

Aging Behavior of a Hot-Cured Epoxy System

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ABSTRACT: The thermal and hydro-thermal aging of a hot-cured epoxy system (diglycidylether of bisphenol A (DGEBA) + dicyandiamide (DDA)) in the glassy state is revisited using DSC and IR attenuated total reflection spectroscopy. Because of the diffusion of DDA from the solid particles into the liquid DGEBA matrix, curing produces a highly crosslinked amorphous matrix that contains low crosslinked amorphous regions. After full curing, the network possesses a relatively low molecular mobility and no residual reactive groups. Thermal and hydro-thermal loading is performed at 60°C, well below the principal glass transition temperature ($T_{g1} = 171^\circ\text{C}$). Both aging regimes cause significant chemical and structural changes to the glassy epoxy. It undergoes a phase separation of relatively mobile segments inside the low mobile matrix, providing a second glass transition that shifts from $T_{g2} = 86\text{--}114^\circ\text{C}$

within 108 days of aging. This phase separation is reversible on heating into the viscoelastic state. Hydro-thermal aging leads to a reversible and a nonreversible plasticizing effect as well. On thermal aging, no chemical changes are observed but hydro-thermal aging causes significant chemical modifications in the epoxy system. These modifications are identified as a partial degradation of crosslinks produced by the cyano groups of the DDA and correspond to the nonreversible plasticitation. These changes in the cured epoxy should exert an influence on the mechanical properties of an adhesive bond. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2726–2736, 2006

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

INTRODUCTION

During the recent years, epoxy adhesives and resins gain an increased application in the bonding technology, for example in the automotive and aircraft industries. It is known by experience that the performance of such structural metal-adhesive joints as well as of epoxy coatings and fiber reinforced composites deteriorate with service time depending on the environmental conditions. This performance loss is called aging and is especially crucial under sustained thermal and hydro-thermal loading.^{1–3}

To develop structural adhesive bonding to a reliable technology, it is essential to understand the aging behavior of epoxy systems under thermal and hydro-thermal conditions. It is the superposition of the aging of the adhesive, of the substrate or the fiber, and of their common interphase. For a variety of epoxies, the literature describes the degradation of mechanical properties under various aging conditions.^{4–7} But mechanical tests give no approach to the structural and chemical changes responsible for that loss of perfor-

mance. For the epoxy bulk, plasticitation by water is reported as an aging effect, which is reversible on re-drying.^{8–11} Additionally, irreversible processes like hydrolysis, thermal degradation, and network scissoring are reported and lead to a permanent modification of the epoxy bulk.¹² However, the details of these processes are not understood well enough.

This article considers the bulk aging behavior of a hot-cured epoxy based on dicyandiamide (DDA) as a usual amine hardener under thermal (elevated temperatures) and hydro-thermal conditions (immersion in distilled water at elevated temperatures). 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. The article complements two similar studies on the aging behavior of a room-temperature-cured epoxy system.^{13,14}

EXPERIMENTAL

The epoxy system investigated is a hot-cured 1-part adhesive. Diglycidylether of bisphenol A (DGEBA) is used as a bi-functional epoxy resin and DDA (Fig. 1) as a multi-functional amine hardener.

Theoretical background

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

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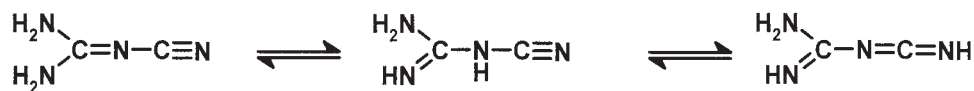


Figure 1 Mesomeric structure of DDA.

ing processes. The solid DDA powder is insoluble in the epoxy resin at low temperatures. Additionally, the amine groups are stabilized by the tautomeric structure of the DDA molecule (cf. Fig. 1). Consequently, no curing reactions take place at low temperatures and mixtures of DGEBA and DDA are stable at room temperature (therefore, it is called a latent curing system). However, curing starts well below the melting point of DDA at 213°C because the hardener diffuses into the liquid epoxy. Inside the diffusion zone a variety of chemical reactions take place. First, the oxirane rings of the DGEBA add to primary or secondary amine groups of the DDA forming hydroxyl groups and, finally, tertiary amines as soon as diffusion starts. Second, the hydroxyl groups react with oxirane rings and produce ether groups at elevated temperature (above ~170°C, cf. Ref. 15). Third, the cyano groups of the DDA are consumed on curing at such high temperatures as well. However, the exact reaction scheme of the cyano groups is still a matter of debate in literature. The diversity of proposed mechanisms are probably caused by the actual curing temperature, by variations of the mixing ratio and by the presence of different accelerators used. However, there is a general agreement that cyano groups react with hydroxyl groups and form one more type of crosslink. According to Gundjian et al.¹⁶ and Lin et al.,¹⁷ these crosslinks should result from an intermolecular addition of cyano and hydroxyl groups. Other workers^{18,19} conclude that an intramolecular addition of adjacent entities is more probable and suppose the formation of 2-amino-oxazolines and/or the tautomeric 2-imino-oxazolidines as five-membered rings. Regardless of the details of the reaction mechanism, a crosslink is formed that includes an imine group (Fig. 2).

With ongoing cure, oligomers and branched macromolecules are generated, which finally form a polymer network.²¹ The crosslinking density rises as the reaction proceeds. As a result, the molecular mobility in the network is more and more restricted. This corresponds to an increasing glass transition temperature T_g . The network vitrifies at the curing temperature T_c . The corresponding T_g is lower than the maximum glass transition temperature $T_{g\infty,ideal}$ that can be achieved by $T_c > T_{g\infty,ideal}$ for the given epoxy system.^{13,22,23}

The following aging mechanisms are reported for epoxy systems. When a glassy network is annealed close to its T_g in dry conditions, an endothermic enthalpy peak appears on the high-temperature end of

the glass transition. This so-called “aging peak” is attributed to short range ordering of segments in the vitrified network.²⁴ Additional thermal loading leads to some degradation due to radical disintegration or oxidative degradation. In the literature, for epoxy systems, several thermo-oxidative degradation mechanisms at temperatures higher than 100°C are proposed.^{12,25,26} However, such high temperatures are uncommon conditions for epoxy systems and are not applied to our epoxy system.

