

Melt Spinnable Spandex Fibers from Segmented Copolyetheresteraramids

M. C. E. J. NIESTEN,* J. KRIJGSMAN, S. HARKEMA, R. J. GAYMANS

University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

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ABSTRACT: Spandex fibers were obtained by melt spinning segmented copolyetheresteraramides with crystallizable aromatic diamide units of uniform length and poly(tetramethyleneoxide) segments. The aramid content was varied from 3 to 22 wt %, and the molecular weight of the polyether segment ranged from 1000 to 9000 g/mol. The influence of the spinning and drawing conditions on the fiber properties was investigated. The aromatic diamide units crystallize very fast. This made the melt spinning of the polymers easy. The aramide units were also found to be very effective in increasing the modulus. For a high elasticity a low aramid content was beneficial, and with a few percent a good elastic behavior is obtained. Orientation by drawing or a spin drawing process improves the elastic behavior. The elastic properties are compared to the values of commercial spandex fibers. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2194–2203, 2001

Key words: spandex fibers; melt spinning; uniform; segmented copolymers; spandex

INTRODUCTION

Synthetic elastic fibers are generally referred to as elastane or spandex fibers in Europe and the United States, respectively. By definition, these fibers have an elongation to break of more than 200%, usually 400–800%, and on release of the deforming stress, return quickly and almost completely to their original length.^{1,2} A major advantage of spandex fibers over rubber yarns is that they are easily spinnable into thin fibers making them suitable for textile applications.

The largest commercial spandex fibers are Lycra™ of DuPont and Dorlastan™ of Bayer. These are segmented polyurethanes consisting of alternating polyurethane hard segments and polyether or polyester soft segments. The hard seg-

ments are made up of aromatic diisocyanates (mostly diphenyl methane-4,4'-diisocyanate; MDI) coupled by extender molecules. If diamines are used as extenders urea-urethane groups are formed and highly elastic fibers with a good heat stability are obtained.^{3–5} The polymerization as well as the spinning process are carried out in solution, dimethyl formamide or dimethyl acetamide being used as the solvent. Most spandex fibers are produced according to the dry spinning process. In this process a highly viscous solution is put through a spinneret and simultaneously, hot air is supplied to evaporate the solvent. Dry spinning is an expensive and environmentally unfriendly process. Hence, melt spinnable alternatives for spandex fibers are interesting.

Segmented polyurethanes can be made melt spinnable by using diols instead of diamines as the hard segment extenders (e.g., Spantel™ of Kuraray Co. Ltd. and Mobilon™ of Nisshinbo). However, the heat stability of these fibers is strongly reduced.⁶ Vieth⁷ reported a melt spinnable copolyetherester fiber based on poly(buty-

Correspondence to: R. J. Gaymans; (r.j.gaymans@ct.utwente.nl).

*Current address: Huntsman Polyurethanes, Everberg, Belgium.

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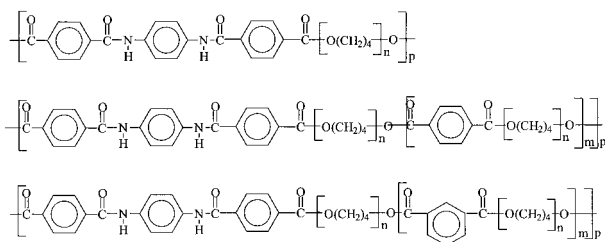


Figure 1 Segmented copolyetheresteraramids with uniform aramid units (TΦT) and PTMO or DMT and DMI extended PTMO soft segments.

lene terephthalate) hard segments and poly(tetramethyleneoxide) soft segments, called Diolen Swing™ (Akzo Nobel). The advantage of this fiber is the solvent-free polymerization and spinning process. The elasticity compared to dry spun polyurethane spandex fibers, however, is poor.

Abhiraman et al.⁸ defined the morphological requirements for a segmented copolymer to provide efficient recovery from deformation. According to them, complete phase separation between the hard and soft segments is necessary to avoid reduction in segmental mobility of the soft segments due to mixing of the hard segments with the soft segments. Chain folding should be eliminated to avoid loops that will not contribute to elasticity. Furthermore, perfect orientation of the hard segment crystals along the fiber direction will eliminate the resistance to recovery from deformation that would result from the nonaxially oriented crystals.

In a recent study melt processable segmented copolyetheresteraramids with aromatic diamide units of uniform length (TΦT) and poly(tetramethyleneoxide) (PTMO) or dimethyl terephthalate (DMT) and dimethyl isophthalate (DMI) extended PTMO soft segments (Fig. 1) were described.^{9–11} The use of uniform crystallizable units has several advantages.^{9–15} The uniform units crystallize very fast and nearly complete over their full length, resulting in a good phase separation and consequently a low T_g , providing low-temperature elasticity. Despite the short length, the TΦT units still crystallize easily into thin lamellae of uniform thickness (1.8 nm).^{9–11,16} The units are too short to chain fold. A very low concentration of TΦT units is sufficient for crystallization to take place and the aramid crystals melt at a relatively high temperature. Hence, using a small amount of diamide units, low modulus materials that are dimensionally stable up to high temperatures can be obtained.^{9–10} The fracture strain of these polymers is extremely high (1300–2000%) and, conse-

quently, the remaining fracture strain after orientation can still be high. Strain-induced crystallization of the soft segments results in a high fracture stress. However, too much strain-induced crystallization can influence the elasticity negatively. In a previous publication it was shown that PTMO segments longer than 1000 g/mol strain crystallize irreversibly while DMT or DMI extended PTMO₁₀₀₀ segments strain crystallize reversibly.¹⁰ Irreversible strain-induced crystallization results in polymers with a high fracture stress; however, at the expense of the elasticity. Reversible strain-induced crystallization might give fibers that combine a high elasticity with a high fracture stress. The tensile strength of these polymers strongly increases with increasing molecular weight.¹¹

