Comparison of Properties of Segmented Copolyetheresteramides Containing Uniform Aramid Segments with Commercial Segmented Copolymers

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ABSTRACT: The thermal (using differential scanning calorimetry), dynamic mechanical (using a dynamic mechanical analyzer), and mechanical properties of segmented copolyetheresteramides with aramid units of uniform length (TΦT) and poly(tetramethylene oxide) (PTMO) segments were compared to those of commercial segmented copolyetheresters (PBT–PTMO) and thermoplastic polyurethanes. The hard segments in TΦT-containing polymers were found to crystallize almost completely, unlike the hard segments of Arnitel and Desmopan. Consequently, the glass-transition temperature of TΦT-containing polymers is lower and the melting temperature higher than those of Arnitel and Desmopan. Furthermore, the rubbery plateau of the TΦT-containing polymers is temperature independent, making the service temperature range wider. In TΦT-containing polymers a lower concentration of hard segment is needed to obtain dimensionally stable polymers with a high melting temperature. No melt phasing occurs during polymerization and therefore long PTMO segments can be used, producing very soft and elastic materials. The polymers crystallize faster than do commercial materials. The elasticity of the TΦT-containing polymers is comparable to the elasticity of Desmopan and better than that of Arnitel. TΦT–(PTMO$_{1000}$/DMT) copolymers are transparent and the solvent resistance is high. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1372–1381, 2001

Key words: segmented copolymer; copolyetheresteramide; uniform; bis(esterdiamide)

INTRODUCTION

This article describes a study of segmented copolymers with crystallizable uniform aramid units (TΦT) and poly(tetramethylene oxide) (PTMO) soft segments (Fig. 1). These polymers are interesting as thermoplastic elastomers (TPEs) as well as for application as a melt-spinnable elastane fiber.

Commercial segmented copolymers used as TPEs are thermoplastic polyurethanes (TPE-U), segmented copolyetheresters (TPE-E), or copolyetheramides (TPE-As).[1] Table 1 has an overview of the main producers of these types of polymers.

TPE-U were the first thermoplastically processible elastomers. The hard segment is formed by
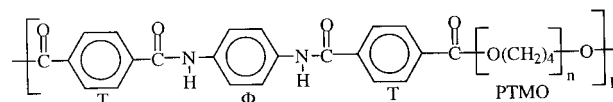
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Figure 1 Structure of segmented copolymer TΦT–PTMO.

Table I   Main Producers of TPE-U, TPE-E, and TPE-A

TPE Type	Company	Commercial Name
TPE-U	Bayer, BASF, Dow, Goodrich	Desmopan, Elastollan, Pellethane, Estane
TPE-E	DuPont, DSM	Hytrel, Arnitel
TPE-A	Elf-atochem, Hüls	Pebax, Vestamid

addition of a chain extender such as butanediol to the diisocyanate, for example, diphenylmethane-4,4′-diisocyanate (MDI). The soft segment is a long and flexible polyether or polyester that connects two hard segments. The hard and soft segments in TPE-U are known to phase-separate through liquid–liquid demixing, often followed by crystallization of part of the hard segments. The resulting morphology is complicated; the glass-transition temperature of the soft phase is broadened because of mixing with some hard segments, and several glassy and/or crystalline hard domains are present.[3] This makes the properties of TPE-U very temperature dependent. Polyurethanes have another disadvantage: they easily degrade during melt processing because of the thermal instability of the urethane groups.

These problems are partly overcome by using segmented copolyetheresters. They consist of fast-crystallizing hard segments such as poly(butylene terephthalate) or poly(ethylene terephthalate) and long, flexible polyether soft segments.[1] The polymers phase-separate through crystallization of the hard segments, resulting in an interconnecting network of polyester lamellae in an amorphous polyether matrix. The morphology is more defined compared to TPE-U: the glass transition is narrower, although some hard segments still mix with the soft phase and there is one crystalline polyester phase.[4] The modulus therefore varies less with temperature, giving these materials a wider service temperature range than do TPE-U. Thermal degradation during melt processing is not a limiting factor as for TPE-U. Copolyetheresters are claimed to have an improved low-temperature flexibility, a higher modulus (because of higher crystallinity), and a better resistance to creep as compared to TPE-U.[1]

Segmented copolymers with amide hard segments (TPE-A) were introduced later. TPE-A possess a morphology comparable to TPE-E. The advantage of this class of TPEs is the availability of a variety of aliphatic and aromatic amides, all having a different crystallinities and melting temperatures, offering a wide variations in properties. TPE-A can be obtained in softer grades than TPE-E, they have very good low-temperature properties, and they are more chemically resistant than TPE-E.[1]

A newer development is the synthesis and evaluation of segmented copolymers with diamide segments of uniform length.[5] This article describes a study of segmented copolyetheresteramides with uniform aramid segments (TΦT-PTMO). Because of uniform crystallizable TΦT units, TΦT–PTMO copolymers possess a very well-defined morphology. The rubbery modulus is temperature independent over a wide temperature range. The fracture strain is exceptionally high (1300%–2000%), which is especially interesting for elastane fiber applications.[6,7,8]

In this study the mechanical dynamic, tensile, and elastic properties of TΦT–PTMO copolymers were compared to some commercially available TPEs: TPE-U (Desmopan of Bayer) and TPE-E (Arnitel of DSM). Desmopan has polyether soft segments,[9] and Arnitel is a PBT–PTMO copolymer.[10] A hard and a soft grade of both types were tested: Desmopan KU2-8672 and Desmopan 955U, and Arnitel EM400 and Arnitel EL550.

