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ORIGINAL PAPER

Characterization of polydimethylsiloxane–polyurethanes synthesized by graft or block copolymerizations

Jianping Zong · Qingsi Zhang · Haifeng Sun ·
Yitao Yu · Shijie Wang · Yunhui Liu

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Abstract We synthesized polydimethylsiloxane–polyurethane dispersions modified with graft copolymerization (PDMS-*G*-PUDs) and polydimethylsiloxane–polyurethane dispersions modified with block copolymerization (PDMS-*B*-PUDs). We systematically investigated the effects of PDMS's structure, content, and molecular weight on properties of copolymer including viscosity, particle size, and stability of dispersions as well as the properties of the film formed by dispersions including gloss, contact angle, water resistance, oil resistance, and mechanical properties. The results demonstrated that the viscosity, particle size, water resistance increased but gloss decreased with the increase of PDMS content and molecular weight. In addition, we compared the properties of PDMS-*B*-PUD films and PDMS-*G*-PUD films with the same amount of PDMS and similar molecular weight. PDMS-*G*-PUD films showed higher water and oil resistance, but lower gloss and poorer mechanical properties. Scanning electron microscopy–energy dispersive spectroscopy analysis (SEM–EDS) indicated that the films of PDMS-*G*-PUD had better microphase separation and PDMS surface enrichment.

Keywords Polydimethylsiloxanes · Polyurethane dispersion · Graft · Block

Introduction

Polyurethane (PU) materials have been widely used as textile coatings, leather finishing agents, and adhesives, etc. because of their excellent properties such as

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J. Zong · Q. Zhang (✉) · H. Sun · S. Wang · Y. Liu
School of Chemical Engineering, Shandong Institute of Light Industry, Jinan 250353, China
e-mail: zqs@sdili.edu.cn

Y. Yu
Department of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou 310027, China

high mechanical resistance, abrasion resistance, and chemical resistance [1, 2]. However, until the late 1970s, almost all of the PU materials are solvent-based, which lead to serious environmental problems. With the development of strict environment protection regulations and the restrictions of volatile organic compounds, water-borne polyurethane (WPU) became one of the most rapidly developing and active branches of PU chemistry and technology because they cause very limited damage to the environment [3]. However, it is well known that conventional WPU, due to introducing hydrophilic groups to the molecular chains, exhibit poor water resistance which seriously limits their applications.

Various methods have been attempted to overcome the limitation over the years. One of the accepted approaches is to modify the molecular structure by introducing low surface energy polymers into WPU. Recently, much attention has been drawn to chemical modification with organic fluorine compounds [4, 5] and polysiloxane [6, 7]. Polydimethylsiloxane (PDMS), as one of major classes of polysiloxane, has a number of unique and superior properties such as high water resistance, heat resistance, high UV stability, low surface free energy as well as biocompatibility [7–10]. However, the low mechanical property and abrasion resistance property of PDMS limit its applications in many fields. Therefore, it is very important to develop copolymers with both the high water and heat resistance of PDMS and the good mechanical property and abrasion resistance of PU.

Recently, many articles on PU focused on the synthesis and application of polysiloxane-modified polyurethanes. Gomes et al. [11] synthesized poly(ether siloxane urethane urea) which could be used for n-C_4H_{10}/CH_4 separation with different polysiloxane contents and studied the correlation between polysiloxane soft segment and the permeation properties. They found that the permeability of the copolymer increased with the increase of polysiloxane content. Stanciu et al. [12] showed either incorporating difunctional PDMS sequence into PU chains or using hard segment with a high crystallizability could increase the thermal stability of PU elastomers. However, it is found that the siloxane-modified PU usually exhibits a high degree of phase separation [13]. In the work of Park et al. [14], a polyurethane based on poly(dimethyl siloxane) as a soft segment was synthesized. The degree of phase separation of this polyurethane increased with the content of hard segments. Li et al. [15] synthesized siloxane-modified polyurethane with different chemical structure of siloxanes, and showed that the microphase separation was the main cause for the improved mechanical properties. However, most of the copolymers were synthesized via block copolymerization. To the best of our knowledge, there is no report in the literature on PDMS-modified polyurethane by graft copolymerization in which PDMS was tailor-made.

In this work, we prepared a series of polydimethylsiloxane–polyurethane dispersions modified with graft and block copolymerization with different PDMS contents and molecular weights by the acetone method in which two types of PDMS were used. One is α-butyl-omega-{3-[2-hydroxy-3-(*N*-methyl-*N*-hydroxy-ethyl-amino)propoxy]propyl}polydimethyl-siloxane with a diol group at only one chain end and the other is bis(methyoxyl hydroxyl)- functionalized polysiloxane with a hydroxyl group at both ends of the chain. In the experiment, toluene 2,4-diisocyanate (TDI) was used as hard segment, polyol (PPG or PDMS) as the soft segment, dimethylol propionic acid (DMPA) as the anionic center and diethylenetriamine as the chain extender. The structures and properties of PDMS-modified polyurethane dispersions (PDMS–PUDs) were characterized by Fourier transform infrared spectroscopy (FT-IR), viscometer, laser particle sizer, transmission electron microscopy (TEM). The films formed by PDMS–PUDs were investigated by gloss measurement, contact angle measurement, water and oil resistance analysis, tensile measurement and scanning electron microscopy–energy dispersive spectroscopy analysis (SEM–EDS). The effects of PDMS chain structure, molecular weight and concentration on the properties and morphologies of PDMS–PUDs and films were studied. Furthermore, the properties of polydimethylsiloxane–polyurethane dispersions modified with graft copolymerization (PDMS-*G*-PUDs) and polydimethylsiloxane–polyurethane dispersions modified with block copolymerization (PDMS-*B*-PUDs) were also compared.

