

Blocked Diisocyanate-Modified Epoxy Resin: Mechanism and Mechanical Properties

CHEN-CHI M. MA,* MING-SHIU LI, YIO-DON WU, and YI-FENG SU

Institute of Chemical Engineering, National Tsing Hua University, Hsin-Chu, 30043, Taiwan

SYNOPSIS

The modification of bisphenol-A-based epoxy resin with isocyanates was investigated. To increase the crosslinking density by a urethane reaction and to conduct the normal crosslinking reaction between the epoxide and the amine during the cure cycle, blocking the isocyanates with active hydrogens is necessary, which may be deblocked and reacted at elevated temperature. The modified reactions involving diisocyanates and hydroxyl groups generated from epoxy cured with an amine system were studied. This mechanism can be identified by the variations of infrared spectra in the carbonyl group stretching region. Furthermore, the effect of the blocked isocyanate incorporation with amine on the reactivity of epoxy was also studied. The thermal and the mechanical properties were characterized. It was found that the glass transition temperature increased with an aromatic blocked-diisocyanate content. The mechanical properties were improved by blocked diisocyanate. The morphology was also investigated, which showed that a homogeneous structure existed in the modified system. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The incorporation of blocked isocyanate into epoxy resins was studied and numerous reports have been published.¹⁻⁶ Kohn and Smearing² used a phenolic hydroxyl compound to block phenyl isocyanate to produce an adduct. The adduct, which was blended with epoxy resin, could be decomposed at elevated temperature and the phenolic hydroxyl compound was then released to cure the epoxy resin. Lee and Baron³ and Lin and Kuo⁴ disclosed the use of latent amine curing agents in single-package epoxy systems, which were prepared by reacting isocyanates with imidazoles and 1-amino-alkylimidazoles, respectively. Geol^{5,6} used phenol carbamates and oxime carbamates in amine-cured epoxy systems for adhesive and coating applications. When the mixture was heated, the carbamates decomposed and released the phenols or oximes. The appearance of phenols or oximes in this mixture would accelerate the curing reaction of epoxy since these active hydrogen compounds have been found to be catalysts for curing. Most literature reports have focused on

the application of blocked isocyanates as latent curing agents or latent accelerators in epoxy resins. To prevent the deterioration of composite properties caused by water, Gilbert and co-workers⁷⁻⁹ proposed a method to reduce the moisture absorption of fiber-reinforced epoxy composites. They used a masked isocyanate to modify the cured epoxy by blocking the residual functional group ($-OH$, $-NH$, oxirane group) by the isocyanate released in the deblocking reaction: It showed that the equilibrium moisture absorption was reduced significantly. However, most of the earlier studies reported on applications of blocked isocyanates in epoxy, and few of them presented spectroscopic identification of the modified system. In this study, the blocked diisocyanate was utilized to modify epoxy. The mechanism of the modification was identified by the infrared spectrum. The thermal and mechanical properties of the modified system were investigated.

EXPERIMENTAL

Materials

The materials used in this study are described in Table I. Blocked diisocyanates were synthesized. A

* To whom correspondence should be addressed.

Table I Materials Used in This Study

Notation	Specification	Supplier
DGEBA (DER 331)	Diglycidyl ether of bisphenol A EEW = 188	Dow Chemical Co., U.S.A.
CPL	ϵ -Caprolactam, MW = 113.2, recrystallized in cyclohexane	China Petroleum Co., Taiwan, R.O.C.
TDI	Toluene diisocyanate	Tokyo Chemical Industry Co., Japan
MDI	4,4'-Diphenylmethane diisocyanate	Tokyo Chemical Industry Co., Japan
HDI	Hexamethylene diisocyanate	Tokyo Chemical Industry Co., Japan
POPA (D-230)	Polyoxypropylenediamine MW = 230	Huntsman Chemicals Co., U.S.A.

blocking agent (ϵ -caprolactam) and a diisocyanate (e.g., TDI, HDI, or MDI) were reacted in an off-stoichiometric manner (i.e., the molar ratio of the blocking agent: diisocyanate is more than 2). Dibutyltin dilaurate was used as the catalyst and diethyl ether was used as the solvent. The blocking agent was evacuated in a vacuum oven at 90°C overnight prior to use. The thermal properties of the blocked diisocyanates are summarized in Table II.

Sample Preparation

DGEBA resin and the desired amount of the blocked diisocyanate were mixed at 80–120°C. The prepolymer mixture was stored in a flask with a

rubber septa at room temperature. The stoichiometric quantity of amine was added to the prepolymer mixture. After mechanical agitation and degassing under a vacuum for 5–10 min, the mixture was poured into a stainless-steel mold, then cured at 60°C for 1 h, 100°C for 2 h, and 160°C for 1 h and then postcured at 175°C for 2 h in the oven. Finally, upon removing from the mold, the samples were kept in the oven and cooled to room temperature progressively.

