Effect of Annealing Conditions on Molecular Structure and Physical Properties of Polypropylene Slit-Film Yarns

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Abstract: The effects of various annealing temperatures and durations on the structure and physical properties of polypropylene (PP) slit-film yarns were investigated. Annealing led to a more developed crystal structure, even when the yarns were drawn before heat treatment. Annealing at 140 °C led to better developed crystal structures than that at 100 °C. Annealing primarily affected the crystalline structure, whereas little change was observed in the molecular orientation of the yarns. The slit-film yarns annealed at 140 °C showed less than 1% shrinkage. A very low-shrinkage slit-film yarn was obtained on annealing for 10 min at 140 °C or 20 min at 100 °C.

Keywords: annealing, polypropylene, slit film yarn, crystalline structure, thermal shrinkage

1. Introduction

Polypropylene (PP) is used in materials as diverse as engineering plastics, packaging, medical equipment, and textiles [1-4]. Most fibers are produced by extruding polymer melts or solutions through spinneret holes. Fibers can also be made from slitting polymer film into film yarns or tape yarns [5]. Rectangular fibers with high width to height ratios are easily produced in this way, with flat film yarn made by slicing such films. Polymer melt extruded through T- or annular dies can be solidified and sliced into film yarns. Slit film yarns are used, for example, to make fabrics for container bags, carpet backings, twines and ropes.

Thermal shrinkage is an important property related to a material’s thermal stability during post processing [6,7]. Annealing has been shown to reduce thermal shrinkage in materials obtained from fiber spinning processes. Thermal shrinkage is also an important consideration for packaging materials such as container bags consisting of PP slit film yarns, as the container bags should not deform upon exposure to hot or humid environments especially for long term transport via marine transportation.

Oriented molecular structures of polymers have been found to shrink and relax easily when annealed without constraint. Studies on annealing effects of PP spun fibers and drawn cast films on molecular structures and physical properties are easily founded elsewhere [8,9], however, research on the effects of constrained annealing on slit film yarns is lacking.

This work reports the annealing of polypropylene (PP) slit film yarns under constrained conditions at different temperatures and durations to reduce thermal shrinkage. The material's structural changes and physical properties were examined.

2. Experimental

2.1. Materials and Sample Preparation

Isotactic PP (Honam petrochemical corporation, melt flow

Figure 1. Schematic of extrusion system for split-film yarns.
A tubular film blowing apparatus was used to form tubular films. The polymer was extruded through an annular die at 240 °C; the blown tubular film was solidified by quenching with water. The film was slit into film yarns, which were then drawn at 90 °C with a draw ratio of 8 and wound on take-up roll. The slit film yarns were wound on bobbins to give the constrained conditions before being annealed in an oven for between 10 and 50 minutes at either 100 or 140 °C. Figure 1 outlines the manufacture of the slit film yarns.

2.2. Tensile Properties
Tensile properties were measured with an Instron tensile tester (UTM Instron 3345), using specimens 50 mm long and a cross-head speed of 100 mm/min.

2.3. Wide Angle X-ray Scattering (WAXS)
WAXS patterns from equatorial scans were measured on a Rigaku Denki-model D/max-2500 X-ray diffractometer system with nickel-filtered CuKα radiation generated at 40 kV and 30 mA. Bundles of fibers were set perpendicular to the beam and scattering intensities were recorded at 0.02° intervals at 3°/min from 5 to 35°. Crystal sizes of (hkl) planes were calculated by [10,11]:

\[ D_{hkl} = \frac{K\lambda}{H_{hkl}\cos\theta} \]  

where, \( D_{hkl} \) is the crystal size of the (hkl) plane, \( K \) the Scherrer constant, \( \lambda \) the wave length, \( H_{hkl} \) the half width, and \( \theta \) the Bragg angle.

2.4. Fourier Transform Infrared Spectroscopy (FT-IR)
FT-IR spectra were recorded on an IFS-66V/S infrared spectrometer (Bruker, Ettlingen, Germany) at a resolution of 1 cm\(^{-1}\) between 650 and 4000 cm\(^{-1}\). A SiC-Glowbar light source and a deuterated L-alanine doped triglycine sulfate (DLATGS) detector were used.

2.5. Differential Scanning Calorimetry
Differential scanning calorimetry (DSC) was performed at 30-270 °C using a DSC 2010 (TA Instruments) with a heating rate of 10°C/min.

2.6. Microscopy
Polarizing microscopy was used to investigate the average molecular orientation of the slit film yarns. Retardation of the optical path of as-spun fibers was measured using a Leica polarizing microscope and a compensator method. Birefringence was calculated using the measured retardation and fiber thickness [12].

2.7. Thermal shrinkage
Slit film yarn samples (initial length, \( L_i \)=25 cm) were immersed in boiling water for 30 min, cooled for 4 h and then dried in air. Their final lengths, \( L_f \), were measured and shrinkage was calculated by:

\[ \text{Shrinkage} \% = \frac{L_i - L_f}{L_i} \times 100 \]  

3. Results and Discussion
Figure 2 shows visual microscopy images of the slit film yarn whose cross-section is rectangular having very large width to height ratios.

