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EXPLORATORY RESEARCH PROJECT

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POLYMER MATERIALS WITH SMART PROPERTIES

- 2014 -

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BRIEF REPORT

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

Objective: Physical and chemical gels from natural and synthetic polymers

Associated Activities:

1. Description of viscoelastic behaviour near the gelation point; investigation of the sol-gel transition
2. Gels based on natural polymer/synthetic polymer/clay mixtures. Preparation and investigation of their properties
3. The effect of copolymer composition and solvent quality on the thermodynamic properties in perturbed and unperturbed state

Introduction

Polysaccharides are macromolecular compounds, generally water soluble, with a large variety of structures and chain conformations in solutions, from flexible random coils (pullulan) to semi-flexible chains (chitosan) or stiff helical chains (xanthan) which provide remarkable physico-chemical and biological properties (biocompatibility, biodegradability and bioadhesivity) [Brunchi et al., *Coll Surf B*, **122**, 512–519, 2014]. The lack of toxicity makes them extremely attractive for various applications in medicine, pharmacy [Morariu et al. *Polym Bull* 2014], food, cosmetics [Bercea et al., *Int J Polym Mater Polym Biomater*, 2014], etc. In recent years, hydrogels have been extensively studied due to their unique properties.

In order to obtain a hydrogel from a homogeneous polymer solution, it is necessary to create some links between different macromolecular chains and to develop a three-dimensional network by chemical or physical methods. Chemical crosslinking is performed in the presence of bifunctional crosslinking agents who are toxic in most cases (e.g. epichlorohydrin, diisocyanates), so other procedures are required.

Many efforts are made to obtain the physical network by creating specific environment (pH, composition, etc.) and thermodynamic conditions (temperature, solvent quality) favorable for intermolecular interactions, able to determine the formation of aggregates, clusters and finally hydrogels. In the most cases, the physical network formation is reversible when the conditions that led to their formation are changed [Morariu et al. *Polym Bull* 2014; Bercea et al., *Polym Plast Technol Eng* 53, 1354-1361, 2014], unlike those chemicals that are irreversible, but can respond in a specific manner to external stimuli [Bercea et al., *Int J Polym Mater Polym Biomater*, 2014].

Hydrogels based on natural or biocompatible polymers are used most often in the controlled drugs release, proteins release, but they present also a high interest for tissue engineering and regenerative medicine. Injectable hydrogels are particularly advantageous for biomedical applications because it can fill any form or defect can be easily combined with cells and they do not require a complicated surgical procedure. If they are biodegradable, surgery is not required for removing them. In-situ formed hydrogels are suitable for such applications, especially if they have elastic properties similar to those of tissues. Investigations carried out by

project team revealed "smart properties" of polymer materials (formation of macromolecular networks thermoreversible or pH sensitive) that occurs under conditions close to those of their use. We present here some results reported in 2014.

Experimental Part

Materials: **Poly(vinyl alcohol)** (PVA, Aldrich and Loba); **Chitosan** (CS, Aldrich); **Xanthan** (Aldrich); **Pluronic F127** (PL, BASF); **Poly(aspartic acid)** (PAS, synthesized by Dr. A. Chiriac); **Poly(ethylene oxide)** (PEO, Fluka); **Laponite RD** (LRD, Rockwood Additives Limited U.K.); **layered double hydroxides** (LDH - Mg/Al, prepared by PhD student E.L. Bibire).

Methods: **Capillary viscometer** Lauda; stress control **rheometer** Bohlin CVO (Malvern); strain controlled **rheometer** MCR 302 (Anton Paar); **Zetasizer Nano-ZS** (Malvern Instruments); HACH 2100AN **turbidimeter**. **SAXS** - system Nanostar U-Bruker; **membrane osmometer** Osmomat 90.

1. Description of viscoelastic behaviour near the gelation point; investigation of the sol-gel transition

We investigated the conditions in which polysaccharide containing systems form hydrogels. One polymer of interest was xanthan for which a double-helix structure was evidenced in aqueous solutions, depending on temperature and salinity conditions. Firstly, dilute solutions were investigated in order to understand its specific behaviour. It has been shown that, at room temperature, the xanthan backbone in aqueous solutions is disordered and highly extended due to the electrostatic repulsions exhibited between charged groups that belong to the side chains [Rocheffort and Middleman, *J Rheol*, 31, 337-369, 1987]. The high extended structure favors the hydrogen bonding and a randomly broken helix is formed. As the temperature increases a transition to coil conformation occurs and the macromolecules are dissociated.

At 25°C, in the presence of salts, the side chains collapse down onto the backbone due to charge screening effects and a disorder–order transition take place when the macromolecules tend to adopt a stable helical conformation. These conformational changes are reflected in rheological and hydrodynamic properties of xanthan chains in solution (Figure 1) [Brunchi et al., *Coll Surf B*, **122**, 512–519, 2014], and their understanding could be very useful in selection of the conditions of aggregation and network formation.

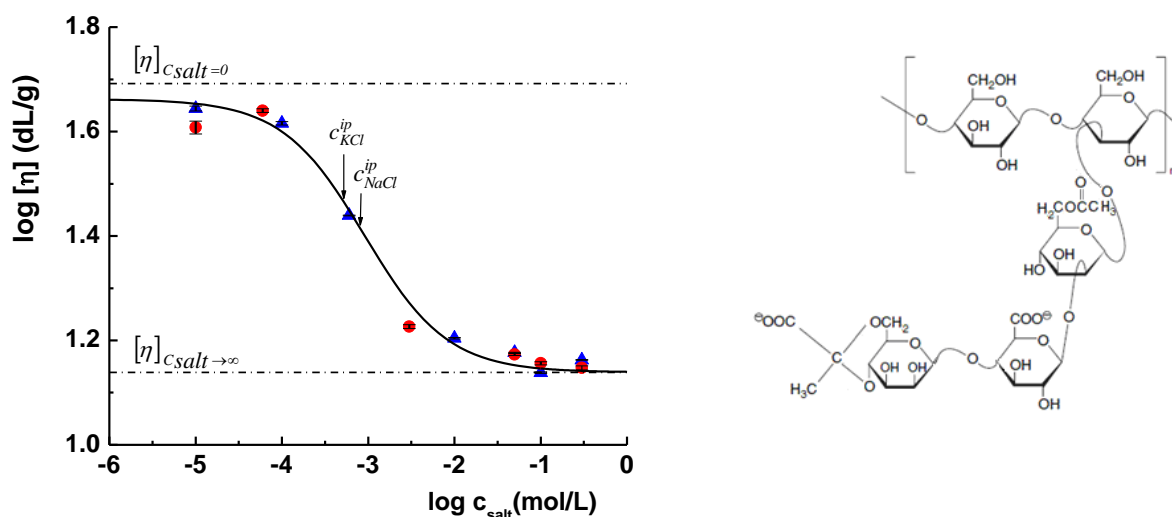


Figure 1. Plot of intrinsic viscosity $[\eta]$ as a function of salt concentration c_{salt} : **NaCl** (triangle), **KCl** (circle), for aqueous xanthan solutions at 25°C [Brunchi et al., *Coll Surf B*, **122**, 512–519, 2014].

