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Morphology of Uni-Directional Drawn "Mixed Melting" Polypropylene Blends

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Beamline(s): X27C

Introduction: Film drawing represents one of the highest volume applications of isotactic polypropylene (iPP), of which biaxially oriented film is most common. In this application, film is often oriented sequentially with machine-direction stretching and subsequent transverse direction stretching. This drawing process creates a film of useful dimensions while imparting desired properties such as barrier and stiffness due to the imposed orientation. The resultant properties of the film are due both to the morphology formed during stretching and during subsequent cooling of the film. Generally a shift of the melting distribution to lower temperatures is known to reduce the crystallinity at the draw temperature, reduce the corresponding yield stress, and promote drawing at lower temperature [1]. However, this shift is often accompanied by a loss in properties implying a processing/property trade-off in the design of resins for film drawing. In flow-induced crystallization of iPP from the melt (differing from solid-state orientation), wide-angle x-ray scattering (WAXS) patterns exhibit a mixture of c-axis and a*-axis orientations [2]. Some reports view the a*-axis orientation as a secondary crystallization event [3]. While a*-orientation is generally thought to be destroyed at high draw ratios for semi-solid-state drawing (particularly for unoriented precursor material), the presence of a*-orientation in drawn film at higher draw temperatures may provide support for the secondary crystallization view-point (in flow crystallization) through the crystallization process on cooling after the drawing stage. In this study Ziegler-Natta iPP, iPP copolymer with ethylene, and equimolecular weight blends are examined by 2D SAXS/WAXS measurements of uni-directional film (a precursor to biaxial film) to probe the influence of polymer melting point on orientation and morphology development in drawn film.

Methods and Materials: Stabilized Ziegler-Natta iPP ($T_m \sim 165$), iPP copolymer with ethylene ($T_m \sim 150$), and a 50:50 "mixed melting" blend (all with $M_w \sim 350,000$) were cast into sheet (~ 0.7 - 0.8 mm) and drawn uni-directionally at $\sim 9000\%$ /min at a draw ratio of 6x with TM long stretching equipment over a range of stretch temperatures (~ 120 - 160 C). Two-dimensional SAXS/WAXS measurements of the as-drawn film were conducted at beamline X27C using 20.1x25.2 cm Fuji imaging plates, processed with a Fuji BAS-2500 reader. The WAXS image plate had a 1.6cm diameter hole cut from the center to allow passage of the primary beam.

Conclusions: Preliminary analysis of WAXS data suggests that crystalline orientation decreases with increasing draw temperature, decreasing more strongly with lower resin melting point. The loss of orientation at the highest draw temperature is also accompanied by the development of some a*-orientation (absent at low draw temperatures), consistent with a model associating the a*-oriented crystals with secondary crystallization of the partially molten fractions following stretching.

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References: 1.)R.A.Phillips, J.Appl.Polym.Sci., **80**, 2400 (2001).; 2.)R.A.Phillips, M.D.Wolkowicz, in Polypropylene Handbook, E.P.Moore Jr. ed., Hanser, Munich, 1996.; 3.)K.Katayama, T.Amano, N.Nakamura, Kolloid-Z.Z.Polymer, **226**, 125 (1967).