Experimental

Materials

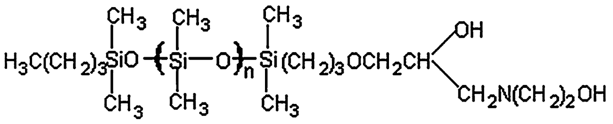
The following chemicals were used without further treatment: tetramethyldisiloxane (from Institute of Chemical Engineering of Wuhan), octamethyltetracyclosiloxane (D_4), hexamethylcyclotrioxysilane (D_3, Xinghuo Incorporation) and chloroplatinic acid, toluene 2,4-diisocyanate (TDI, Tianjin Fuchen Chemicals), dimethylol propionic acid (DMPA, Dow Chemical Company), diethylenetriamine (DEA, Tianjin Damao Chemicals) and trifluoromethanesulfonic acid. Polypropylene glycol with molecular weight 1000 (PPG-1000) and 2000 (PPG-2000), *N*-methylmonoethanolamine, ethylene glycol (EG), and ally glycidyl ether (all industrial grade) were vacuum-distilled before use. *N*,*N*-dimethylformamide (DMF), triethylamine (TEA), toluene, and acetone were immersed in 4-Å molecular sieves for more than 1 week before use.

Synthesis of PDMS

We made α-butyl-omega-{3-[2-hydroxy-3-(*N*-methyl-*N*-hydroxy-ethylamino)propoxy]propyl}polydimethyl- siloxane (PDMSa) and bis(methyoxyl hydroxyl)-functionalized polysiloxane (PDMSb). PDMS with different molecular weight were obtained by adding different amount of raw materials. The detail information regarding the synthetic procedure and characterization of the both polymers was published previously [16, 17]. The molecular weights and structures of PDMS were shown in Fig. 1.

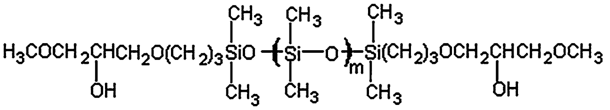
Synthesis of PDMS–PUDs

A 250 mL round-bottom, three-necked flask with a half-moon shaped glass stirrer and a thermometer were used. Reaction temperature was controlled by a thermostat propylene glycol bath.



$H_3C(CH_2)_3Si(CH_3)_2O\text{-}[Si(CH_3)_2\text{—}O]_n\text{-}Si(CH_3)_2(CH_2)_3OCH_2CH(OH)CH_2N(CH_2)_2OH$

PDMS	Molecular weight
a-1	1030
a-2	1492
a-3	2112



$H_3COCH_2CH(OH)CH_2O(CH_2)_3Si(CH_3)_2O\text{-}[Si(CH_3)_2\text{—}O]_m\text{-}Si(CH_3)_2(CH_2)_3OCH_2CH(OH)CH_2OCH_3$

PDMS	Molecular weight
b-1	1188
b-2	1460
b-3	2087

Fig. 1 Structures and molecular weights of various PDMS

Synthesis of PDMS-*G*-PUDs

17.42 g of TDI was added into the flask and heated until molten at about 50 °C. While stirring, proper amount of PPG-1000 and PPG-2000 was added dropwise and stirred for an additional 30 min at 70 °C. After that, PDMSa, DMPA dissolved in DMF and EG were added to the flask at the same temperature and the mixture was continuously being stirred. 2 h later, the NCO content of the prepolymer was determined by the standard dibutylamine back-titration method. The reaction was allowed to proceed until the content of NCO reached the theoretical value (about 2.0%), and subsequently, NCO-terminated prepolymer was obtained. And then acetone was added to reduce the viscosity of the prepolymer and stirring continued until a homogeneous mixture was obtained at ambient temperature. Afterwards, TEA was added to neutralize the carboxylic group in the side chain of prepolymer. After being stirred for 20 min, prepolymer was added into the deionized water and the solution was emulsified by high-speed stirring. At the same time, EDA was added into the solution to extend the chains of copolymer. After removal of acetone from the emulsion by rotary vacuum evaporation, PDMS-*G*-PUDs were prepared.

Synthesis of PDMS-*B*-PUDs

The polydimethylsiloxanes–polyurethane dispersions modified with block copolymerization were synthesized with a similar method of synthesizing the graft copolymers except for feed order of the chemicals. TDI and PDMSb were first introduced into the flask and allowed to react for 30 min at 70 °C. Then, PPG-1000, PPG-2000, DMPA solution (in DMF), EG, and acetone were added to the reactor. The NCO-terminated prepolymer was obtained, followed by neutralization with

Table 1 Basic recipe for the synthesis of PDMS–PUDs

Components	Amounts (g)
TDI	17.42
PPG	Variable[a]
PDMS	Variable[b]
DMPA	3.18
DMF	10
EG	2.10
TEA	2.40
EDA	Variable[c]

[a] Ratio of PPG-1000 and PPG-2000 is 1:2

[b] Ratio of NCO/OH = 1.28

[c] Degree of chain extension (actual): 85%

TEA, aqueous dispersion, and chain extension of the prepolymer. The aqueous PDMS-*B*-PUDs were obtained when acetone was removed.

The recipe for the preparation of PUDs is listed in Table 1. All PDMS–PUDs were synthesized by similar procedures as described.

The PDMS–PUD films were prepared by pouring dispersions on a Teflon plate, followed by drying at room temperature for 1 week. Then the films were removed and placed in a vacuum oven at 60 °C for 24 h. The thickness of membrane was 0.5 mm.

