Processability and Chemical Resistance of the Polymer Blend of Thermoplastic Polyurethane and Polydimethylsiloxane

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Summary: This work is aimed to develop the melt blend of thermoplastic polyurethane (TPU) and polydimethylsiloxane (PDMS) and to study the effect of the chemical resistance on the tensile properties and morphology of the blends. The master batch blends at 2% of PDMS with 98% of TPU were firstly prepared by an internal mixer and then the blends of TPU/PDMS were prepared by melt mixing using a twin screw extruder. The maximum PDMS content that can be mixed with TPU was found to be no higher than 1%. Higher PDMS content leaves an unmelted TPU fraction in the blends due to the short residence time in the twin screw extruder. The resultant blends show an increase in the elongation at break up to 30% and in Young's modulus up to 40% at the optimum PDMS concentration of around 0.6%-0.8%, beyond which these properties diminish. The ultimate tensile strength and the energy to break are decreased by about 20% and 10%, respectively. The Scanning Electron Micrographs of the blends show dispersed phases of PDMS in a TPU matrix. The domain size of the PDMS phase becomes smaller when increasing PDMS content from 0.2% to 0.8%. The morphology of the fractured surface of TPU/PDMS blends shows less fibrous characteristics with increasing PDMS content in the blends.
For the study of the effects of chemical resistance on the tensile properties and morphology of TPU/PDMS blends, two chemical reagents, sulfuric acid (H_2SO_4, 3% v/v) and sodium hydroxide (NaOH, 10% w/v) are selected. The results on the relationship of chemical resistance to tensile properties and morphology of the blends show that NaOH solution has a stronger effect on the tensile properties and morphology of virgin TPU and the blends than H_2SO_4 solution. The ultimate tensile strength and the energy to break of virgin TPU after base immersion was found to be strongly decreased, which could be caused by the base hydrolysis of the polyester soft segment of polyurethane. The effect of PDMS content in the blends on the base resistance and tensile properties is similar to results before immersion, i.e. the effective PDMS content in the blends that can generally improve tensile properties of the blends after immersion in NaOH does not exceed 0.8%. The results are in agreement with the weight loss of TPU/PDMS blends after base immersion and the morphology of the fractured surface of TPU/PDMS blends after base immersion that exhibit very small amounts of a fibrous character. There are also some small particles detached at the surface. This could be the result of an occurrence of a corrosive reaction between the sample surface and NaOH solution.

Keywords: morphology, polydimethylsiloxane, polymer blends, tensile properties, thermoplastic polyurethane

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Introduction

Polymer blends have emerged as an important group of polymeric materials since the late 1970s and have experienced substantial growth since the 1980s. Interests in polymer blending are reflected in the numbers of patent and research publications by both industry and academia.[1-9] Blending of polymeric materials has been shown to be a useful and cost effective route, in comparison with the synthesis of new polymers, for enhancing material properties and developing materials with desired performance.

During the past decades, thermoplastic polyurethane (TPU) has received considerable attention from both the scientific and industrial communities.[10-11] Applications of TPU include automotive exterior body panels, medical implants such as the artificial heart, membranes, ski boots and flexible tubing. TPU features the best physical properties of all elastomers exhibiting high modulus and abrasion resistance, with excellent resistance to aging (ozone), atmospheric factors, typical solvents and oils. Moreover, TPU is capable of bearing greater loads than other rubbers. But the properties of TPU can be changed by the environment in that a physical or chemical process may occur. There are three environmental effects considered particularly important for polyurethane elastomers: the effect of heat, swelling by immersion in certain fluids and hydrolytic resistance. In certain fluids such as alcohols, acids, bases, ketones and esters, polyurethanes tend to show swelling, degradation and changes in some mechanical properties.

From the discussion above, it is interesting to study polymer blends of TPU with other polymers. Polydimethysiloxane (PDMS) was chosen to blend with TPU because PDMS is a polymer with a unique combination of properties resulting from the presence of an inorganic siloxane backbone with organic methyl groups attached to the silicon. This chemical configuration produces polymers which have good chemical stability, in particular good oxidative resistance. Thus, this research is aimed to study the tensile properties and the morphology of TPU/PDMS blends. The effects of chemical reagents on the tensile properties and the morphology of TPU/PDMS blends are investigated.

