

Epoxy Resin Cure. II. FTIR Analysis

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Synopsis

Fourier transform infrared (FTIR) spectroscopy is used to determine the cure rate of an epoxy resin consisting of tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) and diaminodiphenylsulfone (DDS). Cure rates at 120 and 160°C are shown to increase noticeably when 1% BF_3 -MEA is added to either TGDDM or TGDDM plus DDS. Fluoroboric acid is shown to increase the cure rates even more than the BF_3 -MEA. These results combined with the NMR results in the accompanying article indicate that BF_3 -MEA is not a catalyst for epoxy resin cure. Instead it is rapidly hydrolyzed to fluoroboric acid which acts as the catalyst.

INTRODUCTION

Fiber reinforced composites have a variety of industrial uses.^{1,2} The crosslink density of the cured epoxy resins has been shown to increase the epoxy resin's density, compressive modulus, yield point, flow stress, and recoverability.^{3,4} To optimize the crosslink density, different additives and cure cycles have been used. For example, cure processes can be optimized after studying the thermodynamics of the epoxy resin cure. Dynamic dielectric analysis (DDA) and differential scanning calorimetry (DSC) have been used for such studies.⁵⁻⁷ Crosslinking agents and catalysts can be added to optimize the crosslink density. Fourier transform infrared (FTIR) spectroscopy has been used to monitor the reactions which occur when such additives are used.^{8,9} Recent articles describe the use of FTIR to study the cure of tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) when diaminodiphenylsulfone (DDS) and/or boron trifluoride monoethylamine (BF_3 -MEA) are added.^{10,11} These articles show that the epoxide, hydroxyl, ether, and amine bands change after curing the epoxy resin.

The epoxy resin cure in the presence of BF_3 -MEA is of special interest. Several reports have appeared presenting conflicting ideas on the role of BF_3 -MEA in epoxy resin cure. Some reports suggest that BF_3 -MEA dissociates, and the free BF_3 acts as a catalyst,¹²⁻¹⁵ where others maintain that BF_3 -MEA does not dissociate.¹⁶⁻¹⁸ In Part I of this article,¹⁹ it is shown that BF_3 -MEA is hydrolyzed to fluoroboric acid (HBF_4). This hydrolysis is especially fast at the elevated temperatures used to cure epoxy resins. It was concluded that BF_3 -MEA is not a catalyst, but instead HBF_4 and/or other hydrolysis products are acting as the catalyst.

This article gives further evidence that fluoroboric acid is acting as the catalyst. The rates of cure of TGDDM and TGDDM plus DDS were followed

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by using FTIR. This rate is much slower than the rate of hydrolysis of $\text{BF}_3\text{-MEA}$ as previously demonstrated.¹⁷ Moreover, addition of HBF_4 to either the TGDDM or TGDDM plus DDS noticeably accelerates the epoxy resin's cure.

EXPERIMENTAL

FTIR

FTIR spectra were obtained using a Nicolet model 7199 with a TGS detector. All spectra were obtained using 2 cm^{-1} resolution and 100 scans. Samples were dissolved in acetone and cast as a thin film on NaCl plates. The NaCl plates were put in a vacuum desiccator to remove the acetone.

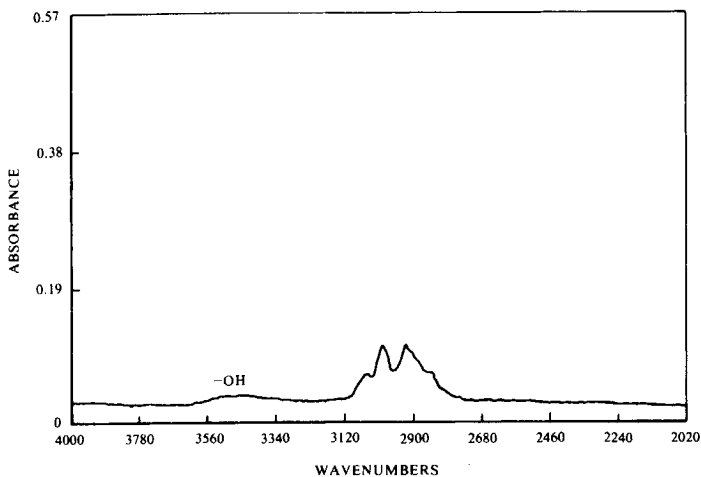
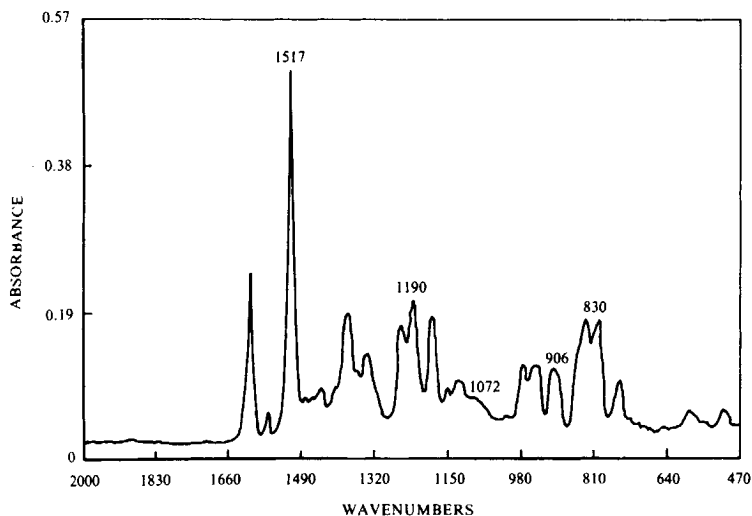


Fig. 1. Room temperature FTIR spectrum of TGDDM.

Each sample was put between two NaCl plates and placed in a Perkin-Elmer temperature controller. After purging the FTIR with nitrogen, a spectrum was obtained at room temperature. The temperature controller was then set at the desired temperature (120 or 160°C), and spectra were recorded at various time intervals.

