Effect of Addition of Polymer on the Rheology and Electrokinetic Features of Laponite RD Aqueous Dispersions

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Rheological properties and zeta potential were investigated for 1 % Laponite RD aqueous dispersions with different contents of poly(ethylene glycol). At low concentrations of polymer (< 1 %), the clay dispersions are stable, whereas an unstable liquid phase appears above 2 % polymer. The samples present a Newtonian behavior, showing more viscous than elastic response. The viscoelastic moduli are influenced by the polymer content and temperature. The longest relaxation time presents a maximum at 2 % poly(ethylene glycol), when the surface of the clay particles is saturated with polymer. Zeta potential decreases significantly as the polymer chains cover the surface of the particles. The flow activation energy depends on polymer concentration, its values being estimated between (15.64 and 26.89) $kJ \cdot mol^{-1}$.

Introduction

During the last years, bulk or solution organic/inorganic nanocomposites have attracted a significant interest due to their unique mechanical, electrical, optical, or thermal properties.[1-5] Clay suspensions are used in a variety of applications including household cleaners, paints, industrial surface coatings, cosmetics, agrochemical, pharmaceuticals, etc. In several of these suspensions, polymer additives are incorporated as rheology modifiers or stabilizers.[6-9]

Laponite RD is a synthetic hectorite type clay that can be used as a model system for disklike colloids having a well-defined thickness of 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 dispersions can exhibit different nonergodic physical states: sol, liquid, repulsive, or attractive glasses, stable gel and flocculation state (unstable gel). The colloidal gels and glasses are solid state of condensed matter with static elasticity. The process of liquid−glass transition is called "aging", and that of sol−gel transition is called "gelation".[10-12] The transitions between states can be induced by changing the concentration of clay, pH, and/or the temperature or inducing the interparticle interactions by adding the salts or polymers.[13,14]

Our previous studies show that the addition of poly(ethylene oxide) (PEO) with a number average molecular weight of 35 $kg \cdot mol^{-1}$ into 2 % Laponite RD dispersion affects significantly the rheological properties.[15] The dynamic response of PEO/Laponite RD/water mixtures with concentrations up to 1 % polymer and 2 % clay is influenced in different ways by temperature and shear conditions, depending on the polymer concentration in the Laponite RD dispersion. Two critical concentration (0.113 and 0.510) % of PEO with molecular weight of 35 $kg \cdot mol^{-1}$ were evidenced, and the temperature influence on the mixtures structures is more important between these concentrations.[16,17]

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Table 1. Composition of the Studied Samples[a]

	initial concentrations[b]		final composition		
	P_i	L_i	P	L	W
sample	% w/v	% w/v	% w/w	% w/w	% w/w
L1	−	1	−	1	99
PEG1-L1	1.02	1.02	1	1	98
PEG2-L1	4.44	1.92	2	1	97
PEG3-L1	6.00	2.17	3	1	96
PEG4-L1	8.00	2.22	4	1	95

[a] P - poly(ethylene glycol) with number average molecular weight of 10 $kg \cdot mol^{-1}$ and polydispersity index of 1.04; L - Laponite RD; W - water. [b] P_i - polymer concentration in initial solution; L_i - clay concentration in initial dispersion.

In this paper, the effect of adding of poly(ethylene glycol) on the viscoelastic and electrokinetic properties of Laponite RD aqueous dispersion is studied.

Experimental Section

Sample Preparation. The clay used in the present investigation is Laponite RD from Rockwood Additives Limited U.K., having the following chemical formula: $Si_8(Mg_{5.45}Li_{0.4})H_4O_{24}Na_{0.75}$. The bulk density and the surface area of the used Laponite RD are 1 $g \cdot cm^{-3}$ and 370 $m^2 \cdot g^{-1}$, respectively.[18]

Poly(ethylene glycol) (PEG) with a number average molecular weight of 10 $kg \cdot mol^{-1}$ and polydispersity index of 1.04 was purchased from Fluka Co.