Similar polyether-aramids were synthesized by Hirt and Herlinger.¹⁵ The fibers of these polymers made by wet spinning turned out to be highly elastic. In this study elastic fibers are melt spun from TΦT-PTMO segmented copolymers. The influence of the spinning conditions on the mechanical properties of the fibers is investigated. Fibers are oriented by drawing and by spin drawing. The time dependence of the elastic recovery as well as the effect of drawing on the elasticity are investigated. As PTMO crystallization strongly influences the deformation behavior of the polymers and the PTMO melts at a low temperature, the influence of temperature on the properties of the fibers is studied. Finally, the tensile properties of spin-drawn fibers are compared to the tensile properties of some commercial spandex fibers.

EXPERIMENTAL

Materials

The synthesis of TΦT-PTMO segmented copolymers is described elsewhere.^{9,10} The studied copolymers are given in Figure 1. The code used for the PTMOs is as follows. The “n” stands for the molecular weight of the PTMO segment and the “m” for the molecular weight of the extended PTMO segment. The PTMO_{2000m} is a modified PTMO with a molecular weight of 2000, which contains 15 mol % methyl side groups. Lycra™ 269B and 136C were generously provided by Dupont and Diolen Swing™ by Akzo-Nobel.

Viscometry

The inherent viscosity of the polymers at a concentration of 0.1 g/dL in a 1/1 (molar ratio) mix-

ture of phenol/1,1,2,2-tetrachloroethane at 25°C, was determined using a capillary Ubbelohde 1B viscometer.

Spinning and Drawing

Threads (~ 0.3 mm in diameter) were obtained by extruding a polymer on a 4-cc DSM res RD11H corotating twin-screw miniextruder. The extruder temperature was set at 60°C above the melting temperature of the polymer. The screw speed was 30 rpm, and threads were wound at 30 m/min.

The as-spun fibers (unoriented) were drawn on a Zwick Z020 universal tensile machine equipped with a 10-N load cell, the strain being measured as the clamp displacement. Samples were drawn by applying the desired draw ratio at a strain rate of 0.06 s⁻¹ and releasing the strain after 5 min.

Spin Drawing

On a semi-industrial scale, fibers were melt spun on an 18-mm single-screw extruder at Acordis Research in Arnhem, The Netherlands. The screw speed of the extruder was 50–60 rpm. The flow of the polymer melt through the extruder was approximately 11 g/min. A spinneret with a diameter of 60 mm with ten 400-μm holes was used. Before the spinneret a filter was placed with 60-120-325-120-60 mazes/square inch. To avoid sticking of the fibers a finish was spread on the fibers. The takeup speed ranged from 100 to 400 m/min.

Tensile Tests

Tensile tests were carried out on a Zwick Z020 universal tensile machine equipped with a 10-N load cell, the strain being measured as the clamp displacement. Stress–strain curves were obtained at a strain rate of 0.16 s⁻¹. For measurements above room temperature an oven was installed on the tensile machine. The tensile stress was expressed in cN/tex (1 tex = 10⁻⁶kg/m, because the density of the polymers is approximately 1 g/cm³, 1 cN/tex corresponds to 10 MPa). The tex of the fibers was determined by carefully weighing 1 meter of fiber. The “true” fracture stress is obtained by multiplying the engineering fracture stress by the draw ratio.

Tensile Set

The tensile set was determined by applying a 300% cyclic strain at a strain rate of 0.06 s⁻¹. Before starting the second cycle, a relaxation time

varying from 0 to 64 h was introduced. The strain at the onset of stress in the second cycle is taken as the residual strain. The tensile set (TS_{300%}) was defined as:

$$TS_{300\%} = \frac{\text{residual strain}}{300} \times 100\% \quad (1)$$

The relaxation rate ($\Delta \log t$ in %/s) of the tensile set was defined as the absolute value of the slope of the line of the TS_{300%} vs. the logarithm of the relaxation time.

DSC

DSC spectra were recorded on a Perkin-Elmer DSC7 apparatus, equipped with a PE7700 computer and TAS-7 software. Two to five milligrams of dried polymer sample were heated at a rate of 20°C/min. The first cooling and second heating scan were used to determine the melting and crystallization peaks. The peak maximum or minimum was used as the melting or crystallization temperature, respectively, the peak area as the enthalpy.

Synchrotron WAXS

Synchrotron wide-angle X-ray scattering (WAXS) measurements were performed on unoriented melt-spun polymer fibers during straining at a straining rate of 10⁻² s⁻¹ at the ESRF in Grenoble (France) on ID11.¹⁶ The wavelength of the beam was 1.00 Å. Every 30 s a measurement was done with an exposure time of 10 s.

DMA

Samples for the DMA test (70 × 9 × 2 mm) were prepared on an Arburg H manual injection molding machine. The barrel temperature of the injection molding machine was set at 50°C above the melting temperature of the polymer, with the mold temperature being held at room temperature.

Using a Myrenne ATM3 torsion pendulum at a frequency of approximately 1 Hz, the values of the storage modulus G' and the loss modulus G'' as a function of the temperature were measured. Dried samples were first cooled to -100°C and then subsequently heated at a rate of 1°C/min, with the maximum of the loss modulus being taken as the glass transition temperature. The flow temperature was defined as the temperature where the storage modulus reached 0.5 Mpa.

