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*FT*i.r.–rheo-optical characterization of the molecular orientation behaviour of amine cured epoxy resins during cyclic deformation

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Rheo-optical *FT*i.r. spectroscopy was used to study molecular orientation phenomena in highly crosslinked epoxies on the basis of the diglycidyl ether of bisphenol-A and a polyetherdiamine. In previous publications, their orientation behaviour during continuous uniaxial deformation was described. The present paper reports on the rheo-optical characterization of these resins during specific cyclic deformation experiments below the glass transition temperature (T_g). Epoxy films were subject to various successive loading–unloading cycles including elongation, recovery, annealing, and stress relaxation in order to study the reversibility of the orientation during relaxation processes. The investigations show that the orientation is only in part reversible upon unloading or stress relaxation below T_g. However, it can be annealed by heating the epoxy resin to above T_g. Furthermore, it was found that no significant fatigue due to chain scission occurs until failure of the sample. The results were discussed with respect to the mechanism of plastic deformation. Copyright © 1996 Elsevier Science Ltd.

(Keywords: epoxy/amine resins; rheo-optical *FT*i.r. spectroscopy; molecular orientation behaviour)

INTRODUCTION

The characterization of orientation effects in polymers on a molecular scale has become a field of intense investigation in order to study the relationships between orientation and mechanical properties. Molecular orientation studies carried out simultaneously with mechanical treatment provide substantial contributions to a more comprehensive knowledge about the underlaying mechanisms of polymer deformation. Rheo-optical Fourier transform infra-red (*FT*i.r.) spectroscopy is one of the most powerful tools for monitoring transient structural changes during the deformation of polymers. It offers a unique possibility to obtain detailed information about molecular orientation and relaxation phenomena occurring during various deformation processes, including elongation, recovery, stress relaxation, and fatigue. Due to the versatility of rheo-optical *FT*i.r. spectroscopy, it has been successfully applied to the characterization of the orientation behaviour of a wide variety of polymers[1–8]. However, up to now highly crosslinked networks have not yet been investigated using this method.

In a series of papers, we reported on the results from the first application of rheo-optical *FT*i.r. spectroscopy to the characterization of complex orientation phenomena in highly crosslinked epoxy networks during uniaxial deformation both above[9] and below[10,11] the glass transition temperature (T_g). In the preceding paper[12], the molecular orientation behaviour of diglycidyl ether of bisphenol-A (DGEBA)/polyetheramine epoxies during continuous deformation in the glassy state was described. The results were discussed on the basis of a simple model for the molecular mechanism of plastic deformation. However, the expected conformational changes could not be observed in the *FT*i.r. spectrum due to the lack of suitable i.r. bands sensitive to such changes.

The present paper deals with an investigation of successive elongation–recovery cycles in order to study the reversibility of the orientation. Rheo-optical *FT*i.r. spectroscopy has proved to be the ideal experimental technique for the characterization of orientation and relaxation phenomena occurring during such cyclic deformation experiments[6,11,13–16]. The question of reversibility of the orientation upon unloading the stretched sample is essential for a more fundamental understanding of the molecular mechanisms involved in polymer deformation. Moreover, rheo-optical investigation of cyclic deformation is expected to confirm the occurrence of conformational changes during plastic deformation in an indirect manner.

THEORETICAL BACKGROUND OF ORIENTATION MEASUREMENTS BY RHEO-OPTICAL *FT*i.r. SPECTROSCOPY

The state-of-art of rheo-optical *FT*i.r. spectroscopy and its applications in the real-time investigation of orientation phenomena in polymers has been summarized in a number of review papers[2,13,17,18]. Here, the basic principles of this specific i.r.–dichroism measurement will be outlined briefly. Although the following approach is based on relatively simple models, it has been successfully used for the characterization of orientation in many different polymers.

The anisotropy of a polymer sample induced by a deformation process may be described by an orientation distribution function $f\ (\theta, \phi, \psi)$. The segmental orientation in uniaxially-oriented samples can be expressed with respect to the orientational axis in terms of the second Legendre polynomial $\langle P_2(\cos\theta)\rangle$ as

$$f = \langle P_2(\cos\theta)\rangle = \frac{3\langle\cos^2\theta\rangle - 1}{2} \qquad (1)$$

where θ is the average angle between the chain axis and the stretching direction. Equation (1) is known as the Hermans orientation function which was defined for the evaluation of orientation measurements by X-ray diffraction and fluorescence polarization[4,18,19].

In i.r. spectroscopy, the dichroic ratio of a well-defined absorption band

$$R = \frac{A_{\parallel}}{A_{\perp}} \qquad (2)$$

is related to the second moment of the orientation distribution function $\langle P_2(\cos\theta)\rangle$ by the expression

$$f = \frac{(R-1)(R_0+2)}{(R+2)(R_0-1)} \qquad (3)$$

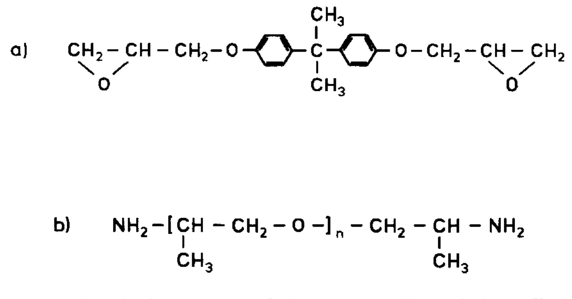
where $A_{\parallel}$ and $A_{\perp}$ are the absorbances with the polarization direction parallel or perpendicular to the stretching direction, respectively. $R_0 = 2\cot^2\alpha$ represents the theoretical dichroic ratio for perfect alignment of the chains, and α is the angle between the local chain axis segment and the transition moment vector of the vibrational mode considered. The orientation of a transition moment vector relative to the chain axis can be obtained from theoretical considerations[1,17]. On the other hand, the angle α can be calculated if the orientation function was determined from an independent experimental method or another well defined absorption band attributed to the same phase of the polymer under investigation.

