

Preparation and Properties of Crosslinkable Waterborne Polyurethanes Containing Aminoplast –Effect of Curing Condition–

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(Received March 30, 2006; Revised May 4, 2006; Accepted May 9, 2006)

Abstract: In order to improve the water swelling, thermal/mechanical and adhesion properties of waterborne polyurethane (WBPU), a series of the crosslinkable WBPUs containing hydrophilic ionic component, dimethylol propionic acid (20 mole%), were prepared by in-situ polymerization using a cross-linker hexakis (methoxymethyl) melamine (HMMM). Effects of the HMMM content (2, 4, and 6 wt%) and curing temperature on these properties of the crosslinked WBPUs samples were investigated. All properties were found to increase with increasing HMMM content. It was found that the optimum curing temperature of the WBPU films and adhesives was near 120 °C, which was not dependent on the HMMM content.

Keywords: Crosslinking, Waterborne-polyurethanes, Aminoplast, Curing temperature

Introduction

Solvent-borne polyurethanes are used in many industrial applications where high abrasion resistance, elastomeric properties, and high extensibility at low temperature are the performance requirements. Most of the solvent-borne polyurethane coatings and adhesives are relatively high in solvent content and do not qualify in low VOC applications [1-4]. From last decade, it is demanding of low VOC products in industry, which potential the process of polymer using low or without volatile organic solvent. For this reason, there is an increased interest in waterborne polyurethanes (WBPUs) system.

However, the WBPUs are deficient in chemical resistance, thermal resistance, and mechanical property compared to solvent based PUs because the WBPUs are linear thermoplastic polymers contained little gel which allows resolubility in solvents. Therefore, improving the exterior durability exhibited by WBPUs is a high priority for research and development [5]. Crosslinking is used in many industrial coatings and adhesive applications to improve solvent and chemical resistance, hardness, and mechanical properties of polymers. It was found that the crosslinked WBPUs achieved the high failure temperature due to the formation of chemical crosslinking [6].

The current study uses alkylated melamine-formaldehyde resin (aminoplast) as crosslinking agents for the WBPU dispersions. Especially, hexakis (methoxymethyl) melamine (HMMM), methylated ether of the fully methylolated melamine resin is reactive with both carboxyl and hydroxyl groups and yield stable waterborne system [7]. However, due to its very recent introduction and use only in industry, the structure/manufacture/performance correlations still need to be investigated, and research on the waterborne system can hardly be

found. In a previous work [8], the in-situ polymerization of the WBPU containing HMMM was found to be a more effective method to improve the properties of the WBPU materials compare to simple blending process.

In this study we focused our tries on correlation of the cross-linker HMMM content along with curing temperature, to the thermal, mechanical, swelling and adhesion properties of the crosslinked WBPUs. A series of crosslinkable WBPU dispersions were prepared by in-situ polymerization using IPDI/PTMG2000/DMPA/EDA/TEA/HMMM. To observe the effect of the heat treating condition on the properties of the crosslinked WBPUs, the samples were treated with different conditions (temperature: 80~150 °C, time: 0~30 min) under pressure 15 kgf/cm². The effects of the HMMM content and the heat treating temperature on the properties of the crosslinked WBPUs were investigated.

Experimental

Materials

The dibutyl tin dilaurate (DBTDL, Aldrich Chemical, Milwaukee, WI) was used without further purification. Isophorone diisocyanate (IPDI, Aldrich Chemical, Milwaukee, WI), triethylamine (TEA, Sigma, Milwaukee, WI), ethylene diamine (EDA, Aldrich Chemical, Milwaukee, WI), methyl ethyl ketone (MEK, Sigma, Milwaukee, WI) and N-methyl-2-pyrrolidone (NMP, Aldrich Chemical, Milwaukee, WI) were used after dehydration with 4 Å molecular sieves for one day. Poly(tetramethylene oxide) glycol (PTMG, $M_n = 2,000$ g/mol, Aldrich Chemical, Milwaukee, WI) was dried over calcium hydride at a room temperature for 24 h. Dimethylol propionic acid (DMPA, Aldrich Chemical, WI) was dried in a vacuum oven for 5 h at 100 °C. The aminoplast used in this study was a commercially available version of hexakis methoxymethyl melamine (HMMM), which has a

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degree of polymerization of approximately 1.5, an average molecular weight of 554 and an average theoretical functionality of 8.3. Amine blocked *p*-toluenesulfonic acid (*p*-TSA, Sigma, Milwaukee, WI) was used as the catalyst for condensation reaction of the methoxy groups of HMMM and carboxyl acid groups of DMPA.

Synthesis of Crosslinkable WBPU Dispersions

Crosslinkable WBPU dispersions were synthesized by the polyaddition reaction using an isophorone diisocyanate, poly(tetramethylene oxide) glycol, dimethylol propionic acid, ethylene diamine, triethylamine, and aminoplast. DMPA (5 g) was dissolved in NMP (6 g) in a 4 necked round-bottom flask equipped with a thermometer, a stirrer, an inlet of dry nitrogen, a condenser, and heat jacket. Then PTMG ($M_n = 2,000$ g/mol, 150 g) was placed in the flask and degassed under vacuum at 80 °C for 1 h. IPDI/MEK (12 g/5.6 g) was added slowly under moderate stirring (300 rpm), and the mixture was allowed to react at 80 °C until the theoretical NCO content was reached. Then TEA was added to the reaction mixture for neutralizing the carboxyl groups of the NCO-terminated polyurethane prepolymer. The water dispersion containing HMMM (0.1~6 wt% per solid)/catalyst *p*-TSA (0.5 wt% per solid) prepared by treating with ultrasonic for 30 min at a room temperature was added into the reaction mixture of polyurethane prepolymers. The polyurethane prepolymer in the reaction mixture was chain-extended by dropping chain extender EDA at 40 °C for 1 h and then the reaction continued until NCO absorption IR peak (2,270 cm^{-1}) had completely disappeared. Finally the methyl ethyl ketone was removed under vacuum to obtain crosslinkable WBPU aqueous dispersion. The feed molar compositions of the WBPU and crosslinkable WBPU dispersions are given in Table 1.

Preparation of Film Samples

Crosslinkable WBPU dispersions were casted on a Teflon disk to make films. Drying was done at 50 °C for 30 min and 60 °C for 60 min, and then the formed films were cured at 80 °C~150 °C for 0~30 min. The three kinds of the cured WBPU films were put at 60 °C and 20 mmHg for 2 days to remove the condensates for ensuring crosslinking reaction. The properties of crosslinked samples were compared to those of the pure WBPU sample. The pure WBPU film was

dried at 50 °C for 1 day, and then the remaining moisture was removed at 60 °C under 20 mmHg for 2 days. The thickness of the films obtained in this study was about 0.1~0.3 mm.

