

# Effects of Polydimethylsiloxane Concentration on Properties of Polyurethane/Polydimethylsiloxane Hybrid Dispersions

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**ABSTRACT:** A series of waterborne polyurethane (WPU) derived from isophorone isocyanate and poly(tetramethylene glycol) were modified by hydroxyl-terminated polydimethylsiloxane (HPMS). The solutions were then cast into films named as PUHS. Rheological behavior of the emulsions were studied using Rheometer and morphology was studied with transmission electron microscope. Meanwhile, the casting films were prepared from the WPU/HPMS hybrid dispersions, and their glass transition behavior, miscibility, water resistance, and medium resistance were studied with differential scanning calorimeter (DSC), wide-angle X-ray diffraction (WAXD), and so on. The results revealed that the emulsions' particle size decreases with increasing HPMS content and the particles are more easily

affixed to each other when the HPMS content is more than 15%, and emulsions are endowed with pseudoplasticity and thixotropy. WAXD and DSC figures manifested that the casting films all exhibited a certain degree of miscibility. The degrees of crystallinity ( $x_c$ ) decreased with increasing HPMS content, and the PUHS films were almost amorphous. It is noticed that water and medium absorption increased in the HPMS/PU compared to pure PU, which demonstrate that the membrane surfaces have excellent water and chemical medium repellency. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5538–5544, 2006

**Key words:** hydroxyl-terminated polydimethylsiloxane; polyurethane; rheology; miscibility; medium resistance

## INTRODUCTION

Waterborne polyurethane (WPU) dispersions, due to their excellent properties and environmental advantages, have become one of the major types of materials used in some fields such as coating.<sup>1–10</sup> To obtain cost/performance benefits, polyurethane (PU) dispersions are blended with polyesters, alkyds, acrylics, and other waterborne polymers.<sup>11</sup> For example, researchers synthesized a series of PU/acrylic blends by a number of routes, such as seeded emulsion polymerization,<sup>11–15</sup> forming interpenetrating polymer networks (IPNs) or semi-IPNs,<sup>16–18</sup> cross-linking,<sup>19</sup> and graft copolymerization of PU onto acrylic polymer chains.<sup>20–23</sup> Recently, excellent properties of polydimethylsiloxane (PDMS) polymers drive the interest of WPU modified with PDMS. PDMS have many applications due to their unique proper-

ties, which arise mainly from its natural structure composed of inorganic Si—O bond and organic graft CH<sub>3</sub> group.<sup>24–27</sup> These properties include low surface energy, very good thermal stability, and excellent flexibility.

The combinations of PU and PDMS would have better heat resistance and lower temperature flexibility than PU and better mechanical properties and abrasion characteristics than PDMS.<sup>28</sup> At present, some researchers have reported related copolymers. For example, Denise investigated the structural characteristics and gas permeation of anionic PU/PDMS blocking membranes; Wang synthesized a kind of anionic aminoalkyl-terminated PDMS-modified PU dispersion.<sup>28</sup> However, as yet, the effects of the concentration of PDMS on the structure and properties of the composites or blends have been scarcely published, and as well as reports about cationic PU/PDMS hybrid dispersions prepared by surfactant-free copolymerization.

To get a systematic knowledge of effects of PDMS on properties of PU, a series of work was carried out. In this work, a series of hybrid dispersions of WPU modified with hydroxyl-terminated PDMS (HPMS) were prepared. Rheological behavior of the emulsions were studied using Rheometer and

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morphology was studied with transmission electron microscope (TEM). Meanwhile, the casting films named as PUHS were prepared from the WPU/HPMS hybrid dispersions, and their glass transition behavior, miscibility, water resistance, and medium resistance were studied with differential scanning calorimeter (DSC), wide-angle X-ray diffraction (WAXD), and so on.

