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Materials

Changes of crystallinity and spherulite morphology in isotactic polypropylene after rolling and heat treatment

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Abstract: The spherulite morphology of the rolled and subsequent heat-treated isotactic polypropylene (iPP) was observed by polarized microscopy, and the crystallinity evolution of materials was also measured by the wide angle X-ray scattering (WAXS). Rolling led to the oblate spherulites in the deformed iPP samples. The sheared crystalline lamellae broke apart into sets of crystalline blocks during rolling. As a result, the crystallinity of the iPP samples was greatly reduced during deformation, which induced the unclear spherulites and spherulite boundaries. Subsequent heat treatment resulted in the strong recrystallization of the rolled iPP samples. But the recrystallization in this work only meant the rearrangement of the macromolecule along the unbroken crystalline lamellae and the existing small crystalline blocks in the deformed spherulites. Heat treatment did not change the shape of the spherulites formed during deformation. The recrystallization also resulted in very clear spherulites and spherulite boundaries.

Key words: isotactic polypropylene (iPP); rolling; heat treatment; X-ray diffraction; crystallinity; spherulites

1. Introduction

Semicrystalline polymers, which contain both crystalline and amorphous components, reveal more complex microstructures, with an amorphous phase between the crystalline lamellae, with most of the macromolecular chains penetrating into both phases [1-3]. Spherulites are the most general type of morphological formations in semicrystalline polymers that are crystallized from a melt. The size of spherulites depends on the supercooling value during crystallization. Spherulites have a scale of ~0.1 to 1000 μm [1, 4]. Spherulites are polycrystalline aggregates consisting of lamellae directed along the spherulite radius [5]. This can be clearly seen in crossed polars but not under the plane-polarized light. In this study, the evolution of the spherulite morphology after rolling and heat treatment is presented. The influence of crystallinity on the spherulite morphology is also discussed. The crystalline morphology is one of the most important aspects of semicrystalline polymers, because the ultimate properties of the material depend mainly on microstructural factors, such as the degree of crystallinity, the size of spherulites, the lamellar thickness, and the crystalline orientation [6-8]. Some work has been done to investigate the crystalline morphology changes of iPP materials during deformation [9-11]. But the relaxation of the deformed iPP crystalline part after subsequent heat treatment is rarely concerned. Therefore, it is one of the purposes of this study to suggest a new way to improve the mechanical properties of iPP materials and iPP serving materials through the investigation of crystallinity and spherulite morphology changes after rolling and heat treatment.

2. Experimental

2.1. Material and processing procedure

The experiment was conducted on commercial semicrystalline iPP sheets (Goodfellow Company, Germany; size: 100 mm×100 mm×10 mm; isotactic index: 95%; density: 0.9 g/cm^3) with an initial thickness of 10 mm. To provide reproducible and homogeneous specimens uninfluenced by the manufacturing process, the iPP sheets were heat-treated at 150°C for 24 h before rolling. The X-ray results show that it is the α form crystalline in the material and the crystallinity degree is about 80vol% after annealing.

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The slices, 100 mm×40 mm×10 mm, designed for the rolling experiments, were machined from the heat-treated sheets. The samples were rolled at room temperature. The total rolling true strain was described by the formula: true strain=ln(h_0/h), where h_0 is the original thickness of the undeformed sample and h the thickness of the rolled sample. Each pass exerted a true strain increasing by about 0.025 at a constant rolling speed. Various true strain levels ranging from 0.4 to 1.5 were obtained. The samples with a true strain of 1.4 were heat treated at 60 and 100°C, respectively, for different annealing times ranging from 2 to 180 min.