EXPERIMENTAL

Sample preparation

DGEBA was cured with Jeffamine curing agents (Texaco, Houston). D-400 and D-2000 are linear aliphatic diamines with poly(propylene oxide) backbones of different chain length. The designation number refers to the approximate molecular weight of each species. The polyetherdiamines were used without further purification. The chemical structures of the materials used are shown in *Figure 1*.

DGEBA was purified by recrystallization from a mixture of acetone and methanol (m.p. = 42°C)[20]. For sample preparation, DGEBA was preheated to 75°C for 30 min in order to completely melt any micro crystals. Then, the D-400 amine was added in the stoichiometric ratio. After stirring, the mixture was vacuum degassed for some minutes.



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

Figure 1 Chemical structure of the epoxy resin and the Jeffamines: (a) DGEBA; (b) D-400 and D-2000

The Jeffamine D-2000 was used in blends with D-400 (95 mol% D-400 and 5 mol% D-2000). The total epoxide/amine ratio was set at the stoichiometric ratio again. At first, the epoxy resin was precured with D-2000 at 95°C for 2 h before adding the D-400. The final mixture was stirred again and degassed under vacuum.

Thin epoxy films suited for both mid-i.r. spectroscopy and mechanical measurements were made by casting the mixture between preheated steel plates. These plates were covered with release films from poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP, Richmond Aircraft Products, Santa Fe Springs, California). The steel device ensures controllable diversion of the heat of reaction and guarantees isothermal curing. DGEBA/D-400 epoxies were cured at 95°C for 20 h whereas the samples containing the amine mixture were cured for 48 h. No post-curing was necessary, since the ultimate glass transition temperatures (T_gs) of the systems investigated are significantly lower than the curing temperature.

Samples for comprehensive analytical characterization of the cured epoxies were made by pouring a part of the epoxy/amine mixture prepared for film casting into small preheated steel frames treated with Frekote release agent (Dexter, Seabrook, New Hampshire). The frames were then covered with FEP release films and placed between steel plates preheated to the curing temperature as well. Crosslinking reactions proceeded simultaneously to film curing under the same conditions.

The deformation behaviour of glassy polymers strongly depends on the thermal history of the sample. In order to ensure equal conditions, the cured epoxy specimens were stored in a desiccator at 40°C for at least 3 months before investigation.

Sample characterization

The final epoxide and amine conversion in the cured specimens was checked by near-i.r. (n.i.r.) spectroscopy. The n.i.r. spectra of samples 2 mm thick were recorded on a Bruker IFS 66 *FT*i.r. spectrometer fitted with a tungsten source, a silicium-coated calcium fluoride beam-splitter and an InSb detector cooled by liquid nitrogen. 32 scans were coadded at 2 cm^{-1} resolution.

The consumption of epoxide and amine functionalities was monitored by the combination band at 2205 nm and the NH_2 overtone at 1530 nm, respectively. The former one is assigned to the combination of the C–H stretching fundamental at 3050 cm^{-1} with the CH_2 deformation band at 1460 cm^{-1}[21]. For quantitative determination of epoxide groups this band is preferred due to its isolated position in the spectrum. The epoxide overtones at 1650 and 1159 nm are partly superimposed by the absorptions of other groups.

In the cured samples no remaining epoxide or amine functionalities were found by means of n.i.r. spectroscopy. Furthermore, during the thermomechanical (t.m.a.) and dynamicmechanical (d.m.a.) mechanical analyses, temperature scans postcuring effects were not observed. The curing kinetics of the DGEBA/Jeffamine system have been investigated by Morgan *et al.*[22]. Within the

Table 1 Glass transition temperatures and network densities

Epoxy resin	T_g (°C)	M_c (g mol^{-1})
DGEBA/D-400	50	605
DGEBA/D-400 + D-2000	42	625

temperature range used throughout the present study, the cure reaction is dominated by the epoxide/amine reaction, and very little side reaction takes place.

The T_gs of the cured epoxies were determined by t.m.a. Measurements in the range of −80°C to 150°C were performed on a Perkin Elmer TMA 7. Flat disk-like samples (2 mm thick) were investigated in the penetration mode with a probe force of 2 N. Every specimen was scanned twice at a heating rate of 10 K min^{-1}. The results are given as mean values in *Table 1*.

D.m.a. was used for the determination of the average molecular weights between crosslinks (M_C)[9]. A Rheometrics Dynamic Analyser RDA II was employed for experimental data collection. The temperature range and heating rate were the same as during t.m.a. measurements. The network densities are included in *Table 1*.

Rheo-optical FT*i.r. spectroscopy*

The rheo-optical measurements were carried out using a variable-temperature electro-mechanical stretching machine developed by Siesler[14]. Polymer films can be studied in deformation and relaxation experiments at variable strain rates and under controlled temperature conditions with an accuracy of ±0.5 K. The sample cell of the stretching apparatus is heated with dry air supplied by the spectrometer purge system. For real-time recording of the stress–strain data and controlling parameters such as temperature, elongation rate etc. the apparatus is equipped with a computer. The specimen is stretched symmetrically along the z-axis in order to observe always the same region of the film. The machine can be moved by micrometer screws to exactly align the central sample area with respect to the i.r. beam. The sample position was carefully adjusted at the convergence point of the incident i.r. radiation. The stretching device has been described in detail elsewhere[14].

The stretching machine was mounted in the sample compartment of a Bruker IFS 66 *FT*i.r. spectrometer equipped with a MCT detector operating at 77 K. Single-channel spectra with 10 scans were run at 2 cm^{-1} resolution. They were taken consecutively in 6.5-s intervals. Upon completion of the experiment, absorbance spectra were calculated using two spectra of the polarizer as references which were recorded with different polarization direction before the rheo-optical experiment.

