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Rheo-optical fourier transform infrared spectroscopy of diol-modified diglycidyl ether of bisphenol-A epoxy resins

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Summary

The molecular orientation behaviour of epoxy networks on the basis of the diglycidyl ether of bisphenol-A (DGEBA) and various linear aliphatic diols was studied by rheo-optical FTIR spectroscopy. Uniaxial deformation was performed above and below the glass transition temperature. The influence of diol chain length and molar ratio on the mechanical properties and the orientation parameter will be discussed.

Introduction

Rheo-optical FTIR spectroscopy is a powerful method to study deformation processes in polymers on a molecular level. It allows the direct observation and quantitative determination of transient orientation effects occurring during the deformation of thin polymer films. The method has been used to characterize the deformation behaviour of numerous polymers (1,2).

In our previous papers, the investigation of the molecular orientation behaviour in various epoxy systems like polyetherdiamine or novolac cured resins and its dependence on parameters such as temperature, strain rate, and the molecular structure of the constituents of the network was reported (3-6). The modification of DGEBA with α,ω-diols (7,8) allows a systematic variation of chain length and molar ratio of the reactants, and thus a methodical change of the network density. Their influence on mechanical properties and molecular deformation behaviour will be discussed in the present paper.

Aliphatic diols with 2 to 12 carbon atoms in the chain were originally used for the modification of DGEBA in order to cover a broad range of network densities. However, it was found (9) that large amounts of 1,2-ethanediol or 1,4-butanediol had escaped from the samples during curing although the curing temperature was much lower than the respective boiling points of the two diols. Consequently, samples modified with these two diols show considerable differences of the network structure and most of the properties as compared to epoxies modified with diols with longer chain length. Therefore, they were not used in rheo-optical experiments.

Experimental

Sample preparation

DGEBA was converted with α,ω-diols of different chain length (HO-$[CH_2]_n$OH ; n = 6, 8, 10, and 12) in a molar ratio (r = $[OH]_o/[Epoxide]_o$) of 1, 0.5 or 0.25, respectively. Magnesium perchlorate (3 mol %) was added as catalyst. Since the diols and the catalyst are insoluble in the molten epoxy resin, prepolymers were prepared by stirring a mixture of all components at 95°C until it became homogeneous. After vacuum degassing, the prepolymers were cast between preheated steel plates covered with release foils of a tetrafluoroethylene-hexafluoropropylene copolymer and cured at 130°C for 48 h. The epoxy films with a thickness of 10 μm were then carefully peeled off the release foil and cut to gauge dimensions of 12 x 8 mm^2.

The preparation of diol-modified epoxy resins was described in detail in refs. 7 and 9. Their glass transition temperatures were given in ref. 9. The manufacture of thin epoxy films suited for rheo-optical spectroscopy has been reported in refs. 3 and 4.

Rheo-optical FTIR spectroscopy

The rheo-optical experiments were performed with a variable-temperature stretching machine (10) installed in the sample compartment of a Bruker IFS 66 spectrometer. Samples were uniaxially stretched with a loading rate of 0.005 mm s^{-1} and under controlled temperature conditions (± 0.5 K). A gold wire-grid polarizer mounted in an electro-mechanical rotator allows a rapid change of the polarization direction of the incident infrared light. Absorbance spectra with 10 scans were recorded with a temporal resolution of 6.5 sec at a spectral resolution of 2 cm^{-1}. The experimental setup has been described comprehensively in refs. 3 and 4.

Determination of the Orientation in Polymers

The orientation of a polymer chain is described by a distribution function f ($\theta\phi\psi$) (2, 11). The segmental orientation in materials with uniaxial alignment is given by the second moment of this distribution function as

$$< P_2 (\cos\theta) > \;=\; \frac{3 < \cos^2\theta > - 1}{2} \qquad (1)$$

where θ is the average angle between the chain axis and the stretching direction. Equation (1) is also known as HERMANS orientation function. It is related to the dichroic ratio R = $A_{\parallel} / A_{\perp}$ by the expression

$$< P_2 (\cos\theta) > \;=\; \frac{(R - 1)(R_0 + 2)}{(R + 2)(R_0 - 1)} \qquad (2)$$

$A_{\parallel}$ and $A_{\perp}$ are the absorbances with the polarization direction parallel or perpendicular to the drawing direction, respectively. $R_0 = 2 \cot^2 \alpha$ is the theoretical dichroic ratio for perfect uniaxial order of the chains, and α is the angle between the vector of the transition moment and the local chain axis segment.