Clay dispersions with concentrations from (1 to 2.22) % were obtained by adding Laponite RD in deionized water followed by high-speed stirring for a few minutes. The clay dispersions were then ultrasonicated for 30 min and used within 2 h from ultrasonication to prevent aging.

Polymer solutions having concentrations in the range from (1.02 to 8) % in deionized water were vigorously stirred and used to prepare the mixtures after one day.

The polymer/clay/water ternary systems were prepared by mixing the clay dispersions with the polymer solutions in different weight ratios to obtain the composition indicated in Table 1. The subsequent measurements were performed one day from the preparation of mixtures.
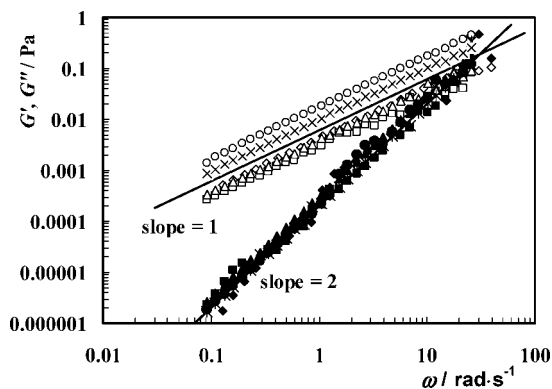
Figure 1. Dependence of the viscoelastic moduli as a function of frequency (ω) of the aqueous dispersions with 1 % Laponite RD and different concentrations of polymer (data obtained at $T = 298$ K): $\diamond$, $\blacklozenge$, L1 sample; $\square$, $\blacksquare$, PEG1-L1 sample; $\triangle$, $\blacktriangle$, PEG2-L1 sample; $\circ$, $\bullet$, PEG3-L1; $\times$, $*$, PEG4-L1. The open and full symbols represent G'' and G' parameters, respectively. The straight lines indicate the slopes of 1 and 2 for G'' and G', respectively.
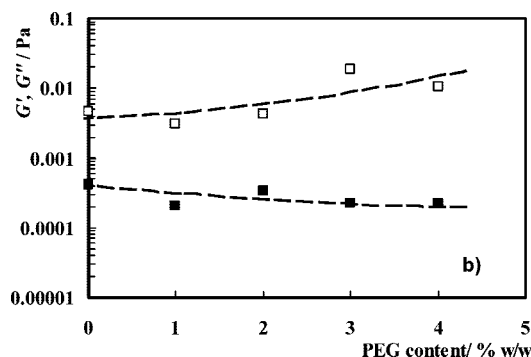
Figure 2. Variation of the viscoelastic moduli as a function of the PEG content in the mixture (data obtained at $T = 298$ K and $\omega = 1$ rad$\cdot$s^{-1}): $\square$, G''; $\blacksquare$, G'. Dotted lines represent a guide for the eye.

Figure 3. Dynamic moduli as a function of frequency (ω) for viscoelastic liquids.[21] The variations of G' and G'' are indicated by the dashed and continuous lines, respectively.

Figure 4. Dependence of the longest relaxation time (τ_1) as a function of the polymer content at $T = 298$ K.

Figure 5. Steady shear viscosity (η) versus shear rate ($\dot{\gamma}$) for samples with 1 % Laponite RD and different concentrations of polymer at $T = 298$ K: $\circ$, L1 sample; $\blacktriangle$, PEG1-L1 sample; $\square$, PEG2-L1 sample; $\blacklozenge$, PEG3-L1; $*$, PEG4-L1 sample.

Rheology. The rheological measurements were performed at different temperatures from (288 to 308) K using a controlled stress CVO Rheometer with parallel plate geometry (60 mm diameter and 500 μm gap) and thermal control by the Peltier effect. The oscillatory shear measurements were performed in the frequency range from (0.08 to 100) rad$\cdot$s^{-1} within the linear viscoelastic regime, where the storage (G') and loss (G'') moduli are independent of the shear stress. Also, steady flow measurements were carried out in the range of shear rates from (10 to 4000) s^{-1} to determine the shear viscosity.