## EXPERIMENTAL

### Materials

The poly(tetramethyleneglycol)s (PTMG) ( $M_n = 1000$ ) were characterized by gel permeation chromatography (GPC) and hydroxyl group number determination. The decompressed distillation was carried out by the decompressed distillation to remove any moisture of PTMG. Isophorone isocyanate (IPDI) and dimethyl sulfate (DS) were vacuum distilled before use. *N*-methyl-diethanolamine (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 WPU/HPMS dispersions

WPU/HPMS dispersions based on IPDI, PTMG, HPMS, MDEA, and TMP was synthesized using surfactant-free emulsion polymerization. In the preparation of the polyurethane (PU) prepolymer, IPDI, PTMG ( $M_n = 1000$ ), and 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 PU 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. Composition of cationic WPU/HPMS dispersions is shown in Table I.

### Preparation of PUHS films

PUHS films were obtained by casting the emulsions on tetrafluoroethylene (TFE) plates and allowing

TABLE I  
Composition of Cationic WPU/HPMS Dispersions

Samples	Designation	Dosage of HPMS (%)
PU	a	0
PUHS-1	b	5
PUHS-2	c	15
PUHS-3	d	20
PUHS-4	e	25

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.

### Particle size measurement

The particle size of the WPU/HPMS emulsions was examined by Hitachi (Model S570) transmission electron microscope (TEM). The sample was diluted to the required concentration with distilled water before measurement.

### Rheology of WPU/HPMS dispersions

The viscosity, pseudoplasticity, and thixotropy of WPU/HPMS dispersions were analyzed in an American Brookfield DV-III Ultra Programmable Rheometer. The measurements were carried out at 20°C in the rotational mode using concentric cylinders type SC4-21. Hundred cubic centimeter of WPU/HPMS dispersions were used in the measurements. Controlled shear rate (CSR) experiments were carried out as follows: shear rate was increased from 50 to 350 s<sup>-1</sup> and maintained for 300 s to provide a uniform and standardized state in all the solutions. Then, the shear rate was gradually increased from 50 to 350 s<sup>-1</sup> in 840 s (up curve in the flow curve) followed by a gradual decrease from 350 to 50 s<sup>-1</sup> (i.e., cessation of flow) in 840 s (down curve in the flow curve). Some experiments were repeated and an excellent reproducibility was always obtained.

Pseudoplasticity of PU emulsions was quantified by means of the shear thinning index (STI). Thixotropic area (TA) is the area between the up and down branches of the flow curve, and it is obtained using the software of the rheometer.

### Wide-angle X-ray diffraction

The wide-angle X-ray diffraction (WAXD) analysis of the samples was performed on D8 discover X-ray diffractometer (Bruker axs, Germany) in the range of  $2\theta = 5^\circ\text{--}45^\circ$ , and the degree of crystallinity was accordingly calculated by the software.

### DSC measurement

The thermal properties were measured with use of a Germany Netzsch differential scanning calorimeter

DSC-204 in a nitrogen atmosphere. All samples of 10 mg were initially scanned over the temperature range from  $-150$  to  $200^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$  and quenched to  $-150^\circ\text{C}$  as rapidly as possible (at a cooling rate of  $100^\circ\text{C min}^{-1}$  from  $200$  to  $20^\circ\text{C}$  and a cooling rate of  $10^\circ\text{C min}^{-1}$  from  $20^\circ\text{C}$  down to  $-150^\circ\text{C}$ ) immediately after the furnace reached  $200^\circ\text{C}$ . All samples were scanned again from  $-150$  to  $200^\circ\text{C}$  with a heating rate of  $10^\circ\text{C min}^{-1}$ . The reported results are taken from the second heating runs of the experiments to avoid experimental artifacts arising from the previous thermal history and incomplete chemical reactions. In this study, the transition temperatures, endothermic peaks, and exothermic peaks of the first and second heating runs are very close, with only the baseline slightly shifted.