The polarization direction of the incident radiation was alternately adjusted parallel and perpendicular to the stretching direction by rapid 90° rotation of a gold wire-grid polarizer (Specac, UK). The polarizer is mounted in a self-constructed electro-mechanical rotator. The change of the polarization direction is automatically initiated by the last scan of each spectrum.

The large number of spectra collected during a rheo-optical experiment requires specific evaluation software for further data processing. The automated data treatment includes all tasks such as transformation to absorbance spectra, normalization to a suitable reference band, band separation and integration, calculation of the dichroic ratio and the orientation function as a function of strain or time, and presentation of the results. Additional software has been developed for evaluation and presentation of the stress–strain–time data.

I.r. dichroism measurements require band absorbances to be sufficiently low to obey the Lambert–Beer law. Therefore, thin epoxy films with a thickness of about 10 μm had to be prepared. Because of the extreme brittleness of such epoxy films they had to be peeled off the release film and handled with great care to avoid any damage of the specimens before mechanical treatment. Specimens for rheo-optical experiments were cut with gauge dimensions of 12 × 8 mm by use of a scalpel. Under a light microscope they were checked for possible defects. Their thickness was determined using a digital length gauge with a resolution of 0.5 μm (Heidenhain model MT 25B). Its accuracy was checked by comparison with the interference fringes in the i.r. spectrum of polyethylene. Only samples with a constant thickness and without any visible flaws were utilized for rheo-optical characterization.

After transfer of the film specimens into the stretching machine they were subjected to successive loading–unloading cycles. The procedures of the various cyclic deformation experiments are reported in Results and Discussion. All samples were stretched with a constant loading and recovery rate of 0.005 mm s^{-1}.

RESULTS AND DISCUSSION

Dichroic behaviour of the investigated bands

One of the major difficulties of rheo-optical *FT*i.r. spectroscopy is to find suitable absorption bands for orientational measurements. Firstly, the assignment of the investigated bands must be well known in order to deduce the exact direction of the transition moment with respect to the local chain segment. Secondly, the band absorbances are required to be sufficiently low to permit the use of the Lambert–Beer law. Only a few absorption bands in the i.r. spectra of the epoxy films used in the present study are suited for orientational measurements. The *FT*i.r. spectrum of an undeformed DGEBA/D-400 film sample taken without polarizer is plotted in *Figure 2*.

Only bands with absorptions smaller than 1.0 were evaluated for calculating the orientation function. The

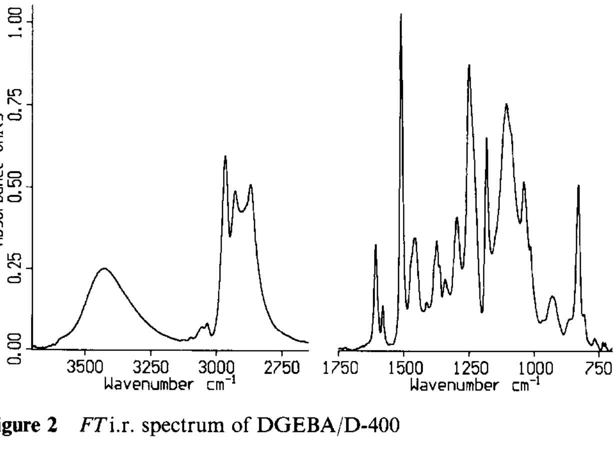


Figure 2 *FT*i.r. spectrum of DGEBA/D-400

absorbances $A_{\parallel}$ and $A_{\perp}$ are determined from integral or peak-maximum intensities of well defined vibrational bands. The intensities of all spectra obtained during a rheo-optical experiment were related to the intensity of a reference band in order to compensate for the decrease of sample thickness during elongation. The absorption at 1610 cm^{-1} attributed to the ν (C=C) stretching mode of the *para*-disubstituted benzene ring in the DGEBA molecule was found to be a suitable reference band.

In comparison with other polymers only very small changes of the dichroic ratio could be observed for epoxy resins during the investigation with rheo-optical *FT*i.r. spectroscopy. The bands selected for evaluation must be well assigned in order to deduce the transition moment direction with respect to the local chain segment. In the present study we have carefully examined the dichroic behaviour of several vibrational bands in the i.r. spectrum of DGEBA/Jeffamine epoxies.

The vibrational modes of the *para*-disubstituted benzene ring in the DGEBA molecule have been analysed using the results by Kulczycki[23] and Varsanyi[24]. Kulczycki assigned the absorption bands of bisphenol-A polycarbonate to the various normal modes given by Varsanyi. DGEBA belongs to the same symmetry group (C_{2v}) as bisphenol-A polycarbonate. Most of the bands are attributed to A_1 or B_2 modes. For A_1 modes the dipole moment vector is localized along the C_1–C_4 axis of the ring. For the B_2 modes the transition moment is perpendicular to this direction and lies in the plane of the ring. No dichroism was observed for absorptions corresponding to A_1 or B_2 modes. The only aromatic absorption in the spectrum which is influenced by the deformation process is the B_1 mode located at 831 cm^{-1}[9]. It is ascribed to an aromatic C–H out-of-plane bending vibration. The vector of the transition moment corresponding to this band stands perpendicular to the plane of the aromatic ring. An increasing dichroism with proceeding extension of the specimen was observed for this absorption.

Absorption bands assigned to various vibrations in the backbone of the chains, e.g. the ether bonds, do not show any variations of the dichroic ratio. Apart from the general intensity decrease due to the thickness reduction of the sample these bands are not at all influenced by the deformation of the network.

The transition moment corresponding to the CH_2 stretching vibrations at 2930 and 2872 cm^{-1} is assumed to be perpendicular to the local chain axis segment ($\alpha = 90°$)[1]. The latter band was used for the calculation of the orientation function.

