# VISCOELASTIC PROPERTIES OF LAPONITE RD DISPERSIONS CONTAINING PEO WITH DIFFERENT MOLECULAR WEIGHTS

Simona MORARIU[*] and Maria BERCEA

"Petru Poni" Institute of Macromolecular Chemistry,
41-A Grigore Ghica Vodă Alley, 700487 Iaşi, Roumania

The effect of poly(ethylene oxide) (PEO) molecular weight on the viscoelastic properties of Laponite RD aqueous dispersion at 25 °C was investigated and discussed. PEO with molecular weight between 0.4×10^3 g/mol and 35×10^3 g/mol was added in concentration of 2% into 2.5% clay aqueous dispersion. The addition of polymer with molecular weight above 4×10^3 g/mol delays the transition from liquid to colloid glass state. It was established that there is a critical molecular weight of added poly(ethylene oxide) which depends on the components concentrations in dispersion from which one chain becomes able to bridge two or more clay particles. The critical PEO molecular weight established by the theoretical calculations considering the molecular weight or the polymer concentration was about 21.45×10^3 g/mol and 25×10^3 g/mol, respectively. The experimental data obtained by rheological measurements were in agreement with theoretical approaches.
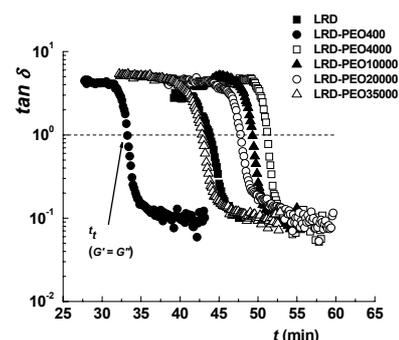
INTRODUCTION

Laponite RD (LRD) has attracted a considerable and growing interest over the past few decades due to its applications in various areas as paints, coatings, cosmetics, pharmaceutical formulations, etc. This synthetic clay can disperse in water as discs with a diameter of 25-30 nm and a thickness of 1 nm having a negative charge on its face and a weakly positive charge on its edge.[1] The manner of the plate-like particles organization in aqueous dispersion is still a matter of debate in the literature. Generally, two competing mechanisms for organization of LRD particles in water are proposed: one assumes a house of cards organization (at low pH) due to direct attractive electrostatic interactions between the oppositely charged edges and faces of the particles and the other considers the electrostatic repulsions

between double layers at high pH.[2-4] LRD aqueous dispersion shows a very complex phase diagram in which it exhibits different ergodic and nonergodic states: sol, liquid, attractive gel, attractive glass, repulsive glass (Wigner glass) and aggregation (phase separation).[5,6] Recently, Ruzicka and Zaccarelli[7] have proposed a phase diagram of LRD aqueous dispersion considering the different experimental and theoretical data reported in literature. Two types of arrested states were distinguished as a result of a spontaneous aging of the LRD dispersion: an equilibrium gel for $1\% \leq c_{clay} < 2\%$ and a Wigner glass for $2\% \leq c_{clay} \leq 3\%$.[8] The rheological parameters of LRD aqueous dispersions which can give useful information concerning the interactions between clay particles are dependent on the clay concentration in dispersion.[9,10]

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[*] Corresponding author: smorariu@icmpp.ro

The addition of a non-ionic polymer such as poly(ethylene oxide) (PEO) to the clay aqueous dispersion modifies significantly its rheological properties as a consequence of the adsorption of polymer chains on the clay particles surface, changing the interactions between clay particles.[11] The polymer chains are adsorbed on the surface of clay platelets forming a layer of polymer with a thickness of 1.5 nm on each face and of 1.5-4.5 nm on edge.[12,13] The associations between PEO chains due to repulsive hydrophobic interactions between the methylene groups and water molecules as well as to attractive hydrogen bonds between the structural units of the polymer and water molecules lead to the formation of the aggregates in aqueous solution.[14] In LRD/PEO aqueous dispersions existing in solid-like state, the clay works as a physical cross-linker for polymer and their viscoelastic properties are dependent on the polymer and clay concentration, temperature or the rest time.[15-18] Recently, some injectable hydrogels based on LRD/PEO aqueous dispersions were developed by addition of a small quantity of chitosan.[19-21] Chitosan confers biocompatibility, biodegradability and non-toxicity to the hydrogels which could be used in medicine.