EXPERIMENTAL

Materials

TΦT–PTMO copolymers have already been synthesized, as described in a previous article.[6,7] Arnitel was kindly provided by DSM and Desmopan by Bayer.

Dynamic Mechanical Analysis

Samples for the dynamic mechanical analysis (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 kept 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 functions of temperature were measured. Dried samples were first cooled to $-100°C$ and then heated at a rate of 1°C/min with the maximum of the loss modulus taken as the glass-transition temperature. The flow temperature was defined as the temperature in which the storage modulus reached 1 MPa.

Differential Scanning Calorimetry

The spectra from differential scanning calorimetry (DSC) were recorded on a PerkinElmer DSC7 apparatus equipped with a PE7700 computer and TAS-7 software. Samples of 2–5 mg of dried polymer 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, respectively, as the melting or crystallization temperature, and the peak area was used as the enthalpy.

Stress Relaxation

Samples (injection-molded test bars) for the stress relaxation experiments were similar to those used for DMA. Stress relaxation was measured on a Zwick Z020 universal tensile machine equipped with a $500N$ load cell, with the strain measured as the clamp displacement with a starting clamp distance of 40 mm. The samples were strained to 100% within 5 s at room temperature. The decay of the stress was measured during 30 min. The measure of stress relaxation ($SR_{x\%}$) used was the absolute value of the slope of the line, obtained from the stress plotted versus the logarithm of time .

$$SR_{x\%} = \frac{|\Delta\sigma_{x\%}|}{\Delta \log t} \qquad (1)$$

Compression Set

A piece of an injection-molded test bar, similar to those used for DMA, was placed between two steel plates and compressed to 1 mm (≈ 55 % compression). After 24 h at 20°C or at 70°C, the compression was released at room temperature. An hour later the thickness of the sample was measured again. The compression set was defined as:

$$\text{Compression set } = \frac{d_0 - d_2}{d_0 - d_1} \times 100\% \qquad (2)$$

where d_0 is the thickness (in millimeters) before compression, d_1 is the thickness (mm) during compression, d_2 is the thickness (mm) 1 h after release of compression.

Tensile Testing

Samples for the tensile tests were prepared by melt-extruding the polymers into threads on a 4-cc DSM res RD11H-1009025-4 corotating twin-screw miniextruder. The extruder temperature was set at 60°C above the flow temperature of the polymers, while the screw speed was kept constant at 30 rpm. The threads were wound at a speed range of 20–50 m/min. To calculate the cross-section of the threads, the titer was determined. The titer (expressed as tex $= 10^{-6}$ kg/m) of the threads was measured by carefully weighing 1 m of thread. The density of the polymers was determined in hexane, and for TΦT-PTMO copolymers it was approximately 1 g/cm³. Arnitel and Desmopan have a density of approximately 1.2 g/cm³ and 1.1 g/cm³, respectively.

Tensile tests were carried out on a Zwick Z020 universal tensile machine equipped with a $10N$ load cell, with the strain measured as the clamp displacement. Stress–strain curves were obtained at a strain rate of 250 mm/min, with a starting clamp distance of 25 mm. The tensile set was determined by applying a 300% cyclic strain at a strain rate of 200 mm/min, with a starting clamp distance of 50 mm. The strain in the second cycle, in which the force becomes positive again, was taken as the residual strain. The tensile set ($TS_{300\%}$) was defined as:

$$TS_{300\%} = \frac{\text{residual strain}}{300} \times 100\% \qquad (3)$$

Cyclic Tensile Tests

Cyclic tensile tests were done on a Zwick Z020 universal tensile machine equipped with a $10N$ load cell, with the strain measured as the clamp displacement. Cyclic stress–strain curves were obtained at a straining rate of 200 mm/min, with a starting clamp displacement of 50 mm. Until 100% strain, the strain increased 20% each cycle, followed by a strain increase of 100% each cycle until the sample broke. The initial modulus at the start of a load cycle was determined manually at approximately 5% strain.

RESULTS AND DISCUSSION

This analysis will first discuss the differences in synthesis and melt processing among TΦT–
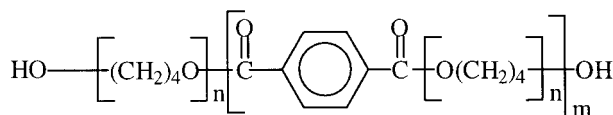
Figure 2 Structure of DMT-extended PTMO (PTMO–DMT).

PTMO, Arnitel, and Desmopan. Then the dynamic mechanical properties of TΦT–PTMO copolymers will be compared to TPE-U and TPE-E, followed by a comparison of their elasticities (stress relaxation, compression set). To make very soft TΦT-PTMO copolymers requires low TΦT concentrations, which means long PTMO segments (>3000 g/mol). Long PTMO segments can be obtained by extending short PTMO blocks with dimethyl terephthalate (DMT), as shown in Figure 2. A previous study[7] showed that the incorporation of DMT in the PTMO phase does not lead to an increase of the T_g.

A series of TΦT–(PTMO$_{1000}$/DMT) copolymers of varying weight percentages— TΦT–(PTMO$_{1000}$/DMT)$_{1000-9000}$ (3–22 wt % TΦT)—was used to compare the elasticity to TPE-U and TPE-E. The tensile properties of the unoriented threads were compared. The composition, DMA, and elastic properties of the TΦT–PTMO, TΦT–(PTMO$_{1000}$/DMT), Arnitel, and Desmopan are summarized in Table II.