Characterization

The particle size of the crosslinkable WBPU dispersions was determined using a laser-scattering equipment (light source He-Ne (633 nm) cw, Autosizer, Melvern IIC, USA). To measure the water swelling of the WBPU samples, the films were immersed in water at a room temperature for 48 h and the percentage of swelling was determined by measuring the weight change;

$$\text{Swelling (\%)} = (W - W_0)/W_0 \times 100 \quad (1)$$

where W_0 is the weight of dried film and W is the weight of the swelled film. FT-IR spectra of both pure and crosslinked samples were recorded in the range of 4000~500 cm^{-1} using a FT-IR spectrometer (Impact 400D, Nicolet, Madison, WI) by the KBr disk method at the resolution of 4 cm^{-1} for 32 scans. XPS spectra were measured by an ESCA 250 X-ray photoelectron spectroscopy (UK), using an Al K (1486.6 eV). The thermal dynamic mechanical behavior of the pure WBPU and crosslinked WBPU was measured at 4 Hz using a DMTA (DMTA MK III, Rheometrics Scientific Inc., USA) with the heating rate of 3 °C/min. The dimension of film sample was 5 × 5 × 0.2 (mm) for DMTA measurement. The thermal behavior of the crosslinked WBPU samples was examined using a DSC 220C (Seiko, Japan) at the heating rate of 10 °C/min under a nitrogen atmosphere. Thermal gravimetric analysis of about 5 mg of the crosslinked WBPU samples were made with TGA (Pyris 6 TGA, Perkin Elmer) under nitrogen atmosphere at the heating rate of 10 °C/min from 30 °C to 550 °C. The mechanical measurements were made in simple extension on dumbbell specimens using a tensile tester (Tinius Olsen 1000, USA) at a crosshead speed of 20 mm/min according to ASTM D-412. Adhesion property was measured at a room temperature using a United Data System Tension Meter (SSTM-1 United Data System, Instron, Japan) according to the ASTM D-1876-01 (the peel resistance of adhesives, i.e., the T-peel test). For adhesion test, the crosslinkable WBPU dispersions containing thickener (L75N, 1 wt%) were coated on Nylon fabrics and another Nylon

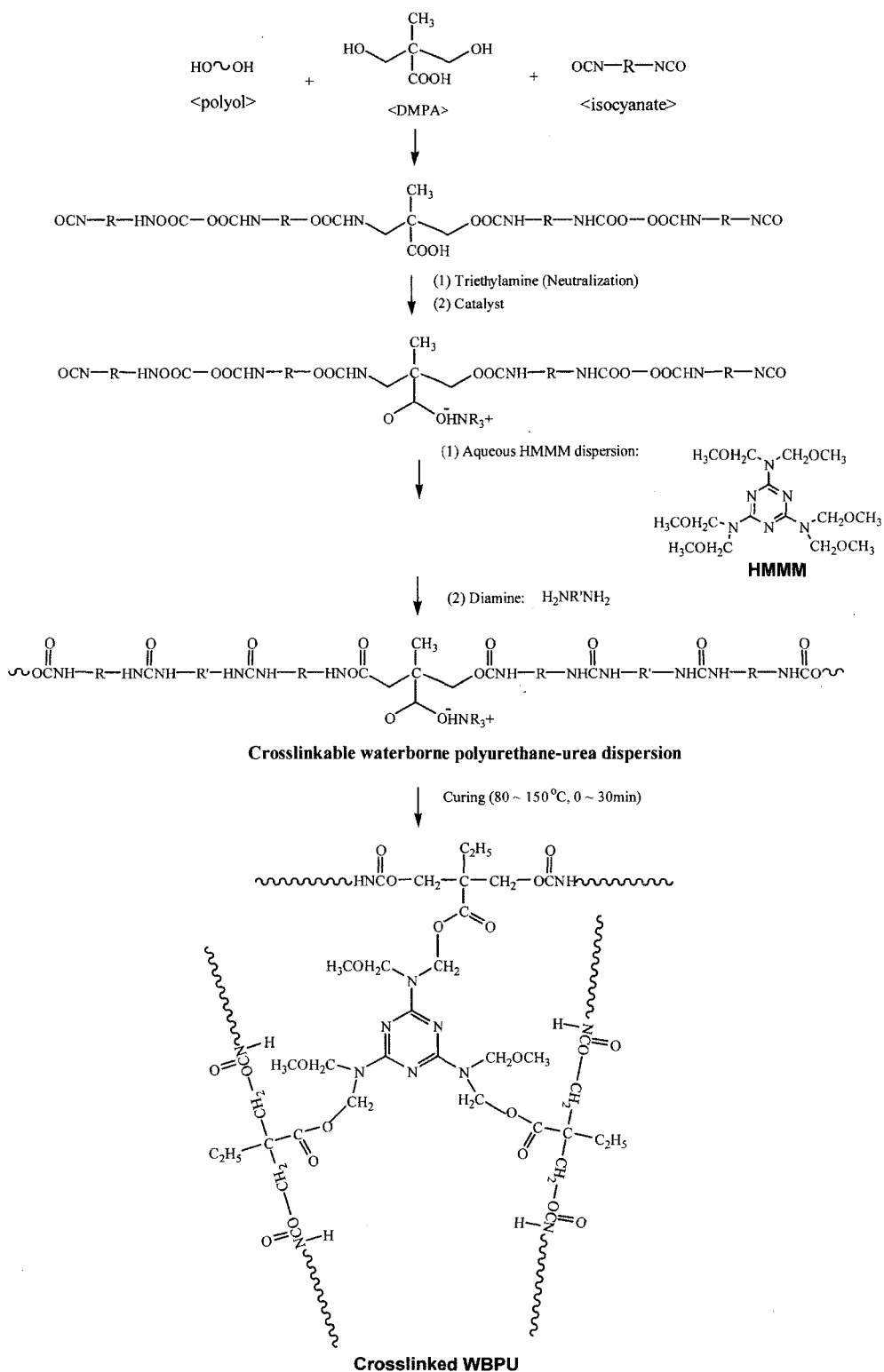
Table 1. Composition of pure waterborne-polyurethane (WBPU) dispersion and crosslinkable WBPU dispersions containing HMMM

Specimens	Composition (mole)					Catalyst		Solid content (wt%)	
	IPDI	PTMG ($M_n = 2,000$)	DMPA	EDA	TEA	HMMM (mole)	HMMM (wt%)		<i>p</i> -TSA (wt%)
WBPU						0.0000	0		30
WBPU2*	2.5	1.0	0.5	1.0	0.5	0.0108	2	0.5	
WBPU4*						0.0215	4		
WBPU6*						0.0323	6		

*Numbers indicate the HMMM content (wt%).

fabrics were laid on the coated surface and then cured at various temperatures for 15 min under 15 kgf/cm² pressure.

The values of the mechanical and adhesion properties are quoted the average value of ten tests.