Owing to the almost uncoupled nature of the methyl group, the transition moment of the CH_3 symmetrical bending vibration modes appearing at 1360 and 1386 cm^{-1} is localized along the C–CH_3 bond[3], i.e. it is situated perpendicular to the polymer chain axis as well. The absorption bands at 1460 and 3400 cm^{-1} also exhibit perpendicular dichroism, but the exact angles α of their transition moments are unknown.

Orientation phenomena during simple continuous deformation

The stress–strain plot of DGEBA/D-400 + D-2000 at $T_g - 20$ K is shown in *Figure 3a*. It is characterized by the appearance of the yield point. In *Figure 3b*, the orientation function f calculated from the *FT*i.r. spectra recorded during this deformation process is plotted. At the beginning, the orientation rises nearly linearly with increasing strain. When passing through the yield point, a change of its slope can be discerned. After the yield point, the orientation curve increases somewhat slower. Similar results were also observed for other DGEBA/Jeffamine resins[10–12]. The orientation functions of all these epoxies show the same characteristic bend of the curve in the vicinity of the yield point.

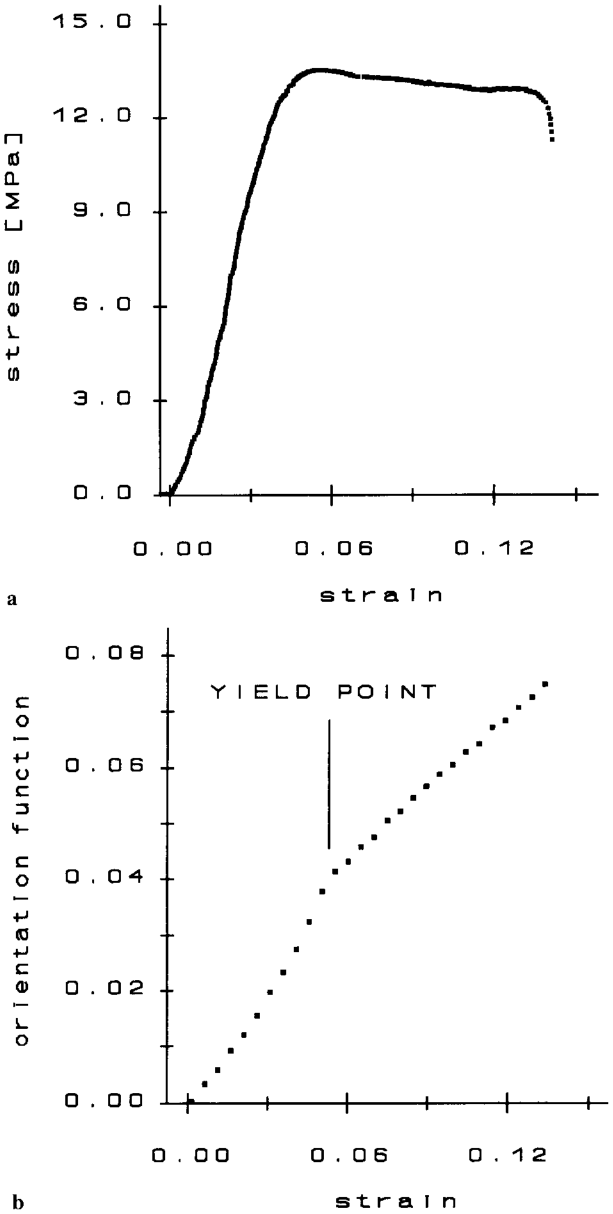


Figure 3 Continuous deformation of DGEBA/D-400 + D-2000 at $T_g - 20$ K: (a) stress–strain curve; (b) orientation function f vs strain

The phenomenon of changing slope in the yield region indicates a significant change of the molecular orientation behaviour and has to be related to the mechanism of plastic deformation. Plastic deformation of glassy polymers is a quite complex process. It has been the subject of numerous investigations. Models for the molecular mechanism of deformation of epoxy resins at temperatures below T_g were discussed by Oleinik[25–27] and Caux *et al.*[28]. These models were applied to the interpretation of rheo-optical data of epoxy resins cured with Jeffamines[12].

Plastic deformation is associated with the formation of specific defects, which store elastic energy without significant changes in the conformational distribution[26,27]. Nucleation and growth of the deformation defects begin to occur after the elastic zone of the stress–strain curve. The defects originate from molecular slip, glide and rotation processes induced by the shear component of the applied stress. From the thermodynamical point of view, the plastic shear defects are metastable states. Due to the molecular slip events, the matter in the defects becomes increasingly oriented. The repeated nucleation of shear defects leads to a rapidly growing defect concentration and results in a steep increase in the orientation function.

The energy of the individual defects increases more and more during further deformation. Upon approaching the yield point region, the internal energy stored in the plastic shear defects levels off. The shear defects terminate their growth and begin to transform. This relaxation process leads to a local conformational rearrangement of the chain segments in the defects[27]. The conformational transitions conserve the microscopic displacement in the defects, but at a considerably lower level of energy.

The change of the molecular mechanism of glassy state deformation in the yield point region is reflected in the changing slope of the orientation function, f. The main contribution to an increase of f results from the formation and propagation of new shear defects. During their growth, the chain segments inside the defects become more and more oriented due to the molecular slip processes. The conformational transitions starting in the yield region predominantly fixed the degree of orientation already achieved. Prior to the yield point, the shear defect concentration rapidly increases because of their continual nucleation. After passing through the yield region, the defect concentration effectively does not increase any more due to the simultaneous conversion of shear defects by conformational rearrangements. Accordingly, the orientation is growing somewhat slower.

The complex conformational rearrangements are expected to be reflected in the spectra since conformational changes are usually easy to detect with *FT*i.r. spectroscopy. Such changes were observed during deformation processes in a wide variety of polymers[2,13,14] including networks such as various rubbers[3] and poly(dimethylsiloxane)[7]. However, no intensity changes originating from stress-induced conformational transitions could be found during the rheo-optical investigation of the deformation behaviour of epoxy networks in their rubbery or glassy state[9–12].