In the present paper we investigate the effect of addition of poly(ethylene oxide) with different molecular weights on rheological properties of Laponite RD aqueous dispersions.

RESULTS AND DISCUSSION

For the present study, samples containing 2.5% LRD and 2% PEO with the molecular weights between 0.4×10^3 g/mol and 35×10^3 g/mol were prepared (Table 1).

It is well known that LRD aqueous dispersions exhibit an aging phenomenon which implies the transition from an initially liquid state to an arrested state (attractive or repulsive glass) of the LRD dispersion within a time which depends on clay and salt concentrations.[7,18] In order to clarify the use of the term "colloidal glass" instead of "gel" it is necessary to specify that two nonergodic states in colloidal dispersions can be distinguished: colloidal glasses and gels. Both nonergodic states show solid-like properties and present soft elasticity while their structures are different (Fig. 1).

The gel state is obtained for low volume fractions of clay and its structure is characterized as a percolated infinite network (Fig. 1a). The colloidal glass state is obtained for high volume fractions of clay particles and inside of its structure a network was not evidenced (Fig. 1b). The difference between the two solid states is difficult to quantify experimentally. Generally, the transition from liquid to the colloidal glass is called "aging" and that from sol (characterized by the presence of clusters with a finite lifetime) to colloidal gel is called "gelation".

According the literature data, the aqueous dispersions with 2.5% LRD undergo a spontaneous aging leading to repulsive colloidal glass (Wigner glass) formation. This spontaneously aging of LRD aqueous dispersions can be evidenced by rheological measurements following the variation of storage (G') and loss (G'') moduli in time. The crossover of G' and G'' is considered as the point when the system undergoes a transition from a liquid-like to a solid-like behavior. According to the phase diagram, the LRD aqueous dispersion in the absence of salt shows a repulsive (Wigner) glass state in which the long-range electrostatic repulsions dominate.[5] Tanaka *et al*.[6] proposed that the aging process of a Wigner glass can be divided into three regimes: 1) a cage-forming regime; 2) a full-aging regime and 3) a final saturation regime. In the first stage of aging, the effective volume fraction increases very rapidly with time reflecting the increase in the repulsive interaction between particles and a transition from a liquid state to a colloidal glass occurs. In the second stage, a slow rearrangement and diffusion of the particles takes place due to the electrostatic and entopic restrictions.

Table 1

Final viscoelastic parameters[a] of investigated dispersions

Sample[b]	G'_{final} (Pa)	G''_{final} (Pa)	$tan\ \delta$ (G''_{final} / G'_{final})
LRD	247.73	23.60	0.095
LRD-PEO0.4	166.10	16.90	0.102
LRD-PEO4	27.00	2.50	0.093
LRD-PEO10	25.44	2.40	0.094
LRD-PEO20	134.70	11.90	0.088
LRD-PEO35	107.90	9.70	0.090

