Melt-Processable Poly(tetrafluoroethylene)

Theo Tervoort,* Jeroen Visjager, Brian Graf, and Paul Smith

Department of Materials, Institute of Polymers, Eidgenössische Technische Hochschule (ETH) Zürich, Universitätstrasse 41, UNO C14, Zürich, CH-8092 Switzerland

Received May 1, 2000

ABSTRACT: The identification of a window of viscosities of poly(tetrafluoroethylene)s is described that permits standard melt-processing of this unique polymer into mechanically coherent, tough objects—a polymer that, heretofore, has been characterized as “intractable” and “not melt-processable”.

Introduction

Conventional and textbook wisdom asserts that poly(tetrafluoroethylene) [PTFE],[1] a polymer with unique chemical and thermal resistance and surface properties, cannot be processed from its molten state into useful articles (e.g., refs 2−8). Hence, products of this material are made through elaborate, shape- and form- restrictive manufacturing techniques that, for example, resemble those employed for metals and ceramics, such as powder compaction followed by sintering and machining, or by ram- and paste-extrusion, suspension spinning, direct plasma polymerization, etc. (cf. the excellent overview in ref 2).

The “intractability” of common PTFE originates in the ultrahigh molar mass (estimated to be $>10^7$ g/mol) and associated extraordinary high melt viscosity ($>10^{11}$ Pa·s) that is stated[9] to be required for this polymer to exhibit useful mechanical properties.

This perceived drawback of PTFE has been noted virtually since its invention in 1938.[10] From that time on, methods have been advanced to circumvent the purported intractability of this polymer. For instance, a variety of comonomers have been introduced in the PTFE macromolecular chains for this purpose, to form copolymers of lower molar mass and reduced viscosity while maintaining adequate mechanical properties. Examples of such copolymers are those comprising hexafluoropropylene (FEP), perfluoro(alkyl vinyl ether)s (PFA’s), or perfluoro-(2,2-dimethyl-1,3-dioxole) (Teflon AF).[2−4,11] Most of these lower molar mass copolymers, indeed, display improved processability and can be shaped with techniques commonly used for thermoplastic polymers. However, a penalty is paid in terms of some or many of the outstanding properties of the homopolymer PTFE, e.g., reduced melting temperature, compromised thermal and chemical stability, etc.

There exist commercial PTFE grades of low molar mass and low viscosity, most often produced by scission of the high molar mass form by γ or electron beam irradiation.[2] These grades—commonly referred to as micropowders—are stated to have molar masses in the range from 2.5×10^4 to 2.5×10^5 g/mol and are widely used as additives in inks and coatings and in thermoplastic and other polymers to incorporate nucleation, internal lubrication, or other desirable properties that stem from the unique physicochemical properties of PTFE.[2] As also shown hereafter, these commercially available low molar mass PTFE grades unfortunately generally exhibit extreme brittleness in their solid form and are categorized as not suited for application as thermoplastic materials.[12]

Here, we report the identification of a window of medium polymer viscosities/molar masses that permits ordinary melt-processing of PTFE into objects with mechanical properties not unlike those of high-density polyethylenes (HDPE). This finding allows the fabrication of a broad spectrum of entirely new products, as well as compounding and recycling, of this unique material.[13]

Experimental Section

Materials. Various grades of PTFE, purchased from Du Pont (Teflon, Zonyl), Ausimont (Algoflon), and Dyneon, were analyzed and employed in this work.

Methods. Because of the well-known difficulties in determining molar mass distributions of PTFE,[2,14] we adopted the common method of measuring the melt flow rate (MFR) for an initial evaluation of the various materials. These MFR values were measured, in accordance with ASTM Standard D1238-88, at a temperature of 380 °C and under a load of 21.6 kg during a maximum extrudate collection time of 1 h using a Zwick 4106 instrument. For more accurate analysis, rheology (previously demonstrated to be useful[15]) was selected as a tool; linear viscoelastic characteristics such as the absolute value of the complex shear viscosity and the shear storage modulus were determined to characterize the different polymer grades. These values were measured from small-amplitude oscillatory shear experiments (Rheometrics mechanical spectrometer RMS 800) at 380 °C for several frequencies between 100 and 10^{-2} rad/s, using standard plate−plate geometry. The linear range was estimated from strain−sweep experiments at 100 rad/s. Thermal analysis was conducted with a Netzsch differential scanning calorimeter (DSC, model 200). Samples of about 5 mg were heated at a standard rate of 10 °C/min. Melting temperatures given hereafter refer to the endotherm peak temperatures of once molten (at 380 °C) and cooled (at 10 °C/min) material. Enthalpies of fusion were determined of the same specimen, and crystallinities were calculated adopting the value of 102.1 J/g for 100% crystalline PTFE.[16] Tensile tests were carried out at room temperature with an Instron tensile tester (model 4411) using dumbbell-shaped specimens of 12 mm gauge length, 2 mm width, and different thickness. The cross-head speed was 12 and 500 mm/min, which corresponds to linear strain rates of respectively 1 and 40 min^{-1}.

