

Preparation and Properties of Polydimethylsiloxane (PDMS)/Polytetramethyleneadipate glycol (PTAd)-Based Waterborne Polyurethane Adhesives: Effect of PDMS Molecular Weight and Content

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ABSTRACT: Waterborne polyurethane (WBPU) dispersions were prepared by pre-polymer process using siloxane polyol, namely polydimethylsiloxane (PDMS), and polyester polyol, namely poly(tetramethyleneadipate glycol) (PTAd), as a soft segment. Three different molecular weights ($M_n = 550, 6000, 110,000$) of PDMS and one fixed molecular weight of PTAd ($M_n = 2000$) was used during preparation of WBPU dispersions. This research aims to explore the potential use of PDMS in complementing WBPU by boosting flexibility, water resistance, and adhesive strength. The water swelling (%), tensile strength, and adhesive strength of WBPU were investigated with respect to PDMS molecular weight and PDMS content (PDMS mol %). The water swelling (%) and tensile

strength decreased with increasing PDMS molecular weight at a fixed PDMS content (mol %) in mixed polyol of WBPU films. By contrast, the peel adhesive strength peaked at 6.64 mol % and 4.43 mol % with molecular weight of PDMS at 550 and 6000, respectively, while it only decreased when the molecular weight of PDMS stood at 110,000. The adhesive strength was almost unaffected with optimum content (6.64 mol %) of lower PDMS molecular weight ($M_n = 550$) in mixed polyol-based WBPU after immersing the adhesive bonded nylon fabrics in water for 48 h among all of the samples. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 88–96, 2012

Key words: polyurethanes; adhesion; strength

INTRODUCTION

The commercial importance of waterborne polyurethane (WBPU) is being increased due to its environment friendly system comparing to its counterpart solvent-borne polyurethane, because this system permits the application of WBPU from an aqueous medium. Only water is evolved during the drying process, which renders the system especially safe with regard to the environment. In last two decades, thousands of articles and patents were issued, which kept steady the improvement of the production technology and the quality of WBPU.^{1–8} However, there still exist many disadvantages such as insufficient

chemical resistivity, thermal stability, mechanical property, and hydrolytic stability and thus restricted their application in various fields. Therefore, research for improving the properties of WBPU always gets priority.^{9–12}

There are different ways to prepare WBPU dispersions using mainly polyol (soft segment), diisocyanate, hydrophilic agent with pendant acid group, counteraction (neutralizing agent), and chain extender.^{9–12} The most preferred method is a prepolymer mixing process. There are three basic steps in this process: (1) formation of isocyanate-terminated prepolymer by reacting polyol, diisocyanate, and hydrophilic agent; (2) neutralization of acid groups by counteractions and emulsification of the NCO-terminated prepolymer for particle formation; and (3) chain extension by reacting amine with prepolymer for higher molecular weight and urea-linkage formation. Depending on the application, polyester polyols or polyether polyols are selected as soft segments in WBPU. It is well known that the polyester polyol-based WBPU provide better mechanical properties, whereas polyether polyol-based WBPU show higher

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hydrolysis resistance, softness, and water-vapor permeability.¹³ To attain better and specific physical properties, a mixed or special type of polyol was used in WBPU. Moreover, various methods such as hydrophobic monomers grafted to polyurethane (PU) main chain,^{14,15} the change of the type and content of ionic center,^{16–18} the adjustment of ionic neutralization degree,^{19–21} the blending^{22–24} and copolymerization of different polymers,^{25–29} and cross-linking^{30,31} have been employed to improve the properties of WBPU.

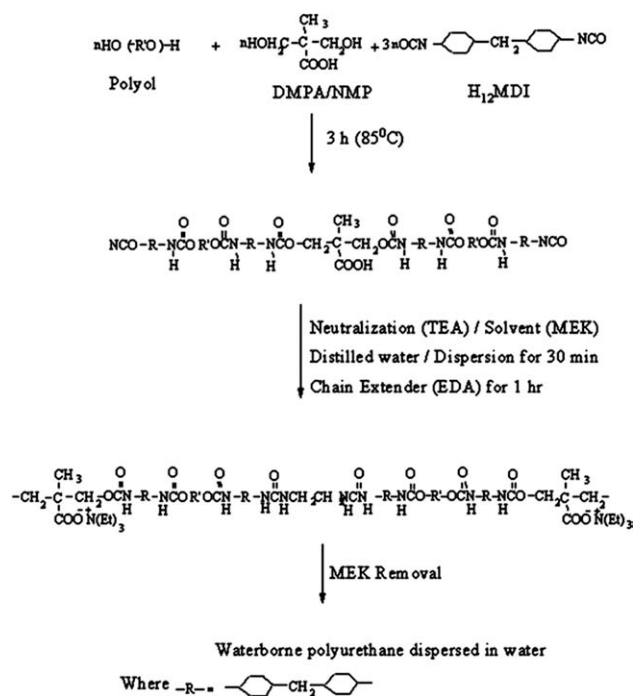
Polydimethylsiloxane (PDMS) is being recognized as having several advantages such as low surface tension, unique flexibility, low glass transition temperature, high temperature stability, good water resistivity, chemical inactivity, and insulating stability.³² The PDMS was also considered in last few years to improve the properties of WBPU.^{33–35} These reports mainly focus on improvement of water resistance and thermal stabilities of the WBPU films. However, there are relatively little efforts on WBPU dispersions modified with PDMS of different molecular weight and their use as an adhesive material.

