

Scientific report

Regarding the project implementation in the period January – December 2012

Project title: **“Advanced researches related to the behavior of multicomponent polymer systems under simulated environmental factors action”**

Objectives:

1. Obtainment of multicomponent polymer systems
2. Characterization of resulted polymer systems and investigation upon structure-properties relationships
3. Dissemination of results
4. Re-actualization and consolidation of managerial and administrative plan

Introduction

Multicomponent polymer systems based on epoxy resins and polyurethanes as films present the best properties by comparison with those showed by other organic coatings and have some practical applications because polyurethanes have remarkable properties related to elasticity, resistance to abrasion and performance in harsh environments, while epoxy resins exhibit good adhesion to metals and high mechanical resistance.

Reactive dyes have applications mainly for cellulosic materials painting, providing above 10% from total dyes amount used for such purposes. The efficiency of dyes fixation represents an evidence of reaction occurred between dyes and cellulosic fibre. The dye's reactivity is an essential feature on which depend to a large extent the working parameters during painting.

Specific applications (biomedical, pharmaceutical, cosmetical) require use of multicomponent polymer systems which are usually obtained through combination of natural polymers properties with those of synthetic ones. In this context, functionality of hydrogels based on poly(vinyl alcohol) (PVA) may be improved through addition of cyclic oligosaccharides such as cyclodextrins (β -CD).

Double sensitive polymer structures constitute basis for obtainment of some materials having controlled properties and suitable for applications in medical and pharmaceutical fields. In this context, we report use of collagen and poly(N-isopropyl acrylamide) as sensitive polymers to environmental changes. Due to their three-dimensional structure conferred by cross-linked polymer network, good absorption capacity, efficient ability to transport and release therapeutic agents, alongside other biological and physico-chemical properties, these polymer substrates are suitable as bio-precursors for materials envisaging tissue engineering applications.

Wood represents a multi-component polymer system, with many potential applications, being regenerable, biodegradable and susceptible to structural modifications. It is very well known that solar radiation (mainly UV ones) and water have harmful effects on wood surfaces under outdoor environmental exposure conditions. For a good protection of wood substrates, there may be applied effective methods such as: 1) surfaces coating and/or 2) chemical treatment. Coating may constitute an efficient physical barrier which protects wood substrate against harmful effects of environmental factors.

1. Obtainment of multicomponent polymer systems

1.1. Semi-interpenetrated polymer networks (SIPN) based on polyurethane (PU) and epoxy resin (ER) were synthesized. PU elastomer was obtained by using 4,4'-diphenyl-methane diisocyanate and poly(ethylene adipate)diol. Epoxy resin (namely Ropoxid 501) was resulted by reaction between 4,4'-isopropylidenediphenol with epichlorhidrin. There were synthesized 6 types of SIPNs through variation of the above-mentioned two polymer components ratio.

1.2. It was performed a study related to the optimal methods in order to achieve a good fixation of some reactive dyes upon polymer substrates based on cellulosic fibres (100% cotton fabric). Thus, were investigated 5 types of reactive dyes, which were applied on polymer substrates by fleet depletion technique. The fixation capacity of reactive dyes decreased following the order: Yellow 143 reactive dye > Red 2 reactive dye > Red 183 reactive dye > Blue 204 reactive dye > Orange 13 reactive dye. The fixation degree (% covalent attached dye on substrate) increased with increasing initial dye concentration, reported to weight of painted fabric samples.

1.3. Multicomponent polymer systems under membrane form were obtained by using poly(vinyl alcohol) (PVA) and β -cyclodextrins (β -CD), in the presence of glutaraldehyde as cross-linking agent. There were resulted 4 types of polymer membranes through variation of PVA/ β -CD ratio.

