Pergamon

Eur. Polym. J. Vol. 30, No. 3, pp. 361–368, 1994
Copyright © 1994 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0014-3057/94 $6.00 + 0.00

STRUCTURAL INVESTIGATION OF EPOXY AMINE NETWORKS BY MID- AND NEAR-INFRARED SPECTROSCOPY

VERONIKA STREHMEL[1]* and TOM SCHERZER[2]

[1]Technical University Merseburg, Department of Chemistry, Institute of Macromolecular Chemistry and
[2]Department of Physics, Institute of Experimental Physics Geusaer Straße, 06217 Merseburg, Germany

(Received 4 February 1993; accepted 27 May 1993)

Abstract—The effects of epoxy amine ratio and accelerator concentration on the chemical structure of networks based on the diglycidylether of bisphenol A cured with 4,4′-diaminodiphenylmethane using imidazole as accelerator were investigated. Mid-i.r. spectra of the networks give qualitative information about the chemical structure of the networks. From near-i.r. spectra the content of residual epoxy groups and the concentration of different amine structures in the networks were calculated. For quantitative analysis of the primary amine concentration in the networks a calibration using a model system was necessary. Therefore a mixture of anisole, 1-aminophenyl-3-phenoxy-propan-2-ol and aniline was used.

INTRODUCTION

Epoxy resins cured with aromatic amines are used as matrix materials in the production of composites [1]. Many factors are responsible for the properties of the resulting epoxy network. One of them is the chemical structure of the network which is influenced by the reactions that occur during the curing process.

Infrared spectroscopy was used for the investigation of the curing process of epoxy resins [2–7] and the structure of epoxy networks [8–13]. In more detailed studies FTIR spectroscopy was applied in addition to solid state ^{13}C-NMR spectroscopy with cross polarization magic angle spinning (CP MAS) for structural analysis of epoxy-amine networks [10, 14]. Infrared spectroscopy is not restricted to the mid-i.r. (MIR) region (400–4000 cm^{-1}). The curing process was followed in the near-i.r. (NIR) (4000–10,000 cm^{-1}) [6, 15, 18] as well and the network structure was determined [18] in this region. Its advantage consists in a considerably simplified spectrum compared with the mid-i.r. region because only overtones and combination bands of hydrogen containing groups (C—H, O—H, N—H) exhibit appreciable intensities in the near-i.r. region.

During amine curing of epoxy resins the primary amino group reacts with the epoxy group forming a secondary amino group in a first step and a tertiary amino group in the second step as well as hydroxylic groups [19]. The influence of an accelerator on the products formed in the epoxy networks has already been studied by FTIR spectroscopy using the diffuse reflection (DRIFT) method [12, 13]. Only a qualitative information about the structure of the networks can be obtained from these spectra because of a strong dependence of band shape and intensity, for example, on the particle size, packing density, refractive index and specular reflection. Relative standard deviations as high as 15% were obtained investigating composites [11]. Therefore, the aim of the NIR spectroscopical investigation is a quantitative analysis of the functional group content in the networks.

EXPERIMENTAL PROCEDURES

Diglycidylether of bisphenol A (DGEBA) was recrystallized from an acetone–methanol mixture with an acetone content of 20 vol% (m.p. 44°C; epoxide equivalent determined by titration: 5.878 mmol g^{-1} = 99.9% of the theoretical value) [20]. 4,4′-Diaminodiphenylmethane (DDM) was recrystallized from a 50% ethanol solution using activated carbon (m.p. 89°C) [21]. Imidazole was recrystallized from benzene containing 1.5% by volume ethanol (m.p. 90°C) [22].

Anisole was distilled $K_p = 154$°C. Aniline was distilled twice *in vacuo* using a Vigreux column $K_p(5\ \text{Torr}) = 80$°C.

1-Aminophenyl-3-phenoxypropan-2-ol was synthesized from aniline and phenylglycidylether. 3 mol aniline and 0.3 mol phenylglycidylether were stirred at 70°C for 4 hr. After cooling, the unconverted aniline was distilled *in vacuo*. The residue from distillation was dissolved in a chloroform–methanol mixture (30:70% by volume). This mixture was dropped into cold hexane. The 1-aminophenyl-3-phenoxypropan-2-ol was fritted. Then it was washed with hexane and dried. After recrystallization from a chloroform–methanol mixture (30:70% by volume) the product was obtained in 47% yield with m.p. of 60–61°C (m.p. 57°C [23]). Epoxy networks were prepared from the DGEBA and DDM ($r = 2[NH_2]_0/[\text{Epoxide}]_0 = 2.0$; 1.0 and 0.33) without an accelerator or in the presence of different amounts of imidazole (0.1–2.5 mol% relative to epoxy groups). The components were mixed at 70°C for 5 min, degassed at the same temperature for 15 min and cured in a preheated mould at 120°C for 5 hr.

---

*To whom all correspondence should be addressed at: Department of Chemical Engineering, Stauffer Building III, Stanford University, Stanford, CA 94305-5025, U.S.A.

NIR spectroscopy

Near-i.r. spectra from 4400 to 10,000 cm^{-1} (2270–1000 nm) were obtained using a Bruker IFS 88 Fourier transform spectrometer equipped with a tungsten source, a silicon-coated calcium fluoride beamsplitter and an InAs detector operating at 77 K. 32 scans were collected at 2 cm^{-1} resolution. NIR spectra were normalized to the aromatic C—H combination band at 5988 cm^{-1} (1670 nm). For calibration measurements using a model system a glass cell with an optical pathlength of 2 mm was employed. The cured samples were measured as specimens of 1 mm thickness.

