SHORT COMMUNICATIONS

High Modulus Films of Polytetrafluoroethylene Prepared by Two-Stage Drawing of Reactor Powder

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In previous papers, we have shown that powder billets and films of ultrahigh molecular weight polyethylene (UHMW-PE) reactor powder, compacted below its melting temperature (T_m), could be successfully drawn by solid-state extrusion,¹ coextrusion,² and by two-stage drawing.^{3,4} Among these techniques, two-stage drawing of the powder film, consisted of an initial solid-state coextrusion at a low extrusion draw ratio (EDR) of ~6 followed by tensile drawing at the controlled temperatures and rates, gave the most effective draw in terms of the maximum achieved tensile properties. The high drawability of UHMW-PE reactor powder was ascribed to the low entanglement density of the virgin morphology.^{5,6}

Polytetrafluoroethylene (PTFE) virgin powder has been reported to be highly crystalline and has a more or less chain-extended conformation,^{7,8} suggesting a low initial entangled state. Indeed, our previous study⁹ has shown that a powder billet of commercial PTFE, which has never been heated above the T_m , could be ultradrawn by solid-state extrusion near the T_m up to an EDR ≤ 60 . However, if the powder billet had been melted, high draw was no longer attainable.

In this Note, we report the preparation of high modulus and strength PTFE films by two-stage drawing of compacted reactor powder films. After the initial coextrusion drawing at 325°C, where the maximum EDR was achieved in a prior study,⁹ PTFE exhibited the highest ductility for second-stage tensile drawing at 45-100°C, below the glass transition temperature ($T_g = 125^{\circ}$ C) and 235—290°C below the melting temperature ($T_m = 335$ °C). Such high ductility, far below the T_g and T_m , is in sharp contrast to other polymers which generally exhibit the highest ductility above their T_g and near T_m . The maximum achieved tensile modulus and strength along the fiber axis at 24°C were 62.5 GPa and 392 MPa, respectively, at the highest total draw ratio (DRt) of 50 achieved in this work. These tensile properties are significantly higher than those achieved by solid-state coextrusion (maximum modulus of 31 GPa and strength of 290 MPa at 24°C).¹⁰ Further, the modulus corresponds to 25 times and the strength is comparable to those of commercial PTFE fibers¹¹ measured at 20°C. Such a highly drawn film exhibits high dynamic Young's moduli at 110 Hz of 136 GPa at -150° C, 84 GPa at 24°C, and 198

6.1 GPa even at 250°C.

EXPERIMENTAL

The two PTFE samples used as-received were powders of commercial grades, 800-J and 6-J, as provided by Mitsui/du Pont Fluorochemicals. The former was prepared by suspension polymerization and the latter by emulsion polymerization. These samples had nominal molecular weights of $\sim 1 \times 10^7$ and $\sim 5 \times 10^6$, respectively. The former powder was compression molded into cylindrical billets, and the latter into films at 320°C, ~15°C below their $T_{\rm m}$ (335°C). For solid-state coextrusion, the compacted powder film was placed between split billet halves of the higher MW-PTFE, and the assembly coextruded to an EDR of 6-20 at the established optimum extrusion temperature (Text) of 325°C.9 Further, the coextruded films and unoriented melt-crystallized samples were tensile-drawn at constant temperatures of 24-370°C, in air ovens equipped with a Tensilon, and an Instron tensile testers, at constant cross-head speeds corresponding to the initial strain rates of $1-10 \text{ min}^{-1}$. The total DR (DRt) was defined by $DRt = (initial EDR) \times (second-stage tensile DR)$. The tensile modulus and strength of drawn products were measured at 24°C and at strain rates of 1×10^{-3} and $1 \times 10^{-2} \, \text{s}^{-1}$, respectively, on a Tensilon tensile tester. Dynamic Young's modulus was measured in the temperature range of $-150-250^{\circ}$ C by an Orientec Vibron DDV-II-EP at a heating rate of 2°C min⁻¹ and a frequency of 110 Hz.

