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Physical Aging of Partially Crosslinked RTM6 Epoxy Resin

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ABSTRACT: The aging behavior of partially and completely crosslinked RTM6 epoxy resin samples in the glassy state is investigated by thermophysical and mechanical analyses. Curing degree, glass transition temperature, density, and micromechanical modulus are investigated as function of aging period, initial curing degree or depth below the sample surface. A clear increase of density and modulus with aging period as well as an enhanced surface stiffness is detected for all curing degrees. Also, the aging period necessary to achieve the steady state modulus is independent from the curing degree. In contrast, the degree of physical aging induced modulus changes shows a significant dependence on the curing degree. A discontinuity is detected in the so-called transition region, which is related to the transition from rubber to glassy state during crosslinking. This emphasizes the importance of curing history for physical aging processes and the high potential of partial curing for the development of new processing routes, in particular for production of samples with low sensitivity to physical aging. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41121.

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INTRODUCTION

Tetra-functional epoxy resins are characterized by outstanding material properties such as high modulus and high tensile strength. They are widely used as matrix materials in aerospace industry for production of fiber reinforced composites, in particular carbon fiber reinforced polymers (CFRP).[1,2] After infiltration of the dry fiber fabric, the thermosetting resin is crosslinked in a thermal curing process. The resulting resin material is in a highly crosslinked, amorphous, glassy state, which is in thermodynamic disequilibrium and instable. When exposed to temperatures below the glass transition temperature for extended periods of time, the resin system gradually approaches equilibrium. A decrease of the specific enthalpy of the system takes place, which can be attributed to a decrease of free volume and/or a decrease in molecular conformational energy. In the first case, the material contracts and thus densifies to achieve a lower energy molecular state, without change of the molecular orientations (volumetric relaxation). In the second case, a volume-independent rearrangement of molecular segments in the network takes place to achieve a lower energy structure (enthalpy relaxation). These reversible, time dependent processes of physical change of the molecular structure are called physical aging.[3–7] The time scales for physical aging increase rapidly with increasing distance to the glass transition temperature. Usually, only for aging temperatures close to the glass transition temperature an equilibrium state can be achieved in a timely manner.[5,7,8] In addition to physical aging, dependent on the environmental conditions, also chemical and/or hydrothermal aging processes can occur, which are caused by a degradation of the chemical structure or the presence of hot and humid conditions.[3] Besides, all aging processes depend on the curing history and the crosslinking degree of the epoxy resin.[5,9,10] Aging results in a time dependent change of the material properties of the epoxy resin system such as mechanical behavior, viscoelastic response, density, permeability, or water absorption and does impact all technical applications.[3]

The surface region of the polymer shows particular aging effects, as the interface of polymer and air also induces material changes. First, the direct contact to environmental settings, e.g., gas atmosphere, humidity, elevated temperatures or irradiation, accelerates chemical and/or hydrothermal aging of the surface layer. Dependent on the resin system analyzed, investigations of chemical aging by oxidation and photo-oxidation experiments report both an increase[11,12] and a reduction of surface elastic modulus.[13,14] However, at room temperature the oxidation rate is expected to be quite small.[15] Moisture absorption results in a degradation of the mechanical properties of epoxy resin systems.[16] Surface postcuring effects for RTM6 are expected to result in a decrease of density and modulus.[17] Secondly, the presence of the polymer–air interface results in a changed molecular mobility and configuration of the polymer chains. It also influences the local monomer segmental packing density and the configurational entropies. A reduction of the glass transition temperature is reported for a thin surface layer of a thickness of about 500 nm for different polymers.[18,19] On glassy

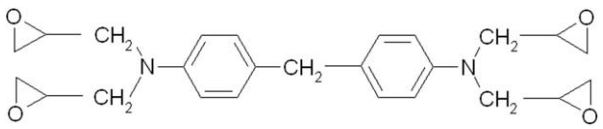

Figure 1. Chemical structure of epoxy resin TGMDA.

polysulfone films a reduction of the free volume elements is detected near the film surfaces, which is suggested to result from enhanced molecular mobility near the surface.[20] The lower free volume state results in a densification of the surface region, which in general is correlated to an increase of modulus.