Instruments and Equipment

Isothermal differential scanning calorimetry was used for the estimation of kinetic parameters. The

Table II The Thermal Properties of Blocked Diisocyanates

Notation	Formula	Melting Point (°C)	Deblocking Temperature ^a (°C)
CPL-TDI		154	146
CPL-HDI		81	165
CPL-MDI		180	153

^a Determined by DSC scans of the blocked diisocyanates and polyol (NCO : OH = 1 : 1).

Table III Peak Temperature of Dynamic DSC Scanning of DGEBA/POPA(D-230) with Various Blocked Diisocyanate Concentrations

Blocked Diisocyanate Concentration (wt %)	Peak Temperature (°C)
DGEBA/POPA virgin system	123
With CPL-TDI	
6%	117
9%	116
12%	114
With CPL-HDI	
6%	122
12%	125
With CPL-MDI	
6%	120
12%	119

epoxy-amine mixtures were prepared previously. A small quantity of the mixture (5–10 mg) was then placed in a sealed aluminum pan. The sample was then either tested immediately or stored in a refrigerator for further study. The isothermal cures of independent samples were conducted at 70, 80, and 90°C, respectively. The calorimetric measurements were done with a DuPont differential scanning calorimeter (2000 DSC).

One drop of the desired mixture was placed between two sodium chloride plates as a thin film and then mounted on a sample holder located in the IR instrument. The IR spectra were measured using a Perkin-Elmer 842 infrared spectrophotometer with a resolution of 2.4 cm⁻¹ in the transmittance mode. IR spectra at elevated temperatures were obtained using a heating cell mounted inside the sample chamber.

The dynamic mechanical analysis (DMA) was conducted using a DuPont 983 with the operating temperature range from -150 to 250°C. The frequency was set at 10 Hz. The dimensions of the sample used were 5 × 1 × 0.2 cm. The crosslinking density of the modified amine-cured epoxy network was characterized through the measurement of elastic moduli in the rubbery state (about *T_g*). According to the theory of rubber elasticity, the equilibrium elastic modulus is given by¹⁰

$$G = \phi dRT/Mc$$

where *d* is the density; *R*, the molar gas constant; *T*, the absolute temperature; and *Mc*, the average molecular weight of chain segments between crosslink points. The actual value of the first factor ϕ is uncertain. However, it may be assumed that when

Table IV Kinetic Study^a of DGEBA/(POPA)D-230 Modified with Various Blocked Diisocyanates

Composition DER331/POPA (D-230)	Reaction Order (<i>n + m</i>)	Activation Energy <i>E_a</i> (kJ/mol)
Pure resin	2.27 ± 0.38	60.1
6 wt % CPL-TDI	1.93 ± 0.19	50.5
12 wt % CPL-TDI	1.87 ± 0.28	53.7
6 wt % CPL-HDI	1.98 ± 0.11	55.7
12 wt % CPL-HDI	1.93 ± 0.18	69.0
6 wt % CPL-MDI	2.24 ± 0.18	57.4
12 wt % CPL-MDI	1.83 ± 0.31	50.2

^a Autocatalytic reaction model: $dC/dt = KC^m(1 - C)^n$.

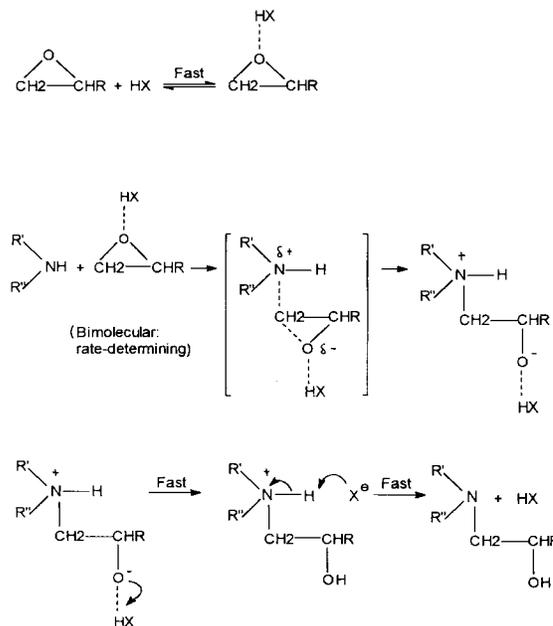
$G < 10^7$ Pa ϕ is close to unity.¹¹ The crosslinking density, *n*, therefore, is given by¹²

$$n = dN/1.5Mc$$

N is the Avogadro's number.

Property Measurement

The thermal properties were measured by using a DSC unit (DuPont 2000) at a heating rate of 10°C/



HX : Urethane group of blocked diisocyanate or the hydroxy group of epoxy .

Figure 1 The mechanism of the amine-cured epoxy resin system.