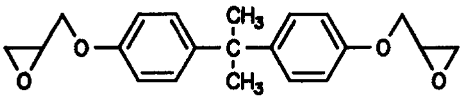
MIR spectroscopy

Spectra in the MIR region (400–4000 cm^{-1}) were recorded using a Bruker IFS 66 spectrometer equipped with a Globar and a DTGS detector. The samples were powdered and mixed with potassium bromide. For DRIFT spectra 100 scans were coadded at 2 cm^{-1} resolution. The band at 1182 cm^{-1} assigned to an in-plane deformation vibration of the para-disubstituted benzene ring was used as reference peak.

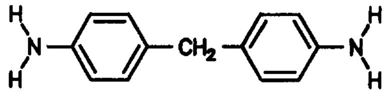
RESULTS AND DISCUSSION

NIR spectral analysis

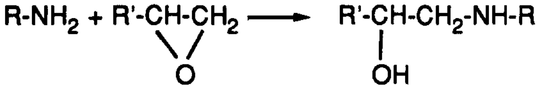
The reaction of DGEBA (1) with DDM (2) can be described by the following equations:



1

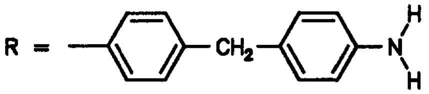


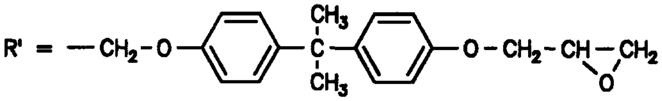
2

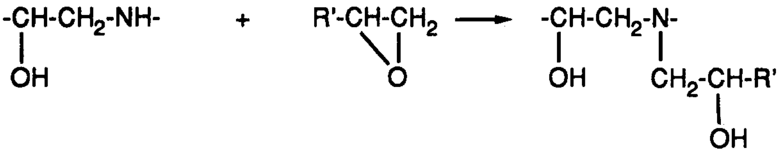


$$R{-}NH_2 + R'{-}\underset{O}{CH{-}CH_2} \longrightarrow R'{-}\underset{OH}{CH}{-}CH_2{-}NH{-}R$$

(1)

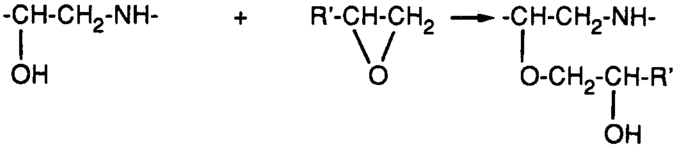






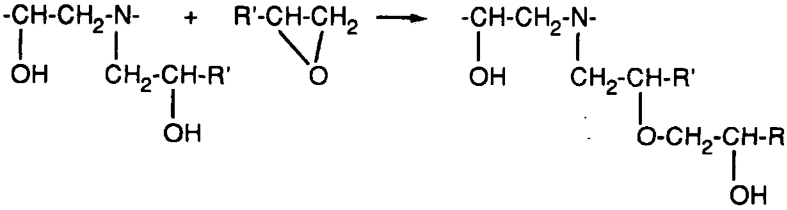
$$-\underset{OH}{CH}-CH_2-NH- \quad + \quad R'-\underset{O}{CH-CH_2} \longrightarrow -\underset{OH}{CH}-CH_2-\underset{CH_2-\underset{OH}{CH}-R'}{N}-$$

(2)



$$-\underset{OH}{CH}-CH_2-NH- \quad + \quad R'-\underset{O}{CH-CH_2} \longrightarrow -\underset{O-CH_2-\underset{OH}{CH}-R'}{CH}-CH_2-NH-$$

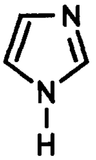
(3)



$$-\underset{OH}{CH}-CH_2-\underset{CH_2-\underset{OH}{CH}-R'}{N}- \quad + \quad R'-\underset{O}{CH-CH_2} \longrightarrow -\underset{OH}{CH}-CH_2-\underset{CH_2-\underset{O-CH_2-\underset{OH}{CH}-R'}{CH}-R'}{N}-$$

(4)

These reactions are influenced by an accelerator in a different way [10, 24]. Imidazole (3) accelerates etherification reactions [equations (3) and (4)] [12, 13].



3

Different functional group concentrations are detected in the networks as a function of the reaction components ratio. Figure 1 shows NIR spectra of networks prepared from DGEBA and DDM and different imidazole concentrations. The band assignments are given in Table 1. The concentrations of unreacted epoxy groups as well as secondary amino groups and primary amino groups are strongly dependent on the accelerator concentration used for network synthesis (Fig. 1).

The content of residual epoxy groups in the networks can be calculated from the intensity of the band at 4535 cm^{-1} (2205 nm) relative to the aromatic CH overtone at 5988 cm^{-1} (1670 nm) using an unreacted mixture of DGEBA and DDM as value for 100% epoxide. The amounts of unreacted epoxy groups remaining in the networks are given in Fig. 2.

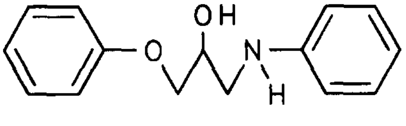
The quantitative analysis of the primary and secondary amino groups is more complicated because of the strong overlapping of the bands assigned to the primary and to the secondary amine, respectively.