Table I DMA and Tensile Properties of TΦT-PTMO, TΦT-PTMO_m, TΦT-(PTMO/DMT), and TΦT-(PTMO₁₀₀₀/DMI) Unoriented

| Polymer | TΦT [% wt] | η_{inh} [dl/g] | T_g^a [°C] | T_f^a [°C] | G' (25°C) ^a [MPa] | σ_b [cN/tex] | σ_{true} [cN/tex] | e_b [-] | TS _{300%} [%] | $\Delta \log t$ [%/s] |
|--|------------|---------------------|--------------|--------------|--------------------------------|---------------------|--------------------------|-----------|------------------------|-----------------------|
| TΦT-PTMO ₁₀₀₀ | 23 | 1.81 | -69 | 220 | 44 | 3.81 | 60 | 13.7 | 46 | 3.0 |
| TΦT-PTMO ₂₀₀₀ | 13 | 2.20 | -65 | 193 | 9 | 5.19 | 97 | 16.6 | 27 | 4.7 |
| TΦT-PTMO ₂₉₀₀ | 9.6 | 2.74 | -65 | 175 | 6 | 5.88 | 100 | 15.6 | 39 | 3.7 |
| TΦT-PTMO ₁₀₀₀ /DMT) ₁₅₃₂ | 17 | 1.74 | -66 | 204 | 17 | 1.70 | 31 | 16.4 | 37 | 4.7 |
| TΦT-PTMO ₁₀₀₀ /DMT) ₁₉₉₆ | 13 | 1.48 | -65 | 190 | 11 | 0.92 | 18 | 17.4 | 29 | 3.3 |
| TΦT-PTMO ₁₀₀₀ /DMT) ₃₁₀₂ | 9.3 | 2.07 | -65 | 178 | 6 | 1.30 | 29 | 20.6 | 21 | 3.3 |
| TΦT-PTMO ₁₀₀₀ /DMT) ₄₂₂₁ | 6.9 | 2.23 | -65 | 160 | 4 | 2.13 | 34 | 13.8 | 14 | — |
| TΦT-PTMO ₁₀₀₀ /DMT) ₆₁₅₆ | 4.9 | 2.29 | -65 | 148 | 3 | 2.52 | 38 | 13.0 | 10 | — |
| TΦT-PTMO ₁₀₀₀ /DMT) ₉₀₂₅ | 3.4 | 1.67 | -65 | 124 | 1.5 | 1.52 | 35 | 20.7 | 9 | — |
| TΦT-PTMO ₁₀₀₀ /DMI) ₂₀₀₀ | 13 | 1.70 | -65 | 190 | 11 | 1.92 | 39 | 18.4 | 26 | 3.3 |
| TΦT-PTMO ₁₀₀₀ /DMI) ₃₀₀₀ | 9.5 | 2.37 | -65 | 178 | 6 | 2.50 | 46 | 17.4 | 20 | — |
| TΦT-PTMO ₆₅₀ /DMT) ₁₉₂₅ | 13 | 1.56 | -65 | 193 | 11 | 0.76 | 17 | 19.9 | 27 | 3.0 |
| TΦT-PTMO _{2000m} ^b | 13 | 2.04 | -75 | 193 | 10 | 2.72 | 51 | 16.6 | 21 | 4.3 |

^a Determined with DMA.^b m refers to modified: 15 wt % of methyl side groups.^c σ_b : fracture stress; σ_{true} : true fracture stress; e_b : fracture strain; TS_{300%}: tensile set after 300% strain; $\Delta \log t$: relaxation rate of tensile set.

RESULTS AND DISCUSSION

Introduction

The inherent viscosity of the copolymers was at least 1.5 dL/g, indicating that the molecular weight of the polymers was high (Table I). The polymers are melt spun easily. Only the polymers with modified PTMO segments (containing 15 wt % of methyl side groups) were a little hard to spin, as the fiber tended to break easily. This was probably due to the poorer strain hardening of the modified PTMO, which is necessary for stabilizing the spin line.

The elasticity of melt-spun fibers as well as the influence of time and drawing on the elasticity was investigated. The influence of the spinning conditions on the fiber properties was studied by spinning TΦT-(PTMO₁₀₀₀/DMI)₃₀₀₀ on a semi-industrial spinning machine. The fiber properties of fibers oriented by drawing and by spindrawing are compared. The orientation on straining was followed by WAXS. The effect of temperature on the fiber properties was investigated. Finally, the fiber properties were compared to some commercial spandex fibers. In Table I some properties of the polymers that were used for the preparation of the fibers are shown.

Elasticity of As-Spun and Drawn Fibers

Extruded threads wound at the very low speed of 30 m/s were assumed to be unoriented, as the

samples at this speed did not show any orientation in the WAXS pattern. On these threads the tensile and elastic properties were measured. In Figure 2 the logarithm of the modulus is plotted vs. the aromatic diamide (TΦT) content. The (log) modulus increases strongly with increasing TΦT content. The increase in (log) modulus is linear with concentration. It is assumed that nearly all the TΦT units are in the crystalline phase.¹¹ Of the polyether phase it is known that PTMO₂₀₀₀ and PTMO₂₉₀₀ segments crystallize just around room temperature,¹⁷ resulting in polymers with a higher overall crystallinity than polymers that contain poorly crystallizing PTMO segments such as (PTMO₁₀₀₀/DMI)_m segments. At room temper-

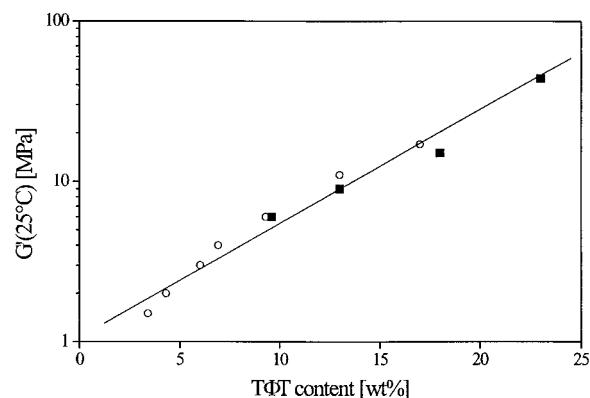


Figure 2 Shear modulus [$G'(25^\circ\text{C})$] vs. TΦT content: ■, TΦT-PTMO; ○, TΦT-(PTMO₁₀₀₀/DMT).