### Water resistance and medium resistance tests

The membranes, with a thickness of  $0.4\text{--}0.8$  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 vacuum oven for  $24$  h to determine their dry weight ( $W$ ). Absorption of the PU-HPMS membranes was determined by immersing the membranes in a baker of medium for  $24$  h. After wiping off the surface water with a piece of filter paper, its weight ( $W_1$ ) was determined. The absorption ( $WS$ ) of the films was calculated by

$$WS = (W_1 - W)/W \times 100\%$$

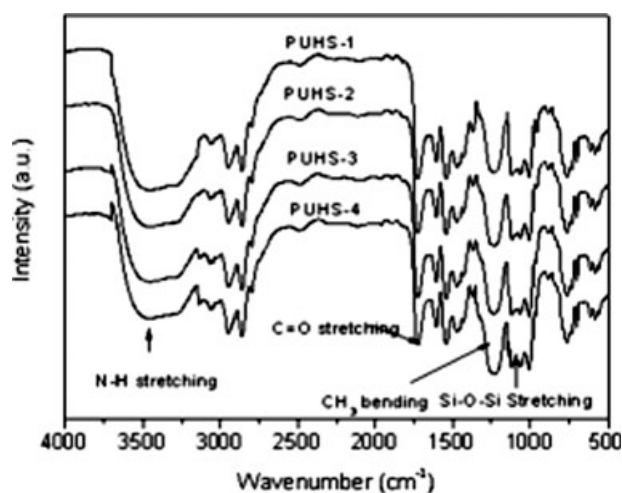
## RESULTS AND DISCUSSION

### Polymer structure analysis

The molecular structure of the PUHS was characterized by FTIR spectroscopy. The spectra of the PUHS synthesized with different proportions of the HPMS are shown in Figure 1. An absence of one NCO peak at  $2270\text{ cm}^{-1}$  indicates that isocyanate reaction was complete. The signals of the urethane linkages appear at  $3451$  and  $1725\text{ cm}^{-1}$  (C=O stretching). The peaks at  $1116$  and  $1004\text{ cm}^{-1}$  (Si—O—Si stretching) is associated to the HPMS, whereas the peaks at  $1231\text{ cm}^{-1}$  (symmetric  $\text{CH}_3$  bending),  $764\text{ cm}^{-1}$  ( $\text{CH}_3$  rocking), and  $2947\text{ cm}^{-1}$  are related to methyl group that is present in both soft segments but is especially present in the main chain of the HPMS soft segment. Thus the intensity of the peaks related to  $\text{CH}_3$  and Si—O—Si stretching vibration increases with the increase of the HPMS content.

### Effect of HPMS on particle morphology

Figure 2 indicate micrographs of PUHS-1, PUHS-2, PUHS-3, PUHS-4, and WPU emulsions. The white



**Figure 1** FTIR spectrum of polyurethane modified by hydroxyl-terminated polydimethylsiloxane.

domains are PUHS. It is found that the emulsions' particle size decreases with increasing HPMS content. It is also found that the particles are more easily affixed to each other when the HPMS content is more than  $15\%$ . The main reason is that the PUHS chain length becomes short and tends to curl up with increasing HPMS content. However, due to the strong hydrophobicity of the PUHS chain, the emulsions' stability is affected to a certain extent. Therefore, the change of particle size is the result of cooperative effect.

### Effect of HPMS on rheological behavior

According to Ostwald–Dewael power-law equation, the rheological behavior can be described as follows:<sup>29</sup>

$$\eta_a = k\dot{\gamma}^{n-1} \quad \text{or} \quad \sigma = k\dot{\gamma}^n \quad (1)$$