For applications of CFRP in aerospace industry, long term stability of the composite components is one of the major material requirements. For airplanes, which are exposed to harsh environments for extended periods of time, the structural integrity of the polymeric materials has to be guaranteed over the whole lifetime. Thus an understanding of the aging behavior of the relevant polymers is essential. In particular knowledge of the changes of bulk and surface mechanical and thermophysical properties, the relevant time scales and the influence of environmental conditions on the aging processes is important to allow the identification of resins with low aging induced changes of material properties.

Besides, for new processing routes, also partial crosslinking of epoxy resins and storing of partially cured CFRP components is of interest.[17] One example is the joining of partially cured CFRP parts to create components with a high integration level.[21] To further develop these new technologies, knowledge of the aging induced material changes of partially cured resin systems is necessary to identify curing degrees and processing routes with low sensitivity to aging processes. This concerns bulk as well as surface properties.

In the actual work, the impact of physical aging on the material properties of partially and completely cured RTM6 epoxy resin samples is addressed. Ambient conditions are the relevant ones for storing of partially and fully cured CFRP components in industry and, therefore, important for the described technical applications. It is shown that the influence of chemical and hydro-thermal aging is small under these conditions. In the following we concentrate on physical aging effects, which influence density and elastic modulus. These aging effects are investigated as function of aging period, initial curing degree and depth below the initial surface. Density and elastic modulus are closely connected to structural changes of the polymer and thus are important quantities for investigation of physical aging by volumetric relaxation processes.[22,23] Of particular interest are initial curing degrees within the so-called transition region. In this region an abrupt increase of density and modulus of the freshly cured epoxy resin occurs.[17] The influence of physical aging on this discontinuity is addressed. The elastic modulus is determined by the micromechanical method of nanoindentation, which has been proven to be very sensitive to aging induced volumetric relaxation processes.[17]

EXPERIMENTAL

Production and Aging of Partially and Completely Crosslinked RTM6 Epoxy Resin Samples

All resin samples discussed in the following are manufactured of the mono-component epoxy resin system HexFlow® RTM6 distributed by the Hexcel Corporation.[24] It is composed of the tetra-functional epoxy resin tetraglycidyl methylene dianiline (TGMDA) (see Figure 1) and the hardeners 4,4′-methylene-*bis*(2,6-diethylaniline) (MDEA) and 4,4′-methyylene*bis*(2-isopropyl-6-methylaniline) (M-MIPA) (see Figure 2).

Modified curing cycles are used to obtain resin samples with defined partial curing degrees α, as described in our previous work.[17] All cycles start with an isothermal curing period at a temperature of 120°C, technically used as infiltration cycle. To create a completely crosslinked sample with a curing degree of nearly 100% the resin is cured subsequently for 2.5 h at the standard heating temperature of 180°C. To obtain samples with partial curing degrees between 50 and 80% the infiltration cycle is followed by isothermal heat treatment at a reduced temperature of 135°C. The different curing degrees result from different durations of these isothermal heating periods, which range between 100 and 150 min, and are measured by differential scanning calorimetry.[17]

To produce samples in different states of physical aging, the partially and completely cured resin samples are stored at ambient conditions (temperature 22 ± 1°C, humidity 35 ± 5%, no irradiation) for up to 13 months. After defined aging periods, ranging between 2 days and several months, micromechanical, and thermophysical investigation of the aged samples is performed.

Micromechanical Testing, Density, and Thermal Analysis

Micromechanical elastic moduli of the partly and completely crosslinked aged epoxy resin samples were measured by nanoindentation, as described in detail in Ref. 17. During the loading–unloading indentation cycles the load–displacement curves $F(h)$ are recorded. From the mainly elastic unloading curve the micromechanical parameters are quantified according to Refs. 25–27.

