

Characterization of Diol Modified Epoxy Resins by Near- and Mid-Infrared Spectroscopy

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SYNOPSIS

Near- and mid-infrared spectroscopy has been used for the characterization of epoxy networks based on diglycidyl ether of bisphenol-A cured with linear aliphatic diols of different chain length in the presence of magnesium perchlorate. Absorption bands due to epoxide, hydroxyl, and ether groups were investigated. The intensity of the hydroxyl absorption and the formation of branched and unbranched ether structures in dependence on the molar ratio and the diol chain length are discussed. A mechanism for the network formation process with respect to diol chain length and concentration is proposed: networks with low density are rapidly formed if long diols are used for modification, whereas the incorporation of short diols into the network takes a longer time but yields networks with a higher density. Glass-transition temperatures of the networks obtained by dynamic thermomechanical analysis confirm the proposed mechanism. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Epoxy resins are one of the most popular classes of thermosets. Their outstanding properties such as chemical and electrical resistance, high strength, and excellent adhesion, have led to a widespread use of these materials in numerous technical applications. The possibilities to choose a suitable cross-linking agent from a large number of compounds that may react with epoxies and to vary the ratio of the diverse reactants allow the design of materials that meet the specific application requirements. On the other hand, the considerable brittleness represents the main drawback for the use of epoxy resins. Therefore, extensive research in the field of modification of epoxy resins has been carried out in the last decade to improve ductility without a loss of strength. Besides the rubber-toughening with carboxyl-terminated butadiene-acrylonitrile copolymers, epoxy resin networks can be made more flexible by diluents. Reactive diluents are particularly advantageous because the incorporation into the network by chemical bonding results in better mechanical properties in contrast with the inclusion of unbonded

particles. Urbaczewski et al.¹ utilized diglycidyl ether of 1,4-butanediol for toughening epoxy/amine networks. The reaction of an epoxy resin with bisphenol-A is reported.^{2,3}

The modification of the most important epoxy resin, diglycidyl ether of bisphenol-A (DGEBA), with linear aliphatic diols allows a broad variation of the mechanical properties because the flexibility can be adjusted by proper choice of the concentration and the chain length of the diol. Investigations on the mechanism of network formation and the structure-property relationships of these networks were carried out by a variety of chemical and physical methods like titration,^{4,5} DSC,⁶ HPLC,^{5,7,8} ¹³C NMR,^{9,10} FTIR spectroscopy,¹¹⁻¹³ and ultrasonic investigations.^{14,15}

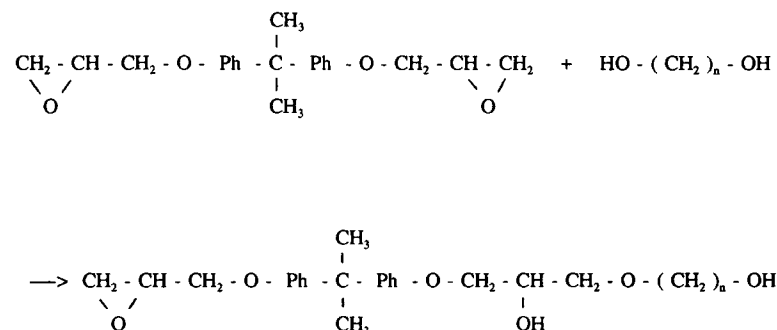
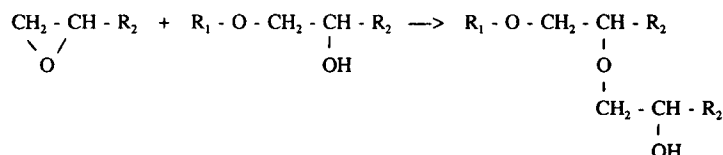
Two main reactions occur in the epoxy/diol system. At the beginning of the curing reaction long oligomer chains with a low degree of branching are predominantly formed (reaction 1 in Fig. 1). The epoxy-secondary hydroxyl reaction (reaction 2 in Fig. 1) represents the only cross-linking reaction in the resin under investigation. If magnesium perchlorate is used as accelerator, this reaction starts first at higher conversions^{5,10} because the etherification reaction only occurs at high temperatures and degrees of cure or in the presence of a large excess of epoxy groups.^{16,17}

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1. primary hydroxyl - epoxide addition2. secondary hydroxyl - epoxide reaction**Figure 1** Scheme of the reactions in the epoxy/diol system.

Tänzer et al.^{4,9} found that only a relatively small amount of diol is chemically bonded into the network. In networks modified with 1,4-butanediol the primary hydroxyl groups have vanished up to a molar ratio ($r = [\text{OH}]_0/[\text{EP}]_0$) of $r = 0.5$.^{9,10} But in samples cured with longer diols, a maximum of only 15–25% diol with regard to stoichiometry is enclosed in the network by covalent bonding.^{4,11} The remaining diol acts as an external plasticizer. Additionally, the network structure depends on the type of accelerator.^{7,9,10,14}

In our last articles^{11,12} FTIR spectroscopy in the mid-infrared (MIR) region was used to study the structure of epoxy/diol networks. For quantitative measurements of certain species by infrared spectroscopy it is desirable to have a band due to a vibration of the functional group of interest that is fairly strong and not overlapped with other bands. In the MIR this is only seldom the case, particularly if complex molecules are under consideration. To achieve more accurate quantification of the results obtained up to now, near-infrared (NIR) spectroscopy, which is superior to MIR spectroscopy in some fields, was utilized.