Results and Discussion

The FTIR spectra of diol-modified epoxy networks are shown in Fig. 1 and 2. In the fingerprint region (Fig. 1), only slight differences between samples modified with 1,6-hexanediol or 1,12-dodecanediol are observed (the spectra of DGEBA with 1,8-octanediol or 1,10-decanediol are omitted for clarity).

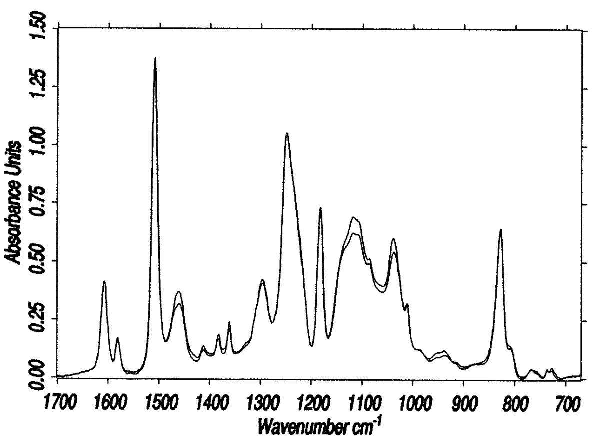

Fig. 1. Fingerprint region of the FTIR spectra of DGEBA modified with 1,6-hexanediol (bottom) or 1,12-dodecanediol (top ; r = 0.5)

In contrast, the bands in the CH_2 stretching region (Fig. 2) show a strong influence of the chain length of the diol used for modification. The peak at 2930 cm^{-1} (υ_{as} (CH_2)) was evaluated for the calculation of $< P_2 (\cos\theta) >$ in the rheo-optical experiments. Its transition moment is known to be perpendicular to the polymer chain axis, i.e. $\alpha = 90°$ (1).

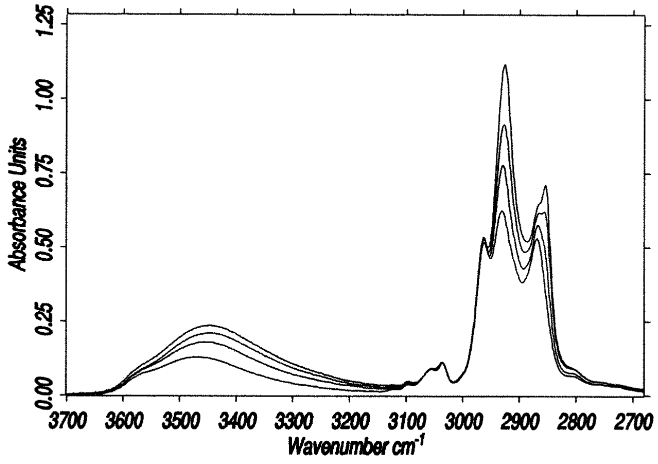

Fig. 2. 3700...2700 cm^{-1} region of the FTIR spectra of diol-modified DGEBA (r = 0.5 ; diol chain length from top to bottom : n = 12, 10, 8, 6)

The dependence of the absorptions assigned to hydroxy and ether stretching vibrations (around 3450 cm^{-1} and 1110 cm^{-1}, respectively) on the diol chain length has already been discussed previously (9, 12). However, both bands are not suitable for the evaluation of rheo-optical FTIR measurements.

Deformation of diol-modified epoxy networks in the rubbery state

The diol-modified DGEBA epoxies were uniaxially stretched until fracture of the sample. As an example, the stress-strain curve and the orientation parameter $< P_2 (\cos\theta) >$ of DGEBA / 1,8-octanediol (r = 0.5) during deformation at T_g + 20 K are plotted in Figs. 3 and 4.

