Development of Wear-Resistant Thermoplastic Polyurethanes by Blending with Poly(dimethyl siloxane). II. A Packing Model

T. BREMNER,[1] D. J. T. HILL,[2] M. I. KILLEEN,[2] J. H. O'DONNELL,[2] P. J. POMERY,[2] D. ST. JOHN,[3,*] A. K. WHITTAKER[4]

[1] Novacor Research and Technology Corporation, 2928 16th St. N.E., Calgary, AB, T2E 7K7, Canada

[2] Department of Chemistry, University of Queensland, Q, 4072, Brisbane, Australia

[3] CRA Research and Technology, ATD Perth Research Centre, W. A. Technology Park, Cannington, W.A., 6107, Australia

[4] Centre for Magnetic Resonance, University of Queensland, Q, 4072, Brisbane, Australia

ABSTRACT: It has been shown in a previous article that melt blending of low levels of commercial poly(dimethyl siloxane)(PDMS) fluid with commercial thermoplastic polyurethanes has a significant positive impact on the coefficient of friction (CoF) and on the mechanical and wear properties of the polyurethanes. The improvements in CoF and wear resistance were expected due to surface modification of the polymer; however, the improvements in the mechanical properties were much more significant than expected. Evidence presented in the earlier publication suggests that the changes in the wear and mechanical properties are not due to surface modification alone, but are largely due to modification of the bulk by PDMS. In this article a model is presented that accounts for the observed relationship between PDMS content and the properties of the blends. It is proposed that the addition of PDMS facilitates an improved packing efficiency (antiplasticization) in the polyurethane soft domain, leading to improved material performance. Beyond an optimum PDMS concentration of 1.5–2.0%, phase separation of PDMS becomes significant, plasticization sets in, and mechanical properties then begin to diminish rapidly. This model has been rigorously investigated and has proven to be highly robust. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65**: 939–950, 1997

Key words: polyurethane; poly(dimethyl siloxane); wear; plasticization; blend

INTRODUCTION

This work is primarily concerned with application of polyurethanes in the Australian mining industry. Applications in this field demand high performance from these materials with respect to their mechanical performance and their wear resis-

tance. Thermoplastic polyurethanes (TPU) are widely employed in these roles due to their excellent performance, which is generally attributed to the phase separation of their hard and soft segments and physical crosslinking through the crystalline hard domains.[1]

Despite the excellent properties of these materials it is desirable to further improve the wear performance of the polyurethanes, because, in many applications, abrasion is the predominant cause of component failure. To this end poly(dimethyl siloxane)(PDMS) has been melt blended with two commercial thermoplastic polyurethanes on a standard Brabender extruder. By us-

ing standard processing equipment and commercial polymers it was hoped to keep the cost of these materials comparable to standard TPUs.

The mechanical and wear properties of these blends, as a function of PDMS concentration in the range 0–4% (w/w), have been previously reported.[2] Significant improvements in wear resistance (by up to 25%) were reported, as well as a reduction in the coefficient of friction (CoF). Similar observations have been reported by other workers.[3–6] In addition, significant increases in mechanical properties were also observed up to an optimal PDMS concentration of 1.5–2%, beyond which the properties begin to become adversely affected by the addition of PDMS. This was unexpected because other published work indicated only small changes in mechanical properties (up to 10%) when low concentrations of PDMS were added,[6] while most workers had observed significant decreases in polymer performance.[7–11] The earlier articles[3–6] did not consider in detail the changes in the mechanical properties, but were rather concerned with optimizing the wear and CoF performance. In the second set of articles,[7–11] high levels of PDMS, as a block copolymer, were used in an effort to improve other properties of the polyurethane at the expense of the mechanical properties. We also have reported the adverse effects of PDMS at higher concentrations ($> \sim 3\%$).[2]

The significant improvements in the mechanical properties reported in the first article of this series[2] is unlikely to be due to surface effects alone, because Young's modulus was also shown to increase with PDMS addition.[2] Evidence was also presented that the improvement in wear performance was related to the bulk properties of the blend rather than simply to a reduction of the surface CoF. In order to understand the relationship between the PDMS concentration and the physical properties, an extensive investigation of the morphology of the blends has been carried out, and a model that explains the observed behavior has been developed. A better understanding of the nature of the TPU/PDMS interactions should allow the design of improved blended materials for specific field applications.

EXPERIMENTAL

Experimental procedures used for sample extrusion, tensile testing, wear testing, measurement of coefficient of friction (CoF), and Shore hardness are outlined in the previous publication[2] along with the descriptions of the TPU and PDMS materials used.

Small-angle X-ray scattering (SAXS) measurements were performed on a Rigaku small-angle scattering goniometer using monochromatic CuKα radiation and a counting tube as described by Mardel et al.[12]

All densities were determined according to the ASTM for density and specific gravity of plastics by displacement[13] in ethanol at 21°C.

$T_{1\rho}$ Measurements

Measurements of ^{1}H $T_{1\rho}$ were made on a Bruker MSL300 operating at 300.13 MHz for ^{1}H. A modified 7 mm solenoid-coil ^{1}H probe was used for all measurements. Typical p/2 pulse times were 3.5 ms, while the probe dead time was less that 10 ms. ^{1}H $T_{1\rho}$ were measured at 298 K by observing the decay of magnetization during spin-locking with a radio frequency field of 70 kHz.

T_2 Measurements

Experiments were only performed for the Pel55D series of blends. Samples were evacuated to 10^{-4} mmHg for a period of 24 h and sealed in 5 mm NMR tubes. NMR measurements were made on a Bruker AC-300 spectrometer, operating at 300.13 MHz for ^{1}H. A 5 mm water-cooled dual (^{13}C/^{1}H) fixed-frequency probe was used for all measurements. Typical p/2 pulse times were 9 ms, while the probe dead time was 18 ms.

All experiments were completed at 423 ± 0.1 K. This temperature was chosen as the minimum temperature at which all peaks in the TPU/PDMS proton spectrum could be resolved, yet it is 8 to 10 K below the onset of the melting endotherm of the hard segment as measured by DSC. Four peaks were detected in the broad-line spectrum, which correspond to the aromatic protons, the methylene protons adjacent to oxygen in the soft segment, the internal methylene protons in the soft segment, and the PDMS protons, ranked from the downfield to the upfield direction.