In contact to water, an epoxy is plasticized because of the interaction of water molecules with branches and loops of the polymer network. For several epoxy systems including DGEBA–DDA (⁹), a chemical reaction with water is discussed. In some cases, this reaction is assumed to cleave the network chains and leach low-molecular-weight products if the chains are cut several times between two crosslinks. Detailed degradation mechanisms are not proposed, however.^{9,10,27}

PROCEDURES

DGEBA and DDA are mixed in a mass ratio of 100 : 7 at 55°C for 30 min followed by degassing and stirring in an ultrasound bath. This mixing ratio, which is common for such commercially available hot-cured epoxy adhesives, provides a lack of amine hydrogen when compared with the stoichiometric ratio of DGEBA:DDA = 100 : 13.5.

To avoid the sedimentation of DDA on curing, the intensively stirred mixture is precured at 150°C for 1.5 h. The resulting prepolymer is solid at room temperature. It contains no visible DDA grains anymore. No network is formed during prepolymerization, since the material possesses low viscosity at 70°C and dissolves fully in organic solvents like THF.

For the bulk specimens, the prepolymer is cast at 70°C into Teflon molds of appropriate size. Disk-like samples (3 mm diameter, 0.8 mm thick, ~6 mg) are prepared for DSC. The samples for IR spectroscopy are disks with 10 mm diameter and 2 mm thickness. For curing, the samples are heated in the molds under dry atmosphere at about 10 K/min from room temperature to 180°C where the temperature is kept constant for 1 h. The small mass per sample, which produces only a small amount of heat of reaction, and the relatively big surface-to-volume ratio avoid any significant overheating in the epoxy during the curing.

Thermal aging is performed at 60°C in dried air (dew point < -70°C) with a CO₂-content < 400 ppm. For

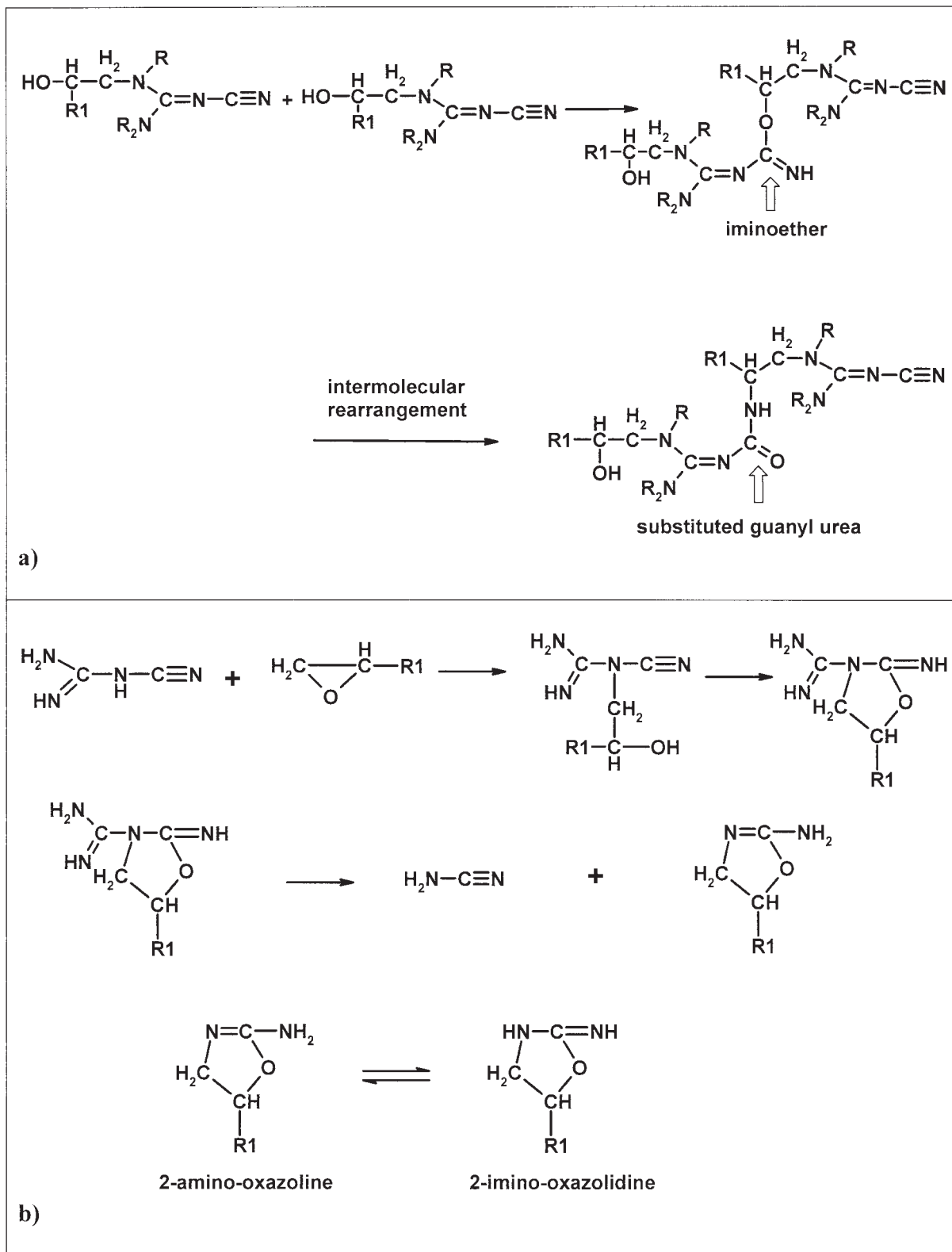


Figure 2 Mechanisms proposed for epoxy curing with DDA. (a) Mechanism of Saunders et al.^{16,20} and (b) mechanism of Zahir.¹⁸

hydro-thermal aging, the samples are immersed in distilled water at the same temperature. The immersion bath is changed weekly to remove leached products.

DSC is carried out on a Perkin-Elmer DSC 7 by heating samples twice (1st and 2nd run) from 5 to 200°C at a rate of 10 K/min.

