

Synthesis and Characterization of Waterborne Polyurethane Adhesive from MDI and HDI

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ABSTRACT: A series of waterborne polyurethane adhesives (WPUAs) were prepared from diphenylmethane-4,4'-diisocyanate (MDI), 1,6-hexamethylene diisocyanate (HDI), poly(1,4-butanediol adipate) diol (PBA), 1,4-butanediol (BDO), and internal-emulsifying agents by the prepolymer mixing method. The viscosity, mechanical properties, thermal properties, and adhesion strength of the samples were measured. The structure–property relationship was discussed primarily. The results indicated

that the MDI/HDI and PBA/BDO molar ratio influenced these properties. The WPUA exhibited excellent T-peel strength and mechanical properties at a suitable MDI/HDI (or PBA/BDO) molar ratio. Moreover, higher MDI/HDI (or PBA/BDO) molar ratio resulted in higher thermal stability. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1396–1402, 2008

Key words: polyurethane; adhesives; adhesion strength

INTRODUCTION

Recently, the manufacture of polyurethane (PU) adhesive is turning from solvent-based type to water-based dispersion with the increasing awareness of environmental issues. The waterborne polyurethane adhesive (WPUA) possesses excellent resistance to low temperature, good flexibility, and adhesion strength as solvent-based PU adhesive. So far, WPUA has been applied in automobile interiors bonding, kitchen, furniture membrane, the composite membrane, and soles/shoe affixed to the fore.^{1,2}

Generally, WPUA is classified into nonionic, anionic, and cationic type. The anionic one is used widely in WPUAs.^{3–8} Anionic WPUA could be prepared from diisocyanate, polymeric polyol, anionic internal-emulsifying agent, and so on. The diisocyanate affects the performance of the adhesive greatly.⁹ In the past decades, the preparation of WPUA has been mainly focused on expensive diisocyanates, such as isophorone diisocyanate (IPDI), tetramethylxylene diisocyanate (*m*-TMXDI), and 1,6-hexamethylene diisocyanate (HDI).^{5–8} Higher price of these diisocyanates hindered its development. Compared with these, diphenylmethane-4,4'-diisocyanate (MDI) is a cheaper substitute. However, MDI cannot be

used directly because its high reactivity would lead to post-chain-extension during the prepolymer mixing process. Considering this problem, Kim et al.¹⁰ tried to synthesize a kind of MDI–HDI aqueous PU adhesive through the OH-terminated polyurethane mixing process to avoid the shortcoming of the utilization of MDI. Except this, few literatures concerned the synthesis and characterization of MDI-based aqueous PU adhesive and its application.

The aim of this work is to synthesize waterborne PU adhesive with low cost and good T-peel strength based on MDI and HDI through the prepolymer mixing method. Here, MDI/HDI molar ratio was reasonably designed to obtain the NCO-terminated prepolymer of lower reactivity and better working properties. At the same time, dimethylol propionic acid (DMPA) and anionic polyester polyol (containing carboxyl) were used together in order to get a much finer dispersion.¹¹

EXPERIMENTAL

Materials

Poly(1,4-butanediol adipate) diol ($M_w = 2000$, PBA, Wuxi Xinxin polyurethane Co., Ltd.), anionic polyester polyol ($M_w = 1970$, JW6-55, Shanfeng polyurethane Inc.), MDI (Yantai Wanhua polyurethane Co., Ltd.), HDI (Bayer), 1,4-butanediol (BDO, BASF), DMPA (Dongying Saimeike Chemical Co., Ltd.), piperazine (AP, Shijiazhuang Hejia Health Productions