Figure 3 shows the tensile strength of the variously annealed samples. Tensile strength ranged from 232 to 303 MPa, increasing slightly with annealing temperature. The effect of annealing time was not significant. Annealing at 140 °C resulted in higher tensile strength than annealing at 100 °C. Tensile strength has been reported not to change significantly with constrained annealing [6]; it has been found to decrease with unconstrained annealing, with relaxation or reorientation of the amorphous phase, which lowered tensile properties, occurring during unconstrained annealing. The constrained annealing reported here slightly increased the fibers’ tensile strength.
The WAXS patterns of the annealed fibers (Figures 4 and 5) show the three major characteristic peaks of the stable monoclinic crystal structure of PP with a highly oriented fibrous structure by tensile drawing. The three characteristic peaks of PP were at $2\theta=14^\circ$, 16.9 $^\circ$, and 18.5 $^\circ$, respectively corresponding to the (110), (040), and (130) planes of the PP crystals [13]. The control sample showed unclear peaks in comparison with annealed ones. The crystal structure developed with increasing annealing time, and annealing at 140 $^\circ$C resulted in more prominent peaks than annealing at 100 $^\circ$C, indicative of a more developed crystal structure.

The increased tensile strength (Figure 3), was due to the development of the crystal structure. Previous work [14,15] has reported that oriented crystalline polymers increased crystalline orientation and decreased crystalline defects by annealing.

Changes of apparent crystal size are shown in Figure 6. Crystal lattices’ lateral sizes were obtained from reflection profiles of the (110) plane and were calculated by equation (1). Lateral crystal size increased with annealing time. Annealing at 140 $^\circ$C resulted in larger crystals that were more affected by annealing time than annealing at 100 $^\circ$C. The observed trend of annealing resulting in larger crystals agrees with previous work [14]. Apparent crystal size increased as the crystals developed (note the sharp and prominent WAXS peaks), indicating that defects were reduced and the crystalline structures improved. Increases of apparent lateral crystal size are generally observed when molecules’ tensile stress is improved by such as increased take-up velocity and drawing with a high draw ratio because of crystal rearrangements and increased orientation.

PP crystals in the control sample did not develop sufficiently and hence did not show prominent WAXS peaks. Crystals developed with increasing annealing time. 10 minutes of annealing resulted in the appearance of peaks representing...
the (040) and the (130) planes. Annealing at 140 °C resulted in the sharper a WAXS pattern of the PP crystal than annealing at 100 °C. Crystal structure development with increasing annealing temperature has been observed in previous work [12,13].

Figure 7 shows DSC thermograms. There were little changes among the annealed samples. Crystallinity can be calculated from the heat of fusion [12,14]. The crystallinity of the control (38%) was increased by annealing (to 46%), but was not significantly affected by annealing time.

The infrared spectra of the variously annealed samples (Figure 8) showed the general features of PP between 650 and 4000 cm⁻¹ with no significant differences between them. Assigned IR bands of PP are easily found in early work and agree with those previously reported for PP [16,17]. The 997 cm⁻¹ band is a helix band [16] resulting from the vibrations of a helical conformation (trans-gauche-trans-gauche) of the isotactic PP. The stable 972 cm⁻¹ band [17] was used as a reference.

The intensity ratio of the 997 cm⁻¹ and 972 cm⁻¹ bands represents isotactic PP’s relative helix band content [18]; it changed little with annealing time or temperature in comparison with the control (Figure 9). The helix band content represents the presence of helical conformations in the oriented amorphous region, a region that relaxes and shrinks with unconstrained annealing, but is little changed by constrained annealing as relaxation is prevented. The WAXS and FT-IR results show that structural changes upon constrained annealing were mainly caused by molecular reordering in the crystalline, rather than the amorphous, phase.

Polarizing microscopy was used to investigate the average molecular orientation of the yarns, which was influenced by crystalline and amorphous orientation. Figure 10 shows birefringence indicating little change in molecular orientation by annealing. Constrained annealing prohibited the relaxation and shrinkage of the amorphous regions, and hence their molecular orientation was not deteriorated by annealing. The
WAXS profiles (Figures 4 and 5) show that the crystalline structure developed with increased annealing time and temperature, though there was no significant change in the birefringence (average molecular orientation) shown in Figure 10. The constrained annealing affected mainly the crystalline structure and had little effect on the amorphous region.

Annealing decreased thermal shrinkage 5.1% to 0.2% (Figure 11). Fibers annealed at 140°C had less shrinkage than those annealed at 100°C. The shrinkage of fibers annealed at 100°C decreased with increasing annealing duration up to 20 min; after 10 min of annealing duration at 140°C had only a slight effect. This is because a higher annealing temperature requires less time to stabilize and reorder the crystalline structure. A previous work [12] reporting the plastic deformation of PP found that annealing for nearly 10³ min at 155°C was needed to obtain sharp crystalline reflections, a commercially unfeasible duration. In the case of PP slit film yarns, annealing for more than 10 min at 140°C was sufficient to improve slit film yarn's tensile strength, crystalline structure, and thermal shrinkage. To improve thermal shrinkage, annealing for 20 min at 100°C or for 10 min at 140°C was required.

4. Conclusions

The effects of constrained annealing on the physical properties and molecular structure of PP slit film yarns were investigated. Tensile strength increased slightly with increasing annealing time and temperature through the development of crystal structure. The amorphous orientation was shown by FT-IR spectroscopy to be unaffected by annealing. Annealing for 10 min at 140°C reduced thermal shrinkage to below 1%. The constrained annealing mainly affected the evolution of the crystalline phase rather than molecular orientation. Crystal structure was improved by annealing and was better developed at higher the annealing temperature.

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References


