New Aspects of Aging in Epoxy Networks. I. Thermal Aging

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ABSTRACT: The thermal aging of an amine-cured epoxy in the glassy state is studied for two network states by using DSC and attenuated total reflection-infrared (IR-ATR). The "low-crosslinked" network possesses a relatively high molecular mobility and a considerable amount of residual reactive groups. In the low crosslinked matrix, the presence of high crosslinked regions is revealed. In contrast, the "highly crosslinked" epoxy system has a reduced molecular mobility and only small reactive groups. The high crosslinked matrix contains low crosslinked regions. Thermal loading for both networks is performed below their glass transition. During thermal aging, an ongoing curing reaction takes place in the low-crosslinked epoxy. Thermooxidative degradation and the disintegration of short-range ordering are observed as

well. The highly crosslinked epoxy system undergoes a phase separation of relatively mobile segments in the low mobile matrix, which is a reversible process on heating. Thermooxidative degradation is also detected for this kind of network. In summary, for the "low" and the "highly" crosslinked epoxy, significant chemical and structural changes take place during thermal aging even though the networks are vitrified. It is convincing that these changes in the cured epoxy should exert an influence on the mechanical properties of a bonded structure. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 361–368, 2004

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

INTRODUCTION

The long-term performance of structural metal-adhesive joints as well as of polymer coatings and fiber-reinforced composites is strongly determined by the aging behavior of the bond.[1,2] In service, the bond properties, especially the bond strength, deteriorate depending on the environmental conditions. By experience, thermal and hydrothermal loading are the most critical conditions in respect to aging.[3] In the following, "aging" comprises all processes in the bond line after preparation, which changes the joint properties. These processes also include "physical aging" as it is commonly defined in literature.[4] The aging behavior of the joint can be understood as a combined aging of the adhesive, the substrate, or the fiber and their interface.

The thermal aging behavior of epoxy systems is of particular interest because of their wide use for structural applications in automotive and aircraft industries where increased temperatures are common environmental conditions. In literature, besides curing and physical aging of epoxy systems,[5] thermal degradation[6] is reported as the main aging effect of the polymer bulk.

This article shows the thermal aging behavior of an amine-cured epoxy adhesive for the bulk in two network states. The first 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 adhesive as used in high-performance applications. During thermal loading, the resulting aging processes of the epoxy system are studied by DSC and by IR spectroscopy to investigate structural and chemical changes in the adhesive.

MATERIALS

The epoxy system investigated is a room-temperature-curing two-part adhesive. Diglycidyl ether of Bisphenol A (DGEBA) is used as a bifunctional epoxy resin and diethylene triamine (DETA, Fig. 1) is used as a trifunctional amine hardener.

Theoretical background

The curing and properties of the resulting epoxy network are important aspects to understanding the aging processes. The curing (which comprises a variety of different chemical reactions) starts when the two components are mixed at a given curing temperature, T_c. The oxirane rings of the epoxy resin are consumed by reacting with the primary or secondary amine
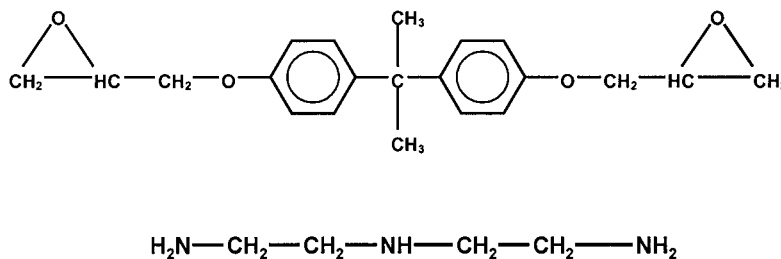
Figure 1 Chemical structure of DGEBA and DETA.

