New Aspects of Aging in Epoxy Networks. II. Hydrothermal Aging

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ABSTRACT: An amine cured epoxy is prepared in two different network states for hydrothermal aging. The "low-crosslinked" network has a considerable amount of residual reactive groups and a relatively high-molecular mobility. The low-crosslinked matrix contains high-crosslinked regions. In contrast, the "highly crosslinked" epoxy system has little reactive groups and a lower molecular mobility. Here, low-crosslinked regions are found in a high-crosslinked matrix. Hydrothermal loading for both networks is performed in demineralized water at temperatures below their glass transition. The water plasticizes both kinds of networks which remain in the glassy state, however. As a consequence, in the low-crosslinked epoxy, the increased molecular mobility promotes an ongoing curing reaction leading to the consumption of epoxy groups until an almost complete network has formed. As a new aging process, phase separation occurs in the highly crosslinked epoxy. The new phase is more mobile than the matrix because it has its own glass transition at a lower temperature. In addition, thermooxidative degradation is observed for both network states. Certainly, these chemical and structural changes in the epoxy networks should influence the performance of an adhesive joint, a coating, or a fiber-reinforced composite. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 369–377, 2004

Key words: phase separation; degradation; curing of polymers; epoxy; hydrothermal aging

INTRODUCTION

In service, structural metal joints, polymer coatings, and fiber-reinforced composites are often operating in humid and warm conditions, which leads to hydrothermal aging of the bond.[1,2] The hydrothermal aging behavior of epoxy systems is often focused because they are widely used in structural applications. For epoxies adhesives, many studies are reported in literature concerning the degradation of the joint strength during a variety of hydrothermal loading.[3,4] When water enters the joint, it causes more or less reversible effects on redrying, such as plasticization, which do not directly alter the joint performance. Also, irreversible effects are described leading to a decline of strength which is caused by corrosion of the substrate material[5] as well as chemical and structural changes of the epoxy resin, especially in the vicinity of the substrate.[6–8]

This article discusses new aspects of the hydrothermal aging behavior of an amine-cured epoxy bulk in two network states under hydrothermal loading (immersion in demineralized water at elevated temperatures). The first network state is obtained by postcuring the room-temperature-cured epoxy slightly above room temperature, representing an adhesive as used in low-performance applications. The second state is set by postcuring at elevated temperatures representing an epoxy as used in high-performance applications. The hydrothermal aging processes are studied by gravimetry, infrared spectroscopy(IR), and calorimetry (DSC and MDSC) over a period of about 3 months. The subsequent redrying of the aged samples allows a separation of reversible and irreversible effects caused by hydrothermal aging.

These investigations continue our previous study on thermally aged samples (elevated temperatures in dry air). The corresponding results are reported in Part I of this series.[9] The combined consideration of thermal and hydrothermal aging allows a more profound discussion of the effects observed. By comparing the results, it can be decided whether the changes in the epoxy are induced by water, temperature, or the combined attack.

MATERIALS

The epoxy system investigated is a room-temperature-curing two-part adhesive. Diglycidylether of Bisphenol A (DGEBA) is used as an bifunctional epoxy resin and diethylenetriamine (DETA) is used as a trifunctional amine hardener.

Theoretical background

The curing and the properties of the resulting epoxy network are important aspects to understand the hy-

drothermal aging processes. The curing reaction (comprising a variety of different reactions) starts when the two components are mixed a given curing temperature T_c. The oxirane rings of the epoxy resin are consumed by reacting with the primary or secondary amine groups of the hardener by formation of hydroxide groups. With ongoing reaction, oligomers and branched macromolecules are generated which finally form a polymer network.[10] As the reaction proceeds, the crosslinking density rises. As a result, the molecular mobility in the network is getting more and more restricted. The restricted mobility leads to an increasing glass transition temperature and to vitrification.[11] Finally, for the epoxy system chosen, a maximum degree of conversion is achieved resulting in a maximum glass transition temperature $T_{g\infty}$ when the curing temperature T_c lies above $T_{g\infty}$. In real samples, this $T_{g\infty,\text{real}}$ is lower than the theoretical limit of $T_{g\infty,\text{ideal}}$ because the crosslinking is accompanied by some degradation at high T_c necessary for complete curing. For curing below $T_{g\infty}$, vitrification takes place when the increasing glass transition temperature reaches T_c. In the vitrified network, curing is dominated by the diffusion of reactive species to each other. Because diffusion in the glassy network is rather slow, the curing reaction proceeds with a much lower rate and the mobility reduces still slowly but continuously. As a consequence, the "final" glass transition temperature exceeds T_c in that case but remains below $T_{g\infty}$. Apart from chemical bonds, attractive forces between polar groups reduce the cooperative mobility by forming physical interaction in the network that act like temporary crosslinks. Consequently, such physical crosslinking increases the glass transition temperature to some degree.