[a] estimated with eq. (1);
[b] the samples were denoted as LRD-PEOX where X represents the molecular weight of added PEO expressed in Kg/mol.
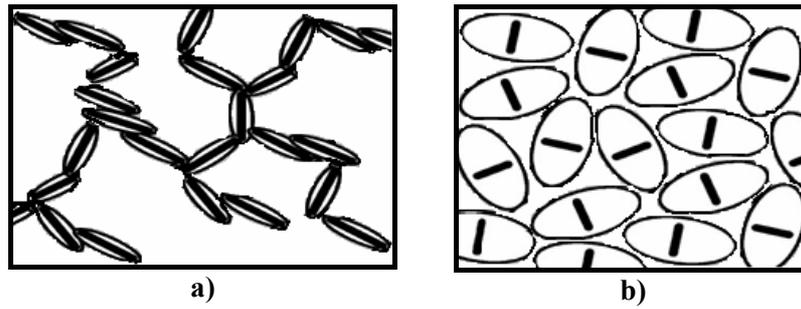
Fig. 1 – Schematic representation of a) the attractive gel and b) the repulsive (Wigner) colloidal glass. The lines represent LRD platelets and the ellipsoid lines show the range of electrostatic repulsions.
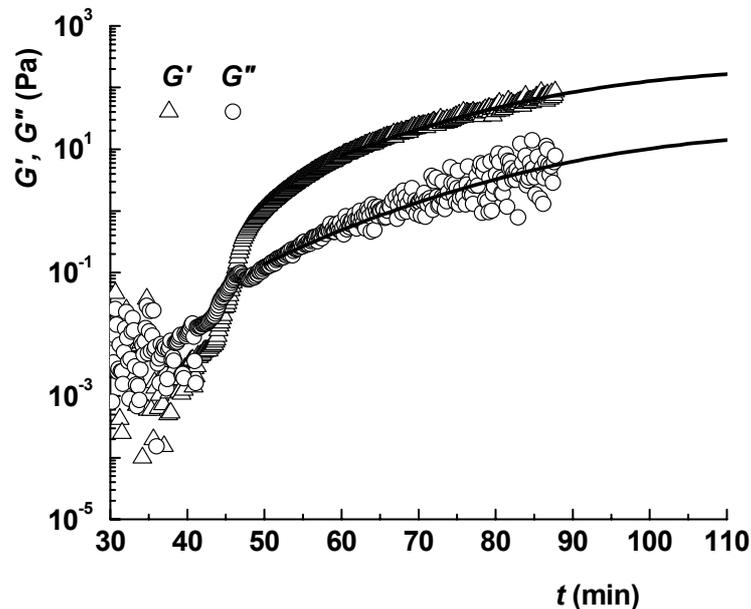

Fig. 2 – Evolution of the storage (*G'*) and loss (*G"*) moduli in time (*t*) for 2.5% LRD dispersion at 25 °C, $\tau = 0.04$ Pa and $\omega = 1$ rad/s. The solid curves were calculated using the Hill equation (eq. (1)).

Fig. 2 illustrates the variation of viscoelastic moduli in time for 2.5% LRD dispersion at 25 °C, a shear stress (τ) and a oscillation frequency (ω) of 0.04 Pa and 1 rad/s, respectively.

In the viscoelastic moduli evolution in time two-steps can be observed: a) the first step when the moduli undergo a rapid rise and b) the second step after the crossing point of *G"* with *G'* when their evolution in time shows more slowly. After about 40 min, *G'* and *G"* start to increase and the LRD dispersion acquires solid-like properties (*G'* > *G"*) after an aging time of 46 min from initial time. The viscoelastic moduli increase slowly above 50 min and they reach the constant values, G'_{final} and G''_{final}, which were calculated by using a modified Hill equation (Microcal Origin version 6.0):[22]

$$G(t) = G_{final}\,\frac{t^n}{t^n + \theta^n} \qquad (1)$$

where *G* represents *G'* or *G"* at time *t*, θ is the time for which $G(\theta) = G_{final}/2$ and *n* is a coefficient relative to the asymptotic slope *P* (in Pa/s) at the time θ by the relationship $P = n \cdot G_{final}/4 \cdot \theta$.

