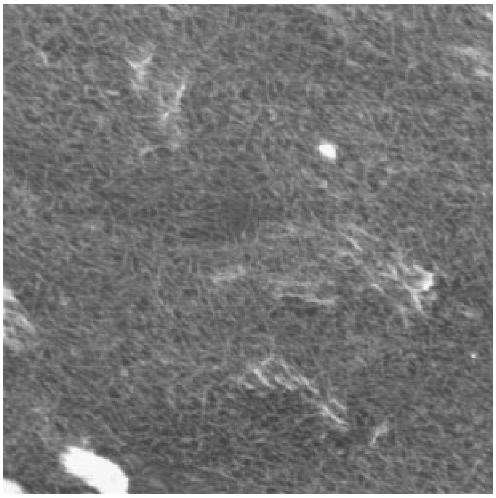
Macromolecular
Journals

Thermoplastic Polyurethanes with Poly(butylene terephthalate) as Crystallizable Hard Phase

Debasish De, Reinoud J. Gaymans*

Polyurethanes were prepared from poly(tetramethylene oxide) end-capped with MDI and PBT extenders. The PBT extenders were random-disperse in length and their length varied from three to seven repeating units. The structure of the polyurethanes was studied by FT-IR and AFM, their thermal and thermomechanical responses were measured by DSC and DMTA, and their elastic behavior was assessed by compression set measurements. The MDI-PBT-MDI hard segments had a ribbon-like crystalline morphology. Increasing the PBT length gave rise to an increase of the storage modulus at room temperature and the melting point. The storage modulus depended strongly on temperature.



Introduction

Thermoplastic polyurethane (TPU) represents an important material within the class of segmented block copolymers. The urethane segments in TPU are mostly made up of diphenyl methane diisocyanate (MDI) and butanediol (BDO), –MDI–(DBO–MDI)n–.[1,2] The properties of segmented block copolymers are dependant on the type and extent of phase separation between soft segments (SS) and hard segments (HS). If this phase separation occurs through crystallization, the modulus increases strongly with the HS content.[2] MDI-based polyurethanes are often slow-crystallizing materials with a low HS crystallinity (≈20%) and this as a result of the bonding angle of the methylene group in the MDI.[2]

Poly(butylene terephthalate) (PBT) has a regular chemical structure, is a fast crystallizing polymer and has a relative high crystallinity (≈40%). PBT has no H-bonding interactions and as a result of this is the miscibility with other polymers better than polyamides and polyurethanes. Due to the increased miscibility between PBT and polyether is in these segmented block copolymers liquid-liquid demixing of PBT segments less likely. Moreover, the melting temperature of the PBT is limited to 228 °C. Thus, long PBT segments can be incorporated in copolymers without liquid-liquid demixing taking place

D. De, R. J. Gaymans
University of Twente, P. O. Box 217, 7500AE Enschede,
The Netherlands
E-mail: r.j.gaymans@utwente.nl
D. De
Dutch Polymer Institute (DPI), P. O. Box 902, 5600 AX Eindhoven,
The Netherlands

DOI: 10.1002/mame.200700356

and without the melting temperature getting too high. PBT segments can also be incorporated in polyurethanes and these copolymers are commercially available but in the open literature, little is reported on them.

The present paper reports on polyurethanes obtained from PTMO end-capped with MDI (2 847 g · mol^{-1}) and PBT-diol extenders. The length (content) of the PBT-diol extenders was varied. The length of the PBT extenders was expected to significantly influence the TPU properties. The PBT extenders were prepared in a separate step. The TPUs were characterized by IR, AFM, DSC, DMTA, Shore A hardness and compression set measurements.

Experimental Part

Materials

Dimethyl terephthalate (DMT), butane diol (BD), anhydrous *N,N*-dimethyl acetamide, diethyl ether, and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) were purchased from Aldrich and used as received. PTMO end-capped with 4,4′-methylene bis(phenyl isocyanate) (MDI) (Adiprene LFM 300) with an NCO content of 3.1 wt.-% and a free MDI content typically <0.5 wt.-% was donated by Crompton.

