Chemorheology on Simultaneous IPN Formation of Epoxy Resin and Unsaturated Polyester

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SYNOPSIS

Study of the simultaneous interpenetrating polymer network (IPN) between diglycidyl ether of bisphenol-A (DGEBA) and unsaturated polyester (UP) was carried out at ambient temperature. Fourier transform infrared (FTIR) spectroscopy was employed to investigate the intermolecular H-bonding and functional group changes. Viscosity changes due to H-bonding and crosslinking were examined with a Brookfield viscometer. Gelation time was measured by a Techne gelation timer. Complexation between Co(II) (the promoter for UP cure) and diamine (the curing agent for DGEBA) was detected with UV-visible spectrometer. Experimental evidence revealed that intermolecular interactions were observed in systems such as DGEBA/UP, DGEBA/diamine, UP/diamine, Co(II)/diamine, DGEBA/uncured UP, and UP/uncured DGEBA. All such interactions had measurable effects on the curing behaviors for both networks, as were indicated by the viscosity changes and gelation time. The IPNs thus obtained were further characterized with rheometric dynamic spectroscopy (RDS) and differential scaning calorimetry (DSC). Partial compatibility between UP and DGEBA networks was evidenced from a main damping peak with a shoulder near glass transition temperature (T_g) for lower UP content; while at higher UP content, only a main damping peak near T_g was observed. DSC revealed a broad glass transition for all IPNs. The resultant IPN materials were all transparent. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Although significant progress has been made in the development of interpenetrating polymer network (IPN) materials in recent years,[1-6] there still is a lack of information concerning the viscosity change during simultaneous IPN formation. Such a viscosity change is important when IPN materials are applied in coatings and/or prepregs. Both epoxy resin and unsaturated polyester are thermosetting polymers. The former exhibits excellent mechanical properties and good adhesion to metals and carbon fiber; while the cost of the latter is lower. Their IPN materials provide balanced performance and cost. Since epoxy undergoes condensation cure and UP undergoes free radical cure, each network formation seems to proceed independently. However, in view of the complicated molecular interactions in the system, apparently this is not the case for each network. Interlocking between the two networks apparently affects curing behavior relative to each other. An IPN composition of equal parts of each component, for example, shows an unusual increase in viscosity and a much shorter gelation time than other compositions. Therefore, we believe an understanding of IPN chemorheology of this system is necessary. Kwok-Wallem and Han reported the chemorheology of unsaturated polyester.[7] In this article we report the effects of molecular interactions and network interlocking on viscosity change and gelation time during IPN formation.

EXPERIMENTAL

Diglycidyl ether bis(phenol-A) (DGEBA) (Epikote 815) liquid epoxy resin with an EEW of 190 and a viscosity of 10 P at 25°C was obtained from Shell

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Chemical Co. Isophronediamine (IPDA) and *m*-xylenediamine (MXDA) purchased from ICI were used directly as curing agents for DGEBA. Stoichiometric equivalent ratio of epoxy to diamine was maintained among all the IPN compositions investigated.
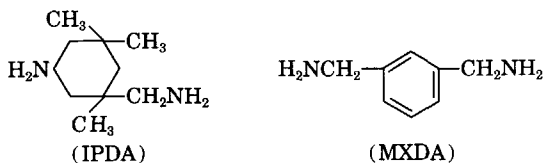
General-purpose unsaturated polyester (157 BQ TC) with a number-average molecular weight of 2000 was obtained from Yong-shun Industrial Co. (Taiwan), which contains phthalic anhydride, propylene glycol, maleic anhydride, and styrene. Cobalt octoate was used as promoter and methyl(ethyl ketone) peroxide (MEKP) was used as peroxide for UP cure.

Fourier transform infrared spectrometry (FTIR) (Bomen model number DA 3-002) with a resolution of 0.5 cm^{-1} was employed to monitor the shifts and changes of IR absorptions. Samples were cast and sandwiched between KBr plates which were then mounted on a cell holder. Samples with various DGEBA/UP ratios were used in this study. Simultaneous IPN formation was induced at ambient temperature.

Viscosity measurements were done with a Brookfield viscometer. Gelation time was measured with a Techne gelation timer. Here, gelation time is defined as the time period from the beginning of cure to the point where the sample's viscosity increases high enough to stop the flow. Essentially a glass rod was immersed in a sample of gel at a specific temperature; the other end of the glass rod was connected to the gelation timer. The curing agent then was added and curing commenced. Simultaneously,

the gelation timer was set to start vibrating up and down. Eventually, the viscosity of the gel increased so high that vibration ceased. This time period was automatically recorded by the gelation timer and is taken as gelation time.

UV-visible spectra were recorded with a Hitachi 330 instrument by using methanol as solvent. DSC thermograms were obtained with a Mettler Model 20 instrument at a heating rate of 10°C/min, under N_2 atmosphere. RDS were recorded with a Rheometric II, at 1 Hz of frequency. The temperature range was −100–200°C.

RESULTS AND DISCUSSIONS

The final transparent IPN materials contained DGEBA, UP, diamine, cobalt octoate, MEKP, cured DGEBA and cured UP networks. Molecular interactions among these species and viscosity changes are discussed below:

Interaction between DGEBA and UP

When pure DGEBA and UP were blended in various ratios, an increase in viscosity was generally observed. Figure 1 shows the nonlinear relationship of viscosity increase versus DGEBA content in the blends before curing. This viscosity increase can be attributed to the intermolecular H-bonding between DGEBA and UP, as evidenced from the shift of carbonyl absorption in the IR spectra in Figure 2. The original carbonyl peak of the UP occurs at 1725.4 cm^{-1}. Upon the addition of an equal part of DGEBA, the carbonyl peak shifts to higher wave number at 1728 cm^{-1}. Since the OH end group of the low-molecular weight UP is believed to originally H-bonded with its own carbonyl group, addition of EGDBA to UP, is believed to replace part of the original tight hydrogen bonds with the weaker intermolecular hydrogen bonds between the OH end group of UP and the epoxide group of DGEBA, as shown in the following expression:
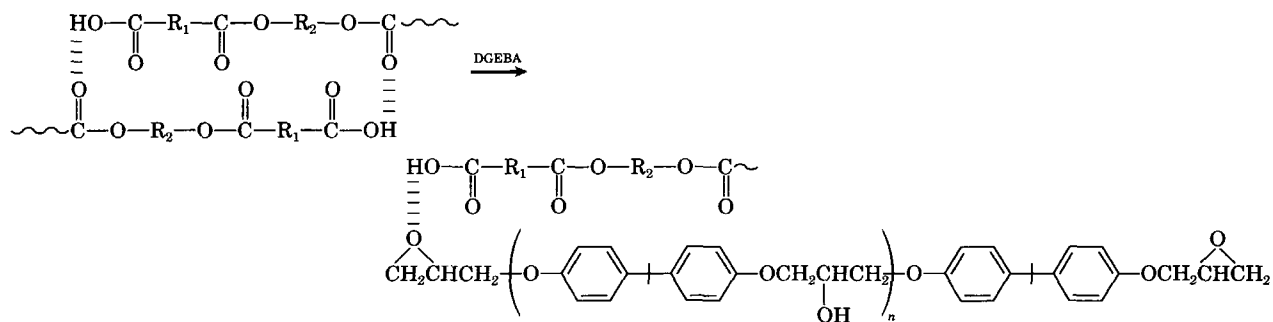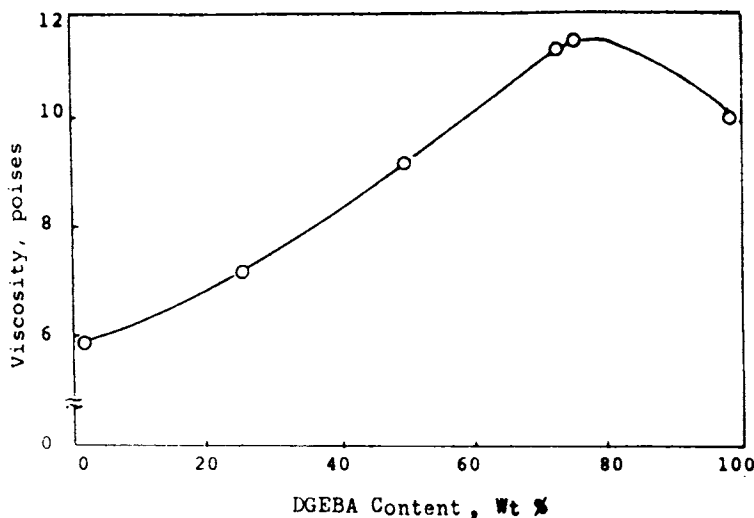
Figure 1   Viscosity of UP/DGEBA blends (uncured) versus DGEBA content.

