

Shear-induced Particle Alignment in a Model Polymer/Clay Nanocomposite

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Introduction

There has been much recent interest in the field of polymer nanocomposites, in which nanoscale organic or inorganic solid particles are dispersed in polymers. Such hybrid materials offer unique opportunities to enhance polymer properties, such as stiffness, heat deflection temperature, and permeability. Many of these enhancements result directly from the fact that the dispersed particulate phase exists on dimensions that are commensurate with the size of polymer molecules. This can lead to confinement effects, whereby even the properties of the polymer matrix are significantly altered through the blending.

A particularly important class of nanocomposites is one in which organically modified clays are dispersed in polymers [1]. The ideal state is one of complete exfoliation, whereby individual inorganic sheets from the layered clay particles are completely dispersed within the polymer matrix. Such a structural state is difficult to achieve. More typical is a state of partial exfoliation and “intercalation,” whereby the polymer penetrates within the clay sheets, but the particles are not completely disrupted.

The rheology of nanocomposite samples is quite different from that of the matrix polymer, owing to the presence of the dispersed particulate phase [2]. Unraveling the origins of the complex rheology of polymer/clay nanocomposites requires an understanding of how flow influences the microscopic structure of the sample, particularly the distribution of particulate orientation. Such information is also vital for the rational design of processing operations, since the desirable properties of nanocomposites will also be strongly affected by the particle orientation distribution induced by flow fields during processing. Here we perform *in situ* x-ray scattering experiments on a model polymer/clay nanocomposite sample in order to probe such flow-induced structural changes.

Materials and Methods

Experiments were performed on several different dispersions of clay in room-temperature polymer melts. The data presented here were collected on an 8-wt% dispersion of organically modified montmorillonite

(2C18M) in a moderate viscosity poly(dimethylsiloxane) (PDMS) fluid.

X-ray scattering experiments were performed in a novel annular cone and plate shear cell that allows the fluid structure to be probed in the flow-gradient (1-2) plane. Details on the construction of the shear cell are available in Ref. 3. Experiments were performed on APS beamline 5-BM-D by using 25-keV bending magnet radiation. A MarCCD detector was used to collect 2-D small-angle x-ray scattering (SAXS) patterns. A vacuum chamber was placed between the shear cell and the detector to reduce air scatter.

Results

Figure 1 presents representative 2-D x-ray scattering patterns observed in the 8-wt% 2C18M/PDMS nanocomposite sample. In this sample, the clay is intercalated by not fully exfoliated. The diffraction peak observed in this pattern reflects the spacing between adjacent inorganic sheets within the clay galleries. Since the layered clay is a 1-D crystal, the peaks in diffraction intensity correspond to a population of clay platelets with normals pointing in that direction within the flow-gradient (1-2) plane of the shear flow. Flow induces net anisotropy in the particle orientation distribution, in which platelets are most likely to be found with normals making an angle about 20° away from the velocity gradient direction. Upon reversal in shear flow direction, the pattern reverses itself.

Performing experiments at a synchrotron provides an opportunity to probe the transient dynamics by which orientation and reorientation occur. Figure 2 presents measures of anisotropy and average orientation angle, extracted from patterns such as those in Fig. 1, as a function of time. In this experiment, flow was initiated in one direction, it reached steady state, and then the shear flow direction was reversed. Finally, shear flow was stopped in order to observe relaxation processes.

On the timescale accessible in these experiments, anisotropy in the particle orientation distribution does not relax. This may be attributed either to the formation of a percolated network of particles that are lightly aggregated by physical interactions or to the formation of a discotic nematic phase in this dispersion of platelike particles.

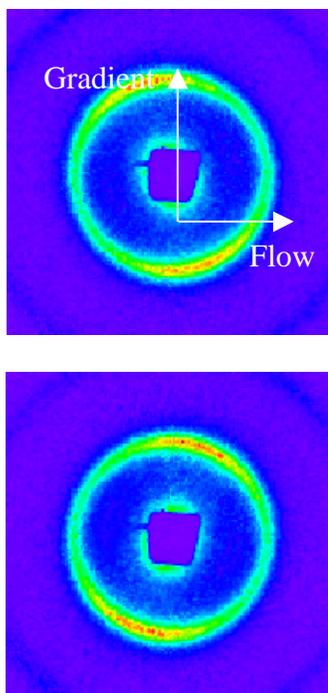


FIG. 1. 2-D x-ray scattering patterns observed in 1-2 plane during shear flow of an 8-wt% dispersion of 2C18M in PDMS at 0.1 1/s. Shear flow is from left to right in upper image and from right to left in lower image.

Given the particle concentrations involved, the former possibility seems more likely to be true. The fact that the sample does not relax completely upon cessation of flow means that there can be no particularly well-defined initial condition for flow inception. Thus, the details of the transient behavior upon flow inception are hard to interpret. Upon flow reversal, however, there is a distinct oscillatory pattern in the average degree of particle orientation, as well as weak oscillations superimposed on the sign change in orientation angle, which occurs as the population of particles adapts its orientation state to the new flow direction. These changes are very reminiscent of the transient dynamics of rodlike and disk-like particles in hydrodynamically dilute solutions, in which the oscillatory character is related to the periodic Jeffery orbits that describe particle trajectories in shear flow [4]. In the present case, the particles are much more highly concentrated and interact strongly with one another.

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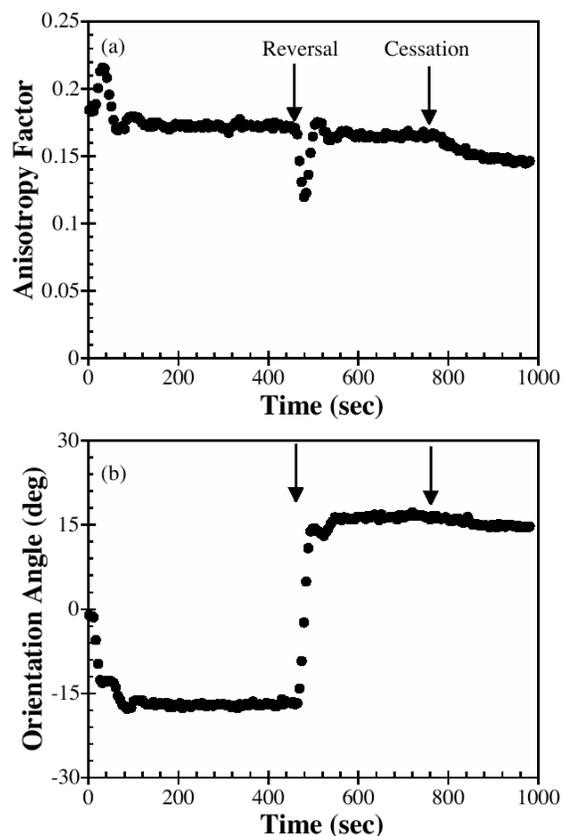


FIG. 2. (a) Anisotropy and (b) average orientation angle in an inception/reversal/cessation experiment at 0.1 1/s.

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