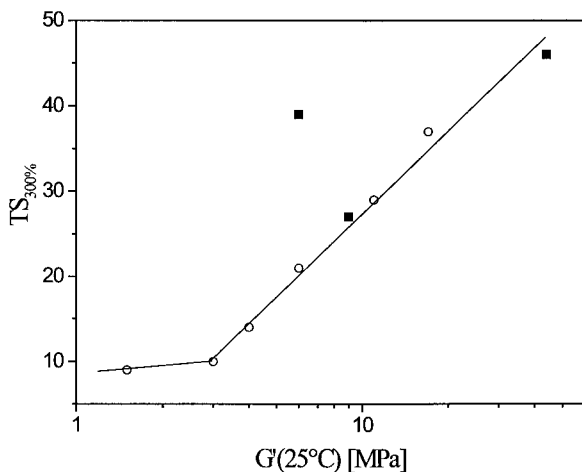


Figure 3 Tensile set of 300% tensile deformation vs. shear modulus [$G'(25^\circ\text{C})$]: ■, T Φ T-PTMO; ○ T Φ T-(PTMO₁₀₀₀/DMT).

ature, however, the PTMO crystallization has little influence on the modulus (Table I).

For the application as elastic fiber, the residual deformation after high deformation (i.e., 300%) is an important parameter. In Table I the set after 300% tensile deformation of melt-spun fibers is given ($TS_{300\%}$). In Figure 3 the $TS_{300\%}$ is plotted vs. the logarithm of the shear modulus. The $TS_{300\%}$ decreases linearly with decreasing logarithm of the shear modulus, leveling off at a very low modulus. The tensile set correlates well with the modulus and probably both depend on the crystallinity. The tensile set of T Φ T-PTMO₂₉₀₀ (9.6 wt % T Φ T) is higher compared to T Φ T-(PTMO₁₀₀₀/DMT)₃₁₀₂ (9.3 wt % T Φ T), which is apparently due to the strain induced crystallization of the PTMO₂₉₀₀ segments. A low $TS_{300\%}$ correlates with a low modulus. Thus, a highly elastic material is also a very soft material, the material might even be sticky. Combining a low $TS_{300\%}$ with a not so low modulus is sought for.

In the standard $TS_{300\%}$ test the relaxation time between unloading and loading is 30 s. The influence of this unloading time (relaxation time) on the elastic properties is studied. In Figure 4 the tensile set is plotted vs. the logarithm of the relaxation time. The relaxation rates of the tensile set (slope of curves in Fig. 4) are given in Table I. The decrease of the tensile set with the logarithm of time follows a straight line. It is clear that relaxation rate of the tensile set is little dependent on the aramide content or type of PTMO. For the polymers containing 13 wt % T Φ T (overall soft segment length of about 2000 g/mol) some slight differences are observed in the starting value of

the tensile set depending on the type of PTMO used. Probably, small differences in relaxation rate of the different PTMO based soft segments account for this. The time effect is caused by a slow relaxation process of the amorphous phase. The amorphous phase seems to exhibit two relaxation processes: a very fast relaxation process (in seconds), which differs for the different PTMO based soft segments, followed by a slow relaxation process that is approximately the same for all the soft segments. Because the starting value of the tensile set varies with the T Φ T content, the relative decrease of the tensile set in time is much higher for the fibers with low T Φ T content compared to the fibers with high T Φ T content. Extrapolating the tensile set to long relaxation times, a polymer with a starting tensile set value of 10%, completely recovers in 3 h.

In a recent study it was shown that the modulus (E) of these polymers decreases on straining (strain softening).¹⁶ Strain softening is attributed to disruption of the crystalline T Φ T network and breaking up of the crystalline T Φ T lamellae into smaller units. Therefore, it is expected that drawn fibers will possess a lower $TS_{300\%}$ than undrawn material because the crystalline phase, which was already deformed during drawing, will plastically deform less during a second straining. In Table II, the $TS_{300\%}$ after drawing is given, and in Figure 5 the tensile set is plotted vs. the draw ratio for fibers containing 13 wt % T Φ T, having different structures of the PTMO segment. A decrease of the $TS_{300\%}$ after drawing was observed for all fibers except for T Φ T-PTMO₁₄₀₀ and T Φ T-PTMO₂₀₀₀. The decrease of the $TS_{300\%}$, however, is quite small considering the strong change in

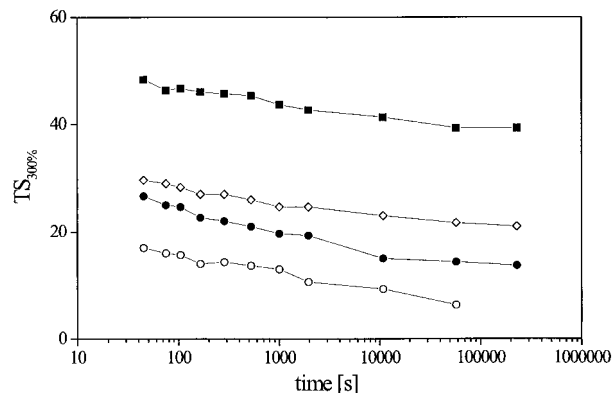


Figure 4 Tensile set after 300% deformation vs. time between first and second loading: ■, T Φ T-PTMO₁₀₀₀; ●, T Φ T-PTMO₂₀₀₀; ◇, T Φ T-(PTMO₁₀₀₀/DMT)₁₉₉₆; ○, T Φ T-(PTMO₁₀₀₀/DMT)₃₁₀₂.