The absorption bands in the NIR region are due to overtones and combinations of the fundamental

MIR molecular vibrations. Although all fundamental vibrational modes can have such bands, only overtones and combination bands of vibrations involving hydrogen appear at appreciable intensities. In polymers, particularly bands of C—H, N—H, and O—H vibrations can be observed. The lower number of bands occurring in the NIR spectrum and the higher spectral separation (approximately twice or three times) due to the physical nature of these bands lead, in spite of the much higher band width in comparison to the MIR spectrum, to a smaller degree of band overlapping. Each overtone is successively weaker in intensity than the preceding one of the same fundamental because higher energy transitions are successively less likely to occur. This smaller absorptivity necessitates larger optical path lengths (1–10 mm)¹⁸ for the NIR spectral region, which represents a considerable advantage over sample handling in the MIR. Additionally, detectors and sources used for the NIR spectral region enable the recording of spectra with a signal-to-noise ratio larger than 10000 compared to 1000 achieved in the MIR.¹⁹ The simplicity of experimental work and spectral interpretation as well as the instrumental advantages have made NIR spectroscopy a valuable tool for analytical purposes. It has been employed

for a large number of qualitative studies as well as quantitative applications in analytical chemistry and polymer science.^{18,20,21}

Because of the much lower degree of band overlapping compared with the appearance in the MIR spectrum, NIR spectroscopy is particularly well suited for evidence and quantification of functional groups in epoxy resins. It has been used for some time for the determination of epoxy groups.²² More recently, quantitative and semiquantitative analysis of epoxy equivalent weight and hydroxyl number of commercial resins^{23,24} as well as monitoring of the cure reaction process in epoxy/amine systems have been performed successfully.²⁵⁻²⁷

As stated above, only overtone and combination bands of fundamentals involving hydrogen atoms may be observed at significant intensities in the NIR spectrum. But in the epoxy/diol system under investigation, ether bonds belong to the most important structures generated during curing. Different ether structures are formed in the two reactions shown in Figure 1. Linear ethers result in chain extension of the unbranched oligomers. The formation of branched ether bonds represents the only cross-linking mechanism in epoxy/diol resins. Therefore MIR spectroscopy was used to study ether structures in the prepolymers and networks and to complete the results obtained by NIR spectroscopy. In particular the influence of the diol chain length on the structure of the network formed will be elucidated in more detail.

EXPERIMENTAL

Sample Preparation

All starting materials were commercially available products. The DGEBA was recrystallized from a mixture of acetone and methanol (m.p. = 42°C). Aliphatic diols (HO—[CH₂]_n—OH) with chain lengths *n* = 2, 4, 6, 8, 10, and 12, respectively, and the accelerator, magnesium perchlorate (Merck, analytical grade), were used as received without further purification.

The linear aliphatic diols were added to DGEBA in a molar ratio, *r*, of 1, 0.5, or 0.25 *M* diol to 1 *M* resin ($r = [\text{OH}]_0 / [\text{EP}]_0$). The concentration of the accelerator was maintained at a level of 3 mol % of the weight of the resin. Diols and magnesium perchlorate are insoluble in molten DGEBA. Therefore, DGEBA, aliphatic diols, and accelerator were stirred at 95°C for 1 h. When the reaction mixture became homogeneous, these prepolymers were poured into

small preheated steel frames treated with a release agent (Richmond Aircraft Products, Santa Fe Springs, CA). The frames covered with release films (Richmond) were placed between steel plates preheated to the curing temperature. The steel device ensures controllable diversion of the heat of reaction and guarantees isothermal curing. Samples were crosslinked at 130°C for 48 h. Their final thickness was 2 mm.

The preparation of thin epoxy films suited for MIR spectroscopy is described in detail by Scherzer et al.^{11,12}

Prepolymer samples used directly for spectroscopic characterization were rapidly cooled to stop further reaction and stored at -12°C until measurements were performed some days later.

Infrared Spectroscopy

NIR spectra from 1000 to 2270 nm (10000 to 4400 cm⁻¹) were obtained using a Bruker IFS 88 Fourier transform spectrometer equipped with a tungsten source, a silicium-coated calcium fluoride beam-splitter, and an InAs detector operating at 77 K. Thirty-two scans were collected at 2 cm⁻¹ resolution. For the measurements of the uncured prepolymer samples a glass cell with an optical pathlength of 2 mm was employed. If necessary, NIR spectra were normalized to the aromatic C—H combination band at 1670 nm.

Additionally, spectra in the MIR were recorded using a Bruker IFS 66 spectrometer equipped with a glowbar and a DTGS detector. Thirty-two scans were coadded at 2 cm⁻¹ resolution. The prepolymer samples were measured in a demountable cell with a thickness of 20 μm. The Lambert–Beer Law was obeyed. In order to account for small path length differences, the intensities of all MIR spectra were normalized to the intensity of the peak at 1182 cm⁻¹ assigned to an in-plane deformation vibration of the *para*-disubstituted benzene ring in the DGEBA molecule.

Determination of Glass-Transition Temperatures

Glass transition temperatures, *T_g*, were determined by dynamic thermomechanical analysis (TMA). A Perkin Elmer TMA 7 apparatus was employed for experimental data collection. Measurements were performed on flat disk-like samples (2-mm thick) at a scanning rate of 10 K min⁻¹ in the penetration mode (probe force 2 N). Every sample was scanned twice.

RESULTS AND DISCUSSION

NIR Spectroscopy

Epoxide Conversion

The NIR spectra of the prepolymer and the fully cured sample of DGEBA modified with 1,8-octanediol at $r = 0.5$ are shown in Figure 2. In Figure 3 spectra of three networks of DGEBA cured with different diols at $r = 0.5$ are plotted.

Three bands due to epoxy groups occur in the spectra of epoxy resins at 2205, 1650, and 1159 nm, respectively. The first one is assigned to a combination of the C—H stretching fundamental at 3050 cm^{-1} with the CH_2 deformation band at 1460 cm^{-1} .²³ The others represent the first and second overtone to the stretching vibration mentioned.²² The peak at 2205 nm is preferred for quantitative use because it is more sufficiently separated from other bands than the overtones.