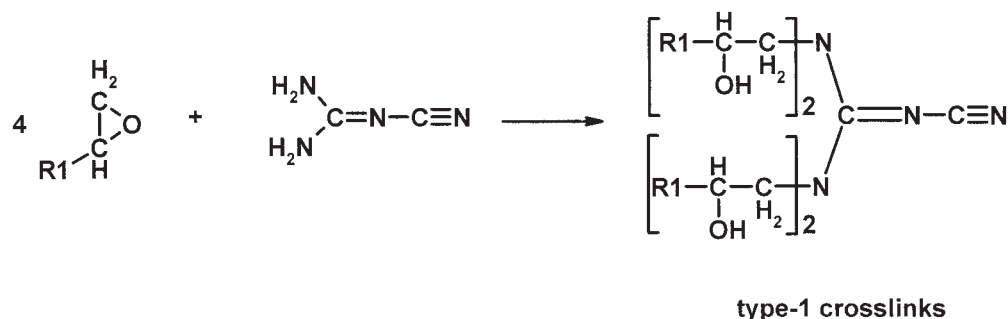


Figure 3 Type-1 crosslinks due to the reaction of primary and secondary amines with oxirane groups.

IR spectra are measured on a Bio-Rad "Excalibur Series FT 3000" spectrometer in attenuated total reflection (ATR) technique 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., $\sim 2.5\text{--}12.5\ \mu\text{m}$. The IR investigation allows to evaluate the consumption of epoxy groups and the chemical modifications due to aging. To make the peak intensities comparable, the spectra are divided by the intensity of the phenyl band at $1510\ \text{cm}^{-1}$ as the internal standard.

RESULTS AND DISCUSSION

Curing of the epoxy system

According to the IR spectra, almost all oxirane rings are consumed and only a few cyano groups are left in the cured network. Therefore, it is concluded that three types of crosslinks are generated by the three curing reactions (see Theoretical background). The type-1 crosslinks result from the addition of primary and secondary amines to oxirane groups (cf. Fig. 3). The type-2 crosslinks are due to the etherification of epoxies with hydroxyl groups (Fig. 4). The type-3 crosslinks result from the reaction of cyano groups with hydroxyl groups and are specific for DDA-cured systems. The details of this reaction mechanism depend on the curing conditions, and therefore, the literature proposes many reaction paths (cf. Theoretical background). For our system cured at 180°C without accelerator, we assume that the mechanism depicted

in Figure 5 is in good agreement with the literature¹⁷ and with our IR spectra. Accordingly, hydroxyl groups are capable to add intermolecularly to the cyano groups. As a special case, an intramolecular addition of adjacent cyano and hydroxyl groups may take place as well and form the five-membered rings proposed by Zahir¹⁸ cf. Fig. 2(b)]. Anyway, a secondary amine group arises in the reaction product (Fig. 5, step a) and reacts very fast with another residual epoxy group (Fig. 5, step b) at the elevated T_c given. As a part of the product, the imino ether is identified by a band at $1680\ \text{cm}^{-1}$ in the IR spectra. Via an unstable intermediate, it can react with another hydroxyl group to an ester species assigned to the IR-band at $1730\ \text{cm}^{-1}$, and another secondary amine (Fig. 5, step c). This reaction is very slow because a considerable amount of imino ether is still present in the epoxy system at the end of curing. It does not change the number of crosslinks.

The $T_g = 171^\circ\text{C}$ in the cured epoxy system corresponds to a complete oxirane conversion indicated by the IR spectra. Hence, T_g is lower than the curing temperature $T_c = 180^\circ\text{C}$ at any time and the curing reactions are not hampered by premature vitrification during network formation. The epoxy does not vitrify before it is cooled down after curing.

On a microscopic scale, the curing reactions depend on the diffusion of DDA molecules from the solid DDA particles into the molten DGEBA. Because of this diffusion, the concentration of hardener decreases with the distance from the DDA grains. This concentration gradient prevails even in the cured network

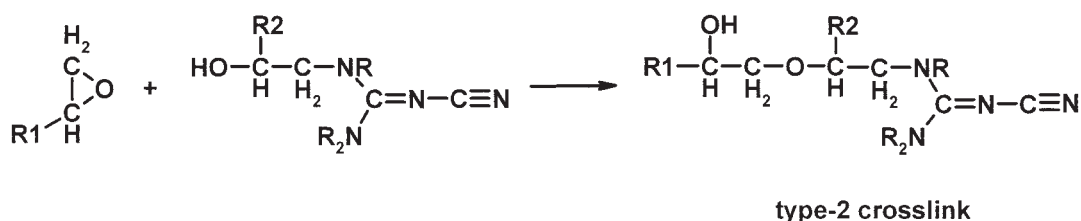


Figure 4 Type-2 crosslinks due to the reaction of hydroxyl groups with oxirane groups.