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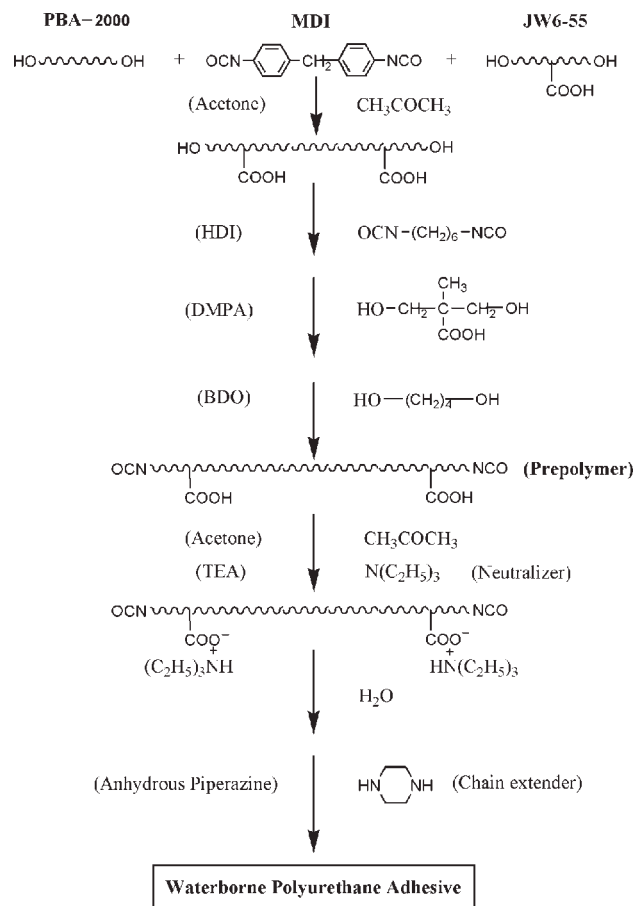


Figure 1 Reaction scheme of waterborne polyurethane adhesive.

Co., Ltd), triethylamine (TEA, AP), acetone (CP), deionized water, used as received.

Synthesis of WPUA

The preparation process of WPUAs was divided into three steps including synthesis of the prepolymer, neutralization, and dispersion. The reaction scheme of WPUA is illustrated in Figure 1.

The prepolymer was prepared in a 500-mL round-bottom, three-necked flask with a mechanical stirrer, thermometer, and condenser. Firstly, PBA and JW6-55 were charged into the dried flask, and then dehydrated for 2 h at 393.15 K under the reduced pressure. When the mixture cooled to the environmental temperature, acetone, and MDI were added, and then MDI reacted with PBA and JW6-55 for 1 h at reflux. Afterwards, HDI was added. After an hour, DMPA was added and reacted about 1 h. Then, BDO was charged into the flask and reacted with diisocyanates for 3 h at reflux. Finally, the NCO-terminated prepolymer was obtained.

When the reaction mixture (prepolymer and solvent) cooled to 303.15 K, TEA was added to neutralize the carboxylic acid. After 15 min, the above

mixture was dispersed into water with strong stirring. The chain extender piperazine was added for further reaction about 30 min at reflux. Finally, the acetone was completely removed under the reduced pressure and waterborne PU adhesive with 40% solid content was obtained.

During the process, JW6-55, DMPA, acetone, TEA, and piperazine were used at a constant amount. The consumption of water changed with a fixed solid content of the aqueous polyurethane dispersion. A series of WPUA were prepared with different designed MDI/HDI and PBA/BDO molar ratios, and the corresponding numbers were listed in Table I.

Preparation of polyurethane films

The polyurethane film was prepared by placing aqueous polyurethane dispersion in a PTFE mould. The sample was dried under infrared lamp for 4 days, and then annealed in an oven at 323.15, 333.15, and 343.15 K for 2 h in turn. Finally, the suitable film was obtained after annealing at 353.15 K for 5 h.

Characterizations

Fourier transform infrared spectroscopy

Absorption peaks of reaction mixture characteristic groups were obtained with a fourier transform infrared (FT-IR) instrument (NICOLET-380, Thermo Electron Corporation).

