

Synthesis and Characterization of Reactive Blocked-Isocyanate Coupling Agents from Methyl Ethyl Ketoxime, Ethyl Cellosolve/ ϵ -Caprolactam Blocked Aromatic and Aliphatic Diisocyanates

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ABSTRACT: A series of water-dispersible blocked polyisocyanates were synthesized from toluene 2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI), dimethylol propionic acid, methyl ethyl ketoxime (MEKO), ethyl cellosolve (EC), and ϵ -caprolactam (CL). The physical properties, such as the viscosity, pH, and storage stability, of the blocked-polyisocyanate adducts were measured. All aqueous dispersions of the blocked polyisocyanates showed good storage stability. The prepared blocked polyisocyanates were characterized by Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry, and thermogravimetric analysis techniques. The FTIR confirmed that the —NCO groups of the original TDI and IPDI molecules were completely blocked by the blocking agents. The thermal analysis measurements revealed that both the blocked TDI- and IPDI-based poly-

isocyanates started to deblock at about 55–85°C. Compared to the CL-blocked polyisocyanates, the MEKO- and EC-blocked polyisocyanates had lower thermal dissociation temperatures and faster deblocking rates. We also found that the initial deblocking temperatures of the TDI-based adducts were lower than those of the IPDI-based adducts. The water resistance and tensile properties of the composite films from the blocked-polyisocyanate crosslinkers and hydroxyl-polyurethane emulsion (HPUE) matrix were studied. The tensile strength increased and the elongation at break were lower in the composites compared to the pure HPUE film. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 748–757, 2011

Key words: crosslinking; polyurethanes; water-soluble polymers

INTRODUCTION

Polyurethanes (PUs) are versatile polymers because of their excellent chemical, solvent, and abrasion resistances and their outstanding hardness and toughness, combined with a low-temperature flexibility,^{1–3} and they have a wide range of applications, including coatings, adhesives, foams, textiles, elastomers, and highly crosslinked plastics.^{4–8} Generally, PUs are hydrophobic. As one of the chief raw materials, isocyanates are highly moisture sensitive. However, it is possible to emulsify and disperse PUs in water if some necessary structural modifications are done with an external emulsifier or by the incorporation of emulsifying groups into the PU backbone.^{3,9,10} Depending on the type of ionic group incorporated, the dispersions can be classified as an-

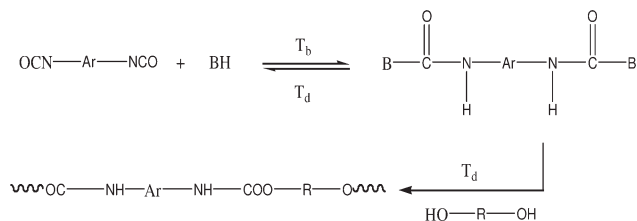
ionic,¹¹ cationic,¹² or zwitterionic.¹³ Anionic dispersions are commercially predominant.^{14,15}

Reactions of isocyanates are widely used to crosslink and chain-extend polymers. However, the high reactivity and toxicity of isocyanates do not allow for their storage and use in one-pack systems, and the effects of the organic solvents of Conventional Pus on the environment are detrimental and have led to the development of alternative techniques that provide eco-friendly systems.

Blocked isocyanates provide a solution for overcoming these drawbacks. Blocked isocyanate is an adduct containing a relatively weak bond formed by the reaction of an isocyanate with a compound containing an active hydrogen atom. At elevated temperatures, this reaction tends to proceed in a way that leads to the regeneration of the isocyanate and the blocking agent. The regenerated isocyanate can react with a coreactant containing hydroxyl functional groups to form urethane, with its thermally more stable bonds. In a typical PU

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heat-curable system, the overall reaction can be viewed in the following way:

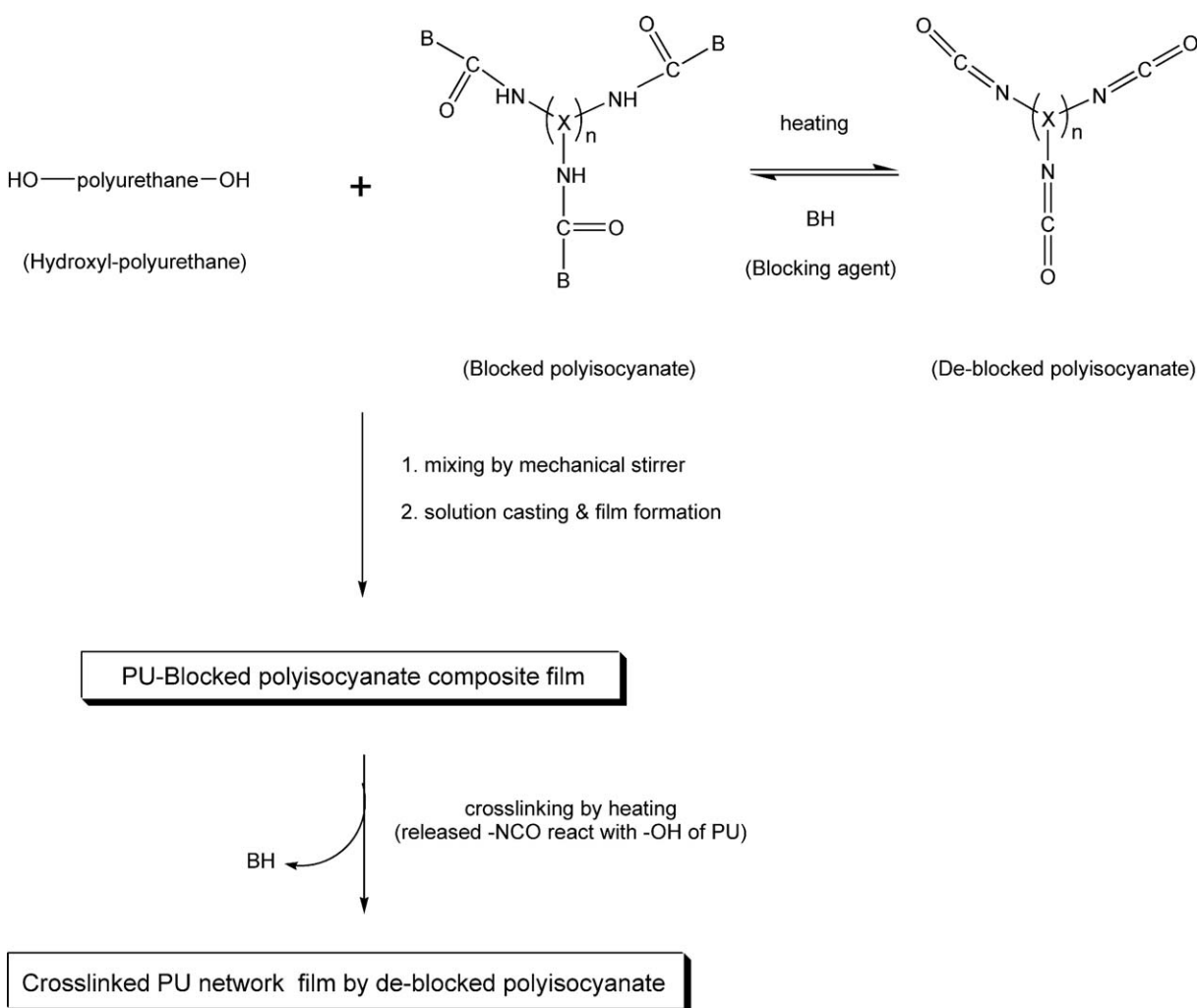


where BH is the blocking agent, T_b is the blocking temperature, and T_d is the deblocking temperature.

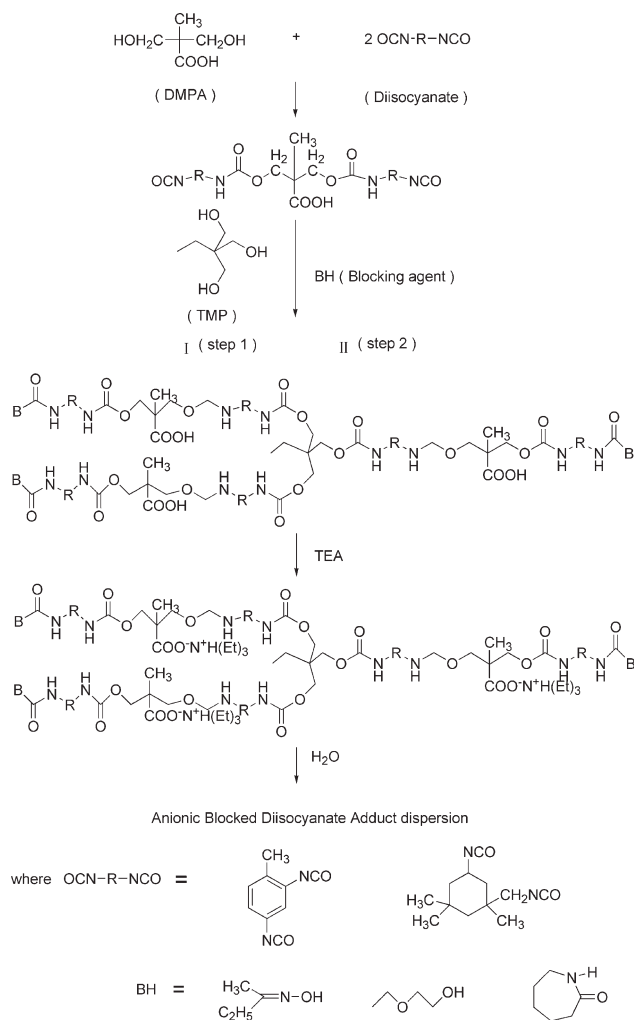
Generally, commercial blocking agents include phenol, ϵ -caprolactam (CL), methyl ethyl ketoxime (MEKO), dimethyl pyrazoles, diethyl malonates, sodium bisulfite, and many others. Imidazoles and amines are ever used as blocking agents.^{16–21} The deblocking temperature of the blocked isocyanates is one of the important limiting factors in industrial applications. The rate and extent of the deblocking

reaction depend on many factors: the structures of the isocyanate and blocking agent, including substituents, solvents, and catalysts; the temperature; and the thermal stability of the isocyanate blocking agent bond.^{22,23}

Recently, water-based PU dispersions are generally made of linear PU chains having ionic groups. However, the tensile and solvent-resistance properties are poor, and hydrophilic modifications lead to poor water resistance for the linear structure. Now, it is highly purified to improve these drawbacks. In our study, a novel method was found for the hydrophobic modification and crosslinking of PUs. All these drawbacks can be improved by the addition of a prepared aqueous blocked isocyanate coupling agent to the PU system. In our study, we prepared a series of novel and eco-friendly water-dispersible blocked polyisocyanates. These blocked-isocyanate coupling agents dispersed well in water, and all aqueous dispersions of the blocked polyisocyanates showed good storage



Scheme 1 Function of the blocked polyisocyanate as crosslinker in the PU film.