The peculiar properties of xanthan are due to its physico-chemical structure, on one hand, and on thermodynamic conditions, on the other hand and they can be they key in designing physical hydrogels. For this purpose, we prepared homogeneous solutions and we investigated them in different conditions of concentration, temperature/thermal history, ionic strength. In Figure 2 we present some results obtained for a semidilute solution of xanthan in frequency sweep experiments at different temperatures and thermal histories.

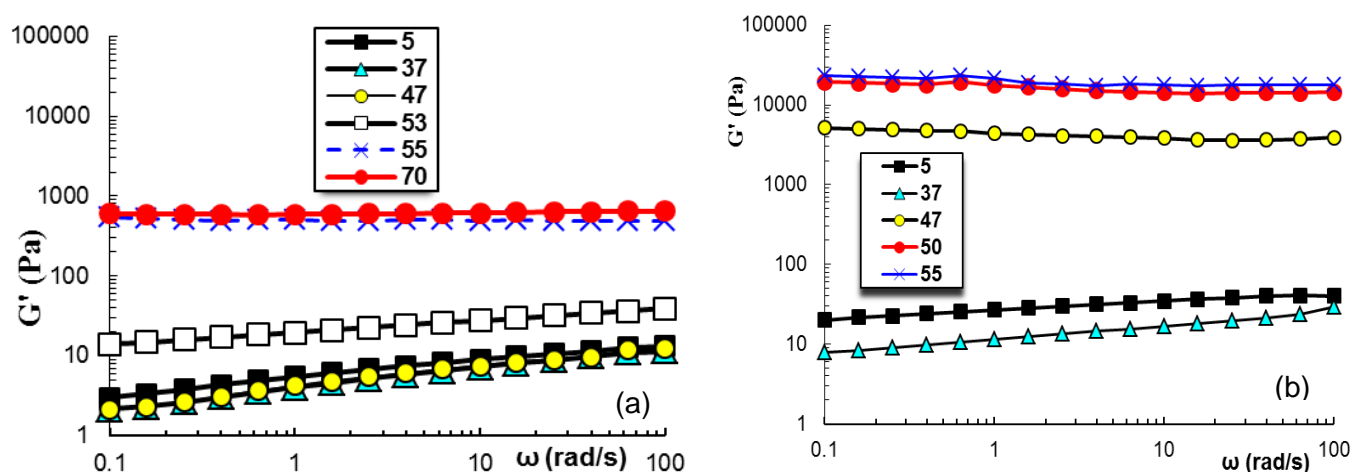


Figure 2. The storage modulus (G') as a function of oscillation frequency (ω) for a semidilute solution of xanthan (a) no thermal history; (b) after a thermal treatment.

An extensive study concerning physical gelation was carried out *in-situ* in the rheometer on CH/PVA mixtures for different thermal histories. For low polymer concentration, a liquid-like behaviour was depicted, whereas for enough high polymer concentration a sol-gel transition can occur.

The gelation temperature interval can be obtained as a function of the practical interest by changing the polymer composition, ionic strength and thermal treatment (Figure 3) [Morariu et al., *Polym Bull*, 2014].

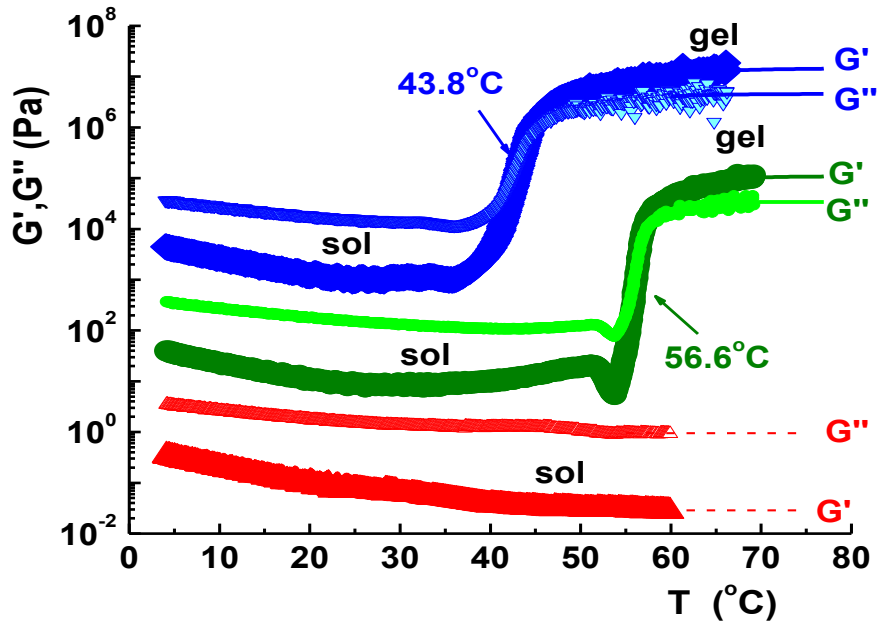


Figure 3. Viscoelastic behaviour as a function of temperature for CH/PVA mixtures with different thermal histories [Morariu et al., *Polym Bull*, 2014].

2. Gels based on natural polymer/synthetic polymer/clay mixtures. Preparation and investigation of their properties

CH, PVA and PEO were selected to prepare hybrid materials based on natural polymer/synthetic polymer/clay mixtures and the obtained materials were tested in order to achieve properties required in targeted applications. Two strategies were adopted:

- chemical gelation of CH/PVA/LDH mixtures and investigation of pH influence of their properties;
 - physical gelation of CH/PEO/argila/LRD mixtures and investigation of rheological and structural properties.
- Firstly, we studied the interactions between the polymers in the absence of clay by viscometry and the experimental data were interpreted by using the following equations:

$$\text{Huggins: } \frac{\eta_{sp}}{c} = [\eta]_H + k_H \cdot [\eta]_H^2 \cdot c \quad (1)$$

$$\text{Wolf: } \ln \eta_r = \frac{c[\eta]_w + Bc^2[\eta]_w[\eta]^*}{1 + Bc[\eta]_w} \quad (2)$$

η_{sp}/c = reduced viscosity; c = concentration of polymer mixture; $[\eta]$ = intrinsic viscosity; η_r = relative viscosity; k_H and B = hydrodynamic interaction parameters; $[\eta]^*$ = characteristic specific hydrodynamic volume.

