Effects of Epoxy Resin on Mechanical and Thermal Characteristics of Poly(propylene oxide)/Poly(butyl acrylate) Networks

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ABSTRACT: We report mechanical and thermal characteristics of a network composed of poly(propylene oxide) (PPG) and poly(butyl acrylate) crosslinked with tolylene diisocyanate. It was found that addition of about 4 wt % of an epoxy resin resulted in a higher mechanical toughness and less discoloration. Furthermore, it was found that the epoxy has a self-restoration function against thermal degradation of the network. The reaction mechanism between the network and the epoxy was investigated with infrared spectroscopy and ^{13}C-NMR and the effect of the epoxy resin on the thermal stability and physical properties is discussed. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1886–1893, 2000

Key words: epoxy; poly(propylene oxide); poly(butyl acrylate); TDI; networks

INTRODUCTION

Various polymer networks are used for construction as a sealing material and are called a "sealant." The components of the most popular sealants are polysiloxane, polysulfide, polyacrylate, and polyurethane. Each has characteristic mechanical and surface properties and is employed depending on the purpose. Among them, networks composed of poly(propylene glycol) (PPG) and poly(butyl acrylate) (PBA) are known to have excellent weather resistance, durability, and heat resistance.[1] Specifically, PPG/PBA networks are prepared by crosslinking PPG and PBA of a triol type with diisocyanate. However, the composite has a defect, that is, it easily turns brown above 100°C. To avoid discoloration, we modified the network with an epoxy of the epichlorhydrin–bisphenol A type.

This article reports the effect of the epoxy resin on the mechanical and thermal characteristics of the PPG/PBA networks prepared with and without epoxy. The reaction mechanisms among the components were investigated using infrared (FTIR) and ^{13}C-NMR spectroscopies. We discuss the relationship between the network structure and the physical properties and seek a method for designing high-performance sealants.

EXPERIMENTAL

Samples

Poly(propylene oxide)diol [PPG(OH)$_2$] with a molecular weight (MW) of 2000 was obtained from Dai-Ichi-Kogyo Seiyaku (Kyoto, Japan). Poly(propylene oxide)triol [PPG(OH)$_3$] with an MW of 3000 was purchased from Takeda Yakuhin Kogyo

(Osaka, Japan). Tolylene diisocyanate (TDI-65), a mixture of 2,4-TDI and 2,6-TDI with the ratio of 65/35, was obtained from Mitsui Chemical Co. (Tokyo, Japan).

For preparation of a sealing material, first, the prepolymer was prepared. $PPG(OH)_2$ and $PPG(OH)_3$ were mixed in the ratio of 60/40 and dried under a vacuum of 0.01 Torr at 120°C for 3 h and then cooled to 80°C. Then, 14.9 parts by weight of TDI-65 was mixed with 100 parts of the PPG prepared above. Thus, PPGs were polymerized and crosslinked through the reaction of the OH groups and the isocyanate groups of TDI-65. This prepolymer still contained 2 wt % of the unreacted isocyanate groups and, hence, was a viscous liquid.

Then, the prepolymer was allowed to react with a hardener composed of 13 parts (by weight) of an epoxy resin (Epicote 828XA, Yuka-Shell Epoxy Co., Tokyo, Japan) and 22 parts of telechelic PBA (TM32BH, Nihon Syokubai Co., Osaka, Japan) with a number-average MW of 2700. Further, 33 parts of dioctylphthalate (DOP) as a plasticizer, 150 parts of calcium carbonate (particle size, 0.05 μm; surface treatment agent, fatty acid, Kalfain 200M, Maruo Calcium Co., Hyogo, Japan) as a filler, and 2 parts of the catalyst, lead octoate 38% (Nikka Octhix Pb 38%, Nihon Kagaku Sangyo Co., Tokyo, Japan), were also added. The structures of the main components are given below:

$PPG(OH)_2$

$PPG(OH)_3$

PBA

TDI

Epoxy resin

n=0.14
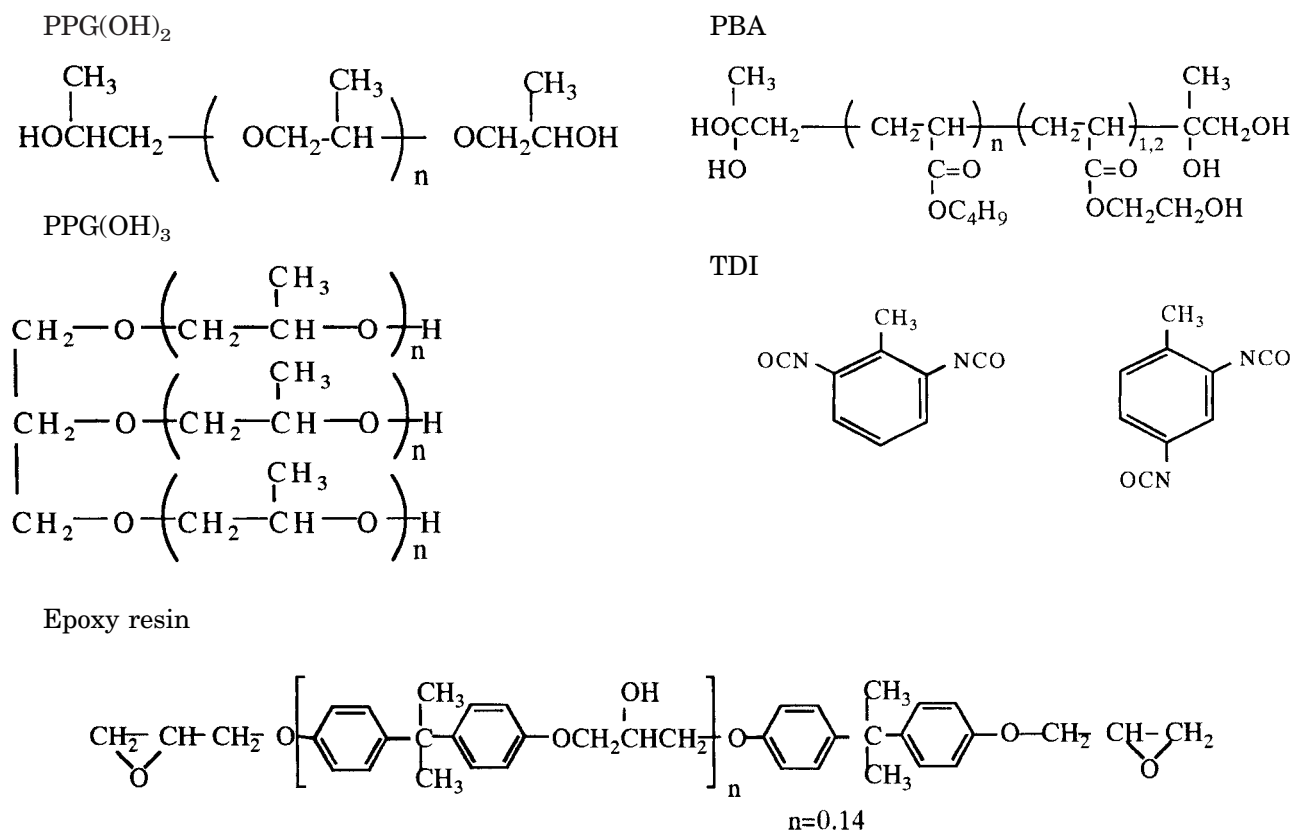
Test samples containing the epoxy were prepared by blending 100 parts of the prepolymer and 220 parts of the hardener. Samples were also prepared from the prepolymer and the hardener which did not contain the epoxy. The thermal stability of these samples was tested at two conditions: "normal" and "high-temperature" agings. In normal aging, the samples were kept at 20°C for 7 days and subsequently at 50°C for 7 days. High-temperature aging was done as follows: The samples subjected to normal aging were further annealed at 90°C for 14 days in a nitrogen atmosphere. For FTIR and NMR analyses, we used samples prepared without adding calcium carbonate (filler).
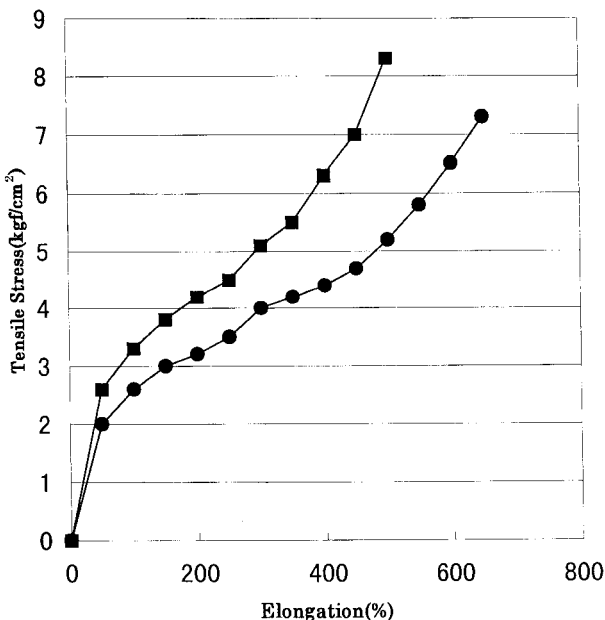
Figure 1   Effect of epoxy resin for tensile property: (■) 0 wt % epoxy resin in sealant after normal aging; (●) 4.1 wt % epoxy resin in sealant after normal aging.