Materials and Experiments

Materials: Thermoplastic polyurethane used in this study is S385A series with the trade name of Skythane, obtained from SK Chemicals Co, Ltd. S385A is a polyester-based thermoplastic polyurethane of which the hard segment is 4,4'-diphenylmethane diisocyanate (MDI) extended with 1,4-butanediol (BO). The soft segment is polyester polyol and 1,4-butanediol.

Polydimethylsiloxane used in this study was obtained from Dow Corning Co, Ltd; it is transparent fluid with a viscosity of 60,000 centistoke.

Sample preparation: The master batch of TPU/PDMS at 2% by weight of PDMS was prepared using the internal mixer of Haake "Rheomix3000p" at 190C for 10 min with a rotor speed of 30 rpm. After that the master TPU/PDMS batch was compressed and cut into pieces. The master batch was used to blend with the virgin TPU, using the counter-rotating twin screw extruder of Haake, to obtain the blends with the final PDMS concentration of 0.2%-1% in 0.2% increments. The extruded blends were cooled and finally cut into pellet form. The virgin TPU sample was treated by the same procedure for use as a reference sample.

Measurements: Tensile properties were measured following ISO 527-1 of the British Standards Institution (BSI) with "Lloyd LR 5K". Chemical resistance of all samples was tested following ASTM D543-95. Chemical reagents used were distilled water, sulfuric acid (H_2SO_4, 3% v/v) and sodium hydroxide (NaOH, 10% w/v). Samples were immersed in chosen chemical reagents at 25C for 168 hr, after which they were dried and tested for tensile strength. Scanning electron microscopy (SEM), using a JEOL JSM-6400 instrument, was used to study sample morphology.

Results and Discussion

Since PDMS is a liquid, the internal mixer is first employed for preparation of the master batch before final blending of the master batch with virgin TPU in the twin screw extruder. Using this procedure, the maximum concentration of PDMS in the TPU/PDMS blend is found to be 1% of PDMS; more than 1% excess PDMS resulted in unmelted TPU due to the short residence time in the twin screw extruder.

Comparison of the ultimate tensile strength, the elongation at break, Young's modulus and the energy to break, of the blended TPU at all compositions before and after immersion in various chemical reagents are shown in Figures 1-4.

Comparing to the virgin TPU, the prepared blends, before immersion, show an increase in the elongation at break up to 30% and in Young's modulus up to 40% at the optimum PDMS concentration of around 0.6-0.8%, beyond which these properties diminish. The ultimate tensile strength and the energy to break are decreased by about 20% and 10%, respectively. The optimum PDMS concentration on a similar system was also reported by Hill *et al*[5] but at higher values than our results. This could arise from differences in the structure and characteristics of the polymer components. The dependence of tensile properties on PDMS

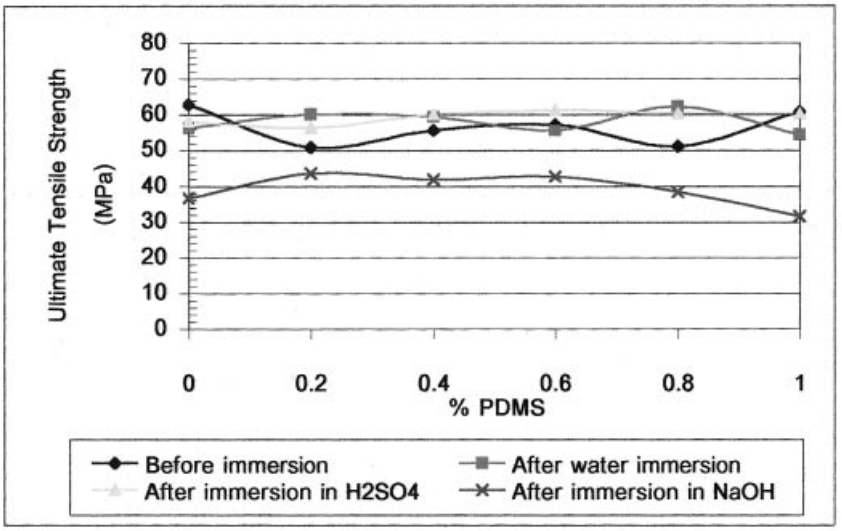

Fig. 1. Comparison on the ultimate tensile strength of the virgin TPU and blended TPU before and after immersion in various chemical reagents

