# Effect of Temperature and Aging Time on the Rheological Behavior of Aqueous Poly(ethylene glycol)/Laponite RD Dispersions

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ABSTRACT: The viscoelastic properties of 2% poly(ethylene glycol) aqueous solutions containing Laponite RD from 1% to 4% were investigated by oscillatory and flow measurements in the temperature range of 15—40 °C. The enhancement of the clay content from mixture causes the increase of the viscoelastic moduli and the change of the flow from liquid-like behavior (Maxwellian fluid) to a solid-like one at a set temperature. The longest relaxation times (τ_1) of the mixtures with low clay concentrations (1% and 2%) are not affected by changes in temperature unlike the samples having high content of clay at which τ_1 increases above 30 °C and below 17.5 °C. The characteristic behavior of the mixtures with the high clay concentration could be explained by considering the effect of Brownian motion on the network structure formed in these dispersions as well as by the poor solubility of poly(ethylene glycol) in water at high temperatures. The flow activation energy was determined and discussed. An abrupt increase of the flow activation energy was evidenced between 2% and 3% Laponite RD. The rheological measurements carried out at different rest times showed a decrease of the gelation time from 1 week to 2 h when the clay concentration increases from 2% to 4%. The aging kinetics of poly(ethylene glycol)/Laponite RD/ water mixtures, investigated at 25 °C, revealed the increase of the viscosity-rate kinetic constant by increasing the clay concentration.
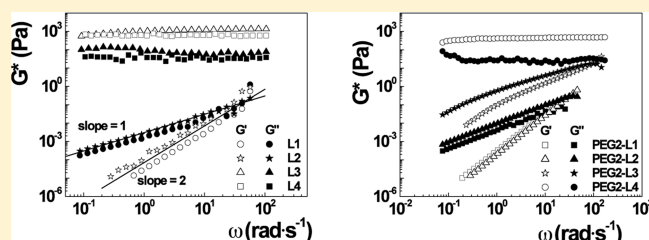
INTRODUCTION

Recently, the clay aqueous dispersions have attracted significant interest due to their use in applications such as paints, cosmetics, agrochemical, pharmaceuticals, etc. Polymers are added to such clay dispersions as rheology modifiers or stabilizers.[1-4]

Laponite RD is a synthetic clay that can disperse in water as disk-shaped particles having a well-defined thickness of 1 nm and a diameter of about 30 nm. Each disk has a strongly negative charge on the faces and a weakly positive charge on the edges. These dispersions can exhibit different physical states (sol, liquid, repulsive or attractive glasses, and stable gel or unstable gel) depending on the clay concentration, pH, temperature, or the presence in medium of the salts or polymers.[5,6] The colloidal gels and glasses are the solid state of condensed matter with static elasticity. Generally, the process of liquid-glass transition is called aging and that of sol—gel transition is called gelation.[7-9]

Poly(ethylene glycol) chains added into a Laponite RD aqueous dispersion are adsorbed on the surface of the clay discs forming a layer of polymer on each face and a rim with a thickness of 1.5 nm and 1.5—4.5 nm, respectively.[10,11]

Our previous studies showed that the addition of poly-(ethylene glycol) with the average molecular weight of 35 kg mol^{-1} into a 2% Laponite RD dispersion affects significantly its rheological properties.[12] The dynamic response of a 2% clay aqueous dispersion with concentrations up to 1% polymer is influenced in different ways by temperature and shear conditions, depending on the polymer concentration. Two critical concentrations of poly(ethylene glycol) with molecular weight of 35 kg mol^{-1} (0.113% and 0.510%) were evidenced, and the

temperature influence on the dispersion structure is more important at concentrations between these two values.[13,14]

The aqueous dispersions containing 1% Laponite RD and different concentrations of poly(ethylene glycol) with the molecular weight of 10 kg mol^{-1} present a Newtonian behavior at 25 °C showing more viscous response than an elastic one. The viscoelastic moduli are influenced by the polymer content and temperature. The relaxation time of the Laponite dispersions is not changed significantly for polymer content lower than 1%, and it presents a maximum at 2% poly(ethylene glycol) when the surface of the clay particles is saturated with polymer. Above this polymer concentration, the longest relaxation time strongly decreases and tends to a constant low value.[15]

In our previous studies,[12-15] we observed that the behavior of the clay based nanocomposites is very complex, being influenced by many factors, such as: composition, molecular weight of the polymer, shear conditions, etc. The aim of the present work is to investigate the effect of temperature and rest time on the rheological properties of the dispersions with different concentrations of Laponite RD when the polymer content is kept constant.

