

Synthetic scientific report

Regarding the project implementation in the period *october 2011 – december 2013*

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

The aging of polymer systems involves different factors: natural (light, heat, humidity), structural and accidental (impurities, oxidation processes occurred during processing), all these being capable to significantly reduce the life-time of materials. The mechanisms of polymers degradation are highly complex.

Thus, there can be initiated photo-cross-linking or photo-oxidative reactions of polymers accompanied by decrease in average degree polymerization, increase of polydispersity and formation of chemical structures capable to modify the properties of polymers.

The present project envisages increasing knowledge in the investigation upon effect of external factors on stability of multi-component polymer systems. It is aimed to create a research team comprising 4 experienced researchers and 3 doctoral students focused to acquire experimental data and to elaborate original theories in order to explain the performance loss of polymer systems during exposure to controlled environmental factors, and to evaluate their life-time prediction.

It is considered that valuable scientific results will be provided, being comparable with those already existing at global level, and will contribute to increasing international visibility of Romanian research activity. The envisaged results will contribute to the finalization of doctoral theses to be realized by the young doctoral students included in the research team.

The present research project is focused on the transformations of polymers with different structures under weathering conditions and especially solar light.

The following objectives were taken into consideration:

- Immobilization of dyes of different structures and concentrations onto natural and/or synthetic polymers
- Obtainment of multi-component systems containing polysaccharides
- Obtainment of semi-interpenetrating networks based on collagen or polyaspartic acid
- Study of the influence of controlled environmental factors upon polymer systems colored with dyes (solar light, heat, humidity)
- Study of the stability of the multi-component systems to weathering conditions

Stage 2011

Objectives:

1. Comparative analysis of the current status on the behavior of polymers under environmental factors;
2. Documentation in modern instrumental techniques and methods;
3. The implementation of a management and administrative plan

Aging is a generic name used to define the slow degradation of various polymeric materials exposed to environmental factors. The mechanism of the degradation process depends on the type of material, but is usually caused by a synergistic combination of natural factors including moisture, sunlight, heating/cooling, chemical agents, biological agents and abrasion by wind exposure

Primary photochemical reactions occur as a result of the activation of macromolecules by direct absorption of light radiation. In an inert atmosphere of nitrogen or argon degradative reactions occur, including splitting of macromolecules and crosslinking, while in the presence of air, oxygen is able to initiate photo-oxidative processes. Photo-oxidative degradation processes of polymers take place by radical intermediates, carried every time by following the steps of a chained mechanism.

The current trend of obtaining multicomponent systems has led to the synthesis and study of some semi-interpenetrated polymer networks based on natural polymer/synthetic polymer with collagen, sensitive to changes in environmental conditions. Such polymeric networks may be obtained by using polymers or monomers sensitive to changes in external parameters, such as temperature, pH, chemical composition of solvent, presence of electric field or of light, with reversible swelling modifications or changes in the chains conformation. In terms of applicability, the semi-interpenetrated networks may be used in various fields, such as pharmaceutical, regenerative medicine, agriculture and wastewater purification or obtaining of sensors.

In recent decades aging studies of polymeric materials have shifted the interest from simple monitoring of properties changes, occurred due to the influence of environmental factors, to structural investigations by using modern techniques such as: Fourier transform infrared spectroscopy (FTIR), mass spectrometry (MS), nuclear magnetic resonance ($^1\text{H-NMR}$), optical and electronical microscopy and atomic force microscopy (AFM) with which

the mechanisms of the degradative reactions are identified. Sophisticated mathematical methods may also be applied in providing the possibility of predicting materials lifetime, the design of new materials, sustainable, and predetermined lifetime intended for specific operating conditions with reduced negative impact on the environment. Analysis of chemical modification of polymeric materials occurred during natural or accelerated aging is not standardized, as is the case of the physico-mechanical properties. FTIR method allows detailed spectral analysis, both qualitative and quantitative. FTIR spectra are frequently used for monitoring photo-chemical and photo-oxidative degradation processes that take place in polymeric materials. The use of FTIR spectroscopy shows major advantages over other methods of investigation. In this case, samples prepared in the form of films or pills may be used by other analysis and investigations (such as Raman spectroscopy etc.). FTIR technique can be extended to the study of photochemical processes occurring on the surface of samples by introducing a cell with attenuated total reflection. With this cell, IR radiation penetrates only 20 μm in depth and sample characterization is made with a high resolution. The IR spectra recorded with a FTIR device equipped with a cell of attenuated total reflection (ATR) have identified functional groups found in very small quantities localized on the samples surface. Photo-oxidative processes of the polymers are limited to surface layers due to the diffusion effect of oxygen and the low penetrability of UV radiation in the material. The specific regions of carbonyl or hydroxyl groups from FTIR or ATR-FTIR spectra provide important information on the photo-oxidative degradation of the studied materials. There exists the possibility to compare signal intensities from these regions with signal intensities specific to other groups (such as: vinyl groups, amide groups, aromatic structures) or other chemical functions which may be associated with products of oxidation reactions.

The elevated temperatures are commonly used to accelerate the aging processes in polymeric materials. Thermogravimetric analysis (TG) studies the mass changes of a polymer as a function of temperature. The following important data may be obtained: T_{onset} (defined as the lowest temperature at which mass loss is identified), T_{max} (the temperature at which decomposition reactions occur with maximum speed) or T_{final} (the temperature at which the thermal degradation process ends). On a thermogram there may be identified one or more T_{max} values, depending on the number of stages of thermal decomposition. T_{max} values are identified with the derivative curve (DTG). The final temperature of thermal decomposition (T_{end}) may be appreciated as the lowest temperature value at which a significant mass loss is not recorded during heating. By applying of simultaneous thermogravimetric analysis (TG) coupled with differential scanning calorimetry (DSC) high precision information may be obtained when compared with the situation in which the results derive from thermograms recorded with different devices. Differential thermal analysis (DTA) is a thermo-analytical technique somewhat similar to DSC. TG-DTA coupled technique allows identification of processes accompanying thermal degradation, unlike the TG-DSC technique which is recommended to be used up to the start of thermal degradation. Assessments about fragmentations of chemical bonds and about secondary reactions, such as cyclizations and crosslinking processes, may be made. To identify the gaseous products resulted from thermal decomposition, thermogravimetric analysis devices may be coupled with other devices, such as FTIR and/or MS, able to characterize evolved volatiles. The X-ray photoelectron spectroscopy (XPS) may measure the ratio between oxygen and carbon atoms. Samples are analyzed to depths up to 100 \AA . Although XPS is superior to FTIR-ATR in terms of resolution, the method does not penetrate deep enough to allow the identification of all oxidation products. An advantage of XPS to FTIR is that the method integrates all oxidation products. At the same time, XPS can not be used to establish the reaction mechanisms in absence of separation and identification possibilities of photo-degradation products.