After vitrification, the resulting glassy epoxy network equals a supercooled liquid in a nonequilibrium state and is characterized by an excess of free volume and free enthalpy as it is discussed for glassy thermoplastics.[12] The excess of free volume provides a surplus mobility in the glassy polymer. This residual mobility allows the polymer segments to approximate equilibrium slowly by reduction of free volume even in the glassy state. The resulting loss in enthalpy is understood as short-range ordering of chain segments. This process in polymers is called "physical aging." The amount of enthalpy relaxation achieved for a polymer is determined by the difference between the aging temperature T_a and the glass transition temperature T_g. With increasing temperature difference $(T_g - T_a)$, the amount of enthalpy relaxation diminishes. This result is obtained for glassy thermoplastics by varying T_a, whereas T_g keeps constant.[13] Compared to thermoplastics, in reactive epoxy systems on curing at a certain temperature T_c, T_g changes, whereas T_a corresponds to T_c and therefore keeps constant. In analogy to thermoplastics, it is concluded for thermo-

sets that physical aging starts when T_g exceeds T_c on curing. For T_g values just above T_c, a large amount of enthalpy relaxation is produced, whereas with ongoing reaction and consequently increasing T_g, the amount of enthalpy relaxation diminishes again.

Compared to thermoplastics, crosslinking in thermosets additionally reduces the ability for physical aging because of a hindered mobility of segments. Therefore, the enthalpy relaxation possible in epoxies reduces with increasing crosslinking density.

Under hydrothermal loading, it has to be considered that physical aging and water uptake influence each other in the following way suggested. The absorbed water reduces interchain physical interactions and therefore plasticizes the network. Thus, the increased molecular mobility facilitates physical aging. Physical aging in turn decreases the free volume and could lower the diffusion rate as well as the uptake capacity of water. Moreover, the epoxy network will be chemically altered by the absorbed water in some way. In the literature, chain scission is reported in this context.

Experimental procedures

The two components of the epoxy DGEBA and DETA are mixed in a mass ratio of 100 : 14 at 55°C for 5 min followed by cooling to room temperature (see ref. 9 for more details). The mixing ratio is derived from supplementary investigation,[14] where an optimum bond strength of this adhesive with aluminum substrates was required. Compared to the stoichiometric ratio of DGEBA : DETA = 100 : 12.12, the preparation provides an excess of amine hardener.

After 48 h of curing at room temperature, two different network states are prepared by varying the postcuring conditions: The first network state forms by postcuring at 40°C for 24 h and possesses a final $T_g \approx 79$°C. The second network state is set by postcuring at 120°C for 1 h and has a $T_g \approx 131$°C.

Hydrothermal aging is performed in the glassy state by immersion in demineralized water at 40°C for the network postcured at 40°C. Hence, no thermally induced crosslinking is expected further. The aging temperature leads to an oxygen content in the water of 3.8 g $(O_2)/L(H_2O)$. The network postcured at 120°C is hydrothermally aged at 60°C by immersion in demineralized water. The higher aging temperature accelerates the aging processes, which are more hampered by the higher crosslinking density in this network. The higher immersion bath temperature reduces the oxygen content of the water to 2.3 g $(O_2)/L(H_2O)$.

The demineralized water has an initial conductivity of about 10 μs/cm, which increases with time due to leaching of the epoxy sample and the glass container. To provide constant aging conditions, the water is changed at a conductivity of 20 μs/cm.

After 3 months of immersion, the samples are redried in dried air (dew point $< -70°C$) with a well-reduced CO_2 content at the temperatures for hydrothermal aging (40 and 60°C, respectively).

DSC is carried out with a Perkin–Elmer DSC 7 by heating samples (discs with a diameter of 3 mm, a height of 0.8 mm, and mass about 6 mg) in the temperature range from 5 to 200°C at a rate of 10 K/min.

For the thermogravimetric investigation, a Perkin–Elmer TGS2 system is used. The thermal program and the samples are the same as for DSC measurements to get information on the mass loss during the DSC heating step.

IR spectroscopy is performed with a Bruker IFS 66v FTIR spectrometer in attenuated total reflection (ATR) technique by using a ZnSe hemisphere and p-polarized light with an incidence angle of 65°. The samples are made as discs (diameter of 10 mm and a height of 2 mm) with a mass of about 250 mg. The ATR technique provides spectral information from a surface layer with a thickness in the order of the wavelength of the infrared light (i.e., $\sim$ 2.5–12.5 μm). Because DSC and IR spectroscopy differ in information depth and sample shape, the time scales of both experimental sets are not comparable.

The IR investigation is used to evaluate the consumption of epoxy groups. To make the peak intensities comparable, the spectra are divided by the intensity of the phenyl band at 1510 cm^{-1} as internal standard. The epoxy group consumption is quantified by the height loss of the epoxy band at 915 cm^{-1} relative to the height of this band in pure DGEBA. The values depict a spectroscopic degree of conversion which is not identical with the chemical degree of conversion.

Prior to DSC and IR spectroscopy, the samples are wiped with a dry tissue and stored in lab atmosphere for 10 min to remove water from the surface and to reach thermal equilibrium.

