The Influence of Composition Ratio on the Morphology of Biomedical Polyurethanes

DARREN J. MARTIN,¹ GORDON F. MEIJS,² PATHIRAJA A. GUNATILLAKE,² SETRIG P. YOZGHATLIAN,³ GORDON M. RENWICK³

¹ Graduate School of Biomedical Engineering, University of New South Wales, Sydney, NSW 2052, Australia

² CSIRO Molecular Science, Private Bag 10, Clayton South MDC, VIC 3169, Australia

³ Department of Materials Science, University of Technology, Sydney, Broadway, NSW 2007, Australia

Received 9 September 1997; accepted 11 November 1997

ABSTRACT: Two series of thermoplastic polyurethane elastomers were synthesized from 4,4'-methylenediphenyl diisocyanate (MDI), 1,4-butanediol (BDO) chain extender, and each of poly(tetramethylene oxide) (PTMO) and poly(hexamethylene oxide) (PHMO) macrodiols. The PTMO and PHMO molecular weights were kept constant at 993 and 852 g/mol, respectively. In the PTMO-based series, the composition ratio was varied between 48 and 58% (w/w) of macrodiol; 2 commercially available PTMO-based polymers were also included. These were Pellethane 2363 80A® and its harder counterpart, Pellethane 2363 55D®. In the PHMO-based series, the composition ratio was varied between 50 and 60% (w/w) of macrodiol. The materials were characterized by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), wide-angle X-ray diffraction (WAXD), and small-angle X-ray scattering (SAXS). Mechanical performance was also assessed by tensile testing, stress hysteresis, and hardness testing. Altering the composition ratio had a similar effect on morphology and properties for both the PTMO and PHMO-based series. An increase in hard segment content was associated with increased hard microdomain crystallinity, hardness, and stiffness. In both series, he beginning of hard microdomain interconnectivity was observed at a composition ratio of 52% soft segment. That is to say, for the processing and annealing conditions employed, macrodiol contents of 52% and below began to produce continuous, rather than discrete, hard microdomains. Pellethane 80A[®] was shown to have a discrete hard microdomain morphology, while Pellethane 55D® was shown to incorporate interconnecting hard microdomains. It is suggested that the superior biostability performance of Pellethane 55D relative to Pellethane 80A may be related to its interconnecting hard microdomain texture. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 937-952, 1999

Key words: pellethane; degradation; morphology

INTRODUCTION

Thermoplastic polyurethanes (TPUs) are a versatile class of thermoplastic elastomer formed by incorporating 2 chemically dissimilar blocks in a linear polymer backbone. These copolymers have an $[H-S]_n$ type structure. At service temperature, the soft segment (S), is viscous or rubbery, while the hard segment component (H) is in a rigid (glassy or semicrystalline) state.

The unique properties of these polymers are due to microphase separation between the hard

Correspondence to: D. J. Martin.

Journal of Applied Polymer Science, Vol. 71, 937-952 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/060937-16



Figure 1 Scanning electron micrographs of explanted P55D (left) and P80A (right) polymers after strained (150% strain) 3-month subcutaneous implantation in sheep in our laboratories.

and soft portions of the macromolecules, which agglomerate to form hard and soft microdomains. Hard domains generally act as reinforcing filler and as thermally reversible crosslinks.

The morphology and properties of TPUs are greatly influenced by many factors. Our previous work has documented the morphological and physical changes caused by altering the soft segment solubility parameter¹ and soft segment length^{2,3} in systematically varying series. In this study, we characterize 2 more series where the hard segment-soft segment composition ratio is varied while keeping the soft segment length constant.

A number of workers have studied series of this nature,⁴⁻¹⁶ although a PHMO-based series has not been examined. Experimental evidence suggests that the onset of hard microdomain continuity occurs somewhere in the region of 40-60% (w/w) hard segment, depending on the system. The 2 series of polyurethanes characterized in this study involve a composition ratio change of only 10% (w/w), which represents a much narrower range than other series studied in the literature. From a biomedical standpoint, characterization of the morphology of these series is important because it is of interest whether it has a bearing on biostability. Many years of use and testing of the Pellethane 2636® series of PTMO-based polyurethanes has shown that P80A is far more susceptible to environmental stress cracking (ESC) in vivo, and its biostability performance more process-sensitive than its harder counterpart, P55D.^{17-20,35} Figure 1 shows scanning electron micrographs of explanted P80A and P55D polymers after a

strained (150% strain) 3-month subcutaneous implantation in sheep in our laboratories. The P80A shows evidence of deep surface cracks where as P55D shows no visible signs of degradation. One intriguing fact is that although these polymers differ greatly in mechanical properties and biostability, they do not differ greatly in composition (11% more polyether macrodiol in P80A by weight).

The chemical effects of *in vivo* degradation in pellethane 80A have been detected using Fourier transform infrared (FTIR) analysis, and they primarily involve localized oxidation of the polyether soft segments.³⁵ Applied or residual stresses on or within this soft material greatly increase its propensity to degrade. It is proposed that the microdomain morphology of the harder but more stable P55D provides more oxidative protection for the soft segments, either by limiting the amount of stress transferred to them during deformation or processing, or by preventing the passage of oxidative species through the polymer so as to slow the degradation rate. Schubert et al.³⁶ have shown recently that (the depth of) polyurethane biodegradation is controlled by diffusion of oxygen into the polymer.