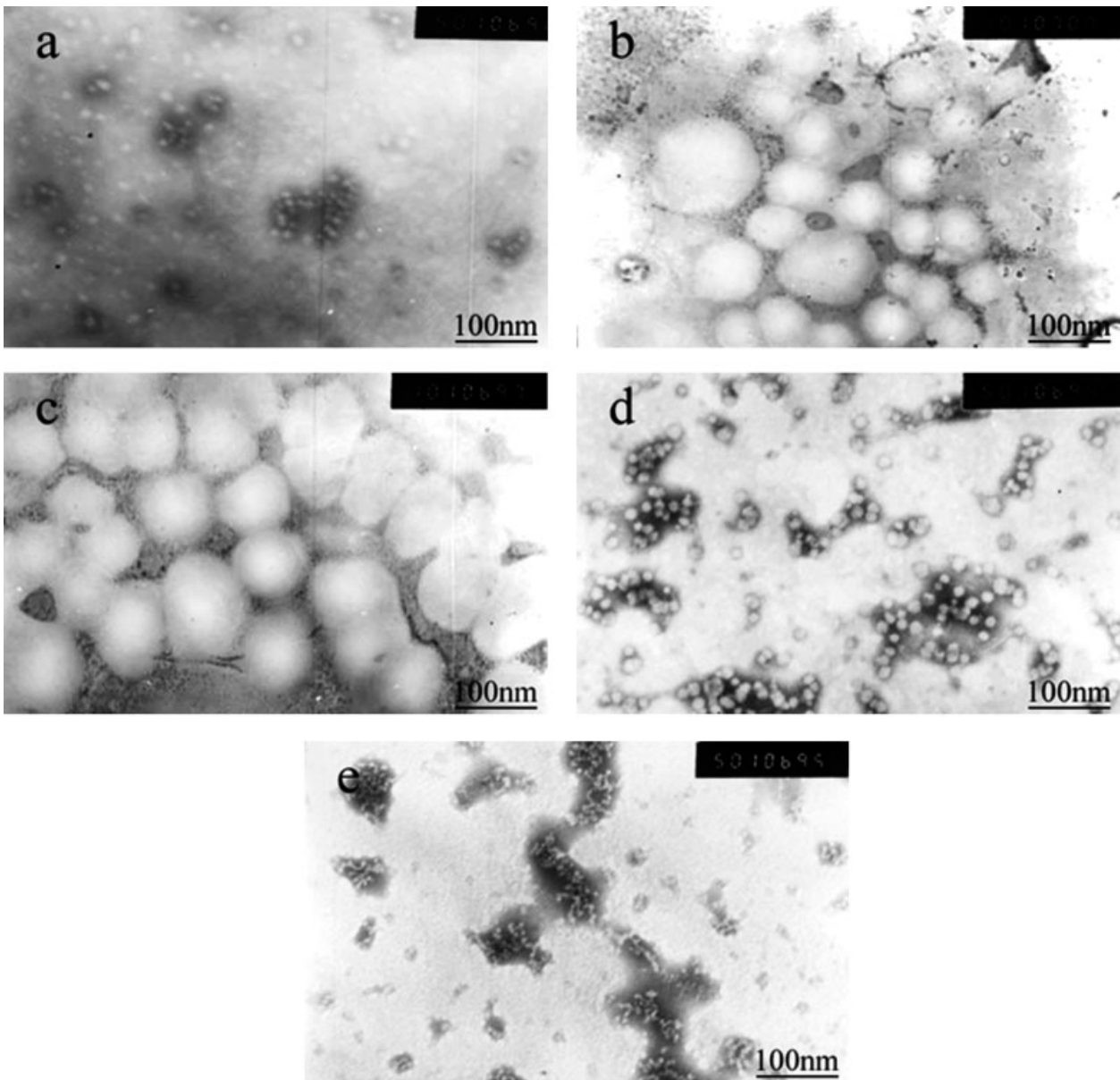
where  $\sigma$  is shear stress,  $\dot{\gamma}$  is shear rate,  $n$  is flow-behavior index (Newtonian fluid,  $n = 1$ ; non-Newtonian fluid,  $n < 1$ );  $k$  is consistency coefficient (the apparent viscosity increases with increasing  $k$ ),  $\eta_a$  is apparent viscosity.

Equation (2) can be obtained from eq. (1):

$$\log \sigma = \log k + \log \dot{\gamma} \quad (2)$$

Since there exists linear relationship between  $\log \sigma$  and  $\log \dot{\gamma}$ ,  $n$ , and  $k$  value can be calculated by linear regression approach.

