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EXPLORATORY RESEARCH PROJECT

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COMPLEX SYSTEMS BASED ON POLYMERS CONTAINING ALICYCLIC STRUCTURES FOR HIGH PERFORMANCE APPLICATIONS

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BRIEF REPORT

concerning the results obtained by the project team between
16 December 2013 – 15 December 2014

Objective 1. Copolyimides (CPIs) morphological modification into micro- and nano- porous particles to obtain materials for high performance applications

Associated Activities:

1.1 *CPIs micro- and nano-structured by suspension cross-linked copolymerization and the correct selection of porogen*

1.2

1.2. *Characterization of micro- and nano-structured CPIs: thermal stability (ATG, DSC), the specific surface area, the morphology (SEM, AFM, EDAX) and nanoparticle size.*

Objective 1. Copolyimides (CPIs) morphological modification into micro- and nano- porous particles to obtain materials for high performance applications

1.1 *CPIs micro- and nano-structured by suspension cross-linked copolymerization and the correct selection of porogen*

The using of a CPI in order to obtain cross-linked porous beads is not mentioned in the scientific literature. The approach proposed in this study is to obtain microspheres cross-linked polymer starts from a polymer chain with potentially reactive due in the C = C double bonds from the backbone.

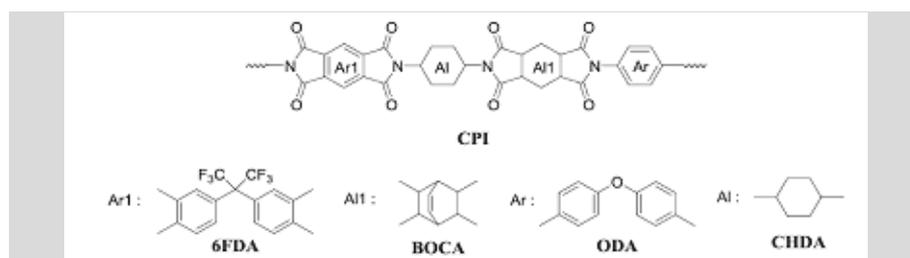
Synthesis and structural characterization of the copolymers

Table 1. Materials used in the copolymers synthesis

Chemical Name	Provider	Abbrev.	Purification method
<i>N</i> -methyl-2-pirolidone	Aldrich	NMP	Vacuum distillation at 10 mmHg, dried on CaH ₂ , stored on 4 Å molecular sieves
Bicyclo[2.2.2]-7-octene-2,3,5,6-tetracarboxylic dianhydride	Aldrich	BOCA	Recrystallization from acetic anhydride, vacuum dried at 160°C, p.t. = 248°C
4,4'-(Hexafluoroisopropylidene)-diphthalic anhydride	Aldrich	6FDA	Recrystallization from acetic anhydride, vacuum dried at 160°C, p.t. = 244°C
4,4'-oxydianiline	Aldrich	ODA	Recrystallization from ethanol; p.t. = 189°C
<i>trans</i> -1,4-cyclohexan-diamine	Aldrich	CHDA	Recrystallization from <i>n</i> -hexane; p.t. = 70°C
1,4-Dioxane	Aldrich	Dx	Used without purification
Benzyl alcohol	Aldrich	BzOH	Used without purification

Linear CPI was synthesized by a copolycondensation reaction of a mixture of dianhydrides (6FDA and BOCA) with two diamine (ODA and CHDA) in NMP under inert atmosphere. The process was carried out in two stages: *preparation of the precursor polymer poly(amic)acid, PAA*, (equimolar amounts of dianhydride / diamine) and *the polyimide* by thermal imidization of PAA to the CPI form.

CPI: Mn = 70000 g/mol. ; Ti > 400 °C; solubility: NMP, DMAc, DMF, DMSO at rt. , Dx at heating.