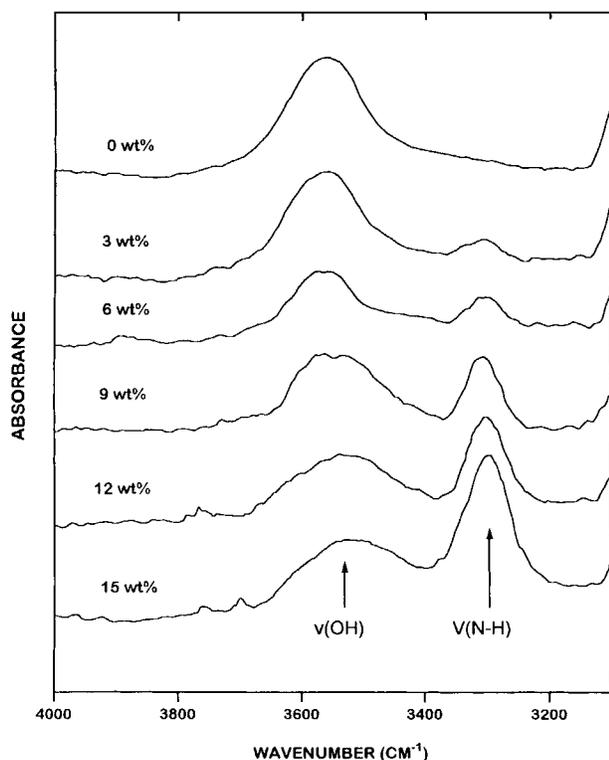


Figure 2 The infrared spectra of DGEBA resin with various CPL-HDI contents.

min. The tensile properties of the specimens were measured by an Instron 4201 universal material testing machine, as described in ASTM D-638, with a crosshead speed of 5 mm/min. The flexural properties were measured as described in ASTM D-790, with a crosshead speed of 2.0 mm/min. The Izod impact strength was measured according to ASTM D-256. SEM photographs were taken on the fractured surface of the Izod impact-tested specimen.

RESULTS AND DISCUSSION

Kinetic Analysis of the Curing Process

The exothermic peak temperatures (T_p 's) of DSC scans for the DGEBA/POPA (D-230) system with blocked diisocyanates at 10°C/min are shown in Table III. In the virgin system, the exothermic peak temperature was at 123°C. With the addition of CPL-TDI (12 wt %) and CPL-MDI (12 wt %), T_p was lowered by 9 and 4°C, respectively. The T_p of the CPL-HDI-modified system was almost the same as that of the virgin system. This reveals that the incorporation of a particular blocked diisocyanate may affect the reactivity of epoxy with amine. The reaction of the amine-cured epoxy system with the addition of aromatic blocked diisocyanate (CPL-

TDI, CPL-MDI) was accelerated, while aliphatic blocked diisocyanate (CPL-HDI) was not.

In addition, the cure kinetics of DGEBA/POPA(D-230) with and without blocked diisocyanate were investigated. An isothermal differential scanning calorimeter was used for the estimation of kinetic parameters by assuming that the exothermic heat evolved during cure was in proportion to the extent of the reaction. However, the reaction of epoxy cured with amine has been found to be autocatalytic.¹³ From the autocatalytic equation, the activation energy and the kinetic order of reaction can be calculated and are summarized in Table IV. The activation energy of DGEBA/POPA (D-230) was 60.1 kJ/mol, which was higher than those of DGEBA/POPA (D-230)/CPL-TDI and DGEBA/POPA (D-230)/CPL-MDI. With the addition of CPL-HDI, the activation energy initially decreased and then increased with CPL-HDI content, as illustrated in Table IV. The reaction orders for DGEBA/POPA (D-230) and DGEBA/POPA (D-230)/blocked diisocyanate systems were found to be between 1.8 and 2.2. Generally, they can be considered as 2.

According to Smith,¹⁴ the mechanism of the reaction was proposed as shown in Figure 1. From investigation on the mechanism, the urea group of the blocked diisocyanate in the reaction plays the role of proton donor, which accelerates the reaction

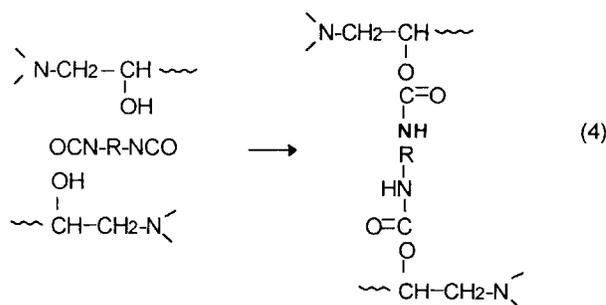
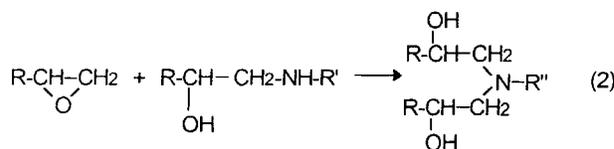
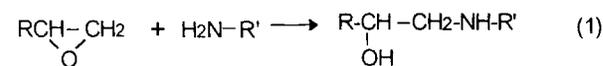


Figure 3 The proposed mechanism of the blocked diisocyanate reacting with the epoxy network.

