

# Mechanical and Surface Properties of Membranes Prepared from Waterborne Cationic Hydroxyl-Terminated Polydimethylsiloxane/Polyurethane Surfactant-Free Micro-Emulsion

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**ABSTRACT:** With the action of catalyst and cosolvent, a series of hydroxyl-terminated polydimethylsiloxane (HPMS) based polyurethane (PU) micro-emulsion were gotten by surfactant-free copolymerization. They were successfully prepared by reacting isophorone isocyanate, poly(tetramethylene glycol), and HPMS with *N*-methyl-diethanolamine (MDEA) as chain extender and trimethylolpropane (TMP) as crosslinker. After neutralizing with dimethyl sulfate and inverting the emulsion polymerization with deionized water, a series of microemulsions were obtained. The emulsions were then cast into membranes named as PU-HPMS. The mechanical properties and water absorption of the PU-HPMS were determined and simultaneously the effects of the content of hard segment, solvent, TMP, MDEA, HPMS, and the molecular weight of soft segment were studied. It is noticed that the tensile strength decreased and elongation at

break increased in the HPMS/PU when compared with pure PU, which confirm that PU was end-capped with PDMS. It is also noticed that water absorption increased in the HPMS/PU when compared with pure PU. As HPMS content increased from 0.0 to 25.0 wt %, the surface free energies decreased from 0.3446 to 0.2317 mN/cm and water absorption decreased from 11.2% to 0.14%. The surface free energies of the membranes were decreased by more than 32.76%, which demonstrate that the membrane surfaces have excellent water and oil repellency. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 40–46, 2006

**Key words:** hydroxyl-terminated polydimethylsiloxane; polyurethane; surfactant-free emulsion copolymerization; membrane; mechanical properties; water absorption

## INTRODUCTION

Polyurethane (PU) materials have a wide application because of their excellent properties such as abrasion resistance, low-temperature flexibility, high strength and chemical resistance, and so on, however, they are water-incompatible materials prepared from organic solvents.<sup>1–5</sup> To reduce volatile organic compound emission, waterborne polyurethane (WPU) has attracted much attention.<sup>5–8</sup> The materials prepared from WPU can be applied in the fields of construction, automotive, packing, transportation, electronics, textiles, tape, paper, and footwear<sup>9–11</sup>; however, some properties of membranes of WPU, such as water resistance and elongation at break, need to be improved further. WPU has been modified by many ways, such

as forming latex interpenetrating polymer networks (IPNs) and semi-IPNs with polystyrene and acrylate rubber.<sup>12,13</sup>

Polydimethylsiloxane polymers (PDMS) have many applications due to their unique properties, which arise mainly from its natural structure composed of inorganic Si—O bond and organic graft CH<sub>3</sub> group (as shown in Fig. 1).<sup>14–17</sup> These properties include low surface energy, very good thermal stability, and excellent flexibility. However, the mechanical properties of PDMS polymers are usually low, especially, with low molecular weights.

The combinations of polyurethane and polydimethylsiloxane would have better heat resistance and lower temperature flexibility than polyurethane and better mechanical properties and abrasion characteristics than polydimethylsiloxane.<sup>18</sup> At present, some researchers have reported related copolymers, but they mainly concentrate on the study of anionic PU/PDMS polymers. For example, Denise P investigated the structural characteristics and gas permeation of anionic PU/PDMS blocking membranes; Wang synthesized a kind of anionic aminoalkyl terminated PDMS modified polyurethane dispersion.<sup>17,18</sup> However, as

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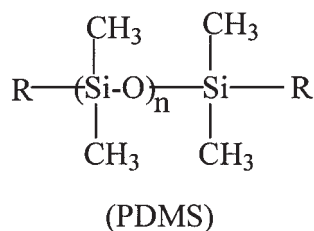


Figure 1 Chemical structure of polydimethylsiloxane.

yet, reports about cationic PU-HPMS micro-emulsion prepared by surfactant-free copolymerization in two-component polyurethane have been scarcely seen.

