Development of Wear-Resistant Thermoplastic Polyurethanes by Blending with Poly(dimethyl siloxane). I. Physical Properties

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SYNOPSIS

Commercial thermoplastic polyurethanes have been melt blended on a standard laboratory extruder with low levels of commercial poly(dimethyl siloxane) fluid. The resultant polyurethanes show improvements in wear resistance of up to 25% (c.f. virgin polyurethane) for an optimal PDMS concentration of 1.5–2.0%, beyond which the properties diminish rapidly. Unexpectedly, the mechanical properties of the blends (as measured by an Instron tensile testing machine) have been even more significantly enhanced, by up to 40% for tensile strength and 50% for elongation to break. Surface studies of the blends are also reported for x-ray photoelectron spectroscopy (XPS), contact angles and coefficient of friction (CoF). © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyurethanes are used widely in the mining industry for the demanding applications of sorting and transporting ore. The thermoplastic polyurethanes (TPU) are successful in this and other industries due to their excellent mechanical properties and high wear resistance. Polyurethane thermoplastics are $(AB)_n$ type block copolymers; these block copolymers are phase separated into soft and hard domains.[1] The phase separation and the physical crosslinking achieved by the crystalline hard domains is generally accepted to be responsible for the materials excellent performance.[1]

There is a large body of literature dealing with the wear of polymers (see reviews [2–5]) and, due to the importance of TPUs, a significant portion of this work deals with the wear of polyurethanes for mining applications.[6–10] Much of this work is involved with modification of morphology, alternative curatives and correlations of various mechanical properties, with wear resistance. Several reports have dealt with the blend modification of TPUs with

poly(dimethyl siloxane) (PDMS) in order to improve wear resistance.[11–14] These articles are primarily applications articles and as such report data on mechanical properties at only one or two levels of PDMS (up to 10-fold improvements in wear resistance have been reported).[11] It has been assumed that the wear performance is enhanced by the significant lowering of the coefficient of friction after the addition of PDMS.[11,14]

A large body of literature exists that deals with polysiloxane-containing copolymers (reviewed [15]) and of this a large amount of work is involved specifically with graft and especially block copolyurethanes containing silicones in the soft domains. This work is predominantly involved with promoting antithrombogenicity in polyurethanes designed for medical applications.[16,17] Other workers have been involved with formation of minimally adhesive surfaces that inhibit the settlement of marine organisms,[18] improved flame retardency,[19] and improved hydrolytic stability.[20]

From a review of the literature, it was predicted that PDMS may modify TPU in several positive aspects that would be desirable for mining applications. An improvement in wear resistance is the most obvious, but a lower coefficient of friction is also desirable to reduce hang up of ore, as is hydro-

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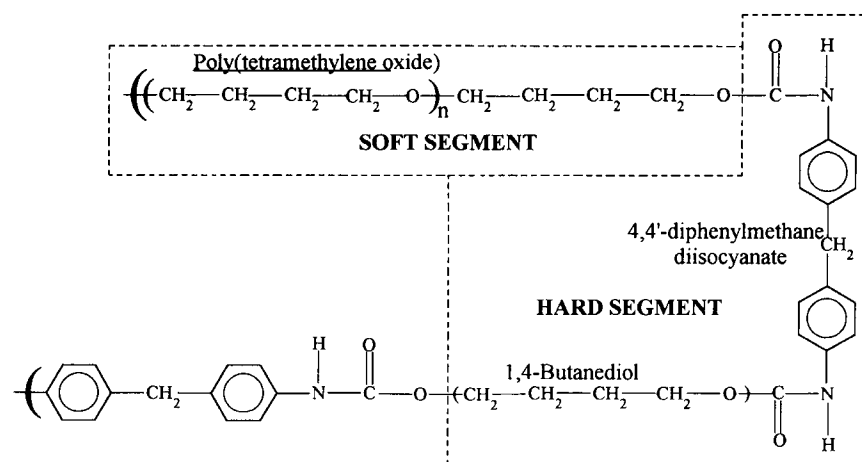
Figure 1 Chemical structure of the TPUs used in this study.

lytic stability because components are often used to handle slurries or are constantly sprayed with water to eliminate dust. Furthermore it appears that these properties could be enhanced without significantly reducing mechanical properties provided only low levels of PDMS are added (∼ 2% [14]). Higher concentrations of PDMS (generally used in block and graft copolymer studies) invariably lead to a significant reduction in mechanical properties.