Measurements

Tensile Test

The tensile strength of the networks was measured according to the Japanese Industrial Standards (JIS A 5758) prescription using a stress–strain tester (Orientech Co., RTM-250).

Fatigue Test

Compression and elongation of ±30% were applied 100,000 times to the specimens prepared as mentioned above, and then the surface was observed by the eye to find cracks.

Dynamic Shear Moduli

The dynamic shear moduli ($G^* = G' + iG''$) were measured at 10 Hz with a rheometer (Reoroji, MR-500) for specimens with a size of $50 \times 50 \times 3$ mm.

Thermal Yellowing Test

Specimens of size $50 \times 50 \times 10$ mm were subjected to normal and high-temperature aging and were used for the test. Some specimens were further annealed at 90°C for 14 days and were observed by the eye to judge the degree of yellowing.

Spectroscopy

FTIR spectra were taken with a spectrometer (JASCO, FTIR 8300). ^{13}C-NMR spectra were also measured with a spectrometer (JPEL, Lambda 500).

RESULTS AND DISCUSSION

Mechanical Properties

Figure 1 shows the engineering tensile stress plotted against the tensile strain for the networks prepared with and without epoxy. We see that the network containing the epoxy exhibits a lower modulus than that with no epoxy. Table I lists the 50% moduli, maximum tensile strength T_{max}, and elongation at break. The maximum elongation before rupture for the network prepared with 4.1% epoxy increases to 650% compared with 500% for the network containing no epoxy. As the amount of the epoxy increases, the 50% modulus decreases but the maximum elongation increases. This indicates that the epoxy reduces the crosslink density and the probability of formation of trapped entanglements. Thus, the epoxy is effective in making the system soft and tough. Table II indicates the effect of the epoxy resin on the stress–strain properties of the specimens after high-temperature aging. Compared with the data listed in Table I, we see that both the 50% modulus and maximum elongation decrease by high-temperature aging. However, the modulus and the elongation for the network prepared with the epoxy is always higher than that without the epoxy.

Table I   Effect of Epoxy Resin on Tensile Property

Epoxy Resin Amount (wt %/Sealant)	Tensile Properties After Normal Aging		
	50% Modulus (kgf/cm^2)	T_{max}[a] (kgf/cm^2)	Eb[b] (%)
0	2.6	8.3	492
2	2.3	9.2	605
4.1	2.0	10.0	738

[a] Maximum tensile strength.
[b] Elongation at break.

