

## Preparation and Properties of Crosslinkable Waterborne Polyurethanes Containing Aminoplast(I)

Ji Yun Kwon and Han Do Kim\*

Department of Textile Engineering, Pusan National University, Busan 609-735, Korea

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**Abstract:** A series of crosslinkable, waterborne polyurethanes (I-WBPUs) were prepared by in-situ polymerization using isophorone diisocyanate (IPDI)/poly(tetramethylene oxide) glycol (PTMG,  $M_n=2,000$ )/ dimethylol propionic acid (DMPA)/ethylene diamine (EDA)/triethylamine (TEA)/aminoplast [hexakis(methoxymethyl)melamine (HMMM)] as a crosslinking agent. Typical crosslinkable, waterborne polyurethanes (B-WBPUs) blended from WBPU dispersion and aqueous HMMM solution was also prepared to compare with the I-WBPUs. The crosslinking reaction between WBPU and HMMM was verified using FTIR and XPS analysis. The effect of the HMMM contents on the dynamic mechanical thermal, thermal, mechanical, and adhesion properties of the I-WBPU and B-WBPU films were investigated. The storage modulus ( $E'$ ), glass transition temperatures of the soft segment ( $T_{gs}$ ) and the amorphous regions of higher order ( $T_{gh}$ ), melting temperature ( $T_m$ ), integral procedural decomposition temperature (IPDT), residual weight,  $T_{10\%}$  and  $T_{50\%}$  (the temperature where 10 and 50% weight loss occurred), tensile strength, initial modulus, hardness, and adhesive strength of both I-WBPU and B-WBPU systems increased with increasing HMMM content. However, these properties of the I-WBPU system were higher than those of the B-WBPU system at the same HMMM content. These results confirmed the in-situ polymerization used in this study to be a more effective method to improve the properties of the WBPU materials compared to the simple blending process.

**Keywords:** crosslinking, waterborne-polyurethanes, in-situ polymerization, aminoplast.

### Introduction

Solvent-borne polyurethanes are used in both coatings and adhesives in thermoplastic and crosslinked form, however, they are relatively high in solvent content and do not qualify in low VOC applications.<sup>1-5</sup> The advantages exhibited by waterborne-polyurethanes (WBPUs) include low viscosities, very low VOC content, reduced flammability, less odor, and easy application using conventional equipment.<sup>6-11</sup> However, WBPUs are deficient in chemical resistance, thermal resistance, and mechanical property compared to solvent based PUs because WBPUs are linear thermoplastic polymers with very little gel content which allows resolubility in solvents. Therefore, improving the exterior durability exhibited by WBPUs is a high priority for research and development.<sup>12</sup> Generally, the cross-linkers react with the polymer chains to form chemically cross-linked polymers, which increase the thermal and mechanical properties of the final products and improve the resistance to grease, oil and solvent.<sup>13</sup> Many diverse adhesive applications for which adhesives are used need a range of parameters to meet their

required specification and function with key factors being the degree of crosslinking in the final polymer film and its hardness. Crosslinked WBPUs achieved the high failure temperature due to the formation of chemical crosslinking.<sup>14</sup>

Many different strategies have been pursued in crosslinking of WBPU dispersions, including crosslinking as dispersion before application.<sup>15-18</sup> Crosslinking of WBPUs can be carried out by a variety of mechanisms. One approach is the reaction of the water-dispersible sites such as carboxyl groups on WBPU dispersions with aziridine,<sup>19</sup> carbodiimide,<sup>20</sup> glycidyl compounds<sup>21</sup> or with amino-formaldehyde resin.<sup>22</sup> Other approaches use special crosslinkable sites such as oxime blocked isocyanates,<sup>23</sup> which can be incorporated by partial reaction of isocyanates with the blocking agent and later incorporation into the polymer. Recent research and development in waterborne coatings have been directed towards stabilizing against changes that occur from induced shear and temperature, improving overall performance, and reducing the amount of organic co-solvents that are required.<sup>24</sup>

Especially, the compatibility of methylated aminoplast with water makes them potential candidates for use in waterborne coatings.<sup>3</sup> The highly alkylated aminoplast offered a number of advantages over the conventional amino form-

\*Corresponding Author. E-mail: kimhd@pusan.ac.kr

aldehyde ones. Highly alkylated aminoplast have tendency for crosslinking rather than self-condensation reactions, more functional sites available for crosslinking, high reactivity with hydroxyl, carboxyl or amine groups of the backbone polymer, potential for high crosslink density, and good storage stability.<sup>25</sup> Particularly, the methylated ether of the fully methylated melamine resin, hexakis (methoxymethyl) melamine (HMMM), is reactive with both carboxyl and hydroxyl groups and miscible with water result in yield stable WBPU dispersion.<sup>26,27</sup> Generally, crosslinkable WBPU dispersions were prepared by simple blending WBPU dispersion with crosslinking agent HMMM. However, there is a problem to make a perfect homogeneous blend from WBPU dispersion/aqueous HMMM dispersion by simple blending. Consequently, it is very difficult to expect a perfect homogeneous reaction of WBPU and HMMM on molecular level.

In this study, in order to improve the homogeneity of HMMM in WBPU and reinforcing effect in crosslinked WBPUs, crosslinkable WBPU (I-WBPUs) were prepared by in-situ polymerization from aqueous medium using isophorone diisocyanate (IPDI)/poly(tetramethylene oxide) glycol (PTMG,  $M_n=2,000$ )/dimethylol propionic acid (DMPA)/ethylene diamine (EDA)/ triethylamine (TEA)/aminoplast [hexakis (methoxymethyl) melamine (HMMM)] as a crosslinking agent. Typical crosslinkable waterborne-polyurethanes (B-WBPUs) containing HMMM were also prepared by simple blending method to compare with I-WBPUs. The effects of the HMMM contents on the dynamic mechanical thermal, thermal, mechanical, and adhesion properties of the I-WBPU and B-WBPU 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 in a vacuum oven (100 °C) for at least 5 hrs. Dimethylol propionic acid (DMPA, Aldrich Chemical, WI) was dried in a vacuum oven for 5 hrs at 100 °C. The aminoplast [2,4,6-trisbis(methoxy methyl)-amino]-1,3,5-triazine (HMMM, TCI, Tokyo, Japan) was used without further purification. Amine blocked *p*-toluenesulfonic acid (*p*-TSA, Sigma, Milwaukee, WI) was used as catalyst for condensation reaction of methoxy groups of HMMM and carboxyl acid groups of DMPA without purification.