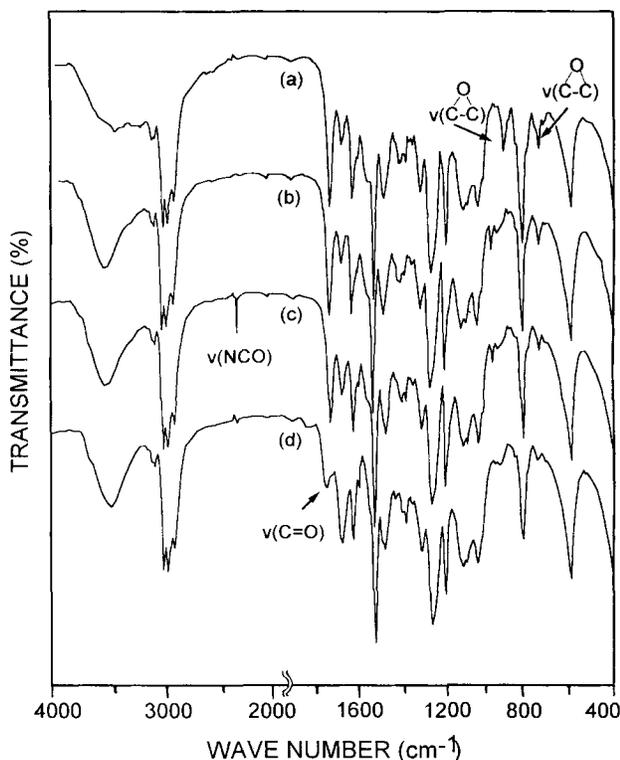


Figure 4 The IR spectra of DGEBA/POPA (D-230)/CPL-TDI (20 wt %) for different curing cycles: (a) beginning; (b) 60°C/1 h, 100°C/2 h, and 140°C/1 h; (c) 60°C/1 h, 100°C/2 h, 140°C/1 h, and 160°C/0.5 h; (d) 60°C/1 h, 100°C/2 h, 140°C/1 h, 160°C/1 h, and 175°C/2 h.

by hydrogen bonding of the epoxy group and weakens the bond strength of the epoxide group, namely, the proton-donor ability determines the efficiency of catalytic behavior. With the same blocked diisocyanate content (6 wt %), the concentration of urea groups introduced by CPL-TDI and CPL-HDI are almost equivalent. However, the reactivity of the modified system was increased by the addition of CPL-TDI to a greater extent than by the addition of CPL-HDI. This phenomenon may be due to the electron-withdrawing effect of the benzene ring of TDI, which, in turn, increases the acidity of a urea. Hence, the incorporation of aromatic blocked diisocyanate in epoxy, to accelerate the curing, is more efficient than that of aliphatic blocked diisocyanate.

Meanwhile, the activation energy of the epoxy system incorporated with 12 wt % CPL-HDI is 69.0 kJ/mol, which is higher than that of the virgin system. This result can be explained from the viewpoint of intermolecular force which was investigated by the IR spectra. Figure 2 shows the IR spectra of various contents of CPL-HDI in DGEBA. As shown in this figure, the absorption of OH group stretching contributed by DGEBA shifts down gradually as the CPL-HDI content increases. This may be due to the

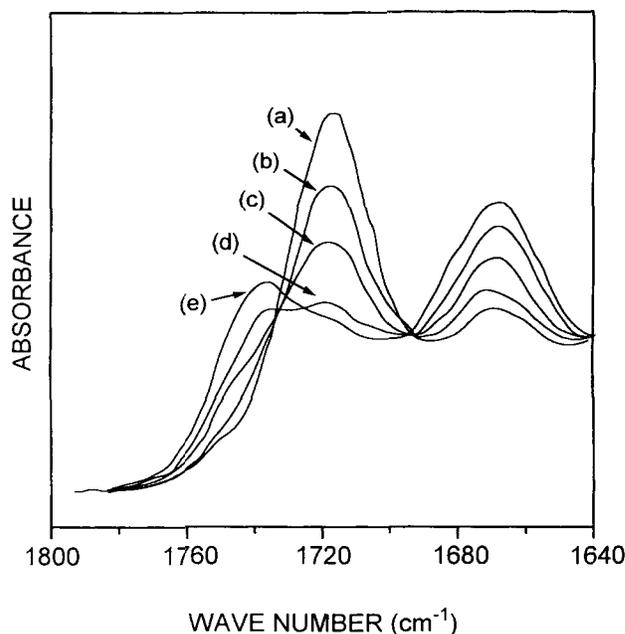


Figure 5 The variation of C=O stretching absorption for different curing cycles: (a) 60°C/1 h, 100°C/2 h, and 140°C/1 h; (b) 60°C/1 h, 100°C/2 h, 140°C/1 h, and 160°C/0.5 h; (c) 60°C/1 h, 100°C/2 h, 140°C/1 h, and 160°C/1 h; (d) 60°C/1 h, 100°C/2 h, 140°C/1 h, 160°C/1 h, and 175°C/1 h; (e) 60°C/1 h, 100°C/2 h, 140°C/1 h, 160°C/1 h, and 175°C/2 h.