Results and Discussion

Table 1 presents an overview of the melting temperatures, enthalpies of fusion, and calculated crystallini-

10.1021/ma000747+ CCC: $19.00

Table 1. Selected Characteristics of Different Commercial Grades of Poly(tetrafluoroethylene)

	PTFE grade	T_m[a] (°C)	enthalpy of fusion (J/g)	crystal-linity[b] (%)	MFR[c] (g/10 min)
I	Zonyl MP 1200	325.9	66.2	64.8	≫1000
II	Zonyl MP 1100	325.0	68.6	67.2	>1000
III	Zonyl MP 1600N	329.0	70.3	68.9	150
IV	Dyneon 9207	329.8	66.5	65.1	55
V	Zonyl MP 1000	329.3	60.7	59.5	52
VI	Dyneon 9201	330.5	62.2	60.9	22
VII	Zonyl MP 1300	329.9	61.8	60.5	10
VIII	Algoflon F5A EX	330.7	63.0	61.7	9
IX	Zonyl MP 1400	330.8	58.5	57.3	2.8
X	Algoflon L206	332.3	62.1	60.8	2.6
XI	ZonylMP 1500J[d]	327.5	45.1	44.2	0.2
XII	Dyneon TFM 1700[e]	327.0	27.0	27.6	0.0
XIII	Teflon 6	328.6	34.4	33.7	0.0

[a] All grades exhibited the well-know thermal transitions around room temperature,[17] typical of PTFE, and only one main melting endotherm at the peak temperatures T_m. [b] Crystallinity: from the enthalpy of fusion of once-molten polymer; assuming 102.1 J/g for 100% crystalline PTFE.[16] [c] MFR: melt flow rate, ASTM Standard D1238−88, at 380 °C and under a load of 21.6 kg. [d] Infrared spectroscopy (method according to ref 18) revealed that this material contained a minor amount (<0.5 mol %) of a comonomer what appears to be hexafluoropropylene. [e] According to the manufacturer,[9] this material contains a minor amount (<0.1 mol %) of the comonomer *n*-perfluoropropylvinyl ether.

ties of the various commercial grades of PTFE that were melted at 380 °C and recrystallized by cooling at 10 °C/min, as well as values of their melt flow rate.

All these materials were examined in terms of their "melt processability" and mechanical characteristics. Melt compression molding experiments were performed at 380 °C with a Carver press (model M, 25 T) for 5 min at 1 metric ton and 10 min at 10 ton and then cooled to room temperature for 4 min at 4 ton into plaques of about 4 × 4 × 0.1 cm and films of a thickness of about 0.25 mm. In addition, extrusion was conducted with a laboratory, recycling twin-screw extruder (MicroCompounder, DACA Instruments, Santa Barbara, CA), the temperature of which was kept at 380 °C, and that was equipped with an exit die of 2 mm diameter (entrance angle 90°). The residence time was 10 min at 75 rpm, after which the material was discharged. It was found that, under the present processing conditions, PTFE grades I−X yielded brittle products, most of which could not be removed from the mold or collected as extrudates without fracture. Because of their high viscosities, PTFE grades XI−XIII could not be extruded without melt fracture or compression molded into homogeneous, defect-free plaques or films with the equipment and under the conditions described above.

We thus established the range of the values of the MFR values outside which, under the present experimental conditions, PTFE is either poorly or not "melt-processable" (<0.2 g/10 min) or yields brittle products (>2.6 g/10 min) and within which this material possibly could be processed from the melt.[18,19]

In the absence of facilities and expertise to synthesize poly(tetrafluoroethylene)s, we opted for creating PTFE of intermediate viscosities and MFR values within the above referred regime through blending of grades of (too) high and (too) low viscosity, thereby producing polymers of pseudobimodal molar mass distributions.

For this purpose, various amounts (total batch quantities 5−7 g) of PTFE grades IX and XI, IX and XII, V and XII, and VII and XIII were introduced into the laboratory, recycling twin-screw extruder, the temperature of which was kept at 380 °C. Mixing was continued for 10 min at 75 rpm, after which the blended product was discharged. Again, values of the MFR of the different blends were determined according to the standard procedure. Table 2 is an illustrative summary of the variety of combinations of PTFE blends that were produced, characterized by an MFR value within the desired range.