The transition time from liquid to colloidal glass of LRD aqueous dispersion is modified by addition of poly(ethylene oxide) with different molecular weights. The viscoelastic moduli of LRD dispersion containing PEO follow the same evolution in time like LRD dispersion (Fig. 3).
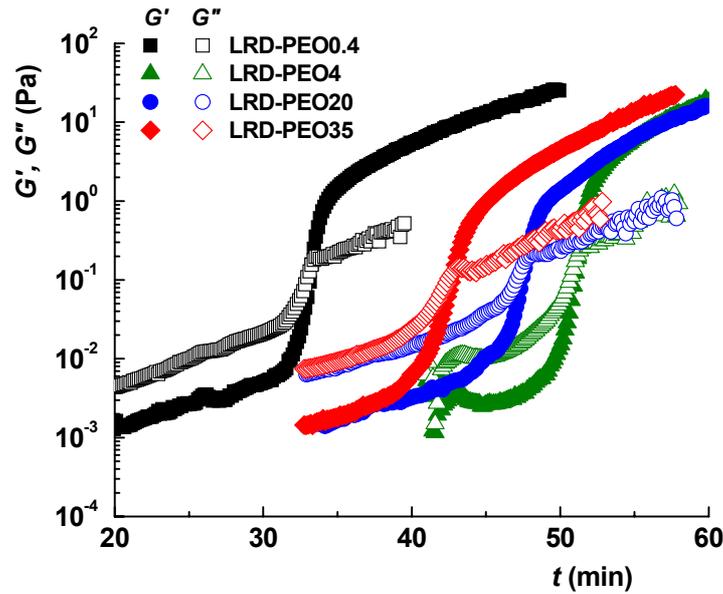
Fig. 3 – Evolution of G' and G'' moduli in time for 2.5% LRD dispersion containing 2% PEO
with different molecular weights at 25 °C, $\tau = 0.04$ Pa and $\omega = 1$ rad/s.
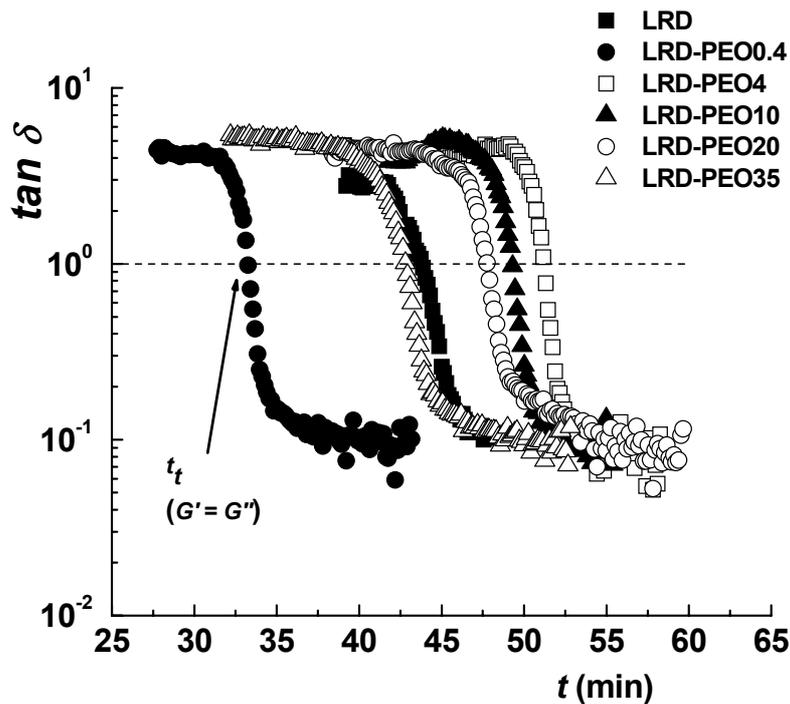

Fig. 4 – Evolution of $tan\ \delta$ in time for 2.5% LRD containing 2% PEO
with different molecular weights at 25 °C, $\tau = 0.04$ Pa and $\omega = 1$ rad/s.

After a period of time, which depends on the molecular weight of added PEO, G' becomes higher than G'' and they tend to constant values which were estimated by fitting the experimental data with Hill equation. G'_{final} and G''_{final} estimated with eq. (1) and $tan\ \delta$ corresponding to these values are shown in Table 1. $tan\ \delta$ was

determined as the ratio between G''_{final} and G'_{final} and the time necessary for the transition from liquid to colloidal glass, t_t, was established as the time corresponding to $G' = G''$ (Fig. 4).

One can observe that the addition of PEO does not change the final $tan\ \delta$ showing that the samples become structured in a similar manner irrespective

of the molecular weight of the added polymer (Table 1 and Fig. 4).

By addition of PEO with very low molecular weight (0.4×10^3 g/mol), the polymer is adsorbed on the surface of clay platelets diminishing the repulsive interactions between them leading to a decrease of aging rate (t_t decreases) (Fig. 5). The addition of PEO with molecular weight above 4×10^3 g/mol causes a slowing of the transition dynamics. The previous rheological investigations showed that the addition of 0.1 g/dL PEO with molecular weight higher than 1×10^3 g/mol into 0.1 g/dL LRD aqueous dispersion in 10 mM NaCl delays the gelation of the clay dispersions.[23] The aggregation of clay platelets in 0.1 g/dL LRD aqueous dispersion in presence of 10 mM NaCl is due to the face-rim attractive interactions. The reduction of the aggregation rate by addition of PEO with molecular weight up to about 1×10^3 g/mol was explained by the increase of the activation energy for face-rim association due to steric hindrance of adsorbed polymers.