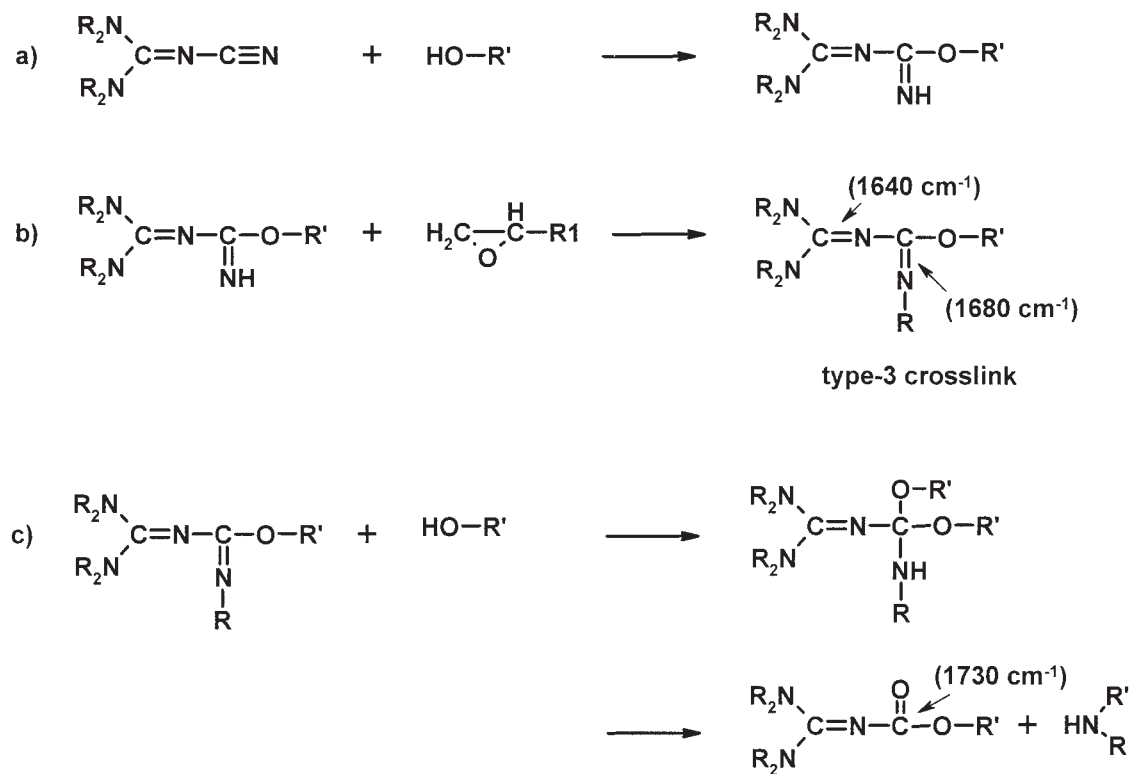


Figure 5 Type-3 crosslinks due to the reaction of cyano groups with hydroxyl groups. (Numbers in brackets represent IR absorption frequencies).

because more and more DDA molecules are fixed by chemical bonds to the growing oligomer and polymer molecules. Consequently, there is an inhomogeneous distribution of crosslinking density according to the distribution of DDA particles in the mixture. The presence of such inhomogeneities in latent curing adhesives is discussed in literature²⁸ and shown there by TEM, small-angle X-ray scattering, and small-angle neutron scattering results.

Thermal aging of the cured epoxy system

During thermal aging at 60°C, no significant chemical changes are detected in the IR spectra of the hot-cured epoxy system. In Figure 6, this is obvious for the spectral region where most changes are expected according to the literature.^{12,26} Moreover, the constant IR-intensity for the cyano band (2210 cm⁻¹) and the unchanged region around 915 cm⁻¹ (epoxy band) reveal that no further crosslinking took place (both regions not displayed in Fig. 6).

In the DSC curves, the principal glass transition temperature T_{g1} remains at the initial value of 171°C (Fig. 7). This corresponds to the stable chemical state. After 1 day of aging, however, a new feature appears at $T = 86^\circ\text{C}$ in the DSC curves. On further aging, it becomes more pronounced and shifts to higher temperature (see Fig. 7). After 108 days, the feature has

reached 114°C and developed into a second glass transition step (T_{g2}) now, which belongs to a new amorphous phase in the inhomogeneous, glassy network. The second glass transition vanishes if the aged sample is heated to the viscoelastic state and then characterized again. Therefore, the phase separation is reversible and this is explained as follows. At the beginning of the phase separation, more mobile segments arrange in the low crosslinked regions in a way that they possess their own cooperative mobility, which is higher than the mobility in the strongly crosslinked matrix. This increased cooperative mobility provides the second glass transition at T_{g2} , well below T_{g1} . With ongoing aging time, the packing density of mobile segments rises in this phase and less mobile segments are included. That results in a decreasing cooperative mobility for the entire new phase. Therefore, T_{g2} shifts to higher values and the height of the c_p -step increases because of the increasing volume part of the second phase. The reversibility of the phase separation proves that it is thermodynamically instable at $T > T_{g1}$ and that the second phase is not caused by any chemical modification of the network. At $T > T_{g1}$, the system forms only one phase in terms of cooperative macromolecular mobility. Phase separation runs again when the system is in the glassy state. Hence, some kind of thermodynamic incompatibility has to be stated as the driving force for the phase separation in the glassy

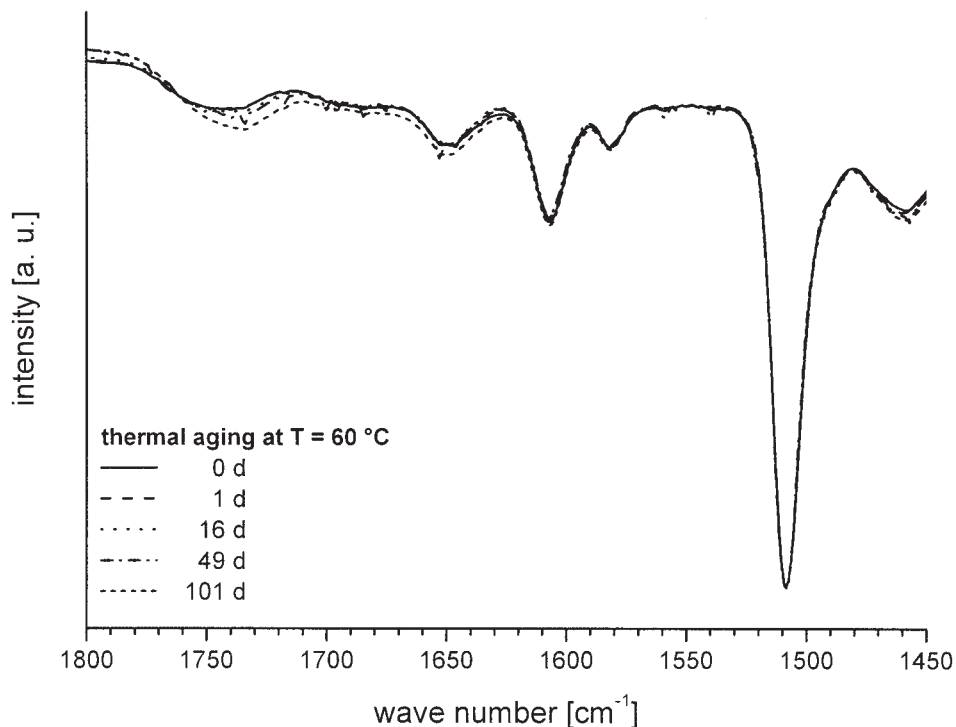


Figure 6 Spectral region (1800–1450 cm^{-1}) during thermal aging of the hot-cured epoxy system at 60°C up to 101 days.

state. Because of the phase separation during thermal aging, the microstructure of the epoxy system changes considerably even though the network is deep in the glassy state.

