Research on Two-Component Room-Temperature Curable Polyurethane-Urea Resins Using Blocked Polyisocyanates

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Introduction

Two-component room-temperature curable aliphatic and/or alicyclic (hereinafter abbreviated as aliphatic) polyurethane-urea resins have not been practically applied except for special applications. This is because aliphatic polyamines are highly reactive toward aliphatic isocyanates, resulting in an excessively fast curing rate. On the other hand, aromatic two-component curable polyurethane-urea resins consisting of an isocyanate-terminated prepolymer using toluene diisocyanate (TDI) and 4,4'-methylenebis(2-chloroaniline) (MOCA) have been in practical use since the 1950s.

Despite toxicity concerns, they are still used today in heat-curable cast elastomers, as well as room-temperature curable waterproofing materials and flooring. Recently, the toxicity of isocyanates has become a major concern, and there is a growing demand for systems that are friendly to both human health and the environment.

Although one-component thermosetting coatings (solution-based, powder, and waterborne) composed of blocked polyisocyanates, polyol compounds, or polyamine compounds have been developed, research on blocked polyisocyanates has been exclusively focused on one-component thermosetting types that are stable at room temperature 1),2). Consequently, there is almost no research on their application to two-component room-temperature curable polyurethane-urea resins.

The authors investigated the effects of isocyanate monomers and various blocking agents on the room-temperature reactivity between blocked polyisocyanates and highly nucleophilic aliphatic diamines. As a result, we discovered that both aromatic and aliphatic blocked polyisocyanates react quantitatively at room temperature by selecting specific blocking agents, yielding polyurethane-urea resins with excellent tensile properties 3),4).

Results and Discussion

1. Influence of Blocking Agents in the Reaction of Aliphatic and Aromatic Blocked Polyisocyanates with 4,4'-Diaminodicyclohexylmethane (H_{12}-MDA)

Various blocked polyisocyanates were synthesized by reacting isocyanate-terminated prepolymers with various blocking agents shown in Figure 1 (blocking agent/NCO = 1.05 equivalent ratio). For the aliphatic blocked polyisocyanates, an isocyanate-terminated prepolymer (Prepolymer A) with an NCO content of 3.6 wt.% was used, which consisted of Kuraray Polyol P-2010 / trimethylolpropane (TMP) / isophorone diisocyanate (IPDI) at an equivalent ratio of 0.8 / 0.2 / 2.0 in 20 wt.% diethylene glycol dimethyl ether (DMDG). For the aromatic blocked polyisocyanates, a PTMG/TDI-based isocyanate-terminated prepolymer with an NCO content of 3.0 wt.% (C-4080, manufactured by Tosoh Corporation) was employed.

The synthesized blocked polyisocyanates were mixed with H_{12}-MDA at an NH_2/blocked isocyanate (BL-NCO) equivalent ratio of 0.98. The mixtures were then cast onto polypropylene (PP) plates to a thickness of approximately 0.3–0.5 mm, and their curability at 25 °C was evaluated. The results are shown in Figure 1.

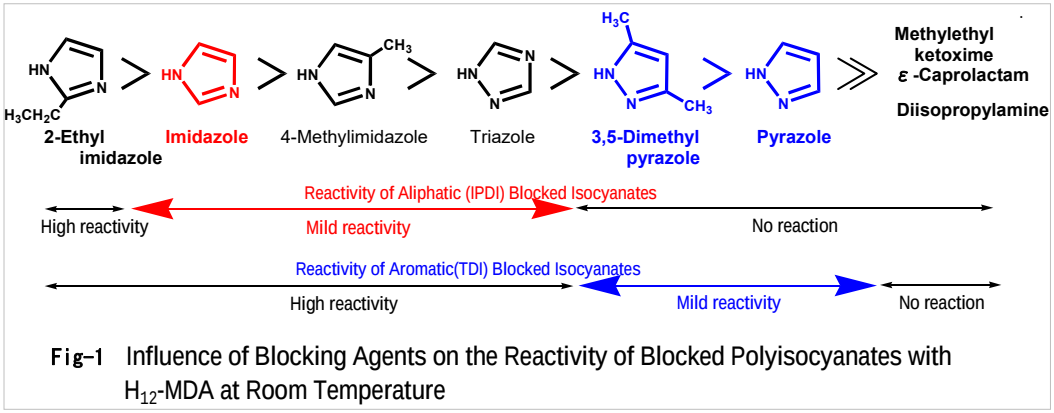


Fig-1 Influence of Blocking Agents on the Reactivity of Blocked Polyisocyanates with H_{12}-MDA at Room Temperature

Aliphatic and aromatic blocked polyisocyanates were synthesized by reacting NCO-terminated prepolymers with various blocking agents at a 1.00 equivalent ratio, using P-2010/TMP/IPDI and PTMG/TDI systems, respectively. These were then mixed with 4,4'-diaminodicyclohexylmethane (H_{12}-MDA) at a 0.98 NH_2/BL-NCO ratio to evaluate 25°C curing performance, as detailed in Figure 1.