Table II Effect of Epoxy Resin on Tensile Property

Epoxy Resin Amount (wt %/Sealant)	Tensile Properties After Heat Aging		
	50% Modulus (kgf/cm^2)	T_{max}[a] (kgf/cm^2)	Eb[b] (%)
0	1.0	4.1	396
2	1.2	5.7	430
4.1	1.5	7.5	463

[a] Maximum tensile strength.
[b] Elongation at break.

Figure 2 shows the temperature dependence of the complex shear moduli $(G' + iG'')$ for the networks prepared with and without the epoxy. As shown in Figure 2, G' below the glass transition temperature of $-60°C$ increases by adding the epoxy. After normal aging, the G'' peak for the network with the epoxy resin shifts to a higher temperature than that without the epoxy resin. This indicates that the components PPG, PBA, and the epoxy are miscible. Increase of the T_g of about 10° by addition of the epoxy can be explained by the blending law of T_g proposed by Fox:

$$1/T_g = \phi_1/T_g(1) + \phi_2/T_g(2) \tag{1}$$

where ϕ is the volume fraction and $T_g(1)$ is and $T_g(2)$ are the T_g's of components 1 and 2. In the present system, component 1 is the network of PPG/PBA prepared without the epoxy and 2 corresponds to the epoxy. From the maximum of G'', we determined $T_g(1)$ to be 216 K. $T_g(2)$ corresponds to the T_g of the crosslinked epoxy and is estimated to be about 400 K. On the other hand, ϕ_1 becomes 0.92, and ϕ_2, 0.08. Here, we have not taken into account the filler for calculation of ϕ. Thus, the T_g of the system containing the epoxy is calculated to be 223 K, in rough agreement with the experiment, 226 K.

In the rubbery region above 0°C, G' of the network with the epoxy became lower than that without the epoxy. This result is consistent with the result shown in Figure 1. From the values of G' at 80°C, we attempted to estimate the molecular weight between entanglements M_x for the networks using the theory of rubber elasticity:

$$G = \rho RT/M_x$$

where ρ ($= 0.82$ g/cm^3) is the density of network in g/cm^3; R, the gas constant; and T, the temperature. The values of M_x for the networks prepared with and without the epoxy are calculated to be 1500 and 3800, respectively. The value of M_x of the former is lower than is the molecular weight of PPG or PBA. This may be reasonable if the trapped entanglement of the network chains is taken into account. The value of M_x of the latter indicates that the full reaction of PPG(OH)$_3$ and TDI is inhibited by the epoxy. The reason for such a phenomenon is ascribed to the reaction between the epoxy and the prepolymer as described later.