MATERIALS AND EXPERIMENTAL METHODS

Materials. Laponite RD used in the present study, with the idealized chemical formula Na$^{+0.7}$[(Si$_8$Mg$_{5.5}$Li$_{0.3}$)O$_{20}$(OH)$_4$]$^{-0.7}$,
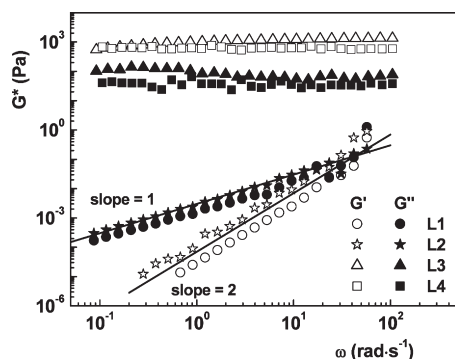
Figure 1. Oscillatory frequency dependence of the viscoelastic moduli for Laponite dispersions at 20 °C (t_{rest} = 1 day).

Figure 2. Oscillatory frequency dependence of the viscoelastic moduli for the PEG/Laponite RD/water ternary mixtures at 20 °C (t_{rest} = 1 day).

was acquired from Rockwood Additives Limited U.K. The bulk density and the specific surface area of the used Laponite RD are 1 g cm^{-3} and 370 m^2 g^{-1}, respectively, and pH for the investigated aqueous dispersions is higher than 9.

Poly(ethylene glycol) with the average molecular weight of 10 kg mol^{-1} and polydispersity index of l.04 was purchased from Fluka Co.

Polymer solutions with concentrations in the range of 4.00–4.76% in deionized water were vigorously stirred for 10 min and kept a day before the mixtures preparation. Clay dispersions with concentrations from 1.89% to 6.90% were obtained by the addition of Laponite RD in deionized water followed by high speed stirring for about 10 min. The clay dispersions were sonicated for 30 min and then mixed with the polymer solutions in different ratios in order to obtain the desired composition. The concentrations were expressed as a w/w %. In the present article, the investigated samples were denoted as PEGX-LY where PEG is poly(ethylene glycol) and L is Laponite RD. The clay dispersions without polymer were denoted only with L. X and Y represent the concentrations of polymer and clay, respectively, in the polymer/clay/water mixtures.

Rheological Measurements. The rheological measurements were performed at different temperatures (15–40 °C) and at different periods of time (up to 7 days) using a controlled stress Bohlin 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 oscillatory frequencies range of 0.05 rad s^{-1} to 500 rad 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 4×10^{-4} s^{-1} to 4×10^3 s^{-1} in order to determine the shear viscosity. The rest time was denoted as t_{rest}.

■ RESULTS AND DISCUSSION

Effect of Temperature. The frequency sweep measurements were achieved at temperatures between 15 and 40 °C in the linear region of viscoelasticity. The variation of the viscoelastic moduli (G' and G'') as a function of the oscillatory frequency (ω) at 20 °C for Laponite RD dispersions in the presence/absence of poly(ethylene glycol) is shown in Figures 1 and 2.

