

Tailoring Plastics at the Molecular Level for Monetary and Environmental Benefits in Industrial Processing^{1,2,3}

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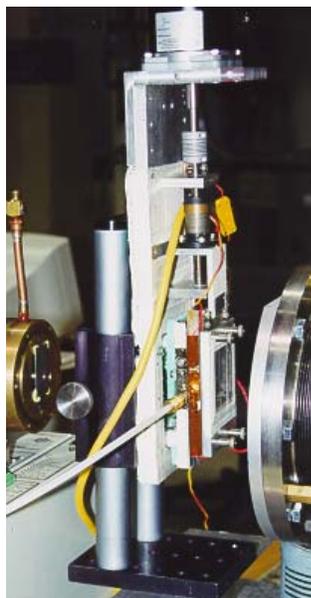


Figure 1: Tensile testing scattering rheometer

Much of our manufactured environment – many metals, plastics, glasses, ceramics, fiberglass, – are extrusion-molded articles. To minimize waste, extrusion-molding plants must balance quality of product, speed of process and cost of production (primarily electricity) for each material. They need to know how fast each material can be processed at what energy cost while maintaining the quality of the finished bulk material.

In the case of plastic materials (polymers) optimizing this task is advantaged by the fact that the macromolecular arrangement of many polymers, including the commonly used polypropylene derivatives reported here, changes fundamentally only at certain critical deformation rates. These critical deformation rates are themselves influenced by the tacticity of the molecule and can therefore be tailored with careful synthesis.

The SSRL-enabled research here correlates the molecular structure of the material with its bulk material properties and uncovers those key shear and extrusion rates.

In this study three distinct tacticity fractions of a polypropylene elastomer were prepared. Deformation of the elastomer was performed *in-situ* in the x-ray probe beam using a custom made tensile testing device on BL1-4 (Figure 1). The tensile tester monitored the rate of applied deformation simultaneously with collecting small angle and wide angle x-ray scattering (SAXS and WAXS) data from which molecular orientations were determined.

Stretching the plastic material yields three sets of scattering: equatorial, off-axis diagonal, and meridional arc (Figure 2). High-tacticity fractions contribute to the equatorial and off-axis diagonal scatterings revealing molecular-scale orientation parallel to the strain axis and crystalline phase transformation from the α -form to the mesomorphic form. The meridional arc is contributed by the low-tacticity fraction with crystalline chains oriented with a preferred direction orthogonal relative to the strain direction. SAXS, which probes long-range ordering, exhibits broad and diffuse meridional peak for the intermediate-tacticity fraction (Figure 3).

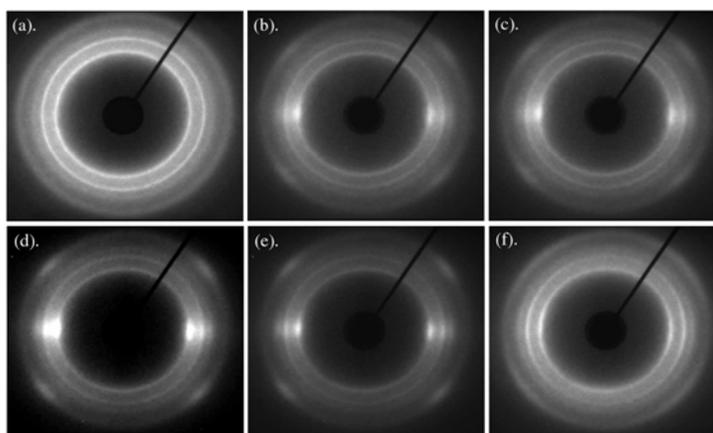


Figure 2: 2d WAXS patterns of the intermediate tacticity fraction of elastomeric polypropylene: (a) unstretched (b) at 100% strain (c) at 200% (d) at 300% (e) at 300% after 1 hr relaxation (f) plus stress free relaxation for 24 hrs. The strain axis is vertical.

