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Flow behavior of poly(ethylene oxide)–laponite nanocomposite solutions

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The flow behavior of poly(ethylene oxide) (PEO)-Laponite RD-water mixtures with polymer concentrations between 0.05 wt% and 1 wt% in the range of temperature 10°C-50°C is investigated. The evolution of the elastic modulus, the viscous modulus and the loss tangent as a function of oscillation frequency for the studied mixtures gives some indications about the dispersions structure. The rheological results allow to evidence of two critical concentrations: c_1=0.113 wt% PEO and c_2=0.51 wt% PEO. Below 30 °C, all mixtures exhibit the gel-like properties. For concentrations lower than c_1, the mixtures containing PEO are also the gels at temperatures above 30°C. The structure for mixtures with PEO concentrations between c_1 and c_2 is strongly influenced by temperature and these systems are considered “critical gels” at temperature higher than 30 °C. The rheological behavior of the mixtures with the polymer concentration above c_2 is affected by the formation of PEO clusters at higher temperatures.

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1. Introduction

Nanocomposite polymer-clay materials in solution represent a new class of materials with a large number of applications including household cleaners, paints, industrial surface coatings, cosmetics, agrochemical, pharmaceuticals, etc. The Laponite RD clay is a synthetic mineral that can be used as a model system for disk-like colloids. At low and moderate ionic strength, the Laponite RD dispersions in water can form an isotropic liquid phase, an isotropic gel phase or a nematic gel phase. At high ionic strength, the aggregation leads to flocculation [1-3]. Usually, the polymer is incorporated into clay dispersions as rheological modifiers, additives or stabilizers.

The purpose of this work is an investigation of the flow behavior of the poly(ethylene oxide) (PEO)–Laponite-water mixtures at different temperatures.

2. Experimental

In this study, the used clay is Laponite RD from Rockwood Additives Limited U.K. The chemical formula of this clay is: $Si_8(Mg_{5.45}Li_{0.4})H_4O_{24}Na_{0.75}$. The typical characteristics of Laponite RD are: the bulk density 1g/cm^3; the surface area 370 m^2/g and pH for 2 wt% dispersion 9.8 [4]. Poly(ethylene oxide) (PEO) with molecular weight M_n=35 000 g/mol and polydispersity index of l.23 was purchased from Fluka Co. The laponite dispersions were prepared by adding the clay in distilled water with moderate stirring for ten minutes. The laponite concentration was of 2 wt % for all samples. PEO was added in the clay dispersion to obtain the polymer concentrations ranging from 0.05 wt% to 1 wt%. The samples were kept at room temperature for 28 days before the rheological measurements. These measurements were performed at different temperatures (10°C-50°C) using a CVO Rheometer with parallel plate geometry (60 mm diameter) and thermal control by Peltier effect. The dynamic properties were determined in the frequency range of 0.01-100 rad/s at a shear stress of 1 Pa.

3. Results and discussion

Laponite RD is a 2/1 type clay consisted of one magnesium octahedral layer between two silicon tetrahedral layers. It is a synthetic disk-shaped clay with a thickness of approximately 1 nm and a diameter of 25 nm. In aqueous dispersion, the Laponite RD particles have a strongly negative charge on the faces and a weakly positive charge on the edges. These clay dispersions can form gels. There are two main discussions about the gelation mechanism of Laponite RD dispersions depending of pH and ionic strength (Fig. 1): a) at low pH and high ionic strength the gelation of clay dispersion is explained by the formation of a linked structure, similar to a „house of cards”, as a result of the electrostatic attraction between the positively charged edges and negatively charged faces of the plate-like particles [5,6]; b) at high pH and low ionic strength the gelation can be explained by the electrical double layer repulsion between clay particles [1,7-10]. The addition of PEO into Laponite RD dispersion determines the change of the clay dispersion properties due to the adsorption of the macromolecular chains on the clay disks surfaces. In the presence of shear, the polymer chains are in a dynamic adsorption/desorption equilibrium with the clay particles and form a „dynamic network” [11]. The rheological studies on the aqueous dispersions of PEO-Laponite RD mixtures can give some indications about the interactions from these systems and about their microstructure.