It is well known that polymers change color under the action of UV radiation. The most popular tools that can analyze color variations are reflection spectrophotometers and colorimeters. To assess color changes, the CIEL*a*b system may be used. In the CIEL*a*b* system, the colors which belong to the visible spectrum are expressed in three-dimensional space and on three perpendicular axes. Each color may be characterized by the combination of parameters L^* , a^* and b^* . In this system the lightness is represented on the vertical axis (L). Lightness is a dimensionless parameter which varies between 100 and 0, values corresponding to white color (100) and black color (0). The color parameters a^* and b^* are represented on the two other horizontal perpendicular axes. The color factor a^* describes the position on the color scale ranging from -a, value that corresponds to pure green, to +a, which corresponds to pure red. The b^* color factor may also vary between the same limits, however value -b signifies pure blue, while +b pure yellow. The global color changes induced by aging may be calculated according with ASTM D 2244 with the formula:

$$\Delta E_{ab} = [(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2]^{1/2}$$

In the formula ΔE represents the color difference, L_2^* , a_2^* and b_2^* represent color parameters of aged samples and L_1^* , a_1^* si b_1^* are the color parameters of the initial sample.

Another characteristic of polymer surfaces that is changing under the influence of light is gloss. From a physical point of view the gloss of a material is a complex quantity that is associated with surface properties and how the spatial distribution of the reflected light is changed by the surface of sample. The gloss observations are often made under an angle of 60°. Usually, the gloss of polymer surfaces decreases during photochemical aging. The decrease of gloss is mainly related to an increase in surface roughness. The data obtained using the methods of characterization are usually represented depending on the exposure time. Most often they are processed by the method of least squares to establish a mathematical relationship between a property and its change during aging. The mathematical relationship allows extrapolation of data resulted from measurements in order to predict from calculus the time evolution of polymer material properties. Such predictions are made on the exposure time needed to reach a certain degree of modification of the monitored properties. Investigations to establish new methods that ensure lifetime prediction of polymer materials with high confidence is underway.

The research team developed a database with recent information on the behavior of polymers under environmental factors. Documentations in modern instrumental techniques and methods for problem definition and elaboration of the experimental study also were made. For this purpose, new specialized articles were purchased and based on these, the techniques and methods for investigating degradability of polymer systems were selected. In order to develop and implement management structure, research team members met monthly and established detailed activity plans. An effective and efficient communication of administrative, technical and financial research problems, both within the team and with the contracting authority was followed. The entire research team was involved in drafting the report of stage. Young doctoral students from the team have developed and presented four scientific papers under the guidance of senior researchers in the scientific session organized by the University "Alexandru Ioan Cuza" Iasi, Faculty of Chemistry - October 28, 2011 and have sent an article for publication toward a journal with international recognition.

The research team has met its objectives with a total degree of achievement.

Stage 2012

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
 - 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 the 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.

2.1. 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

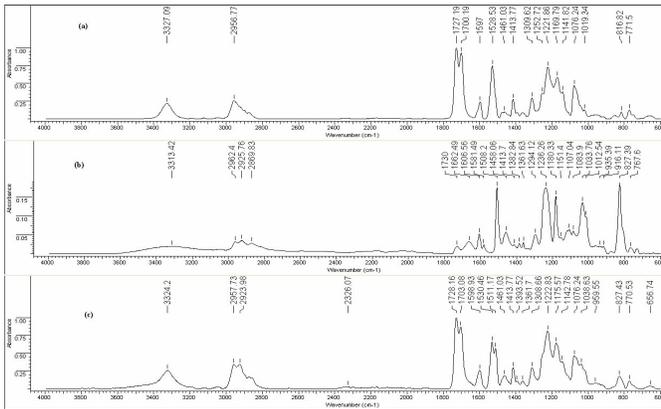


Fig. 2. FTIR spectra for: PU (a); ER (b) and SIPN-3 (c)

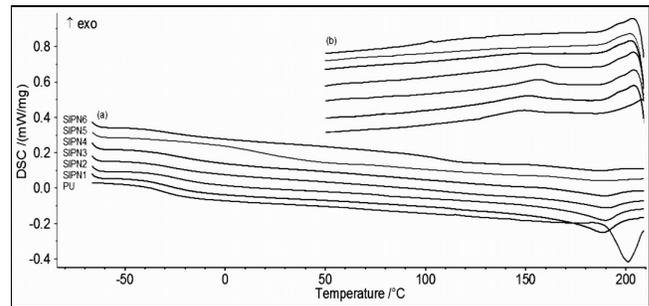


Fig. 3. DSC curves for SIPNs and initial polymers: heating (a) and cooling (b)

The glass transition temperature values (T_g) for the 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**).

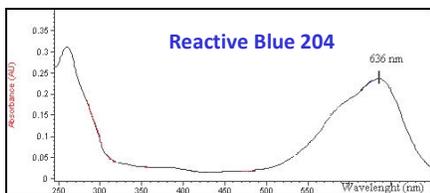
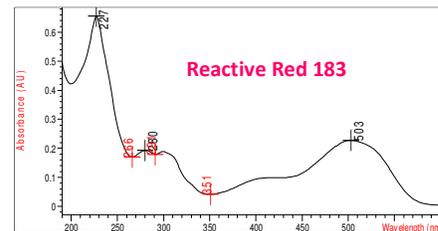
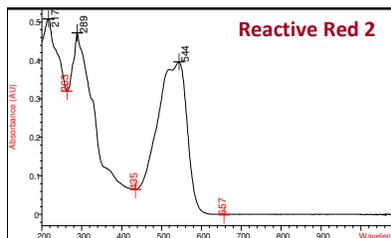
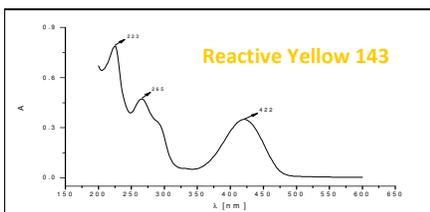
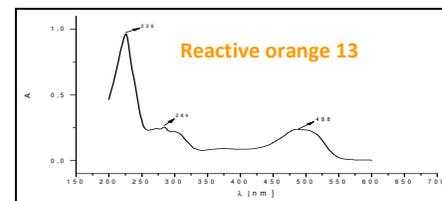


Fig. 4. UV-Vis absorption spectra for reactive dyes

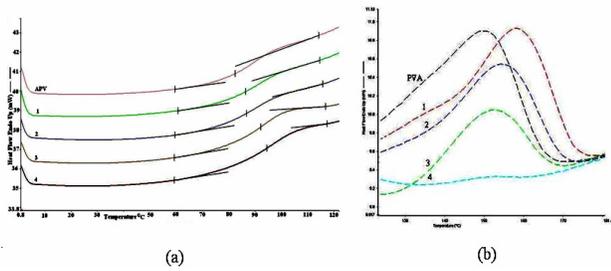
The maximum absorption (λ_{max}) in visible domain for reactive dyes are as follows: 422 nm (Yellow 143 reactive dye); 544nm (Red 2 reactive dye); 503 nm (Red 183 reactive dye); 636 nm (Blue 204 reactive dye); 488 nm (Orange 13 reactive dye).