A total of 100 spectra were recorded for each sample, with each spectrum having an incremented number of spin echoes taken according to the CPMG T_2 pulse sequence.[14,15] The resulting FIDs were then Fourier transformed and baseline corrected. The decays of peak intensities were fitted to either a single or double-exponential decay using the Marquardt–Levenburg algorithm.[16]

Anisotropy

Measurements of the anisotropy in extruded material were made on a Bruker MSL300 spectrome-

ter operating at 300.13 MHz for ^{1}H and 75.46 MHz for ^{13}C, using the method of Harbison and Spiess.[17] A standard 7 mm BB MAS probe was used with typical p/2 pulse times of 3.5 ms. Samples of extruded film were stacked in 7 mm rotors with the draw director perpendicular to the rotor axis. ^{13}C-CPMAS spectra were collected using a CP contact time of 1 ms, and with data acquisition gated so that different spectra were collected at 16 equally spaced orientations of the rotor in a complete rotor period. The resultant 2D data set was analyzed after Fourier transformation in both dimensions. Peaks in the w_1 direction were analyzed using the method described by Harbison and Spiess.

Differential scanning calorimetry (DSC) measurements were performed on a Perkin–Elmer DSC7 at scan rates of 40°C/min from −170 to 100°C and 20 °C/min from 100 to 250°C. Calibrations were made against dodecane, indium, and zinc at the scan rates used. Glass transition temperatures were taken from the point of inflection of the thermograms.

Dynamic mechanical analysis (DMA) scans were made using the 5 mm, three-point bend mode of a Perkin–Elmer DMA7 instrument at a scan rate of 5°C/min, a frequency of 1 Hz, a dynamic stress of 700 mN, and a static stress of 850 mN. The glass transition temperatures were taken from the onset of the peak of the tan δ curve.

RESULTS AND DISCUSSION

In previous work,[2] changes in the physical properties of extruded TPU/PDMS blends were reported over a range of PDMS concentrations between 0 and 4% (w/w). The PDMS used was a nonreactive polymer with a fluid viscosity of 10^3 m^2 s^{-1} and a molecular weight of 139 kg mol^{-1} surplied by Flexichem.[2] Two TPUs of different hardness were studied, the difference in hardness being attributed to differences in the ratio of hard to soft segments. The harder of the two TPUs was from the Dow Pellethane range, with hardness 55D (Pel55D), and the other was from the BASF Elastollan range of TPUs with a hardness of 85A (Ela85A). On blending with PDMS, significant increases in the mechanical properties of up to 50% (cf. pure TPU) were observed. However, at PDMS concentrations greater than the optimal 1.5–2%, all properties (with the exception of the CoF) began to degrade. It was also observed that the softer Ela85A TPU was more prone to physical properties modification by PDMS than was the

harder TPU. A summary of these results and the characteristics of the TPUs are given in Table I. Typical relationships between the inverse of wear rate (i.e., wear resistance) and the tensile product (tensile strength × elongation to break) with the concentration of PDMS are presented in Figure 1. Note the similarity in the curve shapes for the two properties with coinciding optimal PDMS concentrations of 2%.

As outlined in the Introduction, the observed improvement in the mechanical properties was not expected from reports in the literature. Several possible explanations for the observed blend properties upon addition of PDMS have been investigated.

Alternative Models

The first model examined to describe the effect of the addition of PDMS involved only a modification of the polymer surface by the PDMS, as was discussed in an earlier publication[2] and in the Introduction of this article. Although surface modification is apparent, it has been shown not to be responsible for the observed relationship between the mechanical or the wear properties and the PDMS concentration. Evidence of this is in the increase in Young's modulus at the optimum PDMS concentration, and the sustained improvement in wear performance of the blends after the surface had been totally removed by abrasion.

The second model considered was one based on phase separation between soft and hard domains in polyurethane, which is known to enhance the performance of polyurethane.[12,18,19] Shibayama et al.[7,8] have shown that the presence of PDMS (6% w/w) can promote phase separation between MDI based hard domains and PTMO soft domains. Such a phase separation would be consistent with the observed improvements in wear performance,[12] tensile strength, and elongation to break.[19] However, the Young's modulus would be expected to decrease for this model rather than increase[18] and the Shore hardness should be affected, which is not the case.[2]

To confirm that the second model does not apply, measurements were made of the interdomain spacing (d-spacing) between hard domains using SAXS. It was found that the average spacing between hard domains was invariant across the range of blend compositions within the experimental error, quoted as ±20 Å.[12] Values for d-spacing (Table II) were consistent with those reported elsewhere for as-moulded TPU.[12] Secondly, solid-state NMR ^{1}H $T_{1\rho}$ measurements were made

Table I   TPU Characteristics and Summary of the Improvements in the Physical Properties for the Optimum PDMS Concentrations, Compared with Virgin TPUs[2]

TPU[b] ID	TPU Characteristics			% Improvement in Properties[a] (Compared with Virgin TPU)				
	Shore Hardness	% Hard Segment	MW Soft Segment	Wear Rate (down)	CoF (down)	Tensile Strength (up)	Elongat'n to Break (up)	Young's Modulus (up)
Pel55D[c]	55D	55% (w/w)	720	25%	60%	10%	20%	10%
Ela85A[d]	85A (36D)	42% (w/w)	860	15%	25%	40%	50%	10%

[a] All data are for testing longitudinally to the direction of extrusion.
[b] Both polymers are based on poly(tetramethylne oxide) (PTMO) soft segments and 4,4′-diphenylmethane diisocyanate (MDI)/1,4-butanediol hard segments.
[c] Pel55D ≡ Dow Chemical, Pellethane 2103-55D (harder TPU).
[d] Ela85A ≡ BASF, Elastollan 11-85A-10-000 (softer TPU).

to confirm that there were no changes in the size of the microdomains. ^1H $T_{1\rho}$, which in heterogeneous solids is a measure of the size of the slowly relaxing domains (hard domains in this case),[20] was found to be constant at 298 K and typically at 3.0 ms (for the aromatic carbons), across the composition range. This again confirms that there was no change in segregation of the hard blocks on addition of PDMS. Finally, DSC measurements of the melting transitions of the hard segments showed that the T_m of the hard domains were constant at 414 K (Ela85A) and 431 K (Pel55D), and the addition of PDMS did not change the heat absorbed in the melting endotherms (4.7 Jg^{-1} and 16 Jg^{-1}, respectively). It is known that the melt-

ing temperature of the crystalline regions in polyurethane materials is dependent on the size and perfection of the crystalline domains.[21] All of this evidence is consistent with a constant degree of hard/soft domain phase separation over the whole range of PDMS concentrations.