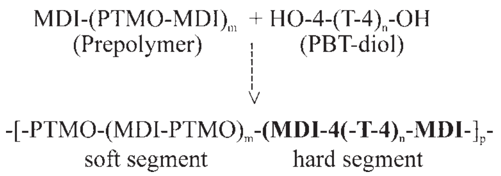
Synthesis of PBT-Diol Segments (Scheme 1)

The preparation of random 4(T4)$_3$ is here given as an example. 1,4-Butanediol (0.4 mol, 36 g) was reacted with 0.3 mol (58.2 g) dimethyl terephthalate (DMT) and titanium tetrabutoxide (catalyst, 0.08 g) at 150 °C for 2 h and at 180 °C for 6 h in a nitrogen atmosphere. The reaction byproduct methanol was removed from the reaction vessel by using a Dean-Stark apparatus. The remaining reaction product was washed with distilled water after cooling.

The polymerization temperature of the longer PBT segments with a higher melting temperature was increased for the oligomers with a repeat length of 4, 5 and 7 to 190, 210, 230 °C, respectively.

Synthesis of PBT-Based Polyurethane (Scheme 2)

The typical synthesis procedure of polyurethane based on 4(T4)$_3$ PBT-diol segments is here described as an example. Segmented polyurethane was synthesized from poly(tetramethylene oxide) (PTMO) end-capped with diphenyl methane diisocyanate (MDI) (2 847 g · mol^{-1}) and extended with PBT-diol. Before polymerization, the prepolymer, extender and polymerization set-up were dried overnight under vacuum at 80 °C. Initially, 20 g (7.02 × 10^{-3} mol) prepolymer was charged to the reactor and 40 mL dry DMAc was added to make a homogeneous solution of the prepolymer. The initial reactor temperature was 100 °C. 5.27 g (7.02 × 10^{-3} mol) of PBT-diol extender was dissolved in 25 mL dry DMAc at a temperature of 140 °C. This solution was added to the reactor and immediately after the addition, a white precipitate formed. Increasing the reactor temperature to 140 °C rendered the reaction mass transparent again. This temperature was maintained for 30 min, after which the reaction was continued for 4 h and 30 min at 120 °C in a dry nitrogen atmosphere. After 5 h of reaction, solvent stripping was performed, initially with low vacuum (by use of membrane pump) and finally with high vacuum (pressure <0.3 mbar). The vacuum was applied for 60 min at 120 °C to ensure that the synthesized polyurethane was completely solvent free. The reactor was subsequently cooled by liquid nitrogen under reduced pressure and the synthesized polyurethane was removed and dried overnight in a vacuum oven at 50 °C prior to further application. The same procedure was followed for the synthesis of the other ester-based polyurethanes. Scheme 2 represents the typical synthesis procedure for the PBT-extended polyurethane.



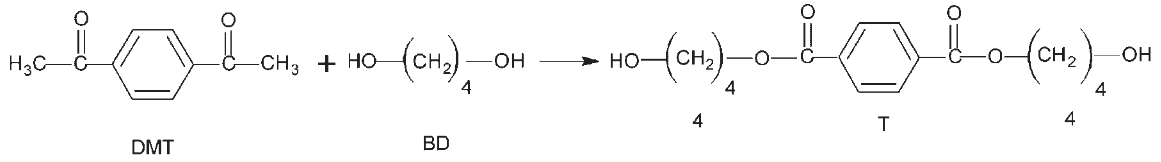
Scheme 2. Synthesis procedure for polyurethane with PBT segments.

Viscometry

The inherent viscosity of the segmented polyurethanes was measured in a mixture of phenol and 1,1,2,2-tetrachloroethane (1:1 mol ratio) at 25 °C with a capillary Ubbelohde type 1A apparatus. Solutions with concentrations of 0.1 g · dL^{-1} were employed for the viscosity measurements.