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.

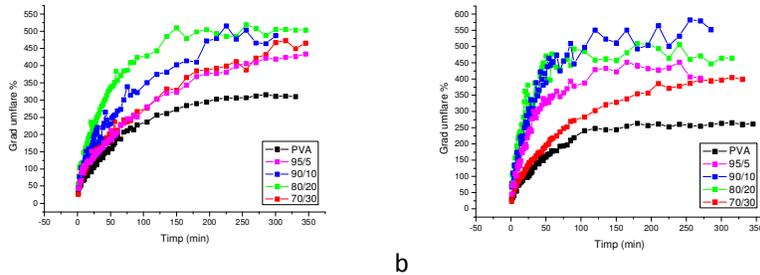


Fig.6. Swelling degree for PVA/ β -CD membranes: (a) at 25 °C, (b) at 37 °C

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).

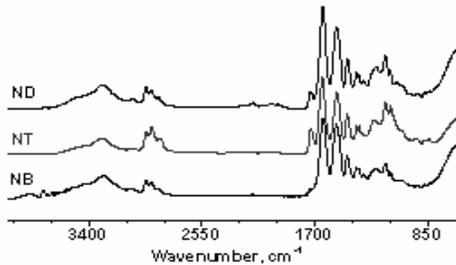


Fig. 7. FTIR spectra for cross-linked polymer networks

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.

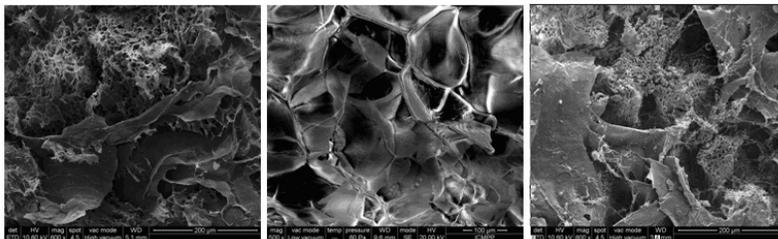


Fig.8. SEM images for polymer networks

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.

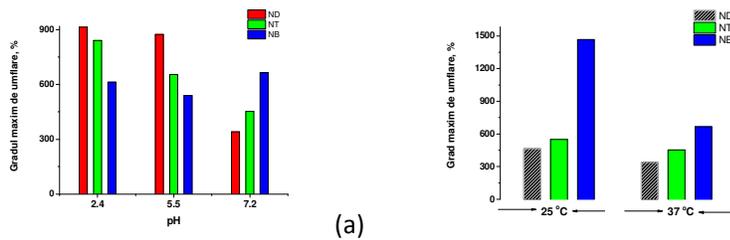


Fig. 9. Swelling degree of polymer networks at equilibrium state: (a) influence of pH and (b) influence of temperature

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, NH₂, 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.

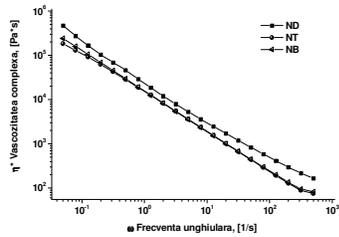


Fig. 10a. Complex viscosity behavior

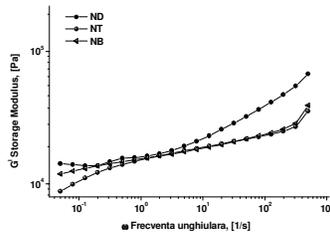


Fig. 10b. Storage modulus evolution

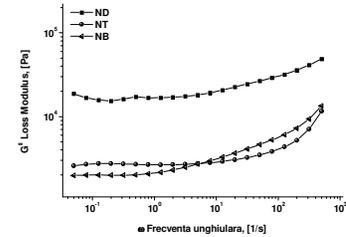


Fig. 10c. Loss modulus evolution

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 11% up to 39% as a function of 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

The Fig. 11 shows 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 -OH groups valence vibrations), 2890 and 2918 cm⁻¹ (characteristic to C-H from CH₃ and CH₂ 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 C=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. 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).

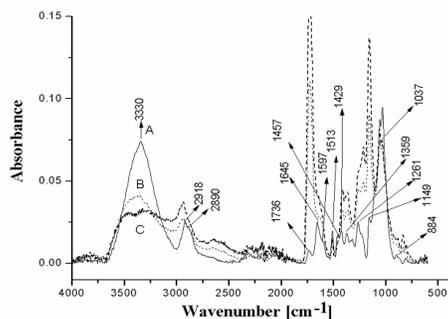


Fig. 11. FTIR spectra for non-treated wood (A), wood treated with SA (B) and wood treated with SA and coated with ESO (C)

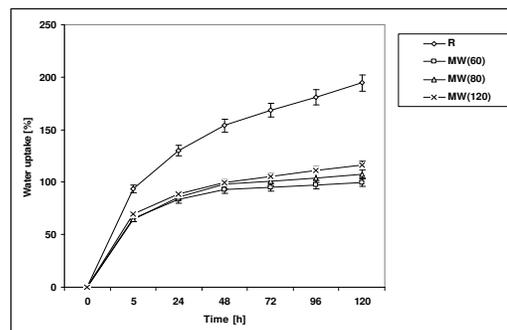


Fig. 12. Water absorption evolution for non-treated wood (R) and wood treated with SA (MW)

In the course stage 2012 were elaborated and presented a total of 11 communications and 15 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 Jun 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. Padurar, 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 for stage 2012 with a full degree of implementation.

Stage 2013

Objectives:

1. Study of the influence of controlled environmental factors upon obtained multicomponent polymer systems.
2. Kinetic modeling of thermal degradation reactions.
3. Modification of properties during photochemical degradation of multicomponent polymer systems.