groups of the hardener by formation of hydroxide groups. The reaction of hydroxide groups with oxirane rings is possible only at high temperatures or in the presence of catalysts. With ongoing reaction, oligomers and branched macromolecules are generated, which finally form a polymer network.[7] As the reaction proceeds, the crosslinking density rises. As a result, the molecular mobility in the network is more and more restricted. The restricted mobility leads to an increasing glass transition temperature and to vitrification.[5] Consequently, above a certain T_c, a maximum degree of conversion is achieved, resulting in a maximum glass transition temperature, $T_{g\infty,ideal}$, depending on the epoxy system chosen. On the other hand, curing at high temperatures also leads to simultaneous thermal degradation in the network, which produces a T_g depression. Hence, the actually measured maximum glass transition temperature $T_{g\infty,real}$ is correlated to the network with the lowest mobility resulting from curing at a certain T_c, where a maximum degree of conversion and the lowest degree of thermal degradation is achieved. For curing below $T_{g\infty,real}$, 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 the curing temperature but remains below $T_{g\infty,real}$ on a reasonable time scale.

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.[4] The excess of free volume provides an additional degree of 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 can be understood as short-range ordering of segments. This process in polymers is called physical aging. The amount and rate 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 and the rate of enthalpy relaxation diminish. This result is obtained for glassy thermoplastics by varying T_a, whereas T_g keeps constant.[8] 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 thermosets 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 due to a hindered mobility of segments. Therefore, the enthalpy relaxation possible in epoxies reduces with increasing crosslinking density.

Experimental procedures

The two components of the epoxy adhesive DGEBA and DETA are mixed in a mass ratio of 100 : 14 at 55°C for 5 min, followed by fast cooling to room temperature. Because of the elevated temperature and the intense stirring, this regimen results in a homogeneous mixture as it is proven by the reproducibility of the curing process at room temperature after mixing and by the reproducible network properties. The mixing ratio is derived from supplementary investigation where an optimum bond strength of this adhesive with aluminum substrates was required.[9] Compared to the stoichiometric ratio of DGEBA : DETA = 100 : 12.12, the preparation provides an excess of amine hardener. The reaction of hydroxide groups with oxirane rings is not observed by IR spectroscopy even at high curing temperatures because no catalysts are added. As the next step, the mixture is cast at 23°C into silicone molds of appropriate size. For DSC, samples are disk-like with 3 mm diameter and 0.8 mm thickness. The samples for IR spectroscopy are disks with 10 mm diameter and 2 mm thickness. The small epoxy mass, which produces only a small amount of heat of reaction, and the relatively large surface-to-

volume ratio, guarantee that no significant rise of temperature occurs during the epoxy curing at room temperature.

After 48 h of room-temperature curing, two different network states are prepared by two different postcuring steps: The first network state forms by postcuring at 40°C for 24 h, resulting in $T_g = 70$°C. The second network state forms by postcuring at 120°C for 1 h possessing a $T_g = 131$°C.

Aging is performed in dried air (dew point < -70°C) with a well-reduced CO_2 content at 40°C for the glassy network postcured at 40°C. Hence, no thermally induced crosslinking is expected further. The glassy network postcured at 120°C is aged at 60°C in the same atmosphere. The higher aging temperature speeds up the aging processes that are more hampered by the higher crosslinking density in this network.

DSC investigations are carried out with a Perkin–Elmer DSC 7 by heating samples (mass about 6 mg) from 5 to 200°C at a rate of 10 K/min. For the MDSC investigation, the constant heating rate of the DSC experiment is replaced by a sawtooth-like heating ramp. A heating step of 1.5 K with a rate of 18 K/min is followed by a cooling step of 0.5 K with a rate of -9 K/min. The resulting mean heating rate is 3 K/min.

IR investigation 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 incident angle of 65°. 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., $\sim$ .5–12.5 μm). 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 the internal standard. Then, the measure of the epoxy group consumption is the height of the epoxy band at 915 cm^{-1} in ratio to the height of that band in pure DGEBA. The values represent a spectroscopic degree of conversion which is only a relative measure for the chemical degree of conversion.