Characterization

The infrared spectra of samples were recorded on a NUXUS 470 Fourier transform infrared (FT-IR) spectrometer (Nicolet, USA). The bulk viscosity of PDMS–PUDs was measured at 25 °C by a Brookfield DV-E viscometer with No. 2 spindle at a shear rate of 100 s^{-1}. Particle size and size distribution of diluted dispersions were detected by Malvern Nano ZS light scattering instrument at 25 °C. The morphologies of the dispersions were observed using transmission electron microscopy (TEM; JEOL JEM 200CX).

The gloss values of films were measured by minityped vancometer (WGG-60) at 25 °C and the results reported were the mean value of five experiments. The contact angles were investigated using Krűss-K_{12} procedure interfacial tensiometer (Germany) by the Wilhelmy plate method. Both advancing and retarding contact angles of the films were detected with deionized water at 25 °C. Five points of different regions of each film were tested and the mean values were reported.

The water resistance and oil resistance properties of the cured films were characterized by the solvent absorptions in water and toluene. The weighted dried films with square shape (20 mm × 20 mm) were immersed in deionized water or toluene at 25 °C for 24 h. The weight of swollen film was measured by wiping off the surface water or toluene with filter paper. The solvent absorption of the film was calculated by the following equation [18]:

$$\text{Solvent absorption (wt\%)} = [(W_t - W_0)/W_0] \times 100 \tag{1}$$

where W_0 and W_t were the film weights before and after being immersed in water or toluene, respectively.

Mechanical properties of PDMS–PUD films were tested on a DWD-10A universal tensile test machine according to the GB/T 528-1992 method, in which tensile strength (MPa) and elongation (%) were evaluated.

Microstructure and element compositions of PDMS–PUD films were examined by nitrogen environmental scanning electron microscope (SEM, quanta 200, FEI co-hooland). The films were immersed in liquid nitrogen and then fractured. The fractured surface of the sample was coated with gold and morphology was imaged by SEM. X-ray energy dispersive spectroscopy was used to analyze the element compositions of the surface and bulk of PU film. Data was collected from a scanned sputtering gold region of about 100 mm^2. The surface enrichment ratio of Si element, f, is defined as

$$f(\%) = \frac{n_1 - n_2}{n_2} \times 100 \tag{2}$$

where n_1 and n_2 represent the atom Si concentration in the surface and bulk of film, respectively.

