Study of Crosslinking AMS/DGEBA System by FTIR

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ABSTRACT: Fourier transform infrared spectroscopy (FTIR) was used to follow the curing of the diglycidylether of bisphenol A (DGEBA) typical epoxide resin by poly(styrene-*alt*-maleic anhydride) (AMS), the reaction being accelerated by triethylamine (TEA) in the presence of methanol. The study was done in an isothermal mode for four temperatures: 85, 82, 80, and 75°C. We followed, for each temperature, the variation of the area of the epoxy band (916 cm^{-1}) versus time. After 200 min of reaction, the degree of conversion of epoxy is 0.5 at 85°C. A postcure at 100°C during 96 h allows one to reach a total conversion of epoxy. The reaction mechanism involves three steps to form the tridimensional network. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1167–1178, 1998

Key words: diglycidylether of bisphenol A; anhydride; curing; FTIR

INTRODUCTION

Properties of a thermoset depend on the degree of crosslinking from the curing reaction. Comprehension of the kinetic and the mechanism of curing is essential to establish the structure–property relationship and to optimize conditions of utilization as an adhesive material, coating, or matrix in fiber-reinforced composites.

Kinetic models allow one to analyze the experimental results obtained by different thermal analysis techniques. Differential scanning calorimetry (DSC), in the isothermal and dynamic modes, has largely been used to take into account the relationship of proportionality between the heat released during the curing and the degree of crosslinking of the reaction.[1–5] In general, reactions of curing show complex kinetics characterized by several stages: induction, gelation, and hardening.

Properties of a thermoset depend on the degree of crosslinking. It is therefore necessary to obtain measurable parameters able to describe the kinetics of the system. Chemical characterization remains limited to the early stage of the reaction, where the conversion is very low. Spectroscopic methods and, particularly, Fourier transform infrared spectroscopy (FTIR) appear as efficient techniques to follow chemical changes occurring during the curing process even at an advanced stage.[6–9]

The present work reports the kinetics study of the curing of the diglycidylether of the bisphenol A (DGEBA) by poly(styrene-*alt*-maleic anhydride) (AMS). Triethylamine (TEA) and methanol are used, respectively, as the catalyst and cocatalyst. Our previous work reports on the results of the kinetic study of this same system by DSC in the dynamic and isothermal modes.[10,11]

EXPERIMENTAL

Instrument

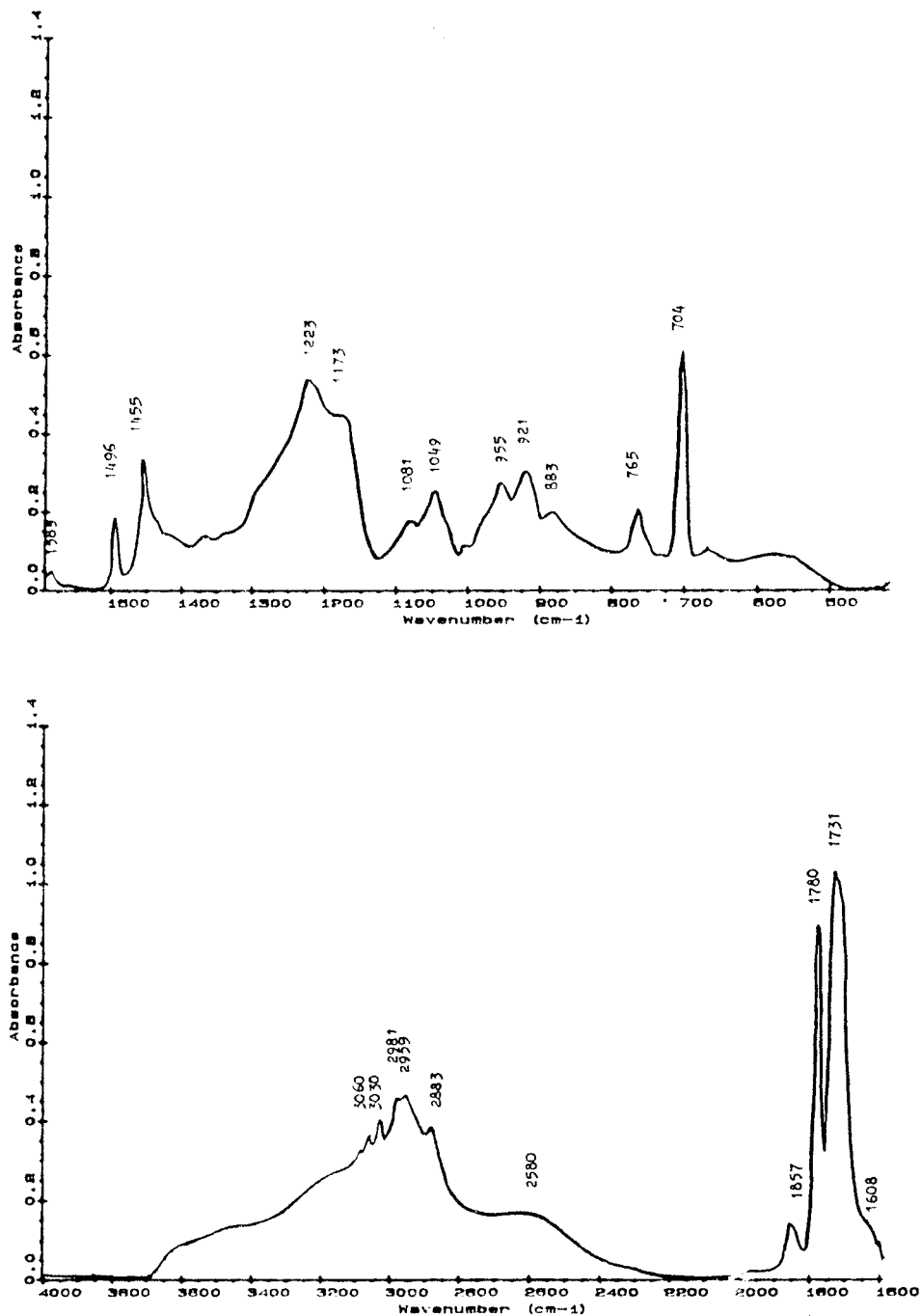Infrared spectra were done using a Nicolet 710 FTIR. Sixty coadded interferograms were