Zeta Potential (ζ). ζ was calculated from the electrophoretic mobility (μ) determined at 298 K by using a Zetasizer Nano NS (Malvern Instruments, UK). For $k\alpha \gg 1$ (k - Debye−Huckel parameter, and α - particle radius), the Smoluchowski relationship was used
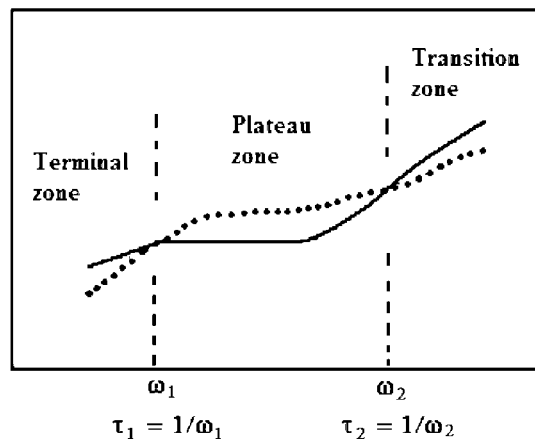
$$\zeta = \eta\mu/\varepsilon \qquad (1)$$

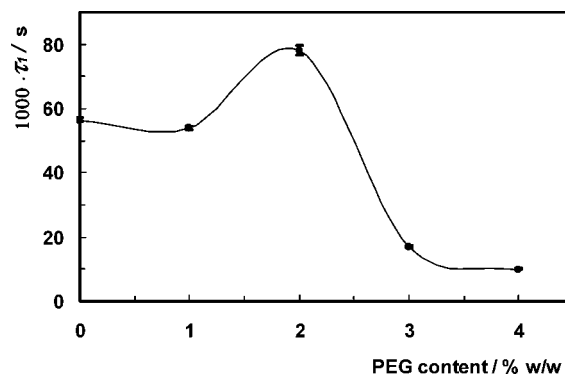where η is the viscosity and ε is the dielectric constant.

Results and Discussion

For the present study, samples with 1 % Laponite RD and different concentrations of the polymer were prepared (Table 1).
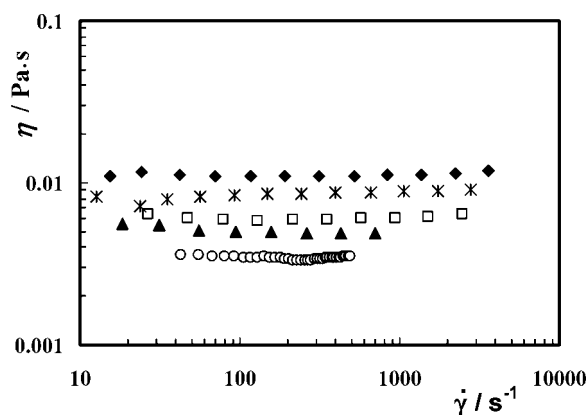
The frequency sweep measurements were achieved at 298 K in the linear region of viscoelasticity (at shear stress of 1 Pa). Figure 1 shows the variation of the viscoelastic moduli (G' and G'') as a function of frequency (ω) for 1 % Laponite RD aqueous dispersion with different contents of poly(ethylene glycol). At 298 K, the samples have a Newtonian behavior showing more viscous than elastic response in the investigated frequency range. The moduli variation with the frequency is typically for viscoelastic Maxwellian fluids, that is, G'' scales with ω^1 and G' with ω^2.

G'' and G' values slowly increase and decrease, respectively, by increasing the polymer content (Figure 2).

