

Preparation and Properties of MDI/H₁₂MDI-Based Water-Borne Poly(urethane-urea)s—Effects of MDI Content and Radiant Exposure

Jae Ho Huh,¹ Hea In Kim,² Mohammad Mizanur Rahman,² Han Do Kim²

¹Busan Branch of Korea Apparel Testing & Research Institute, Busan 1191-6, Korea

²Department of Organic Material Science and Engineering, Pusan National University, Busan 609-735, Korea

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ABSTRACT: Water-borne poly(urethane-urea)s (WBPU)s were prepared by a prepolymer mixing process using aromatic diisocyanate (MDI, 4,4'-diphenylmethane diisocyanate)/aliphatic diisocyanate (H₁₂MDI, 4,4'-methylenebis cyclohexyl isocyanate), polypropylene glycol (PPG, $M_n = 1000$), dimethylol propionic acid, and ethylene diamine as a chain extender, and triethylamine as a neutralizing agent. The effect of MDI on the molecular weight, chemical structure, dynamic thermo, and tensile properties of WBPU)s was investigated. The yellowness index (YI, photo-oxidation behavior) change of WBPU)s under accelerated weathering exposure was also investigated. The WBPU)s containing higher MDI content showed lower molecular weight, which verified the participation of some high reactive isocyanate groups of MDI into side reaction instead of chain growing reaction. As the MDI

content increased, the storage modulus and tensile modulus/strength of WBPU)s film increased, and their glass transitions of soft segments (T_{gs}) and hard segments (T_{gh}) were shifted to higher temperature. The intensity of $\tan \delta$ peak of all three samples increased with increasing radiant exposure. The YI of H₁₂MDI-based WBPU sample (WBPU-0) was not occurred. The YI of WBPU)s containing MDI increased with increasing MDI content and radiant exposure. However, the YI of sample WBPU-25 containing 25 mol % of MDI at 11.3 MJ/m² (radiant exposure) was 6.6 which is a permissible level for exterior applications. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3655–3663, 2008

Key words: water-borne poly(urethane-urea); MDI; H₁₂MDI; radiant exposure; yellowness index

INTRODUCTION

Before 1950, most coatings were solvent borne. The introduction of latex paints for architectural uses was the first major step away from solvent-borne coatings. Since 1970, there has been further trend away from solvent-borne coatings because of higher solvent prices and particularly the need to reduce VOC emissions to meet air quality standards. Water-borne poly(urethane-urea) (WBPU) is regarded as one of the most important industrial polymers nowadays due to its tremendous usefulness as well as environmental benefit compared to its counterpart solvent-borne polyurethane. The WBPU is being widely used in construction, automotive, packaging, transportation, electronics, textile, tape, paper, and footwear industries.^{1–8} Water-borne polyurethane dispersions consist of urethane polymer chains with basic or acidic functionality. After neutralization and entailed salt formulation, these ionomers are hydro-

philically modified sufficient to form stable aqueous dispersions.

Of the large number of commercially available diisocyanates, only a limited number is widely used in polyurethane coatings. They are divided into aromatic and aliphatic isocyanates. Generally, aliphatic diisocyanates such as 4,4'-dicyclohexylmethyl diisocyanate (H₁₂MDI) and isophorone diisocyanate (IPDI) are used for water-borne polyurethane dispersion coating materials. One of the downside of these aliphatic diisocyanates as raw materials is that they cost significantly higher than aromatic isocyanates toluene diisocyanate (TDI) and 4,4'-diphenylmethane diisocyanate (MDI) used in coatings. However, the volatility of TDI which gives it toxicity is the reason why TDI is used for manufacturing resin but not for formulated coatings. Another widely used aromatic diisocyanate is MDI, which has no volatility issue unlike TDI. But still, photo-oxidation of MDI-based polyurethanes has limited their potential for practical use. MDI-based polyurethanes are susceptible to yellowing and ultimately to degradation when exposed to UV.^{9,10} Because of these reasons, MDI is mainly used for manufacturing foams, coatings, adhesives, and elastomers.

Correspondence to: H. D. Kim (kimhd@pusan.ac.kr).

Photo oxidation of polymers is a very complex process involving various factors. The primary factor is weather—mainly daylight, temperature, water (gaseous or liquid), and oxygen (O₂). The secondary factors are atmospheric pollutants, biological agents, acts of nature, high-energy radiations, and mechanical stress (accelerates physical damage). A number of authors have investigated the harmful effects of UV exposure on polyurethanes.^{9–13} For polyurethanes based on MDI, the photosensitivity is thought to be due to an aromatic diurethane bridge. The monoquinone-imide structure is a chromophore that is thought to be responsible for the yellowing of polyurethane during exposure, whereas the diquinone-imide is responsible for the brownish or amber color that polyurethanes exhibit after longer periods of exposure.^{10,13–15} These attacks can be slowed down by the addition of a synergistic blend of light absorbing benzophenone and benzotriazole compounds with UV absorbers and free-radical scavengers such as hindered amines. Pigments and fillers can also be added to mask the effect and in many cases this approach works well for short-term use.

The aliphatic diisocyanates such as H₁₂MDI and IPDI need to be used for high-performance applications with nonyellowing behavior and no degradation in performance.¹⁶ Therefore, the incorporation of MDI into WBPU has both merits (low cost) and demerits (yellowing). This study aims to find out the optimal share of MDI in WBPU to maximize the synergy of aliphatic diisocyanate (H₁₂MDI) and aromatic diisocyanate (MDI) for WBPU coatings.

In this study, a series of WBPU based on various combinations of MDI/H₁₂MDI (MDI/H₁₂MDI: 0/100, 25/75, and 50/50 mol %) were prepared. The effects of MDI content and radiant exposure on the properties such as thermal/mechanical properties and photo-degradation behavior [photo oxidation, yellowness index (YI)] of WBPU film are investigated. These series of materials permit further examination of the permissible content of MDI for exterior coatings.

