

New Epoxy Resins. III. Application of Fourier Transform IR to Degradation and Interaction Studies of Epoxy Resins and Their Copolymers

C. S. CHEN,* B. J. BULKIN, and E. M. PEARCE, *Polytechnic Institute of New York, Brooklyn, New York 11201*

Synopsis

In the Fourier transform infrared (FT-IR) study, diglycidyl ether of bisphenol A (DGEBA) did not show aldehyde or perester absorption when it was normally cured with trimethoxyboroxine (TMB) under a nitrogen atmosphere. Neither alumina nor gold surfaces would cause oxidation of the system. In air, alumina appeared to accelerate the oxidation when compared to gold. The cure of the epoxy in oxygen appeared to cause increased Claisen rearrangement when compared with the same cure in a nitrogen atmosphere. The DGEBA cured with TMB under air or nitrogen atmospheres showed differences in their degradation patterns. The TMB-cured DGEBA and diglycidyl ether of 9,9-bis(4-hydroxyphenyl) fluorene (DGEBF) copolymer had a higher degree of reaction and lower degradation than was shown by the synthetically generated spectra based on the FT-IR summation of the spectra of the respective homopolymers.

INTRODUCTION

The degradation mechanism is the chemical route describing the deterioration of the polymer. An understanding of the mechanism may lead to approaches for the stabilization of the polymers.

The literature in the field of the thermal degradation and the oxidative thermal degradation of epoxy resins up to 1966 has been reviewed.^{1,2} ESR studies support free radical mechanisms.³⁻⁵ Three important degradation mechanisms have been proposed.⁶⁻⁸ Since then, several workers⁹⁻¹⁸ have studied the thermal degradation of epoxy resins, but most of the literature has concentrated on amine-cured systems in which amine initiated the degradation of epoxy resin through dehydration and bond scission. Radiothermal analysis⁹ has been used to study the relative thermal stability of heat-labile groups in isotopically labeled epoxy resins. Both under oxidative and inert conditions, the thermal stability of the epoxy isopropylidene group is greater than that of the reacted glycidyl groups. Other techniques, such as gas chromatography,^{14,19} mass spectroscopy,²⁰ radiochemical analysis,^{9,14} or their combinations, have been also employed for the degradation study of epoxy resins. From their degradation products and the original polymer structure, several degradation mechanisms are proposed. The degradation of material at high temperature may cause rearrangement of the degradation fragments, secondary decomposition of primary products or even more complicated reactions. Therefore, product analysis may lead to erroneous degradation mechanisms. Infrared spectroscopy has been employed^{10,13} to

* In partial fulfillment of the requirements for the Ph.D. degree in Chemistry at the Polytechnic Institute of New York.

monitor the chemical changes during the degradation process, in order to overcome the difficulties existing in the above methods. But the relatively low sensitivity or the fact that the bands of interest are often masked by the strong absorbance of the major component make the application of the conventional dispersive instruments impossible or, at least, extremely difficult for detecting relatively small changes.

Fourier transform infrared spectroscopy (FT-IR) has been widely accepted as a new powerful tool for analysis due to its rapid-scan capability, increased signal-to-noise ratio, high energy throughput, and computer assisted mathematical manipulations of spectral information. The concepts, elementary theory and instrumentation have been discussed.^{21,22} A description of the FT-IR spectrometer together with the underlying theory and advantages over conventional dispersive spectrometers has been well documented by Griffiths²³ and Koenig.²⁴

FT-IR has been applied to the study of polymeric materials in various fields.²⁴⁻³³ These include analysis formaldehyde composites,²⁸ heat and oxidative degradation of polybutadiene,²⁴ polyacrylonitrile,²⁷ and epoxy resins,³¹ oxidative degradation of poly(ethylene terephthalate),³³ and *trans*-1,4-polychloroprene,³⁰ and stress, elevated-temperature, and moisture effects in epoxy resins.³²

In this study, FT-IR is employed for investigating the thermal degradation of the epoxy polymers, as related to different curing conditions on various metal surfaces. In order to understand the reactions leading to the synergistic effect^{34,35} shown by enhanced char formation in the DGEBA and DGEBF copolymer system, subtraction and addition FT-IR spectral techniques²⁷ are used.

EXPERIMENTAL

Curing Process

The epoxy resin diglycidyl ether of bisphenol A (DGEBA), diglycidyl ether of 9,9-bis(4-hydroxyphenyl) fluorene (DGEBF), or their mixtures with 0.164 eq/eq epoxy resin of trimethoxyboroxine (TMB) were dissolved in acetone which had been dried by K_2CO_3 and distilled at 56°C. The epoxy-TMB solution was cast on a smooth, shining, and clean alumina or gold-coated plate, then put into a desiccator to let the epoxy-TMB coating dry on the surface of the alumina or gold plate. The curing procedure was carried out 135°C for 3 h, 180°C for 3 h, and 218°C for another 3 h, in an air-circulated oven or nitrogen-circulated DSC cell.

Application of FT-IR to Cured Epoxy Resin and Degradation of Epoxy Resins

The FT-IR spectrometer was a Digilab Model FTS-20B. In this study, all spectra were collected at 2 cm^{-1} resolution, with 256 accumulated scans, and computed in double precision word size. Disc and tape were used for the data and program storage.

The sample was contained in air environmental chamber for this study, shown

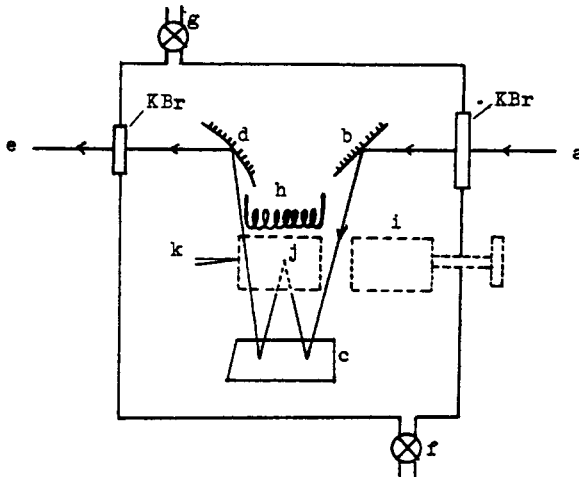


Fig. 1. Diagram of the environmental chamber of FTS IR spectrometer: (a) infrared source; (b,c,d) reflection mirrors; (e) detector; (f,g) gas inlet and outlet valves; (h) microheater; (i) sample plate; (j) blank plate; (k) thermocouple.

schematically in Figure 1. The infrared beam from the source was reflected and passed through the sample on the metal plate, then to the detector. The temperature of the heater was controlled by a Variac and measured by a thermocouple connected to a potentiometer. The environment of this chamber was controlled by evacuation for the thermodegradation study. The difference spectrum was obtained by subtracting the two spectra of interest. The synthetic spectrum was obtained by adding the two spectra.