The elastic (storage) modulus, G', represents the strain energy reversibility stored in the sample, and it depends on the number and strength of the interactions into the system. The liquid-like response is described by the viscous (loss) modulus, G'', which
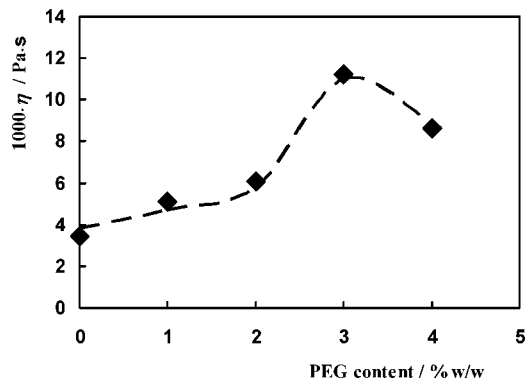
Figure 6. Variation of the steady shear viscosity (η) as a function of the PEG content in the mixture at $T = 298$ K. Dotted line is a guide for the eye.
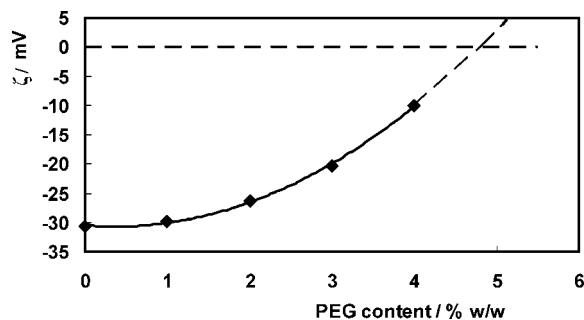
Figure 7. Zeta potential (ζ) of the samples with 1 % Laponite RD and different concentrations of polymer at $T = 298$ K.
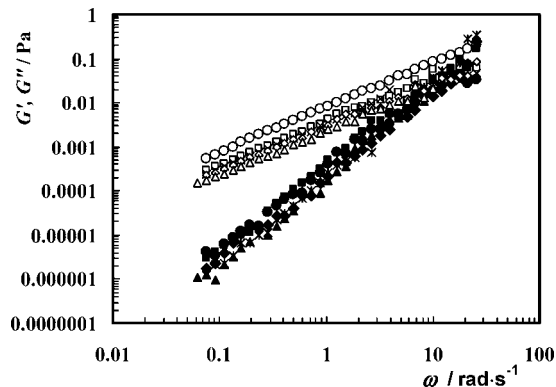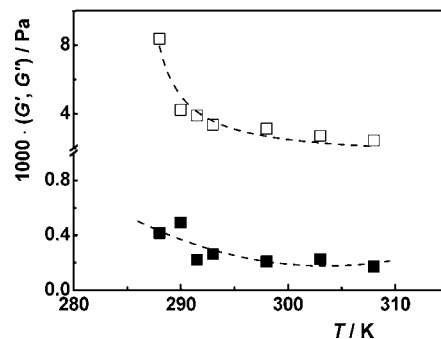

Figure 8. Variation of dynamic moduli of the PEG1-L1 sample as a function of frequency (ω) at different temperatures: $\bigcirc$, $\bullet$, 288 K; $\square$, $\blacksquare$, 290 K; $\times$, $*$, 293 K; $\diamond$, $\blacklozenge$, 298 K; $\triangle$, $\blacktriangle$, 308 K. The open and full symbols represent G'' and G' parameters, respectively.

gives information on the unrecoverable viscous loss. In the presence of the shear, the polymer chains are in an adsorption/desorption equilibrium with the clay particles and form a "dynamic network".[19,20] Due to the dynamic character of the interactions between PEG and Laponite RD during the flow, the differences between the G' values for the studied samples are not so pronounced as those of G''.

