精簡報告

Resole/Epoxy Cocuring Behavior
(NSC-88-2216-E-009-023)

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ABTRACT

Cocuring Materials based on different weight ratios of resole /epoxy were prepared by using NaOH and 4,4'-diaminodiphenylmethane (MDA) as curimg agents. Curing behaviors were investigated with dynamic DSC and viscosity changes during cocuring reactions. Solid samples were characterized with RDS,DSC,FTIR, and gel fraction. Experimantal results revealed that enhanced gel fraction and increased Tg's for each cocured material were generally found. These results are pretty different from the IPN materials which generally reflect in lowered gel fractions and decreased Tg's.

EXPERIMENAL

Resole was prepared according to the method cited in literature [1,2]. Epoxy in the form of diglycidyl ether of bisphenol-A (DGEBA, with an EEW of 914) was obtained fron Shell Co. Weight ratios of resole/epoxy =100/0,75/25, 50/50, 25/75, and 0/100 were blended and were cured simultaneously with NaOH (1% on resole) and MDA (20% on epoxy). Each blend was poured into teflon molds followed by precured at 110 ^{o}C for 5 hrs,then postcured at 160 ^{o}C for 2 hours.

A Nicolet 520 FTIR with a resolution of 0.5 $cm^{-1}$was employed to monitor the band shift. All DSC thermograms were obtained under nitrogen at a heating rate of 10 ^{o}C/min. Gel fractionbs were measured with a Soxhlet extractor by continuous 2 days' extraction ,using acetone as solvent. Viscosity changes were performed with a Brookfield LVT viscometer. The dynamic mechanical properties were studied with rhetric dynamic spectroscopy (RDS, Rheometric II) under a nitrogen atmosphere at a frequency of 1 Hz and a heating rate of 3 $^{o}min^{-1}$, with 0.2 % strain at 31.4 rad sec^{-1}. The temperature ranged from - 100 ^{o}C to 200 ^{o}C.

RESULTS and DISCUSSIONS

Figs. 1 and 2 show resole and epoxide IR band shifts for various resole/epoxy blends. These IR band shifts strongly suggest good miscibility of the two components in molecular level. In view of the single RDS damping peak (Fig. 3) and single Tg (Fig. 4) for each composition,it is believed that this cocured resole/epoxy system has good compatibility. Fig. 5 shows the dynamic DSC thermograms during cocuring reactions. It is noted that an additional exothermic peak at lower temperature was observed for each cocured sample (B,C,D). This appears due to the cocuring reaction of the phenoxide and epoxide.

行政院國家科學委員會專題研究計畫成果報告

酚醛樹脂/環氧樹脂共交聯行爲與物性之研究

計畫類別：☑個別型計畫　□整合型計畫

計畫編號：NSC 88-2216-E-009 -023

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CONTENTS

1. *The Differences of Curing Behaviors between Cocured Materials and IPN Materials*

2. *Protection of Epoxy Resin Against Thermo-Oxidation via Cocuring Epoxy/Resole (I)*

3. *Protection of Epoxy Resin Against Thermo-Oxidation via Cocuring Epoxy/Resole (II)*

The Differences of Curing Behaviors between Cocured Materials and IPN Materials

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SYNOPSIS

This study deals with the blending and cocuring of resole and epoxy, using NaOH and 4,4'-diaminodiphenylmethane (MDA) as curing agents. IR band shifts regarding the molecular interactions were investigated with FTIR. Exothermic peak shifts during cocuring reactions were studied with dynamic DSC. Viscosity increases were measured with a Brookfield LVT viscometer at 100 °C. The dynamic mechanical properties of the cocured samples were investigated with a rheometric dynamic spectroscopy (RDS). Experimental results revealed that the molecular interactions between resole and epoxy resulted in good compatibility as evidenced from the single damping peak in RDS curve and a single glass transition temperature for each cocured sample. Accelerated curing rates were also noticed which led to shifts of exothermic peak to lower temperature and faster viscosity increases. Nevertheless, enhanced gel fractions and increased Tg's of samples were generally observed for this cocured system. Average molecular weight between crosslinkages calculated showed much less than the components. These curing behaviors were different from those of IPN materials, which generally indicate lowered gel fractions and decreased Tg's, and higher average molecular weight between crosslinkages.

INTRODUCTION

Our previous studies on the curing behaviors of fully interpenetrating polymer networks (IPNs) [1] reveals that the exothermic peaks shifts to higher and broader temperature ranges, and a retarded viscosity increases are generally found. These findings are reasonably consistent with the lower gel fractions and lower Tg's for fully IPNs, as compared with the respective components. Our kinetic study for fully IPN consistently show lower rate constants and higher activation energies during IPN formation [2]. Based on these findings we proposed an effect of network interlock to interpret the curing behaviors of IPNs [1,2]. In IPN materials physical chain entanglements between networks result in an increased steric hindrance and a decreased chain mobility, and thus explains the increased activation energies and retarded rate constants during IPN formation.

Our present study concerning the cocuring of two thermosets, resole and epoxy, where chemical crosslinking between networks resulted in a whole network containing two components. For this cocured material, an adverse curing behavior was found. In this article, we would like to report and discuss the different phenomena.

EXPERIMENTAL

Resole was prepared by the method cited in literature [3,4]. Epoxy in the form

of diglycidyl ether of bisphenol-A (DGEBA, Epon 815) with an epoxy equivalent weight of 194 was obtained from Shell Co. Various weight ratios of epoxy/resole in 100/0, 75/25, 50/50, 25/75 and 0/100 were blended. MDA (20 % on epoxy) and NaOH (1 % on resole) were used as curing agents for each indicated component. Each blend was poured into teflon molds, followed by precuring at 110 °C for 5 hours, then an additional postcuring at 160 °C for 2 hours.

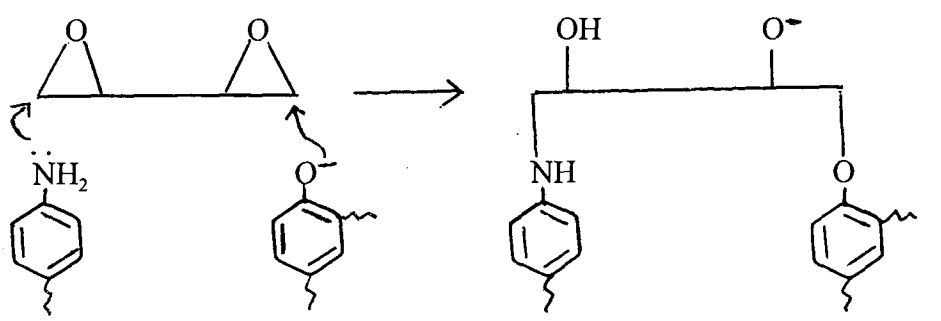
A Nicolet 520 FTIR with a resolution of 0.5 cm^{-1} was employed to monitor the IR band shift. For curing dynamic differential scanning calorimetry (DSC), liquid blends containing curing agents were sealed in the pressured DSC cells. All DSC thermograms were obtained by running the samples in nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Gel fractions were measured with a Soxhlet extractor, after 48 hours of continuous extraction, using acetone as solvent. Viscosity changes during cocuring reactions were measured at 100 °C with a Brookfield LVT viscometer. The dynamic mechanical properties were studied with a rheometric dynamic spectroscopy (RDS, Rheometic II) under a nitrogen atmosphere at a frequency of 1 Hz and a heating rate of 3 °C min^{-1}, with 0.2 % strain at 31.4 rad sec^{-1}. The temperature ranged from –100 to 200 °C.

RESULTS AND DISCUSSIONS

Synthesis and characterization of resole followed the method cited in literature [3,4]. Its FTIR spectrum is shown in Figure 1. The broad absorption band at 3500 to 2500 cm^{-1} indicates a hydrogen bonded resole. The absorption at 800 and 755 cm^{-1} confirms ortho and para CH_2 linkage of phenol. Absorption at 1230 cm^{-1} confirm the C-O-C linkage. ^{13}C NMR spectrum of resole in CD_3OD (solvent peaks at 48.1 to 49.5 ppm) is given in Figure 2. As revealed in literature [4], Peaks at 30.6, 35.6 and 41.1 ppm confirm the CH_2 linkages at 0-0, 0-p, and p-p positions of phenol. The ortho carbon linked to the methylol group occurs at 65.0 ppm. Peaks at 115 to 116, 120.4 to 120.5, 128.8 and 157.6 ppm are the absorptions of carbons on the phenyl ring connected to OH group, and ortho, meta and para positions. For trisubstitut CH_2 linked phenols, he carbon linked to OH occurs at 152 to 157 ppm, while peaks for the other carbons overlap around 127 to 134 ppm. All these confirm the structure of resole.

The good miscibility between epoxy (with a solubility parameter of 9.98) and resole (with a solubulity parameter of 10.5) can be expected by the Small [5] and Hoy [6] method. Figure 3 shows the Shifts of OH absorption in resole. Pure resole has a broad OH stretching absorption around 3600 to 3100 cm^{-1} with a peak at 3300 cm^{-1} (Curve A). When epoxy was blended to resole, the absorption of OH shifts to higher wave number. The more epoxy was incorporated, the higher frequency shifts the

OH absorption, since the miscibility in molecular level between resole and epoxy (Curves B,C,D) dilute the extent of hydrogen bonding. Figure 4 shows the epoxy band shifts. Pure epoxy indicates an epoxy absorption at 917 cm^{-1} (Curve E). When resole was incorporated into epoxy, the epoxide absorption now shifts to lower wave number (Curves B,C,D), presumably because of the hydrogen bonding formed between epoxide and the OH of resole. The compatibility of the cocured resole /epoxy can also be evidenced from the single damping peak in RDS curves (Figure 5) and the single Tg in DSC thermograms (Figure 6) for each composition. Figure 7 shows the dynamic DSC thermograms of resole/epoxy cocuring behaviors. Pure epoxy shows a curing exothermic peak at 160 ° C (Curve A), while resole has an exothermic peak at 164 °C (Curve A). Each cocured composition of resole/epoxy =75/25, 50/50 and 25/75 (Curves B, C, and D) indicates an additional peak at lower temperature which is believed due to the cocuring raction between phenoxide in resole and the epoxide in the epoxy.



The ^{13}C NMR spectra for cured resole and cured epoxy have been extensively studied in literature [7,8,9,10,11]. The crosslinked epoxy cured by MDA shows a residual epoxide carbon at 50.7 ppm (Figure 8). The disappearance of this peak for the cocured 50/50 of resole/epoxy (Figure 9) revealed the opening of the residual epoxide by a strong nucleophilic attack of phenoxide group, since phenoxide is a stronger nucleophile than the amine group transition.

The viscosity increases during cocuring reactions at 100 °C are given in Figure 10. Both pure epoxy and resole cured at relatively slower rates and shows pot-lives at 35 minutes for epoxy (Curve A) and at 33 minutes for resole (Curve E), respectively. Other compositions for resole/epoxy = 75/25, 50/50, and 25/75 (Curves B, C and D) indicate faster cure rates, presumably because the fast nucleophilic attack of phenoxide to epoxide as well as a catalytic effect of the OH on the epoxy/MDA cure as reported in literature [1,12].

A plot of Tg's versus % resole content is given in Figure 11. It is noted that enhanced glass transition temperatures for the cocured materials is observed, which is different from IPN systems. In IPN systems, rather, decreased glass transition

temperatures are generally found [1,13]. A plot of gel fractions versus % resole content is shown in Figure 12. Again, enhanced gel fractions for the cocured samples (B,C, and D) are observed. Whereas, in IPN systems, decreased gel fractions has been known [1,13]. This enhanced gel fractions would mean more crosslinking for each cocured sample and account for the enhanced glass transition.

Hourston proposed a method to calculate the average molecular weight (Mc) between two linkages for a crosslinked polymer [14]:

$$Tg - Tg,o = 3.9 \times 10^4/Mc$$

Where Tg is the glass transition temperature of a specific material, and Tg,o is that of uncured epoxy (-16.6 °C). The calculated Mc values are plotted in Figure 13. It is noted that the Mc value for a cocured sample (resole/epoxy = 75/25, 50/50, and 25/75) are generally smaller than than epoxy. While In Fully and semi-IPNs higher Mc values are generally found [1,13]. These findings of higher Tg's, lower gel fractions and lower Mc values strongly support the fact of higher crosslonking in cocured polymer materials than IPN materials since the chemical crosslinking between the two networks in cocured materials accounts for the experimental results. In IPN materials the physical chain entanglements in the two networks provide a sterically hindered environment and cause difficult and incomplete cure, leading to lower gel fraction, lower Tg's, and higher Mc values [1,2,13].

CONCLUSION

In the compatible resole/epoxy cocured materials, enhanced gel fractions, increased glass transition temperatures, and lower average molecular weight between linkages were found. These phenomena are different from those generally found in IPN systems as reported in literature. Chemical crosslinking between the two networks in a cocured system would lead to higher crosslinking; whereas, physical chain entanglements of the two networks in IPN materials would lead to lower crosslinking, thus account for these findings.

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CAPTIONS OF FIGURES

Figure 1. FTIR spectrum of resole.

Figure 2. ^{13}C NMR spectrum of resole.

Figure 3. ν_{OH} band shifts in resole/epoxy blends.

Figure 4. Epoxide band shifts in resole/epoxy blends.

Figure 5. Damping peaks (tan δ) for various resole/epoxy compositions.

Figure 6. Glass transition temperatures for various resole/epoxy compositions.

Figure 7. Dynamic DSC thermograms showing exothermic peaks for Various resole/epoxy compositions during cocuring reactions.

Figure 8. ^{13}C NMR spectrum for postcured epoxy.

Figure 9. ^{13}C NMR spectrum for cocured 50/50 of resole/epoxy material.

Figure 10. Viscosity increases for various resole/epoxy compositions during cocuring reactions.

Figure 11. Plot of glass transition temperatures versus % resole content.

Figure 12. Plot of % gel fractions versus % resole content.

Figure 13. Plot of average molecular weights between linkages versus % resole content.