EXPERIMENTAL

Materials

Polypropylene glycol (PPG, $M_n = 1000$, Aldrich Chemical, Milwaukee, WI) was dehydrated at 80°C under vacuum (1–2 mmHg) until no bubbling was observed. Dimethylol propionic acid (DMPA, Aldrich Chemical, Milwaukee, WI), 4,4'-methylenebis cyclohexyl isocyanate (H₁₂MDI, 90%, Aldrich Chemical, Milwaukee, WI), ethylene diamine (EDA, Aldrich Chemical, Milwaukee, WI), triethylamine (TEA, Sigma, Milwaukee, WI), and *N*-methyl-2 pyrrolidone (NMP, Aldrich Chemical, Milwaukee, WI)

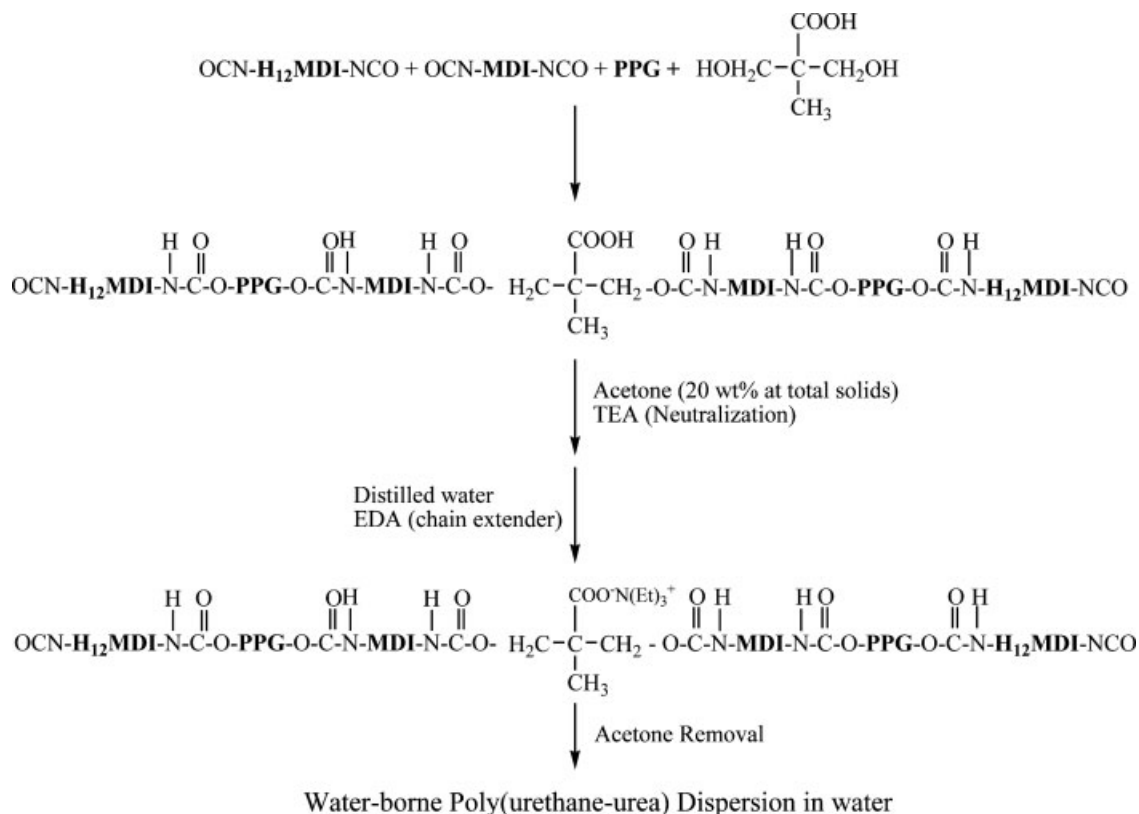
were used after dehydration with 4 Å molecular sieves for 1 day. Dibutyltin dilaurate (DBTDL, Aldrich Chemical, Milwaukee, WI) and 4,4'-methylenebis phenyl isocyanate (MDI, 98%, Aldrich Chemical, Milwaukee, WI) was used without further purification.

Preparation of WBPUs and their films

A series of WBPU was synthesized using the prepolymer mixing process method, which is outlined in Scheme 1. MDI, dissolved in NMP (1 : 1 w/w), H₁₂MDI, and PPG were added to 500 mL, four-necked, round-bottomed flask equipped with a mechanical stirrer, a nitrogen inlet, a condenser, and a thermometer. DMPA dissolved in NMP (DMPA/NMP = 1 : 2 w/w) was then slowly dropped into the system at 40°C for 30 min. After that, the mixture was heated at 90°C, and then DBTDL (less than 0.05 ppm) was added. The reaction mixture was allowed to react at 90°C until the theoretical NCO content was reached as determined using a standard dibutylamine back-titration method (ASTM D 1638). Then, acetone (20 wt %) was added to the reaction mixture to adjust the viscosity of the solution under moderate stirring (175–200 rpm). The NCO-terminated prepolymer, endcapped with aliphatic isocyanate (H₁₂MDI), was cooled down to 50°C. TEA, dissolved in acetone (TEA/acetone = 1 : 2 w/w), was added to neutralize the carboxyl group. After 30 min of neutralization reaction, the mixture was cooled to 25°C and distilled water (70 wt %) was added to the reaction mixture under vigorous stirring (1300–1500 rpm). The neutralized prepolymer was chain extended by dropping EDA, dissolved in water (EDA/water = 1 : 2 w/w) at 40°C for 1 h, and the reaction continued until NCO peak (2270 cm⁻¹) in FTIR spectra had completely disappeared. All the WBPU dispersions (30 wt % solid content) were obtained by the evaporation of acetone and the subsequent addition of an adequate amount of distilled water. Films were obtained by pouring the aqueous dispersion onto a polytetrafluorethylene disk at ambient conditions. The films (typically about 0.1 mm thickness) were dried at 80°C for 1 day and stored in a desiccator at room temperature.

