

Synthesis and Characterization of Novel Organosilicon-Modified Polyurethane

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ABSTRACT: Organosilicon-modified polyurethane have been synthesized using the prepolymer method and characterized by Fourier infrared (FTIR) spectroscopy, wide angle X-ray diffraction (WAXD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), differential thermal analysis (DTA), solvent resistance analysis, and stress-strain tests. The FTIR spectra show that the polyurethane is fully reacted and polydimethylsiloxane (PDMS) is chemically incorporated into the copolymer. SEM reveals a multiphase structure with surface cracking and thermal analysis indicates that the heat resistance proper-

ties are better when the PDMS concentration is low. According to the solvent resistance, water and acetone uptake decreases when the PDMS content is less than 4 wt % while the ethanol uptake changes indistinctively. The mechanical properties of the films are also discussed. A tensile strength up to 6 wt % has the largest effect while the elongation at break decreases. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1486–1492, 2012

Key words: polyurethanes; polymer synthesis and characterization; high-performance polymers; phase separation

INTRODUCTION

Thermoplastic polyurethane (TPU) composed of multiphase, segmented polymers possesses a two-phase microstructure which arises from the chemical incompatibility between the soft and hard segments. The hard rigid segment segregates into a glassy or semicrystalline domain, and the polyol soft segments form amorphous or rubbery matrices in which the hard segments are dispersed.¹ TPU are commonly used as adhesives in many applications because of their versatile properties, flexibility, good behavior at low temperature and high strength.² On the other hand, polyurethane has some disadvantages such as low viscosity and tack, poor wettability, poor fire re-

sistance, and limited thermal, mechanical and electrolytic stability^{3,4} consequently restricting wider applications.

Polydimethylsiloxane (PDMS) has many desirable properties such as low glass transition temperature, low surface energy, high permeability to gas, good insulating properties, good hydrophobic properties, and very good thermal stability as a result of the siloxane bond.^{5,6} However, the mechanical properties of PDMS are usually poor.⁷ Polyurethane and PDMS are different but complementary to one another,⁸ and organosilicon-modified polyurethane are composed of siloxane and urethane, that is, DHPDMS/TPU, possess the advantages of both.⁹ Recently, silicon as modifier have played an important role in improving corrosion resistance, adhesion, and mechanical properties. Silicon-modified polyurethane is widely used as foams,^{10,11} coating,^{12,13} leather finishing,¹⁴ especially, adhesives.^{15,16} However, the effects of PDMS content on the solvent resistance property of TPU are scarcely investigated.

In the study reported here, polyurethane functionalized by organosilicon is prepared by a prepolymer process using TDI and polyester polyols. The morphological characteristics, thermal properties, solvent resistance, and mechanical properties are analyzed and discussed. Moreover, the product synthesized processes improved solvent resistance property, which makes it available in engineering sectors.

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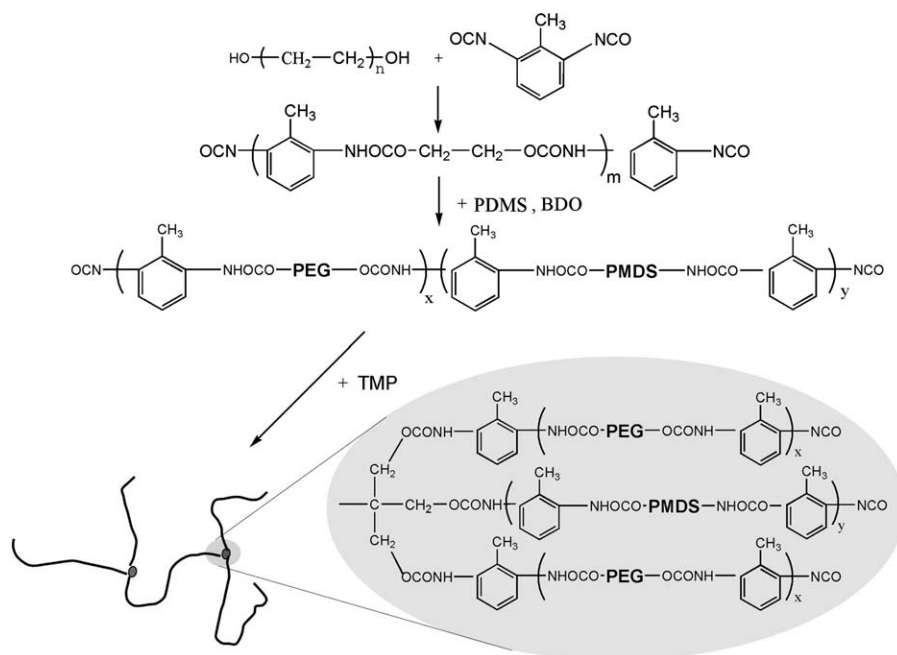


Figure 1 Pictorial representation of the synthesis of PDMS-modified polyurethane.