The phase separation observed for this hot-cured epoxy system is very similar to the phase separation in the fully crosslinked epoxy made of DGEBA and DETA by curing at room temperature and subsequent

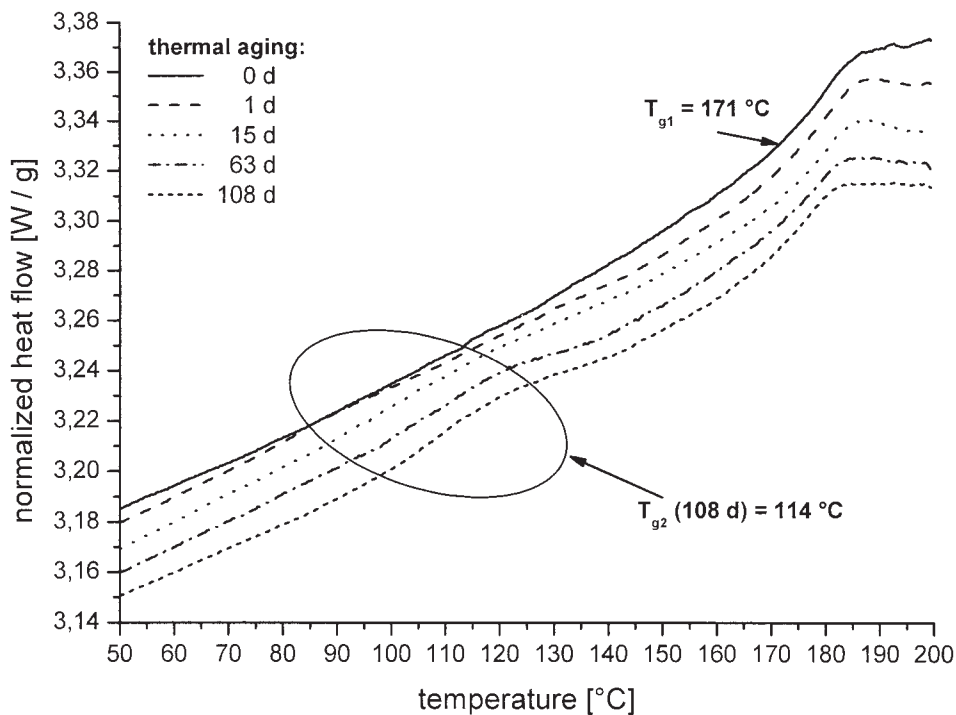


Figure 7 DSC measurement of the hot-cured epoxy system during thermal aging at 60°C up to 108 days.

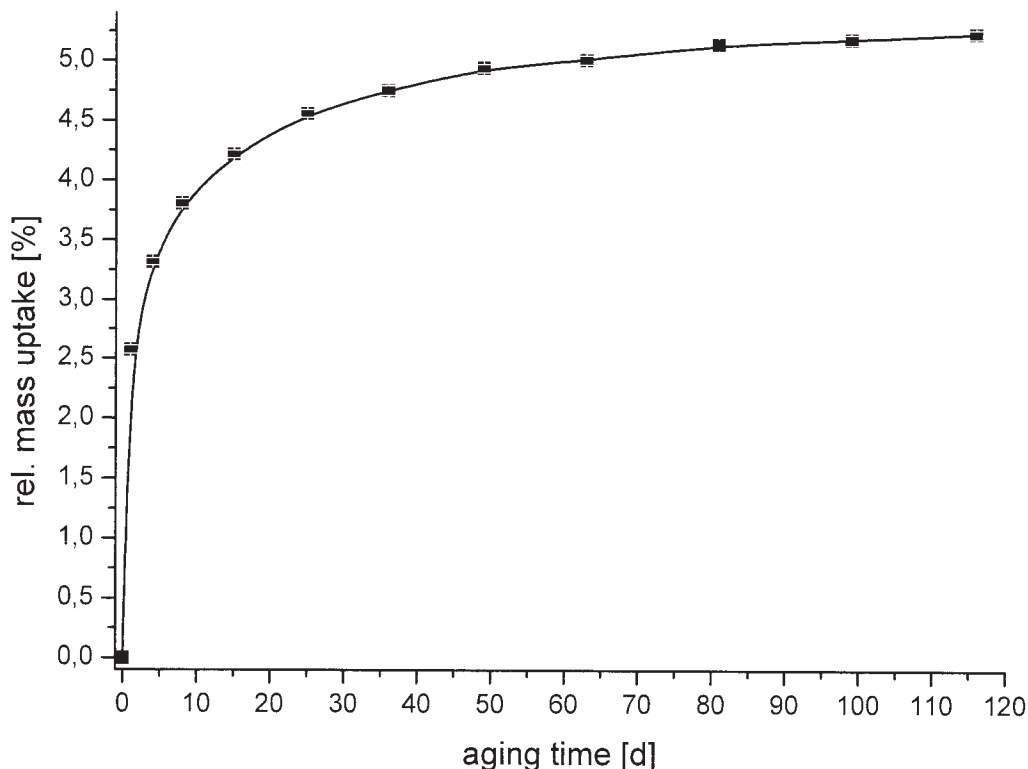


Figure 8 Relative mass uptake of the hot-cured epoxy system during hydro-thermal aging at 60°C.

postcuring at 120°C for 1 h.^{13,14} Therefore, the phase separation could be a characteristic aging mechanism for a wider range of epoxy systems.

Hydro-thermal aging of the hot-cured epoxy system

The water uptake of the hot-cured epoxy system during hydro-thermal aging at 60°C is depicted in Figure 8. After a high initial rate of water diffusion into the bulk, the rate slows down and the water uptake reaches 5.18 mass % after 116 days. Saturation is not reached within this time.