Characterization

Chemical components of WBPU were confirmed by the Fourier Transform infrared spectroscopy (FTIR, JASCO, Japan). FTIR spectra of WBPU were recorded in the range of 4000 ~ 650 cm⁻¹ using a ATR (Silicon crystal) at the resolution of 4 cm⁻¹ and 100 scans. The molecular weight of the WBPU film samples were measured by gel permeation



Scheme 1 The preparation process of water-borne poly(urethane-urea).

chromatography (GPC) on a Waters-515 spectrometer using polystyrene as standard and tetrahydrofuran as eluent. The thermal dynamic mechanical behavior of WBPU were measured at 3 Hz, 20 μm (amplitude) in a tension mode, using DMA Q800 (TA Instrument, USA) with a heating rate of 5°C/min in the temperature range of $-75 \sim 200^\circ\text{C}$. The dimension of the film was a $15 \times 5.3 \times 0.1$ (mm) for DMA measurement. Temperature calibration of DMA was done by using indium (T_m : 156.6°C). The mechanical measurements were made in simple extension on dumbbell specimens using a tensile tester (Instron 5582, Instron, Co. LTD, USA). A crosshead speed of 50 mm/min was used throughout these investigations to determine the ultimate tensile modulus and strength for all the samples. The values quoted are the average of five measurements. Accelerated weathering exposure was done by using the CI 4000 (Xenon lamp, Atlas, USA), and the detail exposure composition is shown in Table I. This composition is generally accepted to test the effects of weathering on automotive interior materials.

All samples were treated in chambers over various radiant durations (energy) [24 h (5.7 MJ/m^2), 48 h (11.3 MJ/m^2), and 72 h (17.0 MJ/m^2)]. Half of the samples were exposed to light, and the other half were light screened.

$$\begin{aligned} & \text{Radiant exposure energy (MJ/m}^2\text{)} \\ & = \text{irradiance (W/m}^2\text{)} \times \text{exposure time (s)} \quad (1) \end{aligned}$$

YI of exposed part and nonexposed part of film samples were measured using Macbeth Coloreye 700 spectrophotometer (illuminant D65, 10° observer) according to ASTM D 1925-70.

$$\text{YI} = 100 (1.28X - 1.06Z)/Y \quad (2)$$

where X , Y , and Z are tristimulus values.

RESULTS AND DISCUSSION

WBPU preparation

Because of the higher cost of aliphatic isocyanates, aromatic isocyanates have the largest market share.

TABLE I
Accelerated Weathering Exposure Conditions
on WBPU Films

Test condition	Note	
Black panel temp. ($^\circ\text{C}$)	89 ± 3	
Chamber temp. ($^\circ\text{C}$)	63 ± 3	
Humidity (%)	50 ± 5	
Irradiance (W/m^2)	65.5 ± 2.5	300–400 nm
Inner/outer filter	Boro silicate/soda lime	

TABLE II
Sample Designation, Composition (mole), Solid Content, and Average Molecular Weight (M_n) of WBPU

Sample designation	Composition (mole)						Solids wt (%)	M_n
	H12MDI	MDI	PPG ($M_w = 2000$)	DMPA	EDA	TEA		
WBPU-0	1	0	0.25	0.25	0.50	0.25	30	14,173
WBPU-25	0.75	0.25	0.25	0.25	0.50	0.25	30	13,049
WBPU-50	0.5	0.5	0.25	0.25	0.50	0.25	30	12,547

The main market trend is to replace TDI by MDI or polymeric MDI which are much less volatile. They are used where oxidative discoloration on exposure to UV radiation is not an issue. To find out the optimal content of MDI in WBPU to maximize the synergy of H₁₂MDI and MDI for application to exterior coating, the WBPU based on MDI/H₁₂MDI blend (MDI/H₁₂MDI: 0/100, 25/75, and 50/50 mol %) were synthesized by a prepolymer mixing process.

The sample composition, solid content, and average molecular weight (M_n) of WBPU prepared in this study are shown in Table II. The reactivity of NCO groups of MDI is notable higher than that of H₁₂MDI NCO groups. The MDI NCO groups reacted first with the diols of polyol/DMPA completely at 40°C without catalyst, whereas almost all H₁₂MDI NCO groups showed no reaction in this condition. When catalyst DBTDL was added to the reaction mixture heated to 90°C, the H₁₂MDI NCO groups reacted with the remaining diols to form urethane groups. The remaining NCO groups of H₁₂MDI located at the end of prepolymer chains reacted with amino groups of chain extender EDA to form urea groups during chain extension.

Consequently, WBPU-0 sample had 50 mol % H₁₂MDI-based urethane groups and 50 mol % H₁₂MDI-based urea groups, WBPU-25 sample had 25 mol % MDI-based urethane groups/25 mol % H₁₂MDI-based urethane groups/50 mol % H₁₂MDI-based urea, and WBPU-50 sample had mainly 50 mol % MDI-based urethane groups/50 mol % H₁₂MDI-based urea groups. The molar ratio of feed monomer indicates that all three samples have the same H₁₂MDI-based urea content (50 mol %).

The WBPU containing higher MDI content showed lower molecular weight, indicating that some high-reactive isocyanate groups of MDI took part in side reaction instead of chain growing reaction. The reaction of isocyanates with hydroxyl compounds is the major reaction found in polyurethane coating. The major hydroxyl groups involved in the reaction with isocyanates are terminal end chains (—OH) such as polyol (—OH) or carboxylic acid (—C(=O)—OH) and water (H—OH). When some highly reactive —NCO groups are involved in the side reaction with water (H—OH), the stoichiometric balance of functional groups (—NCO ratio) is

changed and leads to decrease in the molecular weight of final polymer.

From our preliminary experiment, it was found that unstable WBPU dispersion and brittle low-molecular weight PU material was obtained at the normal reaction condition when 100 mol % MDI was used without catalyst. This should be due to the high reactivity of MDI —NCO groups. However, the investigation about the specific side reactions and their kinetics between MDI —NCO groups and water hydroxyl groups is not within the scope of this study. More detailed studies about the side reactions of MDI —NCO groups should be made in the further study. The aim of this study is to find the permissible range of MDI content in WBPU coatings which is related to the extent of color change (YI) with radiation exposure.