Fourier Transform Infrared (FT-IR) Spectra

Infrared spectra were recorded using a Biorad FTS-60. Polymer films no thicker than 10 μm were prepared from a 5% solution of polymer in hexafluoroisopropyl alcohol (HFIP). The film was placed between two KBr pellets in a nitrogen atmosphere.



Scheme 1. Synthesis procedure for PBT-diol segments.

Atomic Force Microscopy (AFM)

AFM samples were prepared from a 5% polymer solution in HFIP. The film thickness was approximately 30 μm. The AFM measurements were performed with a Nanoscope IV controller (Veeco Inc.) operating in tapping mode. The AFM was equipped with a J-scanner with a maximum size of 200 μm^2. Si-cantilevers (Veeco) were used to obtain height and phase images. The amplitude in free oscillation was 5.0 V. The operating set point value (A/A_0) was relatively low at 0.70. Scan sizes were 1–3 μm^2 in order to obtain the best contrast.

Differential Scanning Calorimetry

DSC thermograms were recorded on a Perkin Elmer DSC apparatus, equipped with a PE 7700 computer and TAS-7 software. A sample of 10–12 mg of dry polymer was heated at 20 °C · min^{-1} to 20 °C above the melting temperature of the polymer. A cooling scan was then performed at 20 °C · min^{-1}. A second heating scan was subsequently carried out and all presented thermal data were taken from this scan. The heat of fusion of the HS in the polyurethanes was calculated as heat of fusion per gram HS.

Compression Molding

Test samples for dynamic mechanical thermal analysis (DMTA) and compression set (CS) measurements were prepared by compression molding with a 40 ton Lauffer 40 press. Prior to the compression molding, the crushed polymer was dried overnight in a vacuum oven at 50 °C. Approx. 1.8 g of the polymer was then uniformly spread into a bar-shaped mold ($80 \times 9 \times 2$ mm^3). The compression molding was carried out by compressing-decompressing the sample four times (in order to remove any air bubbles) at 230 °C for 1 min at 8.5 MPa.

Dynamic Mechanical Thermal Analysis (DMTA)

The compression molded test samples with dimensions of $70 \times 9 \times 2$ mm^3 were dried in a vacuum oven at 50 °C overnight before use. The DMTA spectra were recorded with a Myrenne ATM3 torsion pendulum at a frequency of 1 Hz and 0.1% strain. The samples were cooled to −100 °C and subsequently heated at a rate of 1 °C · min^{-1}. The glass transition temperature (T_g) of the polymer was defined as the temperature at which the loss modulus reached its maximum value, and the flow temperature (T_{flow}) was defined as the temperature at which the storage modulus reached 0.5 MPa. The temperature at which the rubbery plateau began – generally determined as an intercept of two tangents – was defined as the flex temperature (T_{flex}). The decrease in storage modulus of the rubbery plateau with increasing temperature (% change per °C) was quantified by $\Delta G'$, which was calculated from

$$\Delta G' = \frac{G'_{25\,^{\circ}C} - G'_{(T_{flow}-50\,^{\circ}C)}}{G_{25\,^{\circ}C}} \times \frac{1}{\Delta T}$$

where ΔT is defined as the temperature range: $(T_{flow} - 50\,^{\circ}C) - 25\,^{\circ}C$.

Compression Set

Square-shaped samples were cut from the compression molded bars for compression set measurements. The compression set was measured at room temperature and 35 °C according to the ASTM 395 B standard. The compression was applied for 24 h for each measurement temperature, and the thickness of the samples was measured after half an hour's relaxation. The compression set was taken as the average of three measurements. It is defined as

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

where d_0 = thickness before compression (mm), d_1 = thickness during compression (mm), d_2 = thickness after 30 min relaxation (mm).

Shore A Hardness

The hardness of the polymer samples was measured by a Zwick HHP 2001 Shore A meter (ISO R 868/ DIN 53505) on compression molded bars. An average of eighteen measurements was calculated.