The nanoindentation measurements were performed with a NanoTest 600 nanoindenter (Micromaterials) and a Berkovich geometry indenter. The maximal indentation depth was 2.8 μm. The load controlled mode was used with loading and unloading rates of 2 mN/s. In all measurements, a dwell time of 5 s was inserted between loading and unloading. As shown in our previous work, these measurement parameters ensure undistorted, reproducible load–displacement curves and reliable modulus values. The impact of viscoelastic effects is minimized.[17] Before analysis, the raw data of the load–displacement measurement is corrected by the system compliance. To determine the contact stiffness S, the unloading curve was fitted with a power law between $0.8 \cdot F_{max}$ and F_{max}. A Poisson's ratio of 0.35 is used.[28] Average modulus values were obtained by investigating several comparable resin regions. All average values are calculated from more than nine individual values. The measurements were

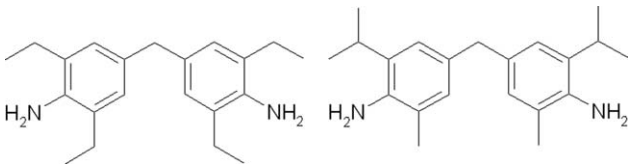

Figure 2. Chemical structure of hardeners MDEA and M-MIPA.

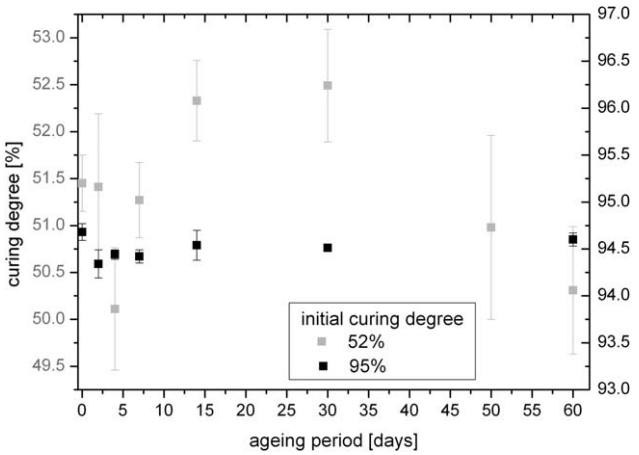

Figure 3. Curing degrees as function of aging period.

performed on plane surfaces of the polymer samples, which were prepared by a grinding and polishing process of the fresh resin sample. After aging no further surface treatment is carried out. To investigate the modulus changes as function of depth below the surface, a subsequent abrasion of the aged surface layer of one sample is done by several grinding and polishing processes. After each abrasion step the micromechanical investigation is done.

Density of the fresh and aged polymer samples of different curing degrees is measured with a helium pycnometer AccuPyc II 1340 (Micromeritics). For each curing degree and aging period at least three resin samples were analyzed.

Thermal analysis was done with a 204F1 Phoenix differential scanning calorimeter (Netzsch). The curing degree of the fresh and aged resin samples was determined according to Ref. 17. The glass transition temperature T_g of the fresh resin samples was determined from the modulated DSC curves as the midpoint of the endothermic shift of the reversing heat flow, when the resin passes from the glassy to the rubbery state.[3,6] For the aged samples a modified procedure is used, since an additional endothermic structure appears in the DSC signal near T_g. It is due to the aging induced decrease of specific enthalpy of the system and the corresponding increase of energy necessary for transformation to rubber state. Also in the modulated DSC curve a related structure appears and merges with the glass transition signature. To separate the two superposed signatures of the reversing heat flow, the points of maximal incline of each signature are determined from the first derivative of the heat flow. The corresponding temperature positions are attributed to the position of the additional aging induced structure and to the glass transition temperature, respectively. For each curing degree and aging period at least three resin samples were analyzed.