Scheme 1. Preparation of crosslinkable waterborne-polyurethane dispersion by an in-situ process and crosslinking reaction of WBPU and HMMM.

Results and Discussion

Particle Size and Water Swelling

The composition of the pure and crosslinkable WBPU having various HMMM contents (2, 4 and 6 wt%) are shown in Table 1. The WBPU dispersions prepared in this study contained 20 mole% ionic component DMPA. Generally, ionic groups need to stabilize the dispersed phase in the presence of water, while they associated in polymers in the solid state acted as a physical crosslinker and improve mechanical properties. Smaller particle sizes are obtained by increasing the hydrophilicity of the WBPU [9], however, the dried films are generally water sensitive due to the presence of ionic groups. In order to improve their properties such as chemical resistance and mechanical properties, the WBPU must be crosslinked. In this study, the HMMM was used as a crosslinker to improve properties of the WBPU. The crosslinking reaction of the WBPU and HMMM are shown in Scheme 1. Figure 1 shows the particle size of the pure WBPU and crosslinkable WBPU dispersions and the water swelling of the crosslinked WBPU films cured at different temperature (100, 120, 150 °C) vs. HMMM content. Larger particles are preferred in surface coating for rapid drying and smaller ones are desirable when the deep penetration of dispersion into a substrate is essential [10]. It was found that the crosslinkable WBPU dispersions prepared here by in-situ polymerization have small particle sizes, which is due to the high content of hydrophilic component DMPA (20 mole%). The particle size increased a little with increasing HMMM content, indicating the inclusion of HMMM in the WBPU particles during in-situ polymerization process [8]. The water swelling of the all WBPU film samples cured at 100, 120 and 150 °C for 15 min under 15 kgf/cm² pressure

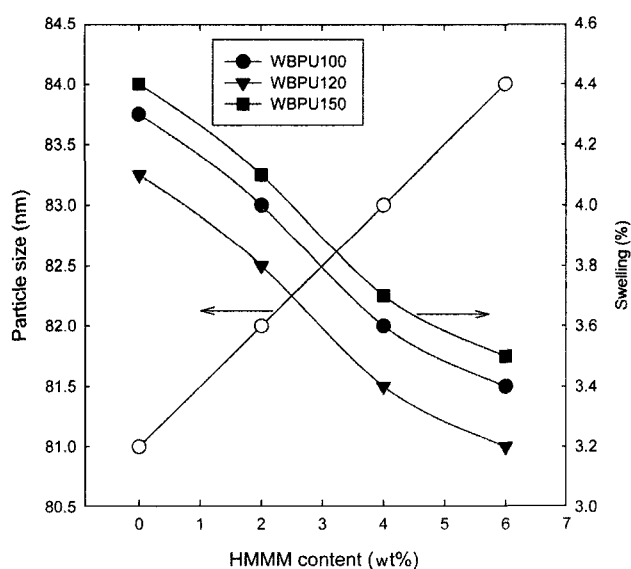


Figure 1. Particle size of WBPU dispersion and water swelling (%) of crosslinked WBPU films cured at 100 °C, 120 °C, and 150 °C as a function of HMMM content.

decreased with increasing HMMM content. This might be due to the increase of crosslinking reaction resulting in the increased crosslinking density of the WBPU chain. However, the WBPU-120 samples cured at 120 °C have the lower water swelling% compared to the other samples cured at 100 and 150 °C.

Identification of Crosslinked WBPU

The FT-IR spectra of the pure WBPU film and a typical crosslinked sample WBPU4-100 films containing 4 wt% of HMMM cured at 100 °C for 15 min are shown in Figure 2. The absorption bands of carbonyl stretching vibrations and hydrogen bonded/free N-H stretching vibration for both pure WBPU and WBPU4-100 films were appeared at 1750~1670 cm⁻¹ and 3600~3100 cm⁻¹, respectively [11]. Especially, in case of the crosslinked sample WBPU4-100, the absorption bands corresponding to the aromatic structure of the HMMM appeared at 1500 cm⁻¹ and 815 cm⁻¹, whereas the strong absorptions at 1240 cm⁻¹ and 1200 cm⁻¹ revealed the formed O=C=O linkages. The characteristic band at near 815 cm⁻¹ was assigned to the absorption band of the triazine ring out-of-plane deformation vibration of the HMMM [12,13]. The aminoplast HMMM component and crosslinking reaction of the crosslinked WBPU samples were identified by these characteristic peaks.

Effects of Curing Condition on the Properties

Adhesion property was measured at a room temperature according to the ASTM D-1876-01 (the peel resistance of adhesives, i.e., the T-peel test). In our earlier study [14], the optimum pressure of the pure WBPU sample was found to be 15 kgf/cm². Therefore, in this study, the applied pressure for curing was fixed at 15 kgf/cm². And we found that the optimum curing temperature of the WBPU adhesives containing various DMPA contents without HMMM decreased

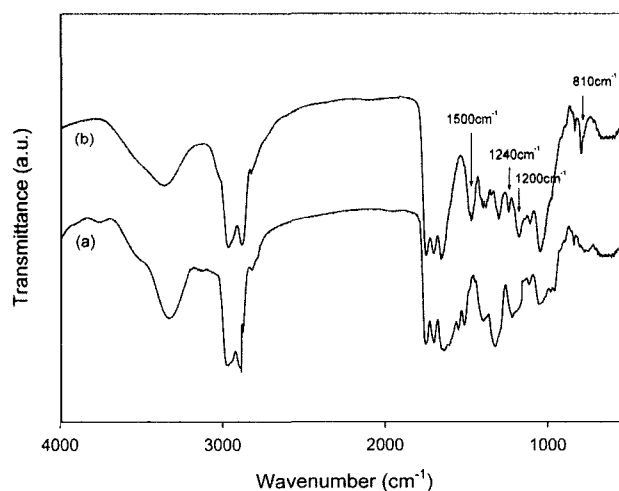


Figure 2. FT-IR spectra of (a) pure WBPU film and (b) crosslinked WBPU4-100 samples.