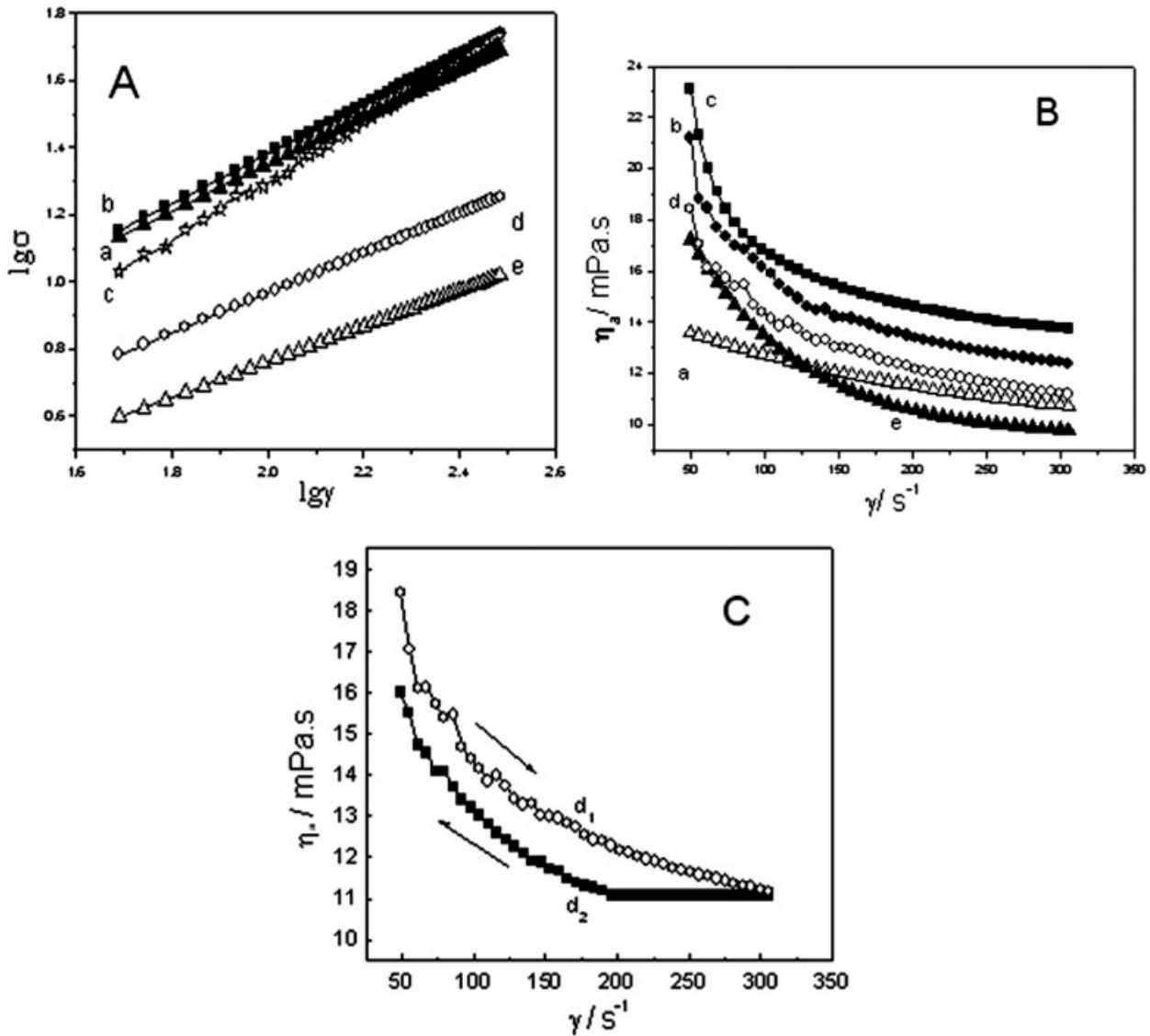
The application conditions of coatings are mainly determined by their rheological properties. Therefore, the rheology of PUHS coatings has been considered in this study. Figure 3 shows the flow curves of emulsions with different HPMS content and their flow-behavior index ( $n$ ) and consistency coefficient



**Figure 2** Effects of HPMS content on the particle size of the emulsions: The TEM micrographs of (a) WPU emulsion, (b) PUHS-1 emulsion, (c) PUHS-2 emulsion, (d) PUHS-3 emulsion, and (e) PUHS-4 emulsion.