In summary, both the model of surface modification and the model of increased segregation of the hard domains are inadequate to describe the experimental data, and are rejected.

Free Volume Model

Measurements of Changes in Free Volume

From the above discussion, it is apparent that the PDMS is present in the bulk TPU and not just confined to the surface, but at the same time, it does not affect the degree of segregation of the TPU into hard and soft domains. If the PDMS mixes with the TPU, it is likely that it will effect the free volume of the system. In the next section several methods are described that were used to probe changes in chain packing, and hence, free volume, in the soft domains of the TPU.
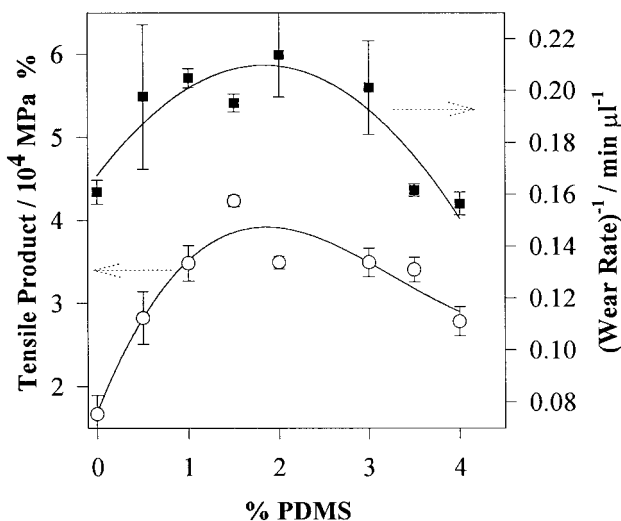

Figure 1   Tensile product (tensile strength × elongation to break) and the inverse of wear rate (≡ wear resistance) for Ela85A vs. the concentration of PDMS (%w/w) in the blends.[2]

Table II   Average Interdomain Spacing (*d*-Spacing) in Extruded TPUs, Calculated from SAXS Data

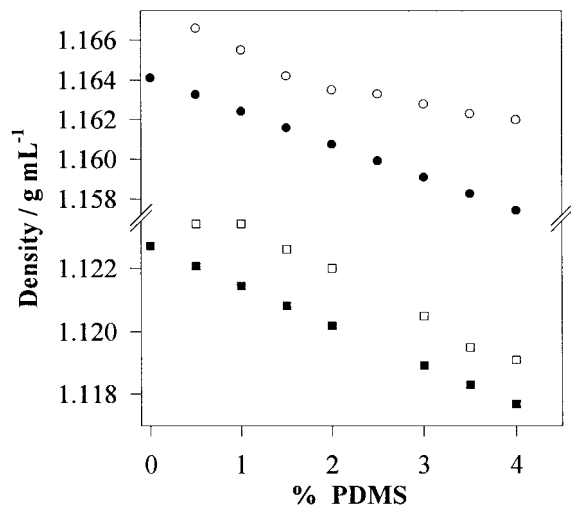|	Longitudinal to Extrusion	Transverse to Extrusion
Ela85A	131 ± 10 Å	125 ± 6 Å
Pel55D	125 ± 10 Å	118 ± 8 Å

d-spacings quoted ± 2 standard deviations.

Figure 2 Density vs. the concentration of PDMS in the blends, (Pel55D and Ela85A). Pel55D, Exp. ○, Calc. ●; Ela85A, Exp. □, Calc. ■.

The first piece of evidence that PDMS mixes with the TPU is the measurements of the density of the blend on the addition of PDMS. In Figure 2 the densities of the blends are plotted as a function of PDMS concentration. Also plotted are the densities expected for these blends based on the additivity rule, calculated from the densities of PDMS (0.977 g/cm^{-3} [22]) and of the two TPUs (Ela85A = 1.123 g/cm^{-3} and Pel55D = 1.164 g/cm^{-3}). It must be stressed that SAXS, NMR, and DSC measurements reported above have confirmed that there is no change in the size or total volume of the hard domains on addition of the PDMS. Furthermore, evidence of the isolation of the action of PDMS to the soft domains of the TPU (rather than the hard domain) can be obtained from the observation that the softer TPU (Ela85A), having the higher soft segment content, is much more prone to modification by PDMS.[2] It is clear from Figure 2 that the density of the blend is greater than that predicted from the additivity rule. Therefore, the PDMS appears to promote improved chain packing in the polytetramethylene oxide [PTMO, (TPU soft segment)].

A sensitive measure of changes in packing, and hence, free volume, is the glass transition temperature (T_g). In an ideal copolymer or blend the partial specific volumes of the two components remain the same as in the homopolymers, and the T_g of a blend is therefore given by[23]:

$$\frac{1}{T_g} = \frac{1}{(w_1 + B_{w_2})} \times \left[\frac{w_1}{T_{g_1}} + \frac{B_{w_2}}{T_{g_2}} \right]$$

where T_{g_1} and T_{g_2} are for the respective homopolymers 1 and 2, w_1 and w_2 are the mass fractions of the homopolymers and B is a constant close to unity. A similar equation given by O'Brian[24] applies for polymer/plasticiser mixtures. Calculations have been made for the T_gs of the PTMO in ideal blends over the range of PDMS concentrations used. Because, as will be been shown below, the PDMS resides only in the soft domain (PTMO), the mass fraction (w_1) of the polymer has been taken as the mass of the PTMO soft segment alone (i.e., ignoring the hard segment). The calculated values of T_g are represented in Figure 3 by the dotted lines. T_g values measured by DSC are also plotted on the same graph and lie above the theoretical curve. Furthermore, a curve drawn through the experimental points is similar in shape to that for the mechanical properties in both series, i.e. there is a maximum deviation from expected behavior at ∼ 1.5–2% PDMS. The increase in the T_g values, compared with theory, can be attributed to the better packing of the PTMO chains. The improved packing would result in a reduction in the free volume available for motion of the chains, and hence, the T_g of PTMO would be shifted towards a higher temperature.