The dispersions free of polymer show different viscoelastic behaviors, depending on the clay concentration: the samples having less than 2% Laponite RD (L1 and L2) present liquid-like
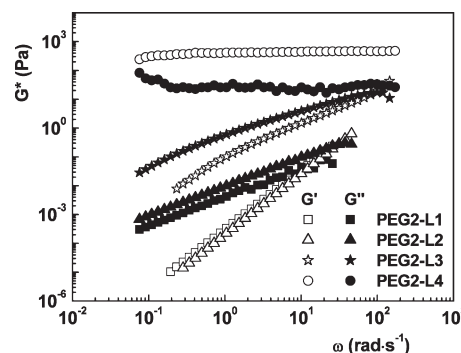
properties and those with higher concentrations of clay (L3 and L4) have solid-like behavior, showing a weak dependence on oscillation frequency.

Generally, the structure and the properties of the clay dispersions are modified by the addition of poly(ethylene oxide) due to the change of the interaction between the clay particles in water. The rheological properties of Laponite dispersion in the presence of PEG depend on the clay concentration in the initial dispersion. Up to 2% Laponite RD, the clay particles are dispersed in water showing a liquid-like behavior. By adsorption of polymer chains, the repulsive double layer potential is screened, and the electrostatic repulsion between clay particles decreases. The addition of PEG with M_n = 10 kg mol^{-1} determines a slight increase of the viscoelastic moduli (Figure 2).

If the polymer is added into a Laponite RD dispersion with concentration higher than 2% (as for example the sample denoted PEG2-L3), the rheological behavior is different. In our study, the pH of all Laponite based dispersions is higher than 9, and in this condition, the formation of the gel structure is caused by long-range electrical double layer repulsion between the clay platelets.[5,6,9,16] The adsorption of PEG onto Laponite RD particles reduces the association between these and a more pronounced decrease of viscoelastic parameters is evidenced (Figure 2). The PEG2-L3 sample shows a liquid-like behavior, whereas the corresponding clay dispersion (L3) presents gel properties. The formation of the clay–polymer–clay bridges in the presence of PEG with the molecular weight of 10 kg mol^{-1} is reduced because the polymer chains are not long enough to connect the Laponite RD particles.

The addition of PEG into 4% clay dispersion does not change significantly the viscoelastic moduli values (sample PEG2-L4). At concentrations higher than 3% Laponite RD, Mourchid et al.[8] evidenced the formation of a nematic phase in which the clay discs or small stacked aggregates of clay particles orient with respect to each other in domain over macroscopic length scales. The presence of PEG chains into such system does not affect the structure of clay dispersion, and as a consequence, the rheological properties are not altered.

One can see that the viscoelastic moduli values of the clay dispersions containing PEG chains increase by increasing the clay content, and the dispersion with 4% Laponite RD shows solid-like properties having $G' > G''$. The samples with a clay concentration lower than 3% present a typical behavior of viscoelastic Maxwellian fluid, that is, G'' scales with ω^1 and G' with ω^2. The longest relaxation time (τ_1) was calculated from the
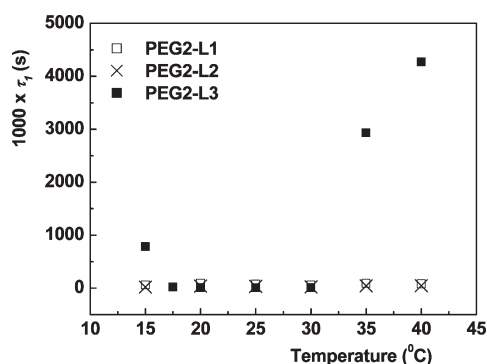
Figure 3. Effect of temperature on the longest relaxation time of the mixtures with different clay concentrations (t_{rest} = 1 day).
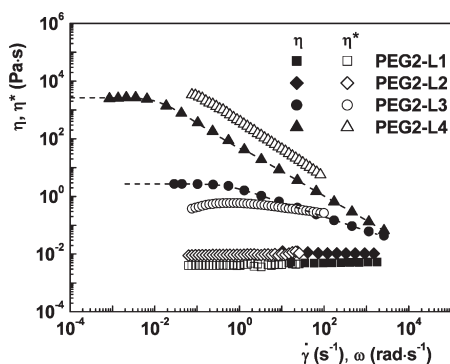

Figure 4. Application of the Cox−Merz rule to samples with different concentrations of clay at 20 °C (filled symbols, steady shear viscosity vs shear rate; open symbols, complex viscosity vs oscillation frequency) (t_{rest} = 1 day). Dotted lines represent the fitting curves according to the Carreau equation.