The higher DGDBA content in the blend, the more extensive is the intermolecular H-bond formation between UP and DGEBA. This leads subsequently to higher viscosity of the system, as shown in Figure 1. Because of the extensive intermolecular H-bonding between DGEBA and UP, no apparent phase separation was observed. The resultant IPN materials were all transparent. This improved compatibility was evidenced from the broad single glass

transition in DSC for all IPNs (Fig. 3). Figure 4 shows the rheometric dynamic spectroscopy of the IPNs. UP has a damping peak at 165°C, and DGEBA shows two damping peaks at 106 and −10°C. The peak at 106°C is believed due to glass transition; while the peak at −10°C is probably due to β-transition. Keenan and Seferis reported a β-transition at −40°C for an epoxy cured by sulfone-based aromatic diamine.[8] An IPN of UP/DGEBA
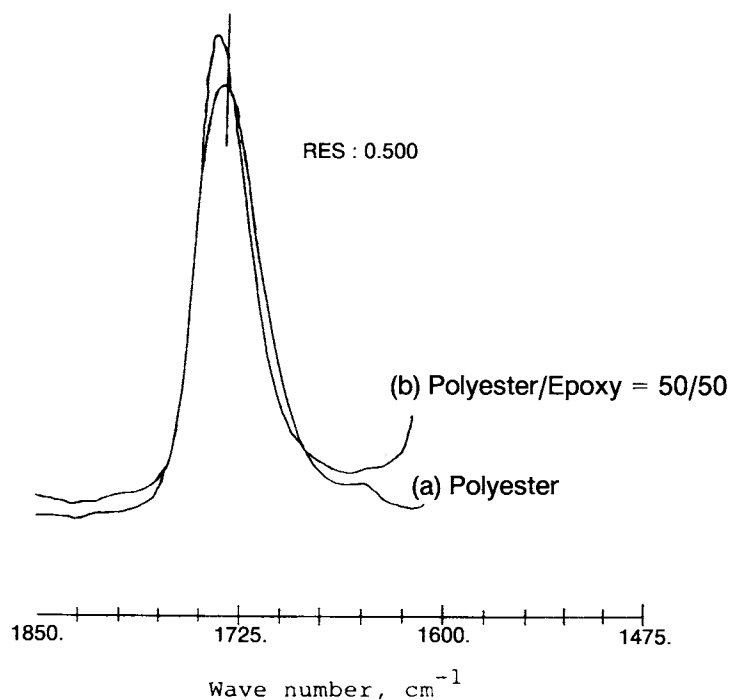

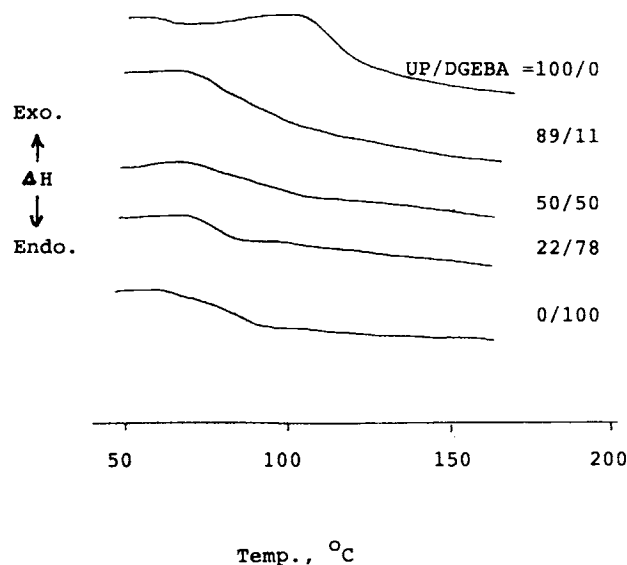**Figure 2**   Shift of IR band for carbonyl absorption in (a) UP, (b) UP/DGEBA 50/50.

Figure 3 DSC thermograms of IPNs at various UP/ DGEBA compositions.

= 89/11 composition indicates an inner shift of a single damping peak at 144°C. The IPN of equal parts of each component (UP/DGEBA = 50/50) shows two peaks at 62 and 94°C; while the IPN of UP/DGEBA = 22/78 has a damping peak at 80°C with a small shoulder at 101°C. It appears that UP and DGEBA are, at least partially compatible and that increasing UP content would enhance compatibility by introducing more OH groups, and hence more H-bondings, into the IPNs.

