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Molecular orientation phenomena in DGEBA/polyetherdiamine epoxies studied by rheo-optical FTIR spectroscopy

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Summary

Rheo-optical FTIR spectroscopy was used to monitor molecular orientation phenomena in highly cross-linked epoxies on the base of the diglycidyl ether of bisphenol-A (DGEBA) and a polyetherdiamine. The paper deals with the characterization of the uniaxial deformation process both above and below the glass transition temperature of the networks. Additionally, the epoxy resins were subjected to successive loading-unloading cycles in order to study the reversibility of the orientation during relaxation.

Introduction

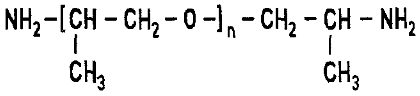
The characterization of the complex orientation phenomena appearing in polymeric systems during their deformation has become a field of intense investigation in order to get more detailed relationships between molecular orientation and mechanical properties. Molecular orientation studies carried out simultaneously with the mechanical treatment provide valuable information on the mechanisms involved in polymer deformation.

Rheo-optical FTIR spectroscopy offers the unique opportunity to monitor transient structural changes occurring during the deformation process (1,2). It is highly sensitive to the orientation of electric dipole moments in molecules and allows quantitative measurement of the developing orientation. Up to now, a wide variety of polymers have been characterized by the means of this technique (1-5). However, highly cross-linked networks such as epoxy resins have not yet been investigated using rheo-optical FTIR spectroscopy. This may be due to the difficulties in preparation of thin epoxy films suitable for both infrared spectroscopy and mechanical measurements.

The present paper deals with the first application of rheo-optical FTIR spectroscopy to monitor orientation phenomena in highly cross-linked epoxies during uniaxial deformation and relaxation both above and below the glass transition temperature of the networks.

Experimental

Epoxy resins were prepared from the diglycidyl ether of bisphenol-A (DGEBA) and a polyetherdiamine (Jeffamine D-400; Texaco). The chemical structure of the amine curing agent is shown in Fig. 1.



$$NH_2-[\underset{CH_3}{\underset{|}{CH}}-CH_2-O-]_n-CH_2-\underset{CH_3}{\underset{|}{CH}}-NH_2$$

Fig. 1. *Jeffamine D-400*

For the preparation of thin epoxy films suited for mid-infrared spectroscopy the mixture (at the stoichiometric ratio of the reactants) was cast between preheated steel plates covered with FEP release films (Richmond Aircraft Products ; type A 5000). Samples were cured at 95°C for 20 h. The final glass transition temperature T_g determined by thermomechanical analysis (Perkin Elmer TMA 7) was found to be 50°C.

The epoxy films obtained have a thickness of about 10 µm. They are extremely brittle and have to be peeled off the release film and handled with great care to avoid any damage of the specimen before mechanical treatment. Samples for rheo-optical investigations were checked for structural defects by a light microscope. Until testing, the cured specimens were stored in a desiccator at ambient temperature.

The rheo-optical measurements were carried out using a variable-temperature electro-mechanical stretching machine developed by SIESLER (6). The apparatus is mounted in the sample compartment of a Bruker IFS 66 FTIR spectrometer. The polarizer (SPECAC gold wire-grid polarizer) is placed in a self-constructed electro-mechanical rotator (7). The polarization direction is automatically initiated after recording of each spectrum. For real-time recording of the stress-strain data and controlling measurement parameters such as temperature, elongation rate, polarizer position et cetera the system is equipped with a computer. The experimental setup is shown schematically in Fig 2.