The aim of this work was to complete a comprehensive assessment of TPU/PDMS blend properties over a low range of PDMS concentrations. For these blends to prove commercially viable in the mining industry it was also aimed to produce the blends as cheaply as possible. To this end only commercially available TPUs and PDMS and standard processing equipment have been used. In this way it was hoped to show that properties can be enhanced to a significant degree for little extra expense, especially when compared with block or graft copolymers.

MATERIALS

Current work has been involved predominantly with two commercially available TPUs. These particular

TPUs both have significant markets within the Australian mining industry for various applications. They are both based on poly(tetramethylene oxide) (PTMO) soft segments and 4,4'-diphenylmethane diisocyanate (MDI) hard segments. The prepolymers have been chain extended with 1,4-butanediol, which is assumed to reside in the hard domains for calculating the fraction of hard segment (Fig. 1).

The PTMO-MDI–based TPUs were selected due to their wide application in the mining industry, their superior hydrolytic stability (c.f. poly(ester)s and other poly(ether)s),[21] and their superior wear resistance.[10]

The basic difference between the two TPUs studied here is their hardness. The differences in hardness arise from different ratios of hard to soft segments, which in turn, is related to different soft segment molecular weights. The compositions of the two TPU materials (Table I) have been calculated from ^{1}H solution NMR (JEOL, GX 400 MHz) in DMSO-d_7 at 80°C using the method previously reported by Mardel et al.[7] The percentage hard segment was confirmed from nitrogen content measured by micro analysis.

The nonreactive, (methyl terminated) poly (dimethyl siloxane) (PS048, ($-$ Si(CH$_3$)$_2$$-O-$)$_n$)

Table I Commercial Thermoplastic Polyurethane Characteristics

	DOW Pellethane 2103-55D (Pel55D)	BASF Elastollan 11-85A-10-000 (Ela85A)
Percent hard segment	55% (w/w)	42% (w/w)
Molecular weight PTMO	720 g/mol	850 g/mol
Shore hardness	55D	85A (36D)

was obtained from Flexichem. The PDMS had a molecular weight of 134 kg/mol and is a fluid with a viscosity of $\sim 10^5$ centistoke.[22]

Due to the large difference in solubility parameters between PDMS ($\delta = 31$ $J^{1/2}cm^{-3/2}mol^{-1}$) and the polar hard segment ($\delta = 55$ $J^{1/2}cm^{-3/2}mol^{-1}$) and the generally reported immiscibility of PDMS with TPU,[23] it was deemed necessary to use a Brabender twin screw extruder to melt blend the PDMS with the TPU at maximised shear.

PDMS fluid was added to TPU pellets (dried over night at 65°C under N_2) at 5% (w/w), and stirred until the TPU pellets were evenly coated with fluid. The pellets were extruded from a 1 mm diameter rod die and pelletized. These 5% PDMS pellets were used to blend with virgin TPU to obtain final PDMS concentrations of 0–4% (w/w) in 0.5% increments. The final blends were extruded from a slit die (25 $\times \sim 1$ mm) onto cold rollers producing ribbons of $\sim 25 \times \sim 0.8$ mm. Temperatures in the four zones of the extruder were in the range 160–220°C, and the extruder was run at 30 rpm. All testing has been performed on these ribbon samples.

EXPERIMENTAL

Wear Testing

All wear tests reported in this article were performed on the dry sand-rubber wheel apparatus (DS-RW).[25] In this test a specimen is forced against a rotating rubber wheel and a curtain of sand is dropped between the wheel and specimen as the abrasive. The DS-RW test is considered to best simulate many mining field applications. However, the ASTM[25] is not designed for polymer testing and, thus, the ASTM conditions have been modified for use with polyurethanes. Modified test conditions are given in Table II; however, a more detailed discussion of the optimisation and choice of conditions can be found in another article.[26] All other conditions are consistent with the ASTM. We have reported results from triplicate tests as wear rates [volume loss (μl) per minute of abrasion]; the details of the testing regime

can also be found in another article.[26] This is also a deviation from the ASTM, in which the volume loss after a particular lineal abrasion distance is calculated from the speed of the wheel, its diameter and the length of testing time. It was found more information could be obtained from the wear rates. For comparison with the ASTM, 1 min of test time is the equivalent of 154.4 m lineal abrasion.