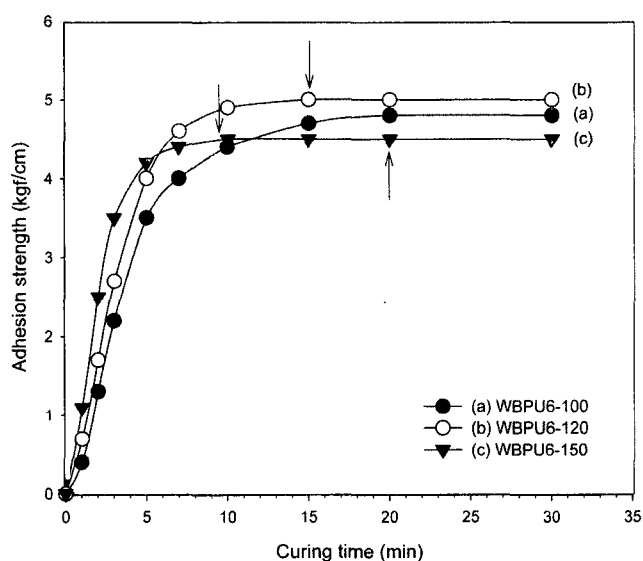


Figure 3. Effect of curing time on adhesive strength of crosslinked WBPU6 samples cured at different temperature (100 °C, 120 °C, and 150 °C); (a) WBPU6-100, (b) WBPU6-120, and (c) WBPU6-150 films.

with increasing the DMPA content, and their adhesive strength and mechanical properties increased with increasing the DMPA content. This indicated that the higher content of ionic groups was, in the formation of ionic and hydrogen bonds, the lower thermal energy got. It was speculated that these optimum points were the most favorable temperatures which were depended on the DMPA content. From this result, we can infer that the optimum temperature will contribute to improve the crosslinking reaction of the carboxylic groups in WBPU and the methoxy groups in HMMM molecules in this study. The effect of the curing time on the adhesive strength of the typical HMMM (6 wt%) contained samples WBPU6 cured at various temperatures under pressure 15 kgf/cm² is shown in Figure 3. As the curing time increased, the adhesive strengths of the typical samples WBPU6-100, WBPU6-120 and WBPU6-150 cured at 100, 120 and 150 °C increased rapidly up to about 7, 10 and 15 min, respectively, and then leveled off. The initial curing rate (initial slope) increased with increasing the curing temperature. However, the WBPU6-120 sample cured at 120 °C showed the highest adhesive strength at the leveled off point. To investigate the effects of the curing temperature and HMMM content on the properties of the adhesive and films, the curing time was fixed at 15 min in this study.

Figure 4 shows the effect of the curing temperature on the adhesive strengths of the crosslinked WBPUs having various HMMM contents (0~6 wt%). The adhesive strength increased with increasing the curing temperature up to near 120 °C, and then decreased sharply. The adhesive strength increased with increasing the HMMM content. From this result, the optimum curing temperature of the crosslinkable WBPUs

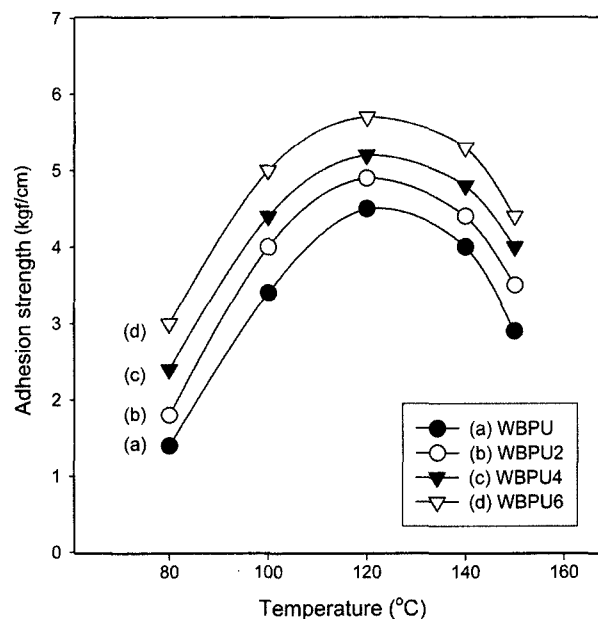


Figure 4. Effect of curing temperature on adhesive strength of crosslinked WBPU films with various HMMM content; (a) WBPU, (b) WBPU2, (c) WBPU4, and (d) WBPU6 films.

prepared in this study was found to be near 120 °C, which was not depended on the HMMM content. It was also found that the breaking was not occurred on the interface of fabrics/adhesive layer but occurred in adhesive layer itself. This indicates that the strength of solid WBPU is more important factor than the attraction force between fabric and adhesive.

The effect of the curing temperature on the tensile strength

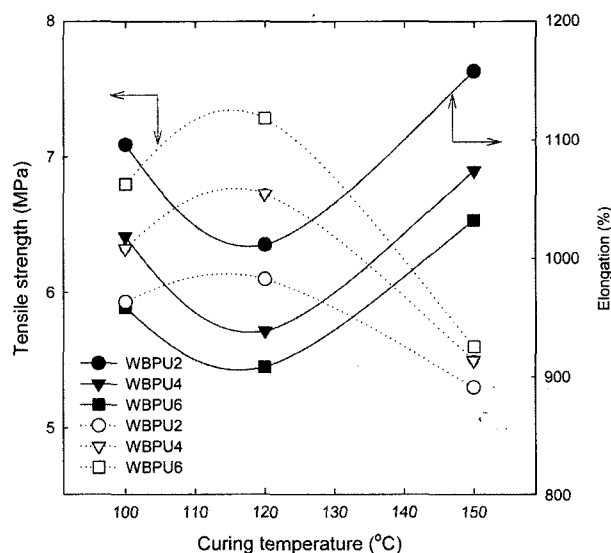


Figure 5. Tensile strength and elongation at break of crosslinked WBPU films with different HMMM content as a function of curing temperature.

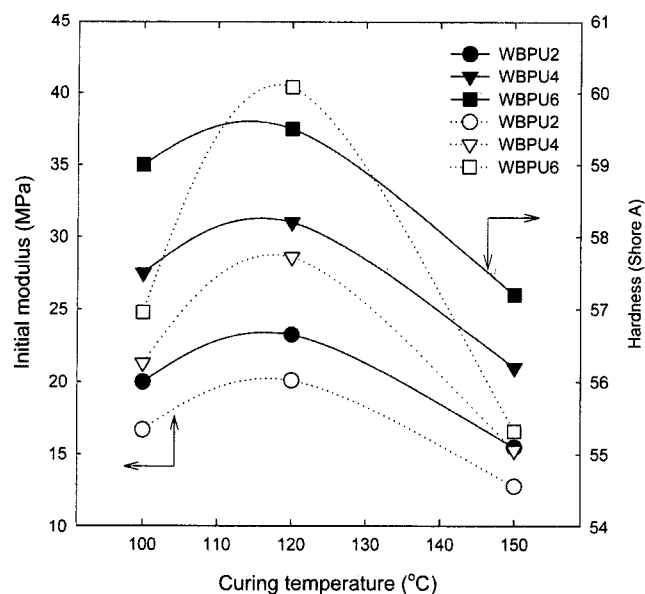


Figure 6. Initial modulus and hardness of crosslinked WBPU films with various HMMM content as a function of curing temperature.

of the crosslinked WBPU films samples having various HMMM contents is shown in Figure 5. It was found that the initial modulus, tensile strength, and elongation at break of the pure WBPU film were 10.1 Mpa, 5.9 Mpa, and 1280 %, respectively. It was found that the higher the HMMM content produced the higher tensile strength and the lower elongation. The tensile strength and tensile initial modulus (see Figure 6) of the samples also increased with increasing the curing temperature up to 120°C, and then decreased markedly. However, the elongation at break decreased with increasing the curing temperature up to 120°C, and then increased sharply.