In our previous reports, we were able to improve the adhesive strength by different ways such as increasing DMPA content,¹⁸ using polyester polyol,¹³ using optimum aliphatic hardener content,³⁶ made crosslink structure,³¹ and using optimum clay,³⁷ and carbon nanotube³⁸ content. Unfortunately, major WBPU adhesive materials are water sensitive³⁹ and the adhesive strength decreased after immersing in water for a while. In taking this problem, the use of PDMS with benefits in boosting water resistivity might be useful. In this study, we prepared WBPU dispersions using hydroxy terminated PDMS ($M_n = 550/6000/110,000$) and poly(tetramethyleneadipate glycol) (PTAd; $M_n = 2000$). We investigated the properties of WBPU films such as water resistance and mechanical strength (tensile strength and Young's modulus). The adhesive strength using these synthesized WBPU dispersions onto nylon fabrics was evaluated after immersing in water for 48 h.

EXPERIMENTAL

Materials

PTAd (number-average molecular weight $M_n = 2000$ g/mol, Sigma-Aldrich, St. Louis, Mo, USA) and hydroxy terminated PDMS ($M_n = 550/6000/110,000$ g/mol, Aldrich) were dried under vacuum at 90°C and 1–2 mmHg for 3 h before use. Triethylamine (TEA; Junsei Chemical, Tokyo, Japan), *N*-methyl-2-pyrrolidone (NMP; Junsei Chemical), 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI, Aldrich), and ethylenediamine (EDA) (Junsei Chemical) were dehydrated with



Scheme 1 The preparation process for a waterborne polyurethane.

4-Å molecular sieves for 1 week prior to use. 2,2-Bis(hydroxymethyl) propionic acid (DMPA, Aldrich), dibutyltin dilaurate (Aldrich), thickener (L75N, Bayer, Leverkusen, Germany), and hardener (ARF 30, polyisocyanate 20 wt %, Dongsung NSC Ltd, Korea) were used without further purification.

Preparation of WBPU dispersion

WBPU dispersions were synthesized using the prepolymer mixing process (Scheme 1).^{12,13} The polyol was placed in a four-necked flask that was equipped with a thermometer, a stirrer, a condenser with a drying tube, an inlet and outlet for dry nitrogen, and a heat jacket, and the system was degassed under vacuum at 90°C for 30 min. DMPA/NMP (1/1 w/w) was added to the flask, and the mixture was allowed to cool to 45°C under moderate stirring (175–200 rpm). Then dibutyltin dilaurate (1 drop) was added to the flask along with H_{12} MDI, and the mixture was heated to 85°C under moderate stirring (175–200 rpm) and reacted for 3 h. The change in the NCO value during the reaction was determined using the standard dibutylamine back-titration method (ASTM D 1638). Then methyl ethyl ketone (MEK, 10 wt %) was added to the NCO-terminated prepolymer mixture at 65°C in order to adjust the viscosity of the solution. TEA was also added to the reaction mixture at 65°C in order to neutralize the carboxyl groups of the NCO-terminated prepolymer. After 30 min of neutralization, distilled water

(70 wt %) was added to the reaction mixture (25°C) with vigorous stirring (1300–1500 rpm). The neutralized prepolymer was chain-extended by dropping EDA (mixed with water) at 40°C for 1 h, and the reaction continued until the NCO peak (2000–2300 cm^{-1}) in the IR spectrum had completely disappeared. The dispersions were obtained (30 wt % solid content) after MEK was evaporated (collected separately).

Preparation of WBPU films

The films were prepared by pouring the aqueous dispersion (10 g) onto a Teflon disk (diameter 7 cm) and drying the dispersion under ambient conditions for about 48 h. The dried films (typically about 0.5 mm thick) were dried at 60°C for 6 h and then vacuum dried for 12 more hours. The vacuum dried films were stored in a desiccator at room temperature. WBPU adhesive materials were formulated from WBPU dispersions, a thickener (L75N, 0.5 wt %), and a hardener (ARF 30, 5.0 wt %) according to our previous reports.^{13,18} An appropriate amount of WBPU dispersion was mixed with the thickener (0.5 wt %) and the hardener (5.0 wt %) to obtain a homogeneous mixture at room temperature. The prepared adhesive material was then coated onto nylon fabric and another nylon fabric was placed on the coated surface and then dried at fixed temperatures (100°C) under constant pressure (15 kg/cm^2) for 10 min.