The experimental results obtained for CH/PVA mixtures were well fitted with Wolf model, as can be observed in the example given in Figure 4.

The formation of intermolecular interaction between CH and PVA is influenced by polymer composition, solution pH, and PVA molecular weight [Bercea et al., *Int J Polym Mat Polym Biomat*, 2014; Morariu et al., *Polym Bull*, 2014].

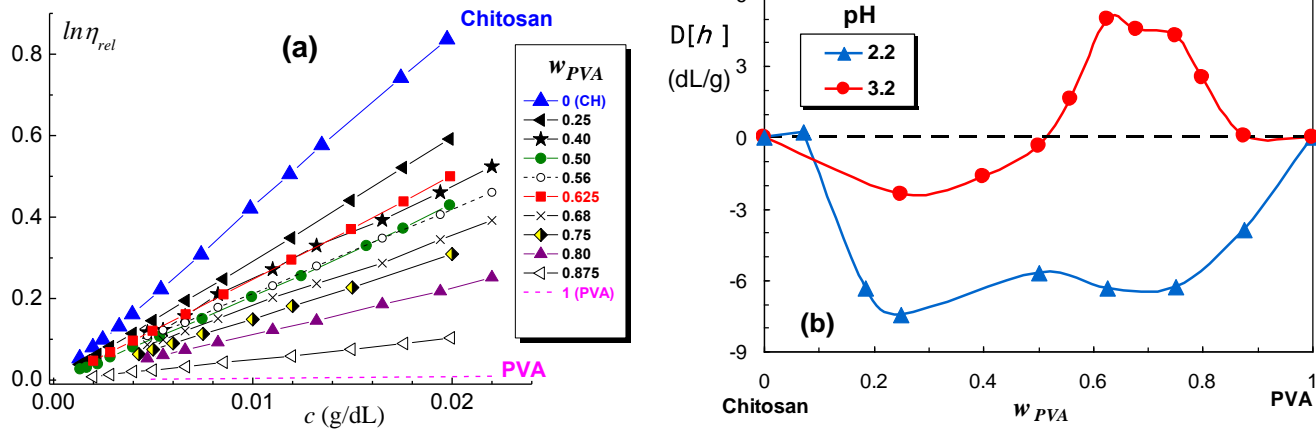


Figure 4. Plots of (a) $\ln \eta_r = f(c)$ (equation (2), pH = 3.2) and (b) $\Delta[\eta] = [\eta]_w - [\eta]_{add} = f(w_{PVA})$ for CH/PVA mixtures, M_w (PVA) = 7.6×10^4 g/mol at 37°C [Bercea et al., *Int J Polym Mat Polym Biomat*, 2014].

The conclusions resulted from viscometric investigations were considered in designing physical and chemical hydrogels from CH/PVA mixture in a LDH matrix. For this study, we present some results obtained for chemical crosslinked systems which showed a solid-like behaviour in oscillatory measurements for pH values between 3 and 7.5 (Figure 5). For pH = 5.5 a maximum value of viscoelastic moduli and swelling degree was observed. This pH-dependent behaviour is the result of two opposite tendencies of hydrogel components: the ability of chitosan to swell at low pH value of the medium, on one hand, and the efficiency of clay to form network at high pH values, on the other hand. For pH < 3 or pH > 7.5 the CH/PVA/LDH mixtures in the presence of the crosslinker collapse and tend to precipitate and hydrogels were not formed [Bercea et al., *Int J Polym Mat Polym Biomat*, 2014].

In creep-recovery tests, a constant shear stress (τ) was applied for a given period of time and then the deformation or compliance were followed when the external force was removed. A high elastic recovery was observed at pH = 5.5 when the degree of recovered strain (γ_{rec}) is around 90% from the maximum value reached by the strain in the creep test (Figure 6). Below shear stress of 50 Pa there is not pH influence in recovery degree; for $\tau > 50$ Pa, γ_{rec} decreases dramatically to approx. 20% at low pH value [Bercea et al., *Int J Polym Mat Polym Biomat*, 2014].

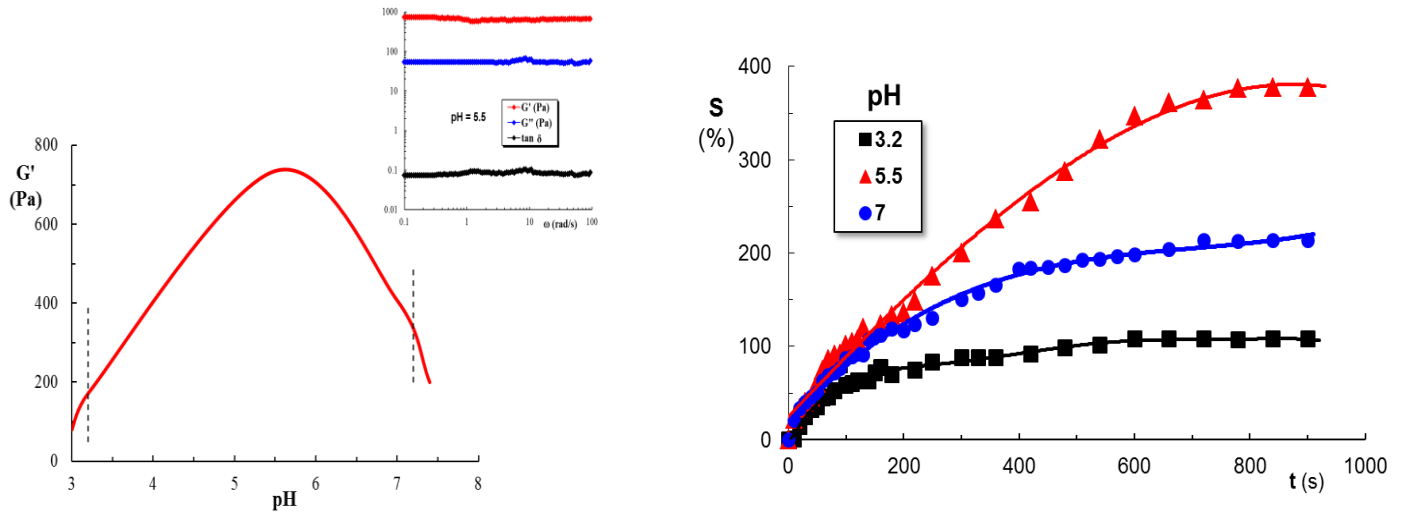


Figure 5. pH influence on viscoelastic parameters and swelling behaviour for chitosan/PVA/LDH [Bercea et al., *Int J Polym Mat Polym Biomat*, 2014].