RESULTS AND DISCUSSION

The two network states of the unaged epoxy system

During mixing of DGEBA and DETA at 55°C, the curing reaction starts immediately and proceeds when the epoxy system is cooled to room temperature. In these early stages, the curing reaction runs chemically controlled. After 160 min, the glass transition temperature of the system reaches room temperature and vitrification takes place (MDSC).[10] Because T_g exceeds T_c at this time, physical aging starts and results in a
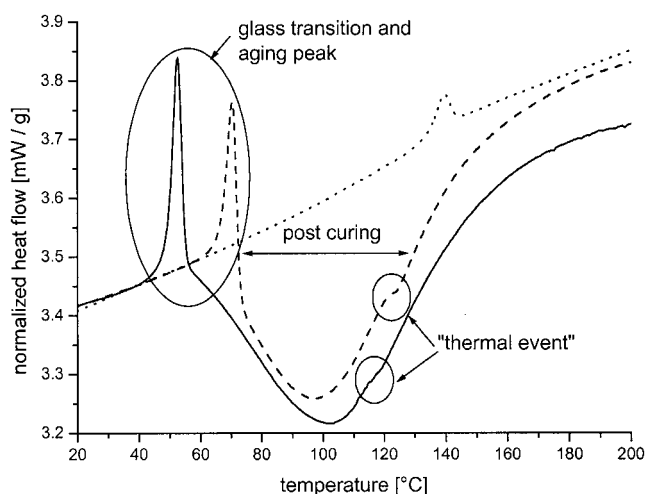

Figure 2 DSC plots for the room-temperature-cured epoxy (solid), the epoxy system postcured 24 h at 40°C (dashed), and the epoxy system postcured 1 h at 120°C (dotted).

pronounced endothermal peak superimposed with the glass transition (see solid DSC curve in Fig. 2). For epoxy systems, such aging peaks are reported in the literature (e.g., ref. 5). For our system, a second heating cycle reveals that the enthalpic peak has disappeared as it has to be the case for physical aging. The enthalpy in the aging peak represents the amount of heat necessary to mobilize short-range ordered polymer segments. Therefore, the height of the aging peak is a measure for physical aging of the network. With ongoing curing time, the reaction proceeds diffusion controlled with a measurable rate in the glassy state and the glass transition temperature reaches 52.7 $\pm$ 0.5°C (DSC) after 48 h. By room temperature, curing at a consumption of 60% epoxy groups (IR-ATR) is obtained.

When the room-temperature-cured epoxy system ($T_g \sim 53$°C) is postcured at 40°C, the viscoelastic state is not reached. Therefore, the curing reaction proceeds under diffusion control and is only little accelerated in the glassy state. As before, the curing reaction slows down because of the small and diminishing mobility and therefore only a slight increase in the degree of conversion (70% epoxy consumption) is obtained. Consequently, the resulting postcured network reaches a glass transition of $T_g = 70.0 \pm 0.2$°C (see dashed DSC curve in Fig. 2). The reduced physical aging peak on the glass transition results from the higher crosslinking density (compare theoretical background) achieved by postcuring at 40°C. In the further discussion, this network state with a relatively low crosslinking density and a large amount of residual reactive groups (about 30%) is denoted as "low crosslinked."

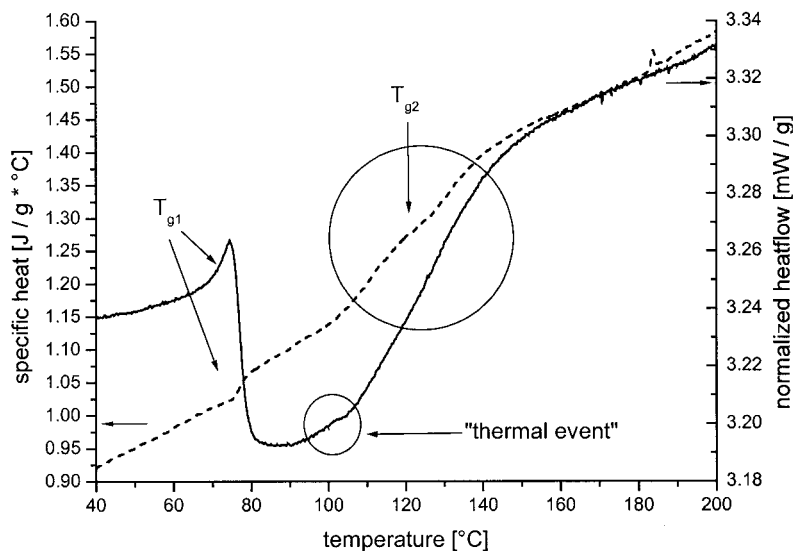The second network state is formed by postcuring the room-temperature-cured epoxy at 120°C for 1 h.