Identification of WBPU

The FTIR spectra of WBPU based on MDI/H₁₂MDI (MDI/H₁₂MDI: 0/100, 25/75, and 50/50 mol %) are shown in Figure 1. Adding MDI component changed the characteristic peak and intensity. The WBPU based on MDI/H₁₂MDI (samples WBPU-25 and WBPU-50), respectively, showed the peaks at 1600 cm⁻¹ and 1410 cm⁻¹ due to C=C and C—C

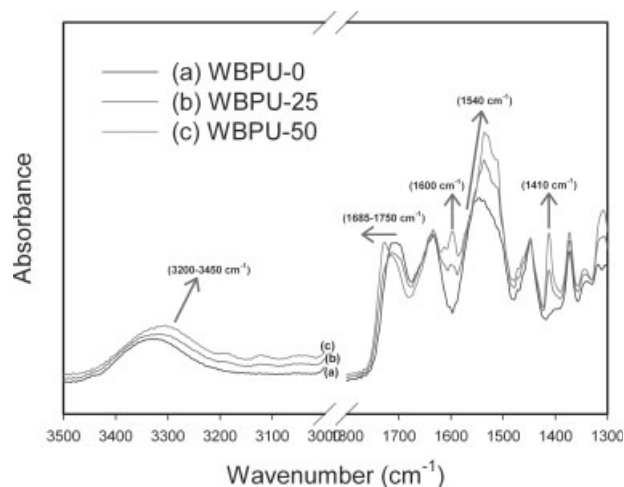


Figure 1 The FTIR spectra of WBPU with MDI/H₁₂MDI blend (MDI/H₁₂MDI : 0/100, 25/75 and 50/50 mol %); (a) WBPU-0, (b) WBPU-25, and (c) WBPU-50 films.

absorption bands of phenyl ring,^{17,18} but WBPU based on pure H₁₂MDI (sample WBPU-0) showed no such peaks. These peaks increased with increasing MDI content. The peak at 1635 cm⁻¹ is assigned to the ordered hydrogen bonded C=O in urea group of WBPU samples.¹⁹ The wavenumber and absorbance at this peak did not change indicating that all three samples contained the same content of H₁₂MDI-based urea group (50%). As shown in other studies as well, the peaks in the range of 1685 ~ 1750 cm⁻¹ and 3200 ~ 3450 cm⁻¹ were assigned to the C=O and N-H groups, respectively.^{17,19} However, the peaks of C=O group shifted to the higher frequency, whereas the peaks of N-H at 1540 cm⁻¹ and 3200 ~ 3450 cm⁻¹ moved to lower frequency. These behaviors should be due to the structural difference between the aromatic phenyl group of MDI and aliphatic groups of H₁₂MDI. According to the study by Zhang et al.,¹⁷ these shifts are attributed to the superconjugation between phenyl of MDI and C=O in urethane. The trend in peak shift in our study is also in line with the result of the study by Zhang et al.¹⁷

DMA analysis

Analysis of DMA results brings us a significant information about molecular motions and phase separation of polyurethane chains.²⁰ Figure 2 shows the dynamic mechanical properties of WBPU-0, WBPU-25, and WBPU-50 as a function of temperature. The thermal and mechanical properties of WBPU film samples are shown in Table III. The storage modulus of film sample increased with increasing MDI content in the temperature range of -75°C–160°C. This might be attributed to the higher rigidity of aromatic MDI structure compared with aliphatic H₁₂MDI. WBPU-0, WBPU-25, and WBPU-50 samples had two tan δ peaks assigned to the glass transition temperatures of the soft segments and hard segments (T_{gs} : about -20 ~ -4°C and T_{hg} : 109 ~ 141°C), respectively. Although the tan δ curves of WBPU-0 and WBPU-25 were almost similar to each other, WBPU-50 showed notably different pattern at high-temperature region (hard segment T_{gh}). Higher structural rigidity of MDI compared with H₁₂MDI made the T_{gs}

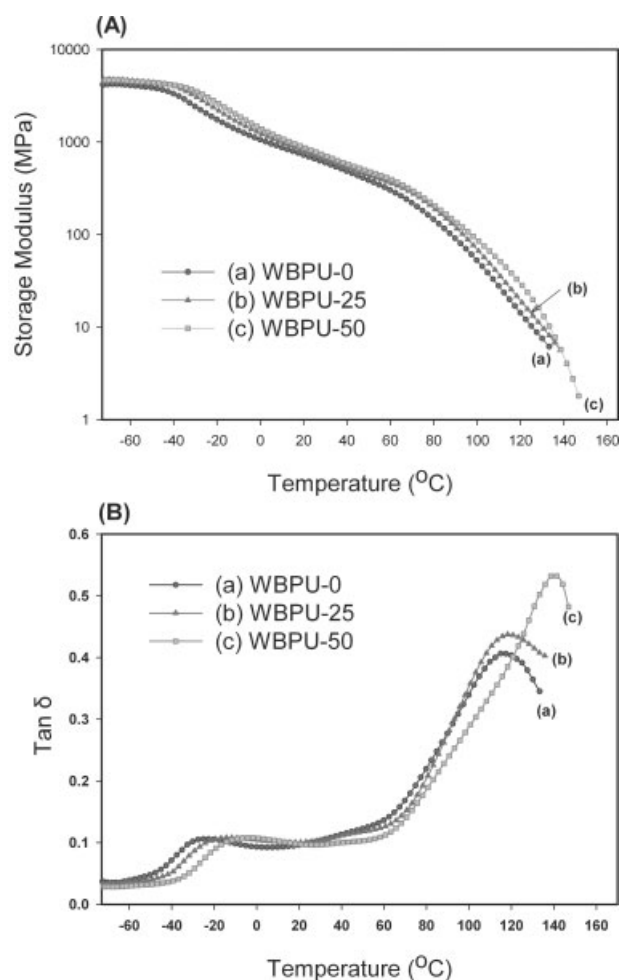


Figure 2 The storage modulus (A) and tan δ curves (B) of WBPUs; (a) WBPU-0, (b) WBPU-25, and (c) WBPU-50 samples.

and T_{gh} shift to higher temperature. Generally, ΔT_g ($T_{gh} - T_{gs}$) was related to the extent of phase separation in the amorphous region, and the intensity of tan δ peak was related to the extent of hydrogen bond, crosslinkage and the rigidity of molecular chain.¹⁸ As the MDI content increased, the ΔT_g increased significantly but the tan δ intensity decreased (see Table III). The results also stem from higher structural rigidity of MDI.