Polymerization and Melt Processing

It was found that during the polymerization of segmented copolymers, melt phasing of the hard and soft segments is likely to occur.[3] Melt phasing might inhibit the formation of high-molecular-weight polymers. As diisocyanates react very rapidly, melt phasing is often not a limiting factor in the polymerization of TPE-U. Esters and amides, however, react much slower, and hence melt phasing can be a problem during the polymerization of TPE-E and TPE-A. Melt phasing is enhanced by using high hard-segment concentrations and/or long PTMO segments.[11] In Figure 3 melt phasing in the polycondensation of PBT–PTMO copolymers as functions of the PTMO content and length is shown. In PBT–PTMO copolymers decreasing the PTMO content while keeping the PTMO length constant results in an increase of the PBT segment length. Longer PBT segments melt-phase at a lower concentration than do short PBT segments. The TΦT units are uniform and short in length. As a result, the PTMO content in the TΦT-PTMO and TΦT–(PTMO$_{1000}$/DMT) copolymers is so high that melt phasing apparently does not occur. To illustrate this, the points of TΦT–PTMO and TΦT–(PTMO$_{1000}$/DMT) are included in Figure 3. The melt-phasing region of TΦT–PTMO and TΦT–(PTMO$_{1000}$/DMT) probably lies at a somewhat different polymer compo-

Table II   Composition, DMA Properties, and Elasticity of TΦT–PTMO, TΦT–(PTMO$_{1000}$/DMT), Arnitel, and Desmopan

| TΦT-Based Polymers Soft Segment	TΦT [wt %]	G' (25°C) [MPa]	T_g [°C]	T_{fl} [°C]	$SR_{25\%}$ [—]	$SR_{100\%}$ [—]	Compression Set 55%, $T = 20°C$	Compression Set 55%, $T = 70°C$
PTMO$_{650}$		29	118	−58	247	—	—	—
PTMO$_{1000}$	22	44	−69	216	0.68	0.82	31	48
PTMO$_{1400}$	17	15	−70	198	0.37	0.70	21	48
PTMO$_{2000}$	13	10	−65	191	0.21	0.48	19	42
PTMO$_{2900}$	9	6	−70	170	0.11	0.37	22	40
(PTMO$_{1000}$/DMT)$_{1532}$	16	17	−66	201	—	—	17	38
(PTMO$_{1000}$/DMT)$_{1996}$	13	11	−65	188	0.21	0.47	13	38
(PTMO$_{1000}$/DMT)$_{3102}$	9	6	−65	172	0.11	0.29	15	47
(PTMO$_{1000}$/DMT)$_{4221}$	7	4	−65	155	0.10	0.27	24	55
(PTMO$_{1000}$/DMT)$_{6156}$	6	3	−66	140	0.09	0.24	—	—
(PTMO$_{1000}$/DMT)$_{7024}$	4	2	−65	119	—	0.15	21	66
(PTMO$_{1000}$/DMT)$_{9005}$	3	1.5	−65	102	0.06	0.14	23	67
Commercial polymers								
Arnitel EM400	—	18	−70	182	0.30	0.43	15	36
Arnitel EL550	—	67	−50	205	0.45	0.52	30	58
Desmopan KU-8672	—	11	−45	150	0.21	0.45	13	41
Desmopan 955u	—	91	−31	176	0.94	1.00	23	60
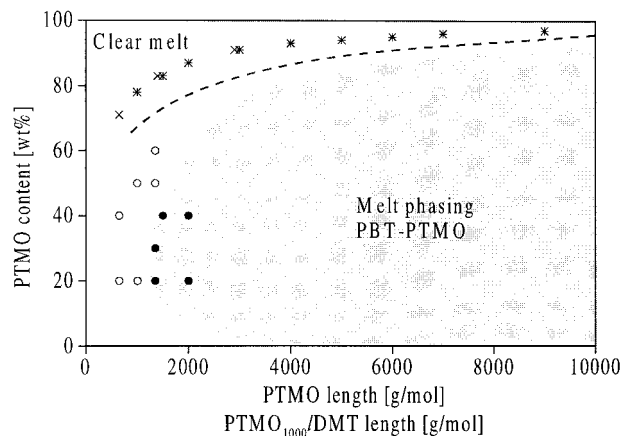
Figure 3 Melt phasing in polycondensation as a function of PTMO or (PTMO$_{1000}$/DMT) content and length for (●,○) PBT–PTMO,[7] (×) TΦT–PTMO, and (∗) TΦT–(PTMO$_{1000}$/DMT). The melt-phasing region of PBT–PTMO is indicated; the dotted line indicates the expected melt-phasing transition of TΦT–PTMO and TΦT–(PTMO$_{1000}$/DMT) copolymers.

sition than does PBT–PTMO, indicated by the dotted line.

In order to obtain a well-crystallizable and high-melting segment in TPE-E, at least four PBT repeat units are needed. Very soft TPE-E cannot be obtained because long PBT segments melt-phase in high-molecular-weight polyether segments. In TΦT–PTMO copolymers melt phasing was not observed because the uniform TΦT units are short. Very low concentrations of TΦT can be used in order to obtain soft materials that are high melting and fast crystallizing.

With DSC the melting and crystallization peaks of TΦT–PTMO copolymers were only visible at a TΦT concentration higher than 20 wt %. Remarkable about the series TΦT–(PTMO$_{1000}$/DMT)$_{1000-9000}$ is that polymers containing less than 17 wt % TΦT are transparent while TPE-E

is generally opaque. Apparently, the TΦT crystals are smaller than the wavelength of visible light. In Table III the DSC results of TΦT–PTMO, Arnitel, and Desmopan are shown.