EXPERIMENTAL

Materials

The polyurethane was synthesized under laboratory conditions using toluene diisocyanate (TDI, Beijing Comens, Beijing) and poly (ethylene glycol) (PEG-1000, $M_n = 2000$, Beijing Comens, Beijing). 1,4-butanediol (BDO) was used as the chain extender and trimethylolpropane (TMP) used as the crosslinker. The solvent used in this experiment is ethyl acetate. Ethyl acetate was heated to 95–100°C by refluxing toluene for 2 h before use. The process effectively dehydrated the solution. Polydimethylsiloxane polymers ($M_n = 1000$) was supplied by Jinan Futao. All the reagents were used as received without further purification.

Polymerization

The TPU was prepared using the prepolymer method.¹⁷ TDI and polyester polyols were added to a four-neck round-bottom flask (30 mL ethyl acetate) containing a mechanical stirrer and placed in a water bath to obtain the prepolymer. An NCO/OH of 1.6 was used. The reaction was carried out at 80–90°C under nitrogen for 2–2.5 h. Afterwards, variable PDMS (2, 4, 6, and 8 wt %) and BDO were added one by one, and the system was cooled to 65–70°C. To avoid crosslinking during polyurethane synthesis, an appropriate amount of ethyl acetate (5–10 mL) was necessary. After cooling down, the resulting solutions/crosslinker with a mass ratio of 1 : 1 were mixed for 30 min. A solution of polyurethane without PDMS was also prepared as the control (Fig. 1).

Most of the properties of the TPU were measured on the solid films, which were prepared by placing about 100 mL of the solution in a PTFE mould and allowed to dry at room temperature for 1 h. The polyurethane films were approximately 0.9 mm thick. The polyurethane films were annealed in an oven at 60°C for 2 h followed by heating at 80°C for 1 day. The films were stored at room temperature for 1 week before the tests. The nomenclature of the oligosiloxane-containing polyurethane were PU0 (i.e. TPU without organosilicon), and PU2, PU4, PU6, and PU8 (TPUs containing organosilicon with 2, 4, 6, and 8%, respectively).

Characterization

The TPU films were characterized by FTIR spectroscopy, SEM, WAXD, TGA, DTA, solvent resistance test, and stress–strain test.

FTIR spectroscopy

The chemistry of the polyurethane films was analyzed using a Shimadzu FTIR system. The measurements were conducted in the attenuated total reflectance (ATR) mode. The incident angle of the laser beam was 45°, and 20 scans were averaged.

Wide angle X-ray diffraction

Wide angle X-ray diffraction (WAXD) analysis was performed with thin film samples of 1.0 mm thickness using a Rigaku D/max-rA X-ray diffractometer. The samples were scanned at 4°/min using Cu K α

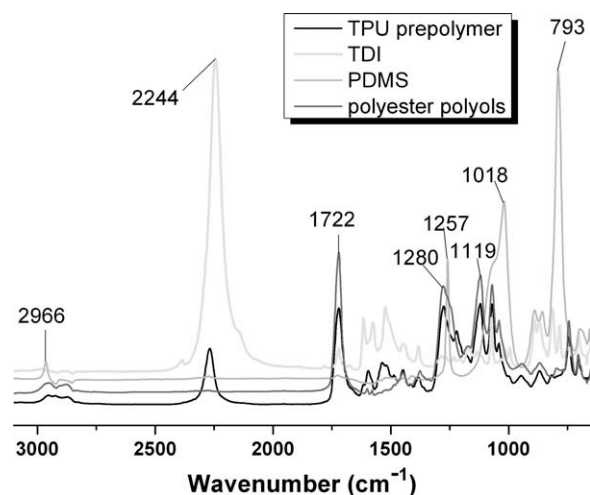


Figure 2 ATR-IR spectra of TDI, PDMS, polyester polyols, and TPU prepolymer.

radiation (0.154 nm) with a filament voltage of 40 kV and current of 100 mA in the range of 10–60°.