Figures 3 and 4 compare the effect of aging on the dynamic shear moduli for the networks prepared with and without the epoxy, respectively. In Figure 3, it is seen that the heat treatment does not affect the shear moduli for the network containing the epoxy. On the other hand, the shear moduli of the network prepared
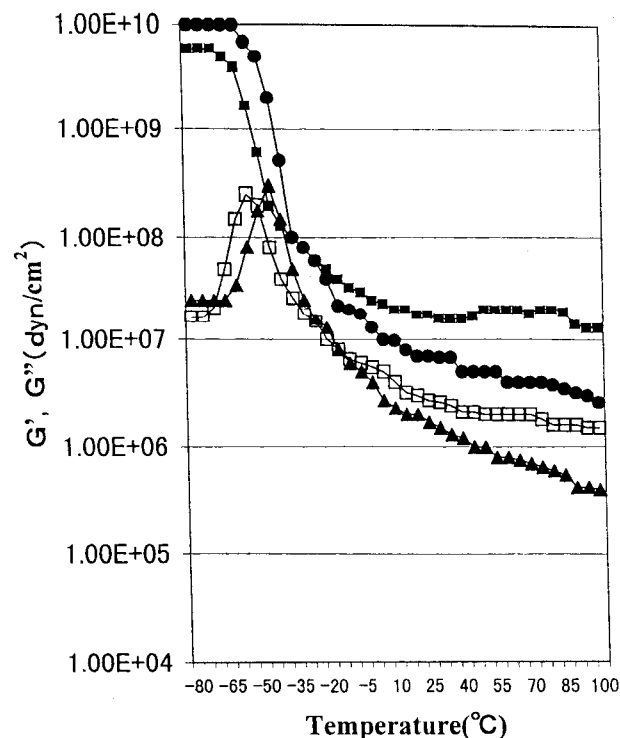
Figure 2 Effect of epoxy resin amount on dynamic viscoelasticity: (●) G' 4.1 wt % epoxy resin in sealant; (■) G' 0 wt % epoxy resin in sealant; (▲) G'', 4.1 wt % epoxy resin in sealant; (□) G', 0 wt % epoxy resin in sealant.
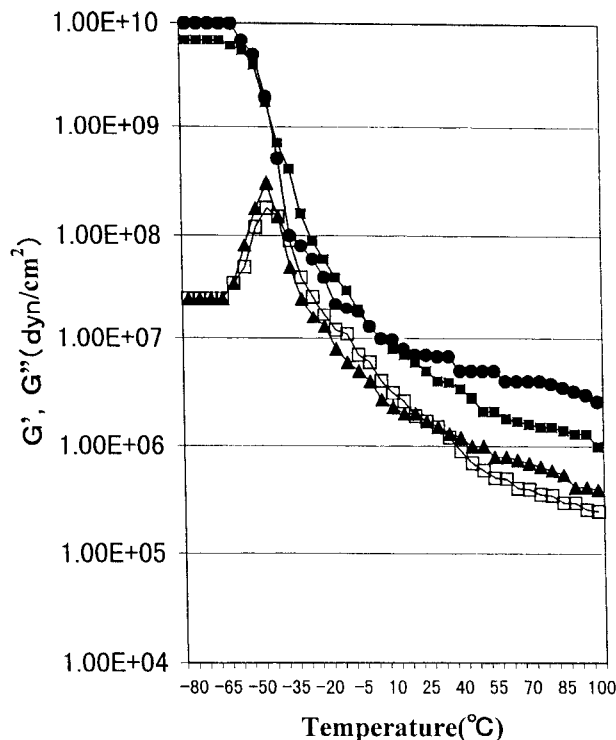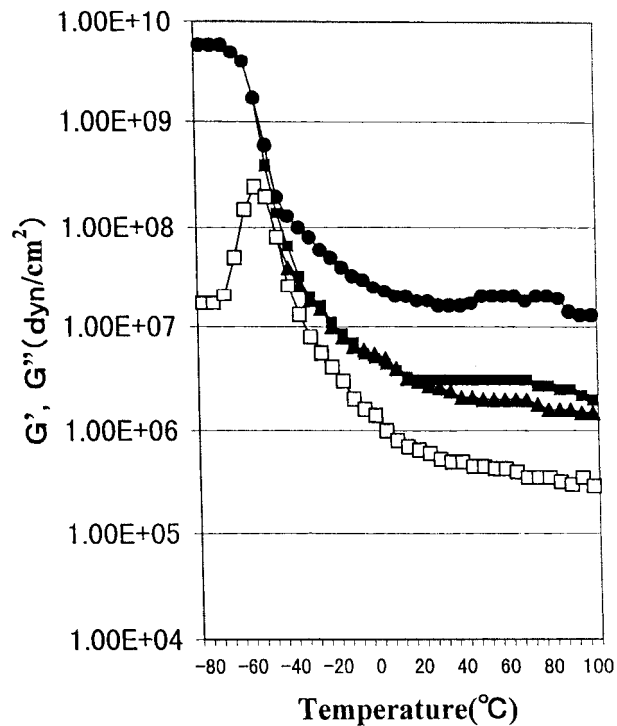
Figure 3 Difference of dynamic viscoelasticity with epoxy resin: (●) G', 4.1 wt % epoxy resin in sealant after normal aging; (■) G', 4.1 wt % epoxy resin in sealant after heat aging; (▲) G'' 4.1 wt % epoxy resin in sealant after normal aging; (□) G'' 4.1 wt % epoxy resin in sealant after heat aging.