Table II Values for Tensile Set of 300% Tensile Deformation after Different Draw Ratios

| Fiber | Draw Ratio | | | |
|---|------------|----|-----|----|
| | 1 | 6 | 8.5 | 11 |
| TΦT-PTMO ₁₀₀₀ | 46 | 40 | 35 | 33 |
| TΦT-PTMO ₁₄₀₀ | 32 | 55 | — | — |
| TΦT-PTMO ₂₀₀₀ | 27 | 60 | — | — |
| TΦT-PTMO ₂₉₀₀ | 39 | — | — | — |
| TΦT-PTMO ₁₀₀₀ /DMT ₁₅₃₂ | 37 | 28 | 35 | 33 |
| TΦT-PTMO ₁₀₀₀ /DMT ₁₉₉₆ | 29 | 23 | 26 | 28 |
| TΦT-PTMO ₁₀₀₀ /DMT ₃₁₀₂ | 21 | 15 | 16 | 15 |
| TΦT-PTMO ₁₀₀₀ /DMT ₄₂₂₁ | 41 | — | — | — |
| TΦT-PTMO ₁₀₀₀ /DMT ₆₁₅₆ | 10 | — | — | — |
| TΦT-PTMO ₁₀₀₀ /DMT ₉₀₂₅ | 9 | 7 | — | — |
| TΦT-PTMO ₁₀₀₀ /DMI ₂₀₅₂ | 27 | 20 | 18 | 17 |
| TΦT-PTMO ₁₀₀₀ /DMI ₃₁₅₂ | 19 | 11 | 10 | 10 |
| TΦT-PTMO ₆₅₀ /DMI ₁₉₂₅ | 27 | 21 | 20 | 19 |
| TΦT-PTMO _{2000m} | 21 | 17 | 17 | 17 |

lamellar structure as read from the strong decrease in modulus. The strain softening experiments showed that the modulus decreases with a factor 6 during the first 200% strain.¹¹

All the polymers with PTMO segments of 1400 g/mol and longer show an increase of the TS_{300%} with increasing draw ratio. The TS_{300%} of DMI extended PTMO₁₀₀₀, DMT extended PTMO₆₅₀, and PTMO_{2000m} decreases with increasing draw ratio. Polymers with (PTMO₁₀₀₀/DMT)_m soft segments have a minimum of the TS_{300%} at a draw ratio of 6. The increase of the tensile set with drawing seems to be caused by strain induced crystallization of the PTMO phase. In a previous publication it was shown that PTMO₁₄₀₀ and longer strain crystallize much more than extended PTMO or modified PTMO (PTMO_m, contains 15 wt % methyl side groups).¹⁰ Also, it was concluded that the strain-induced crystallization of PTMO segments longer than 1400 g/mol is irreversible, while for extended PTMO₁₀₀₀ or modified PTMO the strain-induced crystallization is (partly) reversible. For (PTMO₁₀₀₀/DMT)_m at draw ratios of 6 and higher, the strain-induced crystallization of (PTMO₁₀₀₀/DMT)_m overcompensates the strain softening due to the breaking up of the diamide lamellae. After a draw ratio of 11, the fiber containing (PTMO₁₀₀₀/DMI)₂₀₅₂ has a lower tensile set than the fiber containing (PTMO₁₀₀₀/DMT)₁₉₉₆, while its fracture strain and stress are higher. Therefore, it seems that DMI extended PTMO₁₀₀₀ segments yield polymers with better tensile set properties than DMT

extended PTMO₁₀₀₀ segments. The optimum PTMO length (n) in (PTMO_n-DMI)_m and (PTMO_n-DMT)_m and total length (m) for properties (tensile set, fracture stress, fracture strain, heat stability) still has to be determined.

The tensile properties of fibers after drawing are comparable (Table III). Drawing increases the fracture strength at the cost of the elongation at break. The “true” fracture strain increases only slightly on drawing.

The Influence of the Spinning Conditions on the Properties of As-Spun Fibers

On TΦT-(PTMO₁₀₀₀/DMI)₃₀₀₀ the influence of spinning conditions was studied. In an other part of the study this was carried out on TΦT-(PTMO₁₀₀₀/DMI)₂₀₀₀.¹⁸ The spinning was done at a spinning temperature of 230°C, on a semiindustrial spinning machine with the extruder at a low throughput and at different winding speeds, ranging from 100–350 m/min. These conditions correlate with spinning speeds of 300–1000 m/min on an industrial machine. Also given are the results of an extrusion experiment with a miniextruder at very low take up speeds (30 m/min). The effect of spinning speed on the stress–strain curves of the fibers are shown in Table III and Figure 6. There is clearly a strong effect of spinning speed on the stress strain behavior. With increasing takeup speed the fracture stress increases at the expense of the fracture strain. This spinning speed effect is probably due to increased orientation and crystallization of the PTMO phase. As was observed with WAXS the samples were somewhat oriented after spinning; however, the orientation was difficult to quantify.

