ABSTRACT

The work presented in this thesis is focused on understanding the linkages between the microstructure, processing and properties of polyolefin nanoclay composites.

Polymer nanocomposites are hybrid materials comprising of inorganic components that have nano-dimensions. In contrast to the traditional fillers, nano-fillers such as nano dimensional layered clays are found to be effective even at as low as 5-wt % loading. This happens because of two reasons: (a) Nano-sized clays have dramatically higher surface area compared to their macro-size counterparts like china clay or tale, and (b) the presence of mobile cations on the surface of the clay allows for organic modification of the surface, which can render the clays hydrophobic thereby increasing their potential to mix well in a polymer matrix. Polymer nanoclay composites show significantly higher modulus, thermal stability and barrier properties without increasing weight and in some cases, without affecting the optical clarity.

A nanoclay consists of two dimensional nanometer thick platelets that are stacked up in layers separated about 1 nm apart. Organo-clays have layer spacings (galleries) of upto 4 nm. Based on the state of dispersion of the clay in the polymer matrix, nanocomposites are classified as intercalated composites (in which polymer chains reside in between the silicate layers, while preserving the ordered layered structure to some extent) and exfoliated composites (in which polymer chains completely delaminate the clay layers). It is generally observed that the best enhancement in thermo-mechanical properties are achieved for exfoliated nanocomposites and so the ultimate goal of manufacturing strategies of polymer nanoclay composites is to achieve ideal exfoliation. The three main strategies for synthesis of nanoclay composites are (i) in-situ polymerization, wherein the monomer is allowed to intercalate in between the clay layers and then polymerized, (ii) solution intercalation, wherein the polymer chains are allowed to diffuse in between the clay layers from a solution, and (iii) melt intercalation, where-in the composite is formed at temperature above the softening point of the polymer by the combined action of mechanical shear and diffusion. Of these the melt intercalation route is commercially the most attractive option but does not necessarily result in an ideal exfoliated microstructure.
Polymer nanocomposites ultimately have to undergo many processing operations such as extrusion and injection molding either during their manufacture by melt intercalation or during shaping operations for the manufacturing of a product. During these operations the nanocomposite melt flows through complex geometries and experiences different stress fields. The microstructure of the final product is dictated to a large extent by the processing conditions. Moreover, the microstructure in turn determines the flow properties of the melt. The work presented in this thesis attempts to understand the structure-processing-property relations in polyolefin nanocomposites in a semi quantitative manner.

Polypropylene (PP)-layered silicate nanocomposites were prepared by melt compounding PP and organically modified montmorillonite in the presence or absence of a compatibilizer viz., a high MFI PP-co-maleic anhydride. The hybrid materials were characterized using Transmission Electron microscopy (TEM) and high temperature WAXD. Rheological measurements in shear mode included creep and stress ramp studies using a controlled stress rheometer (Bohlin, CVO-50), step strain and oscillatory studies using a controlled rate rheometer (Rheometric Scientific, ARES) and high shear measurements using a capillary rheometer (Cea, Rheovis). Creep resistance of compatibilized hybrids was found to be significantly higher than that of uncompatibilized hybrids and also increased with annealing time. The creep data together with the micro-structural investigation indicated a small amount of exfoliation from the edges of the clay crystallites during extrusion and annealing. The zero-shear viscosity of the compatibilized nanocomposites was at least three orders of magnitude higher than that of matrix resin and the uncompatibilized hybrids. Importantly, the large increase in zero-shear viscosity was not accompanied with any increase in the flow activation energy compared to the matrix polymer. It is concluded that (a) at low stresses the hybrids exhibit a Newtonian response of high viscosity, (b) presence of confined chains between galleries, if any, do not significantly contribute to the rheological response, and (c) the high viscosity of the molten nanocomposite originates from large frictional interactions of the clay crystallites, which form a percolating network.

At high stresses the compatibilized hybrids showed an apparent ‘yield’ behavior, which is an indirect suggestion for breakage of the network by incipient flow-induced alignment of the clay crystallites. A direct evidence for orientation under shear was obtained from a novel in-situ rheo-x ray technique. The rheo-x ray
data allowed for quantitative measurements of orientation as a function of shear stress after the yield transition. It was found that the clay tactoids oriented quite easily by shear and achieved an average orientation function value of \( \sim 0.85 \) at high stresses. Orientation relaxation after shear revealed an interesting behavior in that the presence of the compatibilizer accelerated the orientation relaxation of the clay tactoids.

The flow-induced orientation and orientation relaxation results are relevant to both processing and product properties of PLS nanocomposites. To complete the story of microstructure-flow-property linkages the effect of clay orientation on the tensile modulus of extruded products was also studied. Tapes of PP-nanoclay composites were extruded through a slit die under different shear stresses using a capillary rheometer. Clay orientation was measured from 2D diffraction patterns obtained by using an image plate. The tensile modulus of the tapes was measured using an Instron UTM. In the range of extrusion speeds tested in this study, both the tensile modulus and the clay orientation were initially found to increase with piston speed and then saturated at higher speeds. Thus, quantification of the dependence of modulus on clay orientation was possible.

Rheological measurements were also made on polyethylene nanocomposites that were prepared by in-situ polymerization of ethylene using a metalloocene catalyst that was heterogenized on montmorillonite by a novel strategy (Saptarshi Ray, Ph.D. thesis, Univ. of Pune, 2003). This study has helped to understand some of the differences in the rheology of intercalated and exfoliated nanocomposites.