

A Small Angle Neutron Scattering Study on Polymer-Clay Solutions

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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 polymer-clay solution. Many structural models have been proposed for such systems. However, this is the first time the alignment of these platelets and polymers under shear has been observed and their orientation characterized. This information could be important in nanocomposite materials.

EXPERIMENTAL

In this study, we use small-angle neutron scattering (SANS) to study solutions of the synthetic hectorite type clay, Laponite LRD (Laporte Industries Ltd.), and poly(ethylene-oxide) (PEO) ($M_w = 10^6$ g/mol). For highly viscoelastic solutions containing a mass fraction of 3 % LRD and 2 % PEO (LRD2) at room temperature, the clay particles produce transparent dispersions of disk shaped particles ca. 300 Å in diameter and ca. 10 Å in thickness [1,2]. The pH and ionic strength of the solutions were controlled by the addition of NaOH and NaCl, respectively.

SANS measurements were made on the NG7 30 m SANS instrument at the National Institute of Standards and Technology Center for Neutron Research [3]. The shear cell used for the solutions is a Couette geometry, which has been described previously [4]. In the standard configuration, referred to as the "radial beam" geometry, the incident beam is parallel to the shear gradient. In a second configuration, referred to as the "tangential beam" geometry, the incident beam is parallel to the flow direction. The primary contrast in the SANS experiment is between D_2O and the other solution components (clay, PEO, salts), thus SANS experiments can detect the orientation of the clay platelets and polymer chains under shear. We will refer to these samples as "regular" ones. SANS on contrast matched samples (clay and solvent have same scattering length density) detect only the polymer structure.

RESULTS AND DISCUSSION

Our current understanding of the SANS results is that the polymer chains are in a dynamic adsorption/desorption equilibrium with the clay particles to form a network. Results obtained from the polymer-clay solutions in the "radial" and "tangential" beam configurations indicate that flow at reasonable shear rates (5 to 30) s^{-1} is sufficient to induce orientation of the polymer-clay network. By using two beam configurations one can determine how the polymer chains and clay platelets orient under shear.

SANS patterns from both configurations (Figure 1) indicate the shear flow results in an unusual alignment of clay platelets: the platelets are oriented in the flow direction with the surface normal in the neutral direction (Figure 1) [5]. SANS results obtained from regular samples are shown in Figure 2. With the sample at rest a maximum in scattering intensity was observed which broadens at low shear rates (full squares). The maximum at $q_{max} \approx 0.007 \text{ \AA}^{-1}$ corresponds to an average spacing between platelets $d = 2\pi/q_{max} \approx 900 \text{ \AA}$. In the high q range we note that $I(q)$ scales with q^{-2} , characteristic of the scattering from randomly oriented discs. With increasing shear rate, the maximum disappears and we observe the onset of anisotropy in the scattering pattern with a systematic increase of the intensity in the neutral direction (Figure 1 and 2). A more linear region develops in the low q range and a slight deviation from q^{-2} is observed in the high q

range. This deviation is due to the orientation of clay platelets under shear.

Contrast matched LRD2 samples show interesting behavior at rest and under shear (Figure 3). Comparing the data from contrast matched samples, where only the PEO is visible, with the "regular samples" where both clay and polymer are visible, leads us to the observation that the clay begins to align first, at around 5 s^{-1} . The PEO doesn't start aligning until shear rates above 30 s^{-1} . The lack of internal flexibility of the rigid clay particles makes them much easier to align than the flexible polymer chains.