Characterization

A Fourier transform infrared spectrometer (Impact 400D, Nicolet, Madison, WI) was used to identify the WBPU structure. The dispersion was coated on the thallium-bromide/thallium-iodide crystal surface as a thin liquid film and dried for the analysis. For each sample, 32 scans were collected at a 4- cm^{-1} resolution in the transmittance mode.

A Hitachi model H-7500 transmission electron microscope (TEM) was used to examine the morphology of the films. The samples for TEM analysis were first prepared by placing the nanocomposite films in epoxy capsules and curing the epoxy at 70°C for 24 h in an oven. The cured epoxies containing WBPU films were then microtomed with a diamond knife into 70–90 nm thick slices at -100°C . Finally, a 3 nm thick carbon layer was deposited on these slices for TEM observation.

The glass transition temperature (T_g) of the WBPU films was measured at 4 Hz by dynamic mechanical thermal analyzer (DMA MK III, Rheometrics Scientific, Inc., Surrey, UK) with a heating rate of 3 $^\circ\text{C}/\text{min}$. The dimension of the film sample was 5 \times 5 \times 0.2 (mm^3). The mechanical measurements

were made in simple extension on dumbbell specimens with a tensile tester (Tinius Olsen 1000, PA) at a crosshead speed of 20 mm/min according to ASTM D 412. The DMA analysis was only done for those samples which had sufficient mechanical strength confirmed by tensile test.

For swelling study, the WBPU films were immersed in water for 48 h at 30°C and the swelling percentage was determined from the weight increase as:

$$\text{Swelling}(\%) = \frac{W - W_0}{W_0} \times 100$$

where W_0 is the weight of the dried film and W is the weight of the film at equilibrium swelling.

The tensile properties were measured at room temperature with a United Data System tension meter (Instron ASTM-1, United Data Systems, Japan) according to the ASTM D 638 specifications. A crosshead speed of 50 mm/min was used throughout these investigations to determine the ultimate tensile strength and modulus and the elongation at break (%) for all the samples. The values quoted are the average of five measurements. The adhesion property was measured with the United Data System tension meter according to the ASTM D 1876-01 (the peel resistance of adhesives, i.e., the T -peel test). The values quoted are the average of five measurements.

RESULTS AND DISCUSSION

In this report, PDMS of different molecular weights was used with PTAd, DMPA, EDA, and H_{12}MDI and reacted to generate NCO-terminated prepolymers, followed by the processes of neutralization and dispersion to produce WBPU dispersion, as shown in Scheme 1. It is known that the physical properties of WBPU films depend on the molecular structure of materials used and the molar ratio of NCO/OH.^{1,18} In this report, the molar ratio of NCO/OH is similar in all the WBPUs. The soft segment (polyol) content varied due to different molecular weight of polyols (see Table I). However, no difficulty was encountered in preparing PDMS-modified prepolymers from the reaction of PDMS with the other materials. The data in Table I showed that all kinds of WBPU dispersions were successfully prepared. The structure of WBPU was identified by characteristic amide and carbonyl IR peaks (Fig. 1). In all cases, the absence of a peak in the range of 2000–2300 cm^{-1} confirmed that all isocyanate groups were reacted in this system. The characteristic N–H and CO peaks appeared at 3321 cm^{-1} and 1707 cm^{-1} , respectively, confirmed the formation of WBPU in all cases.^{10,12,18} Moreover, the WBPU with PDMS had a characteristic PDMS-methyl peak at 802 cm^{-1} ^{33–35} and also