Durability of multicomponent polymer systems (MPS) is diminished as a result of their exposure to aggressive elements of the external environment. Degradation of polymer materials represent all complex processes, reactions and changes that occur in chemical structure, morphology and their properties under the action of various agents of environmental degradation. In the process of degradation under environmental factors results products that retain their macromolecular character, but whose physical and chemical properties are changed. During decomposition new structures are obtained which may resume up to the monomeric unit or even to mineralization. Degradation processes are irreversible and may occur under the action of heat, UV radiation and/or humidity. These processes occur in all life stages of polymeric materials, sometimes initiated just before use. Each degradation process has its own particular characteristics.

1. Influence of environmental factors on multicomponent polymer systems

1.1. Exposure to UV radiation. The majority MPS are affected by ultraviolet radiation. Depending on the wavelength, the radiation intensity, exposure time and chemical structure, respectively, MPS exposed to UV radiation can undergo photo-degradation processes. These processes involve both color and gloss changes that only affect the aesthetic appearance of MPS and major structural changes such as cleavage of macromolecules and Mesh, signified affecting physical-mechanical properties. The latter can affect property to such an extent that cause premature aging or even scrapping of MPS. Photochemical degradation effects of MPS which require long periods of exposure may be tracked by putting samples through accelerated aging tests performed in clean rooms and irradiating them with high intensity UV lamps. Aging speed if MPS can be by significant values (over 60 times). Knowledge of photo-degradation mechanisms and identifying the active species affecting MPS structure is very useful in choosing the most appropriate and effective methods of photo-stabilization.

1.2. Exposure to temperature. MPS thermal stability is important as it determines the maximum processing temperature and environmental conditions under which the materials can be used without spoiling. As long as thermal stability is related to the initial temperature of degradation and the degradation rate of MPS, the determination of kinetic parameters associated with degradation processes under the influence of temperature is a major topic of interest. The results may provide useful information in defining specific processing conditions of MPS for different applications and can establish a correlation between thermal stability and material structure. The data could also be useful for predicting the lifetime of MPS at different temperatures and in the recovery/destruction of polymer waste by pyrolysis or combustion.

1.3. The effect of humidity. Under the action of humidity the degradation MPS is rapid. As a consequence of this process, there result free radicals that can enhance the degradation reactions, affecting both the thermal stability of the MPS and their structure. When wood is exposed to environmental factors conditions without any protection, for example humidity and/or sunlight (especially UV) - its surface is deteriorating rapidly. Action of environmental factors upon wood can cause micro-cracks that subsequently induce cracks in wood mass due processes of swelling and shrinkage of wood as a result of water absorption and drying process. Under the action of humidity, photo-degraded fragments of wood (mainly from lignin) are removed and therefore increase the surface roughness of wood. It is known that low resistance to moisture is one of the main disadvantages of wood, and this can be improved by chemical modification. Wood reaction with succinic anhydride significantly reduced hydrophilic nature of its constituents (**Table 3**). A decrease in the values of water absorption was recorded for modified wood compared with the initial sample.

Chemical and physical treatment and/or wood surface coating are effective methods that can be applied to protect the wood surface from damage. In this way the dimensional stability, resistance to moisture and to fungi action are improved. By chemical treatment, the initial structure of biopolymer components of wood is influenced and some of its properties can be modified (for example, hydrophilicity).

Table 3. Water absorption chemically treated wood samples

Sample/ soak time	5h	24h	48h	120h
LB	92	128	153	178
LB60	64	82	90	98
LB80	60	76	85	90
LB120	58	75	84	87

2. Kinetics of thermal degradation reactions

2.1. Study of thermal transformations that occur in polymers. MPS heating may cause phase transitions, phenomenon indicated by the glass transition temperature (T_g). T_g values can provide an indication of the miscibility of the MPS components. In the case of MPS that have not undergone cross-linking (eg. mixtures of linear polymers) there may be determined the melting and crystallization temperatures. Heat curing and crosslinking kinetics studies may be undertaken. Via thermogravimetric studies the MPS thermal stability may be monitored by correctly assessing the initiation of the thermal decomposition process. Also kinetic studies on the rate of decomposition reaction may be undertaken and feedback on different thermal decomposition mechanisms may be obtained. The apparent kinetic parameters of the decomposition reaction can also be set to develop a kinetic model. Using coupled techniques (TG/FTIR, TG/MS) allows qualitative evaluation of volatile products evolved during thermal decomposition, depending on the temperature. The semi-interpenetrated polymer networks (SIPNs) based on polyurethane (PU) and epoxy resin (ER) obtained during the stage of 2012 show a single composition-dependent T_g . T_g values move slightly towards higher values as crosslinked resin content increases. This is due to the reduction of free volume between chain segments, restricting the movement of polymer chains by steric hindrance. The melting/crystallization profiles of pure PU decrease in intensity with increasing crosslinking density up to a 30% ER content. This is a sign of compatibility between components of S-IPN structures. Miscibility studies were conducted by applying Fox and Gordon-Taylor equations and the results were in good correlation with those obtained from experiments. Crosslinking densities were determined and their values increased with heat capacity values decrease, as expected.

Applying the equation of Fox (**Fig. 13**) has revealed the presents of specific interactions between the components of SIPN networks by obtaining a positive deviations between experimental and theoretical data. An appreciation of the strength of these bonds was achieved by Gordon-Taylor equation (**Fig. 14**). Gordon-Taylor experimental constant value was close to 2 values, suggesting the presence of strong interactions between the two components of the networks.

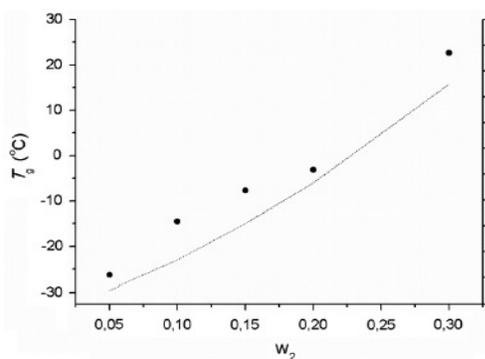


Fig. 13

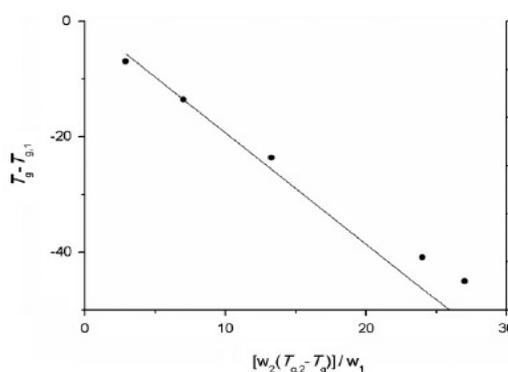


Fig. 14

Heat capacity values and cross-linking density values are given in Table 4. It can be observed that T_g and cross-linking density values increase with the heat capacity values decrease, as expected. The heat capacity is an energetic characteristic of the chain segments movement. Upon increasing values of the cross-linking degree, reduction of free volume between chain segments sterically hinders their movement, thus lowering the heat capacity values (**Table 4**).