Scheme 1. Structure of the CPIs and the used monomers

The cross-linked (co) polymers in the form of "beads" were obtained by suspension radical copolymerization of the CPI with N, N'-4,4'-difenilmetanbismaleimida (BMI), used as cross-linker: * Several reports CPI / BMI (50/50, 60/40, 65/35, 70/30 and 75/25), * and * the same stabilizing conditions and two pairs of porogens: NMP / BzOH, and Dx / BzOH. Were used

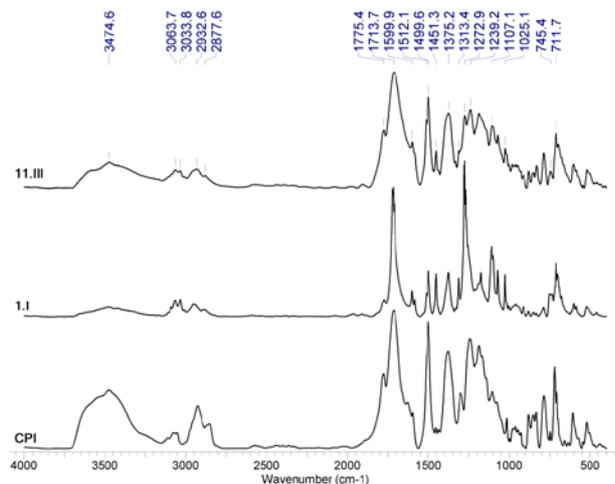


Fig.1. FTIR spectra for CPI and the samples 1.I & 11.III

IR spectra show characteristic absorption peaks for: the *imide structure* to approx. 1775cm^{-1} and 1713cm^{-1} (symmetric and asymmetric stretching vibration of C = O imide), approx. 1378cm^{-1} (stretching vibration of the imide ring C-N) and approx. 723cm^{-1} (imide ring deformation vibration); the *aromatic structure* at approx. 3063cm^{-1} and 3033cm^{-1} (= CH in the benzene ring); *aliphatic structure* to approx. $2925\text{-}2854\text{cm}^{-1}$ (aliphatic groups of BOCA sequences); C=C *double bond* from the aliphatic bicycle from BOCA, at about 711cm^{-1} ; ether bridges at about 1238cm^{-1} (- O-aromatic).

Factors affecting the suspension polymerization. Effect of agitation speed.

It is well recognized that the final particle size and particle size distribution are decisively impacted by the initial drop size distribution of the monomer/water dispersion and the controlled breakage/coalescence processes in the early stages of polymerization. In our experiments, a mechanical agitation was applied throughout the whole process to keep the monomer droplets well dispersed. The results showed that large particles are formed for agitation speeds between 200÷300 rpm and 900 rpm respectively, while at a moderate agitation speed of about 400 rpm, small particles are obtained. One possible explanation could be that at a low agitation speed there is an insufficient splitting of the initial monomer droplets, while at a high agitation speed there is a high probability that many collisions to finish in coalescence, because, the very small initial monomer droplets can be cluttered due to an inadequate stabilization. The results are in agreement with the literature data which report a U-shaped addition of the mean drop size on the agitation speed, typical for the complex nature of breakage/coalescence processes occurring in suspension systems. Figure 2 presents such situations where droplet collision and breakup cannot be prevented. It may also observe that, at different agitation speeds, particles of various sizes which are almost always polydisperse were obtained.

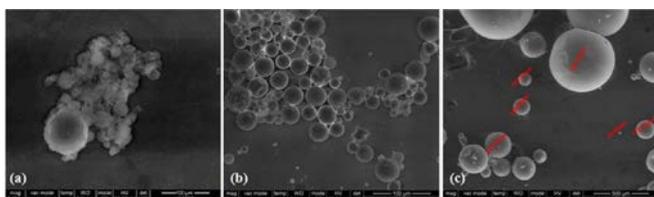


Fig. 2 Effect of the agitation speed on the particle size: a 210 rpm, b 420 rpm and c 900 rpm

Effect of the suspension stabilizer

The morphology of the resulting crosslinked (co) polymers is in a great extent determined by the type of the used suspending agent, since it protects the droplets against collision during polymerization. Throughout the whole process of suspension polymerization, the two phases organic and water, remain separated. The polymerization takes place in the suspended droplets that act like isolated micro reactors. As suspension stabilizer PVA with a hydrolysis degree of 98 and 88 mol %, respectively, were used. leaving 14,650 average degree of polymerization for the 98 % PVA and 50,000 or 88,000 average for the 88 % PVA grade.