Results and discussions

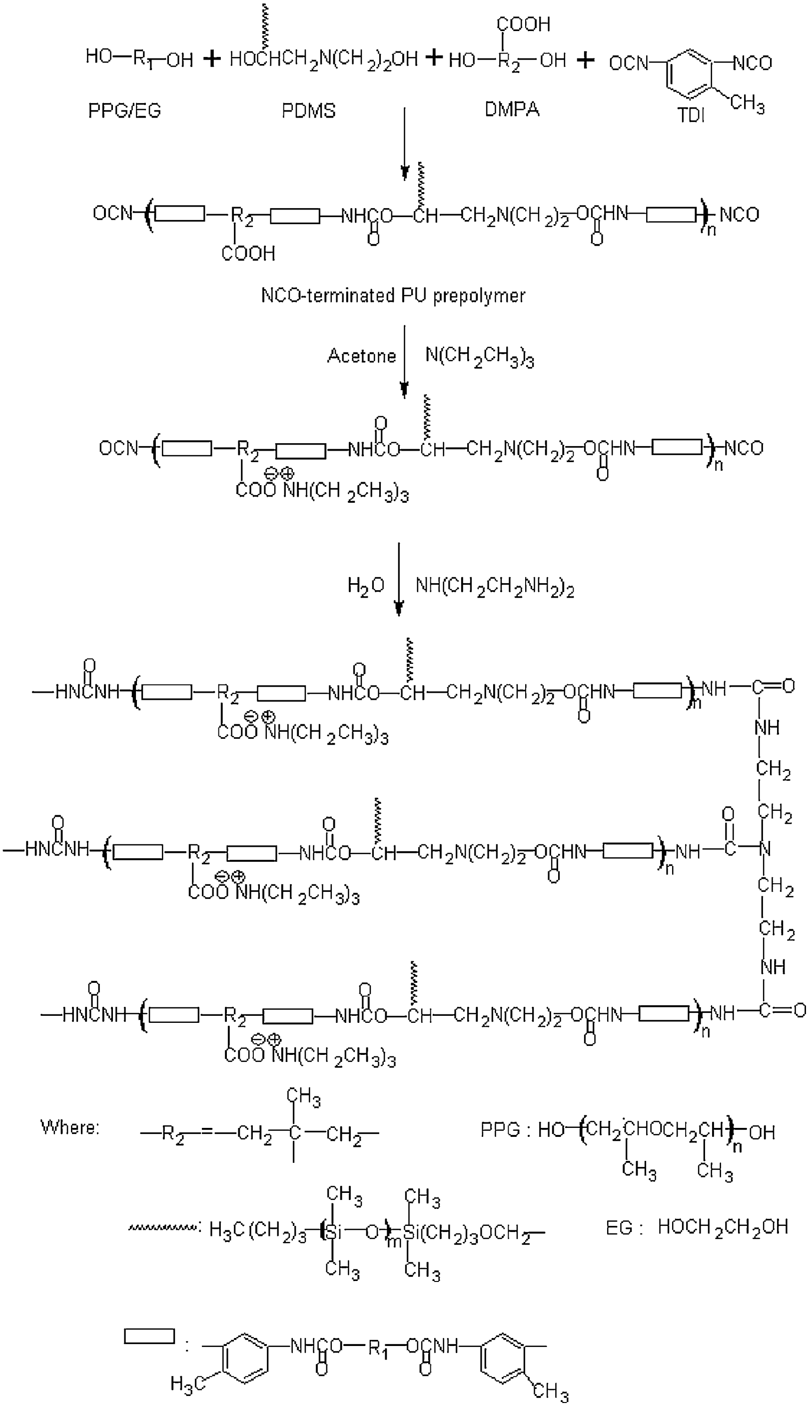
Synthesis and stability of PDMS–PUDs

In this study, PDMS with different chemical structures and molecular weights were formulated with PPG, DMPA, EG, and TDI and reacted to generate isocyanate-terminated prepolymers, followed by the processes of neutralization and dispersion to product PDMS–PUDs, as shown in Schemes 1 and 2. It is known that the physical properties of PU films depend on the molecular structure of materials used and the molar ratio of NCO/OH [17, 18]. The molar ratio of NCO/OH is 1.28 in all the copolymers in the experiment.

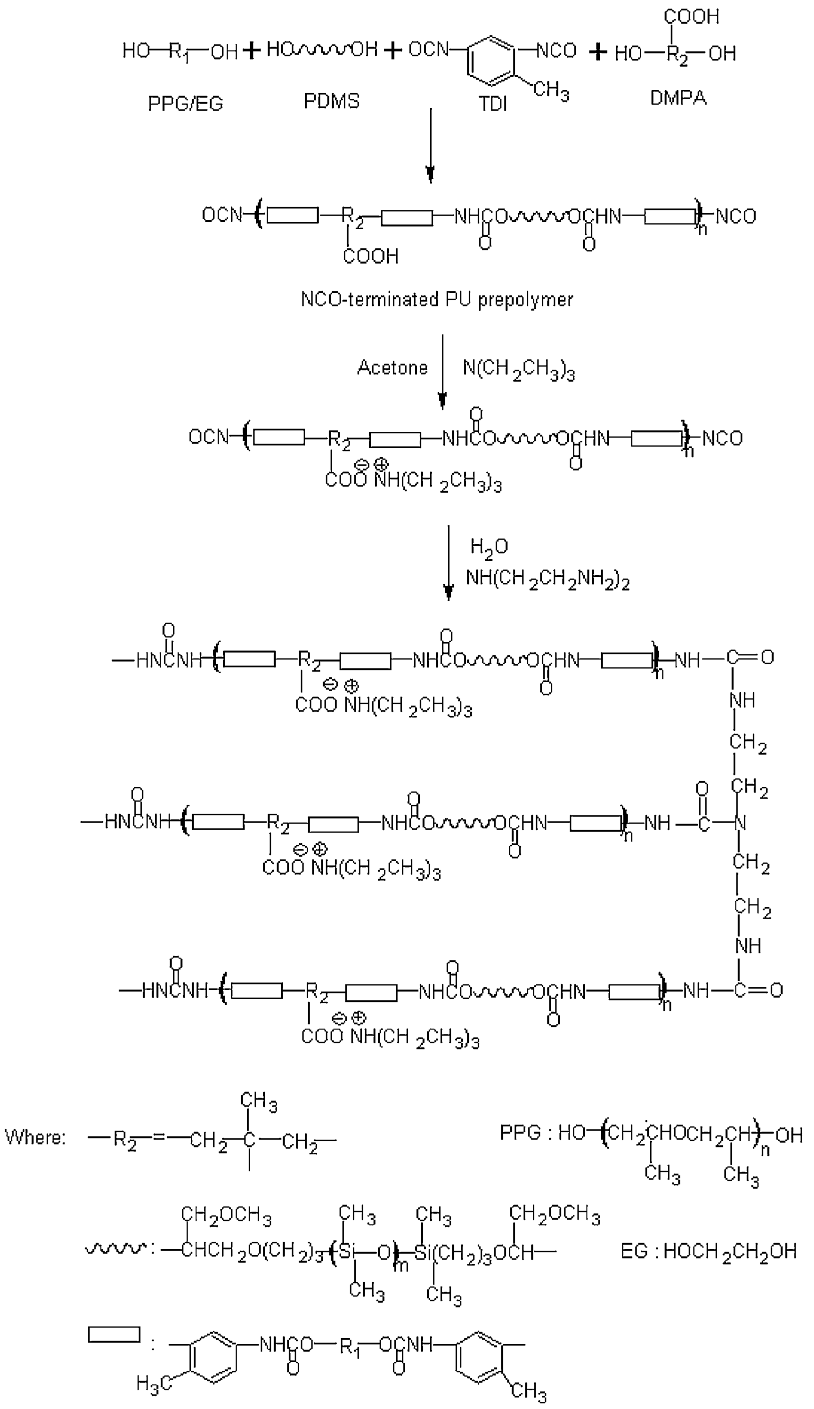
No difficulty was encountered in preparing PDMS-modified prepolymers from the reaction of PDMS with the other materials although the reaction time of obtaining PDMS-*G*-PUDs was prolonged. The data in Table 2 showed that both kinds of polyurethane dispersions were successfully prepared. All the products appeared to be transparent or translucent without any sedimentation when they were placed at room temperature for more than 12 months.