Scheme 2 Synthesis of the anionic blocked-isocyanate adducts.

stability. In addition, all of the synthesized blocked polyisocyanates exhibited moderate deblocking temperatures and excellent mechanical properties (better adhesion, tensile strength, and water and chemical resistance) when they were used as coupling agents in hydroxyl-polyurethane emulsion (HPUE) systems. The isocyanate groups [toluene 2,4-diisocyanate (TDI) and isophorone diisocyanate (IPDI)] were effectively blocked by the blocking agents [MEKO, ethyl cellosolve (EC), and CL] in this study. A sketch map of the blocked polyisocyanates as crosslinkers for PU films is shown in Scheme 1. The detailed synthesis route of the blocked polyisocyanate is presented in Scheme 2. The mechanical and thermal properties of the prepared PU composite films and the effect of the blocked polyisocyanates used in the composite were tested and are discussed. Naturally, the prepared blocked polyisocyanates could also be used as crosslinkers in many other thermally curable systems.

EXPERIMENTAL

Materials

The raw materials used in this study are listed in Table I. The raw materials were laboratory-grade chemicals and were used as received except for HPUE, which was prepared in our laboratory. All of the solvents used were purified and dried according to standard procedures.²⁴

Synthesis of water-dispersible blocked polyisocyanates based on TDI

The reaction scheme shown in Scheme 2 outlines the synthetic process used to prepare water-based blocked anionic PU coupling agent dispersions. TDI and dimethylol propionic acid (DMPA) in acetone were first charged into the reaction kettle equipped with a mechanical stirrer, nitrogen inlet, and reflux condenser. The reaction mixture was heated to 70°C in a constant-temperature water bath, and the reaction was carried out until a theoretical NCO content was reached. The change in NCO content during reaction was determined with a standard di-*n*-butylamine back-titration method.²⁵ Then, 1,1,1-trimethylolpropane (TMP) was added to the reaction mixture. During the reaction, the change in isocyanate content was determined with the same method until the theoretical end point was reached; this was after approximately about 2–3 h of reaction. Then, the reaction mixture was cooled to 50°C, and the calculated amount of blocking agent diluted with 50 mL of acetone was slowly added. The reaction was further carried out under 80°C until no NCO peak could be detected in the Fourier transform infrared (FTIR) spectrum. The obtained blocked polyisocyanate adducts were cooled to 50°C, and the

TABLE I
Raw Materials Used in this Study

Designation	Chemical description	Supplier
DMPA	Dimethylol propionic acid	Aldrich, USA
TDI	Toluene 2,4-diisocyanate	Fluka (Switzerland)
IPDI	Isophorone diisocyanate	Fluka
MEKO	Methyl ethyl ketoxime	Aldrich, USA
CL	ϵ -Caprolactam	Aldrich, USA
EC	Ethyl cellosolve	Aldrich, USA
TMP	1,1,1-Trimethylolpropane	Fluka
TEA	Triethylamine	Aldrich, USA
DBTDL	Dibutyl tin dilaurate	Aldrich, USA
HTPB	Hydroxyl-terminated polybutadiene;	Wako Pure Chemical Industries, Ltd. (Japan)
HPUE	Hydroxyl-polyurethane emulsion	Prepared in our laboratory

TABLE II
Recipe of Each Blocked Adduct

Composition	Adduct					
	T ₁	T ₂	T ₃	I ₁	I ₂	I ₃
TDI	34.80	52.20	69.60	—	—	—
IPDI	—	—	—	44.46	66.69	88.92
DMPA	10.73	16.08	21.44	10.73	16.08	21.44
TMP	5.36	8.04	10.72	5.36	8.04	10.72
MEKO	11.50	—	—	11.50	—	—
EC	—	17.82	—	—	17.82	—
CL	—	—	29.83	—	—	29.83
TEA	8.08	12.12	16.16	8.08	12.12	16.16

I₁, The prepared EC-blocked IPDI adduct.

I₂, The prepared CL-blocked IPDI adduct.

neutralizing agent triethylamine (TEA) was added and allowed to react for 30 min. At the end, water was added to accomplish the dispersion under vigorous stirring. These blocked isocyanates were water-dispersible adducts.

Synthesis of water-reducible blocked polyisocyanates based on IPDI

The synthetic procedure of the IPDI-based adducts were the same as that described for the TDI-based adducts, except for the reaction temperature. The IPDI-based adducts were synthesized at a higher temperature (85–90°C). The recipe of each blocked adduct is given in Table II.

Composites preparation

Films of the HPUE composite samples prepared by the incorporation of 0.5 and 1 wt % blocked-isocyanate coupling agents were prepared by solution casting Cole-Parmer, USA. The composites were mixed and run in a Waring blender for 5 min. The blender was used to thoroughly stir the two dispersions together. The formulations were then cast onto Petri dishes greased with silicon and left to evaporate at room temperature for 24 h. The composite films were then dried in a convection oven to remove all remaining water. After that, the temperature was fixed above the deblocking temperature to accelerate the reaction between HPUE and the blocked-isocyanate coupling agent. After 30 min of baking, the films were removed from the oven and kept *in vacuo* at room temperature for 48 h before the test and characterization.

Characterization

The viscosity of the dispersions was measured with a Brookfield (Brookfield, USA). DV-III viscometer at 25°C. Dispersions in a sealed bottle were kept in an air-circulated oven under 80°C, at room temperature

(25°C) and in a refrigerator under 0°C to examine their storage stability at different temperatures. The FTIR spectra of adducts were recorded with an RFX-65A IR analyzer (Analect, USA) in the range 400–4000 cm⁻¹ at room temperature. The samples were prepared as pellets with potassium bromide.