The cured-epoxy-coated on alumina or gold plate under inert (N_2) or oxidative (air) atmosphere was put beneath the microheater in the sample environmental chamber of the FT-IR spectrometer under the evacuated atmosphere. Degradations at $300^\circ C$ were followed by collecting spectra of the sample every 20 min. The chamber acts as a gas cell. When the sample is in place, the spectrum of

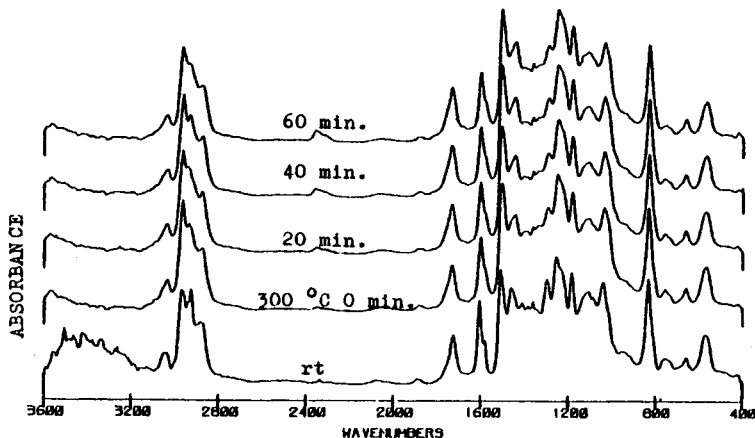


Fig. 2. IR spectra of cured DGEBA on Al surface under air atmosphere at room temperature and during degradation at $300^\circ C$ (MXY = 290, MNY = 10).

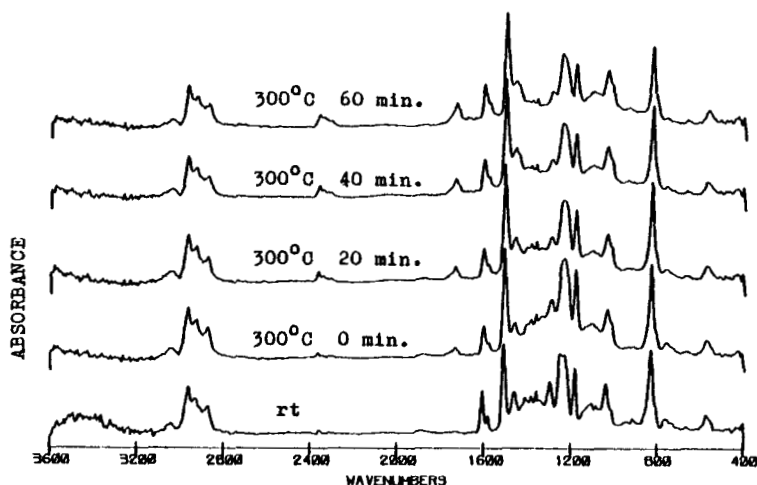


Fig. 3. IR spectra of cured DGEBA on Al surface under N_2 atmosphere at room temperature and during degradation (MXY = 150, MNY = -10).

both volatile and residual products is obtained. The spectra of the gas products were obtained by moving the slide and changing the coated plate to a blank plate. The difference between these yields the spectrum of the residuals.

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy (FT-IR) had been applied to the study of the degradation of epoxy resins.³¹ In that study, the spectra both before and after degradation always showed absorption at 1732 cm^{-1} and 1765 cm^{-1} . These had been assigned to the stretching of the carbonyl groups in aldehyde (1732 cm^{-1}) and perester (1765 cm^{-1}), assumed due to the isomerization of epoxy group and the subsequent oxidation of the aldehyde during the curing process.³¹

Figure 2 shows the IR spectra of the TMB-cured DGEBA on an alumina surface under an air atmosphere (curing cycle 135°C , 3 h, 180°C , 3 h, and 218°C ,

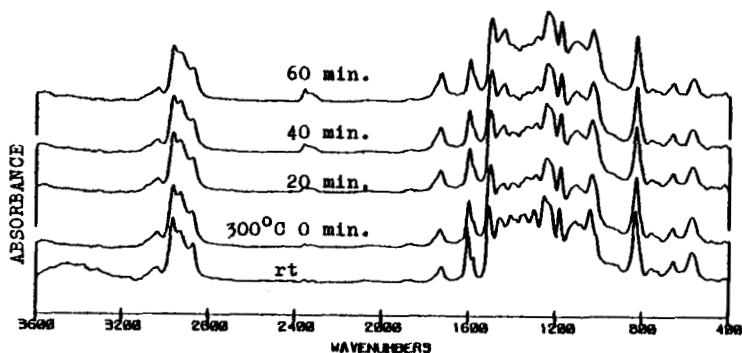


Fig. 4. IR spectra of cured DGEBA on Au surface under air atmosphere at room temperature and during degradation at 300°C (MXY = 360, MNY = -30).

