

# Shake gels based on Laponite–PEO mixtures: effect of polymer molecular weight

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**Abstract**—Disc-shaped clay particles (Laponite) with a thickness of 1 nm and a diameter of 25 nm were bridged into a physical gel (shake gel) by poly(ethylene oxide) (PEO) chains under shear. The shake gels formed transformed again into a liquid when the shear stopped. The critical concentrations of Laponite and PEO required for the shake gel formation were determined. The results show that the molecular weight of the polymer chains significantly affects the critical concentrations, as well as the mechanical properties of gels. Shake gels form under certain concentrations of Laponite and PEO, corresponding to a critical surface coverage value  $\bar{n}_{\text{PEO}}$  of the Laponite particles by the polymer chains. The value of  $\bar{n}_{\text{PEO}}$  decreases as the molecular weight of PEO is increased. It was shown that strong gels with a relaxation time longer than 30 min form if the polymer molecular weight is in the range of  $2 \times 10^5$ – $3 \times 10^5$  g/mol.

**Keywords:** Gels; reversible gels; shear-induced gelation; Laponite; poly(ethylene oxide).

## 1. INTRODUCTION

Polymer–clay interactions in aqueous solutions have received considerable attention in recent years due to both fundamental and technological interest. These mixtures are used as rheological modifiers, as additives in coatings and as stabilizers or flocculators of colloidal dispersions [1]. In addition, these systems exhibit interesting physical properties and, at certain concentrations, they form model reversible networks.

Laponite is a synthetic disc-shaped silicate, with a thickness of approximately 1 nm and a diameter of 25 nm [2–4]. In aqueous dispersions, Laponite has a strongly negative face charge and a weakly, localized positive edge charge. The negative face charge of Laponite originates from the water–particle interactions while the edge charges are generated by the adsorption of the hydroxyl groups where

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the crystal structure terminates. If dispersed in distilled water, the sodium ions ( $\text{Na}^+$ ) on the particle face of Laponite are drawn towards the particle surface due to the electrostatic attractions. Opposing this, the osmotic pressure of water pulls the  $\text{Na}^+$  ions away from the particle. At equilibrium,  $\text{Na}^+$  ions form electrical double layers on both sides of the dispersed Laponite particles. Since the mutual positive charges of the particles repel each other, dilute dispersions of Laponite consists of non-interacting particles and, therefore, have a low viscosity. Addition of water-soluble compounds, such as salts or surfactants, to the Laponite dispersions will reduce the osmotic pressure holding the  $\text{Na}^+$  ions away from the particle surface, so that the electrical double layer becomes thinner. This results in the agglomeration of the particles and formation of a tixotropic gel with a “house of cards” network structure [4–6].

Compared to the low-molecular-weight compounds, addition of water-soluble polymers affects the Laponite dispersions differently, depending on the polymer concentration and on the molecular weight of the polymer chains. It has been shown that the binding between the particles can be inhibited by adding low-molecular-weight poly(ethylene oxide) (PEO) due to the saturation of the particles with an adsorbed layer of polymer chains [7, 8]. Higher-molecular-weight PEO bridges between the particles and leads to the formation of clusters or a weak gel immediately after mixing [7, 8]. Thus, polymers that are long enough to form interparticle bridges will promote formation of a reversible clay–polymer network.

Moreover, depending on the surface coverage of the Laponite particles by the polymer chains, Laponite–PEO mixtures exhibit physical properties ranging from a low viscosity liquid up to an elastic gel [9, 10]. Zebrowski *et al.* showed that, for certain concentrations of Laponite and PEO of molecular weight  $3 \times 10^5$  g/mol, Laponite–PEO mixtures undergo shear-induced gelation and the gels formed transform again into a liquid when the shear stops [9]. Such gels are called as “shake gels”. In the Laponite–PEO mixtures suitable for the shake gel formation, the polymer chains are weakly adsorbed by the particles so that, at rest, small aggregates consisting of several particles will form. When a shear is applied, the chain segments will adsorb additional free particles in the dispersion. Thus, as the shear proceeds, an increasing number of polymer–clay adsorption sites are created so that the polymer chains form bridges between particles belonging to different aggregates, leading to a macroscopic gel formation [9, 11]. However, once the shear stops, the polymer chains desorb, reducing the bridging and attaining their original conformation; this causes the gel to relax back to a fluid. The mechanism of shake gel formation requires that the segment–Laponite bond is weak and the energy associated with the adsorption is much less than that associated with the entropy of the polymer coil [9, 10]. Thus, moderate shear can increase the number of bonds between the polymer and the clay without significantly altering the configuration of the polymer.