Thermal analysis

Differential scanning calorimetry (DSC; TA Instruments model DSC 204C) was used to examine the thermal properties of the blocked-isocyanate coupling agents obtained from the aqueous dispersions and HPUE composites at a heating rate of 10°C/min under a nitrogen purge of 30 mL/min. The temperature range of the DSC test was from 20 to 200°C and from –80 to 20°C, respectively. The sample size was 5–10 mg in a sealed aluminum pan. Thermogravimetric analysis (TGA) was carried out with a TA Instruments model TGA Pyris1 thermogravimetric analyzer. The sample weight was 8–10 mg. The experimental run was performed from 30 to 600°C at a heating rate of 20°C/min under a nitrogen atmosphere with a gas flow rate of 30 mL/min. Blocked-isocyanate samples were dried well in a vacuum oven before testing.

Tensile analysis

The tensile properties of the composites were measured with a universal tensile machine (Instron, USA) at a crosshead speed of 50 mm/min. Sample specimens were prepared from the films with a die 10 mm wide and 50 mm long. The grip distance was set at 25 mm. The thickness of the film was 0.8–1.2 mm. For each sample, four specimens were tested, and the average value is reported.

Water uptake tests

The water resistances of the composites were tested as follows. Preweighed dry slabs (50 × 10 mm² in size) were immersed in deionized water for 1 week to study the water resistance at room temperature. After immersion, the samples were blotted with a laboratory tissue and weighed. The final water uptake was expressed as the weight percentage of water in the swollen sample:

$$\text{Water uptake (\%)} = (W_W - W_D)/W_D \times 100\%$$

where W_D is weight of the dry sample and W_W is the weight of the swollen sample.

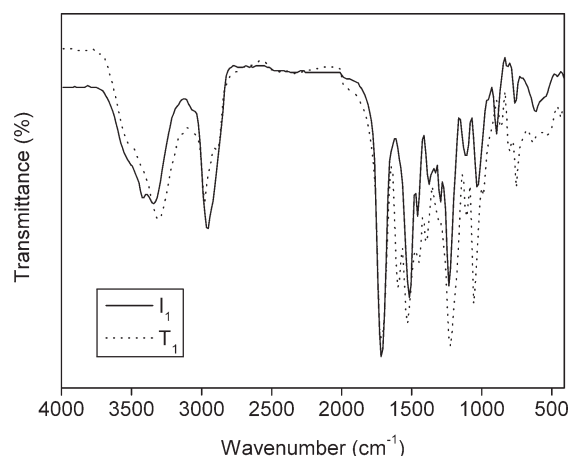


Figure 1 FTIR spectrum of the anionic MEKO-blocked polyisocyanate adducts.

Gel time tests

The gel time studies were done as follows: Anionically water-dispersible blocked-polyisocyanate adducts were mixed thoroughly with hydroxyl-terminated polybutadiene (HTPB) in 1 : 1 NCO:OH ratio in flasks, and then, the beakers were placed in an oil bath maintained at 160°C. We inverted the flasks at regular time intervals to observe the flow behavior of the solutions. The time at which the solution ceased to flow was taken as the gel time. A duplicate experiment was conducted for each synthesized adduct to ensure the accuracy of the collected data.

RESULTS AND DISCUSSION

Synthesis of anionic blocked-isocyanate coupling agents

A series of blocked polyisocyanates were prepared, and their structures were confirmed by FTIR spectroscopy. Representative FTIR spectra of the MEKO-blocked TDI and IPDI adducts are given in Figure 1. The FTIR spectra of all of the blocked polyisocyanates were identical and showed no absorption in the 2250–2270 cm^{-1} range; this indicated that the

–NCO groups of the diisocyanate molecules were completely blocked by the blocking agents. The formation of a urethane linkage could be identified easily by a few main characteristic bands:^{26–28} the bands at 3300–3370 cm^{-1} corresponded to the stretching vibrations of NH, the peaks at 1685–1730 cm^{-1} corresponded to the stretching vibrations of carbonyl (C=O) groups, the bands at 1533–1540 cm^{-1} corresponded to carbamate, and the band at 1223–1267 cm^{-1} corresponded to the stretching vibrations of C=O combined with NH in all of the spectra. The absorption frequencies of the individual prepared blocked-isocyanate adducts are given in Table III. The corresponding FTIR absorption frequencies of the synthesized blocked diisocyanate adducts just confirmed the formation of blocked TDI- and IPDI-based coupling agents.

Physical properties of the blocked polyisocyanate dispersions

The solid content of the synthesized blocked polyisocyanate dispersions was 30 wt %. The carboxylic groups of DMPA were completely neutralized by TEA in all of the experiments. The pH of the dispersions obtained by the neutralization of the weakly acidic pendant COOH groups of DMPA by a strong base, TEA, was weakly basic because of the remnant basicity of the internal salt groups. Blocked-isocyanate dispersions based on TDI were more basic compared to the dispersions based on IPDI in the test. The viscosity, storage stability, and pH of the dispersions are given in Table IV. The dispersion viscosity of the CL-blocked adduct was higher than those of the MEKO- and EC-blocked dispersions for the same diisocyanate. The result was possibly caused by the slow blocking reaction of CL. It was also due to the self-polymerization of CL. In the case of diisocyanates, the viscosities of the dispersions based on IPDI were lower than those based on TDI. This was due to the existence of an aromatic ring in the structure of TDI, which caused a higher reactivity in TDI and resulted in a high viscosity in the dispersions.