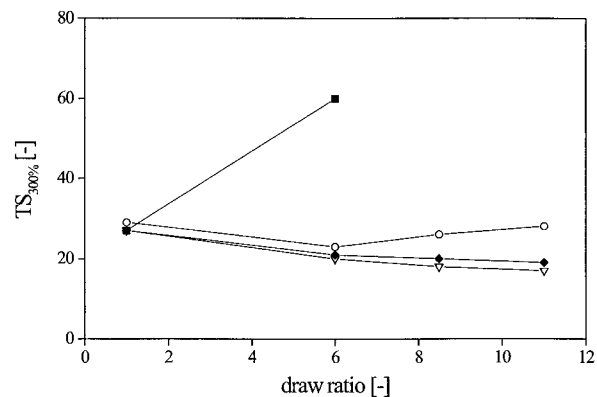


Figure 5 Tensile set after 300% strain vs. draw ratio for fibers containing 13 wt % TΦT: ■, TΦT-PTMO₂₀₀₀; ○, TΦT-(PTMO₁₀₀₀/DMT)₁₉₉₆; ▽, TΦT-(PTMO₁₀₀₀/DMI)₂₀₅₂; ◆, TΦT-(PTMO₆₅₀/DMI)₁₉₂₅.

Table III Tensile Properties of T Φ T-(PTMO₁₀₀₀/DMI)₃₀₀₀ Spun at Different Speeds

| Winding Speed (m/min) | Draw Ratio (-) | ϵ_b (%) | σ_b (cN/tex) | σ_{true} (cN/Tex) | TS _{300%} % |
|--------------------------|-------------------|---------------------|------------------------|-----------------------------|-------------------------|
| 30 ^a | 1 | 1740 | 2.5 | 46 | 20 |
| | 6 | 890 | 4.5 | 45 | 12 |
| | 8.5 | 660 | 5.2 | 40 | 10 |
| | 11 | 560 | 7.2 | 48 | 10 |
| 100 ^b | 1 | 970 | 5.6 | 60 | 24 |
| 250 ^b | 1 | 670 | 7.0 | 54 | 14 |
| 350 ^b | 1 | 530 | 9.0 | 57 | 13 |

^a Mini-extruder.^b Semi-industrial scale spin unit.

The “true” fracture stress is much less dependent on the spinning speed and the observed lower values for the low spinning speeds might well be due to the less uniformity of these fibers.

Some orientation can thus be introduced by drawing and by spin drawing. The fracture properties seem to be dependent on the spinning conditions. The tensile set values decrease with increasing spinning speed. The TS_{300%} values of the spin drawn materials seem to be as low as those of the drawn materials. The fibers made on the semi-industrial machine have better tensile properties probably as these fibers are more homogeneous in thickness. Spin drawing is thus an attractive process, as good fiber properties can be achieved during spinning without an additional drawing step. The fact that the diamide units crystallize very fast might as well contribute to this effect.

Structural Changes during Straining

The structure of the T Φ T phase in unoriented samples is that of lamellae with a very high as-

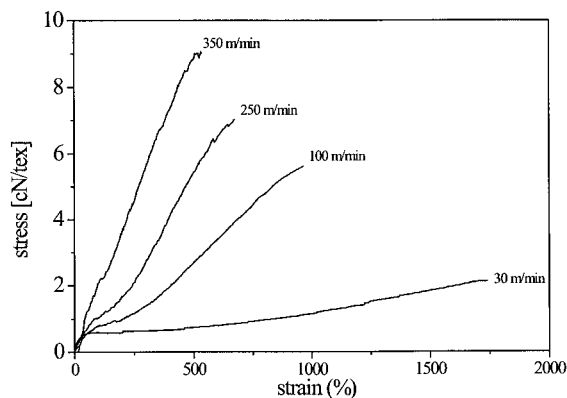


Figure 6 Stress–strain curves of as-spun fibers of T Φ T-(PTMO₁₀₀₀/DMI)₃₀₀₀ melt spun at different winding speeds (m/s).

pect ratio with no spherulitic ordering.¹⁶ The structure development during straining was followed with WAXS using a synchrotron facility (Fig. 7). WAXS pictures were taken at different strains and of a strained sample after relaxation of 6 days. The sample tested was a single fiber thread, which was strained at a strain rate of 0.05 s⁻¹. At 80% strain only a ring is visible, and hence, hardly orientation has occurred yet. On straining 500% and 1000% a very high orientation is visible. The orientation is apparent at the equator, but hardly developed in the fiber direction. The absence in the meridian direction indicates that no long-range order is present in this direction. As the T Φ T units are only 1.8 nm long, an order in this direction is not expected. The black spots on the equator probably are both from the PTMO phase. The absence of T Φ T diffraction peaks is probably due to its low concentration (only 9%) and the very small lamellar size.

After releasing the 1000% strain and measuring 6 days later, a strong diffuse ring is again apparent, combined with four peaks at the equator. The diffuse ring must be due to the relaxed amorphous PTMO phase. The middle two peaks at the equator are expected to be from the crystalline PTMO phase, but now less oriented than under strain. The two outer peaks must be from the T Φ T phase, but now stronger than in Figure 7(a) due to the fact that they are oriented, and stronger than in Figure 7(b) and (c) due to the fact that the lateral lamellar dimensions probably have increased on relaxation.¹⁶ Here, the orientation of the T Φ T is reasonable; thus, some loss of orientation on relieving the strain might also have taken place.