The results revealed that PVA with the highest molecular weight and partially hydrolyzed ($M_w=88,000$, 88 %) is the best suspension agent, whereas PVA with the lowest molecular weight and the highest hydrolysis degree ($M_w=14,650$, 98 %) leads to unstable systems. Two issues should be mentioned (1) CPI -the linear copolyimide - has a pronounced hydrophobic character due to the non-polar alicyclic sequences and the 6 F bridges from the backbone structure, and (2) that PVA, due to its hydrophilic character, adjusts the polymer particles size by its positioning at the surface, outside of the resulting monomer droplets. By varying the hydrolysis degree one can alter the PVA hydrophobicity and by default, its conformation and surface activity at the monomer/water interface. A high hydrolysis degree increases the hydrophilic phenomenon so that, the PVA molecules do not adsorb strongly enough at monomer–water interface to form a coherent film and inhibit the coalescence of droplets. This explains the decrease of suspension stability and the increasing trend of the mean droplet size. By contrast, the moderately hydrolyzed PVA, with a more active surface at the droplet interface, enhances the system stability, and shifts the drop size to smaller values possibly due to a changed interfacial tension which affects the droplet breakage/ coalescence rates (Fig. 3).

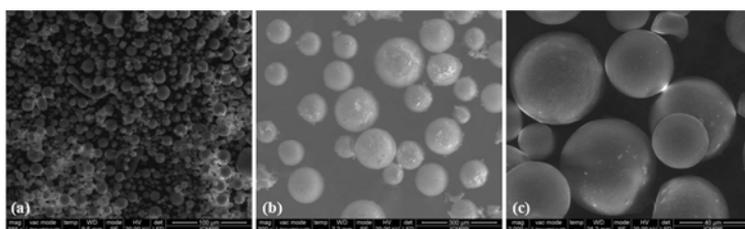


Figure 3. Effects of the PVA molecular weight and hydrolysis degree on the particle size.

The experiments showed that for an aqueous/organic phase ratio of 10/1 and an amount of poor solvent in the diluent mixture between 40÷50 wt.% regular spherical beads were obtained.

As a conclusion, even if the PVA species with low molecular weight are more active surface agents (being prone to a stronger action than the higher molecular weight ones) the hydrolysis degree seems to be the key factor for the adsorption balance of PVA at the monomer–water interface and, implicitly, for the stabilization of the discussed systems.

. A proportion of poor solvent outside this range resulted in agglomerated particles. Agglomerates were also formed at very low concentration of CaCl_2 (4 wt.%) in aqueous phase, while above this value a gradual decreasing in particle size was noticed. Minimum size values for a concentration of 12 wt.% were observed.

Factors influencing the morphology of the resulting polymer beads

Effect of diluents and crosslinker

Porous structures start to form when the amount of diluent and crosslinker pass a critical value. The resulting polymers morphology (studied on samples with mechanical strength, washed and dried), was investigated as a function of: *the pore-forming diluent quality (BzOH/NMP and BzOH/Dx) and *the crosslinking components molar ratio in the reaction mixture (CPI/BMI: 50/50, 60/40, 65/35, 70/30 and 75/25, respectively).

