SHORT COMMUNICATIONS

Unusual Stress–Strain Behavior in Ultra-Drawn Films of High Molecular Weight Poly(4-methyl-1-pentene)

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Recently, ultradrawing of flexible chain polymers has been extensively studied to achieve the maximum mechanical properties.^{1–3} Among many polymers studied, only ultrahigh molecular weight (UHMW) polyethylene^{4–7} and polypropylene^{8–10} have been ultradrawn to the limits in terms of mechanical and physical properties approaching limits.

In our current study of ultradrawing of poly(4-methyl-1-pentene) (P4M1P), it was found that single crystal mats of UHMW–P4M1P could also be drawn to a high draw ratio (DR) of 80 by a two-stage drawing technique.^{5,8} The ultradrawn films exhibited unusual stress–strain curves for ambient tensile testing. The curve was characterized by three distinct regions consisting of an initial elastic region, a yield region, and finally, a post-yield region. A similar stress–strain curve has been reported only in a few polymers such as wool^{11,12} and oriented polypivalolactone¹³ and poly(butylene terephthalate)¹⁴ where the α – β (helix-planar zigzag or *gauche*–*trans*) transformation occurred on extension. In contrast to these polymers, however, ultradrawn UHMW–P4M1P showed tensile moduli of 7.5–9.1 GPa in the post-yield region, which were significantly higher than the crystal modulus of 2.9–6.7 GPa^{15,16} reported for

the ordinary tetragonal form of P4M1P.^{17,18}

In this communication, we report unusual stress–strain behavior observed in ultradrawn films of UHMW–P4M1P and studied in relation to the specific morphology and the crystal structural or conformational changes that occurred during extension at room temperature.

EXPERIMENTAL

The UHMW–P4M1P used was a highly isotactic polymer with viscosity average MW of 1.5×10^6 . Solution-grown crystals (SGC) were isothermally precipitated from a 0.2 wt% solution in xylene kept at 50°C over 20 h. SGC mats were obtained by slowly filtering the crystal suspension followed by drying at 50°C.

A two-stage drawing technique^{5,8} was utilized for uniaxial drawing of SGC mats of UHMW–P4M1P. For the first-stage drawing, a solid-state coextrusion technique developed by Porter *et al.*¹⁹ was used. For the second-stage, a conventional tensile drawing technique was used. Extrudates having an extrusion DR (EDR) of 6 prepared at 180°C were drawn at 180–200°C in an air oven equipped with a Tensilon tensile tester HTM-100. The total DR was defined by $DR_t = EDR \times DR$.

Stress-strain curves for drawn films were measured along the fiber axis at room temperature and at a strain rate of $1 \times 10^{-2} \text{ s}^{-1}$. The modulus was determined from the slope of the stress-strain curve at low and high strain. Wide-angle X-ray diffraction patterns were recorded using a flat plate camera with Ni-filtered Cu- K_α radiation.

RESULTS AND DISCUSSION

Figure 1 shows stress-strain curves characteristic of a low and a high DR film of UHMW-P4M1P prepared by two-stage drawing of the SGC mat. The extrudate with an EDR 6 shows usual stress-strain behavior commonly observed for a variety of polymers with low DR. However, the highly drawn samples exhibited an unusual stress-strain curve as shown for DR_t 50 in Figure 1. The curve was characterized by the three distinct regions including an initial elastic region (0–6% strain) where the stress increased rapidly with strain (Region I), a yield region (6–12% strain) where the stress stayed almost constant (Region II), and finally, a post-yield region (12–20% strain) where the stress again increased rapidly (Region III) until the sample fractured by a repetitive

Figure 1. Stress-strain curves of UHMW-P4M1P films with a low EDR 6 and a high DR_t 50, recorded at room temperature and strain rate of $1 \times 10^{-2} \text{ s}^{-1}$. Note that the curve for the DR_t 50 sample is characterized by three regions: Regions I, II, and III.

partial rupture. The tensile properties of the drawn films are summarized in Table I.

He and Porter^{20,21} have studied solid-state coextrusion of normal MW P4M1P. They report that the tensile modulus and strength increase steadily with EDR and approach 3.7 and 0.25 GPa, respectively, at EDR 30. The unusual stress-strain behavior observed here in UHMW-P4M1P was absent in their samples. A tensile modulus of 3.8 GPa determined in Region I of Figure 1 is in good agreement with the initial modulus of 3.7 GPa reported for an EDR 30 extrudate. It is noted that these moduli are even higher than the lowest reported crystal modulus value of 2.9 GPa¹⁵ determined by X-ray crystal strain measurements. Furthermore, the modulus of 7.5–9.1 GPa in Region III is about twice the initial modulus (Region I) and even markedly higher than the highest crystal modulus value of 6.7 GPa¹⁶ reported for the ordinary crystal form of P4M1P. Such features are in sharp contrast to the stress-strain behavior in ultra-drawn normal MW P4M1P. It has also been shown that in ultradrawn polyethylene⁵ and polypropylene⁸ having a range of DR (30–300), the modulus determined at a higher strain is slightly lower than that at a low strain.