Tensile Testing

Tensile properties were measured on an Instron tensile testing machine (model 4505) using a crosshead speed of 100 mm/min sampling at 25 pts/s at 21°C and 40% humidity. Specimens were cut into rectangular bars of $25 \times 10 \times \sim 0.8$ mm and were clamped with a test length of 17 mm. Rectangular bars were used rather than dumbbell specimens because the extruded ribbons were too narrow to cut dumbbells transverse to the extrusion direction. The ASTM for rubber properties in tension,[24] states that this is acceptable if it is not practical to do otherwise. A series of tests were performed on dumbbell and rectangular specimens cut longitudinal to the extrusion direction and results were found not to be statistically different.

Durometer Hardness

Shore hardness was measured on a stack of specimens greater than 6 mm in thickness following the ASTM.[28] (The Shore A and D ranges are overlapping with the D range being the harder of the two).

Coefficient of Friction.

Measurement of the coefficient of friction (CoF) was based on the ASTM guide for measuring and reporting friction coefficients[27] using standard D1894. The 200 g sled, made for these tests, had three stainless steel spherical points of contact (10 mm diameter) welded to a base plate in a tripod arrangement. This sled design was chosen so that the poly-

Table II DS-RW Test Conditions c.f. ASTM Conditions

	Force N	Counter Weight (kg)	Sand Flow Rate (g/Min)	Lineal Abrasion	Wheel Speed RPM
Modified conditions	86.7[a]	3.2[a]	300–320	1 min = 154.4 m	213.5
ASTM Standard B	130	4.81	300–400	1436 m	200 ± 10

[a] $\frac{2}{3}$ ASTM Standard B.

mer to sled contact would not be effected by any slight surface undulations.

X-Ray Photoelectron Spectroscopy

X-Ray photoelectron spectroscopy (XPS) was carried out on a Perkin–Elmer PHI model 560 multi-technique system with a model 25–270AR double-pass cylindrical mirror analyser. XPS data were generated using a Mg $K\alpha_{1,2}$ (1253.6 eV) 300 W source. Survey spectra were taken with an analyzer pass energy of 100 eV and high resolution multiplex spectra of specific elements at a pass energy of 25 eV (using peaks for Si-2p and C,N,O-1s). The pressure in the vacuum chamber of the XPS was maintained below 10^{-7} Torr. Square samples of one cm dimensions were cleaned by stirring in AR ethanol for 3–4 min and dried under vacuum at room temperature for several days. From the Multiplex data, peak areas were obtained and these, together with experimentally determined sensitivity factors,[29] were used to determine relative atomic concentrations at the blend surfaces (50–100 A depth). The atomic concentrations were used to calculate comparative concentrations of blend components at the surface from the know structures of the hard segment, soft segment, and PDMS.

Contact Angle

Contact angles were measured from photographs of the angles for the advancing edge of water droplets in air at 20°C.

RESULTS AND DISCUSSION

The series of physical testing described and discussed below have been performed in order to quantify any positive or negative effects that blending of PDMS may have compared with the virgin polyurethanes, which are already widely used in the mining industry.

Wear Resistance

Wear testing is of prime importance because wear of components is most often responsible for their failure in the field. Laboratory results for wear resistance of all blends are reported and compared with virgin TPU.

The following protocol was adopted for the measurement of wear resistance: preweighed specimens were subjected to 1.5 min of abrasion before re-

weighing on an analytical balance and allowed to cool for 10 min before another 1.5 min of wear, etc. For both the Pel55D and Ela85A series of blends, there was a good linear relationship between volume loss and wear time. Plots of wear vs. time were constructed for each concentration of PDMS and the wear rate for each blend was calculated. These wear rates have been plotted against the percentage of PDMS in the blends (Fig. 2) and show minima between 1.5 and 2% PDMS. Other workers have reported decreases in wear rate on addition of small amounts of PDMS around this level, but have not reported an optimum concentration of PDMS.[11,14] The minima represent a significant improvement in abrasion resistance for both series (c.f. virgin TPU) and above the optimal PDMS concentration of 1.5–2%, the wear rate of the blends begins to rapidly increase. At the maximum PDMS concentration (4%), the blends show much poorer performance than the virgin TPU.