Results and Discussion

Polyurethanes were synthesized from a MDI end-capped PTMO and a PBT-diol extender. The length of the PBT-diol extender was varied. The PBT-diol extenders were prepared prior to the polymerization.

End-Capped Prepolymer Composition

The specifications of the end-capped PTMO prepolymer used included an NCO content of 3.1 wt.-% and a free MDI content typically <0.5 wt.-%. The composition of the PTMO prepolymer end-capped with MDI was studied by NMR, and for this reason the isocyanate groups had been reacted with hexyl amine. The ^1H NMR spectrum displayed isolated peaks for the MDI CH_2 at 4.08 ppm, the ether CH_2 at 3.84 ppm, and the urethane CH_2 at 4.42 ppm. The PTMO length was found to be 1 980 g · mol^{-1}, which is close to the often used 2 000 g · mol^{-1} on the market. The amount of free MDI relative to the total amount of MDI was determined from the hexyl content and was found to be 1.70%, which corresponds to 3.4% of the NCO groups present. The NCO content in the material was 3.0 wt.-%, excluding the NCO groups in the free MDI. This indicates a molecular weight of the end-capped prepolymer of 2 800 g · mol^{-1}.

PBT-Diol Extenders

The PBT-diol extenders were denoted $4(T4)_n$, where 4 stood for the butanediol and T for terephthalate. The extenders

DOI: 10.1002/mame.200700356

Table 1. Thermal characteristics of the PBT-diol units.

	Repeat length	Molecular weight	T_m	ΔH_m
			°C^a)	$J \cdot g^{-1}$
$4(T4)_3$	3	750	$96_m, 119_m, 157_m$	85
$4(T4)_4$	4	970	$65_w, 90_w, 120_w, 188_s$	85
$4(T4)_5$	5	1 190	$70_{vw}, 100_{vw}, 206_s$	85
$4(T4)_7$	7	1 630	$60_{vw}, 110_{vw}, 145_{vw}, 220_s$	90

a)vw, very weak; w, weak; s, strong.; vs, very strong.

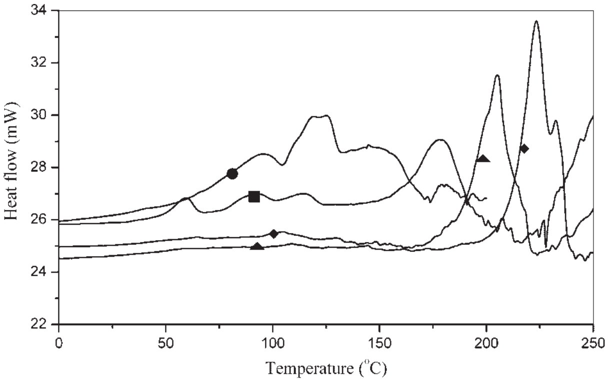


Figure 1. DSC melting of PBT-diol units with random-disperse distributions: ●, $4(T4)_3$; ■, $4(T4)_4$; ▲, $4(T4)_5$; ◆, $4(T4)_7$.

were prepared from butanediol and dimethyl terephthalate: $4(T4)_3$, $4(T4)_4$, $4(T4)_5$, $4(T4)_7$ and the units had a random dispersion. The thermal characteristics of the PBT-diol ester units were measured by DSC and are presented in Table 1 and Figure 1.

The random $4(T4)_n$ showed multiple crystallization and melting transitions, particularly $4(T4)_3$ and $4(T4)_4$. The melting temperatures at approx. 100 °C and 160 °C were believed to come from the 4T4 and the 4T4T4T4 units and the melting transition at 120 °C from the 4T4T4 unit.

The transitions for $4(T4)_5$ and especially $4(T4)_7$ were reasonably narrow. One reason for this was that the effect of the unit length on the melting temperature decreased with increasing length.[3] As most transitions were broad, an accurate determination of the heat of fusion of the PBT-diol units was difficult to carry out. However, an approximate value was 85 $J \cdot g^{-1}$. With increasing $4(T4)_n$ length, the melting temperatures increased.

