Semi-Crystalline Polymers

Semi-crystalline polymers, such as polyethylene and polypropylene are common commercial materials used for consumer products. Polyethylene is the most widely used polymer due to its low cost and the wide range of properties that can be achieved through variation in branch content and processing conditions. Equistar, in Cincinnati, is the largest producer of polyethylene in the US and P&G is a large user of these materials, especially in packaging. There has been a close collaboration between research at UC in polyolefins and local industrial interests that have developed over a number of years of interaction. Most of this work has focused on process control over orientation and the lamellar crystallite morphology in polyethylene. In addition to polyethylene, some work has focused on biosource and biodegradable polyesters, polyhydroxyalkonates, now marketed under the tradename Nodex by P&G. Nodex is targeted as an environmentally friendly replacement for polyolefins in the consumer products packaging field and is in some ways a future competitor for polyolefins.

Due to the length of a polymer molecule, the variability in length between different chains and the presence of branches which act as defects during crystallization, polymers typically crystallize into nanosized crystallites with the chains passing through the thickness of the crystallite (at a slight angle) and with chain folding at the broad surfaces of the lamellae. Typically, lamellar crystals have an aspect ratio similar to a sheet of paper with lamellar thickness on the order of 5 to 50 nm. Such highly asymmetric, plate like structures tend to stack when sufficient crystalline concentration, or degree of crystallinity, exists. Tie chains between crystallites serve to enhance stacking and to make stacking more regular as may epitaxial nucleation. A semi-crystalline polymer can be viewed as a composite with rigid crystallites suspended in a viscous liquid or rubbery phase. Stresses and residual stresses induced in processing can have a dramatic effect and control over the orientation of these lamellar crystallites as can melt stress prior to crystallization. From composite models it is expected that the modulus normal to the lamellae is far lower than the modulus in the plane of the lamellae. Similarly, gas transport through a polymer, such as polymers used to store food or products with a fragrance, is much lower through the crystalline phase and can be controlled by manipulating lamellar orientation during processing Such lamellar control over moisture vapor transmission was first demonstrated in work at UC in collaboration with Equistar Chemicals.

There is much interest in the polymer industry to use nanomaterials as reinforcing fillers in polymers. Interest has focused on exfoliated (chemically treated) clay, layered silicates, due to their low cost and the potential for dramatic improvements in properties. Layered silicates when exfoliated (when the layers are separated) has lamellar crystalline sheets with a thickness on the order of 0.4 nm and a variable width up to the micron scale. The specific surface area for such a sheet structure is proportional to the inverse of the thickness since thickness relates volume to surface area for platelets. For exfoliated clay, surface areas on the order of several football fields per gram are possible. Dispersion of clay in polyolefins is a two fold problem the second of which has only recently been noted, primarily through work at UC. First, the layers must be dispersed and maintain dispersion during processing of the polymer matrix. This can be partly achieved with known chemical treatments and through blending clay and polyethylene compatibilizing polymers in the composite. UC research was the first to note that this exfoliation process, while partially successful, leads to two distinct species of clay, one in micron-scale tactoids and the other exfoliated or intercalated (partially exfoliated). In addition to the degree of exfoliation, orientation of the clay layers is of vital importance to properties for similar reasons that polymer lamellar orientation is of importance to physical properties. Recently graduated PhD student Ayush Bafna, worked in collaboration with Equistar to understand the manipulation of layered silicate orientation by processing. Simultaneous information concerning tactoid and intercalated clay layer orientation, clay crystallographic orientation polymer lamellar and crystalline orientation were obtained from polymer films processed under a variety of conditions as well as for blow molded samples. In addition to highlighting analytic capabilities at UC and developing a new approach to mapping orientation in processed materials, interesting correlations in orientation were seen, for instance that the orientation of clay tactoids on a micron scale mimicked that of the polymer lamellae and was opposite that of exfoliated clay layers.

More recent work, carried out by Ryan Breese, has investigated crystalline lamellar orientation in post processing orientation of polyethylene films. In his MS work Breese developed a dynamic composite model that describes the orientation and structural transition from lamellar to fibrillar crystalline structures in processed films. Ryan intends to pursue a PhD on a similar topic.