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Figure 1 FTIR spectrum of maleic anhydride−styrene copolymer (AMS).

scanned at a 2 cm^{-1} resolution. Functions of the optical bench are entirely automated and the acquisition as well as the processing of the signal is made with the help of data-processing software. A thermostated cell-type ACCUSPEC Model 20, a digital controller temperature-type ACCUSPEC, and a linear temperature programmer are used jointly for the isothermal programming.

Materials

The epoxy resin used is a commercial product (Dow Chemical Co.; DER332) with an epoxy equivalent of 174 g. The hardener is a copolymer poly(styrene-*alt*-maleic anhydride) (AMS), synthesized in our laboratory by the free-radical polymerization method.[10] AMS and DGEBA were mixed at a molar ratio of $r = 0.7$.[10] The TEA is used by 15% to the
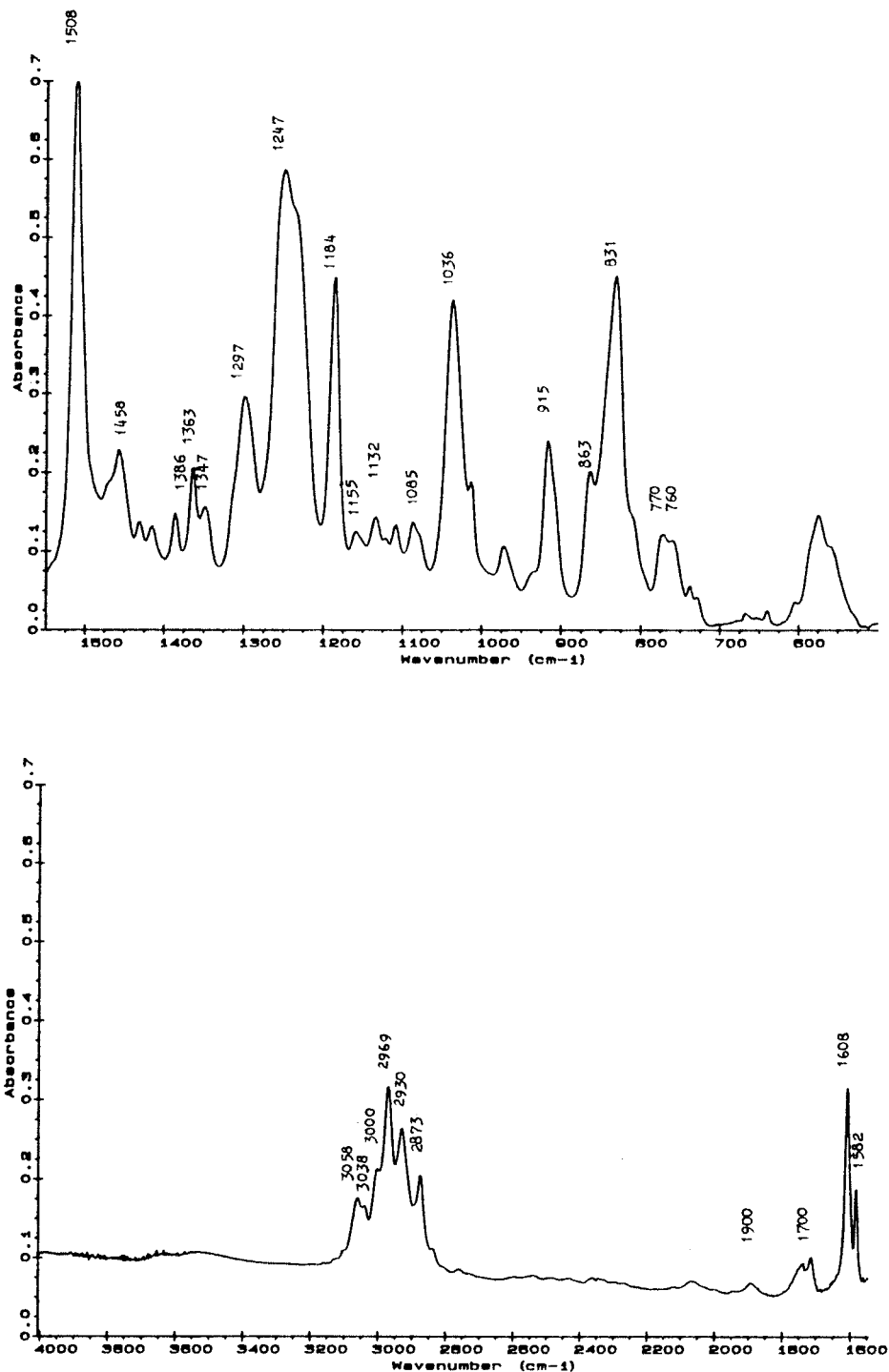
Figure 2   FTIR spectrum of DGEBA resin.