This work, therefore, aims to investigate whether an order-order transition of microphase geometry occurs at a composition ratio somewhere between those of P80A and P55D. The 2 series of polymers prepared bridge the gap between the 2 grades of Pellethane, and small iterations in composition ratio allow a reasonable determination of where, if at all, this transition occurs for the processing conditions imposed.

Materials Preparation

PTMO Series

A series of 6 TPUs were synthesized from 4,4'methylene diphenyl diisocyanate (MDI) and 2,4-butanediol (BDO) chain extender, with polytetramethylene oxide (PTMO) macrodiol soft segments. PTMO was acquired commercially (Terathane 1000). The soft segment molecular weight employed was 993 g/mol. Materials contained 48, 50, 52, 54, 56, and 58% (w/w) of the PTMO macrodiol.

The molar ratio of isocyanate groups with respect to hydroxyl groups was 1.00, and the synthesis method employed was a 1-step bulk synthesis (see below). Processing waxes and catalyst were added to the polymers during synthesis. These were Irganox 1010 (0.2% w/w), Irgawax 280 (0.25% w/w), and stannous octoate catalyst (0.05% w/w).

Two additional commercially available PTMObased polymers were molded and tested for comparative purposes. These were Pellethane 2363 $80A^{\ensuremath{\circledast}}$ and Pellethane 2363 $55D^{\ensuremath{\circledast}}$. Pellethane 80A incorporates a PTMO soft segment with a molecular weight of approximately 1000 g/mol. It has a composition ratio of 56% soft segment (w/w). Pellethane 55D has a shorter PTMO soft segment (approximately 600–650 g/mol) and has a composition ratio of 45% macrodiol (w/w).

All samples were annealed at 135°C for 10 h after compression molding and prior to testing.

PHMO Series

A series of 5 TPUs were synthesized from MDI and BDO chain extender, with poly(hexamethylene oxide) (PHMO) macrodiol soft segments. The PHMO macrodiol was synthesized in-house by condensation polymerization of 1,6-hexanediol.³⁴ The soft segment molecular weight employed was 852 g/mol. Materials contained 50, 52, 55, 58, and 60% (w/w) of the PHMO macrodiol.

The molar ratio of isocyanate groups with respect to hydroxyl groups was 1.00, and the synthesis method employed was a 1-step bulk synthesis. Processing waxes and catalyst were added to the polymers during synthesis as in the case of the PTMO-based series.

All samples were annealed at 135°C for 10 h after compression molding and prior to testing.

1-Step Bulk Synthesis Method

The hydroxyl numbers of all macrodiols were determined by a standard procedure (ASTM D2849method C, 1975).²¹ The MDI and BDO were distilled and degassed, respectively, and the PTMO and PHMO macrodiols were dried thoroughly under a vacuum of better than 0.1 torr at 80°C for at least 12 h prior to synthesis. Dried macrodiol was accurately weighed into a clean, dry polypropylene beaker and kept dry at 105°C in an oven under a vacuum of 0.1 torr prior to polymerization. Degassed BDO was weighed into a pre-wet (with BDO), tared polypropylene syringe and added to the dried macrodiol in the reaction beaker. Freshly distilled MDI was weighed into a wet, tared polypropylene beaker and immediately added to the reaction beaker, which was then stirred continuously with a spatula for 1 min to ensure uniform mixing of all ingredients. The contents of the reaction beaker were poured onto a glass-reinforced Teflon sheet, covered with a second sheet, and pressed by hand to a thickness of less than 5 mm. The as-poured material was then placed in an oven to cure at 100°C for 4 h under a steady flow of dry nitrogen.

Compression Molding

The as-synthesized polyurethane materials were compression-molded into either 0.5-mm- (for SAXS and DSC samples) or 1.3-mm-thick plaques at temperatures of 185–200°C using a watercooled hydraulic press. Before molding, the materials were chopped into small pellets, and welldried in a vacuum oven (0.1 torr at 40°C overnight). The cooling procedure was kept uniform for all materials by keeping the water flow rate the same. The molds employed were simple steel plates with 2 rectangular cavities machined out. The plates were nickel-plated and then Tefloncoated to provide a corrosion-resistant, nonadhesive surface.

Annealing

Annealing was carried out on pre-dried samples (0.1 torr at 40°C overnight) under a dry nitrogen purge at 135°C for 10 h. Samples were placed on a flat sheet of glass fibre reinforced Teflon sheet to prevent possible sticking. Annealed samples were allowed to cool to room temperature slowly in the oven.

Instrumentation and Test Methods

Gel Permeation Chromatograph

Polyurethane molecular weights were determined using a Spectra Physics GPC system with N,N-dimethylformamide containing 0.05M LiBr as the mobile phase at 80°C. Columns of pore size 10^2 , 10^3 , and 10^5 Å were utilized, and the system was calibrated against 6 polystyrene standards.

Differential Scanning Calorimeter

DSC work was performed on a TA Instruments DSC2920. The heating rate employed was 10°C/min. DSC samples were dried (0.1 torr at 40°C overnight) prior to testing, and a sample weight of about 10 mg was used.

Dynamic Mechanical Thermal Analyzer

Dynamic mechanical testing was carried out on a Polymer Laboratories DMTA equipped with tensile head and reducing force option, with a heating rate of 2°C/min and a frequency setting of 2 Hz. Rectangular samples, 1.3 mm thick, 4 mm wide, and 20 mm long were tested.

Wide-Angle X-Ray Diffractometer

Wide-angle X-ray diffraction work was carried out on a Siemens D5000 diffractometer using CuK α radiation and a 2 θ range of 4 to 40° Samples were 1.3-mm-thick discs of 10 mm diameter punched from compression-molded plaques.