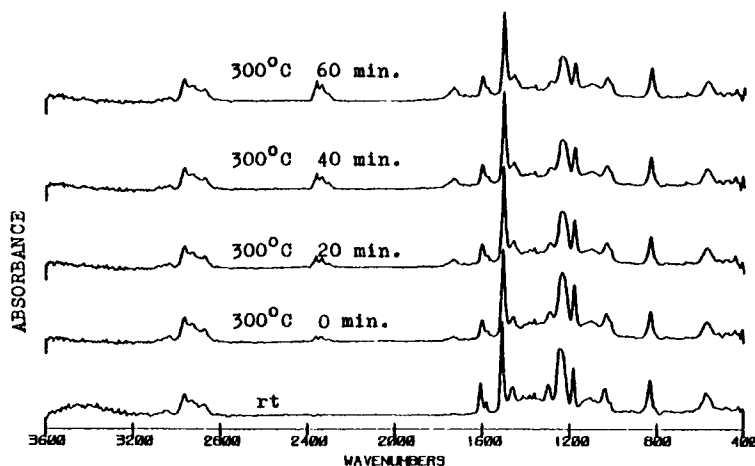
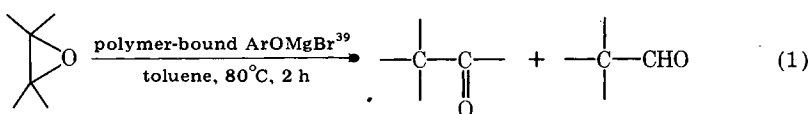


Fig. 5. IR spectra of cured DGEBA on Au surface under N_2 atmosphere before and after thermodegradation at 300°C (MXY = 150, MNV = -10).

another 3 h) before and after thermodegradation at 300°C in vacuum. At room temperature, the spectrum showed broad —OH absorption ($3200\text{--}3600\text{ cm}^{-1}$), which might indicate inter- and intramolecular hydrogen bonding and/or adsorbed water. As the temperature was increased, the intensity of this absorption decreased and it shifted to higher frequency ($3440\text{--}3640\text{ cm}^{-1}$). This might indicate dehydration either through reaction or loss of adsorbed water. There was also less hydrogen bonding of the remaining OH. Water is a major product of the degradation of epoxy resin,^{8,14,36} and the extent of both inter- and intramolecular hydrogen bonding is temperature-dependent.³⁷ The absorptions at 1732 cm^{-1} (aldehyde) and 2345 cm^{-1} (carbon dioxide) increased. The isomerization of the epoxide group to aldehyde might occur at 300°C .³⁸ This rearrangement could also occur through acid–base catalysis—e.g.,



The aldehyde in the presence of methoxide anion might be converted to an ester (Tischtschenko–Claisen aldehyde \rightarrow ester hydride anionotropy),⁴⁰ followed by hydrolysis to acid and pyrolysis to alkane and carbon dioxide or to ketone, water, and carbon dioxide.

The IR spectra of the TMB-cured DGEBA were determined as thin films on an alumina surface with the same curing cycle, but under nitrogen atmosphere, before and after thermodegradation at 300°C under vacuum (Fig. 3). At room temperature, the original spectrum showed broad —OH absorption, interpreted as in the previous spectra (Fig. 2). However, there was no absorption at 1732 cm^{-1} . This indicates that the 1732 cm^{-1} absorption (Fig. 2 and in the study of Lin et al.³¹) was mainly due to the oxidation of the epoxy resin. When the temperature was increased, the absorption at 1732 cm^{-1} (aldehyde) and 2345 cm^{-1} (carbon dioxide) were increased for the same reason as above.

To investigate possible effects of alumina on the reactions, DGEBA (TMB)

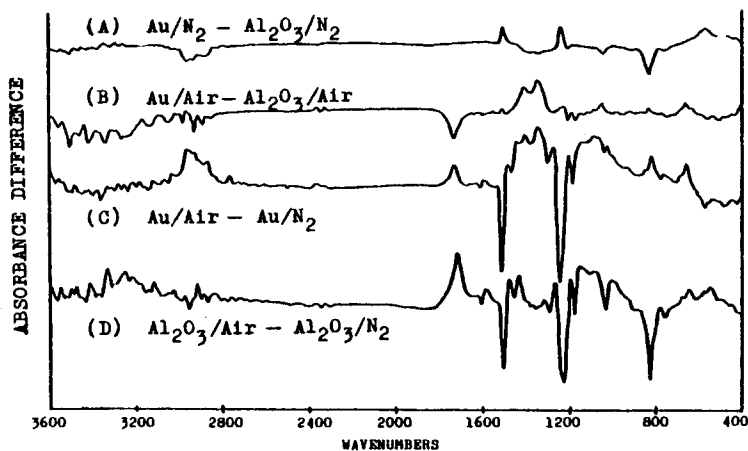


Fig. 6. Difference spectra of cured DGEBA, due to different metal surfaces or curing conditions.

was cured on a gold surface under air atmosphere (Fig. 4). It showed qualitatively similar spectral changes as the same epoxy resin cured on an alumina surface under air atmosphere (Fig. 2). The TMB-cured DGEBA on a gold surface under nitrogen atmosphere (Fig. 5) showed qualitatively similar changes as the same epoxy resin cured on an alumina surface under nitrogen atmosphere (Fig. 3). Thus the oxidation-producing carbonyl groups appeared due to atmosphere rather than surface.

The difference spectra of undegraded cured DGEBA, comparing different metal surfaces or curing conditions, were determined (Fig. 6). From these difference spectra, it appeared that the effect of atmosphere was greater than the metal effect, since the difference of the same epoxy resin cured on the same metal

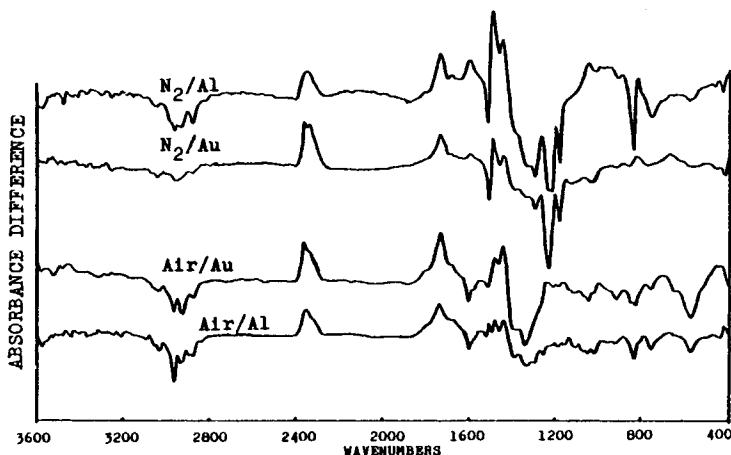


Fig. 7. IR difference spectra of cured DGEBA, before and after 300°C, 60 min degraded, on different metal surfaces or curing condition.