Figure 3 Comparison of DSC (solid; right axis) and MDSC measurement (dashed; left axis) of the unaged "low-crosslinked" epoxy system.

This temperature is well above the initial T_g of ~ 53°C. Therefore, at the beginning of the postcuring step, the reaction runs in the viscoelastic state with an increased rate and the short-range ordered regions (because of physical aging at room temperature) are dissolved. When the glass transition temperature reaches 120°C, the system vitrifies and the reaction proceeds at a lower rate in the new glassy state. At the same time, physical aging starts again. After postcuring, the epoxy system has a glass transition of T_g = 130.9 ± 0.7°C (see dotted DSC curve in Fig. 2). So, compared to $T_{g\infty,real}$ = 136°C,[10] an almost completely crosslinked state has formed. Only a small amount of enthalpy relaxation is indicated by the aging peak because of the increased crosslinking density after postcuring at 120°C. The consumption of reactive groups for this network state is almost complete (IR-ATR). In the further discussion, this network state is called "highly crosslinked."

This more integral view on the reaction discussed must be completed by the aspect that both network states appear to be inhomogeneous with regard to their crosslinking density. An indication for this assumption is found in the DSC curves for the room-temperature-cured and for the low-crosslinked epoxy system. On heating, a "thermal event" is found at about 100°C (see Fig. 2). The origin of this thermal event is not well identified by DSC as it is superimposed by the heat of the ongoing reaction after exceeding the corresponding glass transitions (T_{g1} = 53°C and 70°C, respectively). MDSC provides the advantage of separating the "nonreversing" heat flow, caused by the reaction, from the "reversing" heat flow at the glass transitions.[11] The MDSC investigation (reversing heat flow) on the low-crosslinked network

shows the expected first glass transition at T_{g1} = 70°C and a broad second glass transition from T_{onset} = 100°C to T_{end} = 138°C, which is related to the thermal event in the DSC curve (see Fig. 3). Consequently, the thermal event in the DSC plots is correlated to the initial part of a second glass transition T_{g2}. The reasons for this second glass transition are explained as follows. T_{g2} belongs to regions in the network which have a significantly reduced cooperative mobility compared to the main part of the network with a T_{g1} = 70°C. These different cooperative mobilities should result from a local distribution of crosslinking densities and molecular packing. Because the room-temperature-cured epoxy system shows the thermal event as well, the inhomogeneous structures must have formed in the early stages of reaction. The formation of these inhomogeneous structures is irreversible due to chemical bonding. Consequently, the structure remains on postcuring. Thus, it is convincing to conclude that in principle even in the highly crosslinked epoxy system an inhomogeneous crosslinking distribution prevails. For this network state, DSC plots show only one glass transition as discussed above (see Fig. 3). The existence of an inhomogeneous crosslinking density is only indicated by the broadness of this glass transition (T_{onset} = 105°C; T_{end} = 143°C).

The presence of such inhomogeneities contrasts the literature, where epoxy networks based on diepoxy and diamine are found to be homogeneous as shown by small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) investigation. Moreover, from thermal and thermomechanical measurement typical epoxy-amine networks exhibit only one glass transition and one sharp well-defined aging
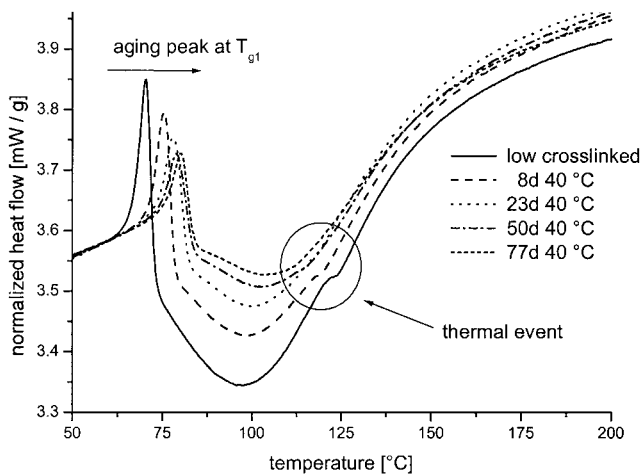
Figure 4 DSC measurement of the low-crosslinked epoxy system during aging at 40°C up to 77 days.