As it is well-known, three zones—terminal, plateau, and transition—delimited by two points for which $G' = G''$ can be distinguished for a viscoelastic liquid in the double logarithmic plot of G' and G'' as a function of frequency (Figure 3).[21] This behavior results from the interactions number and the effect of the entanglements for the polymers with flexible molecular chains and from the chain rigidity and the intermolecular associations for the polymers with rigid chains.

Two sets of relaxation times are evidenced in this plot: the long-range relaxation which occurs at the time scale of the

Figure 9. Variation of dynamic moduli of the PEG1-L1 sample as a function of temperature at $\omega = 1$ rad·s^{-1}: $\square$, G''; $\blacksquare$, G'. Dotted lines represent a guide for the eye.
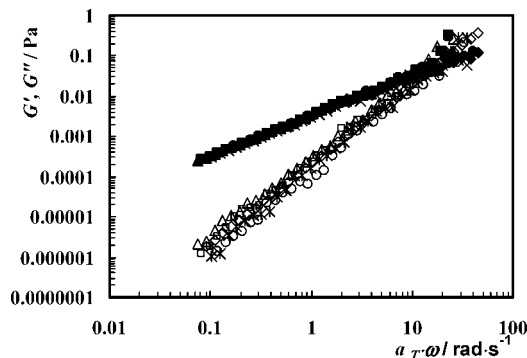
Figure 10. Master curves of viscoelastic moduli for the PEG2-L1 sample as a function of shifted frequency $a_T \cdot \omega$ at the reference temperature of $T = 308$ K: $\bigcirc$, $\bullet$, 288 K; $\times$, $*$, 293 K; $\diamond$, $\blacklozenge$, 298 K; $\square$, $\blacksquare$, 303 K; $\triangle$, $\blacktriangle$, 308 K. The open and full symbols represent G' and G'', respectively.

Table 2. Relaxation Time and Zeta Potential for Samples with 1 % Clay and Different Concentrations of Polymer at $T = 298$ K

PEG content	relaxation time (τ_1)		ζ
	$1000 \cdot \tau_1$	std. error	
% w/w	s	s	mV
0	56.28	0.56	−30.6
1	53.91	0.54	−29.8
2	77.94	1.56	−26.4
3	16.85	0.34	−20.4
4	9.77	0.19	−10.0

terminal zone (τ_1) and the short-range relaxation at the time scale of the transition zone (τ_2). The crossover frequency (ω_{cross}) values for which $G' = G''$ are inversely proportional with the relaxation times.

For the studied dispersions, only the longest relaxation time, τ_1, was determined by using the crossover frequency from Figure 1. The evolution of τ_1 as a function of PEG content is shown in Figure 4, and the corresponding values are given in Table 2 (errors below 2 %).

With up to 1 % polymer added into Laponite dispersion, τ_1 is nearly constant. For polymer concentrations higher than 1 %, the longest relaxation time increases and presents a maximum at 2 % PEG. Above this concentration, a decrease of τ_1 is distinguished, suggesting a change of the clay dispersion structure. Thus, a "saturated network" is reached around 2 % polymer concentration, when the surface of the clay particles is saturated with polymer.[19] According to the literature data,[4] the surface coverage at saturation is of 1.14 g·g^{-1} with PEG of 10 kg·mol^{-1}.