Amine bands appear around 6500 cm^{-1} (overtones) and near 5000 cm^{-1} (combination bands). Both primary and secondary amines are known to absorb in the overtone region [29]. Unfortunately, their absorption coefficients are different and depend strongly on the type and the concentration of the amines used [26, 27, 31]. Tertiary amines do not absorb in the NIR.

Around 5000 cm^{-1} a strong absorption due to primary amines appears. However, a small band at 4995 cm^{-1} was observed in *N*-methylaniline. In *N*-ethylaniline [26] and in 1-aminophenyl-3-phenoxypropan-2-ol a weak absorption was found also. The intensity of this band is more than two orders of magnitude weaker than the absorption due to primary amines at 5045 cm^{-1}. For quantitative analysis a separation of both bands is necessary because in samples with strong conversion of primary amine and high secondary amine content both bands become comparable in intensity.

A model system consisting of 1-aminophenyl-3-phenoxypropan-2-ol (4), aniline and anisole was helpful for quantification. This model system is comparable with the chemical structure of the epoxy amine networks. Different contents of primary and secondary amine structures are preparable in a simple way in the model system. The NIR spectra of some selected compositions are demonstrated in Fig. 3.

The primary amine concentration in the networks was calculated from the intensity of the band at 5045 cm^{-1} relative to the aromatic C—H overtone at 5988 cm^{-1} (1670 nm) after correction for the intensity of the band at 4995 cm^{-1}. Therefore, the intensity ratio of the bands at 5045 and 4995 cm^{-1} relative to the aromatic C—H overtone at 5988 cm^{-1} was compared with the normalized spectrum of the model system. A factor representing the ratio of the secondary amine relative to the sum of primary and secondary amine was calculated from the model system. The normalized spectrum of 4 multiplied with this factor was subtracted from the spectrum of the epoxy network and a corrected band without any shoulder was received.



4

For the determination of the secondary amine from the intensity of the 6635 cm^{-1} band relative to the aromatic CH overtone at 5988 cm^{-1} different absorption coefficients for primary and secondary amine in dependence of their ratios have to be considered. The absorption coefficient ratios were determined using the model system consisting of 4, aniline and anisole. The NIR spectra of the model system are the base for calibration. The calibration curve shows a dependence of the ratio of absorption coefficients of primary and secondary amines at 6635 cm^{-1} on the content of primary amine relative to the total amine content (Fig. 4).

Using the calibration curve the secondary amine content of the networks was calculated from the overtone band at 6635 cm^{-1} after subtraction of the primary amine content.

The tertiary amine content in the networks synthesized is the difference between the amine content before reaction and the primary and secondary amine concentration in the networks determined from NIR spectra. The results of the amine composition in the networks are demonstrated in Fig. 5. The results differ for various ratios of epoxy groups to amino hydrogen. The influence of imidazole will be discussed separately for samples with an equimolar ratio of epoxy group and amino hydrogen as well as amino hydrogen excess and epoxy excess, respectively.

Table 1. Band assignments from NIR spectra of epoxy amine reaction; systems [15, 16, 25–30]

Band cm^{-1}	nm	Assignment
4535	2205	$-\underset{\diagdown O \diagup}{CH-CH_2}$ combination band
4618	2165	aromatic combination band
4677	2138	aromatic combination band
4784	2090	—OH combination band
4878	2050	—OH combination band
4995	2002	—NH combination band
5045	1982	—NH$_2$ combination band
5880. . .5650	1700. . .1770	—CH overtones of —CH$_2$, —CH$_3$
5988	1670	—CH combination band of aromatics
6060	1650	—CH overtone in $-\underset{\diagdown O \diagup}{CH-CH_2}$
6536	1530	—NH$_2$ overtone
6635	1507	—NH$_2$, —NH overtone
6980	1432	—OH overtone