Small-Angle X-Ray Scattering Facility

The SAXS machine at the Research School of Chemistry (Australian national University, (ANU), Canberra, has been briefly described elsewhere.²²

The SAXS data are presented as a function of scattering vector or scattering momentum, Q, as follows:

$$Q = 4\pi \sin \theta / \lambda \tag{1}$$

where θ is half the scattering angle, and λ is the X-ray wavelength. The radiation used was $\operatorname{CuK}_{\alpha}$. The data were corrected for detector sensitivity and electronic background. Transmission and flux measurements were carried out before and after each test. The sample to detector distance was 890 mm. No desmearing of the data was performed. All data were corrected using a water scattering function to an absolute scattering in-

tensity scale (units of cm^{-1}). Data were processed using the BLISS program at the Research School of Chemistry, ANU, and ANU–ORNL data analysis software.

Tensile Testing

Tensile testing was carried out on 5 replicates of each material with an Instron model 4032 universal testing machine. Smaller-than-standard tensile dumbbell samples were punched from the molded sheet stock. The smaller samples (t= 1.3 mm, w = 4.3 mm, l = 30 mm) were required to allow for large elongation behavior and to enable a comparison with previous tensile results involving in vivo and in vitro degradation studies,²³⁻²⁶ which employed the same size dumbbell samples. A 1 kN load cell was used, and the crosshead speed was 500 mm/min. Gauge lengths of 20 mm were used, and pneumatic grips were required to hold the test specimens to prevent slippage. Permanent set measurements were recorded within 1 min of sample breakage.

Tensile Hysteresis

Tensile hysteresis measurements were performed on a MTS 858 Bionix servohydraulic testing machine using a 1 kN load cell calibrated down to 100N. Hysteresis dumbell samples were 0.5 mm thick and 2.1 mm wide, and a gauge length of approximately 6.0 mm was standard. The samples were positioned in the pneumatic grips which were set at 90 psi pressure. Gauge lengths were accurately measured for the sample, which was then stretched and unloaded at 1 mm/min to the required strain for each cycle. This slow ramp rate was employed to minimize buckling and compression of the sample during the unloading cycle. The end point for the cycle was taken where the unloading curve crossed the X-axis (i.e., when stress returned to zero). A separate sample was used for each strain cycle.

The data was collected using the TestStar II data acquisition program. The percentage hysteresis was defined as the ratio of the area bound by the loading–unloading curve to the total area under the loading curve. The areas were calculated using the Image Tools software developed by UTHSCSA.

Shore Hardness Indentor

Shore hardness values were measured at 20°C with calibrated A and D scale indentors by stack-



Figure 2 DSC thermograms for (a) the PTMO-based series, P80A and P55D, annealed at 135°C for 10 h and (b) the PHMO-based series annealed at 135°C for 10 h.

ing 5 1.3-mm-thick moldings together on a flat surface and taking the mean of 5 readings.

RESULTS AND DISCUSSION

Nomenclature Employed

The nomenclature used for this series is of the form T## or H##, where T or H represents a material based on PTMO or PHMO soft segment, respectively, and ## is the weight percent of the macrodiol contained in the material. P80A and P55D codes are used to identify the 2 Pellethane polymers.

Characterization of the Polyurethanes

Differential Scanning Calorimetry

Figures 2(a) and (b) show the DSC thermograms for the two polyurethane series after annealing at 135°C for 10 h. A summary of the DSC features are listed in Table I. An increase in hard segment concentration was associated with an increase in hard microdomain crystallinity (enthalpy of fusion values were calculated per gram of hard segment). A comparatively higher degree of crystallinity was observed for the PHMO-based series in agreement with the results obtained in a previous study.¹ It is believed that if equivalent soft seg-

Material	Soft Phase T _g /°C	Hard Phase T_g /°C	Hard Phase Melting/°C (1st, 2nd)	Hard Phase $\Delta H/Jg^{-1}$ (total 1 + 2) ^a
T58	-39.3	60.0	158.3	19.0
T56	-41.8	58.2	162.4	24.6
T54	-46.2	57.0	162.5	24.8
T52	-36.3^{b}	59.0	143.5,197.5	26.8
T50	-37.0^{b}	58.5	155.2,201.5	32.8
T48	-38.8^{b}	62.5	164.0,195.2	37.0
P80A	-45.0	55.0	159.5	17.3
P55D	_	_	159.5,181.9	36.7
H60	-38.1	60.0	151.0	23.5
H58	-37.4	61.0	161.0,204.5	26.7
H55	-36.2^{b}	61.5	153.8,205.0	33.4
H52	-32.5^{b}	60.0	150.7,205.8	33.9
H50	-31.5^{b}	62.5	155.4,199.2	37.0

Table I Summary of DSC Features for Materials Annealed at 135°C

^a Enthalpy of fusion values for hard phase melting were calculated per gram of hard segment rather than per gram of polymer. ^b Broad soft domain glass transitions were difficult to determine.

ment molecular weights (rather than PHMO 852 and PTMO 993) had been employed in these series, an even greater difference in crystallinity would have been encountered. The effect of segment length has also been reported in previous work.^{2,3}

P80A produced the lowest enthalpy value for hard microphase melting, whereas P55D produced one of the highest.