Generally, the hardness reflects the resistance to local deformation and is related to the crosslinking density of the matrix [15]. The hardness of film samples showed the same trend as the tensile strength changes according with the curing temperature and HMMM content (see Figure 6). From these results, it was concluded that the optimum curing temperature of the WBPU sample containing 20 mole% DMPA prepared in this study was near 120°C. It was also found that the optimum curing temperature was independent on the HMMM content.

X-ray Photoelectron Spectroscopy Analysis

Figure 7 shows the XPS C1s and O1s core-level spectra of the pure WBPU, WBPU6-100, WBPU6-120, and WBPU6-150 films. The C1s core-level spectra have been resolved into three component peaks; the sharp peak near at 285 eV assigned to a hydrocarbon environment (C-C bond), the peak near at 287 eV assigned to a carbon singly bound to oxygen environment (C-O bond) formed by crosslinking reaction, and the broad peak near at 290 eV assigned to a carbon double bond to oxygen environment (C=O bond),

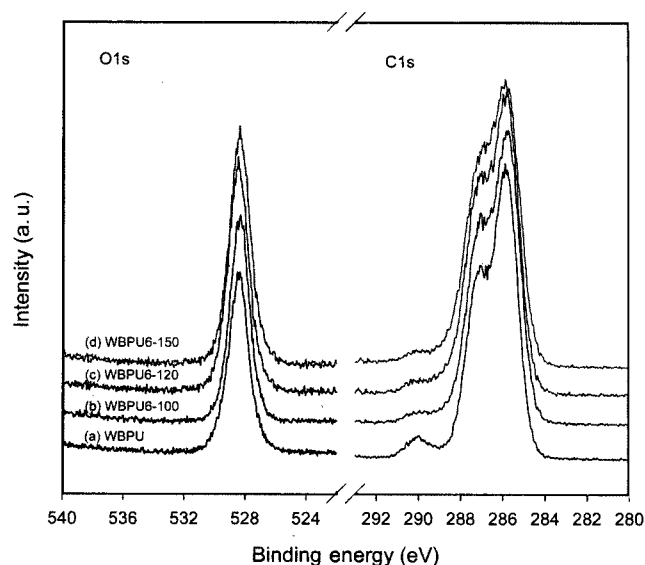


Figure 7. XPS C1s and O1s core-level scan spectra of (a) WBPU, typical samples, (b) WBPU6-100, (c) WBPU6-120, and (d) WBPU6-150.

respectively. The XPS O1s spectrum of the WBPU film shows a peak near at 527–530 eV correspond to the -C-O-, ether-type group with oxygen singly bonded to carbon and the -C=O, carbonyl-type group with oxygen doubly bonded to carbon. The curve fitting of C1s for the pure WBPU, typical crosslinked WBPU6-100, WBPU6-120, and WBPU6-150 samples is shown in Figure 8. Three peaks obtained from curve fitting indicated a carbon of hydrocarbon (C-C), a carbon singly bond to oxygen (C-O), and a carbon double bond to oxygen (C=O), respectively. The values of C, O, N and C-O/(C=O) + (C-C) obtained from curve fitting area are given in Table 2. The sample WBPU6-120 also had the highest values of N content and C-O/(C=O) + (C-C), indicating that the optimum curing temperature was near 120°C for the crosslinking reaction.

Dynamic Mechanical Thermal Properties

Significant information about molecular motions of a WBPU chains can be obtained through the use of a dynamic mechanical thermal analysis (DMTA). The temperature dependences of the dynamic storage modulus (E') and loss $\tan\delta$ for the three kinds of WBPU samples cured at 100, 120 and 150°C are shown in Figure 9 and Figure 10, respectively. E' of all samples increased with increasing the HMMM content, which was due to the increasing of crosslinking density in the WBPU chain. However, the E' values of the WBPU-120 films cured at 120°C were higher than those of the other samples at the same HMMM content. This also indicates that the optimum curing temperature is about 120°C to improve the crosslinking reaction of the WBPU samples containing 20 mole% DMPA content.

The pure WBPU had two $\tan\delta$ peaks near -58°C and

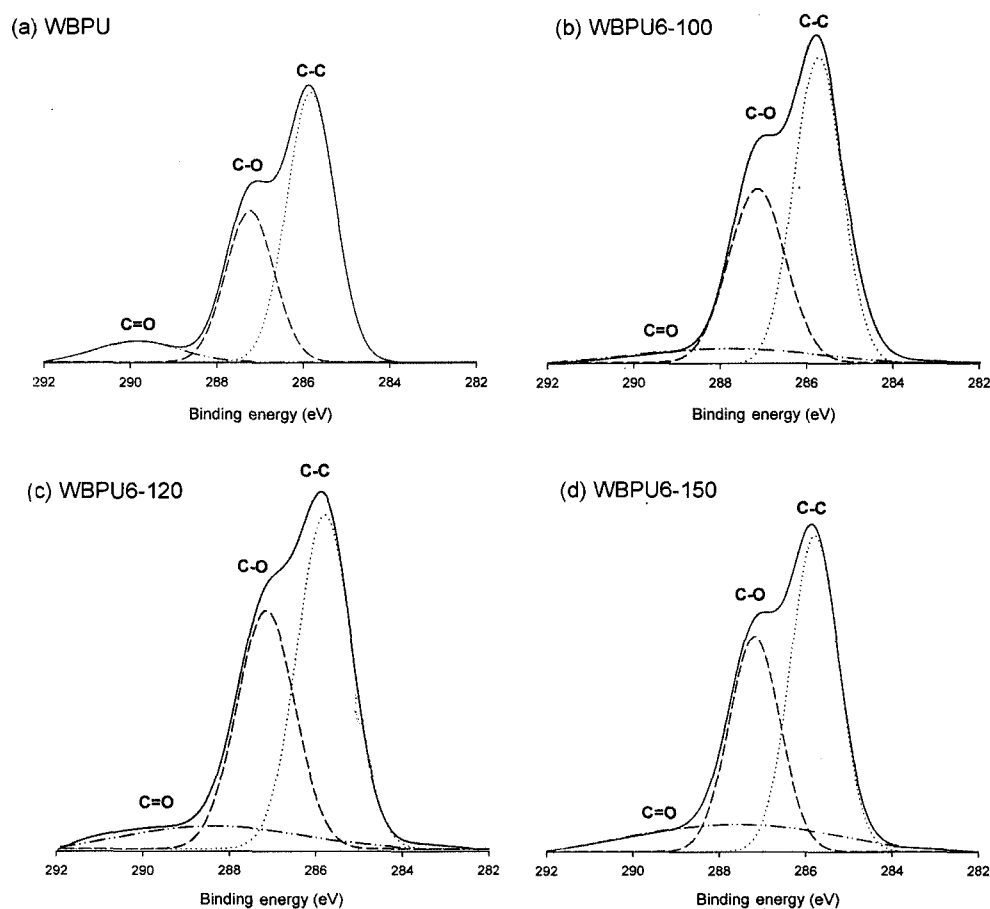


Figure 8. Curve fitting of XPS C1s core-level spectra of (a) pure WBPU and typical samples, (b) WBPU6-100, (c) WBPU6-120, and (d) WBPU6-150.