Fig. 1

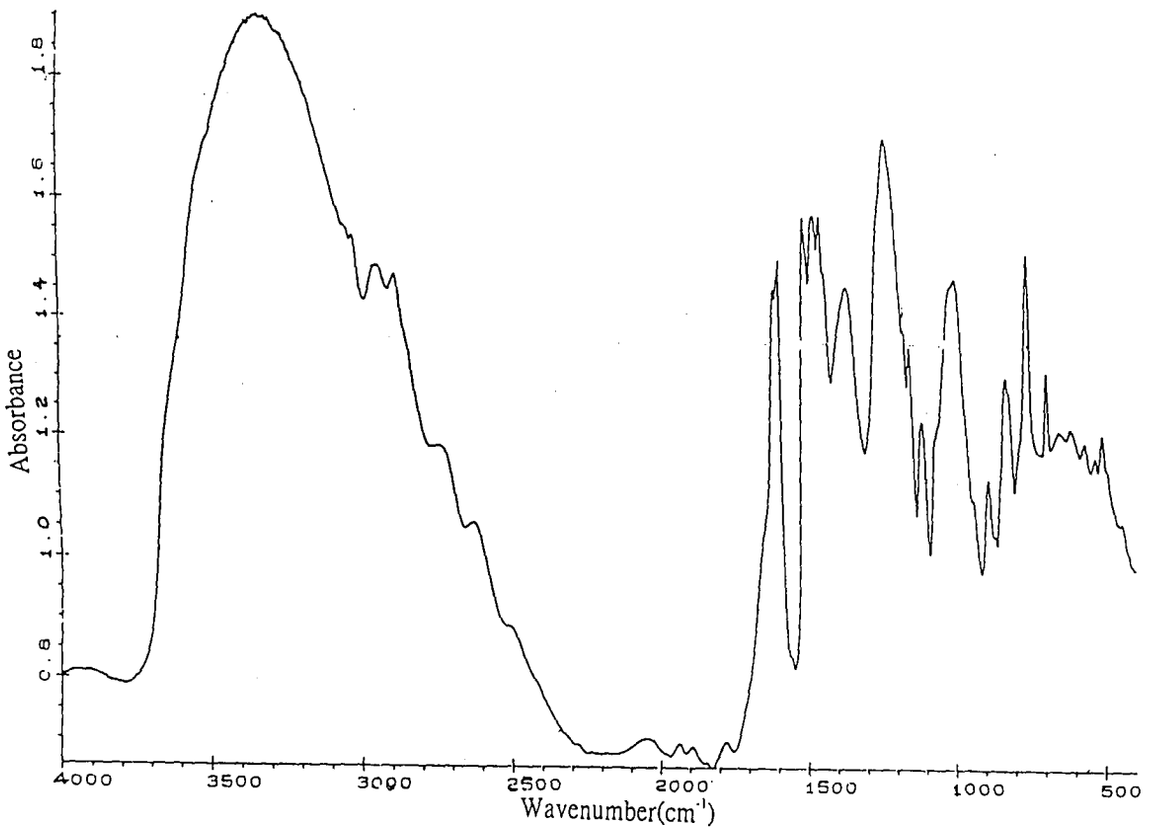
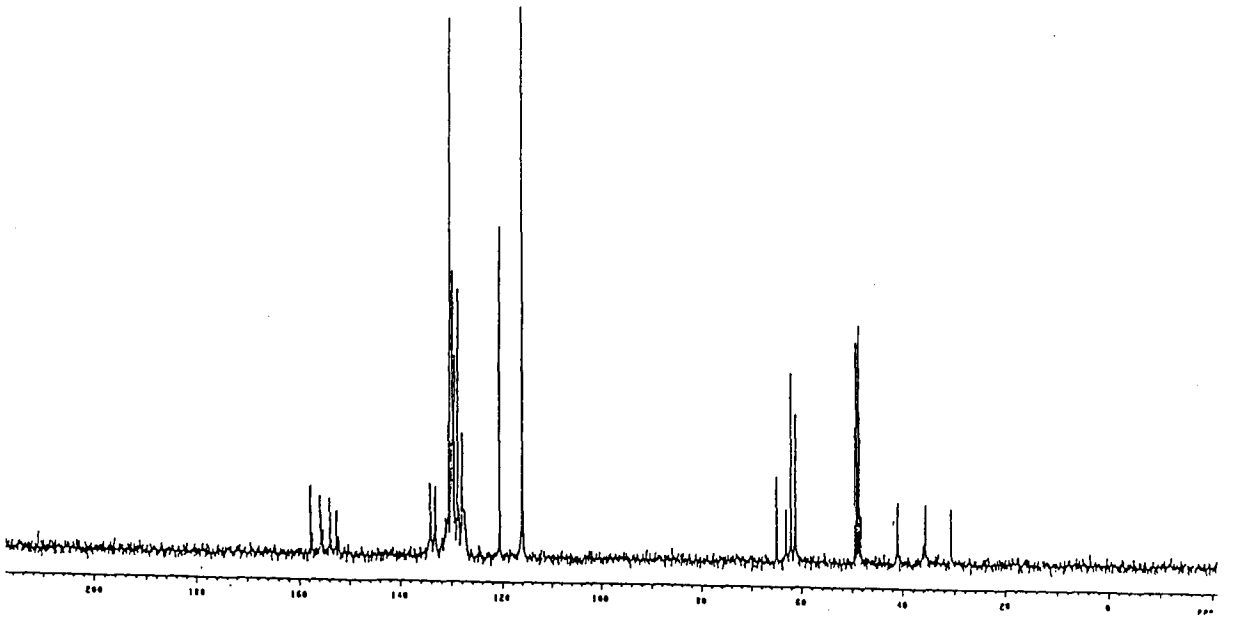

Absorbance
0.8
1.0
1.2
1.4
1.6
1.8
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)

Fig. 2



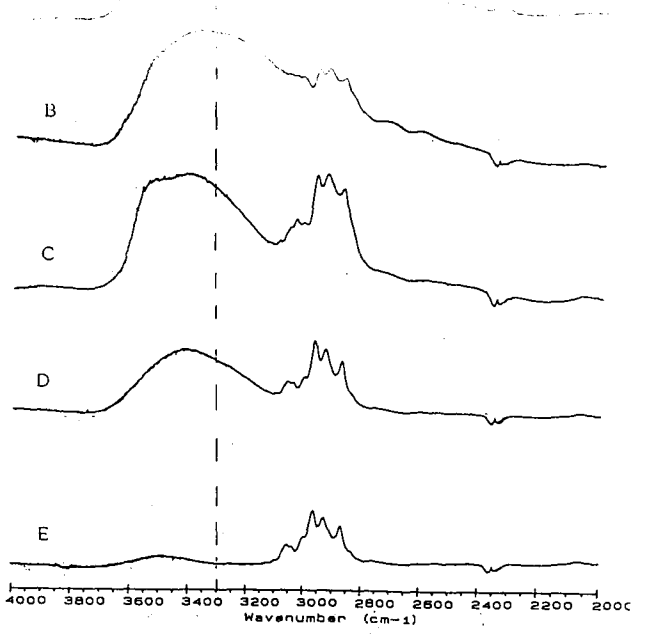

B
C
D
E
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000
Wavenumber (cm-1)

Fig. 4

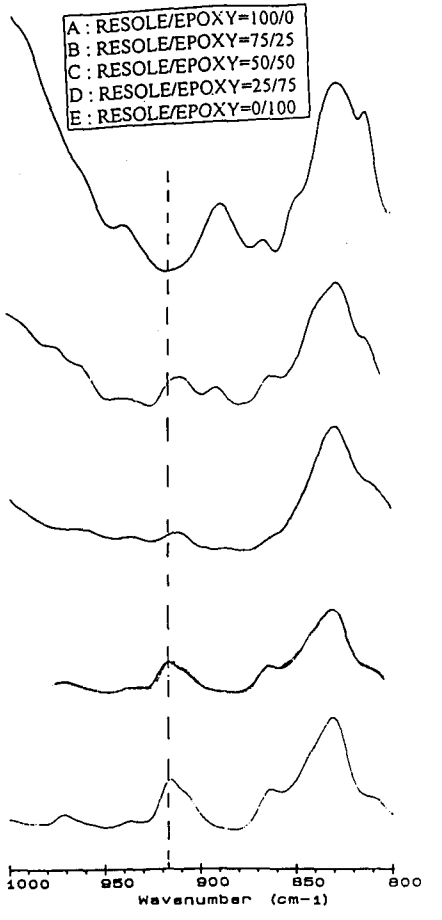

A : RESOLE/EPOXY=100/0
B : RESOLE/EPOXY=75/25
C : RESOLE/EPOXY=50/50
D : RESOLE/EPOXY=25/75
E : RESOLE/EPOXY=0/100
1000
950
900
850
800
Wavenumber (cm-1)

Fig. 5

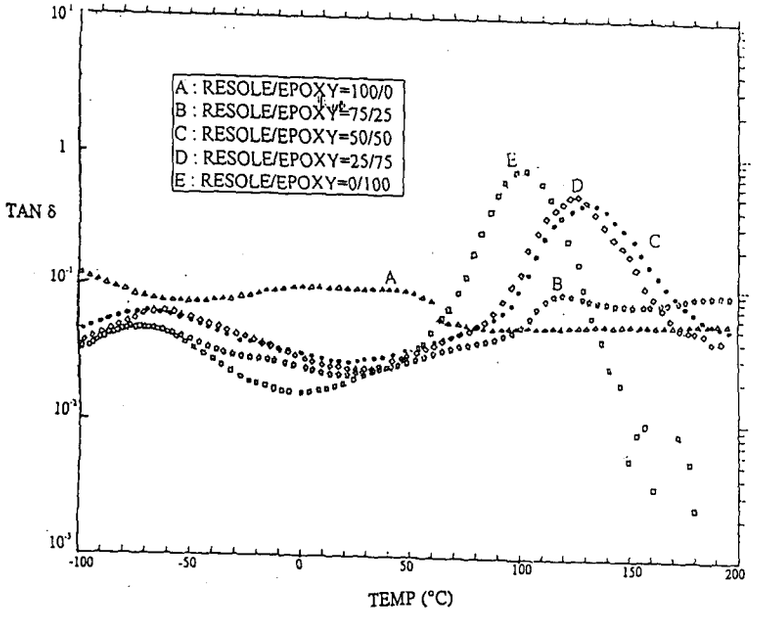

A : RESOLE/EPOXY=100/0
B : RESOLE/EPOXY=75/25
C : RESOLE/EPOXY=50/50
D : RESOLE/EPOXY=25/75
E : RESOLE/EPOXY=0/100
TAN δ
TEMP (°C)
A
B
C
D
E

Fig. 6

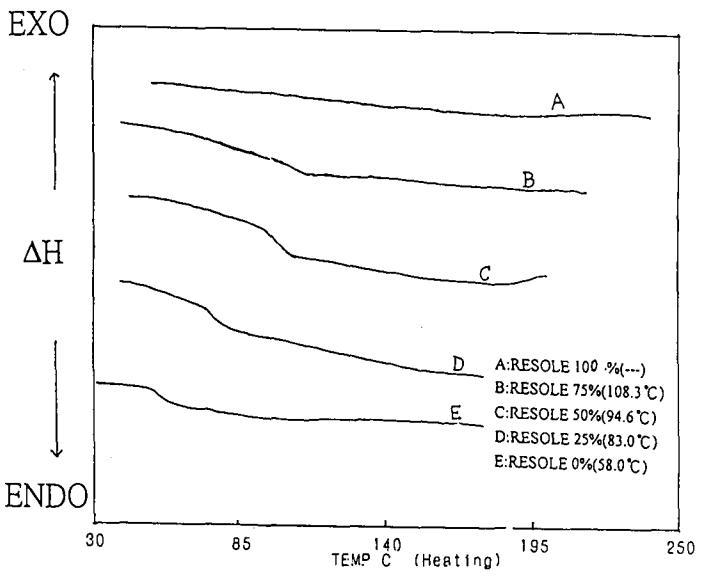

EXO
ΔH
ENDO
A
B
C
D
E
A:RESOLE 100 %(---)
B:RESOLE 75%(108.3℃)
C:RESOLE 50%(94.6℃)
D:RESOLE 25%(83.0℃)
E:RESOLE 0%(58.0℃)
30
85
140
195
250
TEMP C (Heating)

Fig. 7

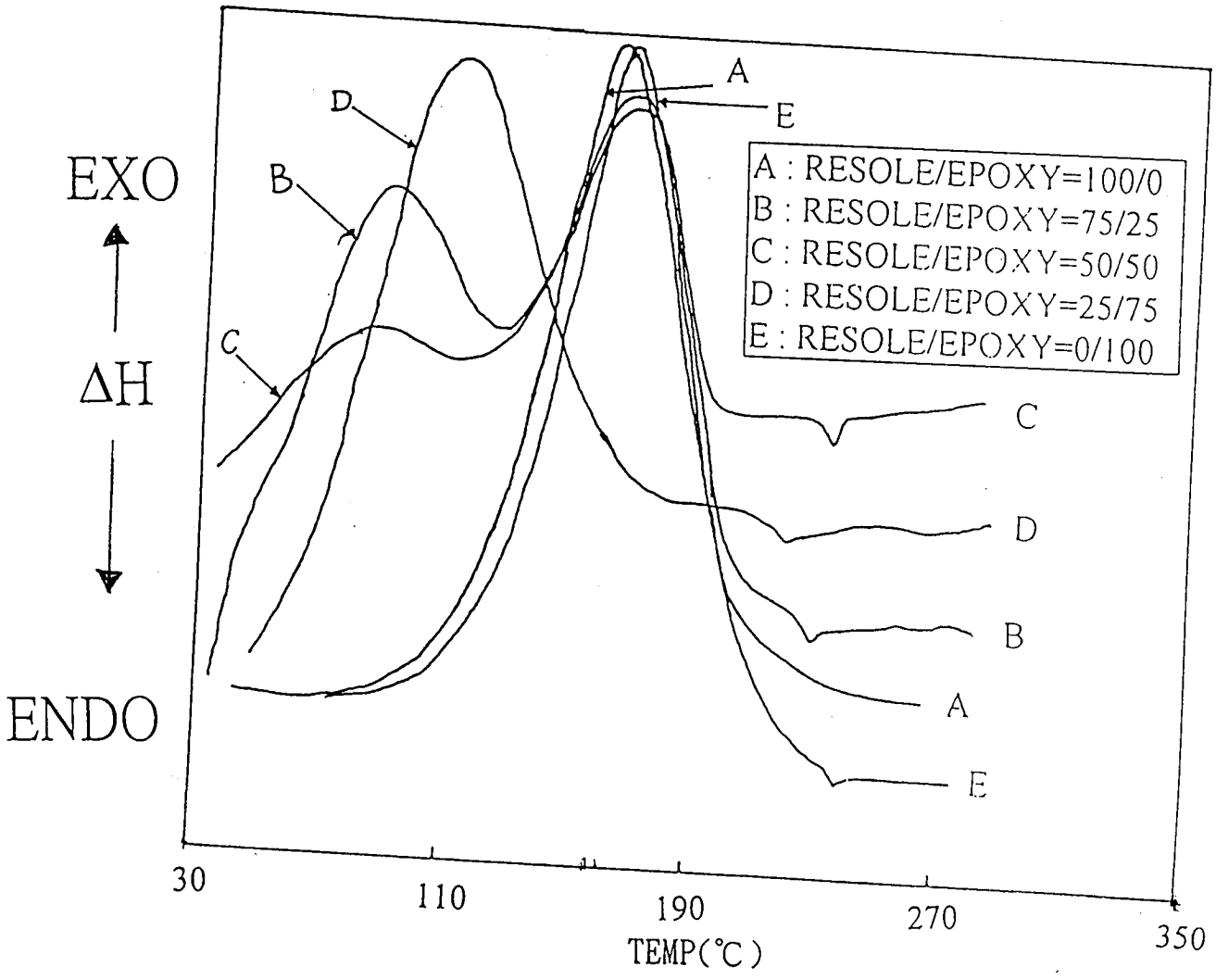

EXO
ΔH
ENDO
A
B
C
D
E
A : RESOLE/EPOXY=100/0
B : RESOLE/EPOXY=75/25
C : RESOLE/EPOXY=50/50
D : RESOLE/EPOXY=25/75
E : RESOLE/EPOXY=0/100
30
110
190
270
350
TEMP(℃)