The epoxy conversions in the prepolymers with $r = 0.5$ derived from the epoxy band at 2205 nm are summarized in Table I. Conversion data for samples modified with different amounts of 1,6-hexanediol are given too. The normalized intensity of pure molten DGEBA was assigned to 100% epoxide level. The results show a remarkable tendency: in contrast with the regular reactivity behavior of alkanediols, in our epoxy system diols with longer chains react faster than diols with shorter chains. Similar behavior was found by ultrasonic investigations.^{14,15} The gel times determined by viscosity measurements¹⁵ confirm these observations. Resins modified with long chain diols reach shorter times to gelation and vitrify earlier than samples cured

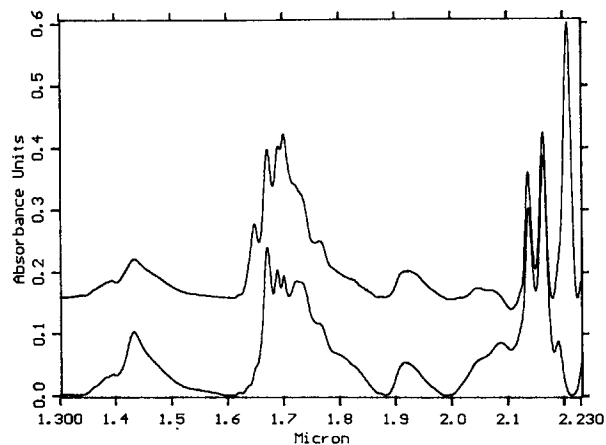


Figure 2 NIR spectra of (top) the prepolymer and (bottom) the fully cured sample of DGEBA modified with 1,8-octanediol ($r = 0.5$).

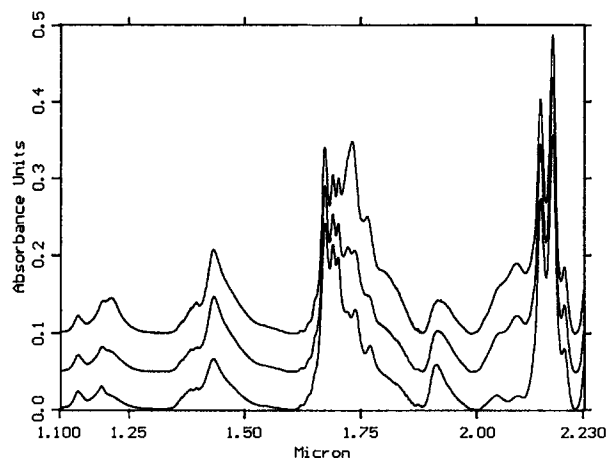


Figure 3 NIR spectra of DGEBA cured with different diols. $r = 0.5$; from bottom to top: 1,2-ethanediol, 1,6-hexanediol, and 1,12-dodecanediol.

with shorter diols due to the more rapid reaction of the first ones.

The epoxy bands have almost completely disappeared in the spectra of all cured resins investigated in this study. Only a very small shoulder in the wing of the aromatic C—H combination band at 1670 nm may be discerned (see Figs. 2 and 3). It is virtually impossible to quantify this residue. However, a maximum content of epoxy groups remaining in the network of 1% may be estimated. This is in accordance with results obtained by both FTIR spectroscopy in the MIR^{11,12} and ¹³C NMR spectroscopy⁹ where a maximum of less than 2% was estimated.

Even in a sample of DGEBA cured only with the accelerator (DGEBA: magnesium perchlorate

Table I Epoxy Conversion Data

Diol	Modification With Different Diols ($r = 0.5$)		Modification With 1,6-Hexanediol	
	Epoxide Conversion (%)	r	r	Epoxide Conversion (%)
1,2-Ethanediol	1	1	1	13
1,4-Butanediol	2	0.5	0.5	9
1,6-Hexanediol	9	0.25	0.25	5
1,8-Octanediol	18			
1,10-Decanediol	23			
1,12-Dodecanediol	24			

Epoxide conversion in prepolymers of diglycidyl ether of bisphenol-A (DGEBA) modified various diols at $r = 0.5$, and of DGEBA modified with different amounts of 1,6-hexanediol, respectively.

= 1 : 0.03) the epoxide groups have completely vanished. Other reactions than those given in Figure 1 must have occurred (epoxy homopolymerization) which will be discussed later.

Absorptions Due to Hydroxyl Groups

Absorption bands of hydroxyl groups appear in the NIR spectrum of epoxy resins at 1432, 2050, and 2090 nm. The latter two arise from combinations of hydroxyl stretching and deformation vibrations.²¹ They are also found as a less intense complex in the spectra of amine cured epoxies.^{23,25-27} In pure diols only the 2090-nm absorption appears.

The 1432-nm band originates from the first overtone of the hydroxyl stretching vibration.²⁰ The correct interpretation of this band is complicated by the occurrence of hydrogen bonding. In liquid diols a very broad asymmetric band appears between 1400 and 1650 nm with a maximum at 1590 nm and a shoulder around 1500 nm. In solution the diols show a completely different behavior. Instead of the broad complex the band at 1432 nm was found. In both the cured epoxy/diol networks and the prepolymers the same band was observed with a weak shoulder at the low frequency side, and in epoxies cured with amine the 1432-nm absorption band also appears with approximately the same intensity.^{23,25-27}

Hydrogen bonding causes a shift of the O—H band to longer wavelengths and an increasing MIR absorption coefficient. Additionally the band position is influenced by the distance between the associated hydroxyl groups.

Bellenger et al.²⁸ studied hydrogen bonding in amine crosslinked epoxies in the MIR region. Three IR bands were identified. The most intense one around 3400 cm^{-1} was assigned to intermolecular hydrogen bonding. A shoulder at 3550 cm^{-1} is caused by intramolecular dimeric association of two hydroxyls linked to the same nitrogen atom. The third band attributed to an (O—H...N) chelate is not relevant to the resin system examined here.

In the NIR spectral region the various O—H bands are more distinctly separated from each other. Their absorptivities are changed in comparison with the MIR too. The intensity of the fundamental bands strongly increase due to hydrogen bonding. Overtone intensities are nearly independent of these interactions.^{29,30} The hydrogen bonded species often show a less intense band than the free O—H. An increase of the absorptivity ratio of free to bonded O—H groups up to a factor of 30 is reported²⁹ for the NIR in comparison to the MIR spectral region.

Considering these facts it is easily realized that

the maximum of the complex found in pure diols is caused by strong intermolecular hydrogen bonding (polymeric association). In the spectra of the networks this band appears as a small tail of the band at 1432 nm, particularly if samples were modified with large amounts of long chain diols.