TABLE III
Thermal and Mechanical Properties of WBPU Film Samples

Sample designation	T_{gs} (°C)	T_{gh} (°C)	ΔT_g (°C) ($T_{gh} - T_{gs}$)	Tan δ intensity			Tensile strength (MPa)	Initial modulus (MPa)	Elongation (%)
				25°C	70°C	90°C			
WBPU-0	-20	109	129	0.0992	0.1691	0.2780	3.9	50	193
WBPU-25	-12	120	132	0.1014	0.1499	0.2761	4.1	60	186
WBPU-50	-4	141	145	0.0962	0.1384	0.2371	4.6	75	185

Mechanical properties

The stress–strain curves of WBPU-0, WBPU-25, and WBPU-50 are shown in Figure 3. The changing trend of initial tensile modulus matches that of storage modulus determined by DMA. Generally, the tensile strength of polymer is dependent on the chemical structure (polarity and rigidity) and the molecular weight of polymer at the fixed composition. The molecular weight of WBPU decreased with increasing MDI content (see Table III). However, the initial tensile modulus and tensile strength of samples increased, whereas the elongation at break decreased a little with increasing MDI content. This indicated that the tensile strength of WBPU sample prepared in this study dominantly hinged upon the structural feature (rigid structure) of MDI rather than its molecular weight.

Effect of radiant exposure

In this study, all samples were exposed over various durations (radiant exposure) [0 h (0 MJ/m²), 24 h (5.7MJ/m²), and 48 h (11.3MJ/m²)] to artificial sun light using the CI 4000 (Xenon lamp, Atlas, USA)—the same conditions under which automotive inte-

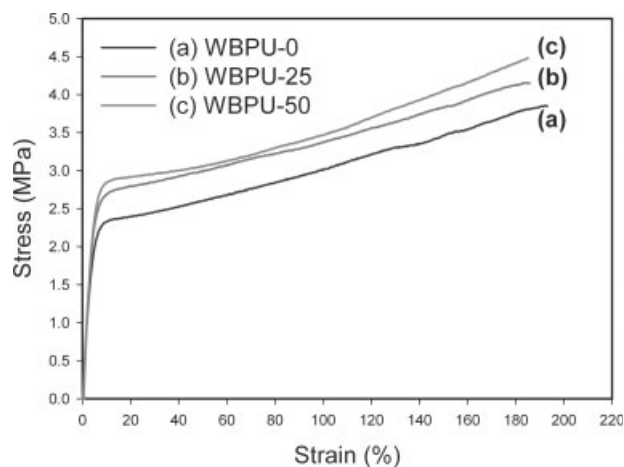


Figure 3 Stress–strain curves of WBPU having various combinations of MDI/H₁₂MDI (MDI/H₁₂MDI : 0/100, 25/75 and 50/50 mol %); (a) WBPU-0, (b) WBPU-25, and (c) WBPU-50 samples.

rior materials go through weathering tests. After exposing film samples to artificial sun lights, the effect of radiant exposure on the properties such as thermal/mechanical properties and photo oxidation (YI) of WBPU film samples having different content

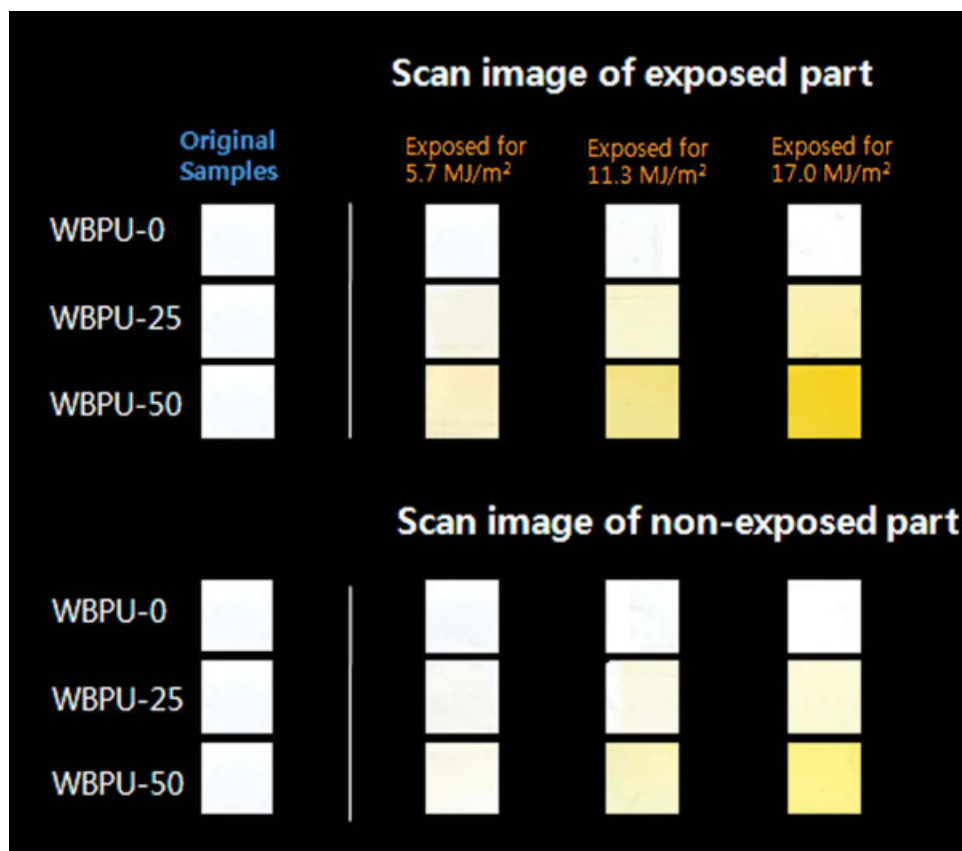


Figure 4 The images of original samples (as-polymerized WBPU film sample) and treated (exposed and screened) samples under various radiant exposures (0, 5.7, 11.3, and 17.0 MJ/m²). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