Brookfield viscosity

The viscosity of the dispersion was measured with a NDJ-1 rotational Brookfield viscometer at 298.15 K. Experiments were carried out at 6, 12, or 30 rpm of the spindle.

Thermal properties analysis

Thermal properties of the films were performed on the thermal gravimetric analysis (TGA, Shimadzu

TABLE I
Directions for Producing the Waterborne Polyurethane Adhesives

Sample	MDI/HDI (molar ratio)	PBA/BDO (molar ratio)	PBA (g)	BDO (g)	MDI (g)	HDI (g)
MH45	4/5	2/3	40.00	2.70	10.00	8.40
MH54	5/4	2/3	40.00	2.70	12.50	6.72
MH63	6/3	2/3	40.00	2.70	15.00	5.04
MH72	7/2	2/3	40.00	2.70	17.50	3.36
PB14	6/3	1/4	20.00	3.60	15.00	5.04
PB23	6/3	2/3	40.00	2.70	15.00	5.04
PB32	6/3	3/2	60.00	1.80	15.00	5.04

Supplement: JW6-55 17.90 g, DMPA 2.68 g, TEA 3.03 g, and piperazine 0.82 g.

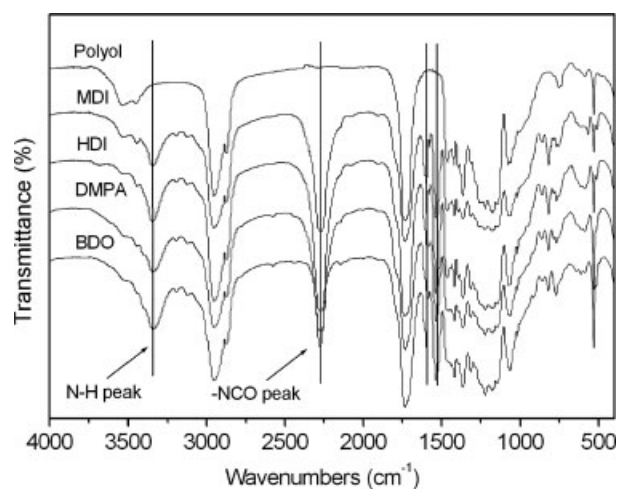


Figure 2 FT-IR spectra collected during synthesis of urethane prepolymer (MDI/HDI = 6 : 3).

TGA-60) and differential scanning calorimetry (DSC, TA-60WS, DSC-60, 100V; Shimadzu). For TGA, the sample was heated from 303.15 to 873.15 K with a heating rate of 10 K/min under N_2 atmosphere (30 mL/min). For DSC, the temperature of sample increased from 178.15 to 473.15 K at 10 K/min.

Measurement of mechanical properties

Mechanical properties of the PU films were performed on an INSTRON 4201 instrument. In the test, each sample was measured five runs for the average value, at a crosshead speed of 250 mm/min.

T-peel adhesion strength

T-peel strength of the WPUA was measured in an INSTRON 4201 instrument. Certain amount of adhesive was applied to each PVC strip treated with acetone. After that, the two PVC strips were kept at a certain temperature for about 10 min. After that, the strips were fixed in contact and a pressure of 0.8 MPa was immediately placed on the strips for 40 s and 24 h, respectively. Finally, green T-peel strength and final T-peel strength value were obtained after measuring at a peel rate of 250 mm/min.

RESULTS AND DISCUSSION

FT-IR analysis

The reaction process was monitored by FT-IR spectroscopy. The characteristic adsorption peaks of the reaction mixture changed with the reaction process. The variation of the adsorption peaks was shown in Figure 2. The related characteristic peaks of functional groups were listed in Table II.