Polyurethanes

Polyurethanes were synthesized from a MDI-endcapped PTMO with a molecular weight of 2 800 $g \cdot mol^{-1}$ (MDI groups included) and a PBT-diol extender. The free MDI content in the prepolymer was low, i.e. 1.7% of the MDI units present. The PBT-diol extender was added to this prepolymer and the synthesis was carried out at 120–140 °C. At first DMAc was present as the solvent and later the solvent was stripped. The thermal properties of these PBT-diol extended polyurethanes are given in Table 2.

All copolymers had high inherent viscosities that only changed slightly with HS length, meaning that the molecular weights were similar.

IR Spectroscopy

The carbonyl bands of the urethane and the ester groups can be visualized with IR spectroscopy. The carbonyl groups of the urethane are sensitive to H-bonding. The

Table 2. Thermal properties of the PBT-diol extended polyurethanes.

	HS^a)	PBT	η_{inh}	T_m^b)	ΔH_m	T_{flow}
	%	%	$dL \cdot g^{-1}$	°C	$J \cdot (g\ HS)^{-1}$	°C
$4(T4)_3$	34.8	20.9	0.87	$108_w, 155_w, 168_w$	17	120
$4(T4)_4$	38.1	25.2	0.65	$90_{vw}, 145_{vw}, 179_s$	28	130
$4(T4)_5$	41.5	29.2	0.73	$160_{vw}, 180_{vw}, 217_s$	23	175
$4(T4)_7$	47.1	36.1	0.71	$140_{vw}, 190_{vw}, 224_s$	36	225

a)Hard segment content;b)vw, very weak; w, weak, s, strong.

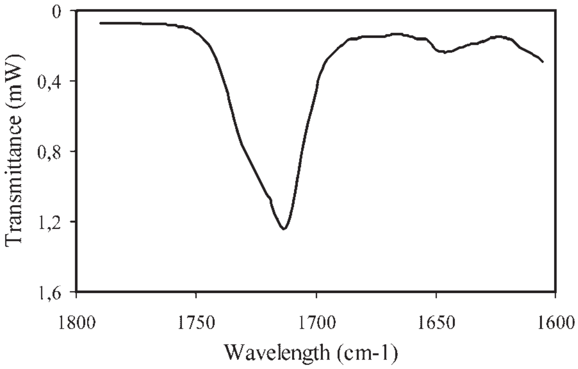


Figure 2. FT-IR spectra for the 4(T4)$_3$-extended polyurethanes (1 600–1 800 cm^{-1}).

non-hydrogen bonded urethane C=O band is located at 1 750 cm^{-1}, the H-bonded band in the amorphous state at 1 725 cm^{-1} and the H-bonded band in the crystalline state at 1 706 cm^{-1}.[4,5] The ester carbonyl peak of PBT is located at approx. 1 720 cm^{-1} and this peak is only slightly dependant on the crystallinity.

The carbonyl peaks of the urethane and ester groups of the copolymers were found to be overlapping. An example of an FT-IR is given in Figure 2.

A peak maximum was observed at 1 716 cm^{-1} and a shoulder at 1 730 cm^{-1}. The peak at 1 716 cm^{-1} corresponded to the ester carbonyl, and the shoulder at 1 730 cm^{-1} was assigned to the amorphous urethane carbonyl. The crystalline urethane carbonyl at 1 706 cm^{-1} was however difficult to detect.