Scanning electron microscopy

The TPU films were mounted onto scanning electron microscopy (SEM) stubs and sputter coated with gold. The micrographs were taken on a Hitachi-450 scanning electron microscope (Hitachi) with the following conditions: 3 mm working distance and 25 kV voltage. For fracture analysis, samples were fractured in liquid nitrogen and gold-sputtered prior to observation.

Thermal analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out in a Mettler TGS DTA thermobalance. The samples (20 mg) were heated from room temperature to 650°C at a heating rate of 10°C/min.

Solvent resistance test

The solubility and performance change of the TPU films (10 mm × 10 mm with uniform thickness) in organic solvents were determined preliminarily to investigate the solvent resistant properties. Some common solvents including water, ethanol, and acetone were used. Changes in the swelling rates during immersion in these solvents at room temperature for different time were calculated. Solvent uptake can be calculated by the following equation:¹⁸

$$\text{Solvent uptake} = (W_s - W_d) / W_d \times 100\% \quad (1)$$

where W_s and W_d are the weights of swollen and dry films, respectively.

Stress-strain test

The mechanical properties of the polyurethane films were determined on an RG 3005 (REGGER, Shenzhen) using dog-bone test pieces 0.9 mm thick and 2 mm wide (in the center of the test sample). The procedures followed the GB/T 528-1998 standard in which a cross-head rate of 100 mm/min was adopted. Three tests were performed on each sample.

RESULTS AND DISCUSSION

Structure characterization

As illustrated in Figure 1, the prepolymer method was progress of two step, before and after adding PDMS. Before adding PDMS, a step-growth polymerization occurred between poly (ethylene glycol) and TDI and oligomers were obtained. The growth of molecular weight rapidly started after addition of PDMS and BDO. Furthermore, crosslinked structure was formed by addition of the crosslinking agent. The structure of the prepolymer was verified by FTIR spectroscopy as shown in Figure 2. The absorption bands around 1722 cm^{-1} (C=O of urethane) and 1000–1200 cm^{-1} (C–O–C stretching) are obtained.^{1,2,4,17,18} It is also noteworthy that the ATR-IR spectrum of the TPU prepolymer shows a high intensity of NCO band at 2244 cm^{-1} , confirming that the prepolymers contains unreacted isocyanate ends.

A typical FTIR spectrum of the TPU films is shown in Figure 3. All the FTIR spectra show the bands corresponding to polyurethane at 3453 cm^{-1} (free N–H stretching), 3383 cm^{-1} (hydrogen-bonded N–H), and 1729 cm^{-1} (C=O of urethane). The bands arising from C–O–C in the polyester at 1155, 1193, and 1432 cm^{-1} also appear. Furthermore, the

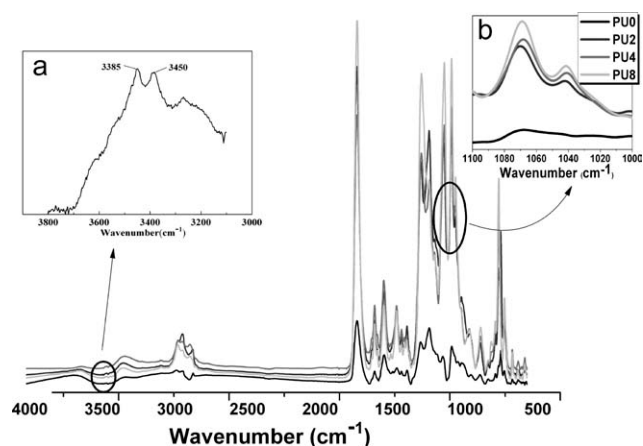


Figure 3 ATR-IR spectra of the polyurethane films with different PDMS content. The insert (a) shows FTIR bands at 3450 and 3385 cm^{-1} and insert (b) shows an increase in Si–O–Si absorbance bands.