Both the PTMO and PHMO series showed similar results in terms of thermogram features. Soft microdomain glass transitions were generally broad and difficult to measure; however, as the hard segment content was increased in both series, a sharp increase in soft microdomain T_{σ} was seen at a composition ratio of 52% soft segment. This observation is consistent with the DMTA results. A soft microdomain T_g was not detected in the DSC thermogram for P55D, and no hard microdomain T_g was detected either. Soft and hard microdomain glass transitions were measurable for P80A, but the hard microdomain T_{σ} was not prominent compared with the other PTMObased polymers. Possibly, differences in synthesis (and pelletization) methods and synthesis volumes for the "T" series may have given rise to their more prominent hard microdomain glass transitions.

At 52% soft segment a well-defined $180-206^{\circ}$ C endotherm appears (T3) in addition to the endotherm attributed to the disordering of agglomerates of mainly MDI-BDO-MDI sequences (T2) and found at lower temperatures (140-165°C) in

all thermograms. As the hard segment length increases, a point is reached ($\sim 52\%$ soft segment), where the hard segment sequence distribution includes a significant number of MDI₃BDO₂ sequences, and crystallization of these sequences is favored, causing the higher melting peak. A further increase in the average hard segment length causes growth of the T3 endotherm. Although P55D incorporates the most hard segment by weight, it did not display a significantly higher hard segment melting enthalpy value or melting temperature. This is mainly because it incorporates a significantly shorter PTMO macrodiol to preserve clarity and processability. Also, the different synthesis and processing (pelletization) procedures used to make the Pellethane materials must be considered.

The relative size of the T3 endotherm compared to the T2 endotherm is greater in the PTMO-based materials since they include slightly longer average hard segment lengths for a given composition ratio. hard segments, which include more than 3 MDI residues, must fold and re-enter the hard domains, thus producing structures that are more disordered than regions where folding does not occur. It is possible that endothermic events that occur between T2 and T3 in this study are a result of the disordering of these folded longer hard segments.^{2,3}

A complementary annealing study was carried out on T48 and H50 to show how annealing at higher temperatures promotes more long-range order in the hard microdomains. The effect of



Figure 3 DSC thermograms for T48 and H50 polymers annealed at 135°C for 10 h.

annealing at 170 and 200°C was studied, and the results are given in Figure 3 and Table II. No T2 endotherm was encountered for materials annealed at 170°C; however, T3 endotherms and a T4 shoulder and T4 endotherm (214°C) were seen for T48 and H50, respectively. Annealing at 200°C produced a large, sharp endotherm in both cases at 220-225°C, believed to be a T5 endotherm. The melting enthalpy calculated for the PTMO-based material annealed at 200°C was greater than that calculated for the PHMO-based material due to the longer average hard segment lengths present in the former. Further evidence for the existence of T3, T4, and T5 endotherms and a discussion of their origin is provided in a SAXS-DSC-annealing study of a series of PHMO-based polyetherurethanes.³

Dynamic Mechanical Behavior

Figure 4(a) and (b) illustrates the dynamic mechanical behavior of each material. The storage modulus is seen to increase with hard segment content for both series, as would be expected. This is a result of more effective reinforcement by the more highly ordered hard microdomains as well as the change in composition ratio. The magnitude of the mechanical damping peaks decreases with an increase in hard segment content. This is due mainly to an increase in hard microdomain order, which imposes restrictions on soft segment mobility. A prominent shift upwards in damping peak position occurs in both series for materials, including 52% macrodiol and less. It could be argued that this shift is a result of the introduction of hard segment crystals of the T3 kind. However, if this was the case, one would expect this effect to increase with an increase in the size of the T3 DSC endotherm. Since this is not the case, the most likely cause for this shift is a morphological change from discrete hard microdomains to more interconnecting ones. Further evidence for this phenomenon is given in the tensile and stress hysteresis results later.

A shoulder is observed on the low temperature side of each damping peak. This shoulder represents the relaxation of soft segments in the center of the soft microdomains, which are purer and less affected by the rigid, hard microdomain structure. The main peak indicates that most of the soft segments are restricted in motion by the hard microdomains, and more so when the hard microdomains become interconnecting.

Wide-Angle X-Ray Diffraction

Diffraction patterns for the annealed materials are shown in Figure 5(a) and (b). WAXD peak positions are tabulate din Table III. A relatively sharp diffraction peak (4.57 Å lattice spacing) occurs for the polymers containing 52% soft segment or less. The intensity of this peak correlates with the comparative size of the T3 melting endotherms, and the peak position compares favorably with reported lattice spacings for MDI–BDO crystals.^{9,29–32} It appears that the hard segment structure involved with the higher melting T3 endotherm is more capable of packing into wellordered crystallites.

Both P80 and P55D show broad, weak diffraction patterns, suggesting minimal long-range ordering when annealed at 135°C.

Material	T2 Melting Peak/°C	$\begin{array}{c} {\rm T3~Melting} \\ {\rm Peak/^{\circ}C} \\ {\rm (\Delta H/Jg^{-1})^{a}} \end{array}$	$ m T4~Melting Peak/^{o}C \ (\Delta H/Jg^{-1})^{a}$	T5 Melting Peak/°C (ΔH/Jg ⁻¹) ^a
		195.2		
T48A135	164.0	$(37.0)^{\rm b}$	_	_
		197.2		
T48A170	_	(17.9)		_
			_	
			220.4	
T48A200		_	(49.8)	
		199.2		
H50A135	155.4	$(37.0)^{\rm b}$	_	—
			213.5	
H50A170		195.3	$(15.9)^{c}$	—
				224.8
H50A200	—	—	_	(36.2)

Table II Summary of DSC Endotherms for T48 and H50 materials Annealed at 135, 170, and 200°C

 $^{\rm a}$ Enthalpy of fusion values for hard phase melting were calculated per gram of hard segment rather than per gram of polymer. $^{\rm b}$ Total enthalpy for T2 and T3 endotherms.