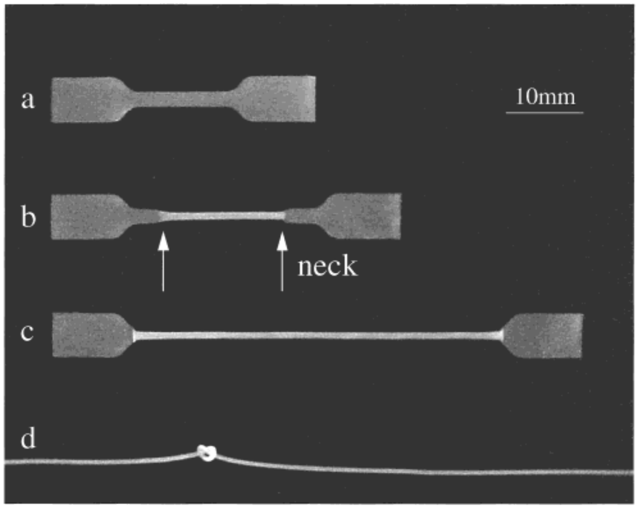

Figure 1. Photographs of melt compression molded tensile bars of poly(tetrafluoroethylene) blend V + XI of MFR = 0.7 g/10 min (Table 3): (a) undrawn; (b) drawn, note the macroscopic "neck"; (c) drawn four times at room temperature; and melt-extruded monofilament (d).

Table 2. Compositions and Melt Flow Rates of Selected Poly(tetrafluoroethylene) Blends

PTFE grades	weight ratio	MFR (g/10 min)	PTFE grades	weight ratio	MFR (g/10 min)
IX + XI	25−75	1.2	VII + XIII	60−40	1.8
IX + XI	10−90	0.8	VII + XIII	50−50	0.8
V + XII	60−40	0.8	VII + XIII	45−55	0.6
IX + XII	60−40	0.4			

Employing the above equipment and experimental conditions, all these (blended) PTFE materials were melt compression molded into plaques and films and spun into monofilaments (cf. Figure 1) without difficulty. The samples we produced were found to be mechanically coherent and tough, and their mechanical properties were measured according to the standard methods described above. Typical stress−strain curves of melt compression molded PTFE films (thickness 0.25 and 1 mm; here of the blend V + XI of MFR = 0.7 g/10 min (Table 3)) are presented in Figure 2a,b; also shown for comparison purposes is the stress−strain curve of a sample of commercial, preformed/sintered, and skived film (Lubriflon; Angst + Pfister, AG; 0.4 mm thickness) (c). Figure 2 shows that the new, melt-processed PTFE films have the typical deformation properties of a thermoplastic, semicrystalline polymer with a distinct yield point, strain softening, and subsequent strain hardening. The mechanical characteristics of the melt-processed (Figure 2a) and skived film were respectively: yield stress 12.6 and 12.8 MPa; nominal tensile strength 15.4 and 46.1 MPa; strain at break 293% and 477%. The present films—formed by simple melt processing—thus exhibited mechanical properties that approach those for the laboriously produced commercial product. Importantly, the mechanical properties of the

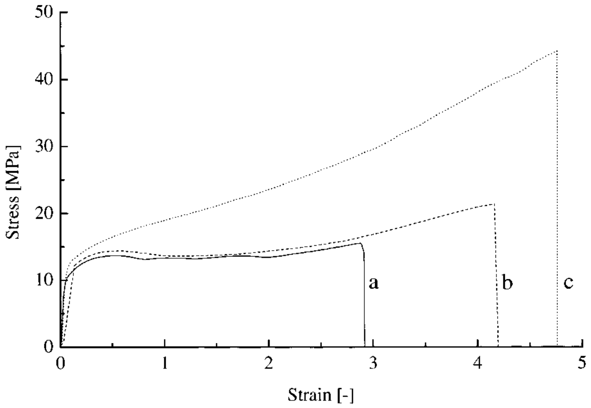

Figure 2. Stress−strain curves recorded at room temperature of PTFE: (a) melt-processed film (0.25 mm thick) of PTFE blend V + XI of MFR = 0.7 g/10 min (Table 3), strain rate 1 min^{-1}; (b) same as (a), but sample thickness 1 mm, and strain rate 40 min^{-1}; (c) commercial, sintered and skived film, thickness 0.4 mm and strain rate 1 min^{-1}.

