The activities undertaken in the proposed objectives were finalized and are summarized in this present report.

The obtaining of multicomponent polymeric systems is important for a sustainable evolvement, taking into account aspects regarding environmental protection and waste management. Polymeric semi-interpenetrating networks (SIPNs) are particular blends formed from one linear and one cross-linked polymer without chemical bonds established between components. Cross-linked epoxy resins and polyurethanes (PU) may form semi-interpenetrating polymer networks with interesting combinations of properties which make them excellent coating materials. Polynvinyl alcohol (PVA) possesses high capacity of hydrogen bonding with other polymers and at the same time being biodegradable, biocompatible and water soluble. All these properties recommend PVA as a candidate for the obtaining of films in blends with other natural polymers, such as cellulose. PVA and cellulose based cryogels may assure mass transport of micro- and nanoparticles, as well as making possible the immobilization of different cells and biomolecules on their surfaces. Such materials may be destined for some specific applications, such as: tissue engineering, biodegradable food packaging, membranes for biosensors or wound dressings, assuring an appropriate level of moisture necessary for cauterization. Natural fibres textiles, such as cotton, silk and wool offer weak protection of human skin from solar spectrum light due to reduced light absorbing capacity of these materials. Improvement of light absorbing capacity is possible by painting the textiles with different coloured dyes. Wavelengths in the range 300-400 nm (~ 5% of the solar light spectrum which reaches the Earth surface), having high energy, act in a destructive manner to both human skin and textiles. Recent studies in the field of composites generate opportunities for the obtaining of materials with significantly improved properties by efficiently exploiting renewable resources and with a wide range of applications. Such systems are obtained based on matrices from renewable resources – biopolymers – having a positive impact on the environment.

Objective 1. Physico-chemical characterization of multicomponent polymeric systems aged under controlled conditions

1.1. Evaluation of optical properties (colour, gloss) and physico-mechanical properties modification

Five semi-interpenetrating polymer networks based on PU and increasing content of cross-linked epoxy resin were synthesized and characterized. Based on the percent content of cross-linked epoxy resin, the networks were noted as SIPN1 (5% resin), SIPN2 (10% resin), SIPN3 (15% resin), SIPN4 (20% resin) and SIPN5 (30% resin). The photochemical behaviour of SIPNs under UV irradiation with $\lambda > 300$ nm is interesting from both practical point of view, especially when the increase of materials photochemical stability is sought, and theoretical point of view, in order to gain new knowledge on different photochemical decomposition mechanisms of polymers, finding of adequate photostabilizers or obtaining of photodegradable materials. Concerning the photochemical stability studies of SIPNs, irradiation was made on 40 mm$^2$ surfaces with a medium pressure Hg vapour lamp of 100 W, model OSRAM HQE-40 with an emission spectra range between 340-370 nm. Irradiations were undertaken in air atmosphere. The more energetic radiations with $\lambda < 300$ nm, absent in natural light spectra, were eliminated with a quartz/borosilicate filter with a maximum transparency at 365 nm. Colour variation analysis ($\Delta E$) was evaluated with Eq. 1, where $L^*$ is the lightness factor, $a^*$ is the chromatic coefficient of redness-greening and $b^*$ is the chromatic coefficient of yellowness-blueness. Indexes 2 and 1 in Eq.1 represent the parameter values measured after and before irradiation, respectively.

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2}$$

Gloss variation on the surfaces of the samples was determined at 60° by comparing the intensity of luminous reflection on the sample surface with the value obtained for the standard (polished black glass). The surface gloss retention (Gr) was calculated with Eq. (1) where $G_r$ and $G_i$ represent the initial and the final gloss values.

$$Gr = \frac{G_f}{G_i} \times 100$$

Figs. 1 and 2 show the variations of colour differences and gloss retention with irradiation time. An increase in $\Delta E$ values with irradiation time may be observed (Fig.1). The most significant increase of these values was observed in the first 25h of UV irradiation for PU. The $\Delta E$ value for PU was 31.1 after 200h irradiation time, indicating major colour differences between irradiated and non-irradiated samples. The $\Delta E$ values of SIPNs were lower than those recorded for PU at the end of the photodegradation process. $\Delta E$ values increased in the following order: SIPN3 (19.9) < SIPN5 (21.3) < SIPN2 (21.5) < SIPN1 (22.3) < SIPN4 (23.6). The $G_r$ value decreased with irradiation time for all samples (Fig. 2) with lowest value for PU (48.7), while for the other samples it varied between 76.9 (SIPN2) and 96.1 (SIPN4).
This decrease in \( G_r \) values was explained by a modification in structures roughness, because there exists a direct relationship between gloss and roughness. An explanation for the decrease in \( G_r \) value for PU compared with the other structures is attributed to the high transparency of the polymer structure, because UV light deeper penetrates the sample, thus generating an advanced deterioration. Irradiation significantly modifies the samples resistance to mechanical effort and deformation. Figs. 3 and 4 show the effort-deformation curves for samples SIPN2 and SIPN5.

