

*Dedicated to the memory of
Professor Maria Brezeanu (1924–2005)*

GELS BASED ON POLY(ETHYLENE OXIDE)-LAPONITE MIXTURES

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The effect of poly(ethylene oxide) with $M_n=35\ 000$ g/mol added to an aqueous laponite clay dispersion was investigated at pH=7. The results have shown that the viscoelastic properties of clay dispersion obtained in oscillatory measurements are influenced by the presence of the polymer. For $\omega > 0.1$ rad/s, formation of gel in the poly(ethylene oxide)/laponite/water mixture was observed. The viscosity of the ternary mixture decreased because the adsorbed poly(ethylene oxide) chains form a steric barrier that affects the interactions between the particles of laponite.

INTRODUCTION

In the last years, the polymer-clay interactions in aqueous solutions have registered high level of fundamental and industrial interest. The clay dispersions are used in many different applications including paints, coatings, cosmetics, food, pharmaceuticals, household cleaners, etc. The polymer is incorporated into clay dispersions as rheological modifiers, additives or stabilizers. The investigations on the polymer-clay dispersions behavior are also important in the development of new applications as fracturing fluids for oil-field and polymer-clay nanocomposites.¹⁻⁴

Laponite is a synthetic disc-shaped clay with a thickness of approximately 1 nm and a diameter of 25 nm. It is known that the laponite dispersions form the isotropic gels in aqueous solutions. At high concentrations of clay in water, the gel structure changes to an ordered nematic system.^{5,6}

The purpose of this work is the investigation of the effect of the poly(ethylene oxide) (PEO) addition on the viscoelastic properties of laponite dispersion.

RESULTS AND DISCUSSION

Laponite RD is a 2/1 type clay, consisting of one magnesium octahedral layer between two silicon tetrahedral layers. The Laponite RD disc-shaped particles have a negative charge on the faces and a positive edge charge in aqueous dispersions and at low pH value. The suspensions are stable up to concentrations of 2.5-3 wt % and they form the irreversible gel above these values. They age slowly in time even at low concentration, finally forming gels.⁷ By adding a polymer into such dispersion, the macromolecular chains are adsorbed on the clay disc faces and their properties are completely changed.⁸

In the present study, PEO with $M_n=35\ 000$ g/mol and polydispersity index of 1.23 was selected as polymer. Three samples were prepared at pH=7: 2 wt % laponite dispersion, 2 wt % PEO solution and ternary mixture of 2 wt % laponite and 2 wt % PEO in water.

To investigate the effect of the PEO addition to the laponite dispersion, oscillatory measurements were performed in the linear viscoelastic regime with small sinusoidal strain, $\gamma(t)$:

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$$\gamma(t) = \gamma_0 \sin(\omega t) \quad (1)$$

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:

$$\tau(t) = \gamma_0 |G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t)| \quad (2)$$

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, $\tan \delta$, is a dimensionless parameter defined as:

$$\tan \delta = \frac{G''}{G'} \quad (3)$$

The values of $\tan \delta$ 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 ($\gg 1$) for liquidlike materials and it becomes very small ($\ll 1$) for solidlike materials.

The magnitude of complex viscosity is given by:

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

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.

Figs. 1-3 show the variations of the elastic modulus, viscous modulus and the loss tangent for 2 wt % laponite dispersion, 2 wt % PEO solution and ternary mixture of 2 wt % laponite–2 wt % PEO in water as a function of frequency (ω).

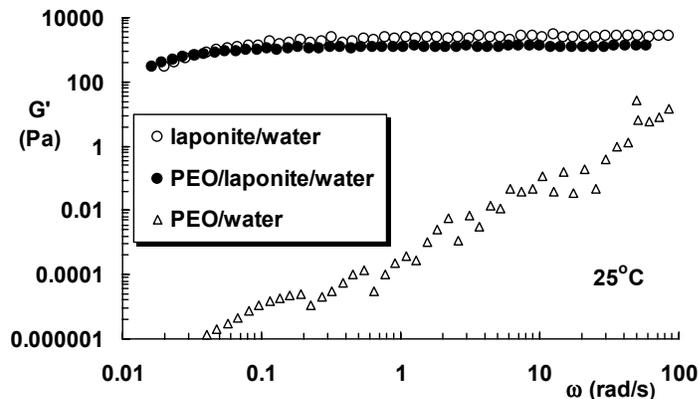


Fig. 1 – Evolution of the elastic modulus as a function of oscillation frequency for the studied samples at 25°C.