In the present study, we investigated the effect of the molecular weight of PEO on the properties of Laponite–PEO-based shake gels. For this purpose, PEOs of

various molecular weights between  $2 \times 10^5$  and  $9 \times 10^5$  g/mol were used. The critical concentrations of Laponite and PEO required for gel formation, as well as the moduli of elasticity of gels were determined. As will be seen below, the molecular weight of PEO significantly affects the liquid–gel boundary concentration of the mixture as well as the mechanical properties of the resulting gels.

## 2. EXPERIMENTAL

### 2.1. Materials

Laponite clay (Laponite XLG, Rockwood Additives) and PEOs (Aldrich) were used as received. The nominal molecular weights ( $\bar{M}_w$ ) of the PEOs were  $2 \times 10^5$ ,  $3 \times 10^5$ ,  $6 \times 10^5$  and  $9 \times 10^5$  g/mol. The intrinsic viscosity  $[\eta]$  and the  $z$ -average square radius of gyration  $\langle S^2 \rangle_z$  of PEOs with  $\bar{M}_w > 6 \times 10^3$  g/mol in water at 25°C were reported as  $[\eta] = 4.33 \times 10^{-4} \bar{M}_w^{0.679}$  (dl/g) and  $\langle S^2 \rangle_z = 4.08 \times 10^{-18} \bar{M}_w^{1.16}$  (cm<sup>2</sup>), respectively [12]. Table 1 shows the  $z$ -average radius of gyration  $\langle S^2 \rangle_z^{1/2}$  of PEOs used in this study together with their overlap concentrations  $c^*$ , calculated using the equation [13]:

$$c^* = \frac{3\bar{M}_w}{4\pi N_A \langle S^2 \rangle_z^{3/2}} \times 10^2 \text{ (w/v, \%)} \quad (1)$$

where  $N_A$  is Avogadro's number.

Laponite stock solution was prepared by adding 2.5 g of Laponite powder to 100 ml of distilled water at high speed with a magnetic stirrer. PEO stock solutions were prepared by dissolving 1.5 g of PEO in 100 ml of distilled water for a few days. The stock solutions were used within one day after their preparation. Laponite–PEO mixtures were prepared by adding PEO stock to Laponite stock solution at 24°C. The concentrations of Laponite and PEO in the mixtures were varied in the range of 1.0–1.88% (w/v) and 0.065–0.45% (w/v), respectively. For example, to prepare a mixture containing 1.5% (w/v) Laponite and 0.30% (w/v) PEO, 2 ml of PEO stock solution was added to 6 ml of Laponite stock solution in a test tube, and the volume of the mixture was completed to 10 ml with distilled water. After preparation of

**Table 1.**

The molecular weight  $\bar{M}_w$ , the  $z$ -average radius of gyration  $\langle S^2 \rangle_z^{1/2}$  and the overlap concentration  $c^*$  of PEOs used in the preparation of Laponite–PEO dispersions