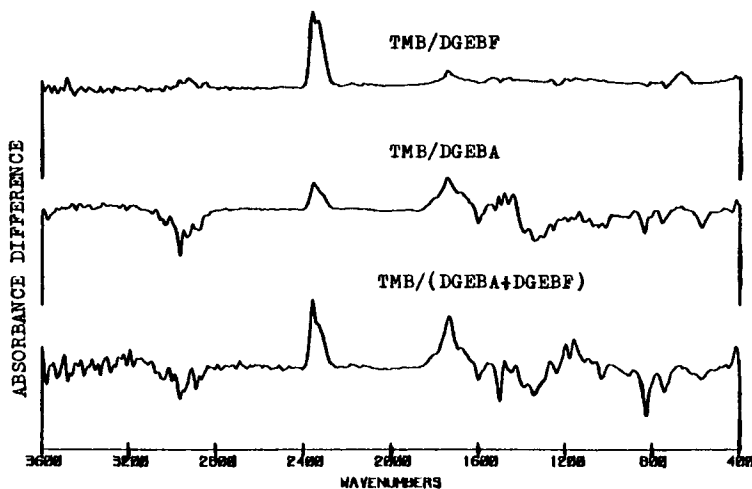


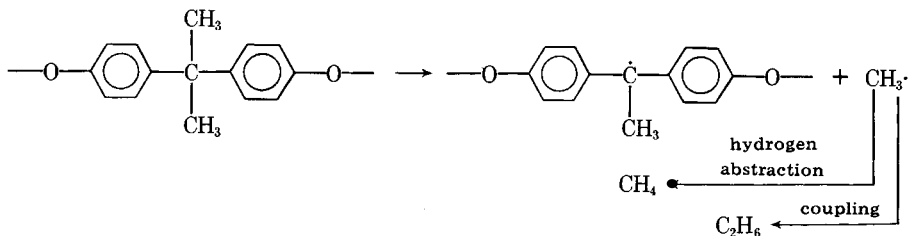
Fig. 8. IR difference spectra of cured copolymer and homopolymers before and after thermodegradation at 300°C: 300°C 60 min–300°C 0 min.

but cured under a different atmosphere was greater than the difference of the same epoxy resin cured on different metals but under the same atmosphere. Alumina or gold showed similar results with the epoxy resin under a nitrogen atmosphere during cure, and thus no unusual catalytic effects could be related to the metal surface. However, alumina caused more oxidation of epoxy resin in an air atmosphere during cure than the effect caused by gold.

The degradation of these cured epoxy resins (Fig. 7), again showed that atmosphere effect was greater than that of the metal. If epoxy resins were cured under the same (nitrogen or air) atmosphere, they would be degraded through similar reactions independent of alumina or gold surface. No matter which metal surface was used, with curing under air or nitrogen, these cured epoxy resins always showed an increase in the 1732 cm^{-1} absorption and the release of carbon dioxide during thermodegradation. If epoxy resins were cured on the same metal surface, but under different atmospheres, then these epoxy resins would, in part, be degraded through different mechanisms.

IR and difference spectra of cured DGEBA before and after 300°C, 60 min degradation (Fig. 8) showed an absorption increase at $2270\text{--}2390\text{ cm}^{-1}$, indicating CO_2 as a pyrolysis product. The absorption at $1870\text{--}1620\text{ cm}^{-1}$ was also increased, indicating increasing acid, ester, or aldehyde and vinyl groups, since the epoxy oxirane ring could be isomerized to aldehyde at this temperature³⁸ and then catalyzed by methoxide anion to ester by the Tischtschenko reaction, followed by hydrolysis to the acid. Vinyl groups were increased, since dehydration of the epoxy system would create vinyl group,¹⁸ and this was a major process for the degradation of epoxy resin. 1425 cm^{-1} absorption was increased indicating possible Claisen rearrangements occurred during pyrolysis of the epoxy resin, since the 1601 cm^{-1} and 827 cm^{-1} and 1256 cm^{-1} absorptions were also decreased indicating the decrease of *p*-substituted aromatic groups and ether groups, but the 1425 cm^{-1} absorption increased at the same time indicating that 1,2,4 trisubstituted benzene increased.

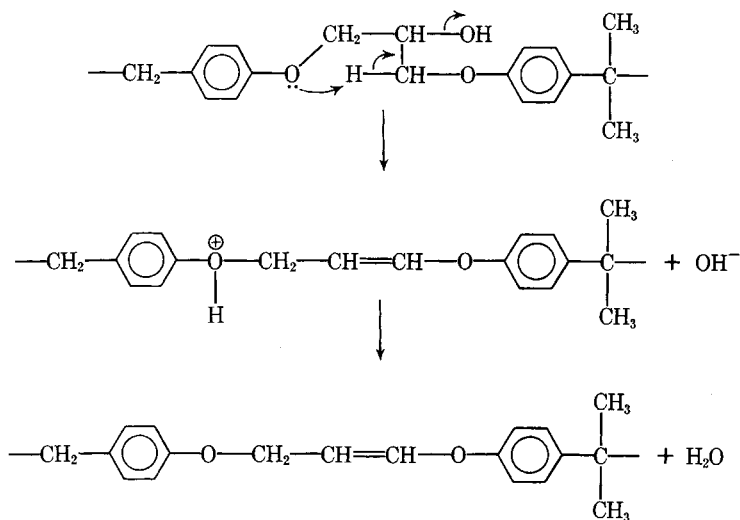
The decreased absorption at 2966 cm^{-1} might indicate pyrolysis of the isopropylidene group



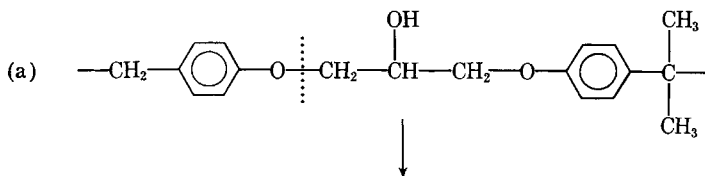
Lin et al.³¹ had stated that a band at 1184 cm^{-1} was due to C—CH₃ stretching shifted to 1170 cm^{-1} during the isopropylidene group degradation. We did not observe this shift. A band at 1178 cm^{-1} decreased gradually. This was assigned to in plane aromatic C—H bending, which would decrease after degradation by Claisen rearrangement or alkyl reaction with the aromatic ring. The absorption at 916 cm^{-1} was decreased, indicating that the oxirane ring was isomerized to aldehyde and further catalyzed by methoxide anion to ester.