( $k$ ) were calculated from Figure 3(A) (as shown in Table II). The  $n$  value of the WPU solution without HPMS approached to 1 and  $n$  value decreased greatly with increasing HPMS content. This indicates that pure PU almost exhibits a Newtonian behavior, i.e., there is little variation of viscosity by increasing the shear rate. Addition of HPMS produces an increase in the apparent viscosity of PUHS emulsions, which can be ascribed to the creation of hydrogen bonds between the silanol groups, the C=O groups in the urethane units. There is no simple relationship between viscosities of PUHS emulsions. The variation of the viscosities in PUHS adhesive solutions is the following:  $\eta_a(c) \geq \eta_a(b) \geq \eta_a(d) \geq$

$\eta_a(e) \geq \eta_a(a)$ . The highest viscosities correspond to the PUHS emulsions containing PUHS-1 and PUHS-2. The emulsions with higher HPMS content (PUHS-3 and PUHS-4) exhibit lower viscosity, for instance, the viscosity of PUHS-4 emulsion is basically close to pure PU emulsion. The main reason is that the difference in structure and polarity of organosiloxane and PU lead to the change of interaction force between the polymer's latex particles. On the one hand, due to solvation and hydrogen bond action of polar PU in water phase, the viscosity increases. On the other hand, the solvation of apolar organosiloxane is feeble, and Si—OR group content increases with increasing HPMS content, which



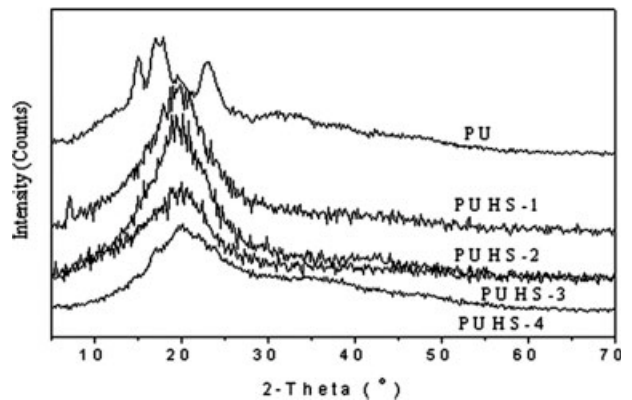
**Figure 3** Flow curves of emulsions with different dosage of HPMS. (A) The  $\lg\sigma \sim \lg\gamma$  relationship of PU, PUHS-1, PUHS-2, PUHS-3 and PUHS-4 emulsion; (B) Variation of viscosity with shear rate for PU, PUHS-1, PUHS-2, PUHS-3 and PUHS-4 emulsion; (C) The  $\eta_a$ - $\gamma$  relationship of PUHS-2 emulsion.

make particle's crustaceous hydrated layer thin. Therefore the interfacial acting force between latex particle and water declines, which manifest the decrease of the apparent viscosity.

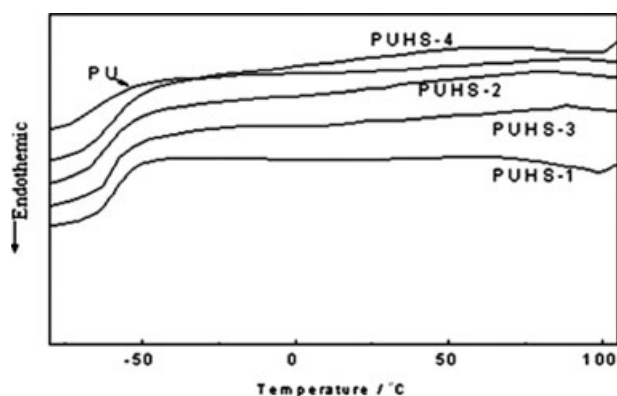
In addition, it is also found that  $\eta_a$  decreased acutely at the beginning and then become invariable with increasing shear rate [as shown in Fig. 3(B)], which manifest that PUHS emulsions are endowed

**TABLE II**  
*n, k* Values for PUHS Emulsions

Samples	Designation	<i>n</i>	<i>k</i>
PU	a	0.885	0.381
PUHS-1	b	0.737	0.811
PUHS-2	c	0.700	0.892
PUHS-3	d	0.590	0.612
PUHS-4	e	0.531	0.501