RESULT AND DISCUSSION

The powder film of PTFE, compacted below its melting point, was too brittle to be drawn directly by tensile drawing. However, it became ductile on solid-state coextrusion to an EDR of 6—20 and at an optimum extrusion temperature of 325° C, ~10°C below the $T_{\rm m}$ of powder. The assembly of a compacted powder film within the powder billet halves could be extrusion drawn to an EDR of 40—60, as reported for solid-state extrusion of compacted powder billets.⁹ However, the cohesion and adhesion between the powder film and the split billet halves became so strong that their separation after extrusion drawing was difficult for highly drawn samples. Thus, the maximum EDR actually obtained by solid-state coextrusion of the powder film was limited to ~ 25 , significantly lower than what we achieved by solid-state extrusion of a compacted powder billet.

The initially coextrusion-drawn samples with an EDR of 6, 12, and 20 at 325°C were further tensile-drawn at constant temperatures of 24—370°C in air ovens. The maximum achieved DRt increased from ambient with drawing temperature, and reached a maximum of 40—50 at 45—100°C, depending on drawing rate and initial EDR. At yet higher drawing temperatures, the ductility decreased rapidly with temperature. When draw was attempted on these extrusion-drawn samples above their $T_{\rm m}$ of ~335°C, they fractured due to melting, combined with an entropic shrinkage force.

It is interesting to note that the optimum drawing temperature of 45-100°C for the second-stage draw is lower than the T_g of PTFE and also remarkably low, 235—290°C, below the $T_{\rm m}$ of powder film (335°C). This is in contrast to other polymers that generally show their highest ductility near their $T_{\rm m}$. The optimum draw temperature is also markedly lower than that of 330-340°C for solid-state extrusion of compacted PTFE powder billets.9 For solid-state extrusion of a PTFE powder billet, draw was possible above 100°C, and the maximum achieved EDR increased with temperature up to near its $T_{\rm m}$. Thus, the ideal draw for solid-state extrusion and second-stage tensile drawing are significantly different. These characteristics of the two techniques are likely related to the different deformation modes and the existence of the reversible crystal/crystal transitions at 19 and 30°C in PTFE. The former deformation proceeds under shear versus extensional fields combined with a compressive force,¹² whereas the latter proceeds under a simple extensional field in a free space. The existence of two crystal/crystal transitions around room temperature indicates that PTFE crystals become fairly ductile above these transition temperatures. However, the intermolecular force in PTFE is significantly lower than other polymers, which may lead to the more rapid decrease in the tensile strength with increasing temperature.¹³ Thus, the competitive effects of ductility increase and strength decrease with increasing temperature, give an optimum drawing temperature around 45-100°C, slightly above the reversible crystal transitions, depending on initial EDR and drawing rate.

The tensile modulus and strength along the fiber axis at 24°C for drawn films, obtained by solid-state coextrusion and two-stage drawing of compacted powder films, are shown in Table I. The maximum achieved DRt is not significantly affected by the initial EDR (6, 12, and 20) for the second-stage drawing at the optimum condition for each of the initial EDR's. However, the maximum achievable tensile properties are remarkably affected by initial EDR and draw temperature. The second-stage drawing of a higher initial EDR of 20 at a higher draw temperature of 100°C gave a significantly higher tensile modulus and strength. Drawing above this temperature resulted in unstable draw. These results differ from those previously observed for the two-stage draw of UHMW-PE single crystal mats,¹⁴ where an initial EDR of 6 provided the highest draw and hence

Table I. Axial tensile modulus and strength at 24°C of PTFE
films drawn by solid-state coextrusion and two-stage
drawing of a compacted reactor powder film.
The first-stage coextrusion draw was made at 325°C.

Draw temp./°C Text-Td	Total draw ratio EDR × DR	Tensile modulus GPa	Tensile strength MPa
325	6	5.8	62
325	12	12.8	120
325	20	23.7	193
325-45	6×3	6.9	116
325-45	6×7	24.6	265
325-100	12×2	24.4	179
325-100	12×4	35.5	303
325-60	20×1.5	30.7	264
325-60	20×2.4	57.2	380
325-100	20×1.5	34.5	270
325–100 325–120ª	$\begin{array}{c} 20 \times 2.5 \\ 20 \times 1.5 \end{array}$	62.5	392

^a Draw was unstable and no uniform samples were obtained.