^c Total enthalpy for T3 and T4 endotherms.

Small Angle X-Ray Scattering

The SAXS camera used had a one-dimensional position sensitive detector, and, therefore, the data collected required Lorentz correction. In this treatment, the intensity is multiplied by Q^2 , where Q is the scattering vector (defined by $Q = 4\pi/\lambda \sin \theta$, where θ is half the scattering angle). The intensity [I(Q)] of the small-angle scattering from a polyurethane depends on the difference in electron scattering length density $(\rho_h - \rho_s)$ between the hard and soft microphases as given by

$$I(Q) = K(\rho_h - \rho_s)^2 S(Q) \tag{2}$$

where Q is the scattering vector, K is an instrument constant, and S(Q) is the scattering function from the atomic particle distribution in the sample. The intensity of the SAXS data also relates to the composition ratio of a material. The mean-square electron density fluctuation, $\langle \rho^1 \rangle$, is described by the following relationship:

$$\langle \rho^2 \rangle = \phi_h \phi_s (\rho_h - \rho_s)^2 \tag{3}$$

where ϕh and ϕs are the respective volume fractions of hard and soft segments, which, in turn, have electron densities ρ_h and ρ_s .¹³ Table IV includes physical density, weight fraction and theoretical volume fraction values for the hard and soft components of the polyurethanes.

The position of the scattering maxima $Q_{\rm max}$ can be used to estimate the average 1-dimensional interdomain spacing, $d_{\rm Bragg}$, by using Bragg's Law. The relationship between $d_{\rm Bragg}$ and $Q_{\rm max}$ for the camera used is

$$d_{\rm Bragg} = 2\pi/Q_{\rm max} \tag{4}$$

where d_{Bragg} represents the average interdomain spacial periodicity or "long period". Calculated long periods for the annealed materials are shown in Table V. The value obtained for this interdomain spacing is not a domain thickness value but rather an average spacial periodicity. If we assume a lamellar morphology, we can estimate the hard microdomain thickness in a well-phase-separated material by the following method:

$$T_h = \phi_h \cdot d_{\text{Bragg}} \tag{5}$$

where ϕ_h is the volume fraction of the hard microphase.

Lorentz corrected SAXS data are shown in Figure 6(a) and (b). Average interdomain spacing values, and hard domain thickness estimates are given in Table V. A large increase in both scattering intensity and average interdomain spacing is observed for the hardest materials (T48 and H50)



Figure 4 Dynamic mechanical behavior of (a) the PTMO-based series, P80A and P55D, and (b) the PHMO-based series.

in each series. The SAXS patterns for H50, and T48 in particular, show scattering functions that appear to have a shoulder on the high Q side of the peak, indicating 2 hard microdomain thickness populations. As hard segment length is increased, the estimated hard microdomain thickness also increases. Values for hard microdomain thickness correspond to an average of between 2 and 4 MDI–BDO repeat units in length based on hard segment length values taken from work by Van Bogart et al.,⁴ who calculated the following values: MDI–BDO–MDI, ~ 30 Å long; MDI–BDO–MDI–BDO–MDI, ~ 47 Å long; MDI–BDO–MDI–BDO–MDI, ~ 64 Å long.

Our method for estimating T_h does not include calculations of interfacial thickness dimensions or of the relative amounts of amorphous and crystalline hard microdomain material. However, it does suggest that at above 50% (w/w) hard segment, the morphology of materials in both series involves a "step up" in hard microdomain thickness, possibly indicating the addition of 1 MDI–BDO unit to the average hard microdomain thickness. If the T_h values presented are converted, then they correspond to an increase in critical hard segment length from the equivalent of an MDI₃BDO₂ sequence to an MDI₄BDO₃ sequence. The large increase in scattering intensity accompanying this change certainly supports the idea of significantly thicker and purer hard microdomains.

The general lack of trend displayed by the maximum scattering intensity of softer formulations suggests that the introduction of longer hard segments, which cause the additional T3 endotherms, serves to produce competing hard mi-



Figure 5 X-ray diffraction patterns for (a) the PTMObased series, P80A and P55D, and (b) the the PHMObased series.

crodomain structures, which prevent an increase in the degree of microphase separation. The composition ratio also affects the scattering intensity in these series to a small extent [see eq. (3)].

The SAXS curves for P80 and P55D, shown in Figure 7, are very similar. Any increase in hard– soft microdomain contrast (phase separation) expected from increasing the length of the hard segments in P55D is obviously offset by incorporating a shorter, more compatible PTMO macrodiol.

Tensile Testing

Table VI summarizes the molecular weights, shore hardness values, and tensile properties of

each series. Typical tensile stress-strain curves for these materials are shown below in Figure 8(a) and (b). An increase in hard segment content causes more hard microdomain reinforcement and, thus, an increase in the stiffness and hardness, as indicated by stress at 100% strain and shore hardness results. A large jump in the stress supported at 100% strain is seen for T52 and H52 since these materials represent the composition where the hard microdomains begin to connect. This was observed and discussed in the dynamic mechanical (DMTA) results.