2.2. X-ray diffraction

The wide angle X-ray scattering (WAXS) diffraction patterns were obtained by means of the X-ray diffractometer system with an area detector on the reflection method. The measurements were carried out using the Co $K_{\alpha 1}$ radiation at a tube current of 40 mA and a voltage of 40 kV. The distance between the sample and the area detector was 158 mm. The X-ray diffraction results were used to calculate the crystallinity of the rolled and heat-treated samples. To avoid the influence of the rolling texture, 119 2θ-intensity X-ray curves were obtained from the 119 Debye-Scherrer frames and the final integrated result was the sum of these 119 curves for all the samples. All the X-ray curves have 2θ ranging from 12° to 32° [12-13]. A smooth curve was used to separate the amorphous and crystalline parts. The degree of crystallinity X_c for each specimen was obtained from the ratio between the area under the crystalline peaks and the total area under the diffraction curve, with different contributions of the crystalline and amorphous regions considered.

2.3. Polarized microscopy

The crossed polarized light was used to observe the spherulites' morphology of the rolled and heat-treated samples. The spherulites' morphology of the undeformed sample was also examined. For this purpose, the sections with 30-μm thickness were cut in planes perpendicular to the normal and transverse directions, respectively. The sections were cut at room temperature using a Leica RM 2165 rotary microtome.

3. Experimental results

Fig. 1 shows the calculated result of the corresponding relative change in crystallinity as a function of rolling true strain. It should be noted that these results come from the integration over the entire pole sphere, that is, the influence of the crystallographic texture is fully accounted for [12]. The crystallinity of the iPP samples is greatly reduced with increasing true strain, varying from an initial value of 80.1vol% for the undeformed sample to the final value of 36.6vol% for the deformed sample with a true stain of 1.5.

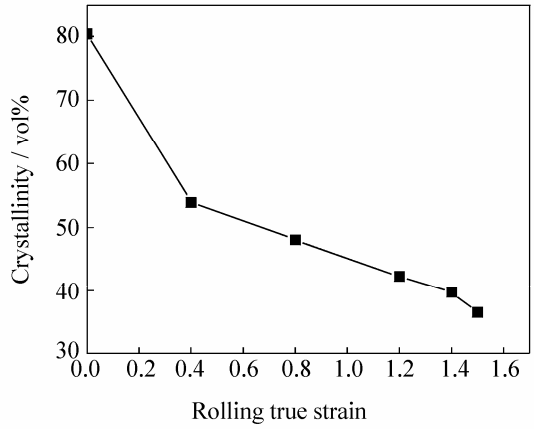

Fig. 1. Changes in crystallinity degree with the rolling true strain calculated from the integrated X-ray diffraction data.

Figs. 2 and 3 present the polarizing micrographs of the undeformed and rolled samples. The initial microstructure of the undeformed sample (Fig. 2(a)) is a well spherulitic structure with the diameter ranging from 100 to 200 μm. For the rolled samples, two sets of sections cut in perpendicular to the transverse and normal directions were investigated, respectively, to evaluate the changes in spherulites' morphology. The arrows on the pictures indicate the rolling direction.

In sections normal to the transverse direction, the spherulites appear elongated along the rolling direction as the rolling true strain increases (Figs. 2(b) and (c)). As the rolling true strain is 1.2 (Fig. 2(d)), the spherulites are long and narrow and elongate along the rolling direction, but the boundaries can also be observed easily. For the samples with a higher rolling true strain (Figs. 2(e) and (f)), no more elongation occurs on the pictures, but it is difficult to distinguish spherulites and spherulite boundaries. However, the outlines of the initial spherulites are highly elongated along the rolling direction.

The spherulites' morphology observed from the normal direction, does not change at low rolling true strain (Fig. 3(a)). At somewhat higher true strain (Fig. 3(b)), the spherulites elongate slightly along the rolling direction. The spherulites do not elongate much even at high rolling true strain (Figs. 3(c) and (d)), but the spherulites and their boundaries are unclear and are difficult to recognize. This phenomenon is because of, first, the lower crystallinity, and second, the much smaller diameter of spherulites in the normal direction. Finally, the size of the rolled spherulites is larger than that of the undeformed ones, but their shape is also