1.4. A new type of hydrogel based on poly(N-isopropyl acrylamide-co-diethylene glycol diacrylate) inserted into a porous membrane of collagen. Polymer networks were obtained through radical copolymerization reaction between poly(N-isopropyl acrylamide) (pNIPAM) and three different cross-linking agents in the presence of a protein based matrix. The cross-linking agents used in reaction are as follows: diethylene glycol diacrylate (DEGDA), tetraethylene glycol diacrylate (TEGDA) and N,N'-methylene-bis-acrylamide (BisAam), respectively. The resulted polymer networks were coded as ND, NT, and NB, respectively, as a function of the cross-linking agent used in reaction.

1.5. Softwood samples were chemically pre-treated with succinic anhydride (SA). The modified wood samples were further treated with epoxy functionalized soybean oil (ESO) (obtained in laboratory by peracid process) in the

presence of triethylamine (TEA) as catalyst. Studies regarding wood behavior under polychromatic light action (UV radiation with $\lambda > 300$ nm) after chemical pre-treatment of wood with SA and further treatment with ESO under controlled accelerated ageing processes are under progress.

2. Characterization of resulted polymer systems and investigation upon structure-properties relationships

2.1. There were synthesized 6 types of SIPNs with composition presented in Table 1, the schematic representation being showed in Fig. 1. Structural characterization was performed by means of FTIR spectroscopy (Fig.2). The absorption band at 3324 cm^{-1} (Fig. 2c) is specific to O-H group vibration in ER and to N-H group vibration from PU.

Table 1. Composition of synthesized SIPN

Sample	PU (%)	Epoxy resin (ER) (%)
SIPN-1	95	5
SIPN-2	90	10
SIPN-3	85	15
SIPN-4	80	20
SIPN-5	70	30
SIPN-6	60	40

Fig. 1 Structure of SIPN: (a) PU; (b) ER

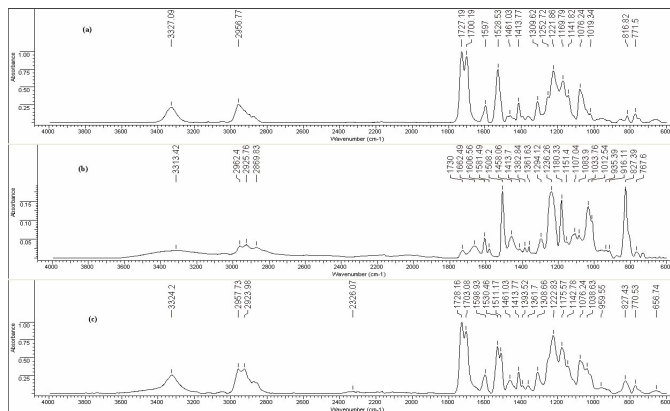


Fig. 2. FTIR spectra for: PU (a); ER (b) and SIPN-3 (c)

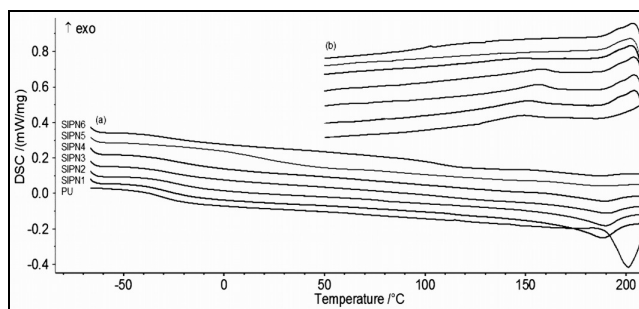


Fig. 3. DSC curves for SIPNs and initial polymers: heating (a) and cooling (b)

The glass transition temperature values (T_g) for synthesized SIPNs based on PU and ER were determined by dynamic differential calorimetry method (DSC) – Fig. 3. It was investigated the influence of ER content upon T_g values. There were initiated miscibility studies by applying Fox and Gordon-Taylor equations. Morphology studies were performed by using electron microscopy (SEM) and optical microscopy (OM) methods.