effect of the hydrogen bonding of the carbonyl group of urea introduced by CPL-HDI. The OH group of DGEBA plays the role of a proton donor that may accelerate the ring-opening reaction of oxirane with amine. The hydrogen bonding formed between the OH group of DGEBA and the C=O group of CPL-HDI will restrict the OH group from donating a pro-

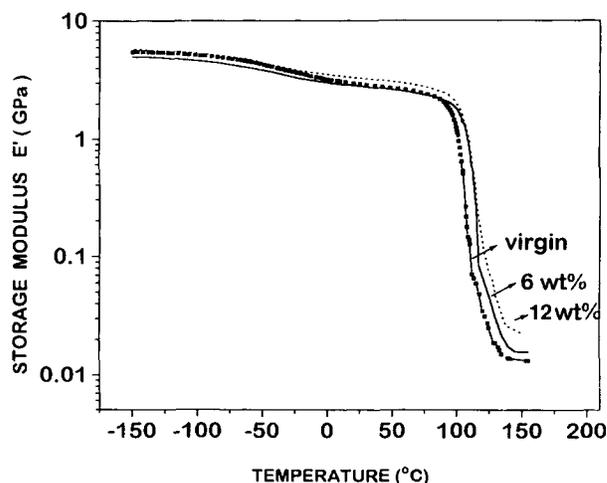


Figure 6 The storage modulus of DGEBA/POPA (D-230) system modified by various CPL-TDI contents.

Table V Properties of Blocked Diisocyanate-modified DGEBA/PDPA (D-230) System

Blocked Diisocyanate Content (Wt %)	Bulk Density (g/cm ³)	tan δ (max)	M_c (g/mer)	n (1/cm ³) $\times 10^{-20}$
0	1.1583	1.028	585	7.95
CPL-TDI				
6	1.1648	1.045	566	8.64
12	1.1679	0.849	439	10.6
CPL-HDI				
6	1.1603	1.137	556	8.79
12	1.1600	0.986	428	10.8
CPL-MDI				
6	1.1652	0.9371	575	8.14
12	1.1677	0.9162	496	9.44

ton to the epoxide group. Since the higher CPL-HDI content incorporated with epoxy decreases the proton-donor ability of the modified system, the reaction of epoxy with amine is retarded.

Infrared Spectra

The proposed mechanism of the reaction of bisphenol-A-based epoxy resin modified by blocked diisocyanate is shown in Figure 3. Equations (1) and (2) of Figure 3 present the normal crosslinking reaction of the epoxide and amine. The blocked diisocyanate incorporated into the epoxy system does not react with epoxy until the curing temperature is raised above the deblocking temperature. It is well known that isocyanate reacts with caprolactam to form a substituted urea. When blocked diisocyanate is incorporated into the epoxy system, the absorption peak of the carbonyl group of the substituted urea does not change during the normal crosslinking reaction of the epoxide with amine. Once the curing temperature is raised above the deblocking temperature, the modified reaction occurs [eqs. (3) and (4) of Fig. 3].

In Figure 4, the IR spectra of DGEBA/POPA (D-230)/CPL-TDI (20 wt %) were recorded for different

curing cycles. From curve (a) to curve (b) of Figure 4, one can see that the absorption peak of the oxirane at 910 cm⁻¹ disappears completely after cure [curve (b)] and the IR absorption in carbonyl region shows almost no change. This phenomenon coincides with the assumption, which was proposed previously, that the blocked diisocyanate does not react during the curing reaction of epoxy resin. As shown in the curve (a) of Figure 4, the C=O stretching of urea in CPL-TDI is evident at 1704 cm⁻¹. The C=O stretching of caprolactam contributed by CPL-TDI and excess CPL is at 1655 cm⁻¹. When the curing temperature is elevated above the delocked temperature, the absorption peak of isocyanate group is evident [curve (c) of Fig. 4]. It indicates that as the deblocking reaction of CPL-TDI occurs isocyanate and caprolactam are released as expressed in [Eq. (3) of Fig. 3]. As the reaction time proceeds, the absorption band of the original C=O stretching of urea in CPL-TDI splits into two regions, the lower-frequency band at 1655 cm⁻¹ corresponding to the absorption range of the C=O stretching of CPL and the higher-frequency band at 1735 cm⁻¹ corresponding to the urethane formed.