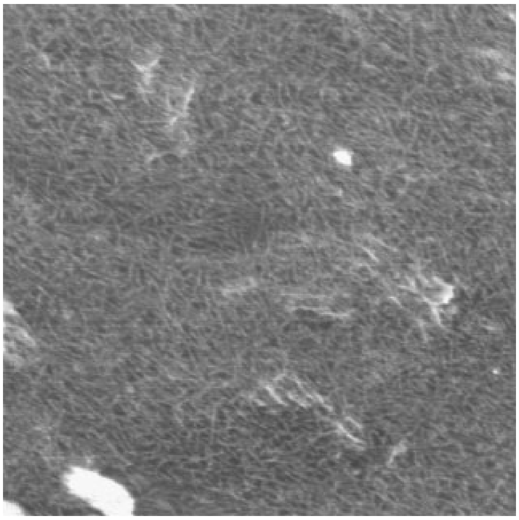


Figure 3. AFM micrograph (1 × 1 μm^2) of 4(T4)$_3$-extended polyurethane.

AFM Results

The crystalline morphology in the polyurethanes was studied by AFM in the phase angle mode. AFM micrographs were taken for 4(T4)$_3$ (34.8% HS) and an example can be seen in Figure 3.

The bright lines represent the crystals. At the surface, numerous randomly oriented long ribbons can be seen. The crystalline ribbons were quite straight and had a length of about 200–300 nm and a thickness of a few nanometers. No clustering or spherulitic structure was observed.

Melting Behavior of Polyurethane

Most of the PBT-extended PU copolymers displayed multiple HS melting transitions (Table 2). Melting temperatures depend strongly on the thickness of the crystallites.[2,6] The multiple melting transition thus suggest a multitude of crystallite thicknesses. The melting temperature of the copolymers increased strongly with increasing ester segment length (Table 2). As the HS contents were low and the melting transition broad, the heat of fusion was difficult to measure. It seemed that the segment length increased on the heat of fusion of the HS somewhat. The melting temperature of the PTMO segment was approx. 20–25 °C.

DMTA Results

The thermomechanical behavior of the synthesized polyurethanes was measured by DMTA (Figure 4 and Table 3).

Three transitions were apparent a T_g of the PTMO a T_m of the PTMO and a melting of the HS. The T_g of the PTMO phase was low (−55 °C) and increasing the PBT length had little effect on this. The T_g of PTMO$_{2000}$ in a segmented block copolymer can be as low as −65 °C.[7] The increase in T_g can be approximated with the Fox relationship.[8] However as both MDI and PBT units are the reason for this T_g increase a calculation of the dissolved content is difficult. The T_g of TPU's are often at 35 °C and higher.[1,2]

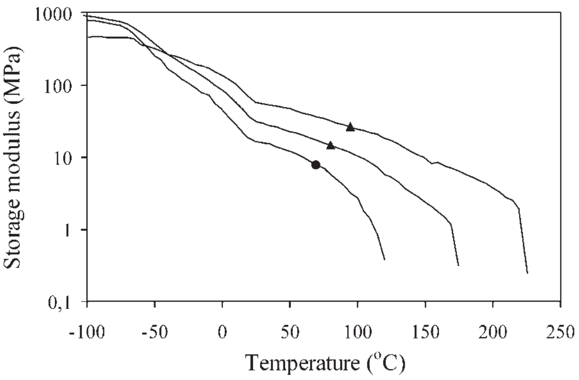


Figure 4. Storage moduli as functions of temperature for various PBT-diol units: ●, 4(T4)$_3$; ▲, 4(T4)$_5$; ◆, 4(T4)$_7$.

DOI: 10.1002/mame.200700356

Table 3. DMTA and elastic data of the polyurethanes.

Random	**HS$^{a)}$**	**PBT**	**η_{inh}**	**T_g**	**T_{flex}**	**$G'_{25\,°C}$**	**T_{flow}**	**$\Delta G^{b)}$**	**$CS_{24\,°C}$**	**Shore A**
	%	**%**	**$dL \cdot g^{-1}$**	**°C**	**°C**	**MPa**	**°C**	**$\% \cdot K^{-1}$**	**%**	
$4(T4)_3$	34.8	20.9	0.87	−55	18	17	120	2.4	40	73
$4(T4)_4$	38.1	25.2	0.65	−56	23	17	130	4.3	28	79
$4(T4)_5$	41.5	29.2	0.73	−56	22	31	175	4.7	36	90
$4(T4)_7$	47.2	36.1	0.71	−56	25	59	225	5.4	59	91

$^{a)}$Hard segment content;$^{b)}$$\Delta G$: decrease in storage modulus with temperature.