Fig. 8

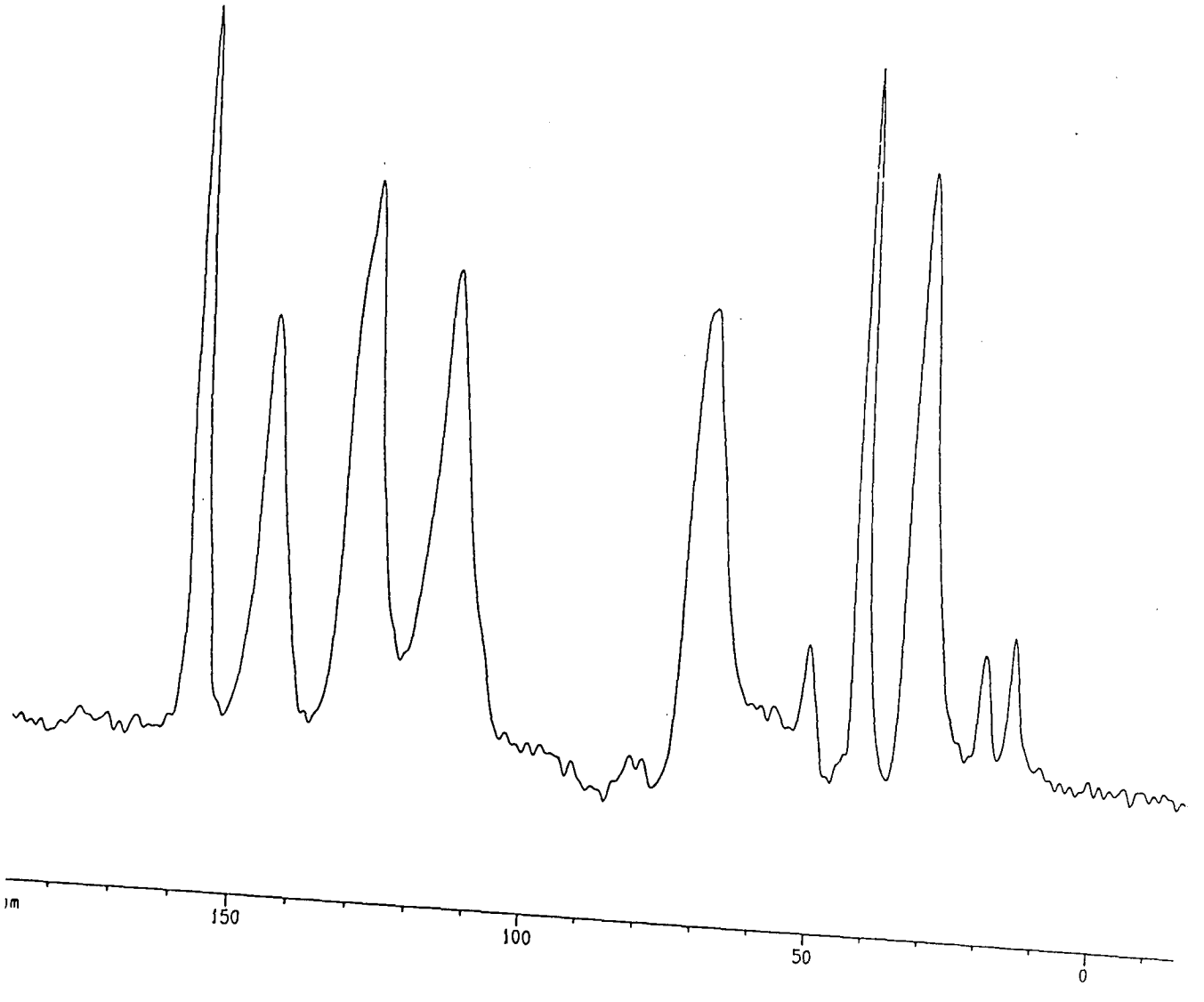


Fig. 9

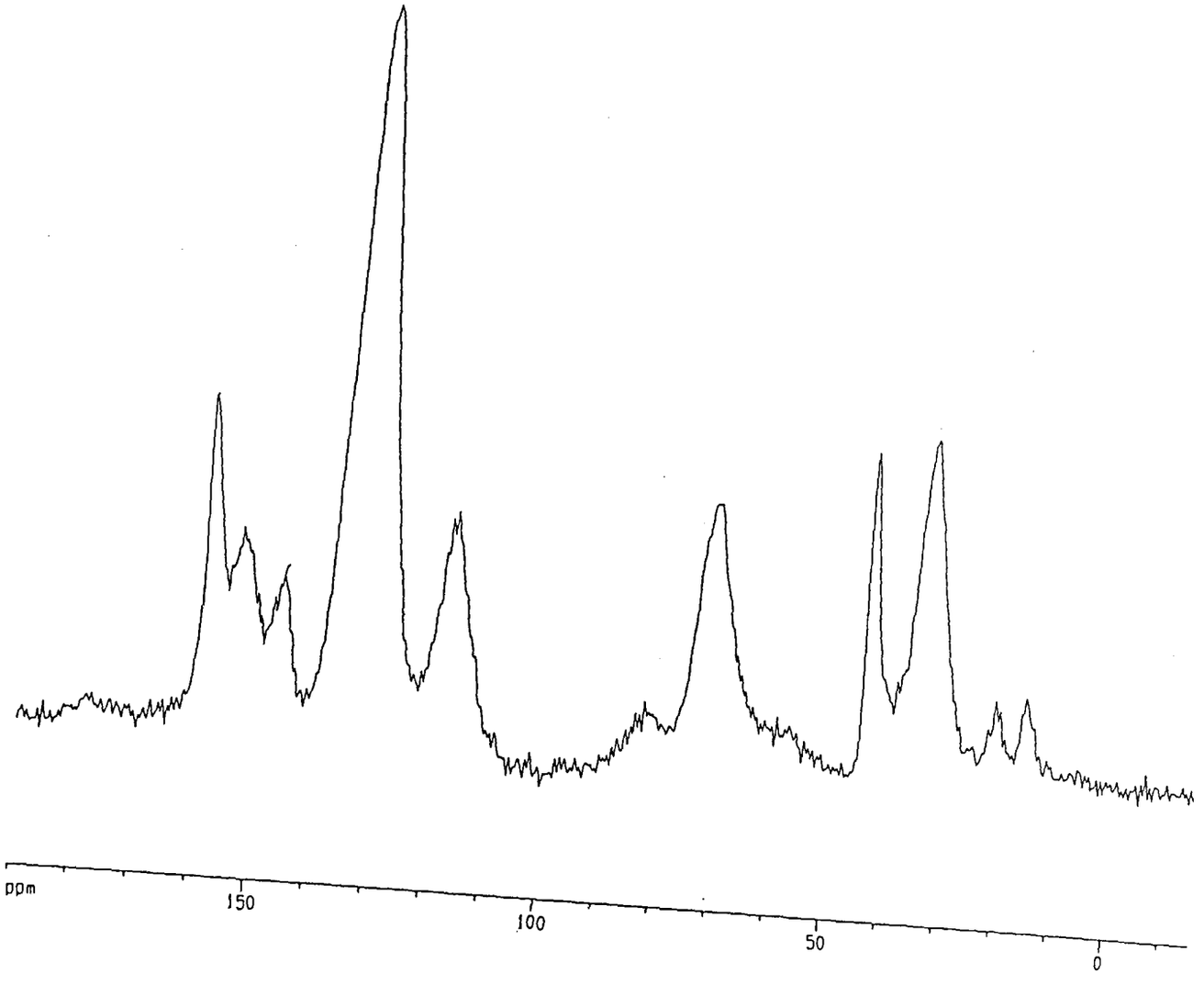


Fig. 10

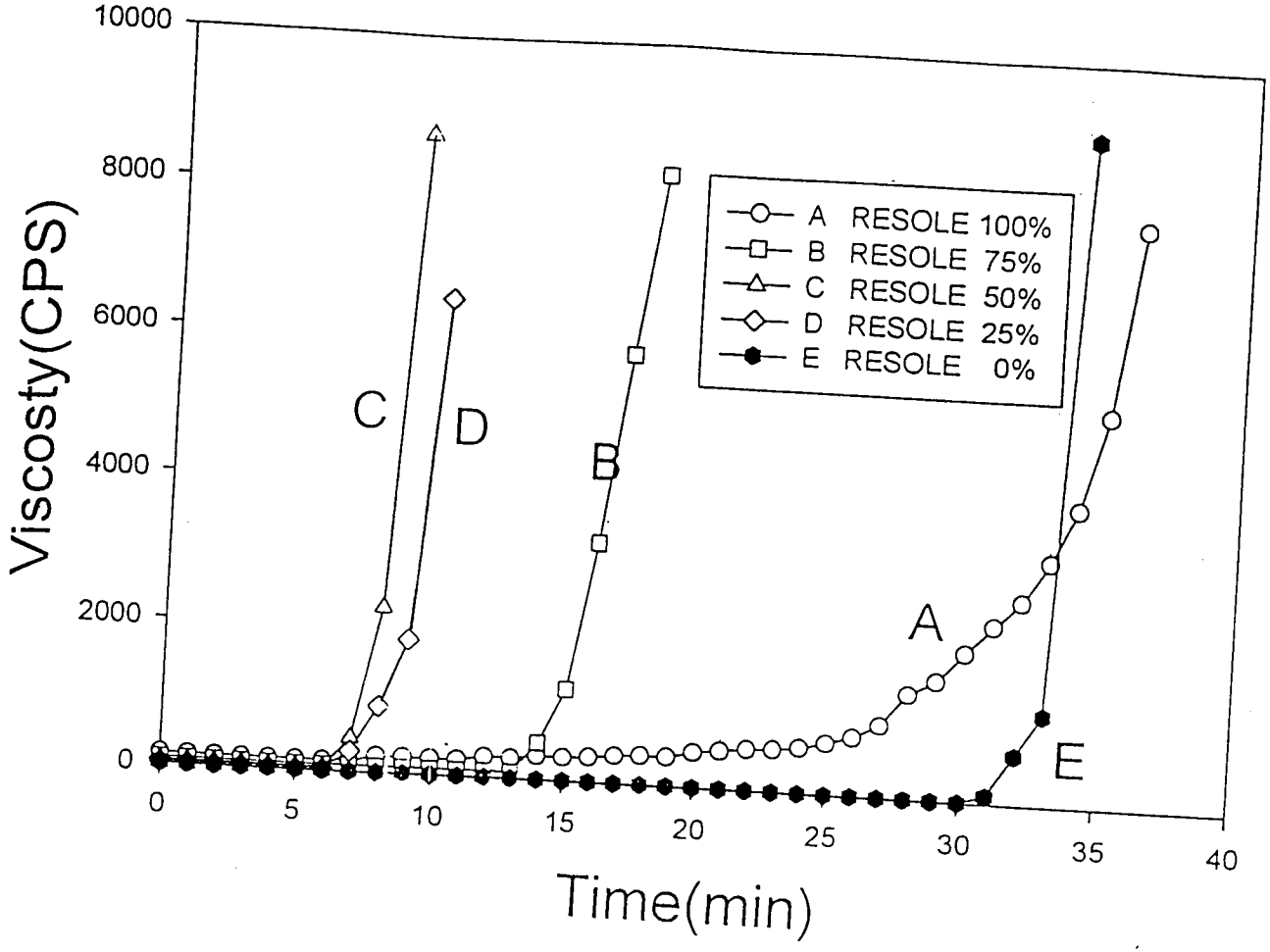

10000
8000
6000
4000
2000
0
Viscosty(CPS)
0
5
10
15
20
25
30
35
40
Time(min)
A RESOLE 100%
B RESOLE 75%
C RESOLE 50%
D RESOLE 25%
E RESOLE 0%
A
B
C
D
E

