Deformation Behaviors in Isotactic Polypropylene During Rolling

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Abstract—Wide angle X-ray diffraction is used to measure the texture evolution of isotactic polypropylene (iPP) during rolling. Pole figures, orientation distribution functions and crystallinities of the rolled iPP are obtained and calculated. The texture evolution is also simulated by the modeling. It can be drawn that the main deformation mechanisms occurred at low strain is the coarse slips on few planes and the amorphization because of the special mother and daughter lamellae of the material, which leads to the crystallinity decreases greatly. As the true strain increases, mother and daughter lamellae are broken, then, the following deformation does not be controlled by the special structure of α-iPP. The basic deformation mechanisms in the rolled iPP is the crystallographic slips, and the main slip systems are (010)[001] and (100)[001] chain slips and (010)[100] transverse slip and so on. Amorphization is also a deformation mechanism which may take place as an alternative to crystallographic slip depending on the crystallographic orientation of a lamella. The [001]||RD fiber texture, which includes several (hk0)[001] texture components is the main texture component in the rolled iPP.

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INTRODUCTION

The understanding of the basic mechanism of plastic deformation of the semi-crystalline polymers has been started in the 1960s. The molecular microstructure, the crystallization behavior, the semi-crystalline morphology, and the mechanism of plastic deformation at the scale of crystalline lamellae were investigated by the diffraction techniques and transmission electron microscopy in the 1970s. Peterlin [1] studied the plastic deformation of single crystals, thin layers, and bulk samples together with mechanical properties, X-ray and infra-red data and found the existence of three stages in the cold drawing of crystalline polymer: the plastic deformation of the original spherulites structure, the discontinuous transformation of the spherulites into fiber structure by micronecking, and the plastic deformation of the fiber structure. Such micronecking had been considered for obtaining large-strain deformation of aggregates of the chain folded crystals. It was considered that micronecking removes kinematical constraints between lamellae and allows them to untangle. However, it was testified by Argon et al. [29] that the micronecking is reasonable in tensile deformation but is not correct for modes of the deformation not producing cavitations. Because the positive normal stress component prevents cavitations. Although WAXS, SAXS, TEM and light microscopy observations indicate that some degree of inhomogeneous deformation in the form of localized shear bands occurs, the crystalline and associated amorphous regions of the material undergo a continuous series of shear induced morphological transformations, without any cavitations [3]. They did a large amount of qualitative studies of the texture evolution during deformation and further analyzing of the deformation mechanisms. Possible plastic deformation mechanisms in the crystalline phase of semi-crystalline polymers were summarized by Bowden and Young [10], Haudin [11], and by Lin and Argon [2]. And the deformation mechanisms in the different rolling stages and layers were studied by Qiu [12]. These authors reported that the crystalline portion of many semi-crystalline polymers, such as PET, HDPE, Nylon-6 and PP, deform mainly by crystallographic shear mechanisms. Although other mechanisms such as twinning and stress-induced martensite transformation were reported as well, they seem to occur predominantly in highly textured samples. According to these publications [2, 4, 10–16], microscopic deformation in the crystalline parts of semi-crystalline polymers occurs in the form of crystallographic shear predominantly on {hk0} planes. This mechanism is often referred to as crystallographic shear slip. Considerations associated with the anisotropy of the interfacial energy suggests that crystalline slip along the (100), (010), and (110) planes should occur preferentially in these materials. Indirect experimental studies have suggested that the two most important chain slip modes are (100)[001] and (010)[001]. The third slip system along the (110) plane, although widely postulated, has not been detected experimentally. It was also reported that transverse slip mechanisms such as,
(100)[010] and (010)[100], can occur in addition to the chain slip process. In addition to the crystal slip, melting-recrystallization is also regarded as a kind of inference of chain unfolding which occurs in the deformation process [17]. The interfibrillar tie molecules were considered as the factor influence the ultimate draw ratio in some flexible-chain semicrystalline polymers [18].