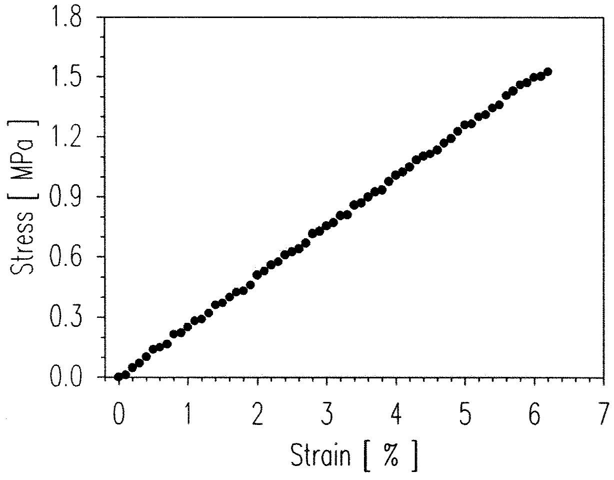

***Fig. 3.** Stress-strain curve of DGEBA / 1,8-octanediol (r = 0.5) at T_g + 20 K*

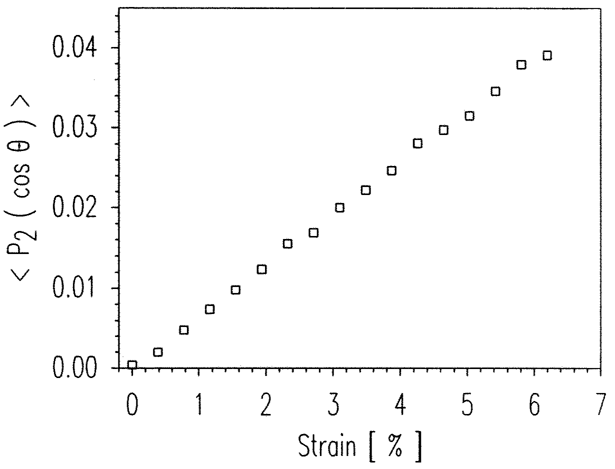

***Fig. 4.** $< P_2(\cos\theta) >$ of DGEBA / 1,8-octanediol (r = 0.5) at T_g + 20 K*

The stress depends nearly linearly on the strain which is typical for highly cross-linked epoxies (3, 4, 6) due to the finite extensibility and non-Gaussian character of the short chain segments in the network (13). The orientation also shows a linear relation to the strain. This has been likewise observed for various other rubbery epoxy networks (3, 4, 6). The deformation of polymer networks is based on the uncoiling and extension of chain segments by rotations around their skeletal bonds. In the present modified resins, the diol sequences are the main elastic component which becomes extended whereas the stiff diphenylpropane units from the DGEBA molecule largely resist any deformation. This is also corroborated by the dependence of the ultimate strain σ_b on the chain length of the diol (Fig. 5).

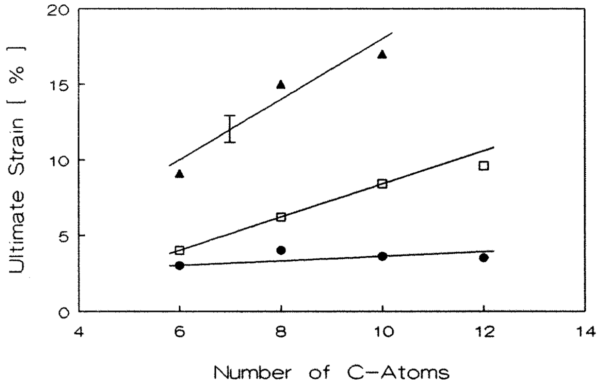

***Fig. 5.** Dependence of the ultimate strain ϵ_b at T_g + 20 K on the diol chain length (● r = 0.25; □ r = 0.5; ▲ r = 1)*

