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Stress–strain behavior of cold-drawn isotactic polypropylene subjected to various drawn histories

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ABSTRACT

Uniaxial tensile properties of cold-drawn isotactic polypropylenes (iPP) subjected to various drawn histories were investigated to elucidate the molecular origin of strain-hardening in the uniaxial stress–strain behavior of semicrystalline polymers. Two series of Ziegler–Natta catalyzed iPP with a wide range of crystallinities and metallocene catalyzed iPP with a wide range of molecular weights were used in this study. We propose a tie molecular model which assumes that tie-chains anchored in adjacent crystalline lamellae are expanded into tautness, and the taut tie-chains are pulled out from the crystalline lamellae within the lamellar units. On the basis of this model, we derive a universal constitutive equation for various cold-drawn iPPs subjected to various drawn histories.

1. Introduction

The influence of crystalline morphology such as lamellar alternating structure, degree of crystallinity, stacked lamellar cluster, and spherulitic superstructure on the tensile properties of various semicrystalline polymers has been extensively studied in the past [1–4]. The Young's modulus and the elastic limit are intimately related to initial morphology such as the degree of crystallinity and the lamellar alternating structure within spherulites. It is likely that the positive dependence of crystallinity on Young's modulus is caused by the thinning of amorphous layers because the applied stress becomes concentrated on the amorphous phases having much lower modulus [5,6]. Further extension above the elastic limit causes the destruction of stacked lamellae (or lamellar clusters) within highly deformed spherulites, resulting in a distinct yield point as a maximum in the conventional stress–strain curves [7]. Beyond the yield point, large scale plastic deformation occurs and a concave contraction then catastrophically initiates on the specimen and coalesces into a well-defined neck [8–10]. During necking processes, macroscopic morphological transformation from isotropic spherulitic structure to anisotropic fibril one takes place accompanied by the fragmentation and/or rearrangement of the stacked crystalline lamellae constructing spherulites. This necking deformation is called 'cold drawing' [8]. The extension ratio is generally defined as the natural draw ratio [11,12]. After the necking boundaries have propagated throughout the entire length of the specimen under constant flow stress, an increase in nominal stress appears up until break. This phenomenon may be termed 'strain-hardening' [13].

The strain-hardening of various polymeric materials has been extensively studied by G'Sell et al. [14–16] and Haward et al. [17,18]. Post-yield deformation of semicrystalline polymers has been often discussed in terms of their molecular network, represented by amorphous chains linking fragmented crystallites and/or entanglements acting as physical cross-links. Hiss et al. [19] rationalized strain-hardening as an effective contribution to the physical network density of tie-chains anchored in adjacent crystallites. Additionally, it is reported that differences in primary structure such as molecular weight and branching influence strain-hardening [20–22].

Considering these previous results, exploitation of the concept of rubber-elasticity theory seems to provide a framework for studying the molecular and structural mechanisms underlying strain-hardening. However, the explicit nature of strain-hardening is not completely understood in molecular terms because the strain-hardening behavior of a polymer depends not only on the initial semicrystalline morphology but also on the tensile conditions such as temperature and tensile speed. The neck generates a highly oriented fibrillar crystalline structure as a result of the large-scale morphological rearrangement of the isotropic spherulitic structure. Hence, the nature of strain-hardening is directly related to the structural morphology in the cold-drawn (or necked) state produced from the initial

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morphology. This makes it more difficult to elucidate the molecular and/or structural origin of the strain-hardening behavior in semicrystalline polymers.

The purpose of this study is to provide a molecular understanding of the strain-hardening in stress–strain curves measured at room temperature of semicrystalline polymers. For the purpose, we have investigated the tensile behavior of cold-drawn samples subjected to various drawn histories in uniaxial extension up to necking at room temperature. The present study is also motivated by the need to structurally understand the effect of predraw processing conditions on the mechanical properties of typical semicrystalline polymer solids. In this work, two typical grades of isotactic polypropylene (iPP) samples with high stereoregularity were chosen for investigation because the crystalline morphology and cold-drawn state of such iPP samples can be widely changed by annealing and drawing preprocesses [23,24]. Using various tensile data for cold-drawn iPPs, we present a novel analytical method for describing the structural origin of the strain-hardening behavior of semicrystalline polymers in molecular terms.

2. Experimental

2.1. Materials and sample preparation

The chosen starting material was Ziegler–Natta catalyzed isotactic polypropylene (ZNPP) with $M_w = 380 \times 10^3$ and molecular weight distribution index $M_w/M_n = 4.9$. To investigate the effects of molecular weight we also employed a set of metallocene-catalyzed isotactic polypropylenes (mPPs), ranging from $M_w = 170 \times 10^3$ to 400×10^3, which had narrower molecular weight distribution ($M_w/M_n = 2.7$–3.2). These iPP samples had high tacticity (98–99%).

The polymer pellets were melted in a laboratory hot press for 5 min at 210 °C and 10 MPa. The molten samples were allowed to equilibrate under pressure for 5 min prior to cooling. On removal from the press, the samples were plunged directly into a hot water bath to produce sheets of approximately 200-μm thickness. Dumbbell shaped specimens with a gauge length of 10 mm and width of 4 mm were cut from these sheets.