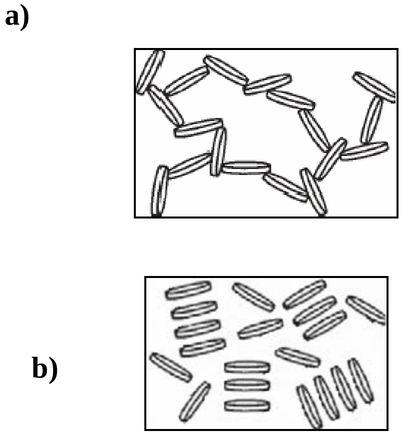


Fig. 1. Schematic structure of Laponite RD dispersions under static equilibrium conditions at: ***a)*** *low pH and high ionic strength and* ***b)*** *high pH and low ionic strength.*

To investigate the effect of temperature on the viscoelastic properties of PEO-laponite-water mixtures, oscillatory measurements were performed in the linear viscoelastic regime with small sinusoidal strain, $\gamma(t)$:

$$\gamma(t) = \gamma_0 \sin(\omega t) \tag{1}$$

where γ_0 represents the strain amplitude, ω is the frequency of oscillation and t is the real time.

The stress, $\tau(t)$ is given by:

$$\tau(t) = \gamma_0 \left| G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t) \right| \tag{2}$$

where: G' is the elastic modulus which represents the strain energy reversibility stored in the sample and G" is the viscous modulus which gives the amount of energy irreversibility given off by the substance to its environment.

The loss tangent, tan δ, is a dimensionless parameter defined as:

$$\tan\delta = \frac{G''}{G'} \tag{3}$$

The values of tan δ give information about the ratio between the amount of dissipated and stored energy, i.e., the ratio between the viscous and the elastic response of the sample. This parameter is very large (>>1) for liquid-like materials and it becomes very small (<<1) for solid-like materials.

The magnitude of complex viscosity is given by:

$$|\eta^*| = \sqrt{(\eta')^2 + (\eta'')^2} \tag{4}$$

where η' is the real part of the complex viscosity, which stands for the viscous behavior, while η'' is the imaginary part of the complex viscosity, which stands for the elastic behavior.

It is known that the Laponite RD aqueous dispersions form isotropic gels at concentrations of clay above 2 wt% [3]. The polymer addition into Laponite RD dispersion determines the change of the rheological properties of the clay dispersion depending on the polymer molecular weight and concentration.

The mixtures compositions prepared for this study are presented in Table 1.

Table 1. Compositions of PEO-Laponite RD-water mixtures[a].

Sample	Laponite RD (wt%)	PEO[b] (wt%)
PEO005-L2	2	0.05
PEO01-L2	2	0.1
PEO02-L2	2	0.2
PEO05-L2	2	0.5
PEO1-L2	2	1.0

[a] pH=9.8

[b] M_n=35 000 g/mol and polydispersity index is l.23.

The radius of gyration (R_g) of PEO with M_n=35000 g/mol, in water at 30°C is about 11 nm and it was determined with the relation (5) with a view to compare the polymer dimension in solution to the clay particles.

$$R_g = 0.022 \cdot M_w^{0.583} \text{ (nm) [12]} \tag{5}$$

The critical concentration, c*, which separates the dilute-semidilute regimes for PEO in water was determined according to Graessley [13]:

$$c^* = \frac{0.77}{[\eta]} \text{ (g/ml)} \tag{6}$$

where:

$$[\eta] = 12.5 \cdot 10^{-3} \cdot M_w^{0.780} \quad \text{in water at 30°C (ml/g) [14]} \tag{7}$$

Moreover the critical concentration, c', which separates the extremely dilute-dilute domains for PEO in water was estimated with the following relation [15]:

$$c' = \frac{0.19}{[\eta]} \text{ (g/ml)} \tag{8}$$

where $[\eta]$ was calculated with relation (7).

The calculated c* and c' values for PEO in water were 1.5 wt% and 0.4 wt%, respectively.

The oscillatory rheological measurements were performed at temperatures between 10°C and 50°C in the frequency range of 0.01-100 rad/s at a shear stress of 1 Pa.

Typically, the gelation point is determined either at the point where G' exceeds G" or when these parameters exhibit the following power law dependence on the frequency:

$$G'(\omega) \sim G''(\omega) \sim \omega^n \quad [16,17] \tag{9}$$

where n is a constant.