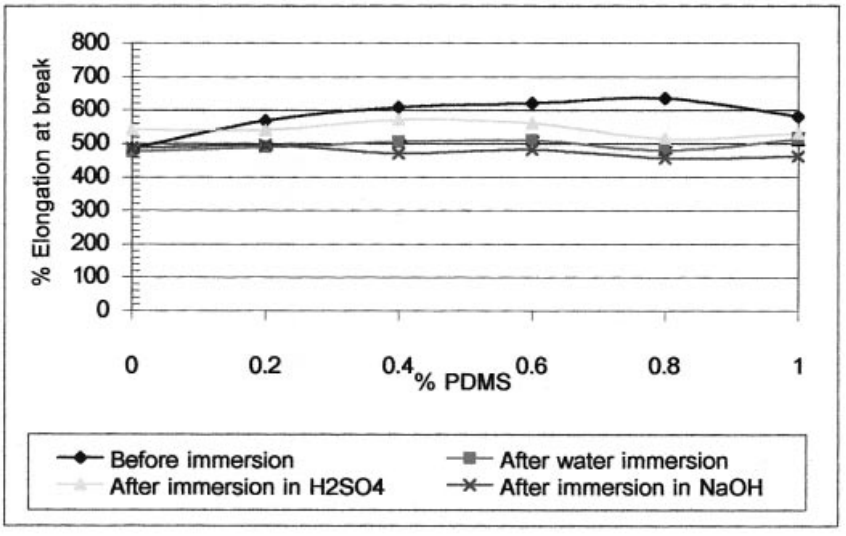

Fig. 2. Comparison on the elongation at break of the virgin TPU and blended TPU before and after immersion in various chemical reagents.

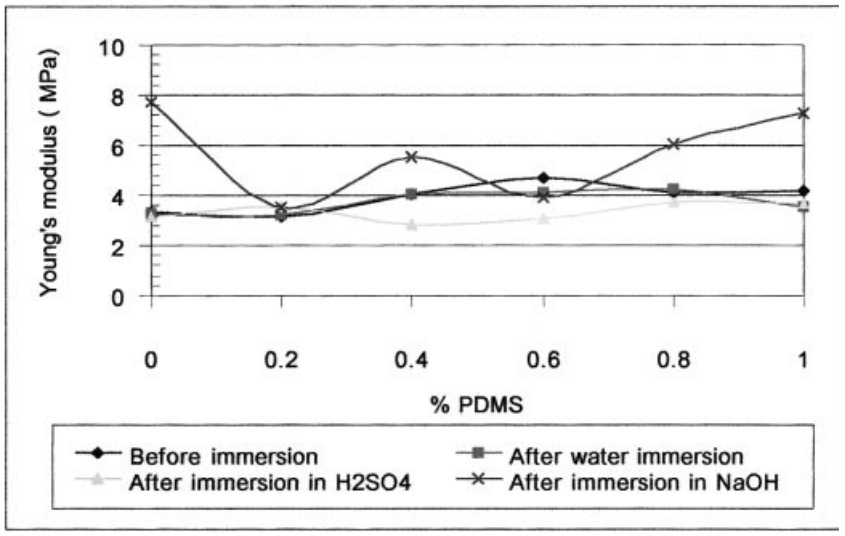

Fig. 3. Comparison on Young's modulus of the virgin TPU and blended TPU before and after immersion in various chemical reagents.