The reasons for the lack of intensity changes due to conformational transitions have been discussed in detail in a preceding paper[9]. The diphenylpropane group in the DGEBA molecule is an extremely rigid structure which largely resists any deformation. Therefore, deformation is predominantly localized in the more flexible polyether chains of the Jeffamine curing agents. The i.r. spectrum of epoxies based on DGEBA is dominated by the very strong absorbances of the diphenylpropane unit. Only one vibrational mode in the fingerprint region of the spectrum is attributed to the aliphatic amine molecules (ν C–O–C at $1105\,\mathrm{cm}^{-1}$). However, although a great number of vibrational bands in the i.r. spectra of polyethers is known to be sensitive to specific conformations, the absorption at $1105\,\mathrm{cm}^{-1}$ is not influenced by conformational changes[29].

Orientation phenomena during cyclic deformation

Since the direct spectroscopic observation of the rearrangement of the conformational distribution during continuous deformation failed due to the lack of suitable conformation-sensitive i.r. bands, specific experiments on the basis of deformation cycles were designed for obtaining indirect evidence. Moreover, the investigation of the reversibility of the orientation during such deformation cycles should substantially contribute to a more fundamental understanding of the molecular mechanisms involved. Rheo-optical *FT*i.r. spectroscopy offers an excellent opportunity to obtain comprehensive knowledge about molecular orientation and relaxation phenomena occurring during cyclic deformation experiments.

The molecular orientation behaviour of DGEBA/D-400 was studied during cyclic deformation at $T_g - 20\,\mathrm{K}$. The sample was subjected to successive loading–unloading cycles, and the appearance and relaxation of the orientation was simultaneously monitored by i.r. spectroscopy. The stress–strain plot and the corresponding second moment of the orientation distribution function calculated from the ν_s CH_2 symmetric stretching vibration at $2872\,\mathrm{cm}^{-1}$ are shown in *Figure 4*.

In the course of five deformation cycles the epoxy film was gradually stretched to higher and higher maximum strain. This procedure leads to a significantly higher ultimate elongation than during simple continuous deformation (about 30% *versus* 9.9%). Obviously, the toughness of the glassy resin considerably increases due to the cyclic process. Analogous observations were reported by Morgan *et al.*[30] and Erina *et al.*[31].

When the stretched sample is unloaded, a marked hysteresis is observed in the stress–strain diagram. The strain does not completely relax. Therefore, a permanent elongation of the film sample can be observed which does not disappear by the beginning of the next cycle. After each cycle, the permanent elongation becomes more pronounced.

The orientation also only partly relaxes upon unloading the epoxy film. In the initial phase of the unloading process, the orientation function decreases in synchrony with the drop of the strain. However, the orientation relaxation rapidly falls behind the decreasing stress and proceeds to occur after the complete disappearance of the stress. Finally, it levels off leaving a residual orientation of about half of the difference between the preceding maximum orientation and the orientation level before the respective deformation cycle. During repeated elongation–recovery cycles, the sample becomes more and more oriented. This leads to a gradual self-reinforcement of the epoxy resin indicated by the behaviour of the Young's modulus increasing from one cycle to the next. The self-reinforcement and the permanent orientation correspond to the incomplete recovery of the shape of the sample upon unloading.

The results of the cycle deformation experiment shown in *Figure 4* are in accordance with the expected molecular mechanism of deformation below T_g. The rise of the orientation is mainly caused by the formation and growth of plastic shear defects. However, these defects are stable under stress only (except for $T \ll T_g$)[26]. Therefore, their contribution to the orientation function quickly relaxes if the stress vanishes. The nearly exponential decay of the orientation is caused by the fact that defects with an internal energy of $\Delta E \leq kT_{\text{def}}$ disappear simultaneously with the decrease of the stress whereas defects having $\Delta E \geq kT_{\text{def}}$ relax somewhat more gradually[26]. The remaining plateau in the plot of the orientation function should reflect the conformational rearrangements as a result of the relaxation of shear defects. These conformational transitions are irreversible below T_g and cause the observed permanent orientation as well as the lasting increase of sample length.

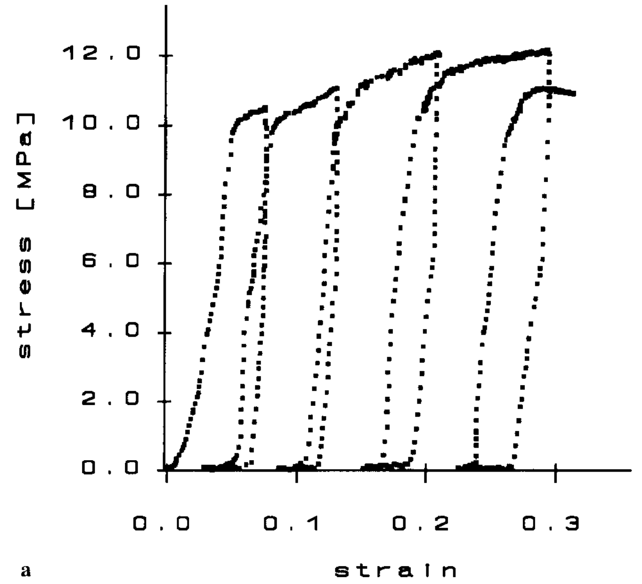
The 'frozen' orientation in the sample can be erased by annealing of the conformational changes only. For that, the sample has to be heated to above the T_g. In *Figure 5*, the results from a rheo-optical experiment including cyclic deformation, orientation relaxation, and heating of the epoxy film sample above T_g are shown. After the first deformation cycle, the sample was allowed to relax for 15 min before starting the next cycle. Following the second elongation–recovery cycle at $T_g - 20$ K, the unloaded sample was rapidly heated up to $T_g + 20$ K. After 2 min, the sample was cooled down (most of the time in the much longer period of interruption was needed for the heating and cooling processes). When the previous deformation temperature was attained, the sample was elongated again until failure of the film.