**Figure 4** X-ray diffraction spectra of the PUHS-1, PUHS-2, PUHS-3, PUHS-4, and PU films.



**Figure 5** DSC thermograms of the PUHS-1, PUHS-2, PUHS-3, PUHS-4, and PU films.

with pseudoplasticity. Mooney equation can explain this phenomenon, which was described as follows:<sup>30</sup>

$$\ln \eta_a = \ln \eta_e + k_e V_i / (1 - V_i / \phi) \quad (3)$$

where  $\eta_a$  is systematic apparent viscosity,  $V_i$  is particles' interior phase volume,  $\phi$  is stacking coefficient,  $k_e$  is shape factor,  $\eta_e$  is particle's outside viscosity. Deformation took part in particles with the action of shear stress,  $k_e$  decreased and  $\phi$  increased, which eventually lead to the decrease of  $\eta_a$ .  $\eta_a$  keeps invariable when the particles keep steady shape. Furthermore, there exist polar groups in polymer molecular chain; hydrogen bond and solvation are then created, which eventually form hydrated layer. The hydrated layers are destroyed when the shear rate increases, which make the particles' relative movement more easy and therefore  $\eta_a$  decrease; however, when shear rate increases to a certain degree, that is, the hydrated layers are totally destroyed,  $\eta_a$  would not decrease any longer.

Thixotropy is also imparted to PUHS emulsions [i.e., up curve of the flow curve is higher or lower than the low curve, respectively, as shown in Fig. 3(C)]. A thixotropic system is characterized by the presence of a positive hysteresis loop between the up and down branches of the flow curves. The area of this loop, called thixotropic area (TA), allows an indirect quantification of the thixotropy or rheopexy in the PUHS emulsions. A positive TA means the ex-

istence of thixotropy, whereas a negative TA value means the existence of rheopexy (i.e., the viscosities in the down branch of the flow curve are higher than in the up one).

#### Effect of HPMS on structure and miscibility

The WAXD patterns of the PUHS-1, PUHS-2, PUHS-3, PUHS-4, and PU films are displayed in Figure 4. The degrees of crystallinity ( $x_c$ ) of the PUHS-1, PUHS-2, PUHS-3, PUHS-4, and PU were 0.081, 0.018, 0.002, 0.0016, and 0.44, respectively. The  $x_c$  decreased with increasing HPMS content, and the PUHS films were almost amorphous. The results indicate that PU's crystalline structure was changed after modified with HPMS. Four diffraction peaks of PU at  $2\theta = 14.8^\circ$ ,  $17.3^\circ$ ,  $17.73^\circ$ , and  $19.4^\circ$  are due to the orderly arrangement of soft segments, and a peak at  $22.9^\circ$  is from hard segments. It is worth noting that the peak at  $22.9^\circ$  in the PUHS films disappeared, which indicates that the HPMS and WPU are miscible, and the recorded decrease in  $x_c$  also implies that the compound films own excellent miscibility on a molecular scale.

#### Effects of HPMS on glass transition behavior

Figure 5 displays some representative DSC thermograms of the PUHS-1, PUHS-2, PUHS-3, PUHS-4, and PU films. Their glass transition temperature ( $T_g$ ), melting points, and melting enthalpies are shown in Table III. Briefly, the typical glass transition temperature ( $T_g$ ) around  $-60^\circ\text{C}$  and broad peaks with a maximum around  $80^\circ\text{C}$  were found. The broad peak can be considered as merged endotherms, which are due to the disruption of short and long range order of hard segments, respectively, as proposed by Seymour and Cooper.<sup>31</sup>  $T_g$  range from  $-57.3$  to  $-67.5^\circ\text{C}$  is substantially higher than that of pure soft-segment (The  $T_g$  of PTMG is about  $-82^\circ\text{C}$ ). This indicates a certain degree of hard and soft segment mixing. These results support the conclusion from the WAXDs. It is worth noting that PUHS-4 exhibited lower  $T_g$ , which indicates an improved microphase separation when HPMS content increased to 25%.