To get a kind of membrane that simultaneously have the advantage of polyurethane and polydimethylsiloxane, one kind of high molecular weight hydroxyl-terminated PDMS (HPMS) was chosen to enveloping the polyurethane prepolymer, and dispersions of WPU end-capped with HPMS was prepared with the surfactant-free micro-emulsion. Finally, the effects of the NCO/OH ratio, cosolvent, trimethylolpropane (TMP), *N*-methyldiethanolamine (MDEA), PDMS on mechanical properties, and water absorption were studied.

## EXPERIMENTAL

### Materials

The poly (tetra ethylene) glycols (PTMG) (and) were characterized by gel permeation chromatography (GPC) and hydroxyl group number determination. The decompressed distillation was carried out to remove any moisture of PTMG. Isophorone isocyanate (IPDI) and dimethyl sulfate (DS) were vacuum dis-

tilled before use. *N*-methyldiethanolamine (MDEA) and Trimethylolpropane (TMP) were dried at 70°C for 16 h. DMF was dried for at least 1 week using four molecular sieves, before use. Hydroxyl-terminated polydimethylsiloxane (HPMS) was normally used after completing drying in vacuum oven at 80°C.

### Preparation of polyurethane/HPMS surfactant-free micro-emulsion

PU-HPMS micro-emulsion based on IPDI, PTMG, HPMS, MDEA, and TMP was synthesized using surfactant-free emulsion polymerization. In the preparation of the PU prepolymer, IPDI, PTMG (P1 and P2), and dibutyltin dilaurate (DBTDL) 0.02 wt % (based on the total reaction mass) were charged into a four-necked reaction vessel equipped with a reflux condenser, a mechanical stirrer, and a digital thermometer. And the DMF solutions of TMP and MDEA were added slowly to the vessel. The reaction was started at 75°C under a dry nitrogen atmosphere. When the isocyanate group content (determined by the di-*n*-butylamine titration method) of the reaction mixture reached 2%, the reaction was terminated and a certain content of HPMS was poured into the vessel to end-cap PU prepolymer at 80°C for 2 h. The unreacted free IPDI was left in the synthesized PU prepolymer to give the PU network a higher hard-to-soft segment ratio.

A part of the polyurethane solution was neutralized with DS, and then deionized water was poured slowly into the vessel and stirred vigorously for several hours. Finally, a kind of semitransparent microemulsion was obtained. The chemical structure of PU-HPMS is shown in Figure 2. Composition of cationic PU-HPMS is shown in Table I.

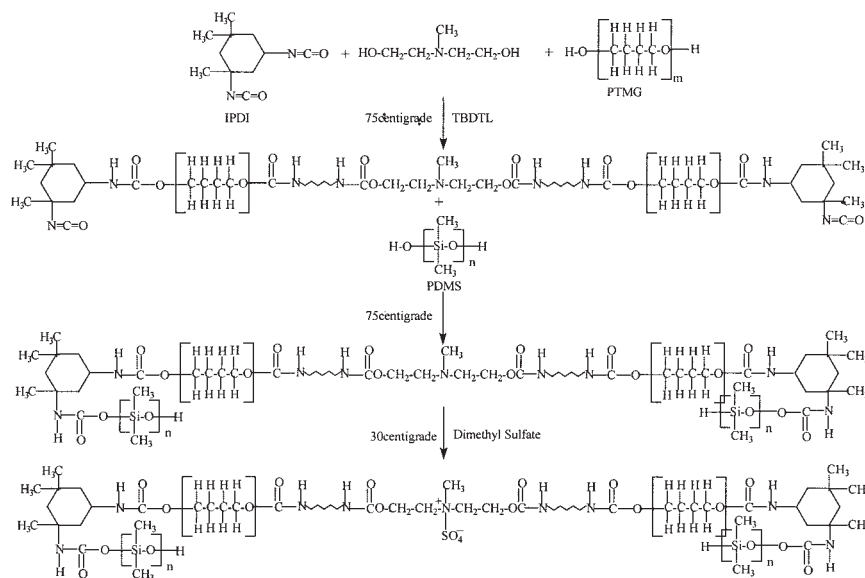


Figure 2 Chemical structure of PU-HPMS prepared in this study.