The molecular weights of the PHMO-based polymers are lower than those of the PTMO-based materials. This is reflected in the higher tensile strengths and lower permanent set values of the latter series, with the exception of T48. The poorer tensile properties exhibited by T48 are probably due to a very rigid interconnecting hard microdomain structure, where, possibly, the hard domains have formed a more brittle matrix. This structure inhibits domain rotation, orientation, and soft segment stress crystallization.

Tensile Hysteresis

Stress hysteresis testing is a useful method for understanding morphology and deformation in multiphase polymers. The hysteresis values obtained relate to the degree of plastic deformation, inelastic recovery, and energy dissipation associated with stretching and unloading a material. A typical hysteresis curve is shown in Figure 9. Hysteresis versus strain curves are shown in Figure 10(a) and (b) for the PTMO-based polymers (including P80A and P55D) and the PHMO-based polymers, respectively. It can be seen in Figure 10(a) that, in general, a higher hard segment content is associated with greater hysteresis, especially at strains of 150% or below. This is the region where hard microdomain reorientation and disruption occurs. More important are the significantly higher hysteresis values at low strains displayed by materials with 52% soft segment or less. This is further evidence of a shift from microstructures incorporating more discrete hard microdomains (P80A, T54, and T56) to morphologies with a greater degree of hard microdomain interconnectivity and crystallinity.

Interconnecting hard microdomains cause plastic deformation to occur at lower strains and to a greater extent. This has been evidenced by Abouzahr et al.,¹³ Wang and Cooper,²⁷ and Lee and Hsu²⁸ in various polyurethane (PU) systems.

Material	Diffraction Angles (2θ)	<i>d</i> -spacings/Å
T58	20.15	4.40^{a}
T56	20.21, 15.68	$4.39.^{\rm a}$ 5.63 ^b
T54	19.90, 15.85	$4.46^{\rm a}, 5.57^{\rm b}$
T52	19.58, 15.68	$4.53,^{\rm c}5.63^{\rm b}$
T50	19.39, 21.65, 15.68	$4.57,^{\rm c}$ $4.10,^{\rm c}$ $5.63^{\rm b}$
T48	19.39, 15.85	$4.57,^{\rm c}5.57^{\rm b}$
P80A	20.21	4.39^{a}
P55D	20.21, 15.68	$4.39,^{\rm a}5.63^{\rm b}$
H60	20.02, 15.85	$4.43^{\rm a}, 5.57^{\rm b}$
H58	19.58, 15.85	$4.53^{\circ}, 5.57^{ m b}$
H55	19.46	4.56°
H52	19.39, 23.35	$4.57,^{\rm c} 3.81^{\rm c}$
H50	19.39, 21.78, 23.79, 25.24	4.57,° 4.08,° 3.74,° 3.53°

Table III WAXD Peak Positions for Annealed Polyurethanes

^a Broad central maximum.

^b Origin unknown

 $^{\rm c}$ d-spacing compares favorably with the values shown in the literature for MDI–BDO lattice spacings. $^{9,29-32}$

This happens because they are not as free to rotate and reorient, and also because they behave more as a rigid reinforcing matrix than as filler particles in a rubbery matrix. At strains greater than 150%, the hysteresis is more constant and similar for the different polymers. The deformation that occurs in this region is of the disrupted domain texture, where chain slippage is the predominant mechanism. For materials such as P80A, where the hard microdomains are quite discrete, the elastic energy stored in the soft rubbery matrix is more entropic in nature, and, therefore, the resulting hysteresis is lower.

The hysteresis behavior of the PHMO-based series, shown in Figure 10(b), seems far less sensitive to the composition ratio. Apart from H60, all hysteresis curves fall within similar bound-

Soft Segment Wt Material Fraction (%) $\rho_s^p/\text{g cm}^{-3}$ $\rho_h^p/\text{g cm}^{-3}$ ϕ_h 1.32^{b} 0.37 T58 58 1.08^{a} T56 56 1.32^{b} 0.39 1.08^{a} $1.32^{\rm b}$ T5454 1.08^{a} 0.41 1.32^{b} 520.43T52 1.08^{a} 1.32^{b} T5050 1.08^{a} 0.45 $1.32^{\rm b}$ T48 48 1.08^{a} 0.47 1.32^{b} 0.39 **P80A** 56 1.08^{a} P55D 45 1.08^{a} 1.32^{b} 0.50H60 60 1.04^{a} 1.32^{b} 0.34 1.32^{b} H5858 1.04^{a} 0.36 1.32^{b} H5555 1.04^{a} 0.39 1.32^{b} H5252 1.04^{a} 0.42H5050 1.04^{a} 1.32^{b} 0.44

Table IVPhysical Density and Theoretical Volume Fraction Valuesfor Soft and Hard Microphases

 ρ_s^{pz} and ρ_h^p are the physical densities of the pure soft and hard segments.

^a Literature values from Kobayashi et al.³³

^b Obtained from Quay et al.³¹

Material	$Q_{ m max}$ /Å $^{-1}$	$d_{ m Bragg}\!/\!{ m \AA}$	$\phi_h{}^{\mathrm{a}}$	$T_h/\text{\AA}^{ ext{t}}$
T48	0.0419	150	0.46	69
T50	0.0510	123	0.44	54
T52	0.0524	120	0.42	50
T54	0.0517	122	0.40	49
T56	0.0517	122	0.38	46
T58	0.0517	122	0.36	44
P80A	0.0525	120	0.39	47
P55D	0.0525	120	0.50	60
H50	0.0412	153	0.44	67
H52	0.0504	125	0.42	53
H55	0.0517	122	0.39	48
H58	0.0517	122	0.36	44
H60	0.0497	126	0.34	43

Table VSAXS Interdomain Spacingand Hard Domain Thickness Values

 $^{\rm a}$ ϕ_h is the calculated hard segment volume fraction based on density values given in Table IV.