Table 3. Compositions, Zero-Shear Viscosities, Molar Masses, and Melt Flow Rates of Selected Poly(tetrafluoroethylene) Blends

PTFE grades	weight ratio	$\eta_0{}^a$ (Pa·s)	molar mass^b M_w (g/mol)	M_w/M_n	MFR (g/10 min)
V	100	5.6×10^4	2.3×10^5	6	52 ± 3
V + XI	60−40	9.3×10^5	5.3×10^5	11	15 ± 4
V + XI	40−60	6.1×10^6	9.3×10^5	20	4 ± 1
V + XI	20−80	8.7×10^6	1.0×10^6	26	0.6 ± 0.1
V + XI	10−90	9.2×10^6	1.0×10^6	46	0.7 ± 0.3
XI	100	1.3×10^7	1.2×10^6	21	0.2 ± 0.1

[a] Absolute values of the complex viscosities from small-amplitude oscillatory shear experiments at 380 °C extrapolated to zero frequency invoking the Carreau−Yasuda model.[22] The linear range was estimated from strain-sweep experiments at 100 rad/s. [b] Calculated employing the formalisms in ref 15.

melt-processed films were not affected by storage for prolonged periods of time (>12 h) at temperatures of 250 °C; their strain and stress at break were within experimental error identical to the respective values of the nontreated films.

For more detailed rheological, processing, and mechanical studies, somewhat larger quantities were prepared of a series of blends of PTFE grades V and XI. The latter material of MFR 0.2 g/10 min was selected as the "high molar mass" component rather then XII or XIII (both of MFR = 0.0 g/10 min), to promote mixing on a molecular level, which is known to be increasingly difficult as the viscosities of the constituents are more dissimilar.[20] Various amounts (total quantity 90 g) of PTFE grades V and XI were introduced into a Brabender melt kneader (model Plasti-corder PL 2000), which was kept at a temperature of about 380 °C, 60 rpm. After about 1 min, a void-free, clear homogeneous viscous fluid formed that behaved like a melt of ordinary thermoplastics. Mixing was continued for 10 min, after which the blended product was discharged. The absolute values of the complex viscosities of the resulting PTFE samples were measured, as well as their MFR values. In addition, employing the results of the approach of Tuminello et al.,[15] we estimated the (weight-average) molecular mass and its distribution of these blended PTFE grades (see Appendix). The weight-average molar mass was obtained from the well-known relationship between zero-shear viscosity, η_0, and weight-average molar mass, M_w, in the entanglement regime, $\eta_0 = K(M_w)^{3.4}$, with a proportionality constant $K = 10^{-13.5}$, as determined by Tuminello et al.[15] Assuming the Cox−Merz relation[21] to apply, values of η_0 were estimated from fitting the measured viscosity data to the Carreau−Yasuda equation:[22]

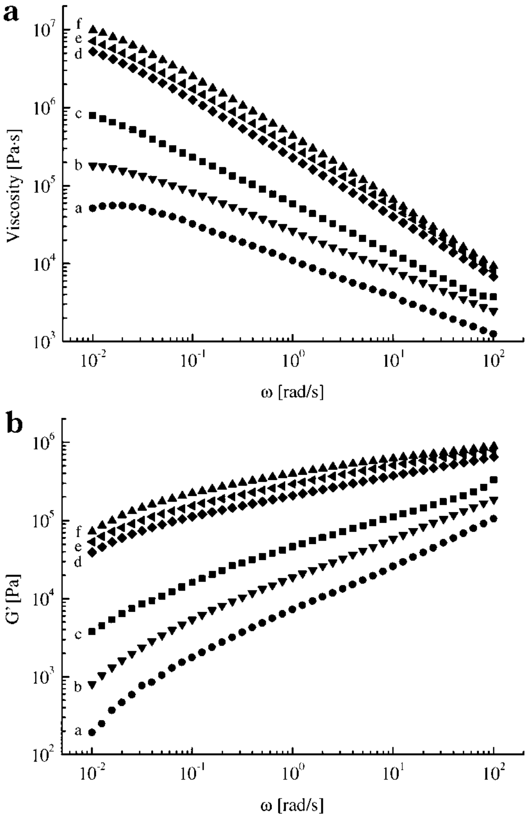

Figure 3. Linear viscoelastic characteristics of various PTFE blends (V + XI) at 380 °C: (a, top) absolute value of the complex shear viscosity versus shear rate; (b, bottom) storage shear modulus, G', versus shear rate. The notations a−f correspond to the following V/XI blend compositions: 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100, respectively.