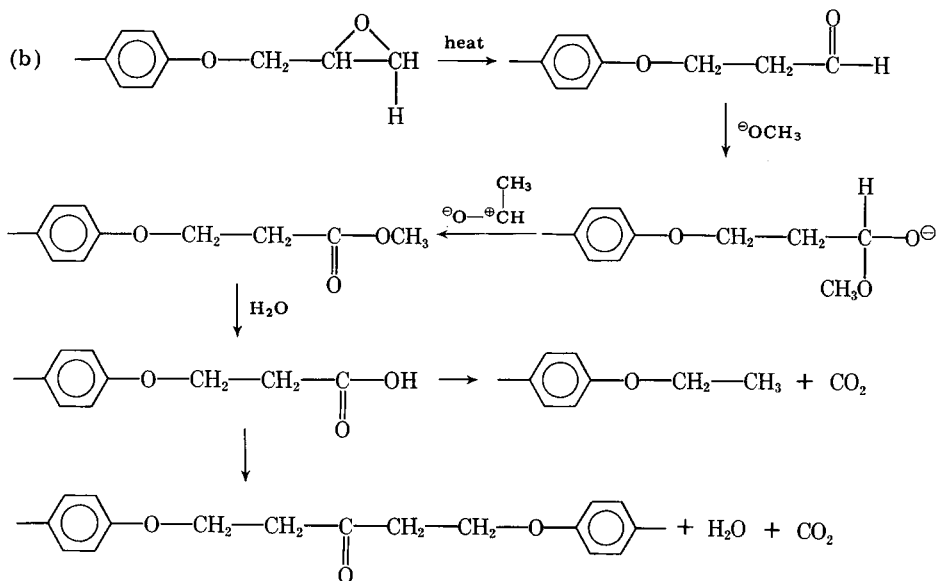
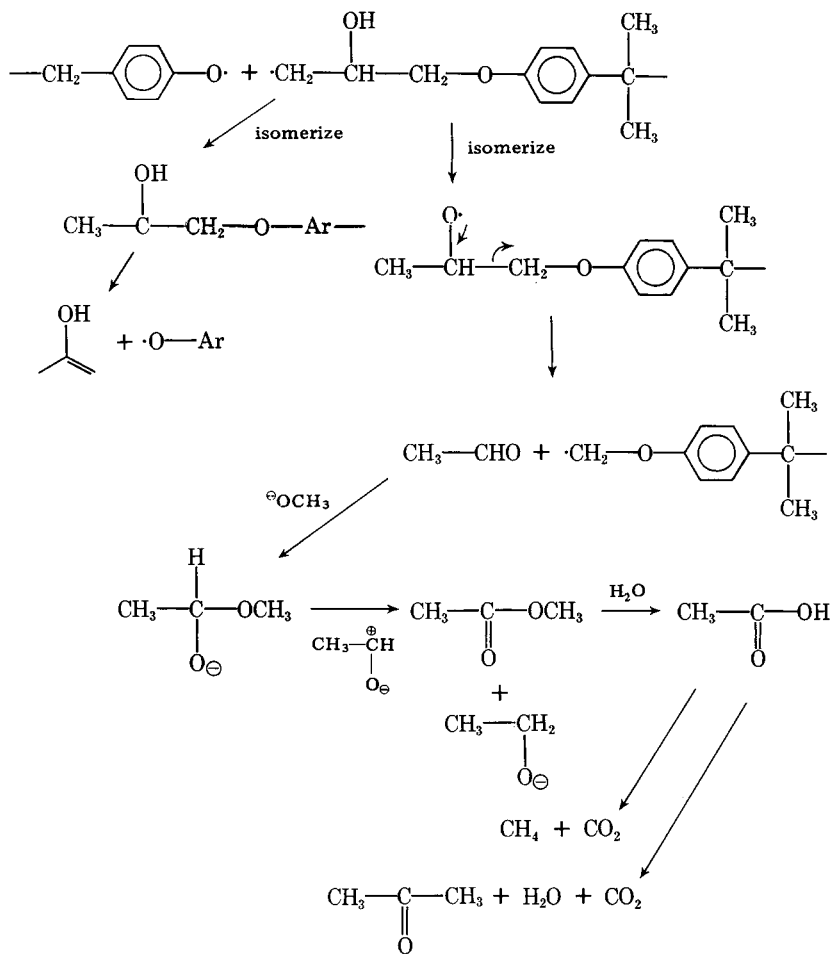
The proposed thermodegradation mechanisms for the TMB-cured DGEBA were as follows:

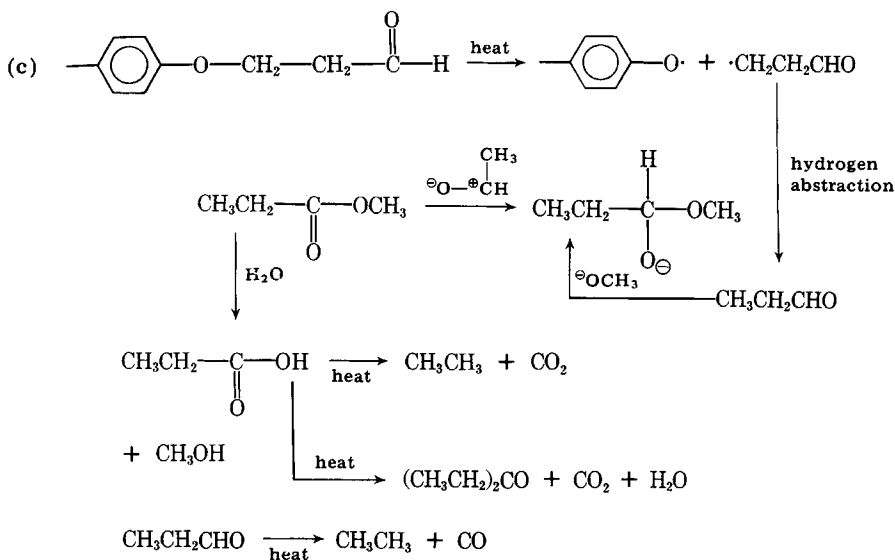
(1) Dehydration



(2) Formation of carbon dioxide, alkane, ketone, water, methanol, and carbon monoxide:



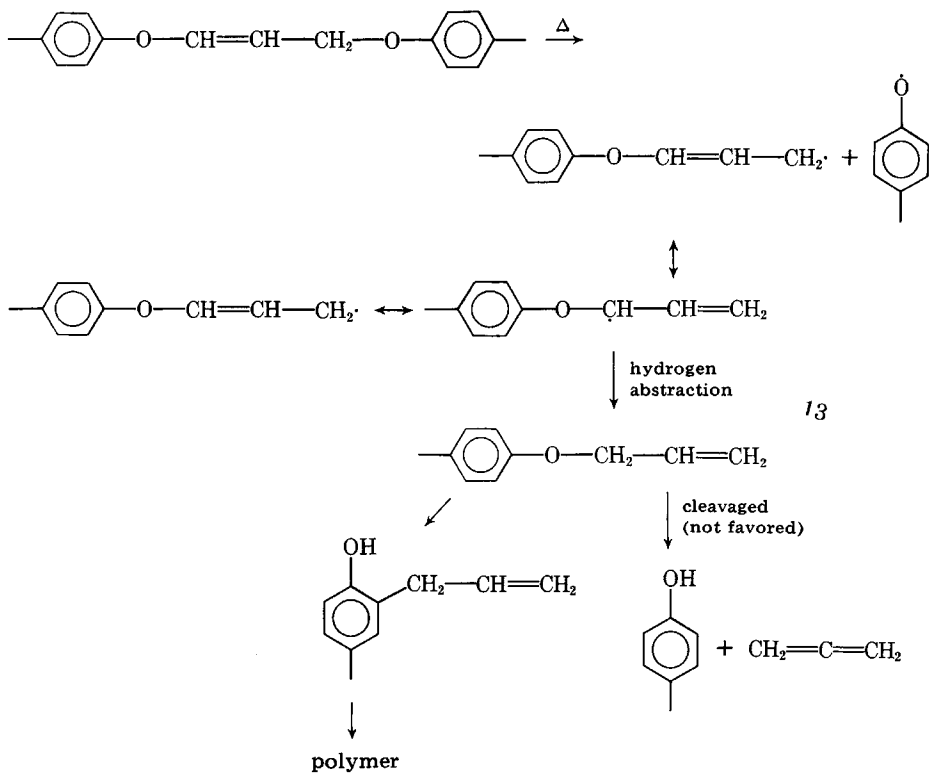




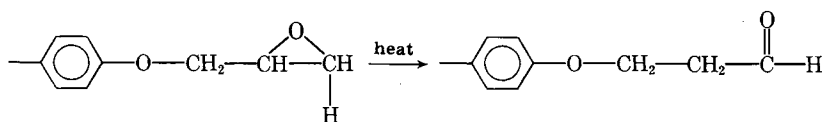
(3) The formation of aldehyde, ester, or acid shown in residue could be the same as in (2).

(4) Trace amount carbon monoxide formation could be seen in (2).

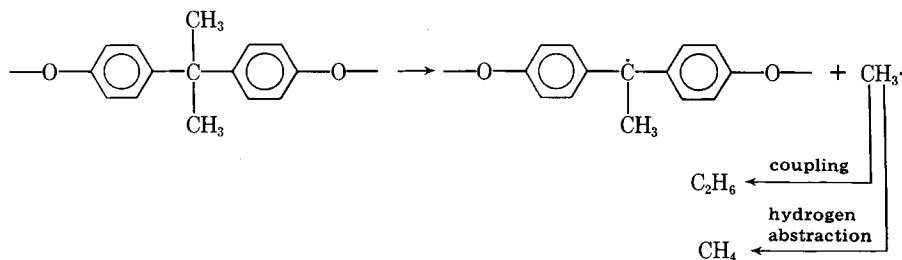
(5) Claisen rearrangement:



(6) Oxirane group decreased:



(7) Loss of methyl:



The char residue at 700°C as a function of mole fraction of DGEBF in the copolymers of DGEBF and DGEBA indicated a synergistic effect for DGEBF with DGEBA in regard to char formation for the TMB curing system.³⁴ Lin et al.³⁴ had found the gel fractions of TMB-cured DGEBA and TMB-cured DGEBF were 84.5% and 33.3%; however, the gel fraction for TMB-cured copolymer (22.9 mol % of DGEBF and 77.1 mol % of DGEBA) was 91.0%. This indicated that this copolymer had a higher crosslinking density than the weighted average one would obtain from the homopolymers.

The IR difference spectra of the TMB-cured copolymer and their respective homopolymers, before and after thermodegradation, are shown in Figure 8. For the copolymer system, the absorptions of 1601 cm^{-1} , 1502 cm^{-1} , 1240 cm^{-1} , and 827 cm^{-1} decreased during degradation. For the DGEBA and DGEBF homopolymer systems, degradation caused the absorptions at 1601 cm^{-1} , 1256 cm^{-1} , and 827 cm^{-1} and 1502 cm^{-1} , 1240 cm^{-1} , and 827 cm^{-1} to decrease.

The IR and difference spectra of cured copolymer and the weighted sum of the cured homopolymer of DGEBA and DGEBF at room temperature (Fig. 9) showed that the copolymer had stronger absorptions at 1601 cm^{-1} , 1502 cm^{-1} , and 827 cm^{-1} . Levy et al.³² had found that the IR absorptions of 1514 cm^{-1} and 823 cm^{-1} would be decreased as DDS-cured tetraglycidyl diamine-diphenylmethane (TGDDM) further polymerized. However, when this epoxy degraded, then these two IR bands increased. This likely indicates that the copolymer had a higher degree of polymerization as previously found by Lin et al.⁴¹ through their gel fraction study.

The thermal stability (measured by TGA) of the sum of homopolymer of TMB-cured DGEBA and TMB-cured DGEBF was worse than that of the corresponding copolymer.³⁴ FT-IR (Fig. 10) showed a similar result to the TGA study. The copolymer showed less pyrolyzed water (1325–2000 cm^{-1}) and carbon dioxide (667 cm^{-1}), products previously reported by Patterson-Jones¹⁸ for the pyrolysis of epoxy resin. Thus the FT-IR study indicated that the copolymer was more thermally stable than the averaged sum based on the homopolymers.