From Figure 2 it can be noted that the softer Ela85A series shows approximately half the wear rate of the harder Pel55D. This is consistent with the literature, which documents (for materials generally and specifically for polyurethanes) that in this hardness range the wear rate will increase with increased hardness.[2,8,9,30]

Because hardness is known to be directly relevant to the wear performance of polyurethanes, it was necessary to measure the hardness of each blend to ensure that changes in hardness were not affecting the observed trends. Shore hardness was measured
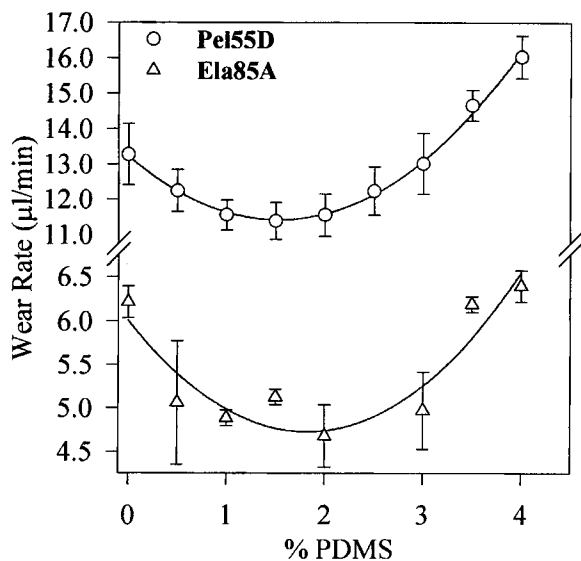
Figure 2 Wear rate vs. % PDMS in blends, (Pel55D and Ela85A, tested longitudinally to extrusion).
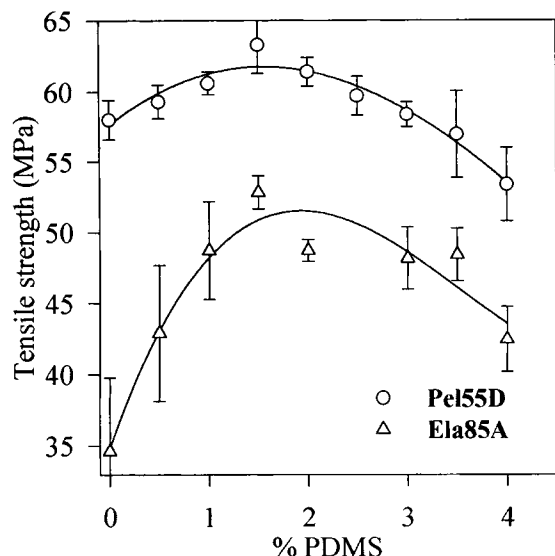
Figure 3 Ultimate tensile strength vs. % PDMS in blends, (Pel55D and Ela85A, tested longitudinally to extrusion).

Figure 4 Ultimate elongation vs. % PDMS in blends, (Pel55D and Ela85A, tested longitudinally to extrusion).
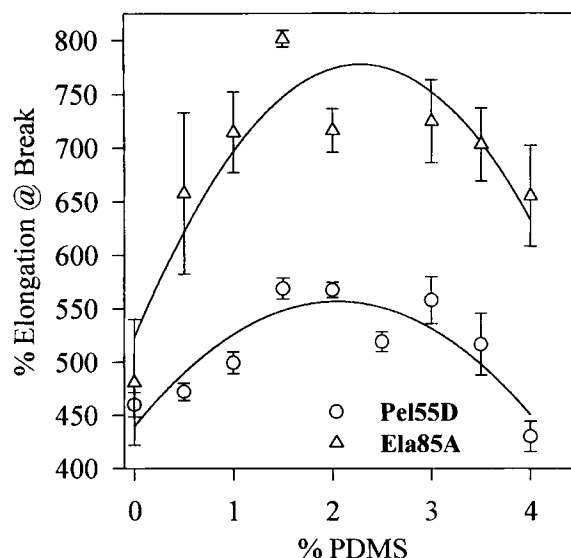
for all samples in both series and found to be constant across the range of PDMS content and were consistent with the specifications given by the manufacturers of the TPUs.

For both series of blends, the optimum improvement in wear performance due to the addition of PDMS is significant. However, the relative improvement for the softer Ela85A series ($\sim$ 25% c.f. pure TPU), was greater than the improvement in the Pel55D series ($\sim$ 15%). This is an important observation and will be discussed in more detail in the next article of this series.[31]

Mechanical Properties

Having established the improved performance of these blends with respect to wear resistance, it is important that they still have appropriate mechanical properties for applications if they are to replace TPUs in the field.