RESULTS AND DISCUSSION

In the following the thermophysical and mechanical investigation of aging induced changes of material properties of partially and completely cured RTM6 epoxy resin samples is presented. We first show aging induced changes of curing degree, glass transition temperature, density, and micromechanical modulus as function of the initial curing degree and the aging period. Then the influence of surface aging for all partially and completely cured resins samples is investigated.

Thermophysical Properties as Function of Aging Period

To allow the investigation of physical aging effects, aging of the partially and completely cured RTM6 epoxy resin samples was performed at ambient conditions. To show the negligible influence of chemical aging processes, in the following the amount of material changes due to postcuring, absorption of moisture and oxidation processes is discussed. To this aim the curing degree and the glass transition temperature of two samples with low and high initial curing degrees of 51.5 and 94.8%, respectively, are analyzed as function of the aging period. The results are shown in Figures 3 and 4.

For the completely cured sample with initial curing degree of 95% only a negligible increase of curing degree of 0.4% is observed within the first 60 days of aging. The sample with an initial curing degree of 52% shows a slightly higher increase of curing degree of 2.4%, which however is still very small. For both analyzed samples, therefore, only small changes of curing degree can be stated which are restricted to the first 30 days of aging. Thus only minimal further postcuring processes occur, primarily on lowly cured resin samples. Based on our previous work, a prediction of density and modulus as function of curing degree is possible.[17] The observed small increases of curing degree of maximal 2.4% would result in a slight reduction of density of 0.0008 g/cm^3 and modulus of 0.067 GPa. As will be shown below, this influence of postcuring on the material properties is very small compared to physical aging effects. Thus chemical aging due to postcuring effects can be neglected in the following.

The glass transition temperature of a thermosetting polymer is directly correlated to its crosslinking degree. An increase of crosslinking results in an increase of T_g. In our previous work this dependency has been measured for a large range of partial curing degrees of the RTM6 epoxy resin samples.[17] Additionally T_g is influenced by environmental effects, e.g., an absorption of water or a chemical degradation. Water absorption reduces the glass transition temperature and causes a decrease of the

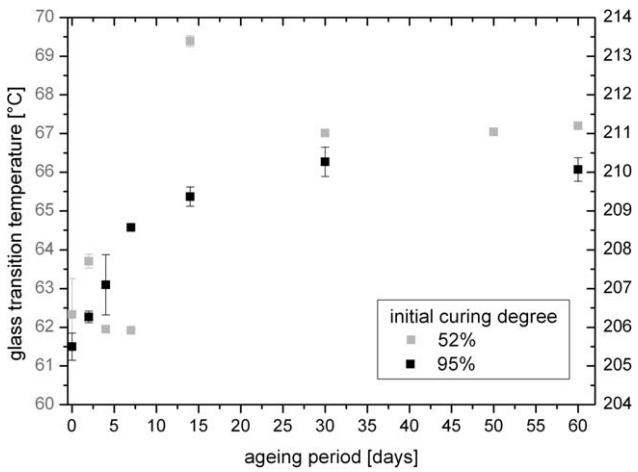

Figure 4. Glass transition temperatures as function of aging period.

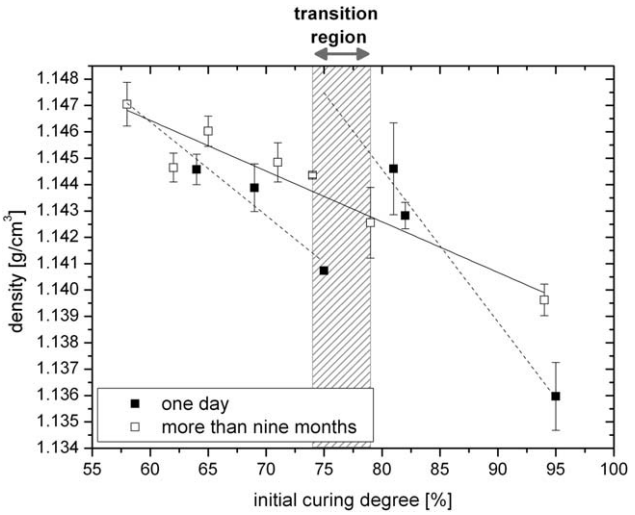

Figure 5. Density of the fresh and long term aged partially and completely crosslinked RTM6 samples as function of the initial curing degree, together with linear fit lines.