Polypropylene is one of the most important commodity semicrystalline polymers, which can be used as engineering material, such as in automobiles, household appliances and in the construction industry [19]. Semicrystalline polymers, for example, polypropylene and polyethylene, are complicated materials, with an amorphous phase interlaying crystalline lamellae, and with most of the macromolecular chains engaged in both phases. The crystalline structure of the isotactic polypropylene (iPP) is one of the most complex among industrially developed polymeric materials, since it displays several allotropic modifications and a variety of spherulitic morphologies. The two most common crystalline phases contain monoclinic (α) and hexagonal (β) unit cells. It is shown that both crystalline structures can coexist in a given specimen, but with each spherulite consisting of a single phase [20]. The α spherulites contain two families of lamellae: the radial (mother) ones and the tangential (daughter) ones which normal to the radial lamellae nearly. In contrast with the α spherulites, the β spherulites consist of the broad, locally parallel stacked radial lamellae, just as in the spherulites of other polymers [21].

In this work, an integral calculation method is used to estimate the crystallinity evolution of iPP samples during rolling based on the integration of wide angle X-ray frames obtained from an area detector. The texture evolution is also analyzed during rolling in terms of pole figures and the orientation distribution function (ODF) derived from them. In addition, the texture evolution is simulated by the modeling. The texture evolution of the simulated results and the experimental results, the crystallinity evolution during rolling and the mother and daughter lamellae structure are considered to discuss the deformation behaviors of the α-iPP comprehensively.

EXPERIMENTAL

Materials and Procedures

One kind of commercial semi-crystalline isotactic polypropylene (iPP) sheets (Goodfellow Company, Germany; size: 100 × 100 × 10 mm, isotactic index 95%, density 0.9 g/cm3, melting temperature: 170–175°C) was used in the study. The iPP sheets were annealed at 150°C for 24 hours before rolling to provide reproducible and homogeneous specimens uninfluenced by the manufacturing process. The X-ray results show that it was α form crystalline in the material and the degree of crystallinity was about 80% after annealing.

The samples, 100 × 40 × 10 mm, designed for rolling experiments, were prepared from the heat treated sheets. The samples were rolled at room temperature. Each pass exerted a true strain increasing of about 0.025 at the constant rolling speed. The total true rolling strain was described by the formula: true strain = ln(h0/h), where h0 is the original thickness of iPP sample and h is the thickness of rolled sample. Various true strain levels (logarithmic) were obtained, from 0.4 to 1.5. After rolling, iPP sheets were also broadened on the transverse direction. All the X-ray samples and tensile samples were machined from the center part of sheets to minimize the influence of broadening.

X-Ray Diffraction

Textures of the crystallographic planes of iPP crystallites (α form) in the deformed samples were determined by means of X-ray diffractometer system with an area detector on the reflection method (Bruker D8; CuKα, tube current: 40 mA; tube voltage: 40 kV)

For reconstructing complete Debye-Scherrer diagrams covering the entire pole sphere we collected 119 frames for each sample condition. The integration time for each single frame amounted to 150 seconds in order to capture sufficient intensity. From the normalized and corrected Debye-Scherrer frames (110), (040), (130), and (−113) pole figures were reconstructed at the diffraction angles: 16.4°, 19.6°, 21.6°, and 49.9°, respectively. The sample symmetry was orthorhombic and the crystal symmetry (α form) was monoclinic. The parameters of the unit cell are: a = 6.65 Å, b = 20.80 Å, c = 6.5 Å, β = 99.8° [21].

Three-dimensional orientation distribution functions (ODF) of grains in polycrystalline aggregates are used to quantify crystallographic textures. They can be calculated from two-dimensional pole figures by means of series expansion methods or direct methods. In this work, the texture component method in the formulation of Helming et al. [22] is used for quantitative texture analysis.

X-ray diffraction results were also used to calculate crystallinity of the rolled samples. For each sample, 119 intensity-20 X-ray curves were obtained from the 119 Debye-Scherrer frames and the final integrated result was the sum of these 119 curves. All X-ray curves have 20 ranging from 12° to 32°. In this work, the two-phase concept is adopted which is usually accepted for polymeric materials. The amorphous contribution to the scattering was taken into account through a broad diffraction band. A smooth curve was used to separate the amorphous and crystallinity parts. The degree of crystallinity for each specimen was obtained from the ratio between the area under the crystalline peaks and the total area under the diffraction curve, with the different contributions of the crystalline and amorphous regions considered.