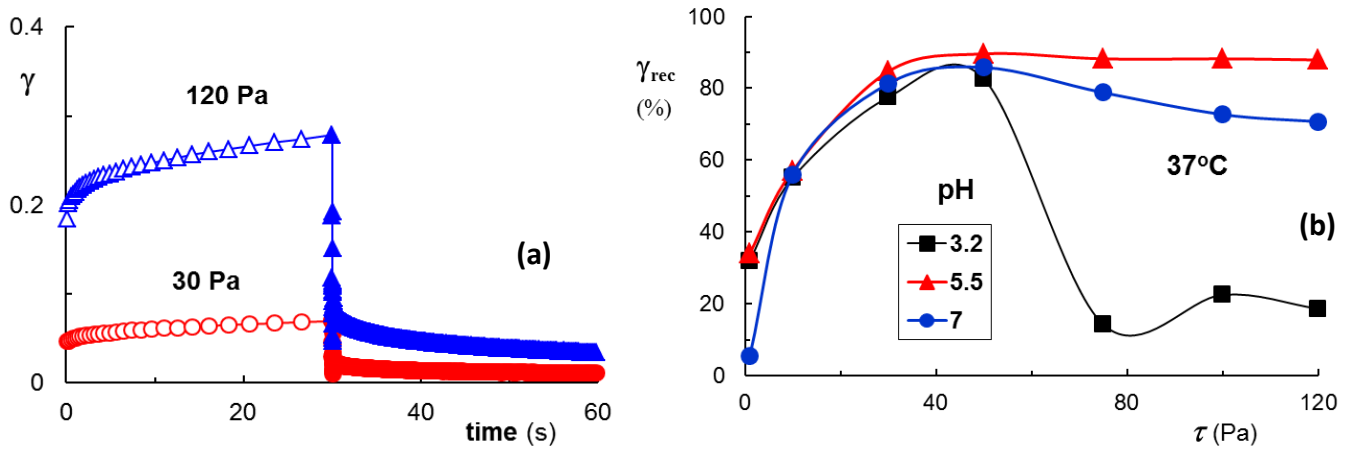


Figure 6. (a) Creep (30Pa and 120Pa) and recovery curves for chitosan/PVA/LDH at pH = 5.5; (b) $\gamma_{rec} - (\tau)$ for different pH values [Bercea et al., *Int J Polym Mat Polym Biomat*, 2014].

For CH/PEO/LRD hydrogels, the chitosan concentration significantly influences the creep-recovery behaviour as well as other rheological parameters (yield stress, shear viscosity), as it was reported in 2013. For this step, electrokinetic and SAXS investigations were carried out and the results were presented in a recently published paper [Morariu et al., *Ind Eng Chem Res* 53(35), 13690-13698, 2014].

SAXS technique was used to determine the size and shape of nano-scale structures, to investigate their tendency to aggregate to submit phase changes and provided structural information. The scattered intensity as a result of interactions between sample and beam can be written as:

$$I(q) = k \cdot S(q) \cdot P(q) \quad (3)$$

where q is the scattering vector, k is a constant, $S(q)$ represents the static structure factor and $P(q)$ describes the form factor.

The length of the scattering vector is given by $q = 4\pi \sin(\theta) / \lambda$ where λ is the scattering wavelength and θ is half of scattering angle. The static structure factor, $S(q)$, is used to determine the overall organization within sample, and the form factor, $P(q)$, depends only on the size and shape of scattering components. In SAXS investigations, intensity from fractal objects can be written by the following simple power-law:

$$I(q) = I_0 \cdot q^{-\alpha} \quad (4)$$

α value can be obtained from the slope of a log-log plot of $I(q)$ versus q and it is related to the fractal dimension (denoted by D) in the gel network.

Figure 7 presents the dependences obtained for 2,8%LRD, 2,8%LRD/2,8%PEO and 2,8%LRD/2,8%PEO/0,007%CS samples, one day after preparation. SAXS measurements were not performed for the samples with higher CS concentrations because the aggregates dimension grows and the sedimentation influences negatively the measurements.

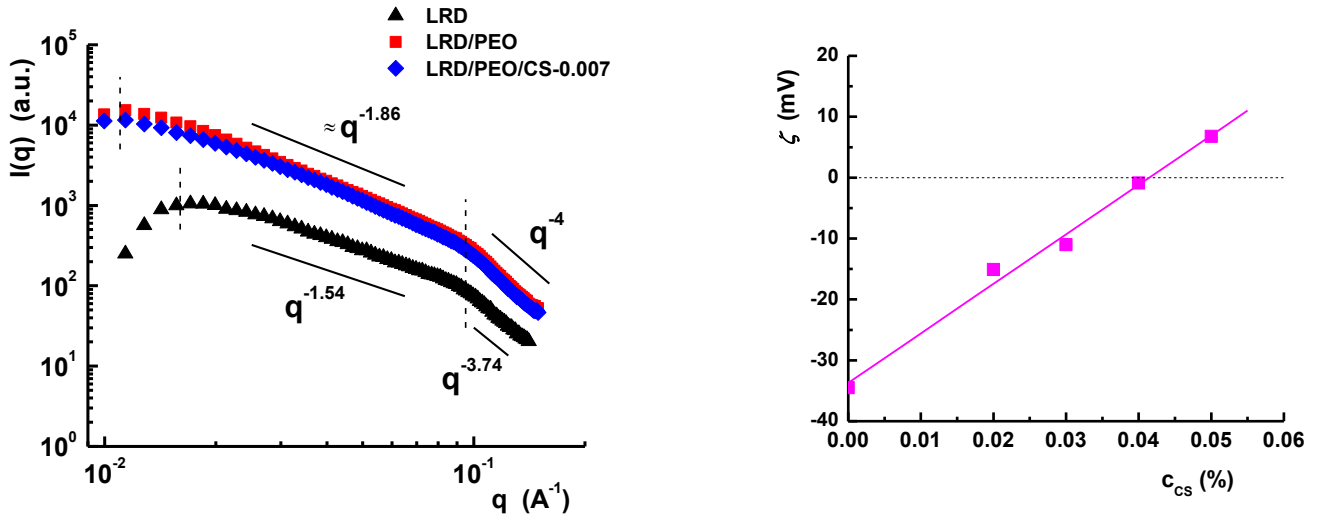


Figure 7. SAXS results for 2,8%LRD, 2,8%LRD/2,8%PEO and 2,8%LRD/2,8%PEO/0,007% and zeta potential (ζ) as a function of chitosan concentration [Morariu et al., *Ind Eng Chem Res* 53(35), 13690-13698, 2014].