The viscoelastic behavior of the investigated dispersions is due to the molecular weight (the chain length), on the one hand, and the polymer concentration which is free in water (non-adsorbed), on the other hand.

In the presence of polymer with high molecular weight, the chains are long enough to form interparticle bridges which increase the elasticity of the system. The mean end-to-end distance of PEO in water, r_o, was calculated and compared with the approximate distance between clay platelets in 2.5% LRD aqueous dispersion in order to investigate the effect of polymer bridging on viscoelastic moduli. r_o values for used PEO samples were calculated by using the relationship given by Swenson $et\ al.$:[24]

$$r_o \approx \sqrt{6}\, R_g \ \ (\text{nm}) \qquad (2)$$

where R_g represents the gyration radius of PEO in water and it was calculated with the following empirical relation:[24]

$$R_g = M^{0.57}/0.45 \ \ (\text{nm}) \qquad (3)$$

The mean end-to-end polymer distances for PEO samples are shown in Table 2.

The approximate distance between clay platelets ($d = 16$ nm) was estimated as the distance between the LRD platelets in the dispersion with 2.5% LRD (46 nm) according to Ramsey and Lindner[25] minus the diameter of the clay particles (30 nm).
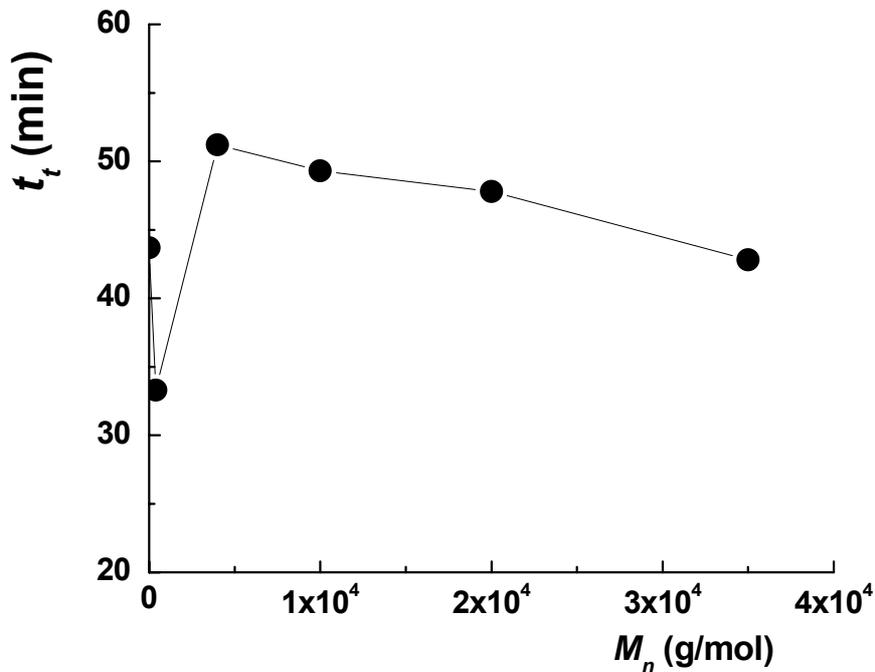

Fig. 5 – Effect of molecular weight of PEO on t_t of the LRD aqueous dispersion.

Table 2

Different parameters calculated for investigated samples

Sample	$r_o{}^a$ (nm)	c_{free} (g/dL)	$c*$ (g/dL)	A^b	B^c
LRD-PEO0.4	1.66	1.10	30.42	985	2200
LRD-PEO4	6.15	1.35	6.37	71	220
LRD-PEO10	10.37	1.43	3.42	25	88
LRD-PEO20	15.40	1.48	2.14	11	44
LRD-PEO35	21.18	1.52	1.46	6	25

[a] calculated with eq. (2);
[b] *A* represents the moles of adsorbed polymer to completely cover the surface of one clay platelet;
[c] *B* represents the polymer moles corresponding to one clay platelet according to the components concentrations from investigated dispersions.