Nuclear Magnetic Resonance (NMR)

NMR spectra were recorded with a Varian FT80A Fourier Transform NMR. The ^1H and ^{19}F NMR spectra were measured at 79.542 and 74.832 MHz, respectively. In every case, deuterated solvents were used for field lock. For ^1H NMR, chemical shifts are reported with tetramethylsilane

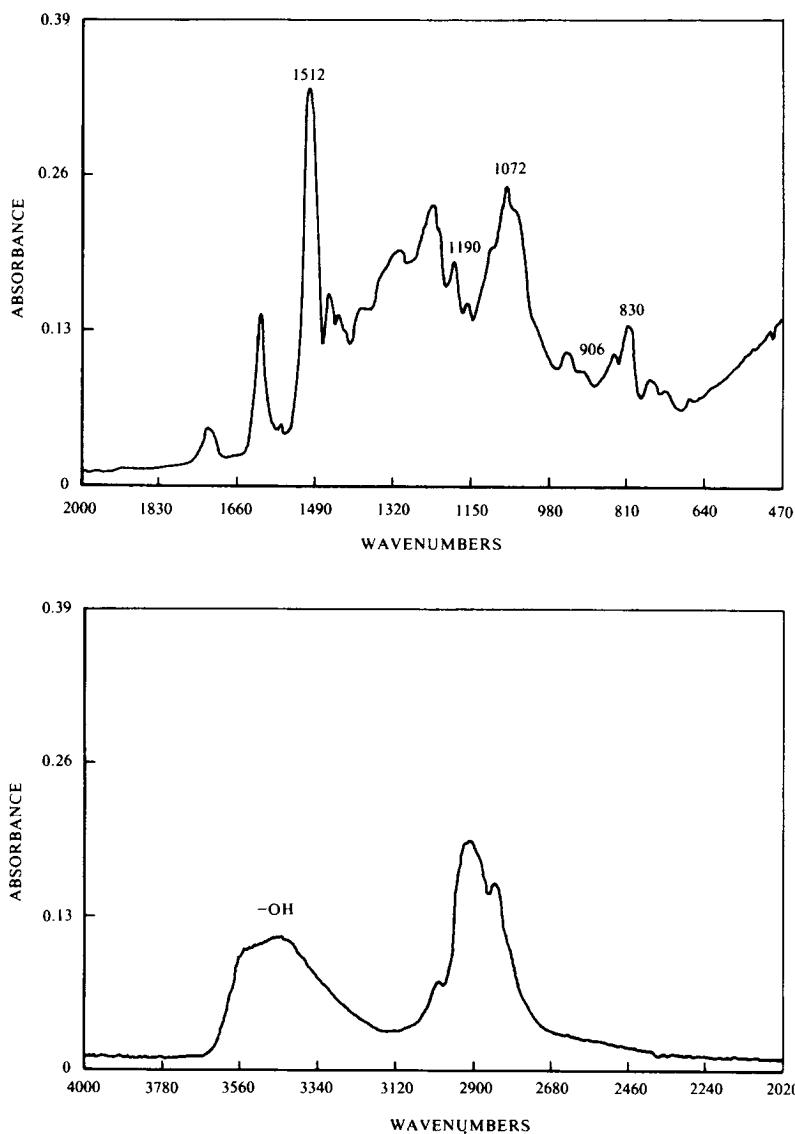


Fig. 2. Spectrum of TGDDM after 75 min at 160°C.