The TΦT undercooling (T_m–T_c) was always lower than 30°C, suggesting that the polymers crystallize faster than Arnitel and Desmopan, whose undercooling ranged from 66°C to 96°C. TΦT–PTMO copolymers crystallize very fast, allowing short injection molding cycles, and the crystallization is nearly complete, unlike Arnitel and Desmopan, which crystallize much more slowly and incompletely. On heating a TPE-E or TPE-U, polyester or polyurethane crystallinity is expected to increase because of an increase of chain mobility, making the properties temperature dependent.

Dynamic Mechanical Analysis

In Table II the DMA and elastic properties of Arnitel and Desmopan are shown. For both types of polymers the softer grades (lower G′ at 25°C)) have a lower glass-transition temperature than the harder grades (higher modulus), which contain a higher concentration of hard segments. Because of incomplete phase separation the concentration of hard segments mixed with amorphous soft segments increases with overall hard-segment content. This explains the observed higher T_g for the harder grades of Arnitel and Desmopan as compared to the softer grades. In TΦT–PTMO copolymers, on the other hand, phase separation is almost complete; virtually no TΦT units are present in the amorphous phase. Therefore, in TΦT–PTMO copolymers the T_g essentially does not depend on the TΦT content and is low (Table II).

In Figure 4 the storage modulus is plotted versus the temperature for Arnitel, Desmopan and

Table III   DSC Results of TΦT–PTMO, Arnitel, and Desmopan

Polymer	T_m (°C)	T_{fl}[a] (°C)	ΔH_m (J/g)	T_c (°C)	$T_m - T_c$ (°C)
TΦT–PTMO$_{650}$	266	247	12	238	28
TΦT–PTMO$_{1000}$	222	216	10	203	19
Arnitel EM400	195	182	16	99	96
Arnitel EL550	204	205	27	138	66
Desmopan KU-8672	166	150	5	100	66
Desmopan 955u	183	176	14	103	80

[a] Determined with DMA.

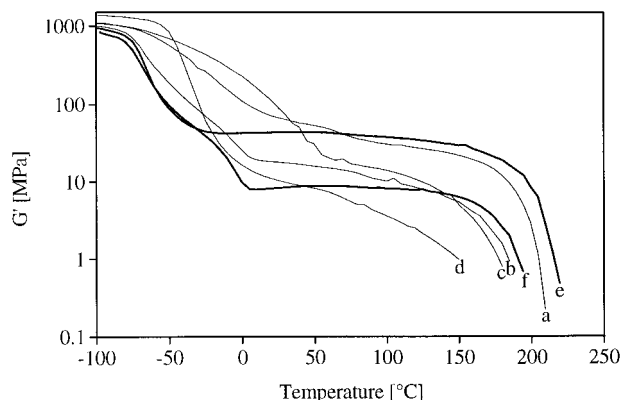**Figure 4** Storage modulus versus temperature for: (a) Arnitel EL550; (b) Arnitel EM400; (c) Desmopan 955u; (d) Desmopan KU-8762; (e) TΦT–PTMO$_{1000}$; and (f) TΦT–PTMO$_{2000}$.

TΦT-PTMO. The storage modulus of Desmopan (curves c and d) shows a very broad glass transition, the absence of a real rubbery plateau, and a poor defined melting transition. The storage modulus of Arnitel (curves a and b) shows a rubbery plateau, although it is temperature dependent, and a melting transition. Finally, TΦT–PTMO copolymers (curves e and f) possess a very sharp glass transition, a temperature-independent rubbery plateau, and a sharp melting transition. The constant rubbery plateau of TΦT–PTMO can be explained by its complete phase separation. Virtually no TΦT units are present in the PTMO phase, resulting in a low and sharp T_g. In addition, the TΦT units form crystalline lamellae of a uniform thickness, melting in a narrow temperature range. In general, the melting temperature of a polymer depends on the lamellar thickness.[12] Arnitel and especially Desmopan do not have a very distinct flow transition since they contain crystalline lamellae with a range of thicknesses.

The absence of a real rubbery plateau in Desmopan confirms that TPE-U possesses a complicated morphology with several glass- and melting transitions because of liquid–liquid demixing and incomplete phase separation of the hard and soft segments. The viscosity of multiphase polymer melt is often higher than that of a homogeneous polymer melt.[13] Therefore, melt processing of a TPE-U can be difficult. TΦT–PTMO copolymers form a homogenous melt and are consequently easily melt processible.

Figure 4 shows that soft TΦT–PTMO copolymers (low TΦT content and thus low rubbery modulus) still have a high melting temperature

(e.g., curve f). The soft grades of Arnitel and Desmopan have a lower melting temperature and consequently a lower heat stability than the TΦT–PTMO copolymers. In Figure 5 the flow temperature is plotted versus the shear rubbery modulus for TΦT–(PTMO$_{1000}$/DMT), Arnitel, and Desmopan. The flow temperature decreases with decreasing rubbery modulus. The decrease of the shear rubbery modulus is caused by a decrease in the physical crosslink density because of a decrease in the hard-segment concentration. According to the solvent effect described by Flory,[14] the melting temperature of a segmented copolymer decreases with decreasing hard-segment content. From Figure 5 it is clear that of the three types of materials, TΦT–PTMO copolymers have the highest flow temperature.