These variations are illustrated in Figure 5. This figure shows the variation of the carbonyl group

Table VI Glass Transition Temperature of Blocked Diisocyanate-modified Epoxy System

Blocked Diisocyanate	Wt % Blocked Diisocyanate in Epoxy				
	0 Wt %	3 Wt %	6 Wt %	9 Wt %	12 Wt %
CPL-TDI	76.3°C	82.3°C	82.8°C	82.3°C	81.7°C
CPL-HDI	76.3°C	74.5°C	70.5°C	67.7°C	63.7°C
CPL-MDI	76.3°C	81.8°C	83.4°C	83.2°C	83.0°C

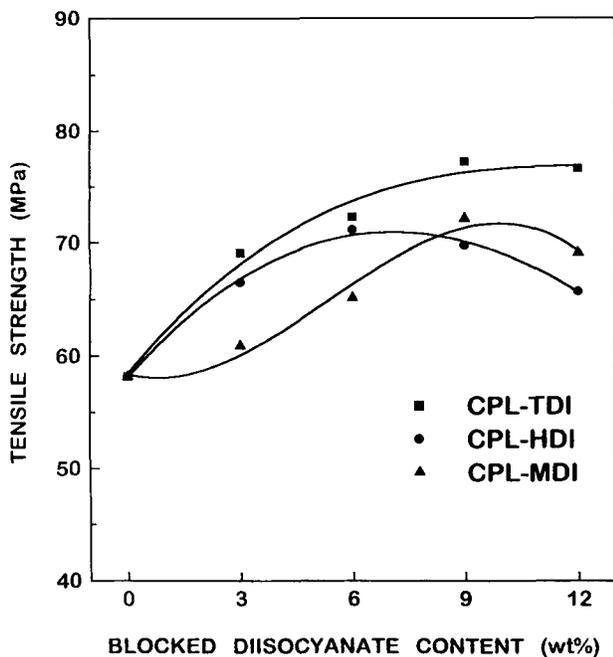


Figure 7 The tensile strength of DGEBA/POPA (D-230) system modified by various contents of blocked diisocyanate.

stretching for different curing cycles. Curves (a)–(e) of Figure 5 show that the peak intensity of the C=O stretching of CPL at 1655 cm^{-1} increases during the curing cycle. The absorption peak of the original C=O stretching of urea contributed by CPL-TDI

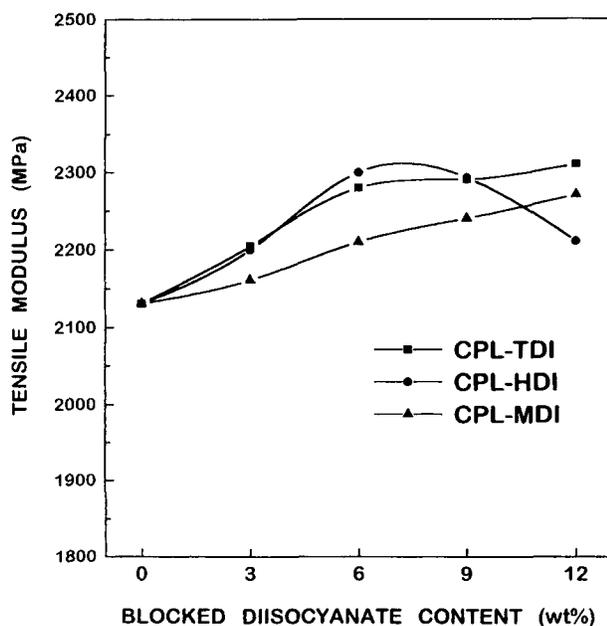


Figure 8 The tensile modulus of DGEBA/POPA (D-230) system modified by various contents of blocked diisocyanate.

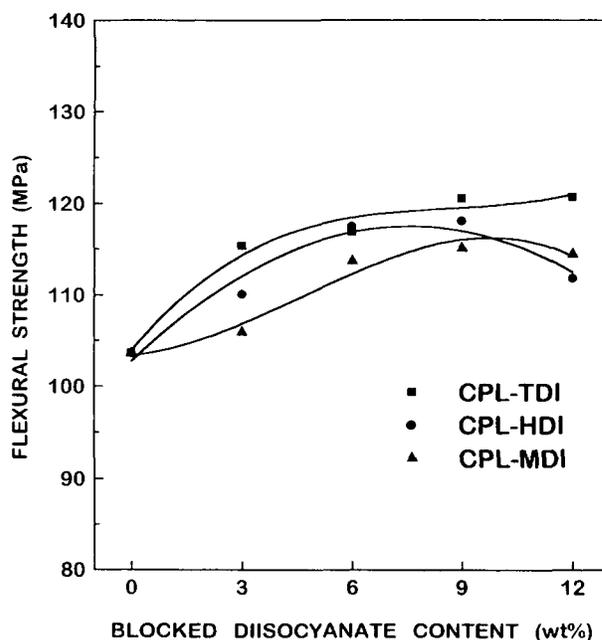


Figure 9 The flexural strength of the DGEBA/POPA (D-230) system modified by various contents of blocked diisocyanate.

shifts from 1704 cm^{-1} to 1735 cm^{-1} . This result indicates the adjacent atom of the carbonyl group changes during the reaction. As illustrated in eqs. (3) and (4) of Figure 3, the original C=O of urea contributed by CPL-TDI with two neighboring nitrogen atom is converted to the urethane structure in which