Figure 5. Effect of temperature on the complex viscosity of PEG2-L1 sample (t_{rest} = 1 day).

Figure 6. Effect of temperature on the complex viscosity of PEG2-L3 sample (t_{rest} = 1 day).

oscillatory shear data as being the inverse of oscillation frequency for which $G' = G''$ (ω_{cross}). For temperatures ranging from 15 to 40 °C, the longest relaxation times of the samples with low clay concentration (1% and 2%) are independent of the temperature (Figure 3).

For all studied samples, the effect of the clay concentration on τ_1 is insignificant at temperatures between 17.5 and 30 °C. In the same time, the temperature effect on τ_1 is more important for the samples with higher clay concentrations at which τ_1 increases for temperatures above 30 °C and below 17.5 °C. The different effect of the temperature on τ_1 for the PEG2-L3 sample could be explained, on the one hand, by the effect of Brownian motion on the strong network structure formed in the dispersion with high clay concentration, and on the other hand, at high temperature the solvency of poly(ethylene oxide) in water decreases. For a slow increase of the temperature from 15 to 20 °C, the Brownian motion induces the breaking of the strong network structure formed between clay particles and the desorption of the polymer that covered the clay discs, leading to the decrease of the relaxation time. By further increases of the temperature, the PEG chains shrink on the Laponite RD particles and the clay disk−clay disk and clay disk−polymer chain interactions increase.

The molecular weight of the added polymer is an important factor that influences the variation of the relaxation time with temperature. Lin-Gipson et al.[17] showed that the relaxation time of a solution with 2% poly(ethylene oxide) having the molecular
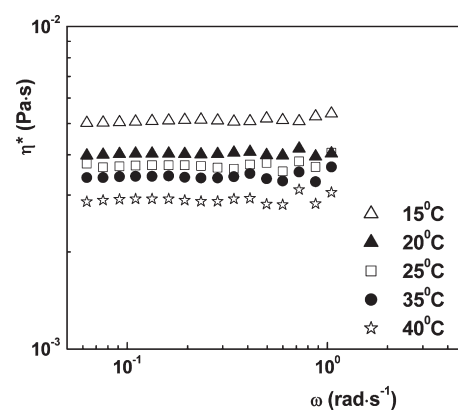
weight of 1000 kg mol^{-1} and 3% Laponite RD increases by the increasing of the temperature indicating some stronger associative interactions between the polymer chains and clay discs. By using the small angle neutron scattering method for a mixture of 3% Laponite LRD and 1.5% poly(ethylene oxide) (molecular weight of 900 kg mol^{-1}) in water, Li et al.[18] evidenced an anisotropic structure at temperatures lower than 20 °C, while at 50 °C, this sample becomes isotropic.

The steady flow measurement allows the investigation of the steady shear viscosity (η) of the studied dispersions. The dispersions with 1% and 2% clay exhibit a Newtonian behavior (the viscosity is independent of the shear conditions), unlike the mixtures with 3% and 4% clay that show a pseudoplastic behavior (the viscosity decreases under shear) (Figure 4). At high enough concentrations ($\geq$3%) the Laponite particles attract each other forming fractal aggregates that can generate a network structure, which is destroyed by application of sufficient strain, and the viscosity decreases with increasing shear rate.