TABLE I  
Composition of Cationic PU-HPMS

Designation	NCO/OH ratio (%)	Molecular weight of PTMG (g/mol)	Ratio of MDEA (%)	Ratio of TMP (%)	HPMS content (%)	The type of membrane
PU	22/1.0	1000 (P1)	10	3.0	0	AR
PU-HPMS-I	2.2/10	1000 (P1)	10	3.0	5	AR
PU-HPMS-2	2.2/1.0	1000 (P1)	10	3.0	8	AR
PU-HPMS-3	2.2/1.0	1000 (P1)	10	3.0	10	AR
PU-HPMS-4	2.2/1.0	1000 (P1)	10	3.0	15	AR
PU-HPMS-5	2.2/1.0	1000 (P1)	10	3.0	20	AR
PU-HPMS-6	2.2/1.0	1000 (P1)	10	3.0	25	AR

### Preparation of PU-HPMS membranes

PU-HPMS films were obtained by casting the emulsions on tetrafluoroethylene (TFE) plates and allowing them to dry at room temperature for 5 days and then at 60°C for 12 h. After demolding, the films were submitted to vacuum drying for 1 day. Three kinds of films were studied: the pure emulsion (SA), the emulsion with DMF added in PU prepolymer (AR), and the emulsion with DMF added previous to casting (AD).

### Tensile tests

The tensile strength and elongation at break of the films were measured on a multifunctional electronic strength tester TS2000-S (Scientific and Technological Limited Company of High Iron in Taiwan). Tensile test bars ( $5 \times 70 \text{ mm}^2$ ) were cut from PU-HPMS films of 0.4–0.8 mm thickness. The standard tensile test performed was an adaptation of ASTM 412–83, D 638–84, and D 882–83 methods.

### Determination of water absorption

The membranes, with a thickness of 0.4–0.8 mm, were cut into circular disks by using a sharp-edged stainless steel die with inner diameter of 20 mm. The samples were dried in a vacuum oven for 24 h to determine their dry weight. Water absorption of the PU-HPMS membranes was determined by immersing the membranes in a beaker of water at 37°C. The wet weight with different immersion times was determined by wiping off the surface water with a piece of filter paper. The water absorption (WS) of the films was calculated by<sup>17</sup>

$$WS = [(W_t - W_d)/W_d] \times 100 \quad (1)$$

As swelling reaches equilibrium, WS (%) approaches the saturated swelling, otherwise known as equilibrium content, (%).

In addition to the equilibrium degree of swelling, the rate at which equilibrium is reached and the transport mechanism are of great importance. The simplest

transport mechanism is Fickian, the rate of approaching equilibrium can be calculated by the diffusion coefficient  $D$ . The value of  $D$  can be obtained from the plots of the degree of saturation (WS) against, where  $L$  is the initial thickness of the membrane and  $t$  the swelling time.

According to Fickian diffusion mechanism, the diffusion coefficient ( $D$ ) of water in the membranes can be determined from the slope of the plot by using the following equation<sup>19</sup>:

$$\frac{WS}{W_{eq}} = \left( \frac{D_t}{16\pi L^2} \right)^{0.5} \quad (2)$$

### Contact angle measurements and evaluation of surface free energy

Contact angles were measured with a JJC-I contact angle goniometer. The samples for contact angle measurement were prepared by casting the polymer onto clean silicon wafers from 10% (w/v) acetone. The silicon wafers were kept in an oven at 25°C for 24 h under vacuum. Contact angles were measured at 20°C, and the results reported are the mean values of five replicates. The contact angle of membrane was measured with two test liquids (water, ethylene glycol). By combining the contact angle data and the eqs. (4) and (7), the surface energy of membranes was calculated.