Corresponding with the major part of water uptake, T_{g1} decreases from the initial value of 171°C to 105°C within 35 days (see Fig. 9). Then, the principal glass transition stays constant at this temperature. The decrease in T_{g1} is due to the plasticizing effect of water (cf. Theoretical background). The plasticitation causes a T_{g1} -shift of -72 K for this hot-cured epoxy system, which is very high as compared with the -20 to -30 K reported for other hot-cured epoxies in literature.⁸

Again, a second glass transition develops below the principal glass transition during hydro-thermal aging. The heights of this second glass step and of an endothermic aging peak increase and its characteristic temperature T_{max2} rises from 90 to 99°C with ongoing aging (see Fig. 9).

The existence of two glass transitions in plasticized epoxies is often overlooked in the literature. Other authors explain the two transitions by the so-called core-shell phenomenon.^{29,30} Accordingly, T_{max2} is attributed to some plasticized "core" of the sample, whereas a "shell" quickly re-dries during the experiment and shows its glass transition at T_{g1} .

Our thermogravimetric analysis confirms, however, that significant drying does not take place in our measurements until the samples reach ~130°C in the 1st DSC heating run, e.g., at temperatures above T_{max2} and even above T_{g1} for the plasticized network. The desorption of water during the 1st DSC run is indicated by an endothermic peak above the principal glass transition (cf. Fig. 9). In a 2nd DSC run (not shown in the figures), only the principal glass transition is found for the aged matrix network confirming that the phase separation is reversible for hydro-thermal aging as well. Therefore, both glass transitions characterize the swollen network, while it contains an almost constant amount of water for the given aging time. Moreover, the core-shell model cannot explain why the second glass transition is also found for thermal aging of dry samples in the same temperature range. In contrary to the core-shell model, the explanation for the phase separation during thermal aging also applies to the development of the second glass transition during hydro-thermal aging. Now, the final

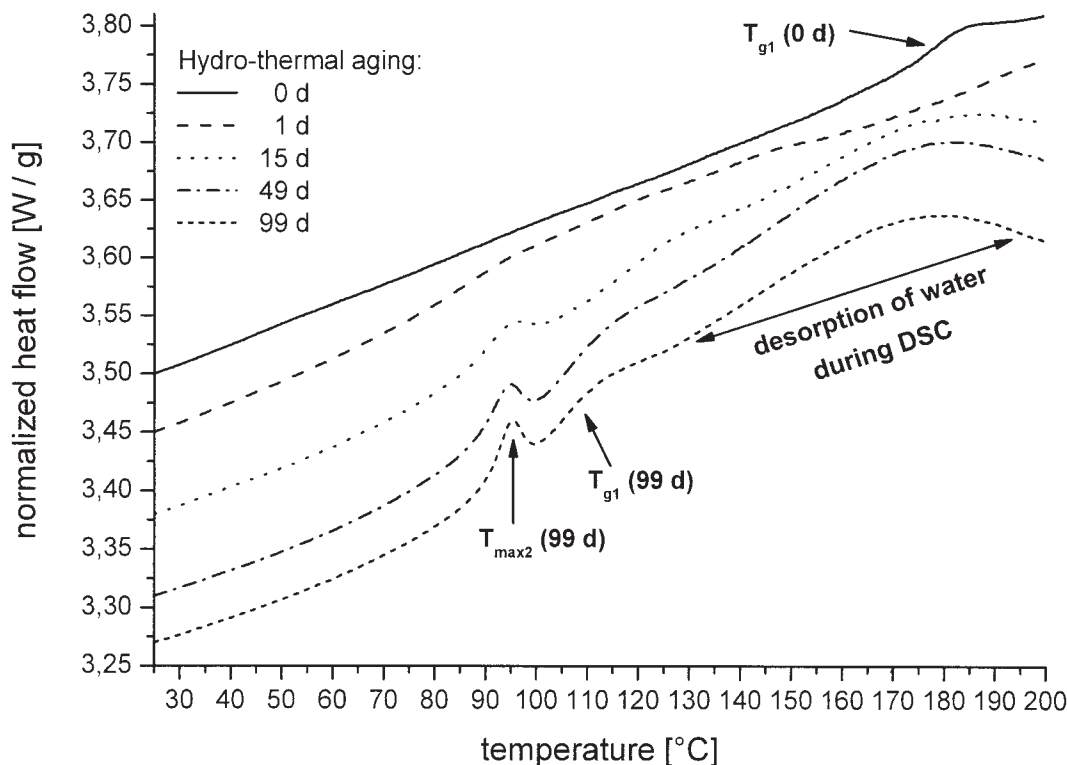


Figure 9 DSC measurement of the hot-cured epoxy system during hydro-thermal aging at 60°C up to 99 days.

$T_{\max 2}$ is about 15 K lower than T_{g2} for thermal aging. That increase in cooperative mobility is due to the plasticizing effect of water in the emerging phase. Moreover, the second glass transition is more distinct in the case of hydro-thermal aging because the aging temperature of 60°C is closer to the principal glass transition of the plasticized epoxy system. As a result, there is more macromolecular mobility in the network and this supports phase separation. The aging peak, which appears at the upper end of the second glass transition after 8 days, indicates enhanced local packing in the second phase.

According to gravimetric analysis, about 1 mass % of water remains in the network after the 1st DSC run and this amount is still present after the 2nd run (cf. Fig. 10). Other time-temperature regimes (e.g., 48 h at 105°C) do not remove this residual water content. Therefore, it is concluded that about 1 mass % of water is bonded irreversibly to the network. This modified state is characterized by a 2nd DSC run that shows only the principal glass transition for the modified matrix network. Figure 10 also depicts the glass transition temperature $T_{g1, \text{re-dried}}$ of the modified matrix after re-drying as a function of hydro-thermal aging time. $T_{g1, \text{re-dried}}$ does not reach $T_{g1} = 171^\circ\text{C}$ of the nonaged network. Therefore, the total plasticitation effect, which corresponds to a maximum T_{g1} -shift of -72 K within 99 days, splits into an irreversible part and a reversible part. The irreversible part is due to

the irreversibly bonded water. It corresponds to the difference ($T_{g1} - T_{g1, \text{re-dried}}$) that amounts to -32 K after 1 day and increases further to -41 K at 100 days. We assume that the aging process responsible for the irreversible plasticitation reduces the network density of the epoxy by breaking bonds under the influence of water. This hydrolytic process deteriorates only a part of the network, however, because the irreversible plasticitation comes to an end within the observed period of hydro-thermal aging.