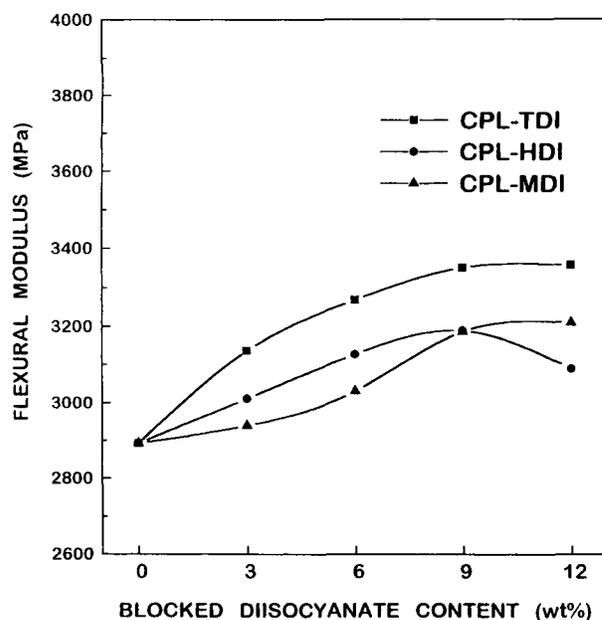


Figure 10 The flexural modulus of DGEBA/POPA (D-230) system modified by various contents of blocked diisocyanate.

C=O has as neighbors one nitrogen and one oxygen atom. Due to the inductive effect of substituent groups between C=O groups, the absorption frequency of carbonyl stretching increases with the increasing amount of the urethane structure. From the IR spectrum, the results coincide with the mechanism of the modification proposed, which represents additional crosslinking in the network structure of epoxy cured with amine.

Dynamic Mechanical Properties

The storage moduli (E') of the unmodified epoxy resin and the epoxy modified by various CPL-TDI contents are compared in Figure 6 which reveals that the modulus in the rubbery state increases with CPL-TDI content. From the dynamic mechanical analysis, the equilibrium moduli in the rubbery state can be obtained and the average weight between crosslinks (M_c) are derived from the equation proposed by Tobolsky et al.¹⁰ The effect of the modification of epoxy resin by blocked diisocyanate on crosslinking density is summarized in Table V. It shows that the CPL-HDI-modified system possesses a higher crosslinking density than that of the others with the same blocked diisocyanate content. This is explained by the fact that the crosslinking density is proportional to the mol number of the isocyanate group introduced by the blocked diisocyanate. The peak height of the damping peak tends to decrease, especially in the epoxy system modified by 12 wt % blocked diisocyanate. This phenomenon may be accounted for by the effect of additional crosslinks which restrict the molecular motion.

Thermal Property

The thermal properties of various blocked diisocyanate-modified epoxy systems are listed in Table VI. Results reveal that the glass transition temperature (T_g) increases in CPL-TDI- and CPL-MDI-modified systems but decreases in the CPL-HDI-modified system. However, the above analysis shows that incorporation of blocked diisocyanate with epoxy may increase the crosslinking density. Neilsen¹⁵ reported a number of results and correlated T_g 's to the degree of crosslinking. He concluded that crosslinking may increase the glass transition temperature of a polymer by introducing restrictions on the molecular motions of a polymer chain.^{16,17} However, the chemical composition is also changed when the crosslinker is incorporated into the modified epoxy system. Hence, the copolymer effect between the original epoxy network and the incorporated modifier should be taken into consideration. In

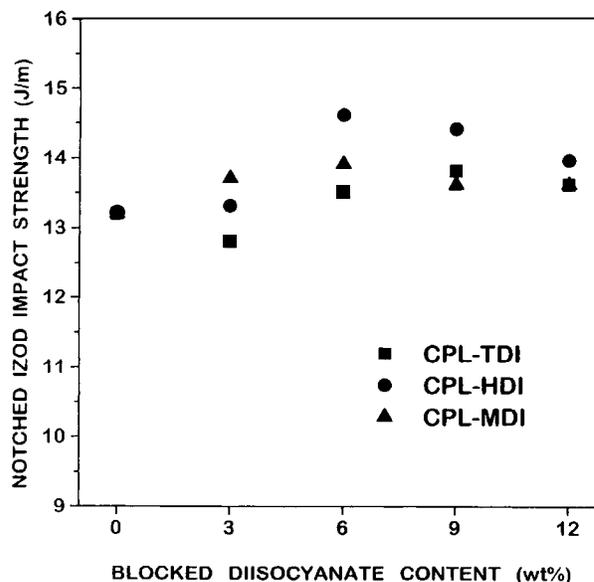


Figure 11 The notched Izod impact strength of the DGEBA/POPA (D-230) system modified by various contents of blocked diisocyanate.

CPL-TDI- and CPL-MDI-modified systems, the increase of T_g may be due to the introduction of additional crosslinks and the rigid benzene ring structure into the epoxy matrix. However, the incorporation of CPL-HDI, possessing a hexamethylene segment in the epoxy system, may change the chemical composition. Due to the copolymer effect, the increase of aliphatic soft segment content in the epoxy matrix lowers the glass transition temperature of the modified system. The plasticization of released CPL may be considered as having the opposite effect on the T_g among the modified systems.