Figure 2 showed the variation of characteristic adsorption peaks of the reaction mixture in different reaction phases: before the reaction of polymeric

polyols; 1 h after adding MDI; 1 h after adding HDI; 1 h after adding DMPA; 3 h after adding BDO. After the addition of MDI, the characteristic peaks belonging to isocyanate, aromatic and urethane groups, such as $N=C=O$ (2275 cm^{-1}), $C=C$ bond (1598 cm^{-1}), and $N-H$ bond (3342 cm^{-1} , 1534 cm^{-1}), appeared. With the introduction of HDI, the intensity of $N=C=O$ was enhanced, although that was weakened markedly after DMPA was charged into the reactor. Meanwhile, characteristic peaks of urethane group, such as $N-H$ peak, increased gradually. After the added DMPA reacted with isocyanates about 1 h, BDO was added. Finally, all the $O-H$ groups were consumed, the adsorption peak of $O-H$ disappeared and the peak intensity of free isocyanate groups ($N=C=O$) reduced to a constant value. The NCO-terminated prepolymer was obtained.

The viscosity of aqueous PU dispersion

Figure 3(a) showed the effect of the MDI/HDI molar ratio on viscosity of the aqueous polyurethane dispersions. Figure 3(b) exhibited the relationship between viscosity and PBA/BDO molar ratio. Generally, the viscosity of aqueous PU dispersion was determined mostly by the hydrophilicity of polyurethane particles.^{12,13} During the experiment, the viscosity of the dispersion increased with increasing MDI/HDI molar ratio at a constant PBA/BDO ratio of 2 : 3. This was probably ascribed to the different molecular structure of MDI from HDI. With the increase of MDI, the polarity of the hard segment was enhanced, and the hydrophilicity was strengthened. It seemed that higher content MDI resulted in higher viscosity of aqueous PU dispersion. From Figure 3(b), it could be seen that the viscosity of aqueous polyurethane dispersion decreased with PBA/BDO molar ratio rising at a constant MDI/HDI ratio of 6 : 3. Meanwhile, the hard segments content and ionic group content decreased. This would make the urethane chains less polarity and weaken

TABLE II
FT-IR Characteristic Bands Assigned to the Polyester Polyols and Aromatic Urethane Prepolymer

Characteristic groups	Wavenumber (cm^{-1})
Polyester $O-H$ stretching	3536, 3446
$N-H$ stretching	3342
$N=C=O$ symmetric stretching	2275
$N-H$ bending and $N=C=O$ asymmetric stretching	1534
Ester $C=O$ and Urethane $C=O$	1700 ~ 1740
Aromatic $C=C$ stretching	1598
$N-H$ bending and $C-N$ stretching	1534
$C-H$ out-of-plane bending in phenyl	819, 512

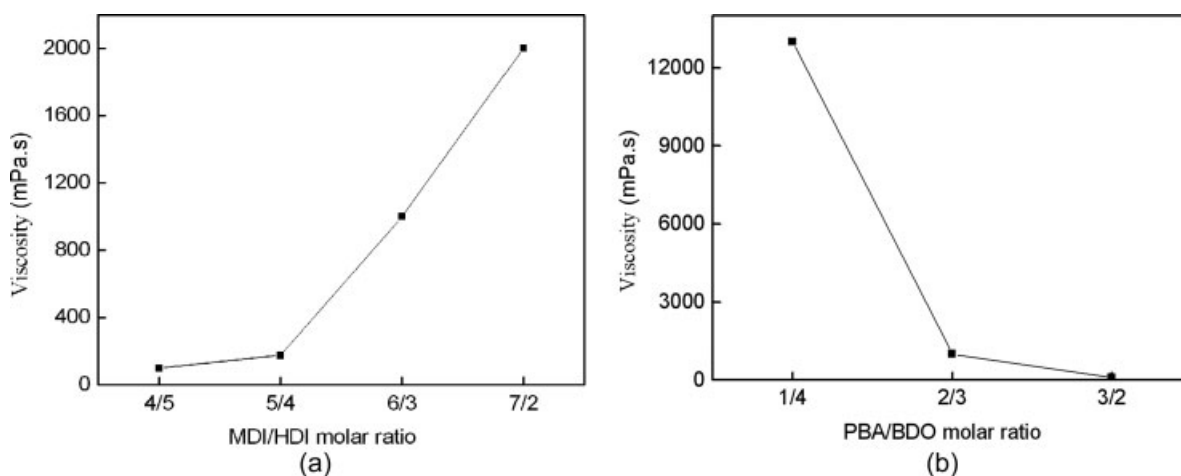


Figure 3 Viscosity as a function of the molar ratios for (a) MDI/HDI and (b) PBA/BDO.