2.2. An evaluation study and quantitative analysis for 5 reactive dyes were performed by using UV-Vis spectrophotometry method, following the maxima absorption values for validation of analytical methods to be further applied for characterization (Fig.4).

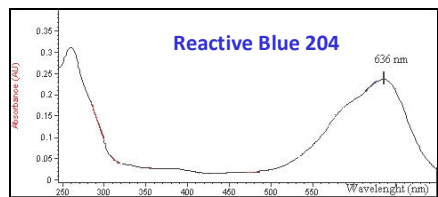
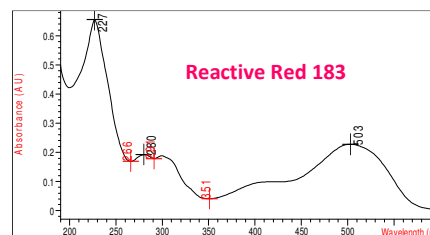
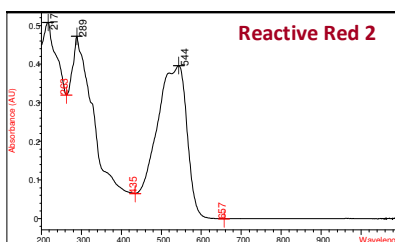
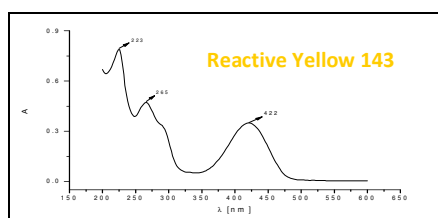
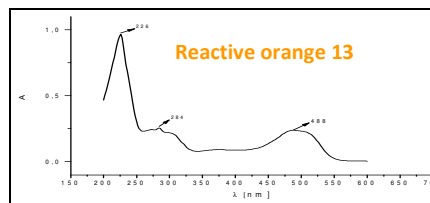


Fig.4. UV-Vis absorption spectra for reactive dyes

The maximum absorption (λ_{max}) in visible domain for reactive dyes are as follows: 422 nm (Yellow 143 reactive dye); 544nm (Red 2 reactive dye); 503 nm (Red 183 reactive dye); 636 nm (Blue 204 reactive dye); 488 nm (Orange 13 reactive dye).

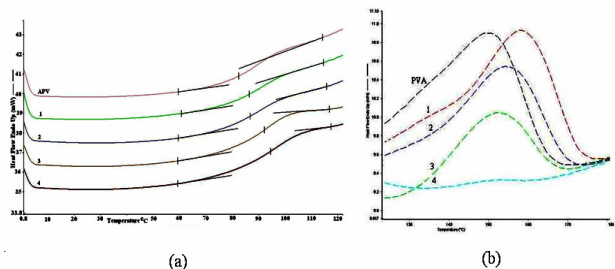


The resulted preliminary data are important for evaluation of biological impact exerted by dyes upon human organism under action of UV radiation from solar light spectrum with occurrence of photo-chemical transformations.

2.3. The effect of β -CD on the thermal stability of PVA based membranes, previously chemically cross-linked in the presence of glutaraldehyde used as cross-linking agent, was investigated. The DSC thermograms recorded for chemically cross-linked PVA/ β -CD membranes are presented in Fig. 5.

Fig. 5. DSC thermograms for PVA and PVA/ β -CD chemically cross-linked membranes:

(a) 0-120 °C, (b) 125-180 °C



It can be noticed an increase of glass transition temperature T_g with increasing β -CD amount in samples. The melting temperature value exhibits the same tendency as T_g . This evolution is due to interactions occurred between the two components of the blend.

The swelling behavior investigation was performed at two different temperature values using bidistilled water, the curves being presented in Fig. 6.