Elasticity

For a thermoplastic elastomer elasticity is one of the most important properties. Stress relaxation gives an indication of elasticity. In an ideal elastomer no stress relaxation occurs because there is no plastic deformation. Generally, a lower stress relaxation corresponds with a lower permanent deformation.[15] Stress relaxation was quantified by the absolute value of the slope of the line obtained by plotting stress versus logarithm of time at 25% or 100% strain. In Figure 6 stress relaxation is plotted versus (a) shear rubbery modulus and (b) flow temperature for TΦT–(PTMO$_{1000}$/DMT), Arnitel, and Desmopan. In general, the modulus increases with increased physical crosslink density. Here the physical crosslinks are either crystals or glassy domains.
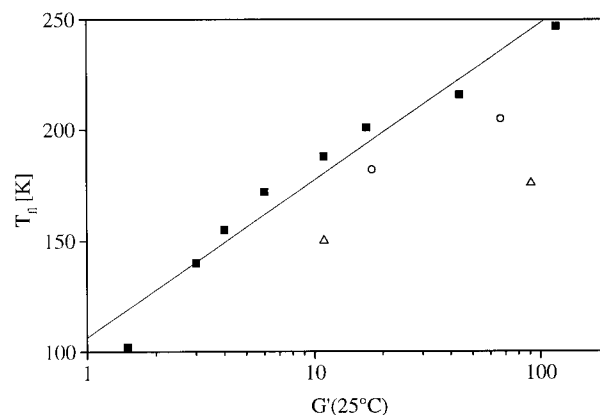

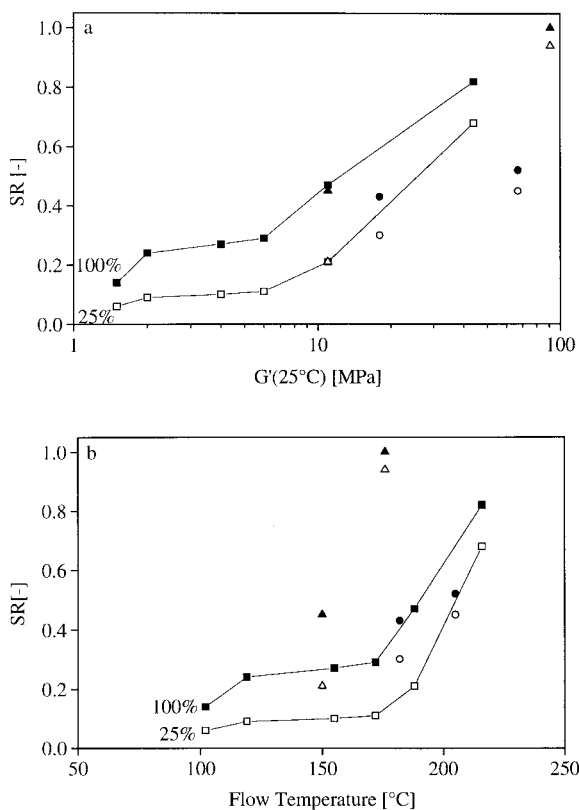**Figure 5** Flow temperature versus shear rubbery modulus for: (■) TΦT–(PTMO$_{1000}$/DMT); (○) Arnitel, (△) Desmopan.

Figure 6 Stress relaxation versus (a) shear rubbery modulus and (b) flow temperature at 25% strain for (□) TΦT–(PTMO$_{1000}$/DMT), (○) Arnitel, and (△) Desmopan; and at 100% strain for (■) TΦT–(PTMO$_{1000}$/DMT), (●) Arnitel, and (▲) Desmopan.

As expected, stress relaxation increases with increasing modulus for all the polymers as a result of an increase in the physical crosslink density. The stress relaxation of Desmopan is similar to that of TΦT–(PTMO$_{1000}$/DMT). Arnitel, however, has a lower stress relaxation. This might be explained by the presence of thick PBT lamellae, which are harder to deform than are the thin TΦT lamellae. Hence, at relatively low deformation (≤100%) the elasticity of Arnitel is better than that of Desmopan and the TΦT–(PTMO$_{1000}$/DMT) copolymers. On the other hand, Figure 6(b) shows that of the polymers with a similar flow (melting) temperature, TΦT–(PTMO$_{1000}$/DMT) copolymers have a lower stress relaxation than Desmopan and a stress relaxation comparable to Arnitel. In TΦT–(PTMO$_{1000}$/DMT) copolymers a high elasticity can be combined with a relatively high melting temperature. Furthermore, in a previous study[16] it was shown that the elasticity of TΦT-PTMO copolymers can be improved by extending the TΦT units with a diol, for instance, 1,12-dode-

canediol. This was attributed to the formation of a multiphase system. A crystalline network in an amorphous matrix is expected to plastically deform more than a multiphase system.

In Figure 7 the compression set is plotted versus the shear rubbery modulus and the flow temperature for TΦT–(PTMO$_{1000}$/DMT), Arnitel, and Desmopan.

For TΦT–(PTMO$_{1000}$/DMT) copolymers a minimum in the compression set at a rubbery modulus of 6 MPa is observed. The decrease of the compression set with decreasing modulus can be explained by a decrease in the TΦT content, resulting in a decrease in crystallinity. Apparently, if TΦT content is very low, the physical crosslink density becomes too low to respond effectively to a compression of 24 h, which might explain the observed increase of the compression set at very low TΦT concentrations. Figure 7(a) suggests that at 20°C the compression set of TΦT–
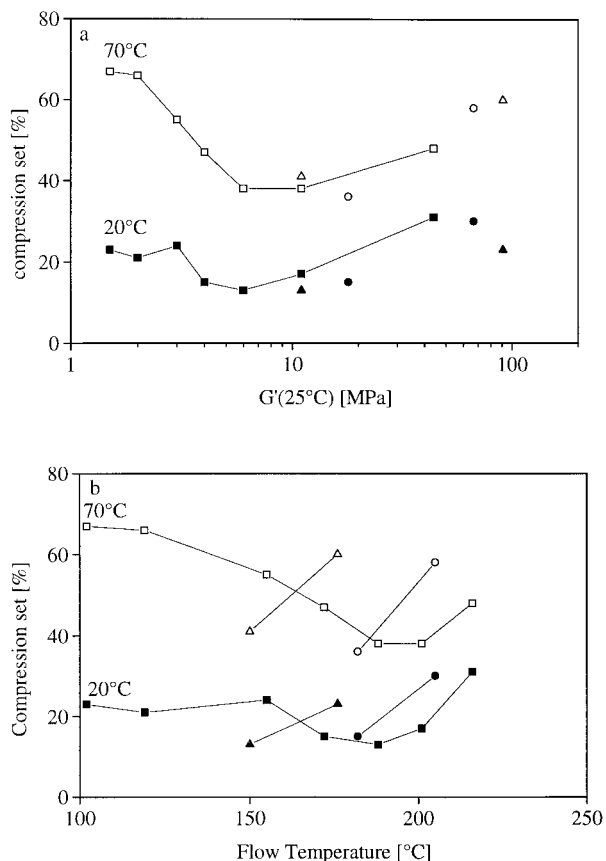