SAXS scattering curves show three q domains delimited by changes of $I(q) = f(q)$ at $q = 0.016 \text{ \AA}^{-1}$ (LRD) or $q = 0.011 \text{ \AA}^{-1}$ (LRD/PEO and LRD/PEO/CS-0.007) and $q = 0.095 \text{ \AA}^{-1}$. For LRD hydrogel appears a pronounced decrease of $I(q)$ at low q values which is attributed to the interference effect between the electric double-layers surrounding the Laponite RD discs. In the mid- q region, $I(q) \sim q^{-1.54}$ which indicates the presence of the clay platelets stacks proving that the clay is not fully exfoliated. A power law dependence of $I(q) \sim q^{-3.74}$ was evidenced at high q values for clay hydrogel in the absence of polymer. LRD hydrogel presents a fractal structure with the mass and surface fractal dimensions of 1.54 and 2.26, respectively.

The addition of PEO into a LRD hydrogel with high clay concentration can cause the increase or decrease of the rheological parameters depending of the molecular weight or the concentration of the polymer in the system. In the present study, the addition of PEO promotes the formation of larger clusters with low mass density causing the decrease of the rheological parameters (η , G' , G''). The PEO concentration (2.8%) is higher than the concentration necessary to cover completely the surface of the clay platelets and the presence of free PEO chains in aqueous dispersion could be responsible for the diminishing of the rheological parameters as compared with those of LRD hydrogel. Moreover, the short PEO chains were not able to form clay interparticles bridges.

By introducing into LRD/PEO hydrogel, interactions between the positive charges of CS chains and the negative ones existing on the surface of the clay platelets occurs. Also, the formation of the hydrogen bonds between PEO and CS chains, on the other hand.

The interactions between clay platelets and CS chains were evidenced by electrokinetic measurements which showed a decrease of zeta potential (ζ) by increasing the CS concentration (Figure 7). ζ is -68 mV for LRD hydrogel indicating that the dispersion has a very good stability. By addition of PEO, ζ becomes -34.50 mV suggesting the screening of the clay surface due to the adsorption of polymer chains. The CS addition determines a change of zeta potential from -34.50 mV for LRD/PEO hydrogel to 6.80 mV for the hydrogel with 0.050% CS, the dependence between ζ and chitosan concentration being linear. The isoelectric point was established for 0.0415% chitosan added to 2,8%LRD/2,8PEO hydrogel. According to SAXS investigations, the maximum aggregates size is of 357 Å for 2,8%LRD/2,8PEO and 390 Å for 2,8%LRD/2,8%PEO/0,007%CS.

The dependence observed in the mid- q region, $I(q) \sim q^{-1.86}$, indicates that the hydrogels with polymer have an exfoliation degree higher than that from LRD hydrogels.

The structure of polymer/clay hybrid hydrogels (2,8%LRD/2,8%PEO and 2,8%LRD/2,8%PEO/0,007%) consists of the agglomerates having a smooth surface with clay platelets wrapped by PEO and CS chains. CS chains are interconnected between the clay platelets which are covered by PEO short chains [Morariu et al., *Ind Eng Chem Res* 53(35), 13690-13698, 2014].

3. The effect of copolymer composition and solvent quality on the thermodynamic properties in perturbed and unperturbed state

A copolymer of high interest for designing smart materials is the triblock linear copolymer consisting of poly(ethylene oxide) (PEO) blocks (70%) and poly(propylene oxide) (PPO) blocks (30%) known as Pluronic F127. Above a certain concentration, aqueous solutions of Pluronic F127 undergo a fully reversible sol-gel transition as a function of temperature. This transition can be exploited for applications in which the solution is injected into a being in the sol state and become a gel at body temperature. In aqueous solution,

the macromolecules associate and form micelles and further increase in concentration the micelles generate supramolecular structures which evolves into networks (Figure 8) [Bercea, Morariu et al., *Polym Plast Technol Eng* 53, 1354-1361, 2014].

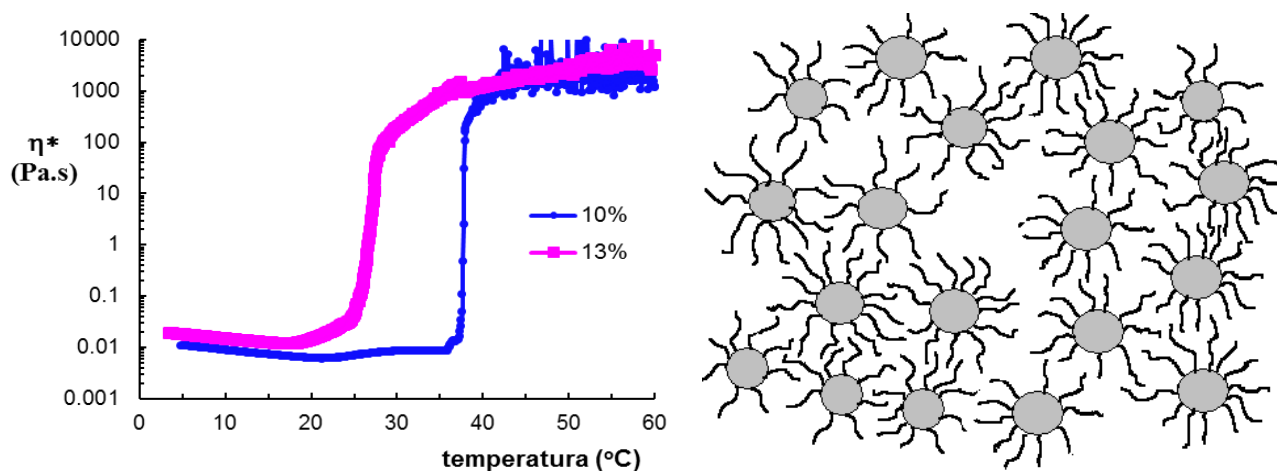


Figure 8. Illustration of the gelation for Pluronic F127 solutions at increasing the temperature.