Aliphatic polyisocyanates blocked with imidazole or triazole, and aromatic ones with pyrazole, cured within one day at

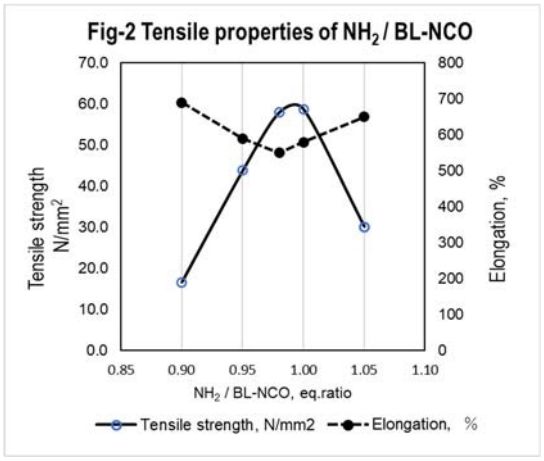
25°C to form transparent films that were easily demolded from PP plates. While reactivity follows the order in Figure 1, unsubstituted imidazole (aliphatic) and pyrazole or 3,5-dimethylpyrazole (aromatic) were identified as the optimal blocking agents, offering a balance of mild reactivity, sufficient pot life, and good strength development.

2. Two-Component Ambient-Curing Aliphatic Polyurethane Urea Resins

2-1 Relationship between NH_2/BL-NCO equivalent ratio and tensile properties during curing.

Using the imidazole-blocked prepolymer A, the effect of varying the NH_2/BL-NCO equivalent ratio of H12-MDA from 0.90 to 1.10 on tensile properties is illustrated in Figure-2.

The tensile strength reaches its maximum near an NH_2/BL-NCO equivalent ratio of 1.0, suggesting that the reaction proceeds quantitatively.



2-2 Properties of Aliphatic Polyurethane Urea Resins Cured at 25°C

Table 1 shows the physical properties of the imidazole-blocked polyisocyanates cured with an alicyclic diamine at 25 °C for 10 days, using polyester polyols or polycarbonate diols as the polyols, and IPDI or 4,4'-methylenebis(cyclohexyl isocyanate) (H_{12}-MDI) as the isocyanate monomers

Table-1 Curing Properties of Aliphatic Polyurethane-Urea Resins at Room Temperature (20°C / 10 days)

A-Parts (Blocked polyisocyanate: BL-NCO)						B-Parts (Polyamine)		Solids	Flow time	Tensile Properties		
NCO-terminated prepolymer Polyol / isociyanate (eq.ratio)	Blocking agents (Imidazole /NCO)	Solids wt.%	DMDG wt.%	BL-NCO wt.%	Viscocity mPa·s / 25°C	Alicyclic diamine	NH_2/ BL-NCO eq.ratio	wt.%	min./ 25°C	Elongation %	100% Modulus N/mm^2	Tensile strength N/mm^2
P-1010 / H_{12}-MDI = 1.0/2.0	Imidazole (1.00/ 1.00)	68	32	3.38	2,450	PACM	0.98	70	44	410	10	48
P-2010 / TMP / IPDI = 0.8/0.2/2.0		68	32	2.56	2,050	PACM	0.98	70	62	480	4	53
P-2010 / TMP / H_{12}-MD = 1.0/2.0		64	36	2.34	2,000	C-260	0.98	66	42	480	7	46
P-3010 / F-2010 / IPDI = 0.8/0.2/2.0		74	26	1.81	5,800	PACM	0.98	75	51	630	3	41
P-3010 / F-2010 / IPDI = 0.8/0.2/2.0		74	26	1.81	5,800	C-260	0.98	75	74	650	3	47
C-2090 / IPDI = 1.0/2.0		63	37	1.93	1,950	PACM	0.98	65	79	400	7	45
C-2050 / IPDI = 1.0/2.0		63	37	1.99	2,350	PACM	0.98	65	77	370	7	60