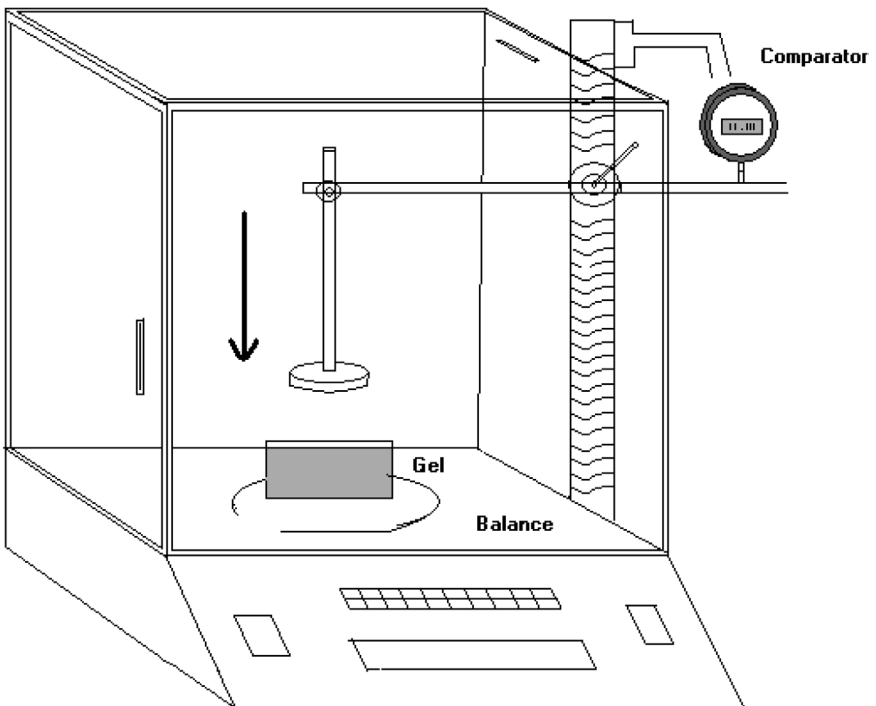
$\bar{M}_w$ (g/mol)	$\langle S^2 \rangle_z^{1/2}$ (nm)	$c^*$ (% w/v)
$2 \times 10^5$	24.0	0.57
$3 \times 10^5$	30.3	0.43
$6 \times 10^5$	45.4	0.25
$9 \times 10^5$	57.4	0.19

the mixtures, they were shaken vigorously for 15–20 s and inspected visually for increased viscosity, as well as for the formation of a gel.

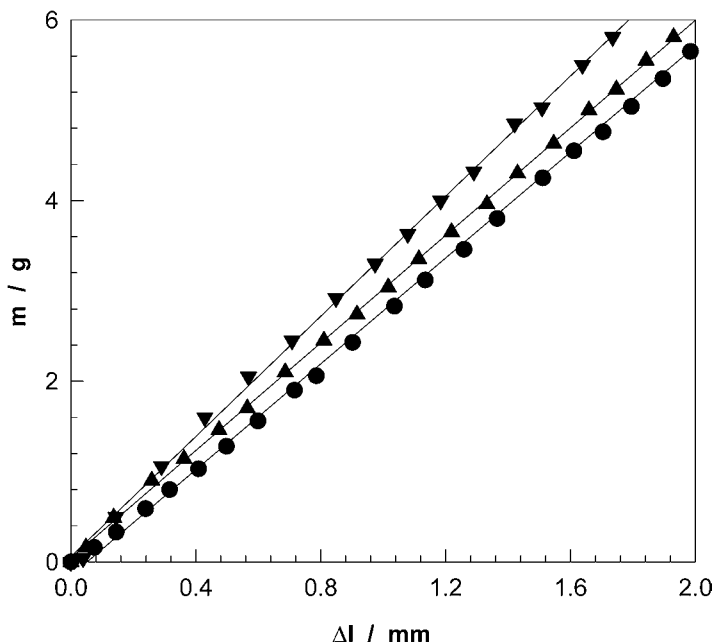
## 2.2. Methods

For the measurement of the relaxation time of the shake gels formed, a metal bead of 4.0 mm in diameter was placed on the surface of the mixture just after completion of shaking. Then, the time required until the metal bead drops to the bottom of the test tube was recorded. Gels with a relaxation time longer than 30 min were classified as strong gels, while those with shorter relaxation times as weak gels.