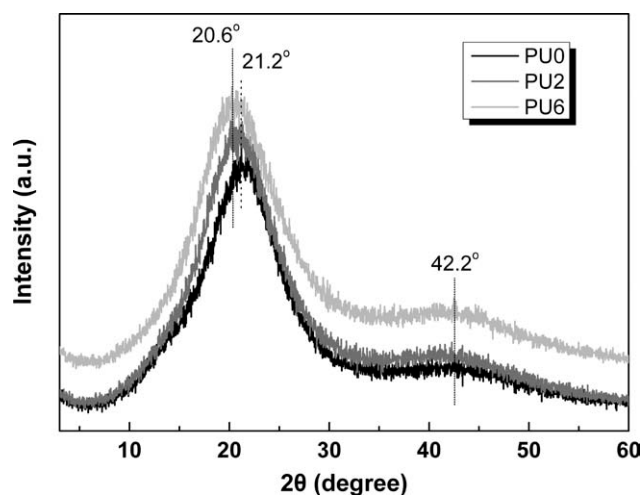


Figure 4 WAXD patterns of PU0, PU4, and PU8.

ATR-IR spectrum of the isocyanate does not show the band at 2250 cm^{-1} (related to free NCO) thereby confirming that the polyurethane is fully reacted.^{1,2,4,17,18} The PDMS-modified TPU shows a relatively similar ATR-IR spectrum than that of pre-

polymer, although some differences in the $700\text{--}1000\text{ cm}^{-1}$ range can be noticed. The peaks at 1063 and 1100 cm^{-1} (Si—O—Si stretching) as well as 823 cm^{-1} (CH_3 rocking) are assigned to the PDMS in the copolymer. In addition, the increase in PDMS promoted an increase in Si—O—Si absorbance bands, as shown in the insert of Figure 3(b).

WAXD was performed to investigate the underlying microstructure of the TPU films. As shown in Figure 4, the WAXD patterns of all samples were similar with a large and a small wide diffraction at around 20° and 42° , respectively, which are typical for amorphous polymeric materials.¹⁹ It has been observed that with addition of PDMS (PU4 and PU8) the characteristic diffraction peak appears at 21.2° is shifted to 20.6° as a result of the introduction of PDMS with narrow molecular width compared to polyurethane.

Morphology characterization

Figure 5 shows the SEM pictures of the PU2 films, and the surface morphology is rough and scaly. It shows a distribution of phase microdomains with

