phenylazo)benzoyl-2,2,6,6-tetramethyl piperidine-1-oxyl (AzO-TEMPO) and 4-[4-(2-thienylazo)benzoyl]-2,2,6,6-tetramethylpiperidine-1-oxyl (TiO-TEMPO), two TEMPO derivatives bearing azobenzene-like chromophores, by free radical post-reactor modifications initiated by peroxide and carried out in the melt. To highlight the grafting and to evaluate its degree (FD) the functionalized polymers were characterized by FT-IR spectroscopy. Then, their photophysical behavior was studied by UV/Vis spectroscopy, and the results compared with the properties displayed in solution by the two free TEMPO analogues. As we hoped for, the trans-cis isomerization was observed in all cases, which proves that the photophysical properties of the two TEMPO derivatives are preserved after grafting onto HDPE and, hence, that our approach enables the possibility of obtaining new classes of light responsive polymeric materials.

Fig. 1. UV-Vis spectra of HDPE-g-(AzO-TEMPO) and HDPE-g-(TiO-TEMPO) films recorded after different irradiation time with a lamp that emits at 366 nm

References
Author Index

Abreu, A.S., 49, 168
Acero, E.H., 124, 125
Adema, K.N.S., 18, 70, 75
Agnello, P.H.L., 22, 119
Akakncı, A., 43
Al-Malaika, S., 5, 81, 131
Amaro, L.P., 131
Anca, V., 137
Anzllovar, A., 20, 102
Araujo, A., 165
Arnaud, M.-A., 111
Arrigo, R., 23, 129, 130, 156
Aulova, A., 5, 25, 164
Aurelian, S., 154
Bab, M., 24, 120, 147
Bakó, P., 100
Bánay, K., 143
Barandiaran, I., 16, 42
Barány, T., 78
Barbera, S., 47
Barbosa, J.M., 89
Barral, L., 159
Baumann, T.F., 108
Beaupré, S., 111
Bégué, D., 111, 112
Bek, M., 5, 25, 163
Bellayer, S., 69
Bellina, F., 183
Benavides, R., 17, 24, 56, 141, 142
Beneš, H., 23, 44, 133, 136
Benezet, J.C., 83
Bereska, A., 18, 52, 71
Bereska, B., 17, 52, 71
Berezin, O., 113
Bergeret, A., 83, 98
Bettini, S.H.P., 23, 139, 140
Bialas, S., 115
Bicu, I., 166
Bigger, S.W., 36
Billingham, N., 5
Bochenek, M., 32
Bocz, K., 19, 78
Bodiilau, R., 26, 175, 176
Bodzay, B., 100
Bohn, M.A., 18, 67
Bonhomme, S., 94
Bonnekessel, M., 148
Bonse, B.C., 19, 89
Botelho, G., 25, 26, 49, 165, 179
Botta, L., 126, 127, 128
Bounor-Legaré, V., 65, 66
Bourbigot, S., 69, 72
Bourgeois, Y., 69
Bouza, R., 159
Brasoveanu, M., 25, 137, 160
Braun, U., 18, 64, 68, 120
Brunclíková, M., 133
Brzuzaud, S., 20, 92, 97, 98
Budai, D., 100
Builes, D.H., 41
Bujiowicz, K., 158