**TABLE III**  
Experimental Results of DSC for the Films

Material	Glass-transition temperature ( $^\circ\text{C}$ )	Melted crystallinity peak ( $^\circ\text{C}$ )			Melting enthalpy (J/g)
		Onset point	Midpoint	Endpoint	
PU	-67.5	28.3	91.9	103.2	10.69
PUHS-1	-58.4	19.5	65.6	94.6	2.473
PUHS-2	-61.6	37.7	80.8	99.6	2.332
PUHS-3	-57.3	57.9	89.8	102.1	1.213
PUHS-4	-59.2	34.0	57.3	79.4	3.209

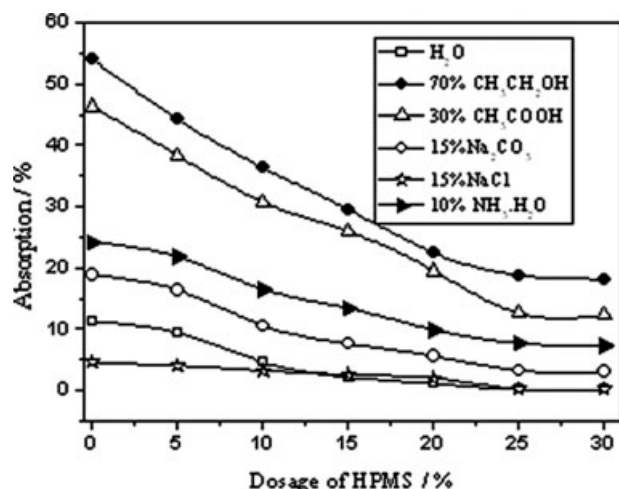


Figure 6 Variation of water and medium absorption with dosage of HPMS.

#### Effects of HPMS water resistance and medium resistance

Figure 6 shows variation of water and medium absorption with dosage of HPMS. As HPMS content increased from 0.0 to 25.0 wt %, water absorption decreases from 11.2 to 0.14% and medium absorption also decreases. The results demonstrate that the membrane surfaces have significant water and medium repellency. On the one hand, water can not immerse into the membranes due to strong hydrophobic Si—O—Si bonds. On the other hand, the organic groups grafted in HPMS are arrayed on the outermost membrane surface, and there does not exist any polar groups in HPMS. Furthermore, the mutual compensation of  $d\pi\pi$  bonds between Si—O and Si—O dipoles make polysiloxane form spiral structure (as shown in Fig. 7), which make interaction force between Si—O chain feeble as well as sur-

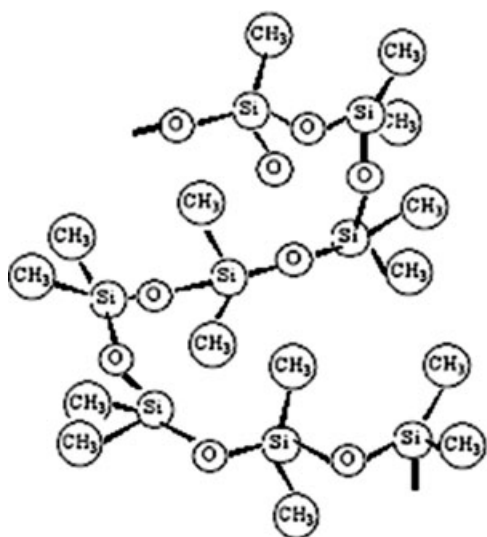


Figure 7 The spiral structure of organosiloxane.

face tension. Therefore, it is advisable to make PU modified with HPMS.

#### CONCLUSIONS

A series of hybrid dispersions of WPU modified with HPMS (PUHS) were prepared, and accordingly the films were cast. The emulsions' particle size decreases with increasing HPMS content and the particles are more easily affixed to each other when the HPMS content is more than 15%, and the emulsions are endowed with pseudoplasticity and thixotropy. WAXD and DSC figures manifested that the casting films all exhibited a certain degree of miscibility. The degrees of crystallinity ( $x_c$ ) decreased with increasing HPMS content, and the PUHS films were almost amorphous. It is noticed that water and medium absorption decreased in the PUHS compared to pure PU, which demonstrate that the membrane surfaces have excellent water and chemical medium repellency.

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