TABLE I
Sample Designation and Composition of Waterborne Polyurethane Adhesives

Sample designation	Composition (molar ratio)						PTAd ^b (wt %)	PDMS ^c (wt %)	PDMS (mole %)
	Polyol ^a		DMPA	H ₁₂ MDI	TEA	EDA			
	PTAd	PDMS							
WP-PTAd	0.040	0	0.054	0.113	0.054	0.019	64.77	0	0
WP-1-550	0.035	0.005	0.054	0.113	0.054	0.019	60.22	2.37	2.21
WP-1-6000	0.035	0.005	0.054	0.113	0.054	0.019	48.78	20.91	2.21
WP-1-110,000	0.035	0.005	0.054	0.113	0.054	0.019	10.55	82.90	2.21
WP-2-550	0.030	0.010	0.054	0.113	0.054	0.019	55.05	5.05	4.43
WP-2-6000	0.030	0.010	0.054	0.113	0.054	0.019	36.70	36.70	4.43
WP-2-110,000	0.030	0.010	0.054	0.113	0.054	0.019	5.00	91.40	4.43
WP-3-550	0.025	0.015	0.054	0.113	0.054	0.019	49.14	8.11	6.64
WP-3-6000	0.025	0.015	0.054	0.113	0.054	0.019	27.25	49.05	6.64
WP-3-110,000	0.025	0.015	0.054	0.113	0.054	0.019	2.87	94.64	6.64
WP-4-550	0.020	0.020	0.054	0.113	0.054	0.019	42.33	11.64	8.85
WP-4-6000	0.020	0.020	0.054	0.113	0.054	0.019	19.66	58.97	8.85
WP-4-110,000	0.020	0.020	0.054	0.113	0.054	0.019	1.75	96.34	8.85
WP-5-550	0.015	0.025	0.054	0.113	0.054	0.019	34.39	15.76	11.06
WP-5-6000	0.015	0.025	0.054	0.113	0.054	0.019	13.42	67.11	11.06
WP-5-110,000	0.015	0.025	0.054	0.113	0.054	0.019	1.06	97.40	11.06
WP-PDMS-5 (PDMS, $M_n = 550$)	0	0.040	0.054	0.113	0.054	0.019	0	33.59	17.70
WP-PDMS-6 (PDMS, $M_n = 6000$)	0	0.040	0.054	0.113	0.054	0.019	0	84.66	17.70
WP-PDMS-11 (PDMS, $M_n = 110,000$)	0	0.040	0.054	0.113	0.054	0.019	0	99.02	17.70

^a PTAd (M_n) = 2000, PDMS (M_n) = 550/6000/110,000.

^b PTAd (wt %) = $\frac{\text{PTAd}(\text{wt})}{\text{PDMS}(\text{wt})+\text{PTAd}(\text{wt})+\text{DMPA}(\text{wt})+\text{H}_{12}\text{MDI}(\text{wt})+\text{TEA}(\text{wt})+\text{EDA}(\text{wt})} \times 100\%$.

^c PDMS (wt %) = $\frac{\text{PDMS}(\text{wt})}{\text{PDMS}(\text{wt})+\text{PTAd}(\text{wt})+\text{DMPA}(\text{wt})+\text{H}_{12}\text{MDI}(\text{wt})+\text{TEA}(\text{wt})+\text{EDA}(\text{wt})} \times 100\%$.

confirmed the successful preparation of WBPU with PDMS. The characteristic Si peak was marched at 1000–1300 cm^{-1} with ether band in same region of WBPUs and could not isolate in IR spectra.

The morphology of WBPU films was analyzed by TEM. The typical TEM micrograph is shown in Figure 2. The dark regions in Figure show the denser polyurethane-rich domains (PTAd) while the lighter areas are the PDMS-rich domains. However, it is very difficult to analyze phase separation with respect to different PDMS molecular weight and their contents by TEM. Thus, we measured the T_g values by DMA to investigate the phase separation with different PDMS molecular weight and their contents. The T_g values are summarized in Table II. The PTAd polyol-based WBPU showed two T_g values, whereas the mixed polyol-based WBPU showed two or three T_g values. This depends on PDMS molecular weight and content. Generally, the lower T_g values come from soft segment (polyol) and higher T_g values come from hard segment.^{12,38} In this study, when we used PDMS with $M_n = 550$ and 6000, the WBPU showed two T_g values (one for soft segment and another for hard segment) up to the certain PDMS content, after that they showed three T_g values (two for soft segment and another for hard segment) (see Fig. 3). This implied that PDMS polyol was phase mixed well up to the certain PDMS

content. In case of higher PDMS molecular weight ($M_n = 12,000$), the WBPU showed always three T_g values. This implied that phase separated well using PDMS higher molecular weight at initial stage.³³

The PDMS molecular weight and their contents used in the experiment played a key role in the mechanical properties of WBPU films. The PTAd-based