Figure 5 shows the steady shear viscosity as a function of shear rate for all dispersions. The steady shear viscosity increases
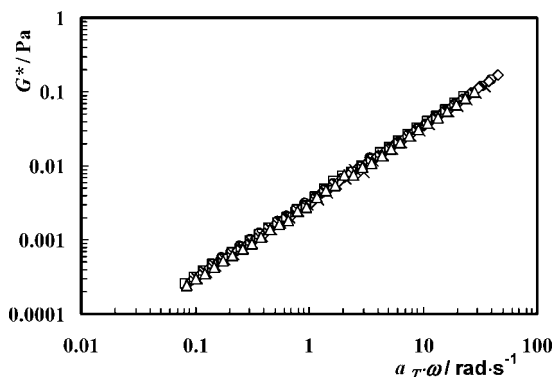
Figure 11. Master curves of complex modulus (G^*) for the PEG2-L1 sample as a function of shifted frequency $a_T \cdot \omega$ at the reference temperature of T = 308 K: ○, 288 K; ×, 293 K; ◇, 298 K; □, 303 K; △, 308 K.
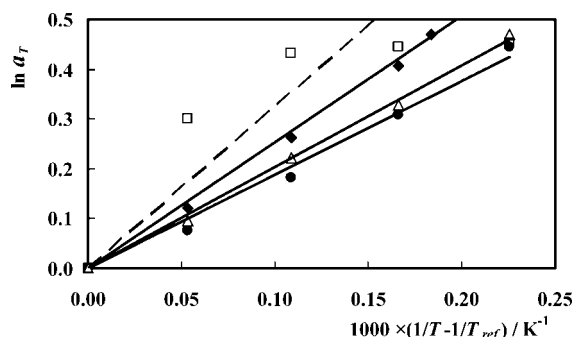
Figure 12. Plots of ln a_T as a function of $(1/T - 1/T_{ref})$: ◆, PEG1-L1 sample; ●, PEG2-L1; △, PEG3-L1 sample; □, PEG4-L1. The trendlines are given by solid (PEG1-L1, PEG2-L1, and PEG3-L1 samples) and broken (PEG4-L1 sample) lines.
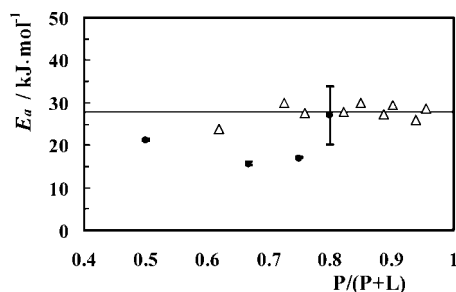
Figure 13. Variation of the flow activation energy (E_a) as a function of polymer content in the polymer/clay mixtures (P, % w/w PEG; L, % w/w Laponite RD); ●, our data (PEG with M_n of 10 kg·mol^{-1}); △, literature data (poly(ethylene oxide) with M_n of 900 kg·mol^{-1}).[22] The solid line represents the average flow activation energy value by considering the literature data.

by increasing the polymer concentration, and a further increase is observed above 2 % PEG (Figure 6).

To understand the rheological behavior, zeta potential measurements were carried out at 298 K. Zeta potential is a parameter that reflects the effective charge on the dispersion particles and can give the information about the electrostatic repulsion between them. The magnitude of zeta potential is influenced by the particle surface charge, the polymer adsorbed layer, and the medium nature in which the particles are suspended and gives indications about the system stability. The values obtained for zeta potential as a function of PEG concentration indicate a negative charge on the surface of clay particles (Figure 7).

Due to the adsorbed PEG chains, the repulsive double layer potential is screened, and the electrostatic repulsion between

Laponite RD particles decreases. Thus, the values of zeta potential decrease significantly as the polymer chains cover the surface of the particles. Also, an unstable liquid phase appears above 2 % PEG ($\zeta < -25$ mV).

The same effect was also observed for Laponite RD suspension in water by adding salt. Thus, at a clay concentration below 2 % and ionic strength higher than $2 \cdot 10^{-2}$ M, the flocculation of the dispersions was observed.[10−12] The increase of polymer concentration involves stronger attractive interactions between the clay particles. The plot of zeta potential versus PEG concentration exhibits an isoelectric point where the net charge on the particle is zero for a concentration of 4.9 % PEG, and the flocculation is most probably to occur.