number of epoxy groups. The methanol is used in a stoichiometric quantity to the anhydride rings.

Procedure

Necessary quantities of AMS and DGEBA are mixed in 2 mL of tetrahydrofuran (THF) and stirred until homogenization and then the TEA and the methanol are added to the solution.[10] Samples to analyze are obtained by depositing, on a Teflon plate, the solution obtained in the form of a thin film. After evaporating the solvent, the film is placed in the temperature controller and then introduced into the thermostated cell. Two
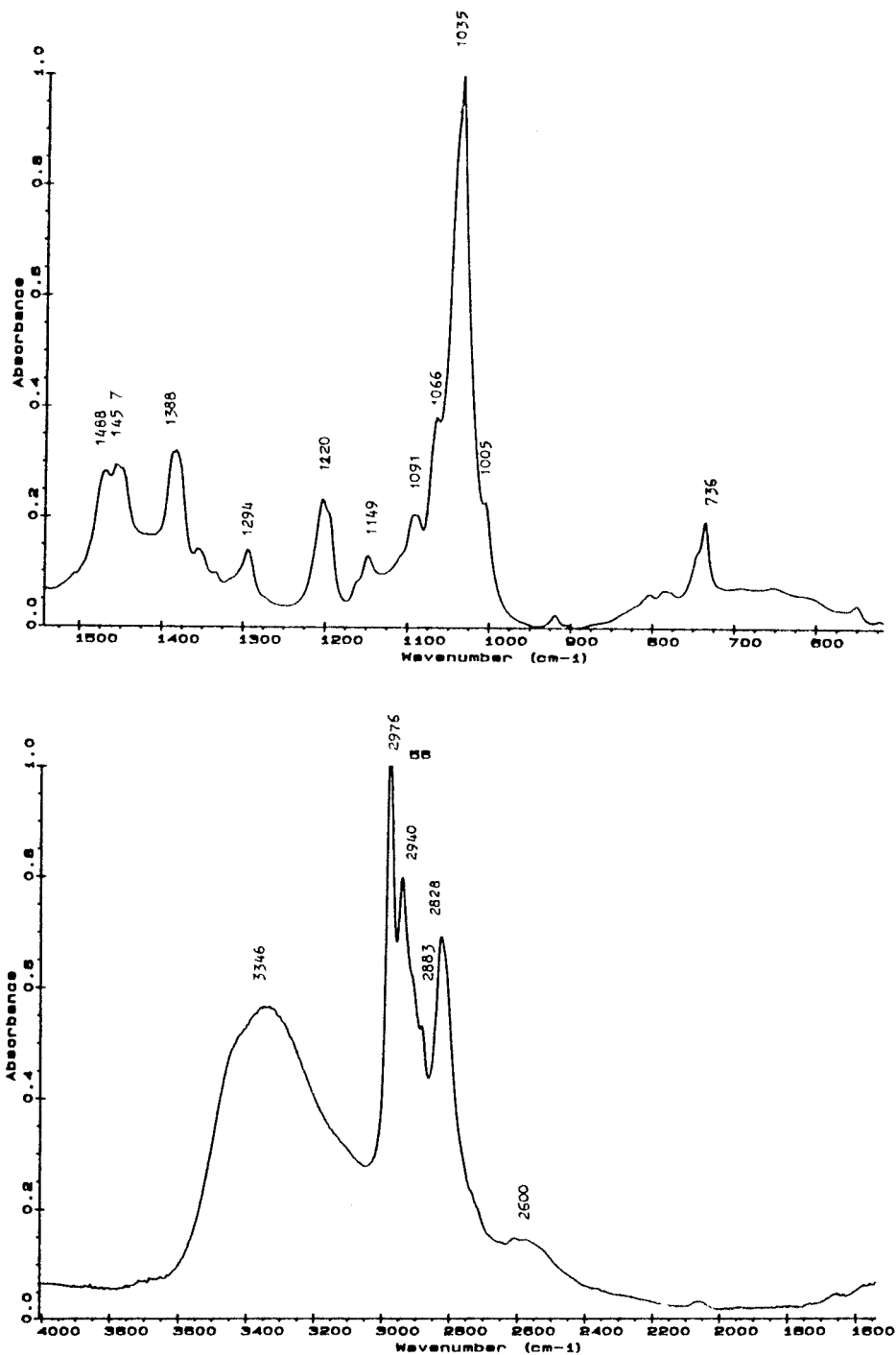
Figure 3   FTIR spectrum of TEA/methanol mix.