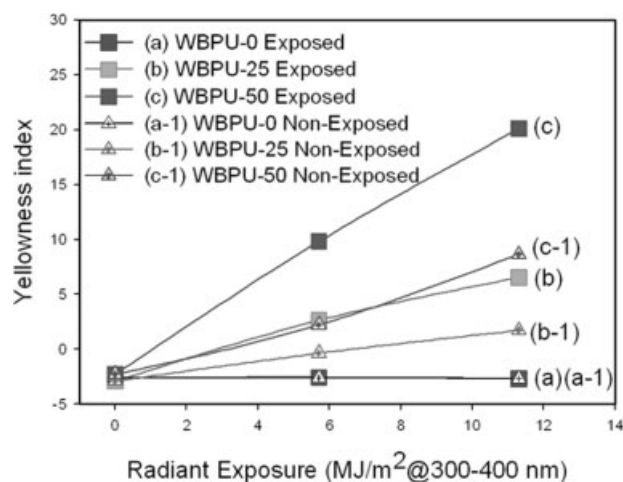


Figure 5 Yellowness index versus radiant exposure (0, 5.7 and 11.3 MJ/m²); (a) WBPU-0, exposed part; (a-1) WBPU-0 nonexposed part; (b) WBPU-25, exposed part; (b-1) WBPU-25, nonexposed part; (c) WBPU-50, exposed part; and (c-1) WBPU-50 nonexposed part.

of MDI were investigated. It was found that all three samples exposed to the highest energy 17.0 MJ/m² were too fragile to measure the yellowness and dynamic mechanical properties. Scan images of three kinds of samples are shown in Figure 4: original samples (untreated samples) and treated samples half of which were exposed to light and the other half nonexposed (light screened). All treated samples, both exposed and nonexposed, were treated at 63°C in the chamber. The color changes of treated samples were compared with those of original samples. The yellowness of treated sample intensified with increasing MDI content. The yellowness was also proportional to the radiant exposure energy.

The YI calculated according to ASTM D 1925-70 indicates the quantitative value of color changes. The YI values of all samples were shown in Figure 5 and Table IV. The YI of WBPU-25 containing 25 mol % of MDI at 11.3 MJ/m² (radiant exposure) was 6.6, whereas WBPU-50 containing 50 mol % of MDI at 11.3 MJ/m² stood at 20.1. As radiant exposure increased, the YI of exposed part rapidly increased in WBPU-50 compared with that of WBPU-25, whereas WBPU-0 remained unchanged. As for the nonexposed part, the YI was smaller than that of exposed part. However, the nonexposed/exposed parts showed almost the same tendency. The humidity and temperature of the chamber were probably the factors that drove up the yellowness of the screened part. These behaviors are probably attributable to MDI's photosensitivity, thought to be caused by aromatic diurethane bridge.^{10,13-15} The YI of samples increased in the

order of WBPU-50 > WBPU-25 > WBPU-0 (not changed), indicating the increase of photo oxidation with increasing MDI content. All of the original WBPU samples showed minus (-) value, indicating their shift towards blue on the chromaticity coordinates.

The storage modulus of samples is shown in Figure 6. With increasing radiant exposure, the rubbery plateau rapidly dropped. In the low temperature (below about 50°C), the samples exposed to higher energy showed higher storage modulus, but their storage modulus decreased rapidly in the higher temperature (above 50°C). The higher storage modulus in the lower temperature range is attributable to the formation of quinone-imide which increases the molecular chain rigidity. However, the rapid decrease of storage modulus in the higher temperature range (above 50°C) might be due to the weakened polymer chain broken by artificial sun light. The storage modulus of (d) nonexposed part in each sample stood at almost the same level with (a) original samples.

Figure 7 shows the tan δ curve of samples as a function of temperature. The changes of T_{gs} , T_{gh} , ΔT_{gs} , and tan δ intensity of WBPU film samples are shown in Table V. As the radiant exposure increased, the lower temperature tan δ peak point (T_{gs}) of treated sample increased, but the higher temperature tan δ peak point (T_{gh}) of treated sample decreased. The intensity of tan δ peak of all three samples increased with increasing radiant exposure. The tan δ peak intensity of WBPU-50 remained nearly unchanged. However, in the case of WBPU-0 and WBPU-25, the increase of the radiant exposure led to a notable increase of tan δ peak intensities at higher temperature, but the tan δ peak intensity at lower temperature decreased with increasing radiant exposure. The tan δ peak intensity was reversely related with storage modulus value. But the changing trend of tan δ peak intensity matches that of storage modulus.

TABLE IV
The Yellowness Index of WBPU Samples for Radiant Exposure (5.7 – 22.8 MJ/m²)

Sample description		Original sample	At 5.7 MJ/m ²	At 11.3 MJ/m ²
WBPU-0	Exposed part	-2.6	-2.6	-2.7
	Nonexposed part	-2.6	-2.6	-2.7
WBPU-25	Exposed part	-2.9	2.6	6.6
	Nonexposed part	-2.9	-0.4	1.7
WBPU-50	Exposed part	-2.3	9.8	20.1
	Nonexposed part	-2.3	2.2	8.6

Minus (-) value indicates the shift toward blue on the chromaticity coordinates.