the intermolecular interactions. It led to the decrease of hydrophilicity of polyurethane particles. The viscosity of the PU dispersions was in the order of $PB14 > PB23 > PB32$.^{14–16}

Thermal analysis

TG analysis

Thermo gravimetric analysis curves of the PU samples were shown in Figure 4(a,b). For all PU samples, a slight weight loss was observed below 473.15 K which was ascribed to the residual water. A rapid weight loss percent appeared between 473.15 K and 732.15 K, which was caused by the decomposition of the polymer.

Considering the whole thermal degradation process, the sample exhibited better thermal stability with the increasing MDI/HDI molar ratio. That is to say, the thermal stability of the WPUAs fell in the order $MH72 > MH63 > MH54 > MH45$. The reason was that the MDI-based polyurethane chains

showed better thermal stability than the HDI-based ones. This phenomenon was also reported by Rogulska et al.¹⁷ From Figure 4(b), it was observed that the weight loss of the sample with lower PBA/BDO molar ratio appeared distinct decrease during thermal degradation process. The thermal stability of PB32 was higher than that of PB23 and PB14. This might be attributed to the poorer thermal resistance of hard segments (urethane and urea) compared with soft segments (polymeric polyols).⁷

DSC analysis

DSC curves of the PU samples with different MDI/HDI and PBA/BDO molar ratios were shown in Figure 5(a,b). The analysis data of the different DSC curves were listed in Table III. The melting endothermic peak appeared in the range of 308.15 K–318.15 K, corresponding to the crystalline melting temperature of the soft segment.

As to the melting enthalpy of the soft segment (ΔH_m SS), ΔH_m SS value of the MH45 sample was

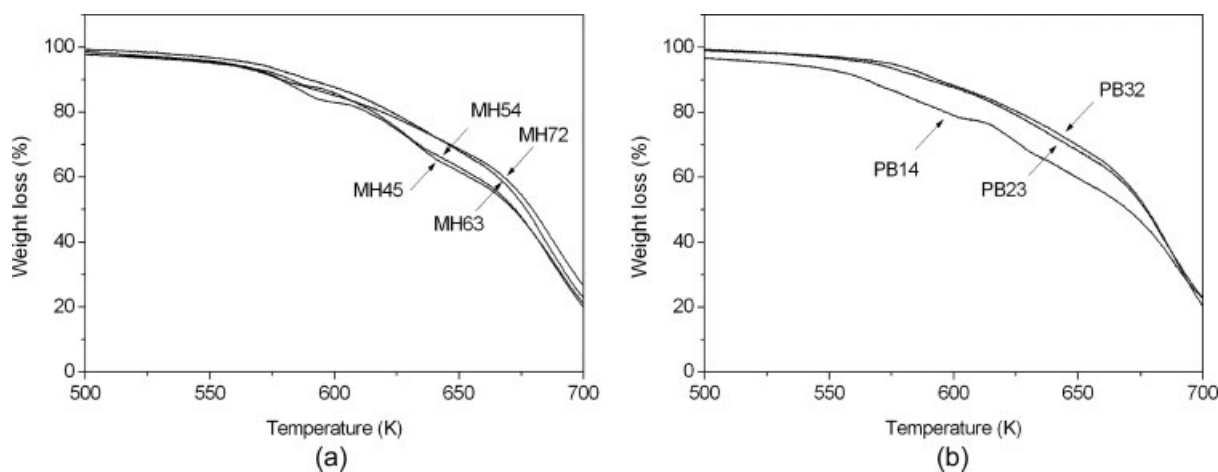


Figure 4 TG curves of the PU films with different (a) MDI/HDI and (b) PBA/BDO molar ratios.