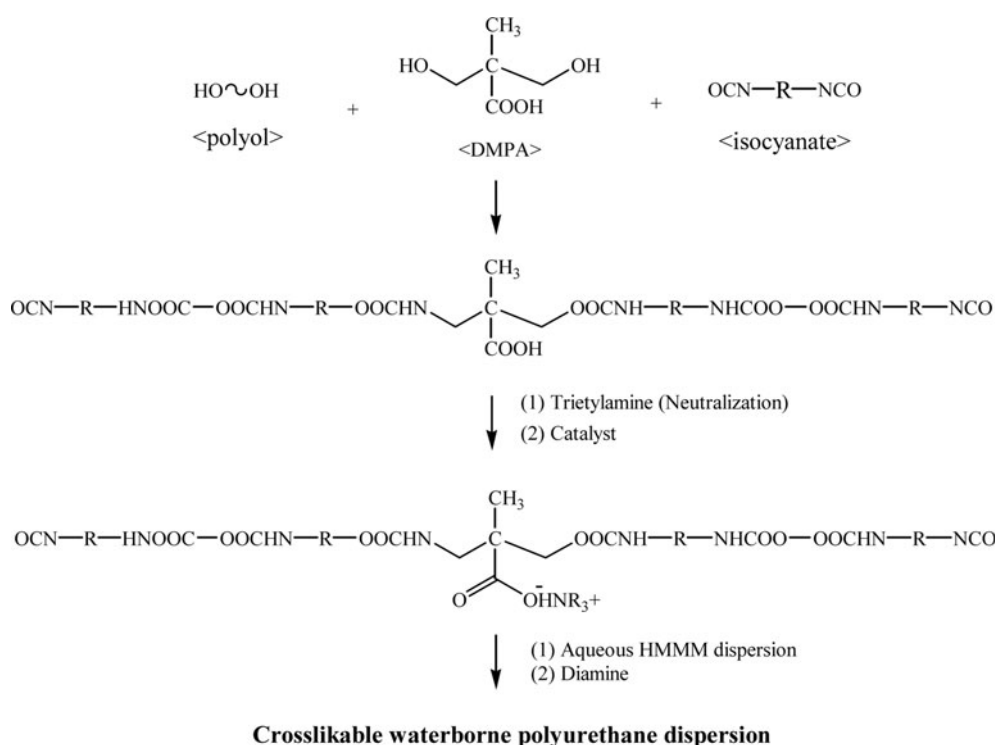
### Preparation of Crosslinkable I-WBPU and B-WBPU

**Dispersions.** Crosslinkable WBPU (I-WBPU) dispersions were synthesized by the polyaddition reaction using 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 hr. 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. The change in the NCO value during the reaction was determined using a standard dibutylamine back-titration method.<sup>28</sup> Upon obtaining the theoretical NCO values, the prepolymers were cooled to 55 °C and a neutralizing solution, i.e. TEA dissolved in MEK (5 wt% based on the total weight), was added and stirred for 1 hr, while maintaining the temperature at 55 °C. 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 room temperature was added into the reaction mixture of polyurethane prepolymers at 55 °C. The polyurethane prepolymer in the reaction mixture was chain-extended by dropping chain extender EDA at 40 °C for 1 hr and then the reaction continued until NCO absorption IR peak (2270  $\text{cm}^{-1}$ ) had completely disappeared. Finally the methyl ethyl ketone was removed under vacuum to obtain the polyurethane anionomer dispersion in water. The in-situ polymerization process for I-WBPU dispersions are shown in Scheme I.

B-WBPUs were prepared by mixing from the WBPU dispersion and aqueous HMMM/*p*-TSA dispersion under magnetic stirring for 30 min, and subsequently, this mixture was treated with ultrasonic vibration for 1 hr at room temperature to enhance the homogeneity of mixture. The feed molar compositions of the WBPU, I-WBPU, and B-WBPU components are given in Table I.

**Preparation of Crosslinked Waterborne-Polyurethane Films.** The crosslinkable WBPU (I-WBPU and B-WBPU) dispersions/thickener (L75N, 1 wt%) 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 formed films were cured at 120 °C for 20 min. Then the cured films were put at 60 °C under 20 mmHg for two days to remove the condensates for ensuring crosslinking reaction. The thickness of the films obtained in this study was about 0.1~0.3 mm.

**Characterization.** The particle size of both crosslinkable WBPU dispersions was determined using laser-scattering equipment (Autosizer, Melvern IIC, USA). FTIR spectrum of both crosslinked WBPU samples were recorded in the range of 4000~500  $\text{cm}^{-1}$  using FTIR spectrometer (Impact 400D, Nicolet, Madison, WI) by KBr pelleting technique at the resolution of 4  $\text{cm}^{-1}$  for 32 scans. XPS spectra were measured by an ESCA 250 X-ray photoelectron spectroscopy

**Scheme I.** Preparation of crosslinkable waterborne-polyurethane (I-WBPU) dispersion by in-situ process.**Table I. Composition of Waterborne-Polyurethane (WBPU), Crosslinkable I-WBPU and B-WBPU Containing HMMM**

Specimens	Composition (mole)					HMMM		Catalyst	Particle Size (nm)	Solid Content (wt%)
	IPDI	PTMG ( $M_n=2,000$ )	DMPA	EDA	TEA	(mole)	(wt%)	<i>p</i> -TSA (wt%)		
WBPU						0.0000	0.0		81	
I-WBPU0.1						0.0005	0.1		81	
I-WBPU0.5						0.0030	0.5		81	
I-WBPU1						0.0050	1.0		82	
I-WBPU2						0.0108	2.0		82	
I-WBPU3	2.5	1.0	0.5	1.0	0.5	0.0162	3.0	0.5	82	30
I-WBPU4						0.0215	4.0		83	
I-WBPU6						0.0323	6.0		84	
B-WBPU2						0.0108	2.0		81	
B-WBPU4						0.0215	4.0		81	
B-WBPU6						0.0323	6.0		81	