Similar conclusions were obtained from measurements of T_g by DMA (Fig. 4). T_g was defined as the temperature at the onset of the tan δ peak in DMA temperature scans. The absolute values of T_g obtained from the DMA are comparable to
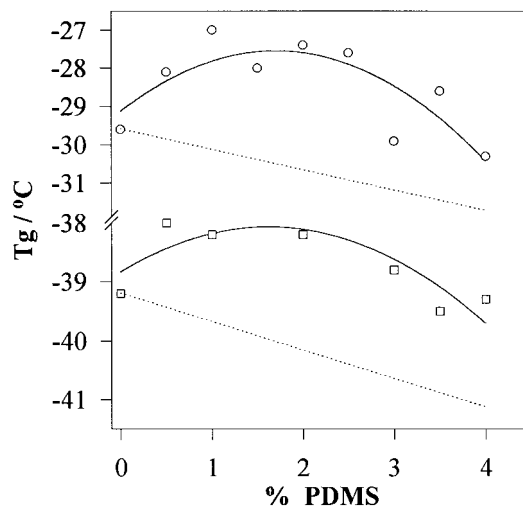

Figure 3 Experimentally measured glass transition temperatures for PTMO (T_g measured from the point of inflection in the DSC thermogram), vs. the concentration of PDMS in the blends (Pel55D, ○ and Ela85A, □). The dotted line represents the theoretically calculated T_g for an ideal blend.
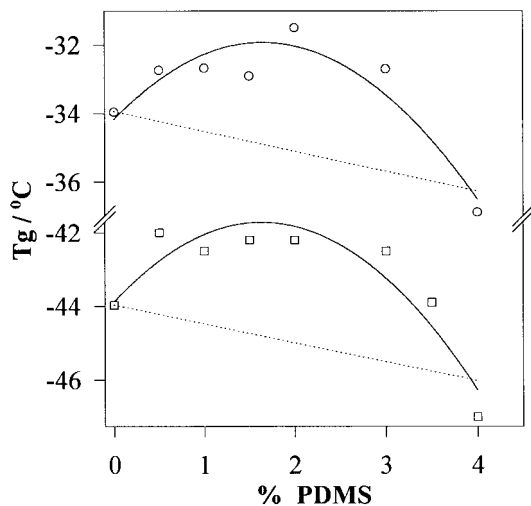
Figure 4 Experimentally measured glass transition temperatures for PTMO (T_g measured from the onset of the tan δ peak by DMA), vs. the concentration of PDMS in the blends (Pel55D, $\bigcirc$ and Ela85A, $\square$). The dotted line represents the theoretically calculated T_g for an ideal blend.

the DSC values, being systematically 4 to 5°C lower. This systematic difference may be associated with the different chain motion frequencies probed by the different techniques, differing scan rates, and differences in defining T_g (i.e., midpoint of the DSC thermogram, cf. onset of DMA tan δ peak). The observed trends are, however, very similar and confirm that blending PDMS increases the packing efficiency and reduces the free volume of the soft PTMO segments.

Further evidence for increases in the packing efficiency in the blend can be obtained from the shape of the tan δ peak with increasing PDMS content. The half-width of the tan δ peak remains almost constant with increasing PDMS content, but the intensity of the peak decreases and the maximum shifts to higher temperature. This behavior is consistent with a lower energy loss and increased elasticity in the blends.

Indirect evidence for the mixing of PDMS with PTMO can also be found from DSC. In blends of Pel55D with PDMS a small endothermic peak was observed at ~ -45°C, which is due to the melting of PDMS, as confirmed from the literature[10,25] and from DSC scans of pure PDMS. For blends of Ela85A with PDMS, no such transition is present at any PDMS concentration. The absence of the PDMS melting endotherm in Ela85A may be explained if PDMS is sparingly miscible with the PTMO of this polyurethane. In Pel55D, which has a lower PTMO content, the PTMO becomes satu-

rated with PDMS, and thus we see a transition for free, phase-separated PDMS. However, with the higher PTMO content of Ela85A, saturation, and hence, phase separation is not achieved in the concentration range of PDMS used, and therefore the melting transition of PDMS is not observed because all of the PDMS is intimately mixed with PTMO. Measurements of NMR T_2 reported below support these conjectures.

It is possible to calculate the energy of the PDMS melting transition in Pel55D blends, and it was found that 28% of the PDMS chains remain phase separated. Therefore, DSC measurements suggest that the ratio of phase-mixed to phase-separated PDMS in Pel55D is roughly 70 : 30.

The above results point to a change in the free volume of the soft segment on the addition of PDMS. The initial increase in the density and the glass transition temperature on addition of PDMS, and the subsequent decrease in these properties at higher concentrations, reflects an initial antiplasticization and subsequent plasticization of the TPUs soft segment by PDMS. Antiplasticization is a phenomena that occurs in many polymers on addition of low levels of plasticiser. Under these circumstances, the Young's modulus and tensile strength are observed to initially increase to a maximum and then decrease at higher plasticiser levels as normal plasticization sets in,[24] as was observed in the TPU/PDMS blends.[2] The most accepted explanation for antiplastisization is that a small amount of plasticiser, below a certain "threshold level," provides enough additional free volume (or lubrication) to the system to permit limited chain mobility. This can result in a greater degree of polymer–polymer interaction and realignment and the development of small increases in localized molecular order or chain packing.[24] For the blends, this means that at the low optimal (or "threshold") PDMS concentrations of 1.5–2%, the PDMS promotes improved packing of the PTMO chains that are associated with it. This would explain the observed relationship between Young's modulus and tensile strength with PDMS concentration. It would also explain the observed trends in wear resistance, because wear resistance is often correlated with increased tensile properties (workers most commonly show correlations between wear resistance and tensile product (or energy to break).[26,27] The variation of tensile product with PDMS concentration can be seen in Figure 1. Note that it varies with PDMS concentration in a very similar fashion to wear resistance. This is an indication that the improved wear resistance is a direct result of

the improved mechanical properties and, hence, a result of antiplasticization.

Although PDMS has a higher molecular weight ($139,000$ g mol^{-1}) than most plasticisers, which are generally considered to be molecules of 300 to 6000 g mol^{-1},[24] it could be rationalized to act as a plasticiser, due to its very low glass transition temperature (T_g). The most widely accepted mechanism for plasticization is based on the Free Volume Theory.[24] The free volume is the difference between the polymer volume (defined by Van der Waals radii) and total volume occupied by the polymer; this difference is the volume associated with the packing of the polymer chains. At or below the T_g the polymer will have a limited free volume because large-scale molecular motions are severely curtailed, the addition of a small plasticiser molecule (which has a greater free volume than the polymer, i.e., lower T_g), will increase the free volume of the plasticized polymer, and so decrease the T_g of the blend. PDMS has a large molar volume (75.5 cm^3/mol[28] due to the ease with which the methyl groups rotate around the Si—O bond[29]), which is manifested as an extremely low T_g of $-123°$C.[29] Therefore, PDMS could act as a plasticizer for the PTMO soft segments in these polyurethanes, which have a much higher T_g; in the range -30 to $-45°$C.

