SHEAR ORIENTATION OF VISCOELASTIC POLYMER-CLAY SOLUTIONS

Shear-induced structural changes in complex fluids of anisotropic species are very general phenomena, occurring in polymer solutions, liquid crystalline materials and block copolymer melts. The purpose of our 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].

In our work, we use 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). The results reported here are 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 thick [5,6]. The pH and ionic strength of the solutions were controlled by the addition of NaOH and NaCl, respectively.

Figure 1 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 work 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.

A double logarithmic plot of viscosity, η, versus shear rate 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.

The SANS shear cell utilized has been described previously [2]. It consists of a cylinder that rotates within an outer cylinder with the sample in the gap between them. The instrument was configured in both "radial" (incident beam parallel to the shear gradient along the cylinder diameter) and "tangential" (incident beam passing between the cylinders, parallel to the flow direction) geometries. Using 9 Å wavelength neutrons gives a Q range between 0.0027 Å^{-1} and 0.0199 Å^{-1}. The primary contrast in the
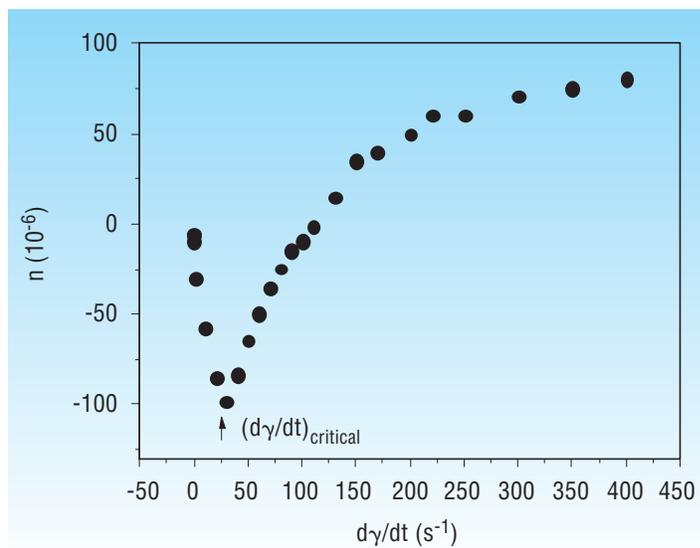
FIGURE 1. Optical birefringence as a function of shear rate. The arrow indicates the shear rate where the minimum in the birefringence occurs.

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.

The results obtained from the polymer-clay solutions in the "radial" and "tangential" beam configurations are summarized in Fig. 2. At low shear rates, a diffuse isotropic ring of SANS intensity is observed (Fig. 2a). 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 (Fig. 2b) and an anisotropic streak develops parallel to the vorticity axis of the flow field (the cylinder axis). If we neglect the main reflected beam which appears as a background streak in the gradient direction for tangential beam measurements (Fig. 2d), the anisotropic streak becomes the dominant feature in both scattering geometries with increasing shear rate. After cessation of shear, the streaks relaxed to an isotropic state in less than 2 min.
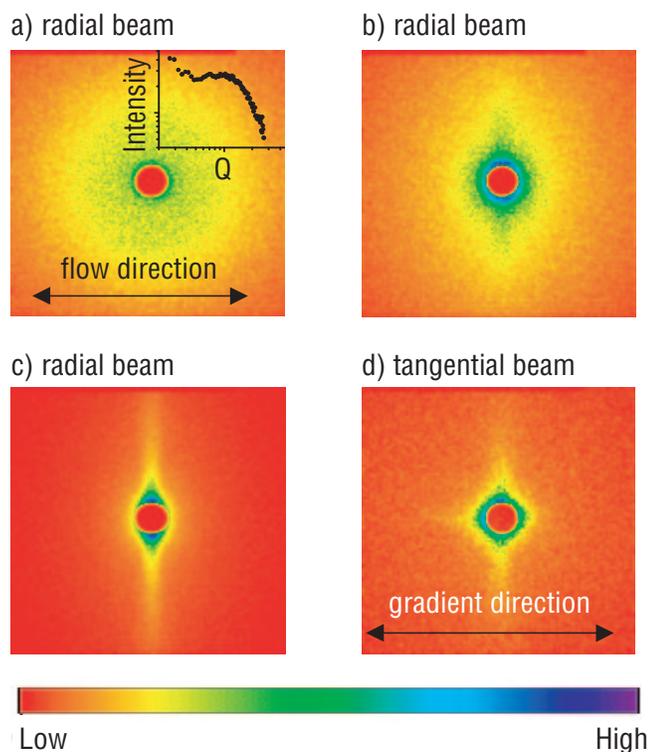
To account for the SANS and birefringence results, our current understanding is that the polymer chains are in a dynamic adsorption/desorption equilibrium with the clay particles to form a network. The peak position in the quiescent scattering pattern in Fig. 2a is an indication of the mesh size of this network ($\approx$ 1000 Å). A 2 % solution of only PEO, at the same pH, polymer and salt concentration showed no anisotropic SANS scattering at

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shear rates up to 100 s^{-1}. Similarly a 3 % 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 strong orientation of the PEO does not occur until the critical shear rate is exceeded. 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 from both beam configurations (Fig. 2) 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 direc-

tion 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 in 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 exhibited macroscopically, and is indicative of the dynamic coupling of the polymer chains to the clay. Future work will compare the relative rates of the relaxation in the PEO and clay with the cooperative adsorption/desorption kinetics which occur during deformation.

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FIGURE 2. SANS patterns of the clay-polymer solutions as a function of shear rate in the radial geometry (a-c) and tangential geometry (d) at shear rates of a) 0.5 s^{-1}, b) 20 s^{-1}, c) 90 s^{-1}, d) 90 s^{-1}.