peak.[12] For the first time in this field of research, our investigations give evidence for these inhomogeneities by DSC and MDSC experiments.

Thermal aging of the low-crosslinked epoxy system

During aging, the low-crosslinked epoxy system at 40°C for 77 days, the glass transition temperature T_{g1} increases from 70.0 ± 0.2 to 80.4 ± 0.4°C, as observed by DSC (see Fig. 4). At the same time, the intensity of the postcuring peak decreases. Both results indicate an ongoing exothermal reaction in the low-crosslinked epoxy system. The consumption of epoxy groups necessary for the ongoing reaction is verified by the decay of the epoxy band intensity at 915 cm^{-1} (IR spectros-
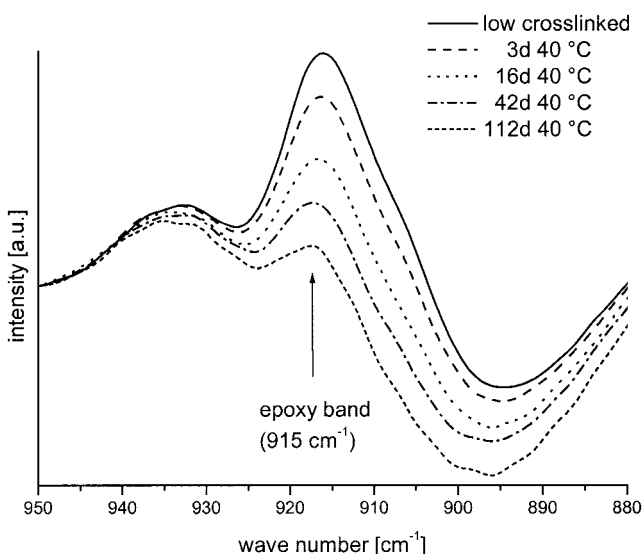

Figure 5 Epoxy band at 915 cm^{-1} during aging of the low-crosslinked epoxy system at 40°C up to 112 days.
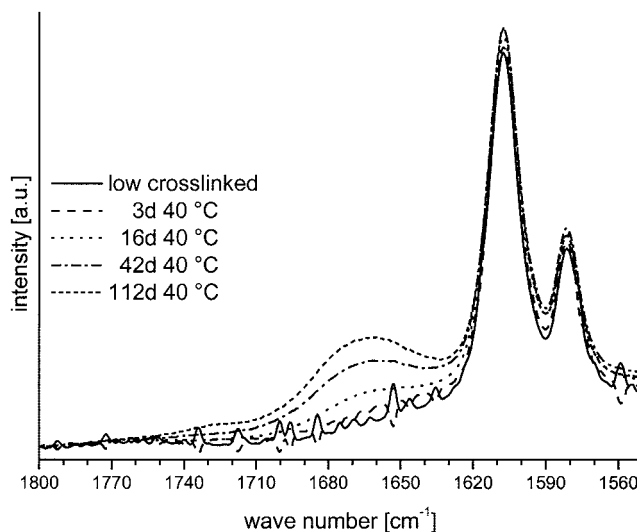

Figure 6 Spectral region (1770 to 1620 cm^{-1}) during aging of the low-crosslinked epoxy system at 40°C up to 112 days.

copy; Fig. 5). The consumption of epoxy groups is still measurable after 77 days of aging. Thus, it is concluded that the curing reaction in the glassy network proceeds at some rate beyond the studied period of aging. Consequently, the glass transition temperature still increases with time.

