The Self-Reinforcement of Polyolefins Produced by Shear Controlled Orientation in Injection Molding

INTRODUCTION

The enhancement of the mechanical properties of polyethylene (PE) that result from the use of oscillating packing pressures in injection molding was recently reported by Guan et al.[1] The procedure used for the molding of high density PE (HDPE) was not described in detail, and it was not evident that the use of an oscillating packing pressure is to simply cause compression and decompression of the melt in the mold cavity,[2] or to give rise to the application of a macroscopic shear to the solidifying melt.[3] A macroscopic shear may be achieved by the out of phase operation of at least two spaced apart pistons connected to a mold cavity as described by Allan and Bevis,[4] and as applied at moderate pressures to a wide range of polymers and polymer matrix composites, including PE.

The mechanical property enhancements referred to with respect to PE in Guan et al.[1] and in Allan and Bevis[4] are similar, and it is reasonable to assume that the mechanism of property enhancement is due to the application of successive macroscopic shears to a solidifying melt. The patented process[4] is referred to as shear controlled orientation in injection molding (SCORIM), and recent reports relate to polypropylene (PP)[5] and thermotropic liquid crystal polymers,[6] where very substantial enhancement of mechanical properties was reported. The enhancement of mechanical properties of polyolefins that result from shear fields in processing[1,4] is attributed to the formation of "shish kebab" morphologies in HDPE[7] and isotactic PP (IPP)[8] converted into moldings by the SCORIM process.

The purpose of this article is to present evidence for shish kebab morphologies in HDPE[7] and IPP[8] when converted into molded bars using the SCORIM process.

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EXPERIMENTAL

Methods

Figure 1 is a schematic diagram of the apparatus used to apply a controlled macroscopic shear to a solidifying melt in a mold cavity. The 180° out of phase reciprocation of pistons A and B causes the most effective shearing to be applied at the melt–solid interface, as it progresses from the surface to the core of the molding during solidification.

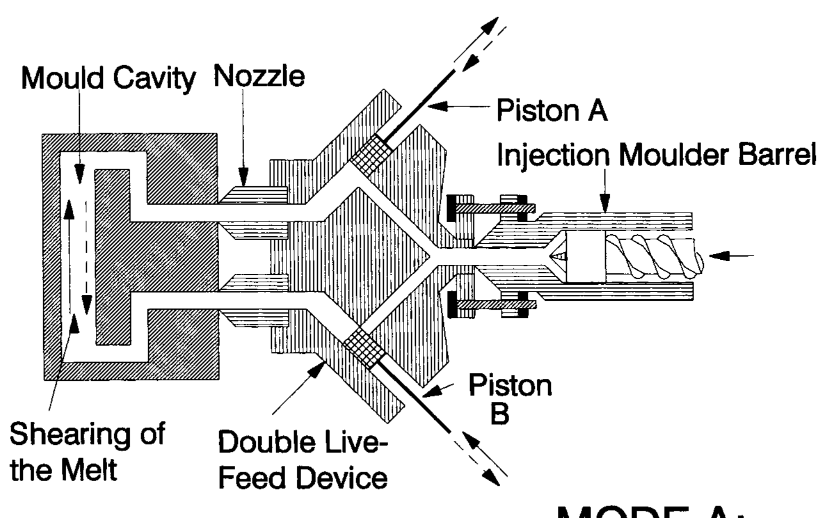

Figure 1 Schematic diagram of the apparatus used to impart a macroscopic shear during solidification of polyethylene and polypropylene moldings. To impart shear on the melt–solid interface as the interface progresses from the surface to the center of the cavity, pistons A and B are operated 180° out of phase.

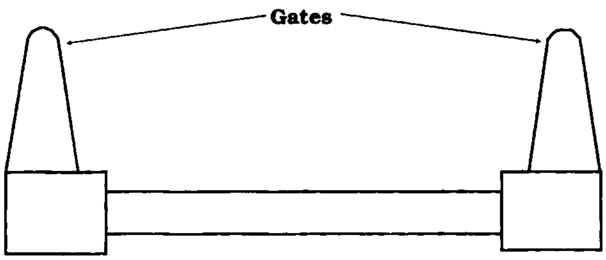

Figure 2 Schematic diagram of the double gated mold cavity arrangement used for molding a 6 × 6 × 90 mm bar of polyethylene, and a 5 mm diameter × 40 mm long bar for polypropylene.