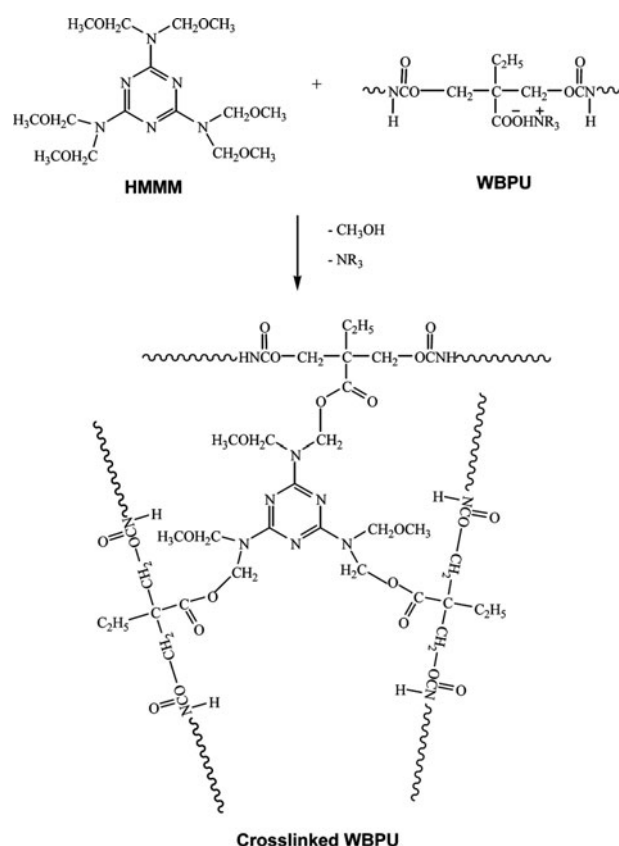
(UK), using Al K (1486.6 eV). The thermal dynamic mechanical behavior of WBPU, I-WBPU, and B-WBPU films was measured at 4 Hz using DMTA (DMTA MK III, Rheometrics Scientific Inc., USA) with the heating rate of 3°C/min. The dimension of film sample was 5 × 5 × 0.2 (mm) for DMTA measurement. The thermal behavior of cross-linked WBPU films was examined using a DSC 220C

(Seiko, Japan) at the heating rate of 10°C/min under a nitrogen atmosphere in the temperature range of 25-350°C. Thermal gravimetric analysis of about 5 mg of both cross-linked WBPU films were made with TGA (Pyris 6 TGA, Perkin Elmer) under nitrogen atmosphere at the heating rate of 10°C/min from 30 to 550°C. The mechanical measurements were made in simple extension on dumbbell speci-

mens 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 room temperature using 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, I-WBPU and B-WBPU adhered materials containing thickener (L75N, 1 wt%) were coated on Nylon fabrics and another Nylon fabrics were laid on the coated surface and then cured at 120°C for 20 min. The values of mechanical and adhesion properties are quoted the average of ten tests.

## Results and Discussion

**Particle Size of Pure WBPU, I-WBPU, and B-WBPU Dispersions.** Crosslinking structure of the WBPU and HMMM was shown in Scheme II. The solid content and particle size of the pure WBPU, I-WBPU, and B-WBPU dispersions used in this study were listed in Table I. Generally, the particle size of the WBPU decreases with increasing hydrophilic component in polyurethane.<sup>29</sup> Larger particles are preferred in surface coating for rapid drying and smaller ones are desirable when the deep penetration of dispersion

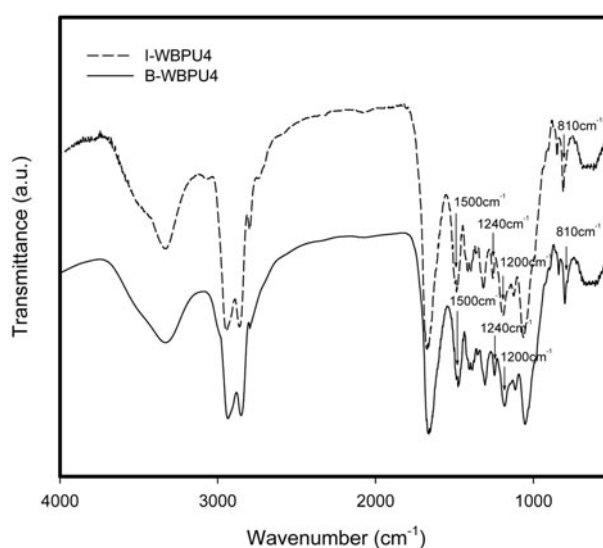


**Scheme II.** Crosslinking of waterborne-polyurethane (WBPU) and HMMM.

into a substrate is essential.<sup>30</sup> The particle size of the I-WBPU dispersions increased a little with increasing the HMMM content at higher HMMM level (above 2 wt%). The increase of particle size of the I-WBPU is possibly attributed to the incorporation of the HMMM into the WBPU particles. From this result, it is speculated that some HMMM in the I-WBPU system are located on both the inner and outer surface of the WBPU particles. However, the particle of the B-WBPU dispersions was the same size as that of the pure WBPU dispersion, indicating the existence of two components particles (WBPU and HMMM particles) separately. This means that the most HMMM are separated from the WBPU particles in the B-WBPU system. From these results, it was found that the I-WBPU system have the higher homogeneous structure consist of the WBPU and HMMM compared to B-WBPU system. It is also supposed that the homogeneousness of the HMMM in WBPU will improve the properties of the WBPU materials.

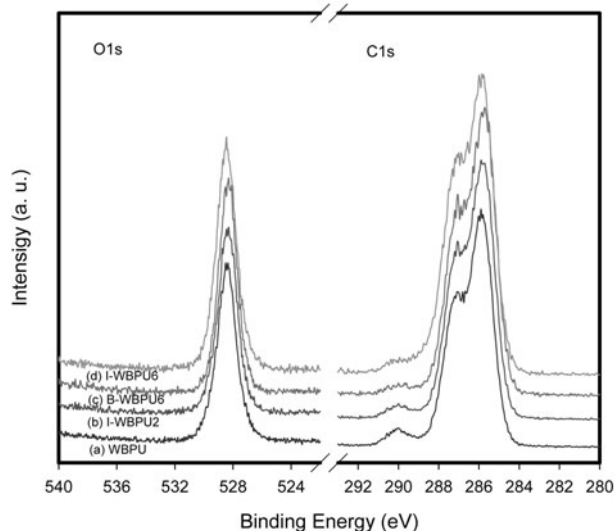
**Identification of Crosslinked WBPU Structure.** Figure 1 shows FTIR spectra of the typical samples I-WBPU4 and B-WBPU4 films containing 4 wt% of HMMM prepared in this study. The absorption bands corresponding to the aromatic structure of the HMMM appeared at 1500 and 815  $\text{cm}^{-1}$ , whereas the formed O-C=O linkages revealed strong absorptions at 1240 and 1200  $\text{cm}^{-1}$ . The characteristic band at near 815  $\text{cm}^{-1}$  was assigned to the absorption band of the triazine ring out-of-plane deformation vibration of HMMM. The aminoplast HMMM component in both I-WBPU and B-WBPU samples were identified by these characteristic peaks, respectively.