Fig. 6 shows the schematic representation of the structure of 2.5% LRD aqueous dispersion in absence/presence of PEO. In repulsive (Wigner) colloidal glass state which is characteristic for LRD dispersion with 2.5% LRD (Fig. 6a) long-range electrostatic repulsions dominate. By addition of low molecular weight PEO, the adsorbed polymer reduces the repulsive interactions between clay particles causing the decrease of the elastic modulus (Fig. 6b). For the higher molecular weight of PEO, the polymer chains are long enough to form the bridges between clay particles and the elastic modulus increases (Fig. 6c).

The formation of a clay-polymer-clay network starts to a critical polymer molecular weight depending on the clay and polymer concentrations. The polymer is able to form the bridges between the clay platelets when $r_o \geq d$. In Fig. 7 it is shown the variation of G'_{final} as a function of r_o for our systems as compared to literature data[26] for 2% LRD dispersion in presence of 2% PEO with different molecular weights.

Baghdadi *et al.*[26] found for 2% LRD aqueous dispersion that G' shows a minimum in its variation with r_o/d at about 0.75 (corresponding to $M_n = 49 \times 10^3$ g/mol) irrespective of pH and the

polymer concentration. For 2.5% LRD dispersion, the G' minimum value is shifted at $r_o/d = 0.60$ (corresponding to $M_n = 10 \times 10^3$ g/mol).

The addition of polymer with low molecular weight into 2.5% LRD dispersion causes in the first stage a depletion attraction between clay particles and it reduces the final elastic modulus. G'_{final} increases by addition of PEO chains with high molecular weight which are able to be adsorbed on more than two clay platelets. The dependence of G'_{final} on the molecular weight of added PEO shows a minimum at about 10×10^3 g/mol (Table 1 and Fig. 7). By addition of PEO with molecular weight higher than approx. 20×10^3 g/mol, the polymer chains are large enough to bridge two or more clay particles. Considering the eqs (2) and (3), one polymer bridge is obtained when

$$d \approx r_o = M_{min}^{0.57} / 18.4 \text{ (nm)} \qquad (4)$$

where M_{min} represents the lowest molecular weight of PEO that is able to bridge two clay particles.