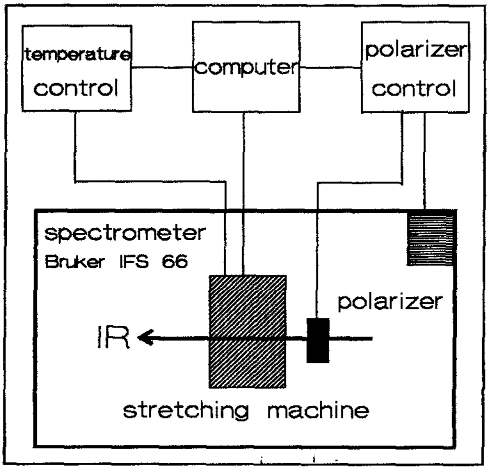


Fig. 2. *Experimental setup*

Single-channel spectra with alternating polarization direction were taken successively in 6.5-second intervals at 2 cm^{-1} resolution. For each spectrum 10 scans were coadded. Absorbance spectra were calculated using two polarizer spectra recorded before the experiment.

Film specimens with gauge dimensions of 12 x 8 mm^2 were stretched with a draw and recovery rate of 0.005 mm/s.

Theoretical Background

The orientation of a polymer chain can be expressed by an orientation distribution function f (θ,ϕ,ψ). The segmental orientation in uniaxially-oriented samples can be written in terms of the second moment $< P_2 (\cos\theta) >$ of the function f 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 drawing direction. This expression corresponds to the well-known HERMANS orientation function defined for X-ray diffraction measurements (3). $< P_2 (\cos\theta) >$ is related to the dichroic ratio $R = A_{\parallel} / A_{\perp}$ by

$$< P_2 (\cos\theta) > = \frac{(R - 1) (R_0 + 2)}{(R + 2) (R_0 - 1)} \qquad (3)$$

where $R_0 = 2 \cot^2 \alpha$ is the theoretical dichroic ratio for perfectly uniaxially ordered chains. The argument α is the angle between the transition moment vector and the local chain axis segment.

For the calculation of $< P_2 (\cos\theta) >$ from the IR spectra of the epoxy resins, the CH_2 symmetric stretching vibration at 2872 cm^{-1} was evaluated. Its transition moment is known to be perpendicular to the chain axis (8).

Results and Discussion

Deformation above the glass transition temperature

The DGEBA / D-400 epoxies were uniaxially deformed in the rubbery state until failure of the sample. The stress-strain diagram at T_g + 20 K is shown in Fig. 3 a. The Legendre polynomial $< P_2 (\cos\theta) >$ calculated from the FTIR spectra recorded simultaneously is plotted in Fig. 3 b.

Both the stress and the orientation show a linear dependence on the strain instead of the nonlinear behavior typical for most rubbers. Similar results were found for the orientation behavior of other DGEBA / Jeffamine resins above their glass transition temperature (9) and for the polyether chains in the soft segments of some polyurethanes (10,11).

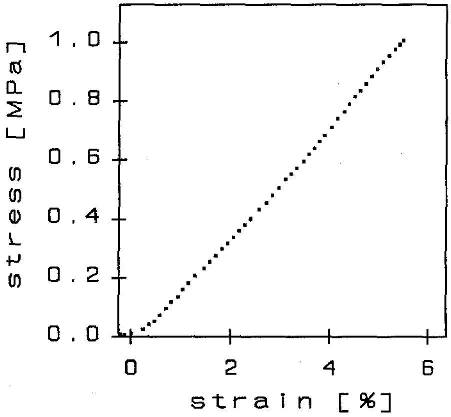


Fig. 3 a. *Stress-strain curve of DGEBA / D-400 at* $T_g + 20$ *K*

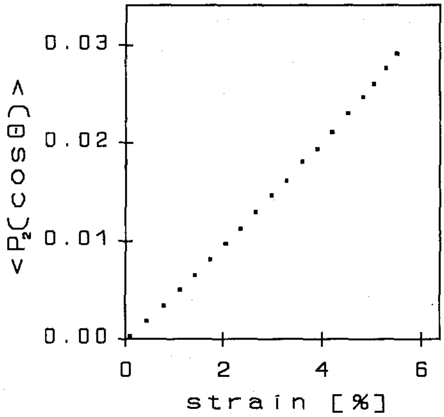


Fig. 3 b. *Orientation function of DGEBA / D-400 bei* $T_g + 20$ *K*

Flexible polymer networks in the rubbery state are relatively easy to deform. However, the underlying molecular mechanisms can be quite complicated. The changes in shape or spatial configuration occurring during the extension process are caused mainly by rotations about skeletal bonds of the individual network chains transforming them from a coiled to a more elongated state. The uncoiled chain segments become more and more oriented, which is reflected in a continuous increase of $< P_2 (\cos\theta) >$. Highly cross-linked epoxies such as those investigated in this study are not expected to behave like ideal elastomers (12). Therefore, restrictions caused by the non-Gaussian character and the finite extensibility of the short network chains have to be taken into consideration.