For the low-crosslinked epoxy system, it is surprising that the "aging peak" decreases with increasing aging time (see Fig. 4). For this behavior, two explanations are proposed. First, it is obvious that the ongoing reaction observed for the whole network proceeds inside the short-range ordered regions, too. With increasing degree of conversion, more and more ordered segments are fixed by chemical bonding. Thus, no excess enthalpy is consumed for dissolving these fixed 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 of the low-crosslinked epoxy system at constant T_a, the glass transition temperature T_g increases. Consequently, the amount of relaxed free volume reduces, resulting in a smaller aging peak.

During aging, the thermal event indicating the existence of a second glass transition at T_{g2} is still present in the DSC plots (see Fig. 4). Thus, the highly crosslinked regions survive in the network during aging. However a detailed analysis of the glass transition is not possible by DSC because of its superposition with the curing reaction, as discussed above.

When the low-crosslinked epoxy system is aged at 40°C, two new peaks show up in the IR-ATR spectra at 1730 and 1660 cm^{-1} (see Fig. 6). In literature,[13] the
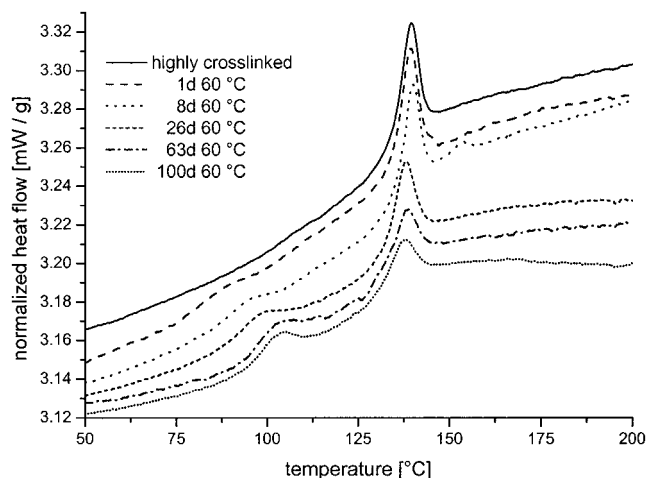
Figure 7 DSC measurement of the "highly crosslinked" epoxy system during aging at 60°C for 77 days.

peak growth in the wavelength ranging from 1770 to 1620 cm^{-1} is attributed to a thermal degradation in epoxy networks. The correlated breaking of chemical bonds is considered to provide a wide range of chemical groups including carbonyl- (C=O), imine- (C=N), and C=C groups.[13] All these double bonds have their characteristic absorption band in the above described wavelength range around 1700 cm^{-1}. In literature, no clear correlation between the arising bands, the degradation mechanism, and the forming chemical groups is found. A brief discussion on this topic is given in ref. 12.

In our investigation, it is surprising that already after room-temperature curing a small intensity of these bands exists even though no thermal loading was supplied. Moreover, a thermal degradation in the bulk is correlated to a decreasing glass transition temperature.[6] This is not observed by our investigation. However, the information depth of IR-ATR spectra lies in the range of about 10 μm and IR transmission spectra of epoxy dispersed in KBr pellets show no peaks at 1730 and 1660 cm^{-1}. So it is concluded that the degradation mechanism takes place on the surface under the influence of oxygen and temperature.

Thermal aging of the highly crosslinked epoxy system

During thermal aging at 60°C, the highly crosslinked epoxy system behaves very differently. It shows a stable glass transition at its initial temperature T_{g1} = 130.9 ± 0.7°C (see Fig. 7). This indicates that further curing is not measurable. Only the intensity of the aging peak at T_{g1} decreases but is still measurable after 100 days of aging. Consequently, on aging of the highly crosslinked epoxy network at 60°C far below T_{g1} = 131°C, no additional enthalpy relaxation takes

place. Moreover, the existing enthalpy relaxation is unstable (i.e., the short-range ordered regions break down at a slow rate).