CONCLUSIONS

The use of aromatic diisocyanates (MDI, TDI) in coating applications, especially in WBPU systems, was clearly limited due to their high reactivity toward water during dispersion process and their susceptibility to thermal degradation and photo

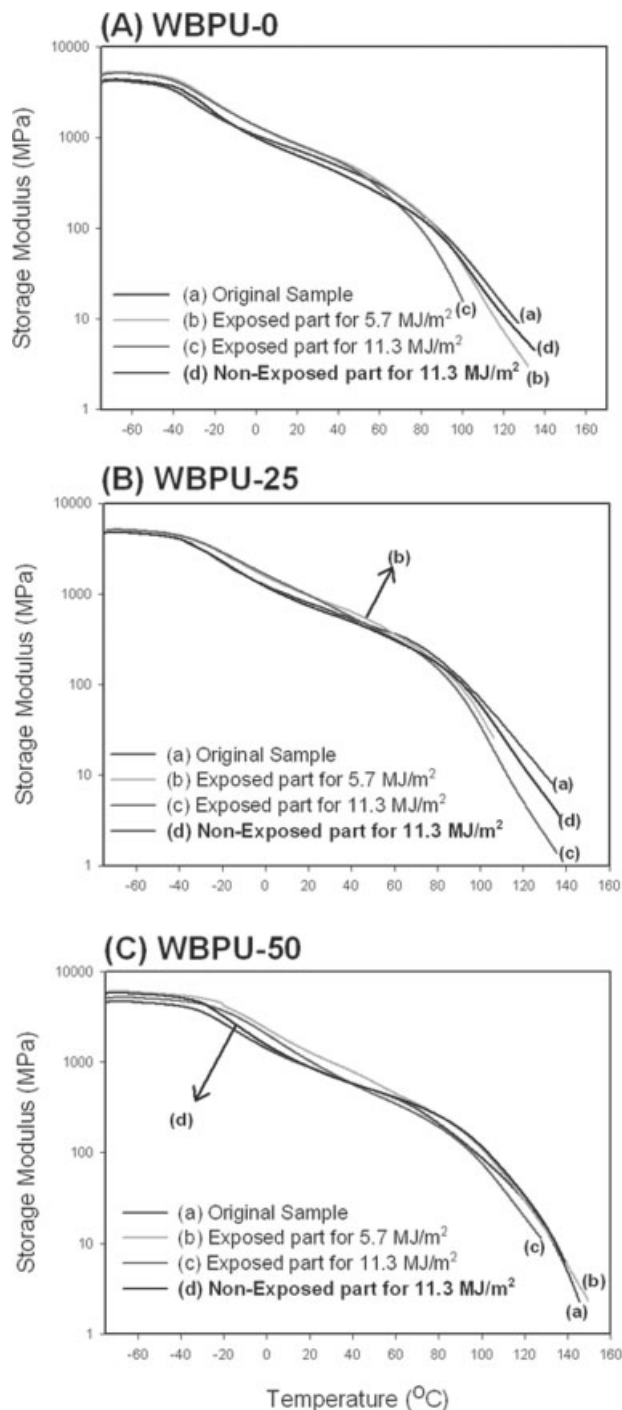


Figure 6 The storage modulus curves for various exposure times (radiant exposure): (A) WBPU-0, (B) WBPU-25, and (C) WBPU-50, [(a) original sample: 0 h (0 MJ/m²), (b) 24 h (5.7 MJ/m²), (c) 48 h (11.3 MJ/m²), and (d) nonexposed part for 48 h (11.3 MJ/m²)].

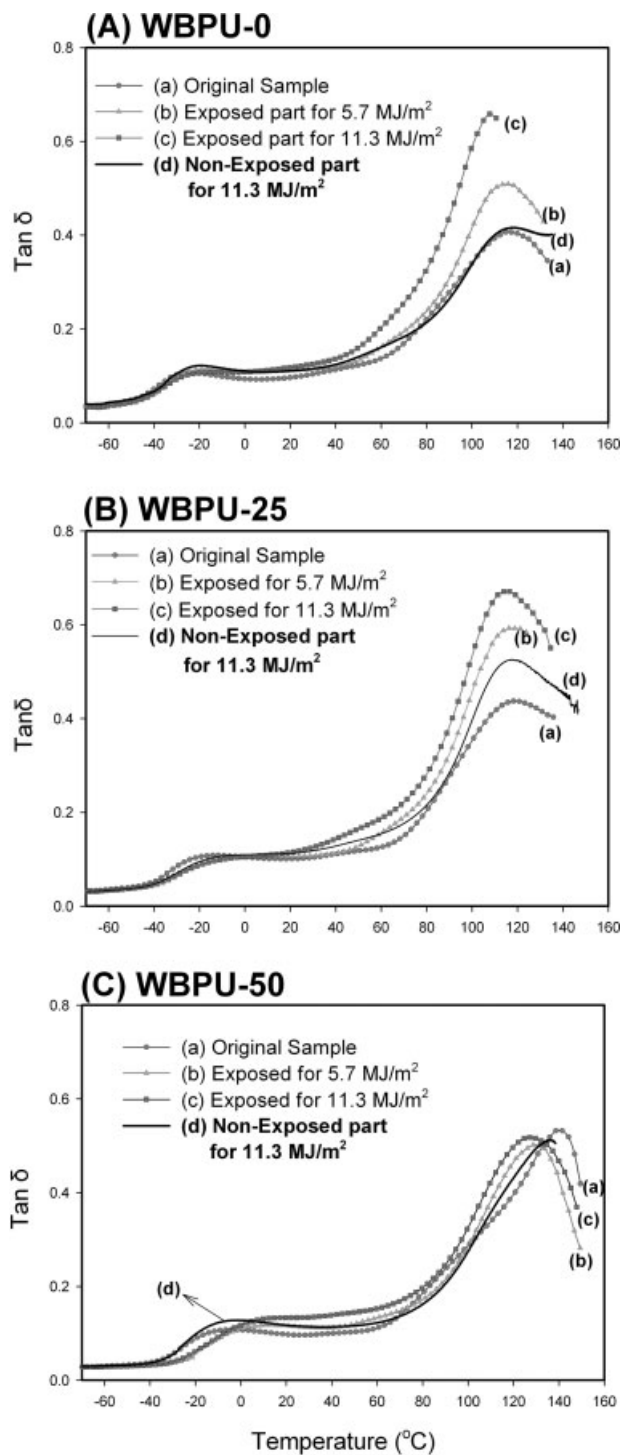


Figure 7 The tan δ curves for various exposure times (radiant exposure): (A) WBPU-0, (B) WBPU-25, and (C) WBPU-50, [(a) original sample : 0 h (0 MJ/m²), (b) 24 h (5.7 MJ/m²), (c) 48 h (11.3 MJ/m²), and (d) nonexposed part for 48 h (11.3 MJ/m²)].