Fig. 11

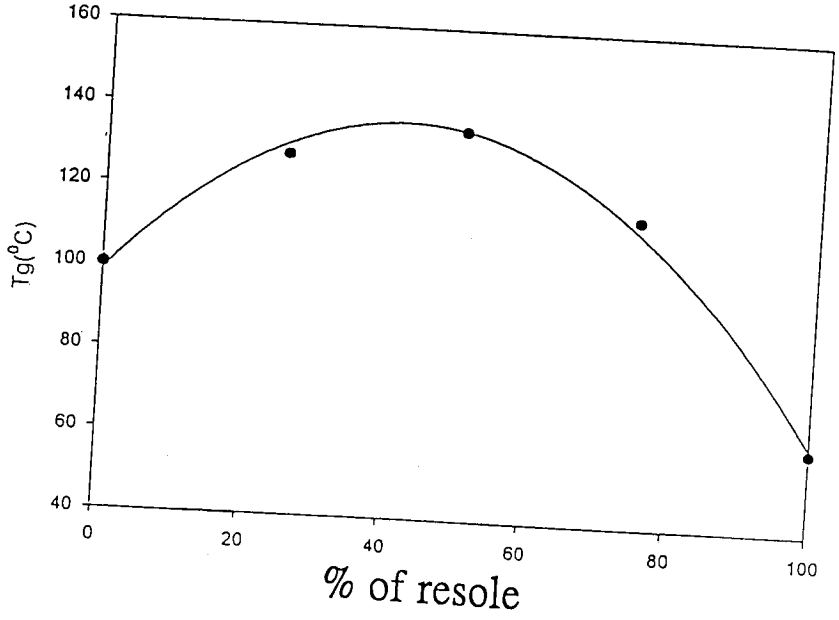


Fig.12

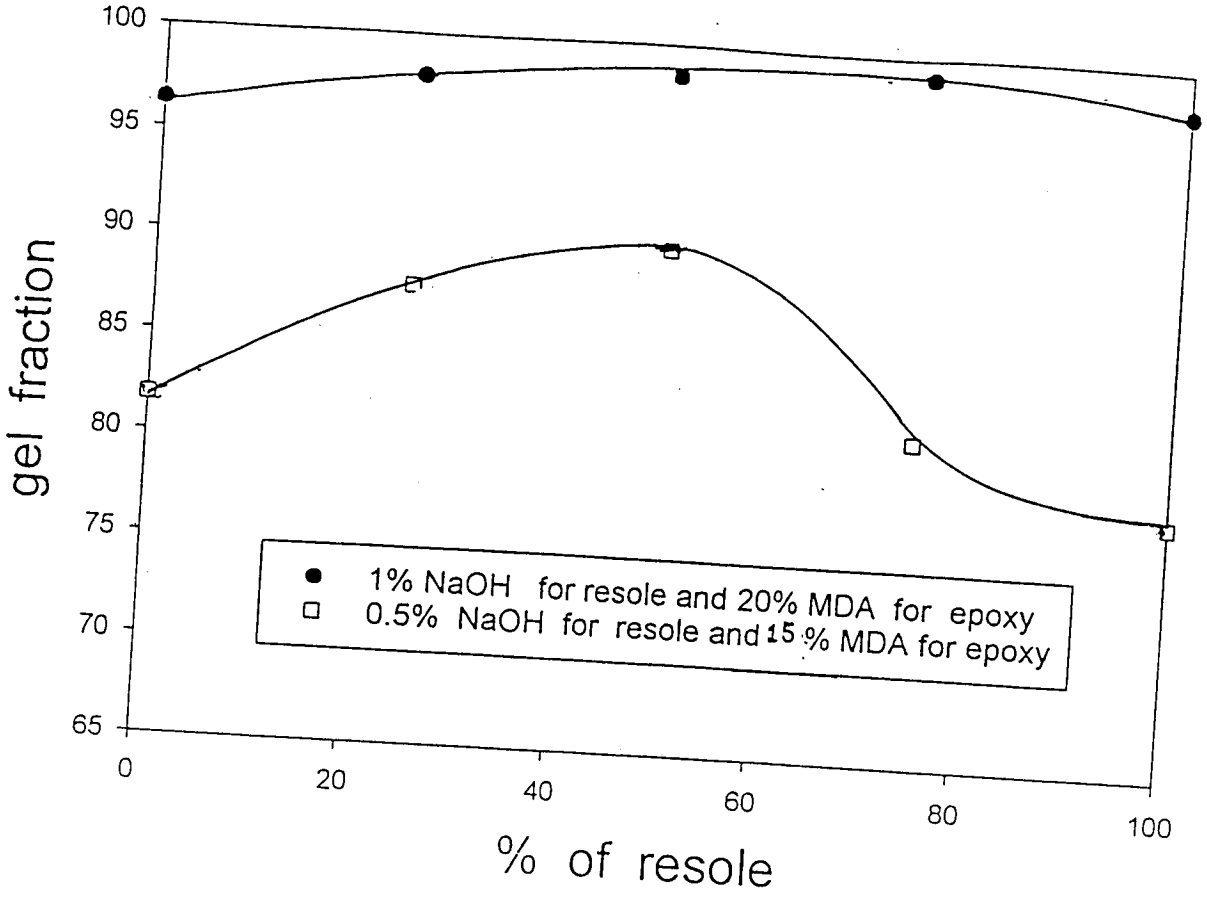
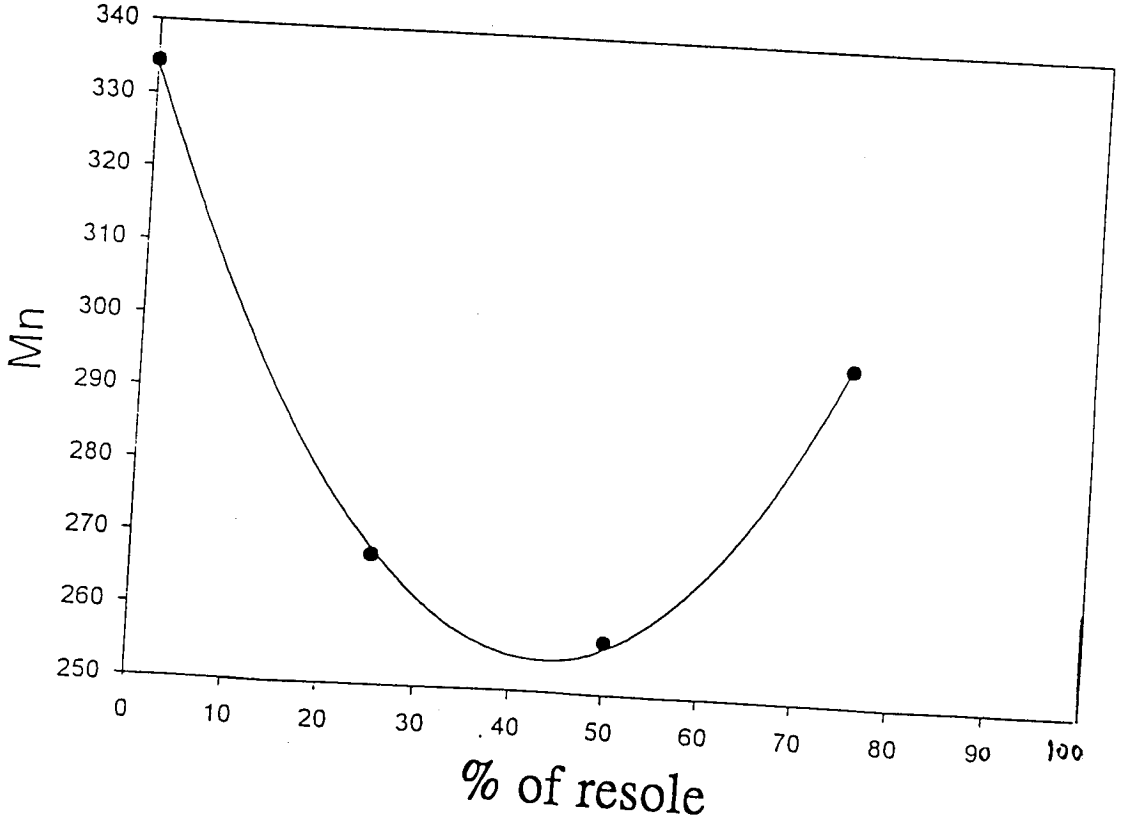

100
95
90
85
80
75
70
65
gel fraction
0
20
40
60
80
100
% of resole
1% NaOH for resole and 20% MDA for epoxy
0.5% NaOH for resole and 15% MDA for epoxy

Fig. 13


340
330
320
310
300
290
280
270
260
250
Mn
0
10
20
30
40
50
60
70
80
90
100
% of resole

Protection of Epoxy Resin Against Thermo-Oxidation via Cocuring Epoxy/Resole (I)

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ABSTRACT

Cocured materials based on 100/0, 50/50 and 0/100 weight ratios of resole/epoxy were prepared by using NaOH and 4,4'-diaminodiphenylmethane (MDA) as curing agents. Samples were spin-coated on Al plates and were accelerated aging at 150 °C in air circulation for 49 days. The functional group changes during thermal oxidation were monitored with FTIR at various times. Difference spectra were obtained by using benzene absorption at 1608 cm^{-1} as internal standard. Kinetic study was performed, and a first order of degradation was evaluated. Experimental results revealed that the degradation rate constants for pure epoxy, 50/50 of resole/epoxy and pure resole are $9.32x10^{-3}$, $4.29x10^{-3}$, and $2.03x10^{-3}$ hr^{-1}, respectively, indicating a significant protection of epoxy against thermal oxidation via cocuring resole/epoxy.

INTRODUCTION

Hindered phenols are well known as stabilizers for plastics and rubbers [1,2] Since resole is a thermosetting resin with hendered phenol moiety on the backbone, it would be expected as a proper radical scavenger and also as a stabilizer for polymers. On the other hand, epoxy resin is a strong material and has been widely used in thermosetting plastics, composites, adhesives, coatings, ...,etc.. However, incorporating of low molecular weight hindered phenols into polymer may have leaching problem [3]. Therefore, we are interested in incoprorating polymeric resole into epoxy resin and cocuring the two resins into a network structure to avoid leaching problem. In this article we would like to repot the result of our study.

EXPERIMENTAL

Resole was synthesized by the method reported in literature [4,5]. Epoxy in the form of diglycidyl ether of bisphenol-A (DGEBA, Epon 815) with an epoxy equivalent weight (EEW) of 194 was perchased from Shell Co.. Weight ratios of resole/epoxy in 100/0, 50/50, and 0/100 were blended and were cured simultaneously by using NaOH (1 % on resole) and MDA (stoichiometric balance on DGEBA) as curing agents. Film samples on Al plates were spin-coated and were placed in accelerated aging oven at 150 °C under air circulation for 49 days.

A Nicolet 520 FTIR with a resolution of 1 cm^{-1} was employed to monitor the functional group changes during thermal oxidation. Difference spectra were obtained by subtracting the absorbances at various time t from that at time zero, using

benzene absorption at 1608 cm^{-1} as internal standard. Integration of peak areas for the increasing carbonyl absorbance were related to the carbonyl concentration changes. The conversion, α, is defined as

$$\alpha = (A_t - A_o)/(A_\infty - A_o) = (C_t - C_o)/(C_\infty - C_o)$$

Where A_o, A_t and A_∞ are peak areas of carbonyl groups at the initial time, time t and after 49 days, respectively; C_o , C_t and C_∞ are the corresponding concentrations.

by incorporating resole into epoxy via cocuring. Further report on the improved retention of mechanical properties by the same protection method will be submitted.

FTIR RESULTS AND DISCUSSIONS

Thermal oxidation of diamine cured epoxy resin has been reported in literature [6,7]. The initial stage of degradation leads to loss of H_2O resulting in the formation of C=C, later degradation stages lead to the production of substituted aldehydes, ketones and acids, which cause the increasing absorbances at ca. 1700 to 1740 cm^{-1} [6,7]. However, literature [8,9,10] reveals extensive thermal oxidation products of resole, which consists mainly of carbonyl groups at ca. 1625 cm^{-1} in the type of substituted benzophenones and quinod-type moieties at ca. 1660 to 1690 cm^{-1} [8,9,10]. Difference spectra for the cured epoxy, cured resole and cocured resole/epoxy (50/50) are given in Figures 1, 2 and 3, respectively. It appears that increasing carbonyl absorbances confirm the reports in literature. However, in comparison of Figures 1 and 3, obviously, increasing of carbonyl absorbance at ca. 1700 to 1740 cm^{-1} is significantly decreased for the cocured 50/50 of resole/epoxy, based on the same period of thermal oxidation. Plots of increasing conversions versus time for the three samples are given in Figure 4. It appears that the formation rates of carbonyl groups are in the order: epoxy > 50/50 of cocured resole/epoxy > resole. In view of the chemical structure of resole, this order is reasonable since resole consists of hindered phenol type moiety in its backbone which, of course, is able to act as stabilizer against thermal oxidation [3,4]. Plots of $-\ln(1-\alpha)$ versus time for the increasing carbonyl groups at ca. 1700 to 1740 cm^{-1} indicate straight lines which fit the first order of degradation. The thermal-oxidation rate constant for each sample can be measured directly from the slope of specific line. The measured rate constants are $k_1 = 9.31 \times 10^{-3}$ hr^{-1} for epoxy, $k_2 = 4.29 \times 10^{-3}$ hr^{-1} for 50/50 of cocured resole/epoxy, and $k_3 = 2.03 \times 10^{-3}$ hr^{-1}. Therefore, it is obvious that significant protection of epoxy resin against thermal oxidation can be achieved by incorporating resole into epoxy via cocuring. Further report on the improved retention of mechanical properties by the same protection method will submitted.

CONCLUSION

Significant protection of epoxy resin against thermo-oxidation via cocured resole/epoxy was found by monitoring the rates of carbonyl group formation with FTIR. Thermo-oxidation rate constants for different samples were also determined from kinetic study, indicating lower thermo-oxidation rate constant after resole was cocured into epoxy resin.

ACKNOWLEDGEMENT

The authors would like to thank the National Science Council for financial support under contract number NSC 88-2216-E-009-023.

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Captions of Figures

Figure 1. Difference spectra ($A_t - A_o$, t in days) for epoxy during thermo-oxidation

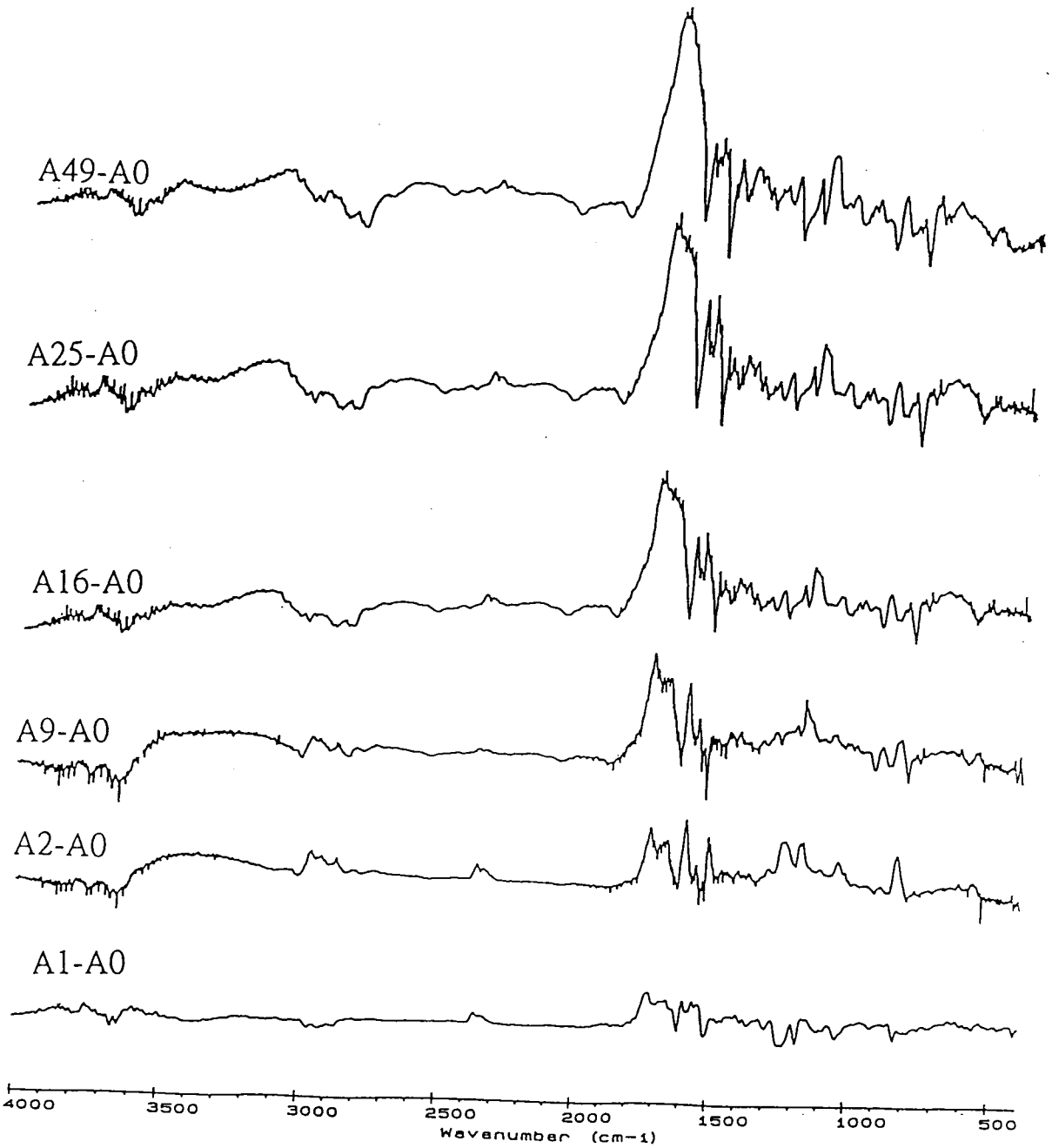
Figure 2. Difference spectra ($A_t - A_o$, t in days) for resole during thermo-oxidation.