The ratio between diluent (D) and monomers (M) was constantly equal to 10:1 (ml/g). All the other parameters were kept unchanged. In suspension polymerization pores are formed in the presence of a suitable porogen (usually called diluent, inert medium, etc.), which causes phase separation during the polymerization process. The quality of the solvent used as porogen depends on the thermodynamic quality (affinity), expressed as the relationship between the solvent and solute (solubility parameter). The co-reactants quantity and the polymer solvent interaction in the reaction mixture, determine the porous network structure. The structure formation can be explained in terms of differences between the solvent and polymer interaction parameters. The Hildebrand solubility parameter theory proved in many cases, extremely useful in predicting the physical characteristics of the crosslinked polymers. Depending on the values of the solubility parameter (δ) for diluents and reaction components and according to this theory, BzOH can act as good solvent due to its almost similar thermodynamic properties as the crosslinked compounds, in contrast with the other two solvents, NMP and Dx, which behave as poor solvents. The results revealed that only the mixtures of those diluents containing BzOH ensure the porous polymeric beads formation with mechanical strength. Both, NMP and Dx respectively, used alone as pore-forming diluents, resulted in very incoherent pore structures caused by a much too earlier phase separation, while BzOH, used alone as porogen, led to porous networks without resistance (possible due to a large interconnected pores number). Figure 4 presents SEM images as detail for the internal structure of two fractured samples with the same chemical

composition, but synthesized using different porogen systems. It is noticed the porogen effect of a thermodynamically good solvent which allows to obtain fine-meshed network structures, with high surface area and small pore size (Fig. 4a), because the polymer remains fully solvated up to a high degree of conversion in the reaction system.

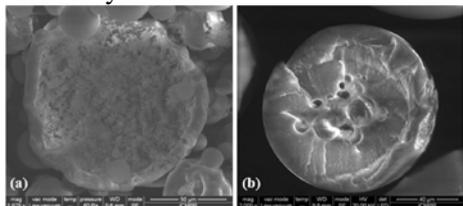


Figure 4. SEM of fractured beads samples containing 50 % BMI: (a) in BzOH/NMP: 60/40; (b) in BzOH/Dx: 60/40

Figure 4 b presents a more coarsely porous structure, with a small surface area and a large pore volume, which is in fact, the porogen effect of a poor solvent, reflecting the incompatibility between its molecules and the resulting polymer network segments.

1.2. Characterization of micro- and nano-structured CPIs: thermal stability (ATG, DSC), the specific surface area, the morphology (SEM, AFM, EDAX) and nanoparticle size.

In order to investigate the influence of variation of the parameter value δ on the morphology were synthesized three series of porous polymers using two pairs of diluants. There are obtained matrix with different morphological characteristics, by change the quality and the ratio of the components in the mixture of solvents (see Table 2 below).

Table 2. Recipe used in reaction systems to prepare the polymer samples

Sample's code	Series	BMI (%)					BzOH (X ₁)	NMP (X ₂)	Dx.(X ₂)	* $\delta_{mix.}$ (MPa ^{1/2})
		5	30	35	40	50				
I	1	2	3	4	5	0.6	0.4	-	23.45	
II	6	7	8	9	10	0.5	0.5	-	23.37	
III	11	12	13	14	15	0.6	-	0.4	22.64	

Particles size

Table 3 Effects of stabilizer and initiator on the yield and particle size of the cross-linked beads

Factor	Stabilizer ^{a)}			Initiator ^{b)}				
Quality	M _w PAV 14,650 50,000 88,000			BOP				
Quantity (%)	1.5 % PAV+12 % Ca Cl ₂			1.4	2	3	4	5
Yield (%)	66	73	78	52	57	64	69	73
*Particle size, μ m	5–60	35–500	20–200	30–700				

a) Polymerization system: crosslinker (BMI) 30 %, initiator (BOP) 5 %;

b) Polymerization system: crosslinker (BMI) 30 %, stabilization system (1.5%PAV+12%CaCl₂); PAV: Mw 50,000, 88 % hydrolysis degree