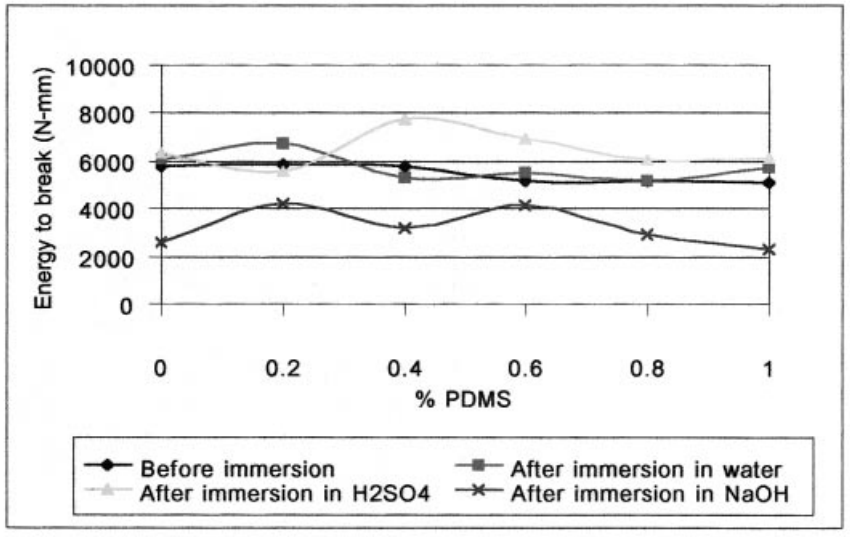

Fig. 4. Comparison on the energy to break of the virgin TPU and blended TPU before and after immersion in various chemical reagents.

concentration in the blends can be preliminary explained by the change of the morphology and the fractured mechanism of the blends, as observed by SEM (Figures 5-8).

Fractured surface of blended TPU at 0.2% and 0.4% PDMS concentrations in Figure 6 and Figure 7 is different from that of virgin TPU (Figure 5), with less fibrous characteristic in the blends and with, in addition, areas of craze structure. In contrast, the fibrous characteristic and craze formation in blended TPU at 0.8% PDMS concentration, shown in Figure 8, is not visible. In this case the fractured structure appears in a chunky crack form. It is evident that there are three different fracture characteristics. The first, of a fibrous nature, occurs with the virgin TPU. The second, craze formation with some fibrous characteristics, is observed in the blended TPU at 0.2% and 0.4% of PDMS. The third, the chunky formation without any of the fibrous characteristics observed in virgin TPU, occurs in the blended TPU with 0.8% of PDMS. A change in the phase morphology of the TPU blend at the optimum PDMS concentration corresponds to the results on tensile properties, where the reduced effect of PDMS content on the tensile properties of TPU blends occurred at around 0.6%-0.8% PDMS concentration.

The ultimate tensile strength, Young's modulus and the energy at break of the blends at all compositions after immersion in water and acid (3% H_2SO_4), comparing to those before immersion, are not significantly different. In the case of acid immersion, a slight effect of PDMS contents on the acid resistance to the tensile properties is noticed.

In the case of base immersion (10% NaOH), the results on tensile properties show that base immersion has a significant effect on tensile properties. The effect of PDMS concentrations on the base resistance to the tensile properties is marked, i.e. the effective PDMS contents in blended TPU does, more or less, not exceed 0.8%. At 1% PDMS concentration, the effect on each property diminishes, with the value of each property being close to that of pure TPU. This is similar to the results found in the case of TPU/PDMS blends before immersion.

Comparing immersion in different chemical reagents, NaOH (10% w/v) has the strongest influence on the tensile properties of virgin TPU and blended TPU. For virgin TPU after base immersion comparing to before base immersion the ultimate tensile strength and energy at break is strongly decreased by 42% and 55%, respectively. This could be caused by the base hydrolysis of the polyester soft segment of polyurethane[12]. The effect of PDMS concentration on the base resistance to tensile properties is similar to results before immersion, i.e. the effective PDMS contents in the blends that can generally improve tensile properties of the blends after immersion in NaOH does not excess 0.8%. The results are in agreement with the weight loss of TPU/PDMS blends after base immersion and the morphology of the fractured