Figure 4 Difference of dynamic viscoelasticity with epoxy resin: (●) G', 0 wt % epoxy resin in sealant after normal aging; (■) G', 0 wt % epoxy resin in sealant after heat aging; (▲) G'' 0 wt % epoxy resin in sealant after normal aging; (□) G'' 0 wt % epoxy resin in sealant after heat aging.

without the epoxy decreases about one order by the heat treatment as shown in Figure 4. This indicates that the thermal stability increases much by addition of the epoxy. As discussed below, the epoxy has a function of self-restoration against deterioration.

Discoloration

Table III shows the effect of the epoxy resin on the discoloration of the surface of the networks after heat aging. With an increasing amount of the epoxy resin, the networks remained colorless. It is expected that the primary amine is generated by contamination with water and also by the heat treatment. As generally suggested, the primary amine forms complicated compounds and causes discoloration by the heat treatment.[2] Since the epoxy resin reacts easily with the amine group, the epoxy prevents discoloration.

Reaction Mechanisms

As mentioned above, the epoxy resin results in a high-performance network for sealing. The epoxy is expected to react with the isocyanate, urethane, and amine groups. To test the reaction between the epoxy and isocyanate groups, we carried out gel permeation chromatography (GPC) measurements on the reaction products of 2.4 g (0.013 mol) of TDI-65, 10 g (0.027 mol) of Epicote 828XA, and 40 g of toluene. The mixture was allowed to react at 50°C for 3 days. The GPC diagram indi-

Table III Effect of Epoxy Resin Amount on Acrylic Urethane Sealant

| Epoxy Resin Amount (wt %/Sealant)	Appearance After Heat Aging
0	Brown
2	Light brown
4.1	Colorless
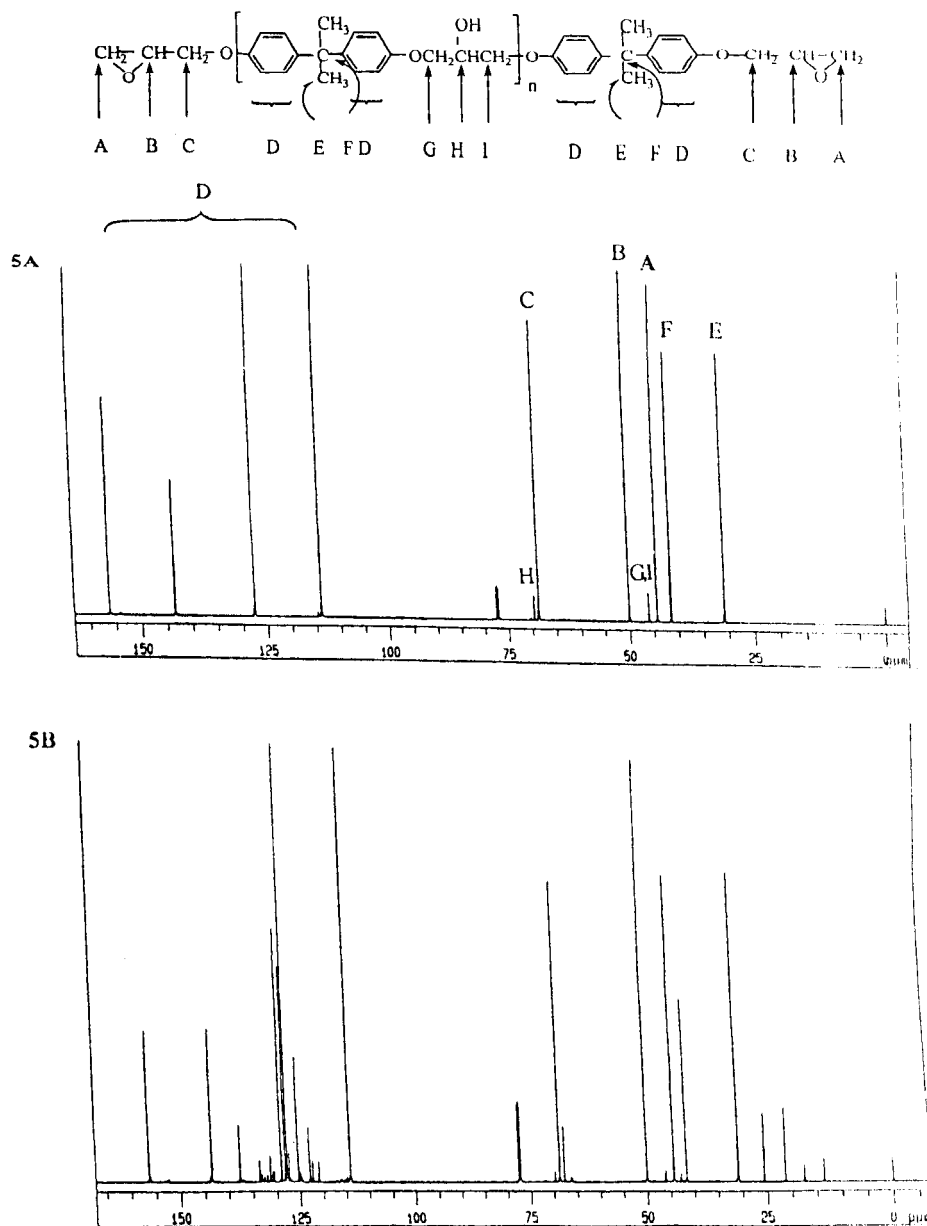
Figure 5 ^{13}C-NMR spectra of the reaction products of TDI and epoxy resin: (A) spectra of only epoxy resin; (B) spectra of the reaction products of TDI and epoxy resin.