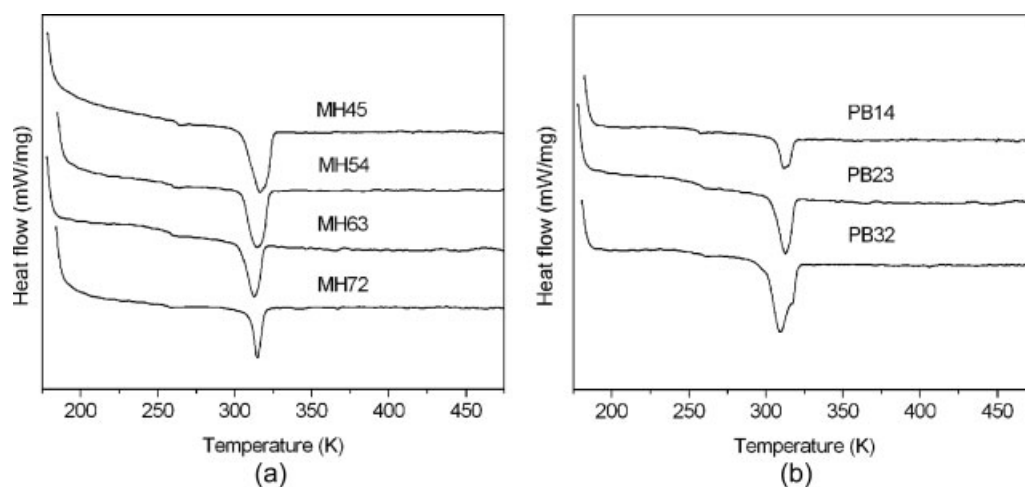


Figure 5 Differential scanning calorimetry (DSC) curves of the PU films with different molar ratios of (a) MDI/HDI and (b) PBA/BDO.

higher than other MH-series samples, and ΔH_m SS value of the PB-series (PB14 < PB23 < PB32) increased with the increase of PBA/BDO molar ratio. For the MH-series samples, the sample with higher molar ratio of MDI/HDI exhibited lower crystallinity than the other samples, because the bulky double phenyl ring of MDI increased rigidity of polymer molecule and hindered the crystallization of soft segments significantly.^{17,18} The other reason was probably that higher MDI content made good molecular weight distribution of polyurethane chains and enhanced interactions between hard segments and soft segments. This influence hindered the crystallization of soft segments. For the PB-series PU samples, the crystallinity increased with increasing of soft segment content. The higher soft segment content weakened the intermolecular interactions and enhanced PU chain flexibility, which made the soft segments easy to crystallize.^{19,20}

Mechanical properties of PU films

Mechanical properties of the PU films were tested and shown in Table IV. With the rise of MDI/HDI molar ratio (from 4/5 to 6/3), tensile strength and tear strength of the films were strengthened, obviously. The bulky double benzene ring structure of MDI, not only hindered the molecular slippage, but also increased rigidity of the hard segment, which

favored tensile strength and tear strength of film.^{18,21} The tensile strength and tear strength of MH72 was lower than that of MH63 because of the poor compatibility between MDI-segments and HDI-segments. At a fixed NCO/(OH + NH) total molar ratio, the hard-soft segments ratio affected mechanical properties mainly. When a certain amount of BDO was replaced by PBA, the soft segment content increased and the hard segment total content lowered. The polar groups in macromolecule chain were reduced and the crystallinity of soft segment was enhanced. It resulted in lower intermolecular interactions and higher molecular flexibility. However, too high soft segment content led to poor micro-phase separation and weakened mechanical properties. The tensile strength and tear strength increased firstly and then decreased for the PB-series samples.

