INFLUENCE OF POLY(ETHYLENE OXIDE) ON THE AGGREGATION AND GELATION OF LAPONITE DISPERSIONS IN WATER

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The influence of poly(ethylene oxide) the aggregation and gelation of Laponite RD aqueous dispersions temperature in the range 10°C-50°C using rheology, under different experimental conditions is studied. PEO adsorbs onto the Laponite particles and inhibits aggregation by steric hindrance. The diminution of the aggregation phenomenon depends on the polymer concentration and temperature. Bellow 30°C, the polymer concentration has no significant effect on the viscoelastic behavior. Above 30°C, a critical concentration, c_p, necessary to completely cover the clay particles surface was established. For $c < c_p$, the samples have a gel-like behavior. Above c_p, a "critical gel" behavior is observed. Higher polymer concentrations (≥ 1 wt%) leads to the formation of clusters or a weak gel.

INTRODUCTION

Laponite is an additive that improves the performances of a wide range of industrial and consumer products being non-toxic, non-yellowing, non-inflamable, and also not supporting the microbial growth. This clay is used as a model for disk-like colloids,[1-6] having a well-defined thickness of 1 nm and a diameter of 30 nm. As dispersion in water, the laponite can form an isotropic liquid phase, with increasing of the clay content, an isotropic and a nematic gel at low salt concentration (low ionic strength).[1, 2] At high salt concentration (high ionic strength) the aggregation leads to flocculation.[3-6]

Laponite is known as the has as result highly shear thickener of commonly used rheological additives. At shear rates close to those caused by gravity (10^{-4} s^{-1}, *e.g.* when the product is in storage), a 2% gel of Laponite in water has a viscosity of over 10^5 Pa·s; under high shear rates conditions ($> 10^3$ s^{-1}) the viscosity falls to less than 0.03 Pa·s.[7]

A synergistic increase in efficiency can be obtained by combining Laponite with certain polymers thickeners and this can provide a significant cost saving. The polymer is incorporated into the clay dispersions as rheological modifier, additive or stabilizer. Many properties of the polymer/ clay/water systems depend on the structural changes such as the orientation of the clay disks within the material, a property which can be greatly affected or controlled by shear flow.

In this paper we investigate the effect of poly(ethylene oxide) (PEO) on the aggregation and gelation of Laponite RD aqueous dispersions at different temperatures and under various equilibrium conditions.

RESULTS AND DISCUSSION

In aqueous dispersions, the Laponite RD disk-like particles have negative charges on the faces and positive ones on the edges, being able to form gel-like structures. There are two main explanations about the gelation mechanism of Laponite RD dispersions, depending of pH and ionic strength: 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

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of cards", as a result of the electrostatic attraction between the positively charged edges and negatively charged faces of the plate-like particles;[8-10] b) at high pH and low ionic strength the gelation can be explained by the electrical double layer repulsion between clay particles.[11, 12] The second mechanism can explain the gelation of the 2 wt% Laponite RD aqueous dispersion at a pH value of 9.8 used in the present study (high pH and low ionic strength).

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 the shear, the polymer chains are in a dynamic adsorption/desorption equilibrium with the clay particles and form a „dynamic network".[13]

The liquid-solid transition strongly affects the molecular mobility, which leads to large changes in rheological parameters. Exactly at the transition point, the material behaves not as a liquid and not yet as a solid. The relaxation modes are not independent any more, but they are somehow coupled over a wide range of time scale. The coupling is expressed by a power law distribution of relaxation modes:[14]

$$G(t) = St^n, \text{ for } \lambda_o < t < \infty \tag{1}$$

where $G(t)$ is the relaxation modulus, S is the gel strength parameter, n is the relaxation exponent and λ_o is the characteristic material time.

The relaxation exponent, n, is restricted to values between 0 and 1: $n = 0$ corresponds to the limiting behavior of a Hookean solid when the relaxation modulus is a constant. The restriction of

n values to less than unity assures a diverging zero-shear viscosity at the gel point. At times shorter than λ_o the sol-gel transition can not be observed by rheological measurements because this parameter characterizes the molecular building block of the critical gel.

$$G'(\omega) = \frac{S \cdot \pi \cdot \omega^n}{2 \cdot \Gamma(n) \cdot \sin(\frac{\pi \cdot n}{2})} \tag{2}$$

$$G''(\omega) = \frac{S \cdot \pi \cdot \omega^n}{2 \cdot \Gamma(n) \cdot \cos(\frac{\pi \cdot n}{2})} \tag{3}$$

The elastic modulus, G' (the strain energy reversibility stored in sample) and the viscous modulus, G'' (the amount of energy irreversibility given off by substance to its environment) can be expressed as:

$$\tan \delta = \frac{G''}{G'} \tag{4}$$

where $\Gamma(n)$ is the Legendre Gamma function.