For understanding the thermodynamic behaviour of this copolymer, we used the viscometric results obtained in dilute aqueous solutions at different temperatures. Figure 9 presents the intrinsic viscosity at different temperatures, values resulted by using equation (2) to model the experimental data obtained at different concentrations of copolymer $\text{PEO}_{99}\text{-}b\text{-PPO}_{69}\text{-}b\text{-PEO}_{99}$ (PL).

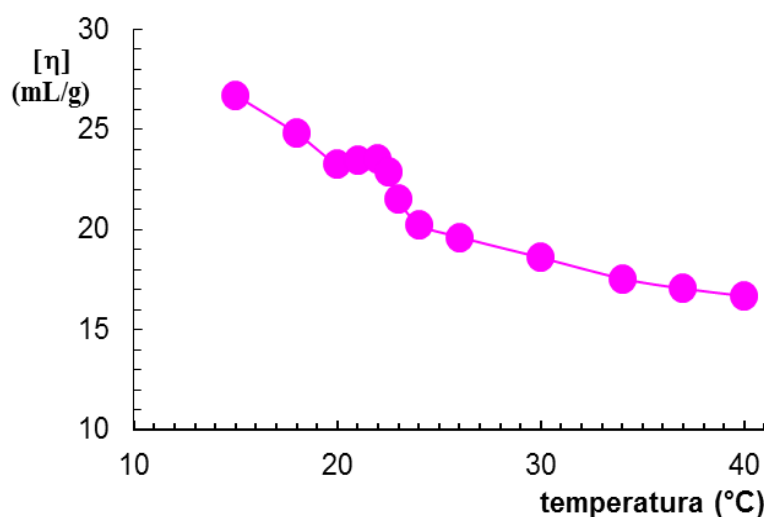


Figure 9. intrinsic viscosity as a function of temperature for Pluronic F127 aqueous solutions.

An interpretation of $[\eta]$ – temperature dependence on the basis of the excluded volume analysis allows the discussion of the solvent quality as a function of the temperature and the evaluation of theta temperature (Θ) of copolymers. The viscosity–temperature behaviour of copolymer solutions depends on the chemical structure of the copolymer and on the change of the physical interactions under the influence of both temperature and comonomer nature [Bercea si Morariu, *Rev Roum Chim* 51(1), 31-37 2006]:

$$\left\{ T \left[\left(\frac{d \ln [\eta]_T}{dT} - \delta \right) \left(\frac{\kappa}{\gamma} \right) - \varepsilon + \delta \right] \right\}^{-1} = \frac{T}{\Theta} - 1 \quad (5)$$

where: $\frac{d \ln [\eta]_T}{dT} = \frac{3}{2} \times \frac{d \ln \langle r_o^2 \rangle}{dT} + \frac{\varepsilon}{\kappa} \times \frac{d \ln z}{dT} = \delta + \gamma \frac{d \ln \alpha}{dT}$;

$$\kappa = \frac{d \ln f(\alpha)}{d \ln \alpha};$$

$$\frac{\langle r_o^2 \rangle}{M} = \left(\frac{K_\theta}{\phi_o} \right)^{2/3};$$

$$\delta = \frac{d \ln K_{\theta,T}}{dT}$$

with $\phi_o = 2.51 \cdot 10^{23} \text{ mol}^{-1}$ for $[\eta]$ expressed in mL/g, α is the viscometric expansion factor:

$$\alpha = \left(\frac{[\eta]_T}{[\eta]_{\theta,T}} \right)^{1/\gamma} \quad (6)$$

and

$$\ln [\eta]_{\theta,T} = \ln [\eta]_{\theta,T_o} + \delta(T - T_o) \quad (7)$$

where $[\eta]_{\theta,T_o}$ and $[\eta]_{\theta,T}$ represent the values of the intrinsic viscosity at T_o and T ; the value $[\eta]_{\theta,T_o}$ is experimentally obtained, and γ is a parameter to which the value 3 was assigned.

In order to discuss $f(\alpha)$ and κ , we applied the Flory theory (equation (8)) and Fixman (equation (9)) and Figure 10 shows the resulted dependences.

$$f(\alpha) = \alpha^5 - \alpha^3 \text{ and } \kappa = \frac{5\alpha^2 - 3}{\alpha^2 - 1} \quad (8)$$

$$f(\alpha) = \alpha^3 - 1 \text{ and } \kappa = \frac{3\alpha^3}{\alpha^3 - 1} \quad (9)$$

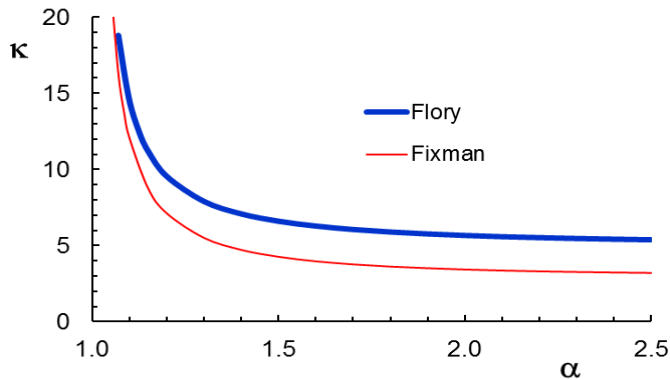


Figure 10. The dependence of the parameter κ on α , according to Flory and Fixman theories.

At low temperatures, the PPO blocks form the "core" of the micelle and PEO blocks form the hydrophilic part located in the outer shell of the micelle (Figure 8). The decrease of the solvent quality with increasing the temperature above 20°C (Figure 11) is attributed to the hydrophobicity of PPO blocks.

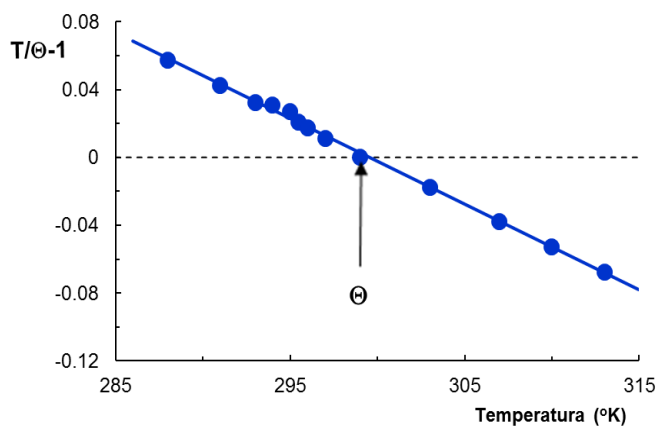


Figure 11. $(T/\Theta-1)$ as a function of T according to equation (5) for aqueous solutions of PL.