 $^{\rm b}\,T_h$ is the average hard microdomain thickness estimated using equation (5).

aries. One explanation for this is that the PHMO macrodiol employed is a more viscous (less rubbery) compound than PTMO. It has a T_g of -35° C compared to -96° C for PTMO.¹ Because of this, one might expect more effective transferral of loads to the hard domains and for small changes in composition to show less difference in hysteresis behavior.

Figure 11 shows a schematic 2-dimensional representation of the microdomain morphology of Pellethane 80A and Pellethane 55D based on the results generated in this study.

CONCLUSIONS

The following conclusions have been drawn from this study.

Changing the composition ratio in PTMObased and PHMO-based MDI-BDO systems has a similar effect on morphologies and properties in the range 50-60% soft segment.

An increase in hard segment content (length) for a given soft segment length was associated with an increase in hard microdomain crystallinity (per gram of hard segment). A comparatively higher degree of crystallinity was observed for the PHMO-based series. An increase in hard segment content also involved an increase in hardness and stiffness. The PTMO-based series displayed supe-



Figure 6 Lorentz-corrected SAXS data for (a) the PTMO-based series and (b) the PHMO-based series.



Figure 7 Lorentz-corrected SAXS data for P80A and P55D. Typical tensile stress–strain curves for (a) the PTMO-based series, P80A and P55D, and (b) the PHMO-based series.

Material	M_n /1000	Shore Hardness (23°C)					Stress at
		Shore A	Shore D	UTS (MPa)	Fail Strain (%)	Permanent Set (%)	100% Strain (MPa)
T58	189	89	43	35.5	423	45	7.7
T56	190	90	43	34.6	409	43	8.3
T54	156	90	44	36.4	446	51	9.1
T52	182	93	46	32.8	338	40	10.9
T50	205	95	48	40.0	312	38	13.8
T48	174	95	50	19.3	160	25	15.8
P80A	207	82	_	33.7	430	_	8
P55D	192	_	55	40.3	328	_	20
H60	89	91	42	19.5	528	76	7.0
H58	85	93	43	20.8	490	76	8.3
H55	84	94	44	15.8	293	53	9.9
H52	89	95	47	24.3	430	81	13.8
H50	100	96	49	24.1	354	65	15.1

 Table VI
 Molecular Weight, Hardness, and Tensile properties



Figure 8 Typical tensile stress-strain curves for materials listed in Table VI.

rior tensile strengths and higher molecular weights than the PHMO-based series.

In both series, for the processing conditions imposed, a sharp increase in soft microphase T_g was observed at a composition ratio of 52% soft segment. Similarly, a prominent increase in the tensile stress at 100% strain was encountered at the same 52% composition in both series, and stress hysteresis results suggest the development of more intricate hard domain texture in this region. This was interpreted as a morphological change from discrete to interconnecting hard microdomains.

The SAXS and WAXD peak intensities for the hardest materials in each series (T48 and H50) were significantly greater than those measured



Figure 9 Typical stress hysteresis curve for a segmented polyurethane (T56).



Figure 10 Percentage of stress hysteresis versus applied strain curves for (a) the PTMO-based series, P80A and P55D, and (b) the PHMO-based series.

for other members of each series. These hardest materials also involved larger average interdomain spacings. These results indicated the addition of 1 MDI–BDO unit to the average hard microdomain thickness. Estimated hard microdomain thickness values suggested that this step probably involved an increase from the equivalent of an MDI_3BDO_2 sequence to an MDI_4BDO_3 sequence.

Our commercial test materials, Pellethane 80A[®] and Pellethane 55D[®], were the softest and hardest samples characterized, respectively. It was shown that P80A has a discrete hard microdomain morphology, while P55D incorporates an interconnecting hard microdomain structure. Given the poor biostability of P80A and the excellent biostability of P55D, this result suggests that incorporating an interconnecting hard microdo-



Figure 11 Schematic 2-dimensional representation of the microdomain morphology of Pellethane 55D (left) and Pellethane 80A (right).

main structure in PTMO-based biomedical PUs improves their biostability. This may be because of a reduction in the stress transferred to the more oxidatively unstable soft segments when they tie interconnecting hard microdomains together. Alternatively or additionally, an interconnecting hard microdomain may hinder the passage of oxidative species through the polymer, thus greatly slowing the degradation process. Ongoing biostability testing and morphological characterization of strained polymers aims to fully understand this relationship.

The authors thank Professor John White for assistance and helpful discussions, Mr. Trevor Dowling regarding the SAXS results, and Dr. Bill Walsh regarding the stress hysteresis work.