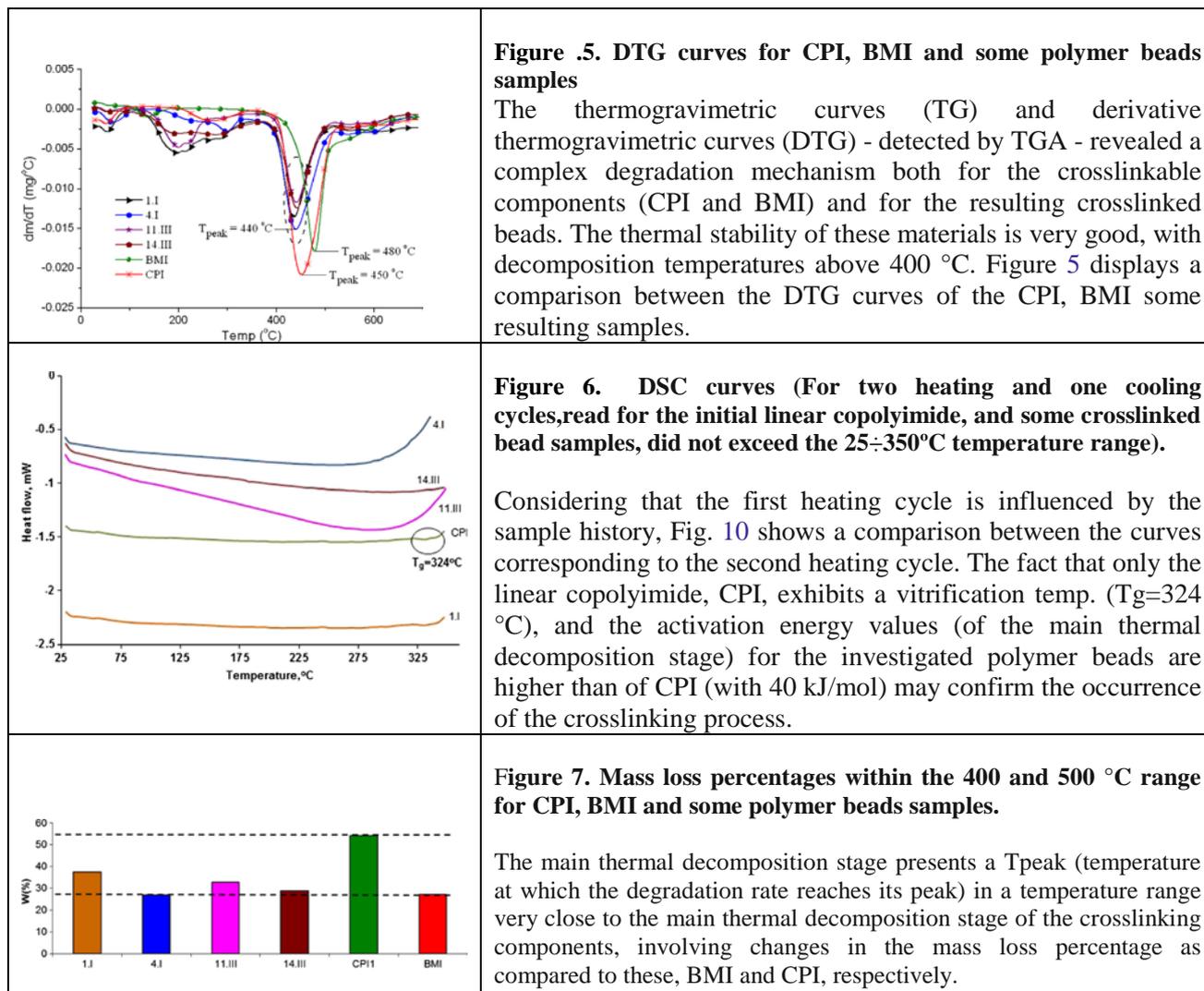
Considering the polyunsaturated nature of CPI and the steric accessibility of the double bonds into the macromolecular chain as compared with small molecules, a larger amount of benzoyl peroxide (BOP) was used comparatively with conventional free radical polymerization. This allowed better performances providing more reaction centers and by default, an increased polymerization rate.

All the reactions occurred in isothermal regime at 90°C for 20 h.

The temperature value was selected to assure a high decomposition rate of the initiator and also, a high solvating power of the diluents., affecting te particles size due to the increase of the polymerization rate.