polymers mechanical properties.[16,29] As shown in Figure 4, aging of the epoxy resin samples results an increase of glass transition temperatures. For the completely cured sample an aging induced increase of T_g of about 4.8°C is found. The sample with 52% initial curing degree shows a slightly higher increase of T_g of about 7.4°C. Considering the observed aging induced increases of curing degree of the two samples of 0.4% ($\alpha = 95\%$) and 2.4% ($\alpha = 52\%$), increases of the glass transition temperatures of 2.9° and 6.3°C, respectively, are expected according to our previous work.[17] The measured increases agree quite well with the expected values and are even slightly higher. Since for both samples no aging induced reduction of glass transition temperature is observed, it can be concluded that only a negligible moisture uptake takes place. Therefore, no moisture induced degradation of the epoxy resin and the corresponding reduction of its mechanical properties are expected. For both samples, the aging induced changes of glass transition temperature occur during the first 30 days of aging, in agreement with the aging induced changes of curing degree. After 30 days, a steady state is reached.

Chemical aging can also occur due to oxidation of the polymer. However, at room temperature the oxidation rate is expected to be quite small. For two bisphenol A diglycidyl ether (DGEBA) based epoxy systems after 9 months of aging an oxidation of only 0.2 and 0.05% is reported. The influence of oxidation processes thus is expected to be negligible.[15]

The results confirm the minimal influence of postcuring, chemical aging, and degradation due to moisture absorption for the RTM6 epoxy resin system at ambient conditions. The small effects observed are restricted to the first 30 days of aging. Long term aging induced changes of material properties, which will be analyzed in the following, are thus expected to be caused by physical aging of the glassy epoxy network.

Density and Micromechanical Modulus of Long-Term Aged Partially and Completely Cured Epoxy Resin

Modulus and density of polymers are closely connected, as they both are determined by the molecular structure, intermolecular forces, and intramolecular forces.[22,23] Density and modulus are particular sensitive to volumetric relaxation processes due to physical aging. Therefore, in the following these quantities will be used to investigate physical aging induced changes of partially and completely cured aged RTM6 samples. Micromechanical testing by nanoindentation represents a valuable tool for modulus investigation of polymers, as it has been shown to be sensitive to changes of the molecular arrangement of polymers, e.g., during annealing or aging.[17]

As shown in our previous work, density and modulus of freshly cured RTM6 epoxy resin samples vary significantly as function of the curing degree.[17] First, both parameters decrease with increasing curing degree. This is caused by the growing three-dimensional network and the increase of glass transition temperatures, which reduce the possibility of molecular arrangements, increase the specific volume and thus decrease the density and modulus.[30,31] Secondly, a discontinuity of density and modulus is found, which is correlated to a transition from rubber to glassy state during the isothermal curing treatment. For the presented partially cured samples this transition region corresponds to a curing degree of 76.5 ± 2.5%. For lower curing degrees, the resin is in its rubber state at the end of curing and transition to glassy state takes place during cooling to room temperature. For higher curing degrees, the resin transforms to glassy state during curing and the ongoing curing acts as an annealing treatment. Therefore, structural relaxation processes of the polymer network start, resulting in a discontinuity of density and modulus in the transition region. The density and the micromechanical modulus of the fresh resin samples (1 day after curing) as function of the curing degree are shown in Figures 5 and 6. Also the transition region is indicated in both figures.