The differences between the values of the steady-state viscosity for these samples are considerably higher at low shear rates. Cox and Merz[19] observed for many polymer systems that a correspondence between η plotted against shear rates ($\dot{\gamma}$) and the magnitude of η^* plotted against ω occurs, and the following empirical relationship was proposed:

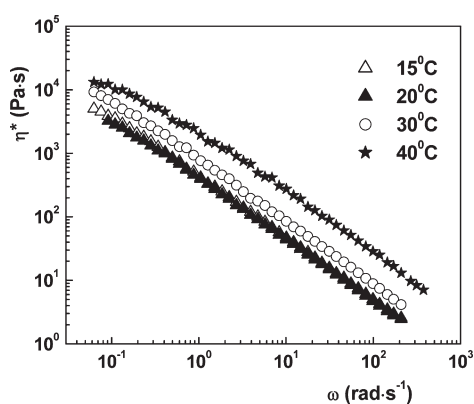$$\eta^*(\omega) = \eta(\dot{\gamma})|_{\omega = \dot{\gamma}} \tag{1}$$

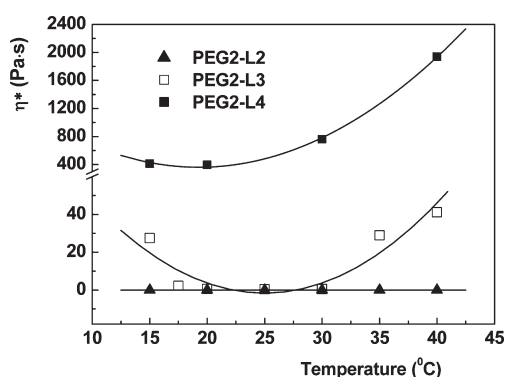**Figure 7.** Effect of temperature on the complex viscosity of PEG2-L4 sample (t_{rest} = 1 day).

Figure 8. Effect of temperature on the complex viscosity of the mixtures for an oscillation frequency of 1 rad s^{-1} (t_{rest} = 1 day).

The deviation from Cox—Merz relationship was observed for the systems characterized by the existence of the ordered structures, large aggregates, or the high particle—particle interactions.[20,21] In our case, the dispersions having low clay concentration obey the Cox—Merz rule. This rule is not valid for the dispersions with the clay concentration higher than 3%, behavior that is characteristic to the complex structured fluids.[22]

Figures 5—7 show the evolution of the complex viscosity (η^*) of the mixtures with low (PEG2-L1) and high (PEG2-L3 and PEG2-L4) clay concentrations at different temperatures.

The complex viscosity decreases by increasing the temperature for the samples with low concentrations of Laponite RD (Figure 5). For these samples, the interactions between clay particles are not very strong and the enhancement of Brownian motion by increasing the temperature causes the continuous decrease of the complex viscosity.

By increasing the clay concentration, a network structure is realized in the aqueous dispersion due to the increase of the interactions between clay discs. For the systems having the clay concentrations higher than 2%, the increase of the temperature until 20 °C induces the decrease of the complex viscosity followed by its increase at higher temperature (Figures 6 and 7). This decrease of the complex viscosity is more important for the sample with 3% Laponite RD. The complex viscosity of this mixture at 20 °C is 2 orders of magnitude lower than that measured at 15 °C. Chang et al.[23] evidenced the same behavior for the concentrated attapulgite aqueous suspension.

Table 1. Zero Shear Viscosities Values and Flow Activation Energy for the Investigated Dispersions

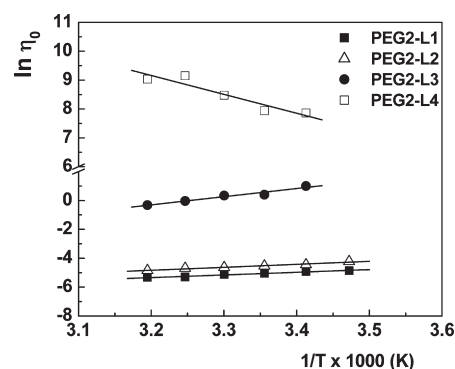| sample	η_o (Pa s)						E_a (kJ mol^{-1})
	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	
PEG2-L1	0.0077	0.0073	0.0064	0.0059	0.0050	0.0048	15.32 ± 0.34
PEG2-L2	0.0146	0.0117	0.0108	0.0097	0.0091	0.0079	16.99 ± 0.49
PEG2-L3		2.7208	1.4820	1.3970	0.9650	0.7227	47.05 ± 2.29
PEG2-L4		2590.26	2791.29	4792.23	9385.50	8407.04	−54.44 ± 6.16

Figure 9. Arrhenius plot used to determine the flow activation energy for PEG/Laponite RD/water mixtures.