Figure 3. Difference spectra ($A_t - A_o$, t in days) for 50/50 of cocured resole/epoxy during thermo-oxidation.

Figure 4. Conversion of carbonyl formation, α, versus time for (A) epoxy, (B) 50/50 of cocured resole/epoxy, and (C) resole.

Figure 5. Plots of - ln (1 - α) versus thermo-oxidation time at 150 °C for (A) epoxy, (B) 50/50 of cocured resole/epoxy, and (C) resole.

Fig. 1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A25-A0
A16-A0
A9-A0
A2-A0
A1-A0
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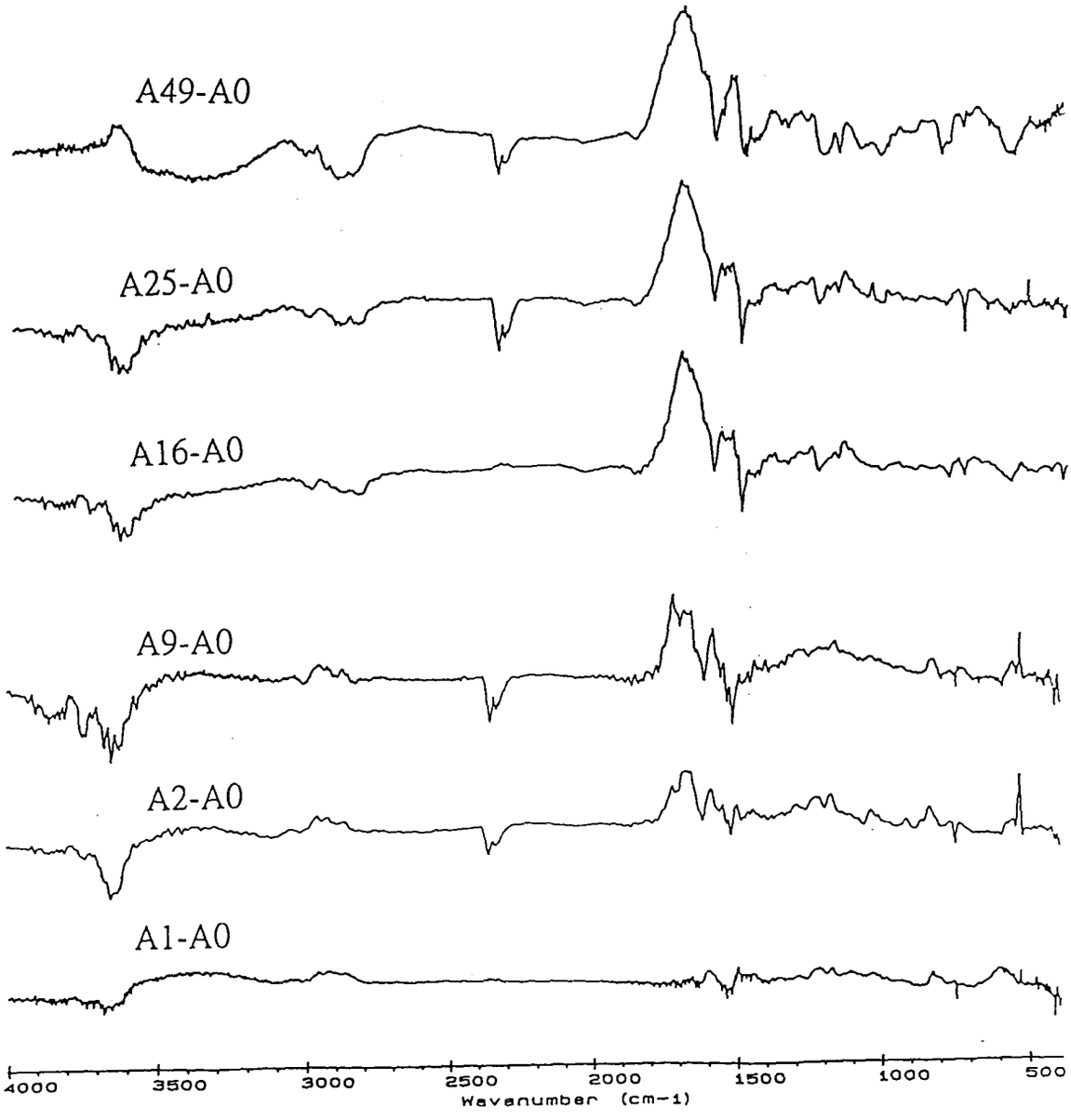
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

Fig-2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4000
3500
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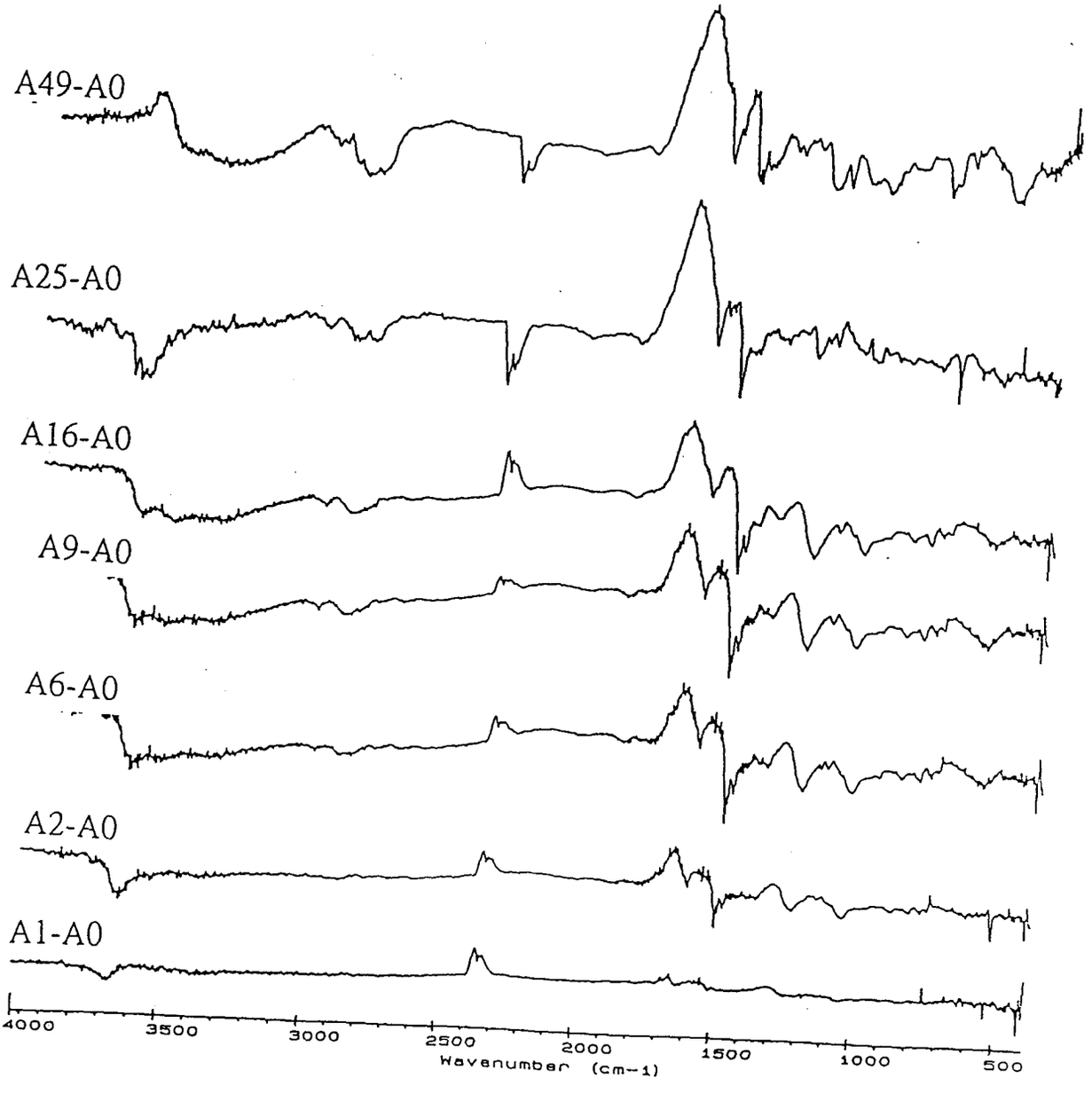
1000
500
Wavenumber (cm-1)

Fig. 3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4000
3500
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2500
2000
1500
1000
500
Wavenumber (cm-1)

Fig.4

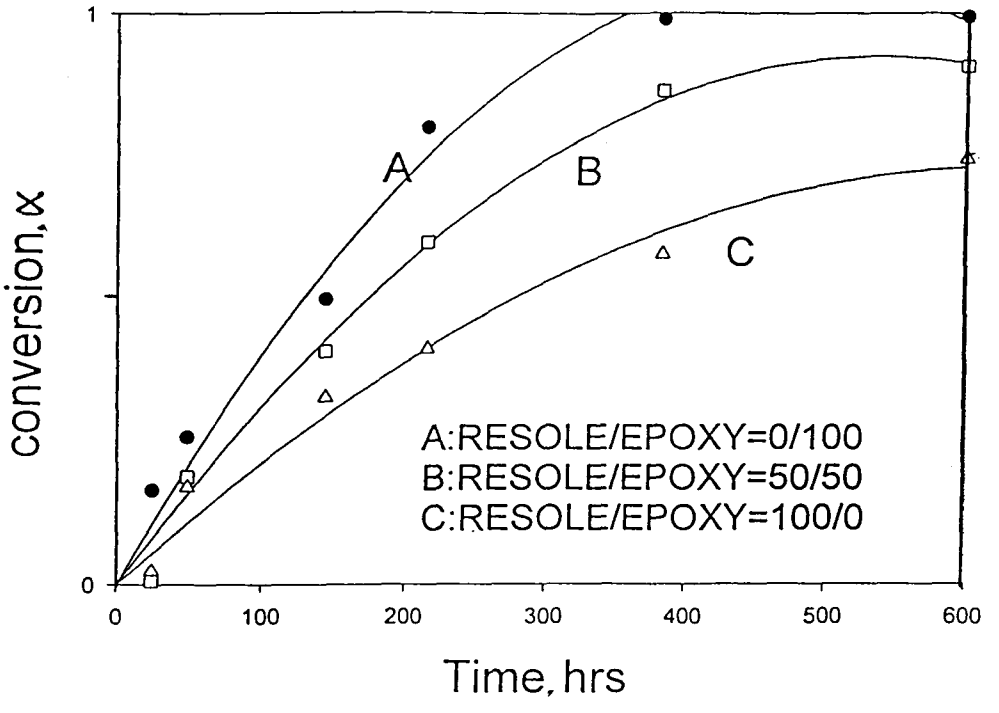
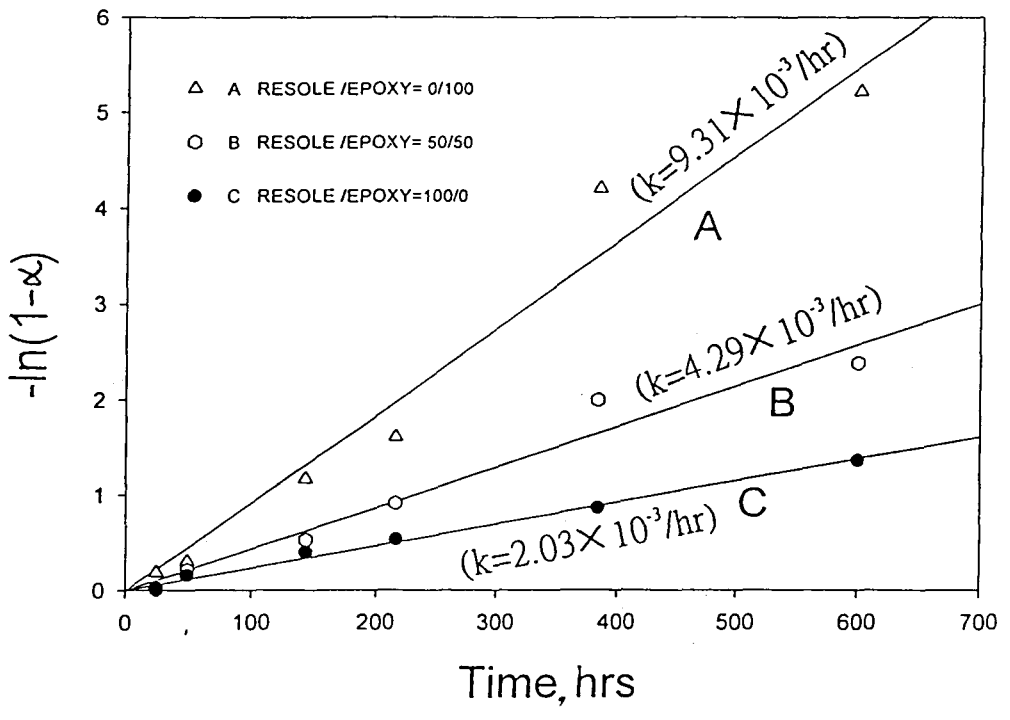

conversion, α
1
0
0
100
200
300
400
500
600
Time, hrs
A
B
C
A:RESOLE/EPOXY=0/100
B:RESOLE/EPOXY=50/50
C:RESOLE/EPOXY=100/0

Fig. 5


A RESOLE /EPOXY= 0/100
B RESOLE /EPOXY= 50/50
C RESOLE /EPOXY=100/0
(k=9.31X 10-3/hr)
A
(k=4.29X 10-3/hr)
B
(k=2.03X 10-3/hr)
C
-ln(1-α)
Time, hrs
0
1
2
3
4
5
6
0
100
200
300
400
500
600
700

Protection of Epoxy Resin Against Thermo-Oxidation via Cocurig Epoxy/Resole (II)

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* To Whom correspondence should be addressed

ABSTRACT

Cocured materials based on resole/epoxy in weight ratios of 100/0, 50/50 and 0/100 were prepared by using NaOH and 4,4'-diaminodiphenylmethane (DMA) as curing agents. These cocuered samples were accelerated aging at 150 °C in air circulation for 45 days. Continuous enhancement of ir absorption at $\nu_{c=o}$ 1700 to 1740 cm^{-1} indicated thermal oxidatiom, leading to the formation of carbonyl groups. The sample with reole/epoxy = 50/50 showed retarded formation of carbonyl absorption significantly. Mechanical property tests of samples during the course of aging, including tensile stress-strain, modulus, and impact resistance confirmed a significant protection of epoxy by incoporating resole into epoxy via cocuring.