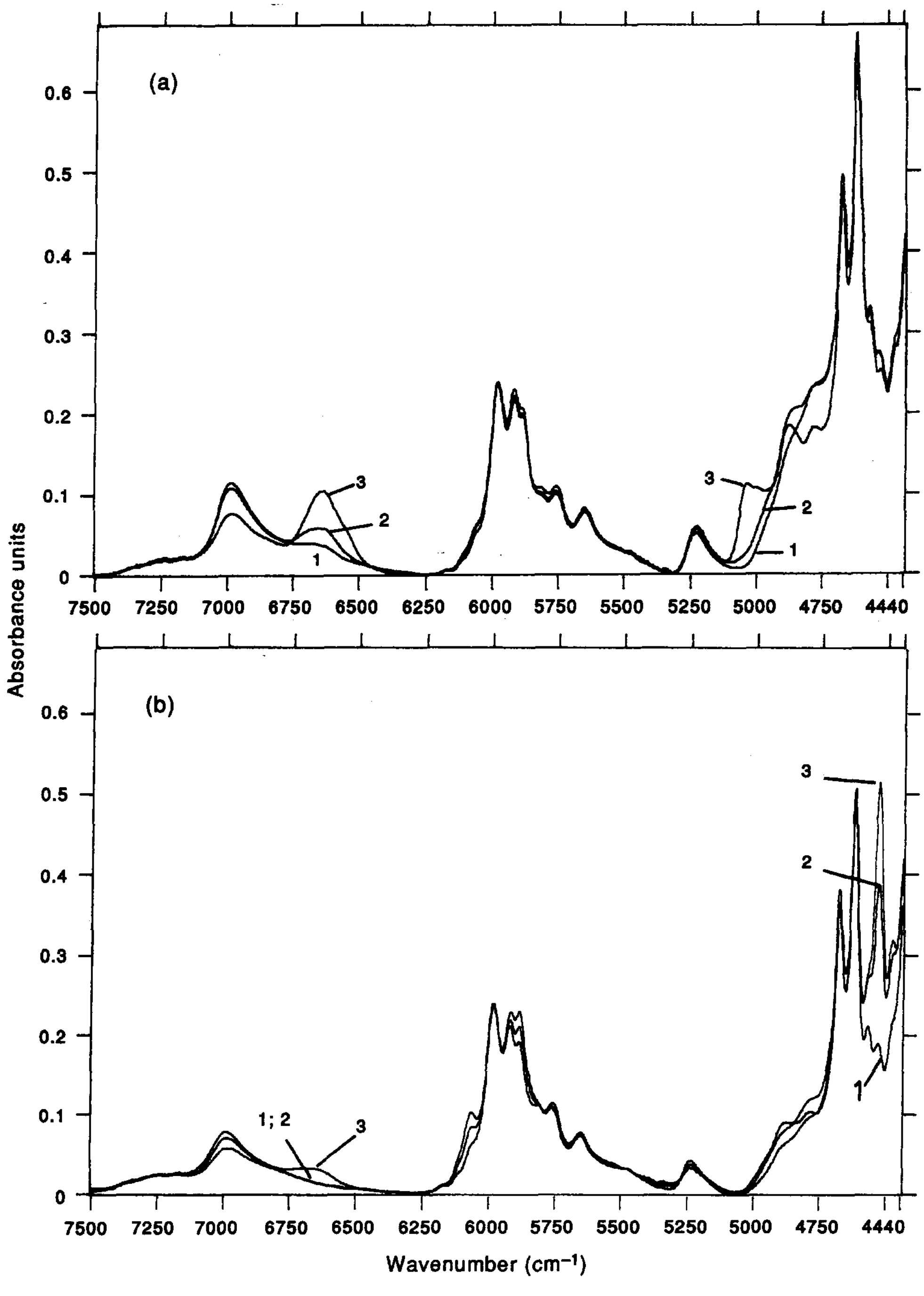


Fig. 1. NIR spectra of networks prepared from DGEBA and DDM [(a): $r = 1$; (b): $r = 0.33$] using different amounts of imidazole at 120°C and a curing time of 5 hr. (1) Without accelerator; (2) 0.65 mol% and (3) 2.00 mol% imidazole relative to epoxy groups.

Networks prepared from an equimolar ratio of epoxy groups and amino hydrogen

The chemical structure of the networks prepared from DGEBA and DDM with $r = 1$ using different imidazole concentrations for network synthesis has already been investigated by FTIR spectroscopy [12, 13]. It was shown that in the absence of an accelerator the degree of etherification is very low. The addition of imidazole during network synthesis leads to the formation of more ether structures and to an incomplete amine conversion.

The quantitative NIR spectroscopical analysis of the residual epoxy content shows only a weak dependence of the unreacted epoxy group content on accelerator concentration (Fig. 2). In all cases $< 3\%$ of unreacted epoxide groups were determined. The primary amino groups are all reacted in the absence

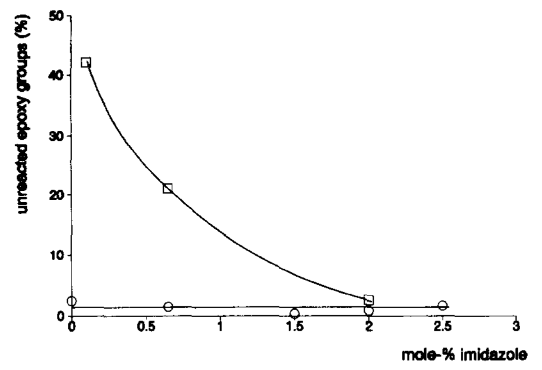


Fig. 2. Content of unreacted epoxy groups in DGEBA-DDM networks (cured 5 hr at 120°C) as a function of imidazole concentration. (1) $r = 1$ (○); (2) $r = 0.33$ (□).

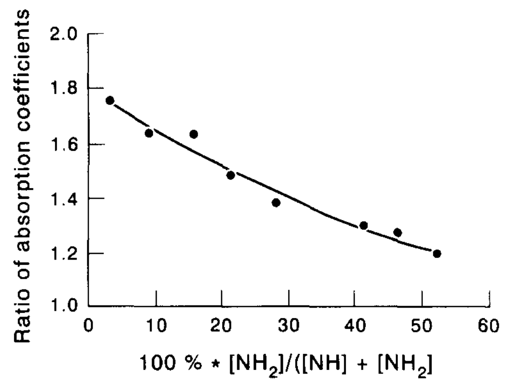


Fig. 4. Ratio of the absorption coefficients of primary to secondary amino groups around 6600 cm^{-1} determined from the NIR spectra of the model system consisting of aniline, anisole and 1-aminophenyl-3-phenoxy-propan-2-ol (calibration curve). The primary amine content is given in mol% aniline with regard to the total amine.

of an accelerator and in the presence of 0.65 mol% imidazole relative to epoxy groups in the starting mixture. Using a higher imidazole concentration (1.5 mol% imidazole or more) a considerable amount of primary amino groups remain in the networks [Fig. 5(a)]. Only a small amount of secondary amino groups was determined from NIR spectra of a network synthesized without an accelerator. Mostly tertiary amine structures were formed. The concentration of secondary amine structures increases up to an imidazole concentration of 1.5 mol%. The content of tertiary amino groups decreases. When > 1.5 mol% imidazole is added during network synthesis, the content of tertiary amine structures remains nearly on the same level as in the networks using 1.5 mol% imidazole, but the content of secondary amino groups in the networks decreases with increasing content of primary amino groups. Similar results were obtained by solid state ^{13}C-NMR spectroscopy with CP/MAS investigation of networks prepared of DGEBA, 4,4'diaminodiphenylsulphone networks and *N*,*N*-dimethylbenzylamine or the monoethylamine complex of boron trifluoride [10].