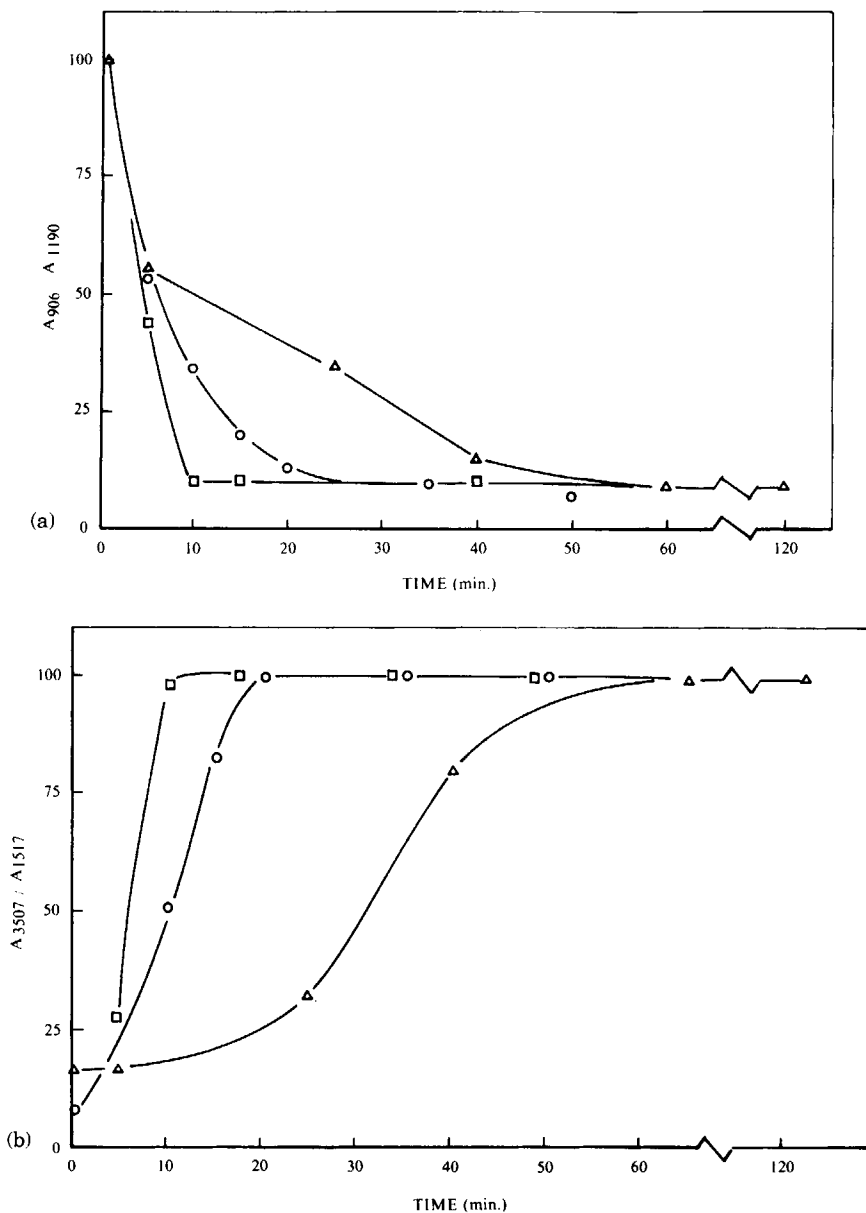


Fig. 3. Homopolymerization of TGDDM at 160°C: (a) epoxide absorbance; (b) hydroxyl absorbance; (c) ether C—O—C absorbance. (Δ) No catalyst; (\square) 1% HBF_4 ; (\circ) 1% $\text{BF}_3\text{-MEA}$.

$\ast(\text{TMS})$ at 0 ppm being used as the reference. For ^{19}F NMR, hexafluorobenzene at -163 ppm is used as the reference.

RESULTS

Homopolymerization of TGDDM

The homopolymerization of TGDDM should be accompanied by a loss of epoxide (oxirane) ring, and an increase in hydroxyl and ether (C—O—C stretch) bands in the FTIR spectrum. At room temperature, before any

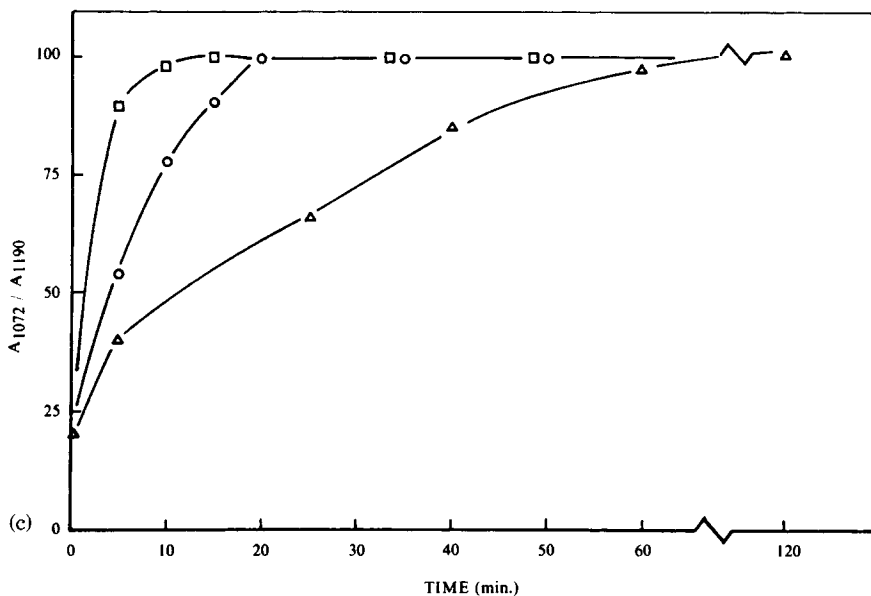


Fig. 3 (Continued from the previous page.)

polymerization has occurred, the spectrum of TGDDM has a noticeable epoxide band at 906 cm^{-1} as well as small hydroxyl and ether bands in the region of 3400 cm^{-1} and at 1072 cm^{-1} , respectively (Fig. 1). The hydroxyl and ether functions are caused by the presence of impurities in the TGDDM and are expected to make the TGDDM more reactive. In addition to other bands, phenyl bands at 1190 cm^{-1} and 1517 cm^{-1} are present and remain constant regardless of epoxide reactions. The absorbances at these frequencies are used as references. The absorbance at 3507 cm^{-1} caused by hydroxyl is divided by the absorbance at 1517 cm^{-1} , and the absorbances at 1072 cm^{-1} and 906 cm^{-1} are divided by the absorbance at 1190 cm^{-1} to estimate changes in the ether and epoxide concentrations. It is also possible to use the absorbance at 830 cm^{-1} as an internal standard, and similar results are obtained if the ether and epoxide absorbances are divided by the phenyl absorbance at 830 cm^{-1} .

Upon heating TGDDM in the presence of $\text{BF}_3\text{-MEA}$ (100 parts TGDDM to 1 part $\text{BF}_3\text{-MEA}$) homopolymerization occurs. After 75 min at 160°C , the FTIR spectrum is noticeably different (Fig. 2). A broad -OH band appears along with an ether (C-O-C) band at 1072 cm^{-1} . The phenyl band at 1517 cm^{-1} is shifted to 1512 cm^{-1} , but the bands at 1190 cm^{-1} and 830 cm^{-1} are not shifted. The epoxide band at 906 cm^{-1} has almost disappeared.

The rate of homopolymerization of TGDDM can be estimated by following the loss of epoxide along with the increase in hydroxyl and ether absorbances. In the absence of any additives, TGDDM polymerizes slowly at 160°C , requiring 1 h for the epoxide absorbance to reach its minimum and hydroxyl and ether absorbances to reach their maximum (Fig. 3, a-c).

The addition of $\text{BF}_3\text{-MEA}$ to TGDDM (1% $\text{BF}_3\text{-MEA}$ by weight) accelerates the homopolymerization of TGDDM. The addition of HBF_4 to TGDDM accelerates the homopolymerization even more. Therefore, HBF_4 can clearly act as an accelerator (or possibly a catalyst) for this homopolymerization.