Interaction between DGEBA and Diamines

The original epoxide group of DGEBA absorbs at 915.1 cm^{-1}. Addition of the curing agent MXDA to DGEBA, before curing, shifts epoxide absorption to 914.5 cm^{-1}. This shift is believed to be due to the intermolecular H-bonding between the epoxide group of EGDBA and the amino group of MXDA. In their study of epoxy/amine curing behavior, Bel-
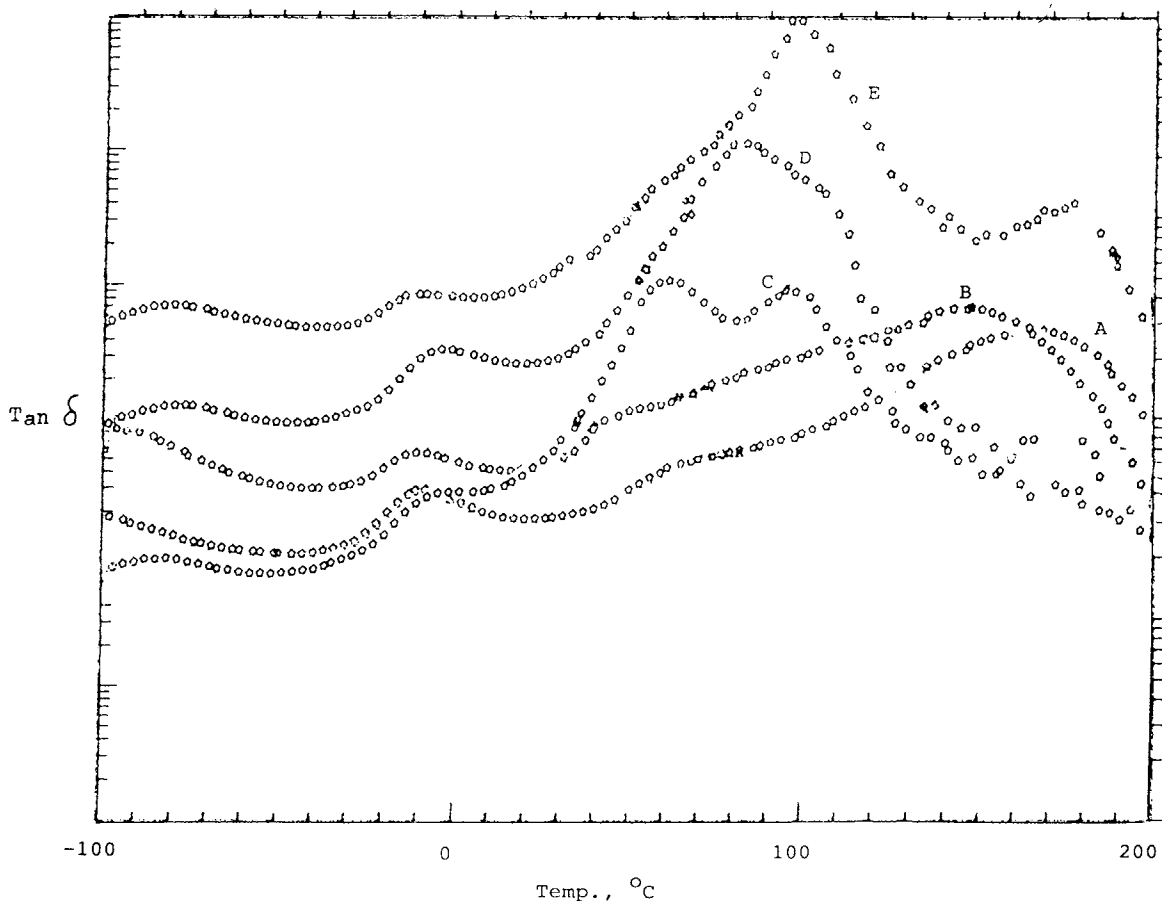

Figure 4 Rheometric dynamic spectroscopy of IPNs at various UP/DGEBA ratioa: (A) 100/0, (B) 89/11, (C) 50/50, (D) 22/78, (E) 0/100.
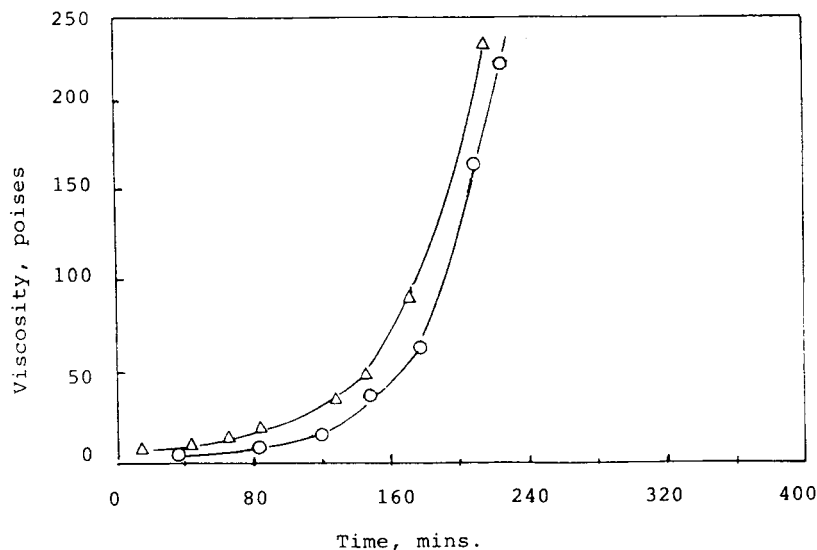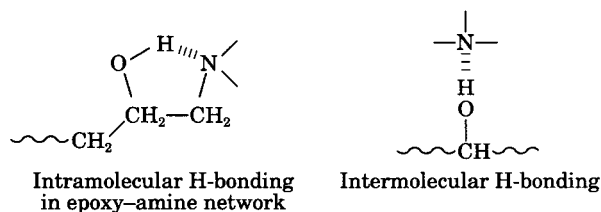
Figure 5 Viscosity change versus cure time for DGEBA. (△) DGEBA/IPDA 1/1, (○) DGEBA/IPDA 1/2.

lenger and co-workers reported an intramolecular H-bonding in epoxy–amine networks and an intermolecular H-bonding in epoxy–amine,[9] as indicated below:

Intramolecular H-bonding in epoxy–amine network   Intermolecular H-bonding

Both types of hydrogen bonds retard the reactivity of diamine and slow down the cure rate; therefore,

the addition of excess diamine reflects a lower viscosity increase (Fig. 5) and a longer gelation time (Fig. 6) for epoxy cure.

Interaction between UP and Diamines

Addition of diamine to UP results in new H-bonding between carbonyl group of UP and diamine as evidenced from the shifts of the carbonyl peak to a higher wave number in IR spectra as shown in Table I. The greater amount diamine in UP results in higher wave numbers indicating the presence of more extensive hydrogen bonds. Similar interactions
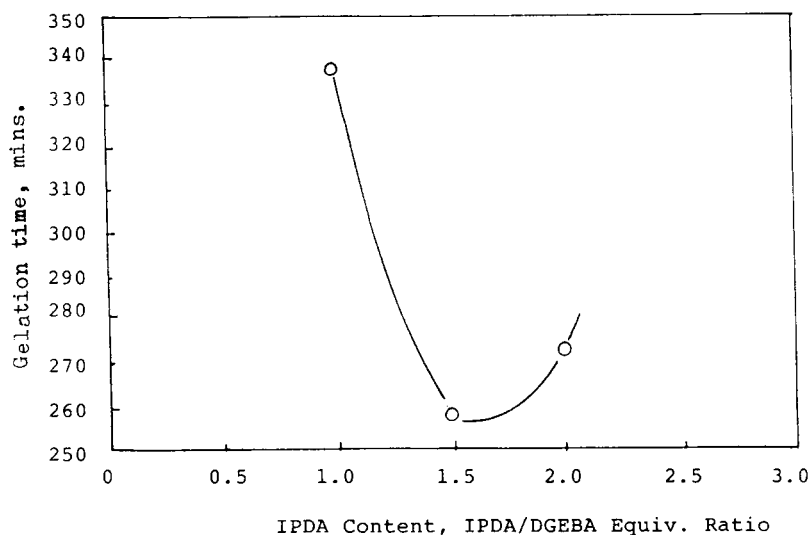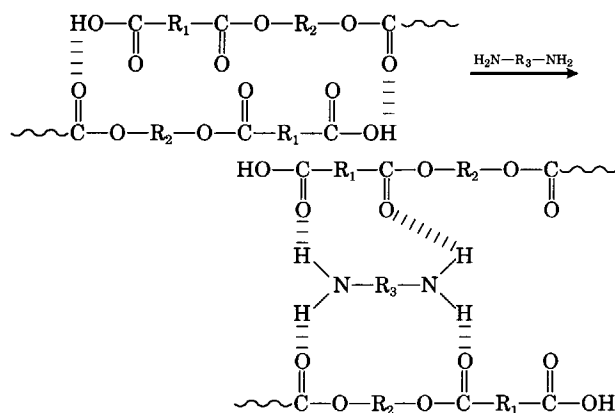