Table 4. Heat capacities and related cross-linking data.

Sample	Heat capacity, C_p ($J g^{-1} ^\circ C^{-1}$)	ρ_c ($mol cm^{-3}$)
PU	1.485	-
S-IPN-1	1.466	0.0128
S-IPN-2	1.417	0.0458
S-IPN-3	1.335	0.101
S-IPN-4	1.290	0.131
S-IPN-5	1.172	0.210

2.2. Calculation of kinetic parameters for establishing reaction mechanisms

Thermogravimetric analysis conducted in an inert atmosphere (N_2) and at 4 heating rates (5, 10, 15 and $20^\circ C/min$) in a temperature range between 30 and $700^\circ C$ was used for the determination of the apparent kinetic parameters (activation energy, pre-exponential factor, conversion function form) of the MPS thermal decomposition reactions (**Fig. 15** and **Fig. 16**).

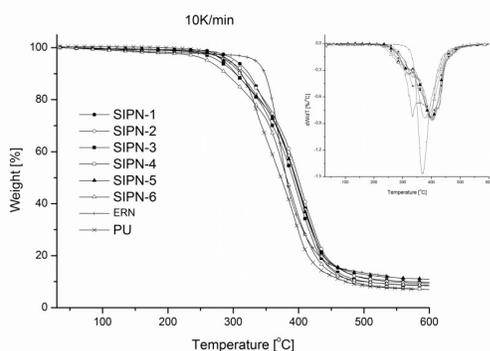


Fig. 15

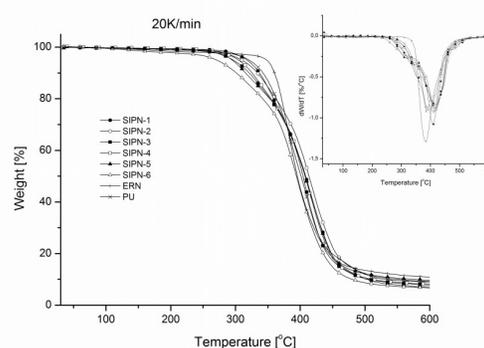


Fig. 16

Initial decomposition temperatures, the temperatures corresponding to each stage of decomposition and the residual masses were also determined. Global kinetic parameters were calculated by isoconversional methods of Friedman (**Fig. 17**) and Ozawa-Flynn and Wall (**Fig. 18**) which use the thermograms registered at four different heating rates. The conversion function was determined by multiple nonlinear regression method.

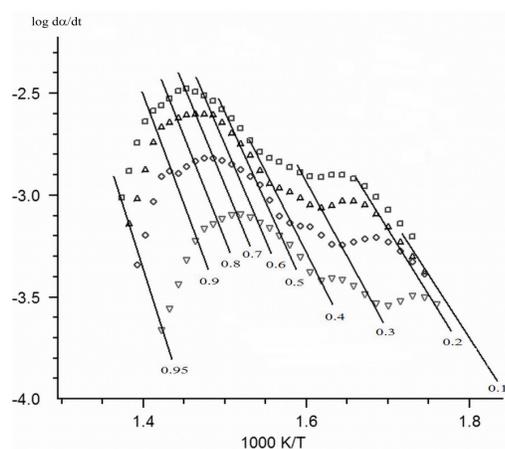


Fig. 17

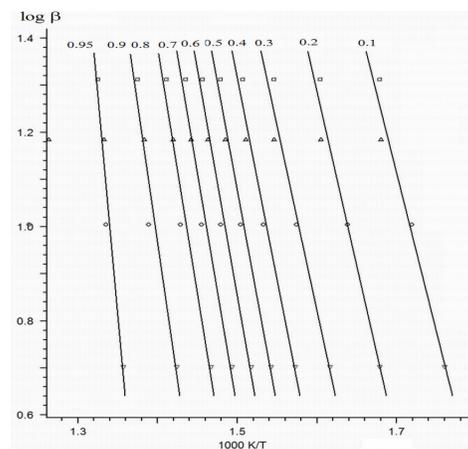


Fig. 18

2.2.1. Semi-interpenetrated polymer networks (SIPNs) based on polyurethane (PU) and epoxy resin (ER)

It was found that thermograms shifted towards higher temperature domains with heating rate increase. Based on those shifts the values of global kinetic parameters were calculated (**Table 5**).

Table 5. Values of global kinetic parameters

α	Kinetic parameters			
	Friedman		Flynn-Wall-Ozawa	
	Log A (s ⁻¹)	E (kJ mol ⁻¹)	Log A (s ⁻¹)	E (kJ mol ⁻¹)
0.1	12.56	121	6.64	107
0.2	20.86	136	8.11	126
0.3	18.5	166	7.63	123
0.4	12.71	177	7.65	125
0.5	16.46	181	8.92	141
0.6	23.40	186	10.02	155
0.7	30.73	177	10.72	166
0.8	30.45	192	10.79	168
0.9	36.65	199	10.70	170
0.95	36.48	211	14.66	230

Kinetic parameters values increased with conversion degree, thus suggesting a complex mechanism of thermal degradation in three successive stages. After testing 14 kinetic models by multivariate linear regression method, it was found that the overall process of thermal decomposition is characterized by a kinetic model of n order:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} (1 - \alpha)^n$$

2.2.2. Cryogels obtained from polyvinyl alcohol (PVA) and microcrystalline cellulose

Cryogels containing PVA and cellulose show 4 stages of thermal degradation. The residual mass depends on the amount of cellulose in the composition of cryogels and the DTG curves peaks decrease for all stages of thermal degradation with natural polymer content increase. These issues highlight the presence of hydrogen bonding interactions between the two components, leading to an increase in the thermal stability in the presence of cellulose. Figs. 19 and 20 show the graphs obtained with the Friedman (Fig. 19) and Flynn-Wall-Ozawa (Fig. 20) methods at the conversion degree (α) values between 0.1 and 0.9. Both isoconversional methods indicate the dependence of activation energy (E) on the conversion degree.