Part I of this report shows that $\text{BF}_3\text{-MEA}$ is rapidly hydrolyzed at 100°C

to HBF_4 , and it was proposed that the HBF_4 is the true catalyst. To test this further, a 1:20 mixture of BF_3 -MEA plus TGDDM was dissolved in deuterated orthodichlorobenzene (d_2 -ODCB). The ^1H and ^{19}F NMR spectra were recorded (Fig. 4, a and b). The multiplet at 2.7 to 2.9 ppm in the ^1H NMR is caused by two methylene protons of the epoxide group. This multiplet can be used to determine the epoxide equivalent weight of glycidyl ethers (20,21). The ^{19}F NMR spectrum shows the BF_3 quartet and HBF_4 peak as expected.¹⁹

After 7 min at 120°C , the ^1H and ^{19}F NMR spectra were recorded again (Fig. 5, a and b). The ^1H NMR shows no appreciable change in the epoxide equivalent weight, but the ^{19}F NMR shows that all the BF_3 -MEA has been hydrolyzed to HBF_4 . These data provide direct evidence that BF_3 -MEA is hydrolyzed to HBF_4 before the polymerization of TGDDM can occur.

Polymerization of TGDDM + DDS

When TGDDM is polymerized in the presence of DDS, there is the possibility for homopolymerization reactions to occur between epoxide groups as well as heteropolymerization to occur between epoxide and primary amine.¹⁰ The rate of homopolymerization can be determined from the increase in the ether bands. The heteropolymerization can be studied by following the secondary amine absorbance at 3409 cm^{-1} . The total polymerization can be observed through the absorbances at 906 cm^{-1} and 3507 cm^{-1} caused by epoxide and hydroxyl, respectively.

The FTIR spectrum of TGDDM + DDS + BF_3 -MEA (100:58.7:1) at room temperature is shown in Figure 6. The presence of DDS gives rise to peaks at 3464 cm^{-1} and 3368 cm^{-1} which might interfere with the hydroxyl band (which appears upon polymerization). The phenyl bands at 1570 cm^{-1} , 1190 cm^{-1} , and 830 cm^{-1} are still available as reference peaks. In addition, there is a primary amine band at 1614 cm^{-1} along with the ether and epoxide bands at 1072 cm^{-1} and 906 cm^{-1} .

This mixture of TGDDM, DDS, and BF_3 -MEA was then heated to 120°C and spectra were recorded periodically. After 30 min at 120°C , there are numerous changes in the FTIR spectrum (Fig. 7). The absorbance in the region of 3200 cm^{-1} to 3500 cm^{-1} has increased. There is no longer a peak at 1614 cm^{-1} , but instead the peak at 1595 cm^{-1} has a broad shoulder. The phenyl band that was at 1517 cm^{-1} is shifted to 1512 cm^{-1} , and the 830 cm^{-1} band is shifted to 832 cm^{-1} . (The 1190 cm^{-1} band is not shifted.) The epoxide band at 906 cm^{-1} has almost disappeared.

It is apparent from these spectra that the ether and epoxide bands (at 1072 cm^{-1} and 906 cm^{-1}) can be used to estimate degrees of polymerization. One might also be tempted to use the primary amine band at 1614 cm^{-1} . However, the band at 1595 cm^{-1} has such a broad shoulder that what actually is observed is an increase in the absorbance at 1614 cm^{-1} after heating the sample.

It might seem that the region of 3200 cm^{-1} to 3500 cm^{-1} is useless in estimating degrees of polymerization; however, the hydroxyl and secondary amine bands should be located in this region. If the spectrum at room temperature is subtracted from the spectrum at 120°C after 30 min, peaks