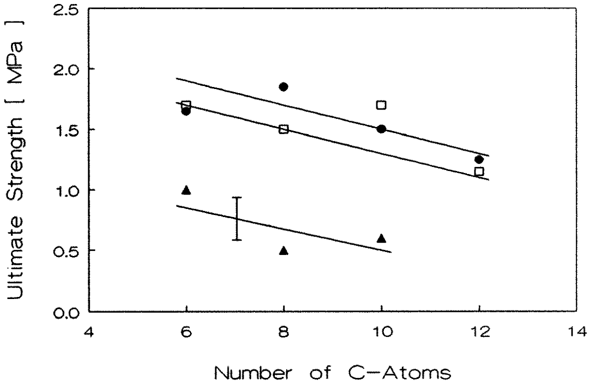

***Fig. 6.** Dependence of the ultimate strength σ_b at T_g + 20 K on the diol chain length (● r = 0.25; □ r = 0.5; ▲ r = 1)*

ϵ_b rises with increasing diol chain length and molar ratio r. Both of them lead to networks with wider meshes, i.e. higher M_c values (8). For the networks with the lowest diol content, the chain length is of minor importance. Here, the network structure is mainly determined by the branched ethers resulting from the homopolymerization of the excess DGEBA (14). At higher molar ratios the diol is only partly covalently bound into the network (7, 15). The sol content increases, and looser networks are formed (8, 9). Such a structure of the networks allows large extensions of the films. However, it also causes a strong decrease of the ultimate strength σ_b (Fig. 6) and the elastic modulus E (Fig. 7) of the epoxies when the chain length and percentage of the diol increase.

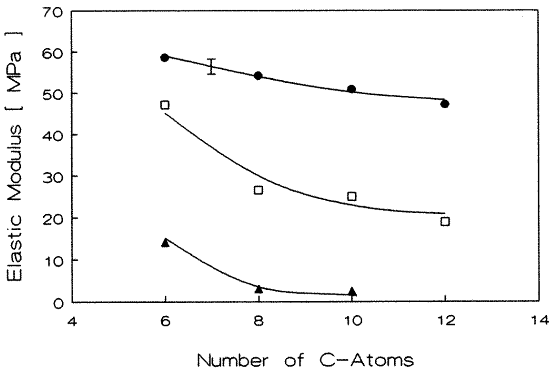

Fig. 7. Dependence of the elastic modulus E at T_g + 20 K on the diol chain length (● r = 0.25; □ r = 0.5; ▲ r = 1)

The heterogeneous structure of the networks with the higher molar ratios leads to an inhomogeneous stress distribution in the sample and causes the films to break at lower tensile strength.

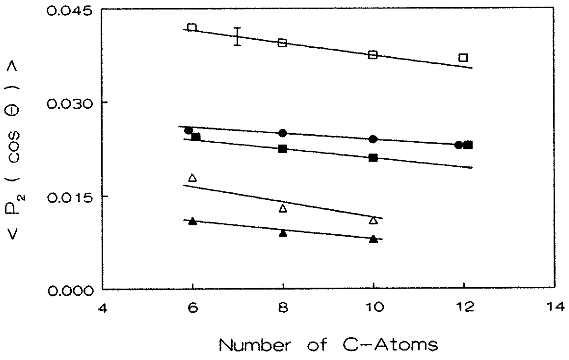

Fig. 8. Dependence of $< P_2 (\cos\theta) >$ on the diol chain length (deformation at T_g + 20 K ; ● r = 0.25, ■ r = 0.5, ▲ r = 1; filled symbols ϵ = 3 %, empty symbols ϵ = 5 %)

Fig. 8 shows the effect of the molar ratio of the constituents and the chain length of the diol on the orientation parameter $< P_2 (\cos\theta) >$ at two reference strains. Obviously, the orientation behaviour is only weakly influenced by the chain length. $< (P_2 (\cos\theta) >$ only slightly decreases with increasing length of the diol. In contrast, the orientation is strongly dependent on the molar ratio, in particular on changing it from r = 0.5 to r = 1.

These observations are closely correlated to the M_c values of the networks (8) which were also found to vary only slightly with the molecular weight of the diol and between the two lower molar ratios. However, they are about one order of magnitude higher for the samples of stoichiometric composition. This indicates the formation of increasingly incompletely cross-linked networks with a high content of network imperfections.