As described in the previous section, the stress-strain curve for the DR_t 50 film shown in Figure 1 is analogous in several respects to those of wool^{11,12} and polypivalolactone¹³ which undergo alpha-beta transformation

Table I. Tensile properties of uniaxially drawn UHMW-P4M1P films

DR	Modulus in Region I	Modulus in Region III	Strength at Break	Strain at Break
	GPa	GPa	GPa	%
1 (mat)	1.7		0.01	4
6	2.5		0.1	19
50	3.8	7.5–9.1	0.70–0.81 ^a	20

^a This value should be regarded as a minimum because the ultra-drawn sample fractured by repetitive partial rupture as shown in Figure 1.

during extension. The plateau region in the stress-strain curves of these oriented polymers has been ascribed to the process of conformational transformation from the initial helix to the planar zigzag.^{12,13} Subsequent increase in the stress (Region III in Figure 1) has also been discussed. Significantly different mechanisms have been proposed for these two polymers with different morphologies¹¹⁻¹³; *i.e.*, chain extended *vs.* chain folded. Several polymers, such as poly(ethylene glycol)²² and syndiotactic polypropylene²³ have been shown to undergo similar conformational transformation on drawing. However, the unusual

stress-strain curve has not been reported for these polymers probably due to differences in morphology.

Cyclic load experiments were performed at room temperature on a DR₁ 50 film to determine the change in the stress-strain curve. The film was extended to a strain of 15% at a strain rate of $1 \times 10^{-2} \text{ s}^{-1}$, then the strain was released to zero at the same rate, and the film was restrained to 15% strain followed by release of the strain to zero, and so on. Figure 2 shows the stress-strain curves for the DR₁ 50 sample recorded during the first, fifth and tenth extension cycles. During cyclic loading, the plateau Region II gradually diminishes and the curve becomes a straight line after repeated cycles. It is important to note that although the sample length at zero stress increases slightly (7%) during the cycles, the stress-strain curve in Region III is not affected at all. It thus appears that the structural change may be reversible in nature, as will be discussed below based on X-ray diffraction study. Furthermore, the increase of the sample length and the corresponding change in the shape of the stress-strain curves during the loading cycles, suggest that the structural recovery from the strained state to the initial one may

Figure 2. Changes in the shape of the stress-strain curves for an ultradrawn UHMW-P4M1P film with DR₁ 50. The curves were recorded on the first, fifth and tenth extension cycle during cyclic loading.

Figure 3. Wide-angle X-ray diffraction patterns of a DR₁ 50 film recorded at zero strain (A), and at $\sim 10\%$ strain (B). The scattering around the direct beam was due to air scattering.

require a time longer than that expended from the maximum strain (15%) to zero strain (15 s). These features are further studied by wide-angle X-ray diffraction.

Figure 3 shows wide-angle X-ray diffraction patterns of the DR₅₀ sample obtained before (Figure 3a) and after (Figure 3b) cyclic loading. The latter pattern was recorded on the sample kept at a constant strain of 10%, after repeating the loading cycle 30 times. The X-ray pattern of the original sample shows that the crystal structure has the ordinary tetragonal form. Further, the sharp spots indicate that the ultradrawn sample is highly crystalline and the chains are extremely well oriented, suggesting high chain extension. The pattern recorded with the sample kept under tension (Figure 3b) clearly shows that the crystal structure has been transformed to a new form. This new form is characterized by strong and continuous streaks on the equator and first layer, and also by strong reflection ($d=5.0\text{ \AA}$) elongated along the first layer line and fairly strong reflections ($d=9.2\text{ \AA}$) on the equator. The fiber period is $6.4\text{ \AA}$ compared with $13.8\text{ \AA}$ for the initial tetragonal form. The appearance of the very weak tetragonal (122) reflection ($d=5.32\text{ \AA}$) just below the strong $5.0\text{ \AA}$ reflection of the new form (Figure 3b) shows the coexistence of a small amount of the initial form. It has been reported that P4M1P takes several crystal forms depending on crystallization^{24,25} and annealing²⁶ conditions. The present modification observed in ultradrawn UHMW-P4M1P under tension, however, does not correspond to any of these reported forms. Although the detailed crystal structure of this new modification is not clear, the appearance of strong streaks on the equator and layer lines with only two clear reflections indicates a nematic structure in which the molecular chains are arranged irregularly both along and perpendicular to the chain axis.

It is also important to note that the new modification is only stable under tension. When the stress was released, most of the new

form quickly transformed back to the initial form. Such a reversible transformation between the two crystal forms, observed here by the X-ray diffraction, well explains the stress-strain behavior in Regions II and III in Figures 1 and 2. The fact that the tensile modulus of 7.5–9.1 GPa in Region III is remarkably higher than the crystal modulus of 2.9–6.7 GPa for the tetragonal form^{15,16} indicates that the initial 7/2 helical chain conformation is significantly elongated in the new crystal form. In oriented polypivalolactone¹³ and wool,^{11,12} the slope of the stress-strain curve was lower in Region III than in Region I. This has been explained by the chain unfolding in the former and by the interfibrillar slippage in the latter polymer, which occurred during extension. Such mechanisms are not important in ultradrawn UHMW-P4M1P where the molecular chains are highly extended and oriented. Thus, the different behavior in Region III between these polymers is likely related to differences in their microstructures. It is recalled that the unusual stress-strain behavior observed in UHMW-P4M1P was absent in the lower MW samples.²⁰ As seen in Figure 1, the crystal transformation occurs at a stress level of 0.25 GPa, which is comparable to the fracture stress of the ultradrawn lower MW P4M1P.²⁰ This is likely the reason that such an unusual stress-strain behavior was observed in the UHMW-P4M1P but absent in the lower MW P4M1P.

In conclusion, UHMW-P4M1P has been ultradrawn to DR 80 by two-stage drawing of single crystal mats. The ultradrawn films exhibited unusual stress-strain curve characterized by three distinct regions. Such behavior has been discussed on the basis of (1) reversible transformation from the ordinary crystal form in the initial state to the new crystal form during extension and (2) the specific morphology of ultradrawn UHMW-P4M1P.

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