NaCl pellets are placed on the two splits of the cell.

FTIR purging is undertaken by nitrogen before each test. IR spectra of each pure used reactant, DGEBA, AMS, and a methanol/TEA mix, are taken first in order to compare them with the cured products. The kinetic study was performed at four isothermal temperatures[11]: $T = 85, 82, 80$, and 75°C.

After recording the spectrum at room temperature, the temperature programmer was set off. The initial reaction time ($t = 0$) corresponds to the time when the chosen isothermal temperature is reached. Measures are ended when the varia-

Table I Attribution of Frequency Bands of TEA/MethOH Mix

Wavenumber (cm^{-1})	Attribution
736	γCH_{2r} (rocking) (TEA) + δO—H participating to a hydrogen bond (methanol)
1035	νC—OH (methanol)
1066–1149	νC—N (TEA)
1220	γCH_{3r} (methyl rocking) (TEA)
1294	$\gamma CH_{2t} + \gamma CH_{2w}$ (twisting and wagging) (TEA)
1388	$\delta_{sym}CH_3$ (TEA and methanol)
1457	$\delta_{asym}CH_3$ (TEA and methanol)
1488	δCH_2 (scissoring) (TEA)
2400–3000	νO—H in the case of associated OH (hydrogen bonds and chelation)
2828	$\nu_{sym}CH_2$ (TEA) + $\nu_{sym}CH_3$ (methanol)
2883	$\nu_{sym}CH_3$ (TEA)
2940	$\nu_{asym}CH_2$ (TEA)
2972	$\nu_{asym}CH_3$ (TEA and methanol)
3100–3600 centered on 3346	νO—H associated (hydrogen bonds) (methanol)

γ, out-of-plane bending vibration; δ, in-plane bending vibration; ν, stretching vibration or elongation bond vibration.

tion of the epoxy band area becomes negligible. The cured sample at 85°C during 200 min is post-cured at 100°C for 96 h.

RESULTS AND DISCUSSION

The spectra of DGEBA, AMS, and the methanol/TEA mixture are represented, respectively, in Figures 1–3. Tables I–III give corresponding positions of the absorption bands.[12–14]

Figure 4 represents the spectrum at room temperature of the AMS/DGEBA system. Table IV reports the wavelength of the main absorption bands. As an example, we have represented in Figure 5 the spectra at $T = 85°C$ for three reaction times ($t = 0$, 60, and 150 min) as well as the spectrum corresponding to the postcuring at 100°C for 96 h.

The study concerns the epoxy reactivity vis-à-vis the anhydride groups. The analysis of the IR spectra is based on the peak area variation of the epoxy groups' absorption at 916 cm^{-1}. The baseline joins the starting and ending points of the epoxy band. To quantify this variation, we considered as the internal standard (band that remains unchanged during the reaction) the band corresponding to the stretching vibration of the bond C=C at 1506 cm^{-1}, which is characteristic of the aromatic nucleus. The epoxy fractional conversion is calculated as follows:

$$\alpha = 1 - \frac{(A_{\text{epoxy}}/A_{\text{aromatic}})_t}{(A_{\text{epoxy}}/A_{\text{aromatic}})_{t=0}}$$

with A_{epoxy} the area corresponding to the absorption of the epoxy groups and A_{aromatic} the area corresponding to the absorption of the aromatic cycles.

The decreasing of the methanol and TEA band intensities, respectively, at 670 and 1034 cm^{-1} and 2800–2200 and 1067 cm^{-1} during the reaction, indicates that they take part in the curing process. The continual decreasing of the epoxy band area at 916 cm^{-1} and that of the anhydride at 1778 cm^{-1} ($\nu_{asym}C$=O) shows that there is progressive consumption of the epoxy and anhydride during the curing reaction (200 min).

The increasing intensity of the two characteristic bands of ester at 1186–1157 and 1727 cm^{-1} and the increasing of the intensity of the characteristic band of the hydroxyl at 3650–3100 cm^{-1}, produced by the curing reaction, indicate that there is an addition esterification reaction. We have also observed a perceptible decreasing of the intensity of the O—H methanol band in the beginning of the reaction.

In the zone 1252–1230 cm^{-1}, we have an overlapping of the vibration of epoxy ring, the stretching vibration of the C—O anhydride, and the stretching vibration of the C—O ester. Changes are observed within this band during the reaction. We observed both a decreasing of the epoxy and anhydride absorption bands, due to their consumption by the curing reaction, and a simultaneous increasing with widening of the ester-group band.