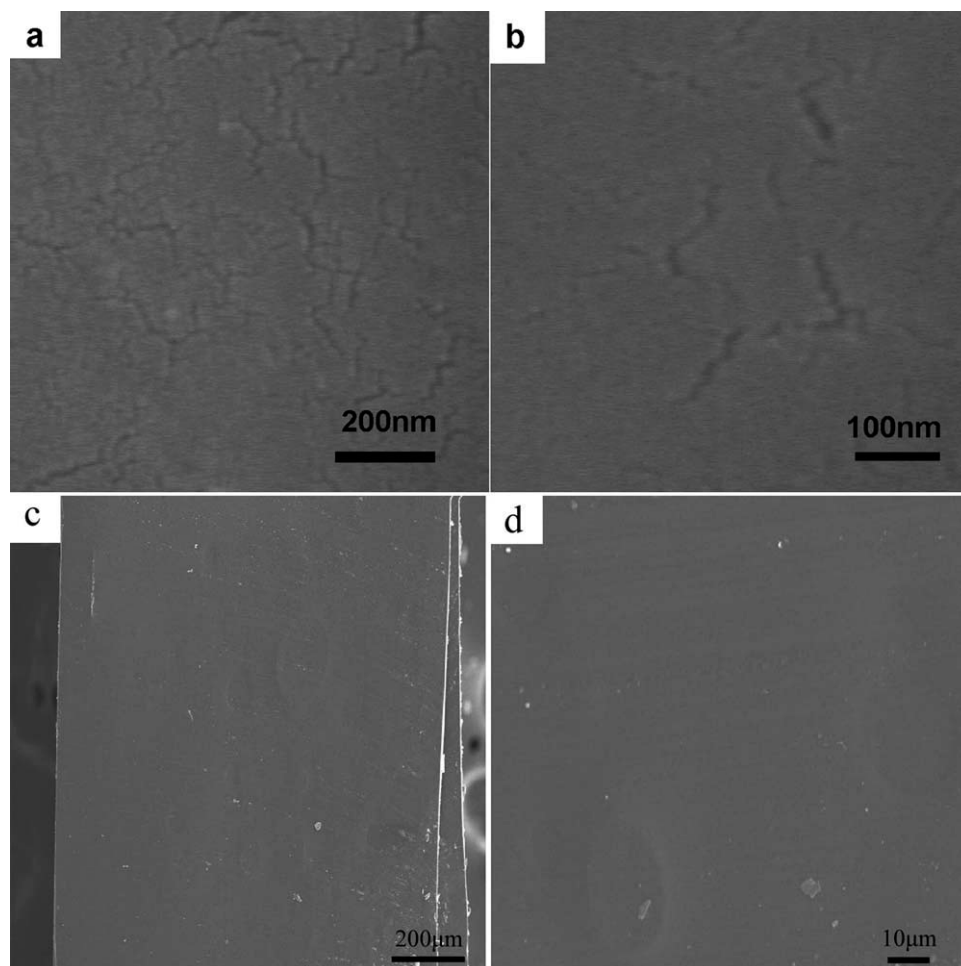


Figure 5 SEM images of the top surface revealing cracks (a, b) and fractured surface (c, d) showing a smooth topography at two different magnifications.

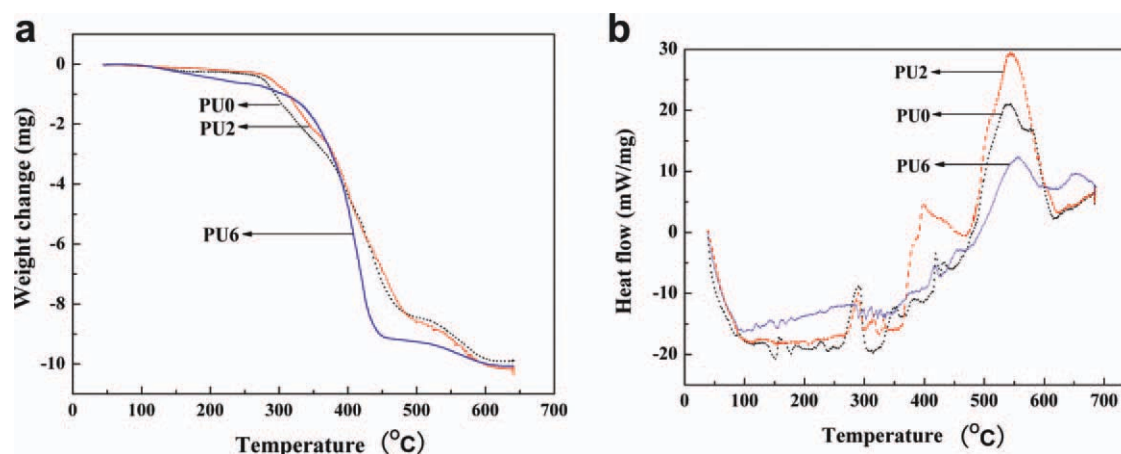


Figure 6 (a) TG and (b) DTA curves in air obtained from the organosilicon-modified polyurethane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

some small balls. This is due to a higher incompatibility between soft segment and hard segment because of large differences in the chemical structure.²⁰ When the TPU solution is placed in a PTFE mould, volume contraction due to evaporation of solvent occurs at the top surface of the films and cracks obtained. The hard-segment-rich domains are dispersed in a soft-segment-rich matrix, acting as the physical tie points as well as the reinforcing filler.²¹ The degree of phase separation (DPS) affects the thermal properties and crystallinity of the polyurethanes. As DPS increases, the tie points decrease allowing increase in chain slippage and disentanglement and vice versa.²² Because the FTIR bands at 3450 and 3385 cm^{-1} (the insert a in Fig. 3) correspond to free and hydrogen-bonded N–H stretching, respectively, it is possible to calculate the DPS. The DPS is 49.4% (PU2) using the following relationship.^{23,24}

$$\text{DPS} = \frac{\text{NH}_{\text{bonded}}}{[\text{NH}_{\text{bonded}} + \text{NH}_{\text{free}}]} \quad (2)$$

On the other hand, cracks develop on the film surface. Crack formation is usually attributed to the combined functions of UV radiation, oxygen, and humidity breaking down macromolecules and producing gaseous products such as carbon monoxide or carbon dioxide.²⁵ SEM images of fractured surfaces show a smooth topography for the PU2 film [Fig. 5(c,d)].