Above Θ , the intermolecular distance decreases due to the increase of the size or the number of micelles, PPO blocks dehydrated and the formation of an extended network occurs. This phenomenon is thermoreversible and rheological investigations evidenced the fast answer of the PL solutions at temperature change. A combination of the spontaneous self-assembling ability of Pluronic F127 in water with the mechanical properties of PVA, hydrogels with high elasticity and thermoresponsive behavior can be designed [Bercea, Morariu, et al., *Polym Plast Technol Eng* 53, 1354-1361, 2014]. These extraordinary properties can be used in the elaboration of materials used as drug release systems, as for example thermosensitive nanocarriers. The practical interest for such drug carriers is to be easily obtained, fast and precise in response to the stimuli, especially when an urgent need is required for disease control.

Self-assembling phenomena between Pluronic F127 solutions in the presence of poly(aspartic acid) (PAS) were investigated as a function of pH, temperature and PL/PAS mixture composition. Multifunctional materials can be thus systematically assembled and optimized, even when multiple co-assembling constituents are present, compounds which are also able to be functionalized with ligands or chemical groups either post-assembly or pre-assembly [Nita, Chiriac, Bercea, *Coll Surf B* 119, 47–54, 2014]. PAS is a biodegradable, biocompatible polypeptide and for the present study a sample was synthesized by a team member (Dr. A. Chiriac). Specific intermolecular interactions determine the increase of the macromolecular coils as compared with those of the PL. The complex formed between these two variants of macromolecules is also a system of interest as giving a particular demonstrative example of interaction between a polymer with dissociation capacity and a structure with surfactant ability (Figure 12).

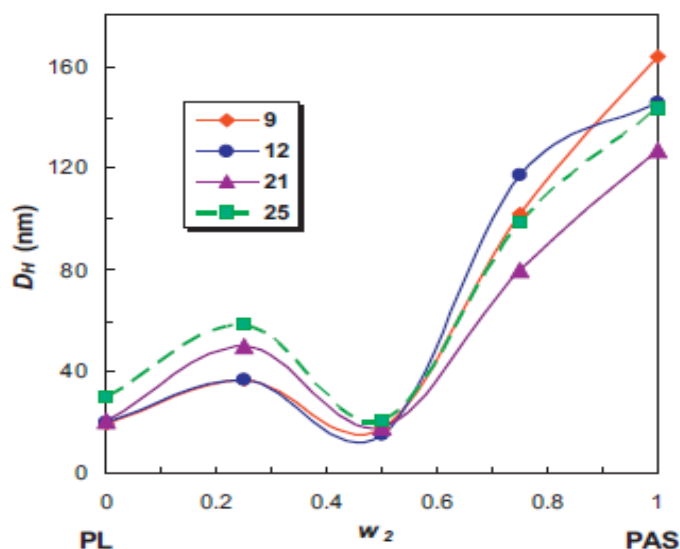


Figure 12. Hydrodynamic diameter (D_H) of macromolecules as a function of PL/PAS mixtures composition at different temperatures [Nita, Chiriac, Bercea, *Coll Surf B* 119, 47–54, 2014].

The PL/PAS mixtures were investigated systematically by using different techniques: viscometry, rheology, light scattering and electrokinetic measurements and favorable interactions were depicted around $w_2 = 0.5$. The intermolecular aggregates are formed through hydrogen bonds between $-\text{COOH}$ and $-\text{NH}_2$ groups from PAS macromolecules and $-\text{O}-$ from PEO blocks (Figure 13).

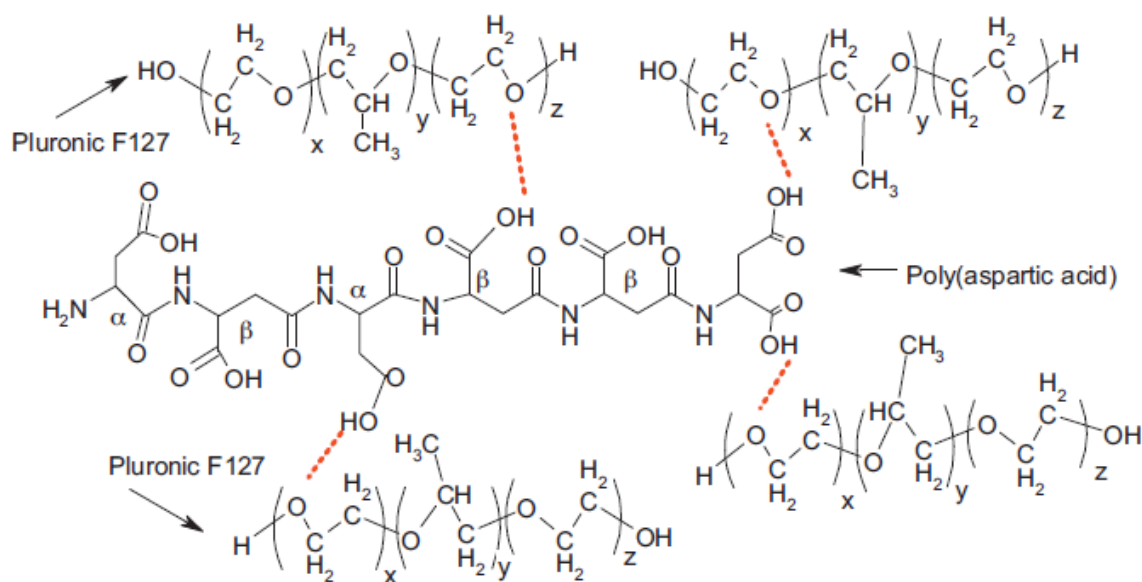


Figure 13. Schematic representation of the hydrogen bonds between PAS and PL.

At the stoichiometric ratio strong interactions between PAS and PL occur and core-shell particles are formed with PL as shell and PAS inside of the micelle. Zeta potential becomes zero for $w_2 = 0.5$ (Figure 14) [Nita, Chiriac, Bercea, *Coll Surf B* 119, 47–54, 2014], showing that there are no charges at the particle surface.