Figure 2 is a schematic diagram of the double gated mold cavity layout used for the production of HDPE and IPP moldings with respective dimensions 6 × 6 mm square cross section × 90 mm long, and 5 mm diameter circular cross section, 40 mm long.

On completion of mold filling in the SCORIM molding, a macroscopic shear was applied throughout the packing stage by the out of phase oscillation of pistons A and B. Molecular weight data and molding conditions used for the conversion of the two study materials selected for presentation are given in Table I.

Distinct morphologies are associated with regions of moldings where a macroscopic shear is applied during solidification. The extents of the cross-section areas of the shear-induced morphologies are indicated in Figure 3, and the techniques used to characterize these regions were transmission light microscopy of microtomed sections, wide angle X-ray scattering (WAXS) Debye patterns, microhardness measurements, Young's modulus measurements, differential scanning calorimetry (DSC), and permanganic etching in combination with transmission electron microscopy of replicas of etched surfaces.

RESULTS

The Young's moduli of conventional and SCORIM moldings are given in Table II.

Table I Molecular Weight Data and Molding Conditions

Study Materials	HD PE	Shell KF6100
Melt flow index	7.0	3.1
M_w	120,000	352,000
M_n	71,000	45,000
Density (g L^{-1})	0.962	0.905
Frequency of piston oscillations (Hz)	0.2	1.0
Temperature (°C)		
Melt	200	195
Mold	25	60

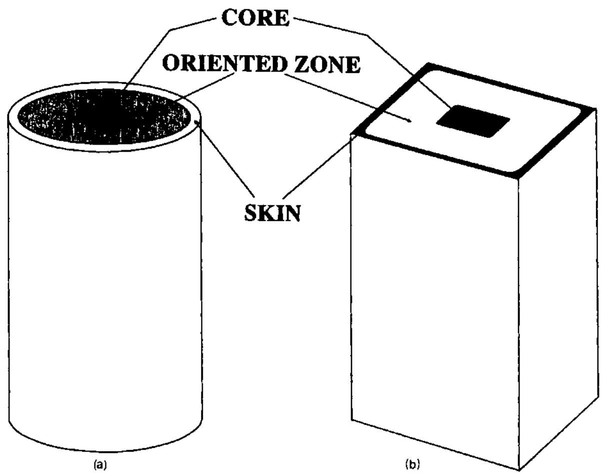

Figure 3 (a,b) Diagrams showing the areas of different microstructure areas of different microstructure across the section of two bar moldings that resulted from the action of the SCORIM processing of PP and HDPE, respectively.

Table II Young's Moduli

	HDPE	IPP
E (GPa)		
Conventional molding	1.39	1.9
SCORIM	2.43	3.3

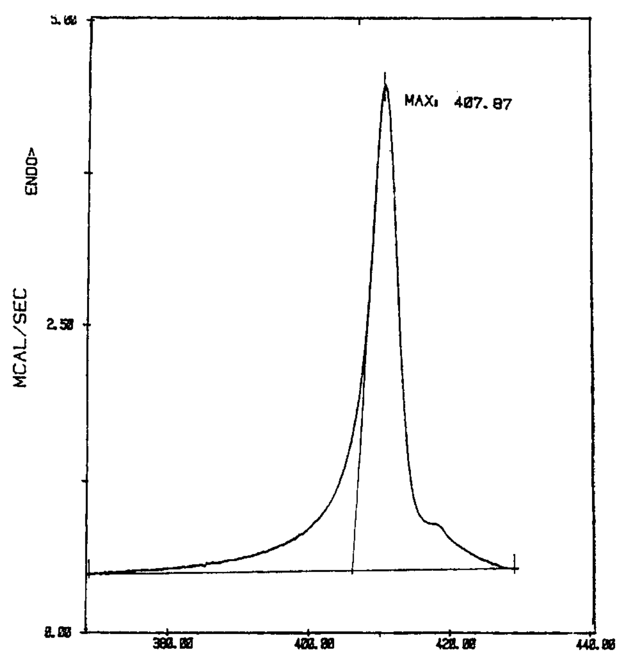

Figure 4 DSC melting endotherm obtained from the shear influenced region of a polyethylene molding.