To prepare various cold-drawn specimens with different drawn histories, we stretched the undrawn dumbbell shaped specimens at various fixed crosshead speeds at room temperature (25 ± 0.5 °C) using a Model 4466 Instron tensile machine. Specimens were elongated up to an extension ratio of $\lambda = 3.5$, which is in the necking region, and the necked specimens were held for 10 min. The specimens were then released from the clamps and kept under unloading conditions for one day at room temperature to remove elasticity-aftereffects. The length of the cold-drawn specimens shrank just after being released and reached a constant value after more than 3 h. After holding for one day, no shrinkage in the cold-drawn specimens was observed during the time-scale of the present tensile experiment. The tensile properties of these pre-drawn specimens were investigated under various elongation speeds at room temperature using the same tensile machine. The procedure used to prepare the cold-drawn specimens is schematically illustrated in Fig. 1.

The ZNPP sheets quenched at 80 and 100 °C were annealed in an oven at 100 and 130 °C for 4 h to prepare iPP sheets with a wide range of crystallinities. Cold-drawn specimens of these sheets were prepared by drawing samples at a strain rate of 0.1 min^{-1} (or elongation speed of 1 mm/min). All mPP samples were quenched in 100 °C water to maintain their crystallinity at 58–59 vol% to allow the molecular weight to be treated as an isolated variable. Cold-drawn mPP specimens were obtained by drawing the samples at a common strain rate of 0.1 min^{-1}.

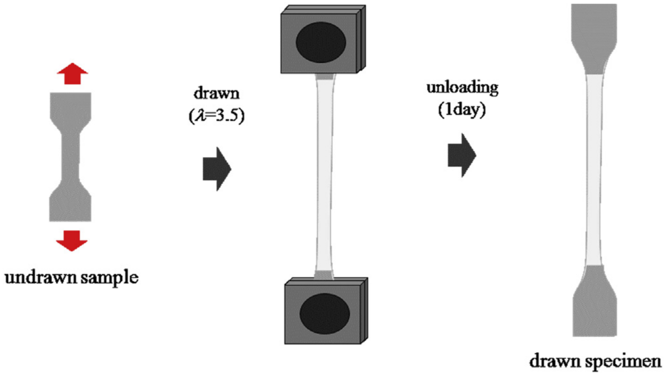

Fig. 1. Schematic illustration of cold-drawn sample preparation.

2.2. Sample characterization

The degree of crystallinity of the sheet samples in volume fraction was estimated using Archimedes' method using a Mettler XS205 electrobalance, with ethanol as the solvent. The densities of the crystalline and amorphous regions were taken as 936 and 856 kg/m^3, respectively [25].

Long period was characterized by small angle X-ray scattering (SAXS) measurements using Rigaku Nano-Viewer (CuKα radiation). The scattered X-rays were detected using a one-dimensional position sensitive proportional counter (PSPC). After appropriate correction (e.g., Lorentz correction), the SAXS profiles of all of the samples were characterized by one or more diffuse peaks, and the maximum peak was converted into the long period according to Bragg's law. Assuming that the crystalline lamellae were space filling with a single thickness population, the lamellar thickness L_c and amorphous layer thickness L_a were determined using the following relations: $L_c = \chi_v L_p^0$ and $L_a = (1 - \chi_v) L_p^0$ where χ_v is the crystallinity in volume fraction and L_p^0 is the long period of the original iPP sheets.

Differential scanning calorimetry (DSC) measurements were carried out using a Perkin Elmer Diamond DSC to obtain the melting point of the samples. Samples of about 3 mg were cut from sheets prepared for the measurements, sealed in aluminum pans, and heated at 20 °C/min.

The structural characteristics of the undrawn iPP samples are summarized in Table 1. The end numeral of the sample code indicates the weight-average molecular weight in the 10^{-3} order of magnitude. The end numerals of the ZNPP380 samples indicate the crystallinity in volume %. In this work, infrared dichroism was used in addition to the SAXS long period results to characterize the chain orientation state of the cold-drawn specimens. The Herman's orientation factors of the crystal *c*-axis within the lattice f_c and amorphous chains between crystalline lamellae f_a were estimated from the dichroic ratios of the 841 cm^{-1} and 1154 cm^{-1} bands,

Table 1
Characteristics of undrawn samples.

Sample	L_p^0/nm	L_c/nm	L_a/nm	T_m/°C	χ_v/vol%
mPP170	14.5	8.4	6.1	148	58
mPP240	14.8	8.6	6.2	148	58
mPP330	15.0	8.7	6.3	148	58
mPP400	15.3	9.0	6.3	148	59
ZNPP380-58	15.1	8.8	6.3	165	58
ZNPP380-61	17.8	10.9	6.7	164	61
ZNPP380-64	19.6	12.5	7.0	163	64
ZNPP380-66	20.5	13.5	7.0	163	66