The band occurring in amine crosslinked epoxies at 1432 nm due to the epoxide ring cleavage by the amine groups was attributed by Dannenberg²³ to intramolecular bonded species. But the situation in diol modified epoxies is quite different. Internal H-bonds between hydroxyl groups attached to the same atom or to neighboring atoms cannot be formed because such groups do not occur in this system. However, in prepolymers and cured samples intramolecular H-bonds may extend toward the ether bond formed by the addition of DGEBA and the diol.

The band found in diols in solution at 1432 nm cannot be attributed to an internal H-bonded hydroxyl group only. In the spectra of short chain diols this interaction appears at a wavelength below 1420 nm. If the number of C atoms is larger than three, no internal bonds were found by NIR spectroscopy.³⁰ However, dimeric intermolecular association that absorbs in this spectral region may also occur. In solid-state organic compounds its wavenumber increases with the hydrogen bond distance. In cured epoxies the steric hindrance results in a higher average O—H...O—H distance. Accordingly, the band at 1432 nm and its weak shoulder in the low frequency wing are assigned to both dimeric intermolecular and intramolecular bonded species.

Free hydroxyl groups show an absorption at 1400 to 1410 nm. But in epoxy networks practically all O—H groups are involved in H-bonding because there are sufficient proton acceptors available.³¹ No free hydroxyl was found in the spectra of epoxy/diol networks. Only the 1432-nm absorption band in the dissolved diols has a slight shoulder in this region, which is attributable to small amounts of unbonded O—H groups.

Dependence of Hydroxyl Absorption on Molar Ratio

The integrated intensity of the hydroxyl band at 1432 nm is plotted versus molar ratio in Figure 4. The aromatic combination band at 1670 nm was used to correct for small pathlength differences between the different samples. In both prepolymers and networks the intensity increases with the concentration of the diol.

Because both the primary and secondary hydroxyl groups absorb at 1432 nm, it is evident that the in-

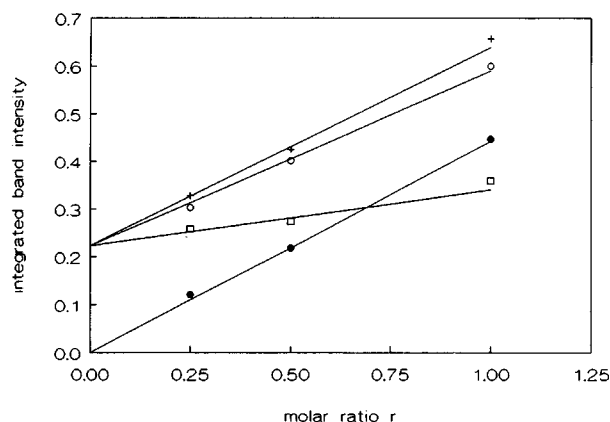


Figure 4 Dependence of the integrated intensity of the hydroxyl band at 1432 nm in the NIR spectra of epoxy/diol prepolymers and networks on the molar ratio r : networks modified with (□) 1,4-butanediol; (○) 1,6-hexanediol; (+) 1,8-octanediol/(●) prepolymers prepared with 1,6-hexanediol. All spectra are normalized to the intensity of the aromatic combination band at 1670 nm.

tensity of this band has to increase with increasing molar ratio, r . The number of secondary alcohol groups formed during both the addition of epoxide and diol and the branching reaction is supposed to be equivalent to the primary hydroxyl content present in the initial mixture because each O—H group consumed in reaction 1 or 2 (see Fig. 1) generates a new one. Consequently it is expected that the intensity at 1432 nm is proportional to the molar ratio. However, as is obvious from the curves in Figure 4, proportionality was found in the prepolymers, but not in the cured samples. Moreover, from Figure 2 it can be seen that the networks show a stronger absorbance than the corresponding prepolymer. That means the content of hydroxy groups in the networks is considerably higher than the portion of primary alcohols in the starting mixture, especially if only small amounts of diol are added. This disagrees with the mechanism of reaction given in Figure 1. Therefore side reactions must have occurred.

The structure of products that may be formed in the side reactions is not yet quite clear. Epoxy homopolymerization is known to occur in the presence of Lewis acid (magnesium perchlorate) or base type catalysts.³² Though the degree of homopolymerization of the epoxide is reported to be low,⁵ particularly in the absence of diol, the curing of DGEBA with 3 mol % magnesium perchlorate results in a dark, insoluble product without remaining epoxy groups ($T_g = 133^\circ\text{C}$). In samples containing diol the hydroxyl should have a catalytic effect on the homooligomerization reaction of DGEBA.⁵ Although homopoly-

merization generates ether structures, hydroxyl groups should also be formed due to chain termination. The appearance of hydroxyl, ether, and double bonds have been reported during homopolymerization of epoxides.^{33,34}

Additionally, reactions of DGEBA with small amounts of water that is always present in the initial mixture (e.g., in the accelerator, $\text{Mg}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$) may occur increasing the concentration of hydroxyl groups. These assumptions are supported by investigations on the system DGEBA/diol/magnesium perchlorate by methods such as GPC,¹³ HPLC,⁸ and ^{13}C NMR spectroscopy⁹ indicating the additional occurrence of various reactions other than that given in Figure 1. In networks cured with a large excess of epoxide ($r = 0.25$) considerable amounts of α -glycol functionalities were observed.⁸ Their formation should be caused by the reaction of epoxide with water from the magnesium perchlorate-dihydrate. (Moreover, the accelerator is hygroscopic. It was stored in a desiccator for this reason.) Oligomers resulting from the reaction of α -glycol with DGEBA are also terminated by hydroxyl groups. The α -glycol and the oligomers are supposed to be the main reason for the deviations from proportionality between the hydroxyl band intensity and the molar ratio observed, particularly if only small amounts of diol are added. Besides, considerable quantities of cyclic DGEBA dimers were found.⁵

Isomerization of epoxide groups as a possible origin of the hydroxyl band increase can be excluded. Double bonds due to isomerization were detected only in dimethylbenzylamine-accelerated systems.⁹ Epoxy/diol networks cured in the presence of magnesium perchlorate do not show bands between 1640 and 1660 cm^{-1} due to C—C bonds in FT-Raman spectra (taken by a Bruker Raman Modul FRA 106 connected to the IFS 88 FTIR spectrometer).