Uniaxial compression measurements were performed on shake gels with relaxation times longer than 15 min. All the mechanical measurements were conducted in a thermostated room of  $24 \pm 0.5^\circ\text{C}$ . The key parts of the apparatus used are shown in Fig. 1. Briefly, a fixed amount of the shake gel just after its preparation was transferred into a cylindrical vial of 56 mm in diameter and 46 mm in high and then the vial was placed on a digital balance. A load was transmitted vertically to the gel through a rod fitted with a PTFE end-plate. The force acting on the gel was recorded from the reading of the balance in terms of the mass  $m$ , while the resulting deformation  $\Delta l$  was measured using a digital comparator (IDC type Digimatic Indicator 543-262, Mitutoyo), which was sensitive to displacements of  $10^{-3}$  mm.



**Figure 1.** Uniaxial compression apparatus for measuring stress–strain data on shake gels just after their preparation.

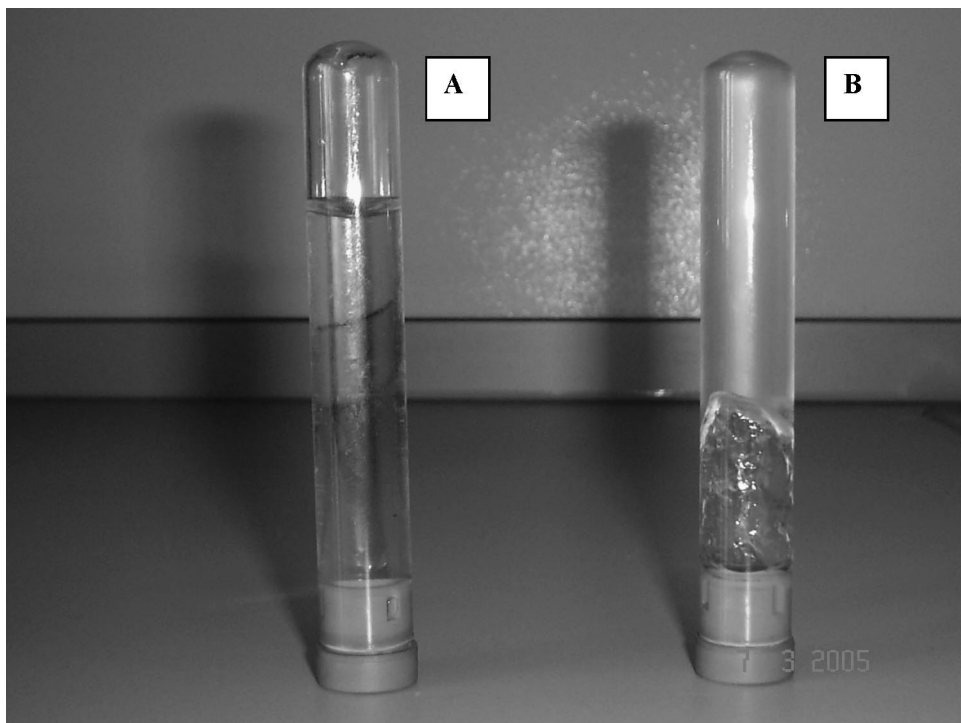


**Figure 2.** Typical stress-strain data for shake gel samples.  $\bar{M}_w = 2 \times 10^5$  g/mol, PEO concentration = 0.3%, Laponite concentration = 1.25 (●), 1.38 (▲) and 1.50% (▼).

Measurements gave reproducible results if the amount of the gel subjected to the deformation and the duration of the measurement (less than 5 min) are fixed. Typical  $m$ - $\Delta l$  data are shown in Fig. 2 for gels formed from various Laponite-PEO mixtures. The slope of the linear relationships was taken as the modulus  $G$  of shake gels.