- **Polyols**:P-1010 (Mn:1000, f=2)), P-2010 (Mn:2000,f=2)), P-3010 (Mn:3000, f=2)), and F-2010 ((Mn:2000, f=3)) are polyester polyols manu factured by Kuraray Co., Ltd.C-2050 (Mn:2000,f=2)) and C-2090 (Mn:2000, f=2)) are polycarbonate diols manufactured by Kuraray Co., Ltd.
- **Polyamines**:Amicure PACM: 4,4'-diaminodicyclohexylmethane manufactured by Air Products Japan, Inc.Laromin C-260: 4,4'-diamino-3,3'-dimethyldicyclohexylmethane manufactured by BASF SE.
- **Solvent**:DMDG: Diethylene glycol dimethyl ether
- **Film** preparation:Prepared using an applicator to a thickness of 0.3 to 0.5 mm.
- **Tensile test**:Measured using a No. 3 dumbbell specimen at a tensile speed of 500 mm/min.
- **Flow time:**The time required until the flow velocity of the mixed solution decreases to 10 mm/10 sec. or less when 15 g of the mixture containing predetermined amounts of Liquid A and Liquid B is inverted in a disposable cup and allowed to flow down the inner wall.
- **BL-NCO (%)** represents the weight percentage of blocked isocyanate groups, calculated as isocyanate groups.

According to Table 1, the reaction between the aliphatic imidazole-blocked polyisocyanate and the alicyclic diamine is

mild, showing a flow time of 42 minutes or more at 25°C. The products cured at 25°C for 10 days demonstrate excellent transparency and favorable tensile properties.

3. Physical Properties of Aromatic Polyurethane-Urea Resins Cured at 25°C

Table 2 shows the physical properties of the pyrazole-blocked polyisocyanates cured with an alicyclic (aliphatic) diamine at 25 °C for 10 days, using polyether diols (modified PTMG, PPG), polyester diols, or polycarbonate diols as the polyols, and TDI as the isocyanate monomer.

Table-2 Curing Properties of Aliphatic-Aromatic Polyurethane-Urea Resins at Room Temperature (20°C / 10 days)

A-Parts (Blocked polyisocyanate：BL-NCO)						B-Parts (Polyamine)		Solids	Flow time	Tensile Properties			
NCO-terminated prepolymer Polyol / Isocyanate (eq.ratio)	Blocking agents (Pyrazole/ NCO)	Solids wt.%	DMDG wt.%	BL-NCO wt.%	Viscocity mPa·s / 25°C	Alicyclic diamine	NH_2/ BL-NCO eq.ratio	wt.%	min./ 25°C	Elongation %	100% Modulus N/mm^2	Tensile strength N/mm^2	Tear strength N/mm
C-4080 (PTMG/TDI prepolymer by Tosoh Corp.)	Pyrazole	75	25	2.11	2400	C-260	0.98	76	125	410	7	41	87
C-4080 (PTMG/TDI prepolymer by Tosoh Corp.)	3,5-Dimethyl pyrazole	75	25	2.07	2400	C-260	0.98	76	75	410	7	47	87
PTG-L2000 / T-100 = 1.0/2.0	Pyrazole	81	19	2.75	2700	C-260	0.98	82	124	410	8	42	70
PPG-D1000 /PPG-D2000 / T-100 = 0.5/0.5/2.0	Pyrazole	90	Isopar–G 10	3.67	7000	C-260/ D-400 =7/3	0.98	91	116	570	6	22	71
P-2010 / T-100 = 1.0/2.0	Pyrazole	81	19	2.57	3350	C-260	0.98	82	135	500	6	37	94
C-2090 / T-100 = 1.0/2.0	3,5-Dimethyl pyrazole	76	24	2.46	6250	C-260	0.98	78	69	370	10	54	107