Measurement of Mixing of PDMS with Soft Segments

The proposed model of interaction of PDMS with TPU requires that these two polymers be miscible with each other. The large differences in the solubility parameters of PDMS and TPU [δ(PDMS) $= 31$ J$^{1/2}$cm$^{-3/2}$mol^{-1}, δ(TPU hard segment) $= 55$ J$^{1/2}$cm$^{-3/2}$mol^{-1}) and the reported immiscibility of PDMS with TPU[30] may suggest that the model, based on antiplasticization, could not apply, because by definition plasticizers must be miscible with the polymer.[24] However, evidence detailed above suggests that the PDMS is miscible with the PTMO soft domain of the TPU. The miscibility and mobility of the blend components have been studied using a solid-state NMR technique.

A comprehensive study has been made of the NMR T_2 relaxation times of the Pel55D blends. The NMR method used in this work is sensitive to molecular motion (chain segment reorientation and curvilinear diffusion in the system) occurring on a time scale of hundreds to tens of thousands of microseconds. This type of analysis is certainly not new, and has been applied to a variety of systems in the past, including examination of ther-

mally initiated crosslinking,[31] effects of chain orientation on morphology,[32] effects of carbon black in rubbers,[33] and the determination of molecular weight using calibration standards.[34] It has been shown, for example, that a good descriptive model of molten polyethylenes follows a multicomponent relaxation,[35] of the general form:

$$I = I^f \times \exp(-t/T_2^f) + I^s \times \exp(-t/T_2^s)$$

where $I^f =$ the intensity of the fast relaxing component, assigned to regions of high segmental density in the molten polymer; $I^s =$ the intensity of the slowest relaxing component, assigned to relatively mobile chains with no involvement in entanglements; T_2^f, T_2^s, $=$ the spin-spin relaxation time constants associated with each component.

In the above analysis, the fast and slow regimes in the inhomogeneous polyurethane material are related to more or less constrained polymer chains and chain segments within the polymer. In a two-component system, the T_2 time constant is indicative of the motional freedom of the chains, and the preexponential constant is a relative measure of the number of protons contributing to the motional frequencies described by T_2.

NMR T_2 measurements were made at 423 K, which is below the melting transition of the hard segments, and is sufficiently high a temperature to increase the resolution in the proton NMR spectrum. Measurements were made of the T_2 relaxation times of each of the four resolved peaks using the CPMG sequence,[14,15] and the resultant decays were fitted to either a single or, where necessary, a double exponential decay. Table III shows the intensities and time constants (T_2) of these decays.

Aromatic Protons

The aromatic protons in this polymer are resident in the hard segments of the TPU materials, and thus are in a highly constrained environment. The T_2 relaxation of this region is well defined by a single exponential decay, indicating that the aromatic protons are in a single morphological environment. The T_2 relaxation times, of the order of 1.8 ms, are the shortest of those measured, as expected for a relatively rigid environment, and most importantly show no variation with PDMS content. This is a reasonable indication that the hard segment region is unaffected by the addition of PDMS, and more precisely that the PDMS does not enter the hard domain.

The T_2 value, of 1.8 ms, is much longer than

Table III T_2 **Relaxation Times and Associated Intensities (I_o) for Various PDMS Blends with Pel55D**

% PDMS	Aromatic Peak T_2 (ms)	Aliphatic Peak at 3.3 ppm				Aliphatic Peak at 1.5 ppm				PDMS			
		I_o^s %	I_o^f %	T_2^s (ms)	T_2^f (ms)	I_o^s %	I_o^f %	T_2^s (ms)	T_2^f (ms)	I_o^s %	I_o^f %	T_2^s (ms)	T_2^f (ms)
PDMS										100		32	
Pel55D													
(virgin)	1.8	50	50	19	3.7	70	30	19	2.3				
1%	1.8	29	71	15	2.8	34	66	18	3.4	33	67	36	3.9
1.5%	1.9	35	65	16	3.1	36	64	20	3.7	32	68	39	3.4
2%	1.8	36	64	15	2.7	32	68	21	3.2	31	69	38	2.4
3%	1.9	35	65	17	3.1	42	58	18	3.2	50	50	62	2.6
4%	1.8	37	63	13	2.5	37	63	20	3.5	63	37	80	3.2

that expected for totally rigid, crystalline blocks. But at the elevated temperature at which these experiments were performed, there is significant motion of the blocks and of the chains within the blocks.

Aliphatic Protons

Two peaks are resolved in the ^{1}H-NMR spectra due to the methylene protons from the PTMO soft segment:

$$(-CH_2-CH_2-CH_2-CH_2-O-)_n.$$

The peak at 3.3 ppm is due the methylene protons adjacent to the ether linkage (external protons), while the peak at 1.5 ppm is due to the other protons in the aliphatic sequence (internal protons). The data obtained from the T_2 experiments showed that even in the pure Pel55D material, two exponential time constants are required to describe the data. It is possible to assign the two components in terms of relative motional freedom, with the faster relaxing component being due to protons that are within or adjacent to the hard domains, or involved in chain entanglements. The component with the longer T_2 time constant (T_2^s) has a higher degree of motional freedom, and is ascribed to material effectively isolated in the soft domains. The I_o values given are the intensities (as percentages) associated with the two relaxation decays and correspond to the amount of material in each environment. Comparing the percentage of signal for the longer T_2 relaxation (I_o^s) for pure TPU with I_o^s for the TPU/PDMS blends (Fig. 5), it can be noted that there is a decrease in I_o^s with the addition of

PDMS. This indicates that the PDMS has acted on the soft segment of the TPU so that the motional freedom is decreased. This decrease in motion is attributed to an increased packing efficiency, as suggested previously.