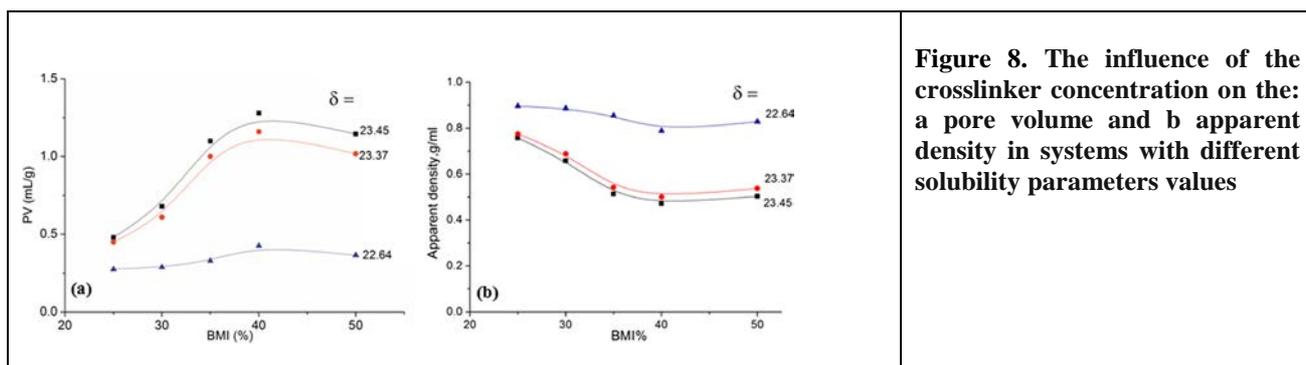
Thermal behavior

The thermal behavior of the synthesized crosslinked CPI/BMI microbeads was studied by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), in order to reveal the structural changes occurring in heating.



The resulting crosslinked (co) polymers exhibit different morphologies according to porogens used (implicitly its solvating power) and the crosslinked content used in the reaction mixture. Considering the solubility parameter δ as basic factor in the formation of porous morphology, the graphics representation of experimental results for different degrees of crosslinking shows dependence of these synthesized parameters and morphological characteristics of the obtained polymers.

Specific surface area and average pore size



The variation of specific surface area for the same degree of crosslinking indicates maximum values of (co) polymers in the series I, system with the best solubility parameter value. At various crosslinker concentrations and the same degree of the monomer dilution and diluent quality, the experimental data showed that the pore volume and the specific surface area increase with raising the BMI amount to a certain threshold, of about 40 % (after these this characteristics decrease).

The average pore size changes from small pores to large pores as show the curves shape from Fig. 9 a, b.

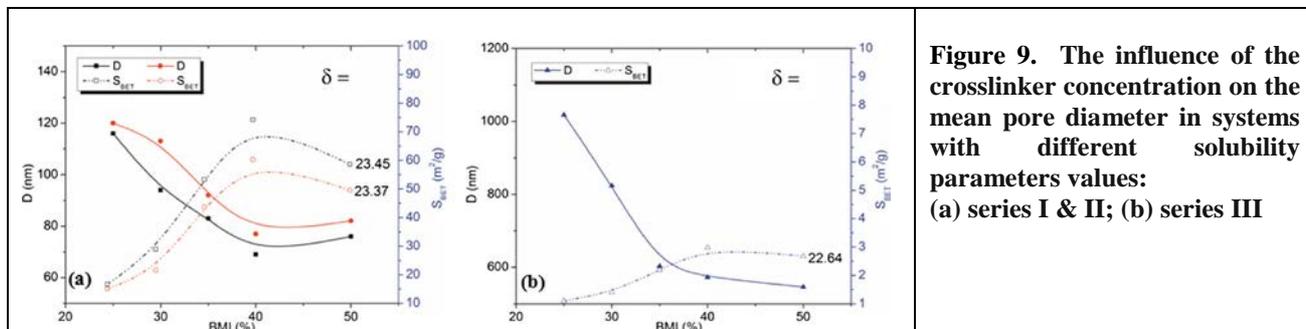


Figure 9. The influence of the crosslinker concentration on the mean pore diameter in systems with different solubility parameters values: (a) series I & II; (b) series III

The apparent density decreases simultaneously up to the same BMI concentration (Fig. 8). The results are consistent with the literature data which confirm such a threshold related to the solvent and crosslinker content in macroporous structures synthesis.