If n→1, the gel is viscous, while for n→0, the gel is elastic or rigid. The gelation can also be described by the evolution of tan δ. Thus, tan δ becomes independent of frequency at the gelation point.

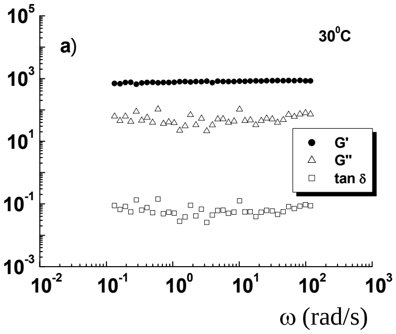
Monitoring the evolution of G', G" and tan δ of the studied samples as a function of ω it was observed that all mixtures have the gel properties at temperatures below 30 °C.

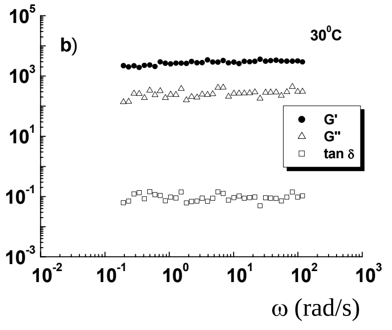
The variations of G', G" and tan δ for PEO005-L2, PEO05-L2 and PEO1-L2 mixtures as a function of ω at 30°C are shown in Fig. 2. Thus, a dependence of G' and G" with ω described by the relation (9) was observed and the G' values are almost 1 order of magnitude higher than G" values (tan δ<<1). The mixtures have a preponderant elastic character, as it can be seen from the values of tan δ, suggesting the existence of a gel structure. For all samples, the tan δ values are independent of frequency at temperatures below 30°C.

The Fig. 3 shows the variation of G', G" and tan δ with ω of PEO005-L2, PEO05-L2 and PEO1-L2 samples at 50 °C. The increase of the temperature above 30°C modifies the mixtures microstructure in different manners. The PEO005-L2, PEO01-L2 samples keep the gel structure by increasing the temperature. The samples with 0.2 wt% and 0.5 wt% PEO have a "critical gel" structure which represents a critical state of matter between liquids and solids (tan δ→1 and tan δ=constant). The evolution of rheological parameters for PEO1-L2 sample at the temperatures higher than 30 °C suggests the formation of the polymer clusters that can be seen by visual observation. In this case the rheological parameters exhibit the following power law dependences on the frequency:

$$\tan\delta \ll 1;\ G'(\omega) \sim \omega^{n1};\ G''(\omega) \sim \omega^{n2} \qquad (10)$$

where n1 and n2 are constants and n1≠n2.





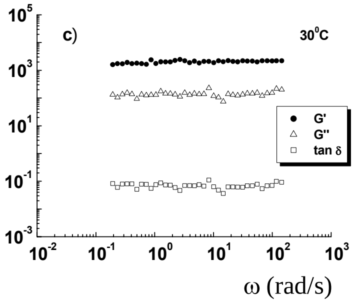


Fig. 2. Evolution of the elastic modulus (G'), the viscous modulus (G") and the loss tangent (tan δ) as a function of oscillation frequency (ω) for the following samples: ***a)*** *PEO005-L2,* ***b)*** *PEO05-L2 and* ***c)*** *PEO1-L2 at 30°C.*