Figure 7 Compression set versus (a) shear rubbery modulus and (b) flow temperature at 20°C for (■) TΦT–(PTMO$_{1000}$/DMT), (●) Arnitel, (▲) Desmopan; and at 70°C for (■) TΦT–(PTMO$_{1000}$/DMT), (○) Arnitel, and (△) Desmopan.
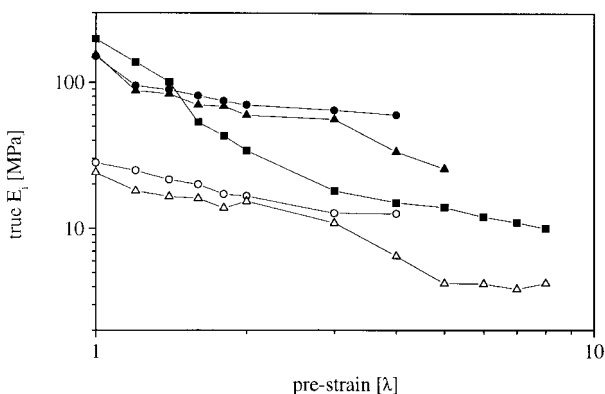
Figure 8 Decrease of true initial modulus ($E_{5\%}$) in a cyclic tensile test as a result of prestraining for: (■) TΦT–PTMO$_{1000}$; (●) Arnitel EL550; (▲) Desmopan 955u; (○) Arnitel EM400; and (△) Desmopan KU-8762.

(PTMO$_{1000}$/DMT) is somewhat higher than that of Arnitel and Desmopan. However, Figure 7(b) shows that this is only the case for the polymers with a relatively low melting temperature. TΦT–(PTMO$_{1000}$/DMT) copolymers with a flow temperature of 170°C and higher have a lower compression set than do Arnitel and Desmopan with a similar melting temperature.

Strain Softening

During straining of a segmented copolymer, the soft segments are stretched, thereby exercising forces on the crystalline domains. This process, which is called strain softening, leads to disruption of the crystalline network. In a cyclic tensile test the "second" initial modulus is lower compared than the original initial modulus.[3] In Figure 8 the decrease of the true initial modulus ($E_{5\%}$) in a cyclic tensile test is given for TΦT–PTMO$_{1000}$, Arnitel, and Desmopan.

The decrease of the modulus of TΦT–PTMO$_{1000}$ is stronger than that for Arnitel and Desmopan, which might be explained by the TΦT crystalline network being more easily disrupted than that of Arnitel or Desmopan because of the extremely thin TΦT lamellae (1.8 nm). In general, yield stress decreases with decreasing lamellar thickness[17]. These results are in good agreement with the higher stress relaxation of TΦT–PTMO copolymers as compared to Arnitel types with a similar rubbery modulus.

Tensile Properties

In Table IV the tensile properties of Arnitel, Desmopan, TΦT-PTMO, and TΦT–(PTMO$_{1000}$/DMT) copolymers are given. The fracture strain of TΦT–PTMO and TΦT–(PTMO$_{1000}$/DMT) is very high and higher than that of Arnitel and Desmopan. A previous study[8] explained that the thin TΦT lamellae are easily deformed, leading to high stretchability of the PTMO soft segments, which in turn results in a high fracture strain. Apparently, the hard phase in Arnitel and Desmopan is more difficult to deform. The fracture stress of Arnitel and Desmopan is higher than that of TΦT–PTMO and TΦT–(PTMO$_{1000}$/DMT), probably because of more strain-induced crystallization. However, the true stress of TΦT–PTMO and TΦT–(PTMO$_{1000}$/DMT)$_{2000}$ copolymers is higher, and therefore the fracture energy is also expected to be higher.

The yield stress of a polymer depends on crystallinity and lamellar thickness.[17] In TΦT–PTMO copolymers lamellar thickness is constant, and consequently yield stress increases with TΦT concentration. In Figure 9 yield stress is plotted versus shear rubbery modulus for TΦT–(PTMO$_{1000}$/DMT), Arnitel, and Desmopan. The increase of yield stress with increasing rubbery modulus of Arnitel EL550 is much higher than that of TΦT–(PTMO$_{1000}$/DMT), suggesting that lamellar thickness as well as crystallinity is increased in Arnitel EL550.