Morphological investigation (SEM, AFM, EDAX)

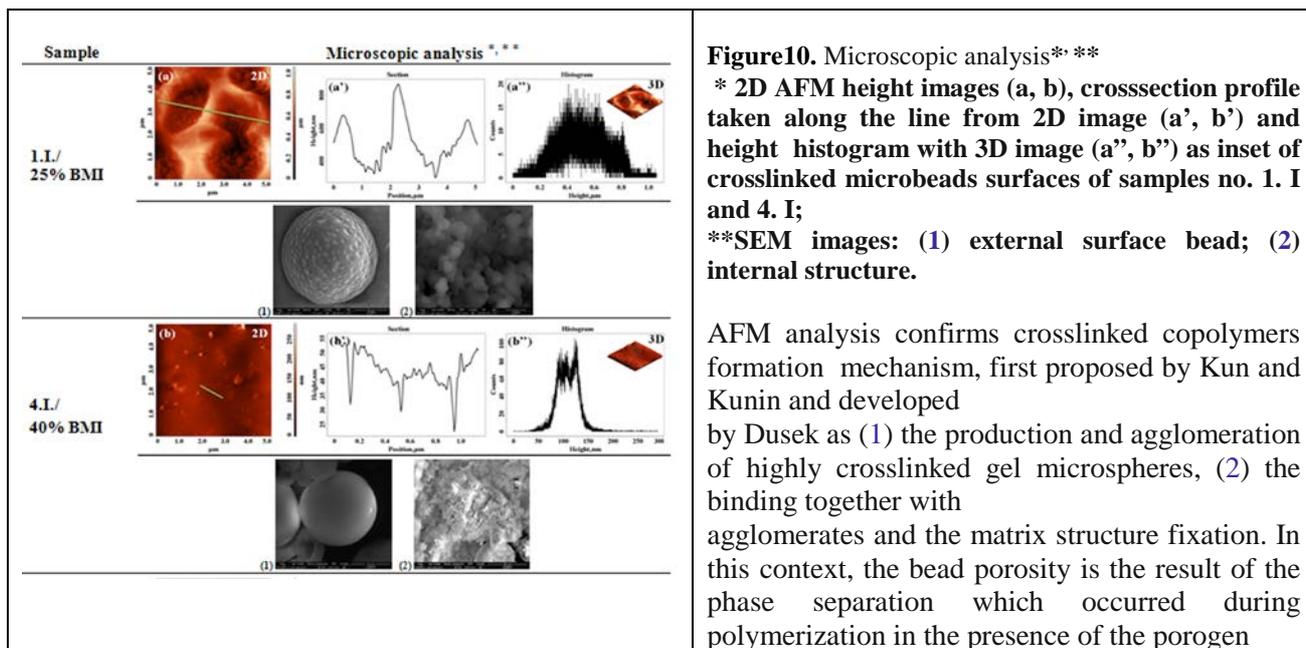


Figure 10. Microscopic analysis***

* 2D AFM height images (a, b), crosssection profile taken along the line from 2D image (a', b') and height histogram with 3D image (a'', b'') as inset of crosslinked microbeads surfaces of samples no. 1. I and 4. I;

**SEM images: (1) external surface bead; (2) internal structure.

AFM analysis confirms crosslinked copolymers formation mechanism, first proposed by Kun and Kunin and developed by Dusek as (1) the production and agglomeration of highly crosslinked gel microspheres, (2) the binding together with agglomerates and the matrix structure fixation. In this context, the bead porosity is the result of the phase separation which occurred during polymerization in the presence of the porogen

Morphological changes of microbeads were evidenced by AFM and SEM. AFM images were processed correction plan to get better accuracy. For a fair comparison of the surface roughness, the roughness parameter was determined as the ratio of actual surface area and geometric surface area. SEM. Analyzing the results, we see very clearly porous structures of these materials.