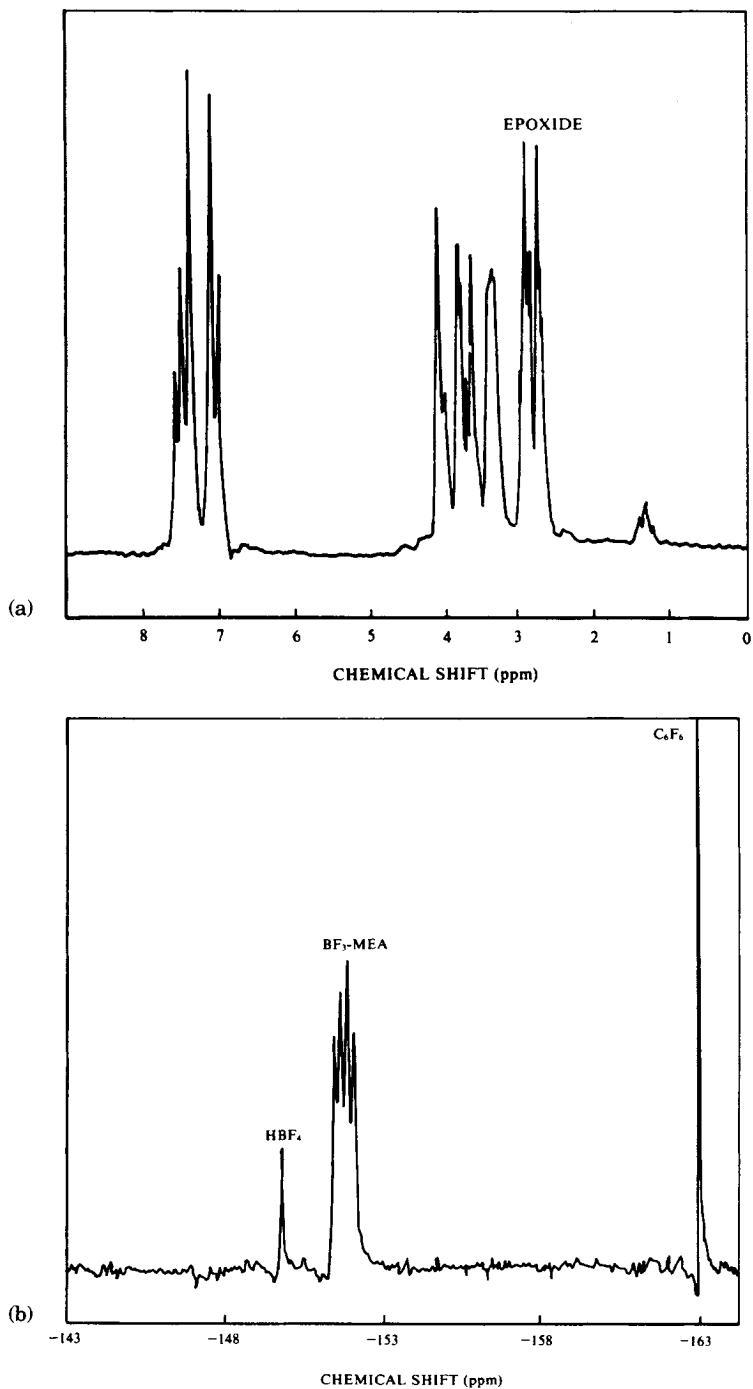


Fig. 4. (a) ^1H NMR of TGDDM containing 1/20 $\text{BF}_3\text{-MEA}$ at room temperature in $\text{d}_2\text{-ODCB}$ solvent. (b) ^{19}F NMR of $\text{BF}_3\text{-MEA}$ (1/20 of TGDDM) at room temperature in $\text{d}_2\text{-ODCB}$ solvent.

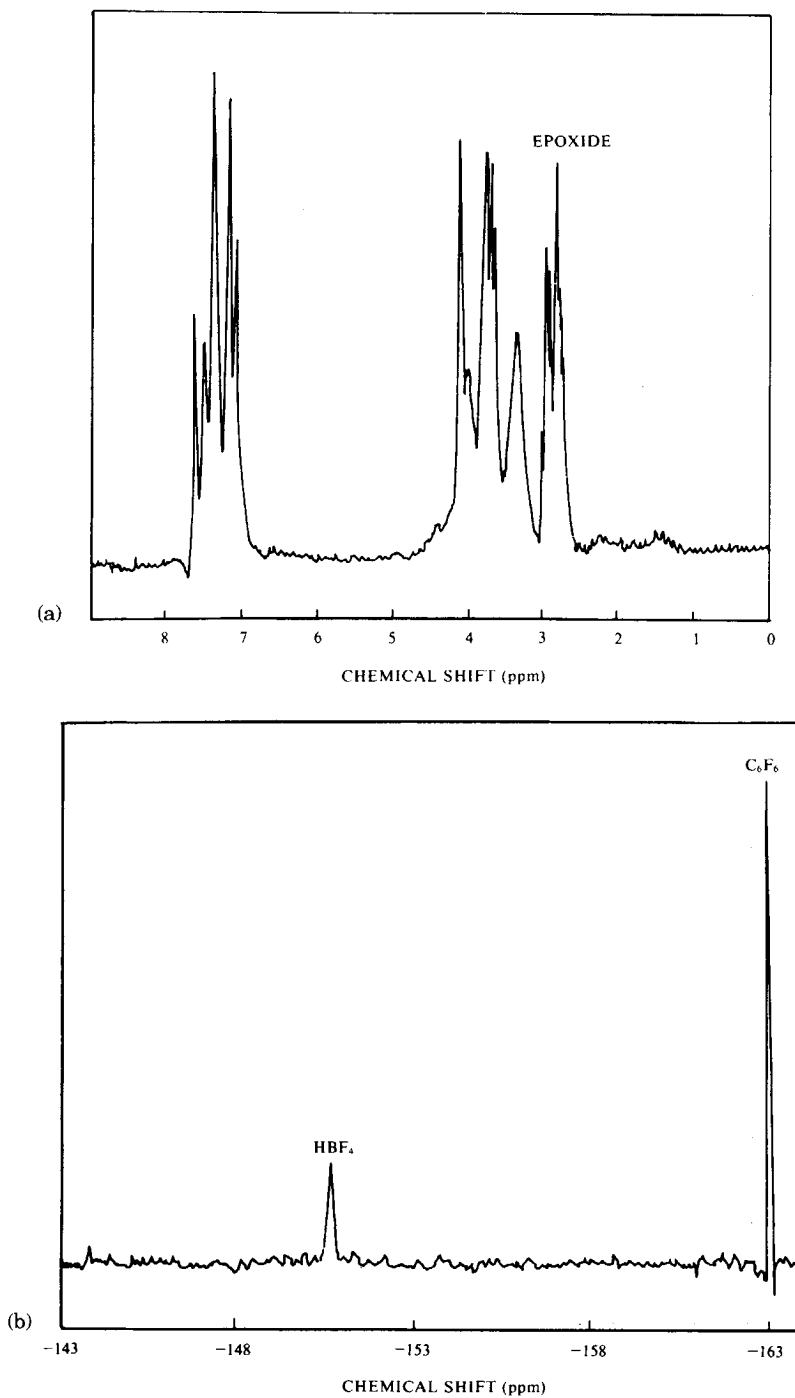


Fig. 5. (a) ^1H NMR of TGDDM containing 1/20 $\text{BF}_3\text{-MEA}$ after 20 min at 120°C . (b) ^{19}F NMR of $\text{BF}_3\text{-MEA}$ (1/20 of TGDDM) after 20 min at 120°C .