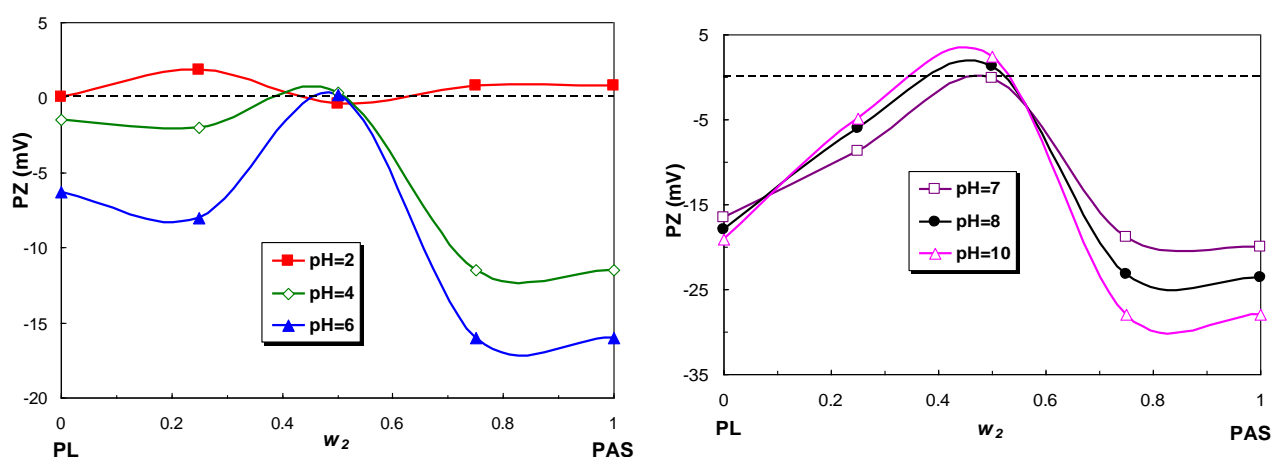


Figure 14. Zeta potential (PZ) as a function of PL/PAS mixtures composition for different pH values of aqueous solutions [Nita, Chiriac, Bercea, *Coll Surf B* 119, 47–54, 2014].

As conclusion, in 2014 the project team investigated different intelligent materials which incorporate either natural polymers (xanthan, chitosan) and/or clays, either biodegradable, biocompatible polymers (Pluronic F127, poly(aspartic acid), poly(vinyl alcohol). The properties of the designed materials were investigated in different conditions of temperature and pH.

All objectives were fully realized and most results were used in manuscripts submitted to publication.

Results dissemination

- 8 papers were elaborated and submitted to journals indexed by web of knowledge (5 published, 1 published on-line, 2 accepted), the total Impact Factor being of 24.313.
- 2 papers accepted in the first number of a new journal: – *Journal of Hydrogels* (American Scientific Publishers)
- The team members participated at scientific events with 3 oral presentations and 3 posters.

Articles published in Journals indexed by Web of Science (Thomson Reuters) with Acknowledgements to UEFISCDI: 8

1. Effect of pH and temperature upon self-assembling process between poly(aspartic acid) and Pluronic F127; L.E. Nita, A.P. Chiriac, M. Bercea; *Colloids and Surfaces B: Biointerfaces*, 119, 47–54 (2014); **FI = 4,287; SI = 1,06991**
2. Intrinsic viscosity and conformational parameters of xanthan in aqueous solutions: Salt addition effect; C.-E. Brunchi, S. Morariu, M. Bercea; *Colloids and Surfaces B: Biointerfaces*, 122, 512-519 (2014); **FI = 4,287; SI = 1,06991**
3. Tailoring of clay/poly(ethylene oxide) hydrogel properties by chitosan incorporation; S. Morariu, M. Bercea; L. Sacarascu; *Industrial & Engineering Chemistry Research*, 53, 13690-13698 (2014); **FI = 2,235; SI = 1,91195**
4. Thermodynamics of copolymer solutions: How the pair of interactions can contribute to the overall effect; M. Bercea, B.A. Wolf; *The Journal of Physical Chemistry B*, 118, 9414-9419 (2014); **FI = 3,607; SI = 1,95448**
5. Investigation of poly(vinyl alcohol)/Pluronic F127 physical gels; M. Bercea, S. Morariu, L.E. Nita, R.N. Darie; *Polymer-Plastics Technology and Engineering*, 53, 1354-1361 (2014); **FI = 1,481; SI = 0,41275**
6. Chitosan/poly(vinyl alcohol)/LDH biocomposites with pH-sensitive properties; M. Bercea, L.E. Bibire, S. Morariu, G. Carja; *International Journal of Polymeric Materials and Polymeric Biomaterials*, xx, 00-00 (2015); **FI = 2,784**
7. Review: Poly(vinylpyrrolidone) – a versatile polymer for biomedical and beyond medical applications; M. Teodorescu, M. Bercea; *Polymer-Plastics Technology and Engineering*, xx, 00-00 (2015); **FI = 1,481; SI = 0,41275**
8. Dependence of Solvent Quality on the Composition of Copolymers: Experiment and Theory for Solutions of P(MMA-*ran*-t-BMA) in Toluene and in Chloroform; M. Bercea, B.A. Wolf; *Soft Matter*, xx, 00-00 (2015); DOI: 10.1039/c4sm02568g; **FI = 4,151; SI = 5.30501**

Participations at scientific events mentioning the projet at section „Acknowledgements”

Oral presentations: 2

The 2nd CEEP Workshop on Polymer Science, Iasi, Romania, 24-25. 10. 2014

1. Thermodynamic aspects concerning the xanthan behavior in dilute solution; C.-E. Brunchi, S. Morariu, M. Bercea
2. Physical hydrogels of poly(vinyl alcohol)/poly(vinylpyrrolidone); M. Teodorescu, M. Bercea, S. Morariu

2nd International Conference on Chemical Engineering “Inovative Materials and Processes”, Iasi, Romania, 5-8 Nov. 2014

3. Hybrid nanoarchitectures based on polymers/layered double hydroxides for applications in innovative technologies; L.E. Bibire, M. Bercea, M. Puscasu, G. Carja

Posters: 3

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

1. Effect of salt and heat treatment on aqueous xanthan solutions; C.-E. Brunchi

EMRS Fall Meeting 2014, Inorganic nanoarchitectonics : from design and fabrication to sustainable solutions, Warsaw, Poland, 15-19ept. 2014

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