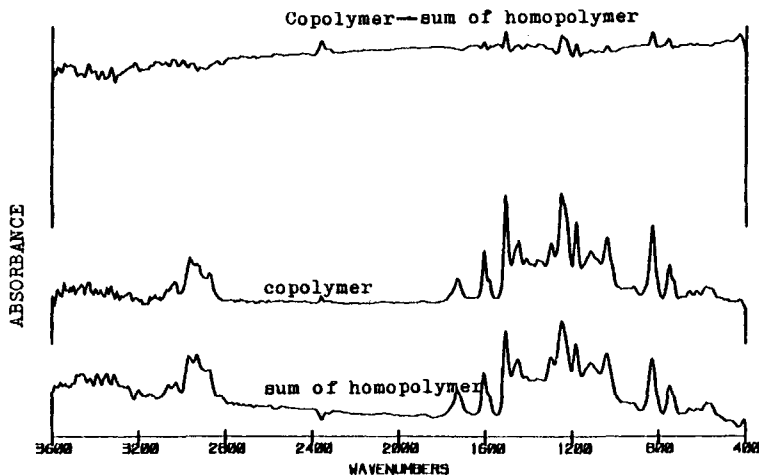


Fig. 9. IR and difference spectra of cured copolymer and sum of cured homopolymer DGEBA and DGEBF at room temperature (MXY = 260, MNY = 30).

The gaseous products of pyrolysis for the cured copolymer and homopolymers of TMB-cured DGEBA and DGEBF were obtained and in the environmental chamber by FT-IR (Fig. 11). Methane and ethane are seen in the 2840–3000 cm^{-1} region, carbon dioxide was seen in the 2270–2390 cm^{-1} region, the 2070–2210 cm^{-1} absorption indicate a small amount of carbon monoxide, and the bands at 1320–2000 cm^{-1} indicated water vapor. Methyl acetate, methyl propionate, or a similar ester were probably among the gaseous products. Figure 11 shows absorptions at 1030, 1088, and 1260 cm^{-1} , which were characteristic of these esters. The C=O stretching absorption at 1740 cm^{-1} was also present though partially hidden by water absorption bands. The band at 667 cm^{-1} is from

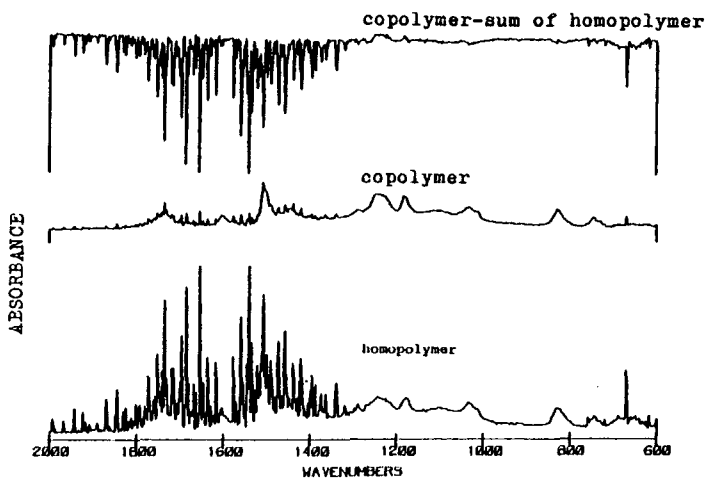


Fig. 10. IR and difference spectra of cured copolymer and sum of homopolymer of DGEBA and DGEBF at 300°C, 60 min (MXY = 490, MNY = 0).

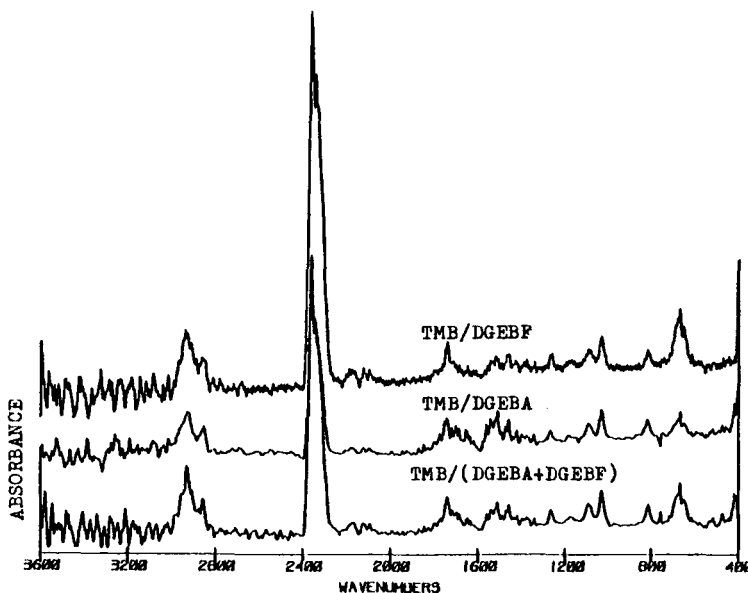
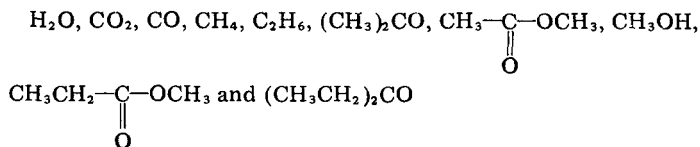


Fig. 11. IR spectra of gaseous products of cured copolymer and homopolymers of DGEBA and DGEBF (MX_Y = 40, MNY = -20).

carbon dioxide. Bands arising from volatile aldehydes or ketones are partially masked by the strong absorbance of water.

CONCLUSION

In the FT-IR study, DGEBA did not show aldehyde or perester absorption when it was cured with TMB under a nitrogen atmosphere. Neither alumina nor gold would cause oxidation of the system. In air, alumina did appear to accelerate the oxidation when compared to gold. The cure of the epoxy in oxygen appeared to cause more Claisen rearrangement than the cure in a nitrogen atmosphere. The DGEBA-cured with TMB under air or nitrogen atmosphere showed differences in their degradation patterns.



appeared to be among the gaseous products which occurred during the thermodegradation of the TMB cured epoxy resin. (DGEBA AND DGEBF).

