Engineering the Microstructure of Semicrystalline Polymers

Guruswamy Kumaraswamy
Polymers and Advanced Materials Laboratory, National Chemical Laboratory, Pune 411008, INDIA.
g.kumaraswamy@ncl.res.in

Polymers with chemical and stereo/regio-structural regularity can crystallize on cooling below the crystallization temperature, and are called semicrystalline polymers. Semicrystalline polymers include commodity materials such as polyethylene, isotactic polypropylene and PET and engineering plastics such as polyacetals, and nylons, and, comprise about 70% of all synthetic polymers produced today, viz. about 150 million tons/annum. Polymer crystallization is a non-equilibrium process, frustrated by the long chain nature of polymer chains. Therefore, it is possible to design polymer processing conditions that result in specific semicrystalline microstructure, and therefore in specific property profiles. For example, in Nature, the glands that extrude the silk fiber from spiders and silkworms have evolved such that the silk dope that is spun experiences extensional deformation. This determines the crystallinity and crystal orientations in the silk fiber, that give rise to its extraordinary combination of stiffness and toughness.

Recent advances in the chemistry and technology of polymer synthesis, and a deeper understanding of microstructure development in semicrystalline polymers have rendered it possible to extract improved performance from existing polymers. Such microstructure engineering in semicrystalline polymers enables the use of existing polymers in more demanding applications – for example, in replacing metal in automotive applications to reduce the weight and improve the fuel efficiency of cars. I will use a few examples to demonstrate how industrially practical changes in processing conditions, and/or clever use of additives, exploit the non-equilibrium nature of polymer crystallization to controllably alter semicrystalline morphology and thereby, enhance material properties. Work from our group on polyoxymethylene, an engineering polyacetal used in applications that demand high fatigue endurance, has demonstrated that a wide distribution of lamellar thickness characterizes the microstructure of this polymer under conventional processing conditions. This limits the use of this polymer to below its deflection temperature of around 100^{o}C. We demonstrate that this “safe use” temperature is not intrinsic to polyoxymethylene – rather, it is a consequence of its semicrystalline microstructure. Thus, processing conditions and additives that resulted in a different semicrystalline morphology allow the use of polyoxymethylene at temperatures above 100^{o}C. In another example from our work, we demonstrate that it is possible to exercise control over the crystal orientation in a commodity polymer, isotactic polypropylene (iPP), using additives based on sorbitol. The sorbitol derivative dissolves in iPP above the polymer melting point, but precipitates to form a nanofibrillar mesh as the polymer is cooled. Orientation of this solid mesh allows us to control iPP crystallization and realize controllable crystal orientation, and therefore, achieve controllable mechanical modulus and failure properties.

Thus, an improved understanding of the physics of microstructure formation allows us to design strategies to engineer semicrystalline morphology and enables us to push the envelope of polymer performance.