During the first two elongation–recovery cycles, the same behaviour as in the experiment plotted in *Figure 4* is observed. Upon unloading, the orientation only in part relaxes, and the initial length of the epoxy film is not completely recovered. Even during the break following the first cycle, no significant relaxation can be discerned. In an additional experiment, the plateau of the orientation function was found to show only a very weak decrease when the stretching machine was stopped for 90 min.

However, upon heating the unloaded sample to above T_g for some minutes, both the remaining orientation and the permanent increase of the sample length disappear immediately. During the following reloading the sample seems to behave just as in the initial cycle.

The plateau in the orientation function below T_g and its instantaneous disappearance just on reaching the glass transition region correspond to the behaviour of conformational transitions. Thus, the results from the two cyclic deformation experiments clearly confirm the occurrence of conformational changes during the plastic deformation process which could not be observed directly in the spectrum of the epoxies due to the lack of suitable i.r. bands sensitive to such changes. In addition, Oleinik[26] found an exotherm peak near T_g in the differential scanning calorimetry (d.s.c.) curve of polystyrene samples after stretching them well below T_g reflecting the release of the conformational rearrangements induced during the glass state deformation.

The nearly complete recovery of the initial sample length in *Figure 5* demonstrates that chain scissions in the deformed polymer network are of minor importance. When the sample is elongated again, the maximum stress is a little bit lower than in the preceding cycles, indicating slight fatigue of the material during the previous thermal and mechanical treatment of the sample. However, the



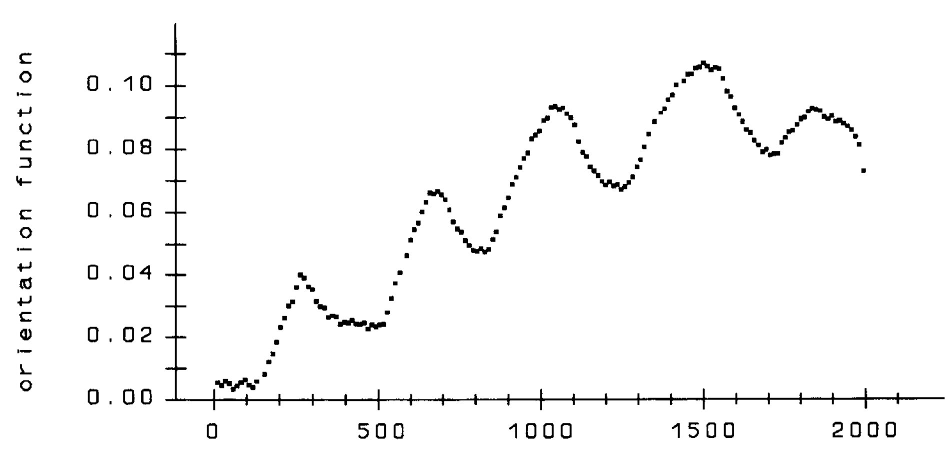
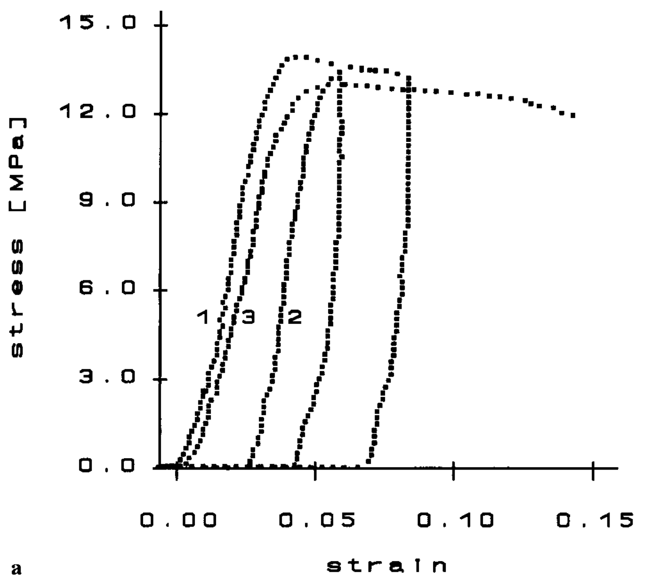


Figure 4 Cyclic deformation of DGEBA/D-400 at $T_g - 20$ K (5 successive loading–unloading cycles): (a) stress–strain curve; (b) orientation function f vs time

slope of the orientation function during the third cycle resembles that in the first cycle, and no other significant fatigue effects can be observed.

The molecular orientation behaviour in amine cured epoxy resins during cyclic deformation in the rubbery state was investigated too. Results have already been published in a previous paper[9]. The networks were also subjected to several successive loading–unloading cycles, and the increasing and decreasing orientation was studied by *FT*i.r. spectroscopy. The stress–strain curves for elongation and recovery of all subsequent cycles are identical and do not show any hysteresis effect. The strain completely disappears during unloading, and no remaining elongation of the samples could be detected.

The behaviour of the orientation function f exactly reflects the rise and fall of the strain; f is nearly linear with respect to the strain. Upon unloading, the orientation totally vanishes without any time lag to the disappearance of the stress. Clearly, the deformation behaviour of the epoxy networks above T_g is completely reversible. This corresponds to the molecular mechanism of deformation in the rubbery state, i.e. the excitation and entropy-driven relaxation of conformational states during a loading–unloading cycle. Furthermore, indications for the occurrence of fatigue effects such as disentanglement or successive chain rupture in overstrained network segments were not found.