The Tischtschenko reaction⁴⁰ might account for the CO₂ formation whereas the Claisen rearrangement might explain the decrease of the absorptions at 1601, 1256, and 827 cm⁻¹ and the increase of the absorption at 1425 cm⁻¹ during the thermodegradation of epoxy resin.

The TMB-cured DGEBA and DGEBF copolymer had a higher degree of reaction and lower degradation than was shown by the synthetically generated

spectra based on the FT-IR summation of the respective homopolymer systems.

The authors acknowledge support in part by the NASA Ames Research Center, Moffett Field, Calif., under Grant No. NSG-2147.

References

1. D. P. Bishop and D. A. Smith, *Ind. Eng. Chem.*, **59**(8), 32 (1967).
2. R. T. Conley, "Thermosetting Resins," in *Thermal Stability of Polymers*, R. T. Conley, Ed., Marcel Dekker, New York, 1970, Vol. 1, Chap. 11, p. 507.
3. P. L. Jain, *J. Polym. Sci.*, **31**, 210 (1958).
4. M. B. Neiman, B. M. Kovarskaya, A. S. Strizhkova, I. I. Levanotoskaya, and M. S. Akutin, *Dokl. Akad. Sci. SSSR*, **135**, 1419 (1960).
5. D. W. Ovenall, *Polym. Lett.*, **1**, 37 (1963).
6. M. B. Neiman, B. M. Kovarskaya, L. I. Golubenkova, A. S. Strizhkova, I. I. Levantorskaya, and M. S. Akutin, *J. Polym. Sci.*, **56**, 383 (1962).
7. H. C. Anderson, *J. Appl. Polym. Sci.*, **6**, 484 (1962).
8. L. H. Lee, *J. Polym. Sci.*, *A-1*, **3**, 859 (1965).
9. D. O. Bowen, *Mod. Plast.*, **44** (Aug.), 127 (1967).
10. M. A. Keeman and D. A. Smith, *J. Appl. Polym. Sci.*, **11**, 1009 (1967).
11. J. C. Patterson-Jones and D. A. Smith, *J. Appl. Polym. Sci.*, **12**, 1601 (1968).
12. A. S. Vlastaras, *Vac. Microbalance Tech.*, **8**, 229 (1969).
13. E. Cerceo, *Ind. Eng. Chem., Prod. Res. Dev.*, **9**(1), 96 (1970).
14. D. P. Bishop and D. A. Smith, *J. Appl. Polym. Sci.*, **14**, 205 (1970).
15. J. C. Patterson-Jones, V. A. Percy, R. G. F. Giles, and A. M. Stephen, *J. Appl. Polym. Sci.*, **17**, 1867 (1973).
16. J. C. Patterson Jones, V. A. Percy, R. G. F. Giles, and A. M. Stephen, *J. Appl. Polym. Sci.*, **17**, 1877 (1973).
17. P. S. Theocaris, S. A. Paipetis, and J. M. Tsangaris, *Polymer*, **15**, 441 (1974).
18. J. C. Patterson-Jones, *J. Appl. Polym. Sci.*, **19**, 1539 (1975).
19. J. M. Stuart and D. A. Smith, *J. Appl. Polym. Sci.*, **9**, 3195 (1965).
20. L.-H. Lee, *J. Appl. Polym. Sci.*, **9**, 1981 (1965).
21. E. D. Becker and T. C. Farrar, *Science*, **178**, 361 (1972).
22. R. J. Bell, *Introductory Fourier Transform Spectroscopy*, Academic, New York, 1972.
23. P. R. Griffiths, *Chemical Infrared Fourier Transform Spectroscopy*, Wiley, New York, 1975.
24. J. L. Koenig, *Appl. Spectrosc.*, **29**, 293 (1975).
25. M. M. Coleman, *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.*, **17**(2), 732 (1976).
26. M. M. Coleman and P. C. Painter, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C16**(2), 197-313 (1978).
27. M. M. Coleman and P. E. Painter, "Fourier Transform Infrared Spectra of Macromolecules," in *Applications of Polymer Spectroscopy*, E. G. Brame, Jr., Ed., Academic, New York, 1978, Chap. 10.
28. S. A. Liebman, D. H. Ahlstrom, and P. R. Griffiths, *Appl. Spectrosc.*, **30**, 355 (1976).
29. H. W. Siesler, "Characterization of Chemical and Physical Changes of Polymer Structure by Rapid-Scanning Fourier—Transform IR (FTIR) Spectroscopy," in *Proceedings of the 5th European Symposium on Polymer Spectroscopy*, D. O. Hummel, Ed., Verlag Chemie, Weinheim, 1978.
30. M. M. Coleman and P. C. Painter, "Computer Assisted Vibration Spectroscopy," in *Proceedings of the 5th European Symposium on Polymer Spectroscopy*, D. O. Hummel, Ed., Verlag Chemie, Weinheim, 1978.
31. S. C. Lin, B. J. Bulkin, and E. M. Pearce, *J. Polym. Sci.*, *A-1*, **17**, 3121 (1979).
32. R. L. Levy, D. L. Panter, and C. J. Summers, *J. Appl. Polym. Sci.*, **24**, 1643 (1979).
33. M. Y. Ng, M.S. thesis, Polytechnic Institute of New York, June 1979.
34. S. C. Lin and E. M. Pearce, *J. Polym. Sci.*, *A-1*, **17**, 3095 (1979).
35. D. A. Kourtidis and J. A. Parker, 11th National SAMPE Technical Conference, 1979, p. 551.

36. E. C. Leisegang, A. M. Stephen, and J. C. Patterson-Jones, *J. Appl. Polym. Sci.*, **14**, 1961 (1970).
37. R. M. Silverstein and G. C. Bassler, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 1967, Chap. 3.
38. H. C. Anderson, *Anal. Chem.*, **32**, 1592 (1960).
39. A. Pochini and R. Ungaro, *IUPAC Int. Symp. Macromol., Prepr.* **4** (Part 2), 170 (1980).
40. H. Krauch and W. Kunz, *Organic Name Reactions*, Translated from the second revised German edition (with Addendum) by J. M. Harkin, Wiley, New York, 1964, p. 453.

Received April 22, 1982

Accepted October 12, 1982