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

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.

The gelation process is well described by the evolution of $\tan \delta$ as a function of frequency or time. 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:[14, 15]

The gelation point can be also identified when G' and G'' are parallel in their frequency dependences.

$$G'(\omega) \sim G''(\omega) \sim \omega^n \tag{5}$$

$$\tan \delta = \tan(\frac{\pi \cdot n}{2}) \tag{6}$$

At the gelation point, tan δ becomes independent of frequency and $\delta = n \pi/2$.

The loss tangent becomes very small (<< 1) for solid-like materials. If tan δ → 1 and tan δ = constant, the material has a "critical gel" structure which represents a critical state of matter between liquids and solids.

Influence of temperature and polymer concentration on the viscoelastic properties

Frequency sweep measurements were achieved at temperatures between 10°C and 50°C in the linear region of viscoelasticity (at shear stress of 1 Pa). In Fig. 1 is shown the variation of tan δ with temperature for the Laponite RD dispersion and for samples with different content of PEO (Table 1) at the constant frequency $\omega = 1$ rad/s.

From Fig. 1, it can be observed that below 30°C there are not significant differences in the behavior of the different samples. A transition from a gel to a "critical gel" state is evidenced at a temperature located between 30°C and 40°C for the Laponite RD aqueous dispersion.

This transition temperature was better determined from the representation of the loss tangent as a function of temperature for different frequencies (Fig. 2). All curves give a point of intersection at 38°C and this can be considered as the transition temperature from the gel to the "critical gel" state.

The tan δ values of the mixtures with concentration of PEO higher than 0.05 wt% are not influenced by increasing of temperature. For the mixtures with 0.2 wt% and 0.5 wt% PEO, the gel - "critical gel" transition was observed at 47°C, as can be seen from the some Fig. 3 for 0.2% PEO.

The gelation point is independent on frequency as it can be observed figure where the loss tangent as a function of temperature is shown.

To explain this behavior, we calculated the critical PEO concentration, c_p, as being the concentration necessary to completely cover the clay particles surface, by knowing the specific surface area of 370 m^2/g, the diameter of 25 nm and the thickness of 1 nm for Laponite RD disks and the radius of gyration of PEO (R_g) of 11 nm.

Table 1

Samples prepared for rheological measurements

Sample[a]	PEO[b] (wt%)
L2	0
PEO005-L2	0.05
PEO01-L2	0.1
PEO02-L2	0.2
PEO05-L2	0.5
PEO1-L2	1.0

[a]clay concentration = 2 wt%; $pH_{dispersions} = 9.8$;
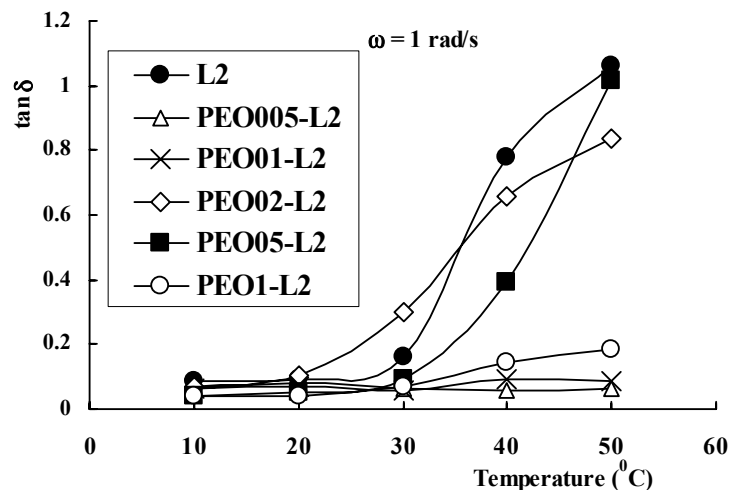[b]$M_n = 35\ 000$ g/mol and polydispersity index is 1.23.