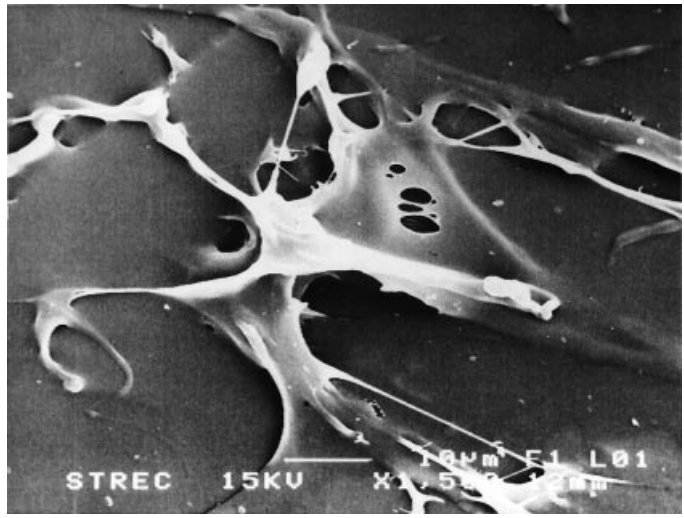

Fig. 5. SEM photograph of fractured surface of virgin TPU.

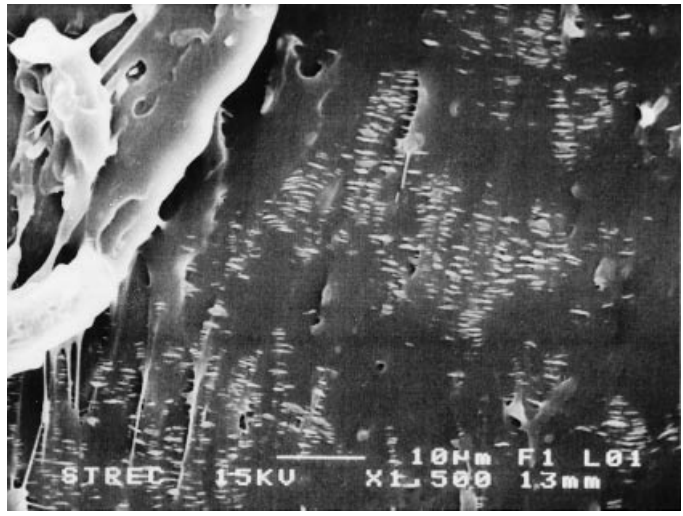

Fig. 6. SEM photograph of fractured surface of TPU/PDMS blends at 0.2% PDMS.

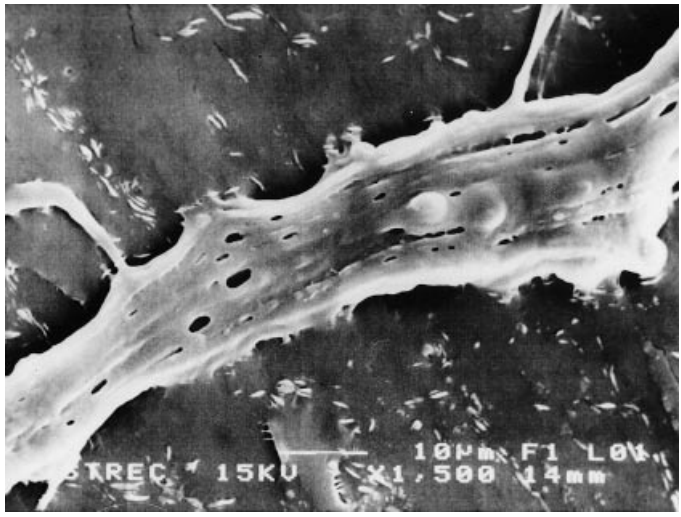

Fig. 7. SEM photograph of fractured surface of TPU/PDMS blends at 0.4% PDMS.

