CHARACTERIZATION OF POLYMER-CLAY SOLUTIONS BY RHEOLOGY, FLOW BIREFRINGENCE AND SANS

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Introduction

The objective of this work is to investigate the influence of shear on the structure of a highly viscoelastic, aqueous clay-polymer solution. Many structural models have been proposed for such solutions,[1-3] but little is definitively known about mesoscopic properties or shear behavior. This information is important in the production of nanocomposite materials.[4]
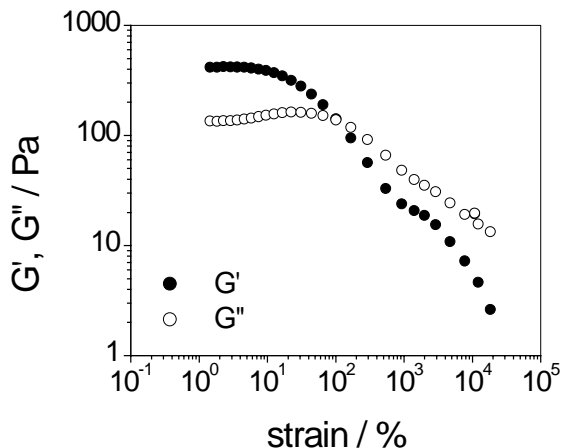
Experimental

In this study, we use rheology, flow birefringence (Δn) small-angle neutron scattering (SANS) to study a solution of the synthetic hectorite type clay, Laponite LRD (Laporte Industries Ltd.), and poly(ethylene-oxide) (PEO) ($M_w = 10^6$ g/mol). For a highly viscoelastic solution containing a mass fraction of 3 % LRD and 2 % PEO at room temperature, the clay particles produce transparent dispersions of disk shaped particles ca. 300 Å in diameter and ca. 10 Å in thickness[5,6]. The pH and ionic strength of the solutions were controlled by the addition of NaOH and NaCl, respectively.

Results and Discussion

A viscoelastic range with a high plateau modulus was observed in a stress controlled oscillatory shear experiment. **Figure 1** shows the storage (G') and loss moduli (G") at a frequency of 1 rad/s as a function of strain. At low strains up to 10 %, the sample behaves as an elastic solid (G' > G"). At strains higher than ca. 30 % which corresponds to a shear stress > 200 Pa the sample starts to flow (G' < G").
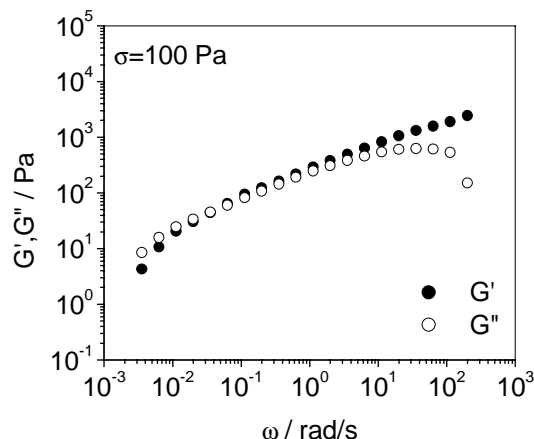
The frequency dependence of G' and G" of the same sample at a stress of 100 Pa is shown in **Figure 2**. A nearly linear frequency dependence could be detected for G' with a power law exponent of 0.45.


Figure 1. Strain dependence of G' and G" from an oscillatory stress sweep experiment at 1 rad/s.

Figure 3 shows the shear rate dependence of the birefringence of the clay-polymer solution. A distinct minimum in the birefringence is observed at a critical shear rate of approximately 40 s^{-1}. The source of the shear dependence of the birefringence is due to the alignment of the clay particles

and the PEO. Previous experiments demonstrated that the sign of the birefringence of the clay particles oriented along a flow field is negative, therefore at low shear rates, the orientation of the clay dominates the birefringence. Above the critical shear rate, the birefringence due to the orientation of the polymer chains dominates. The inlay of **Figure 3** is a double logarithmic plot of viscosity, η, versus shear rate which shows that the solution is shear-thinning over the entire range according to a power law with exponent m = -0.65. No signature of the critical shear rate is observed in the viscosity behavior.