TABLE III
Absorption Frequencies of the Individual Prepared Blocked-Isocyanate Adducts

Adduct	Urethane (S) stretching (<N–H; cm^{-1})	Carbonyl (VS) stretching (<C=O; cm^{-1})	Carbamate (S; –NH–COO–; cm^{-1})	Amide (S) stretching (–NH–CO–; cm^{-1})
T ₁	3301	1727	1533	1226
T ₂	3305	1712	1536	1228
T ₃	3307	1712	1540	1226
I ₁	3338	1716	1515	1240
I ₂	3363	1712	1536	1242
I ₃	3338	1706	1540	1240

VS, very strong; S, Strong.

TABLE IV
Viscosity, Storage Stability, and pH of the Dispersions

Adduct dispersion	pH	Gel time (h)	Viscosity (Cps)	Storage stability (months)			Deblocking temperature (°C)	
				RT	80°C	0°C	DSC	TGA
T ₁	8.15	11	150	>6	>1	>1	55–160	60
T ₂	7.84	10.5	265	>6	>1	>1	60–170	70
T ₃	7.58	9	650	>6	>1	>1	70–180	110
I ₁	7.98	>24	100	>6	>1	>1	60–170	75
I ₂	7.73	>24	185	>6	>1	>1	65–170	80
I ₃	7.55	>24	320	>6	>1	>1	85–180	120

RT, room temperature.

The storage stability of the blocked-isocyanate dispersions, which is a very important parameter in practical applications, depended on many factors, such as the pH, solid content, and viscosity of the medium.²⁹ The storage stability was studied under three conditions, namely, at room temperature (25°C) for 6 months, at 80°C for 1 month, and at 0°C for 1 month, to evaluate the storage stability of the dispersions, and the results are presented in Table IV. The experimental data obtained suggested that all of the prepared dispersions were stable. The stability proved indirectly that the deblocking of the blocked-isocyanate adducts did not occur in the dispersion. All of the blocked-isocyanate dispersion samples were stable for more than 6 months without any gelation under room temperature.

Thermal behaviors of the blocked polyisocyanates

Many analytical techniques have been used to study deblocking temperatures. The most common methods used for determining deblocking temperatures are as follows: gel time, FTIR, TGA, DSC, FTIR spectroscopy in combination with dynamic mechanical analysis, solid-state NMR, and carbon dioxide evolution.³⁰ Deblocking temperatures mostly depend on the method of analysis, the heating rate, and some other variables. Different analytical techniques may produce different deblocking temperatures for the same sample. In our study, DSC and TGA techniques were applied to determine the deblocking temperatures of the prepared blocked polyisocyanate adducts.

The DSC technique was used to study the deblocking properties because the synthesized compounds contained different adduct structures, and therefore, they should have exhibited energy variations in the DSC curve when they deblocked. The deblocking temperature of the blocked polyisocyanate depended on the isocyanates and blocking agents. The DSC curves are depicted in Figure 2.

All of the DSC curves in Figure 2 did not show a significant broad endotherm. The broad endotherm range may have been caused by the slow and controlled release of the blocking agents. For anionic blocked polyisocyanate samples, the melting of the short- and long-range order in the hard-segment

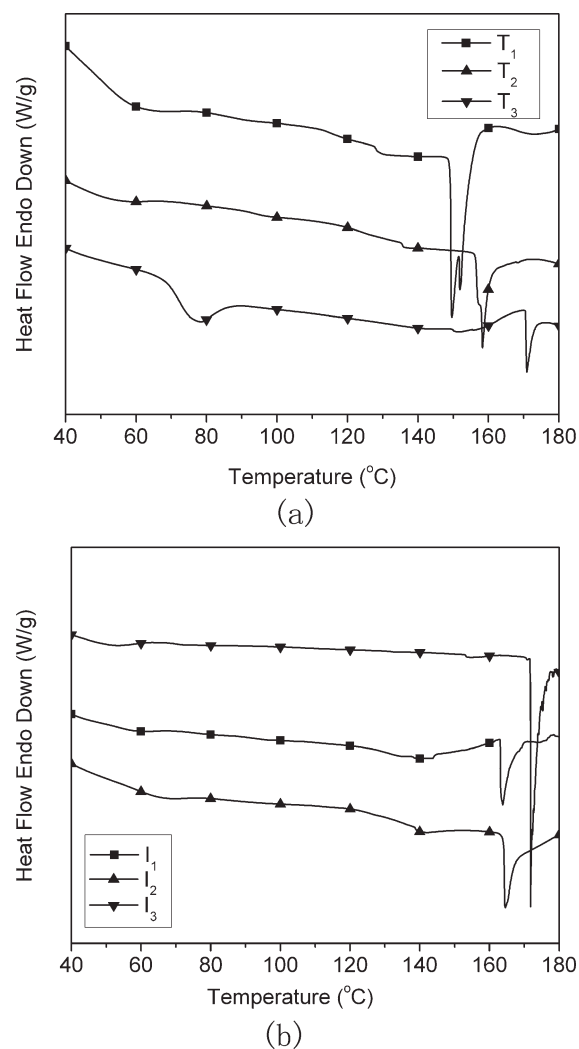


Figure 2 DSC curves of the anionic blocked-isocyanate adducts: (a) TDI and (b) IPDI based.