INTRODUCTION

Hindered phenols are well known as effective antioxidants since they are able to scavenge radicals produced during thermal oxidation of polymers [1,2]. However, incorporation of low molecular weight hindered phenols into polymers has the drawback of additive migration problem during processing ,or after long-term service [3]. Since resole is a polymeric type of hindered phenol, incorporating of resole into epoxy resin via cocuring would avoid such a drawback. Our previous kinetic studies on the thermo-oxidation for resole/epoxy samples indicated a lower degradation rate constant for the sample of resole/epoxy = 50/50. In this article we would like to further report the results of a series of mechanical tests, which confirmed a significant stabilization of epoxy.

EXPERIMENTAL

Resole was synthesized by the method reported in literature [4,5]. Epoxy in the form of diglycidyl ether of bisphenol-A (DGEBA, Epon 815) with an epoxy equivalent weight (EEW) of 194 was purchased from Shell Co.. Resole/epoxy in weight ratios of 100/0, 50/50, and 0/100 were blended and were cured simultaneously by using NaOH (1% on resole) and MDA (20% on DGEBA) as cocuring agents. Films of the above three samples were coated on Al plates, respectively. Dumbell specimens according to ASTM-D638 type 1, and specimens for falling dart impact tests in 50mm x 50 mm x 3 mm were cast in Teflon molds. All samples were cured at 110 °C for 5 hours and then post-cured at 160 °C for 3 hours. Both film samples and mechanical test samples were then placed in an accelerated aging oven at 150 °C under air circulation for 45 days.

A Nicolet 520 FTIR with a resolution of 1 cm^{-1} was employed to monitor the carbonyl group changes during thermal oxidation of the above film samples. Difference spectra were obtained by subtracting the absorbances at various time t

from that at time zero, using benzene absorbance at 1608 cm^{-1} as internal standard. The impact resistance was examined with a computer-added falling dart type impat tester, with a dart weight of 3.3 kg. The value of the dart weight times the height measures the impact energy, which was automatically recorded as newtons vs ms during the cracking process. The area under this curve (newton vs ms) was integrated and taken as the cracking energy. The tensile stress-strain tests were measured according to ASTM-D 638 type 1 dumbell specimen. The test speed was set at 5 mm min^{-1}. In all tests, an average of values of five specimens was reported for each sample.

RESULTS AND DISCUSSIONS

Resole can be cured by NaOH [6], while epoxy can be cured by diamines [7,8,9]. Thus, the blend of resole/epoxy were able to be cocured by NaOH/MDA. Our previous kinetic studies on the thermo-oxidation of resole, cocured 50/50 of resole/epoxy and epoxy indicated a first-order of thermal oxidation, with degradation rate constants in the order: (A) resole (2.03×10^{-3} h^{-1}) < (B) cocured 50/50 of resole/epoxy (4.29×10^{-3} h^{-1}) < (C) epoxy (9.31×10^{-3} h^{-1}) [10]. In order to reveal how the effect of this kinetic significance is on the retention of mechanical properties, tensile and impact tests were conducted. Figure 1 compares the continuous growth of carbonyl absorbances for (A) resole, (B) cocured 50/50 of resole/epoxy and (C) epoxy. It is noted that after the same period of aging, resole indicated a retarded increase of carbonyl absorbance, epoxy showed a rapid increase of carbonyl absorbance, while the cocured 50/50 of resole/epoxy exhibited a carbonyl absorbance increase in between. Figure 2 compares the retention of tensile moduli for the three samples during 45 days of continuous accelerated thermal oxidation. Sample B with 50/50 of cocured resole/epoxy shows a much better modulus retention than epoxy, indicating a significant protection upon incorporating of resole. This is because of the fact that resole is basically a polymeric type of hindered phenol which is a stable antioxidant. Even after 45 days of accelerated thermal aging, the incoporated resole still exhibited its stabilization effect without evaporation or leaching from the cocured material. Although resole had the lowest thermo-oxidation rate constant, its modulus retention is less than the cocured 50/50 of resole/epoxy because resole is substantially not a strong material. In comparison of Figures 3 and 4, for the tensile stress and tensile strain, similar results were observed, with the fact that sample B showed the best retention of tensile stress and strain. Figure 5 shows the percentage retention of cracking energies for falling dart impact tests. Again, sample B exhibited much better retention of cracking energy than resole and epoxy. This is because resole is not a strong material, while epoxy experienced serious thermal

oxidation. Results on mechanical behavior tests are rather consistent with the findings of increased carbonyl absorbance as discussed in Figure 1.

CONCLUSION

Although resole showed the lowest thermo-oxidation rate, it indicated poor retention of mechanical properties because resole is a brittle material. Significant protection of epoxy against thermo-oxidation was observed by incorporating resole into epoxy via cocuring, which subsequently led to significant retention of mechanical properties.

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ACKNOWLEDGEMENT

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CAPTIONS OF FIGURES

Figure 1. Difference spectra of FTIR ($A_t - A_0$, with t in days.) showing the enhanced ir carbonyl absorbance at ca. 1700-1740 cm^{-1} , (A) resole, (B) cocured 50/50 of resole/epoxy, (C) epoxy.

Figure 2. Plots of % retention of tensile modulus versus aging time. (A) resole, (B) cocured 50/50 of resole/epoxy, (C) epoxy.

Figure 3. Plots of % retention of tensile stress versus aging time. (A) resole, (B) cocured 50/50 resole/epoxy, (C) epoxy

Figure 4. Plots of % retention of tensile strain versus aging time. (A) resole, (B) cocured 50/50 resole/epoxy, (C) epoxy.

Figure 5. Plots of % retention of cracking energy versus aging time. (A) resole, (B) cocured 50/50 resole/epoxy, (C) epoxy.

Fig. 1

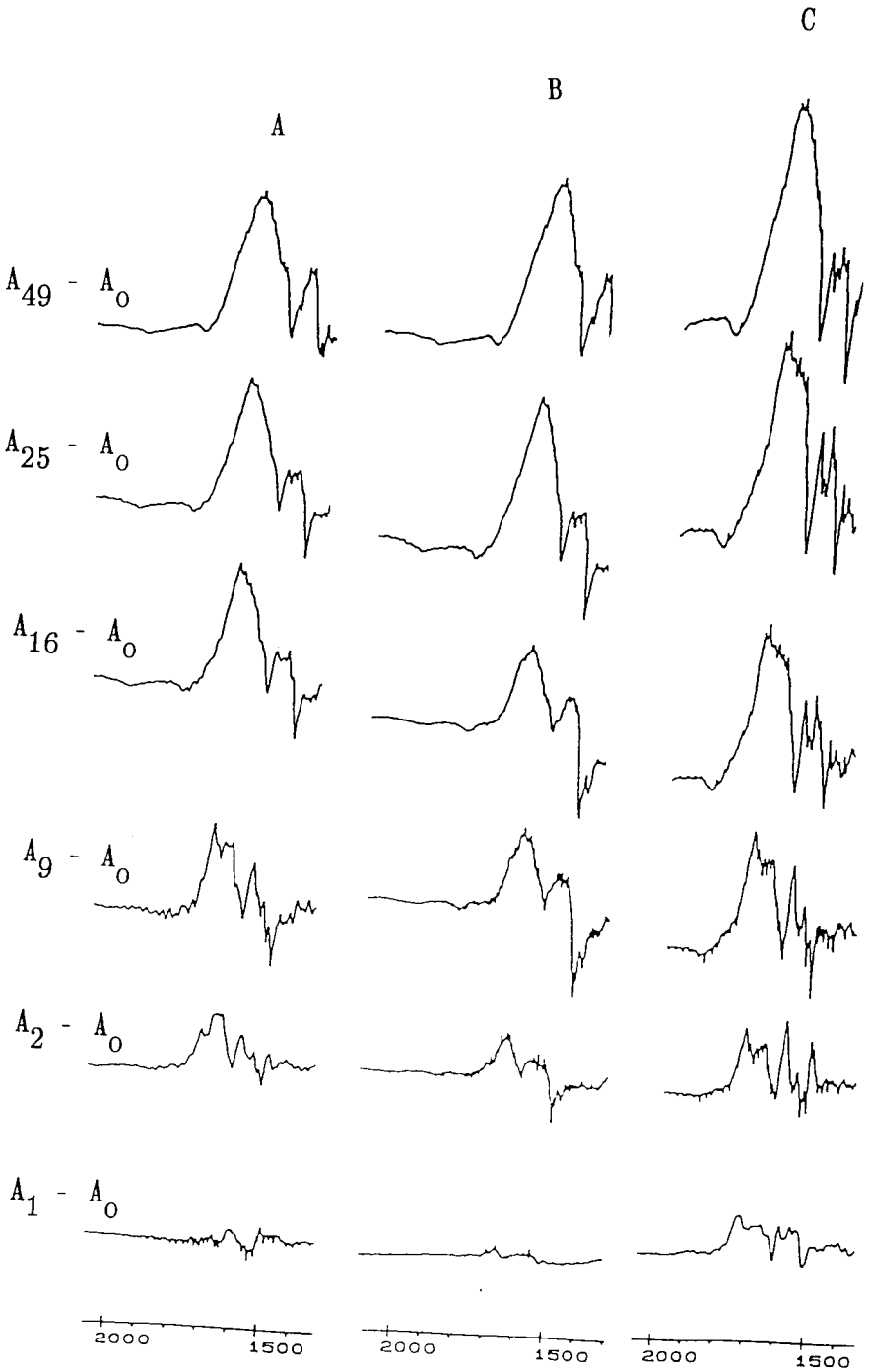

A
B
C
$A_{49} - A_0$
$A_{25} - A_0$
$A_{16} - A_0$
$A_9 - A_0$
$A_2 - A_0$
$A_1 - A_0$
2000
1500
2000
1500
2000
1500
Wavenumber, cm^{-1}

Fig. 2

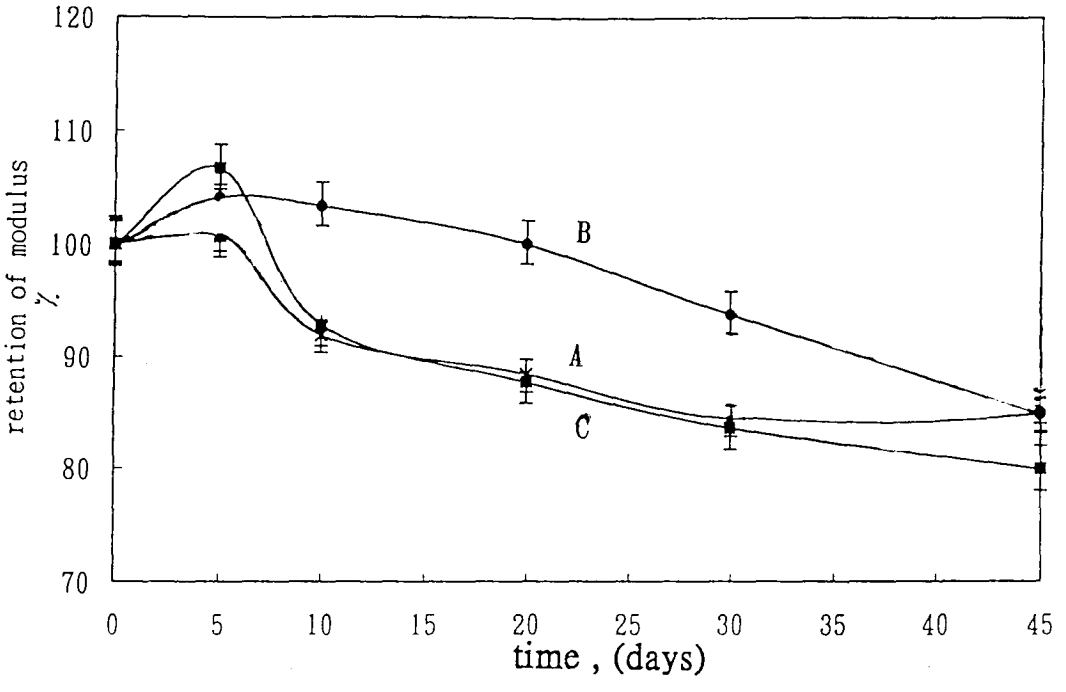

120
110
100
90
80
70
retention of modulus
%
0
5
10
15
20
25
30
35
40
45
time , (days)
A
B
C

Fig. 3

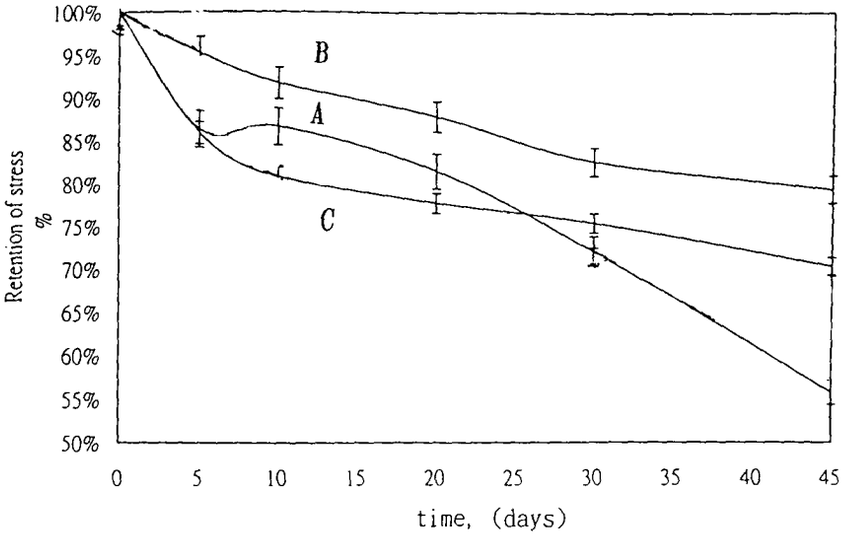

100%
95%
90%
85%
80%
75%
70%
65%
60%
55%
50%
Retention of stress %
B
A
C
0
5
10
15
20
25
30
35
40
45
time, (days)