cated that the molecular weight of the product was higher than that of the original epoxy. This indicates that the isocyanate group can react with the epoxy resin. Two possibilities for the reaction are raised: (1) the reaction between the isocyanate group (—NCO) and the epoxide group[3] and (2) that between —NCO and the hydroxyl group of the epoxy resin.[4,5] It has been known for some time that the isocyanate group reacts with the epoxide group and forms an oxazolidinone[4,5]:
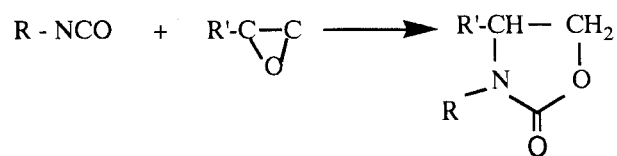
We also measured the ^{13}C-NMR spectra of the sample used for the GPC measurement. After toluene was removed under a vacuum, the ^{13}C-NMR measurement was conducted in deuterated chlo-
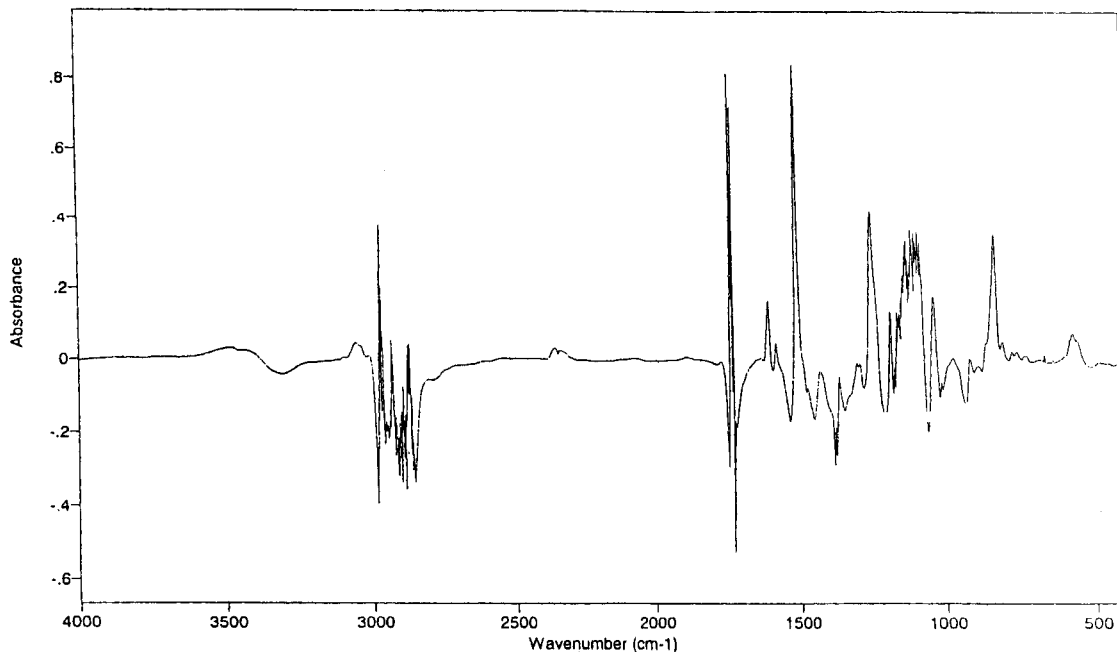
Figure 6 Difference IR spectrum between the spectra for the sample prepared with and without the epoxy resin.