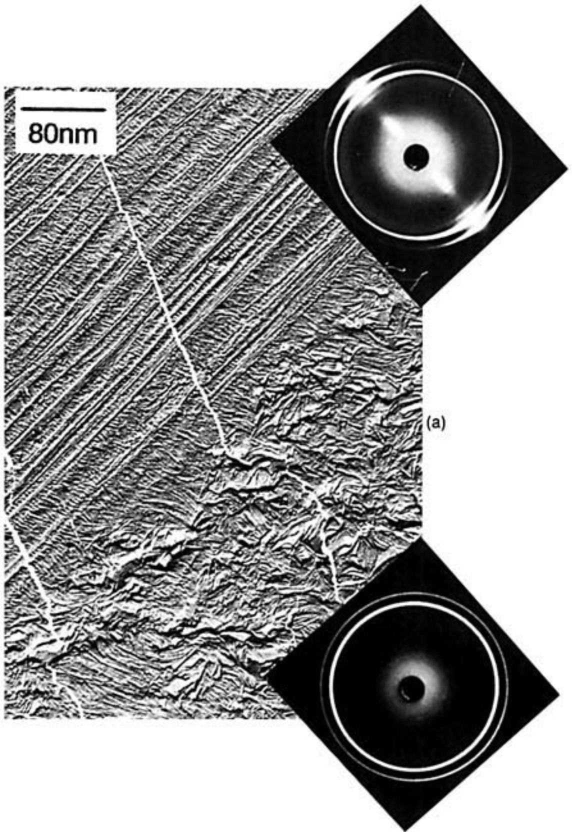

Figure 5 (a) Transmission electron micrograph of a replica from an etched section of HDPE molding, showing shish kebab micromorphology with shishes parallel to the macroscopic shear direction, and the spherulitic core, where shear was not maintained during solidification. Inset are the Debye patterns produced from the respective regions.

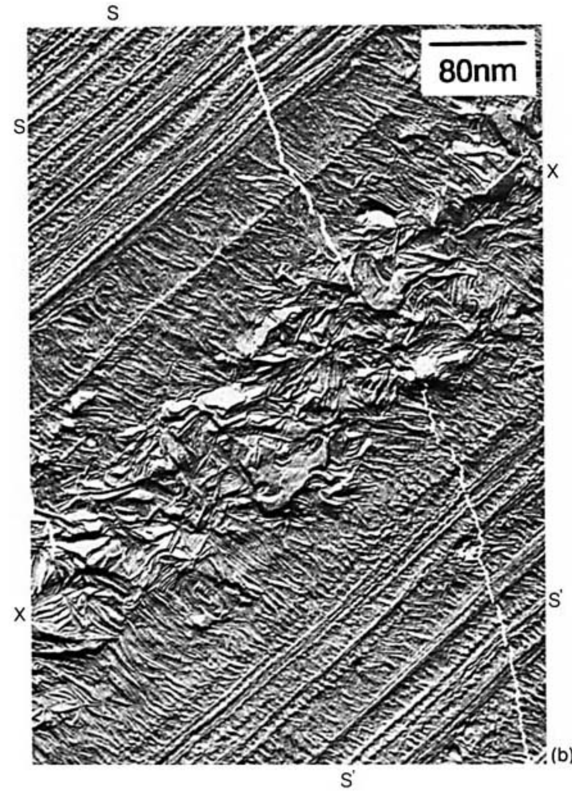

Figure 5 (b) As in Figure 5(a) showing the influence of intermittent application of shear on the micromorphology through the thickness of the HDPE molding. A band of spherulites X–X forms when shear is interrupted, whereas shish kebab micromorphologies S–S and S^1–S^1 arise before and after interruption of macroscopic shear during solidification.