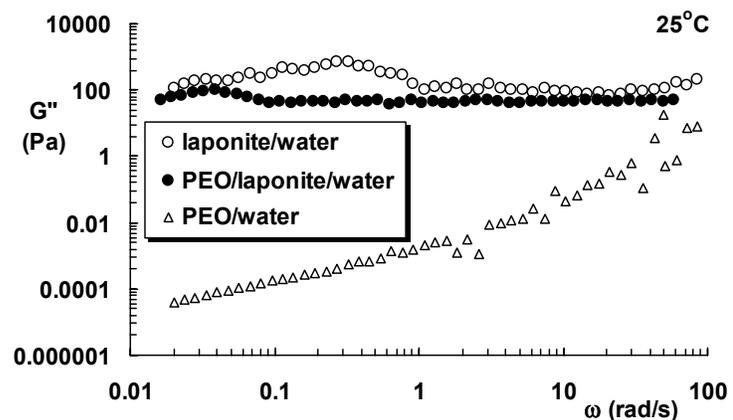
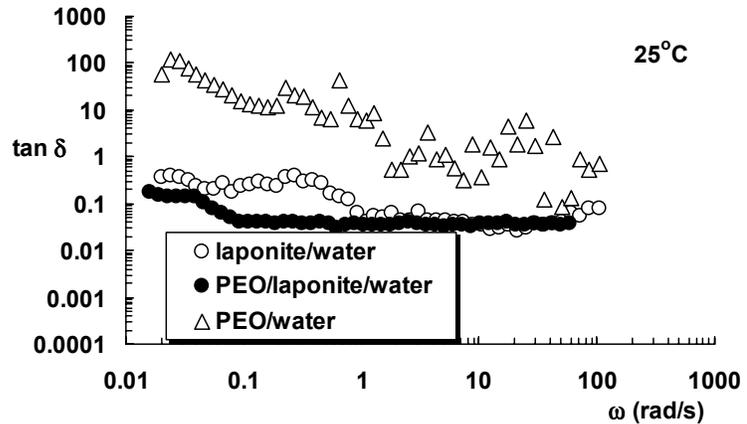


Fig. 2 – Evolution of the viscous modulus as a function of oscillation frequency for the studied samples at 25°C.

Fig. 3 – Loss tangent as a function of oscillation frequency for the studied samples at 25°C.



As already shown,^{7,9} above a certain concentration, colloidal suspensions of laponite undergo gel transition. Below this value, the suspension is slightly viscous and G' and G'' are weak. For higher concentrations, the elastic modulus strongly increases and the appearance of a yield stress was observed. In our case, for 2 wt % laponite, G' and G'' present high values and do not vary much with frequency in the investigated dynamical range because the gelation of systems occurred. This behavior is completely different as compared with a solution of 2 wt % PEO; for this system, both G' and G'' continuously increases with increasing ω and the solution has a preponderant viscous character as can be seen from the evolution of $\tan \delta$.

In the presence of polymer chains, for a ternary system containing PEO, laponite and water, G' and G'' values decrease as compared with those of laponite suspensions and are independent of frequency for $\omega > 0.1$ rad/s. The loss tangent is around 0.04, suggesting the existence of cross-linked network.

The evolution of complex viscosity (η^*) as a function of the oscillation frequency for the studied samples is shown in Fig. 4.