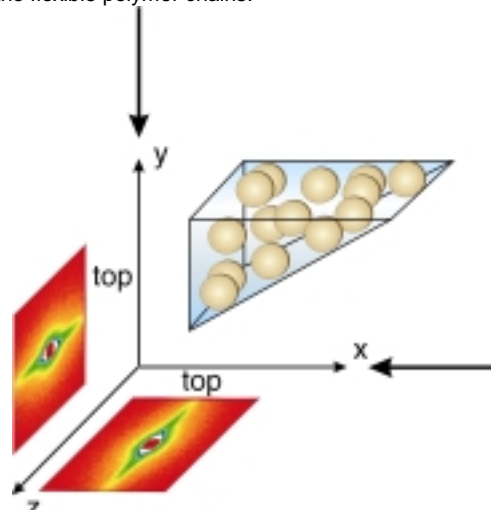


Figure 1. As the platelets align with surface normal along neutral direction, we observe a vertical streak in radial SANS pattern (y) and a vertical streak in tangential SANS pattern (x).

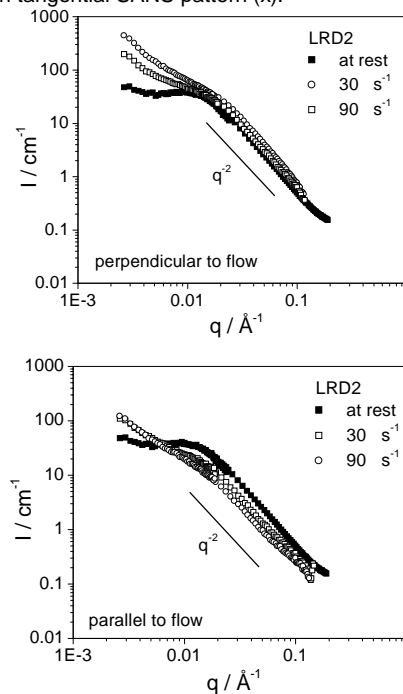


Figure 2. LRD2, regular samples: SANS intensities under static conditions (full squares) in the radial configuration and averaged in 30-degree sectors parallel to the flow direction and perpendicular to the flow direction. Relative standard deviation: $\pm 3\%$. Slopes are shown for reference.

A Guinier analysis of the quiescent contrast matched sample (Figure 3a) yields an apparent "Rg on the order of 400 Å. Literature

values for the unperturbed "Rg" of linear PEO chains at $M_w = 10^6$ g/mol in water are around 888 Å [6]. One possibility is that the much smaller apparent "Rg" observed here represents the dimension of PEO clustered around a platelet particle that builds up the network. (platelet diameter is ca. 300 Å). An alternate interpretation is that the scattering is due to "holes" in the polymer/solvent matrix where the "holes" are PEO poor (clay rich) regions. In this case the PEO would be entangled through the whole volume. With increasing shear rate a linear region develops (Figure 3b,c) and the scattering function is characterized by an asymptotic behavior $I(q) \propto q^{-5/3}$ at low q and $I(q) \propto q^{-1}$ at high q . The $-5/3$ exponent corresponds to a perturbed coil with excluded volume, in our case a perturbed soft PEO shell. The -1 exponent at high q is characteristic of scattering from a rigid rod, and its presence in this q range indicates a relatively large effective persistence length (fairly "stiff" chains).