The melting of the PTMO phase is a shoulder on the storage modulus graph and is characterized by the T_{flex}. The T_{flex} increased a little bit with HS length.

The room temperature modulus increased strongly with increasing HS length. However, this is not so much a length effect but more a crystalline content effect (Figure 5).

Crystallites reinforce the soft segments and this reinforcing effect depends more on the HS content than the HS length.[9] An unmodified PTMO has an extrapolated modulus of 1 MPa.[10] For the longer PBT segments with HS contents of about 50 wt.-%, G' moduli of about 60 MPa were reached. With increasing temperature the modulus gradually decreased and the $\Delta G'$ values were relatively high (Table 3). This diminution was due to the gradual melting of the HS.[2,6] The $\Delta G'$ values were not lower for the longer PBT extenders, this despite the sharper melting temperatures of the PBT-diol units with a long length. The onset of flow of the copolymer at T_{flow} increased with increasing HS length. The T_{flow} as measured by DMTA and the T_m as measured by DSC are normally close. However, in the PBT extended copolymers the T_{flow} was approachable lower than the T_m as measured by DSC (Figure 6).

That the T_{flow} as measured by DMTA were for the shorter PBT segments lower than the T_m as measured by DSC suggest that some high melting PBT segments in these copolymers were not part of a network. However, at long PBT length the transitions convert to 225 °C the melting temperature of high molecular weight PBT.

Compression Set

The compression set (CS) was investigated as a measure of the elastic behavior (Table 3). The CS values were for the PBT extended polyurethanes not low. The compression set values of TPE's generally increase with the modulus.[11] However, by increasing the HS length increases at a constant SS length and the CS values decrease with increasing modulus.[9] The CS values are generally also dependant on the PTMO melting temperature. If the PTMO melting temperature (T_{flex}) is close to or above the measuring temperature, the CS values normally increase.[9,10,12] The high-melting temperatures of PTMO segments in the studied TPU's effect might have played a role in the observed high CS values and this particular for the $4(T4)_7$ copolymer (Table 3).

Shore A Hardness

In the characterization of segmented copolymers an often used stiffness parameter is the Shore A hardness. In Shore

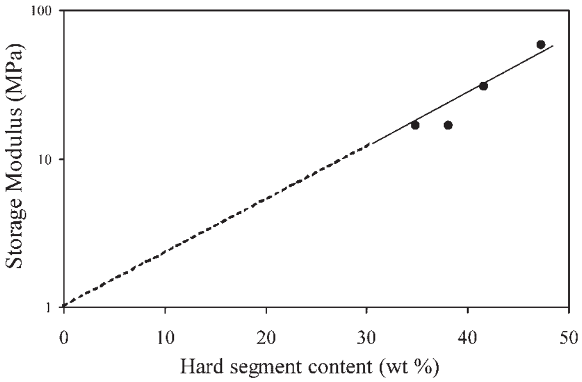


Figure 5. Effect of the HS content of the polyurethanes on the storage modulus at room temperature.

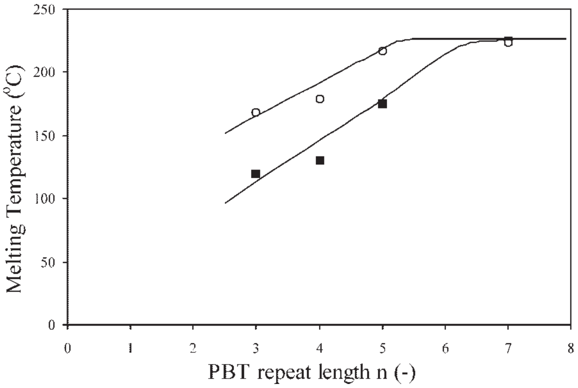


Figure 6. Influence of the PBT unit length on the melting temperature: ○, T_m by DSC; ■, T_{flow} by DMTA.

hardness tests the deformation strain is much higher than for storage modulus measurements. For the prepared copolymers, an increasing HS content gave rise to a strong increase in the Shore hardness (Table 3). These results were in line with the storage modulus data at room temperature.