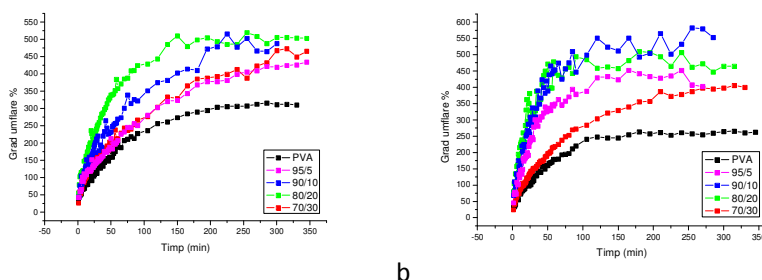


Fig.6. Swelling degree for PVA/ β -CD membranes: (a) at 25 °C, (b) at 37 °C

The swelling process is slightly influenced by temperature, a significant decrease of swelling degree being noticed at 37°C for membrane comprising 30% β -CD.

An increase of swelling degree with increasing β -CD content up to 20% is observed, while it decreases for membrane with 30% β -CD, probably due to a phase separation occurring at a high concentration value of β -CD.

2.4. Investigation of polymer structures was performed by spectral, morphological, thermal (calorimetry) rheological analyses, as well as by determination of water uptake evolution using simulated biological media.

The cross-linking reaction occurred between pNIPAM and DEGDA was confirmed by appearance of a new absorption band at 1731 cm^{-1} , attributed to the C=O group from the structure of cross-linking agent (Fig. 7).

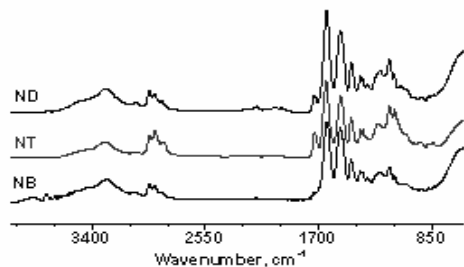


Fig. 7. FTIR spectra for cross-linked polymer networks

FTIR spectra recorded for hydrogels based on collagen and pNIPAM after cross-linking using different cross-linking agents present absorption bands at 2855 , 1366 and 838 cm^{-1} , respectively. FTIR spectrum for NB polymer network type present absorption bands at $3645 - 3839$, 2361 and 1338 cm^{-1} , respectively.

Fig. 8 present the SEM micrographs recorded for the transversal sections of cross-linked polymer networks based on pNIPAM and collagen. The observed morphological differences due to the cross-linking agents are obvious. The SEM images show clearly the collagen fibres embedding within the polymer networks.

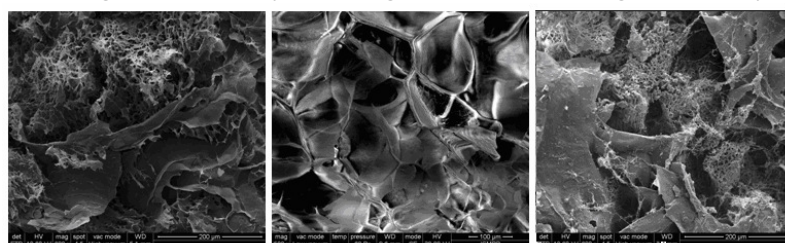


Fig.8. SEM images for polymer networks

The average pores dimension, randomly measured for 12 pores within the polymer networks, indicates a value of $3 \div 6\ \mu\text{m}$ for ND hydrogels, $10 \div 15\ \mu\text{m}$ for NT hydrogels, and $2 \div 4\ \mu\text{m}$ for NB hydrogels, respectively.

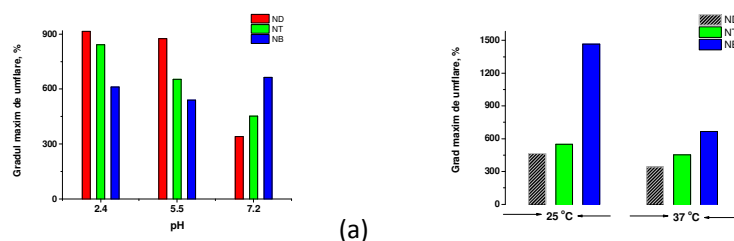


Fig. 9. Swelling degree of polymer networks at equilibrium state: (a) influence of pH and (b) influence of temperature

The hydrogels swelling occurs rapidly in the first 10 min., then the swelling degree remains approximately constant.