Ultimate tensile strength, percent elongation to break, and Young's modulus were measured for each blend using the Instron tensile testing machine. They are plotted against the percentage PDMS in the blends in Figures 3 to 5. As would be expected, the harder Pel55D series shows higher tensile strength and Young's modulus and lower percentage elongation compared to the Ela85A series. Trends in all of the above properties as a function of PDMS content are well pronounced and are analogous to the trends in wear properties as follows: (1) both series show optimum properties at a PDMS blend

concentration of 1.5–2%; (2) properties diminish rapidly at PDMS concentrations above the optimal level; (3) the softer Ela85A series shows a significantly greater percentage improvement in mechanical properties than the Pel55D series compared to the virgin TPU (Table III).

It is often observed that the tensile strength and the ultimate elongation of polymers exhibit opposite behaviors to one another, for instance, when tensile strength is increased, the ultimate elongation tends to decrease. However, in Figures 3 and 4, this is not the case. In the next article of this series, a model
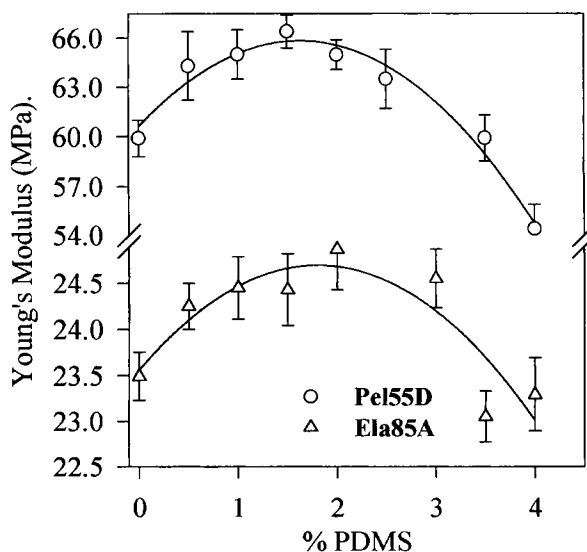

Figure 5 Young's modulus vs. % PDMS in blends, (Pel55D and Ela85A, tested longitudinally to extrusion).

will be presented that accounts for the behaviors observed above for the physical and wear properties of the blends.[31] It is proposed that the addition of PDMS facilitates an improved packing efficiency (analogous to antiplasticization) in the poly (urethane) soft domain, leading to improved material performance. Beyond the 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. The PDMS is also observed to reduce the crystallinity of the TPU soft domain, and this in combination with the additional lubrication from the PDMS, can account for the initial increase in the ultimate elongation of the blends. This model has been rigorously investigated and has proven to be highly robust.[31]

All of the results shown here are for tests carried out in a direction longitudinal to the extrusion direction. Measurements in the transverse direction show similar trends for wear, tensile strength, and elongation to break. Young's modulus, however, shows a linear decrease with PDMS content for transverse testing; this phenomenon will be discussed in the next article.[31] Although similar trends are observed in the longitudinal and transverse directions, the absolute values of these properties differ in the two directions; for instance, there is a degree of anisotropy of properties in the extruded blends. The stress–strain curves (Figure 6) show that in the transverse direction, a lower modulus is observed over the entire strain range to break leading to a lower ultimate tensile strength and slightly higher ultimate elongation in the transverse direction.

The above trends in tensile properties vs. PDMS are at first unexpected. As already discussed in the introduction, most previous work with TPU/PDMS systems has involved block or graft copolymers with higher siloxane contents than that used in this work (generally greater than 10% siloxane concentrations).[16-20] In previous work, mechanical properties have been found to significantly decrease, but this is accepted as a reasonable price for other positive
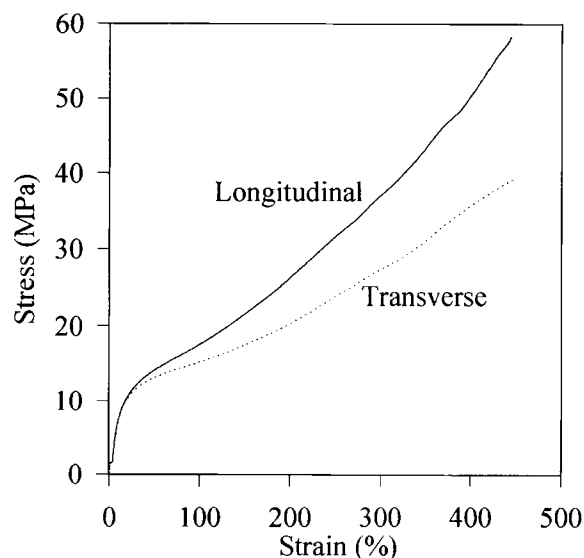