$$|\eta^*(\omega)| = \eta_0/(1 + (\tau\omega)^a)^{(n-1)/a} \tag{1}$$

where $|\eta^*(\omega)|$ denotes the absolute value of the complex viscosity, τ is a time constant, "a" is a dimensionless parameter that describes the transition from the Newtonian plateau (constant viscosity) to the power-law region, and n is the power-law coefficient, i.e., the slope of $|\eta^*(\omega)|$ in the power-law region. The measured data together with the Carreau−Yasuda fits and the obtained zero-shear viscosity values are given in Figures 3 and 4 and Table 3. The zero-shear viscosity of the blends was found to follow a relation proposed by Menefee[23] (solid line in Figure 4):

$$\eta_0{}^{1/3.4} = w_1\eta_{01}{}^{1/3.4} + w_2\eta_{02}{}^{1/3.4} \tag{2}$$

where η_{0i} is the zero-shear viscosity of blend i and w_i is the weight fraction of component i. The estimated molar mass distributions are displayed in Figure 5. From this last figure, the bimodal nature of all blends is evident. Somewhat surprisingly, the high molar mass component XI itself also appeared to be of a bimodal nature.

A most illustrative set of data, revealing the development of mechanical characteristics at increasing viscosities and their variation with the PTFE blend composi-

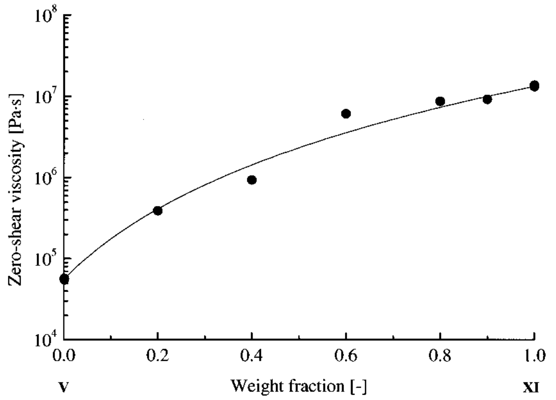

Figure 4. Zero-shear viscosity vs composition of PTFE blends (V + XI, weight fraction XI). The solid line is the zero-shear viscosity−composition relation calculated according to Menefee (ref 23).

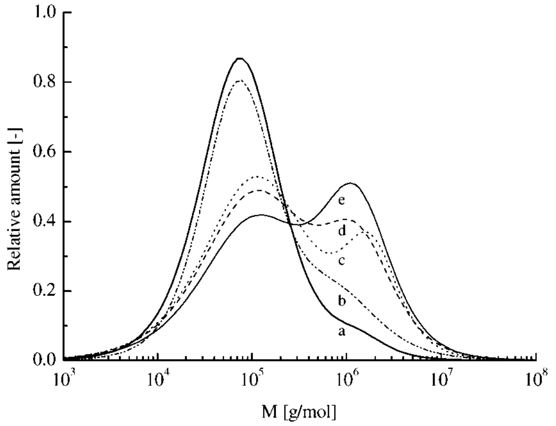

Figure 5. Molar mass distribution of PTFE compositions calculated from the storage shear modulus using the Tuminello transform (see Appendix). The notations a−e correspond to the following V/XI blend compositions: 100/0, 60/40, 40/60, 20/80, and 0/100, respectively. Compositions c and d were found to be melt processable and yielded mechanically coherent and tough products (see, for example, stress−strain curve (c) in Figure 6).

tion, is presented in Figure 6. This figure displays a series of stress−strain curves, recorded at room temperature, of melt compression molded films (thickness 0.25 mm) of (most of) those blends. The gradual and smooth increase in the zero-shear viscosity (Figure 4) and strain to break (Figure 6) indeed appears to indicate that molecular mixing of the different PTFE grades was achieved for the blends at hand.

It is instructive to compare the present results, obtained with PTFE's of a very wide range of viscosities (molar masses), with characteristics, notably their mechanical behavior, of its hydrogen analogue, i.e., linear polyethylenes (PE). In Figure 7 are shown stress−strain curves, recorded at room temperature and at strain rates of 1 and 40 min^{-1}, of melt compression molded films (as above, except at a molding temperature of 180 °C) of two polyethylenes of weight-average molar masses, M_w, and viscosities respectively of (a) and (b) 9.1×10^4 g/mol, 3.4×10^3 Pa·s ("high density/HD PE") and (c) 2.1×10^6 g/mol ("ultrahigh molecular weight/UHMW PE"), 10^8 Pa·s. Evidently, and really not surprisingly, there appears to be relatively little distinction between the behavior of UHMW PE and common (in fact, "UHMW") PTFE (Figure 2c). Both materials display prominent strain hardening immediately after the yield stress has been exceeded. This apparent homogeneous plastic deformation behavior (absence of necking) of both UHMW polymers is commonly associated with microvoiding, i.e., inhomogeneous mechanical behavior on a very small scale, induced by the porous character of sintered objects of UHMW polymers.[24] The high initial void content of UHMW polymers, in its turn, stems from incomplete sintering due to its extremely high melt viscosity. Close resemblance also is noted between the mechanical behavior of lower molar mass polyethylene (Figure 7a,b) and that of the present, melt-processable grades of PTFE (Figure 2a,b). A distinct yield point is observed, after which strain softening sets in, resulting in the commonly associated formation of a macroscopic "neck", which then consumes the tensile bar at approximately constant force until it reaches the wider sections of the tensile bar (cf. Figure 1). The observed neck formation and subsequent cold drawing indicates that the medium molar mass PTFE, in contrast to UHMW PTFE, is virtually free of voids, which is evident also from the clarity of the films. It should be noted that important design parameters, such as the yield stress and the Young's modulus (cf. Table 4), are equal to or even slightly higher for melt-processed medium molar mass PTFE material compared to UHMW PTFE samples (due to the lower crystallinity of the latter; see below).