After 1 day of aging, a second glass transition arises at T_{g2} = 80°C and shifts to 100°C with continuing aging. Simultaneously, the height of its c_p step increases. The development of that second glass transition can be understood as the separation of another amorphous phase in the inhomogeneous network. When the phase separation starts, mobile segments rearrange in the low crosslinked regions, resulting in a particular cooperative mobility as compared with the highly crosslinked matrix. The cooperative mobility of this new mobile phase leads to the new glass transition observed below T_{g1}. As the aging time prolongs, segments with a lower mobility join this mobile phase and become less dependent on the matrix. As a glass transition is a cooperative process, the mobility of the whole phase is reduced when more and more segments with lower mobility are incorporated. Consequently, both the c_p step and the value of T_{g2} increase simultaneously. After heating the aged epoxy network above T_{g1}, this glass transition remains at T_{g1} = 131°C (see Fig. 8) but the corresponding aging peak is no longer observed. The second glass transition also disappeared. By aging reheated samples a second time under the above described conditions, the second glass transition T_{g2} arises again and shows the same behavior as observed during the first aging run. No aging peak forms at T_{g1}. The reversible behavior of the phase separation is explained as follows: When the segregated phase and the matrix phase are heated above the glass transition temperature of the matrix, the system forms a uniform viscoelastic phase again. The phase separation in the inhomogeneous network will start again when the system is cooled to the glassy state.
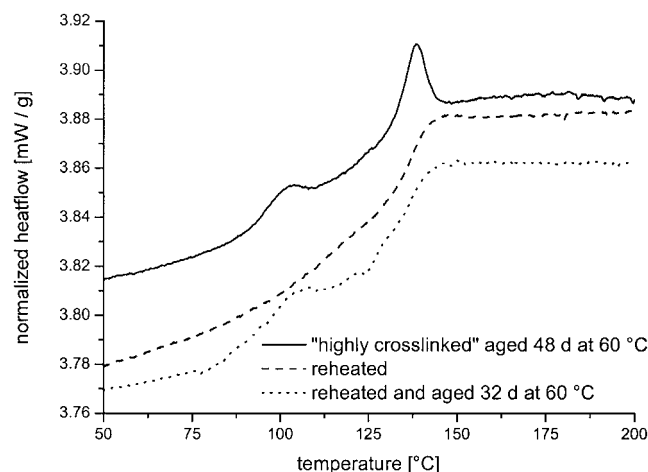

Figure 8 DSC measurement on 48 days at 60°C aged highly crosslinked sample (solid) and a subsequent heating run (dashed). Measurement after second aging cycle at 60°C for 32 days (dotted).
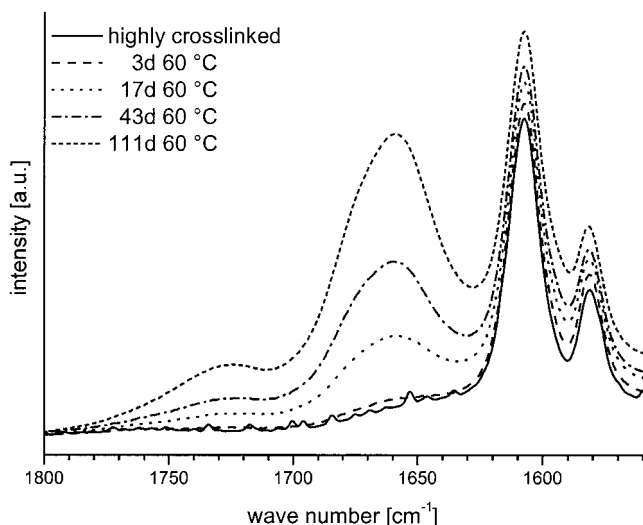
Figure 9 Spectral region (1770 to 1620 cm^{-1}) during aging of the highly crosslinked epoxy system at 60°C up to 112 days.