Buscarino, G., 126
Bussière, P.-O., 25, 85, 88, 112, 150, 156, 161
Cano, L., 16, 41
Cappelletti, A., 42
Cardoso, R.S., 89
Carroccio, S., 95, 129
Cassagnau, P., 65, 66
Catalanotto, F., 156
Cavaletti, E., 85
Cavodeau, F., 20, 91
Cazacu, M., 53, 122
Celina, M., 5, 18, 73, 149
Cerailo, M., 121, 152
César, G., 97
Chadeyron, G., 114
Chapel, A., 21, 114
Chassé, T., 180
Chazeau, L., 19, 86
Chiellini, E., 15, 34
Chivas-Joly, C., 84, 101
Cicogna, F., 95, 129, 183
Ciechanska, D., 172
Cochez, M., 79
Coiai, S., 20, 95, 183
Coiffier, F., 83
Colin, A., 19, 85
Colin, X., 19, 31, 62, 74, 76, 77
Corre, Y.-M., 97
Courtat, J., 18, 65
Courvoisier, E., 18, 76
Cran, M.J., 36
<table>
<thead>
<tr>
<th>Name</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hu, G.-H.</td>
<td>144, 145</td>
</tr>
<tr>
<td>Huber, D.</td>
<td>138</td>
</tr>
<tr>
<td>Huskić, M.</td>
<td>102</td>
</tr>
<tr>
<td>Iervolino, R.</td>
<td>47</td>
</tr>
<tr>
<td>Iggui, K.</td>
<td>20, 98</td>
</tr>
<tr>
<td>Ihssen, J.</td>
<td>148</td>
</tr>
<tr>
<td>Iłowska, J.</td>
<td>52</td>
</tr>
<tr>
<td>Imholz, V.</td>
<td>24, 153</td>
</tr>
<tr>
<td>Isselmou, M.O.</td>
<td>150</td>
</tr>
<tr>
<td>Iván, B.</td>
<td>134, 135, 143, 174</td>
</tr>
<tr>
<td>Jäger, C.</td>
<td>80</td>
</tr>
<tr>
<td>Jakubowicz, I.</td>
<td>99</td>
</tr>
<tr>
<td>Janecska, T.</td>
<td>63</td>
</tr>
<tr>
<td>Janiga, M.</td>
<td>172</td>
</tr>
<tr>
<td>Jentsch, A.</td>
<td>21, 110</td>
</tr>
<tr>
<td>Jeziórksa, R.</td>
<td>5, 21, 109</td>
</tr>
<tr>
<td>Jin, H.</td>
<td>164</td>
</tr>
<tr>
<td>Joly, C.</td>
<td>103</td>
</tr>
<tr>
<td>Joubert, A.</td>
<td>84</td>
</tr>
<tr>
<td>Kaci, M.</td>
<td>92, 98</td>
</tr>
<tr>
<td>Kaczmarek, B.</td>
<td>15, 38</td>
</tr>
<tr>
<td>Kaczmarek, H.</td>
<td>96, 115, 147</td>
</tr>
<tr>
<td>Kafarski, P.</td>
<td>71</td>
</tr>
<tr>
<td>Kaluzna, I.</td>
<td>124</td>
</tr>
<tr>
<td>Kasza, G.</td>
<td>23, 134, 135</td>
</tr>
<tr>
<td>Katančić, Z.</td>
<td>26, 177</td>
</tr>
<tr>
<td>Kaya, D.</td>
<td>16, 43</td>
</tr>
<tr>
<td>Kaźmierczak, D.</td>
<td>123</td>
</tr>
<tr>
<td>Khatibi, R.</td>
<td>126, 128</td>
</tr>
<tr>
<td>Kicko-Walczak, E.</td>
<td>15, 35</td>
</tr>
<tr>
<td>Kmetty, Ā.</td>
<td>78</td>
</tr>
<tr>
<td>Komisarczyk, A.</td>
<td>172</td>
</tr>
<tr>
<td>Kortaberrria, G.</td>
<td>42</td>
</tr>
<tr>
<td>Kos, T.</td>
<td>102</td>
</tr>
<tr>
<td>Kotzian, C.</td>