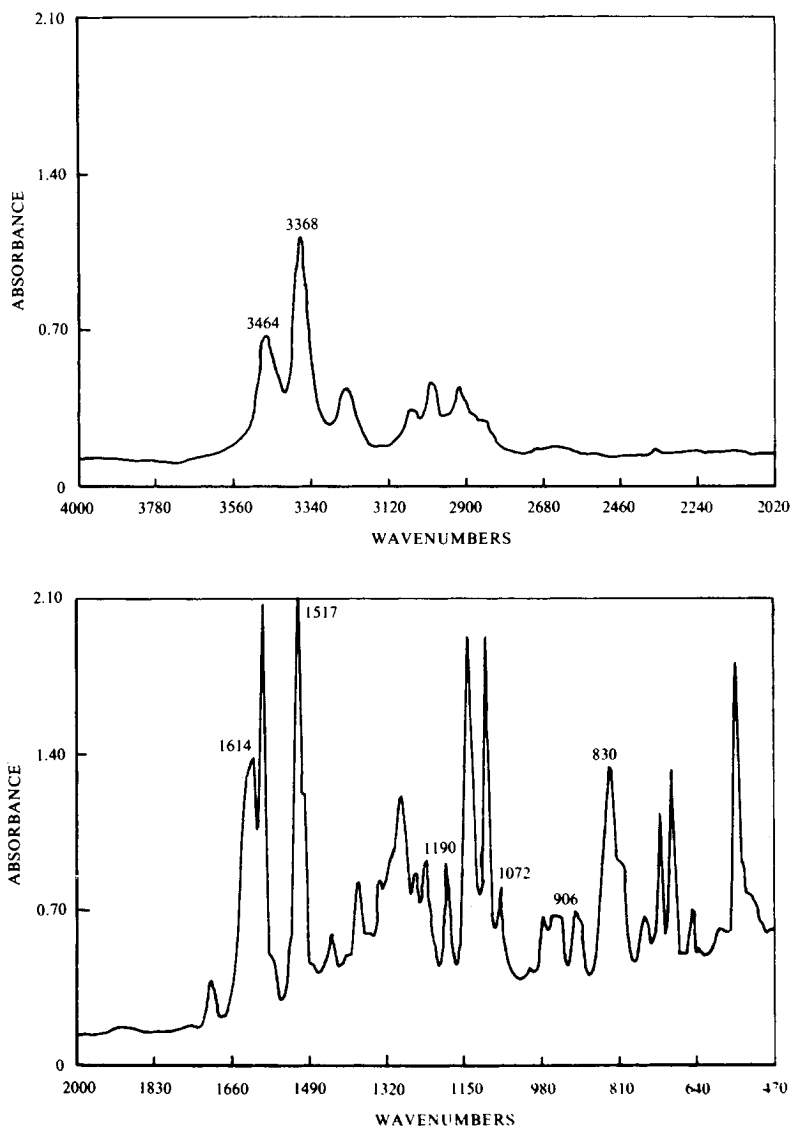


Fig. 6. FTIR spectrum of the mixture TGDDM + DDS + $\text{BF}_3\text{-MEA}$ at room temperature.

at 3507 cm^{-1} and 3409 cm^{-1} , caused by hydroxyl and secondary amine, respectively, become apparent (Fig. 8). In fact, these peaks have been used by other workers studying reactions between TGDDM and DDS.^{10,11} Thus, polymerization of this system can be studied by following the hydroxyl (3507 cm^{-1}), secondary amine (3409 cm^{-1}), ether (1072 cm^{-1}), and epoxide (906 cm^{-1}) bands.

It is interesting to compare the rates of polymerization of TGDDM plus DDS when no catalyst is present, when $\text{BF}_3\text{-MEA}$ is added, and when HBF_4 is added. It has been established that HBF_4 accelerates the homopolymerization of TGDDM. By observing the IR bands previously described it can

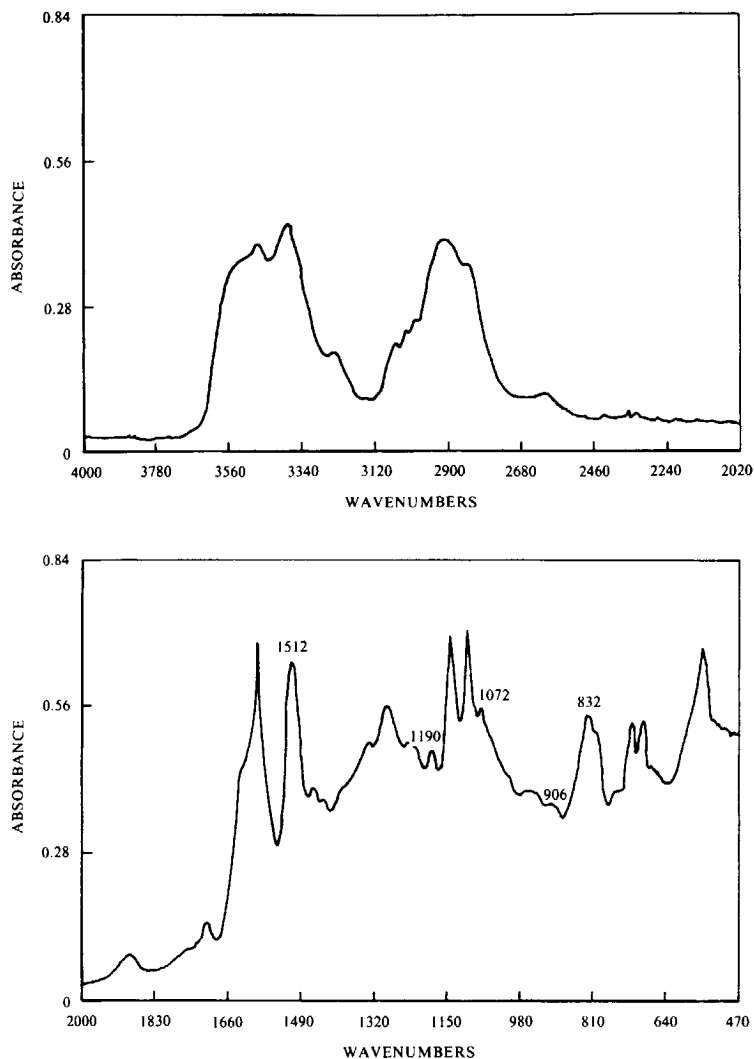


Fig. 7. FTIR spectrum of the mixture TGDDM + DDS + BF_3 -MEA after 30 min at 120°C .

be determined whether HBF_4 also accelerates the polymerization of TGDDM plus DDS.

A comparison of polymerization rates is shown in Figure 9. When no catalyst is present, polymerization at 120°C requires 1 h for completion.