The NT hydrogels present an uniform structure and a good pores dispersion with very-well individualized walls, while the ND polymer networks exhibit an adequate embedding of collagen fibers within the pNIPAM polymer matrix. The NB hydrogels have a similar morphology with that of ND polymer networks, excepting the pores dimension which is

smaller and a weak embedding of the two polymers. The presence of some supplementary functional groups (isopropyl, NH_2 , CO) influences directly the swelling capacity due to the degree of ionization as a function of solution pH (Fig. 9). The polymer networks present a pseudo-plastic behavior (Fig. 10 a-c), evidenced by viscosity decreasing with strain increasing.

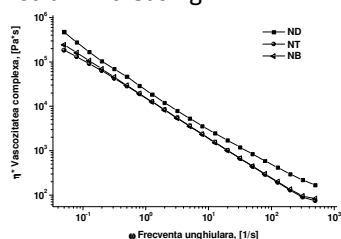


Fig. 10a. Complex viscosity behavior

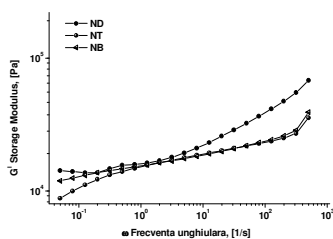


Fig. 10b. Storage modulus evolution

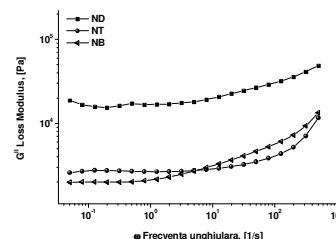


Fig. 10c. Loss modulus evolution

The mechanical properties of hydrogels were described considering both the storage modulus (G') and the loss modulus (G''). The polymer networks exhibit a viscous behavior at lower strain values and an elastic behavior at high strain values. The complex viscosity of hydrogels depends on the composition of each hydrogel type, the polymer structure, and the structural changes occurred during synthesis, respectively.

2.5. The chemical pre-treatment of wood was performed using a solution of succinic anhydride SA at 100°C , under continuous stirring (200 rpm) for 1h. There were applied 3 values of concentration as follows: 60%, 80%, and 120% (w/w), respectively. After chemical modification reaction, wood samples coded as MW(60), MW(80) and MW(120), were kept at room temperature. Further, wood samples were immersed in ESO in the presence of 5% TEA at 100°C for 1h. There were considered 40 wood samples as follows: 10 non-treated samples coded as R (control), and 10 wood samples treated with SA and coated with ESO, for each SA concentration value, coded as MW(60)CESO, MW(80)CESO and MW(120)CESO, respectively. Structural changes were evidenced by FTIR spectroscopy method. Thermal behavior of wood samples was investigated by thermal analysis (TG-DTG). After chemical reaction of wood with SA, the weight percent gain value (WPG) increased from approx. 11% up to 39%, depending on the SA concentration. The WPG values calculated for wood samples after pre-treatment with SA and coating with ESO varied from 3.25% to 4.74% (Table 2).