IPDA Content, IPDA/DGEBA Equiv. Ratio

Figure 6 Gelation time of DGEBA vs. IPDA content.

Table I   Shift of Carbonyl Absorption Peak in UP

Samples	$V_{c=o}$ (cm^{-1})
UP	1725.4
UP + 10% MXDA	1727.4
UP + 15% MXDA	1727.4
UP + 10% IPDA	1726.3
UP + 15% IPDA	1730.0

between poly(ethylene glycol) diacrylate and diamine were observed in our laboratory:[10]

HO—C—R$_1$—C—O—R$_2$—O—C $\sim\sim$

$\qquad\quad$ O $\qquad$ O $\qquad\qquad$ O

O

$\sim\sim$C—O—R$_2$—O—C—R$_1$—C—OH

$\qquad\qquad$ $\xrightarrow{\text{H}_2\text{N}-\text{R}_3-\text{NH}_2}$

HO—C—R$_1$—C—O—R$_2$—O—C $\sim\sim$

$\qquad\quad$ O $\qquad$ O $\qquad\qquad$ O

$\qquad\quad$ H $\qquad\qquad$ H

$\qquad\qquad$ N—R$_3$—N

$\qquad$ H $\qquad\qquad$ H

$\qquad$ O $\qquad\qquad$ O $\qquad$ O

$\sim\sim$C—O—R$_2$—O—C—R$_1$—C—OH

This effect also reflects in the viscosity change as a function of diamine level as shown in Figure 7. For UP/MXDA mixture, the viscosity increases with the increase of MXDA. The maximum viscosity of UP/DGEBA occurs at 4 phr of MXDA, after which, excess free MXDA acts as a plasticizer for UP, and the viscosity decreases. For UP/IPDA mixture, less H-bonding was observed in the early stage, presumably due to the steric methyl group in IPDA. The maximum viscosity occurs at an IPDA level of 6 phr. Similar decrease in viscosity was also noted when excess IPDA was added.

Interaction between Cobalt Salt and Diamine

Mixing cobalt octoate with diamine results in complexation as is evidenced from its UV-visible spectra. Figure 8 shows the absorption spectra of Co(II)/MXDA and Figure 9 shows those of Co(II)/IPDA, where curves a, b, and c are spectra of diamine, cobalt octoate, and Co(II)-diamine complex, respectively. A series of similar Co(II)-amine complexes have been known to inorganic chemists.[11,12] A reasonable inference is that in DGEBA/UP IPN systems, the formation of Co(II)-diamine complex is inhibitory to bonded Co(II) and diamine; hence
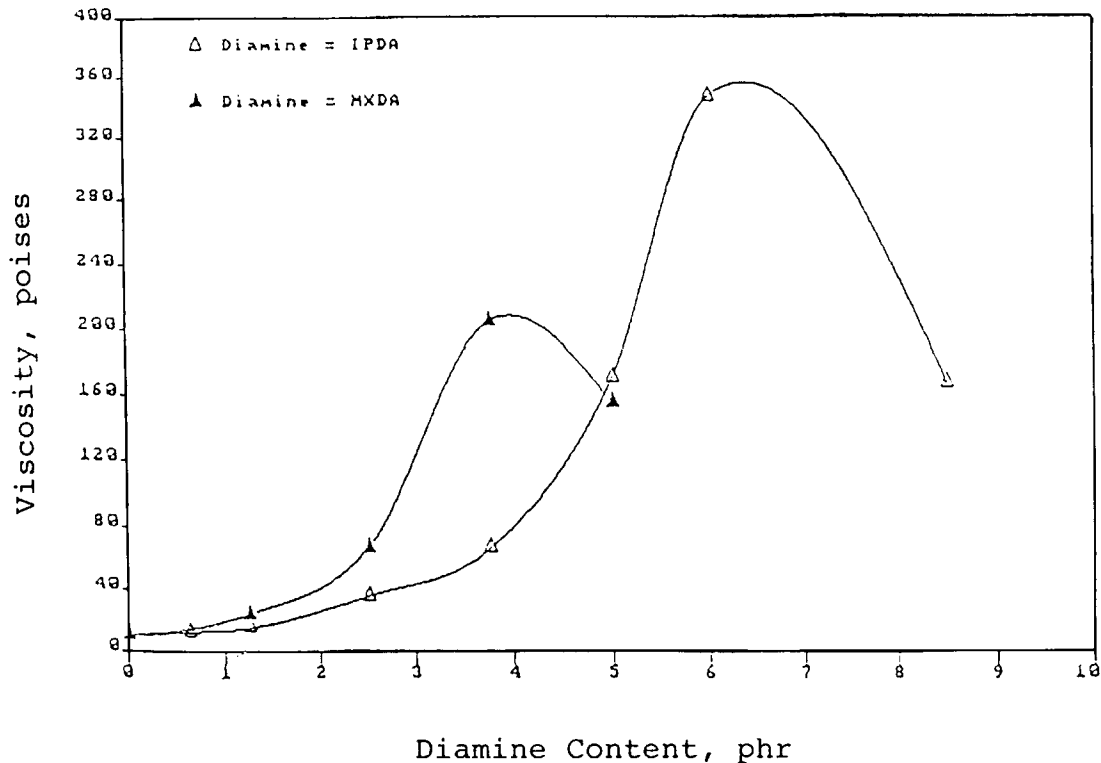