<td>56</td>
</tr>
<tr>
<td>Kowalczuk, A.</td>
<td>181</td>
</tr>
<tr>
<td>Kozłowska, J.</td>
<td>26, 169, 170</td>
</tr>
<tr>
<td>Kraemer, R.</td>
<td>64</td>
</tr>
<tr>
<td>Kredatusová, J.</td>
<td>23, 133</td>
</tr>
<tr>
<td>Krehula, L.K.</td>
<td>177</td>
</tr>
<tr>
<td>Kričej, B.</td>
<td>107</td>
</tr>
<tr>
<td>Krucinska, I.</td>
<td>172</td>
</tr>
<tr>
<td>Kruliš, Ζ.</td>
<td>133</td>
</tr>
<tr>
<td>Kubicek, C.P.</td>
<td>125</td>
</tr>
<tr>
<td>Kudanga, T.</td>
<td>124</td>
</tr>
<tr>
<td>Kun, D.</td>
<td>54</td>
</tr>
<tr>
<td>Kunaver, M.</td>
<td>102</td>
</tr>
<tr>
<td>Küper, U.</td>
<td>148</td>
</tr>
<tr>
<td>Kutnar, A.</td>
<td>21, 106</td>
</tr>
<tr>
<td>La Mantia, F.P.</td>
<td>5, 22, 24, 48, 81, 121, 152, 157, 164</td>
</tr>
<tr>
<td>Lacoste, J.</td>
<td>94</td>
</tr>
<tr>
<td>Lanceros-Mendez, S.</td>
<td>179</td>
</tr>
<tr>
<td>Laven, J.</td>
<td>70, 75</td>
</tr>
<tr>
<td>Le Bihan, O.</td>
<td>84</td>
</tr>
<tr>
<td>Le Coq, L.</td>
<td>84</td>
</tr>
<tr>
<td>Le Duigou, A.</td>
<td>97</td>
</tr>
<tr>
<td>Le Gac, P.Y.</td>
<td>62, 153</td>
</tr>
<tr>
<td>Le Gac, P.-Y.</td>
<td>97</td>
</tr>
<tr>
<td>Le Moigne, N.</td>
<td>98</td>
</tr>
<tr>
<td>Le Nevé, S.</td>
<td>101</td>
</tr>
<tr>
<td>Leclerc, M.</td>
<td>111</td>
</tr>
<tr>
<td>Legocka, I.</td>
<td>22, 39, 118</td>
</tr>
<tr>
<td>Lemaire, J.</td>
<td>94</td>
</tr>
<tr>
<td>Lessi, M.</td>
<td>183</td>
</tr>
<tr>
<td>Lewicki, J.</td>
<td>21, 108</td>
</tr>
<tr>
<td>Li, Z.</td>
<td>24, 146</td>
</tr>
<tr>
<td>Lima, A.C.</td>
<td>179</td>
</tr>
<tr>
<td>Lin, Q.</td>
<td>19, 79</td>
</tr>
<tr>
<td>Livi, S.</td>
<td>136</td>
</tr>
<tr>
<td>Longuet, C.</td>
<td>82, 84</td>
</tr>
<tr>
<td>Lopes, A.C.</td>
<td>179</td>
</tr>
<tr>
<td>Lopez-Cuesta, J.-M.</td>
<td>84, 91, 101</td>
</tr>
<tr>
<td>Louisy, J.</td>
<td>69</td>
</tr>
<tr>
<td>Lucas, A.A.</td>
<td>139</td>
</tr>
<tr>
<td>Ludwig, R.</td>
<td>138</td>
</tr>
<tr>
<td>Łukaszek-Chmielewska, A.</td>
<td>162</td>
</tr>
<tr>
<td>Macedo, M.J.</td>
<td>168</td>
</tr>
<tr>
<td>Machado, A.V.</td>
<td>49, 165, 168</td>
</tr>
<tr>
<td>Maciejewski, G.</td>
<td>123</td>
</tr>
<tr>
<td>Maciejewski, H.</td>
<td>158</td>
</tr>
<tr>
<td>Mahiou, R.</td>
<td>114</td>
</tr>
<tr>
<td>Maio, A.</td>
<td>22, 23, 126, 127, 128</td>
</tr>
<tr>
<td>Makki, H.</td>
<td>18, 70, 75</td>
</tr>
<tr>
<td>Mani, S.</td>
<td>83</td>
</tr>