Table 2. WPG evolution (%) for softwood samples after chemical pre-treatment and coating

Sample	R	MW(60)CESO	MW(80)CESO	MW(120)CESO
wood treated with SA	0	10.93	21.83	39.45
wood treated with SA, coated with ESO	4.74	4.53	3.56	3.25

Fig. 11 show the FTIR spectra recorded for initial wood samples (A), wood samples modified with SA (B) and wood samples modified with SA and coated with ESO (C). The spectrum A presents absorption bands specific to wood: 3330 cm^{-1} (attributed to the $-\text{OH}$ groups valence vibrations), 2890 and 2918 cm^{-1} (characteristic to C-H from CH_3 and CH_2 groups), between 1800 and 1100 cm^{-1} (attributed to the main polymer components from wood structure). In spectrum B, the intensity of absorption band from 3330 cm^{-1} decreases and shifts to lower wavenumber values, evidencing a lower amount of OH groups in wood structure after chemical reaction with SA. The band from 1736 cm^{-1} , attributed to the carbonyl groups $\text{C}=\text{O}$, significantly increases as intensity. All these spectral changes evidence the occurrence of the chemical reaction between wood and SA. In spectrum C, the signals from 2918 , 2890 and 1736 cm^{-1} , respectively, increase as intensity due the reaction occurred between succinic monoester and ESO.

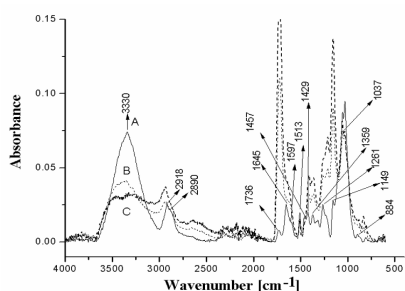


Fig. 11. FTIR spectra for non-treated wood (A), wood treated with SA (B) and wood treated with SA and coated with ESO (C)

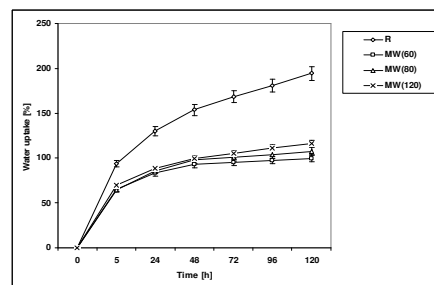


Fig. 12. Water absorption evolution for non-treated wood (R) and wood treated with SA (MW)

The chemical pre-treatment of wood can reduce its hydrophilic properties. A significant decrease of water absorption is noticed (Fig. 12) when hydrophilic OH groups are substituted with hydrophobic succinyl groups by increasing SA concentration in reaction medium. Thermal analysis evidenced that chemical pre-treatment of wood with SA influence its thermal stability, wood becoming more susceptible to degradation as a function of SA

concentration value. Wood properties under environmental factors action (humidity, UV radiation) can be improved by chemical modification and coating with ESO (on-going study).

3. Dissemination of results

There were elaborated and presented 11 oral papers and 16 posters at:

- national scientific symposia: 21st *Symposium on Thermal Analysis and Calorimetry*, Feb. 17, 2012, Bucuresti; *Seminary "Thermal analysis: Characterization of materials by using thermal analysis techniques"*, May 24, 2012 Iasi (organized in cooperation with Netzsch Company); *National Conference on Chemistry Valcea*, Oct. 3–5, 2012

- international scientific symposia: *Fifth Cristofor I. Simionescu Symposium "Frontiers in Macromolecular and Supramolecular Science"*, June 11–13, 2012, Bucuresti; COFrRoCA – 2012, Septième Colloque Franco-Roumain de Chimie Appliquée, 27–29 Juin 2012, Bacau; 7th MoDeSt Conference, 2-6 Sept., 2012, Prague, Czech Republic; 15th *International Conference Polymeric Materials*, Halle, Germany, Sept. 12-14, 2012; 4th *Bilateral Symposium on Functional Heterocyclic and Heterochain Polymers for Advanced Materials*, Iasi; 2^{eme} *Colloque Franco-Roumain de Chimie Medicinale, CoFrRoCM 2012*, Iasi, Romania. The detailed informations are presented on the project's web page mentioned below.