Stress and orientation relaxation during cyclic deformation

Several measurements were carried out in the stress relaxation mode. For these experiments, stretching was stopped at different strains for a definite time interval, and the behaviour of stress and orientation function was observed. A typical elongation/stress relaxation experiment is plotted in *Figure 6*. The DGEBA/D-400 + D-2000 epoxy film was pretreated in a loading–unloading cycle at $T_g - 20$ K. After reloading the sample beyond the yield point, the stretching machine was stopped for 300 s. Then, deformation was continued. When the stress had levelled off, the elongation process was interrupted again for 5 min. Upon renewed loading, the sample broke. During the complete duration of the experiment, i.r. spectra with alternating direction of polarization were collected in 6.5-s intervals in order to determine the orientation function.

Upon stopping the stretching device, a rapid decay of the stress is observed. After 300 s, it has nearly reached a constant level. When the elongation is continued, the stress shows a very steep increase, i.e. the tensile modulus is considerably higher than during the initial cycle.

In contrast to the exponential decay of the stress, the orientation function shows a quite different behaviour (*Figure 6b*). After stopping the stretching apparatus, surprisingly the orientation further increases at first. However, after 20 or 30 s the behaviour changes and a slight decrease of the orientation function can be discerned. Upon continuation of the deformation, no delay between the increase of the orientation and the rise of the stress was found.

The observed behaviour of the orientation function will be discussed in terms of the molecular mechanism of glassy state deformation. It was mentioned above that the plastic shear defects can exist under stress only[26]. Therefore, they rapidly relax upon unloading the sample during the first deformation cycle. Their contribution to

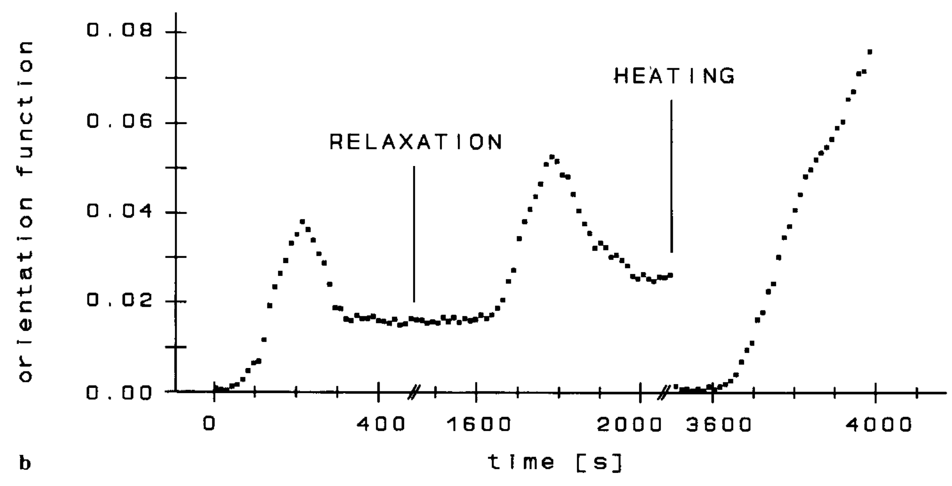


Figure 5 Cyclic deformation of DGEBA/D-400 + D-2000 at $T_g - 20$ K with 15 min relaxation after the first deformation cycle and heating to above T_g between the 2nd and 3rd cycle (see text): (a) stress–strain curve; (b) orientation function f vs time

the orientation function completely vanishes. The residual orientation reflects the conformational transitions being irreversible below T_g.

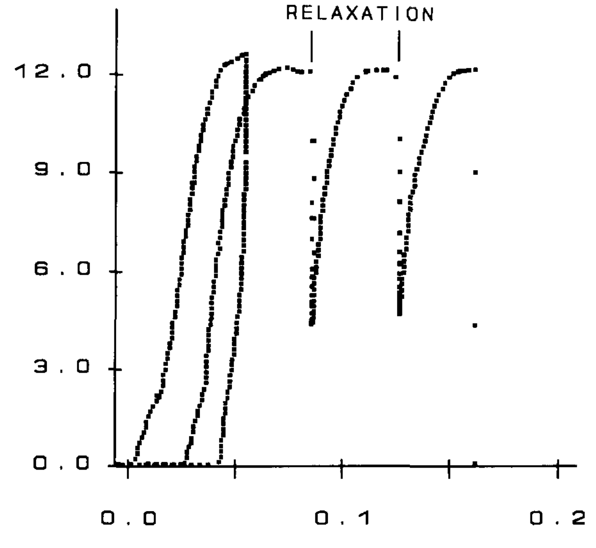
During stress relaxation, the shear defects do not immediately disappear due to the remaining stress. The increase of the orientation function, however, should be a consequence of the stress distribution in the samples. Epoxy resins show a rather irregular structure compared with other polymer networks. During deformation of epoxies, an inhomogeneous stress distribution can develop in the sample causing local stress concentrations. Upon interruption of the stretching without unloading the sample, the local maxima of the internal stress induce molecular slippage events and cause continued nucleation of plastic shear defects. This leads to a further increase of the orientation. The shear defect formation and the conformational rearrangements absorb the excess elastic energy and lead to a more uniform distribution and a rapid decay of the stress. Simultaneously, various orientation relaxation processes start to occur. Due to the considerably reduced level of stress, relaxation of some of the shear defects should happen causing a slight decrease of the orientation. Both processes are superimposed resulting in the observed behaviour of the orientation function. Band shifts due to over-stressed bonds or their relaxation, however, were not found in the i.r. spectra recorded during stress relaxation of the epoxy films.

Siesler performed similar rheo-optical *FT*i.r. investigations during repeated elongation/stress relaxation sequences on poly(butylene terephthalate)[1,2]. He found pronounced conformational changes during elongation of the sample. However, in the stress relaxation intervals, no intensity changes of the conformation-sensitive absorption bands could be detected despite the considerable decrease of the stress.