Nevertheless, the elastic strain energy is stored in rubbery networks largely by conformational changes of the network chains. Such changes in the conformational distribution of polymers are usually easy to detect by infrared spectroscopy, and a lot of results concerning this subject are reported in the literature. Conformational changes were observed during the deformation of a wide variety of polymers (1,2,6) including networks like natural and synthetic rubber (4) or poly(dimethylsiloxane) (13,14). However, in this study intensity changes due to conformational transitions induced by the deformation process were not found.

This unexpected result is caused by the lack of suitable conformation-sensitive infrared bands. The spectrum of epoxies on the base of DGEBA is dominated by the strong absorbances of the diphenylpropane unit. The diphenylpropane group is an extremely rigid structure which largely resists any deformation. That means that deformation is predominantly localized in the more flexible polyether chains of the Jeffamine D-400. But, only one vibrational mode of the amine curing agent is observable in the fingerprint region of the spectrum (ν C-O-C at 1105 cm^{-1}). In the infrared spectra of polyethers a great number of vibrational bands is known to be sensitive to specific conformations. Unfortunately, the ν C-O-C absorption is completely independent of changing conformation (15). Therefore, the conformational changes can not be directly detected in the FTIR spectrum.

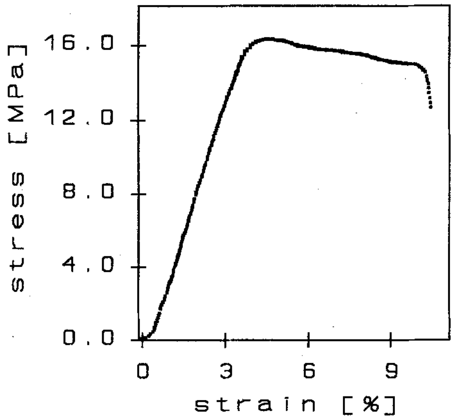


Fig. 4 a. Stress-strain curve of DGEBA / D-400 at T_g - 20 K

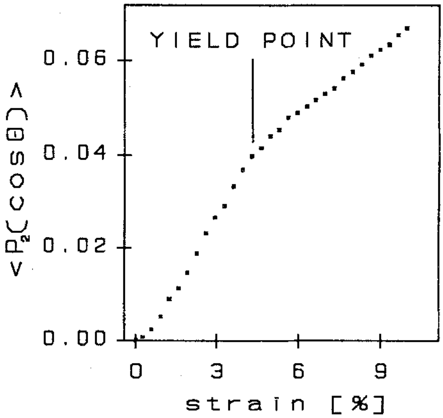


Fig. 4 b. Orientation function of DGEBA / D-400 at T_g - 20 K

Deformation below the glass transition temperature

The deformation and orientation behavior of DGEBA / D-400 was also investigated below T_g. In the glassy state the epoxy films are extremely brittle. At room temperature, they break before yielding at strains up to 2 %. Therefore, the film samples were stretched at a temperature close to the glass transition temperature at T_g - 20 K. In Fig. 4 the stress and $< P_2 (\cos\theta) >$ are plotted versus strain.

Both curves completely differ from the linear behavior of the corresponding curves at $T > T_g$. The stress-strain plot is characterized by the appearance of the yield point indicating a significant change in the mechanism of deformation. The orientation function $< P_2 (\cos\theta) >$ shows an abrupt change of its slope. The strain at this bend precisely coincides with the yield strain. Before and behind the bend, $< P_2 (\cos\theta) >$ depends nearly linear on the strain. After the yield point, the orientation increases considerably slower.