They explained the existence of a minimum in the evolution of the relative viscosity of 10% attapulgite suspension in water as a function of temperature by the effect of the Brownian motion on the strong network structures. For the systems with strong network, the Brownian motion may not be able to raise the viscosity further but rather disrupts the network structure and decreases the system viscosity. As the intensity of Brownian motion increases, the interactions between clay particles increase leading to an increase of the systems viscosity.[23] For better evidence of this behavior, in Figure 8, it shows the evolution of the complex viscosity measured at 1 rad s^{-1} as a function of temperature for the PEG2-L2, PEG2L3, and PEG2-L4 samples.

The complex viscosity of the mixtures with low clay concentration is nearly independent of the temperature unlike those with 3% and 4% Laponite RD.

The flow activation energy was determined by using an Arrhenius-type equation

$$\eta_o = A \, e^{E_a/RT} \qquad (2)$$

where η_o is the zero shear viscosity (Pa s), E_a is the activation energy of the flow (J mol^{-1}), T is the absolute temperature (K), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and A is the pre-exponential factor.

The values of zero shear viscosity of the mixtures with 1% and 2% Laponite RD were determined by the extrapolation of the shear viscosity to zero shear rate, according to

$$\eta_o = \lim_{\dot{\gamma} \to 0} (\eta) \qquad (3)$$

The zero shear viscosity values of the samples with 3% and 4% Laponite RD which have a non-Newtonian behavior were
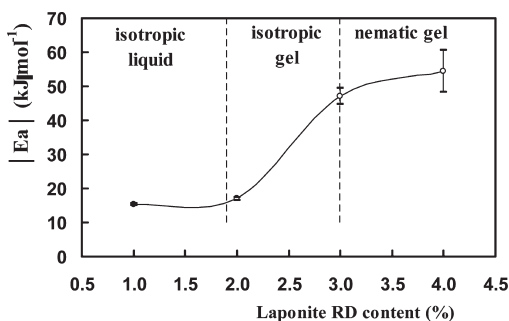
Figure 10. Variation of the flow activation energy (absolute value) with the Laponite RD concentration in the polymer/clay/water mixtures. Dotted lines delimit the physical states of Laponite RD aqueous dispersions according to the literature.[8,16]

determined by using the Carreau method[24]

$$\eta = \frac{\eta_o - \eta_\infty}{(1 + a(\dot{\gamma})^2)^m} + \eta_\infty \qquad (4)$$

where η_∞ refers to the asymptotic values of the shear viscosity at very high shear rates, a is a constant parameter with the dimension of time, and m is a dimensionless constant.

The η_o values and the calculated flow activation energies (E_a) for all investigated mixtures are presented in Table 1. The flow activation energy of the mixtures with the highest clay concentration was determined by applying the Arrhenius relationship at temperatures higher than 20 °C (Figure 9).

For the samples PEG2-L1 and PEG2-L2, one observes a slight decrease of the viscosity by increasing the temperature. This decrease is more pronounced for higher clay content (sample PEG2-L3). The flow activation energy increases with the increase of the clay concentration.

A different behavior can be observed for the sample with the highest content of Laponite RD (sample PEG2-L4) for which the viscosity strongly increases from 20 to 40 °C. For this system, the high temperatures cause an increase of the interparticle attractive forces, which determine an increase of the effective viscosity.[25]

The evolution of flow activation energy (absolute value) as a function of the clay concentration is shown in Figure 10.