Fig. 4

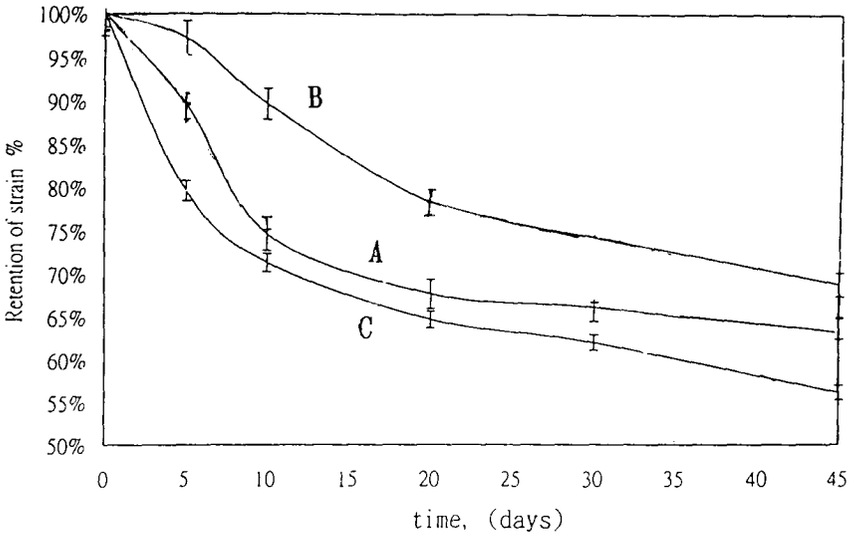
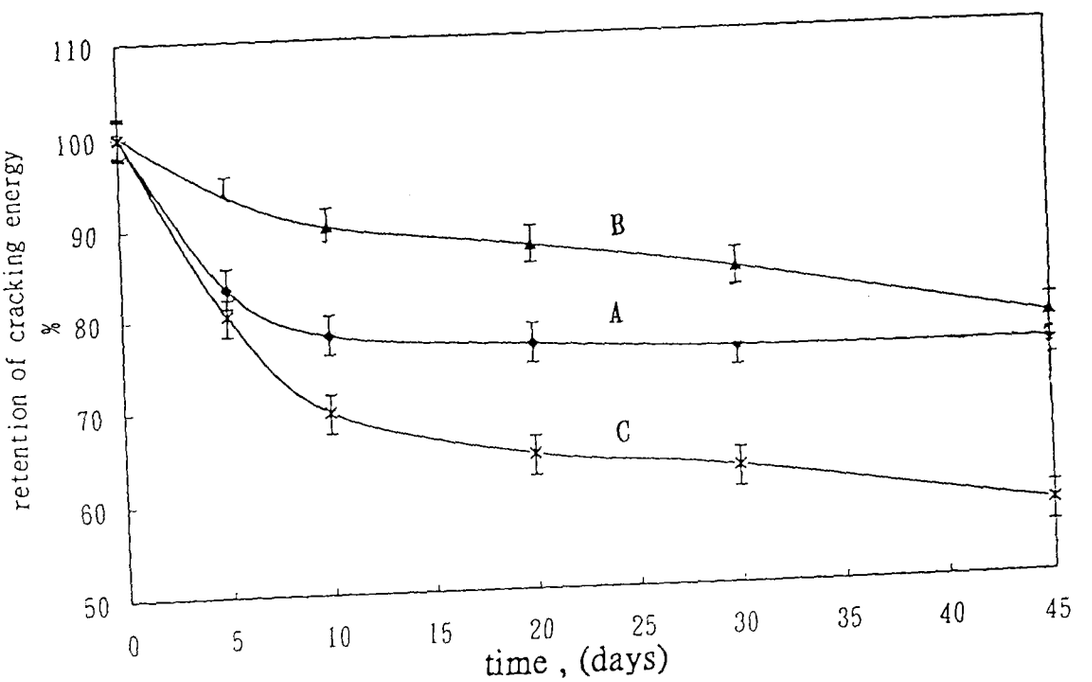

100%
95%
90%
85%
80%
75%
70%
65%
60%
55%
50%
Retention of strain %
B
A
C
0
5
10
15
20
25
30
35
40
45
time, (days)

Fig.5


110
100
90
80
70
60
50
retention of cracking energy
%
B
A
C
0
5
10
15
20
25
30
35
40
45
time , (days)

Resole/Epoxy Cocuring Behavior
(NSC-88-2216-E-009-023)

Mu-Shih Lin and Chun-Chen Chiu, Department of Applied Chemistry, National Chiao-Tung University, Hsinchu, Taiwan 30050

ABTRACT

Cocuring Materials based on different weight ratios of resole /epoxy were prepared by using NaOH and 4,4'-diaminodiphenylmethane (MDA) as curimg agents. Curing behaviors were investigated with dynamic DSC and viscosity changes during cocuring reactions. Solid samples were characterized with RDS,DSC,FTIR, and gel fraction. Experimantal results revealed that enhanced gel fraction and increased Tg's for each cocured material were generally found. These results are pretty different from the IPN materials which generally reflect in lowered gel fractions and decreased Tg's.

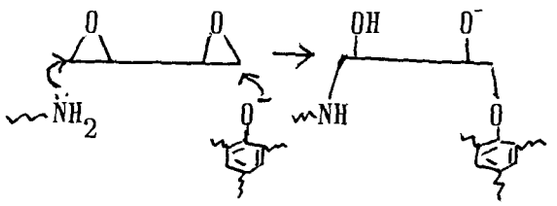
EXPERIMENAL

Resole was prepared according to the method cited in literature [1,2]. Epoxy in the form of diglycidyl ether of bisphenol-A (DGEBA, with an EEW of 914) was obtained fron Shell Co. Weight ratios of resole/epoxy =100/0,75/25, 50/50, 25/75, and 0/100 were blended and were cured simultaneously with NaOH (1% on resole) and MDA (20% on epoxy). Each blend was poured into teflon molds followed by precured at 110 ^{o}C for 5 hrs,then postcured at 160 ^{o}C for 2 hours.

A Nicolet 520 FTIR with a resolution of 0.5 $cm^{-1}$was employed to monitor the band shift. All DSC thermograms were obtained under nitrogen at a heating rate of 10 ^{o}C/min. Gel fractionbs were measured with a Soxhlet extractor by continuous 2 days' extraction ,using acetone as solvent. Viscosity changes were performed with a Brookfield LVT viscometer. The dynamic mechanical properties were studied with rhetric dynamic spectroscopy (RDS, Rheometric II) under a nitrogen atmosphere at a frequency of 1 Hz and a heating rate of 3 $^{o}min^{-1}$, with 0.2 % strain at 31.4 rad sec^{-1}. The temperature ranged from - 100 ^{o}C to 200 ^{o}C.

RESULTS and DISCUSSIONS

Figs. 1 and 2 show resole and epoxide IR band shifts for various resole/epoxy blends. These IR band shifts strongly suggest good miscibility of the two components in molecular level. In view of the single RDS damping peak (Fig. 3) and single Tg (Fig. 4) for each composition,it is believed that this cocured resole/ epoxy system has good compatibility. Fig. 5 shows the dynamic DSC thermograms during cocuring reactions. It is noted that an additional exothermic peak at lower temperature was observed for each cocured sample (B,C,D). This appears due to the cocuring reaction of the phenoxide and epoxide.



The crosslinked epoxy remained a residual epoxide group and showed a ^{13}C NMR at 50.7 ppm (Fig. 6) [3,4], while the disappearance of this peak for the cocured sample (Fig.7) strongly supports the reaction between resole and epoxy networks.

The viscosity changes during curing reactions are given in Fig. 8. The faster viscosity increases for cocured samples (B,C,D) are believed due to the strong nucleophilic attack of the phenoxide on epoxide as well as the catalytic effect of OH on the curing of epoxy by diamine [5,6]. A plot of Tg's versus % resole shows the enhanced Tg's which is quite different from the genenarlly decreased Tg's for IPN materials [7,8]. A plot of gel fraction versus % resole (Fig. 9) shows a decreased gel fraction for the cocured samples. It has been known that IPN materials have lower gel fractions because only physical chain entanglements exists between the two networks, which subsequently leads to incomplete cure because of increased steric hindrance [7,8]. The incomplete cure of IPN materials account for the lower gel feractions and lower Tg's. While in cocured materials, the chemical crosslinking betweeen the two networks largely enhance the the gel fractions as well as the Tg's.

CONCLUSIONS

In the compatible resole/epoxy cocured materials increased gel fractions and Tg's were observed. Whereas in IPN materials decreased gel fractions and Tg's are generally found. Chemical crosslinking between the two networks in the cocured materials would lead to higher crosslinking, while physical chain entanglements in IPN materials would result in incomplete cure. These account for the observed cocuring behaviorsfor resole/epoxy materials.

ACKNOWLEDGEMENT

The authors would like to thank the National Science Council for the financial support under contract no. 88-2216-E -009-023.

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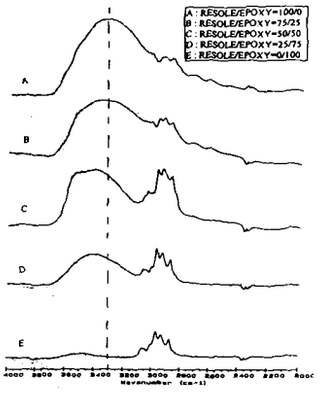


Fig.1 hydroxy band shifts at ca. 3500 cm^{-1}

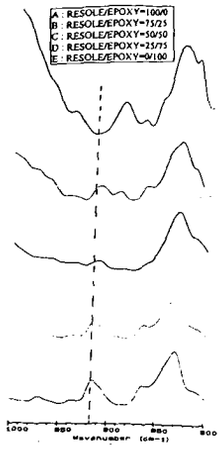


Fig.2 epoxide band shifts at ca. 917 cm^{-1}

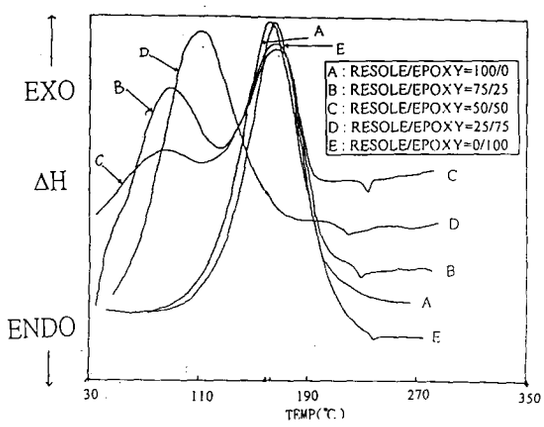


Fig.5 Dynamic DSC showing the shifts of exothermic peaks.

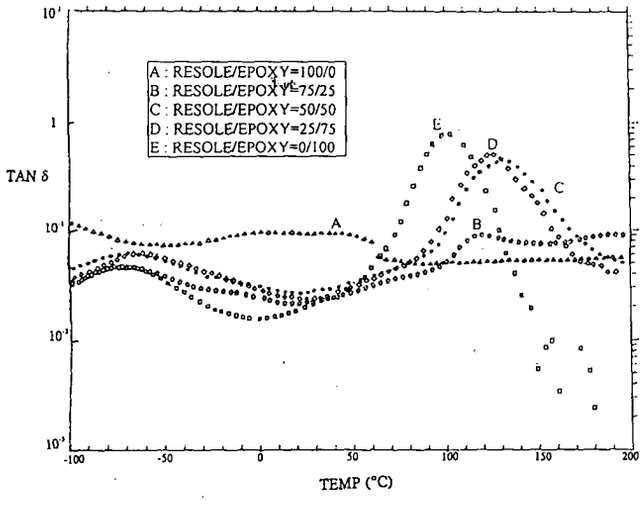


Fig.3 RDS curves.

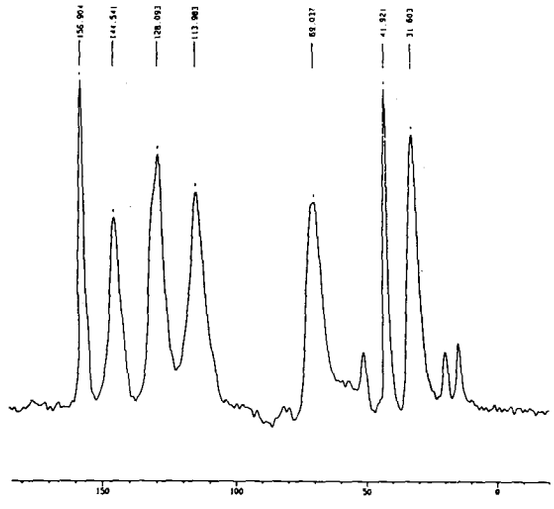


Fig.6 ^{13}CNMR spectrum for DGEBA.

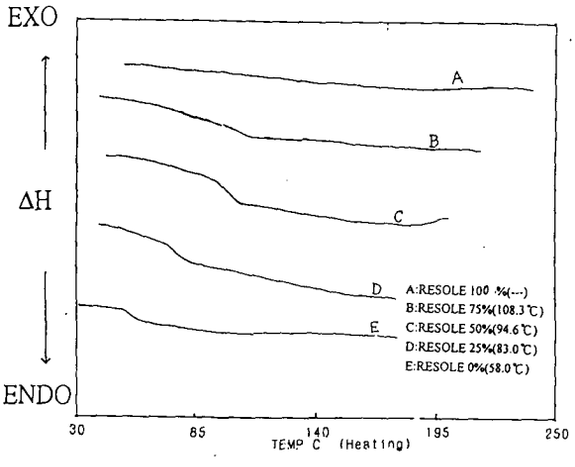


Fig.4 DSC thermograms.

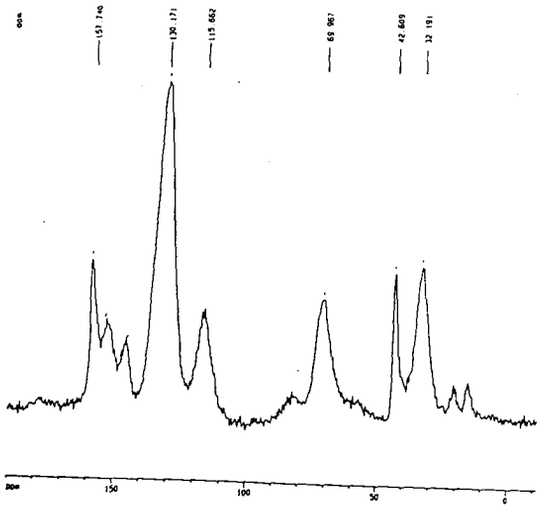


Fig.7 ^{13}CNMR spectrum for cocured resole/DGEBA.

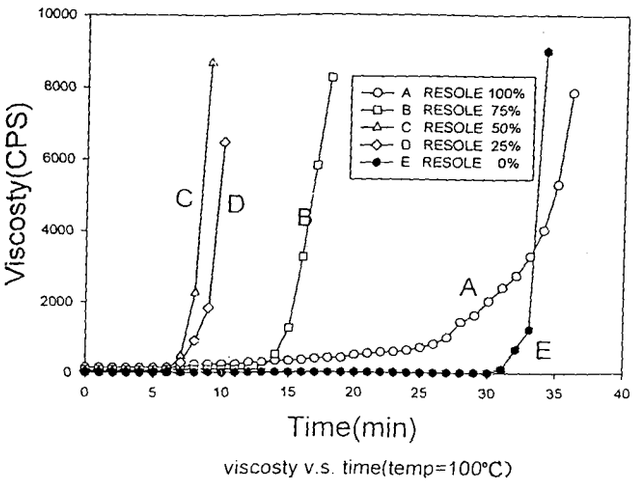


Fig.8 Viscosity increases during cocure at 100 ^{o}C.