Other DGEBA / amine systems studied show the same typical bend in the plot of $< P_2 (\cos\theta) >$ in the vicinity of the yield point (9). Analogous results were also obtained for the orientation behavior of epoxy resins based on novolacs (7).

The characteristic change of the molecular orientation behavior in the yield region has to be related to the mechanism of plastic deformation. The deformation of glassy polymers is a very complex process. It is associated with the formation of specific defects (16,17), which store the elastic energy without significant changes of the conformational distribution. These plastic deformation defects begin to nucleate and to grow in the sample prior to the yield point. Thermodynamically, the deformed local regions of the sample are metastable states.

During further elongation, the energy of the individual defects more and more increases until the internal energy stored in the plastic shear defects reaches a plateau. At this stage of deformation, which macroscopically corresponds to the yield point region, the defects begin to transform. The defect relaxation leads to a local conformational rearrangement of the polymeric chains in the core of the defects (16). The conformational transitions conserve the microscopic deformation in the volume element concerned, but at a significantly lower level of energy.

The main contribution to an increase in the orientation results from nucleation and growth of the plastic shear defects. Due to molecular slip and glide events the matter in the shear defects becomes more and more oriented. The repeated nucleation of such defects prior to the yield point leads to a rapid growth of the defect concentration and, consequently, to a steep increase in the orientation function. After passing through the yield region, the process of shear defect nucleation is continued. However, the defect concentration effectively does not increase any more due to the simultaneous decomposition of defects by complex conformational rearrangements. The conformational transitions predominantly preserve the degree of orientation already achieved. Accordingly, the orientation in the epoxy films is growing slower beyond the yield point, and the curve of $< P_2 (\cos\theta) >$ changes its slope in this region.

The rearrangement of the conformational distribution can not be directly observed in the FTIR spectrum. The reasons for the lack of intensity changes due to conformational transitions have already been discussed above.

Cyclic deformation

The investigation of the reversibility of the orientation during unloading of the sample may contribute to a more detailed understanding of the molecular mechanisms involved in the deformation process above and below the glass transition temperature. Rheo-optical infrared spectroscopy offers the opportunity to obtain comprehensive information on molecular orientation and relaxation phenomena occurring during deformation cycles, including elongation, recovery, stress relaxation, and fatigue.

Therefore, DGEBA / D-400 was subjected to four successive loading - unloading cycles at $T_g + 20$ K, and the appearance and relaxation of the orientation was simultaneously monitored by FTIR spectroscopy. The stress-strain curve and the second-order moment of the orientation function are plotted in Fig. 5.

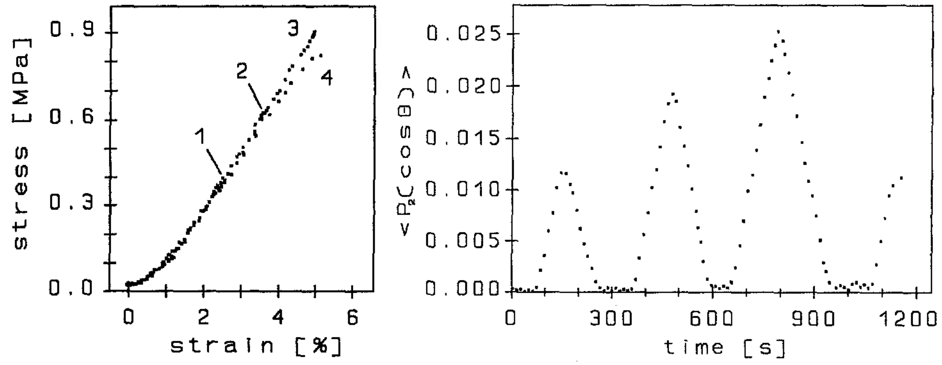


Fig. 5. Cyclic deformation of DGEBA / D-400 at T_g + 20 K
a) stress-strain curve ; b) orientation function

In each cycle, the film sample was stretched to a higher maximum strain than in the preceding one. The stress again depends linearly on the strain. The curves for elongation and recovery are identical without any hysteresis effect, and the curves of all subsequent cycles are in congruence as well. The strain completely disappears upon unloading. Obviously, fatigue effects like disentanglement or successive chain rupture in overstrained network segments did not occur.