We also noticed a decrease of the OH band at 1034 cm^{-1}, but after the postcuring, this same

Table II Attribution of Frequency Bands of DGEBA

Wavenumber (cm^{-1})	Attribution
760–770	γCH_{2r} (rocking) + γC—H of the dissubstituted benzene; 1-4-substituted benzene (four adjacent hydrogens)
831	γC—H of the 1-4-substituted benzene + γCH_{2r} of the epoxide group
915	Characteristic vibration of the epoxide ring corresponding to ν_{asym} $\overset{\displaystyle C-C}{\underset{\displaystyle O}{\diagdown\,\diagup}}$
1036	δC—H of the 1-4-substituted benzene + $\nu_{sym}C$—O—C in the case of an aromatic ether
1085	δC—H benzenic
1132	νC—O of the epoxide ring
1155 and 1184	δC—H benzenic
1247	ν_{sym} $\overset{\displaystyle C-C}{\underset{\displaystyle O}{\diagdown\,\diagup}}$ of the epoxide ring + ν_{asym} C—O—C in the case of an aromatic ether
1297	γCH_{2t} + γCH_{2w} (twisting and wagging)
1347	δCH_{2t} (twisting of the epoxy group)
1363 and 1386	$\delta_{sym}CH_3$, doublet in the case of *gem*-dimethyl groups
1458	δCH_2 (scissoring) + $\delta_{asym}CH_3$ + νC=C of the 1-4-substituted benzene
1508, 1582, 1608,	νC=C of the 1-4-substituted benzene
1650–2000	The overtone and combination tone bands. Characteristic bands of substitution pattern
2873, 2930, 2969	νC—H aliphatic
3000	νC—H of the epoxy group
3038, 3058	νC—H aromatic

See footnote to Table I for symbols.

band becomes wide. The decrease is due to the consumption of the methanol (νC—OH) during the cure, while the widening is due to the hydroxyl groups formed by the reaction and is present after the postcuring.

Figure 6 gives the variation of the epoxy fractional conversion versus time at different temperatures. The fractional conversion increases with time and temperature. The rate of conversion is rapid in the beginning of the reaction. A fractional

Table III Attribution of Frequency Bands of AMS

| Wavenumber (cm^{-1})	Attribution
563	δH—C—C and δC—C—C skeletal
704	γC—H of the monosubstituted benzene (five adjacent hydrogens)
765	γC—H of the monosubstituted benzene + γCH_{2r} (rocking)
883	νC—C—O—C—C + γC—H in the case of an alkene (double bonds formed during
921	termination:; synthesis of the copolymer)
955	
1173	δC—H of the monosubstituted benzene
1173–1300	νC—O anhydrid (very intense and large) + δC—H of the monosubstituted benzene
1417	δC—H in the case of a monsubstituted alkene
1455	δCH_2 (scissoring) + νC=C of the monosubstituted benzene
1496, 1585, 1608	νC=C of the monosubstituted benzene
1731	$\nu_{sym}C$=O
1780	$\nu_{asym}C$=O
1650–2000	The overtone and combination tone bands. Characteristic bands of substitution pattern
2883, 2959, 2981	νC—H aliphatic
3030, 3060	νC—H aromatic

See footnote to Table I for symbols.
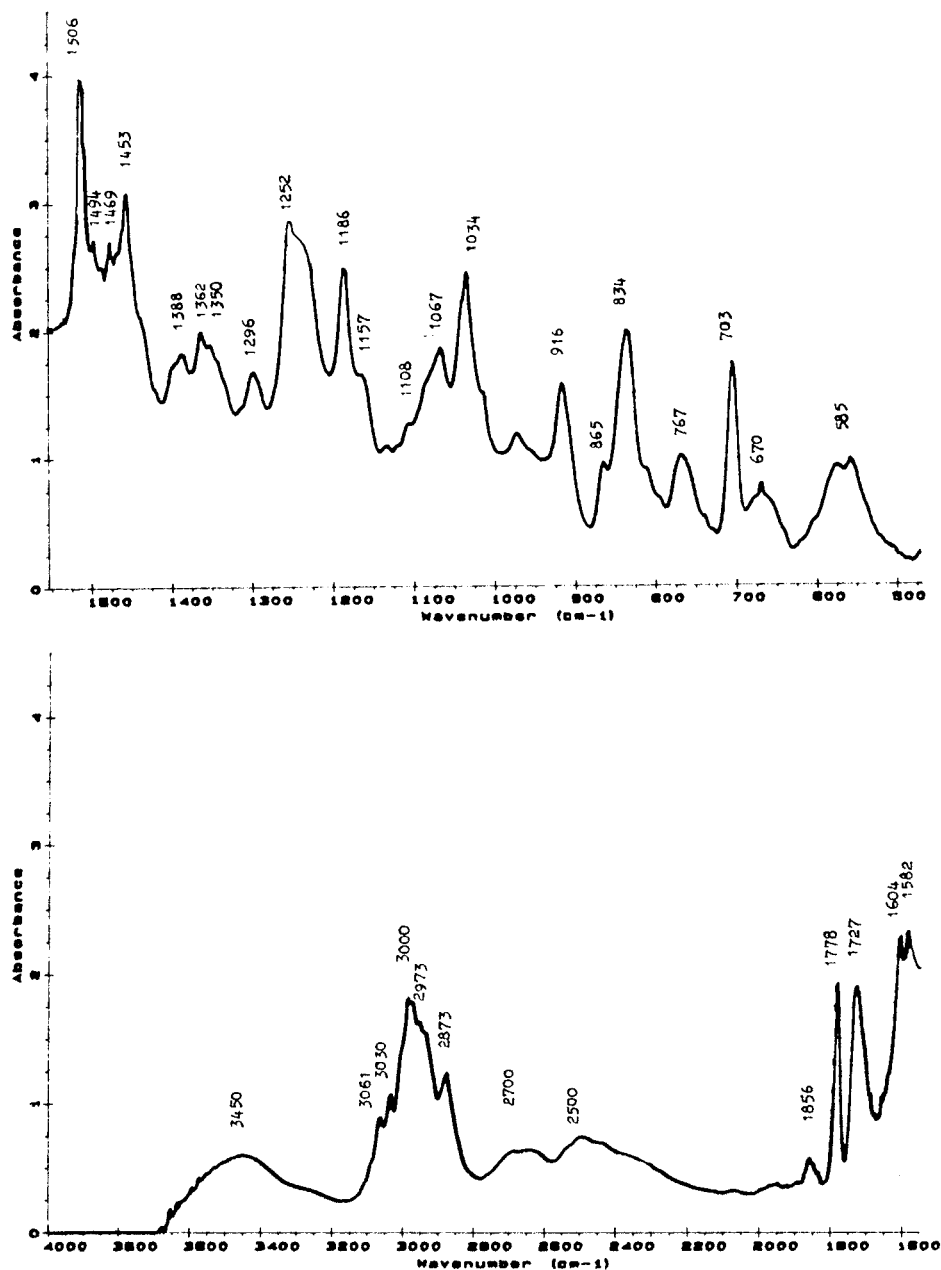
Figure 4 Room-temperature FTIR spectrum of AMS/DGEBA system.