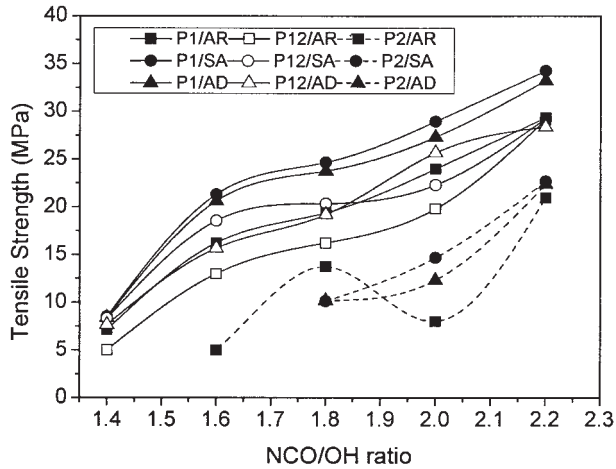
In general, the surface tensions of liquid and solid can be described as follows<sup>20</sup>:

$$\gamma_L = \gamma_L^d + \gamma_L^p \quad (3)$$

$$\gamma_S = \gamma_S^d + \gamma_S^p \quad (4)$$

where  $\gamma_L$  and  $\gamma_S$  are surface tensions of liquid and solid respectively,  $d$  is apolar component and  $p$  is polar component. While the relationship of adhesion energy ( $W_0$ ) to surface tensions and interfacial tension was as follows:

$$W_0 = \gamma_S + \gamma_L - \gamma_{SL} = \gamma_L(1 + \cos\theta) \quad (5)$$



**Figure 3** Variation of tensile strength with NCO/OH for all series.

where  $\gamma_{SL}$  is interfacial tension, and  $\theta$  is the contact angle of the membranes with water or ethylene glycol.

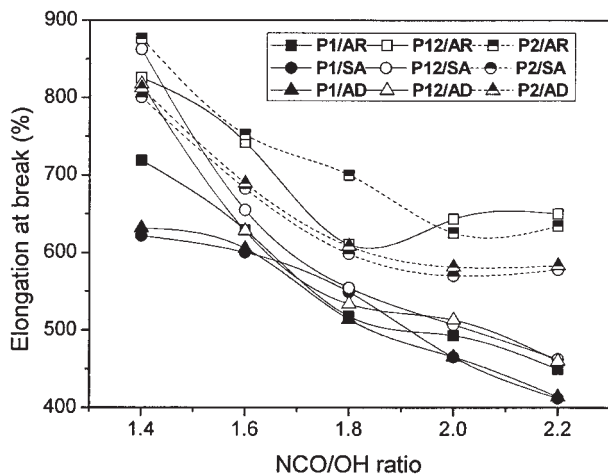
At the same time, adhesion energy ( $W_0$ ) can also be described as follows:

$$W_0 = 2[(\gamma_L^d \cdot \gamma_s^d)^{0.5} + (\gamma_L^p \cdot \gamma_s^p)^{0.5}] \quad (6)$$

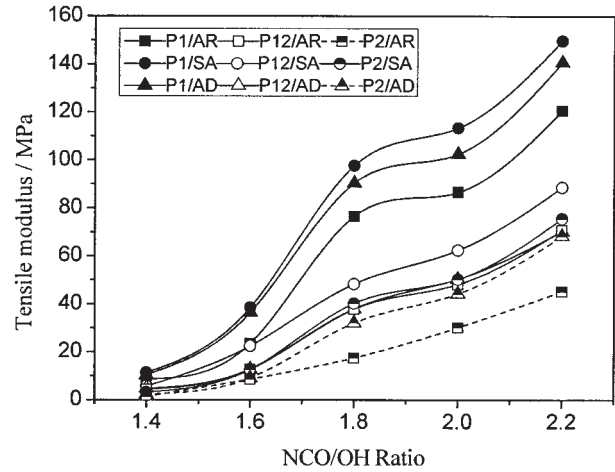
Consequently, the eq. (7) can be obtained by combining eqs. (5) and (6):

$$\frac{\gamma_L(1 + \cos\theta)}{2(\gamma_L^d)^{0.5}} = (\gamma_s^d)^{0.5} + \frac{(\gamma_L^p \cdot \gamma_s^p)^{0.5}}{(\gamma_L^d)^{0.5}} \quad (7)$$

The numerical values of water used are  $\gamma_L = 0.727$  mN/cm and  $\gamma_L^d = 0.239$  mN/cm; the numerical values of ethylene glycol are  $\gamma_L = 0.482$  mN/cm and  $\gamma_L^d = 0.310$  mN/cm.