Mechanical Property

The mechanical properties of the modified system increase significantly. As illustrated in Figures 7 and 8, the tensile strength and modulus are higher than in the virgin system. Flexural strength and modulus also increase and the highest value occurs at 9 wt % of the blocked diisocyanate content, as shown in Figures 9 and 10. This behavior may be due to the increase of the crosslinking density and the hydrogen bonding between the urethane group and the hydroxyl group. It may be concluded that the modulus of the glass state depends on intermolecular forces.¹⁸ The impact strength of the CPL-HDI-modified epoxy system is slightly higher than those of the other systems, as illustrated in Figure 11, which is due to the effect of the soft hexamethylene segment introduced into the epoxy matrix.



(a)



(b)

Figure 12 Microphotograph of various blocked diisocyanate-modified DGEBA/POPA (D-230) system: (a) 12 wt % CPL-HDI, $\times 300$; (b) 12 wt % CPL-TDI, $\times 300$.

Morphology

Figure 12 shows the SEM micrographs of the fracture surface of the modified epoxy matrix. The fracture surfaces exhibit some flat and river patterns, which imply that the modified system is homogeneous. The density of striated lines in the CPL-HDI-modified system [Fig. 12(a)] is higher than that in the CPL-TDI-modified system [Fig. 12(b)]. This microphotograph indicates that the CPL-HDI-modified system possesses a higher fracture energy. This phenomenon explains the different impact behaviors that may occur among various blocked diisocyanate-modified epoxy systems.

CONCLUSIONS

The incorporation of blocked diisocyanate with epoxy resin may reduce the activation energy of the reaction of epoxy/amine by a proton donor effect.

As the blocked diisocyanate content increases, the hydrogen bonding between the carbonyl group and the hydroxy group increases and retards the reaction, especially in the CPL-HDI-modified system. The mechanism of modification is confirmed by IR spectra. It indicates that the incorporation of blocked diisocyanate with epoxy/POPA increases the crosslinking density of the amine-cured epoxy network structure, which coincides with the result of the dynamic mechanical analysis. The glass transition temperature is also increased in the CPL-TDI- and CPL-MDI-modified systems. The mechanical properties of the modified system increase significantly. A homogeneous structure exists in the modified system as can be seen from the SEM photograph.

This research was financially supported by the National Science Council, Taiwan, R.O.C., under Contract No. NSC 84-2622-E-007-001. The authors express their gratitude to the Epolab Chemical Co. for the supply of materials.

REFERENCES

1. B. J. Bremmer, U.S. Pat. 3,442,974 (1969).
2. L. S. Kohn and R. W. Smearing, U.S. Pat. 4,335,228 (1982).
3. F. W. Lee and K. S. Baron, U.S. Pat. 4,533,715 (1985).
4. S. C. Lin and P. L. Kuo, U.S. Pat. 4,797,455 (1989).
5. A. B. Geol, U.S. Pat. 4,683,283 (1987).
6. A. B. Geol, U.S. Pat. 4,683,284 (1987).
7. H. P. Hu, R. D. Gilbert, and R. E. Fornes, *J. Polym. Sci. Part A Polym. Chem.*, **25**, 1235-1248 (1987).
8. S. V. Lonikar, N. Rungsimuntakul, R. D. Gilbert, and R. E. Fornes, *J. Polym. Sci. Part A Polym. Chem.*, **28**, 759-775 (1990).
9. S. S. Sankar, S. V. Lonikar, and R. D. Gilbert, *J. Polym. Sci. Part B Polym. Phys.*, **28**, 293-302 (1990).
10. A. V. Tobolsky, D. W. Carlson, and N. Indictor, *J. Polym. Sci.*, **54**, 175-192 (1961).
11. D. Katz and A. V. Tobolsky, *J. Polym. Sci. A 2*, 1595 (1964).
12. G. Levita, S. D. Petris, A. Marchetti, and A. Lazzeri, *J. Mater. Sci.*, **26**, 2348-2352 (1991).
13. K. Horie, H. Hiura, M. Sawada, I. Mita, and H. Kambe, *J. Polym. Sci. A 1*, **8**, 1357 (1970).
14. I. T. Smith, *Polymer*, **2**, 95 (1961).
15. L. E. Nielsen, *J. Macromol. Sci. Rev. Macromol. Chem. C*, **3**(1), 69 (1969).
16. W. Fisch, W. Hofmann, and R. Schmid, *J. Appl. Polym. Sci.*, **13**, 295 (1969).
17. J. P. Bell, *J. Appl. Polym. Sci.*, **14**, 1901 (1970).
18. L. E. Nielsen, *Mechanical Properties of Polymer and Composite*, Marcel Dekker, New York, 1975, Chap. 4.

Received December 11, 1995
Accepted March 12, 1996