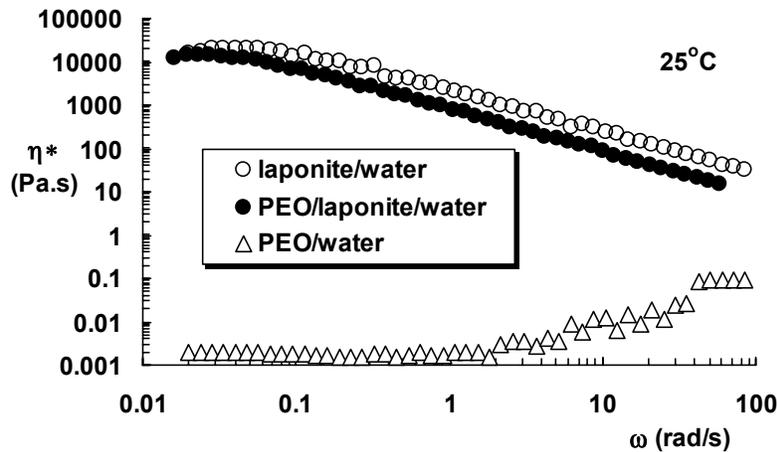


Fig. 4 – Complex viscosity versus the oscillation frequency for the studied samples, at 25°C.

Up to 2 rad/s, PEO solution has a Newtonian behavior and after this value the complex viscosity increases according to the following power law:

$$\eta^* \sim \omega^{0.911} \quad (5)$$

This behavior was attributed to the flow induced aggregation of the macromolecular chains at high values of oscillation frequency ($\omega > 2$ rad/s).

Up to 0.05 rad/s the values of complex viscosity of the systems containing laponite are independent of the applied stress, the dispersions having a Newtonian behavior. For $\omega > 0.05$ rad/s the following dependences were obtained:

$$\eta^* \sim \omega^{-0.914} \quad \text{for laponite (2 wt \%)/water system} \quad (6)$$

$$\eta^* \sim \omega^{-0.964} \quad \text{for PEO (2 wt \%)/laponite (2 wt \%)/water system} \quad (7)$$

In the free polymer laponite dispersion (2 wt %) at pH=7, the electrostatic attraction between the faces and the edges of clay discs leads to formation of aggregates, in the absence of external stress. By addition of PEO with low molecular weight into a such laponite dispersion, the adsorbed polymer layer will screen the interparticle attractions. This will determine a break of the network structure in solution, resulting a decrease of the elastic modulus and complex viscosity of PEO/laponite/water system. When a shear is applied, some bonds between polymer and the clay discs break, new adsorption sites appear on the clay faces and other free polymer chains from solution will be adsorbed on the clay particles. Thus, as the oscillation frequency increases, the attraction between clay particles decreases and as a consequence, the viscosity decreases. For PEO sample used in this investigation with $M_n=35\,000$ g/mol a value of 9.5 nm for the radius of gyration was calculated according to the relationship given in the literature.¹⁰ The dimension of the polymer chains in solution is lower than those of the clay particles and the macromolecular chains are not long enough to form interparticle bridges. According to the literature data,¹¹ the critical molecular weight of PEO at which the interparticle bridges occur is around of 50 000 g/mol.

CONCLUSIONS

It was shown that the addition of poly(ethylene oxide) into laponite dispersion affects significantly the rheological properties. The systems containing laponite show a gel behavior for the frequency higher than 0.1 rad/s (elastic and viscous moduli and the phase angle are independent of frequency). The addition of PEO chains having the radius of gyration lower than the laponite particles dimensions decreases the elastic and viscous moduli because the adsorbed polymer layer forms a steric barrier screening the attractive interactions in laponite gels. Also, it was observed that the presence of the polymer into the laponite dispersion determines a decrease of the complex viscosity.

EXPERIMENTAL

The used clay in this study was Laponite RD from Rockwood Additives Limited U.K. The chemical formula of this clay is: $\text{Si}_8(\text{Mg}_{5.45}\text{Li}_{0.4})\text{H}_4\text{O}_{24}\text{Na}_{0.75}$. Poly(ethylene oxide) was purchased from Fluka Co. PEO is a linear chain polymer with molecular weight $M_n=35\,000$ g/mol and polydispersity index of 1.23. The laponite dispersions were prepared by adding the clay into water at pH=7 with moderate stirring for ten minutes. The laponite concentration was of 2 wt % for all samples. PEO was added into the clay dispersion and these samples were kept for four days and they were shaken before the rheological measurements.

Three samples were prepared: 2 wt % laponite dispersion, 2 wt % PEO solution and ternary mixture of 2 wt % laponite and 2 wt % PEO in water. The rheological measurements were performed at 25°C by 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.

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