RESULTS AND DISCUSSION

The two network states of the unaged epoxy system

In the following, the properties of the two network states are summarized briefly. A detailed discussion of network formation and properties is given in Part I of this series.[9]

The network state obtained by postcuring at 40°C is characterized by a lower crosslinking density (DSC: T_g = 78.6 ± 0.2°C). Enthalpy relaxation due to short-range ordering on curing and postcuring is indicated by the endothermal peak superimposed on the glass transition (DSC). This aging peak represents the amount of heat necessary to remobilize short-range ordered polymer segments. Therefore, the height of the aging peak is a measure for physical aging in the
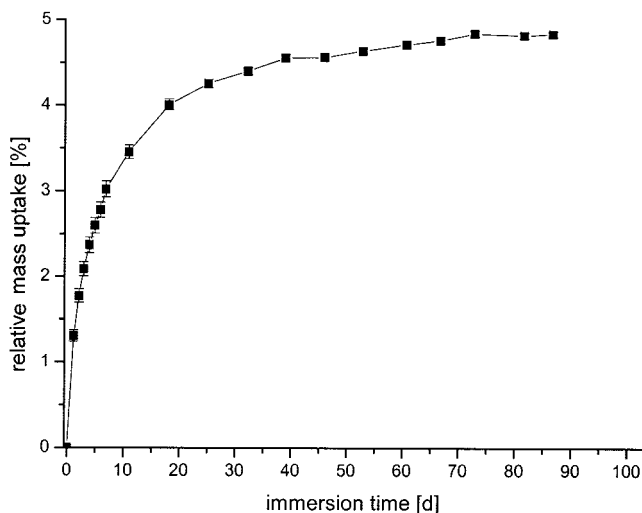

Figure 1 Relative mass uptake of the "low-crosslinked' epoxy system during hydrothermal aging at 40°C.

network. The IR spectroscopy provides 70% of epoxy group conversion. This means that about 30% of residual reactive groups remain in the network. In the further discussion, this network state is denoted as "low crosslinked."

Postcuring the room-temperature-cured epoxy system at 120°C for 1 h results in a system with a glass transition temperature of T_g = 130.9 ± 0.7°C. So, compared to $T_{g\infty,\text{real}}$ = 136°C (derived from supplementary investigation[15]), an almost completely crosslinked network has formed. Only a small amount of enthalpy relaxation remains due to the increased crosslinking density after postcuring at 120°C (compare theoretical background). The consumption of epoxy groups in this network is almost complete (IR-ATR). In the further discussion, this network state will be denoted as "highly crosslinked."

DSC and MDSC investigation on the room temperature cured and the low-crosslinked epoxy system lead to the conclusion that the microstructure of both network states is inhomogeneous with regard to crosslinking density. For the low-crosslinked epoxy system, highly crosslinked regions exist in a low-crosslinked matrix. The highly crosslinked epoxy system is assumed to consist of low-crosslinked regions which are embedded in a highly crosslinked matrix.

Hydrothermal aging of the low-crosslinked epoxy system

During 90 days of water immersion at T_a = 40°C, the low-crosslinked epoxy system absorbs about 4.84 ± 0.03 wt % of water (see Fig. 1). After that time, the sample mass seems to increase only slightly. Therefore, it is assumed that saturation is not fully completed within 90 days. On redrying the epoxy system
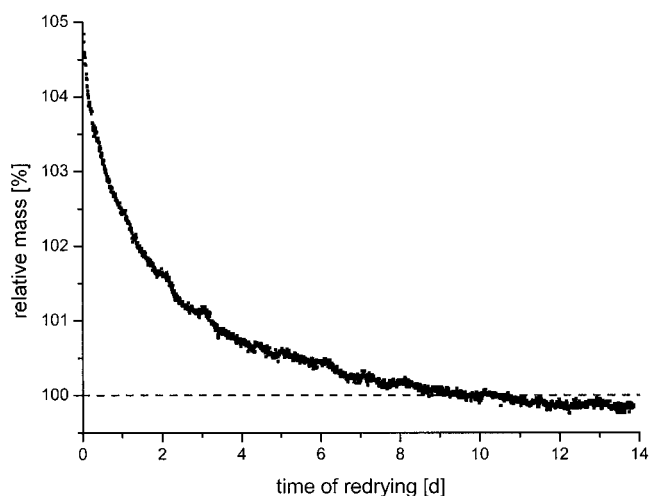
Figure 2 Relative mass loss of the low-crosslinked epoxy system after 100 days hydrothermally aging during redrying at 40°C.

Figure 4 Epoxy band at 915 cm^{-1} during hydrothermal aging of the low-crosslinked epoxy system at 40°C.

at 40°C, the sample mass reaches the initial value within 10 days (see Fig. 2). On further drying, the mass falls below the initial value. Supplementary investigation by ESI mass spectroscopy detects small quantities of DETA, DGEBA, and network components with higher masses in the immersion bath. Hence, a part of the remaining resin, hardener, and network components are leached during hydrothermal aging of the low-crosslinked epoxy system.