It can also be noted from Table III that for the pure TPU, the external aliphatic protons (3.3 ppm) have a lower I_o^s than the internal protons (1.5 ppm). This indicates that the external protons are more restrained than the internal, which would be expected because the external protons are either adjacent to hard domains when they are in terminal tetramethylene groups, or they are adjacent to weak hydrogen bonded ether linkages. Once PDMS is added, the I_o^s for the internal methylene groups (1.5 ppm) is halved as the
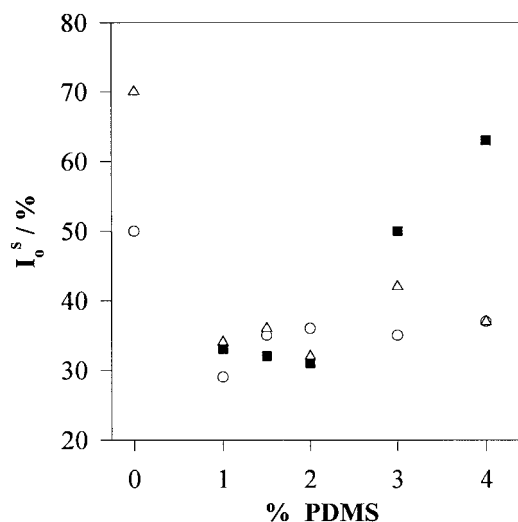

Figure 5 Intensity of the slow relaxing protons (I_o^s), measured from T_2-NMR experiments for the aliphatic protons of PTMO (3.3 ppm ○ and 1.5 ppm △) and for the PDMS protons, ■, vs. the concentration of PDMS in the Pel55D blends.

PTMO becomes more tightly packed and the internal protons lose motional freedom.

PDMS Protons

The pure PDMS fluid has a single exponential T_2 decay with a time constant of approximately 32 ms. If, on blending, the PDMS material is located in phase separated pools, time constants would be expected to have a similar magnitude to that observed for pure PDMS. However, the T_2 decay of the PDMS in all of the blends required two exponentials to describe the data adequately. The presence of a fast relaxing T_2^f component indicates that most of the PDMS is intimately mixed with the Pel55D blend ($I_o^f = \sim 70\%$, below the optimum) and it is in a more restrained environment than in pure PDMS fluid. Thus, the PDMS is closely associated with the more tightly packed PTMO chains.

The relaxation times of the slowly relaxing component (T_2^s) for PDMS blends, at or below the optimal PDMS level required for enhancement of properties (1.5–2%), is of a similar magnitude to that for pure PDMS. This indicates that there is some phase-separated PDMS below the optimum PDMS concentration. The data indicates that $\sim 30\%$ of the PDMS is in phase-separated domains. This result is in excellent agreement with the measurement of 28% in phase-separated domains obtained by DSC, discussed above. Beyond the optimum concentration of PDMS, a dramatic increase in I_o^s intensity is observed (shown in Fig. 6), indicating the onset of gross phase separation of PDMS.

The reason why the T_2^s values for PDMS in blends at concentrations above the optimal PDMS level should be two to three times that for pure PDMS is unclear. The data indicate that the phase separated pools of PDMS have even more motional freedom than pure PDMS. Knaub et al.[36] have reported a decrease in the T_g of PDMS in similar blended systems, however, they were also unable to explain their results. The systems they studied were reactive blends of poly(urethane-ureas)(PUR) and vulcanized PDMS compatibilized with PUR-b-PDMS; PDMS concentrations were in the range 10 to 90%. At and below 40% PDMS the PUR was the continuous phase with PDMS dispersed as nodules of between 5 and 30 μm, and above 40% PDMS phase inversion occurred and the PDMS network became the continuous phase. The T_g of PDMS in the blends were measured by DSC. For blends with greater than 40% PDMS (i.e., PDMS is the continuous phase) the T_g was
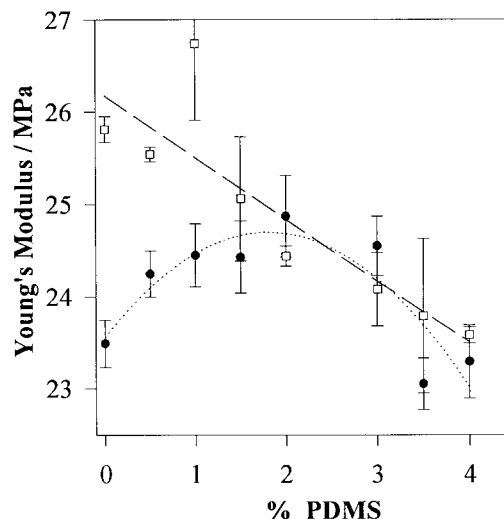

Figure 6 Young's modulus of Ela85A from tensile tests in the longitudinal, ●, and the transverse, □, directions to extrusion.

found to be equal to that of pure PDMS. However, for blends containing less than 40% PDMS, the T_g was displaced to a lower temperature than that of pure PDMS (by some 6°C). This is consistent with a greater degree of motional freedom in the phase separated nodules of PDMS, and therefore consistent with the increased T_2 after gross phase separation sets in. Further work will be required to explain these phenomena. It may be speculated that the shear of the blending process (extrusion in this work or prolonged mixing with prepolymer in the case of Knaub et al.) may leave the phase separated pools of PDMS in a less tangled state, resulting in higher motional freedom, and thus longer T_2 relaxation times and lower T_gs.

Effects of Phase Separation of PDMS

The measurements of the T_2 relaxation times of PTMO indicate that the PDMS mixes with the soft segments of the TPU, and improves the chain-packing efficiency. This phenomenon can account for the observed experimental results, for example, the wear performance, tensile properties at low PDMS concentrations, densification, and the increase in the T_g of PTMO for the blends. At higher concentrations of PDMS there is evidence of gross phase separation of the PDMS. This has a profound negative effect on the blend properties, particularly the elongation to break.

The elongation to break has been observed to decrease on addition of PDMS at levels above the optimum concentration.[2] If PDMS acts as a classi-

cal plasticiser, elongation to break should continue to increase throughout the range of PDMS concentrations.[24] The observed decrease in elongation to break is therefore ascribed to the formation of phase separated domains of PDMS, as detected by DSC and NMR. The phase separation of the PDMS would also act in synergy with plasticization to reduce the other physical properties of the blends. The adverse effect of phase separation of PDMS on polyurethane properties has been previously reported, usually for block copolymers. Knaub et al.[36] found that the immiscibility of the PDMS with the polyurethane system (they used ≥10% PDMS) caused high interfacial tension and poor adhesion between the phases. The poor interfacial adhesion prevents efficient transfer of stress between the phases, and hence, results in a reduction in the mechanical properties.