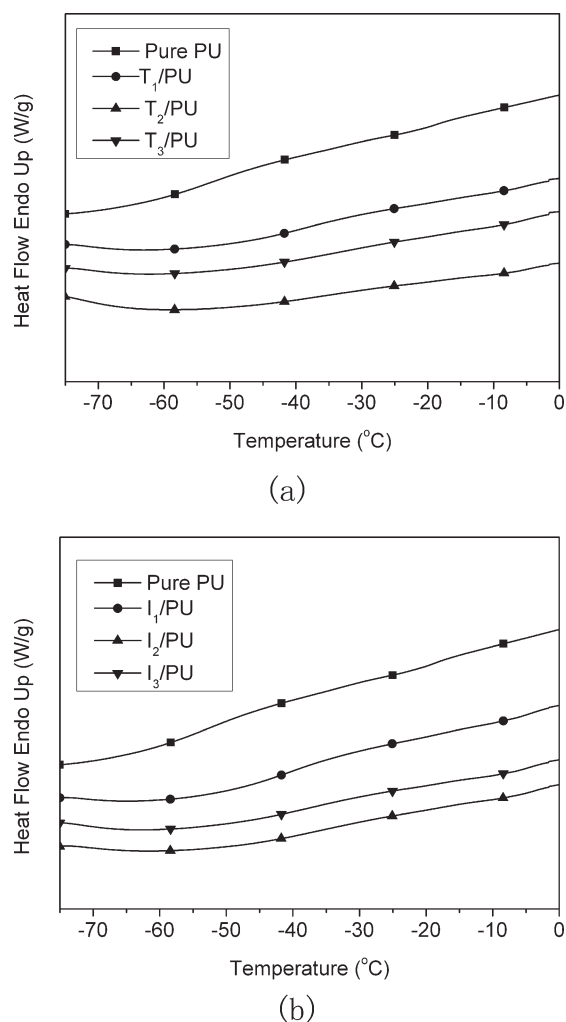


Figure 3 DSC curves of the pure and crosslinked PUs by blocked polyisocyanates: (a) TDI and (b) IPDI based.

domains of the polyisocyanate^{31,32} might take place at these temperature ranges where unblocking might occur; this is another reason for the broadening of the DSC curve, and it affects the determination of the deblocking temperature range by DSC measurement. In the case of blocking agents, from Figure 2(a), we found sharp endotherms around 148°C for T_1 , 158°C for T_2 and 171°C for T_3 , which were the maximum deblocking ratio temperatures of the MEKO-, EC-, and CL-blocked polyisocyanates, respectively. The result indicated that the order of the blocking agent reactivity was as follows: MEKO > EC > CL. A similar trend is shown in Figure 2(b). In the case of isocyanates, for the same blocking agent, the deblocking temperatures of the blocked-isocyanate adducts based on TDI were lower than the adducts based on IPDI, such as 148°C for T_1 and 162°C for I_1 . The prepared MEKO-blocked IPDI adduct as the recipe given in Table 2. This was due to the high reactivity of TDI.

The glass-transition temperature (T_g) of the samples of the pure and crosslinked PUs by the prepared blocked polyisocyanates are shown in Figure 3. The data are summarized in Table V.

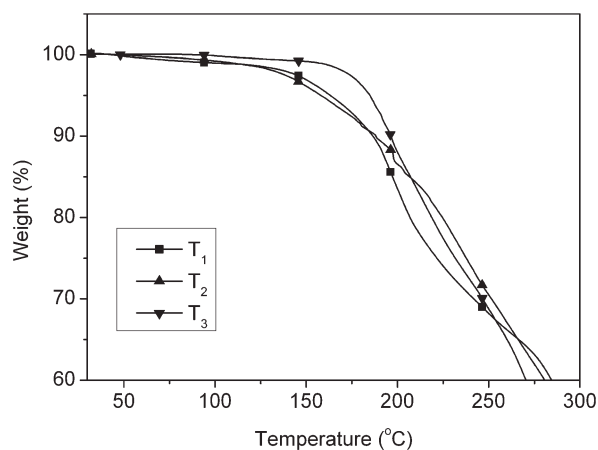
The T_g values of all of the crosslinked HPUE samples were higher than that of pure PU. This was because the linear structure of the pure HPUE provided greater flexibility and mobility to the chains, whereas the PU containing polyisocyanate coupling agent formed an additional more rigid crosslinked network structure, which restricted the movement of the chain. In the case of the blocking agents, the PU film crosslinked by the CL-blocked isocyanate coupling agent exhibited a higher T_g than the PU film crosslinked by the MEKO- and EC-blocked isocyanate coupling agent. This may have been due to the better controlled released of the CL-blocked polyisocyanate, which led to a higher crosslinking density. Between the two isocyanates, for the same blocking agent, the PU film crosslinked by the TDI-based polyisocyanates showed higher values of T_g than the PU film crosslinked by the IPDI-based polyisocyanate. In the PU sample crosslinked by the TDI-based polyisocyanate, the hard segments were more ordered; this led to hard-segment cohesion, whereas in the IPDI-based polyisocyanate crosslinked PU sample, the hard segments were less ordered. This led to a low T_g of the sample. The high reaction nature of TDI, which could introduce a more rigid structure into the PU chain, may have been another reason for the higher T_g of the sample crosslinked by TDI-based polyisocyanate.

TGA was also a very useful technique for observing the deblocking temperature of the blocked polyisocyanates. However, TGA can not be applied for compounds that do not exhibit volatility over the deblocking temperature range. The rate and extent of the elimination reaction may be affected by some factors: the structures of the isocyanates and blocking agents, including substituents; residual solvents; the presence of catalysts; and the temperature. The TGA curves of the blocked polyisocyanate adducts are depicted in Figure 4.