Figure 6 Typical stress–strain curves for Pel55D (longitudinal and transverse to the direction of extrusion).

changes in properties. In one brief report on PDMS/polyurethane blends at concentrations of 2 and 4% PDMS, mechanical properties are reported to be changed by up to 10%. However, it is stated that most applications would be unaffected by this because urethanes are often overdesigned for their end use.[14] It has been generally assumed, therefore, that the PDMS is acting at the polymer surface and the improved wear performance is due to the lower CoF, and the mechanical properties are slightly reduced due to the effect of the immiscible PDMS on the TPU matrix. This is clearly not the case because we have shown that the wear rate remains constant, even after the surface has been removed by abrasion. This indicates that the PDMS predominantly affects the bulk polymer as well as the surface. This is supported by the results for Young's modulus, which would be unlikely to increase if the PDMS acted only at the surface (Figure 5). In the next article in this series, a model of the blended system is presented that is able to successfully explain these observed trends.[31]

Table III Relative Effect of PDMS [at Optimal Concentration (1.5–2%)] on the Physical Properties of the Blended TPUs

	Percentage Improvement in Properties			
	Wear	Tensile Strength	% Elongation at Break	Young's Modulus
Ela85E	Down 25%	Up 40%	Up 50%	Up ~10%
Pel55D	Down 15%	Up 10%	Up 20%	Up ~10%
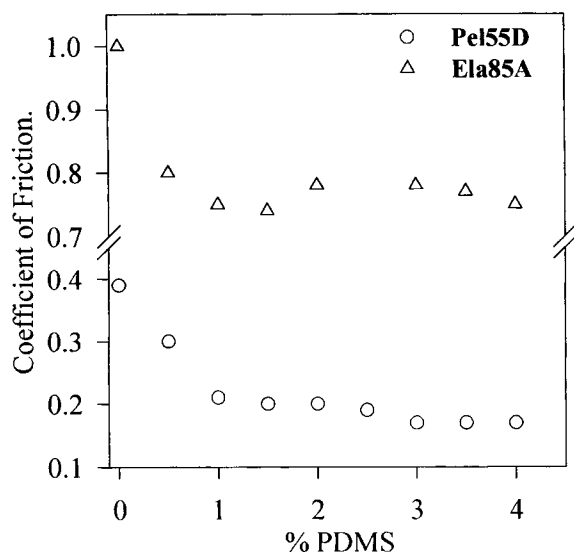
Figure 7 Coefficient of friction (CoF) vs. % PDMS (Pel55D and Ela85A).

Coefficient of Friction

The blending of PDMS with polyurethane has previously been shown to lead to a significantly lower coefficient of friction (CoF),[11-14] which would be advantageous in various mining applications. We have also observed a reduction in the CoF (Figure 7) with the addition of PDMS. The Ela85A initially has a high CoF, and with the addition of increasing amounts of PDMS reaches a plateau at a 25% lower CoF of ~ 0.75. The Pel55D material has an initial CoF of 0.4 and also reaches a plateau with the addition of PDMS at the very low CoF of ~ 0.15. This compares well with that measured for ultra high molecular weight polyethylene (UHMWPE) (~ 0.15),[26] which is often used for applications in the mining industry requiring a low CoF. As discussed above, we do not believe the modification of the CoF is primarily responsible for the improved wear resistance, but it may have some synergistic effects. Furthermore, as mentioned in the introduction, a lower CoF can be a desirable property in its own right.

X-Ray Photoelectron Spectroscopy (XPS)

Although the action of the PDMS appears to be dominant in the bulk of the blends as far as wear and tensile performance are concerned, the surface of the blends are still greatly affected by the presence of PDMS and is of importance for other properties of these blends. The predominance of the PDMS at the surface of siloxane/polyurethane systems is ex-

tremely well documented by the many XPS and contact angle studies.[11,12,17-20,32-38] This is due to the very low surface tension of PDMS [(1.9–2.1)(10^{-2} Nm^{-1}),[39] which is at least 10^{-3} Nm^{-1} lower than that of most other polymers[40] and half that of polyurethane.[41] The concentration of the PDMS at the surface results directly in the observed decrease in CoF noted above and, as will be seen below, may be an important factor in rendering the polyurethane more hydrolytically stable.