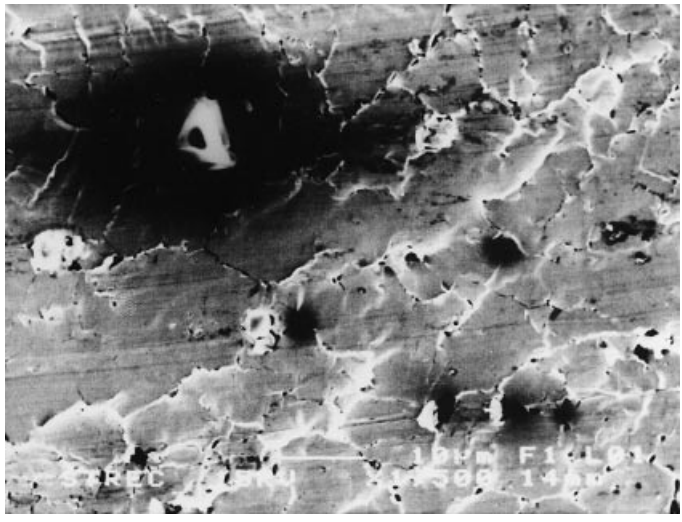

Fig. 8. SEM photograph of fractured surface of TPU/PDMS blends at 0.8% PDMS.

surface of TPU/PDMS blends after base immersion that exhibits very small amount of fibrous characteristic and there are some small particles detached at the surface (Figure 9). This could be the result of a corrosive reaction between the sample surface and NaOH solution or the degradation of the soft domain of polyurethane in base solution as mentioned previously. Further study will be performed to clarify this point.

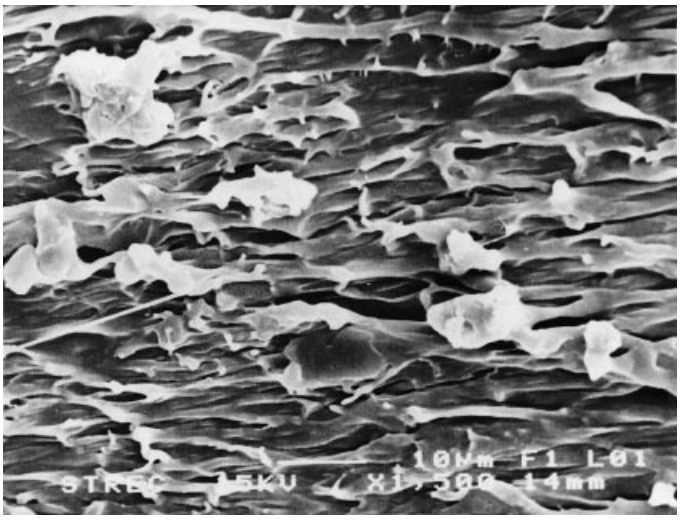

Fig. 9. SEM photograph of fractured surface of TPU/PDMS blends at 0.8% PDMS after base immersion.

Acknowledgements

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[1] D.R. Paul, C.B. Bucknall, "*Polymer Blends volume 1 :Formulation*", J. Wiley & Sons, New York 2000.
[2] L.A. Utracki, "*Polymer Alloys and Blends*", Hanser Publishers, New York 1990.
[3] D.J. Walsh, J.S. Higgins, A. Maconnachie, "*Polymer Blends and Mixtures*", Martinus Nijhoff, Dordrecht 1985.
[4] G. Oertel, "*Polyurethane Handbook*", Hanser Publishers, Germany 1985.
[5] D.J.T. Hill, M.I. Killeen, J.H. O'Donnell, P.J. Pomery, D.S.T. John, A.K. Whittaker, *Journal of Applied Polymer Svience*, **1996**, *61*, 1757-1766.
[6] S.N. Jaisankar, G. Radhakrishnan, *Polymer Engineering and Science*, **2000**, *40*, 621-626.
[7] Y. Kim, W.J. Cho, C.S. Ha, *Journal of Applied Polymer Science*, **1999**, *71*, 451-422.
[8] P. Potschke, K. Wallheinke, H. Fritsche, H. Stutz, *Journal of Applied Polymer Science*, **1997**, *64*, 749-762.
[9] A. Stanciu, A. Airinei, D. Timpu, A. Ioanid, C. Ioan , V. Bulacovschi, *European Polymer Journal*, **1999**, *35*, 1959-1965.
[10] C. Hepburn, "*Polyurethane Elastomers*", Applied Science Publication, England 1982.
[11] Z. Wirpaza, "*Polyurethanes (Chemistry, Technology and Applications)*", Ellis Horwood, Great Britain 1993.
[12] M. Furukawa, T. Yokoyama, *Journal of Polymer Science: Polymer Letters Edition*, **1979**, 17, 175-180.