The results of the DSC measurement during hydrothermal aging are summarized in Figure 3. The initial glass transition (1. glass transition in Fig. 3) drops from 78.6 $\pm$ 0.2 to 68.5 $\pm$ 0.4°C within 12 h. The increased mobility in the network reveals the plasticizing effect of the absorbed water. On plasticizing the
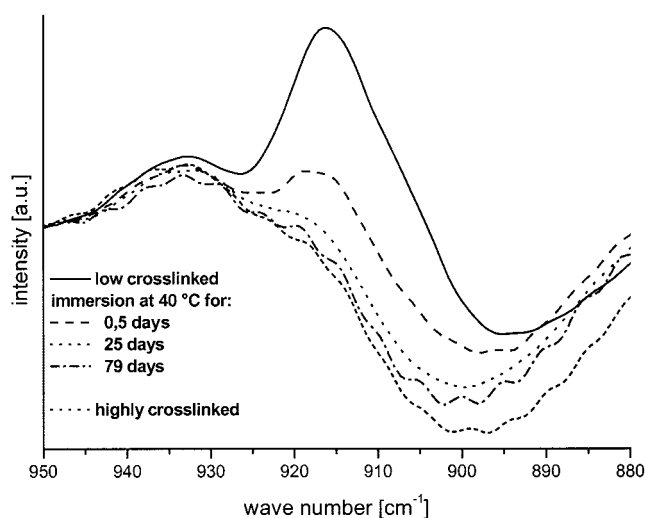
water, molecules interrupt the physical crosslinking by interacting with the polar groups of the epoxy network. The reduced physical crosslinking leads to a depression of the glass transition temperature as discussed above in the theoretical background. During hydrothermal aging, the intensity of the exothermal postcuring peak decreases steadily (DSC curves) and the glass transition temperature shifts slowly upward to 74.7 $\pm$ 0.2°C within 250 days. The loss of mobility in the hydrothermally aged low-crosslinked epoxy system is accompanied by a consumption of oxirane rings (peak at 915 cm^{-1}) as observed by IR spectroscopy (see Fig. 4). After 25 days of immersion, the consumption of epoxy groups in the low-crosslinked epoxy system equals the value of the highly crosslinked sys-
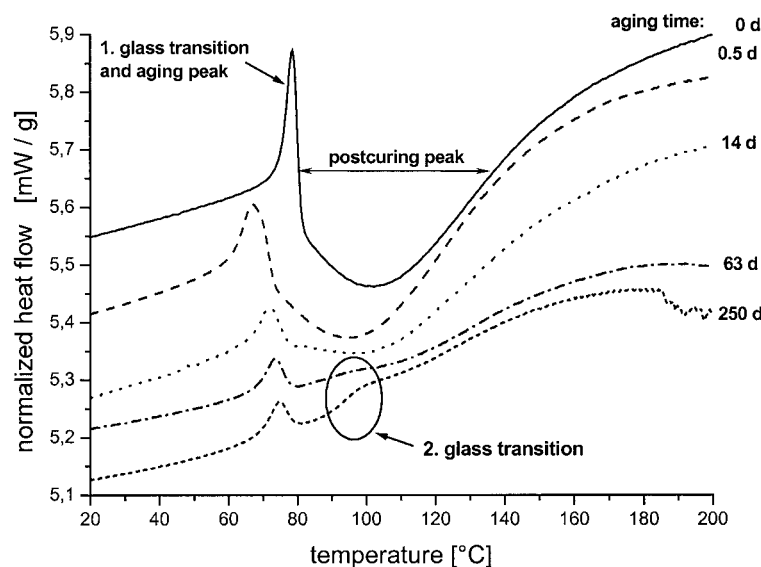

Figure 3 DSC measurement of the low-crosslinked epoxy system during hydrothermal aging at 40°C up to 250 days.

tem and remains constant with ongoing immersion time. Additionally, redried samples which were hydrothermally aged for 100 days have a glass transition temperature at 135°C. Both results confirm the almost complete consumption of epoxy groups during the ongoing curing reaction in the glassy but plasticized network. Hence, it is concluded that during hydrothermal aging at 40°C an almost completely crosslinked network develops from an initially low-crosslinked epoxy system.

Compared to this hydrothermal aging, thermal aging of the low-crosslinked epoxy system over the same period of time leads only to a slight increase of the degree of epoxy conversion and a weak rise of the glass transition temperature (80.4 ± 0.4°C). Consequently, the presence of water in the network increases the rate of ongoing curing significantly. This rate increase is explained by the plasticizing effect of water that promotes the diffusion-controlled reaction by an increased molecular mobility. According to literature, the presence of water in a not fully cured epoxy system is expected to provide only slight additional crosslinking.[16] Consequently, in this investigation, the extraordinary influence of water on the curing reaction in a glassy epoxy network is shown for the first time.

Surprisingly, the aging peak declines with ongoing hydrothermal aging (see Fig. 3). During thermal aging, a decrease of the aging peak is found as well. Consequently, the process is not affected by the presence of water only. Two possible explanations are proposed for this behavior: First, it is obvious that the observed ongoing reaction proceeds inside the short-range ordered regions, too. With increasing degree of crosslinking, more and more ordered segments are fixed by chemical bonds. Thus, no excess enthalpy is consumed for dissolving this part of the short-range ordered regions when the network is heated to the viscoelastic state. Consequently, the aging peak reduces with increasing aging time. Second, as discussed in the paragraph "Theoretical background," the amount of relaxed free volume decreases in a network with increasing temperature difference $T_g - T_a$. During aging, the low-crosslinked epoxy system at constant T_a, the glass transition temperature T_g increases. Consequently, the amount of relaxed free volume reduces, which results in a smaller aging peak.

After 63 days of hydrothermal aging at 40°C, a secondary glass transition appears at about 95°C. This new glass transition appears ~ 23 K lower than the second glass transition, which was observed during thermal aging.[9] The reduced T_{g2} is attributed to the plasticization caused by the penetrated water. Obviously, a low-mobile phase is present in the plasticized high-mobile matrix also during hydrothermal loading.