Figure 2 shows the XPS C1s and O1s core-level spectra of the WBPU, typical I-WBPU2, I-WBPU6, and B-WBPU6 films. The C1s core-level spectra have been resolved into three component peaks. The sharp peak near at 285 eV



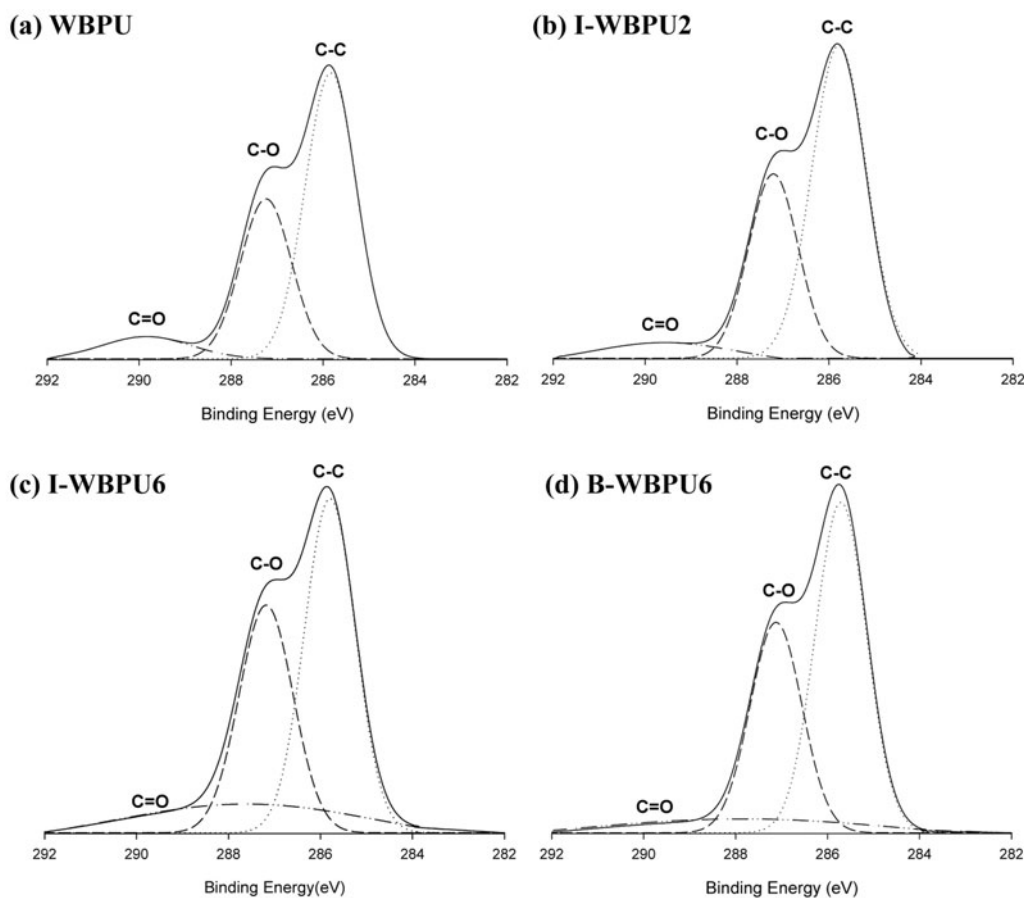
**Figure 1.** FTIR spectrum of I-WBPU4 and B-WBPU4 samples.

assigned to a hydrocarbon environment (C-C bond), the peak near at 287 eV assigned to a carbon singly bound to



**Figure 2.** XPS C1s and O1s core-level scan spectra of (a) WBPU, (b) I-WBPU2, (c) B-WBPU6, and (d) I-WBPU6 samples.

oxygen environment (C-O bond), and the broad peak near at 290 eV assigned to a carbon double bond to oxygen environment (C=O bond), respectively. The intensity of the peak at 287 eV increased with increasing the HMMM content. This is probably due to the formation of crosslinkages from the reaction of the carboxylic groups in the WBPU and the methoxy groups in the HMMM molecules. Crosslinking reaction between WBPU and HMMM is described in Scheme II. The XPS O1s spectrum of the WBPU film shows a peak near at 527~530 eV corresponding 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 intensity of O1s peak of the I-WBPU films increased with increasing the HMMM content. This indicates that the crosslinking reaction increased with HMMM content. The curve fitting of C1s for pure WBPU, typical crosslinked I-WBPU and B-WBPU samples is shown in Figure 3. 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 II. The values of N content and C-O/(C=O) + (C-C) increased



**Figure 3.** Curve fitting of XPS C1s core-level spectra of (a) WBPU, (b) I-WBPU2, (c) I-WBPU6, and (d) B-WBPU6 samples.