Adhesion strength of waterborne PU adhesives

The green T-peel strength was deemed to the ability of the adhesive to hold two surfaces together, when first contacted and before the adhesive developed its ultimate bonding properties.⁹ Final T-peel strength

TABLE IV
Mechanical Properties of Waterborne Polyurethane Films

Sample	Tensile strength (MPa) ^a	Tear strength (kN/m) ^b
MH45	5.36	39.31
MH54	6.27	42.25
MH63	9.20	60.71
MH72	8.36	59.94
PB14	7.58	53.97
PB23	9.20	60.71
PB32	7.94	47.65

^a All these standard deviations are not more than 0.2.

^b All these standard deviations are not more than 1.5.

TABLE III
DSC Data of the Polyurethane Films with Different MDI/HDI and PBA/BDO Molar Ratios

	MDI/HDI			PBA/BDO			
Molar ratio	4/5	5/4	6/3	7/2	1/4	2/3	3/2
ΔH_m SS (J/g)	43.34	37.65	28.22	19.30	14.22	28.22	47.92

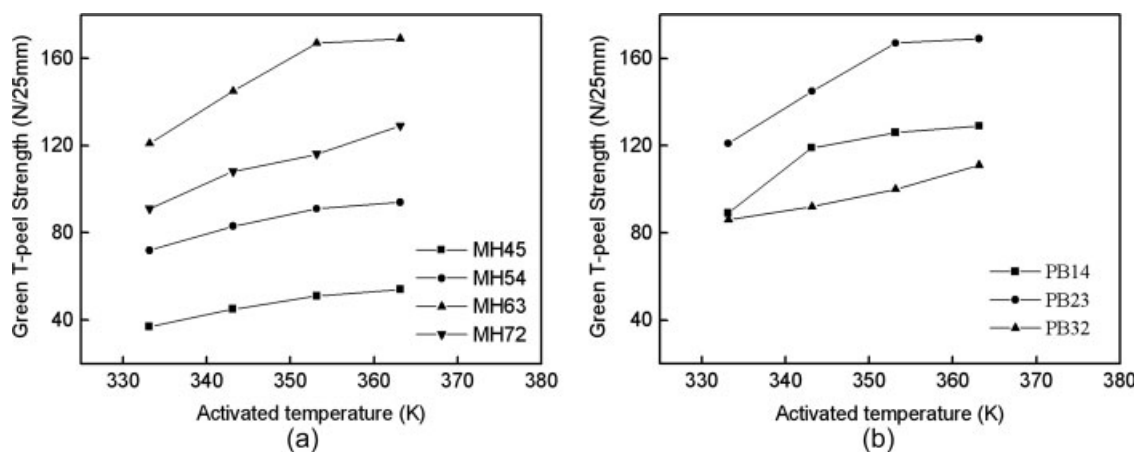


Figure 6 Green T-peel strength as a function of the activated temperature for (a) MH-series and (b) PB-series.

meant the ultimate adhesive strength value here, which was obtained after 24 h joint formation.

Generally, the green T-peel strength was determined mainly by the adhesive strength (adhesive to PVC) and cohesive energy (cohesive in the adhesive bulk). The crystallinity of soft segments, the soft/hard segments molar ratio and the activated temperature are main factors for adhesive strength and cohesive energy. Figure 6 showed green T-peel strength values of PVC/WPUA/PVC joints, depending on the activated temperature. The green T-peel strength increased with the activated temperature increased from 333.15 K to 363.15 K. It was also observed that the green T-peel strength increased firstly and then decreased with increasing MDI/HDI and PBA/BDO molar ratio. For the same sample, the higher activated temperature led to better green T-peel strength, owing to higher adhesive strength and cohesive energy.⁷ The MH63 sample held the highest green T-peel strength among MH-series adhesives. This reason was probably that the suitable