The conclusions on the effects of penetrated water get additional support from the IR spectra. An increas-
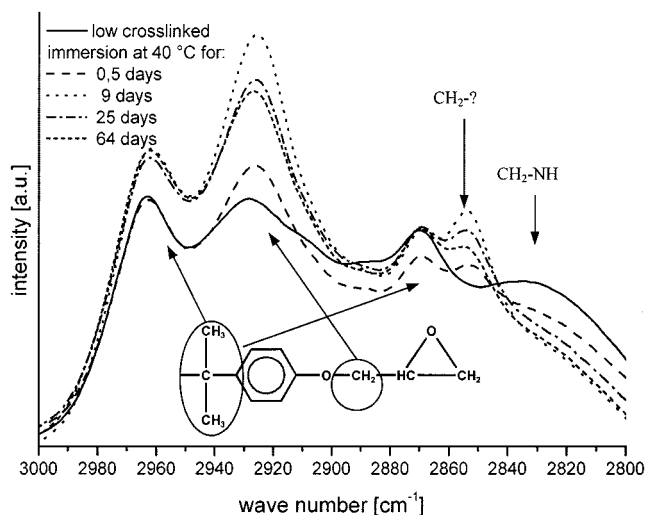

Figure 5 Intensity changes of the CH-bands of the low-crosslinked epoxy system during hydrothermal aging at 60°C.

ing OH band (IR-ATR, 3600 to 3100 cm^{-1}) indicates the water uptake in condensed form during immersion and the additional OH group production during further crosslinking between oxiran and amine groups.

Intensity changes of several bands in the CH-vibration range (3000 to 2800 cm^{-1}) take place during hydrothermal aging (see Fig. 5). The symmetric stretching vibration of CH_2 groups at the secondary amine of DETA (2830 cm^{-1}) loses intensity. This is explained by the ongoing reaction of epoxy with these amines that changes the chemical surrounding of the CH_2 groups adjacent to the amine. A similar effect is observed in the spectra for thermally aged samples. Other changes include that spectral regions are not observed during thermal aging. However, on hydrothermal aging, the peak for the methylene group at the phenyl-ether group gains intensity relative to the peaks of the isopropyl group (2967 and 2877 cm^{-1}). At the same time, a new band arises at 2850 cm^{-1} and grows with immersion time. It is obvious that this band corresponds to a CH stretch vibration but its exact chemical surrounding cannot be established from this investigation. The isopropyl bands themselves change intensity in an arbitrary manner during immersion. All these intensity variations in the CH stretching region are not caused by concentration changes due to any kind of chemical reaction. It is assumed that the intensity variations reflect the complex local structural changes in the arrangement of atom groups and segments. For instance, an ordering of segments affects the transition dipole moment of the CH groups and consequently leads to variations in their IR intensity. In support, it is reported in ref. 17 that ordering effects are mainly depicted in the intensity of the CH bands. We note
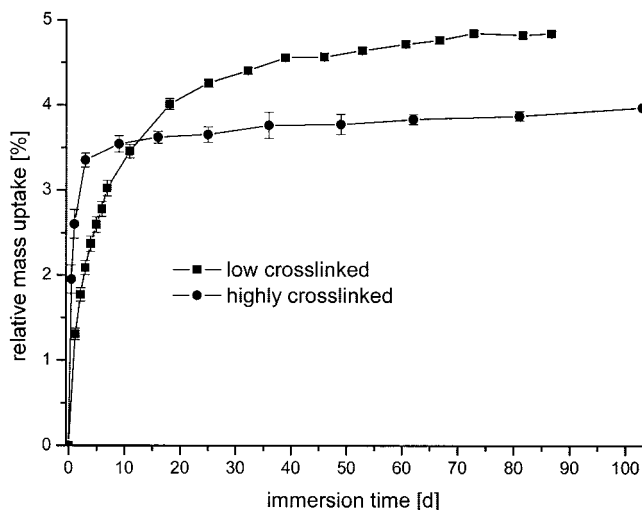
Figure 6 Relative mass uptake of the highly crosslinked epoxy system during hydrothermal aging at 60°C in comparison to the low-crosslinked epoxy system at 40°C.

that changes in short-range orientation and phase separation are observed by DSC during hydrothermal aging (see above). Moreover, no such changes in the CH band intensities are found during thermal aging of the low-crosslinked epoxy system. Therefore, it is concluded that these orientation phenomena occur in the low-crosslinked epoxy network only in the presence of water.

For thermal aging, two new bands develop in the range from 1750 to 1620 cm^{-1}, indicating a thermooxidative degradation. In contrast to thermal aging, no changes in intensity in this spectral region are detected by IR-ATR during hydrothermal aging of the low-crosslinked epoxy system. Although the hydrothermal

aging includes some oxygen dissolved in the water, the water suppresses the thermooxidative degradation to some extent.

Hydrothermal aging of the highly crosslinked epoxy system

In Figure 6, the uptake of water is compared with the curve for the low-crosslinked epoxy. The initial slope is steeper for the highly crosslinked samples, indicating that $T_a = 60°C$ results in an accelerated penetration of water. During 100 days of hydrothermal aging at 60°C, the highly crosslinked epoxy network absorbs 3.97 $\pm$ 0.06 wt % of water (see Fig. 6). This final water uptake is lower than for the low-crosslinked epoxy. Hence, the highly crosslinked network contains less volume that is accessible for penetrating water molecules. On redrying this aged network at 60°C, the absorbed water is lost within 5 days. Similar to for the low-crosslinked epoxy system, on further redrying, the mass falls below the initial value, indicating a leaching of soluble network components. ESI mass spectroscopy detects DGEBA and sequences with higher mass in the immersion bath of the highly crosslinked epoxy system but no DETA is found as in the case of low-crosslinked samples. This confirms that the network contains no more free amine in the initial state.