The side reactions are proposed to cause the intensity behavior observed for the hydroxyl band at 1432 nm. In the prepolymers proportionality between the intensity and the molar ratio was found. Accordingly, the extent of side reactions should be small at this stage.

Dependence of Hydroxyl Absorption on Diol Chain Length

No influence of the diol chain length on the hydroxyl content was expected. At a given molar ratio the total sum of primary and secondary hydroxyl groups and the hydroxyl groups generated by the side reaction courses discussed should be the same for the different diols. In spite of the lower reactivity of the

short chain diols this also applies to the prepolymers. But the hydroxyl absorption band at 1432 nm was found to be dependent on the number of C atoms in the diol chain. The integrated intensities of this band in the NIR spectra of both prepolymers and networks are shown in Figure 5. The spectra were normalized by using the aromatic combination band at 1670 nm.

In the NIR spectra of the prepolymers ($r = 0.5$) the intensity of the hydroxyl band increases with the diol chain length, but only minor changes are observed if diols longer than 1,8-octanediol are used for modification. In the network spectra a sharp increase in the absorbance at 1432 nm was found between 1,4-butanediol and 1,6-hexanediol. For longer diols the hydroxyl intensity remains nearly constant.

It is obvious that the main deviations from the expected behavior occur in samples modified with short chain diols. The greater the molar ratio, the more pronounced are these deviations. As mentioned above, only a certain amount (15–25% with regard to stoichiometry) of diol is incorporated into the network. The excess diol either reacts with DGEBA molecules forming oligomers or remains unreacted. Because of the lower reactivity of the short chain diols the portion of unreacted diol should be large in comparison to the longer diols. The mobility of the smaller molecules is significantly higher, and accordingly it could be supposed that the differences between samples modified with short and long chain diols, respectively, may be caused by a loss of diol in the first ones. In order to verify this assumption

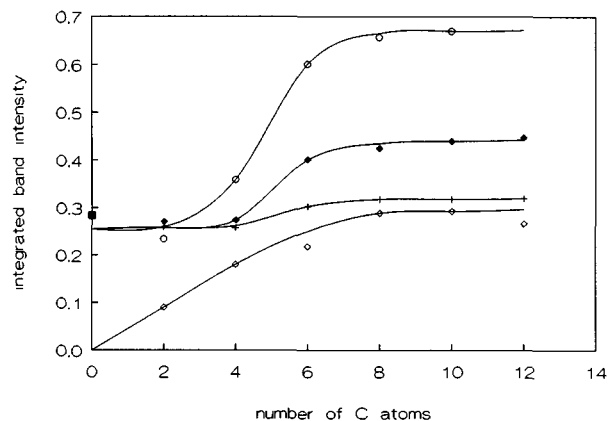


Figure 5 Dependence of the integrated intensity of the hydroxyl band at 1432 nm in the NIR spectra of epoxy/diol prepolymers and networks on the diol chain length: networks with (+) $r = 0.25$; (◆) $r = 0.5$; (○) $r = 1$; (◇) prepolymers with $r = 0.5$. All spectra are normalized to the intensity of the aromatic combination band at 1670 nm.

the weight of mixtures of stoichiometric amounts of DGEBA and 1,2-ethanediol or 1,4-butanediol, respectively, was followed during all steps of sample preparation. Considerable weight losses of 17.5 and 19%, respectively, of the initial total mass were found. The values correspond to 85% of the 1,2-ethanediol and 75% of the 1,4-butanediol used for the formulation of the two resins. Although the boiling point of 1,2-ethanediol (197°C) is 100 K above the temperature during stirring and 70 K above the curing temperature (for 1,4-butanediol these differences are even higher; b.p. = 235°C), a considerable part of the diol has to be volatilized. The percentage of diol remaining in the sample is in precise accordance with the amount of diol incorporated into the network by covalent bonding.

Evaporation of diol as well as hydroxyethers from the cured networks observed by pyrolytic methods is reported.³⁵ No weight loss was found for resins modified with 1,2-ethanediol, which is explained by evaporation of the diol during the curing process. For resins containing longer diols a loss in the range 4–20% of the total sample mass was observed. By thermogravimetric measurements⁴ a decreasing sample weight was found even at 50°C.

Therefore the low intensity of the band at 1432 nm in samples modified with 1,2-ethanediol or 1,4-butanediol should be a consequence of the evaporation of parts of the diol. Because of the higher boiling point and the much lower chain mobility no or only insignificant loss of diol occurs in resins cured with longer diols. Accordingly, the predicted independence of the absorbance at 1432 nm on the chain length was confirmed for these samples.

The evaporation of diol might also influence the epoxy conversion. In that case the low conversion value in the DGEBA/ethanediol prepolymer (see Table I) could be explained not only by the lower reactivity of the diol but also by volatilization of the diol. The concentration of diol decreases already at this stage of reaction and could reduce the rate of conversion. But only a small amount (~15%) of diol is really necessary for the initiation of the reaction.

The quantification of unreacted diol present in the cured networks is difficult. In the MIR region the absorption bands of primary alcohol groups (like the C—O stretching vibration near 1050 cm^{-1} and the O—H deformation vibration in the region from 1200 to 1400 cm^{-1}) are overwhelmed by bands of the ether structures formed in the reaction and by various peaks due to the DGEBA molecule, respectively. In the NIR spectra hydroxyl bands appear between 1400 and 1500 nm (first overtones) and at

2050 and 2090 nm (combination bands). In pure diols only one combination band at 2090 nm was observed, which is the most intense absorption in the spectrum. Cross-linked epoxies show both combination bands irrespective of the curing agent used. For example, the two absorptions were also found in amine cured epoxy resins.²⁷ Consequently they have to be assigned to secondary hydroxyl groups as well. That means that quantitative evaluation of the primary hydroxyl remaining in the networks is possible neither by the overtone bands discussed above nor by the 2090-nm absorption observed in pure diols.