When BF_3 -MEA is present, the polymerization is accelerated. However, after 10 min the polymerization is far from complete. The ^{19}F -NMR of a similar mixture of BF_3 -MEA, TGDDM, and DDS indicated that the BF_3 -MEA is completely hydrolyzed to HBF_4 in the first 5 min. (Because of the low BF_3 -MEA content, 5 min were required to obtain enough scans of the NMR spectrum for an adequate signal-to-noise ratio.) This supports the idea that HBF_4 is acting as the true catalyst in this system.

To further support this idea, it can be seen in Figures 9a-d that HBF_4 accelerates the polymerization of TGDDM plus DDS more effectively than

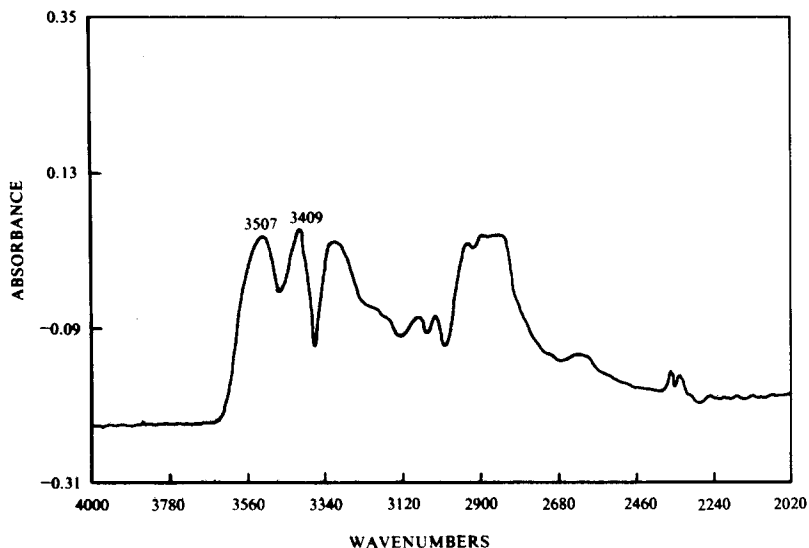


Fig. 8. Difference between FTIR spectra of the TGDDM + DDS = $\text{BF}_3\text{-MEA}$ at room temperature and after 30 min at 120°C . This spectrum shows that the hydroxyl and secondary amine peaks occur at 3507 and 3409, respectively.

$\text{BF}_3\text{-MEA}$. The polymerization is essentially complete within 10 min. These experiments were then repeated at 160°C to determine the effect of temperature on the relative amount of homopolymerization vs. heteropolymerization. As seen in Table I, an increase in temperature causes an increase in the relative amount of heteropolymerization (secondary amine band). HBF_4 seems to cause a preferential increase in homopolymerization (ether band). Thus, the relative amounts of homo- vs. heteropolymerization seems to be controllable by adjusting the temperature or the catalyst (HBF_4) content.

The results reported in these two articles demonstrate that $\text{BF}_3\text{-MEA}$ is not acting as a catalyst in this epoxy resin system. In fact, $\text{BF}_3\text{-MEA}$ is hydrolyzed so fast at temperatures above 80°C , that it probably cannot act as a catalyst in any resin system cured at high temperature. Debates about whether $\text{BF}_3\text{-MEA}$ dissociates or remains intact during polymerization miss the real point. In fact, $\text{BF}_3\text{-MEA}$ is rapidly hydrolyzed to HBF_4 and HBF_3OH . Thus, it is the HBF_4 and/or HBF_3OH which catalyze or accelerate the polymerization.

This conclusion may be very significant to industry. $\text{BF}_3\text{-MEA}$ is a solid at room temperature. It must be quite difficult to blend $\text{BF}_3\text{-MEA}$ uniformly into TGDDM and DDS, or into almost any other resin system. HBF_4 , on the other hand, can be purchased as a 48% solution. HBF_4 can be manufactured by reacting HF with boric acid in a variety of solvents. It should be much easier to uniformly mix an HBF_4 solution into epoxy resins than to mix the $\text{BF}_3\text{-MEA}$ uniformly. Also, HBF_4 is much less expensive than $\text{BF}_3\text{-MEA}$ and its composition has been found to vary very little in different lots. However, the composition of $\text{BF}_3\text{-MEA}$ varies much more in different lots acquired from different vendors.