Irradiation of SIPN samples determines a growth of some physical and chemical properties such as: initial elasticity modulus, the resistance of elasticity limit, resistance to shearing and reducing the elongation break at elasticity limit. These properties modifications decrease with cross-linked epoxy resin content increase in SIPNs. This behaviour is explained by a weak photostabilizing effect of PU by the cross-linked epoxy resin.

1.2. Establishing interaction types between polymeric components

The influence of the components ratio and that of the interactions established between them on the photochemical stability of cryogels has been studied. The most significant structural modifications consist of macromolecular chain scission, cross-linking and oxidation reactions. During UV irradiation of PVA and cellulose based cryogels there were identified significant colour modifications, evidenced through the increase in lightness factor (\( L^* \)) values, accumulation of instable red chromophores (\( a^* \)) and surface yellowing (\( b^* \)). Figs. 5-7 show the modification of chromatic coefficients values with irradiation time for the cryogels. Structural modifications during UV irradiation were monitored via FTIR, UV-Vis and XPS techniques. Due to interruption of oxygen diffusion through the PVA surface, cellulose in the cryogels exhibited a slower photooxidation process. Photooxidation was possible via intermediate hydroperoxidic structures formation, confirmed through an iodometric method. Individual cellulose has also suffered photooxidation phenomena via continuous hydroperoxides formation and depolymerization. Due to its oxygen diffusion barrier properties, PVA protected cellulose fibres from UV radiations up to a concentration of 70% PVA in the cryogel.

SEM micrographs demonstrated that up to a 70% concentration in the cryogel, PVA interacts with cellulose fibres adhering as film to their surface. Above this concentration value, the interactions between components significantly
1.3. Crosslinking degree evaluation
In order to determine SiPNs cross-linking density values it is firstly necessary to calculate absolute heat capacity values and introduce them in Eq. 3, where $C_p$ and $C_p^0$ are the absolute heat capacities of pure PU and that at a given crosslinking density value ($\rho_c$).

\[
P_c = \frac{C_p - C_p^0}{C_p^0} = \frac{\Delta C_p}{C_p^0}
\]

Eq. 3

Determination of absolute heat capacity values may be undertaken via DSC method by recording three consecutive measurements: (1) a scan with empty aluminium crucibles with pierced unsealed lids, (2) a scan with a reference material consisting of pure sapphire and (3) a scan with a same sample mass as that of the reference material. The relationship between the sample caloric capacity, noted $C_p$ (proba), which adds up the heat capacity of sample crucible support, that of sample crucible, that of analysed sample and of the reference material, noted $C_p$ (safrir), which in turn adds up the heat capacity of the reference materials crucible support, that of reference material crucible and that of the reference material and the heating rate, $\beta$, is given in Eqs. 4 and 5.

\[
C_p \text{(proba)} - C_p \text{(safrir)} = (T \text{(proba)} - T \text{(safrir)})/(B)
\]

Eq. 4

\[
C_p \text{(proba)} - C_p \text{(safrir)} = kD
\]

Eq. 5

Since the caloric capacities of crucible with sample and of crucible with sapphire may be noted with $C_p$ (proba) and $C_p$ (safrir) and specific heat values of sample and sapphire with $c_s$ and $c_a$ and their mass values with $m_s$ and $m_a$, Eqs. 6-9 may be obtained, in which by $D_1$, $D_2$ and $D_3$ the thermal displacements between DSC curves of correction, reference and sample were noted.

\[
[C_p \text{(proba)} + m_s c_s] - C_p \text{(safrir)} = D_2
\]

Eq. 6

\[
[C_p \text{(proba)} + m_a c_a] - C_p \text{(safrir)} = D_3
\]

Eq. 7

\[
\frac{m_s c_s}{m_a c_a} = \frac{D_2 - D_1}{D_3 - D_1}
\]

Eq. 8

\[
\frac{m_s c_s}{m_a c_a} = \frac{D_2 - D_1}{D_3 - D_1}
\]

Eq. 9

Since the $c$ values are known, the sample caloric capacity may be calculated with Eq. 10.

\[
C_p \text{(proba)} = \frac{m_s c_s}{m_a c_a} \frac{D_2 - D_1}{D_3 - D_1}
\]