conversion of 40% is reached within 60 min of the reaction at 85°C, but we observed a slowing down of the reaction after this period of time. The appearance of a new band at 1126 cm^{-1} (Fig. 5), characteristic of ether, is observed during the postcuring (96 h at 100°C).

Bands at 916 and 1350 cm^{-1} corresponding to epoxy groups disappear after the postcuring, while the intensity of the band at 1727 cm^{-1}, characteristic of ester groups, increases. However, the anhydride band after having decreased is still vis-

ible in the spectrum. We have also noticed the continued presence of the hydroxyl band at 3650–3100 cm^{-1}. All these changes indicate that during the postcuring there has been an addition esterification reaction with a parallel etherification reaction.

These results show that the cure reaction in the isothermal mode over 200 min is an addition esterification reaction generating ester and hydroxyl groups. The postcuring (96 h at 100°C) results in total consumption of the epoxy groups.

**Table IV   Attribution of Frequency Bands of AMS/DGEBA System**

Wavenumber (cm^{-1})	Attribution
558	δH—C—C and δC—C—C skeletal (AMS and DGEBA)
671	δO—H (methanol)
703	γC—H of the monosubstituted benzene (AMS)
767	γC—H of the monosubstituted benzene (AMS) + γC—H of the 1-4 substituted benzene (DGEBA) + γCH$_{2r}$ (AMS and DGEBA)
834	γC—H of the 1-4 substituted benzene (DGEBA) + γCH$_{2r}$ of the epoxy group
916	ν_{asym} C—C epoxide / O (DGEBA) + δC—H in the case of an alkene (AMS) + νC—C—O—C—C (AMS)
1034	νC—OH (methanol) + δC—H of the substituted benzene (AMS and DGEBA)
1067	νC—N (TEA)
1157	+ δC—H of the substituted benzene (AMS and DGEBA)
1173–1290	δC—H of the substituted benzene + νC—O anhydrid (AMS) + ν_{sym} C—C epoxide / O (DGEBA) + ν_{asym} C—O—C in the case of an aromatic ether
1296	γCH$_{2t}$ + γCH$_{2w}$ (AMS, DGEBA, and TEA)
1350	δCH$_{2t}$ (twisting of the epoxy group)
1362, 1388	Doublet in the case of a *gem*-dimethyl groups corresponding to δ_{sym}CH$_3$
1453	νC=C of the substituted benzene (AMS and DGEBA) + δ_{asym}CH$_3$ (TEA/MethOH)
1469	δCH$_2$ (scissoring) (AMS and DGEBA) + δ_{asym}CH$_3$ (DGEBA)
1494, 1506; 582, 1604	νC=C of the substituted benzene (AMS and DGEBA)
1728	ν_{sym}C=O (AMS)
1778	ν_{asym}C=O (AMS)
1650–2000	The overtone and combination tone bands. Characteristic bands of substitution pattern
2200–3000	νO—H in the case of associated OH (hydrogen bonds and chelation)
2873, 2973	νC—H aliphatic
3030, 3061	νC—H aromatic
3200–3700	νO—H associated OH (hydrogen bonds)

See footnote to Table I for symbols.

Studies have been performed on the mechanism of cure for monoepoxide–anhydride systems[15–17] catalyzed by a tertiary amine in the presence of a proton donor-type HA utilized as a cocatalyst. The mechanism implies an initiation step in which the amine is linked to the polymer chain by a covalent bond. The amine is not therefore regenerated.