Figure 1. Dynamic Young's modulus vs. temperature for a series of drawn PTFE samples measured at 110 Hz. \diamond , melt-crystallized; \Box , compacted powder; \bigcirc , EDR = 6; \triangle , EDR = 20; \blacksquare , DRt = 48 samples. The mechanical relaxations, α , ($\beta_1 + \beta_2$), and γ are shown by arrows.

the highest tensile properties. The highest room temperature tensile modulus and strength of 62.5 GPa and 392 MPa, respectively, were obtained by the secondstage tensile drawing of an initially extrusion-drawn film with an EDR of 20, prepared by coextrusion of a compacted reactor powder film at 325°C. It is noted that the highest tensile modulus corresponds to 25 times those of commercial fibers, although the tensile strength is comparable to them.

The previous study on solid-state extrusion of PTFE reactor powder showed that the modulus of a drawn sample is sensitive to the test temperatures.⁹ Thus, the dynamic Young's modulus was measured on these new drawn samples in the range of $-150-250^{\circ}$ C at a frequency of 110 Hz. Figure 1 shows results for several samples of different morphologies.

PTFE has been known to exhibit three mechanical relaxations, γ , β ($\beta_1 + \beta_2$), and α around -75, 25 (19 and 30), and 125°C, respectively.^{15,16} They have been ascribed to the local mode motion, crystal/crystal transitions, and T_g and/or crystal transition, respectively. The crystal modulus measured by X-ray diffraction show-

ed a sharp decrease in the β region and an even more drastic drop around 125°C, corresponding to the crystal/crystal transitions.¹⁵

The dynamic Young's modulus in Figure 1 decreased in the relaxation regions depending on the sample. With increasing draw ratio, the modulus increases. It is noted that the sample with a high DRt of 48, prepared by tensile draw of an extrudate from an EDR of 20 at 100°C, is 136 GPa at -150° C. This corresponds to 80% of the X-ray chain direction crystal modulus of 170 GPa.¹⁵ The modulus decreased gradually with increasing temperature, dropping rapidly around 25°C, corresponding to the crystal/crystal transitions at 19 and 30°C. At 24°C, where the tensile modulus was determined, the dynamic modulus was 84 GPa, significantly higher than the tensile modulus of 62 GPa. At yet higher temperatures, the modulus decreased monotonously with increasing temperature, and retained a value of 6.1 GPa even at 250°C, the highest test temperature.

It is noted that the X-ray crystal modulus drops drastically around 125° C from 135 GPa at 100° C to 42 GPa at 130° C.¹⁵ However, no such a drastic decrease in modulus was observed in highly drawn samples in this temperature region. The EDR 6 sample at about 125° C and a melt-crystallized film showed a detectable, but only slight decrease in modulus in this temperature region. The modulus changes with temperature in the crystal and in the drawn samples are likely related to the crystallinity, the crystal perfection and their size.¹⁰ Indeed, recently, Nakamae *et al.*¹⁷ have measured the X-ray crystal modulus of these highly drawn samples and found that the crystal modulus drop around 125° C depends significantly on sample DRt, and hence the sample morphology.

CONCLUSION

A two-stage technique has successfully been applied to ultradrawing of PTFE reactor powder films, prepared by compaction below its $T_{\rm m}$. The drawability and efficiency for the second-stage tensile drawing of samples prior extrusion-drawn at 325°C were sensitive to drawing temperature. It was found that the optimum draw temperature, giving the highest achievable DRt, was in the range of 45—100°C, depending on the initial EDR. These optimum temperatures are by 235—290°C below the $T_{\rm m}$ and even lower than the $T_{\rm g}$ of PTFE, in sharp contrast with results on other polymers which generally exhibit the highest ductility near their $T_{\rm m}$. Such high ductility of PTFE at low temperatures is related to its reversible crystal/crystal transitions at 19 and 30°C.

Further drawing of solid-state extrusion-drawn samples above their T_m was not possible due to their fracture upon heating. The maximum achieved DR for melt-drawing of an unoriented sample was 4—6. The modulus at a given DRt of the two-stage drawn sample measured at 24°C was significantly affected by the initial EDR and draw temperature. The highly drawn film with a maximum achieved DRt of 50, prepared from an EDR 20 extrudate, showed the highest tensile modulus and strength of 62.5 GPa and 392 MPa, respectively, at 24°C. Such a highly drawn sample showed high dynamic moduli of 136 GPa at -150° C, 109 GPa at 0°C, 84 GPa at 24°C, and 6.1 GPa at the highest test temperature of 250°C.

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