Eq. 10

The $C_p$ values corresponding to glass transition temperatures ($T_g$) were thus calculated for the SiPNs (Table 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ ($^\circ$C)</th>
<th>$C_p$ ($\text{Jg}^{-1}\text{C}^{-1}$)</th>
<th>$\rho_c$ (mol cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU</td>
<td>-32.7</td>
<td>1.485</td>
<td></td>
</tr>
<tr>
<td>SIPN1</td>
<td>-29.5</td>
<td>1.466</td>
<td>0.0128</td>
</tr>
<tr>
<td>SIPN2</td>
<td>-25.7</td>
<td>1.417</td>
<td>0.0458</td>
</tr>
<tr>
<td>SIPN3</td>
<td>-23.5</td>
<td>1.335</td>
<td>0.101</td>
</tr>
<tr>
<td>SIPN4</td>
<td>-21.3</td>
<td>1.290</td>
<td>0.131</td>
</tr>
<tr>
<td>SIPN5</td>
<td>-15.7</td>
<td>1.172</td>
<td>0.210</td>
</tr>
</tbody>
</table>

Objective 2. Selection criteria establishment for the studied multicomponent polymeric systems, considering specific applications
2.1. Investigations on the effects of immobilized dyes on polymeric substrates in correlation with physical and chemical properties

The influence of UV irradiation time and dose on the interaction of the cellulose substrate (cotton) and 4 different reactive azo-triazine structures with the following commercial names: Reactive Yellow 143 (RY-143), Reactive Orange 13 (RO-13), Reactive Red 183 (RR-183), Reactive Red 2 (RR-2) was studied. These dyes possess the capacity to covalently bond to the textile substrate through stable etheric and/or sulphonic bonds. Fig. 8 shows the modification in VIS absorbance spectra of the studies dyes after 200h irradiation time. Studies have demonstrated that UV irradiation affects, depending on the dose, both dye chemical structure, leading to material colour modification, and that of the textile substrate resulting in dye detachment (Fig. 9) together with glucose units, offering the possibility of the latter to be solved by human perspiration, thus producing adverse irritable effects on skin.
2.2. Testing of the multicomponent polymeric systems

Multicomponent polymeric systems based on biopolymeric matrix of plasticized starch (S) and filler materials which include lignocellulosic fibres (fine beechwood sawdust - BS, firtree needles - FTN) and lignin extracted from the beechwood sawdust (BL) with different concentrations (15%, 30% and 45%). The structure and properties of these materials were investigated via spectroscopy techniques (FTIR, SEM), X-ray diffraction (XRD) and simultaneous thermal analysis (TG/DTG/DTA) and through determination of surface characteristics (resistance to humidity, transparency). Evaluation of optical properties (transparency/opacity) for the obtained systems is shown in Fig. 10.

Table 2 shows the results of humidity resistance tests of the multicomponent polymer systems.

<table>
<thead>
<tr>
<th>System/ Absorption</th>
<th>Immersion time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5h</td>
</tr>
<tr>
<td>$</td>
<td>52.70</td>
</tr>
<tr>
<td>$/FTN15</td>
<td>49.51</td>
</tr>
<tr>
<td>$/FTN30</td>
<td>45.01</td>
</tr>
<tr>
<td>$/FTN45</td>
<td>44.24</td>
</tr>
<tr>
<td>$/BL15</td>
<td>41.61</td>
</tr>
<tr>
<td>$/BL30</td>
<td>38.88</td>
</tr>
<tr>
<td>$/BL45</td>
<td>45.98</td>
</tr>
<tr>
<td>$/BS15</td>
<td>41.61</td>
</tr>
<tr>
<td>$/BS30</td>
<td>38.88</td>
</tr>
<tr>
<td>$/BS45</td>
<td>45.98</td>
</tr>
</tbody>
</table>

The presence of vegetable filling materials in the plasticized starch polymer matrix determines a slight increase in humidity resistance and may improve the application possibilities of these materials. This behavior is due to the presence of interactions consisting in hydrogen bonding formation between the starch polymer matrix, the structural crystalline part of wood (beechwood sawdust) and the firtree needles (which possess cellulose in their chemical composition).