REFERENCES

- Martin, D. J.; Meijs, G. F.; Renwick, G. M.; Gunatillake, P. A.; McCarthy, S. J. J Appl Polym Sci 1996, 60, 557.
- Martin, D. J.; Meijs, G. F.; Renwick, G. M.; Mc-Carthy, S. J.; Gunatillake, P. A. J Appl Polym Sci 1996 62, 1377.
- Martin, D. J.; Meijs, G. F.; Renwick, G. M.; Gunatillake, P. A.; McCarthy, S. J. J Appl Polym Sci 1997 64, 803.
- Van Bogart, J. W. C.; Gibson, P. E.; Cooper, S. L. J Polym Sci Polym Phys Ed 1983, 21, 65.
- Seymour, R. W.; Cooper, S. L. Polym Lett 1971, 9, 695.
- 6. Wagener, K. B. Macromolecules, 1992, 25, 5591.
- 7. Petrovic, Z. S.; Javni, I. J Polym Sci Polym Phys Ed 1989, 27, 545.

- Harris, R. F.; Joseph, M. D.; Davidson, C.; Deporter, C. D.; Dais, V. A. J Appl Polym Sci 1990, 41, 509.
- Christenson, C. P.; harthcock, M. A.; Meadows, M. D.; Spell, H. L.; Howard, W. L.; Creswick, M. W.; Guerra, R. E.; Turner, R. B. J Polym Sci Polym Phys Ed 1985, 24, 1401.
- Seefried C. G. Jr.; Koleske, J. V.; Critchfield, F. E. J Appl Polym Sci 1975, 19, 3185.
- Huh, D. S.; Cooper, S. L. Polym Eng Sci 1971, 11, 369.
- 12. Ferguson, J.; Hourston, D. J.; Meredith, R.; Patsavoudis, D. Eur Polym J 1972, 8, 369.
- Abouzahr, S.; Wilkes, G. L.; Ophir, Z. Polymer 1982, 23, 1077.
- Kazmierczak, M. E.; Fornes, R. E.; Buchanan, D. R.; Gilbert, R. D. J Polym Sci Polym Phys Ed 1998, 27, 2188.
- 15. Leung, L. M.; Koberstein, J. T. J Apolym Sci Polym Phys Ed 1985, 23, 1883.
- Koverstein, J. T.; Galambos, A. F.; Leung, L. M. Macromolecules, 1992, 25, 6195.
- Stokes, K. B.; Urbanski, P. W.; Davis, M. W.; Coury, A. J. in Pacemaker Leads, Aubert, A. E.; Ector, H. Eds., Elsevier, Amsterdam, 1985, p. 279.
- Stokes, K.; Urbanski, P.; Cobain, K. in Polyurethanes in Biomedical Engineering II, Planck, H. Ed., Elsevier, Amsterdam, 1987, p. 109.
- Zhao, Q.; Agger, M. P.; Fitzpatrick, M.; Anderson, J. M.; Hiltner, A.; Stokes, K.; Urbanski, P. J Biomed Mater Res 1990, 24, 632.
- Zhao, Q.; Casa-Bejar, J.; Urbanski, P.; Stokes, K. J Biomed Mater Res 1995, 29, 467.
- ASTM D2849-69. Standard Methods of Testing Urethane Foam Polyol Raw Materials, American Society for Testing and Materials, Philadelphia PA, 1969.
- Aldissi, M.; Henderson, S. J.; White, J. W.; Zemb, T. Mater Sci Forum 1988, 27/28, 437.
- Meijs, G. F.; Gunatillake, P. A.; Rizzardo, E.;. Mc-Carthy, S. J; Chatelier, R. C.; Brandwood, A.; Schindhelm, K. Improved Polymers for Medical Implants–Polyurethanes; Progress in Pacific Polymer Science 2, Imanishi, Y. Ed., Springer-Verlag, Berlin, 1992.
- Meijs, G. F.; McCarthy, S. J.; Rizzardo, E.; Chen, Y.; Chatelier, R. C.; Brandwood, A.; Schindhelm, K. J Biomed Mater Res 1993, 27, 345.
- Gunatillake, P. A.; Meijs, G. F.; Rizzardo, E.; Chaterlier, R. C.; McCarthy, S. J.; Brandwood, A.; Schindhelm, K. J Appl Polym Sci 1992, 46, 319.
- Gunatillake, P. A.; Meijs, G. F.; Rizzardo, E.; Mc-Carthy, S. J.; Chatelier, R. C.; Brandwood, A.; Schindhelm, K. J Appl Polym Sci 1993, 47, 199.
- Wang C. B.; Cooper, S. L. Macromolecules, 1983, 16, 775.
- Lee, H. S. Hsu, S. L. J Polym Sci Polym Phys Ed. 1994, 32, 2085.

- 29. Koberstein, J. T.; Galambos, A. F. Macromolecules, 1992, 25, 5618.
- Blackwell J.; Lee, C. D. J Polym Sci Polym Phys Ed 1984, 22, 759.
- Quay, J. R.; Sun, Z.; Blackwell, J.; Briber, R. M.; Thomas, E. L. Polymer, 1990, 31, 1003.
- 32. Hwang, K. K. S. Wu, G. Lin, S. B.; Cooper, S. L. J Polym Sci Polym Chem Ed 1984, 22, 1677.
- Kobayashi, S.; Tadakoro H.; Chatani, Y. Makromol Chem 1968, 112, 225.
- Gunatillake, P. A.; Meijs, G. F.; Chatelier, R. C.; McIntosh, D. M.; Rizzardo, E. Polym Int 1992, 27, 275.
- McCarthy, S. J.; Meijs, G. F.; Mitchell, N.; Gunatillake, P. A.; Heath, G.; Brandwood, A.; Schindhelm, K. Biomaterials, 1997, 18, 1387.
- Schubert, M. A.; Wiggins, M. J.; Anderson, J. M.; Hiltner, A. J Biomed Mater Res, 1997, 34, 519.