Conclusion

Polyurethanes were synthesized from PTMO end-capped with MDI and extended with PBT-diol. The PBT-diol ($4(T4)_n$) units were random-disperse $4(T4)_n$ in length and the length was increased from $n = 3$ to $n = 7$. The copolymers had all high inherent viscosities. Short $4(T4)_n$ units displayed multiple melting temperatures but with increasing length the melting transition became narrower, especially for repeat lengths of 5 and 7.

Multiple melting transitions were observed for the HS in the TPU's. The melting temperatures of the MDI-PBT-MDI increased strongly with PBT length. The morphology of the HS as observed by AFM was a fine ribbon-like (crystal) structure. The polyether glass transition temperature was not affected by the ester segment length. The T_{flex}, the melting temperature of the PTMO increased a bit with increasing PBT length. This might be due to a slightly reduced amount of dissolved HS.

The storage modulus increased strongly with PBT length (content) as was the Shore A hardness. The temperature dependence of the storage modulus was high for all copolymers ($\Delta G' \approx (4\text{–}5\%)$ per °C). This suggests that a part of crystallites that melt at temperatures lower than the T_{flow}. The compression set values were relatively high and these values were probably influenced by the high melting temperature of the PTMO segments.

Increasing the PBT unit extender length increased the melting temperature and the modulus. Interesting would be to study polyurethanes extended with mono disperse PBT segments, as than the HS melting transition is expected to be sharper, the modulus even higher and the CS lower.

Acknowledgements: This research is part of the research programme of the *Dutch Polymer Institute* (DPI), The Netherlands, project nr. #490.

Received: November 5, 2007; Revised: December 18, 2007; Accepted: December 19, 2007; DOI: 10.1002/mame.200700356

Keywords: polyurethane; PBT; thermoplastic

[1] C. Hepburn, "*Polyurethane Elastomers*", Elsevier, Amsterdam 1992.
[2] W. Meckel, W. Goyert, W. Wieder, "*Thermoplastic Elastomers*", 2nd edition, G. Holden, N. R. Legge, R. P. Quirk, Eds., Hanser, München 1996, Chapter 2.
[3] H.-W. Haeslin, M. Droescher, G. Wegner, *Makromol. Chem.* **1980**, *181*, 301.
[4] B. D. Kaushiva, S. R. McCartney, G. R. Rossmy, G. L. Wilkes, *Polymer* **2000**, *41*, 285.
[5] M. Szycher, "*Szycher's handbook of polyurethanes*", CRC Press LLC, Baca Raton 1999.
[6] C. D. Eisenbach, H. Nefzger, "*Multiphase Macromolecular Systems, Contemporary Topics in Polymer Science*", Vol. 6, W. M. Cumbertson, Ed., Plenum Publishing, New York 1989, p. 339.
[7] M. C. E. J. Niesten, J. Feijen, R. J. Gaymans, *Polymer* **2000**, *41*, 8487.
[8] L. H. Sperling, "*Introduction to Physical Polymer Science*", 3rd edition Wiley New York 2001.
[9] J. M. van der Schuur, R. J. Gaymans, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4769.
[10] M. C. E. J. Niesten, R. J. Gaymans, *Polymer* **2001**, *42*, 6199.
[11] J. M. van der Schuur, E. van der Heide, J. Feijen, R. J. Gaymans, *Polymer* **2004**, *45*, 2721.
[12] G. J. E. Biemond, J. Feijen, R. J. Gaymans, *J. Appl. Polym. Sci.* **2007**, *105*, 951.