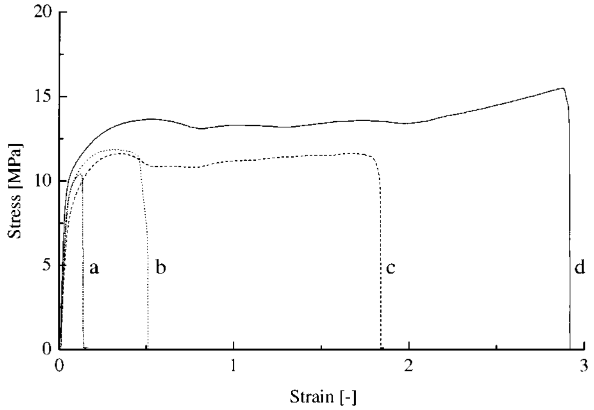

Figure 6. Stress−strain curves of different melt-processed PTFE blends. The designations a−d correspond to the following V/XI blend compositions: 60/40, 40/60, 20/80, and 10/90, respectively. All films were about 0.25 mm thick and were tested at a strain rate of 1 min^{-1}.

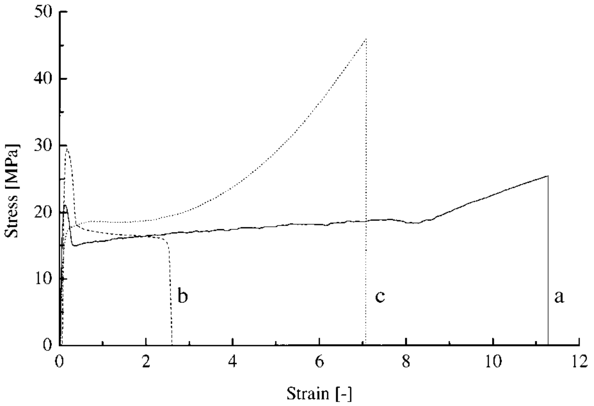

Figure 7. Stress−strain curves recorded at room temperature of polyethylenes of different weight-average molar masses, M_w, and zero-shear viscosities, η_0: (a) HDPE, $M_w = 9.1 \times 10^4$ g/mol, $\eta_0 = 3.4 \times 10^3$ Pa·s, film thickness 0.12 mm, strain rate 1 min^{-1}; (b) same as (a), but film thickness 1 mm and strain rate 40 min^{-1}; (c) UHMW PE, $M_w = 2.1 \times 10^6$ g/mol, $\eta_0 = 10^8$ Pa·s, film thickness 0.2 mm, strain rate 1 min^{-1}.

Table 4. Compositions and Mechanical Properties[a] of Selected Poly(tetrafluoroethylene) Blends

PTFE grades	weight ratio	Young's modulus (MPa)	yield stress (MPa)	tensile strength (MPa)	strain to break
V + XI	60−40	360 ± 33	9.5 ± 0.8	10.4 ± 1.1	0.1 ± 0.02
V + XI	40−60	340 ± 24	11.6 ± 0.4	12.4 ± 1.2	0.4 ± 0.1
V + XI	20−80	265 ± 38	11.1 ± 0.4	11.1 ± 0.4	1.4 ± 0.5
V + XI	10−90	333 ± 28	13.6 ± 0.2	15.0 ± 1.1	2.7 ± 0.5
XI	100	225 ± 5	11.0 ± 0.1	19.7 ± 0.8	4.0 ± 0.4

[a] All tests were carried out at a strain rate of 1 min^{-1}; the above values were averaged from four measurements.

Comparing Figures 2 and 7, it is clear that, in contrast to HDPE, the strain to break of medium molar mass PTFE improves upon increasing the tensile speed (for this tensile bar geometry and under the present experimental conditions). This interesting feature will be further investigated in future studies.