The structural differences of the networks are reflected by their physical properties. The glass transition temperature decreases with increasing imidazole concentration because of the higher flexibility of the ether bridges in comparison with tertiary amine cross-link [10, 32].

It is known that the ratio of amino hydrogen to epoxy groups used for network synthesis influences

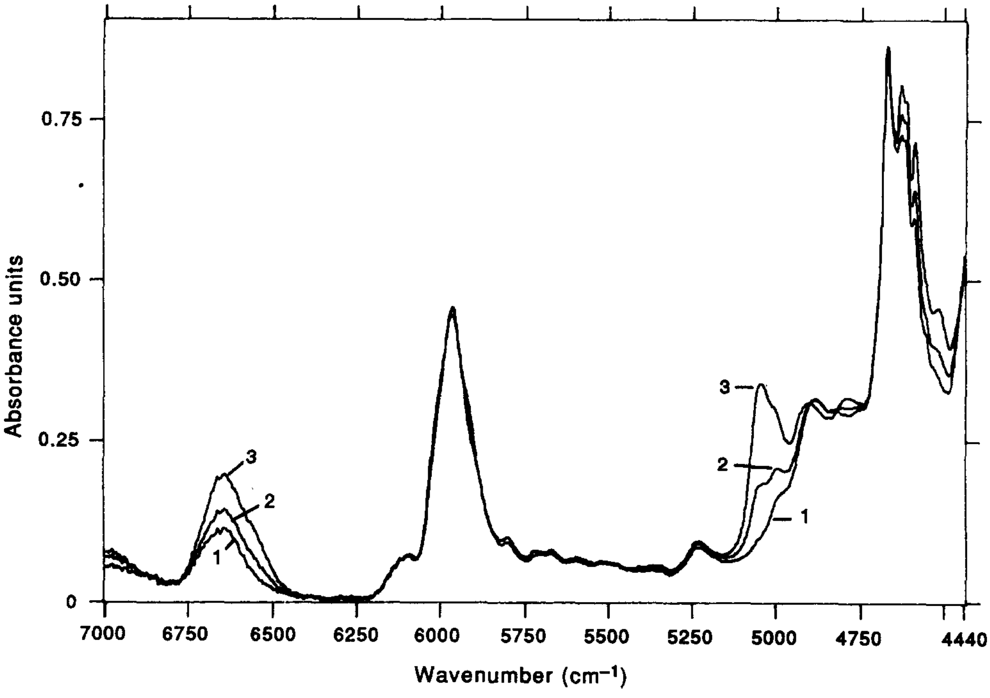


Fig. 3. NIR spectra of different amounts of aniline in an equimolar mixture of anisole and 1-aminophenyl-3-phenoxypropan-2-ol. (1) 9.3 mol%; (2) 28.2 mol% and (3) 52.2 mol% aniline with regard to the total amino groups.

the properties of the networks [33–38]. The results of investigation of networks prepared using excess of amino hydrogen are discussed in the following part.

Networks prepared using an excess of amino hydrogen

Nearly all epoxy groups are converted in the networks prepared from DGEB and DDM with $r = 2$ using different imidazole concentrations. The concentration of unreacted epoxy groups determined by NIR spectroscopy is $< 1\%$.

It is surprising that the imidazole concentration does not significantly influence the content of tertiary amine structures formed. Only a decrease of the secondary amine content and an increase of the primary amine content with increasing imidazole concentration is observed [Fig. 5(b)]. FTIR spectroscopic investigation of these networks by the DRIFT-method show an increasing ether band intensity at 1132 cm^{-1} (Fig. 6). So it can be concluded that etherification reaction occurs in the presence of imidazole even if an excess of amino hydrogen is used.

The part of the FTIR spectrum between 3100 and 3600 cm^{-1} is a complicated one, because bands of unreacted primary and secondary amino groups as well as hydroxylic groups are overlapped as a broad band (Fig. 6). Comparing the spectra of the networks with those of the starting materials and model compounds the maximum around 3380 cm^{-1} can be contributed to unreacted amino groups.