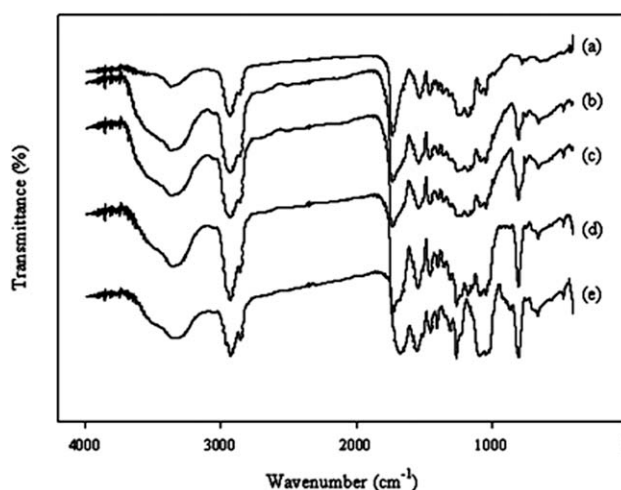


Figure 1 FTIR spectra of WBPU using PTDA (a), mixture of PTAd and PDMS polyol ($M_n = 550$) at PDMS 2.37 wt % (b), 5.05 wt % (c), 8.11 wt % (d), and only PDMS 100.00 wt % (e).

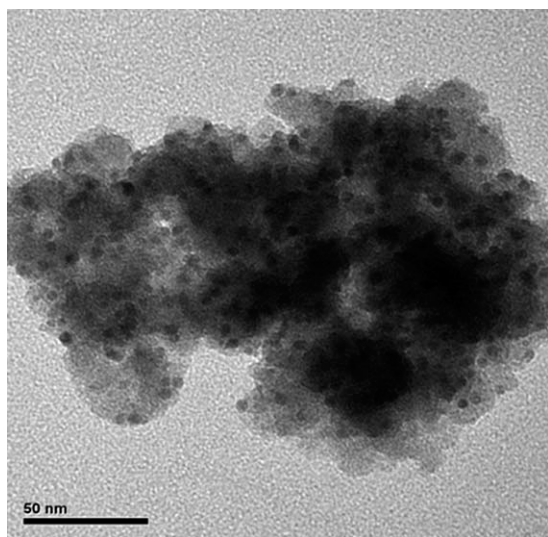


Figure 2 TEM micrograph of WP-3-550.

WBPU showed the highest tensile strength and Young's modulus comparing to those for any of PDMS ($M_n = 550, 6000, 110,000$)-based and mixed polyol-based WBPU films. This might be due to the presence of polar ester groups which can make more hydrogen bonds in polymer and thus increased the resistivity of polymer chain against the applied stress in PTAd-based WBPU [13]. Additionally, the

proper soft segment content made the film high stress capable and increased the tensile strength and Young's modulus.⁴⁰⁻⁴² The low molecular weight PDMS ($M_n = 550$)-based WBPU film was almost brittle and could not count for tensile test. This can be ascribed by very high hard segment content. Slightly higher molecular weight PDMS-based WBPU film was not brittle, but showed small values of tensile strength and Young's modulus. Surprisingly, the WBPU with very high molecular weight PDMS ($M_n = 110,000$) showed a very low tensile strength and Young's modulus values (not measurable). Thus, the WBPU with three different PDMSs showed different response in tensile test. Generally, the tensile strength and Young's modulus increased with increasing macrodiol molecular weight.⁴³ The tensile strength and Young's modulus also depend on soft segment content in PU.⁴⁰ The tensile strength and Young's modulus decreased with increasing soft segment content.⁴⁰ Thus the tensile strength and Young's modulus values were slightly higher using higher molecular weight ($M_n = 6000$) of PDMS which has a larger chain length. But the values were not increased as expected due to higher soft segment (PDMS) content. A high molecular weight PDMS (larger chain length) made the phase separation high and thus decreased the tensile strength and Young's modulus of WBPU films rapidly.⁴² The WBPU film

TABLE II
Mechanical Properties and Glass Transition Temperature of WBPU Films

Sample designation	Young's modulus (kgf/cm ²)	Tensile strength (kgf/cm ²)	Elongation at break (%)	Glass transition temperature		
				T_{gs1}	T_{gs2}	T_{gh}
WP-PTAd	426	405	1015	-39	-	135
WP-1-550	415	363	999	-40	-	132
WP-1-6000	350	341	950	-49	-	128
WP-1-110,000	1	16	1210	-55	-122	120
WP-2-550	337	307	944	-42	-	131
WP-2-6000	307	304	840	-52	-	124
WP-2-110,000	-	-	-	-	-	-
WP-3-550	280	275	891	-43	-	129
WP-3-6000	210	240	710	-57	-108	121
WP-3-110,000	-	-	-	-	-	-
WP-4-550	70	233	861	-46	-106	128
WP-4-6000	40	160	457	-64	-110	116
WP-4-110,000	-	-	-	-	-	-
WP-5-550	42	83	781	-50	-107	125
WP-5-6000	12	32	250	-69	-111	111
WP-5-110,000	-	-	-	-	-	-
WP-PDMS-5 ($M_n = 550$)	Brittle	-	-	-	-	-
WP-PDMS-6 ($M_n = 6000$)	5	59	150	-	-113	105
WP-PDMS-11 ($M_n = 110,000$)	-	-	-	-	-	-

T_{gs1} = Glass transition temperature of PTAd soft segment. T_{gs2} = Glass transition temperature of PDMS soft segment. T_{gh} = Glass transition temperature of hard segment.