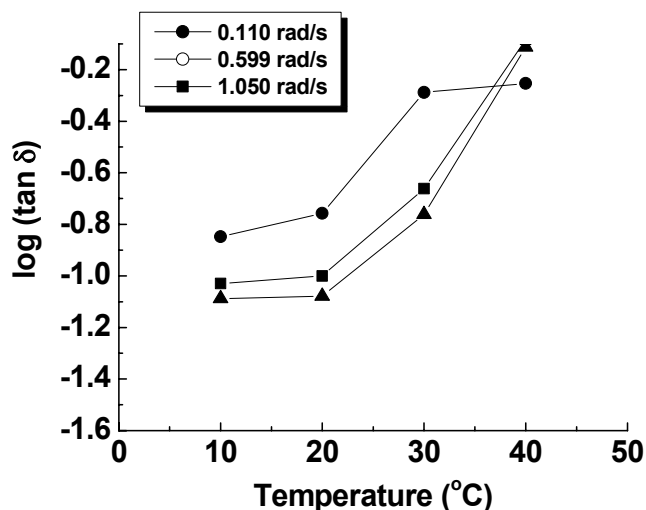Fig. 1 – Loss tangent of the polymer/clay/water mixtures as a function of temperature.

Fig. 2 – Loss tangent as a function of temperature at different frequencies for the L2 sample.

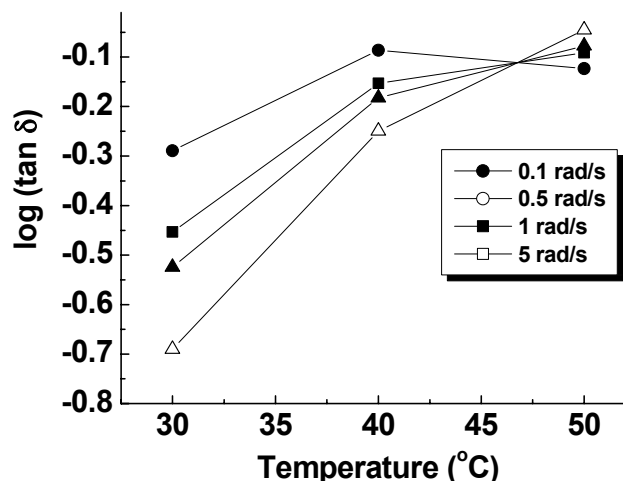Fig. 3 – Loss tangent as a function of temperature at different frequencies for the PEO02-L2 sample.

For PEO with M_w = 35 000 g/mol in water at 30°C, the radius of gyration was determined with the following relation:[16]

$$R_g = 0.022 \cdot M_w^{0.583} \text{(nm)} \tag{7}$$

Thus, it was found that the critical polymer concentration for covering all clay particles is c_p = 0.113 wt%. This value of concentration corresponds to the extremely dilute regime for PEO.[17]

Below c_p, the polymer introduced into the Laponite RD dispersion decreases the repulsions between the clay particles when a strong gel, stable at high temperatures, is obtained. In the samples having the polymer concentration above c_p, there are also free PEO chains in solution. Below 30°C these ternary mixtures behave as weak and stable gels and at higher temperatures as "critical gels".

The formation of PEO clusters at higher temperatures could be responsable for the rheological behavior of PEO1-L2 sample (in this sample, the clusters are visible with the naked).