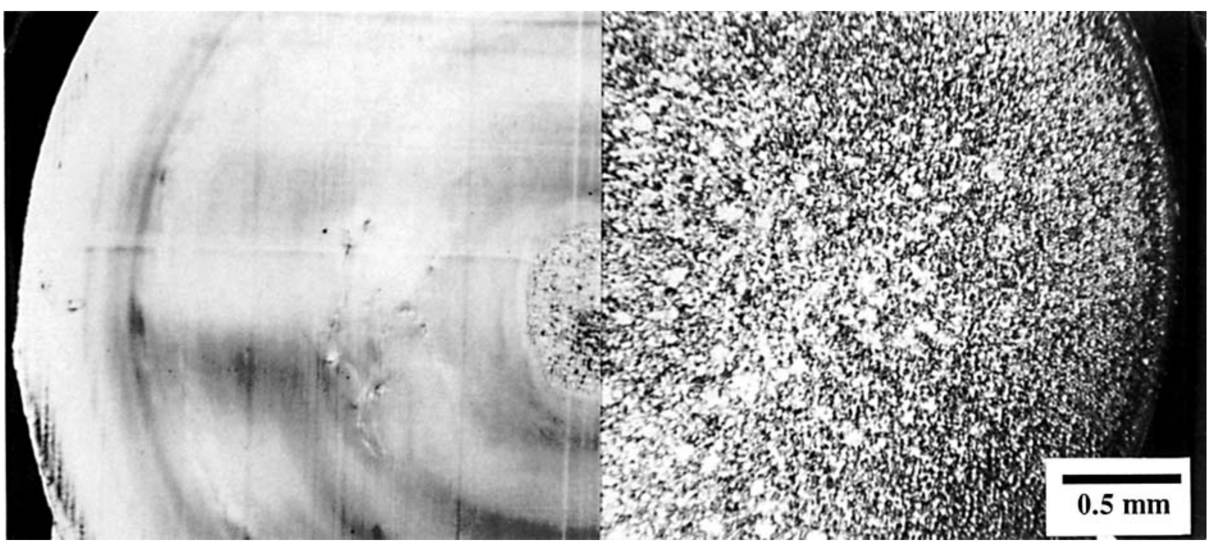

Figure 6 Transmitted light micrographs of representative cross sections of conventional and SCORIM moldings showing the marked difference in polypropylene morphologies produced by the different molding processes. The right side of the figure relates to the conventional molding and the left side to SCORIM, showing the much larger region of highly oriented nonspherulitic polymer that arises with SCORIM.