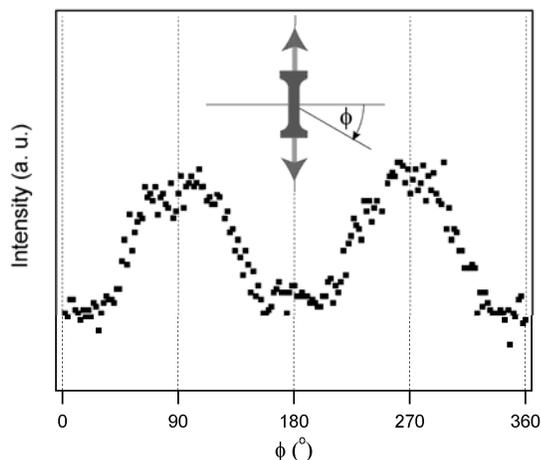


Figure 3: Azimuthal intensity distribution of SAXS for intermediate tacticity fraction in case (f) of Figure 2

These scattering results were combined with birefringence measurements, and wide-angle diffraction data also collected at BL1-4 to complete the characterization of the molecular organization of the elastomeric material to physical deformation. The resulting data allowed determination of the precise degree to which lamellae are oriented to the strain direction, and the surprising revelation that in certain cases this orientation is reproducibly orthogonal to the direction of strain. Permanent deformation of the elastomer after stretching, as measured by the residual strain (tensile set), originates from permanently oriented crystallites and chains pinned within crystalline networks. This model is adopted from the work of Schultz⁴ and is shown in Figure 4. There is also evidence of co-crystallization in the lowest tacticity polypropylene fraction which proportions can be controlled through the application of step strain shear.

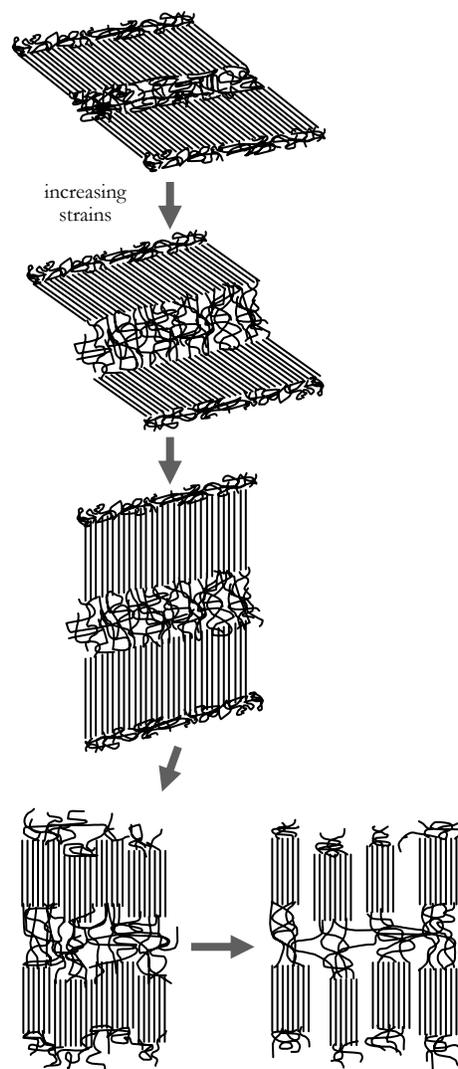


Figure 4: Lamellar deformation model adopted from Schultz.⁴

Plants currently operating above the revealed optimum deformation rates are thereby enabled to save substantial electrical and environmental costs by reducing extrusion speed while retaining or improving the desired bulk rheological qualities in the finished product. The quality, profit and environmental implications of this procedure for industry are difficult to overemphasize.

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¹ W. Wiyatno, G. G. Fuller, J. A. Pople, A. P. Gast, Z. Chen, R. M. Waymouth, C. L. Myers, *Macromolecules* 2003, 36, 4, 1178-1187.
² W. Wiyatno, J. A. Pople, A. P. Gast, R. M. Waymouth, G. G. Fuller, *Macromolecules* 2002, 35, 22, 8488-8497.
³ W. Wiyatno, J. A. Pople, A. P. Gast, R. M. Waymouth, G. G. Fuller, *Macromolecules* 2002, 35, 22, 8498-8508.
⁴ Schultz, J. M., "Polymer Materials Science," 1974, Prentice Hall, Englewood Cliffs, NJ.