**Table II. XPS Results, Thermal and Mechanical Properties of WBPU, I-WBPU, and B-WBPU Film Samples**

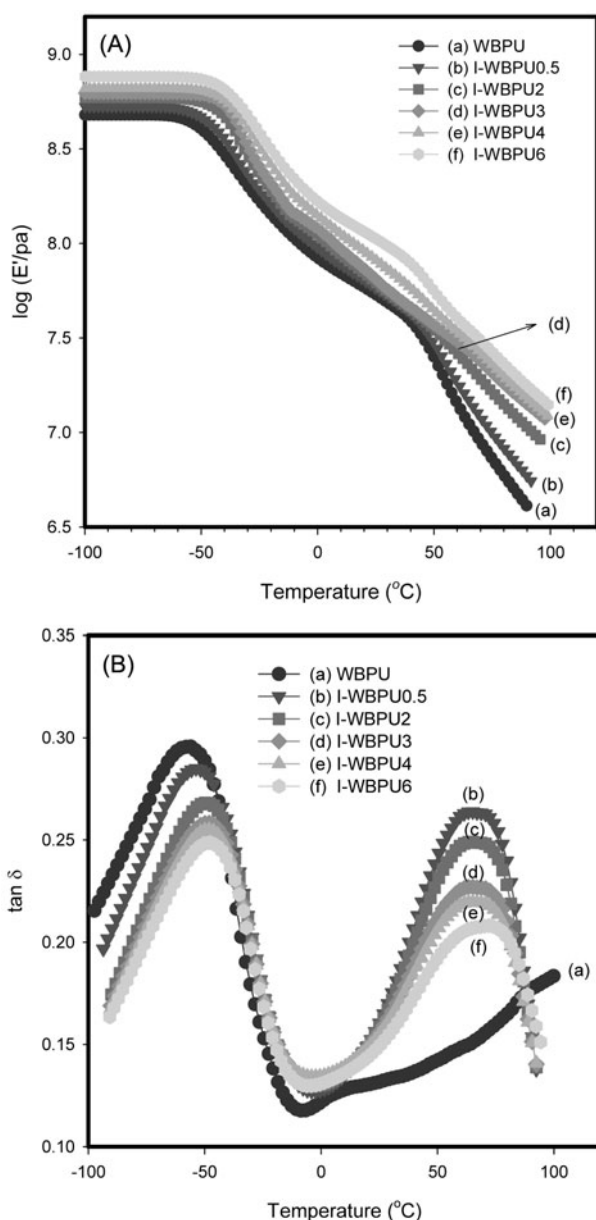
Specimens	Atomic %			C-O/ (C=O) +(C-C)	$T_{gs}$ (°C)	$T_{gh}$ (°C)	$T_m$ (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	Residue at 550 °C (wt%)	IPDT (°C)	Initial Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
	C	O	N											
WBPU	75.1	20.8	4.1	0.47	-58.0	8.7	208.3	323.8	415.1	2.6	425	10.1	5.9	1229
I-WBPU0.1	-	-	-	-	-56.2	32.0	209.0	324.9	416.2	2.7	427	-	-	-
I-WBPU0.5	-	-	-	-	-52.9	64.0	211.4	325.8	417.5	3.0	430	10.8	6.0	1172
I-WBPU1	-	-	-	-	-50.3	66.1	214.7	328.6	422.7	3.5	434	-	-	-
I-WBPU2	75.2	20.1	4.7	0.50	-48.0	67.4	218.7	331.5	427.2	3.8	438	20.1	6.3	1042
I-WBPU3	-	-	-	-	-48.0	68.7	223.0	334.8	431.6	4.3	443	-	-	-
I-WBPU4	76.1	18.9	5.0	0.57	-46.2	70.6	227.4	351.1	450.7	5.9	468	28.6	6.9	949
I-WBPU6	77.1	17.6	5.3	0.59	-45.5	73.1	238.8	359.3	472.7	14.1	540	40.4	7.3	908
B-WBPU2	75.2	20.2	4.6	0.48	-54.9	59.1	206.7	331.0	424.0	3.5	436	10.6	6.0	1177
B-WBPU4	75.7	19.4	4.9	0.52	-51.0	64.4	209.0	338.7	433.0	4.3	445	17.3	6.1	1065
B-WBPU6	76.6	18.3	5.1	0.57	-49.5	68.2	215.0	346.3	441.8	5.1	451	21.0	6.3	994

with increasing the HMMM content, indicating the increase of the crosslinking reaction. It was found that these values of the I-WBPU samples were a little higher than those of the B-WBPU samples at the same HMMM content. This might be due to the good homogeneousness of the HMMM in WBPU matrix polymer of the I-WBPU samples compared to B-WBPU samples. Consequently, the higher homogeneousness of the HMMM in WBPU matrix will give the higher opportunity of crosslinking reaction between their functional groups, resulting in the increased crosslinking density in the WBPU polymer chain.

**Dynamic Mechanical Thermal Properties.** Significant information about molecular motions of a WBPU chains can be obtained through the use of dynamic mechanical thermal analysis (DMTA). For comparison, the dynamic mechanical properties of the I-WBPU and B-WBPU films with various content of the HMMM were determined as a function of temperature. The temperature dependences of the dynamic storage modulus ( $E'$ ) and loss  $\tan\delta$  of the I-WBPU and B-WBPU films are shown in Figures 4 and 5, respectively. The  $E'$  of the I-WBPU and B-WBPU films increased with increasing the HMMM content, which was due to the increasing of crosslinking density in WBPU chain. The  $E'$  values of the I-WBPU films were higher than those of the B-WBPU films at the same HMMM content, indicating the better crosslinking density of the I-WBPU samples compared to the B-WBPU samples. The pure WBPU had two  $\tan\delta$  peaks near -58 and 8.7 °C assigned to the glass-transition temperatures ( $T_{gs}$  and  $T_{gh}$ ) of the soft segments and the amorphous regions of higher order, respectively. In general, their difference,  $\Delta T_g$  ( $T_{gh} - T_{gs}$ ), was related to the extent of phase separation in the amorphous regions. The  $T_{gs}$  and  $T_{gh}$  of the WBPU, I-WBPU, and B-WBPU films are given in Table II. With increasing the HMMM content,

the  $T_{gs}$  and  $T_{gh}$  of the I-WBPU and B-WBPU films shifted to higher temperature. The chain mobility of the soft segments was restricted by the crosslinking of segments, resulting in an elevated  $T_{gs}$  of the both systems. The increases of  $T_{gs}$  and  $T_{gh}$  of the I-WBPU system were higher than those of the B-WBPU system. The  $\Delta T_{gh}$  of I-WBPU and B-WBPU systems also increased significantly with increasing the HMMM content. The increase of the  $T_{gh}$  might be caused by the increased crosslinking density which resulting in decreased mobility of the higher order amorphous regions of the WBPU chain. The  $\Delta T_g$  of both systems increased with increasing the HMMM content, and the  $\Delta T_g$  of the I-WBPU system was a little higher than that of the B-WBPU system with the same HMMM content. This is also likely attributed to the favorable homogeneous reaction of the HMMM in the I-WBPU system. With increasing the HMMM content, the  $\tan\delta$  peak intensities of both systems were decreased indicating the decrease of the amorphous region in WBPU. The peak drop of the I-WBPU system was found to be larger than that of the B-WBPU system. These results also might be due to the increase of crosslinking density, resulting in the decreased amorphous region of the WBPU polymer. From the DMTA results, it was also speculated that the in-situ polymerization system produced higher crosslinking reaction in WBPU chain compared to the simple blending system.