**Figure 4** Variation of elongation at break with NCO/OH for all series.



**Figure 5.** Variation of tensile modulus with NCO/OH for all series.

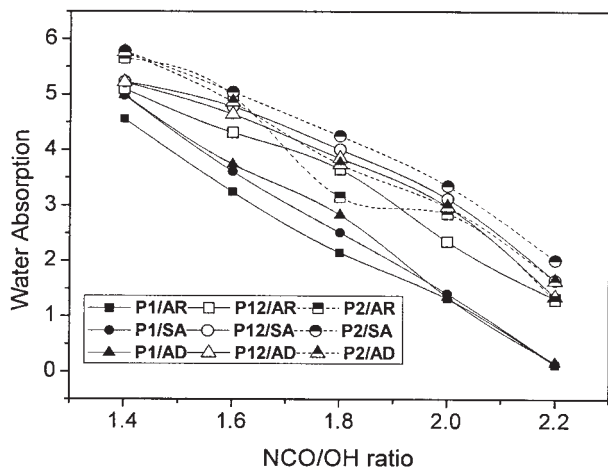
## RESULTS AND DISCUSSION

### Effects of PU-HPMS molecular structure and cosolvent on mechanical properties and water absorption

The mechanical properties of PU-HPMS are directly related to the amount of the hard-segment domains, which are extensively hydrogen-bonded with the neighboring chains and determine the content of NCO groups.

Figures 3–5 show the variation of tensile strength, modulus of elasticity and elongation at break of all series with NCO/OH ratio, for AR, SA, and AD, respectively. As shown in the figures, some conclusions could be drawn as follows: (i) As the NCO/OH ratio increases, there is a reduction in the values of elongation at break and an increase in the values of tensile strength as well as modulus of elasticity. This indicates that the more hard segments allow more effective hydrogen bonds. As shown in Figure 3, the films' tensile strength can not reach 10 MPa when the NCO/OH ratio is 1.4. By comparison, when the NCO/OH ratio is 2.2, their tensile strength can reach 33.8 MPa. (ii) Compared with P12 and P2 systems, the P1 system displays higher tensile strength and modulus elasticity. The inverse behavior is observed for elongation at break. The main reason is that the ether-based soft segment displays feeble polarity, the increase of molecular weight, which indicates reduction of the hard-to-soft segment ratio, would result in decrease in tensile strength. (iii) The sequence of adding solvent also influenced films' mechanical properties. Compared with SA and AD systems, AR system owns higher elongation at break; tensile strength and modulus elasticity are the opposition, particularly for P2 system. The main reason is that the solvent acted as an internal plasticizer dispersing PU-HPMS molecular, lowering the chain interactions, and enhancing the freedom of chain mobility, which results in the in-





**Figure 6** Variation of water absorption with NCO/OH for all series.

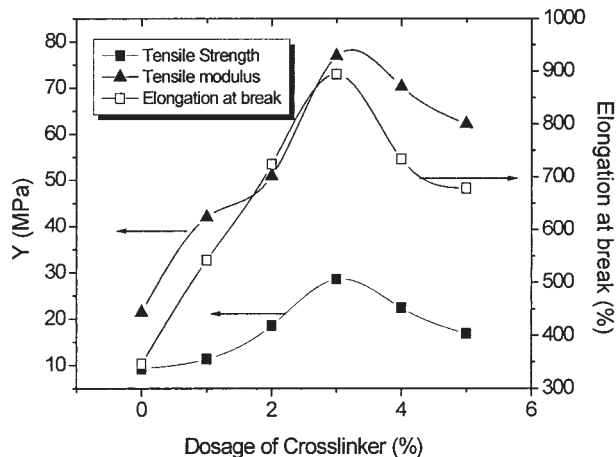
crease of elongation at break. However, no representative difference is found between SA and AD systems, which shows that the solvent did not have a significant interaction with the chains when it was added before casting.