Structure analysis

The chain structures of PDMS-*G*-PUD and PDMS-*B*-PUD were confirmed by FT-IR analysis. As an example, the FT-IR spectra of A4 and B4 are shown in Fig. 2**.** There was no obvious difference in the spectra between A4 and B4. The absorption peaks of typical polyurethane at 3300 cm^{-1} [ν (NH)], 2870–2970 cm^{-1} [ν (CH_2)



Scheme 1 Synthesis of PDMS-*G*-PUD



Scheme 2 Synthesis of PDMS-*B*-PUD

Table 2 Properties of PDMS–PUDs

Sample code	Type of copolymer	PDMS	PDMS content ratio (wt%)	Brookfield viscosity (cps)	Storage stability (months)	Diameter (nm)	PDI
A0	PDMS-*G*-PUD	a-1	7	43.2	>12	159.1	0.471
A1			9	61.5	>12	197.4	0.442
A2	PDMS-*G*-PUD	a-2	3	47.4	>12	56.5	0.178
A3			5	58.2	>12	149.9	0.407
A4			9	64.1	>12	388.2	0.431
A5	PDMS-*G*-PUD	a-3	5	51.2	>12	210.3	0.455
A6			7	56.8	>12	281.5	0.270
A7			9	66.0	>12	361.2	0.479
A8			11	70.1	>12	405.7	0.285
B1	PDMS-*B*-PUD	b-1	5	67.3	>12	98.81	0.461
B2			7	73.2	>12	103.3	0.242
B3			9	82.5	>12	109.2	0.257
B4	PDMS-*B*-PUD	b-2	9	84.4	>12	164.7	0.279
B5	PDMS-*B*-PUD	b-3	5	82.4	>12	88.2	0.343
B6			7	86.0	>12	116.0	0.283
B7			9	88.4	>12	122.6	0.324

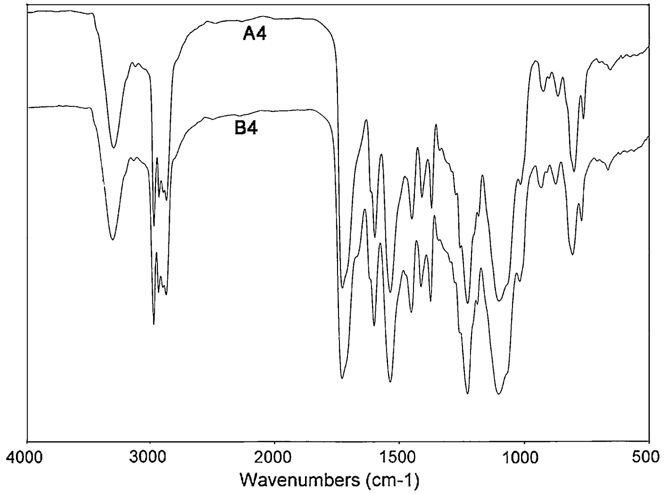


Fig. 2 FT-IR spectrum of A4 and B4

and v (CH_3)], 1729 cm^{-1} [v (C=O)], 1536 cm^{-1} [δ (NH)], and 1103 cm^{-1} [v (C–O–C)] can be seen clearly in the spectra. Furthermore, the peaks at 1017 cm^{-1} [v (Si–O)] and 805 cm^{-1} (Si–CH_3 rocking)] indicated that siloxane groups had been successfully introduced into the polyurethane chain.

Viscosity analysis

The viscosity values of samples with different content of PDMS were listed in Table 2**.** The data demonstrated that the viscosity of PDMS–PUDs was affected by the content and structure of PDMS. The results showed that the viscosity increased with the increase of PDMS presence and molecular weight. Compared with PDMS-*G*-PUD, the PDMS-*B*-PUD exhibited a higher viscosity when the same amount of PDMS with similar molecular weight was added. The reason is that the PDMS-*B*-PUDs, with PDMSb chains in backbones of PU, have longer backbones than PDMS-*G*-PUDs, which have PDMSa located in PDMS-*G*-PUDs as side chains. It also indicated that the chain branching did not show a significant effect on the bulk viscosity of PDMS-*G*-PUDs since all of PDMS chains were not as long as PU main chains in the present work.

The particle sizes and morphologies of PDMS–PUDs

The data of particle size and dispersity index (PDI) of PDMS–PUDs were illustrated in Table 2. Particle size and the distribution of samples A7 and B7 were also shown in Fig. 3**.** From these results we conclude that the particles of PUDs increase with

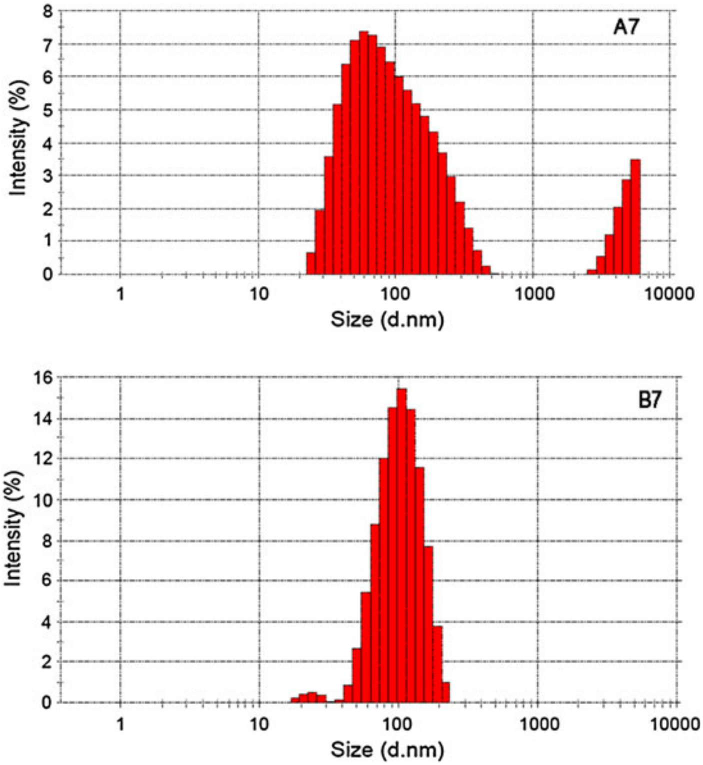


Fig. 3 Particle distribution of A7 and B7

the increase of PDMS content and molecular weight. The size distribution of PDMS–PUDs was not monodisperse and bimodal particle size distributions were obtained, as shown in Fig. 3**.** There are some small particles at about 20 nm in diameter in B7 dispersions and some big particles at about 5000 nm in diameter in A7 dispersions.