Since the orientation in stretched polymer networks is determined by conformational changes and consequently depends on the network density, the orientation behaviour of the various samples can be attributed to the different M_c values. Systems with a low diol content show only minor dependence on the diol chain length since their M_c is mainly determined by the homopolymerized excess DGEBA. Consequently, the network densities and the orientation parameters $< P_2 (\cos\theta) >$ of those samples show only minor variation.

Deformation of diol-modified epoxies in the glassy state

The deformation behaviour of the diol-modified DGEBA epoxy resins was also studied below the glass transition temperature at T_g - 20 K. The epoxies consisting of equimolar amounts of DGEBA and 1,8-octanediol, 1,10-decanediol, or 1,12-dodecanediol have glass transition temperatures of 42°C, 33°C, and 9°C, respectively (9). Since the stretching machine can only be heated, no investigation of those samples at T_g - 20 K could be performed. The other samples were uniaxially stretched until fracture.

The elastic moduli of the diol-modified epoxy resins are shown in Fig. 9. The modulus seems not to depend on the diol content in the samples and is only slightly influenced by the molar mass of the diol used.

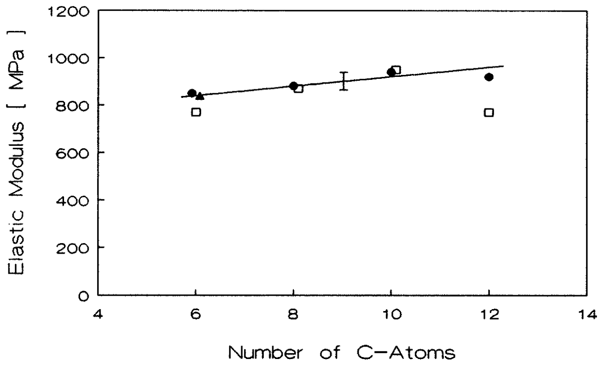

Fig. 9. Dependence of the elastic modulus E at T_g - 20 K on the diol chain length
(● r = 0.25; □ r = 0.5; ▲ r = 1)

The elastic modulus is a typical low strain property. It was determined in the range up to about 2 to 3 % strain. An almost pure elastic deformation without a contribution of plastic deformation is observed there. The slight dependence of E on the diol chain length could indicate a better packing efficiency in resins containing longer diols due to less steric constraints. In contrast, the variation of the amount of diol obviously has no effect on the packing behaviour.

Simultaneously to the stretching of the epoxy films, the increase of the orientation was determined. The orientation parameter is plotted in Fig. 10 at a reference strain of 2.5 % in order to enable a comparison of all resins. Some of them are rather brittle in the glassy state (see below).

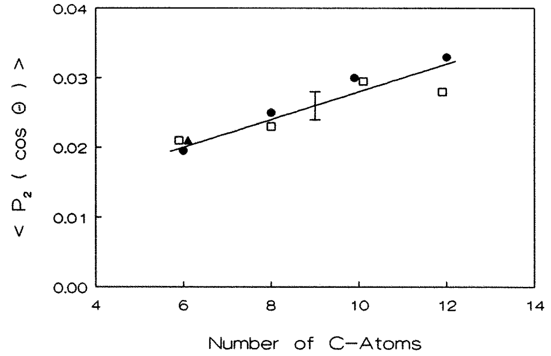

Fig. 10. *Dependence of < P_2 (cosθ) > at 2.5 % strain on the chain diol length (deformation at T_g - 20 K; ● r = 0.25; ☐ r = 0.5; ▲ r = 1)*

The similarity of the behaviour of the orientation parameter to that of the elastic modulus is quite obvious. < P_2 (cosθ) > slightly depends on the molecular weight of the diol component too. In contrast to the behaviour of the modified epoxies above T_g, the degree of orientation increases with increasing diol chain length. This behaviour is due to the different deformation mechanism in the glassy state and is directly related to the observed behaviour of the modulus. Due to the strong intermolecular cohesion, no plastic deformation occurs at those low strains, and only an elastic contribution is observed. The increasing stress at the reference strain which was observed for increasing chain length of the diol in the resin (see Fig. 9) directly causes also a higher orientation in those samples (see Fig. 10).