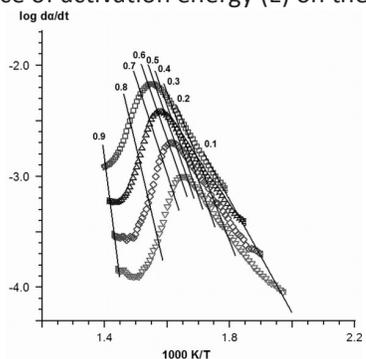


Fig. 19

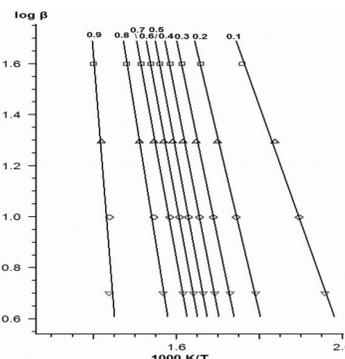


Fig. 20

2.2.3. Wood – a multicomponent polymer system

2.2.3.1. Study of thermal stability of treated wood surface with succinic anhydride (SA)

Thermal degradation of wood is a very complex process, given its chemical structure. Fig. 21 shows the TG curves (Fig. 21A) and DTG curves (Fig. 21B). Data on behavior of wood thermal degradation are presented in Table 6. Chemical modification of wood favorably influenced thermal stability, especially at high concentrations of SA.

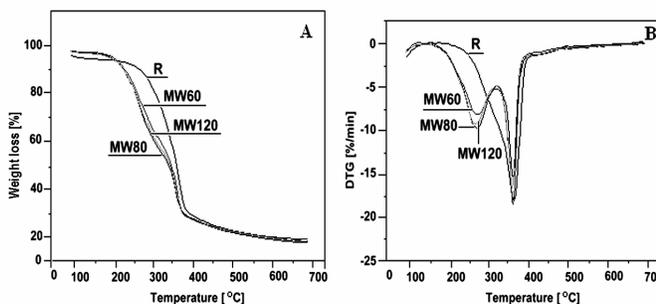


Fig.21

Table 6. Data resulted from the analysis of thermal degradation behavior of wood

Wood sample	T _i (°C)	T _{50%} (°C)	T _{ml} (°C)	W _{ml} (%)	T _{mII} (°C)	W _{mII} (%)	T _f (°C)	T _f - T _i (°C)	W _{Tf-Ti} (%)	W _{rez} (%)
R	109	365	372	75.5	-	-	388	229	75.5	19.4
MW60	203	355	279	33.7	368	43.9	383	180	77.6	19.3
MW80	199	352	276	38.2	368	41.50	380	181	78.7	19.0
MW120	196	350	277	38.8	368	40.0	381	185	78.8	19.1

2.2.3.2. Study of thermal stability of wood treated with the ionic liquid

Thermal analysis of wood species showed that the effect of ionic liquid is dependent on the type of wood (for example its chemical composition). Ionic liquid lowers the specific energy of water removal process. This is due to the ability to transform ionic liquid bound water into free water, helping the release of water from wood. The ionic liquid increased the initial temperature of the beechwood by changing the reaction mechanism of decomposition. The new compounds were identified, and the time of initiation of the evolution of volatile compounds was delayed for beechwood. Identification of volatile compounds resulting from thermal degradation was performed using 3D FTIR spectroscopy (Fig. 22). It may be observed that signals intensity change with wood degradation temperature.

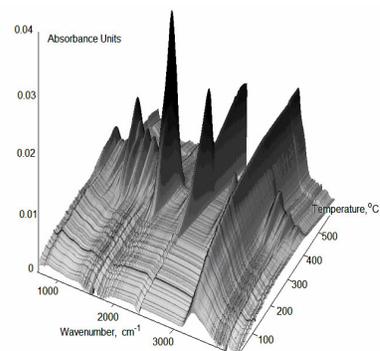


Fig.22

2.3. Determination of the factors influencing the results of thermogravimetric analysis

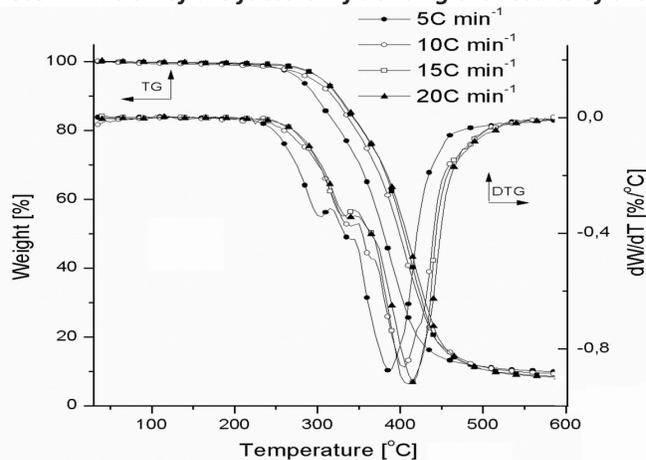


Fig.23

Thermogravimetric analysis results can be influenced by: the shape of analyzed samples and rate of heating. Sample characteristics exert a complex influence on TG curves. It was found that the thermal properties of powders differ substantially from those of larger samples. Effect of heating rate on the position and shape of TG curves is explained by the fact that the change of this parameter affects the processes of heat and mass transfer. In general thermograms shift towards higher temperatures with heating rate increase (Fig. 23).

3. Properties modification during photochemical degradation of multicomponent polymer systems

3.1. Establishment of the influence of wavelengths and doses of radiation on the studied polymers

Sunlight and especially the UV component of the sunlight spectrum are responsible for initiating photochemical degradation. In principle, photo-degradation of polymers is an effect of energy dissipation of photo-chemically excited molecules and is one of the primary photochemical process steps. This can lead to either to the split of the excited macromolecule, with the emergence of new macromolecular fragments with low molecular weights, which modifies the system polydispersity, or formation of interchange chemical bonds with neighboring polymer chains and the formation of crosslinked structures, resulting in increased final molecular weight and low solubility. Once initiated in this manner, degradation of polymers usually continues through secondary photochemical processes (eg. photo-oxidation) in which also participates, together with the initial polymer chains, oxygen and substances derived from primary photochemical process. The structure of most polymers consists mainly of covalent bonds of C-X type (where X can be: C, O, halogen, N or P) and these bonds absorb more or less radiation with wavelengths higher than 200 nm.

3.2. Photo-degradation kinetics study

In the photo-degradation kinetic studies of semi-interpenetrated polymer networks (SIPN) based on polyurethane (PU) and epoxy resin (ER), there were followed by FTIR technique the signals variation in the specific wavenumber range $1492-1570\text{ cm}^{-1}$ and $1750-1716\text{ cm}^{-1}$, specific to urethane bond and ester entities from polyurethane.