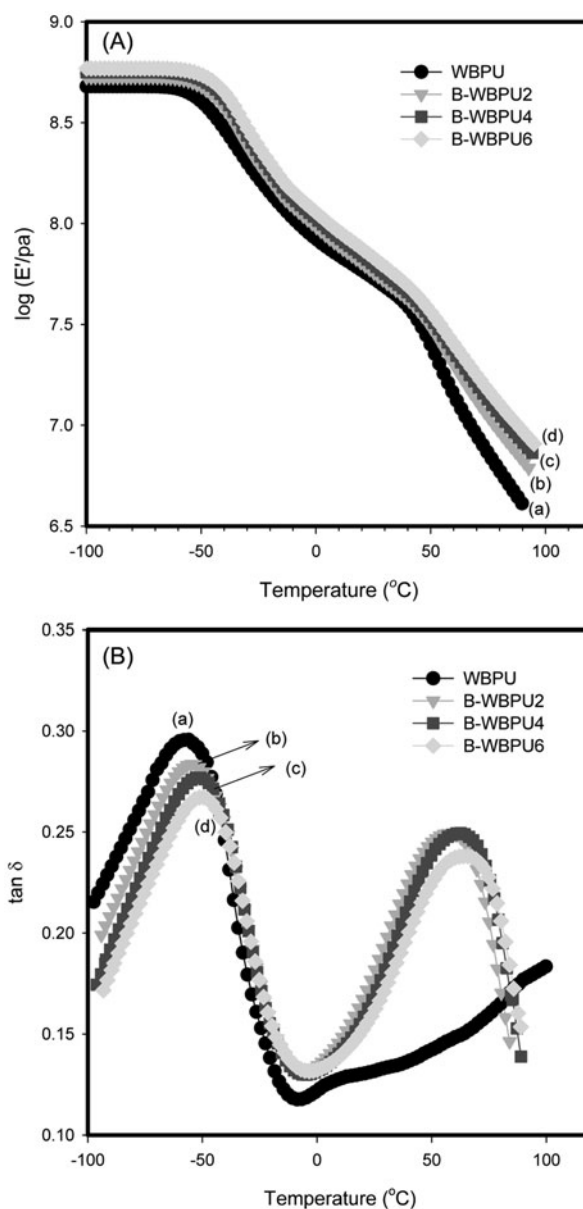
**Thermal Property.** Figure 6 shows the DSC thermograms of the pure WBPU, I-WBPU, and B-WBPU films, respectively. A broad endothermic peak corresponding to melting temperature ( $T_m$ ) of the WBPU at around 208~240 °C was appeared. The increase of  $T_m$  of the I-WBPU system was higher than that of the B-WBPU system at the same HMMM content. The  $T_m$  of the I-WBPU and B-WBPU films shifted to higher temperatures as the HMMM



**Figure 4.** (A) Storage ( $E'$ ) modulus and (B)  $\tan\delta$  peaks of (a) WBPU, (b) I-WBPU0.5, (c) I-WBPU2, (d) I-WBPU3, (e) I-WBPU4, and (f) I-WBPU6 samples.

content increased. This might be due to the rigidity of HMMM component reacted to hard segment component DMPA in WBPU chains. The correct reason why  $T_m$  increases with increasing the HMMM content is not clear at the present moment. More detailed studies should be made.

Figure 7 shows the TGA curves for WBPU, I-WBPU, and B-WBPU films, respectively. The TGA results for WBPU, I-WBPU, and B-WBPU films are summarized in Table II. For the I-WBPU and B-WBPU samples, no appreciable weight loss was observed at temperatures below 250 °C. The  $T_{10\%}$ ,  $T_{50\%}$ , and 10 and 50% weight loss temperatures of

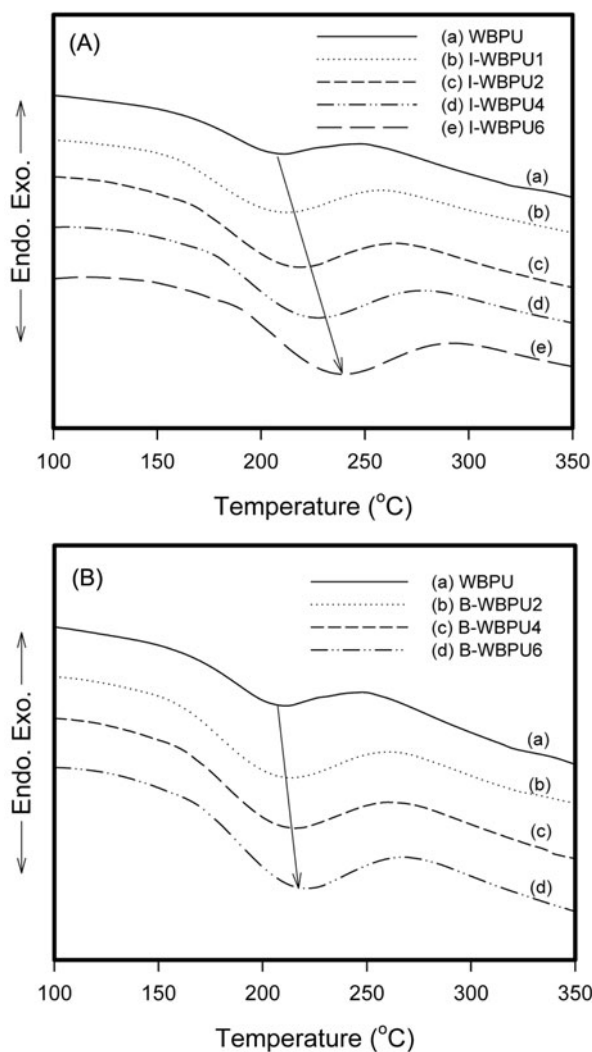


**Figure 5.** (A) Storage ( $E'$ ) modulus and (B)  $\tan\delta$  peaks of (a) WBPU, (b) B-WBPU2, (c) B-WBPU4, and (d) B-WBPU6 samples.