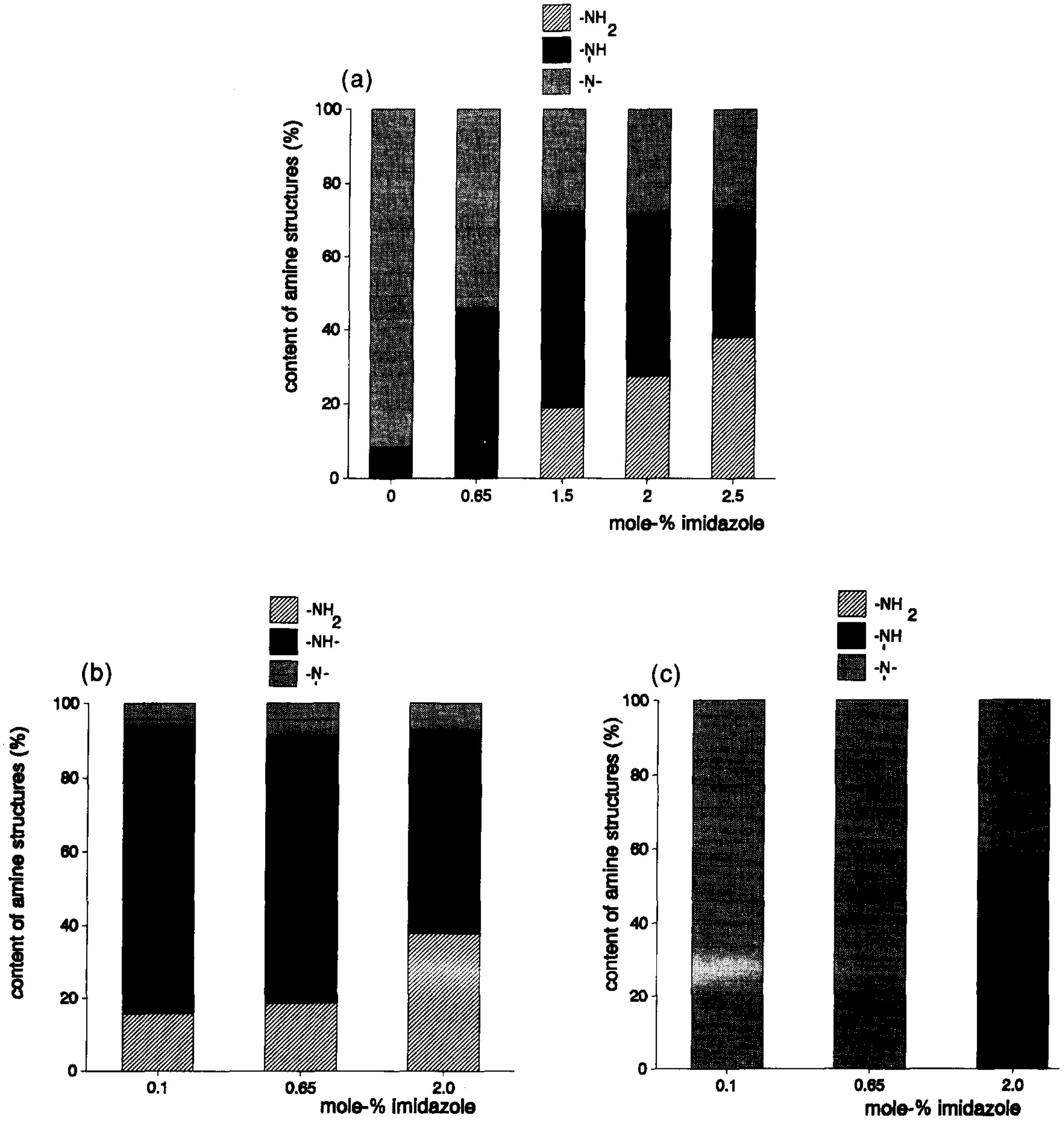


Fig. 5. Relative content of primary (▨), secondary (■) and tertiary (▩) amine structures in networks prepared from DGEBA and DDM in the presence of different amounts of imidazole at 120°C (curing time 5 hr) (a) $r = 1$; (b) $r = 2$ and (c) $r = 0.33$.

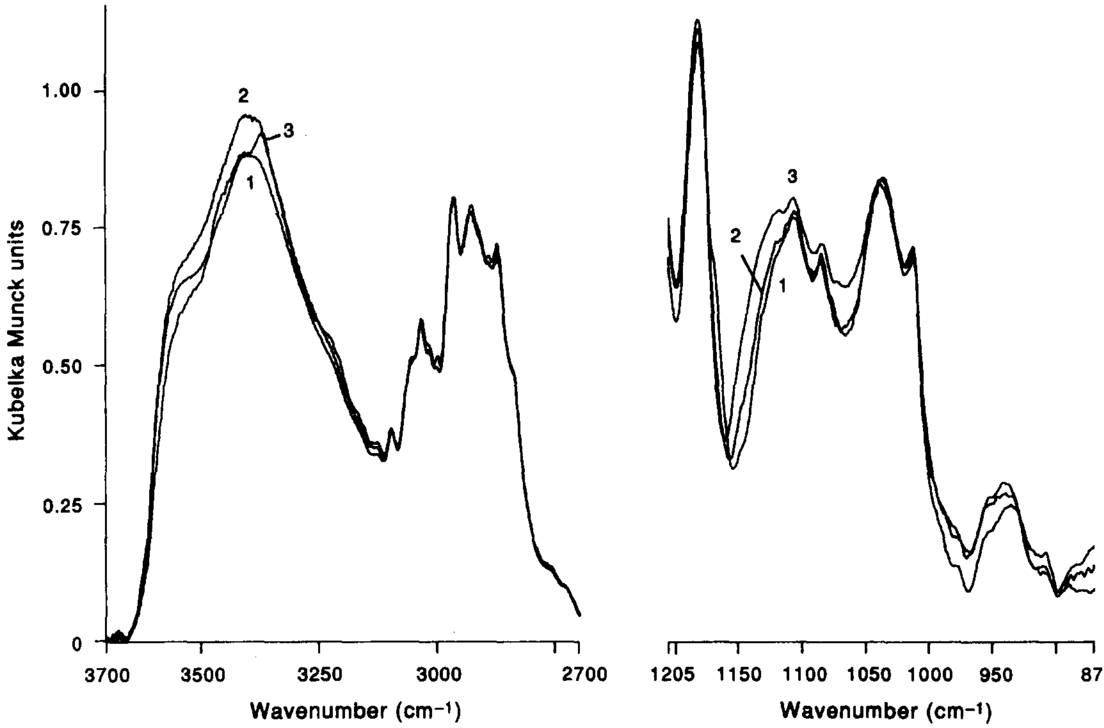


Fig. 6. FTIR spectra of networks prepared from DGEBA and DDM ($r = 2$) using different amounts of imidazole (curing 5 hr at 120°C). (1) 0.1 mol%; (2) 0.65 mol% and (3) 2.0 mol% imidazole relative to epoxy groups in the starting mixture.