According to Tanaka and Kakiuchi,[18,19] epoxyde/anhydrid/amine/HA systems lead to the following reaction steps:

Activation:

$$R_3^1N + HA \rightleftharpoons [R_3^1N\text{----}HA] \qquad (1)$$

$$(2)$$

Propagation:

$$(3)$$

$$(4)$$
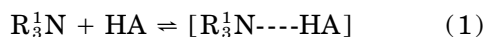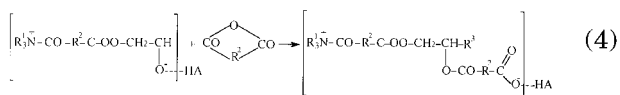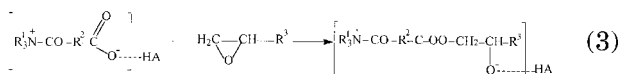
Feltzin[20] proposed a crosslinking mechanism in which a complex of ammonium–carboxylate is formed during the activation step, the amine being regenerated at the terminaition step. The reaction scheme is as follows:

Activation:

$$R_3^1N + HA \rightleftharpoons [R_3^1N\text{----}HA] \rightleftharpoons R_3^1\overset{+}{N}_HA^- \quad (1)$$
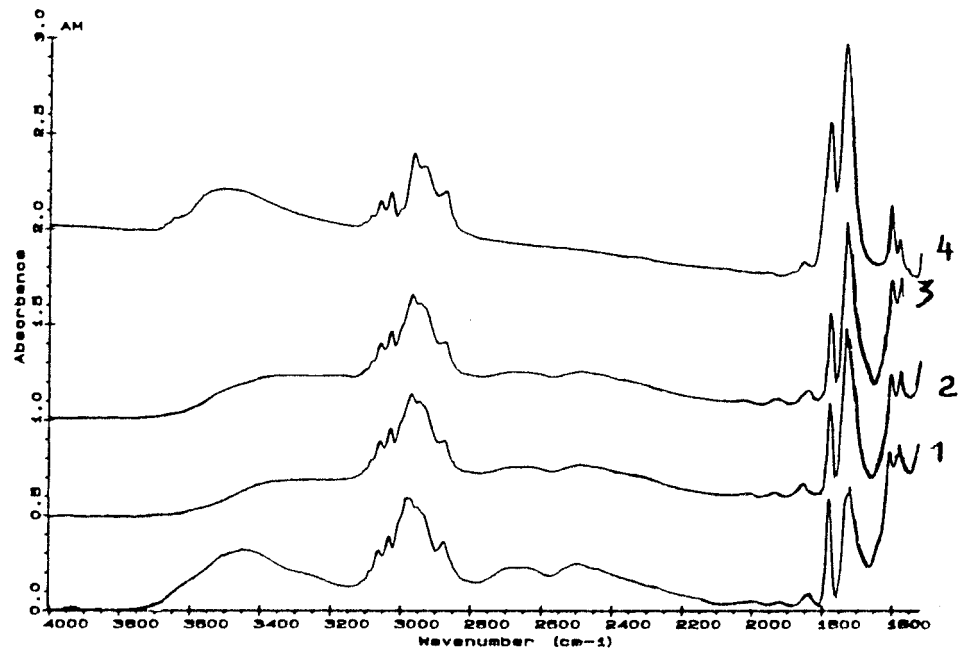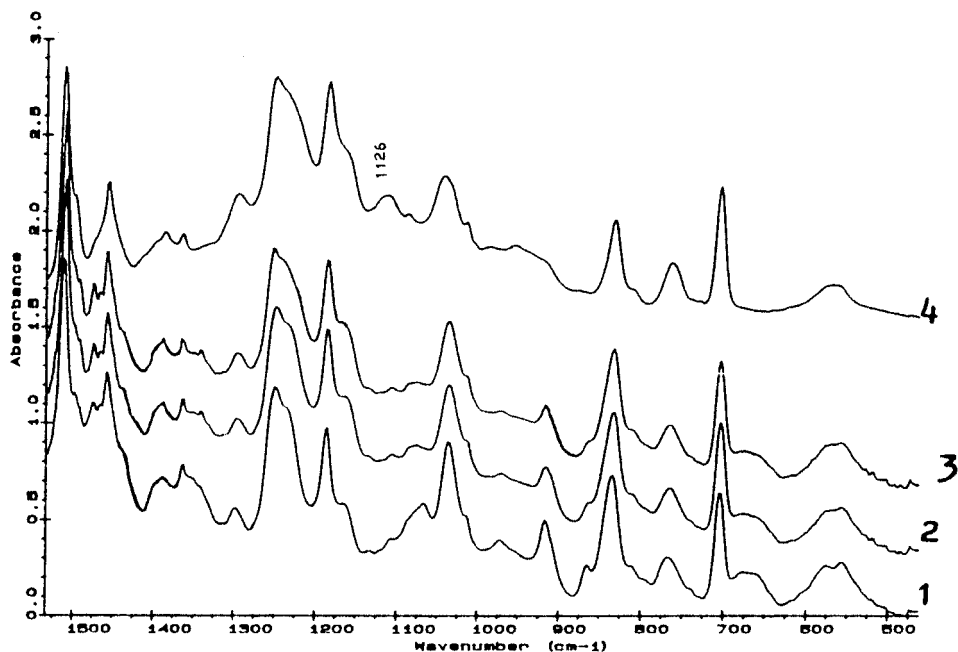
Figure 5 FTIR spectra of AMS/DGEBA system: (1) 0 min at 85°C; (2) after 60 min at 85°C; (3) after 150 min at 85°C; (4) after postcure (96 h at 100°C).