### 3. RESULTS AND DISCUSSION

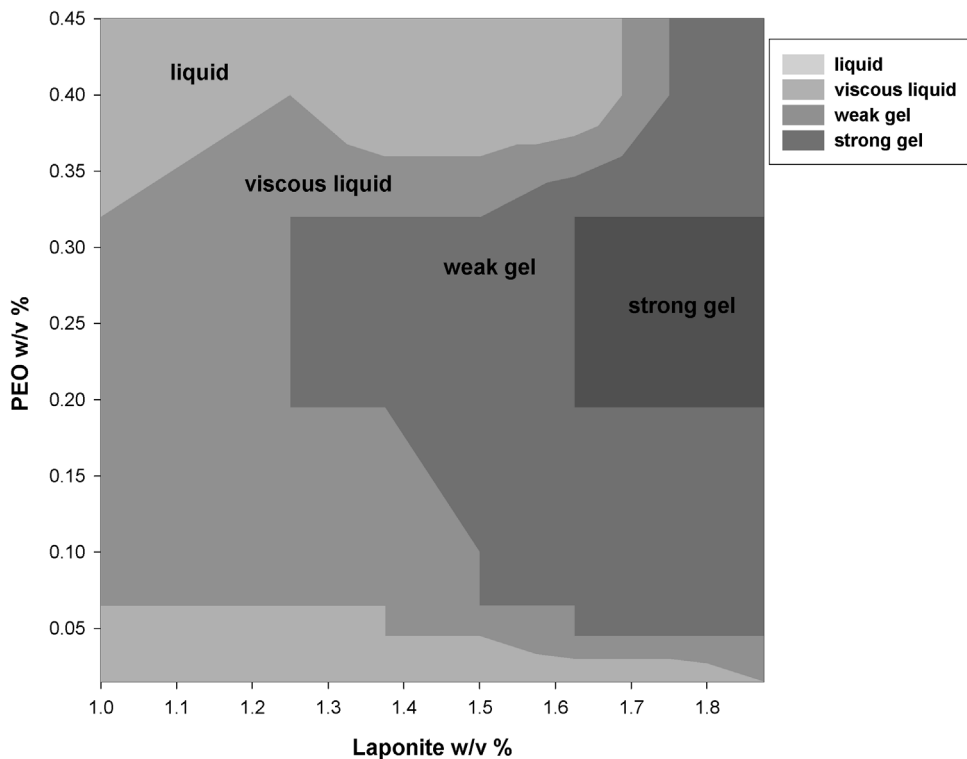
All the Laponite-PEO mixtures prepared in this study were low viscosity liquids. However, when shaken vigorously, they transformed, at certain Laponite and PEO concentrations, into a viscous liquid, a weak gel, or a strong gel. The pictures in Fig. 3 show a mixture containing 1.87% Laponite and 0.25% PEO of  $\bar{M}_w = 3 \times 10^5$  g/mol before (A in Fig. 3) and after completion of shaking (B in Fig. 3). It is seen that the gel formed due to the applied shear carries its own weight upon inverting the tube. This gel relaxed back into a liquid within 40 min. The contour plot in Fig. 4 shows the phase diagram of Laponite-PEO ( $\bar{M}_w = 3 \times 10^5$  g/mol) mixtures. The concentrations at the liquid-viscous liquid and viscous liquid-gel phase boundaries thus found are in accord with those reported before for the same dispersion system [9, 10]. The shear-induced gelation occurs at Laponite concentrations above 1.25%; the amount of PEO required for the gel formation is in the range of between 0.2 and 0.3%. This critical range of PEO becomes broader as



**Figure 3.** An aqueous Laponite–PEO mixture before (A) and after completion of shaking (B). The mixture contains 1.87% Laponite and 0.25% PEO of  $3 \times 10^5$  g/mol. The gel formed due to the applied shear carries its own weight upon inverting the tube.

the Laponite concentration in the mixture is increased. Below this range of PEO, the mixture remains as a liquid due to the very low surface coverage of the particles by the adsorbed PEO chains, while at higher PEO concentrations, the saturation of the Laponite surfaces leads to the steric stabilization of the particles in the dispersion. Shake gels form between these two regimes where the particles adsorb insufficient number of PEO chains. Thus, the free adsorption sites on the particles provide adsorption of additional polymer chains under shear. Figure 4 also shows that strong gels start to form at Laponite concentrations above 1.63%.