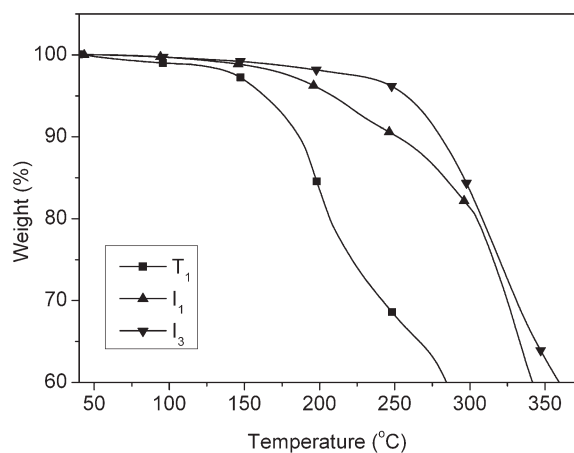
Generally, the deblocking temperatures of a blocked aromatic isocyanate are always lower than those of blocked aliphatic isocyanates. The TGA

TABLE V
 T_g Values of the Samples of the Pure and Crosslinked PUs by Prepared Blocked Polyisocyanates

Samples	Baking temperature/time (°C/min)	T_g (°C)
HPUE	120/30	-48
T_1 /PU	120/30	-38
T_2 /PU	120/30	-35
T_3 /PU	120/30	-30
I_1 /PU	120/30	-42
I_2 /PU	120/30	-40
I_3 /PU	120/30	-38



(a)



(b)

Figure 4 TGA curves of the anionic blocked-isocyanate adducts: (a) TDI and (b) IPDI based.

curves showed that the initial deblocking of the MEKO-blocked TDI and IPDI adducts occurred around 60 and 75°C, respectively. The deblocking of the EC-blocked TDI and IPDI adducts was observed around 70 and 80°C, respectively. The CL-blocked

TDI and IPDI adducts deblocked at 110 and 120°C, respectively. These values were comparable to the reported deblocking values by TGA.^{33,34} For the same diisocyanate, in the case of the blocking agent, we found that the deblocking temperatures of MEKO, EC, and CL were in the following order: MEKO-blocked < EC-blocked < CL-blocked. At the same time, we also observed that the order of deblocking temperatures of the blocked polyisocyanate adducts obtained by DSC and TGA measurements were comparable: The CL-blocked adducts dissociated at a higher temperature than the MEKO- and EC-blocked adducts. Compared to the blocked isocyanates based on IPDI, the coupling agent based on TDI decomposed at a lower temperature. This was possibly due to the stronger electron-withdrawing ability of the phenyl ring in the structure of TDI, which made the coupling agent based on TDI have higher reactivity and a lower deblocking temperature.

Tensile properties of the blocked polyisocyanates and HPUE composites

The sample films were prepared by the incorporation of 0.5 and 1 wt % of the blocked polyisocyanates into the HPUE matrix with solution casting and baked at the deblocking temperature for 30 min. Their tensile properties were evaluated and are tabulated in Table VI. The composites, which contained blocked polyisocyanates, exhibited higher tensile strengths and moduli and lower elongations than the pure PU film. This was because, at high temperature (over the initial deblocking temperature), the regenerated NCO groups reacted with the hydroxyl of PU and led to a more rigid structure network.

In general, the tensile strength and modulus increased with increasing crosslinking density, whereas the elongation at break increased with decreasing crosslinking density. During the crosslinking reaction, the crosslinking density increased; this resulted in a high tensile strength, modulus, and

TABLE VI
Tensile Properties of the Samples

Composite	No crosslinker			0.5% crosslinker ^a			1% crosslinker ^a				
	120°C ^b			120°C ^b			120°C ^b			150°C ^b	
	M (MPa)	TS (MPa)	EL (%)	M (MPa)	TS (MPa)	EL (%)	M (MPa)	TS (MPa)	EL (%)	TS (MPa)	EL (%)
PU	2.71	3.80	> 700	—	—	—	—	—	—	—	—
T ₁ /PU	—	—	—	10.02	14.41	> 500	10.86	14.55	432	15.73	382
T ₂ /PU	—	—	—	9.55	13.32	> 500	9.72	13.45	435	14.21	402
T ₃ /PU	—	—	—	7.81	8.93	> 500	8.43	9.28	421	10.80	375
I ₁ /PU	—	—	—	8.62	10.65	> 500	9.14	10.77	452	12.03	408
I ₂ /PU	—	—	—	8.45	9.93	> 500	8.96	10.05	450	11.12	421
I ₃ /PU	—	—	—	7.60	8.62	> 500	7.67	8.73	436	9.05	395

M, modulus, TS, tensile strength, EL, elongation at break.

TABLE VII
Swelling Properties of the Samples

Composites	No crosslinker	0.5% crosslinker ^a		1% crosslinker ^a	
	120°C ^b	120°C ^b	150°C ^b	120°C ^b	150°C ^b
	Water uptake (%)	Water uptake (%)	Water uptake (%)	Water uptake (%)	Water uptake (%)
HPUE	17.10	—	—	—	—
T ₁ /HPUE	—	7.14	6.85	6.76	6.02
T ₂ /HPUE	—	7.83	7.04	7.02	6.35
T ₃ /HPUE	—	8.26	7.58	7.54	7.18
I ₁ /HPUE	—	7.92	7.12	7.08	6.47
I ₂ /HPUE	—	8.26	7.72	7.46	6.94
I ₃ /HPUE	—	9.15	8.50	8.03	7.46

^a Crosslinker content.