The ternary mixtures with PEO−Laponite nanoclay dispersions in the presence or in the absence of counterions have been studied at a wide range of PEO concentrations through rheology, flow birefringence, small-angle neutron scattering (SANS), and molecular modeling. SANS investigations show that PEO adsorbs and can bridge between Laponite particles, leading to the formation of a polymer−nanoparticle network in solution. By adding Laponite, a weakly increase of the relaxation time up to a critical relative concentration was observed.[22] The complex behavior of this mixture was interpreted as a competition between PEO adsorption on Laponite particles removing PEO from the entanglement network vs forming new bridging networks. The relaxation time can be attributed to the relaxation of the polymer and of the clay and a relaxation due to polymer−clay interactions. Thus, the relaxation time cannot be decoupled.[19,20]

By taking into account our system, by increasing the polymer concentration, the number of the adsorbed chains also increases. Up to a certain concentration (around 2 %), when the surface of the clay particles is saturated with polymer, the relaxation time increases due to the polymer−clay preponderant interactions. The PEG chains are not long enough to form interparticle clay bridges. The radius of gyration of PEG with the molecular weight of 10 kg·mol^{-1} is of 4.31 nm, being shorter than the radius of clay discs (12.5 nm). At concentrations of PEG higher than 2 %, the absence of the long-range electrostatic interactions and of the bridges between clay particles could be responsible for the decrease of the relaxation time and the reduced suspension stability.

The viscoelastic moduli values are slightly affected by the temperature change (Figure 8). Thus, they decrease slowly by increasing the temperature as is shown in Figure 9 for the PEG1-L1 sample.

The rheological master curves were constructed using the experimental data obtained at different temperatures. As it is known, there is equivalence between the effect of the time and the temperature on the rheological properties of the viscoelastic materials. At low temperatures, the material behaves in the same fashion as at high frequency, and at high temperature this behaves as at low frequency. To predict the long-term behavior from short-term experiments, the rheological data obtained in a temperatures range over a narrow frequency range can be represented by a procedure known as "time−temperature superposition".[23,24] The viscoelastic moduli ($G'(\omega)$ and $G''(\omega)$) values at different temperatures can be shifted horizontally (with a shift-factor a_T) and vertically (with a shift-factor b_T) along the frequency axis into one master curve at a certain reference

Table 3. Horizontal Shift Factors and the Flow Activation Energy for the Studied Dispersions

	a_T							flow activation energy	
								E_a	std. error
sample	288 K	290 K	291.5 K	293 K	298 K	303 K	308 K	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
PEG1-L1	3.21	1.70	1.60	1.50	1.30	1.13	1	21.07	0.21
PEG2-L1	1.56	−	−	1.36	1.20	1.08	1	15.64	0.31
PEG3-L1	1.60	−	−	1.39	1.25	1.10	1	16.96	0.17
PEG4-L1	1.57	−	−	1.56	1.54	1.35	1	26.89	6.72

temperature T_{ref}. The master curves can be described by the following equations

$$G^*(\omega, T) = b_T \cdot (T, T_{ref}) \cdot G^*(\omega, a_T(T, T_{ref}), T_{ref}) \quad (2)$$

$$b_T = \frac{T_{ref} \cdot \rho_{ref}}{T \cdot \rho} \quad (3)$$

where ρ_{ref} and ρ are the densities of samples at T_{ref} and T, respectively. The vertical shift factors, b_T, are equal to unity for small differences between T_{ref} and T.

In the present study, 308 K was considered as T_{ref}. As an example, the master curve for the PEG2-L1 sample is shown in Figure 10. For all samples, G' values do not obey time−temperature superposition, especially in the low frequency domain. To obtain accurate values of a_T, the superposition procedure was applied for the complex modulus, G^* (Figure 11).

A relationship between the horizontal shift factor, a_T, and the test temperature, T, is given by the Wiliams−Landel−Ferry (WLF) equation[23]

$$\log a_T = \frac{-c_1(T - T_{ref})}{c_2 + (T - T_{ref})} \quad (4)$$

where c_1 and c_2 are constants. For the composite materials (polymer/clay mixtures), the application of this equation to calculate the a_T parameter is not indicated.[23] For these systems, the use of the Arrhenius-type equation is preferred to the WLF one.