A second observation that appears to be inconsistent with the antiplastisization model is that Young's modulus shows a linear decrease with respect to PDMS content in tensile tests carried out in the transverse direction to extrusion (Fig. 6). However, this may be explained by the PDMS acting as a lubricant, both during processing and afterwards, which allows the PTMO chains to move relative to one another more readily. At the optimum level of PDMS, the PTMO chains are able to attain a higher degree of orientation and packing (i.e., antiplasticization) in the extrusion direction during melt processing, due to shearing through the die and drawing onto the cold rollers. The extruded conformation is then locked in on the cold rollers by the rapid crystallization of the hard domains. During tensile testing this orientation in the PTMO soft segments in the longitudinal direction results in the observed typical antiplasticization behavior of the longitudinal Young's modulus, as seen in Figure 6. However, when tested in the transverse direction to extrusion, the transverse Young's modulus is observed to decrease with the addition of PDMS due to a combination of increased lubrication and a reduction in entanglement density, which allows the polymer chains to slide over one another more easily.

It has been suggested above that the PTMO chains are orientated in the longitudinal direction on extrusion of the blend samples. This is strongly supported by comparing the stress–strain diagrams for the longitudinal and transverse tests (Fig. 7),[2] showing that in the longitudinal direction, stress develops more rapidly than in the transverse direction. This would be expected if
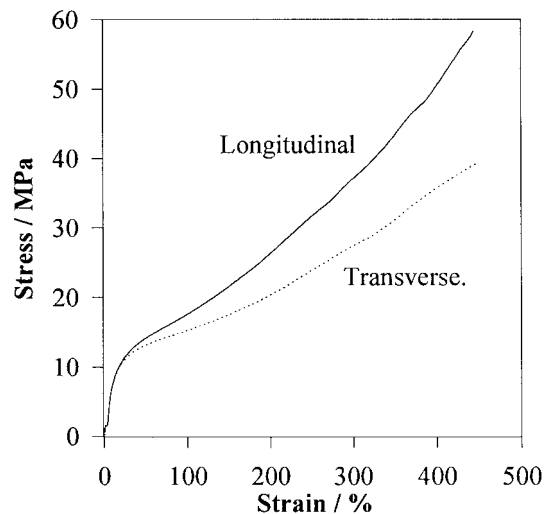

Figure 7 Typical stress–strain curves for Pel55D (longitudinal and transverse to the direction of extrusion).[2]

there was a degree of orientation in the longitudinal direction.

Solid-state NMR has been used to detect orientation in the extruded tapes with the aim of demonstrating that the mechanical anisotropy observed from tensile testing is confined to the soft segment as required by the packing model. The method of Harbison and Spiess [17] relies on the angular dependence of the ^{13}C chemical shift tensor. MAS spectra of aligned samples were recorded at a series of orientations with respect to the magnetic field, defined by the MAS rotor position. A Fourier transform with respect to the rotor position revealed peaks associated only with the chemical shift tensor of the PTMO in the soft segment, that is, the orientation was confined to the soft segments. No peaks were observed for the hard segment, indicating a lack of macroscopic order. The degree of order in the soft segments is low (estimated < 0.05), and could not be quantified due to possible errors in aligning the samples in the rotor.

Crystallinity of PTMO

DSC scans of the TPU have shown a small degree of PTMO crystallinity, with a melting endotherm at ∼ 70°C, which disappears in the second scan. The disappearance of this transition in the second scan has been documented by other workers and it cannot be detected in DMA scans.[30] A plot of the enthalpy of this transition versus the PDMS content of the blends (Fig. 8, Ela85A) shows a linear decrease in the degree of PTMO crystallin-
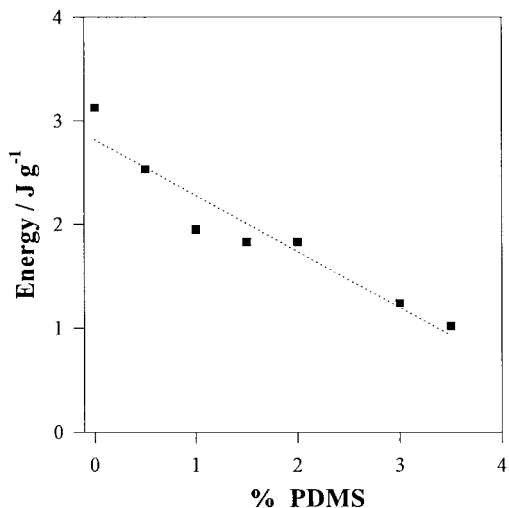
Figure 8 Enthalpy of the melting transition of PTMO in Ela85A blends vs. the PDMS content. Gradient = −0.54 J/g%.

ity with increasing PDMS concentration (r^2 = 0.92), which is consistent with the findings of other workers.[37–39] The melting transitions of PTMO in the Pel55D materials were very small, as would be expected because of the lower PTMO molecular weight and the lower PTMO content in this polymer.

This result indicates that PDMS reduces the degree of crystallinity of the PTMO in the blends, and others have found that PDMS inhibits stress crystallization of PTMO.[37–39] This is a good indication that stress crystallization will also be inhibited in the blends produced in the current work. The lower degree of crystallinity may contribute to an increased flexibility of the blends and an increased elongation to break, which was the most improved property measured for the blends. PTMO has previously been shown to decrease elongation to break in poly(urethane)s.[37,38] Finally, decreased crystallinity of PTMO has also been shown to promote better fatigue performance of poly(urethane)s.[40]

CONCLUSIONS AND SUMMARY OF MODEL

It has been reported previously[2] that blending low concentrations of PDMS with TPU results in a large improvement in mechanical properties, while at higher levels of PDMS (>3%), physical properties begin to be adversely affected. In this study the PDMS has been shown to act predominantly in the bulk of the polymer rather than solely at the surface of the blends. A model of the behavior of PDMS has been proposed that is consistent with all of the observed relationships between the physical properties and the PDMS concentration in the blends. Evidence has been presented that strongly supports this model.

It has been proposed that the addition of small concentrations of PDMS to the TPU promotes more efficient packing of the PTMO, the soft domain of the TPU. This mechanism can be described as an antiplasticization of the PTMO, which is then locked in by physical crosslinks provided by the hard segments. The model is successful in describing the improvements in mechanical properties and wear resistance up to an optimal concentration of PDMS of 1.5 to 2%. Beyond the optimal PDMS concentration, the physical properties begin to deteriorate due to plasticization and due to gross phase separation of PDMS. The model is also successful in explaining why the softer TPU (Ela85A), with a higher soft domain content, is more prone to modification by PDMS.