For application as an elastane fiber the tensile set after 300% strain is an important parameter as a measure of elasticity. In Figure 10 the tensile set is plotted versus shear rubbery modulus and flow temperature for Arnitel, Desmopan, and TΦT–(PTMO$_{1000}$/DMT). The tensile set decreases with decreasing rubbery modulus because of a decrease of the physical crosslink density. After 300% strain the tensile set of Arnitel is higher than that of TΦT–(PTMO$_{1000}$/DMT). There are two explanations for this. First, Arnitel might strain-crystallize more than TΦT–(PTMO$_{1000}$/DMT), which also explains the higher fracture stress of Arnitel. Second, the PBT lamellae of Arnitel are thicker than the TΦT lamellae. This makes them harder to deform, resulting in better elasticity at relatively low deformations [<100% (Fig. 6)], but at higher deformations they are also deformed, and once they are deformed the plastic deformation is higher than that of the TΦT crystalline lamellae. For Desmopan the situation is different. At low deformation [<100% (Fig. 6)] the elasticity is comparable to TΦT–(PTMO$_{1000}$/DMT), but the tensile set after 300% strain is lower than that of TΦT–(PTMO$_{1000}$/DMT). Desmopan possesses a complicated morphology, with

Table IV   DMA and Tensile Properties of Threads of Arnitel, Desmopan, TΦT–PTMO, and TΦT–(PTMO$_{1000}$/DMT)

TΦT-Based Polymers	TΦT (% wt)	η_{inh} (dL/g)	T_g (°C)	T_{fl} (°C)	G' (25°C) (MPa)	σ_y (MPa)	σ_b (MPa)	λ_b [—]	$TS_{300\%}$ (%)
TΦT–PTMO$_{1000}$	22	1.81	−69	216	44	9.8	38.1	14.7	46
TΦT–PTMO$_{2000}$	13	2.20	−65	191	9	5.7	51.9	17.6	27
TΦT–PTMO$_{2900}$	9	2.74	−65	170	6	3.4	58.8	16.6	39
TΦT–(PTMO$_{1000}$/DMT)$_{1532}$	16	1.74	−66	201	17	6.6	17.0	17.4	37
TΦT–(PTMO$_{1000}$/DMT)$_{1996}$	13	1.48	−65	188	11	5.5	9.2	18.4	29
TΦT–(PTMO$_{1000}$/DMT)$_{3102}$	9	2.07	−65	172	6	3.7	13.2	21.6	21
TΦT–(PTMO$_{1000}$/DMT)$_{4221}$	7	2.23	−65	155	4	3.1	21.3	14.8	14
TΦT–(PTMO$_{1000}$/DMT)$_{6156}$	5	2.29	−65	140	3	2.7	25.2	14.0	10
TΦT–(PTMO$_{1000}$/DMT)$_{9025}$	3	1.67	−65	102	1.5	1.2	15.2	21.7	9
Commercial polymers									
Arnitel EM400	—	—	−70	182	18	5.7	61	9.6	41
Arnitel E550	—	—	−50	205	67	16.5	106	5.7	76
Desmopan KU-8672	—	—	−45	150	11	5.0	79	10.5	18
Desmopan 955u	—	—	−31	176	91	10.0	86	9.3	30

σ_y: yield stress; σ_b: fracture stress, λ_b: fracture strain, TS: tensile set

several glass and melting transitions, as a result of phase separation through liquid–liquid demixing. In a previous study[16] it was shown that such a multiphase structure yields an improved elasticity compared to materials with a simple two-phase structure (one crystalline phase and one amorphous phase). Apparently, for Desmopan the improved elasticity is applicable at strains above 100%. By incorporating a diol, that is, 1,12-dodecanediol, as an extender of the TΦT units, a multiphase structure can be introduced into TΦT–PTMO copolymers, and these polymers have an improved elasticity.[16] On the other hand, Figure 10(b) shows that
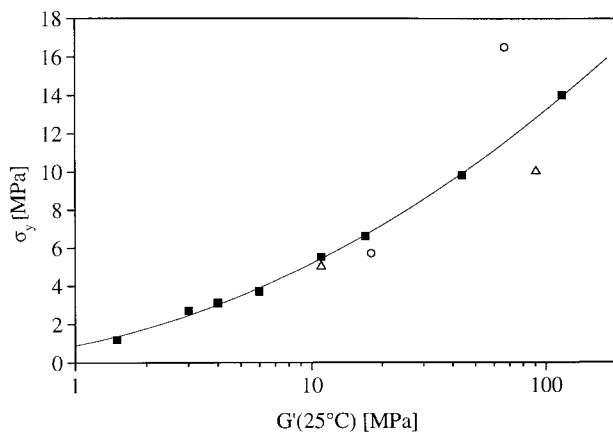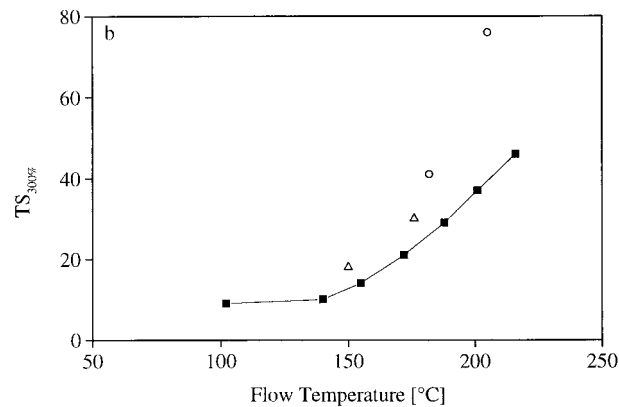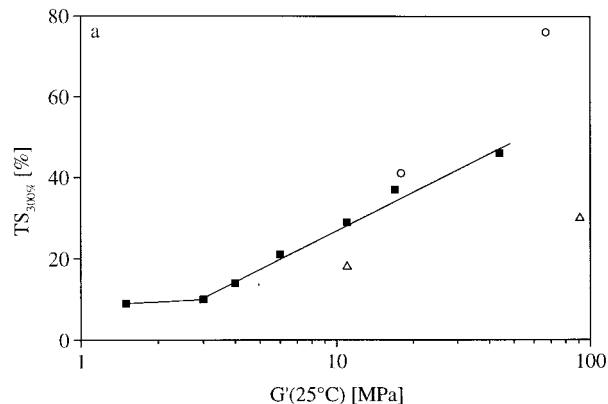

Figure 10   Tensile set after 300% strain versus (a) shear rubbery modulus and (b) flow temperature for: (■) TΦT–(PTMO$_{1000}$/DMT); (○) Arnitel; and (△) Desmopan.