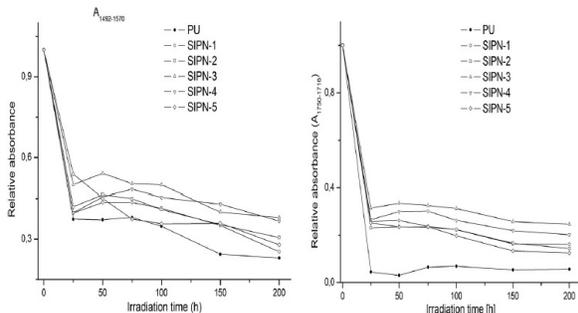


Fig. 24 The highest changes occurred in the first 25h of irradiation. After 200h irradiation times the most important loss of urethane bonds occurred in the PU structure due to photo-Fries rearrangement. One explanation of this behavior may be related to the high transparency of the PU film compared to the studied networks that are more opaque, UV radiation causing a more advanced penetration of the PU film than for the networks. The significant decrease in the absorbance value at 1727 cm^{-1} specific to ester structure may be observed in the first 25 hours of irradiation (**Fig. 24**).

The highest loss of ester linkages have been identified for the network comprising 40% cross-linked ER. It may be observed that above 20% cross-linked ER concentration, there occurs a protection phenomenon of the PU "soft" segments, due to increasing opacity with cross-linked ER content increase and micro phase separation. This may explain a decreasing trend in the concentration of carbonyl entities of soft segments of PU from the sample containing 40% crosslinked ER during irradiation (**Fig. 24**).

3.3. Establishment of photo-degradation mechanisms

After 200h irradiation time the most important loss of urethane bonds occurred in PU structure due to photo-Fries rearrangement, which consists of formation of ortho-amino ester structure and chain branching. This process leads to an increase in affinity of SIPNs for water molecules. Photo-degradation of ester structures by Norrish type reactions occurs by CO_2 elimination, leading to mass variations in the studied structures, reducing of molecular weight and polydispersity increase.

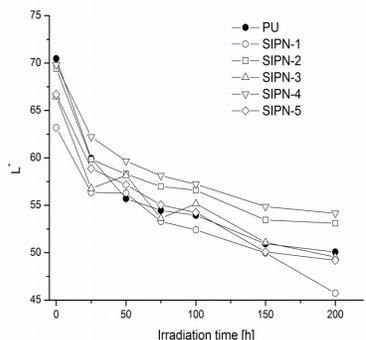
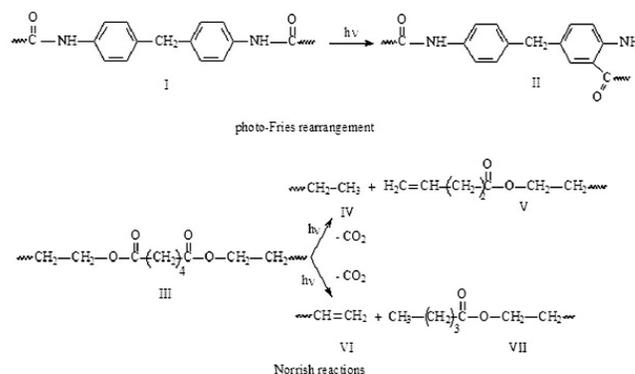


Fig. 25

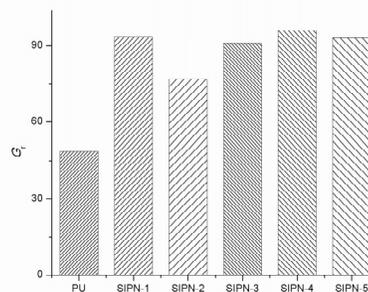


Fig. 26

Table 7. The variation of chromatic coefficients with irradiation time

Sample	a*							b*						
	0	25	50	75	100	150	200	0	25	50	75	100	150	200
PU	-0.576	1.563	2.135	3.750	4.243	4.314	4.421	11.680	30.864	31.001	31.371	31.790	34.532	35.012
SIPN-1	0.291	0.868	0.902	1.003	1.063	3.241	7.194	13.503	22.103	23.798	24.802	25.558	27.101	29.798
SIPN-2	-2.499	1.257	1.474	2.003	2.273	5.668	6.001	16.795	22.343	23.111	26.115	27.972	28.003	28.595
SIPN-3	-2.202	0.013	0.423	0.585	0.814	0.951	0.963	15.928	17.324	19.235	22.043	24.143	25.005	25.870
SIPN-4	-1.493	0.023	0.520	1.243	1.827	3.353	5.380	11.959	19.222	23.384	25.252	26.095	27.312	28.2248
SIPN-5	2.2785	2.345	2.446	2.502	2.5884	4.582	6.3001	16.9252	17.555	22.128	25.399	29.282	28.887	28.4201

The lightness factor decreased for all the studied samples during irradiation (**Fig. 25**). The behavior is an indication of the darkening of all samples after UV irradiation. The irradiation caused the increase of chromatic coefficients values (a^* and b^*) for all the studied samples. (**Table 7**). The chromatic coordinate's variation shows the tendency of reddening and yellowing of the irradiated samples. The gloss decreased during the irradiation of the studied samples (**Fig.26**). The gloss decrease on the surface during irradiation can be explained by changing their roughness because there is a direct relationship between gloss and roughness. It is well known that the rough surfaces are less glossy.

4. Insurance of the project implementation framework. Improving the implementation process.

4.1. Completing the project database

Project database has been updated and can be found at: <http://www.icmpp.ro/mcps/ro/>