Plots of surface composition against added PDMS (Figs. 8 and 9) show that the concentration of PDMS at the surface is much greater (by up to 40 times) than the concentration of PDMS added to the blends at the extruder. These observations are consistent with other earlier reports.[11,12,17-20,32-38]

The relationship between surface compositions and PDMS content for Pel55D and Ela85A differ significantly in Figures 8 and 9. The cause of this different behaviour is difficult to explain; however, we believe it is due to the differing degrees of miscibility of PDMS with the hard and the soft segments. The surface compositions for the pure TPUs indicate that the soft segment has a much higher tendency to concentrate on the surface than the hard segment (as would be expected from values of surface tension for PTMO and TPU, 32 and 39 mNm^{-1}, respectively).[41] Ela85A, which has a bulk composition of 58% PTMO, has 80% PTMO on the surface and Pel55D, which has a composition 45% PTMO, has 70% on the surface. The preference of urethane soft segments for the surface is established in the
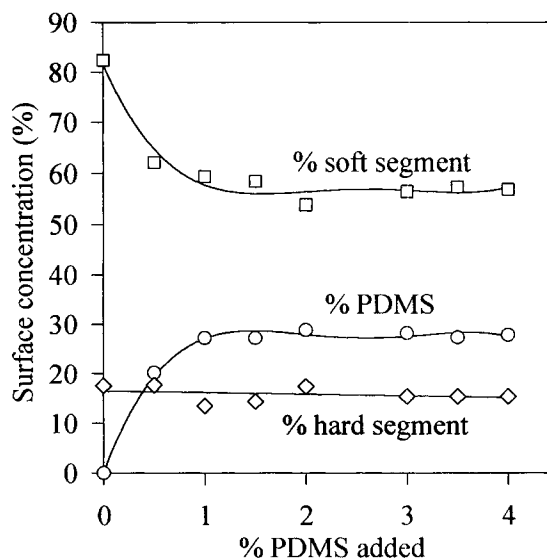
Figure 8 Surface composition of Ela85A vs. % PDMS in the blends, (calculated from atomic concentrations at blend surfaces measured by XPS).
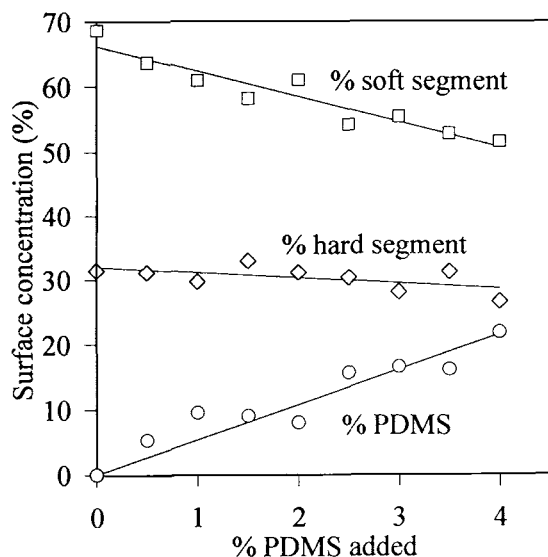
Figure 9 Surface composition of Pel55D vs. % PDMS in the blends, (calculated from atomic concentrations at blend surfaces measured by XPS).

literature.[20] DSC and solid-state NMR studies have established significant miscibility between PTMO and PDMS and no interactions between the PDMS and the hard segment.[31] Therefore, besides the tendency of PDMS to partition towards the surface due to its low surface tension, as discussed above, there are miscibility effects as well. The affinity of PDMS for the surface will also be promoted by preferential enrichment of PDMS into the soft segment, which is more concentrated on the surface. This may explain the more rapid saturation of the surface of the PTMO rich Ela85A and the more gradual buildup of PDMS on the Pel55D surface. This is manifested for Ela85A (Fig. 8) as a rapid buildup of PDMS at the surface (to be more concentrated than the hard segment) followed by a plateau in the PDMS concentration. On the other hand, Pel55D (Fig. 9) shows a slower linear buildup of surface PDMS, not reaching the saturation point within the range of PDMS concentration investigated here, and not exceeding the hard segment concentration at the surface.

Contact Angle Measurements

It has been observed by other work[37] that the low surface tension and hydrophobic nature of the PDMS leads to an increase in water-in-air contact angles when PDMS is added to polyurethane. We have confirmed this for our blends, as shown in Figure 10.