Figure 9   Yield stress versus shear rubbery modulus for (■) TΦT–(PTMO$_{1000}$/DMT) and TΦT–PTMO$_{650}$, (○) Arnitel, and (△) Desmopan.

for polymers with a similar flow temperature, the tensile set of the TΦT-containing polymers is lower than those of Arnitel and Desmopan. Consequently, TΦT-containing polymers possess high elasticity combined with good heat stability.

CONCLUSIONS

The properties of TΦT–PTMO copolymers were compared to a commercial copolyetherester (Arnitel) and a segmented polyurethane (Desmopan). TΦT–PTMO copolymers form a homogeneous melt during polymerization as well as during melt processing. Consequently, high-molecular-weight copolymers are easily formed; even polymers containing very long PTMO segments can be synthesized and processed easily. The undercooling of the TΦT crystals in the polymers is low, suggesting the crystallization rate is higher than for TPE-E and TPE-U, leading to a shorter injection molding cycle. At a low TΦT content TΦT–(PTMO$_{1000}$/DMT) copolymers are transparent. Furthermore, the presence of TΦT crystals makes these materials very chemically resistant.

Compared to Arnitel and Desmopan, TΦT–PTMO copolymers have a low and sharp glass=transition temperature, a temperature-independent rubbery plateau, and a high and sharp melting transition. These give them a large service temperature range. All this can be attributed to the uniform TΦT crystals, which almost completely crystallize into lamellae of uniform thickness, melting in a narrow temperature range.

The flow temperature (melting temperature) of TΦT–PTMO copolymers is higher than those of Arnitel and Desmopan, which means the heat stability of TΦT–PTMO copolymers is better. The TΦT units already crystallize at extremely low concentrations, and consequently very soft materials with a relatively high melting temperature can be obtained. These soft polymers combine a high elasticity with a relatively high melting temperature as compared to TPE-E and TPE-U. At relatively low deformations (<100%) the harder TΦT–PTMO copolymers [G′ (25°C) > 10 MPa] have an elasticity similar to Desmopan but a somewhat lower elasticity than Arnitel. It is probable that the thin TΦT

lamellae (1.8 nm) are already easily deformed at lower deformations, resulting in a relatively high degree of plastic deformation. After a tensile strain of 300%, however, the tensile set of Arnitel is higher than that of TΦT–PTMO copolymer. Along with an extremely high fracture strain (>1300%), TΦT–PTMO copolymers are also interesting materials for melt-spinnable elastane fibers. After orientation in the spin line, a fiber with a low tensile set and a high fracture strain can be obtained.[18] The tensile set of Desmopan is lower than that of the TΦT-PTMO copolymer; however, the heat stability of Desmopan is insufficient.

REFERENCES

1. Holden, G. In Thermoplastic Elastomers, 2nd ed.; Holden, G.; Legge, N. R., Quirk, R., Schroeder, H. E., Eds.; Hanser: Munich, 1996; Chapter 16.
2. Creemers, H. M. J. C., Kunststoffe 1996, 86, 1845.
3. Grady, B. P.; Cooper, S. L. In Science and Technology of Rubber; Mark, J. E., Erman, B., Eirich F. R., Eds.; Academic Press: San Diego, 1978; Chapter 13.
4. Cella, R. J. J Polym Sci: Polym Symp 1973, 42, 727.
5. Gaymans, R. J.; de Haan, J. L. Polymer 1993, 34, 4360.
6. Niesten, M. C. E. J.; Feijen J.; Gaymans, R. J. Polymer 2000, 41, 8487.
7. Niesten, M. C. E. J.; Te Brinke, J. W.; Gaymans, R. J., Polymer 2001, 42, 1461.
8. Niesten, M. C. E. J.; Gaymans, R. J. Polymer, in press.
9. Bayer, product information.
10. DSM, product information.
11. Adams, R. K.; Hoeschele, G. K., In Thermoplastic Elastomers, 1st ed.; Legge, N. R., Holden, G., Schroeder, H. E., Eds.; Hanser: Munich, 1987; Chapter 8.
12. Hiemenz, P. C. Polymer Chemistry, the Basic Concepts; Marcel Dekker: New York, 1984; Chapter 4.
13. Utracki, L. A., In Two Phase Polymer Systems; Utracki, L. A., Ed.; Hanser: Munich, 1991; Chapter 1.
14. Flory, P. J. Trans Faraday Soc 1955, 51, 848.
15. KubÁt, J.; Rigdahl, M. In Failure of Plastics; Browstow, W., Corneliussen, R. D., Eds.; Hanser: Munich 1986; Chapter 4.
16. Niesten, M. C. E. J.; Bosch, H.; Gaymans, R. J. Appl Polym Sci, in press.
17. Young, R. J. Mater Forum 1988, 11, 210.
18. Niesten, M. C. E. J.; Krijgsman, J.; Gaymans, R. J. Chemical Fibers International 2000, 50, 256.