Thermal analysis

Thermal degradation of the TPU was assessed using TGA experiments. Figure 6(a) shows the weight loss as a function of temperature and two degradation stages occurring at about 315°C and 510°C are observed. The initial 5% weight loss occurs at around 300°C, suggesting that incorporation of PDMS does not influence the values. In addition, the TG profile of PU6 shows a continuous weight loss up to 300°C, unlike to PU0 and PU2, which is probably due to some substances with low melting points. A small increase in the decomposition temperature of the organosilicon-modified polyurethane is produced indicating a small improvement in stability in the thermal degradation of the TPU (Table I). In addition, PU2-PU8 shows similar residue yields.

Figure 6(b) depicts the DTA thermograms of the TPU. In fact, the TGA experiments agree well with the DTA thermograms. There are two exothermic peaks at around 400°C and 480°C, respectively, and this is caused by the burning heat. Previous studies² have demonstrated that in ionomeric polyurethanes, the hard segments (i.e. isocyanate+chain extender) decompose thermally earlier than the soft segments (i.e. polyol). Therefore, the first decomposition process at about 400°C should correspond to the hard segments and the second one is associated with the soft segments.

TABLE I
Decomposition Temperature and Weight Loss Obtained from the TG Results

Sample code	PDMS (wt %)	Temperature (°C)					Residue (wt %)
		T_0	T_5	T_{10}	T_{15}	T_{30}	
PU0	0	275.0	292.7	328.4	368.4	430.2	41.5
PU2	2	291.8	312.5	343.5	379.0	431.7	49.3
PU4	4	317.2	305.1	346.0	367.1	397.0	51.8
PU6	6	323.0	305.6	355.3	376.3	410.5	49.4
PU8	8	312.5	277.1	344.6	369.4	405.1	51.0

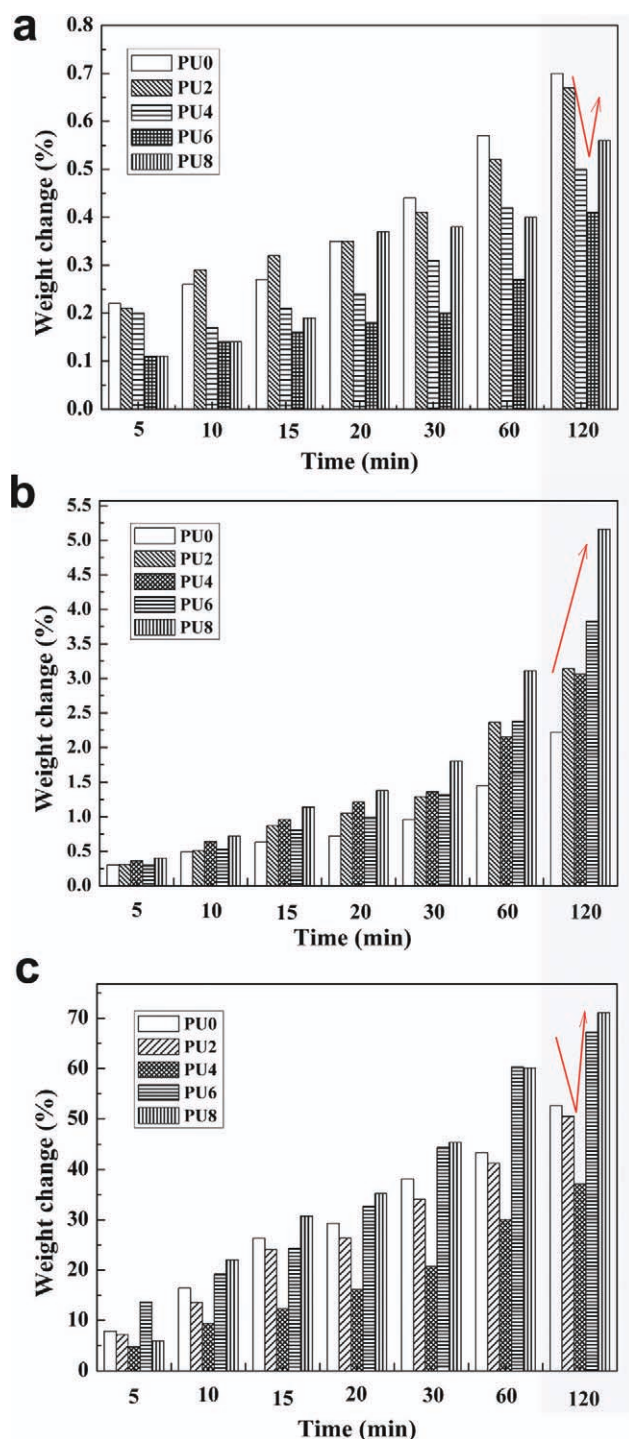


Figure 7 Solvent uptake rate calculated from the TPU films in (a) water, (b) ethanol, and (c) acetone, respectively. Arrows show the variation trend of solvent uptake in different solvents at 120 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Solvent resistance analysis