Figure 6 shows variation of water absorption with NCO/OH for SA, AR, AD. The water absorption decreases as the NCO/OH ratio increases. The PU-HPMS with greater NCO/OH ratio absorbed less water because of the increase of the content of hydrophobic hexatomic-ring, carbamate bond and urea bond. It is also clear that PU-HPMS (PTMG2000) membranes absorb much less water than PU-HPMS (PTMG1000) films. However, the effect of the polyol molecular weight on the water absorption is less significant.

#### Effects of crosslinker on mechanical properties and water absorption

Figure 7 shows variation of mechanical properties with dosage of crosslinker for P1/AR. The tensile strength, tensile modulus, and elongation at break reach the peak while the dosage of crosslinker is 3% (based on total reaction mass, the follows are as the same). To a certain degree, crosslinkages prevent molecules from sliding, which results in the increase of stress and strength. However, excessive crosslinkages make macromolecular chain hardly oriented under external force, and make the emulsion particles hardly transformed. As a result, the chain can not be effectively crossed with each other when casting membranes, and the membranes become brittle, which leads to the decrease of tensile strength, tensile modulus, and elongation at break.

As is shown in Figure 8, the water absorption decreased with the increase of the dosage of TMP when lower than 3%, and the water absorption increased with the increase of the dosage of TMP when larger

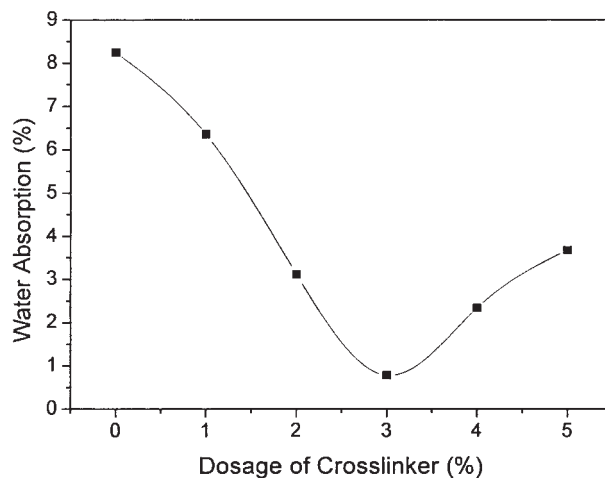


**Figure 7** Variation of mechanical properties with dosage of crosslinker for P1/AR.

than 3%. The main reason is that the increase of the dosage of TMP lead to the increase of crosslinkages when less TMP is added, which effectively restrains the penetration of water; However, if the crosslinking density is too high, the emulsion would be unstable, water can easily penetrate into water phase instead, which consequently lead to the increase of water absorption.

#### Effects of MDEA on mechanical properties and water absorption

Figure 9 shows the relationship between the mechanical properties and the dosage of MDEA for P1/AR. It is found that the tensile strength greatly decreases with the increase of chain extender. It is also found that elongation at break increases with the increase of chain extender at the beginning, and



**Figure 8** Variation of water absorption with dosage of crosslinker for P1/AR.

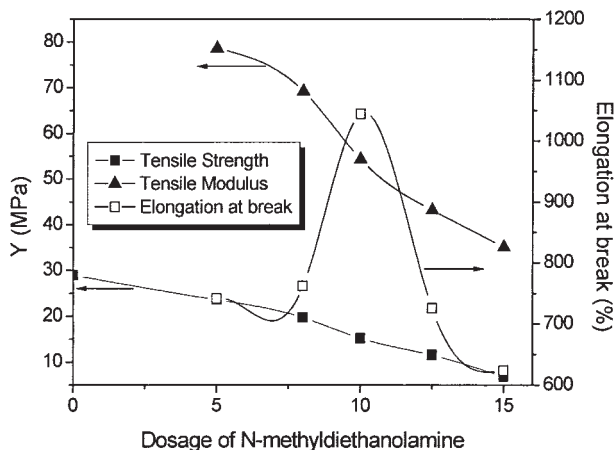


Figure 9 Variation of mechanical properties with dosage of MDEA for P1/AR.