4.2. Dissemination of the results

Scientific papers: 12

1. 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.* **100**, 103-110 (2013); (IF: 2.560); (SI: 1.244)
2. 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.* **111(2)**, 1561-1570 (2013); (IF: 1.982); (SI: 0.548)
3. 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* **8(1)**, 1478-1507 (2013); (IF: 1.309); (SI: 1.322)
4. S.F Patachia, M.-T. Nistor, C. Vasile, Thermal behavior of some wood species treated with ionic liquid, *Ind. Crops and Prod.* **44**, 511-519 (2013); (IF: 2.468); (SI: 1.731)
5. M.-T. Nistor, C. Vasile, TG/FT-IR/MS study on the influence of nanoparticles content on the thermal decomposition of the starch/poly(vinyl alcohol) montmorillonite nanocomposites, *Iranian Polym. J.* **22(7)**, 519-536 (2013); (IF: 1.053); (SI: 0.540)
6. 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: Eng.* **50**, 273-278 (2013); (IF: 2.143); (SI: 2.722)
7. O. M. Paduraru, A. Bosinceanu, G. Tantar, C. Vasile, Effect of hydroxypropyl-cyclodextrin on the solubility of an antiarrhythmic agent, *Ind. Eng. Chem. Res.* **52**, 2174-2181 (2013); (IF: 2.206); (SI: 1.911)
8. C.-D. Varganici, O. Ursache, C. Gaina, V. Gaina, D. Rosu, B.C. Simionescu, Synthesis and characterization of a new thermoreversible polyurethane network, *Ind. Eng. Chem. Res.* **52(15)**, 5287-5295 (2013); (IF: 2,206); (SI: 1.911)
9. R. Bodirlau, C.-A. Teaca, D. Rosu, L. Rosu, C.-D. Varganici, A. Coroaba, Physico-chemical properties investigation of softwood surface after treatment with organic anhydride, *Central Eur. J Chem.* **11(12)**, 2098-2106 (2013); (IF: 1.167); (SI: 0.655)
10. M.-T. Nistor, A. Chiriac, L. Nita, I. Neamtu, C. Vasile; Semi-interpenetrated network with improved sensitivity based on poly(N-isopropylacrylamide) and poly(aspartic acid), *Polym. Eng. Sci.* **53(11)**, 2345-2352 (2013); (IF: 1.243); (SI: 1.349)
11. M.-T. Nistor, C. Vasile, A.P. Chiriac; Hybrid collagen-based hydrogels with embedded montmorillonite nanoparticles, *Appl. Clay Sci.* (2013), sent to publication (IF: 2.342);(SI: 1.268)
12. O. Ursache, C. Gaina, V. Gaina, N. Tudorachi, A. Bargan, C.-D. Varganici, New Diels-Alder thermoresponsive networks based on ether-urethane bismaleimide-functionalized poly(vinyl alcohol), *Ind. Eng. Chem. Res.* (2013), sent to publication; (IF: 2.206); (SI: 1.911)

Papers presented at scientific conferences: 9 (communications: 3 and posters: 6)

European Polymer Congress – EPF 2013, Pisa, Italia, 16-21 Iunie, 2013

1. C.-D. Varganici, L. Rosu, D. Rosu, B.C. Simionescu; Semi-interpenetrating polymer networks based on an aromatic polyurethane and epoxy resin. Miscibility studies (**COMMUNICATION**)
2. D. Rosu, C.-C. Gavati, L. Rosu, C.-D. Varganici; Cellulose fabrics painted with some reactive azotriazine dyes. Photochemical behaviour (**POSTER**)
3. L. Rosu, C.-D. Varganici, D. Rosu; Semi-interpenetrating polymer networks based on an aromatic polyurethane and epoxy resin. Surface properties modifications (**POSTER**)
4. F. Mustata, I. Bicu, D. Rosu, C.-D. Varganici; Epoxy monomers based on methyl ester of corn oil (**POSTER**)
5. R. Bodirlau, C.-A. Teaca, D. Rosu; Organic anhydride treatment of softwood to improve its weathering protection (**POSTER**)
6. C.-A. Teaca, R. Bodirlau, I. Spiridon, N. Tudorachi; Multi-component polymer systems comprising modified starch microparticles and different natural fillers (**POSTER**)

Academic Days Iasi, A XXIV Scientific Session of the Institute of Macromolecular Chemistry "Petru Poni", "PROGRESS IN SCIENCE AND MACROMOLECULAR ORGANIC COMPOUNDS", Iasi, 3-5 Oct. 2013

7. C.-D. Varganici, A. Coroaba, R. Bodirlau, C.-A. Teaca, L. Rosu, D. Rosu; Study of structural and thermal properties of chemically modified wood (**POSTER**)
8. C.-D. Varganici, D. Rosu, L. Rosu, B.C. Simionescu; Epoxy and polyurethane based S-IPNs as coating materials. Miscibility through thermal studies (**COMMUNICATION**)
9. O.-M. Mocanu (Paduraru), C.-D. Varganici, L. Rosu, D. Rosu; Study of thermal degradation of hydrogels based of PVA/cellulose by TG/FTIR-MS analysis (**COMMUNICATION**)

Other activities:

This research project supported the following doctoral stages:

1. Miscibility studies of semiinterpenetrating polymer networks based on aromatic polyurethane and crosslinked epoxy resin, PhD. Cristian-Dragos Varganici

2. Thermal stability of semi-interpenetrated based aromatic epoxy resin and polyurethane, PhD. Cristian-Dragos Varganici

Public doctoral thesis:

1. Interpenetrated networks based on collagen or polyaspartic acid with applications in medicine and pharmacy, June 18, 2013, PhD. Manuela-Tatiana Nistor

2. Multicomponent polymer systems containing polysaccharides, June 20, 2013, PhD. Oana-Maria Paduraru

Master Dissertation thesis:

X ray diffractometry study of polymers and polymer composites, June 2013, Elena Marlica

Part of these theses represents results obtained and reported in this project.

4.3. Ensure resources. Preparation of report stage

The involved research team in the project realized the following activities:

- Monthly work sessions with team members;
- Counseling activities for doctoral/postdoctoral students by senior researchers;
- Organizing panels of senior scientific team problem solving;
- Elaboration and submitting articles for publication in ISI journals;
- Establishing and procurement of the necessary materials for the development research program;
- Human resource, financial and material planning for the next stage;
- Acquisition activity planning, preparing documentation for procurement;
- Tracking the supply flow and the use of funds;
- Preparing stage report 2013 (scientific, financial) and synthetic scientific report for period 2011-2013.

In order to develop and implement management structure, team members met monthly and established detailed activity plans. It was followed effective and efficient communication of administrative, technical and financial research both within the team, and with the contracting authority. The entire research team was involved in drafting the report stage. It was compiled the file necessary to achieve independent financial audit in 2013.

The research team met its objectives with a total degree of achievement.

Main indicators of the results obtained during project implementation between 2011-2013:

<i>Indicators type</i>	<i>Name</i>	<i>No./year</i>			<i>Total</i>
		2011	2012	2013	
Indicators of results	Accepted and published articles in ISI journals		3	10	13
	Participation to scientific symposia	4	27	9	40
	Other results:				
	Doctoral thesis			2	2
	Research project		1	1	2
	Research report			1	1
	Master dissertation thesis			1	1

Cumulated Impact Factor (IF): 26.279

Cumulated Influence Score (SI): 17.844

Project Director,
Dr. Dan Rosu