As in the case of the modulus, no significant effect of the molar ratio on < P_2 (cosθ) > was found. Again, this is a consequence of the fact that the orientation parameter was determined at such low strains where plastic deformation did not occur yet. However, due to the high brittleness of most of these epoxy resins, they cannot be extended far enough to study their orientation behaviour in the plastic deformation zone. For this reason, the missing effect of the molar ratio on the orientation parameter just reflects the independence of the elastic modulus of the diol content.

Generally, all epoxy films were stretched until fracture. Their strains and strengths at fracture at T_g - 20 K are shown in Figs. 11 and 12.

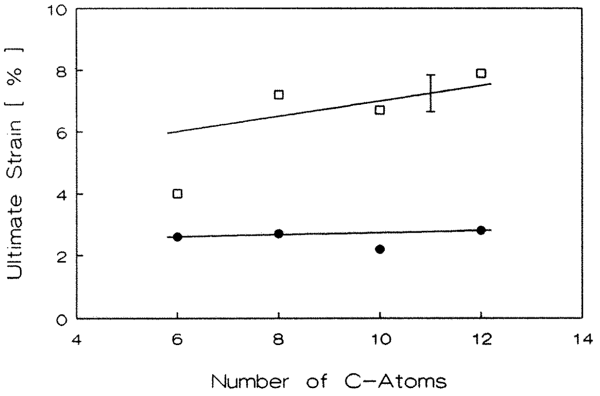

Fig. 11. *Dependence of the ultimate strain ϵ_b at T_g - 20 K on the diol chain length (● r = 0.25; ☐ r = 0.5)*

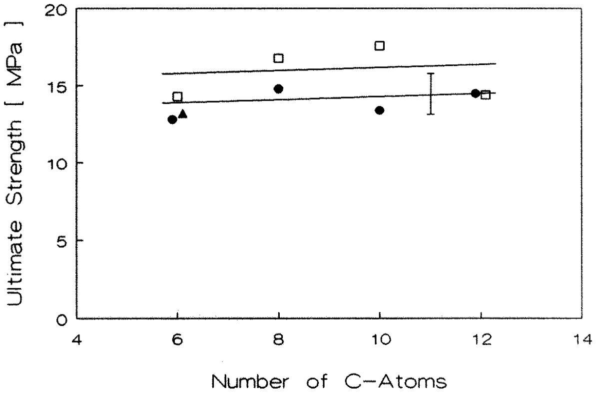

Fig. 12. *Dependence of the ultimate strength σ_b at T_g - 20 K on the diol chain length (● r = 0.25; ☐ r = 0.5; ▲ r = 1)*

In contrast to the rubbery samples, only a weak dependence of both quantities on the diol chain length is observed. In part, this may be due to the different microscopic mechanism of deformation in glassy polymers which is based on molecular slip and glide processes (16, 17). These molecular motions are controlled by the free volume in the material. However, the ultimate properties in the glassy state are not only determined by the chemical structure and the molecular architecture of the resins but also by the statistical nature of fracture processes in those materials. Many polymer glasses show brittle behaviour due to their low resistance to crack nucleation and propagation. Such effects possibly mask a weak influence of the diol chain length on the packing density (and consequently on ϵ_b and σ_b too) which might be expected from the results of the modulus.

A somewhat more pronounced effect on ϵ_b is found for the diol content in the resins. As was already mentioned, only a part of the diol, i.e. 15 to 25 % of the stoichiometric amount (7), is incorporated into the network by covalent bonds. The excess diol forms oligomers with DGEBA and may act as plasticizer which leads to a flexibilization of the resins and to a higher crack resistance. The effect becomes more apparent with increasing molar ratio. This is reflected in the higher ultimate strain of resins with r = 0.5 in comparison to the rather brittle samples with r = 0.25 (Fig. 11).

Nevertheless, in the glassy state the mechanical properties and the molecular orientation of the modified epoxies are less influenced by diol chain length and molar ratio than above T_g. This indicates that both parameters have a stronger effect on the network density than on the packing density.

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