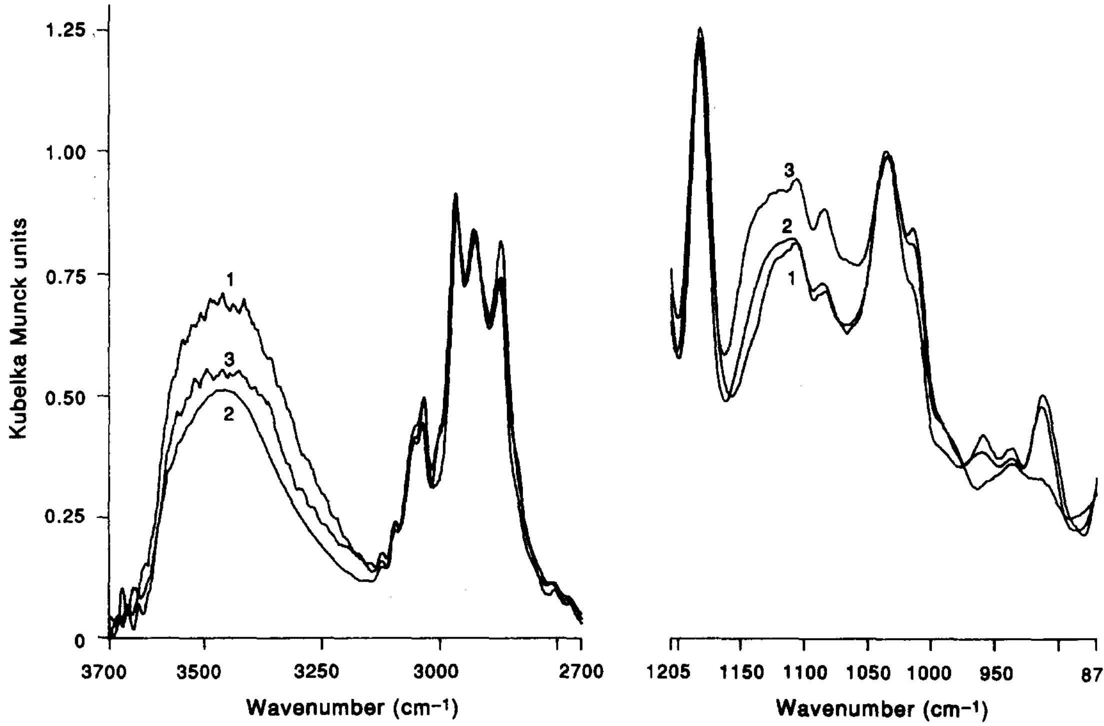


Fig. 7. FTIR spectra of networks prepared from DGEBA and DDM ($r = 0.33$) using different amounts of imidazole (curing 5 hr at 120°C). (1) 0.1 mol%; (2) 0.65 mol% and (3) 2.0 mol% imidazole relative to epoxy groups in the starting mixture.

Etherification reactions are more important in epoxy excess curing systems. The influence of the accelerator concentration in such systems is shown in the next section.

Networks prepared using an excess of epoxide

Networks prepared from DGEBA and DDM ($r = 0.5$) show a significant increase of ether structures with increasing imidazole concentration. This agrees with a higher conversion of epoxy groups resulting from etherification reactions accelerated by imidazole [12, 13].

Also in the case of an amine to epoxy ratio of $r = 0.33$ a lower concentration of unreacted epoxy groups was found with increasing imidazole content (Fig. 2). The content of secondary and tertiary amine groups is shown in Fig. 5(c). It is remarkable that at low imidazole concentrations only tertiary amine groups are formed. 2.0 mol% imidazole lead to acceleration of etherification reactions in such a way that a high concentration of secondary amine groups remain in the networks.

The FTIR spectra of the networks (Fig. 7) show a considerable increase of ether structures with increasing imidazole concentration used for network synthesis. The band with a maximum around 3460 cm^{-1} is explained only by hydroxylic groups if low imidazole concentrations are used for network synthesis because the primary and secondary amino groups are converted. In the FTIR spectrum of the network prepared in the presence of 2 mol% imidazole a shoulder around 3380 cm^{-1} is seen contributed to secondary amino groups remaining in the networks.

CONCLUSIONS

It was shown that imidazole accelerates etherification reactions during amine curing of epoxy resins not only in the cases of epoxy excess and a stoichiometric ratio of epoxy groups to amino hydrogen but also in the case of excess amino hydrogen. Using epoxy excess this reaction leads to a better conversion of epoxy groups during network synthesis. In networks prepared with a stoichiometric ratio of epoxy group to amino hydrogen the primary amine groups are not fully converted if a higher imidazole concentration is added. In the case of an amino hydrogen excess the content of tertiary amine groups formed is nearly independent of the imidazole concentration. The increasing content of unreacted primary amine groups with raising imidazole concentration in those networks is accompanied by a decrease of secondary amine group content.