The dotted lines delimit the physical states of Laponite RD aqueous dispersions from the first phase diagram proposed by Mourchid et al.[8] For Laponite RD dispersions in water free of salts, they identified three phases, depending on the clay concentration (C_c): (a) an isotropic liquid phase at $C_c < 2\%$; (b) an isotropic gel phase for $2\% < C_c < 3\%$; and (c) a nematic gel phase for $C_c > 3\%$. In the isotropic liquid state, the dispersion presents small aggregates formed by several clay discs suspended in water. The isotropic gel phase is characterized by the existence of the percolating gel in which the clay discs have a random orientation. The last phase from the diagram presents a macroscopic nematic ordering of the clay discs.[26] One can observe from Figure 10 that the flow activation energy (absolute value) increases significantly in the isotropic gel phase.

Effect of Rest Time. It is known that the aqueous dispersions of some clays (with or without polymer) show aging and undergo a change from a liquid-like state to a solid-like structure in different periods of time.[27−34] The aging process consists in the structural rearrangement of each clay particle within the sample in time in order to lower the total energy. Low Laponite concentrations (1%) slowly evolve from a viscoelastic fluid to a
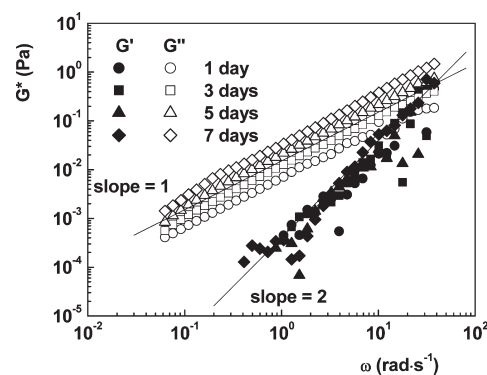

Figure 11. Dependence of the viscoelastic moduli as a function of frequency for PEG2-L2 sample at 25 °C at different rest times.
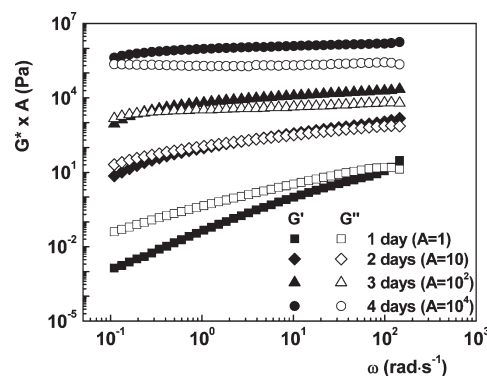

Figure 12. Dependence of the viscoelastic moduli as a function of frequency for PEG2-L3 sample at 25 °C at different rest times.
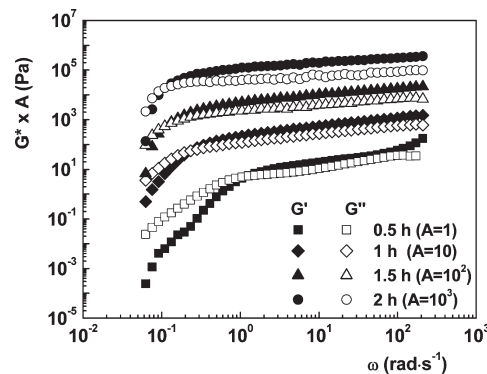

Figure 13. Dependence of the viscoelastic moduli as a function of frequency for PEG2-L4 sample at 25 °C at different rest times.

glass formed by clusters acting as constituent elements interacting via long-range repulsion. The samples with higher Laponite concentration (as for example 3% Laponite dispersion) quickly form a glass of individual particles. Intermediate concentrations of Laponite form a glass that is a mixture of clusters and individual particles.[31] The aging behavior of Laponite aqueous dispersions is strongly influenced by the preparation procedure of the sample,[35] the temperature,[36] and the stress/deformation field.[37,38]