The DSC curves for the highly crosslinked network state during hydrothermal aging at 60°C are summarized in Figure 7. The initial glass transition at T_{g1} drops from 130.9 $\pm$ 0.7 to 99.2 $\pm$ 0.7°C within 9 days and stays constant then. As for the low-crosslinked samples, water plasticizes the network by shielding the physical crosslinks, which leads to a higher mo-
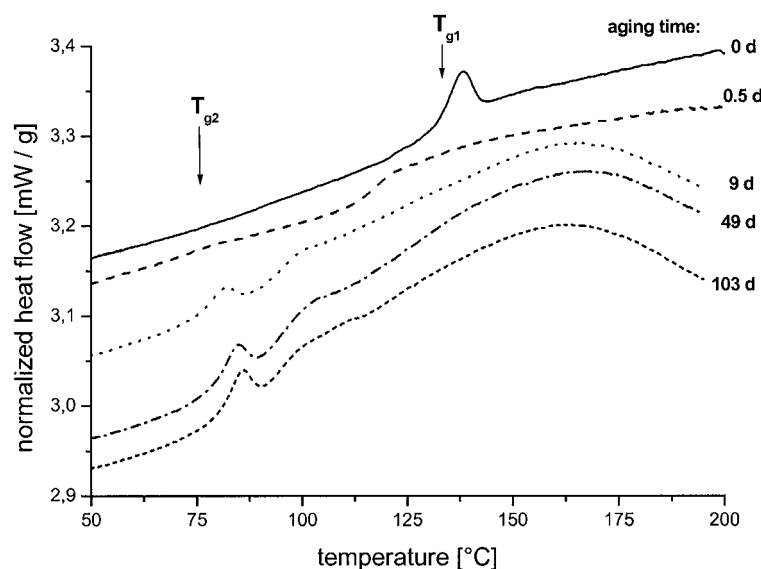

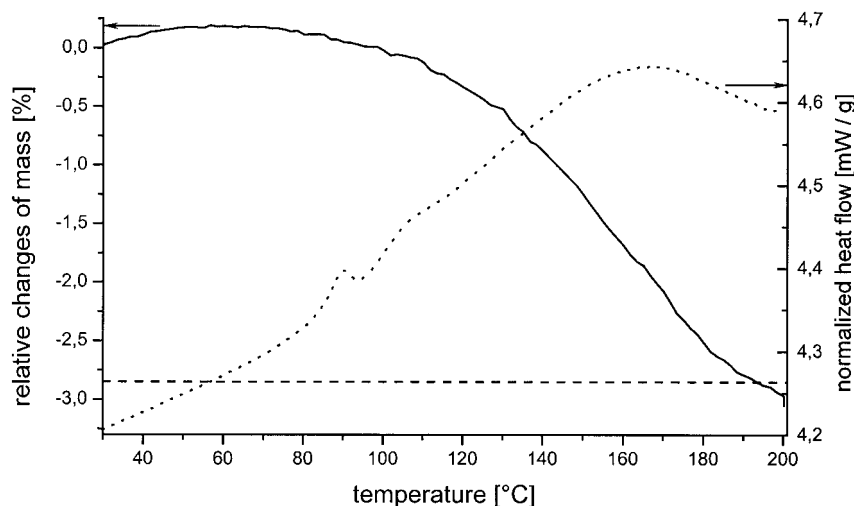**Figure 7** DSC measurement of the highly crosslinked epoxy during hydrothermal aging at 60°C up to 103 days.

Figure 8 Comparison of caloric (dotted) and gravimetric (solid) measurements during a heating run from 20 to 200°C with 10 K/min for a highly crosslinked epoxy system after 36 days of hydrothermal aging.

bility. After redrying, T_{g1} reaches the value of the nonaged samples again (not shown in Fig. 7). Thus, plasticizing is reversible in the highly crosslinked epoxy network.

The aging peak, which is attributed to enthalpy relaxation on postcuring the epoxy system at 120°C, disappears within 12 h of hydrothermal aging. The corresponding decay of the short-range ordered regions indicates their instability at this aging temperature of 60°C far below the glass transition. During thermal aging, the decline of the aging peak is also found but it runs with a much lower rate. Consequently, the mobility is larger in the plasticized network and the presence of water accelerates the breakdown of short-range order.

Further, Figure 7 reveals that a second glass transition arises at $T_{g2} = 80°C$ during hydrothermal aging and shifts with increasing aging time to 90°C. The existence of two glass transitions in plasticized epoxies is often overlooked by many authors. Some workers explain the two transitions by the so-called "core shell phenomena."[18,19] According to this explanation, T_{g2} is attributed to some plasticized "core" of the sample, whereas the "shell" quickly redries during the experiment and has a glass transition at T_{g1}. In our investigation, thermogravimetry confirms that drying takes place during the DSC heating run at temperatures above T_{g2} and T_{g1}, respectively (see Fig. 8). Consequently, both glass transitions characterize the swollen network containing nearly the full amount of water at the particular aging time. During thermal aging, a second glass transition forms as well, which is another contradiction to the core shell explanation. A varying water content across the sample cannot be responsible for the two glass transitions because water is totally absent during thermal aging. The second