The solvent resistance properties of the TPU films are investigated. They are usually determined by solvent uptake.²⁶ The method is applicable if the sol-

vent does not really dissolve the polymer but only diffuses into it.²⁷ Figure 7 shows the weight changes after the films are immersed in water, ethanol, and acetone, respectively. Figure 7 illustrates that the degree of swelling depended both on the time and the concentration of PDMS introduced. It can be seen that TPU films have good solvent resistance in water and ethanol better than that of acetone due to the increase of polarity similarity. The order of solubility parameter values is as following: water > ethanol > acetone \approx TPU. So the decrease in polarity and solubility parameter of the solvents used promoted an increase in solvent uptake. Not only that, the solvent resistance properties are improved appreciably in water and acetone when the PDMS content is less than 4 wt %, which can be attributed to the hindered path of the solvent molecules through the polymer matrix. For instance, as the PDMS content is increased from 0 to 4 wt %, the acetone uptake rate diminishes from 52.58% to 37.11% at 120 min. In Li-Hong Bao's study,²⁸ the solvent absorptivity (SA%) of the aqueous anionic polyurethane in water is 38.6% (MCPU1.15), but organosilicon-modified polyurethane in our study is just 0.4–0.7%. However, when the PDMS content is more than 6 wt %, the solvent resistance property deteriorates. Therefore, it can be said that moderate PDMS (<4 wt %) has improved the solvent resistance property of the TPU films. On the other hand, the introduction of PDMS does not result in a significant change in the ethanol uptake [Fig. 7(b)]. It is probably because that there is a larger gap between the films and PDMS in the solubility parameter.

Mechanical properties

The tensile strength (σ) and elongation at break (ϵ_u) of the TPU films are measured by stress–strain tests. Figure 8 shows the variations in the tensile strength

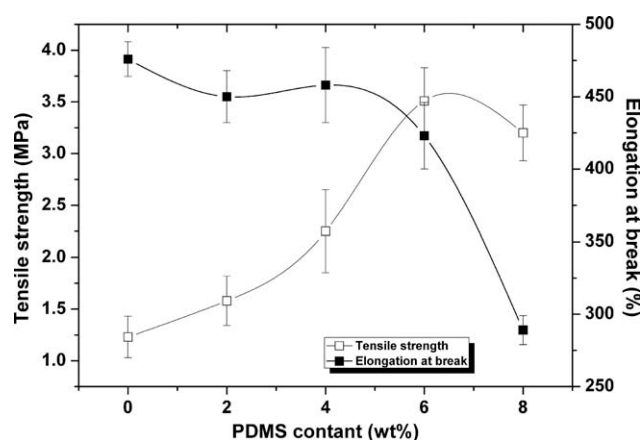


Figure 8 Variation of the tensile strength and ϵ_u (%) as a function of PDMS contents.

and elongation at break as a function of the PDMS contents, respectively. Addition of PDMS increases the tensile strength of the TPU films. The increase is not only attributed to the enlarged chain induced from PDMS but to the interactions between the silanol groups and polyurethane. In fact, a tensile strength up to 6 wt % has the largest effect. All the films show typical rubbery characteristics with high elongation. The elongation at break decreases probably as a consequence of the development of aggregated PDMS leading to phase separation.²⁹

CONCLUSIONS

Organosilicon-modified polyurethane has been synthesized by the prepolymer method mainly using toluene diisocyanate, poly (ethylene glycol), and polydimethylsiloxane. The structure, morphology, thermal and solvent resistance were studied in detail. Phase separation and improved thermal properties of the resultant films were observed. The solvent resistance of the films shows controversy toward water, ethanol, and acetone as the content of PDMS increase due to the differences between polymer chain and solvent in the polarity. Addition of PDMS to the polyurethane decreases water and acetone uptake but increases ethanol uptake. The water adsorption of the product in our study is just 0.4–0.7%. The results suggest that the PDMS show a positive contribution to solvent resistance property. All the films exhibit typical rubbery characteristics with high elongation. The materials with 6 wt% PDMS show the largest effects on the tensile strength.

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