Similar results are reported for the epoxy system hexahydrophthalic acid diglycidylester (HHPD)/hexahydrophthalic anhydride (HHPA) by the investigation of Kreibich and Schmid.[14] According to Kreibich and Schmid,[14] the phase separation is a prestate of short-range orientation, whereas short-range ordered networks are unable to separate into two phases. This conclusion contradicts our study on an amine-cured epoxy system, where phase separation is a reversible aging process. It cannot be concluded whether the decreasing enthalpy relaxation has a causal connection with the phase separation observed at the same time. However, it is assumed that during phase separation mobile segments that were short-range ordered during enthalpy relaxation join the arising high mobile phase.

When the highly crosslinked epoxy system is aged at 60°C, IR-ATR spectroscopy confirms by the constant epoxy band (915 cm^{-1}) that no further crosslinking takes place. As for the low-crosslinked epoxy system, the growth of the same two bands at 1730 and 1660 cm^{-1} in a depth of 10 μm beneath the surface is observed (see Fig. 9). Again, the growth of both bands is referred to the thermooxidative degradation of the epoxy networks by an unknown mechanism. Compared to the low-crosslinked epoxy system, aging at 60°C leads to a double band intensity but the intensity ratio of the two keeps constant. Thus, the increasing aging temperature accelerates the degradation of the network by a factor of 2. However, as for the low-crosslinked epoxy system, the constant glass transition and IR transmission spectra from ground epoxy confirms the thermooxidative network degradation in a few micron thick layer at the surface.

CONCLUSION

To investigate the thermal aging behavior of the two-part epoxy DGEBA and DETA in the bulk, two network states are prepared: In the low-crosslinked epoxy system, a relatively high molecular mobility remains in the glassy state, containing 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. Our DSC experiments reveal the presence of highly crosslinked regions in the less crosslinked matrix. This is an important result because there is an ongoing controversy in literature about the structure of diamine-cured epoxies. The majority of the articles come to the conclusion that these networks should be homogeneous.

The highly crosslinked epoxy system has a reduced molecular mobility and little reactive groups. During postcuring at 120°C, short-range ordering also takes place. Hence, inhomogeneities are assumed as for the low-crosslinked epoxy network.

During aging, the low-crosslinked epoxy system at 40°C, a slow chemical reaction of the residual epoxy groups with amine species takes place. The ongoing reaction reduces the mobility in the glassy network more and more, which leads to an asymptotical climbing of the degree of conversion. The content of initial short-range ordered regions diminishes. For this behavior, two reasons are proposed: First, the ongoing curing reaction immobilizes a part of the short-range ordered segments. Consequently, these segments stay packed and are not disintegrated by heating. Second, the glass transition increases relative to the aging temperature, which reduces the amount of possible enthalpy relaxation. Hence, the still uncured short-range ordered parts dissolve.

During aging at 40°C, a thermooxidative degradation within at least 10 μm thickness is found at the surface, whereas the bulk properties remain intact during our experiments.

A phase separation is observed in our highly crosslinked epoxy system during aging at 60°C. This effect has not been reported in literature before. A new concept of this phenomenon is presented in this article: Starting from the inhomogeneous glassy network, relatively mobile segments achieve a cooperative mobility on aging independent of the low mobile matrix. This renders the formation of a new phase that is reversible on heating and aging. The short-range ordered regions are unstable because the ability for enthalpy relaxation is strongly reduced for aging the network far below its glass transition temperature. The elevated aging temperature of 60°C intensifies the thermooxidative degradation at the surface compared to aging the low crosslinked epoxy system at 40°C.

Regarding the macroscopic rigid mechanical behavior of the glassy epoxy system, especially for the highly crosslinked network state, it is surprising that enough molecular mobility prevails, which enables processes such as phase separation and changes in short-range ordering.

In summary, for the low and the highly crosslinked epoxy networks, significant chemical and structural changes take place during thermal aging far below their glass transition temperatures in well-dried air with reduced CO_2 content. It is convincing that these changes in the epoxy exert an influence on the mechanical properties of an adhesive joint, the coating, or the fiber-reinforced composite. Further, during hydrothermal aging, similar effects have to be expected. The additional influence of water at elevated temperature is described in a supplementary investigation (see Part II: "Hydrothermal Aging"[16]).

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