roform. The spectrum showed some lines which are not seen for the pure epoxy and TDI-65, indicating that some reaction took place between them. Among the lines, we pay attention to the line around 70 ppm. For the pure epoxy resin, the lines from 25 to 75 ppm may be assigned as indicated in Figure 5(A). The intensities for the lines H, I, and G are about 10% of the others since the content of this block is 14%. After the reaction with TDI-65, line H at 70 ppm almost disappeared and a new line appeared at 66 ppm. This indicates that the OH group attached to the carbon H reacts with isocyanate and, hence, the chemical shift for the carbon H shifted. The other lines observed for the reaction products are those seen below 25 ppm. These are assigned to the line due to methyl or methylene groups. This indicates that except for the reaction with the OH group of the carbon H the other reaction took place at the same time. At present, it is clear yet what reaction has occurred. We speculate that the oxazolidinone formed between the epoxide and isocyanate groups reacts further with the epoxy.

Then, we examined whether all the epoxy groups are consumed in the initial stage of the reaction between the prepolymer and the hardener. Figure 6 shows the difference IR spectrum between the spectra for the samples prepared

with and without the epoxy. The bands due to the epoxy group are clearly seen at 1510, 1248, and 830 cm^{-1}. Therefore, the epoxy remains after the reaction of the prepolymer and the hardener. Probably, most of the epoxy resin exists as dangling chains, that is, one end is linked with the network. This reduces the crosslink density of the network as described for the mechanical properties.

Role of Epoxy Resin

It was found that the epoxy resin is effective in increasing the mechanical toughness, heat resistance, and resistance to discoloration. The reason why the heat resistance is thus improved by adding epoxy resin is explained as follows: Judging from the above dynamic viscoelasticity data, we expect that heat deterioration occurs regardless of the epoxy resin. However, the epoxy reacts with the groups formed by the degradation such as the NH_2 groups. Thus, the degradation of the network can be restored by additional crosslinking reactions between the epoxy and reactive groups. The epoxy also reacts with the NH_2 groups and prevents discoloration. Thus, the epoxy plays an important role for the high-performance sealing materials composed of PPG/PBA.

CONCLUSIONS

We found that 4.1 weight % of epichlolhydrin–bisphenol A type epoxy resin added in PPG/PBA networks gives high flexibility and toughness. Furthermore, the epoxy improves the thermal stability and the resistance to discoloration. Thus, in designing an acrylic urethane network with plastic acryl polyol, the epoxy resin has an important technological role.

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