INTRODUCTION

Thermotropic liquid crystalline polymers (TLCPs) combine the virtues of superior tensile properties with the ability to injection mold with very easy flow through the spontaneous ordering of molecules. A critical processing issue is the development of high anisotropy during TLCP processing and its effects on the physical properties of injection molded parts. Although the concurrence of high tensile properties and high directional orientation is of great benefit in fiber spinning, severe anisotropy can be a plague in obtaining balanced properties in many injection molded parts. The rigid nature of the mesogenic segments in TLCP molecules usually leads directly to a high orientation bias favoring the direction of flow with injection molding and other directional processing of thermotropes. A “skin-core” morphology usually develops on the surface and the interior, respectively, of the article during melt processing by extrusion, fiber spinning, injection molding, etc.

Layer orientation in injection molded plaques of 6-hydroxybenzoic acid (HBA/HNA) (58 mol % HBA and 42 mol % HNA) random type copolyesters was determined by Pirnia and Sung using Fourier transform Infrared (FT-IR) attenuated total reflection (ATR) dichroism. This technique enabled these researchers to determine relative orientation encompassing a depth of material 5 µm below the sample surface. Using measured dichotic ratios to calculate the orientation function, the skin, intermediate layers and core were characterized for a series of samples cut from positions along injection-molded plaques by progressively removing material by milling. Generally, Pirnia and Sung reported that: (1) orientation was highest for the skin and progressively decreased as one proceeded from the intermediate layers to the core; and (2) orientation was lowest in the gate region of the moldings. The highest orientation was usually observed in the region beyond the immediate gate area, with orientation parameters on the average of 0.77 to 0.88 being reported for the skin layer. Pirnia and Sung characterized the “skin” that had encompassed
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a depth of 5μm in sampling surface orientation using their FT-IR technique.4

Similar measurements were performed on our samples to determine if the magnitude of the “skin” orientation is similar to what Pirnia and Sung found for their injection-molded samples.

EXPERIMENTAL

Materials and Fabrication

The TLCP primarily utilized in this study is a copolyester containing 4,4’-dihydroxy-α-methylstilbene (DHαMS) as the mesogen and a terephthalate/isophthalate/2,6-naphthalenedicarboxylate molar ratio of 65/10/25.5,6 Sample plaques 76 mm by 76 mm were fabricated using a Boy 30T2 injection molding machine with which both melt and mold temperatures were readily controlled. A mold with an insert with polished faces was utilized permitting the fabrication of plaques of various thicknesses from 0.8 mm to 3.2 mm.

Polymers with molecular weights of about 35,000 g/mol were evaluated. Fill times of 1 s were utilized.

It was ascertained that the samples required surface cleaning to remove contaminants before examination. The cleaning was performed using a 1% solution in de-ionized water of Alconox Liqui-Nox® cleaning agent with a Bransonic 220 ultrasonic cleaner for duration of 10 min. Both the initial presence of contaminants and their effective removal were verified for selected samples by atomic force microscopy using a Topometrix 2000 AFM.

Surface Orientation

Samples were cut from an area down the centerline of a 0.8 mm thick plaque molded with a melt temperature of 290°C and a mold temperature of 45°C. The positions are shown in Figure 1. The direction of melt flow during injection-molding progresses from position 1 towards position 4.

ATR Spectroscopy

The samples were analyzed by infrared spectroscopy using the Seagull Variable Angle Reflectance Accessory (see Figure 2) in a Nicolet Nexus 670 FTIR spectrometer. The Seagull was equipped with its ATR Rotator (see Figure 3), a ZnSe ATR crystal and a Wire Grid Polarizer. The polarizer was set for s-polarization and the Seagull was set for an incident angle of 55°. This incident angle was selected since it was slightly above the experimental critical angle for the samples examined.

Each sample was oriented on the sampling stage of the ATR Rotator so its cut edges corresponded to the 0° and 90° degree settings. A background spectrum was recorded using the clean ATR crystal and then sample spectra were collected with the ATR Rotator set to 0°, 45°, and 90°. The spectra collected were signal averaged over 32 scans at 8 cm⁻¹ resolution, over a spectral range from 4000 cm⁻¹ to 650 cm⁻¹.

For comparison to the results of Pirnia and Sung, the spectra were converted to absorbance units and baseline corrected. Then the dichroic ratio and orientation parameter were calculated as described by Pirnia and Sung.

RESULTS AND DISCUSSION

Figure 4 shows the unprocessed fingerprint region of the spectra collected from the from the position 4 sample. These spectra show distinct differences as a function of the position of the sample in the sampling plane. In particular, the band at 1500 cm⁻¹ is much weaker at the 0° position than at the 90° position. This is expected, since this band is associated with the skeletal vibration of the benzene and naphthalene rings in the copolymer. These rings are oriented roughly parallel to the polymer chain axis. The band at 1730 cm⁻¹, on the other hand, shows very little change in
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intensity due to the rotation of the sample in the sampling plane, indicating that it is not strongly associated with an oriented species within the copolymer.

The orientation differences in these particular samples are extremely easy to observe by FTIR spectroscopy. The rotation of the sample could be tuned to maximize and/or minimize the intensity of the band at 1500 cm⁻¹, to position the sample more precisely along its oriented axis than the mechanical alignment used herein.

The spectra were processed to compare the orientation function to that published in the literature. The orientation function for the band at 1500 cm⁻¹ is shown in Figure 5. The orientation function is approximately the same as that reported by Pirnia and Sung. In addition, the orientation is lowest in the gate region as expected.

**SUMMARY**

The orientation of injection-molded polymers can be analyzed in a straightforward manner by ATR dichroism. Using a variable angle accessory and sample holder, like the Seagull and its ATR Rotator, allows the incident angle to be optimized for a given sample and also makes it possible to determine if the orientation axis is along the axis predicted.

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**REFERENCES**