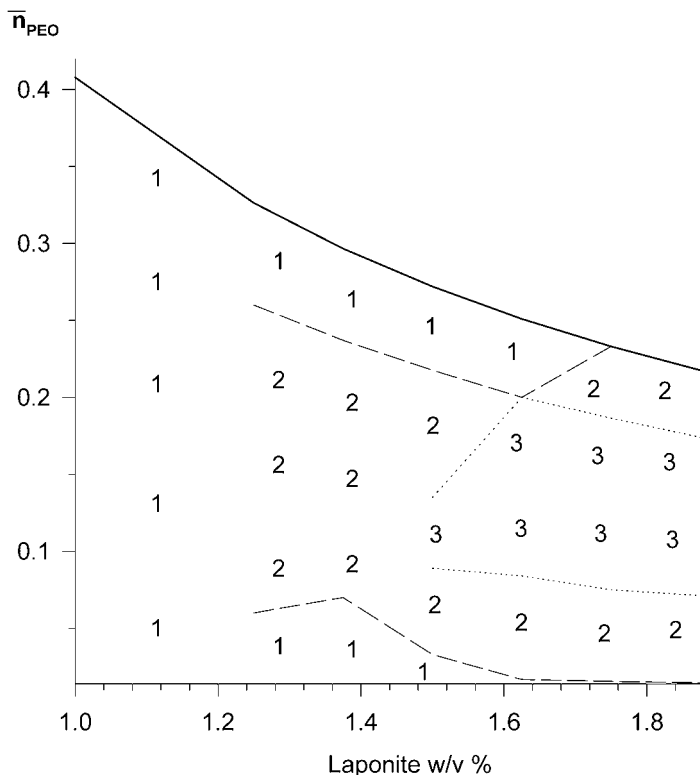
To estimate the surface coverage of the particles by PEO chains, we calculated the average number of polymer chains adsorbed by a Laponite particle  $\bar{n}_{\text{PEO}}$ . For calculations, the diameter and the thickness of a Laponite particle were taken as 25 nm and 0.92 nm, respectively, and the bulk density of Laponite as 1.00 g/ml [4]. The results are collected in Fig. 5, showing the variation of  $\bar{n}_{\text{PEO}}$  depending on the Laponite concentration. The numbers 1, 2 and 3 represent the liquid + viscous liquid, weak gel and strong gel phases, respectively. It is seen that shake gel forms if  $\bar{n}_{\text{PEO}}$  equals 0.1–0.2, i.e., if, on average, 5 to 10 Laponite particles are adsorbed by a single PEO chain. As the Laponite concentration is increased at a fixed value of  $\bar{n}_{\text{PEO}}$ , a weak gel transforms into a strong gel, i.e., the stability of PEO bridges



**Figure 4.** Phase diagram of Laponite–PEO mixtures. The molecular weight of PEO is  $3 \times 10^5$  g/mol. The various phases are indicated in the Figure.

increases. This is probably due to the decreasing distance between the adjacent particles in the gel, which reduces the effective length of PEO bridges so that their stability increases.

In order to elucidate the effect of the polymer molecular weight on the properties of gels, PEOs of molecular weights between  $2 \times 10^5$  and  $9 \times 10^5$  g/mol were used for the gel preparation. In these experiments, PEO concentrations were fixed at 0.2 and 0.3%, while the Laponite concentration was increased from 1.25 to 1.88%. The results are shown in Fig. 6 as the dependence of the modulus of elasticity of gels  $G$  on the  $\bar{n}_{\text{PEO}}$  value. The PEO concentrations were 0.2 and 0.3% in Fig. 6A and 6B, respectively. Several interesting features can be seen from the figures. Increasing molecular weight shifts the critical range of  $\bar{n}_{\text{PEO}}$  for the gel formation towards smaller values. The decrease of  $\bar{n}_{\text{PEO}}$  with increasing PEO molecular weight is rapid between  $\bar{M}_w = 2 \times 10^5$  and  $6 \times 10^5$  g/mol, while higher molecular weight PEO decreases only slightly the  $\bar{n}_{\text{PEO}}$  value. Moreover, the modulus  $G$  of gels decreases as the polymer molecular weight is increased and, only weak gels form if high molecular weight PEOs were used in the gel preparation. Comparison of Fig. 6A and 6B also shows that increasing PEO concentration increases the  $\bar{n}_{\text{PEO}}$  values for the gel formation but decreases the elastic moduli of gels.