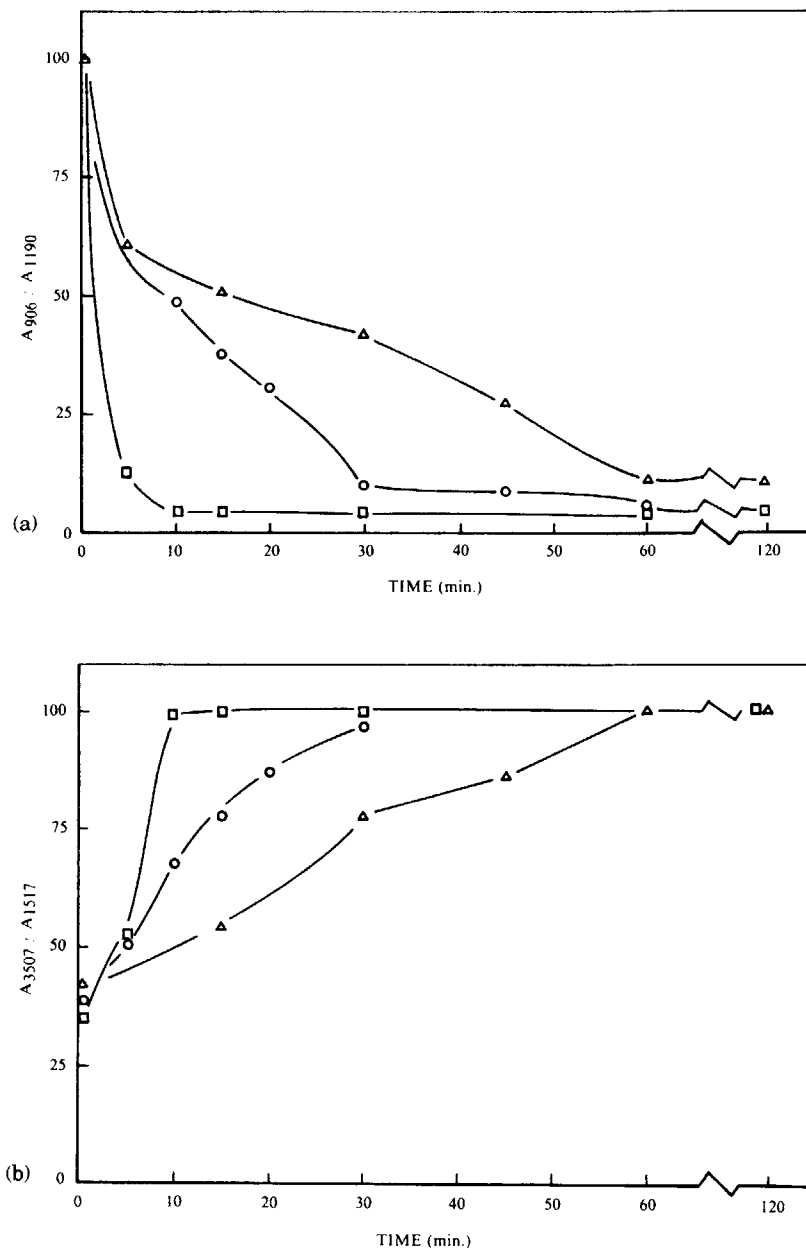


Fig. 9. Polymerization of TGDDM + DDS at 120°C total polymerization. (a) Epoxide absorbance ratios are normalized to 100 at time zero. (b) Hydroxyl absorbance ratios are normalized to 100 at 2 h. (c) Homopolymerization-ether absorbance; absorbance ratios are normalized to 100 at 2 h. (d) Heteropolymerization-secondary amine absorbance; absorbance ratios are normalized to 100 at 2 h. (Δ) No catalyst; (\square) 1% HBF_4 ; (\circ) 1% $\text{BF}_3\text{-MEA}$.

Since $\text{BF}_3\text{-MEA}$ is rapidly converted to HBF_4 , it can be expected that very similar resins could be obtained by using HBF_4 . We have shown that this epoxy resin system is cured faster using 1% HBF_4 than by using 1% $\text{BF}_3\text{-MEA}$. To get equal cure rates, one need only use less HBF_4 .

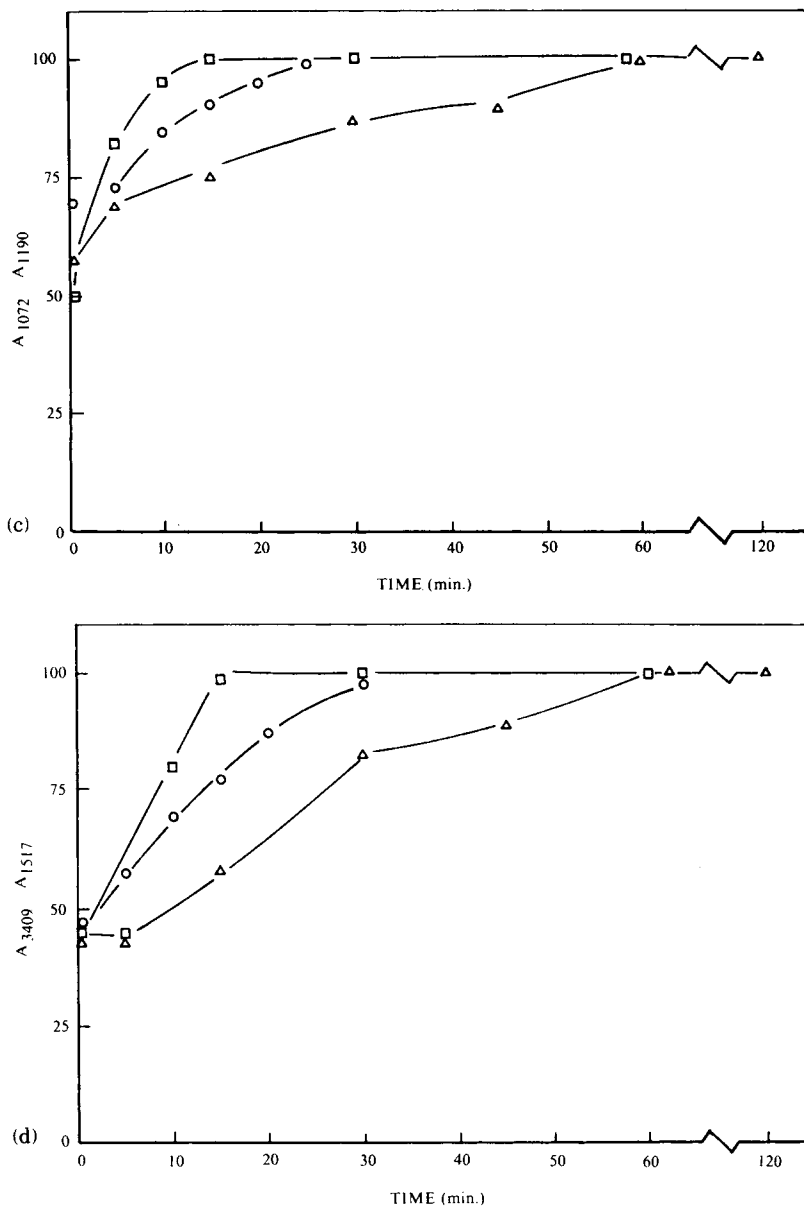


Fig. 9 (Continued from the previous page.)

TABLE I
Degree of Homopolymerization vs. Heteropolymerization

Formulation	Temperature (°C)	Increase in ether band (%)	Increase in secondary amine band (%)
TGDDM+DDS	120	68	121
	160	62	327
TGDDM+DDS+HBF ₄	120	100	125
	160	70	164

It would be useful to cure several different epoxy resins using HBF_4 in place of BF_3 -MEA and test their functional properties (strength, adhesion, etc.).

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