Comparing PUDs modified by PDMSa and PDMSb with similar molecular weight, we found that the particles of PDMS-*G*-PUDs are bigger. It is because of the free volume in the particle and nature of chain packing. As the dispersions are water-based, the outer layers of copolymers contain more hydrophilic –$COO^{-}HN^{+}(C_2H_5)_3$ ions while the inner layers contain more hydrophobic PDMS [19, 20]. With PDMSa as the side chain, the PDMS-*G*-PUD had a dendritic chain structure which results in a higher free volume and lower chain packing density and thus larger particles.

TEM photographs of PDMS–PUD particles were shown in Fig. 4 at 5.8 × 10^5 magnifications. With the molecular weight and content of PDMS increasing,

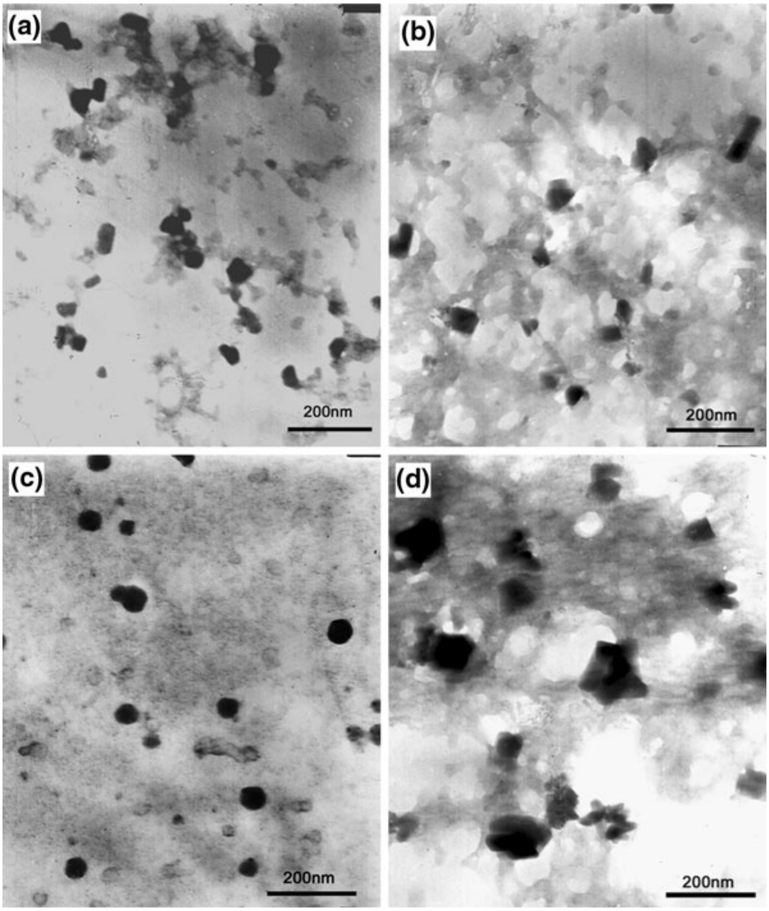


Fig. 4 TEM images of A1 (**a**), A7 (**b**), B3 (**c**), B7 (**d**)

the shape of particle became more irregular. It is believed that incorporated polysiloxane influenced carboxyl distribution in the particles, and thus particle morphology.

Gloss analysis of PDMS–PUD films

The gloss values of films decreased with the increase of PDMS content, as shown in Table 3. It is found that the degree of surface gloss depends on roughness, and the surface gloss decreases with increasing surface roughness. The surface heterogeneity in PDMS–PUD membranes caused by microphase separation between nonpolar PDMS and polar urethane groups can lead to surface roughness. The more serious is the phase separation, the lower is the gloss. The degree of phase separation would become higher when more PDMS were added, resulting in lower gloss of film surface. The lower gloss of PDMS-*G*-PUD film suggested that the grafting samples had higher degree of microphase separation in comparison with PDMS-*B*-PUD. We speculate that PDMSa migrated to the film surface more easily during film casting.

Contact angle analysis of PDMS–PUD films

To describe surface wettability of the PDMS–PUD films, the advancing contact angle (θ_A) and retarding contact angle (θ_R) were measured. We found that the molecular weight and content of PDMS had a significant effect on contact angle, as