Figure 7   Viscosity of UP/diamine mixture versus diamine content. (▲) MXDA, (△) IPDA.
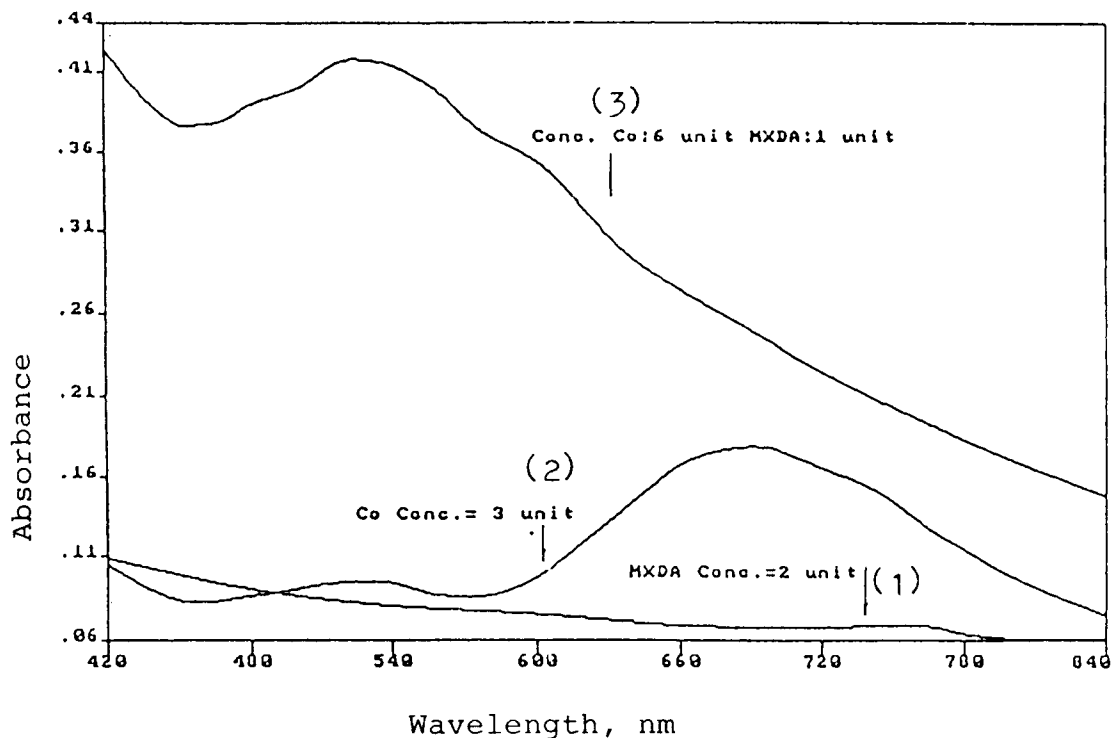
Figure 8   UV-visible spectra of (1) MXDA, (2) cobalt octoate, (3) cobalt octoate/MXDA 6/1.

their reactivities decrease and both network growth are slowed during IPN formation.

Comparison of DGEBA Cure Behavior by MXDA and IPDA

Dynamic DSC thermograms of DGEBA cured by MXDA and by IPDA are given in Figures 10(a) and

10(b). It was found that in the DGEBA/MXDA curing system, the maximum exothermic peak occurs at 108.5°C; while for the DGEBA/IPDA system, two maximum exothermic peaks (104 and 132°C) were found. In DGEBA/IPDA systems, the 104°C peak probably is due to the reaction of the less steric NH_2 and the second peak at 132°C due
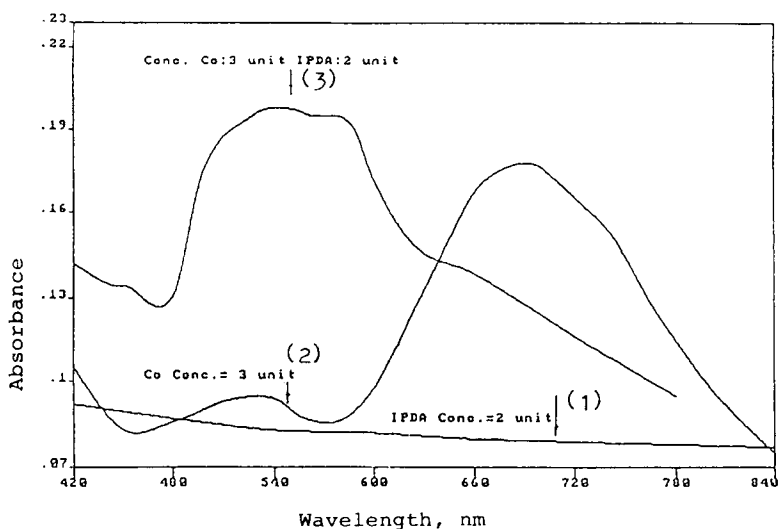

Figure 9   UV-visible spectra of (1) IPDA, (2) cobalt octoate, (3) cobalt octoate/IPDA 3/2.
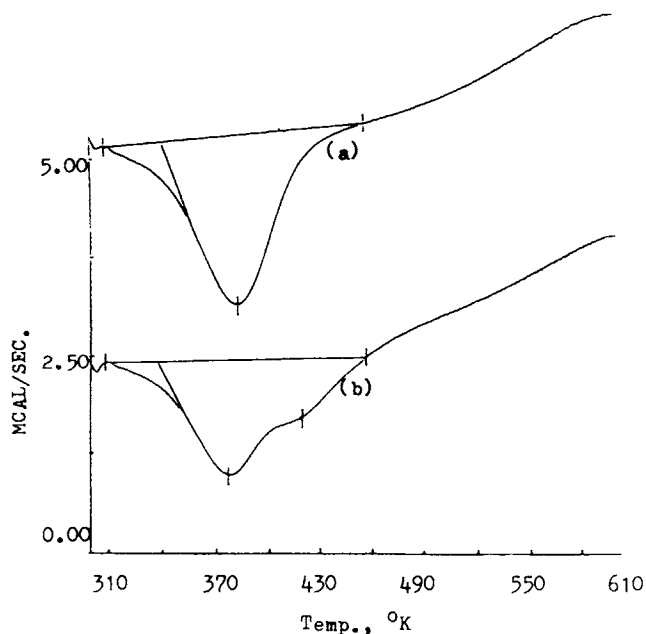
Figure 10   (a) Dynamic DSC thermogram of DGEBA cured by MXDA. (b) Dynamic DSC thermogram of DGEBA cured by IPDA.

to the reaction of the NH₂ near the methyl group. A single exothermic peak was observed in the case of DGEBA/MXDA, because the two NH₂ groups are equivalent. The gelation time in MXDA/DGEBA was 190 minutes, compared with 373 minutes in IPDA/DGEBA system, which confirms the retarded curing rate by the steric methyl group in IPDA.