The Effect of Temperature on the Fiber Properties

The fracture properties of these segmented copolymers are highly dependent on the strain-induced

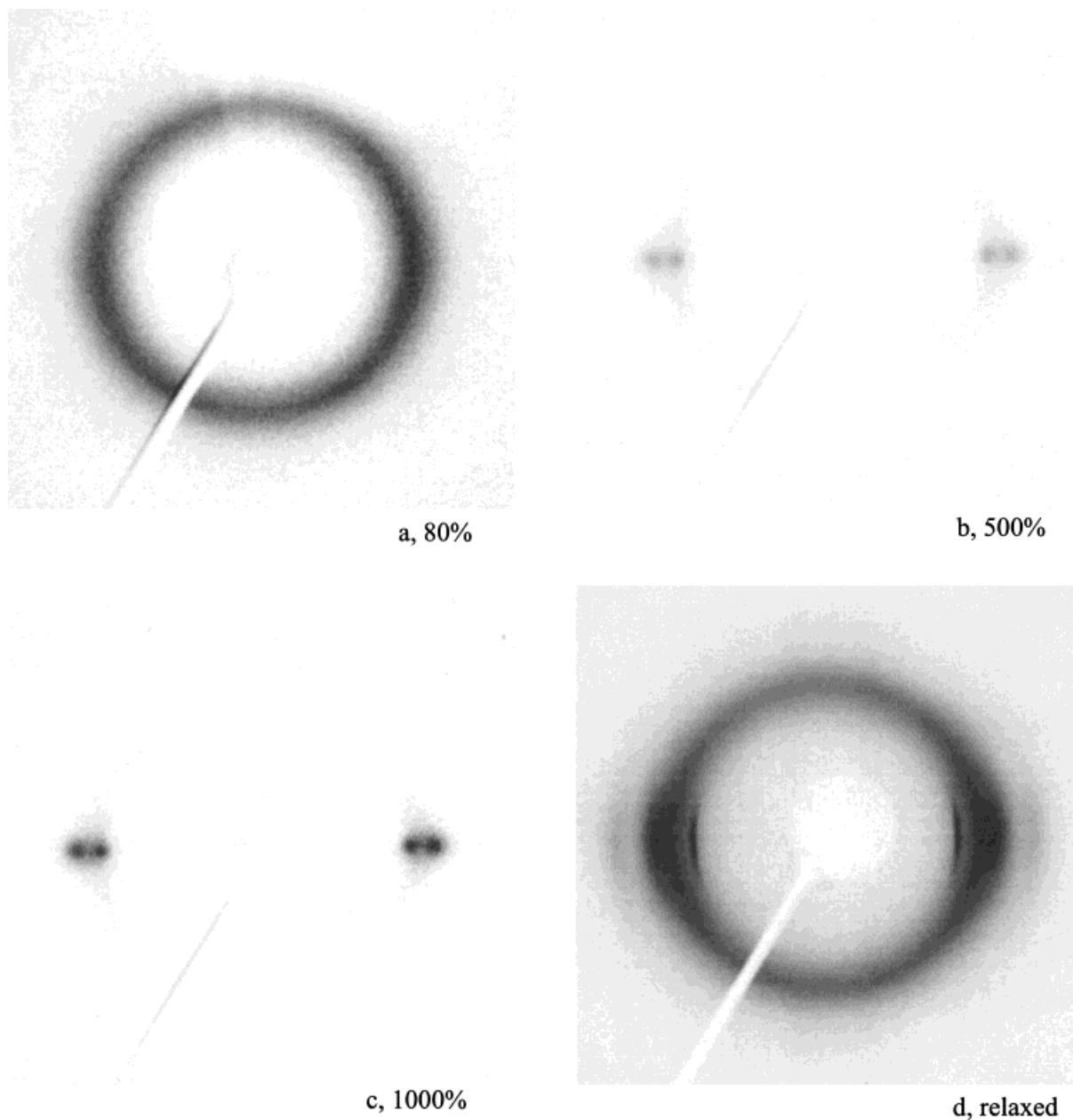


Figure 7 WAXS diagrams of TΦT-(PTMO₁₀₀₀/DMI)₃₀₀₀ at different strains: (a) 80%; (b) 500%; (c) 1000%; (d) 6 days after a 1000% strain.

crystallization. However, the strain-induced crystallized PTMO phase has a melting temperature near room temperature,¹⁶ and thus one expects a loss of the strain-induced crystallization effect on increasing the temperature. The fracture stress and strain of TΦT-(PTMO₁₀₀₀/DMI)₃₀₀₀ spun at high speed (~350 m/min) were measured over a temperature range (Fig. 8, Table IV). On increasing the test temperature the fiber material, which is partly oriented, shows on increasing the test temperature first an increase in the fracture

strain. This probably due to a weaker strain-hardening effect. At higher temperatures the fracture strain decreases strongly. The stress strain curve up to 100% deformation seems to be little affected. At high-test temperatures no strain hardening of the PTMO phase is possible, and strain hardening seems to be important for delocalization of the deformation. With increasing temperature the fracture stress strongly decreases. The fracture stress is directly dependent on the amount of strain induced crystallization of

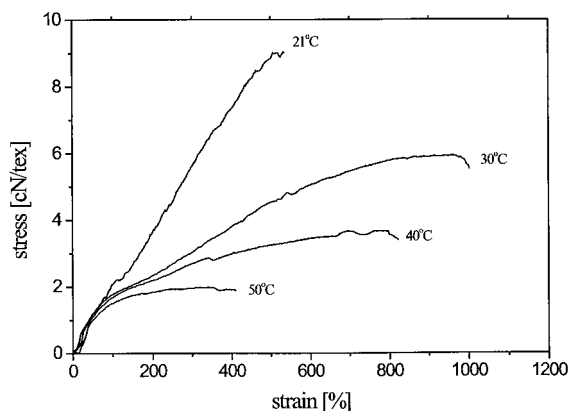


Figure 8 Stress–strain behavior of TΦT-(PTMO₁₀₀₀/DMI)₃₀₀₀ fibers (winding speed 350 m/s) tested at different temperatures.

the PTMO phase. The “true” fracture stress also decreases strongly with increasing test temperature. The tensile properties of these PTMO polymers at a strain higher than 100% are thus highly dependent on test temperature.