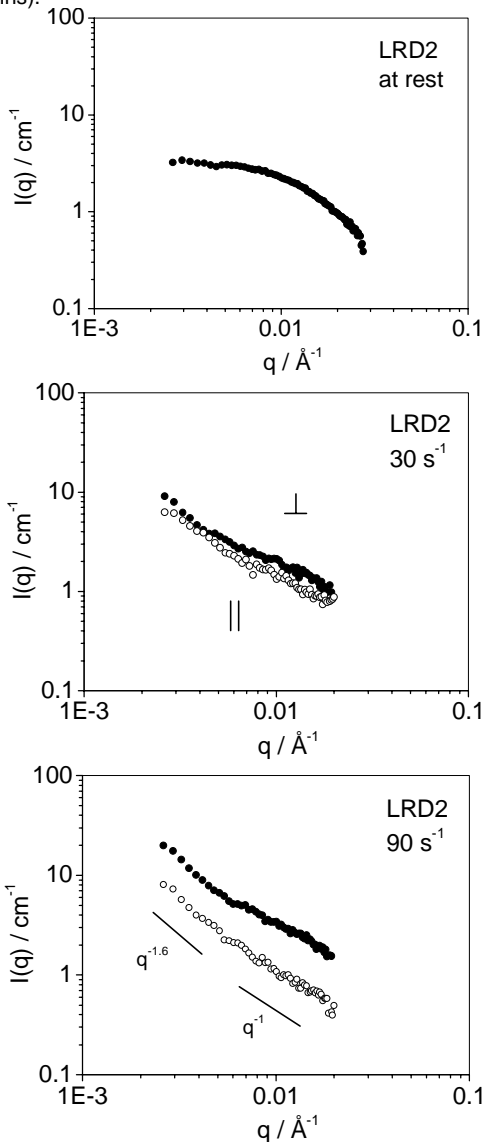


Figure 3. LRD2, contrast matched samples in radial configuration: a) circularly averaged SANS intensity for the sample at rest. b) and c): Intensities as averaged in 30-degree sectors parallel to the flow direction (open circles) and perpendicular to the flow direction (full circles). Relative standard deviation: $\pm 3\%$. Slopes are shown for reference.

Scattering from a 3% reference sample of PEO, at the same pH and salt concentration as LRD2, is given in Figure 4. The -2 exponent

at low q is characteristic of the gaussian coil. Comparison with Figure 3a shows the dramatic conformational change in PEO caused by the presence of clay. The PEO reference sample exhibited no anisotropic scattering at shear rates up to 100 s^{-1} (Figure 4) indicating that the applied shear rate is not high enough to overcome randomizing effects caused by the first normal mode of single chain relaxation (characteristic time τ_1) when the clay is absent.

The orientational alignment of the platelets is a competition between i) flow alignment and ii) orientational and configurational relaxation. In the case of clay/PEO samples that equilibrium is altered by the clay polymer interactions with increasing adsorption times of the PEO attached to the clay driving the equilibrium towards i) while desorption favors ii). Using arguments similar to Hayter and Penfold [7] these competing effects can be characterized by $\Gamma_x = g \tau_x$ with g being the shear rate and τ the relaxation time (τ_0 for the adsorption/desorption process - i.e. the attachment time). Full alignment will occur when $\Gamma \gg 1$. SANS on regular samples as well as birefringence show the clay alignment starts at shear rates of 5 s^{-1} . This implies that $\tau_0 \approx 0.05 \text{ s}$ for PEO on the Laponite surface under experimental conditions. SANS data on contrast matched samples on the other hand show no evidence of the polymer chains stretching until shear rates of ca. 30 s^{-1} . This is due to the flexibility of the PEO chains giving them many internal modes of relaxation, which can partially compensate for their ends being tethered to clay particles. Nonetheless, the chains do align at shear rates well below those for chains whose ends are not tethered (reference sample).

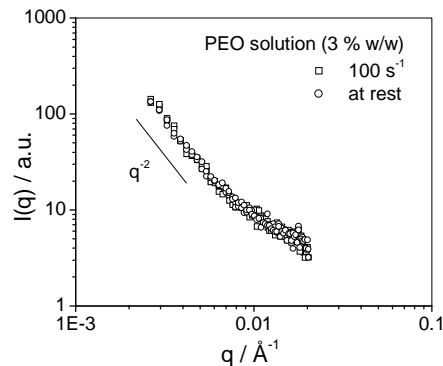


Figure 4. Circularly averaged $I(q)$ vs. q for a pure PEO solution (3%). Relative standard deviation: $\pm 3\%$. Slope is shown for reference.

Finally, a 3% aqueous clay reference solution was measured and showed no evidence of anisotropy. Therefore, we can conclude that the anisotropic SANS pattern observed in the polymer-clay solution is due to the coupling between clay platelets and polymer, allowing a higher orientation than either single component in solution can produce.

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Certain equipment and instruments or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are the best available for the purpose.