Conclusion. This research opens perspectives for studies on chemical modification of the surface area of the microparticles (internal and external surface) so that a large number of imide groups are active clamping and become places for different functional molecules.

All objectives were fully realized in this stage and some results were included into manuscripts submitted to publication.

Results dissemination

- 1 papers published in journal indexed by web of knowledge.
- The team members participated at 4 scientific events with 2 oral presentations and 6 posters.

- A patent application has been submitted.

Original articles published in journals with impact factor

New polyimide-based porous crosslinked beads by suspension polymerization: physical and chemical factors affecting their morphology; C. Hulubei, C D Vlad, I Stoica, D Popovici, G Lisa, S L Nica, I A Barzic, *J Polym Res*, 21(9), 2014, DOI:10.1007/s10965-014-0514-4

Scientific meetings

Conferences, communications:

New materials based on polyimides containing alicyclic units; C.Hulubei, D.Popovici, C. D. Vlad,I. Stoica, M. Bruma, S. Ioan; *THE 2nd CEEP WORKSHOP ON POLYMER SCIENCE* : Iasi, , ICMPP; 24-25.10.

2014:<http://www.icmpp.ro/events/conferences/ps2014.html>

Biomaterials based on partial cycloaliphatic polyimides with enhanced antimicrobial properties; D Popovici, C Hulubei, M Aflori, S Ioan, D S Vasilescu, S Dunca; Conferinta Nationala de Chimie, Calimanesti Caciulata 01 – 03.10 2014

Posters

Morphological surface features impact on cytocompatibility of an epiclone-based polyimide film; I Stoica, A I Barzic, M Butnaru, C Hulubei; 6th International Conference “Biomaterials, Tissue Engineering & Medical Devices” BiomMedD’2014, on September 17-20, 2014.

Structural, magnetic, electrical and humidity sensing characteristics of polyimide/iron oxide composites; S L Nica, V Nica, D Popovici, C V Grigoraş, C D Varganici, C Hulubei, S Ioan; Conferinta Nationala de Chimie, Calimanesti Caciulata 01 – 03.10 2014

Improve the antimicrobial activity of partially cycloaliphatic co-polyimide films by plasma treatment; D Popovici, C Hulubei, A I Barzic, S Ioan, D S Vasilescu, S Dunca; *THE 2nd CEEP WORKSHOP ON POLYMER SCIENCE* : Iasi, ICMPP;

24-25.10.2014 :<http://www.icmpp.ro/events/conferences/ps2014.html>

Thermal behavior of semiaromatic polyimides; C D Varganici, D Rosu, C Barbu–Mic, L Rosu, D Popovici, C Hulubei, B C Simionescu; *THE 2nd CEEP WORKSHOP ON POLYMER SCIENCE* : Iasi, ICMPP; 24-25.10.2014:

The synthesis and characterization of hybrid organic/inorganic composites polyimide/iron oxide (Fe₃O₄/γ-Fe₂O₃); S L Nica, V. Nica, C Hulubei, S Ioan; Innovative Materials and Processes 2nd International Conference on Chemical Engineering, România, Iaşi, 05-08 November 2014

Porous microspheres and transparent materials based on partially alicyclic copolyimides; C Hulubei, C D Vlad, I Stoica, D Popovici, G Lisa, S L Nica, A I Barzic, S Ioan; Innovative Materials and Processes 2nd International Conference on Chemical Engineering, România, Iaşi, 05-08 November 2014

<http://www.icmpp.ro/events/conferences/ps2014.html>

PATENT (Brevet OSIM): Procedeu de sinteză a unor materiale poliimidice transparente și flexibile; C Hulubei, D Popovici, M Bruma. Cerere de Brevet Nr. A/00864/17.11.2014

Director proiect,