Therefore only some qualitative remarks will be given. The behavior of the band at 2090 nm confirms the results obtained by utilizing the overtones. The longer the diol or the larger its percentage in the sample, the more intense is the band at 2090 nm; that is, the more unreacted primary hydroxyl groups are present in the network. However, only minimum changes were observed if the number of C atoms in the diol chain is larger than eight. In epoxies modified with 1,2-ethanediol or 1,4-butanediol a very low absorption was found at 2090 nm due to the loss of diol during the curing process.

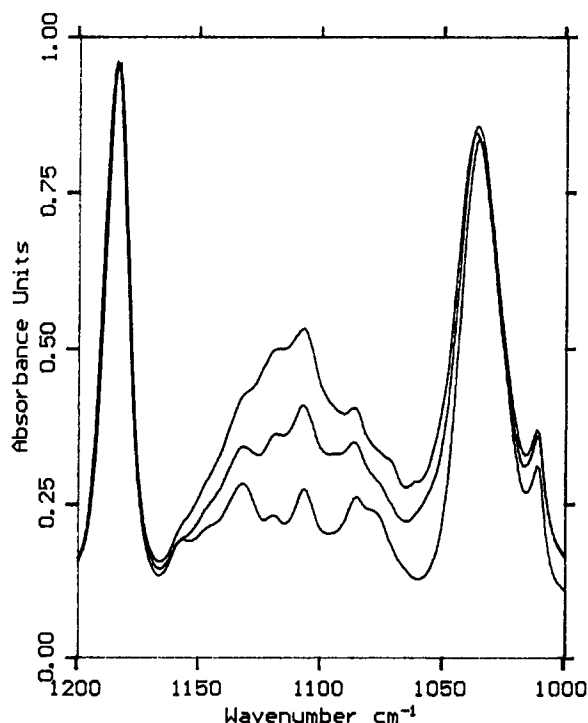


Figure 6 Ether absorption region in the MIR spectra of epoxy/diol prepolymers. $r = 0.5$; from bottom to top: 1,2-ethanediol, 1,6-hexanediol, and 1,12-dodecanediol.

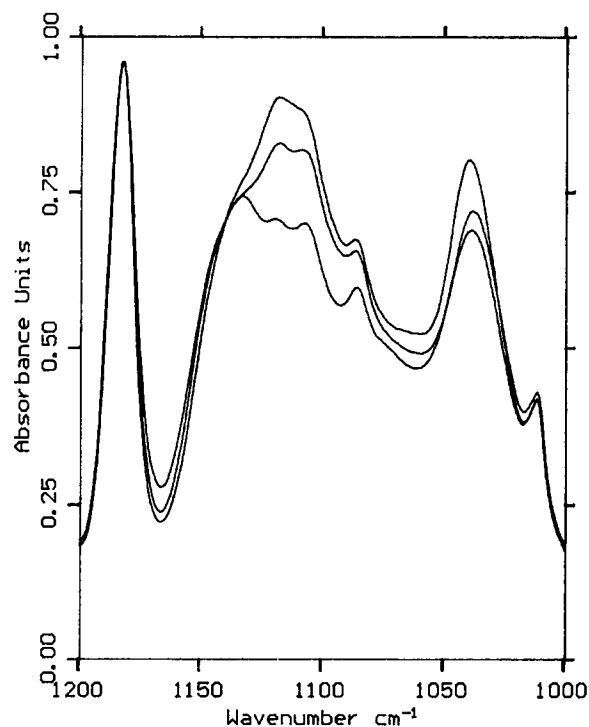


Figure 7 Ether absorption region in the MIR spectra of epoxy/diol networks. $r = 0.5$; from bottom to top: 1,2-ethanediol, 1,6-hexanediol, and 1,12-dodecanediol.

MIR Spectroscopy

Formation of Ether Bonds

The two reactions predominantly occurring in the resins during prepolymerization and cross-linking (see Fig. 1) result in different ether structures that can be separated by MIR spectroscopy. Whereas the epoxy–primary hydroxyl reaction creates unbranched ether bonds, the reaction of epoxy groups with secondary hydroxyl groups yields branched ethers. MIR spectra of the prepolymers and of cured epoxy films were recorded to elucidate these differences and to propose a reaction mechanism in dependence on diol chain length and concentration. In Figures 6 and 7 the ether absorption region between 1100 and 1150 cm^{-1} is plotted for three epoxy/diol prepolymers ($r = 0.5$) and the corresponding networks, respectively. All spectra are normalized to the intensity of the deformation vibration of the disubstituted benzene ring at 1182 cm^{-1} .

The total intensity of the band complex assigned to various ether structures depends on both diol chain length and molar ratio. According to the results of the epoxy conversion in the prepolymers

obtained by NIR (Table I), the formation of ethers progresses more rapidly in resins modified with long diol chains due to their higher reactivity. Similar behavior was found for prepolymers containing different amounts of the same diol: more ether structures are formed when the reaction was started with stoichiometric amounts of diol and DGEBA. In the spectra of cured networks the total intensities of the ether peaks differ much less, especially if longer diols than 1,6-hexanediol are used.

In the MIR spectra of epoxy resins three absorption bands due to ether groups may be distinguished in the region between 1100 and 1150 cm^{-1} . For a more detailed analysis of the mechanism of reaction, precise knowledge about the origin of these bands is required. Whereas the peaks at 1107 and 1117 cm^{-1} are assigned to both unbranched ethers and secondary hydroxyl groups, the shoulder at 1132 cm^{-1} is caused by branched ether groups as a consequence of crosslinking.^{11,12} The three bands are strongly overlapped. For quantification the band complex plotted in Figures 6 and 7 had to be separated into elementary absorption bands. Additionally, the intensity at 1132 cm^{-1} was corrected for the intensity of a small band appearing in the spectrum of pure DGEBA at the same position. The results are shown in Figure 8.

