Shear-Induced Crystallization Precursor Studies in Model Polyethylene Blends by *In-Situ* Rheo-SAXS and Rheo-WAXD

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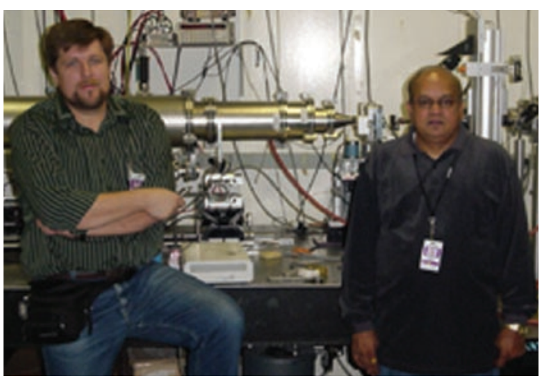
The development of the shear-induced crystallization precursor structure of crystallizing, high molecular-weight binary polymer blends and non-crystallizing, low molecular-weight polyethylenes was investigated by in-situ rheo-small-angle x-ray scattering (SAXS) and wide-angle x-ray diffraction (WAXD) techniques. A "shish-kebab" structure, detected by both SAXS and WAXD, was observed in the blend containing the non-crystalline matrix of relatively higher viscosity, while only a twisted lamellar structure was seen in the rest of the blends. These results suggest that the matrix viscosity plays an important role in the formation of the crystallization precursor structure from the high molecular-weight chains under flow.

Prior to crystallization, the initially formed precursor structures, with a molecular orientation induced by flow during polymer processing – such as extrusion, injection molding, fiber spinning, and film blowing – can often dictate the subsequent morphology and, thus, the final properties of the polymer. Although extensive research on orientation-induced crystallization has been conducted, the nature of the earliest events during crystallization under flow is still not fully understood. In this study, a unique polymer blend system, inspired by studies of dilute polymer solutions under flow, was used to simulate the formation of precursor structures at the initial stage of flow-induced crystallization. In these blends, two low molecular-weight polyethylene copolymers, containing 2 mol % of hexene, with average molecular weights (M_w) of 50,000 (MB-50k) and 100,000 (MB-100k) and a polydispersity of 2, were used as the matrix material of different viscosity. A high molecular-weight polyethylene homopolymer with a Mw of 250,000 (MB-250k) and a polydispersity of 2, which is miscible with both low molecular-weight polyethylene matrices, was used as the crystallizing minor component. Two series of model blends, MB-50k/MB-250k and MB-100k/MB-250k, each containing weight ratios of 100/0, 97/3, 95/5, and 90/10, were prepared by solution blending to ensure thorough mixing at the molecular level. A Linkam CSS-450 high-temperature shear stage, modified for



Authors (left to right)
(top) Igors Sics and Rajesh Somani,
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in-situ x-ray scattering measurements, was used to control the shear conditions of the polymer samples. Two-dimensional WAXD and SAXS measurements (not measured simultaneously) were carried out at beamline X27C using a MAR CCD x-ray detector.

At the chosen shear conditions (rate = 60 s^{-1}, duration = 5 s, T = 120°C, which is greater than the melting point of the matrix), while no flow-induced structures were seen in pure MB-50k and MB-100k melts, the blends in both series showed distinct but different shear-induced structures. Our results indicate that the high molecular-weight MB-250k chains are responsible for the formation of crystallization precursor structures in the blend under shear, which can act as a template for further crystallization. A "shish-kebab" structure, detected by both WAXD (**Figure 1A**) and SAXS (**Figure 1B**), was observed in the MB-100k/MB-250k (90/10) blend, while only a twisted lamellar structure was seen in the rest of the blends under the same shear conditions. These findings suggest that the matrix viscosity plays an important role in influencing the formation of the crystallization precursor structure from the high molecular-weight chains under flow. The evolution of the shish-kebab structure from SAXS, consistent with the appearance of two equatorial (110) reflection peaks in WAXD, can be explained by the *coil-stretch* transition that is induced by flow. The observed "shish" is due to the extended chain crystallization of the stretched chains, whereas the kebabs are due to the folded chain crystallization of the coiled chains. In other blends, because the stretched chains could not aggregate rapidly, no detectable shish was observed. In the MB-100k/MB-250k (90/10) blend, the length of the shish was estimated from the equatorial streak in SAXS, and showed a noticeable decrease with time, possibly due to the relaxation of stress distribution or the overall crystal orientation.

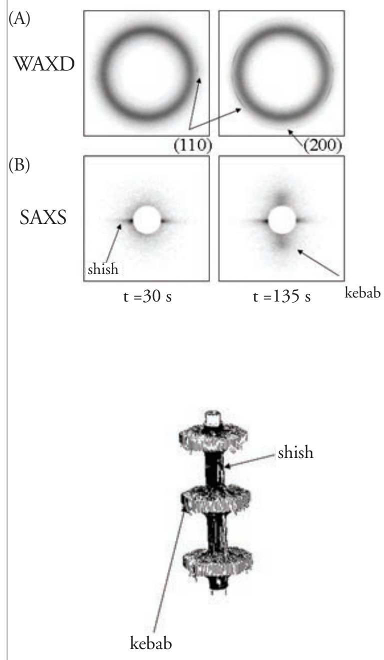

Figure 1. Selected two-dimensional (A) WAXD and (B) SAXS patterns, which illustrate the development of the "shish-kebab" morphology in the MB-100k/MB-250k (90/10) blend under shear (rate = 60 s^{-1}, duration = 5 s, T = 120 °C).