Acknowledgements—The authors wish to thank Professor H. W. Siesler, University Essen, for the use of the near-infrared spectroscopic equipment of the Institute of Physical Chemistry and the "Stiftung für die Deutsche Wissenschaft" for financial support.

REFERENCES

1. V. Strehmel, L. Krukowka and M. Fedtke. *Chem. Techn.* **42,** 416 (1990).
2. H. Dannenberg and W. R. Harp. *Anal. Chem.* **28,** 86 (1956).
3. J. Klaban, J. Smrcka and J. Mleziva. *Makromolek. Chem.* **111,** 1 (1968).
4. A. Gupta, M. Cizmecioglu, D. Coulter, R. H. Liang, A. Yavrounian, F. D. Tsay and J. Moacanin. *J. appl. Polym. Sci.* **28,** 1011 (1983).
5. R. E. Smith, F. N. Larsen and C. L. Long. *J. appl. Polym. Sci.* **29,** 3713 (1984).
6. D. W. Schiering, J. E. Katon, V. B. Gupta and L. T. Drzal. *J. appl. Polym. Sci.* **34,** 2367 (1987).
7. E. Mertzel and J. L. Koenig. *Adv. Polym. Sci.* **75,** 73 (1986).
8. S. C. Lin, B. J. Bulkin and E. M. Pearce. *J. Polym. Sci.; Polym. Chem. Edn.* **17,** 3121 (1979).
9. V. Bellenger, J. Verdu, J. Francillette, P. Hoarau and E. Morel. *Polymer* **28,** 1079 (1987).
10. A. Sabra, T. M. Lam, J. P. Pascault, M. F. Grenier-Loustalot and P. Grenier. *Polymer* **28,** 1030 (1987).
11. K. C. Cole, A. Pilan, D. Noel, J.-J. Hechler, A. Chouliotis and K. C. Overbury. *Appl. Spectrosc.* **42,** 761 (1988).
12. T. Scherzer, V. Strehmel, W. Tänzer and S. Wartewig. *Progr. Polym. Colloid Sci.* **90,** 202 (1992).
13. T. Scherzer, V. Strehmel, W. Tänzer and S. Wartewig. *Proc. SPIE* **1575,** 387 (1992).
14. J. Ancelle, A. J. Attias, B. Bloch, C. Cavalli, B. Jasse, F. Laupretre and L. Monnerie. *Crosslinked Epoxies,* p. 213. Walter de Gruyter & Co, Berlin (1987).
15. H. Dannenberg. *SPE Transactions* **3,** 78 (1963).
16. G. A. George, P. Cole-Clarke, N. St John and G. Friend. *J. appl. Polym. Sci.* **42,** 643 (1991).
17. N. A. St John and G. A. George. *Polymer* **33,** 2679 (1992).
18. J. Zelenka, M. Ilavsky, V. Spacek, S. Stokrova, J. Klaban and K. Dusek. *Progr. Polym. Colloid Sci.* **269,** 1013 (1991).
19. B. Rozenberg. *Adv. Polym. Sci.* **75,** 113 (1986).
20. Dow Chemical Co., Invs.: J. E. Lastovica Jr. *US 3 142 688 Chem. Abstr.;* **61,** 8278e (1964).
21. W. Eberhard. *Chem. Ber.* **27,** 1804 (1894).
22. H. R. Snyder, R. G. Handrick and L. A. Brooks. *Org. Synth. Coll.* **3,** 471 (1955).
23. P. Freres and E. Fourneau. *Chem. Zentralblatt* **81,** 1790 (1910).
24. K. Fryauf, V. Strehmel and M. Fedtke. *Polymer* **34,** 323 (1993).
25. R. F. Goddu and D. A. Delker. *Anal. Chem.* **32,** 140 (1960).
26. K. Whetsel, W. Roberson and M. W. Krell. *Anal. Chem.* **30,** 1594 (1958).
27. K. Whetsel, W. Roberson and M. W. Krell. *Anal. Chem.* **30,** 1598 (1958).
28. O. Crisler and A. M. Burrill. *Anal. Chem.* **31,** 2057 (1959).
29. L. G. Weyer. *Appl Spectrosc. Rev.* **21,** 1 (1985).
30. J. E. Sinsheimer and A. N. Keuhnelian. *Anal. Chem.* **46,** 89 (1974).
31. F. H. Lohmann and W. E. Nortemann. *Anal. Chem.* **35,** 707 (1963).
32. V. Strehmel, E. Zimmermann, K.-G. Häusler and M. Fedtke. *Progr. Polym. Colloid Sci.* **90,** 206 (1992).
33. J. P. Bell. *J. appl. Polym. Sci.* **14,** 1901 (1970).
34. J. P. Bell. *J. Polym. Sci., Part A-2.* **6,** 417 (1970).
35. T. Murayama and J. P. Bell. *J. Polym. Sci., Part A-2* **8,** 137 (1970).
36. E. F. Oleinik. *Adv. Polym. Sci.* **80,** 49 (1986).
37. V. Bellenger, W. Dhaoui, J. Verdu, J. Galy, Y. G. Won and J. P. Pascault. *Polymer* **30,** 2013 (1989).
38. C. I. Vallo, P. M. Frontini and R. J. J. Williams. *J. Polym. Sci.; Polym. Phys.* **29,** 1503 (1991).