Effects of the Presence of Uncured UP on DGEBA Cure Behavior

The presence of uncured UP has measurable effects on the gelation time for DGEBA cure behavior. Figure 11 shows the gelation time of DGEBA cured by IPDA in the presence of different amounts of uncured UP. Below 30 phr of uncured UP, the OH end
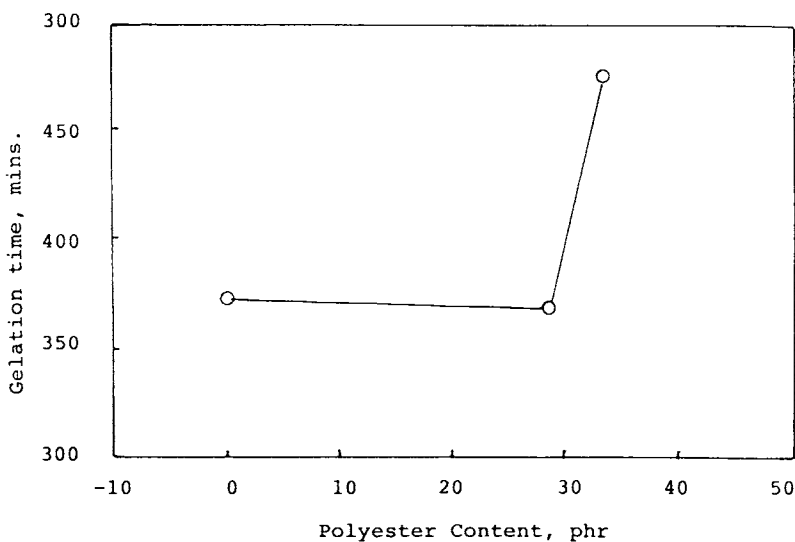

Figure 11   Gelation time of DGEBA cured by IPDA, containing different amounts of uncured UP.
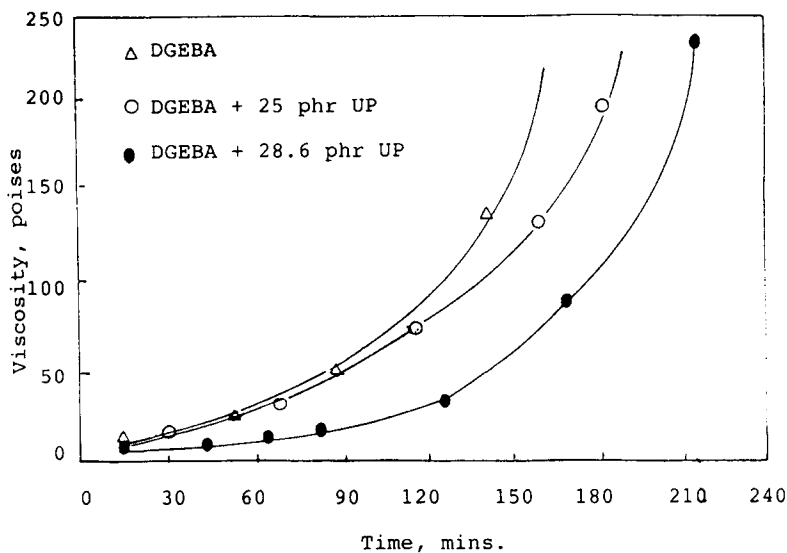
Figure 12 Viscosity change of DGEBA cure, containing different amounts of uncured UP. (△) DGEBA, (○) DGEBA + 25 phr UP, (●) DGEBA + 28.6 phr UP.

group in UP acts as a catalyst for the DGEBA–diamine cure system, accelerating the cure reaction. This catalytic effect is known in the literature.[13] On the other hand, above 30 phr of uncured UP, first, the excess UP probably acts, at least in part, as a diluent for DGEBA, hence effectively lowering the concentrations of both DGEBA and diamine. Second, the excess uncured UP H-bonds with diamine as previously indicated in Table I. Third, excess uncured UP also H-bonds with DGEBA, as was previously shown from the shift of carbonyl peak in IR absorption (Fig. 2), thus increasing the viscosity of the UP/DGEBA blend (Fig. 1). This H-bonding is reflected in the decreased mobility of both diamine and DGEBA chains. Therefore, excess uncured UP slows the curing rate of DGEBA, as indicated by longer gelation time (Fig. 11) and the slower increase in viscosity (Fig. 12).

Effects of the Presence of Uncured DGEBA on UP Cure Behavior

Figure 13 shows the increase of viscosity of UP cured by 0.5 phr MEKP in conjunction with 0.1 phr cobalt octoate. Curve a is the viscosity change of UP, while curves b, c, and d are those of UP containing 12.5, 25, and 37.5 phr of uncured DGEBA, respectively. It was found that the more uncured DGEBA in the UP/MEKP/cobalt system, the slower the rise in viscosity. The presence of uncured DGEBA dilutes both the free radical and UP concentrations. Furthermore, the H-bonding between DGEBA and UP

restricts the chain mobility of UP. Therefore, the presence of uncured DGEBA retards the curing rate of UP, leading to slowed increase of viscosity (Fig. 13) and a longer gelation time (Fig. 14).

Effect of Diamine on the Cure Behavior of UP

Figure 15 shows the gelation time of UP cured by 0.5 phr MEKP and 0.1 phr cobalt octoate in the presence of various IPDA levels. Below 1 phr of IPDA, the gelation time decreases presumably because the H-bonding between UP and diamine increases the viscosity of the system and leads to a decreased termination rate, which subsequently leads to an earlier autoacceleration stage (i.e., Tromsdorff effect). At IPDA content above 1 phr, the formation of Co(II)–amine complex is enough to reduce the active cobalt ions and slow the curing rate. Therefore, an increase of gelation time is observed with higher diamine contents.

Amounts of Cobalt Salt on UP Cure Behavior

Figure 16 shows the viscosity increase of UP cured at room temperature by 0.5 phr MEKP with two different cobalt octoate levels. It was found that 0.2 phr cobalt octoate (curve a) was much more effective in enhancing the viscosity increase than 0.1 phr (curve b). It is known that cobalt salt acts as a promoter in UP/peroxide cure systems, inducing in-
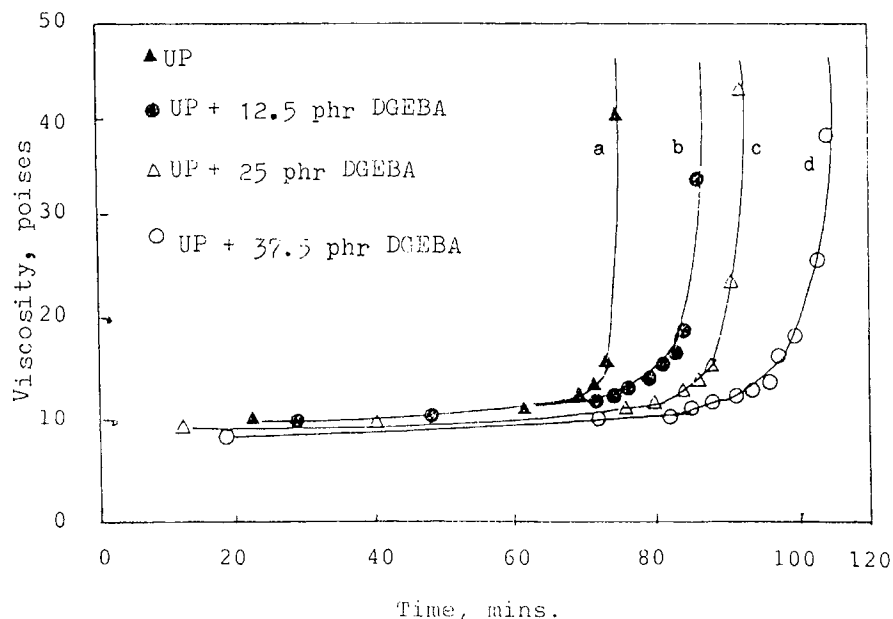
Figure 13 Viscosity change of UP cure, containing different amounts of uncured DGEBA. (▲) UP, (●) UP + 12.5 phr DGEBA, (△) UP + 25 phr DGEBA, (○) UP + 37.5 phr DGEBA.

creased viscosity. This increase causes difficulty in chain diffusion for free radical polymerization, especially near the gel point. The increase of cobalt salt shifts the gel effect to an earlier stage. Figure 17 shows the gelation time of UP versus MEKP content for 0.35 phr and 0.2 phr cobalt octoate. When MEKP concentration is higher than 0.3 phr, the effect of cobalt salt becomes insignificant.