The ratio between branched and unbranched ethers is strongly influenced by the number of C atoms in the chain of the diol used for modification. It is shifted in favor of the latter, if longer diols are employed (Fig. 8). Even in the spectra of the pre-

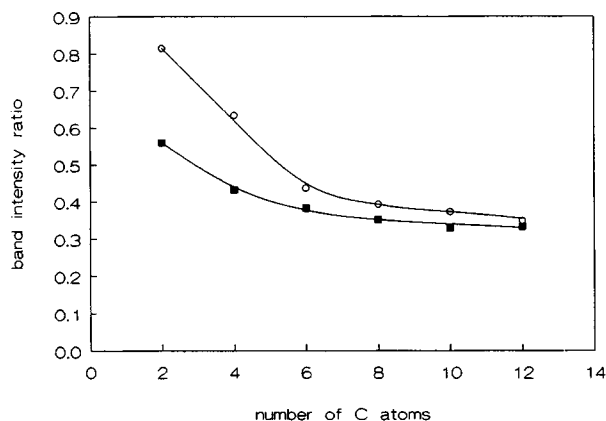


Figure 8 Dependence of the MIR band intensity ratio $I(1132 \text{ cm}^{-1})/I(1107 \text{ and } 1117 \text{ cm}^{-1})$ of epoxy/diol prepolymers and networks on the diol chain length: $r = 0.5$; (■) prepolymers; (○) networks. The intensity at 1132 cm^{-1} was corrected for the intensity of a small band appearing in the spectrum of pure DGEBA at the same position.

polymers shown in Figure 6, a decrease in this ratio with increasing diol chain length is observable. For longer diols the spectra of the prepolymers and networks exhibit nearly the same intensity ratio though the degree of etherification is much higher in the latter. That means in these samples chain extension and branching occur at a constant ratio at the advanced stage of reaction if an epoxide conversion of at least $\sim 20\%$ is reached.

The decrease of the intensity ratio with increasing chain length is explained by the higher reactivity of longer diols mentioned above. Large amounts of unbranched oligomers are formed during the first stage of their cure indicated by the strong absorbance at 1107 and 1117 cm^{-1} . The resulting deficiency of DGEBA at the advanced stage of reaction limits subsequent branching and cross-linking. Consequently, in the MIR spectra of networks prepared with long diols only a rather weak shoulder appears at 1132 cm^{-1} . In contrast, this band is the most intense absorption due to ether structures in the spectrum of the resins modified with 1,2-ethanediol. However, in the latter system the intensity of this band should be influenced by the loss of diol during curing because the reaction of DGEBA with secondary hydroxyl groups becomes even more pronounced.

Tänzer et al.³⁶ determined the ratio of the reactivities of primary and secondary hydroxyl groups, respectively, with epoxide by two separate model reactions. For short diols a ratio of 8.7 was found, which is reported to be independent of temperature in the range from 70 to 130°C. The reactivity ratio is presumably somewhat greater if longer diols are used. In the initial mixture of DGEBA/diol resins no or only a few secondary hydroxyl groups are present, that is, the branching reaction is insignificant at this stage of reaction.

The reactivity ratio in Tänzer et al.³⁶ is much smaller than those given by Alvey² for the reaction of DGEBA with bisphenol-A covering a range from 17 to 1100 in dependence on the catalyst used. Therefore the degree of branching in the diol-modified epoxies is much greater than in the phenol-cured resin. Whereas the latter reaction can yield both linear products (thermoplastics) and cross-linked structures (thermosets) according to the conditions of reaction,^{2,3} the conversion of epoxies with linear aliphatic diols always leads to networks.

The ratio between branched and unbranched ethers was found to have a strong influence on the structure of the network formed. On the basis of these findings a mechanism of reaction with respect

to chain length and molar ratio will be proposed. But previously the T_g of the networks will be given that were determined to verify the results obtained by IR spectroscopy.

Glass-Transition Temperatures

The T_g of the epoxy/diol networks obtained by dynamic thermomechanical analysis are summarized in Table II. Additionally, the T_g of the network cured only with 3 mol % accelerator is given. For all samples the difference between the values of the two temperature scans did not exceed 3 K. The average values are listed in the table. These results correspond quite well to the T_g obtained for some of the samples by DSC at the same heating rate (10 K min⁻¹).⁶ In Figure 9 the dependence of the T_g on the chain length of the diol is shown for samples with a diol content of 1, 0.5, and 0.25 mole per 1 mole DGEBA, respectively. Its dependence on the concentration of various diols is plotted in Figure 10.

T_g decreases with increasing number of C atoms in the diol chain and with increasing concentration of diol. First, the decrease of the T_g with increasing number of C atoms in the diol can be explained by the chain lengthening causing a softening of the cross-linked network due to the formation of larger meshes. But networks modified with short or long diols, respectively, exhibit a completely different behavior. If short diols are used as curing agent, T_g depends linearly on r , but the decrease is much smaller in comparison with networks modified with longer diols. Additionally, a sharp decrease in T_g between networks modified with 1,4-butanediol and

Table II T_g of Epoxy/Diol Networks

Diol	T_g (°C)		
	$r = 1$	$r = 0.5$	$r = 0.25$
1,2-Ethandiol	119	140	148
1,4-Butanediol	125	134	141
1,6-Hexanediol	60	103	122
1,8-Octanediol	42	82	110
1,10-Decanediol	33	64	99
1,12-Dodecanediol	—	60	95
DGEBA + 3 mol % Mg(ClO ₄) ₂ ·2H ₂ O		133	

Glass-transition temperatures (T_g) of epoxy networks of diglycidyl ether of bisphenol-A (DGEBA) modified with linear aliphatic diols in the presence of 3 mol % magnesium perchlorate.

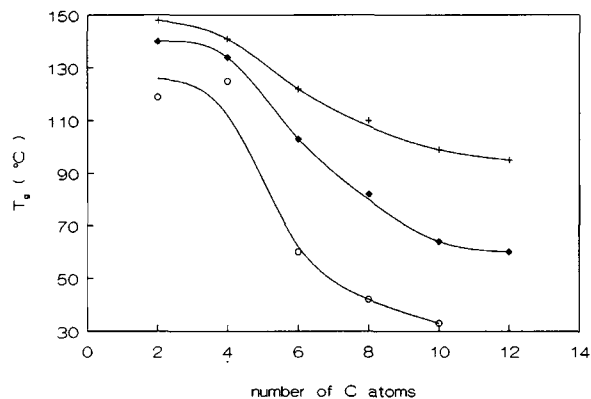


Figure 9 Dependence of the T_g of diol-modified DGEBA on the chain length of the diol: (+) $r = 0.25$; (◆) $r = 0.5$; (○) $r = 1$.