MDI/HDI molar ratio resulted in high adhesive strength and cohesive energy. For the PB-series adhesives, the higher molar ratio of PBA/BDO caused the higher crystallinity of soft segments. So, the green T-peel strength increased with increased PBA/BDO molar ratio. However, too many soft segments were also unfavorable to the green T-peel strength, which resulted in lower mechanical properties and cohesive energy (intermolecular interactions). Therefore, the maximum green T-peel strength was obtained at the molar ratio 2 : 3, due to a relative balance between adhesive strength and cohesive energy.²²

The final T-peel strength was investigated at the activated temperature 343.15 K. Figure 7(a,b) showed that the final T-peel strength changed with the MDI/HDI and PBA/BDO molar ratio. Once the ultimate bonding properties of PU adhesive were developed, the adhesive strength and cohesive energy would be enhanced. The final T-peel strength was higher than the green T-peel strength for the

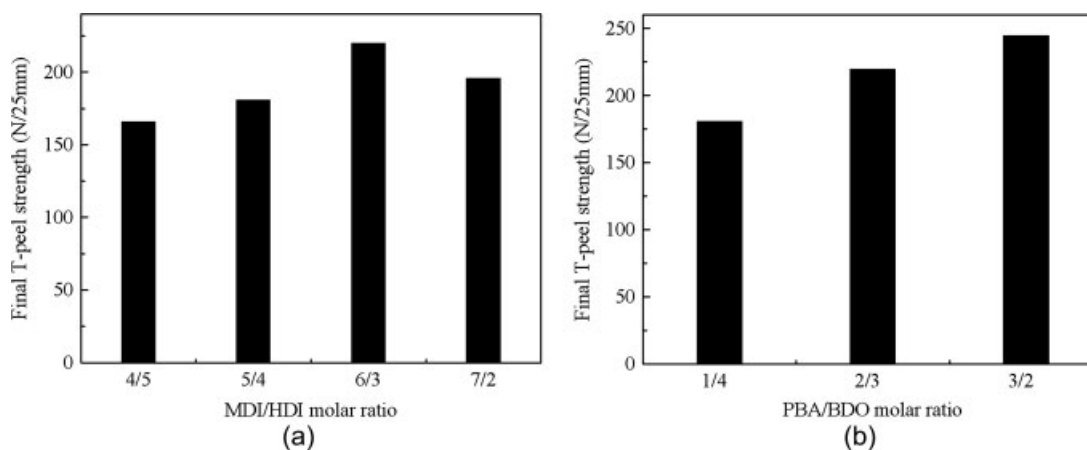


Figure 7 Final T-peel strength as a function of the (a) MDI/HDI and (b) PBA/BDO molar ratios.

same WPUA at a certain activated temperature. At the same time, the MH63 sample held the highest final T-peel strength. However, as to the PB-series PU adhesives, the adhesive strength was the determining factor when the cohesive energy was high enough. The final T-peel strength value of the PB32 sample was higher than that of PB23 and PB14. The higher content of soft segments led to higher crystallinity, improved the mechanical seal of these crystalline domains with the substrates, and enhanced the adhesive strength.¹⁰

CONCLUSIONS

MDI-based WPUAs with promising performance were prepared. The properties of polyurethane samples were influenced markedly by the molar ratio of MDI/HDI and PBA/BDO.

Higher MDI/HDI molar ratio was helpful to the improvement of viscosity, but not to crystallinity. Higher molar ratio of PBA/BDO led to different influence on them. WPUA with higher MDI/HDI (or PBA/BDO) molar ratio showed better thermal stability. Moderate MDI/HDI (or PBA/BDO) molar ratio was necessary for higher tensile strength and tear strength.

WPUA with higher activated temperature exhibited outstanding green T-peel strength. Suitable MDI/HDI and PBA/BDO molar ratio was the key to get a kind of WPUA with promising green T-peel strength and final T-peel strength.

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