Figure 2. Frequency dependence of G' and G" at a stress of 100 Pa.
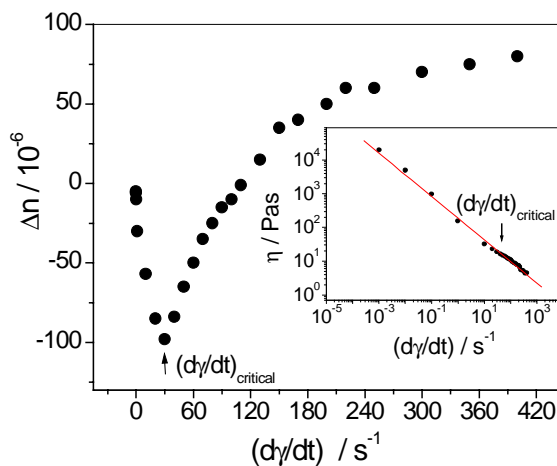
Figure 3. Optical birefringence as a function of shear rate. The arrow indicates $(d\gamma/dt)_{critical}$, the shear rate where the minimum in the birefringence occurs. Inlay: Steady state viscosity as a function of shear rates, $d\gamma/dt$. The double logarithmic plot gives a power law exponent of -0.65. Relative standard deviation < ± 3 %.

The SANS shear cell utilized has been described previously.[2] The instrument was configured in both "radial" and "tangential" geometries using 9 Å wavelength neutrons to give a Q range between 0.0027 Å^{-1} and 0.0199 Å^{-1}. The primary contrast in the SANS experiment used to detect the orientation of the clay platelets and polymer chains under shear is between D_2O and the other solution components. At low shear rates, a diffuse isotropic ring of SANS intensity is observed. The diffuse ring corresponds to an average spacing between platelets of 800 Å to 1100 Å. With increasing shear rate the ring becomes more diffuse and an anisotropic streak develops parallel to the vorticity axis of the flow field (the cylinder axis). The anisotropic streak

increases with increasing shear rate. After cessation of shear, the streaks relaxed to an isotropic state in less than 2 min.

To account for the SANS and birefringence results, our current understanding is that the polymer chains are in a dynamic adsorption/desorption equilibrium with the clay particles to form a network. The peak position in the quiescent scattering pattern is an indication of the mesh size of this network ($\approx$ 1000 Å). A 2 % (mass fraction) solution of only PEO, at the same pH, polymer and salt concentration showed no anisotropic SANS scattering at shear rates up to 100 s^{-1}.

Similarly a 3 % (mass fraction) aqueous clay solution shows no evidence of an anisotropic SANS pattern. Therefore, we can conclude that the anisotropic SANS pattern observed in the clay-polymer solutions is due to this coupling between clay platelets and polymer, allowing a higher orientation than either single component in solution can produce. From the birefringence data, the clay particles orient at low shear rates, while significant orientation of the PEO occurs above the critical shear rate. Since the clay platelets and the PEO chains are of comparable size (both about 300 Å), the lack of internal flexibility of the rigid clay particles makes them much easier to align than the flexible polymer chains.

According to SANS patterns, the shear flow results in an alignment of clay platelets orienting with their surface normals in the vorticity direction. One would expect the surface normals to orient along the gradient direction of the flow field. However, the type of orientation observed in these clay-polymer solutions is also observed in some liquid crystalline lamellar phases, block copolymer solutions, and melts. The critical shear rate is the shear rate at which the rate of chain desorption is slower than the terminal relaxation time of the chain, hence chain extension is observed in the birefringence.

On cessation of shear, the stress on the network decays almost immediately, and the recovery of the isotropic structure is controlled by the relaxation of the stretched chains. As the chains retract, the coupling of the chains to the clay allows the platelets to randomize in orientation under the local viscous environment.

The recovery from anisotropy is much faster than expected from simple Brownian motion of only the clay particles in a medium of the same viscosity as the clay-polymer solution exihibited macroscopically, and is indicative of the dynamic coupling of the polymer chains to the clay.

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