1,6-hexanediol can be observed. A more detailed discussion of the influences on the T_g is necessary.

Two reasons should be responsible for the observed differences. As mentioned above it was shown that only a certain part of the diol is covalently bonded to the network. Although in networks modified with 1,4-butanediol, primary hydroxyl groups have vanished up to a molar ratio of $r = 0.5$ a much lower percentage of diol actually takes part in the network build-up.^{9,10} In samples cured with longer diols a maximum of only 15–25% diol is enclosed in the network by chemical bonding.^{4,11} The excess diol forms short oligomers with DGEBA or remains unbonded. Blaszcó³⁵ found large amounts of free chain ends terminated by diols, mainly in resins modified with longer chain diols. These lower molecular species act as external flexibilizer markedly affecting the T_g .

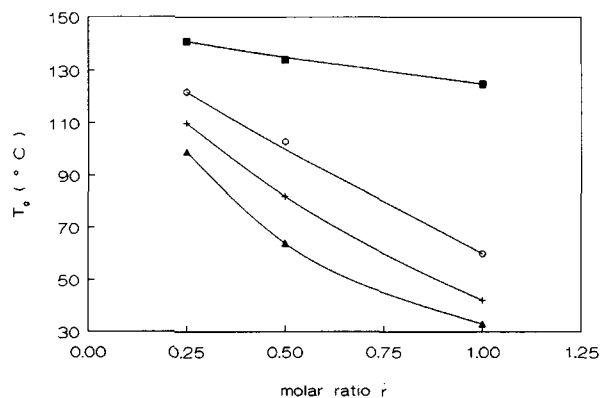


Figure 10 Dependence of the T_g of diol modified DGEBA on the molar ratio r : (■) 1,4-butanediol; (○) 1,6-hexanediol; (+) 1,8-octanediol; (▲) 1,10-decanediol.

The dramatic decrease in T_g between networks modified with 1,4-butanediol and 1,6-hexanediol is caused by the volatilization of considerable percentages of 1,2-ethanediol and 1,4-butanediol during prepolymerization and curing. It was stated above that presumably all excess diol not necessary for the network build-up has been evaporated, and consequently plasticization by unreacted diol with its deleterious effect on T_g should not occur in these networks. In contrast, resins cured with longer diols are strongly plasticized. The higher the molar ratio, the more diol remains in the network, and the sharper is the drop in T_g .

Second, the observed behavior of the T_g should be caused by the different curing behavior of the various diols used for modification; due to the strong oligomer formation in samples modified with longer diols the subsequent cross-linking is limited because a high percentage of epoxide is already consumed in the first step. The reactivity of short diols is much lower, and a considerably higher degree of cross-linking can be reached during the later stage of cure (see Fig. 8). Additionally, the observed loss of diol favors the cross-linking in these samples even more. The network density strongly increases with decreasing chain length and concentration of the diol used for modification.

CONCLUSIONS

DGEBA reacts with linear aliphatic diols in the presence of an accelerator (magnesium perchlorate) to form flexible epoxy resins. NIR and MIR spectroscopy has been used for the characterization of the epoxy/diol prepolymers and networks. Additionally, T_g 's of the networks were determined by dynamic thermomechanical analysis.

The following mechanism of network build-up may be proposed. At the beginning of the curing reaction, predominantly long oligomer chains with a low degree of branching are formed (reaction 1 in Fig. 1). Branching reactions (reaction 2 in Fig. 1) start first at higher conversions if magnesium perchlorate is used as accelerator.¹⁰ Both the restricted mobility of the terminal epoxide groups due to the viscosity increase and the increasing abundance of the secondary hydroxyl groups formed during the reaction with respect to the decreasing amount of primary O—H groups of the diols available at increasing conversion favor the branching and cross-linking reaction at the advanced stage of reaction. Due to the branching mechanism the viscosity in-

creases even more rapidly and may reduce the linear chain growth.^{4,15} The reaction with secondary hydroxyl must occur for a percentage of the epoxy groups present in the initial mixture at least equal to the extent of epoxide conversion above the amount of available diol in the sample. Because the conversion of epoxy groups was found to be nearly complete, branching should become the dominant reaction, particularly in samples with low diol content ($r = 0.25$).

This mechanism has to be specified with respect to diol chain length and concentration. The higher reactivity of long chain diols leads to a more pronounced oligomer formation during the first stage of cure and causes a deficiency of DGEBA at the advanced stage of reaction. This high epoxy conversion limits subsequent branching and cross-linking. In contrast, samples modified with short diols exhibit stronger branching during the later stage of curing (see Fig. 8) due to its slower reaction. The shorter the diol, the higher the degree of cross-linking achieved and the higher the T_g of the network. If 1,2-ethanediol or 1,4-butanediol are used for modification, the reported loss of considerable amounts of diol causes an even stronger cross-linking.

It is evident that the network formation process varies with the chain length of the diol: networks with low density are rapidly formed if long diols are used for modification, whereas the incorporation of short diols into the network takes a longer time but yields networks with a higher density. This interpretation is confirmed by the observed T_g : the decrease of T_g with increasing number of C atoms in the diol can be explained by (i) the chain lengthening causing a softening of the cross-linked network due to the formation of larger meshes, (ii) the different curing behavior of the various diols, and (iii) the influence of the residual diol swelling and plasticizing the network.

Increasing the diol concentration in the sample leads to an influence on the reaction behavior similar to the use of long chain diols: the strong oligomer formation at the beginning of the reaction reduces the percentage of epoxy groups available for cross-linking at the advanced stage of curing. In addition to the lower degree of cross-linking, the networks with $r = 1$ or 0.5 contain significant amounts of unreacted diol as well as addition products from DGEBA and diol not covalently bonded to the network. However, the relatively low concentration of branching points is not much affected by the diol content.¹⁴ But the T_g of the networks reacts very

sensitively to both the different network densities and the dilution by free diol and other products without network-forming properties.

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