<tr>
<td>Maria, H.J.</td>
<td>15, 37</td>
</tr>
<tr>
<td>Marlica, E.</td>
<td>25, 147, 166</td>
</tr>
<tr>
<td>Marosi, Gy.</td>
<td>78, 100</td>
</tr>
<tr>
<td>Marque, G.</td>
<td>86</td>
</tr>
<tr>
<td>Martinez, G.</td>
<td>141</td>
</tr>
<tr>
<td>Martínez, I.</td>
<td>27</td>
</tr>
<tr>
<td>Matějka, L.</td>
<td>55</td>
</tr>
<tr>
<td>Maxwell, R.S.</td>
<td>108</td>
</tr>
<tr>
<td>Medlej, H.</td>
<td>111</td>
</tr>
<tr>
<td>Melo, L.</td>
<td>141</td>
</tr>
<tr>
<td>Méndez, G.</td>
<td>142</td>
</tr>
<tr>
<td>Mendrek, B.</td>
<td>181</td>
</tr>
<tr>
<td>Michálková, D.</td>
<td>133</td>
</tr>
<tr>
<td>Michniewicz, M.</td>
<td>26, 172</td>
</tr>
<tr>
<td>Militz, H.</td>
<td>21, 104</td>
</tr>
<tr>
<td>Mistretta, M.C.</td>
<td>121, 152</td>
</tr>
<tr>
<td>Mocanu (Paduraru), O.M.</td>
<td>60, 147</td>
</tr>
<tr>
<td>Mogon Patel, 17</td>
<td></td>
</tr>
<tr>
<td>Montero, B.</td>
<td>159</td>
</tr>
</tbody>
</table>

186
Morici, E., 23, 25, 81, 131, 157
Morreale, M., 121
Mota, C., 168
Motzkus, C., 84, 101
Moustafa, H., 16, 50
Mucha, M., 22, 115
Mühlhaupt, R., 90
Muñoz, P.A.R., 139, 140
Nádor, A., 23, 134, 135
Naik, A.D., 18, 69
Neira, G., 56
Nemțanu, M.R., 23, 137, 160
Nerín, C., 171
Nevoralová, M., 133
Niedermann, P., 100
Nizeyimana, F., 85
Nowakowski, K., 172
Nyanhongo, G.S., 124, 138
Oblak, P., 5, 17, 58, 164
Ohtani, H., 19, 87
Okamba Diogo, O., 16, 45
Okruszek, A., 167
Oleszko, N., 32
Oliveira, E., 171
Oliveira, M., 16, 25, 49, 165
Oprea, S., 24, 25, 154, 155
Oprea, V., 154, 155
Ortiz, J., 142
Ortner, A., 22, 124, 125
Oseli, A., 5, 163
Osváth, Z., 24, 143
Otazaghine, B., 91
Ounoughene, G., 19, 84
Pampalone, V., 130
Papaspyrides, C., 103, 173
Partal, P., 27
Passaglia, E., 95, 131
Patel, M., 17, 57
Paula, M.M.S., 141
Paula, M.S., 142
Pavlíč, M., 107
Peisert, H., 180
Perchacz, M., 16, 44, 136
Perrin, D., 83
Perz, V., 148
Peters, E.A.J.F., 70, 75
Petersen, H., 20, 99
Petrič, M., 21, 107
Piazza, A., 126
Piechowicz, K., 170
Pilař, J., 16, 40
Pinzino, C., 95
Pólk, M., 25, 35, 162
Ponyrko, S., 17, 55
Pori, P., 107
Prodan, T., 163
Prokeš, J., 178
Przyłucka, A., 125
Puchinger, H., 46
Pukánszky, B., 17, 54, 63
Quintana, A., 73
Ramírez, C., 159
Rapi, Z., 100
Ribitsch, D., 148
Richaud, E., 17, 45, 62, 77, 149, 153
Rico, M., 25, 159
Rigolin, T.R., 140
Risso, S., 139
Rivaton, A., 21, 111, 112, 180
Rizzarelli, P., 95
Robinson, M., 57