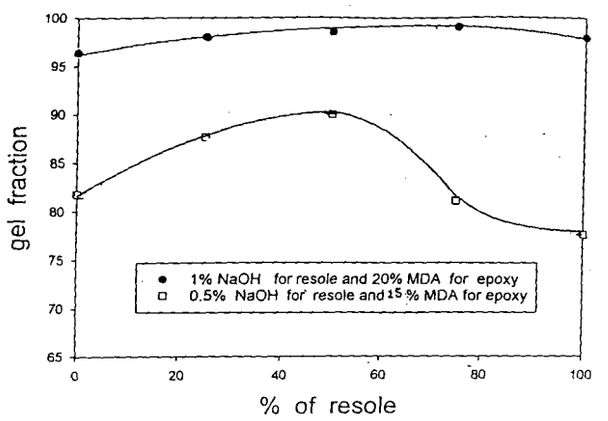


Fig.9 Gel fractions vs. % resole content.

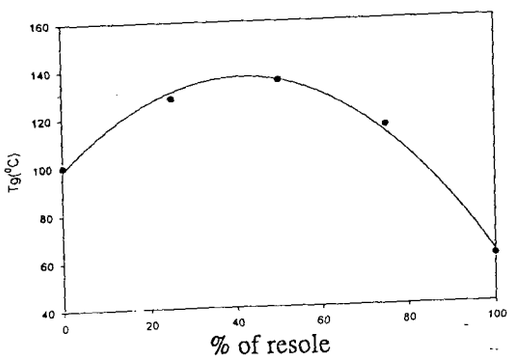
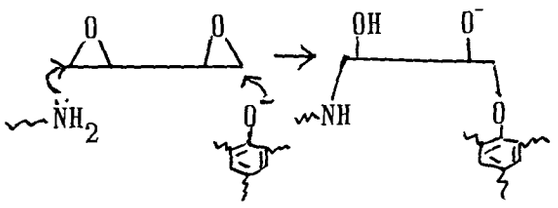


Fig.10 Tg's vs. % resole.



The crosslinked epoxy remained a residual epoxide group and showed a ^{13}C NMR at 50.7 ppm (Fig. 6) [3,4], while the disappearance of this peak for the cocured sample (Fig.7) strongly supports the reaction between resole and epoxy networks.

The viscosity changes during curing reactions are given in Fig. 8. The faster viscosity increases for cocured samples (B,C,D) are believed due to the strong nucleophilic attack of the phenoxide on epoxide as well as the catalytic effect of OH on the curing of epoxy by diamine [5,6]. A plot of Tg's versus % resole shows the enhanced Tg's which is quite different from the genenarlly decreased Tg's for IPN materials [7,8]. A plot of gel fraction versus % resole (Fig. 9) shows a decreased gel fraction for the cocured samples. It has been known that IPN materials have lower gel fractions because only physical chain entanglements exists between the two networks, which subsequently leads to incomplete cure because of increased steric hindrance [7,8]. The incomplete cure of IPN materials account for the lower gel feractions and lower Tg's. While in cocured materials, the chemical crosslinking betweeen the two networks largely enhance the the gel fractions as well as the Tg's.

CONCLUSIONS

In the compatible resole/epoxy cocured materials increased gel fractions and Tg's were observed. Whereas in IPN materials decreased gel fractions and Tg's are generally found. Chemical crosslinking between the two networks in the cocured materials would lead to higher crosslinking, while physical chain entanglements in IPN materials would result in incomplete cure. These account for the observed cocuring behaviorsfor resole/epoxy materials.

ACKNOWLEDGEMENT

The authors would like to thank the National Science Council for the financial support under contract no. 88-2216-E -009-023.

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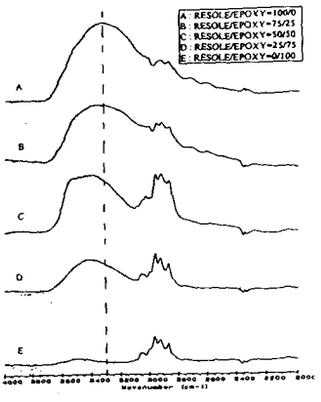

Fig.1 hydroxy band shifts at ca. 3500 cm^{-1}

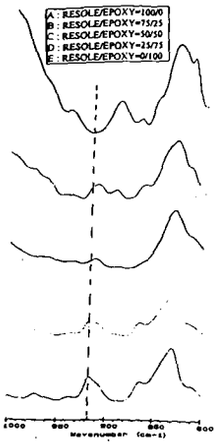

Fig.2 epoxide band shifts at ca. 917 $cm.^{-1}$

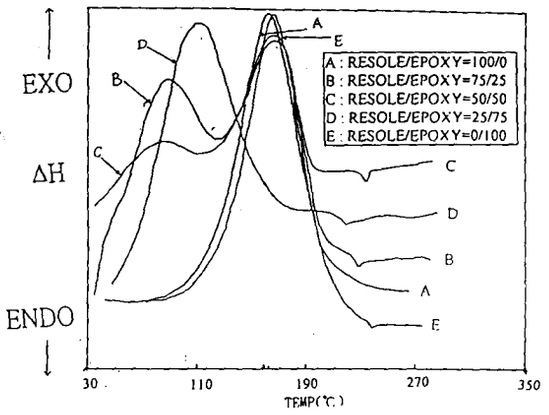

Fig.5 Dynamic DSC showing the shifts of exothermic peaks.

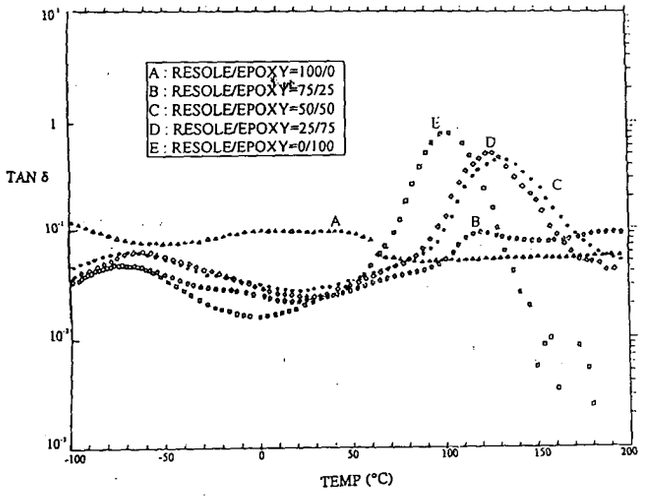

Fig.3 RDS curves.

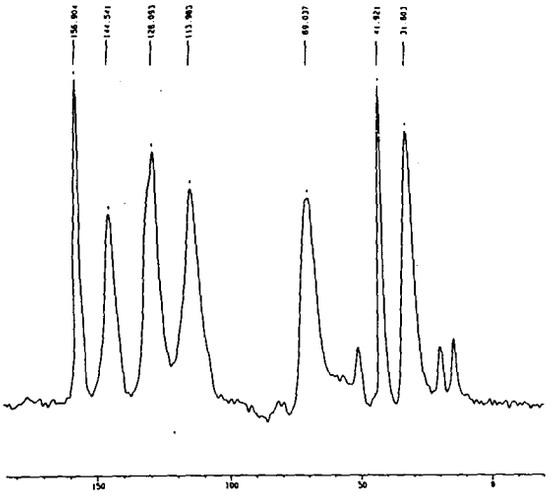

Fig.6 ^{13}CNMR spectrum for DGEBA.

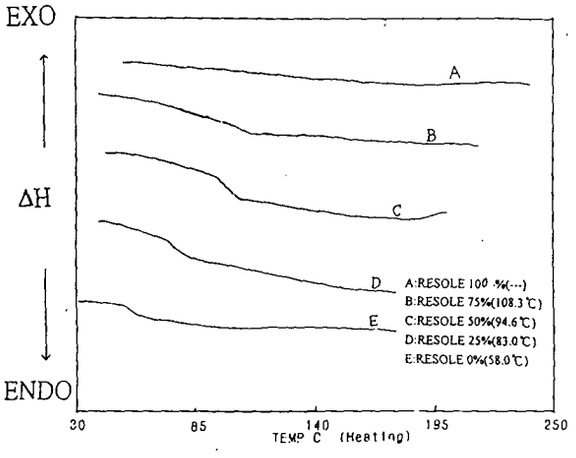

Fig.4 DSC thermograms.

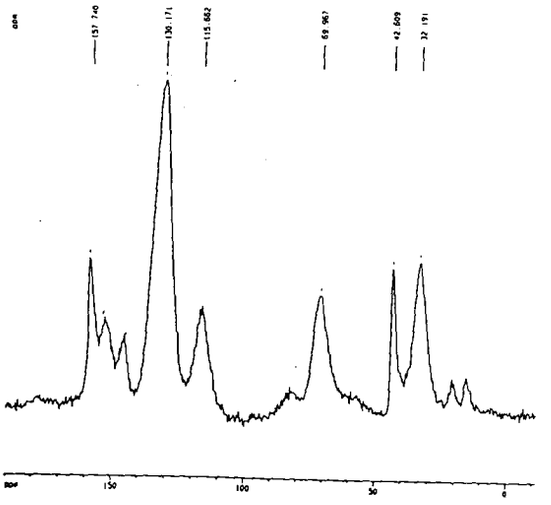

Fig.7 ^{13}CNMR spectrum for cocured resole/DGEBA.

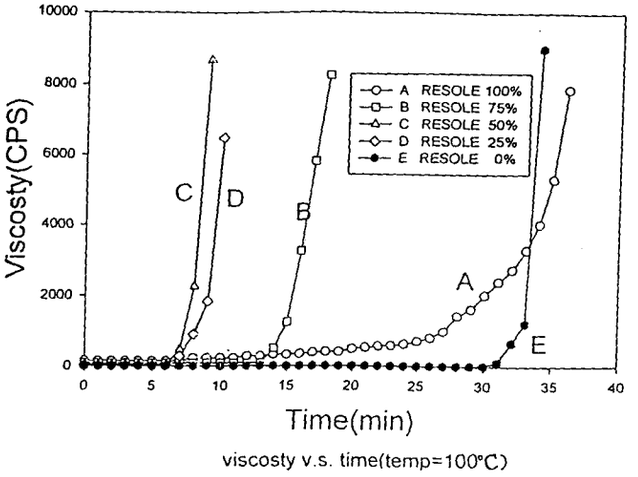

Fig.8 Viscosity increases during cocure at 100 ^{o}C.

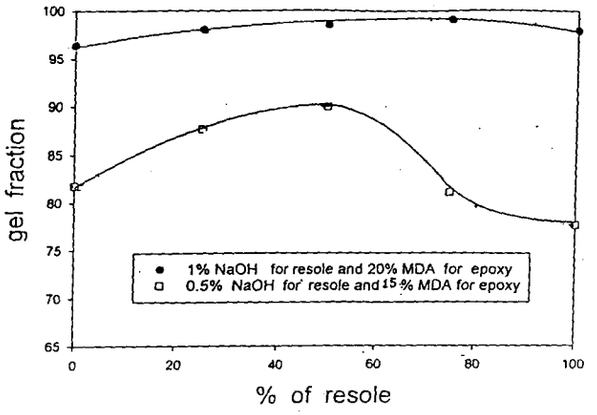

Fig.9 Gel fractions vs. % resole content.

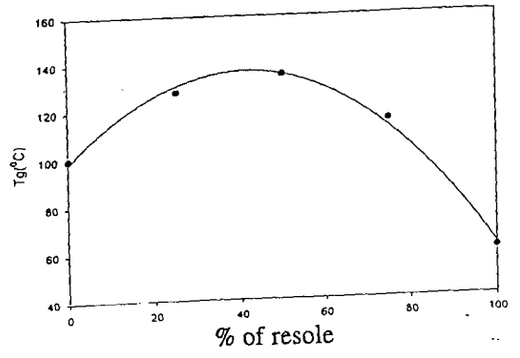

Fig.10 Tg's vs. % resole.

精簡報告

Resole/Epoxy Cocuring Behavior
(NSC-88-2216-E-009-023)

Mu-hih Lin and Chun-Chen Chiu, Department of Applied Chemistry, National Chiao-Tung University, Hsinchu, Taiwan 30050

ABTRACT

Cocuring Materials based on different weight ratios of resole /epoxy were prepared by using NaOH and 4,4'-diaminodiphenylmethane (MDA) as curimg agents. Curing behaviors were investigated with dynamic DSC and viscosity changes during cocuring reactions. Solid samples were characterized with RDS,DSC,FTIR, and gel fraction. Experimantal results revealed that enhanced gel fraction and increased Tg's for each cocured material were generally found. These results are pretty different from the IPN materials which generally reflect in lowered gel fractions and decreased Tg's.

EXPERIMENAL

Resole was prepared according to the method cited in literature [1,2]. Epoxy in the form of diglycidyl ether of bisphenol-A (DGEBA, with an EEW of 914) was obtained fron Shell Co. Weight ratios of resole/epoxy =100/0,75/25, 50/50, 25/75, and 0/100 were blended and were cured simultaneously with NaOH (1% on resole) and MDA (20% on epoxy). Each blend was poured into teflon molds followed by precured at 110 ^{o}C for 5 hrs,then postcured at 160 ^{o}C for 2 hours.

A Nicolet 520 FTIR with a resolution of 0.5 $cm^{-1}$was employed to monitor the band shift. All DSC thermograms were obtained under nitrogen at a heating rate of 10 ^{o}C/min. Gel fractionbs were measured with a Soxhlet extractor by continuous 2 days' extraction ,using acetone as solvent. Viscosity changes were performed with a Brookfield LVT viscometer. The dynamic mechanical properties were studied with rhetric dynamic spectroscopy (RDS, Rheometric II) under a nitrogen atmosphere at a frequency of 1 Hz and a heating rate of 3 $^{o}min^{-1}$, with 0.2 % strain at 31.4 rad sec^{-1}. The temperature ranged from - 100 ^{o}C to 200 ^{o}C.

RESULTS and DISCUSSIONS

Figs. 1 and 2 show resole and epoxide IR band shifts for various resole/epoxy blends. These IR band shifts strongly suggest good miscibility of the two components in molecular level. In view of the single RDS damping peak (Fig. 3) and single Tg (Fig. 4) for each composition,it is believed that this cocured resole/ epoxy system has good compatibility. Fig. 5 shows the dynamic DSC thermograms during cocuring reactions. It is noted that an additional exothermic peak at lower temperature was observed for each cocured sample (B,C,D). This appears due to the cocuring reaction of the phenoxide and epoxide.