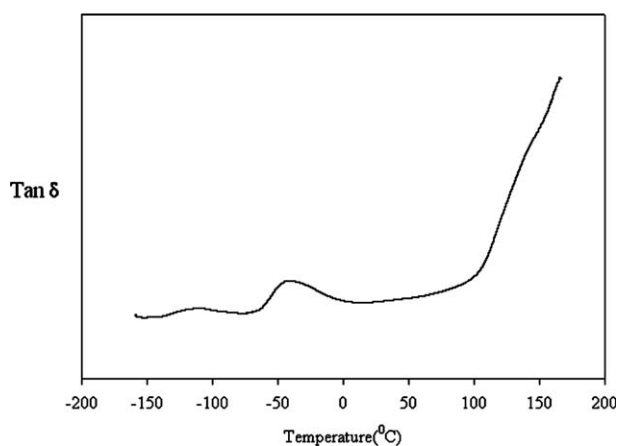


Figure 3 Tan δ of WP-4-550 films.

with high molecular weight PDMS ($M_n = 110,000$) performed like a soft material due to a very high soft segment content. Both PDMS molecular weight and a high soft segment content made the film very soft and the tensile strength and Young's modulus values were very low (not counted in test machine). The mechanical properties of WBPU films were also affected with different PDMS content using mixed polyols (see Table II and Fig. 4). Both the tensile strength and Young's modulus values of WP-550 films were higher than that of WP-6000 films, as shown in Table II. This can be attributed to the relatively high degree of the microphase separation in WP-6000 films. It is known that the microphase separation affects the mechanical properties of WBPU, and only appropriate microphase separation is beneficial to higher mechanical properties.⁴² The tensile strength would be poor when the microphase separation is higher. The WBPU with largest chain length of PDMS ($M_n = 110,000$) showed different behavior. From initially, the mechanical properties (tensile strength and Young's modulus) were dropped down from the value of using only PTAd-based WBPU film. Due to a higher molecular weight of PDMS the soft segment content was also higher (83%) in WP-1-110,000 sample and the tensile strength and Young's modulus had a very small value. An increase of the molecular weight of soft segment led to a higher phase segregation and also a lower proportion of the hard segments decreased the mechanical properties rapidly. Above 2.21 mol % PDMS (WP-110,000 samples) the soft segment content was very high and made the film very soft; and the tensile strength and Young's modulus values were not counted in test machine. The elongation at break (%) is also affected using different PDMS molecular weight and their contents in WBPU films (see Table II and Fig. 4). The elongation at break (%) of WP-PDMS-6 had a lower value using PDMS of $M_n = 6000$; whereas this value increased highly in WP-

PDMS-11 using PDMS of $M_n = 110,000$. To explain this behavior we have to count both soft segment content and PDMS effect. When we used PDMS 6000, the PDMS mainly act as a plasticizer and increased the elongation at break slightly.^{41,44} However, using PDMS 110,000 the soft segment content is also very high and the material has no resistivity on stress. Thus, this film just showed a very high elongation at break (%). Using mixed polyols, both factors (soft segment content and PDMS effect) also have effect on elongation at break (%) of WBPU films. Up to the optimum PDMS content using PDMS 550 and 6000, the PDMS act as a mainly plasticizer and decreased the elongation at break (%) slightly. Above optimum PDMS content the hard segment content is lower and thus the elongation at break (%) increased rapidly with increasing PDMS content. Thus this is very important to use optimum PDMS content to obtain the proper mechanical properties of films.

The water swelling (%) data in Table III demonstrated that the PDMS concentration and their molecular weight played an important role in water resistance for mixed polyol-based WBPU films: the water absorption of most samples decreased with more PDMS (except WP-110,000 samples) added up to the optimum content. Comparing single polyol-based WBPU-films, the PTAd polyol-based WBPU showed higher water swelling than for each PDMS ($M_n = 6000, 110,000$) polyol-based WBPU. This might be due to the presence of hydrophilic ester