In addition to a close resemblance of their molar mass dependent mechanical characteristics, poly(tetrafluoroethylene) and polyethylene display strong similarities in their degrees of crystallinity, as determined by differential scanning calorimetry, for example. Typically, virgin (as-polymerized), ultrahigh molar mass versions of both PTFE and PE are of a very high degree of crystallinity[16,25] (often >80%), whereas the same polymer materials after crystallization from the melt exhibit a relatively low crystallinity of about 40%. On the other hand, melt-crystallized medium and lower molar mass grades of both PTFE and PE display degrees of crystallinity of 60% and more (cf. Table 1 and refs 16, 26) and, therefore, are of a (relatively) higher density than their corresponding UHMW forms; for this reason the term "HDPE" is used in common parlance to refer to these grades of PE. Analogously and logically, the designation "HD-PTFE" accurately describes the present melt-processable grades of PTFE. (It will not escape the reader that this terminology could be sensibly applied to certain copolymers of PTFE; e.g., FEP could adequately be classified as belonging to the family of linear low-density poly(tetrafluoroethylene)s, or LLD-PTFE.)

Having noted salient similarities in the conformational energies of PE and PTFE macromolecules[27] and their behavior in the molten[15] and solid forms (this work), the question (re)emerges as to why PTFE requires a substantially higher molar mass, or, rather, longer chain length than PE and most other polymers, to form (semi)crystalline solids of adequate mechanical properties. A long time ago, it was argued[8] that the very weak interchain bonds in PTFE are responsible for this necessity. An additional, or perhaps alternative, origin may be found in the macromolecular requirements for "elastic percolation", as explained hereafter. It is well-known that isotropic, organic molecular solids that are composed of extended-chain crystals are brittle, because applied stresses are transmitted via the crystal grain boundaries only. Toughness of such materials develops solely when the length of constituent molecular chains exceeds the "thickness" of the crystals and form covalent bridges between them. Upon crystallization from the molten phase—under ambient conditions—linear polyethylene typically forms (orthorhombic) crystalline regions of characteristic thickness of about 10 nm; thus, this polymer forms tough solids only at chain lengths that are about 4−5 times that value corresponding to molar masses of approximately 5×10^3 g/mol. When PTFE is crystallized from the melt, it first forms a hexagonal crystal phase[28] in which the chains display an extremely high mobility (hence its high melting temperature[27]), leading in turn to the formation of crystals of a thickness that are larger, often by a factor of 10−20 or more, than those of PE.[29,30] (It should be noted that when PE is crystallized under conditions, for example, at high pressures,[31] where it also first forms a similar hexagonal, highly mobile phase, crystals thicknesses very similar to those of PTFE are obtained.) Because of the dramatically larger thickness of PTFE crystals in comparison with those of commonly solidified PE, one must expect that the minimum chain *length* for PTFE to form tough solids also be at least 10−20 times larger than that of PE (in terms of molar *mass*, $>(2-4) \times 10^5$ g/mol). A cursory view of the data in Tables 3 and 4 and Figure 5 reveals that this estimate, in view of the very crude analysis and assumptions, appears satisfactory.

Note: handling of fluoropolymers may be hazardous.[32]

Acknowledgment. The authors very much appreciate the assistance of Messrs. Aitor Andueza and Magnus Kristiansen (ETH-Zürich) and invaluable discussions with Dr. Kees Bastiaansen (TUE/ETH-Zürich). They also have the pleasure to acknowledge F. Kinsey Haffner, Esq. (Pillsbury, Madison & Sutro, LLP), for critical reading of the manuscript.

Appendix

The molar mass distribution of the PTFE blends was estimated from the storage modulus as a function of frequency, $G(\omega)$, using the storage modulus transform according to Tuminello et al.[15] To this extent, the square root of the reduced modulus, $W_u = (G'(\omega)/G_N^0)^{0.5}$, as a function of $\log(\omega)$, was fitted to the following two-component hyperbolic tangent function, using a non-linear least-squares Levenberg−Marquardt (LM) algorithm:

$$W_u^{0.5} = \sum_i A_i[1 + \tanh(B_i(X + C_i))]/2 \qquad (3)$$

where $\sum_i A_i = 1$, $0 \le A_i \le 1$, $B_i > \ln(10)/6.8$ (to ensure convergence of M_w and M_n), and $X = \log(\omega)$. Next, the logarithmic frequency axis was transformed to a logarithmic relative molar mass axis using an arbitrary proportionality constant, according to $1/\omega \propto M_w^{3.4}$. Subsequently, the cumulative molar mass distribution, $\text{CMD}(M) = 1 - W_u$, was obtained by plotting $1 - W_u$ versus the logarithm of relative molar mass. The derivative of CMD(M) with respect to log(M) resulted in the differential molar mass distribution. Finally, the relative molar mass was transformed into absolute molar mass by matching the relative weight-average molar mass to the experimental value, obtained from the zero shear viscosity (see text). For the plateau modulus, G_N^0, a critical parameter in the analysis, a value of $G_N^0 = 1.7$ MPa was adopted, as determined by Tuminello et al.[15]

References and Notes

(1) The designation "poly(tetrafluoroethylene)" refers to polymers of tetrafluoroethylene comprising less than 0.5 mol % of a comonomer; ISO 12086.