both systems increased with increasing the HMMM content. The final residual weight of the I-WBPU and B-WBPU films increased from 3.5 to 14.1 wt% and from 3.5 to 5.1 wt% according to the content of the HMMM. These rises were caused by the increase of crosslinking density, resulting in the increase of decomposition temperature of the WBPU. The integral procedural decomposition temperature (IPDT) of the WBPU, I-WBPU, and B-WBPU films was calculated with following Doyle's eq. (1),<sup>31</sup>

$$\text{IPDT (}^\circ\text{C)} = A^* \times K^* (T_f - T_i) + T_i \quad (1)$$

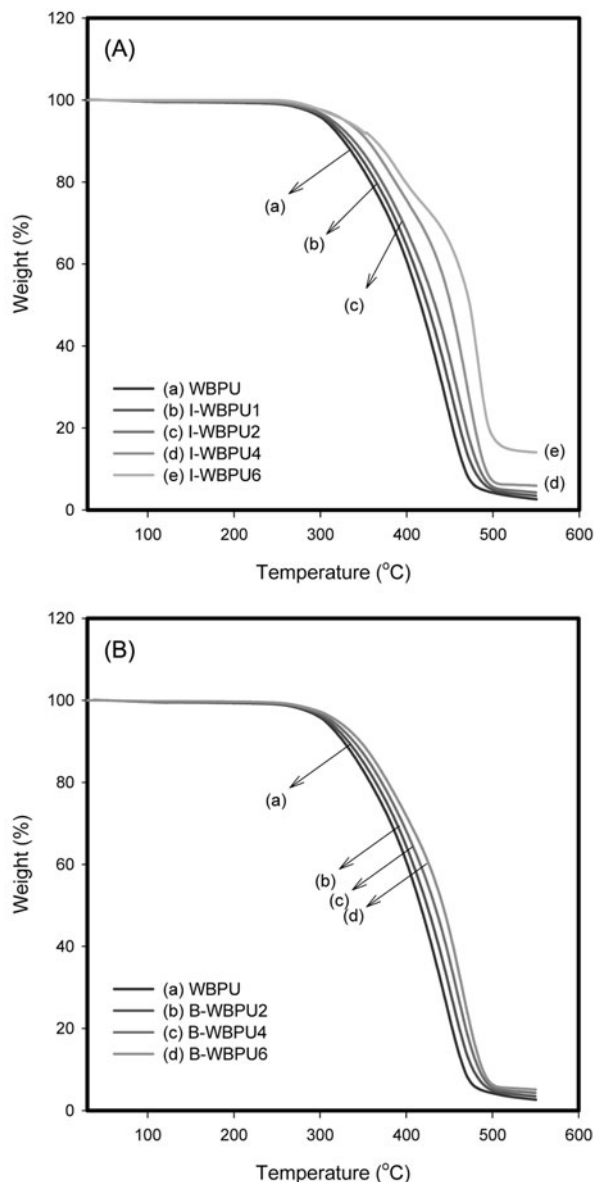
where  $A^*$  is  $[(A_1 + A_2)/(A_1 + A_2 + A_3)]$ ,  $K^*$  is a coefficient,  $T_i$



**Figure 6.** DSC thermograms of (A) I-WBPU and (B) B-WBPU samples.

and  $T_f$  are initial temperature and final temperature, respectively. The area of  $A_1$ ,  $A_2$ , and  $A_3$  are shown in Figure 8. The IPDT of both systems increased with increasing the HMMM contents. This indicates that the crosslinking reaction using HMMM has contributed to the higher thermal stability of the WBPU. However, the  $T_{10\%}$ ,  $T_{50\%}$ , and IPDT values of the I-WBPU system were higher than those of the B-WBPU system at the same HMMM content. This is probably due to the higher crosslinking density of the I-WBPU system compared to the B-WBPU system.

**Mechanical Property.** The stress-strain curves for WBPU, I-WBPU, and B-WBPU films are shown in Figure 9, respectively. The initial modulus, tensile strength, and elongation at break are summarized in Table II. It was found that the initial modulus, tensile strength, and elongation at break of the WBPU film were 10.1 MPa, 5.9 MPa, and 1280%, respectively. In both systems, with increasing the HMMM



**Figure 7.** TGA thermograms of (A) I-WBPU and (B) B-WBPU samples.

content, the tensile strength and initial modulus increased, and elongation at break decreased. This result is possibly originated in the increase of crosslinkage formation between HMMM and WBPU. The changes of these mechanical properties of the I-WBPU system were higher than those of the B-WBPU system at the same HMMM content. This result also might be due to the higher crosslinking density of the I-WBPU system compared to the B-WBPU system.

Generally, hardness reflects the resistance to local deformation and is related to the crosslinking density of the matrix.<sup>32,33</sup> Figure 10 shows the dependence of hardness on the HMMM content for the I-WBPU and B-WBPU films. The hardness of both systems increased with increasing the



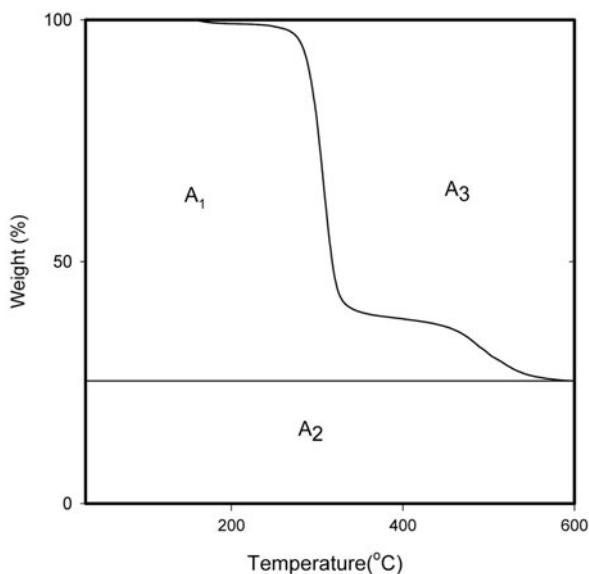


Figure 8. Schematic representation of TGA area for calculation of IPDT values.