The IR spectroscopic results support the partial hydrolysis assumed for the epoxy network. A new IR band grows at 1730 cm^{-1} during hydro-thermal aging, while the band assigned to the imino ether at 1680 cm^{-1} decreases (see Fig. 11). The changes are very similar to those observed on curing when a hydroxyl group is added to the imino ether (cf. "Curing of the epoxy system"). But now these changes are induced by water, since no such changes occur at thermal aging. Hence, we propose that water reacts with the imino ethers adjacent to the type-3 crosslinks (s. Fig. 12). This reaction is well known in organic chemistry as the splitting of Schiff's base and runs at low temperatures. Water hydrolyzes the type-3 crosslinks, which means that some network chains are irreversibly cleaved. Because of the hydrolysis, water is chemically bonded to the network and that causes the measured irreversible water uptake of 1 mass %, which equals 0.055 mol of water per 100 g of the epoxy

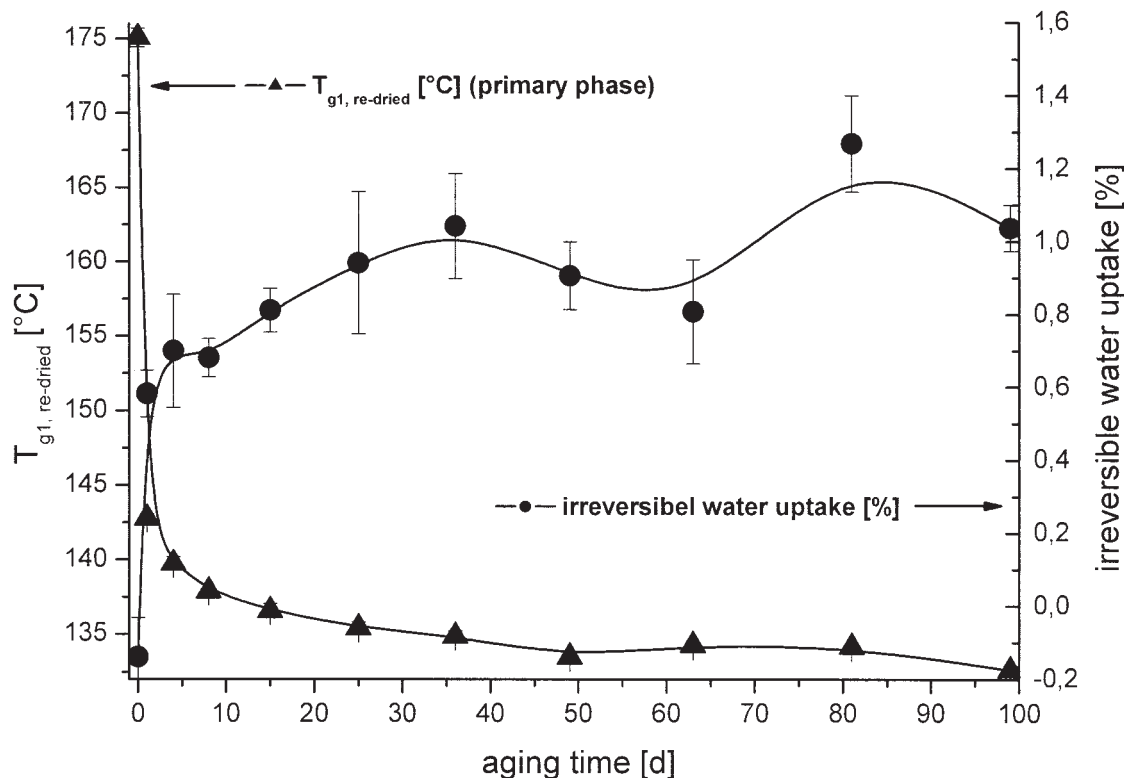


Figure 10 Glass transition temperature of the primary phase (left axis) and irreversible mass uptake (right axis) of the hot-cured epoxy system after hydro-thermal aging up to 99 days and re-drying.

system. This amount of water matches well to the content of imino ether groups in the fully cured network (0.078 mol/100 g). Cleaving the crosslinks increases the polymer mobility and this explains the irreversible decrease observed for T_{g1} during hydro-thermal aging. $T_{g1, \text{re-dried}}$ reaches a plateau at long aging times, indicating that only the type-3 crosslinks are hydrolyzed. The crosslinks of types 1 and 2 remain stable under the applied conditions of hydro-thermal aging. This prevents the total disintegration of the network.

The proposed hydrolysis mechanism has to be distinguished from a similar mechanism mentioned in the literature for an epoxy system containing DDA.³⁰ There, water, which has to be present at curing, is considered to prevent the formation of type-3 crosslinks. Accordingly, the cyano groups do not react with hydroxyl groups but with water molecules thus forming a carbonyl group and a primary amine already during the curing. The water molecules will win the race because they are very mobile when compared with the hydroxyl groups at the growing epoxy oligomer or polymer molecules.

Therefore, in this article, the reaction type proposed for adsorbed water in the epoxy network is assigned for the first time to an aging mechanism that leads to a hydrolysis of crosslinks, thus explaining the observed depression of glass transition temperature and the irreversible water uptake.

CONCLUSIONS

The effects of thermal and hydro-thermal loading on a hot-cured epoxy adhesive consisting of DGEBA and DDA are studied over a period of 100 days. Curing at 180°C over 1 h via a prepolymer state leads to almost full conversion of reactive groups and to a relatively low macromolecular mobility ($T_g = 171^\circ\text{C}$). An inhomogeneous network density results from a diffusion gradient of DDA from the solid DDA-particles into the liquid DGEBA on cure.