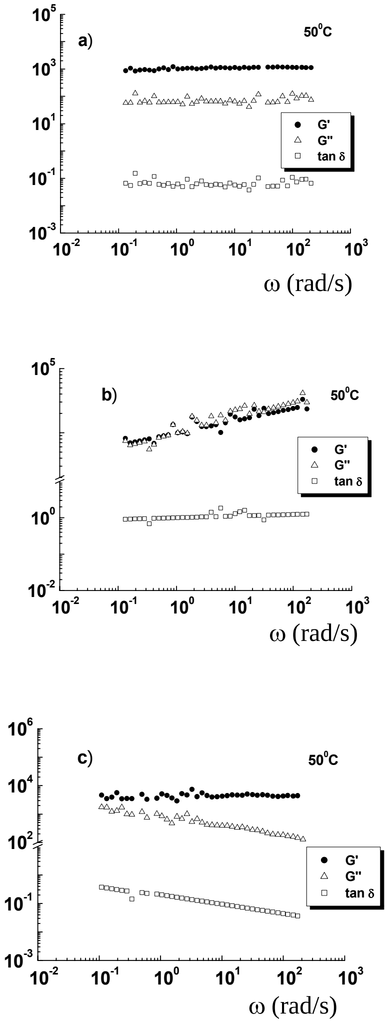


Fig. 3. Evolution of the elastic modulus (G'), the viscous modulus (G") and the loss tangent (tan δ) as a function of oscillation frequency (ω) for the samples a) PEO005-L2, b) PEO05-L2 and c) PEO1-L2 at 50°C.

Fig. 4 shows the effect of temperature on the G’ of PEO005-L2 and PEO1-L2 samples. One can see that the G’ values increase with increasing the temperature and this effect is more important for the sample with higher content of polymer. The same effect of the temperature was also observed on the G” values (Fig. 5).

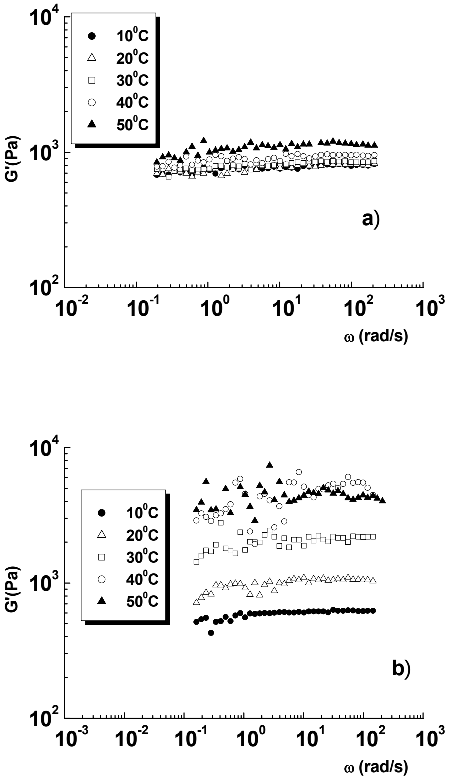


*Fig. 4. Temperature effect on the elastic modulus (G’) for the samples **a)** PEO005-L2 and **b)** PEO1-L2.*

The temperature effect on the tan δ at different polymer concentrations is shown in Fig. 6.

One can observe that the samples containing PEO below of 0.1 wt% and at 1 wt% present the solid-like properties (tan δ<<1) in the studied temperature range. At PEO concentrations between 0.1 wt% and 1 wt% the samples structures are strongly influenced of temperature and they behave as “critical gels” at temperatures higher than 30 °C (tan→1).

For understanding this behavior it is necessary to consider the structure of Laponite RD dispersion in used experimental conditions. According to literature [1,7-10] the gelation mechanism of the 2 wt% Laponite RD dispersion at a pH value of 9.8 can be explained by the formation of a colloidal gel due to the long-range electrostatic repulsion between overlapping double layers (Fig. 1b). The addition of PEO to this gel causes either the diminution or the increasing of this repulsion depending of the molecular weight or the concentration of the polymer in system.

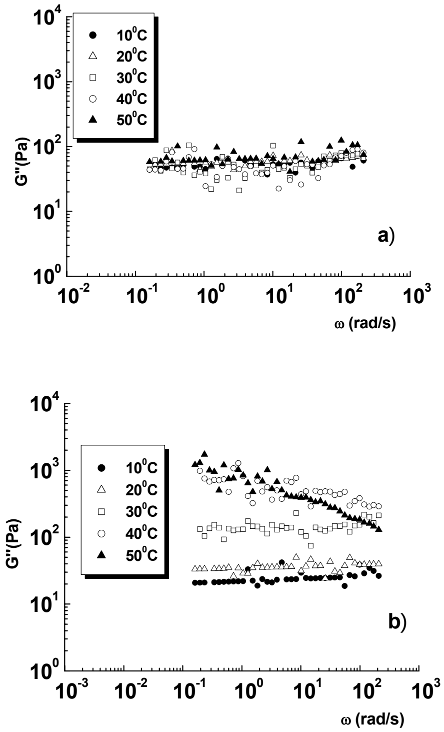


Fig. 5. Temperature effect on the viscous modulus (G”) for the samples a) PEO005-L2 and b) PEO1-L2.