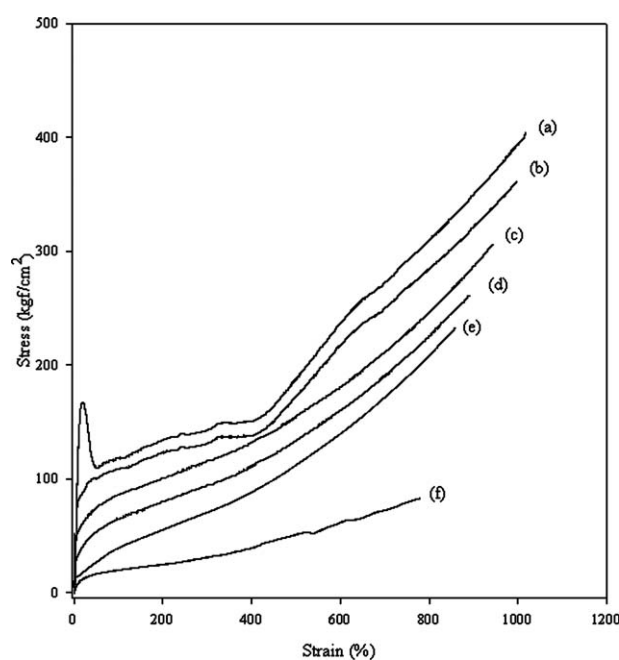


Figure 4 Stress-strain curve of WBPU using PTAd (a) and mixture of PTAd and PDMS polyol ($M_n = 550$) at PDMS 2.37 wt % (b), 5.05 wt % (c), 8.11 wt % (d), 11.64 wt % (e), and 15.76 wt % (f).

TABLE III
Water Swelling (%) and Adhesive Strength (kgf/cm)
After Immersed the Adhesive Bonded Nylon Fabrics
Under Water

Sample designation	Water swelling (%)	Adhesive strength (kgf/cm)		
		16 h	32 h	48 h
WP-PTAd	14.2	10.1	6.8	3.7
WP-1-550	12.1	12.2	9.1	7.9
WP-1-6000	13.2	6.1	1.3	0.5
WP-1-110,000	15	0.7	0	0
WP-2-550	9.8	13.6	10.2	8.8
WP-2-6000	14.1	6.8	1.5	0.7
WP-2-110,000	21	0.5	0	0
WP-3-550	5.5	16.8	16.7	16.7
WP-3-6000	15.1	6.2	1.6	0.5
WP-3-110,000	21.5	0.3	0	0
WP-4-550	5.5	14.3	12.4	9.5
WP-4-6000	17.1	3.5	1.1	0
WP-4-110,000	22.1	0.2	0	0
WP-5-550	5.6	12.4	9.3	7.5
WP-5-6000	20	0.8	0.2	0
WP-5-110,000	22.8	0.2	0	0
WP-PDMS-5 ($M_n = 550$)	Brittle	0.3	0.3	0.1
WP-PDMS-6 ($M_n = 6000$)	10	0.6	0.1	0
WP-PDMS-11 ($M_n = 110,000$)	12.1	0	0	0

group in WP-PTAd. It was also observed that the water swelling was lower for WP-PDMS-6 than for WP-PDMS-11. This is probably due to lower micro-phase mixing using shorter chain length of PDMS in WP-PDMS-6.⁴³ Additionally, the shorter chain length of PDMS also increased the chain packing and resisted water penetrating.⁴³ However, the WP-PDMS-5 (using lower molecular weight PDMS) was brittle and not considered for water swelling test. The mixed polyol (PTAd and PDMS) based WBPU showed an interesting behavior. Initially, the water swelling was decreased with increasing PDMS content in WP-550 and WP-6000 samples. The decrease of water swelling might be due to the presence of hydrophobic siloxane chain which prevents the water molecule getting into the bulk. In addition, after certain amount of PDMS an increase in water swelling was further observed for both series and indicated that the higher PDMS content made phase separation and decreased the water resistance.⁴³ The water swelling (%) of WP-11 films using a very high molecular weight PDMS in mixed polyol decreased at initial stage. The larger chain length of PDMS made high phase separation, as well as loose chain packing and thus decreased the water resistance.

The adhesive strength of WBPU adhesive onto nylon fabrics depends on polyol, molecular weight of PDMS, and polyol ratio. It was observed that the adhesive layer was torn instead of breaking the nylon fabric–adhesive interface for all samples. This