oxidation. It is in this context that this study aims to find out the optimal share of MDI in WBPU to maximize the synergy of aliphatic diisocyanate and MDI for WBPU coatings. WBPUs based on various combinations of MDI/H₁₂MDI (MDI/H₁₂MDI: 0/100, 25/

TABLE V
The Dynamic Thermal Mechanical Properties of WBPU Film Samples for Radiant Exposure (5.7 – 11.3 MJ/m²)

Sample designation	T_{gs} (°C)	T_{gh} (°C)	ΔT_g (°C) ($T_{gh} - T_{gs}$)	Tan δ intensity		
				25°C	70°C	90°C
WBPU-0	-20	109	129	0.0992	0.1691	0.2780
WBPU-0, exposed for 5.7 MJ/m ²	-18	113	131	0.1125	0.1939	0.3075
WBPU-0, exposed for 11.3 MJ/m ²	-14	109	123	0.1212	0.2551	0.4383
WBPU-0, nonexposed part for 11.3 MJ/m ²	-20	117	137	0.1122	0.1829	0.2640
WBPU-25	-12	120	132	0.1014	0.1499	0.2761
WBPU-25 exposed for 5.7 MJ/m ²	-7	117	124	0.1065	0.1900	0.3245
WBPU-25 exposed for 11.3 MJ/m ²	-7	115	122	0.1190	0.2217	0.3832
WBPU-25 nonexposed part for 11.3 MJ/m ²	-8	118	126	0.1148	0.1765	0.2846
WBPU-50	-4	141	145	0.0962	0.1384	0.2371
WBPU-50 exposed for 5.7 MJ/m ²	7	130	137	0.1140	0.1480	0.2142
WBPU-50 exposed for 11.3 MJ/m ²	8	128	136	0.1333	0.1688	0.2466
WBPU-50 nonexposed part for 11.3 MJ/m ²	-2	136	138	0.1153	0.1364	0.2056

75, and 50/50 mol %) were synthesized by a prepolymer mixing process. The effect of MDI on the molecular weight, chemical structure, dynamic thermal mechanical properties, and tensile properties of WBPU was investigated. The change of WBPU's YI (photo-oxidation behavior) under accelerated weathering exposure was also investigated. The WBPUs containing higher MDI content showed lower molecular weight, indicating the participation of some high-reactive isocyanate groups of MDI into side reaction instead of chain growing reaction. As the MDI content increased, the storage modulus and tensile modulus/strength of WBPU film increased, whereas the elongation at break decreased a little, and the glass transitions of soft segments (T_{gs}) and hard segments (T_{gh}) shifted to higher temperature. With increasing radiant exposure, the T_{gs} of exposed samples increased, but the T_{gh} decreased. Although the YI of all original samples (as-polymerized WBPU film sample) showed minus (-) value which indicates their shift toward blue on the chromaticity coordinates. The YI of WBPU-25 and WBPU-50 sample increased with increasing radiation exposure, and H₁₂MDI-based WBPU sample (WBPU-0) remained unchanged. The YI of WBPU containing MDI increased with increasing MDI content and radiant exposure, however, the YI of sample WBPU-25 containing 25 mol % of MDI at 11.3 MJ/m² (radiant exposure) was 6.6 which is a permissible level for exterior coatings.

References

- Coutinho, F. M. B.; Delpech, M. C. *Polym Test* 1996, 15, 103.
- Delpech, M. C.; Coutinho, F. M. B. *Polym Test* 2000, 19, 939.
- Shao, C. H.; Huang, J. J.; Chen, G. N.; Yeh, J. T.; Chen, K. N. *Polym Degrad Stab* 1999, 65, 359.
- Coutinho, F. M. B.; Delpech, M. C. *Polym Degrad Stab* 2000, 70, 49.
- Chen, G. N.; Chen, K. N. *J Appl Polym Sci* 1997, 63, 1609.
- Diterich, D.; Keberie, W.; Witt, H. *Angew Chem Int Ed (Eng)* 1970, 19, 40.
- Crowther, B. G. *Rapra Rev Rep* 1996, 8, 6.
- Frisch, K. C.; Xiao, H. X.; Czerwinski, R. W. *Adhes Age* 1988, 3, 41.
- Osawa, Z. *Dev Polym Photochem* 1980, 3, 209.
- C. R. Newman, D. Forciniti. *Ind Eng Chem Res* 2001, 40, 3346.
- Gajewski, V. *Rubber World* 1990, 202, 15.
- Abu-Zeid, M. E.; Nofal, E. E.; Tahseen, L. A. *J Appl Polym Sci* 1984, 29, 2443.
- Hoyle, C. E.; Kimm, K. J.; No, Y. G.; Nelson, G. L. *J Appl Polym Sci* 1987, 34, 763.
- Nevskii, L. V.; Tarakanov, O. G.; Belyakov, V. J. *J Polym Sci* 1968, 23, 193.
- Nevskii, L. V.; Tarakanov, O. G.; Kafengauz, A. P. *Soviet Plastics* 1972, 1, 46.
- Randall, D.; Bosman, J. *Polyurethane Technol Appl* 2002, 125.
- Zhang, S.; Ren, Z.; He, S.; Zhu, Y.; Zhu, C. *Spectrochim Acta A* 2007, 66, 188.
- Oertel, G.; Hoffman, J.; Maier, U.; Prager, F. H.; Vogel, J. *Polyurethane Handbook*, 2nd ed.; Hanser Publishers: Munich, Vienna, New York, 1994; p 481.
- Yilgor, E.; Burgaz, E.; Yurtsever, E.; Yilgor, I. *Polymer* 2000, 41, 849.
- Menard, K. P. *Dynamic Mechanical Analysis*; CRC Press LLC: Boca Raton, Florida, 1999, p 112.