- **Polyols**:P-2010 (Mn:2000, f=2) is a polyester polyol manufactured by Kuraray Co., Ltd.C-2090 (Mn:2000, f=2)) is a polycarbonate diol manufactured by Kuraray Co., Ltd.PTG-L2000 (Mn:2000, f=2)) is a PTMG-based diol manufactured by Hodogaya Chemical Co., Ltd.PPG-D1000 (Mn: 1000, f=2) and PPG-D2000 (Mn:2000, f=2)) are polypropylene glycols manufactured by Mitsui Chemicals, Inc.
- **Blocking Agents**:Pyrazole3,5-DMP:3,5-Dimethylpyrazole **Blocking agent/NCO**=1.0(eq.ratio)
- **Polyamines**:Amicure PACM:4,4'-diaminodicyclohexylmethane manufactured by Air Products Japan, Inc.Laromin C-260: 4,4'-diamino-3,3'-dimethyl dicyclohexylmethane manufactured by BASF SE.Polyetheramine D-400: A polyether diamine with an (Mn:400) manufactured by Mitsui Fine Chemicals, Inc.
- **Solvents**:DMDG: Diethylene glycol dimethyl ether. Isopar G: An isoparaffinic hydrocarbon manufactured by ExxonMobil Chemical
- **Film preparation**:Prepared using an applicator to a thickness of 0.3 to 0.5 mm.Tensile test:Measured using a No. 3 dumbbell specimen at a tensile speed of 500 mm/min.
- **Flow time**:The time required until the flow velocity of the mixed solution decreases to 10 mm/10 sec. or less when 15 g of the mixture containing predetermined amounts of Liquid A and Liquid B is inverted in a disposable cup and allowed to flow down the inner wall.
- **BL-NCO**: represents the weight percentage of blocked isocyanate groups, calculated as isocyanate groups.

According to Table 2, the reaction between the aromatic pyrazole-blocked polyisocyanate and the alicyclic iamine is mild. The products cured at 25°C for 10 days demonstrate excellent transparency and favorable tensile properties.

4． Reaction Mechanism of the Blocked Polyisocyanates with H12-MDA

The thermal curing of blocked isocyanates with polyols reportedly involves competitive elimination-addition and bimolecular nucleophilic substitution reactions.

The results suggest that the blocked polyisocyanates in this study react quantitatively with aliphatic diamines via the nucleophilic substitution mechanism illustrated in Figure- 3.

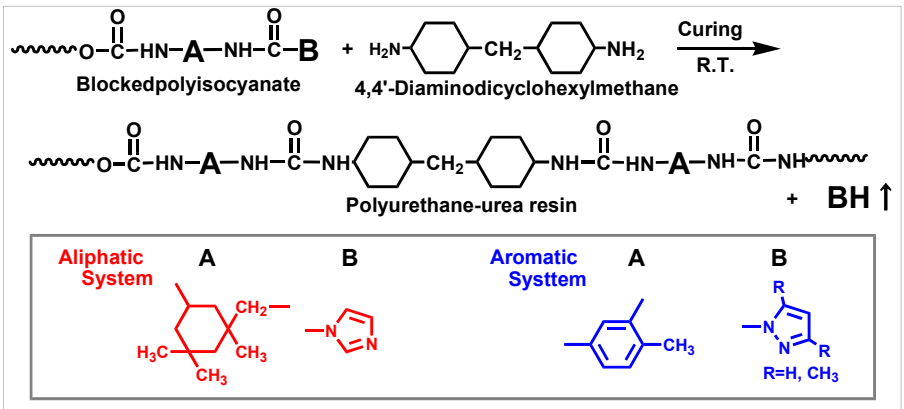


Fig-3 Reaction Mechanism of Blocked Polyisocyanates with H_{12}-MDA

Summary

The two-component, room-temperature-curable polyurethane-urea resins comprising the blocked polyisocyanate compounds and aliphatic polyamines developed in this study exhibit the following characteristics:

- High-strength polyurethane-urea resins with excellent transparency
- An eco-friendly and human health-safe two-component system that is free of isocyanate groups and composed of highly safe components
- Capable of being molded at ambient to elevated temperatures in high-solid or solvent-free formulations due to its moderate reaction
- Low risk of foaming due to the selective reaction with aliphatic polyamines
- Applicability to a wide range of uses through structural design

1) "Latest Technologies for Functional Polyurethanes 2015," published by CMC Publishing Co., Ltd., covers content on pages 17–19.
2) "Recent Technical Developments in Blocked Polyurethane Resin Coatings" English title for 1992 article in *Netsukohasei Jushi (Journal of Thermosetting Plastics, Japan)*, Vol. 13, No. 2, pp. 47–60.
3) Japanese Patent No. 6624469 (Welgreen Corporation)
4) Japanese Patent No. 6716818（Welgreen Corporation.）