Influence of experimental procedure on the viscoelastic behavior

In the second step, the temperature sweep measurements were carried out for PEO/Laponite RD/water mixtures at constant frequency (ω = 1 rad/s) and shear stress (σ = 1 Pa), with a heating rate of 1°C/min, in the temperature range 10-50°C. The evolution of tan δ as a function of temperature for different mixtures by considering both type of experiments, frequency sweep and temperature sweep tests in Fig. 4 is shown.
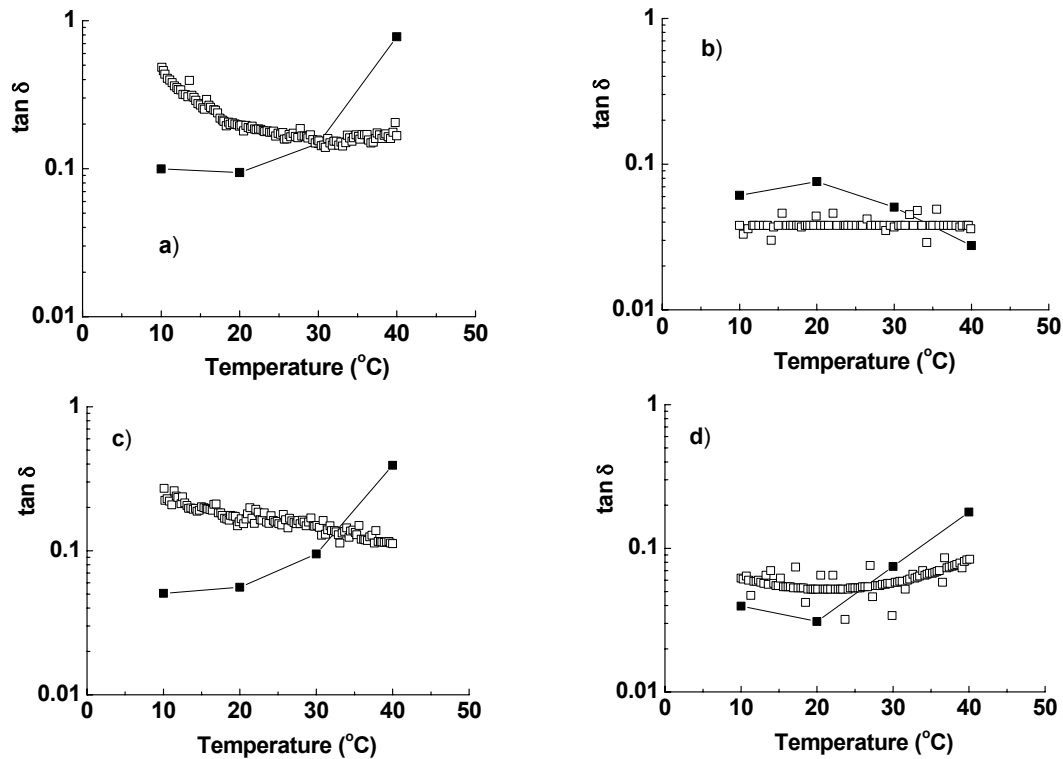
Fig. 4 – Evolution of the loss tangent (tan δ) as a function of temperature at ω = 1 rad/s and σ = 1 Pa for the samples: a) L2; b) PEO005-L2; c) PEO05-L2; d) PEO1-L2; ■ – data obtained in frequency sweep test at constant temperature; □ – data obtained in temperature sweep test with 1°C/min at constant frequency.

The L2 and PEO05-L2 samples present in frequency sweep a stronger gel structure than in temperature sweep tests for the same shear stress conditions. In frequency sweep tests, the system attains a thermal equilibrium, whereas in the conditions of continuous increase of temperature the time is not enough for a strong aggregation of the clay disks. The gel structures of the PEO005-L2 and PEO1-L2 samples are less influenced by the experimental procedure used in rheological measurements.

EXPERIMENTAL

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 typical characteristics of Laponite RD are: the bulk density $1 g/cm^3$; the surface area $370 m^2/g$ and pH for 2 wt% dispersion 9.8.[7] Poly(ethylene oxide) (PEO) with molecular weight $M_n =$ 35 000 g/mol and polydispersity index of 1.23 was purchased from Fluka Co.

The laponite dispersions were prepared by adding the clay in distilled water with moderate stirring for ten minutes. For all samples, the laponite concentration was of 2 wt %. PEO was added in the clay dispersion to obtain samples with polymer concentrations ranging from 0.05 wt% to 1 wt%. The

binary (clay/water) and ternary (polymer/clay/water) mixtures were kept at room temperature for 28 days to reach the equilibrium.

The rheological measurements were performed at different temperatures (10°C-50°C) using a CVO Rheometer with parallel plate geometry (60 mm diameter and 500μm gap) and thermal control by Peltier effect. The dynamic properties were determined in the frequency range of 0.01 - 100 rad/s at constant shear stress (in the linear region of viscoelasticity) in two different ways: (a) frequency sweep at constant temperature; (b) temperature sweep at constant frequency.

CONCLUSIONS

The dynamic response of the poly(ethylene oxide) (PEO)/Laponite RD/water mixtures is influenced in a different manner by temperature and shear conditions, depending on the polymer concentration in the Laponite RD dispersion. Below a critical concentration, c_p (0.113 wt% for PEO used in this study), the gel structure realized at low temperatures (from 10°C to 30°C) is also mantained at higher temperatures (above 30°C).

The temperature strongly influences the structures in the case of the L2, PEO02-L2 and PEO05-L2 samples, which become "critical gels"

at a certain temperature (L2 at 38°C and PEO02-L2, PEO05-L2 at 47°C). The rheological behavior of PEO1-L2 sample is explained by the formation of PEO clusters at higher temperatures.

For the PEO005-L2 sample, having the polymer concentrations below c_p, and for the PEO1-L2 sample, with a high content of PEO, the structure is less influenced by the experimental procedure used to investigate the rheological properties.

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