glass transition on thermal and hydrothermal aging supports our explanation that there is a phase separation in the inhomogeneous network under the influence of both kinds of aging. When the phase separation starts, mobile segments are thought to rearrange in the low-crosslinked network regions, resulting in a particular cooperative mobility which is higher than in the highly crosslinked matrix. The cooperative behavior of this new mobile phase leads to the new glass transition T_{g2}, which is observed well below T_{g1} of the highly crosslinked matrix. As aging prolongs, segments with a lower mobility join this mobile phase and become less dependent on the matrix. The mobility of this whole phase is reduced when more and more segments with lower mobility are incorporated. Consequently, the c_p-step and T_{g2} increase simultaneously. Compared to thermal aging, the glass transition temperature T_{g2} is 10 K lower now and an aging peak arises. These differences in mobility are due to different water contents and result from the plasticizing effect of water in the developing mobile phase. The aging peak indicates that enthalpy relaxation occurs in the highly mobile phase. On redrying, the mobile phase produced by hydrothermal aging disappears quickly at some water content. Then, another mobile phase arises (DSC plot not shown) with a T_g $\approx 83°C$. A similar mobile phase is observed during thermal aging. It is concluded that the phase produced by hydrothermal aging is different from the phase obtained in thermal aging.

During hydrothermal aging of the highly crosslinked epoxy system, a constant epoxy IR band indicates no further curing reaction in the network. In the region of the CH group vibration (from 3000 to 2800 cm^{-1}; Fig. 9), intensity variations of several peaks take place similar to the low-crosslinked epoxy system.
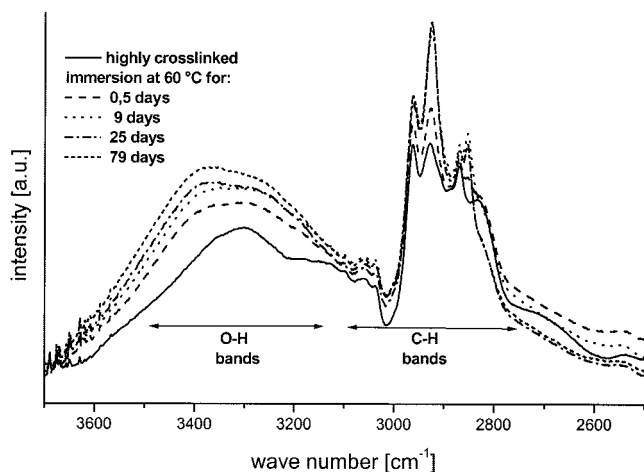
Figure 9 Spectral region (3700 to 2500 cm^{-1}) during aging of the highly crosslinked epoxy system at 60°C up to 79 days.

These changes are not reversible on redrying. Intensity variations of the CH bands cannot be explained by concentration changes because of any kind of chemical reaction. It is assumed that these intensity variations result from an irreversible rearrangement of segments as discussed for the low-crosslinked epoxy network. Obviously, these structural changes are induced by water because no spectral variations occur in the CH-stretching region during thermal aging. Again this interpretation agrees with the short-range orientation and the phase separation as observed by DSC during hydrothermal aging (see above).

During hydrothermal aging of the highly crosslinked epoxy system, a new IR band at 1660 cm^{-1} arises (see Fig. 10), which is irreversible on redrying. On thermal aging, this band occurs as well but with higher intensity. As for thermal aging, this band indicates a thermooxidative degradation of the epoxy network which affects at least the upper 10 μm beneath the surface. According to the peak position, the formation of several groups such as C=O, C=N, or C=C is possible. In literature, no clear correlation between the bands arising and the degradation mechanism is found. A review on this topic is given in ref. 20. The lower peak intensity is attributed to the reduced oxygen content in the immersion bath compared to the dried air. On thermal aging, a second band at 1730 cm^{-1} develops that is not observed for hydrothermal aging. Therefore, it is concluded that the presence of water during aging alters the mechanism of the thermooxidative degradation in the epoxy network.

CONCLUSION

Two network states are prepared for the study of the hydrothermal aging behavior of the two-part adhesive

DGEBA and DETA in bulk: In the low-crosslinked epoxy system, a relatively high-molecular mobility remains in the glassy state and it contains a considerable amount of residual reactive groups. Short-range ordered regions are present in the network because of enthalpy relaxation during room temperature curing and postcuring at 40°C. Highly crosslinked regions are embedded in a less crosslinked matrix (details discussed in ref. 9; part I of this series).

The highly crosslinked epoxy system has a reduced molecular mobility and epoxy groups are not detected. During postcuring at 120°C, enthalpy relaxation takes place. As for the low-crosslinked state inhomogeneities are assumed: low-crosslinked regions are included in a highly crosslinked matrix.

During hydrothermal aging of the low-crosslinked epoxy system, water is physically absorbed and plasticizes the network. This results in an increased polymer mobility and promotes the ongoing curing reaction in the glassy state, which leads to the consumption of the epoxy groups and to an almost complete network. This effect is shown for the first time. As the crosslinking density rises, the amount of enthalpy relaxation diminishes. During thermal aging, an ongoing curing reaction is observed as well, but it has a lower rate. The second glass transition which appears during hydrothermal aging of the low-crosslinked epoxy system verifies the existence of an inhomogeneous network with at least two phases. No thermooxidative degradation is found for hydrothermal aging at 40°C but for thermal aging. Consequently, the presence of water inhibits this kind of degradation, although some oxygen is dissolved.