If the tensile properties change so strongly with temperature due to melting of the strain-induced PTMO crystallites one can wonder whether simply giving a heat treatment above the melting temperature of the PTMO also changes the properties of the oriented material permanently. The tensile properties at room temperature of the fibers after a heat treatment (2 h at 65°C) show surprisingly little change in properties (Table IV). Apparently the PTMO orientation is fixed by the oriented TΦT crystals, and the strain hardening is affected by the test temperature and not a heat treatment.

Comparison with Commercial Spandex Fibers

The properties of TΦT-(PTMO₁₀₀₀/DMI)₃₀₀₀ are compared to some fully developed commercial spandex fibers (Table V). Lycra™ is a segmented polyurethane that is spun by dry spinning. For the DMA analysis, strips (unoriented material) were pressed from fiber material in a hot press at 200°C. The Lycra™ materials combine a high flow temperature with an extremely low tensile set. The moduli (unoriented) however are very low. Thus, in Lycra™, too, a low tensile set is combined with a very low modulus. The disadvantage of low modulus materials is their stickiness, which makes them difficult to handle. Diolen Swing™ is a melt-spinnable spandex fiber from a segmented copolyetherester [poly(butylene terephthalate)-PTMO]. The tensile set and modulus values of Diolen

Swing™ are high. Our TΦT-(PTMO₁₀₀₀/DMI)₃₀₀₀ fibers have tensile set values approaching those of Lycra™.

CONCLUSION

Spandex fibers were made by melt spinning of segmented copolyetheresteramides with uniform crystallizable TΦT units and PTMO-based soft segments. These polymers are easily melt-spinnable, and due to the fast crystallization of the TΦT units easy to handle even at very low diamide contents.

The modulus of the polymers increases with increasing TΦT content and thus increasing crystallinity. The tensile set of the polymers was found to follow a linear relationship with the log shear modulus, leveling off at very low TΦT contents (<4%). At 4–6% TΦT the tensile sets is very low, but the modulus is also low.

The fibers can be oriented by drawing after spinning or during spinning by applying a high spinning speed (≈350 mm/min). Drawing yields fibers with a relatively high fracture stress, a low tensile set while the remaining tensile strain is still high (>500%).

The tensile set is time dependent; it decreases linearly with the logarithm of time due to relaxation of the soft segments. The soft segments seem to relax via two relaxation processes, a very fast one (within seconds) causing differences in the tensile set between polymers with different PTMO types and a relaxation process that is slow and independent of the PTMO type and TΦT content.

PTMO segments longer than 1400 g/mol strain crystallize irreversibly yielding fibers with a high fracture stress, however, at the expense of the elasticity. DMT or DMI extended PTMO₆₅₀ and PTMO₁₀₀₀ or PTMO_m strain crystallize reversibly, offering the possibility to combine a high fracture stress with high elasticity.

Table IV Tensile Properties of TΦT-(PTMO₁₀₀₀/DMI)₃₀₀₀ at Different Temperatures

| Test Temperature (°C) | σ_b | ϵ_b | σ_{true} | TS _{300%} |
|--------------------------|------------|--------------|-----------------|--------------------|
| 20 | 9.0 | 530 | 57 | 13 |
| 30 | 5.9 | 960 | 63 | — |
| 40 | 3.7 | 740 | 31 | — |
| 50 | 2.0 | 410 | 10 | — |
| 20 after 2 h at 65°C | 8.8 | 670 | 68 | 13 |

Table V Properties of Different Spandex Fibers

| Fiber | G' (25°C) ^a [MPa] | T_{fl} ^a [°C] | TS _{300%} ^b [%] |
|---|--------------------------------|----------------------------|-------------------------------------|
| TΦT-(PTMO ₁₀₀₀ /DMI) ₃₀₀₀ | 6 | 178 | 10–13 |
| Lycra™ 269B (DuPont) | 2.5 | 300 | 4 |
| Lycra™ 136C (DuPont) | 2 | 210 | 7.5 |
| Diolen Swing™ (Akzo-Nobel) | 18 | 188 | 52 |

^a Determined on melt pressed test bars.^b Determined on fibers.

One way to obtain a highly elastic material is thus to reduce the crystallinity, however, at the cost of having a very low modulus material. The tensile set can also be lowered by drawing or spin drawing. Another parameter is to avoid strain-induced crystallization of the PTMO phase; however, this has a negative influence on the tensile properties. Reversible strain-induced crystallization seems to have some advantages. Therefore, an optimum (PTMO₁₀₀₀/DMI)_m segment length (m) for spandex fibers seems to be about 5000 g/mol ($T_m \approx 150^\circ\text{C}$, $G'(25^\circ\text{C}) \approx 3$ Mpa).

Uniform TΦT units in PTMO copolymers result in polymers that are melt synthesizable, easily melt processable. The tensile properties are within the range of Lycra™ and the tensile set values approach that of Lycra™. The properties are superior to Diolen-Swing™, a commercial melt-spun spandex fiber.

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