Table 2. XPS results and thermal properties of WBPU and WBPU films crosslinked at various curing temperatures

Specimens	Atomic%			C-O/(C=O) +(C-C)	T_{gs} (°C)	T_{gh} (°C)	T_m (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	Residue at 550 °C (wt%)
	C	O	N							
WBPU	75.1	20.8	4.1	0.47	-58.0	8.7	208.3	323.8	415.1	2.6
WBPU2-100*	-	-	-	-	-53.8	57.0	215.2	329.3	424.7	3.6
WBPU4-100	-	-	-	-	-51.9	62.0	224.5	340.2	438.4	4.8
WBPU6-100	76.8	18.2	5.0	0.57	-48.7	63.0	229.7	349.8	455.5	11.0
WBPU2-120	-	-	-	-	-48.0	67.4	218.7	331.5	427.2	3.8
WBPU4-120	-	-	-	-	-46.2	70.6	227.4	351.1	450.7	5.9
WBPU6-120	77.1	17.6	5.3	0.59	-45.5	73.1	238.8	359.3	472.7	14.1
WBPU2-150	-	-	-	-	-54.7	41.0	210.0	326.7	416.3	6.0
WBPU4-150	-	-	-	-	-52.2	48.1	221.8	332.1	417.4	9.6
WBPU6-150	76.3	18.9	4.8	0.55	-50.8	50.5	223.9	337.5	426.0	11.9

*Numbers (100, 120, and 150) of specimens are curing temperatures, respectively.

8.7°C assigned to the glass-transition temperatures (T_{gs} and T_{gh}) of the soft segments and hard segments, respectively. In general, their difference, the ΔT_g ($T_{gh} - T_{gs}$), was related to the extent of phase separation in the amorphous region. The T_{gs} and T_{gh} of the WBPU, WBPU-100, WBPU-120, and

WBPU-150 samples are given in Table 2. With increasing the HMMM content, the T_{gs} of all samples shifted to higher temperature. This behavior could be probably attributed to the restriction of chain mobility of the soft segments by the crosslinking. The T_{gh} of the all samples also increased signifi-

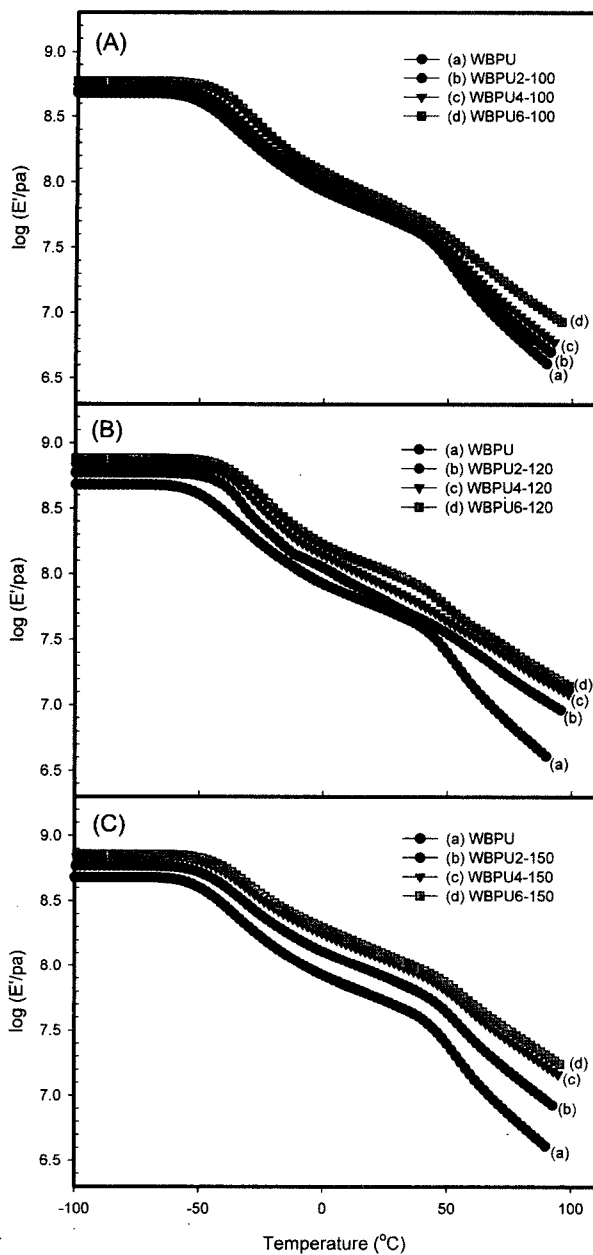


Figure 9. Storage (E') modulus of the crosslinked WBPU having various HMMM content with various curing temperatures; (A) (a) WBPU, (b) WBPU2-100, (c) WBPU4-100, (d) WBPU6-100; (B) (a) WBPU, (b) WBPU2-120, (c) WBPU4-120, (d) WBPU6-120; (C) (a) WBPU, (b) WBPU2-150, (c) WBPU4-150, (d) WBPU6-150 samples.

cantly with increasing the HMMM content. The increase of the T_{gh} might be caused by the increased cross-linking density which resulting in decreased mobility of hard segment of the WBPU chain. ΔT_g of the WBPU-100, WBPU-120, and WBPU-150 samples also increased with increasing the HMMM content, but the ΔT_g of the WBPU-120 samples were a little higher than those of the other samples at the same HMMM