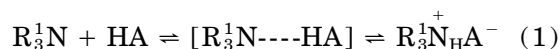$$R^1_3NH\ A^- \ +\ \overset{O}{\underset{R^2}{CO\diamond CO}} \ \rightleftharpoons\ \left[A-CO-R^2-\overset{O}{\underset{O^-}{C}}\right]\cdots\overset{+}{HNR^1_3} \qquad (2)$$

Propagation:

$$\left[A-CO-R^2-\overset{O}{\underset{O^-}{C}}\right]\cdots H\overset{+}{N}R^1_3\ -\ H_2C\diamond CH-R^3 \longrightarrow \left[A-CO-R^2-C-OO-CH_2-\overset{|}{C}H-R^3\right]_{O^-\cdots H\overset{+}{N}R^1_3} \qquad (3)$$

$$\left[A-CO-R^2-C-OO-CH_2-\overset{|}{C}H-R^3\right]_{O^-\cdots H\overset{+}{N}R^1_3}\ +\ \overset{O}{CO\diamond CO} \longrightarrow A-CO-R^2-C-OO-CH_2-CH-R^3_{O-CO-R^2-COO^-H\overset{+}{N}R_3} \qquad (4)$$

Termination:

$$A-CO-R^2-C-OO-CH_2-\overset{|}{C}H-R^3_{O-CO-R^2-COO^-H\overset{+}{N}R_3} \longrightarrow A-CO-R^2-C-OO-CH_2-\overset{|}{C}H-R^3_{O-CO-R^2-COOH}\ +\ R^1_3N \qquad (5)$$
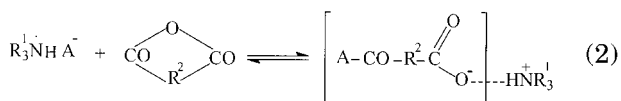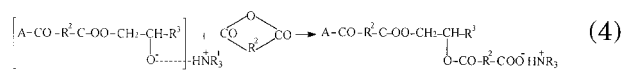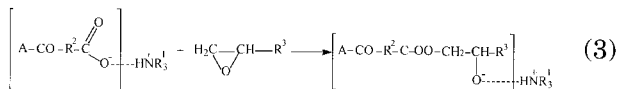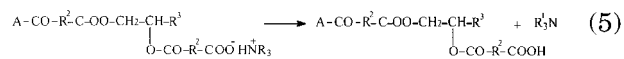
In our study, the FTIR spectrum after the

Figure 6 Epoxy fractional conversion versus time at 85, 82, 80, and 75°C.

crosslinking reaction (200 min) of the AMS/ DGEBA system does not show the presence of the two characteristic bands of a carboxylate ion COO^- at 1600–1550 cm^{-1} and 1420–1350 cm^{-1}. However, we observed the vibrational mode of νN^+—H of a quaternary ammonium at 2800–2200 cm^{-1}.

In addition, an increase of the intensity of the two ester bands at 1186–1157 and 1727 cm^{-1} is observed. The neat presence of the hydroxyl band at 3650–3100 cm^{-1} after postcuring allows us to deduce that the main reaction of curing is a poly-addition esterification reaction which generates both ester and hydroxyl groups. The mechanism proposed by Feltzin[20] might be well adapted for describing our reaction system.

Some tests carried on in the absence of TEA or methanol or both have shown that crosslinking does not occur. These two components have an essential contribution in the mechanism through its activation step.

The reaction scheme of our polymeric system is described as follows:

Activation:

$$N(C_2H_5)_3 + CH_3OH \rightleftharpoons$$

$$[(C_2H_5)_3N\text{------}HOCH_3]$$

$$\rightleftharpoons (C_2H_5)_3\overset{+}{N}H\ \overset{-}{O}CH_3 \quad (1)$$

(2)

Propagation:

(3)

Termination:

(4)

The regenerated amine reacts with the residual methanol, allowing the reaction to continue.

As the characteristic bands of the carboxylate

Figure 7   Structure of the crosslinking product.

have not been observed, we can deduce that the propagation rate is greater than the activation rate. The generated carboxylate ion is instantly followed by the opening of an epoxy ring to give, respectively, ester and hydroxyl groups.

The resin and the hardener are polyfunc-

tional; hence, the anhydride/epoxy reaction gives several ester and hydroxyl groups. The schematic structure of the network produced is shown in Figure 7.

CONCLUSION

Several articles [18,19,21,22] on the cure kinetics of epoxy–anhydride systems of small molecules imply a reaction mechanism wherein the tertiary amine links chemically and irreversibly to the polymer chain during the activation step, generating quaternary ammonium salt. Then, the main product of the reaction is a polyester.

Our study has shown that the curing of the polymeric anhydride/DGEBA system, according to a three-step mechanism, would lead to the crosslinked network constituted of polymeric chains where the moieties consist of monoester and hydroxyl groups. Complete consumption of the epoxides has been shown after the postcure during 96 h at 100°C.

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