Viscosity Changes during Simultaneous IPN Formation

Figure 18 shows typical viscosity changes of this IPN system cured at 30°C. The DGEBA was cured by a stoichiometric equivalent of IPDA, and UP was cured by 0.5 phr MEKP with 0.1 phr cobalt octoate. Since DGEBA undergoes condensation cure and UP
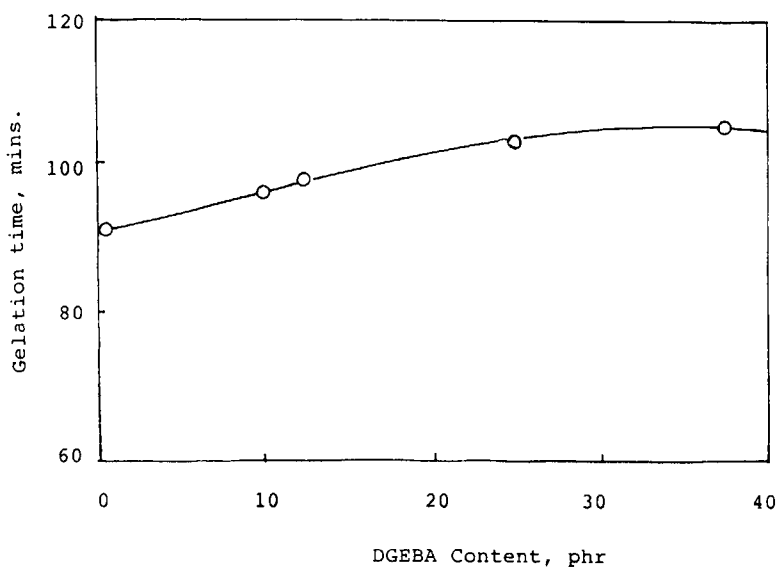

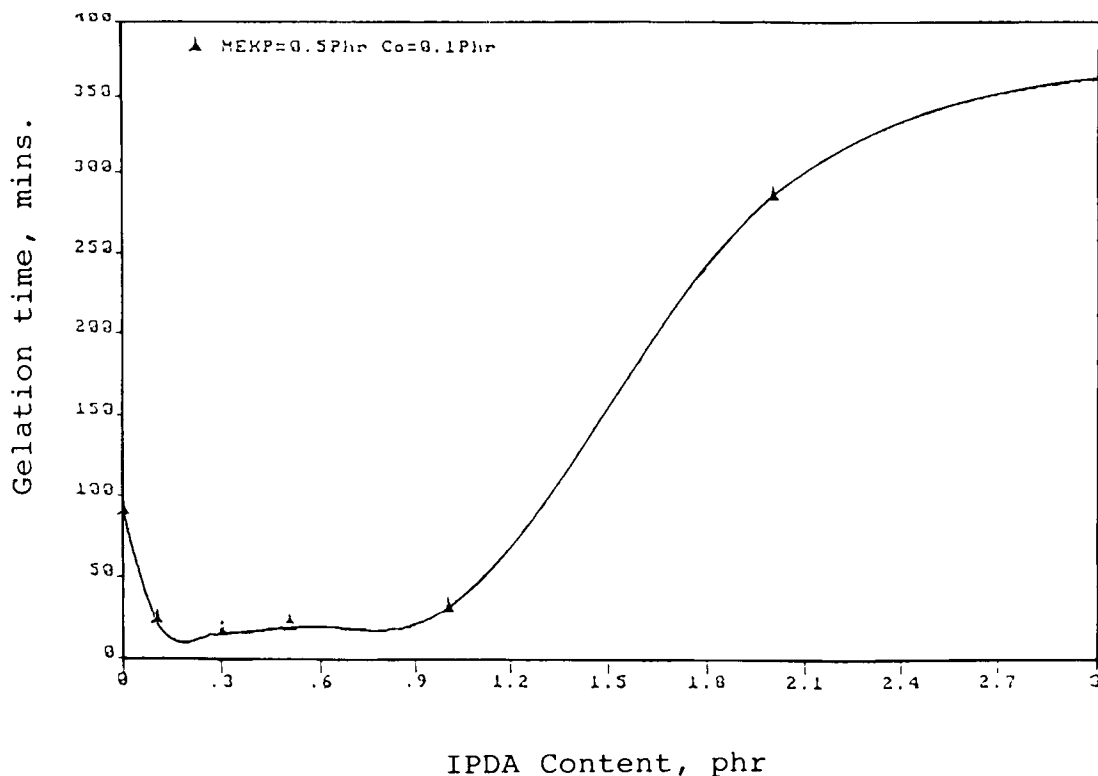**Figure 14** Gelation time of UP cure, containing various amounts of uncured DGEBA.

Figure 15 Gelation time of UP containing different amounts of IPDA.

undergoes free radical cure, both networks grow by different mechanisms. The two networks appear to be fully simultaneous IPNs. Curve a (Fig. 18) shows the viscosity change of the pure DGEBA; while curve e shows that for the pure UP. UP shows a much higher curing rate especially near the gel point, and its viscosity increases faster than the pure DGEBA. When UP is the minor component in the DGEBA/UP system (curve b, DGEBA/UP = 78/22), the initial viscosity increase is believed to be due partly to the H-bonding between DGEBA and UP as mentioned previously (Figs. 1 and 2), and partly to the
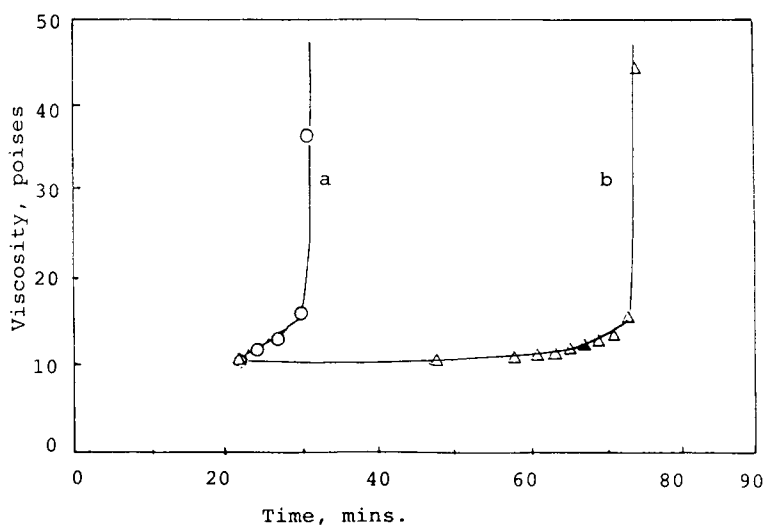