The rise and fall of the $< P_2 (\cos\theta) >$ values shown in Fig. 5 b exactly reflect the increase and decrease of the strain. Upon unloading, the orientation totally vanishes without any time lag to the disappearance of the stress. Consequently, the molecular orientation of the DGEBA / D-400 networks is completely reversible above the glass transition temperature. This corresponds with the excitation and the entropy-driven relaxation of conformational states during deformation. The results of the cyclic deformation experiments indirectly confirm the occurrence of conformational changes whose direct observation failed due to the lack of suitable infrared bands sensitive to such changes.

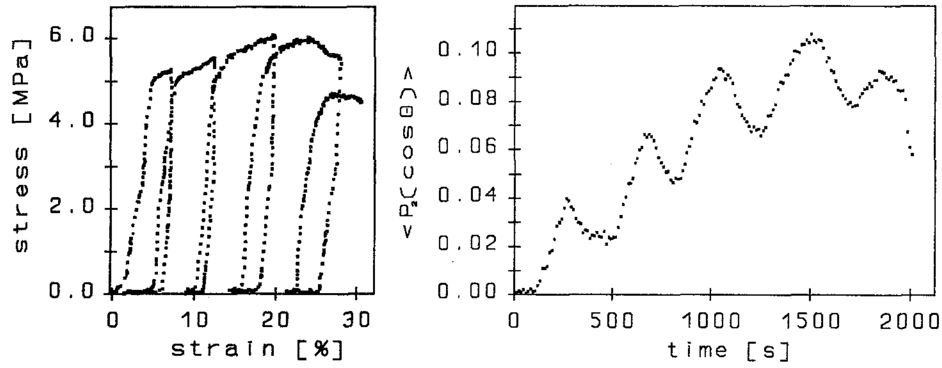


Fig. 6. Cyclic deformation of DGEBA / D-400 at T_g - 20 K
a) stress-strain curve ; b) orientation function

The molecular orientation behavior during cyclic deformation of DGEBA / D-400 was also studied in the glassy state. Again, the sample was subjected to successive loading - unloading cycles until failure of the film. The stress-strain diagram at T_g - 20 K and the corresponding Legendre polynomial $< P_2 (\cos\theta) >$ are shown in Fig. 6.

In the course of five loading-unloading cycles the epoxy film was gradually stretched to higher and higher maximum strain. This procedure leads to a significantly higher elongation-to-break than during simple continual deformation. Obviously, the toughness of the system considerably increases due to the cyclic process.

Upon unloading the sample, a hysteresis can be observed in the stress-strain plot. The strain does not completely disappear, and a permanent elongation of the samples was observed which does not vanish up to the beginning of the next cycle. After each cycle, the permanent elongation effect becomes more marked.

The orientation also only partly relaxes when the sample is unloaded. A residual orientation of approximately 50 % of the preceding maximum value of $< P_2 (\cos\theta) >$ remains in the sample. In an additional experiment, this plateau orientation was found to be nearly constant during stop of the stretching machine for at least 90 min. So, the epoxy film becomes more and more oriented during the five deformation cycles. This causes a self-reinforcement of the sample indicated by the behavior of the elastic modulus increasing from cycle to cycle. The permanent orientation and the self-reinforcement phenomenon correspond to the incomplete recovery of the shape of the sample.

The results of the cyclic deformation of DGEBA / D-400 at $T < T_g$ are in accordance with the presented molecular mechanism of deformation in the glassy state. The orientation mainly results from nucleation and growth of the plastic shear defects. However, these defects are stable under stress only. Therefore, its contribution to $< P_2 (\cos\theta) >$ quickly relaxes if the stress vanishes. The remaining plateau in the plot of the orientation function reflects the conformational changes, being irreversible below T_g. When the sample is heated up to 20 K above the glass transition temperature for some minutes, the orientation plateau disappears immediately due to the relaxation of the conformational changes (9).

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