Thermal aging in dry air at 60°C does not cause any chemical changes in the cured epoxy system. However, a new phase is formed and indicates a remarkable modification of the microstructure of the network. A new explanation is presented for this phenomenon: starting from the inhomogeneous glassy network, relatively mobile polymer segments separate to very small regions inside the stiff network and achieve an increased cooperative mobility on aging. This renders the formation of a new phase, which is reversible on heating above T_g . Regarding the high mechanical stiffness of the glassy epoxy system, it surprises that enough molecular mobility prevails to enable such a phase separation. Most probably, the new phase is finely dispersed in the stiff epoxy matrix.

During hydro-thermal aging in distilled water at 60°C, phase separation takes place again and results in a microstructure similar to thermal aging. Simulta-

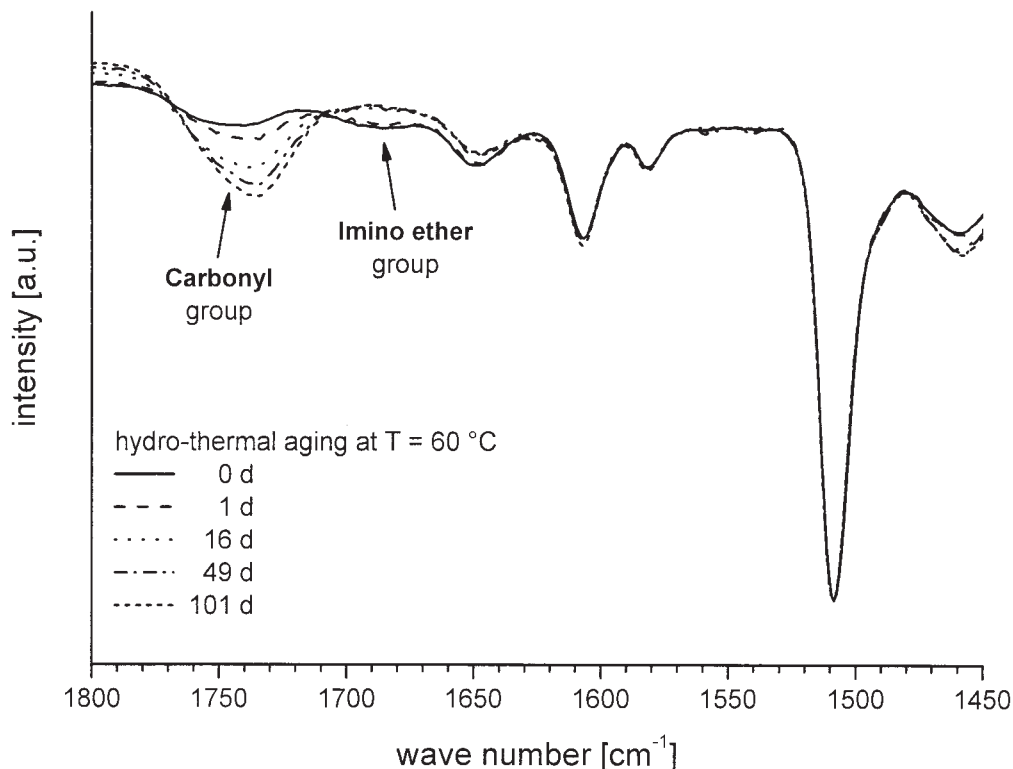


Figure 11 Spectral region (1800–1450 cm⁻¹) during hydro-thermal aging of the hot-cured epoxy system at 60°C up to 101 days.

neously, hydrolysis cleaves a kind of imino-ether-like crosslinks that is specific for the DDA-cured epoxy. The chemical mechanism for this hydrolysis is presented for the first time. It gives an interpretation of the aging behavior of these epoxies because it includes all the observed effects of chemical modification, irreversible part of plasticitation, which is observed besides reversible plasticitation, and irreversible water uptake. Additionally, it is understood why there is no total disintegration of the network: The hydrolysis

affects only the imino-ether-like crosslinks but not the amine-like or the ether-like crosslinks that are also formed during curing.

In summary, significant chemical and structural changes take place in the DGEBA–DDA epoxy network during thermal and hydro-thermal loading far below its glass transition temperature. It is convincing that these changes exert an influence on the mechanical properties of an adhesive joint, a coating or a fiber-reinforced composite made of this epoxy system.

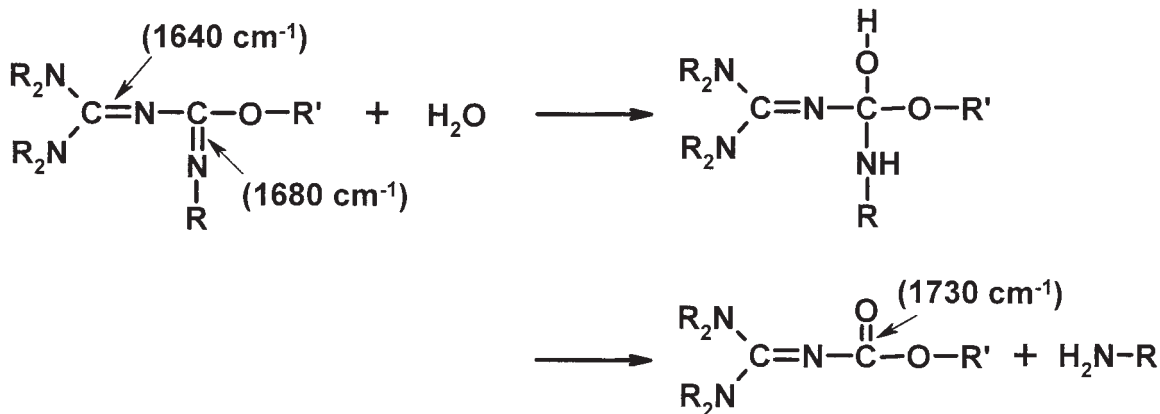


Figure 12 Schematic sketch of the hydrolysis mechanism going on in the hot-cured epoxy system during hydro-thermal aging. (Numbers in brackets represent IR absorption frequencies).

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