Figure 16 Viscosity change of UP cured by 0.5 phr MEKP in conjunction with different amounts of cobalt octoate. (O) 0.2 phr cobalt octoate, (△) 0.1 phr cobalt octoate.
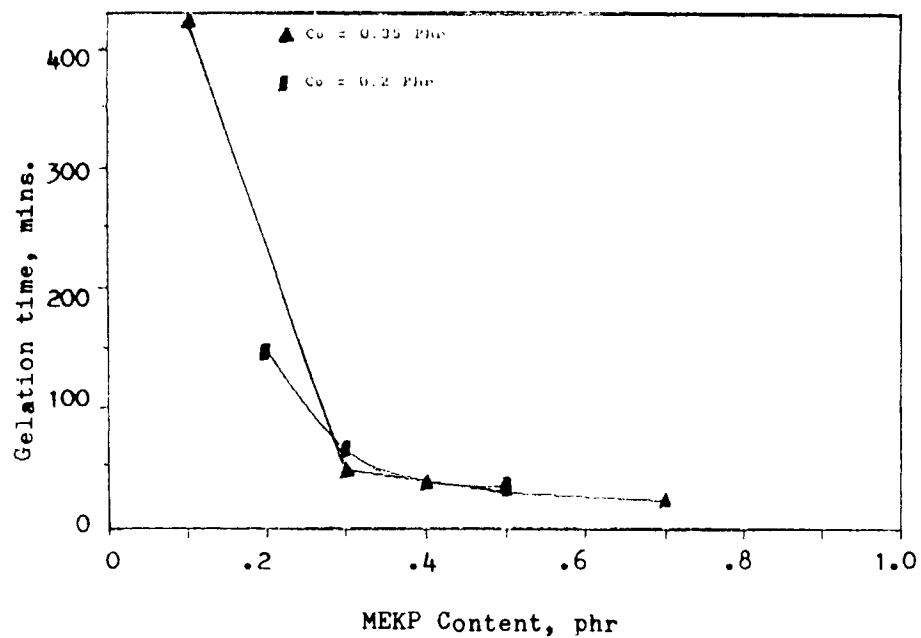
Figure 17   Gelation time of UP cured by various amounts of MEKP in conjunction with (▲) 0.35 phr cobalt octoate, (■) 0.2 phr cobalt octoate.
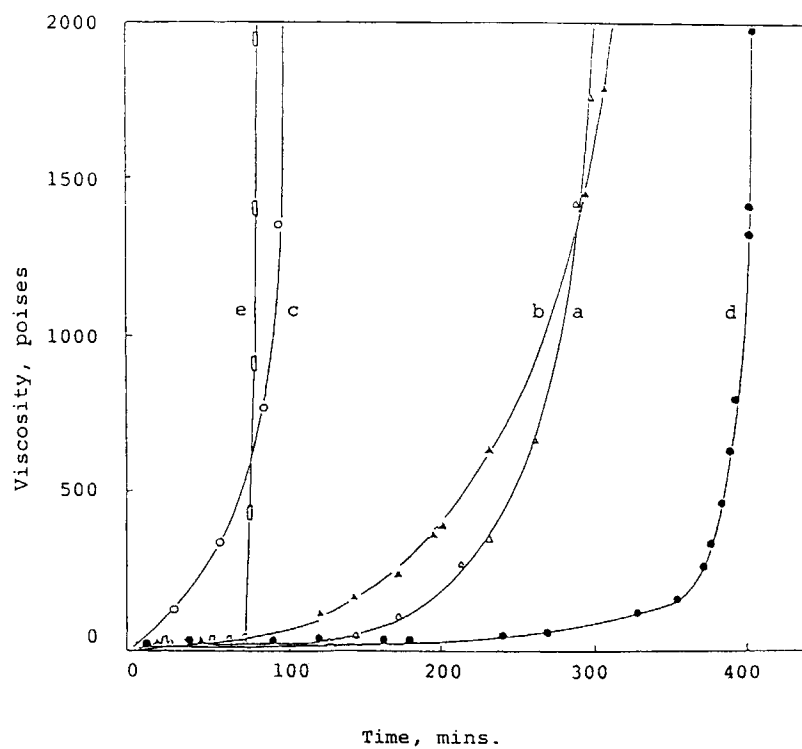

Figure 18   Viscosity changes during DGEBA/UP IPN formation at 30°C. The IPN compositions in ratio of DGEBA/UP: (a) 100/0, (b) 78/22, (c) 50/50, (d) 11/89, (e) 0/100.

Table II Gelation Time of DGEBA/UP IPNs Cured at 30°C

Ratio of DGEBA/UP	Gelation Time (min)
100/0	337
78/22	405
50/50	149
11/89	453
0/100	91

interlock of DGEBA and UP networks. Such network interlocking in later stages of IPN formation results in a decreased curing rate because of high viscosity and, subsequently leads to a longer gelation time than the pure DGEBA as shown in Table II. The blend of equal parts of DGEBA and UP (curve c, DGEBA/UP 50/50) shows an unusual increase in viscosity in the early stages, which can be interpreted as resulting from the extensive H-bonding in systems such as DGEBA/UP and UP/IPDA (Table I) and network interlocking. When the UP is the major component, as in curve d (DGEBA/UP 11/89), a significantly slow curing behavior was observed. This phenomenon can be attributed to the extensive H-bonding between UP and diamine (Table I; Fig. 7). Since the ratio of DGEBA to diamine is maintained by stoichiometric balance, the H-bonded diamine is not totally free to react with DGEBA. On the other hand, the complexation between IPDA and cobalt ions (Fig. 9) retards cure reactions of both DGEBA by IPDA and UP by Co (II)/MEKP. In addition, the extensive H-bonds in UP/DGEBA, UP/IPDA probably presents an extra barrier to free radical attack of UP. Furthermore, network interlocking between cured DGEBA and cured UP should provide additional steric hindrance and restriction of chain mobilities, which further retards curing reactions. Consequently, a much retarded curing behavior and a long gelation time of 453 minutes were found in this IPN composition (Table II).

CONCLUSIONS

During the simultaneous IPN formation of DGEBA and UP, extensive intermolecular interactions in

such pairs as DGEBA/UP, DGEBA/diamine, UP/diamine, cobalt ion/diamine, DGEBA/uncured UP, and UP/uncured DGEBA were observed. Essentially all such interactions and network interlocking showed measurable effects on IPN cure behavior, which was reflected in an increased viscosity and decreased gelation time.

The extensive molecular interactions, H-bonding, and network interlocking led these IPNs to be, at least, partially compatible at lower UP contents; while at higher UP content the IPNs became totally compatible.

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