2.3. Investigations of life cycle assessment (lifetime prediction) for the studied polymeric systems

For the estimation of lifetime of the SIPNs, the samples were aged under controlled conditions by exposure to UV irradiation at different temperatures (40°C, 70°C, 100°C and 130°C). A simplified form of the Arrhenius equation was used, based on the time-temperature relationship (Eq. 11), in which $t$ is the lifetime, $t_0$ is pre-exponential factor, $T$ is aging temperature, $E$ is activation energy and $R$ is the gases constant (8.314 J·K$^{-1}$·mol$^{-1}$).

$$ t = t_0 e^{rac{E}{R T}} $$  \hspace{1cm} \text{Eq. 11}$$

The period corresponding to an increase in colour difference ($\Delta E$) from 0 to 5, when the modification becomes visible by the human eye, was taken into account. Parameters calculated with Eq. 11 are shown in Table 3.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$E$ ,(kJ mol$^{-1}$)</th>
<th>$\ln t_0$</th>
<th>$t$ at 25°C ,(h)</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIPN1</td>
<td>19</td>
<td>-3.987</td>
<td>39</td>
<td>0.949</td>
</tr>
<tr>
<td>SIPN2</td>
<td>38</td>
<td>-9.580</td>
<td>308</td>
<td>0.861</td>
</tr>
<tr>
<td>SIPN3</td>
<td>67</td>
<td>-19.514</td>
<td>1568</td>
<td>0.954</td>
</tr>
<tr>
<td>SIPN4</td>
<td>19</td>
<td>-3.955</td>
<td>127</td>
<td>0.837</td>
</tr>
<tr>
<td>SIPN5</td>
<td>29</td>
<td>-7.110</td>
<td>116</td>
<td>0.954</td>
</tr>
</tbody>
</table>

Objective 3. Insurance of the project implementation framework. Improving the implementation process

3.1. Completing the project database

Project database has been updated and can be found at: http://www.icmpp.ro/mcps/ro/
3.2. Dissemination of the results

Scientific papers: 7


2. Multicomponent bio-based polymer systems comprising starch and wood polymers-structure and thermal behavior; C.-A. Teaca, R. Bodirlau, D. Rosu, L. Rosu, C.-D. Varganici; J. Biobased Mater. Bioenergy, 8(2), 253-260 (2014); IF=0.536; SI=0,761

3. A new way to synthesize of poly(urethane-imide)s based on nitoethyl carbamate intermediary; C. Gaina, O. Ursache, V. Gaina, C.-D. Varganici; Polym.-Plastics Technol. Eng., 53(11) 1160-1168; (2014); IF=1.481; SI=0,555


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

8th International Conference on Modification Degradation and Stabilization of Polymers – MoDeSt 2014, 31 August – 4 September 2014, Portorož (Slovenia)

1. Accelerated photoaging of dyed textiles; D. Rosu, C.–D. Varganici, L. Rosu (COMMUNICATION)

2. On the thermal stability of poly(vinyl alcohol) and cellulose based cryogels; C.–D.Varganici, D. Rosu, O.M. Mocanu (Paduraru), L.Rosu

COMMUNICATION

3. On the photodegradation of poly(vinyl alcohol) and cellulose based cryogels; L.Rosu, C.–D.Varganici, O.M. Mocanu (Paduraru), E. Marlica

POSTER

4. Curing reactions of epoxidized methyl esters of corn oil and thermal characterization of the obtained crosslinked products; F.Mustata, E. Marlica, N. Tudorachi, I. Bicu, C.-D. Varganici


POSTER

6. Investigation of structural changes occurred in wood due to chemical treatment; C.-A. Teaca, R. Bodirlau, D. Rosu, L. Rosu

POSTER

The 2nd CEEP Workshop on Polymer Science, october 24-25, 2014, Iasi, Romania.


POSTER


9. Wood treatment with vegetable oils and its protective effect under environmental factors action; R. Bodirlau, C.-A. Teaca, E. Marlica, L. Rosu, D. Rosu

POSTER

Other activities:

1. Ph.D. Thesis: Thermal and photochemical stability of multifunctional polymeric materials; October 27 , 2014; Ph.D. Student C.-D. Varganici. Part of this thesis represents results obtained and reported in this project. Distinction: Summa Cum Laude; Qualitative: Excellent

2. Book Chapter: Thermal degradation of thermosetting blends; authors: D. Rosu, C.-D. Varganici, L. Rosu, O.-M. Mocanu (Paduraru); In: Thermal Degradation of Polymer Blends, Composites and Nanocomposites; Publisher: Springer-Verlag (2015). Accepted

3. Book Chapter: Multi-component polymer composite systems using polymer matrices from sustainable renewable sources; authors: C.-A. Teaca, R. Bodirlau; In: Eco-friendly Polymer Nano-composites: Processing and Properties; Publisher: Springer-Verlag (2015); Accepted

3.3. 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 2014 (scientific, financial)

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 2014.

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

Project director,

Dr. Dan Rosu

[Signature]