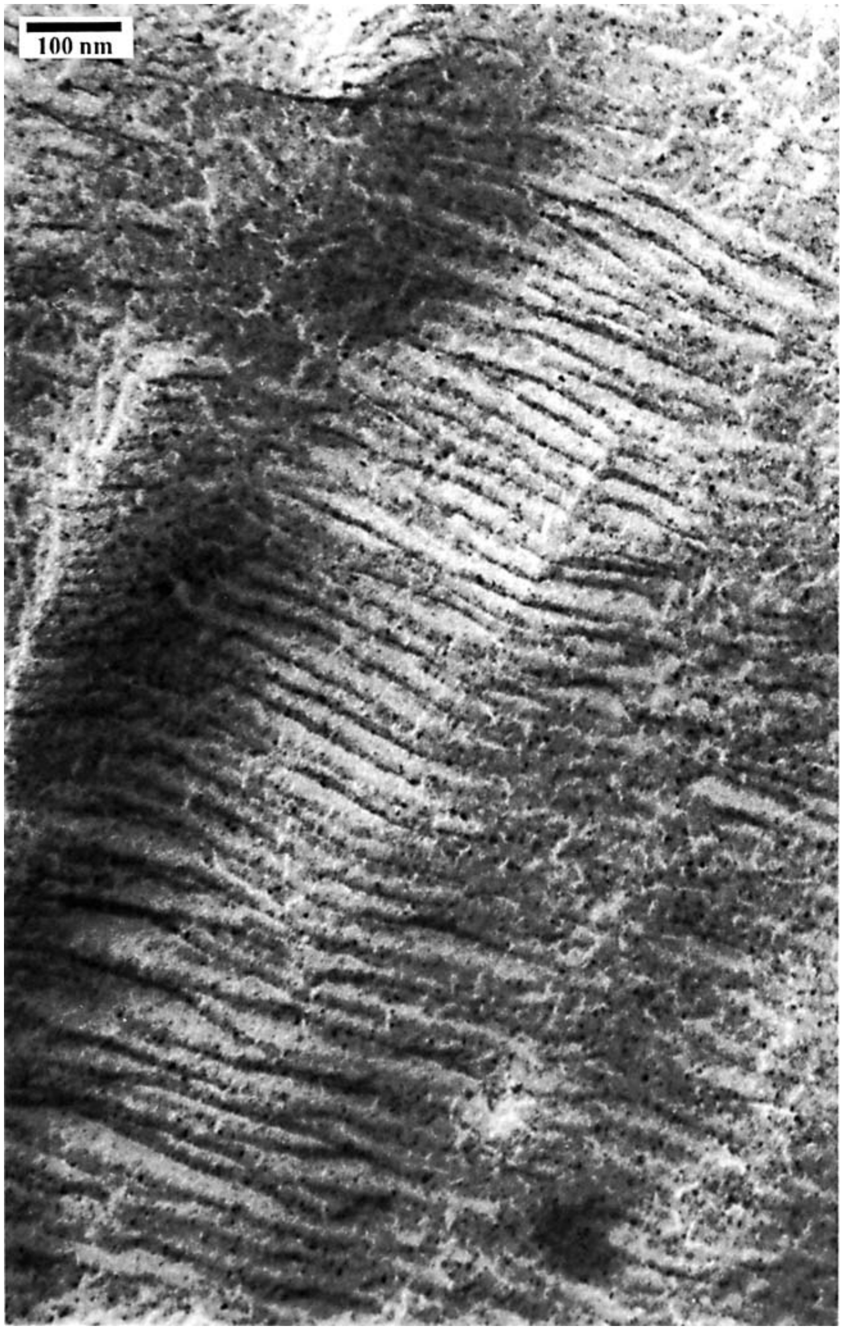

Figure 7 Transmission electron micrograph of a replica from a permanganic etch surface parallel to the direction of macroscopic shear in a polypropylene molding. The micrograph clearly reveals a shish kebab morphology associated in part with the enhancement of Young's modulus, and the occurrence of the γ-phase.

HDPE

The Young's modulus of the region where the micromorphology was influenced by macroscopic shear [Fig. 3(b)], was estimated to be 6 GPa, and responsible for enhancing the modulus of the HDPE molded bar to 2.43 GPa, compared with a modulus of 1.23 GPa for the spherulitic core.

Optimization of cavity and gate dimensions and the SCORIM processing conditions will provide for a greater proportion of the shear-modified morphology, and hence enhanced physical properties.

The shear-induced micromorphology in the HDPE is characterized by the DSC melting endotherm in Figure 4 that exhibits a multiplicity of melting peaks, as in Guan et al.,[1] including a higher temperature melting peak that is not present in the endotherm obtained from the central equiaxed spherulitic core.

The high temperature peak is associated with the shear-induced shish, within the shisk kebab morphology shown in Figure 5(a). Figure 5(a,b) shows transmission electron micrographs of replicas obtained from etched longitudinal sections of HDPE moldings.

The micrograph shows a classical shish kekab morphology within the region influenced by SCORIM, with the shishes parallel to the macroscopic shear direction (indicated by the arrow), and the spherulitic morphology that applies within the central unoriented core of the molding. Inset are the WAXS Debye patterns that represent the substantial differences in the preferred orientation existing within the shear and core regions. The incident X-ray beam was set normal to the macroscopic shear direction.

Figure 5(b) represents the morphology arising when the SCORIM process is interrupted, and represented by the band of spherulites X–X. Prior to interruption of the SCORIM process, the shish kebab morphology S–S applies, and on resumption of the shearing action, the shish kebab morphology S^1–S^1 is restored. Figure 5(b) illustrates the fine degree of control over micromorphology that is possible, and the potential for controlling micromorphology and physical properties using a multiplicity of pistons.[9]

IPP

The marked differences in the macromorphology of the IPP moldings prepared by conventional and SCORIM routes is illustrated in Figure 6. Comparison of the right and left halves of the figure, representing cross sections of conventional and SCORIM moldings, shows the much smaller spherulitic core that can be induced by SCORIM. WAXS diffractometry identified a substantial γ-phase content,[10,11] coupled with a significant increase in crystallinity in the SCORIM moldings. As in HDPE, an examination of transmission electron micrographs of etched sections[8] revealed a shish kebab micromorphology, as shown in Figure 7. This figure shows the first microstructural evidence in the published literature for the presence of shish kebab morphology in injection-molded PP.

CONCLUSIONS

The results presented above are representative of results obtained from a wide range of PEs[7] and PPs,[8] and support the generality of the application of the SCORIM process for the management of the micromorphology and physical properties of molded semicrystalline polymers. The concept of applying macroscopic shears to solidifying melts for the purpose of controlling morphology and physical properties, may be extended to continuous extrusion processes.[12]

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