The temperature dependence of a_T can be described by the following relationship

$$\ln a_T = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right) \quad (5)$$

where E_a is the flow activation energy and R is the gas constant ($R = 8.314$ $J \cdot mol^{-1} \cdot K^{-1}$).

Variation of $\ln a_T$ as a function of ($1/T - 1/T_{ref}$) for the polymer/clay/water ternary mixtures is represented in Figure 12.

Excepting the PEG4-L1 sample, $\ln a_T$ values describe a linear dependence as a function of ($1/T - 1/T_{ref}$) from which the flow activation energy can be calculated. For PEG4-L1, an approximate value for E_a was estimated as being 26.89 $kJ \cdot mol^{-1}$, this value being close to literature data obtained for poly(ethylene oxide) with $M_n = 900$ $kg \cdot mol^{-1}$.[22]

The horizontal shift factor and the flow activation energy for Laponite aqueous dispersions with different contents of PEG are given in Table 3.

For the dispersion with 1 % polymer, a value of (21.07 ± 0.21) $kJ \cdot mol^{-1}$ was obtained, being close to the lower limit of literature data reported for systems containing poly(ethylene oxide) with molecular weight of 900 $kg \cdot mol^{-1}$.[22] With increasing the polymer concentration, we observe a slow decrease of the flow activation energy, (15.64 ± 0.31) $kJ \cdot mol^{-1}$ and (16.96 ± 0.17) $kJ \cdot mol^{-1}$, in the case of 2 % and 3 % polymer,

respectively. By adding low content of polymer (up to 3 %) to the L1 sample, the errors in determining E_a values are relatively small (max. 1.2 %). However, for the PEG4-L1 sample, the errors in determining the activation energy are considerably higher due to the scattering of the experimental data, as observed in Figure 12. For this sample, the value of E_a is only roughly approximated. Even by taking into account these errors, a further increase of E_a can be observed. The calculated values of E_a as compared with those reported in the literature[22] for similar systems are summarized in Figure 13. By considering only the literature data reported for poly(ethylene oxide) with $M_n = 900$ $kg \cdot mol^{-1}$, an average value of 27.83 $kJ \cdot mol^{-1}$ is obtained (the horizontal line).

According to the present data, the E_a value initially decreases with increasing polymer concentration, goes through a minimum, and then increases. A convex downward curve with a minimum at low concentrations was previously observed in the plot of E_a as a function of polymer concentration for polystyrene and poly(methyl methacrylate) in poor solvents.[25]

The minimum is located to lower values of polymer concentration if the molecular weight increases,[25] and this can explain the differences between the data obtained in the present paper and the literature.[22]

Conclusions

In this paper, Laponite RD aqueous dispersions with different contents of poly(ethylene glycol) with M_n of 10 $kg \cdot mol^{-1}$ were prepared, and their rheological properties as well as zeta potential were investigated. The samples present a Newtonian behavior showing more viscous than elastic response. The viscoelastic moduli are influenced by the polymer content and temperature.

The relaxation time of Laponite dispersions is not changed significantly for polymer content lower than 1 % and presents a maximum at 2 % PEG when the surface of the clay particles is saturated with polymer. Above this value of concentration, the longest relaxation time strongly decreases and tends to a constant low value for higher polymer content.

Zeta potential indicating negative charges on the surface of clay particles decreases significantly as the polymer chains cover the surface of the particles. The absence of the long-range electrostatic interactions could be responsible for the appearance of an unstable liquid phase above 2 % PEG. The flocculation is likely to occur by adding approximately 4.9 % PEG, when the isoelectric point was found.

The rheological master curves were constructed, and the horizontal shift factors were calculated to determine the flow activation energy. The value of the flow activation energy initially decreases with increasing polymer concentration, goes through a minimum, and then increases, as was previously observed for polymers in poor solvents.

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