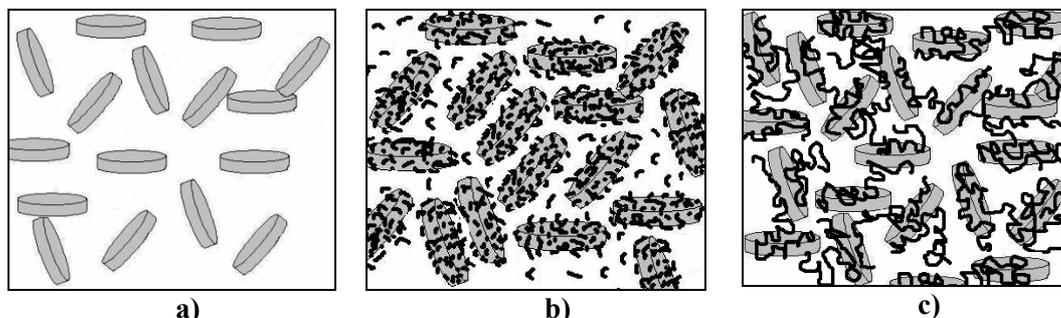|		
a)	**b)**	**c)**

Fig. 6 – Schematic representation of 2.5% Laponite RD aqueous dispersion: a) in absence of PEO, and in presence of 2% PEO with b) low molecular weight ($r_o < d$) and c) high molecular weight ($r_o \geq d$).
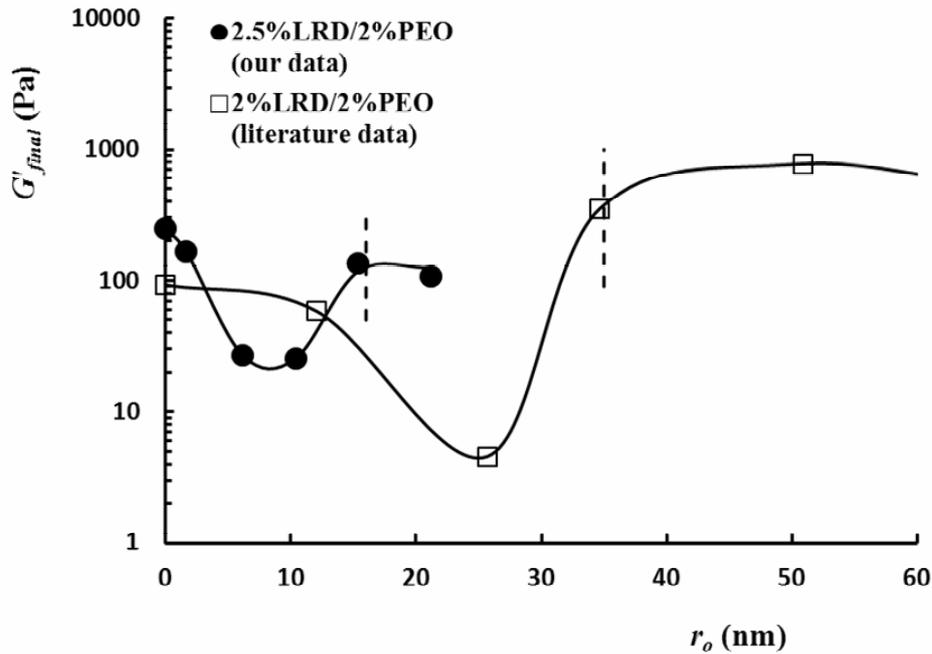
Fig. 7 – Variation of G'_{final} as a function of the mean end-to-end distance of PEO in water for 2% PEO in LRD aqueous dispersions with the concentration of 2.5% (our experimental data) and 2% (literature data[26]). The dot lines represent the limits from which $r_o \geq d$.

M_{min} was established as being about 21.45×10^3 g/mol for the aqueous dispersion with 2.5% LRD and 2% PEO. PEO chains start to bridge two or more clay particles from this molecular weight which corresponds to $r_o = 15.40$ nm (Table 2). G'_{final} becomes constant from M_{min} as indicated in Fig. 7. The dot lines from Fig. 7 represent the distance r_o corresponding to the molecular weight from which the chains can be adsorbed onto two clay particles. For addition of PEO characterized by $r_o \geq d$, the elastic modulus increases as a result of the bridging clay platelets.

The concentration of free PEO in water (non-adsorbed on clay particles) can influence the viscoelastic properties of clay dispersion. Firstly, it was calculated the PEO concentration necessary to completely cover the clay particles surface by considering that the polymer chain occupies a spherical volume with the radius equal to the gyration radius and the area occupied by the a polymer chain can be considered the circular projection of a sphere on the clay platelet surface.

By using the gyration radius of PEO calculated with eq. (3) and LRD platelets diameter of 30 nm, the theoretical number of PEO moles for every clay platelet, denoted with A, has been calculated (Table 2):

$$A = S_c / S_p \quad \text{(PEO moles/one LRD platelet)} \quad (5)$$

where S_c represents the surface area of one clay platelet and S_p is the surface area of polymer sphere projection.

Considering the components concentrations of 2.5% LRD and 2% PEO and the molecular weight of LRD of 1.1×10^6 g/mol[27], it was calculated the experimental number of PEO moles, B, corresponding to one clay platelet from investigated clay dispersions. One can observe that, for 2% PEO, all clay platelets are completely covered ($B > A$).

The concentration of non-adsorbed polymer, c_{free}, and the critical concentration, c^*, which separates the dilute-semidilute regimes for the samples containing PEO have been also calculated (Table 2). The following relation was used to calculate c^* values for PEO in water:[28]

$$c^* = 0.77 / [\eta] \quad \text{(g/mL)} \quad (6)$$

where the intrinsic viscosity, $[\eta]$, was calculated with the following equations:

$$[\eta] = 1.56 \times 10^{-3} \times M^{0.500} \quad \text{in water at 25 °C}[29] \text{ for } 190 < M < 1000 \quad \text{(dL/g)} \quad (7)$$