^b Baking temperature.

low elongation at break. In addition, the tensile strength, modulus, and elongation at break were affected by the change in isocyanate, blocking agent, and curing temperature. The composites modified by the TDI-based coupling agent showed a higher tensile strength and modulus and lower elongation than the composites modified by the IPDI-based coupling agent for the same blocking agent. It is well known that the structure and reactivity of isocyanates can affect the tensile properties.³⁵ Compared to the aliphatic structure of IPDI, the aromatic structure of TDI led to better polymer chain ordering and a rigid structure that favored better tensile properties. Also, a more ordered structure of the hydrogen bonds between the urethane groups in the hard segment of the TDI-based coupling agent resulted in better tensile properties, whereas because of the aliphatic ring structure of IPDI, the hydrogen bonds were partly disrupted.³⁶ However, the higher reactivity of TDI might have resulted in an increased rigidity of the polymers, which subsequently reduced the percentage elongation. As a fact that resulted from the electronic effect, the blocked isocyanates based on the aromatic isocyanates deblocked at lower temperature, and thus, the reactivity of the regenerated aromatic-NCO group was higher than that of the aliphatic-NCO group toward the hydroxyl group. In the case of the blocking agents, the MEKO- and EC-blocked composites showed a higher tensile strength, modulus, and percentage elongation at break than the CL-blocked composites. Generally, the blocking and deblocking reactions of MEKO- or EC-blocked isocyanates were faster than the CL-based reactions. Hence, the MEKO- or EC-blocked polyisocyanate adduct deblocked at a faster rate and readily reacted with HPUE to form a deep crosslinking structure; this accounted for the better tensile properties. In addition, the films baked at 150°C showed a higher tensile strength than those baked at 120°C. The results show that with increasing deblocking temperature, the ten-

sile strength increased, and the elongation at break decreased. This may have been due to the fact that the crosslinking process was related to the deblocking reaction, which increased with increasing deblocking temperature. An increase in the curing temperature led to rapid deblocking and increased the concentration of regenerated —NCO groups.

Water uptake and gel time studies

The composite films containing 0.5 and 1 wt % blocked isocyanates and the pure HPUE film were used to conduct this experiment. As shown in Table VII, the films containing a coupling agent exhibited much lower swelling in water than the pure HPUE film. The pure HPUE film showed an almost threefold increase in the percentage swelling in water compared to the crosslinked samples. The water uptake of the HPUE samples containing a crosslinking agent baked at different deblocking temperatures (120 and 150°C) decreased with increasing baking temperature. As known, with increasing baking temperature, the deblocking reaction and the reaction with blocked-isocyanate adducts were complete; this led to a high crosslinking density. In the case of isocyanates, the TDI-based composites showed more resistance to water compared to the IPDI-based composites. All of the results confirmed that the reduced swelling was due to the effective crosslinking of —NCO groups with the hydroxyls in the process of deblocking. For different blocking agents, the MEKO- and EC-blocked composite samples showed better water resistance than the CL-blocked composites because the blocking and deblocking reactions of MEKO and EC were faster than the CL-based reactions. Hence, the MEKO- or EC-blocked coupling agent deblocked at a faster rate and readily reacted with HPUE to form a deeper crosslinked network structure. This result was accordance with the tensile testing. Hence, the crosslinking of HPUE by the incorporation of blocked coupling agents could be an efficient pathway for improving

the properties of aqueous PU dispersions. The detailed results are presented in Table VII.

The gel times for the isocyanate–HTPB prepolymer were determined. The reason we chose HTPB was that it could make a short potlife because of the high reactivity of the primary hydroxyl groups of HTPB toward the isocyanate groups. During the course of the gel time studies, the viscosity increased, and the free flow of the mixture was arrested gradually. The gel times of the blocked isocyanate–HTPB mixture are presented in Table IV. The gel time depended on the reactivity of isocyanate. Between the two isocyanates, the adducts based on TDI showed a lower gel time than those based on IPDI because the electrophilicity of the aliphatic –NCO groups was smaller. Hence, they reacted more slowly with hydroxyl groups than the aromatic isocyanates. Considering adducts based on TDI, we observed that the gel time was in the following order: MEKO-blocked adducts > EC-blocked adducts > CL-blocked adducts. The possible reason for this order was the different structures of the blocking agent, which led to different electron-withdrawing abilities. For the adducts blocked by CL, the low gel time was due to its stronger electron-withdrawing ability, which drained the electron density from the nitrogen of CL and left a partial positive charge on it.

CONCLUSIONS

In this study, a series of water-based MEKO-, EC-, and CL-blocked aromatic and aliphatic diisocyanate (TDI and IPDI) coupling agent dispersions was successfully synthesized and characterized. The viscosities of the TDI-based dispersions were higher than those of the IPDI-based dispersions because of the high reactivity of TDI. These blocked-isocyanate adducts were deblocked and could be the crosslinkers of HPUE at different deblocking temperatures. The excellent water resistance and high tensile strength of the composite films confirmed that HPUE was crosslinked well by the prepared blocked polyisocyanates. The initial deblocking temperatures of the blocked-polyisocyanate adducts were determined by DSC and TGA. We found that the deblocking temperature increased in the following order: MEKO < EC < CL. The storage stability results show that all of the prepared dispersions were stable for more than 6 months at room temperature and for more than 1 month at 0 and 80°C. The blocking of isocyanate functionality allowed us to make one-package compounds with the required stability in aqueous media. Gelation test results confirmed that the TDI-based blocked-isocyanate adducts deblocked at lower temperatures and cure at faster

rates than the IPDI-based blocked-isocyanate adducts. All of the prepared anionic blocked polyisocyanates could be used as potential crosslinkers in many fields.

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