368c Structure and Rheology of Supercritical CO2 Exfoliated Polymer/Clay Nanocomposites

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Nanoscale fillers such as clay, graphite, and carbon nanotubes tend to aggregate due to a variety of clay-clay interactions. Effective dispersion of the fillers in a polymer matrix has been a key challenge. Supercritical carbon dioxide (scCO2) processing appears to be an environmentally friendly, economical, and effici technique that helps lower the kinetic barrier to achieve intercalated and exfoliated polymer/silicate nanocomposites.

Wide-angle X-ray diffraction (WAXD) and Transmission Electron Microscopy (TEM) are typically used to investigate the structure of polymer/silicate nanocomposites . However, WAXD can be misleading because it does not provide quantitative information about the degree of exfoliation vs. intercalation. Moreover, TEM is labor intensive and special equipment is often necessary to image a sample. Rheology is emerging as a tool that can provide insight into the predominant clay structure in the nanocomposite, since the degree of dispersion appears to affect the moduli and the relaxation time significantly. as well as the processability of the nanocomposite.

We have prepared PDMS/silicate nanocomposites via scCO2 and probed their rheological properties via small amplitude oscillatory shear and steady-shear measurements. At high frequencies, PDMS/silicate nanocomposites demonstrated a factor of two increase in the storage (G') and loss moduli (G") while at low frequencies the enhancements were more pronounced (factor of 3). These moduli improvements are significant better than those obtained with conventional, chemically-modified intercalated clay nanocomposites. In the case of Polyvinyl methylether (PVME)-clay nanocomposites, the rheological improvements were even more significant. Interestingly, the characteristic relaxation time of the exfoliated samples strongly agreed with that of the matrix polymer (i.e. their crossover frequencies were in good agreement). Since exfoliated systems do not have clay galleries (i.e. no stacking), the polymer chains are not confined to spaces significantly smaller than their radius of gyration and small changes in relaxation dynamics are primarily a result of surface interactions. Furthermore, highly exfoliated systems often have a plateau in the terminal zone due to frustrated clay platelets that do not relax on the time scale of the experiment. In stark contrast, the characteristic relaxation time of intercalated samples was an order of magnitude lower than that of the pristine matrix. This is likely owing to the inability of the polymer chains to move three dimensionally because they are confined to a region much smaller than their radius of gyration. Therefore, careful analysis of rheological behavior may provide insights into the structure and clay dispersion in the nanocomposites. Towards this, the clay and the polymer orientation in the nanocomposites are also being probed using rheo-optical FTIR spectroscopy.