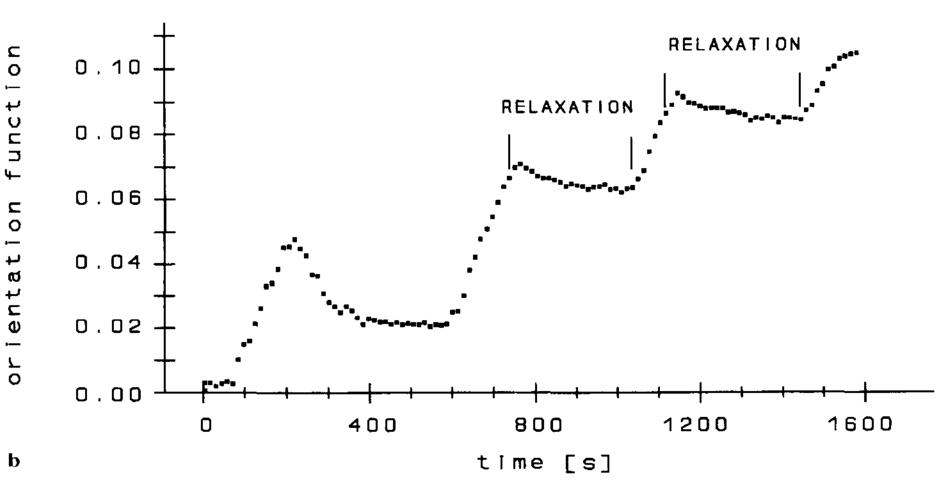
In contrast, Xu *et al.*[32] reported on relaxation of the stress-induced conformational changes in atactic polystyrene when stretching is stopped at the yield point. The initial conformational equilibrium was found to be recovered completely, although a residual stress remained in the sample.

Wool and Statton[33] investigated the stress relaxation behaviour of isotactic polypropylene. They divided the stress relaxation into two stages: a rapid decay region followed by slow relaxation. During the rapid decay, the aligned chains develop an overstress and the non-oriented chains quickly relax. In the slow decay region, the aligned chains tend to relieve the stress by disorientation. The orientation function was found to increase rapidly during the initial stage of fast stress relaxation, then it passed through a maximum, and finally decreased gradually with stress in the slow decay period.

The mentioned homogenization of the stress during the relaxation period becomes evident from the stress–strain diagram. It is reflected in the rapid increase of the stress upon reloading the sample. The stress increases up to the same level as before the onset of stress relaxation. This fact indicates that chain rupture of overstressed bonds does not play an important role during stress relaxation. Obviously, no significant fatigue of the sample occurs until failure of the film. These findings are also supported by the behaviour of the orientation function.



a



b

Figure 6 Cyclic deformation/relaxation experiment with DGEBA/D-400 + D-2000 at T_g − 20 K (for detailed explanation see text): (a) stress–strain curve; (b) orientation function f vs time

CONCLUSIONS

Molecular orientation phenomena in amine cured epoxy resins were studied by rheo-optical *FT*i.r. spectroscopy. In particular, the relaxation behaviour of the orientation during specific cyclic deformation processes was investigated.

Below T_g, the stress–strain plot is characterized by the appearance of the yield point. During simple continuous elongation, the orientation function f shows a characteristic change of its slope in the vicinity of the yield point. This bend indicates a significant change of the molecular orientation behaviour and was discussed with respect to the mechanism of plastic deformation.

The process of plastic deformation consists of two stages. The initial phase is associated with the formation of shear defects without significant changes of the conformational distribution. In the yield point region, transformation of the defects by complex conformational rearrangement starts to occur. However, the main contribution to an increase of the orientation function results from newly induced shear defects. The conformational transitions only conserve the orientation already achieved. Consequently, the orientation increases somewhat slower beyond the yield point.

Unfortunately, the conformational changes could not be observed directly due to the lack of suitable conformation-sensitive bands in the infrared spectrum of the epoxies. Therefore, specific experiments based on deformation cycles were developed for obtaining indirect evidence.

Samples were subjected to various consecutive elongation–recovery cycles in order to study the reversibility of the orientation during these processes. In each cycle, the films were stretched to a higher maximum strain than in the preceding one. Upon unloading, the strain does not completely disappear, and a permanent elongation of the samples is observed. After every deformation cycle, this effect becomes more marked. The orientation is also only in part reversible. A residual orientation remains in the sample. Therefore, the epoxy film becomes more and more oriented during the successive loading–unloading cycles.

The results from the cyclic deformation experiments are in accordance with the presented molecular mechanism of deformation in the glassy state. The orientation mainly results from the formation of shear defects. However, these defects are stable under stress only. Therefore, their contribution to f 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. However, when the sample is heated up to 20 K above T_g, both the permanent increase of the sample length and the plateau in the orientation function disappear immediately due to the annealing of the conformational changes. Thus, the results from the cyclic deformation experiments confirm the occurrence of conformational changes.

Some measurements were carried out in the stress relaxation mode, i.e. stretching was stopped for a definite time interval, and the behaviour of stress and orientation function was studied. Whereas for the stress an exponential decay was observed, the orientation function shows a quite different behaviour. Upon stopping the stretching machine, the orientation function was found at first to increase further, then passed through a maximum, and finally decreased slightly.

As a possible mechanism responsible for stress relaxation in the various polymer systems investigated, specific molecular slippage processes were discussed. Thereby, relaxation leads to a more uniform distribution of the stress over the chain segments. This process is characterized by a rapid decay of the stress and minimum absolute orientation changes. The observed curve of the orientation function is caused by the superposition of the initially continued nucleation of plastic shear defects induced by molecular slip and glide events and the beginning occurrence of various orientation relaxation processes.

Furthermore, it was found that no significant fatigue of the sample due to chain scission effects occurs until failure of the sample.

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