Table 3 Properties of the PDMS–PUD films

Sample code	Gloss	Advancing contact angle (°)	Retarding contact angle (°)	Water absorption (%)	Toluene absorption (%)	Tensile strength (MPa)	Elongation (%)
A0	40.2	93.3	41.6	83.10	87.12	9.06	282.0
A1	38.1	95.7	43.3	44.59	79.12	9.40	201.5
A2	74.3	91.5	39.7	29.83	168.15	12.28	341.1
A3	54.2	94.3	41.2	22.62	99.23	12.48	279.41
A4	48.7	96.8	44.1	16.41	87.35	8.02	252.7
A5	50.3	95.6	43.2	23.93	111.18	16.24	357.55
A6	46.8	96.6	43.7	19.25	107.16	8.11	340.40
A7	35.7	98.7	48.6	17.34	97.13	7.96	259.20
A8	29.7	97.5	47.4	18.28	96.35	6.28	251.10
B1	72.7	91.3	51.3	138.72	138.10	19.52	330.6
B2	60.7	92.6	52.3	106.61	131.12	18.92	331.4
B3	52.3	94.8	52.8	103.27	128.42	15.23	335.2
B4	53.9	91.5	55.6	81.68	96.25	14.89	416.2
B5	55.6	91.3	51.3	87.48	127.04	18.02	421.6
B6	43.9	93.6	53.4	77.48	120.31	15.96	434.2
B7	37.3	93.2	54	68.60	115.23	13.93	450.3

the data in Table 3 demonstrated. Both θ_A and θ_R of PDMS–PUD films increased with the increase of PDMS molecular weight. Generally, the surface water–air contact angle measurement is more surface-sensitive, probably responding to the outmost monolayer of surface [10, 21]. The increase in contact angle demonstrated that the surface of film had more hydrophobic PDMS chains since PDMS was the only hydrophobic segment in copolymers and it could migrate to the surface owing to its surface activity. The larger the molecular weight of PDMS, the more Si–O–Si chains in the surface of films, leading to a larger contact angle.

In our study of the polyurethane films modified by PDMSa-2, PDMSa-3 and PDMSb-3, we noticed that the advancing contact angles reached maximum when the concentration of PDMS was 9% in PDMS-*G*-PUD films and 7% in PDMS-*B*-PUD films. This result is likely due to the lower PDMS distribution density on the surface in less concentration and reduced surface roughness in higher concentration. Therefore, maximal contact angle can be obtained with proper PDMS concentration.

The data presented in Table 3 also indicated that PDMS-*G*-PUD films were more hydrophobic than those of PDMS-*B*-PUD with the same amount of PDMS and similar molecular weight. For example, θ_A of A7 was 98.7°; in contact, the value of B7 was 93.2°. The reason is that the siloxane chains in PDMS-*G*-PUD were free out of the film while the siloxane chains of PDMS-*B*-PUD were bounded by chemical bound at each terminal which restricted the surface segregation of siloxane chains to some extent.

The θ_A values of all the PDMS-*G*-PUD films were larger than that of PDMS-*B*-PUD films while the θ_R values were smaller, as shown in Table 3. This indicated that the PDMS-*G*-PUD film had a higher contact angle hysteresis (θ_A–θ_R). Our explanation of this result is that the surface of PDMS-*G*-PUD film is rough. The contact angle hysteresis is caused by surface roughness of the film [22–24]. The rougher the surface of the sample, the higher the contact angle hysteresis is.

The water resistance and oil resistance properties of PDMS–PUD films

The water absorption data in Table 3 demonstrated that the PDMS concentration played an important role in water resistance: the water absorption of most of samples decreased with more PDMS added. Lin et al. [25] had reported the similar trend. Compared with PDMS-*B*-PUD films, the values of water absorption of PDMS-*G*-PUD films were lower. In addition, the water absorption of sample A7, the advancing contact angle of which was the biggest of all, reached the minimum value (17.34%). It is suggested that the PDMSa can improve the water resistance property more efficiently. The results are consistent with results from the contact angle analysis.

The values of toluene absorption were much higher in comparison with water absorption. In opposition to the water resistance property, the toluene absorption of PDMS-*G*-PUD films increased with increasing molecular weight of PDMS. The oil resistance of both types of PDMS–PUD films became better when more PDMS were added. It is suggested that PDMS can also improve the oil resistance of polyurethane.

Taking a comparative study on PDMS-*B*-PUD films and PDMS-*G*-PUD films, we found that PDMS-*G*-PUD films showed better water resistance and oil resistance, as the data in Table 3 indicated. As discussed above, PDMSa chain was bounded to PU chain by one chain end and could migrate to the surface easily, thus it became a barrier to prevent the water and toluene molecular from getting into the bulk. In contract, PDMSb chain was bounded by both terminals. When it migrated, the other parts of PU chain restricted its movement to some extent, resulting in relatively lower water and oil resistance.

Mechanical properties of PDMS–PUD films

The type of PDMS used in the experiment played a key role in the mechanical properties of polyurethane films. Both of the tensile strength and elongation of PDMS-*B*-PUD films were higher than that of PDMS-*G*-PUD, as shown in Table 3.

Tensile strength of PDMS-*G*-PUD film was lower than that of PDMS-*B*-PUD which can be attributed to the relatively high degree of the microphase separation. It is known that the microphase separation affects the mechanical properties of PU, and only appropriate microphase separation is beneficial to higher mechanical properties. The tensile strength would be poor when the microphase separation is substantial. In this study, PDMS-*G*-PUD films had higher degree of microphase separation than polyurethane films modified with block copolymerization, which is seen in the SEM photographs. In addition, the amounts of hydrogen bond in copolymers also affect the mechanical properties. Steric hindrance of PDMSa reduced the amount of hydrogen bonds, which further reduced the mechanical properties of PDMS-*G*-PUD films.

The tensile strength of PDMS-*B*-PUD films decreased, but the elongation at break increased with the increase of PDMSb molecular weight and concentration, as shown in Table 3. It was mainly due to the poor mechanical properties of PDMS. The longer the PDMS chain, the poorer is the mechanical property and the better is the flexibility. As PDMS was located at the backbone of PU, the chain flexibility was increase, but the tensile strength decreased with the increase of PDMS chain length and concentration. On the other hand, the amount of hydrogen bonds was dominated by the amount of urethane groups, which increased with the decrease of the molecular weight of PDMS [18]. More hydrogen bonds would improve the tensile strength, but damage the elongation of copolymer.