Rodrigues, P., 49
Rojewski, S., 158
Rolon-Garrido, V.H., 17, 59
Rosu, D., 17, 60, 61, 147, 175, 176
Rosu, L., 24, 60, 61, 147, 175, 176
Rouillon, C., 19, 88
Roussaki, M., 173
Rymarz, G., 35
Sahyoun, J., 18, 66
Salazar, H., 179
Salivon, T., 18, 74
Samuel, G., 94
Samyn, F., 69
Sancelme, M., 94
Santos, E., 165
Scaffaro, R., 126, 127, 128
Schartel, B., 80, 90
Scuracchio, C.H., 24, 144, 145
Senz, R., 64
Sinkel, C., 148
Sionkowska, A., 169, 170
Siročić, A.P., 177
Skorupska, M., 169
Šlouf, M., 133
Smith, T., 57
Soccalingame, L., 19, 83
Sonnier, R., 65, 66, 82, 91
Sousa, A.C., 139
Starman, B., 163
Stein, M., 20, 93
Štejskal, J., 178
Štengl, V., 136
Štok, B., 163
Strlič, M., 15, 28
Strumia, M., 42
Sturm, H., 64
Suba, P., 63
Sut, A., 19, 80
Sygmund, C., 138
Szabó, G., 54
Szadkowska, A., 109
Szarka, Gy., 26, 134, 135, 174
Szolnoki, B., 20, 71, 100
Szweda, D., 32
Targosz, M.-M., 20, 101
Tátraaljai, D., 63
Taviot-Gueho, C., 111
Tawakkal, I., 15, 36
Teacă, C.-A., 26, 175, 176
Tegl, G., 23, 138
Tercjak, A., 41
Th Thérias, S. rias, S., 15
Thérias, S., 33, 51, 85, 88, 112, 114, 150, 161
Thomas, S., 37
Tkacz, B., 71
Toldy, A., 100
Topham, P.D., 112
Topolniak, I., 17, 51
Torres, S., 141
Tóth, T., 143
Tournebize, A., 26, 111, 112, 180
Traikia, M., 94
Trchová, M., 26, 178
Trzebicka, B., 32, 181
Tsai, C.-C., 117
Tudorachi, N., 166
Twarowska-Schmidt, K., 22, 123
Uribe, R.M., 56
Utrata-Wesolek, A., 32, 182
Vadas, D., 78
Vagner, C., 79
Vahabi, H., 79
van Bentheim, R.A.T.M., 70, 75
van der Ven, L.G.J., 70, 75
Van Mierloo, S., 23, 132
Varganici, C.-D., 17, 60, 61, 147, 166, 176
Verdu, J., 45, 62, 153
Vigier, G., 86
Violeta, P.O., 154
Viretto, A., 19, 82
Vlad, A., 22, 53, 122
Voit, B., 110
Vollmer, S., 30
Voskoboïnik, M., 113
Vouyiouka, S., 20, 26, 103, 173
Vuković-Kwiatkowska, I., 20, 96
Wagner, M.H., 59
Wafach, W., 32, 182
Waldman, W.R., 151
Walentowska, J., 158
Walsmsley, A., 57
Wang, C.-K., 22, 117
Wang, J., 16, 46
Wartig, K.-A., 90
Wesołek, D., 158
Wierzbicka, E., 16, 39, 118
Wójcik, R., 158
Worsley, M.A., 108
Yang, C., 95
Yang, Rongjie, 116, 146
Yang, Rui, 16, 47, 48
Yarahmadi, M., 99
Yee, M., 119
Yeh, J.-T., 117
Yona, A.M.C., 107
Yu, J., 48
Yu, W., 117
Žagar, E., 102
Zakowska, H., 172
Zaltariov, M.-F., 17, 53, 122
Zembovai, I., 92
Zeren, G., 43
Zhao, J., 16, 47, 48
Zielecka, M., 109
Zorlescu, B., 155
Zupančič, B., 58, 164
Notes
Notes