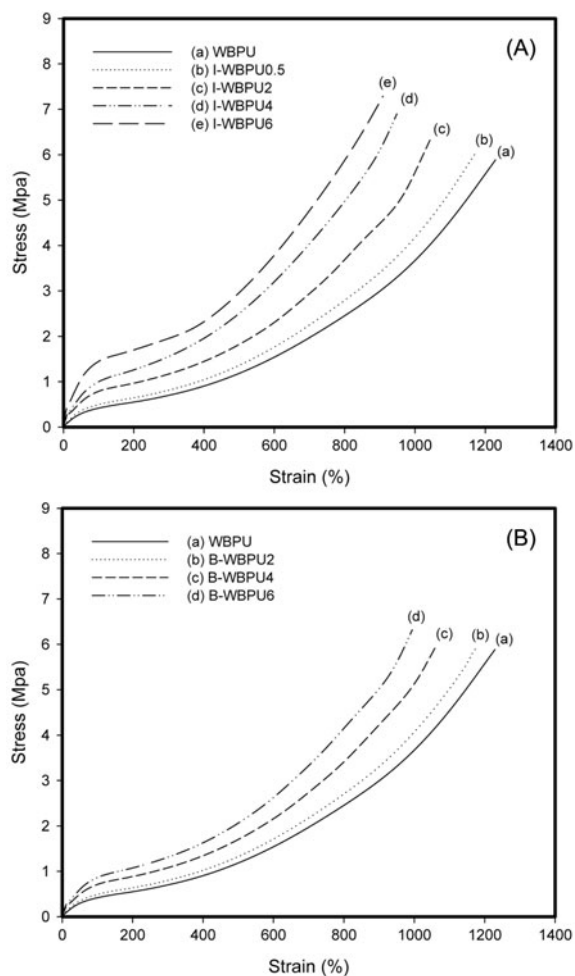


Figure 9. Stress-strain curves for (A) I-WBPU and (B) B-WBPU samples.

HMMM content. The increase in hardness was presumably due to the increase of crosslinking density, resulting in the increase of rigidity/stiffness of main chain of the WBPU. The hardness of the I-WBPU system was higher than that of the B-WBPU system at same HMMM content. This is also likely attributed to the higher crosslinking density of I-WBPU system.

**Adhesion Property.** The adhesion property was measured at room temperature according to the ASTM D-1876-01 (the peel resistance of adhesives, i.e., the T-peel test). Figure 11 shows the relationship between the adhesive strength and crosslinking agent HMMM content. The adhesive

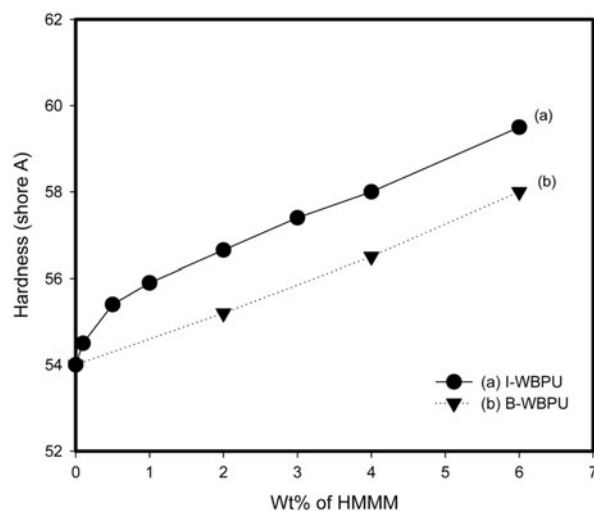


Figure 10. Effect of HMMM content on the hardness of (a) I-WBPU and (b) B-WBPU films.

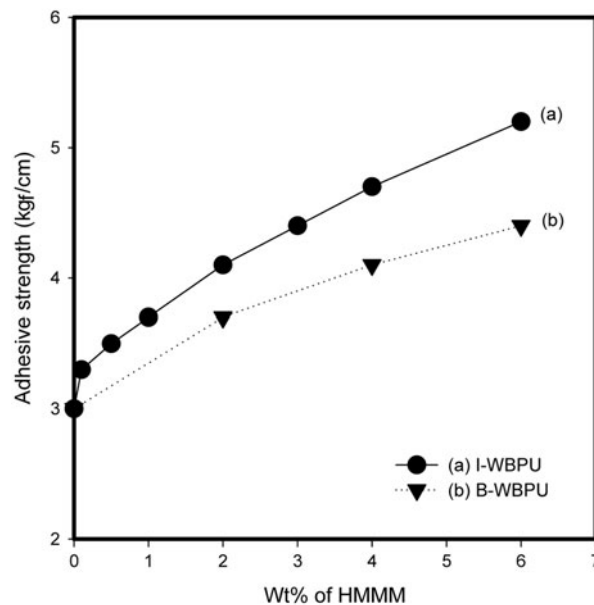


Figure 11. Effect of HMMM content on the adhesive strength of (a) I-WBPU and (b) B-WBPU films.

strengths of the I-WBPU and B-WBPU systems were remarkably increased with increasing the HMMM content. It was found that the adhesive layer was torn instead of breaking the Nylon fabric-adhesive interface for all samples. The adhesive strength of the I-WBPU system was found to be better than that of the B-WBPU system at the same HMMM content. The higher adhesive strength of the I-WBPU system was interpreted to be due to the higher strength of the I-WBPU film sample compared to the B-WBPU film sample.

## Conclusions

In this study, crosslinkable WBPUs containing aminoplast (HMMM) as a crosslinking agent were prepared by in-situ polymerization and simple blending method, respectively. The effects of the HMMM content on the thermal behavior, thermal stability, dynamic mechanical thermal property, mechanical property, hardness, and adhesive strength of the crosslinked WBPUs (I-WBPU and B-WBPU) system were investigated. The confirmation of crosslinking reaction between WBPU and HMMM was executed using a FTIR and XPS analysis. The storage modulus,  $T_{gs}$ ,  $T_{gh}$ ,  $T_m$  and thermal stability of the I-WBPU and B-WBPU systems increased with increasing the HMMM content. As the HMMM content increased, the initial tensile modulus, tensile strength and hardness of the two kinds of crosslinked WBPU films increased, however, the elongation at break decreased. Adhesion strength of the both systems increased with increasing the HMMM contents. The adhesive strength of the I-WBPU system was found to be better than that of the B-WBPU system at the same HMMM content. These superior properties of the I-WBPU system might be due to the better dispersion of the HMMM in the WBPU matrix of the I-WBPU system compared to the B-WBPU system. From these results, it was concluded that the in-situ polymerization using HMMM as a crosslinking agent was a more effective method to improve the properties of the WBPU materials compared to simple blending process.

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