(2) Gangal, S. V. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. 16, p 577.

(3) Banks, R. E.; Willoughby, B. G. In *The Encyclopedia of Advanced Materials*; Bloor, D., Brook, R. J., Flemings, M. C., Mahajan, S., Eds.; Pergamon: Oxford, 1994; Vol. 2, p 862.
(4) Scheirs, J., Ed.; *Modern Fluoropolymers*; Wiley: New York, 1997.
(5) Grulke, E. A. *Polymer Process Engineering*; PTR Prentice Hall: Englewood Cliffs, 1994; p 42.
(6) Seymour, R. B. *Engineering Polymer Sourcebook*; McGraw-Hill: New York, 1990; pp 13, 214.
(7) Doban, R. C.; Sperati, C. A.; Sandt, B. W. *SPE J.* **1955**, *Nov*, 17.
(8) Sperati, C. A.; Starkweather, H. W., Jr. *Fortschr. Hochpolym.-Forsch.* **1961**, *2*, 465.
(9) Hintzer, K.; Löhr, G. In ref 4, p 240.
(10) Plunket, R. J. U.S. Patent 2,230,654, 1941.
(11) In ref 3, p 863.
(12) E.g.: Zonyl MP *Technical Information Sheets*, DuPont, 1998.
(13) Smith, P.; Visjager, J.; Bastiaansen, C.; Tervoort, T. Int. Pat. Appl. WO 00/08071.
(14) E.g.: (a) Suwa, T.; Seguchi, T.; Machi, S. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 2183. (b) Chu, B.; Wu, C.; Buck, W. *Macromolecules* **1988**, *21*, 397.
(15) Tuminello, W. H.; Treat, T. A.; English, A. D. *Macromolecules* **1988**, *21*, 2606.
(16) Starkweather, H. W., Jr.; Zoller, P.; Jones, G. A.; Vega, J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 751.
(17) Bunn, C. W.; Howells, E. R. *Nature* **1954**, *174*, 549.
(18) Doughty, T. R., Jr.; Sperati, C. A.; Ho-Wei Un, H. U.S. Patent 3,855,191, 1974.
(19) Polymers of such relatively low MFR values are by no means unusual, and their characteristics are not prohibitive for processing these materials in their molten form, as is evident not only from the results presented here but also from a cursory examination of the multitude of commercial, so-called "low MFR" polymers (cf. *Polymat, Werkstoffdatenbank*, Deutsches Kunststoff-Institut, 1989).
(20) Grace, H. P. *Chem. Eng. Commun.* **1982**, *14*, 225. Starita, J. M. *Trans. Soc. Rheol.* **1972**, *16* (2), 339.
(21) Cox, W. P.; Merz, E. H. *J. Polym. Sci.* **1958**, *28*, 619.
(22) Yasuda, K.; Armstrong, R. C.; Cohen, R. E. *Rheol. Acta* **1981**, *20*, 163.
(23) Menefee, E. J. *Appl. Polym. Sci.* **1972**, *19*, 277.
(24) Smit, R. J. M.; Brekelmans, W. A. M.; Meijer, H. E. H. *J. Mech. Phys. Solids* **1999**, *47* (2), 201.
(25) E.g.: Smith, P.; Chanzy, H. D.; Rotzinger, B. P. *Polym. Commun.* **1985**, *265*, 258.
(26) E.g.: Capaccio, G.; Ward, I. M. *Polymer* **1974**, *15*, 233; **1975**, *16*, 239.
(27) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969; pp 153−157.
(28) Bunn, C. W.; Cobbold, A. J.; Palmer, R. P. *J. Polym. Sci.* **1958**, *28*, 365.
(29) Melillo, L.; Wunderlich, B. *Kolloid-Z. Z. Polym.* **1972**, *250*, 417.
(30) Bassett, D. C.; Davitt, R. *Polymer* **1974**, *15*, 721.
(31) Wunderlich, B.; Melillo, L. *Makromol. Chem.* **1968**, *118*, 250.
(32) *Guide to the Safe Handling of Fluoropolymers*, 3rd ed., Soc. Plastics Industry, Inc.: Washington, 1998.

MA000747+