Considering the obtained results, there were published and submitted for publication the following scientific papers:

1. C.-D. Varganici, A. Durdureanu-Angheluta, D. Rosu, M. Pinteala, B.C. Simionescu; Thermal degradation of magnetite nanoparticles with hydrophilic shell; *J. Anal. Appl. Pyrol.* **96**, 63–68 (2012) (IF: 2.487)
2. D. Rosu, L. Rosu, F. Mustata, C.-D. Varganici; Effect of UV radiation on some semi-interpenetrating polymer networks based on polyurethane and epoxy resin; *Polym. Degrad. Stab.* **97**, 1261–1269 (2012) (IF: 2.769)
3. O.M. Paduraru, D. Ciolacu, R.N. Darie, C. Vasile; Synthesis and characterization of polyvinyl alcohol/cellulose cryogels and their testing as carriers for a bioactive component; *Materials Science and Engineering C.* **32**, 2508–2515 (2012) (IF: 2.686)
4. C.-D. Varganici, O. Ursache, C. Gaina, V. Gaina, B.C. Simionescu; Studies on new hybrid materials prepared by both Diels-Alder and Michael addition reactions; *J Therm Anal Calorim.* **2012**, <http://dx.doi.org/10.1007/s10973-012-2532-y> (IF: 1.604)
5. S.F. Patachia, M.-T. Nistor, C. Vasile; Thermal behavior of some wood species treated with ionic liquid; *Industrial Crops and Products*, Available online 29 October 2012, <http://dx.doi.org/10.1016/j.indcrop.2012.10.003> (IF: 2.469)
6. D. Rosu, L. Rosu, C.-D. Varganici; The thermal stability of some semi-interpenetrated polymer networks based on epoxy resin and aromatic polyurethane; *J. Anal. Appl. Pyrol.* **2012**, <http://dx.doi.org/10.1016/j.jaap.2012.12.003> (IF: 2.487)
7. C.-A. Teaca, D. Rosu, R. Bodirlau, L. Rosu; Structural changes in wood under artificial UV light irradiation determined by FTIR spectroscopy and color measurements –a brief review; *BioResources*, **2012**, *submission needing revision 1* (IF: 1.328)
8. O. Ursache, C.Gaina, V.Gaina, C.-D.Varganici; New hybrid materials obtained by Diels-Alder and Michael addition reactions. A comparative study; *Polym. Bull.*, **2012**, *submitted* (IF: 1.532)
9. M.-T. Nistor, C. Vasile; TG/FTIR/MS study on the influence of nanoparticles content on the thermal decomposition of the starch/poly(vinyl alcohol) montmorillonite nanocomposites; *Iranian Polymer Journal*, **2012**, *submitted* (IF: 0.936)
10. C.-D. Varganici, L. Rosu, D. Rosu, B.C. Simionescu; Miscibility studies of some semi-interpenetrating polymer networks based on an aromatic polyurethane and epoxy resin; *Composites Part B*, **2012**, *submitted* (IF: 1.731)

It was elaborated the project's web page: <http://www.icmpp.ro/mcps/ro/>

4. Re-actualization and consolidation of managerial and administrative plan

The research team involved in the project has performed the following activities:

- monthly working meetings with research team members;
- advisory activities performed by senior researchers for training PhD students ;
- establishment of panels by senior researchers for solving scientific issues;
- writing and submission of scientific articles for publication in ISI journals;
- establishment and providing the materials' supply for development of research program;
- planning the human, material and financial resources for the next stage;
- planning of acquisition activity, elaboration of documentation for acquisitions;
- following the supply chain and the mode of implementation project's funds;
- elaboration of the stage report (scientific, financial).

In order to develop and implement the management structure, the research team members have established monthly meetings for elaborating the detailed activities plan. It was envisaged an efficient and operational communication of administrative, technical and financial issues both within the research team, and with the contracting authority. All research team was involved in elaboration of the stage report. It was completed the documentation necessary for independent audit report related to financial statements 2011-2012.

The research team has fulfilled the proposed objectives with a full degree of implementation.

Director proiect,
Dr. Dan Rosu