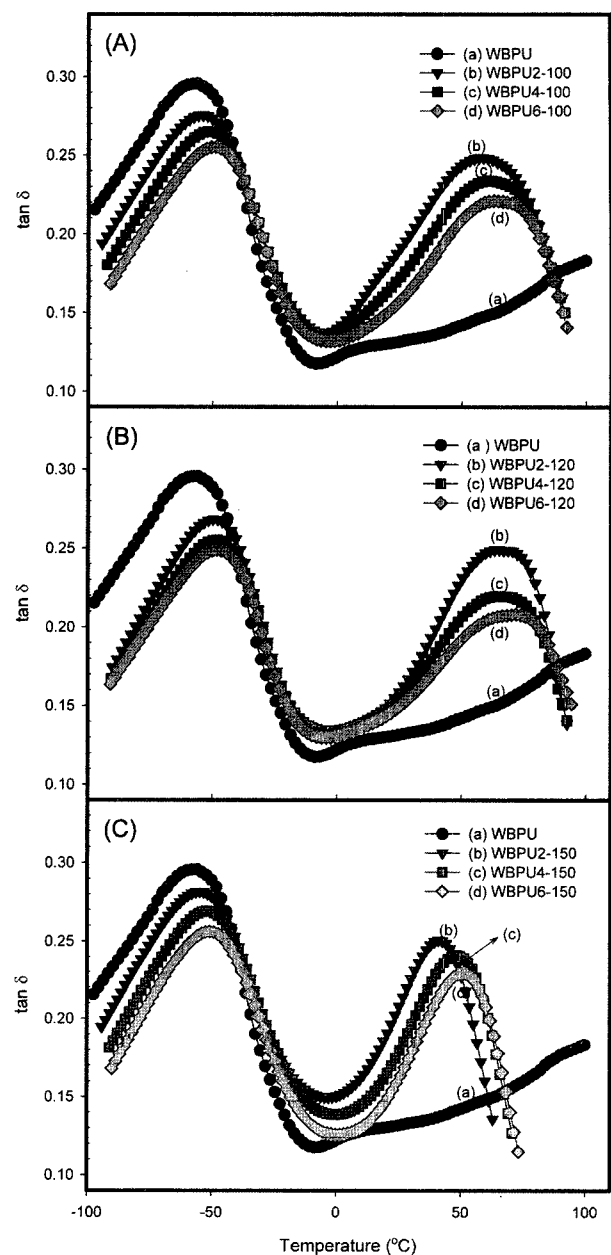


Figure 10. $\tan\delta$ peaks of the crosslinked WBPU having various HMMM contents with various cure temperatures; (A) (a) WBPU, (b) WBPU2-100, (c) WBPU4-100, (d) WBPU6-100; (B) (a) WBPU, (b) WBPU2-120, (c) WBPU4-120, (d) WBPU6-120; (C) (a) WBPU, (b) WBPU2-150, (c) WBPU4-150, (d) WBPU6-150 samples.

content. With increasing the HMMM content, the decreases of the $\tan\delta$ peaks intensities of the all samples were obtained indicating the decrease of amorphous region of the WBPU. The peak intensity drop of the WBPU-120 sample was found to be higher than those of the WBPU-100 and WBPU-150 sample. From these results, it is concluded that the temperature 120°C is the best condition for the crosslinking

reaction of WBPU/HMMM and the formation of dense structure of the polymer WBPU.

Thermal Properties

Figure 11 shows the DSC thermograms of the pure WBPU film and typical crosslinked WBPU-100, WBPU-120, and WBPU-150 samples, respectively. A broad endothermic peak corresponding to melting temperature (T_m) of the pure

WBPU was appeared at around 208 °C~240 °C. The T_m of all samples shifted to higher temperature as the HMMM content increased. This might be due to the rigidity of HMMM component reacted to hard segment component DMPA in WBPU chains. The increase of the T_m of the WBPU-120 sample was higher than those of the WBPU-100 and WBPU-150 samples at the same HMMM content. This is possibly attributed to the higher crosslinking density of the WBPU-120 samples

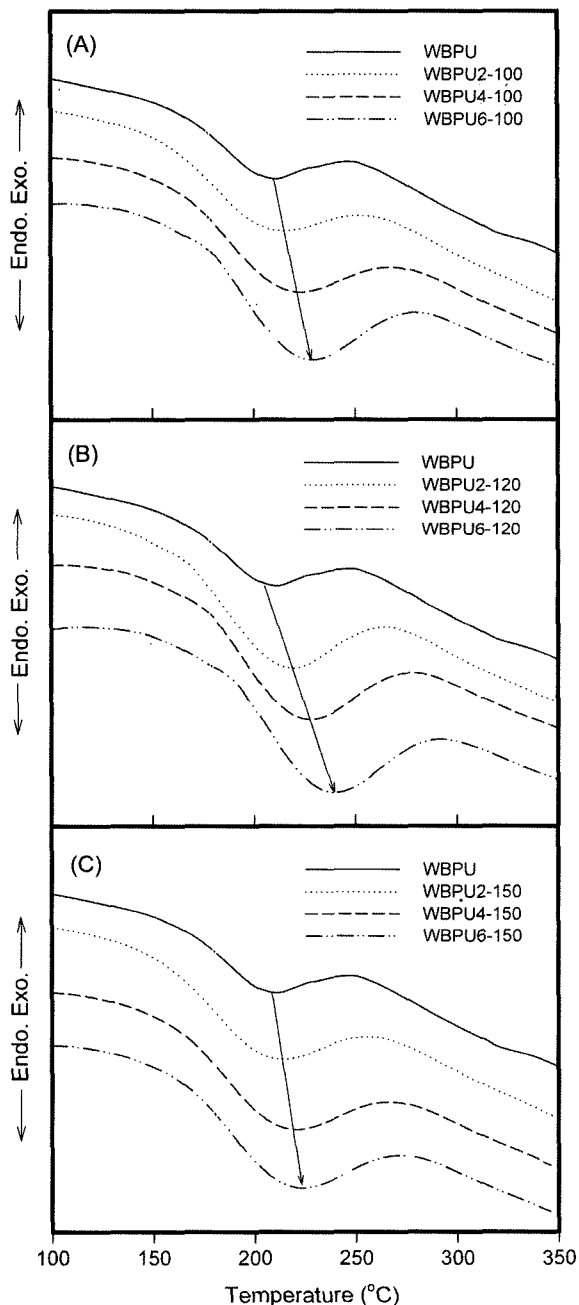


Figure 11. DSC thermograms of crosslinked WBPU films cured at various temperatures; (A) WBPU-100, (B) WBPU-120, and (C) WBPU-150.