The frequency sweep tests of PEG2-L2, PEG2-L3, and PEG2-L4 samples at different rest times evidence the gelation process in
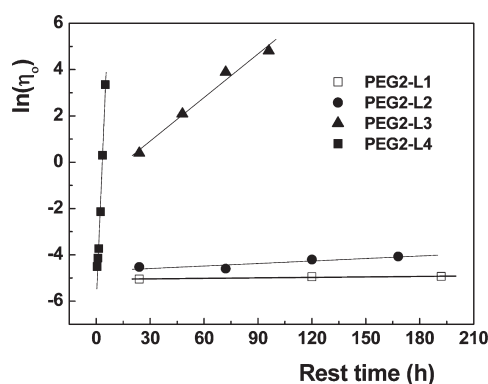
Figure 14. Variation of the zero-complex viscosity as a function of time for the PEG/Laponite RD/water ternary mixtures at 25 °C.
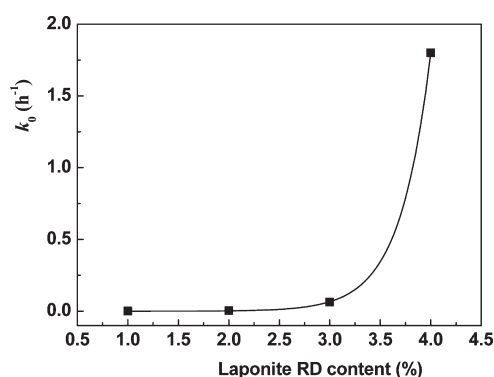

Figure 15. Effect of the Laponite RD content on the viscosity-rate kinetic constant at 25 °C.

time (Figures 11−13). The gelation time decreases by increasing the clay content in the mixtures. Unlike the PEG2-L2 sample that displays the rheological characteristics of a liquid even after 1 week (Figure 11), the PEG2-L3 and PEG2-L4 mixtures begin to exhibit solid-like properties in about 4 days and 2 h, respectively (Figures 12 and 13).

The aging kinetic in time of the PEG/Laponite RD/water mixtures was investigated at 25 °C by following the evolution of the zero shear viscosity as a function of the rest time and the clay concentration. The dependence of η_o of the time (t) can be described by an exponential equation

$$\eta_o = \eta_i \exp(k_o t) \tag{5}$$

where η_o is the zero shear viscosity for the mixtures kept at rest time, t_{rest}, η_i is the zero shear viscosity at the zero rest time ($t_{rest} = 0$), k_o is the viscosity-rate kinetic constant, and t is the time.

Zero-shear viscosity at different rest times was determined by steady-flow measurements for all mixtures.

The η_o values of the mixtures with low clay concentrations, which present Newtonian behavior, were established by extrapolation of the shear viscosity to zero shear rates. The zero shear viscosities of the samples with high clay concentrations that have pseudoplatic behavior were calculated by using the Carreau method (eq 4). The dependence of η_o values as a function of the rest time proves the existence of the aging phenomena for the samples with clay concentrations higher than 2% (Figure 14). The viscosity-rate kinetic constant increases by increasing the

clay concentration, and the fastest aging was evidenced at the mixture with 4% Laponite RD (Figure 15).

CONCLUSIONS

The rheological properties of four mixtures of 2% poly-(ethylene glycol) and Laponite RD (1%, 2%, 3%, and 4%) in water were investigated by oscillatory and flow measurements in the temperature range of 15−40 °C at different rest times. By increasing the Laponite RD concentration, the viscoelastic parameters increase, and the flow behavior changes from liquid-like to solid-like. The effect of temperature on the longest relaxation time is more important for the samples with clay concentrations higher than 3%. The effect of Brownian motion on the formed strong network structure and the modification of the solubility of poly(ethylene glycol) in water at high temperature could be responsible for the behavior of the mixtures with high clay concentration at different temperatures. The absolute values of the flow activation energy of all samples showed an abrupt increase at clay concentrations between 2% and 3%.

The effect of the rest time on the rheological properties of the studied mixtures was also investigated. The gelation time decreases by increasing the clay concentration in the dispersion. The aging kinetic of poly(ethylene glycol)/Laponite RD/water mixtures was investigated at 25 °C, and an augmentation of the viscosity-rate kinetic constant by increasing the clay content was evidenced.

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