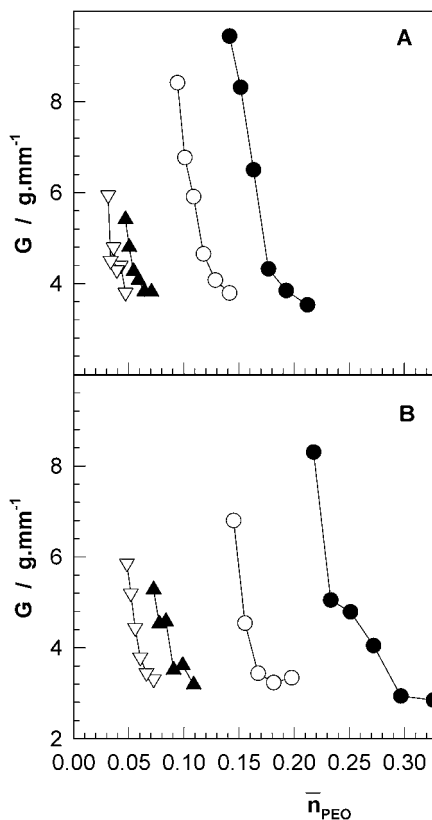


**Figure 5.** Phase diagram of Laponite-PEO mixtures in terms of the dependence of  $\bar{n}_{PEO}$  on the Laponite concentration. The numbers 1, 2 and 3 represent the liquid + viscous liquid, weak gel and strong gel phases, respectively.

The decrease of  $\bar{n}_{PEO}$  with increasing polymer molecular weight can be interpreted as a result of increasing number of free adsorption sites on the PEO chains. As seen in Table 1, the radius of gyration of PEO in water increases from 24.0 nm to 57.4 nm as the molecular weight is increased. Since larger polymer coils subjected to a shear will interact with more Laponite particles than the smaller coils,  $\bar{n}_{PEO}$  decreases with increasing molecular weight. Moreover, at small values of  $\bar{n}_{PEO}$ , that is, at a low surface coverage of the particles by PEO chains, the bridges between the particles will be unstable so that the resulting gels will exhibit a low resistance against shear.

The overlap concentrations  $c^*$  collected in Table 1 indicate that the PEO samples with  $\bar{M}_w < 6 \times 10^5$  g/mol are in the dilute regime so that their coil size are effective in the gel formation process. However, when the polymer chains enter the semi-dilute regime, as those with  $\bar{M}_w = 9 \times 10^5$  g/mol (Table 1), the chains overlap with each other. Since the characteristic size in semi-dilute solution is the mesh size and is much smaller than the individual polymer coil size, increase of polymer molecular weight above  $6 \times 10^5$  does not change the shake gel properties much.





**Figure 6.** Variation of the elastic modulus  $G$  of shake gels depending on the degree of surface coverage of Laponite particles  $\bar{n}_{\text{PEO}}$  by PEO chains. PEO concentration = 0.2 (A) and 0.3% (B). Molecular weight of PEO:  $2 \times 10^5$  (●),  $3 \times 10^5$  (○),  $6 \times 10^5$  (▲) and  $9 \times 10^5$  g/mol (∇).

In conclusion, we have shown that addition of PEO of  $\bar{M}_w = 3 \times 10^5$  g/mol can cause significant changes in the physical properties of Laponite dispersions. Shake gels form under certain Laponite and PEO concentrations, corresponding to a critical surface coverage value of the particles, i.e.,  $\bar{n}_{\text{PEO}} = 0.1\text{--}0.2$ . This range of  $\bar{n}_{\text{PEO}}$  further decreases as the molecular weight of PEO is increased. Strong gels with a relaxation time of longer than 30 min only form if the polymer molecular weight is in the range of  $2 \times 10^5\text{--}3 \times 10^5$  g/mol.

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