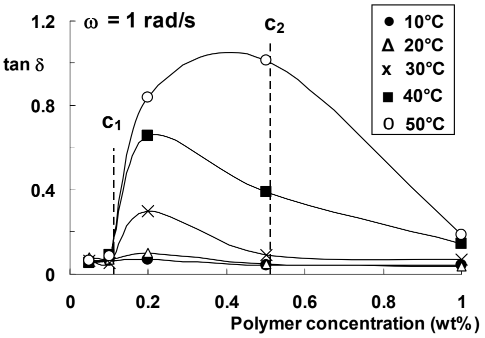


*Fig. 6. Loss tangent (tan δ) as a function of polymer concentration at different temperatures; (**c_1** is the PEO concentration necessary to completely cover the clay particles surface and **c_2** is the concentration corresponding to c’ for the free PEO chains in solution).*

If the added polymer molecular weight into similar Laponite RD dispersion (pH=9.8) is higher than a critical value (about 83 000 g/mol), the formation of clay interparticles bridges can occur resulting a PEO-clay network and an increase in the elastic modulus [18]. By adding low molecular weight PEO, the macromolecular chains are adsorbed on the clay particles surface decreasing the repulsion between clay particles and an increase of the elastic modulus occurs. In our investigation the gelation occurs by the diminution of the clay particles repulsions because the used PEO with M_n=35 000 g/mol can not form the clay interparticles bridges.

For establishing the polymer concentration effect on the gelation mechanism it was calculated the PEO concentration necessary to completely cover the clay particles surface and those corresponding the free macromolecular chains in solution. Using the specific surface area of 370 m^2/g, the diameter of 25 nm and the thickness of 1nm for Laponite RD and R_g of 11 nm (relation (5)) for PEO it was found that the polymer concentration for covering all clay particles (c_1) is 0.113 wt%. The added polymer until this concentration decreases the repulsions between the clay particles and a strong gel stable at increasing the temperature is obtained (Fig. 6).

Above c_1 there are also free PEO chains in solution. The calculated concentrations of the free polymer in solution are 0.09 wt%, 0.39 wt% and 0.89 wt% PEO corresponding to PEO02-L2, PEO05-L2 and PEO1-L2 samples. The critical concentrations, c' (which separates the extremely dilute-dilute domains) and c* (which separates the dilute-semidilute regimes) for PEO in water were calculated as 0.4 wt% and 1.5 wt% PEO, respectively (relations 6, 8).

The PEO concentration in the mixture PEO-Laponite RD-water corresponding to c' for the free polymer in solution (c_2) is 0.51 wt% PEO.

One can observe that the free polymer in solution is in dilute regime for the mixtures with the PEO concentrations higher than c_2. Moreover, it is known that the PEO chains in dilute aqueous solution can form the clusters. Thus, the formation of PEO clusters at higher temperatures is responsible for the rheological behavior of PEO1-L2 sample (the clusters are visible with the naked in this sample).

The samples with the PEO concentrations between c_1 and c_2 are weak gels which are stable until 30°C and "critical gels" at higher temperatures.

4. Conclusions

Monitoring the variation of G', G" and tan δ as a function of ω it was observed that the rheological behavior of the studied poly(ethylene oxide) (PEO)–Laponite RD-water mixtures is dependent on temperature and PEO concentration. The samples with the polymer concentrations between 0.05 wt% and 1 wt% PEO were studied at temperatures in the range 10°C-50°C. It was observed that all mixtures have the gel properties at the temperatures below 30 °C. The increase of the temperature above 30 °C modifies the mixtures microstructure in different manners depending of PEO concentration. Thus, the mixtures with PEO concentrations lower than a critical concentration (c_1) are still the gels at temperatures above 30 °C.

The mixtures structures with PEO concentrations between c_1 and c_2 (this is the concentration corresponding to c' for the free PEO in solution) are strongly influenced by temperature and they are "critical gels" at temperature higher than 30°C. The rheological behavior of the mixture containing PEO above c_2 is due the formation of PEO clusters at higher temperatures.

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