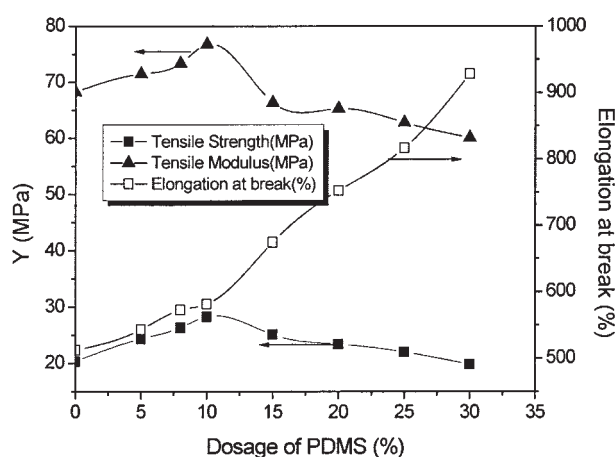


Figure 11 Variation of mechanical properties with dosage of HPMS for P1/AR.

then decreased when the dosage of MDEA more than 10%. These observations may be explained as follows:

- i. The tensile strength of PU-HPMS greatly depend on intermolecular interactions, such as hydrogen bond. In fact, the more chain extender will lead to the less NCO groups, which indicated that less carbonyl group have participated in the hydrogen bonding with more MDEA with chain extender.
- ii. With the increase of the dosage of chain extender, the polymer's relative molecular mass gradually increases and its chain is inclined to develop in linear orientation. As a result, polymer chain can be easily oriented in the pulling process, which results in the increase of the elongation at break. However, at the same time, the ionic groups become excessive with the dosage

of chain extender increased, which arise from the reduction of elongation at break.

As shown in Figure 10, water absorption increased with the dosage of MDEA increased. The hydrophilic property of PU-PDMS membranes was gradually enhanced with the dosage of MDEA increased, and water was easily adsorbed and transferred by hydrophilic groups in PU molecular chain, which consequently lead to the increase of water absorption.

**Effects of HPMS on mechanical properties and water resistance**

Figure 11 shows the tensile strength and modulus of elasticity of PU-HPMS membranes increased with the increase in dosage of PDMS, when the dosage of HPMS was lower than 10%, the elongation at break increased. The main reason is that certain crosslinking

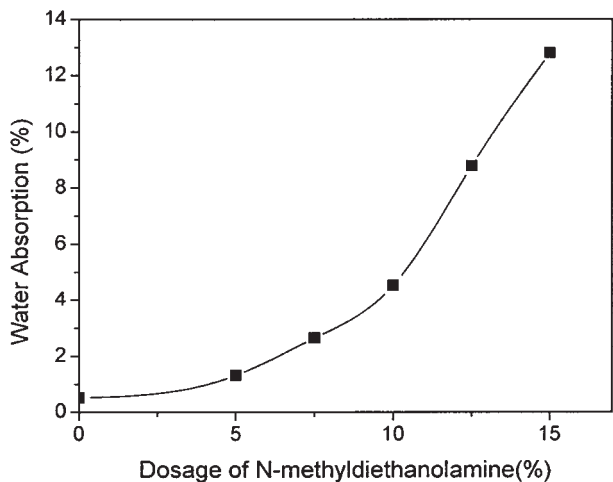


Figure 10 Variation of water absorption with dosage of MDEA for P1/AR.