The inhibition of the crystallization of PTMO by PDMS has also been established and evidence from other workers suggests that it may work in synergy with improved packing to promote flexibility and elongation properties of the blends. It may also improve the fatigue resistance of the blends.

An understanding of the interactions between the TPU and the PDMS in these blends, and especially the mechanism leading to the observation of an optimal PDMS concentration, and its dependence on TPU hardness, will be of great importance in designing materials for field applications in the mining industry.

Further work is required to show that the model is applicable across a range of processing techniques and a range of commercial polyurethanes (e.g., thermoplastics vs. cast thermoset polyurethanes). Preliminary results for changes in the mechanical properties, wear, density, and glass transition temperatures suggest that the packing model does apply to moulded TPUs as well as to cast thermoset materials.[41]

REFERENCES

1. S. L. Cooper and A. V. Tobolsky, *J. Appl. Polym. Sci.,* **10,** 1837 (1966).
2. D. J. T. Hill, M. I. Killeen, J. H. O'Donnell, P. Pomery, D. St. John, and A.K. Whittaker, *J. Appl. Polym. Sci.,* **61,** 1757 (1996).
3. D. J. Gordon, *AFP Tech. Paperm.,* **FC76–505,** 1 (1976).
4. M. Yamada, T. Makumoto, T. Kurosaki, Y. Iwasaki, A. Sejimo, and H. Okada, *Meiji Rubber and Chemical Co., Tech. Rep.,* **14**(1), 27 (1991).
5. D. Feldman, *Proc. 28th IUPAC, Macromol. Symp.,* **671,** (1982).
6. N. E. Lake and J. G. Uhlmann, *High Perform. Plast., Natl. Tech. Conf., Soc., Plast. Eng.* [*Prepr.*]*,* 98 (1976).
7. S. Sakurai, S. Nokuwa, M. Morimoto, M. Shibayama, and S. Nomura, *Polymer,* **35,** 532 (1994).
8. M. Shibayama, M. Suetsugu, S. Sakurai, T. Yamamoto, and S. Nomura, *Macromolecules,* **24,** 6254 (1991).
9. X. Chen, J. A. Gardella, T. Ho, and K. J. Wynne, *Macromolecules,* **28,** 1635 (1995).
10. R. Benrashid and G. L. Nelson, *J. Polym. Sci., Part A: Polym. Chem.,* **32,** 1847 (1994).
11. A. K. Sha'aban, S. McCartney, N. Patel, I. Yilgor, J. S. Riffle, D. W. Dwight, and J. E. McGrath, *Polym. Prepr.,* **24,** 130 (1983).
12. J. I. Mardel, A. J. Hill, K. R. Chynoweth, M. E. Smith, C. H. J. Johnson, and T. J. Bastow, *Wear,* **162–164,** 645 (1993).
13. ASTM D 792–91.
14. H. Y. Carr and E. M. Purcell, *Phys. Rev.,* **94,** 630 (1954).
15. S. Meiboom and D. Gill, *Rev. Sci. Instrum.,* **29,** 688 (1958).
16. W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in C. The Art of Scientific Computing,* 2nd ed., Cambridge University Press, Cambridge, 1992, p. 683.
17. G. S. Harbison and H. W. Spiess, *Chem. Phys. Lett.,* **124,** 128 (1986).
18. S. L. Cooper and A. V. Tobolsky, *J. Appl. Polym. Sci.,* **10,** 1837 (1966).
19. R. A. Assink and G. L. Wilkes, *J. Appl. Polym. Sci.,* **26,** 3689 (1986).
20. V. J. McBrierty and D. C. Douglass, *Phys. Rep.,* **63,** 61 (1980).
21. B. Hartmann, J. V. Duffy, G. F. Lee, and E. Balizer, *J. Appl. Polym. Sci.,* **35,** 1829 (1988).
22. Flexicem Product Catalogue, 1994, p. 262.
23. I. M. Ward and D. W. Hadley, *An Introduction to the Mechanical Properties of Solid Polymers,* John Wiley & Sons, Chichester, 1993.
24. J. L. O'Brian, in *Thermoplastic Polymer Additives; Theory and Practice,* J. T. Lutz, Jr., Ed., Marcel Dekker, Inc., New York, 1989.
25. H. Kazama, T. Ono, Y. Tezuka, and K. Imai, *Polymer,* **30,** 553 (1989).
26. D. C. Evans and J. K. Lancaster, *Treatise Mater. Sci. Technol.,* **13,** 85 (1978).
27. B. Brisco, *Tribol. Int.,* **14,** 231 (1981).
28. C. B Hurd, *J. Am. Chem. Soc.,* **68,** 364 (1946).
29. I. Yilgor and J. E. McGrath, *Adv. Polym. Sci.,* **86,** 1 (1988).
30. J. P. Pascault and Y. Camberlin, *Polym. Commun.,* **27,** 230, (1986).
31. J. P. Cohen−Addad and C. Schmit, *J. Polym. Sci., Part C: Polym. Lett.,* **25,** 487 (1987).
32. H. Tanaka and K. Takagi, *Br. Polym. J.,* **21,** 519 (1989).
33. S. Kaufman, W. P. Slichter, and D. D. Davis, *J. Polym. Sci., Part A-2,* **9,** 829 (1971).
34. A. Charlesby and J. Steven, *Int. J. Radiat. Phys. Chem.,* **8,** 719 (1976).
35. T. Bremner and A. Rudin, *J. Polym. Sci., Part B: Polym. Phys.,* **30,** 1247 (1992).
36. P. Knaub, Y. Camberlin, and J.-F. Gerard, *Polymer,* **29,** 1365 (1988).
37. T. Ho and K. J. Wynne, *Polym. Mater. Sci. Eng.,* **67,** 445 (1992).
38. T. Ho and K. J. Wynne, *Polym. Adv. Technol.,* **6,** 25 (1995).
39. G. Spathis, M. Niaounakis, E. Kontou, L. Apekis, P. Pissis, and C. Christodoulides, *J. Appl. Polym. Sci.,* **54,** 831 (1994).
40. S. Sakurai, S. Nokuwa, M. Morimoto, M. Shibayama, and S. Nomura, *Polymer,* **35,** 533 (1994).
41. M. I. Killeen, PhD Thesis, University of Queensland (1996).