Physically absorbed water in the highly crosslinked epoxy system also leads to a reversible plasticization. The mobility gained by plasticization leads to an accelerated disintegration of short-range ordered re-
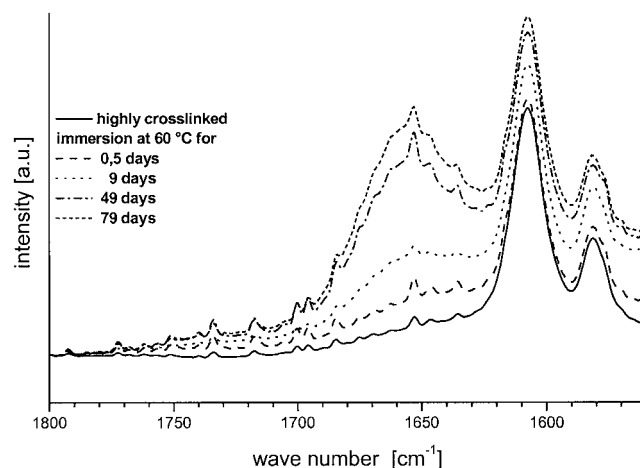

Figure 10 Spectral region (1800 to 1550 cm^{-1}) during hydrothermal aging of the highly crosslinked epoxy system at 60°C up to 79 days.

gions as compared to thermal aging. Phase separation in the inhomogeneous highly crosslinked epoxy network is a new aspect of aging and occurs under the influence of temperature and water as well. Compared to the matrix, a more mobile phase establishes with an independent cooperative mobility. However, the character of these mobile phases depends on the aging regime. Chemical changes (i.e., thermooxidative degradation) are observed both for hydrothermal aging at 60°C and for thermal aging at 40 and 60°C. The mechanisms are different. For thermal aging, two degradation products are observed but only one for hydrothermal loading. Moreover, the quantity of the degradation product common for both regimes is larger in the case of thermal aging. Consequently, water alters the mechanism of thermooxidative degradation.

In summary, for the low-crosslinked and for the highly crosslinked epoxy system, significant chemical and structural changes are induced by hydrothermal loading despite the fact that the network is in the glassy state.

Compared to thermal aging, two major differences are stated: First, water speeds up structural changes because of the increased polymer mobility in the plasticized glassy network. Second, chemical degradation mechanisms are affected.

It is convincing that these changes exert influence on the performance of an adhesive joint, a coating, or a fiber-reinforced composite made by this epoxy.

References

1. Allen, R. C.; Bauer, R. S. in Engineered Materials Handbook, Vol. 2: Engineering Plastics; 2001; Chapter 8.
2. Siddaramaiah; Suresh, S. V.; Atul, V. B.; Srinivas, D.; Girish, S. J Appl Polym Sci 1998, 73, 795.
3. Brewis, D. M.; Comyn, J.; Raval, A. K.; Kinloch, A. J. Int J Adhes Adhes 1990, 10, 4 247.
4. Browning, C. E. Polym Eng Sci 1978, 18, 1 16.
5. Venables, J. D. J Polym Sci, Part B: Polym Phys 1984, 19, 2431.
6. Bremont, M.; Brockmann, W. J Adhes 1996, 58, 69.
7. Chateauminois, A.; Vincent, L.; Chabert, B.; Soulier, J. P. Polymer 1994, 35 (22), 4766.
8. Xiao, G. Z.; Shanahan, M. E. R. J Appl Polym Sci 1998, 69, 363.
9. Bockenheimer, C.; Fata, D.; Possart, W. J Appl Polym Sci 2004, 91, 361.
10. Ellis, B. Chemistry and Technology of Epoxy Resins; Chapman and Hall, New York, 1993.
11. Montserrat, S. Polymer 1995, 36, 2 435.
12. Struik, L. C. E. Physical Aging in Amorphous Polymers and Other Materials; Elsevier Scientific: Amsterdam, Oxford, New York, 1978.
13. Haward, R. N.; Young, R. J. The Physics of Glassy Polymers; Chapman and Hall: London, Weinheim, New York, 1997.
14. Possart, W.; Brockmann, W.; Bockenheimer, C.; et al. Grundlagen zum Verständnis der Wirkungsweise mechanischer Oberflächenvorbehandlungsverfahren auf Haftfestigkeit und Versagensmechanismen adhäsiver Verbindungen, ASPG Universität des Saarlandes; AWOK Universität Kaiserslautern, DFG report, 2001.
15. Bockenheimer, C.; Goebel, M.; Possart, W. Preprints Poster Presentation; EURADH '98 4th European Conference on Adhesion and WCARP-1; 1998, 1, 18.
16. McMaster, G. M.; Soane, D. S. IEEE Trans Components Hybrids Manufac Technol 1989, 12 (3), 373.
17. Scherzer, T. Polym Bull 1995, 35, 621.
18. Soulier, J. P.; Berruet, R.; Chateauminois, A.; Chabert, B.; Gauthier, R. Polym Commun 1998, 29, 243.
19. Ivanova, K. I.; Pethrick, R. A.; Affrossman, S. J Appl Polym Sci 2001, 82, 3477.
20. De Neve, B.; Shanahan, M. E. R. Polymer 1993, 34, 24 5099.