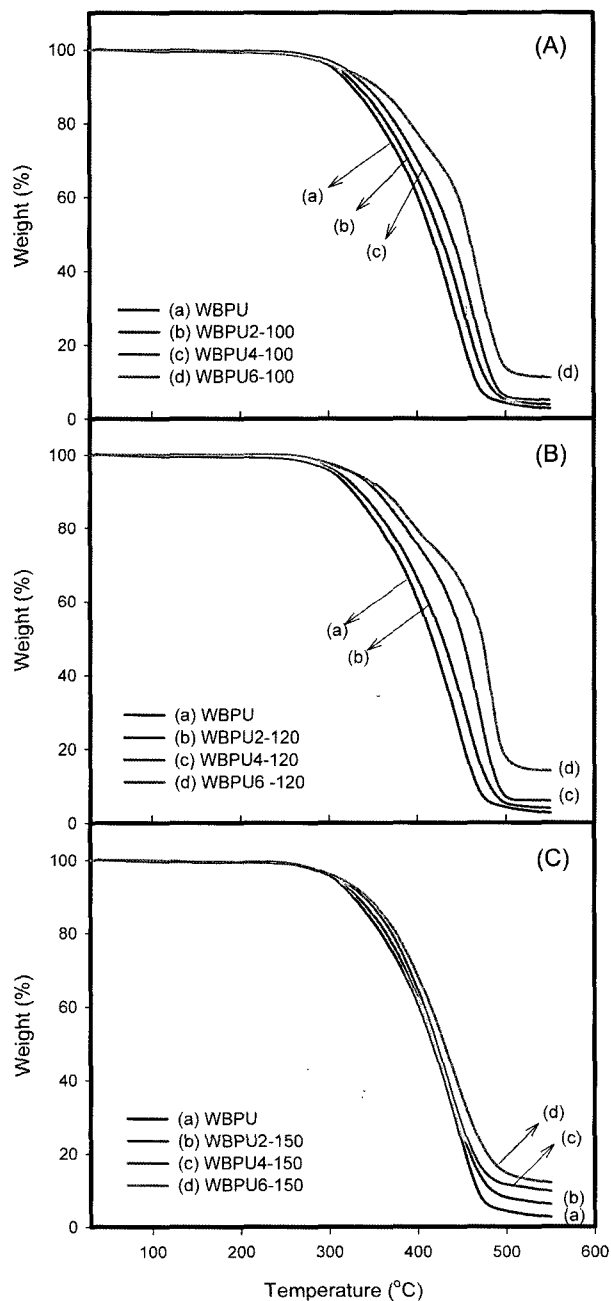


Figure 12. TG thermograms of crosslinked WBPU films cured at various temperatures; (A) WBPU-100, (B) WBPU-120, and (C) WBPU-150.

cured at 120 °C than the other samples.

Figure 12 shows the TGA curves for the WBPU, WBPU-100, WBPU-120, and WBPU-150 samples, respectively. The TGA results for the all samples are summarized in Table 2. The first stage of the degradation of a PU is mainly a reaction of polymerization [16]. This depolymerization starts generally between 200 and 250 °C, and corresponds to the failure of urethane links, which leads to the release of a polyol and isocyanate. The monomers then slowly volatilize, and there is a profusion of secondary reactions (urea formation) and rearrangements. The crosslinked WBPU samples present a similar thermal decomposition behavior with pure WBPU, but they are more thermally stable. Appreciable weight loss of all samples was not observed at temperatures below 250 °C. The $T_{10\%}$ and $T_{50\%}$ (10 % and 50 % weight loss temperatures) of all samples increased significantly with increasing the HMMM content, but the WBPU-120 sample has the highest values. This result also might be due to the higher crosslinking density of the WBPU-120 cured at 120 °C compared to the WBPU-100 and WBPU-150 samples at the same HMMM content. From these results, it is also concluded that the optimum curing temperature is near 120 °C regardless of being with various HMMM contents. The reason why the optimum curing temperature fixes regardless of being with various HMMM contents is not clear at the present moment. More detailed studies should be made.

Conclusions

The crosslinkable WBPU dispersions containing 20 mole% DMPA was synthesized by an in-situ polymerization from IPDI/PTMG/DMPA/EDA/TEA/crosslinker HMMM/catalyst P-TSA. The effects of the HMMM content (0~6 wt%) and curing temperatures on the thermal properties, dynamic mechanical thermal property, mechanical property, water swelling, hardness and adhesive strength of the WBPUs (WBPU-100, WBPU-120, and WBPU-150) cured at different temperatures (100 °C, 120 °C and 150 °C) were investigated. With increasing the HMMM content, the increases of N content and C-O/(C=O) + (C-C) of the all cured WBPU samples were observed indicating the increase of crosslinking reaction between the carboxylic groups in WBPU and the methoxy groups in the HMMM molecule. It was found that these values of the WBPU-120 sample cured at 120 °C were higher than those of the other samples (WBPU-100 and WBPU-150). It has been shown that the thermo-mechanical properties, thermal stability, water swelling and mechanical property of the all crosslinked WBPU samples were affected by the HMMM content and curing temperature. The E' , T_{gs} , T_{gh} , T_m , tensile strength, initial modulus, water swelling, hardness of the WBPU-100, WBPU-120, and WBPU-150

samples increased with increasing the HMMM content. However, these all properties of the crosslinked WBPU-120 samples cured at 120 °C were higher than those of the other samples cured at 100 and 150 °C at the same HMMM content. From these results, the optimum curing temperature for the crosslinkable WBPU containing 20 mole% DMPA content was found to be near 120 °C regardless of being with various HMMM contents.

Acknowledgement

This work was financially supported by Pusan National University in program. Post-Doc. 2005.

References

1. W. H. Chang and M. E. Harman, *U. S. Patent*, 5401576 (1975).
2. W. H. Chang and M. E. Hartman, *U. S. Patent*, 3954899 (1976).
3. W. H. Chang and M. E. Harman, *U. S. Patent*, 3962521 (1976).
4. S. Porter, W. H. Chang, J. R. Dywer, and K. W. Lee, *U. S. Patent*, 4410667 (1983).
5. W. Otterbein and G. Pollano, *Modern Paint and Coatings*, March, 32 (1995).
6. B. Eling in "Polyurethane Technology & Applications", (S. Lee, Ed.), Chap. 25, pp.379-383, Huntsman International, Everberg, Belgium, 2002.
7. W. J. Blank and W. Hensley, *J. Paint Technol.*, **46**, 593 (1974).
8. J. Y. Kwon and H. D. Kim, *Macromolecular Research*, submitted (2006).
9. W. Chen, K. C. Krisch, D. J. Kenney, and S. J. M. S. Wong, *Polymer*, **29**, 567 (1992).
10. Y. S. Kwak, E. Y. Kim, H. D. Kim, and J. B. Lee, *Colloid Polym. Sci.*, **283**, 880 (2005).
11. J. Muszynski, A. W. Grabczyk, and P. Penczek, *J. Appl. Polym. Sci.*, **71**, 1615 (1999).
12. L. V. Daimay, N. B. Colthup, W. G. Fateley, and J. G. Grasselli, "The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules", pp.299-301, Academic Press, Boston, 1991.
13. P. J. Larkin, M. P. Makowski, N. B. Colthup, and L. A. Flood, *Vibrational Spectroscopy*, **17**, 53 (1998).
14. R. M. Mizanur and H. D. Kim, *J. Appl. Polym. Sci.*, accepted (2006).
15. L. Valentini, I. Armentano, J. Biagiotti, A. Marigo, S. Snatucci, and J. M. Kenny, *Diamond and Related Materials*, **13**, 250 (2004).
16. J. H. Saunders, *Rubber Chem. Technol.*, **32**, 337 (1959).