indicates that the bond strength of WBPU adhesives mainly depends on the adhesive thin layer prepared from the WBPU dispersion. The adhesive strength of any PDMS-based WBPU was lower than that of PTAd-based WBPU. Additionally, the adhesive strength gradually decreased with increasing molecular weight of PDMS. The adhesive strength of mixed polyol (PTAd and PDMS)-based WBPUs is shown in Figure 5. The mixed polyol (PTAd and PDMS) based WBPU showed different adhesive strength than that of each separated PTAd- or PDMS-based WBPU. The adhesive strength increased up to the optimum PDMS content in mixed polyol using PDMS when it's $M_n = 550$ and 6000. Using $M_n = 550$, the maximum adhesive strength was found at 6.64 mol % PDMS, whereas for $M_n = 6000$, the maximum adhesive strength was found at 4.43 mol % PDMS. This indicates that the optimum PDMS content for maximum adhesive strength was decreased with increasing chain length of PDMS soft segment. Though the optimum PDMS content was decreased with increasing PDMS molecular weight, the adhesive strength was higher using lower PDMS molecular weight ($M_n = 550$) than that of higher molecular weight of PDMS ($M_n = 6000$) using mixed polyols. However, the adhesive strength decreased from initially using higher PDMS molecular weight ($M_n = 110,000$) in mixed polyols of WBPU. The adhesive strength of WBPU materials depend on hydrophilic agent,¹⁸ preparation conditions (pressing temperature and pressure),¹³ and mechanical strength.⁴⁵ Here we observed that the adhesive strength also depends on polyol ratio and the polyol plasticizer effect. The initial improvement of adhesive strength using mixed polyol with lower PDMS molecular weight ($M_n = 550$ and 6000) was mainly governed by good compatibility of soft and hard segments and also plasticizing effect of PDMS.

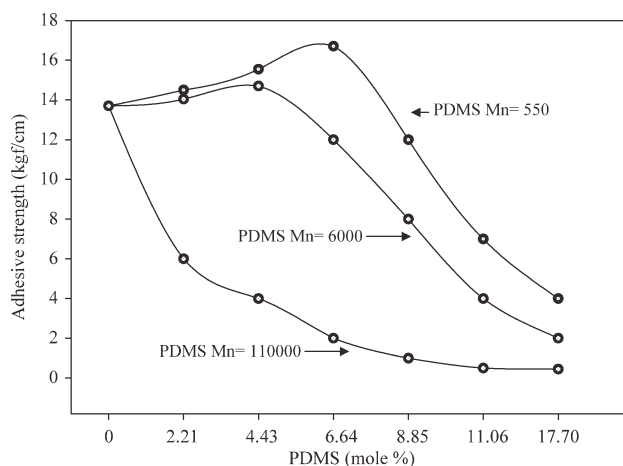


Figure 5 Adhesive strength onto nylon fabrics using various PDMS content in mixed polyol of WBPU.

Our previous report⁴⁵ confirmed that the adhesive strength depends on proper mechanical strength (tensile strength, Young's modulus, and elongation at break) which might be best at optimum PDMS content in WBPU (WP-3-550). However, above optimum PDMS content and high molecular weight of PDMS ($M_n = 110,000$), the phase separation might be dominated and decreased the adhesive strength.

The adhesive strength after immersing the adhesive bonded nylon fabrics under water was also investigated at room temperature (see Table III). This was conducted after various defined intervals (0–48 h). It was observed that the adhesive strength was decreased after immersion in water for most of the samples. The adhesive strength decreasing rate varied with respect to polyol, PDMS molecular weight, and polyol ratio as well as immersion time. The adhesive strength of WP-3-550 which has the optimum PDMS content (6.64 mol %) of lower molecular weight PDMS ($M_n = 550$) in mixed polyols remained unchanged for periods longer than 48 h. This might be due to the highly water resistance of the bulk adhesive polymer film and proper ratio of the soft and hard segment content, (the mechanical interlocking of polymer chains remains almost unaffected). The adhesive strength of all other samples had a tendency to decrease from initially in this condition. It was also observed that there was not any more adhesive strength for some samples prepared by WP-6000 and WP-110,000. Therefore, the WBPU (WP-3-550) with optimum PDMS content (6.64 mol %) in mixed polyol (PTAd and PDMS, $M_n = 550$) can be used as a good adhesive material for specific applications in which the adhesive bonded materials need to be in contact with water.

CONCLUSION

The PTAd and PDMS polyols ($M_n = 550, 6000, 110,000$) and their different ratio was used during preparation of WBPU dispersions. The maximum water resistance, tensile strength, and Young's modulus were found in mixed polyol with optimum PDMS content (6.64 mol %) with lower PDMS molecular weight ($M_n = 550$). The tensile strength and Young's modulus values decreased with inclusion of PDMS. Slightly lower tensile strength and Young's modulus values were observed using PDMS up to the optimum content and after then dropped down rapidly. The adhesive strength was significantly affected by polyol, PDMS molecular weight, and polyol ratio. The adhesive strength increased with increasing PDMS content using low molecular weight PDMS ($M_n = 550, 6000$). However, the adhesive strength of WP-3-550 retained almost original value with optimum PDMS content (6.64 mol %) with low molecular weight PDMS ($M_n = 550$) after

immersion in water for 48 h. Thus, maintaining the proper content of PTAd and PDMS polyol ($M_n = 550$) the WBPU adhesive material can be used as an alternative of current solvent-based adhesives.

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