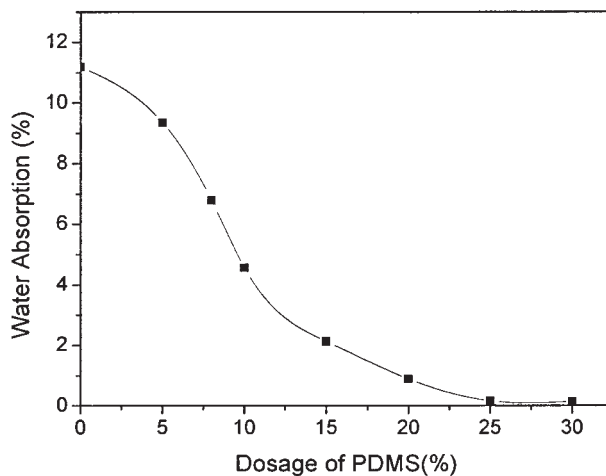


Figure 12 Variation of water absorption with dosage of HPMS for P1/AR.

**TABLE II**  
Contact Angles and Surface Free Energies of PU-HPMS Membranes<sup>a</sup>

Designation	Contact Angle (°)		Surface free energy (mN/cm)		
	Water	Ethylene glycol	$\gamma^d$	$\gamma^p$	
				$\gamma^p$	$\gamma$
PU	75.0	48.1	0.2523	0.0923	0.3446
PU-HJPMS-1	83.4	56.3	0.2616	0.0498	0.3114
PU-HPMS-2	90.2	64.7	0.2417	0.0306	0.2723
PU-HPMS-3	93.4	70.4	0.2050	0.0299	0.2349
PU-HPMS-4	94.8	71.3	0.2124	0.0238	0.2362
PU-HPMS-5	95.4	72.0	0.2086	0.0231	0.2317
PU-HPMS-6	96.5	72.7	0.2354	0.0189	0.2543

<sup>a</sup> The membranes are cured at 120°C for 12 h.

action enhances the flexibility of PU-HPMS membranes and excessive crosslinking bonds make membranes brittle.

Figure 12 shows variation of water absorption with dosage of HPMS for P1/AR. Table II shows the surface free energies calculated from contact angles of the membranes with water and ethylene glycol. As HPMS content increased from 0.0 to 25.0 wt %, the surface free energies decreased from 0.3446 to 0.2317 J/m<sup>2</sup> and water absorption decrease from 11.2% to 0.14%. The surface free energies of the membranes were decreased by more than 32.76%. The results demonstrate that the membrane surfaces have significant water and oil repellency. On the one hand, water can not immerse into the membranes because of strong hydrophobic Si—O—Si bonds. On the other hand, the organic groups grafted in HPMS are arrayed on the outermost membrane surface, and no polar groups exist in any HPMS. Therefore, it is advisable to make PU end-capped with HPMS.

## CONCLUSIONS

An increase in the hard-to-soft segment ratio caused an increase in tensile strength and modulus elasticity and a decrease in water absorption elongation at break.

An increase in the molecular weight of the soft segment led to a decrease in tensile strength and modulus elasticity and an increase in water absorption and elongation at break.

The dispersion effect of the cosolvent can obviously improve the elongation at break.

The tensile strength and modulus elasticity reach the peak while the dosage of crosslinker is 3% (based on total reaction mass), and elongation decreases as the dosage of crosslinker increases. The water absorption increased with the increase of the dosage of TMP when it was lower than 3%, and the water absorption decreased with the increase of the dosage of TMP when it was larger than 3%.

The tensile strength greatly decreased with the increase of chain extender, elongation at break increased with the increase of chain extender, water absorption increased with the increase in dosage of MDEA.

Water absorption of the PU membranes containing HPMS is lower than that of membranes without PDMS. As HPMS content increased from 0.0 to 25.0 wt %, the surface free energies decreased from 0.3446 to 0.2317 J/m<sup>2</sup> and water absorption decreased from 11.2% to 0.14%. The surface free energies of the membranes were decreased by more than 32.76%, which demonstrate that the membrane surfaces have excellent water and oil repellency.

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