$$[\eta] = 4.33 \times 10^{-4} \times M^{0.679} \quad \text{in water at 25 °C}[30] \text{ for } M > 4000 \quad \text{(dL/g)} \quad (8)$$
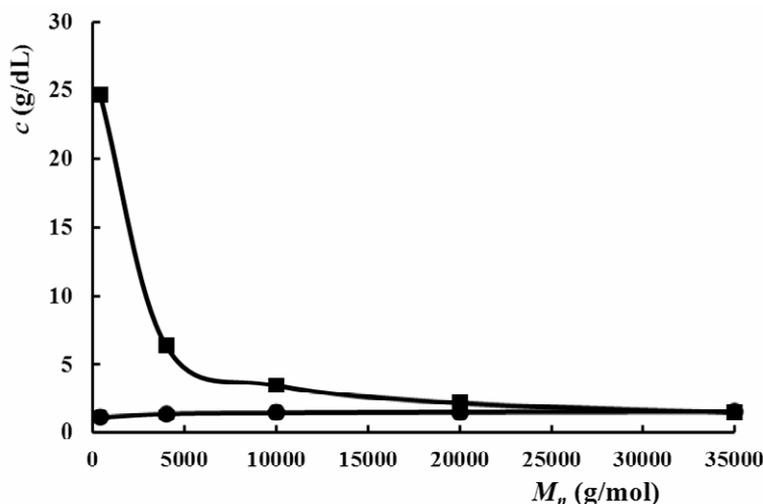
Fig. 8 – Variation of c_{free} (●) and c^* (■) as a function of molecular weight of PEO added to
LRD aqueous dispersions.

Above c^* the polymer coils begin to overlap.

In Fig. 8 is illustrated the variation of c_{free} and c^* as a function of molecular weight of PEO added into clay dispersions.

One can observe that the two concentrations become equal from about 25×10^3 g/mol when the polymer chains which are free in water start to overlap.

EXPERIMENTAL

Laponite RD (LRD) with the chemical formula $Na^{+0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{-0.7}$ which was used in the present investigation was acquired from Rockwood Additives Limited U.K. pH for the studied aqueous dispersions was higher than 9. Poly(ethylene oxide)s (PEO) with the average molecular weights between 0.4×10^3 g/mol and 35×10^3 g/mol were purchased from Fluka Co.

The clay dispersion with the concentration of 2.5% was prepared by addition of LRD in deionized water. LRD dispersions with polymer were obtained by addition of clay into 2% PEO aqueous solution prepared one day before the experimental investigation. All clay dispersions (in presence/ absence of polymer) were homogenized by a moderate stirring for about 2 min and they were placed immediately in rheometer for the measurements.

The rheological measurements were performed at 25 °C by using a Bohlin CVO Rheometer with parallel plate geometry (60 mm diameter and 500μm gap) and thermal control by Peltier effect. The time sweeps were carried out at a constant shear stress (τ) and frequency (ω) of 0.04 Pa and 1 rad/s, respectively. The starting aging time ($t = 0$) was considered the time when the stirring process (about 2 min) was finished.

CONCLUSIONS

The viscoelastic behavior of aqueous dispersions containing 2.5% Laponite RD and 2%

poly(ethylene oxide) with molecular weights between 0.4×10^3 g/mol and 35×10^3 g/mol at 25 °C was investigated and discussed. The rheological measurements have evidenced two-steps in the evolution of viscoelastic moduli as a function of time: 1) the first characterized by a rapid increase of moduli and 2) the second evidenced after $G'' = G'$ point which shows a more slowly increase of moduli. The time necessary for the transition from liquid to colloidal glass was established for LRD aqueous dispersions in absence/presence of PEO with various molecular weights. 2.5% LRD aqueous dispersion with 2% PEO having the molecular weight lower than 35×10^3 g/mol showed closed values of $tan \, \delta$. The addition of PEO with molecular weight above 4×10^3 g/mol causes the increase of the time necessary to transition from liquid to colloidal glass state.

The molecular weight (the chain length) and the concentration of free polymer in water (non-adsorbed) are the factors which influence the viscoelastic properties of investigated dispersions. The polymer chains become able to bridge two or more clay particles above a critical molecular weight of PEO which depends on the clay and polymer concentrations of studied dispersions. For the dispersions with 2.5% LRD and 2% PEO the critical molecular weight was evidenced at about 21.45×10^3 g/mol or 25×10^3 g/mol as a function of the method used for the determination. The rheological data were in agreement with those calculated theoretically.

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