The virgin Ela85A TPU has a greater contact angle than the virgin Pel55D, due to the higher concentration of the less polar soft segment (c.f. hard segment) on the surface of the Ela85A, as confirmed by XPS above. As PDMS is added, both series show a linear increase in contact angle (or hydrophobicity), as would be expected, because PDMS has a very low polarity compared to polyurethane (polarity, $\chi^P \sim 0.05$ and 0.18, respectively).[41] The Pel55D plot has a steeper increase than that for the Ela85A, which may be due to the combination of two factors: (1) the XPS data shows that after an initial change in surface composition, Ela85A tends to have a fairly constant surface composition over the rest of the PDMS range. This would result in a more constant contact angle and, hence, a lower slope for Ela85A than for Pel55D, which has a linear increase in nonpolar PDMS surface concentration over the whole range; (2) In Pel55D, PDMS is partitioning to a more polar surface than in Ela85A. This is indicated by the lower initial Pel55D contact angle and the higher MDI surface concentration found by XPS. Therefore, the relative polarity of the Pel55D surface is decreased more effectively by the build up of nonpolar PDMS, resulting in the steeper slope in Figure 10.

The Pel55D series of blends is observed to have a larger spread in the contact angle data than the Ela85A series of blends. The uncertainties associated with the Pel55D data have been estimated from the standard error of Y and are $\sim \pm 2.6°$ compared with the Ela85A data, which have associated errors of only $\pm 0.6°$. The greater uncertainty associated with
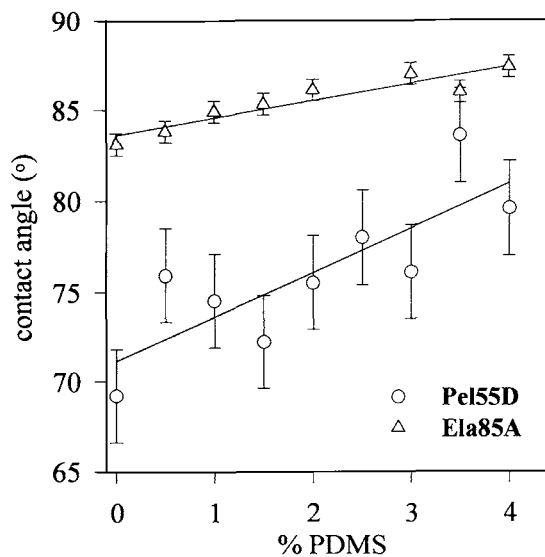
Figure 10 Contact angles (water-in-air) vs.% PDMS in blends (Pel55D and Ela85A).

the Pel55D data is probably due to topographical effects at the blend surfaces; the Ela85A blends had a slightly better surface finish than the Pel55D blends.

An important possible consequence of the increased hydrophobicity of the TPU surface with the addition of PDMS, is that the polyurethanes may be rendered less prone to hydrolysis. This has already been suggested by other workers;[20] however, no aging experiments have been performed to confirm it. Furthermore, PDMS is quite miscible with TPU at low concentrations,[31] so the protection against hydrolysis may extend beyond the surface layers to the bulk, which is also rendered more hydrophobic.

CONCLUSIONS

This work has clearly shown that significant improvements in the performance of TPU can be achieved through the blending of standard, commercially available polyurethanes and commercial siloxane fluid. These blends can, furthermore, be produced on standard polymer processing equipment. Although a twin screw extruder and a double pass were used here to enhance blending, better than expected miscibility between TPU and PDMS suggests that the same ends may be achieved from a single pass on a single screw extruder or on an injection moulder.

To gain the maximum benefit from the addition of PDMS, it is imperative to keep to an optimal concentration range between 1.5 and 2.0% PDMS. Additions of PDMS above this level heavily impacts on the tensile and wear performances of the materials. This low level of PDMS has often been exceeded by other workers, because they were looking to enhance other properties at the expense of mechanical properties, so missing the improved performance of the systems at low concentrations of PDMS.

Properties that have been shown to be significantly enhanced at optimal PDMS concentrations are wear resistance (as measured by the DS-RW test), coefficient of friction, and ultimate tensile strength and elongation. The larger water-in-air contact angle for the blends is evidence of an increased hydrophobicity, which may render the TPU less prone to hydrolysis.

Although the improvements in wear and CoF were expected, the literature does not indicate the enhancement in mechanical properties, and especially to such a significant degree. In previous work it has been generally assumed that the PDMS has its influence on the surface of the polyurethane, leading to changes in the materials surface performance. Evidence presented in this article suggests that PDMS is, in fact, also active in the bulk when wear and tensile properties are considered. In the next article of this series a model will be presented that accounts for these unexpected results and further evidence that strongly supports the model will also be provided.[31]

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