In contrast, the elongation values of PDMS-*G*-PUD films decreased with the increase of the content of PDMSa. The reason may be the relatively small amount of soft segment domains in the backbone of PDMS-*G*-PUD. The tensile strength values of the PU films modified by PDMSa-3 decreased with the increase of PDMS concentration. However, the PU films modified by PDMSa-2 did not show similar regulation. This is because of the combined effects of microphase separation and the amounts of soft domains in main chains.

SEM–EDS analysis

Nitrogen environmental scanning electron microscope was used to examine the morphology and element compositions of PDMS–PUD film. The result of X-ray

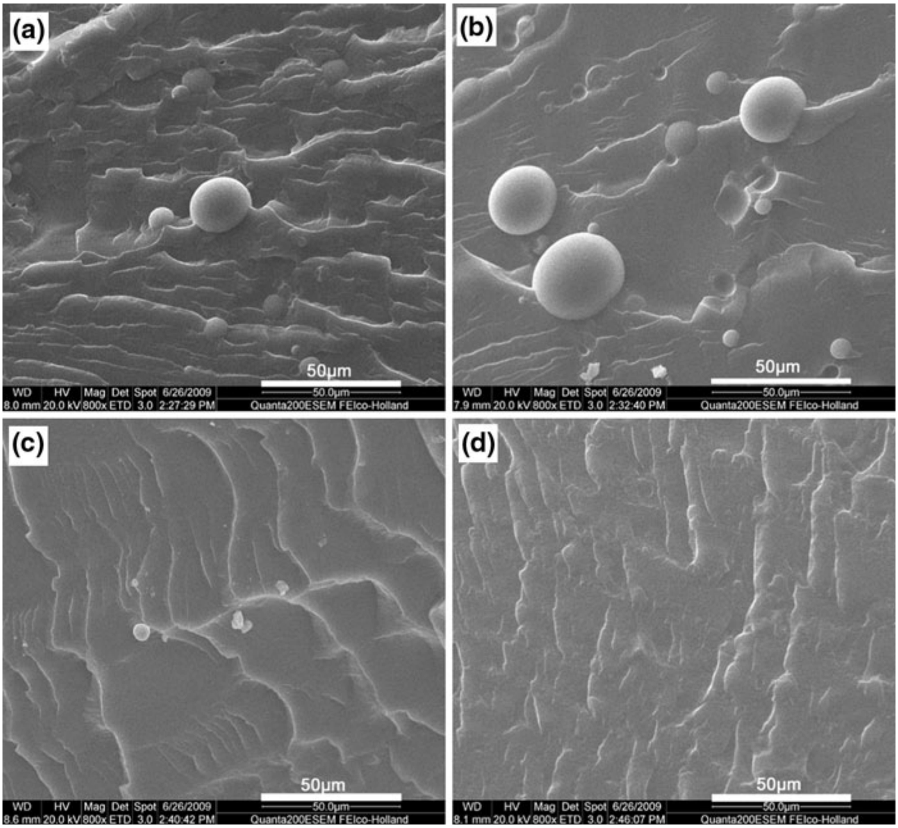


Fig. 5 SEM images of A5 (**a**), A7 (**b**), B5 (**c**), B7 (**d**)

EDS analysis demonstrated that f value of PDMS-*G*-PUD film was 259.56% while that of PDMS-*B*-PUD film was 94.68%. It is clear that the percent of atom Si in the surface of film was much higher than in the bulk. This suggested that most of siloxane chains migrated to the surface of the film during film curing because of its low surface energy [26]. Higher Si enrichment ratio of PDMS-*G*-PUD film confirmed that PDMSa was more prone to surface segregation due to its special structure, as mentioned previously.

The morphologies of the cross-sections of PU films were shown in Fig. 5. The cross-sections of both PDMS-*B*-PUD and PDMS-*G*-PUD films were rough because of the microphase separation between the nonpolar siloxane segment and the polar urethane groups. The images also showed that the microphase separation of film was affected by the content and chemical structure of PDMS. That the cross-sections of sample A5 and B5 were relatively smooth suggested the degree of microphase separation was low when small amount of PDMS (5%) was present in the films. However, the cross-sections became rougher when the PDMS content reached 9%. The relatively serious microphase separation can explain this fact.

Comparing the images of PDMS-*B*-PUD films and PDMS-*G*-PUD films, we noticed that the cross-sections of PU films modified by PDMSa were rougher. This result indicated that the PDMSa aggregated more easily, leading to relatively serious microphase separation. The siloxane domains caused a high contact angle and improved water and oil resistance, but reduced the mechanical properties. From the SEM observation, the microphase separation was the main cause for the improved surface properties.

Conclusions

Both PDMS-*B*-PUD and PDMS-*G*-PUD were successfully synthesized by the acetone method. The effects of chemical structure and molecular weight of PDMS on the properties and morphology of PDMS–PUD were investigated. The values of viscosity and molecular size of polyurethane dispersions increased with the increase of molecular weight and content of PDMS. The sample A7 had the maximum value (98.7°) of contact angles and showed best water resistance of all.

Compared with PDMS-*B*-PUD films, PDMS-*G*-PUD films had larger advancing contact angles and showed better water and oil resistance but lower gloss and poorer tensile strength with the same amount of PDMS and similar molecular weight. Data of EDS indicated that PDMSa was more prone to surface segregation. SEM images showed that PDMS-*G*-PUD film had better microphase separation than that of PDMS-*B*-PUD film.

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