To investigate the influence of physical aging processes on the partially and completely cured RTM6 samples, density, and micromechanical modulus were analyzed after an aging period of more than nine month. After this time period of aging a steady state of the polymer structure near equilibrium is

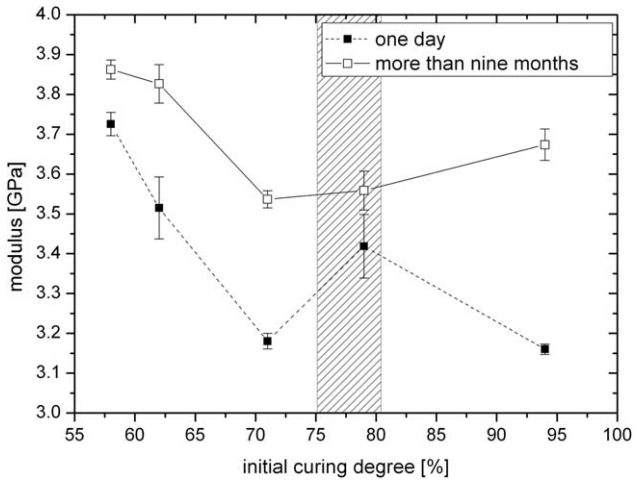

Figure 6. Micromechanical modulus of the fresh and long term aged partially and completely crosslinked RTM6 samples as function of the initial curing degree.

achieved, as will be shown below. The resulting density and modulus values are included in Figures 5 and 6.

A comparison of the aged and fresh resin samples shows in general an increase of density after long term aging. Also all moduli of aged resin samples lie clearly above the corresponding values of the fresh resin samples. This increase of density and modulus after long term ageing is attributed to volumetric relaxation processes, which allow a closer packing of the polymer chains of the three-dimensional network.[20] Also in literature ageing induced density and modulus increases are reported.[3,20,32–34]

The maximal aging induced increase of density and modulus is found for the completely cured sample. A modulus increase of 16% is detected, which is in contrast to a much lower density increase of only 0.3%. This discrepancy is partly attributed to the surface sensitivity of modulus measurements compared to the bulk sensitivity of density measurements as will be discussed in detail below.

A continuous, nearly linear decrease of the density of the aged resin samples is observed as function of the initial curing degree. This is in agreement with literature, where a similar decrease of density with increasing curing degree is reported for epoxy resins in the glassy state.[22,23,33] The modulus values also show a decrease as function of the curing degree for curing degrees below the transition region, following the behavior of density. For curing degrees above the transition region, however, a slight increase of moduli is observed. Again, surface aging effects could influence the modulus values and prohibit a direct correlation with the density values.

In contrast to the fresh resin samples, for the aged resin samples no step-like increase of density and modulus exists in the transition region. As already mentioned, the discontinuity observed for the fresh samples is caused by an annealing effect of the glassy samples (with curing degrees above the transition region) during the curing process and the resulting structural relaxation processes. In contrast, during physical aging samples of all curing degrees undergo comparable structural relaxation processes. Therefore, the discontinuity of density and modulus does not occur. The step-like increase is a nonequilibrium feature of the polymer network, which decays by the structural relaxation processes taking place during physical aging.

Micromechanical Moduli as Function of Initial Curing Degree and Aging Period

To investigate the degree of structural relaxations during physical aging and to identify the relevant time scales to achieve a steady state near equilibrium, the micromechanical moduli of partially and completely cured RTM6 resin samples were investigated as function of the aging period. In Figure 7, the micromechanical moduli of five samples with different curing degrees ($\alpha = 58$, 62, 71, 79, and 94%) are shown for aging periods between one day and nine months.

For the fully cured sample ($\alpha = 94\%$) the modulus of the fresh resin sample amounts to 3.16 ± 0.131 GPa. This is slightly higher than the value of 2.89 GPa given in literature.[24,28] Possible reason is the sensitivity of nanoindentation to structural changes of the polymer, as caused by the annealing treatment of

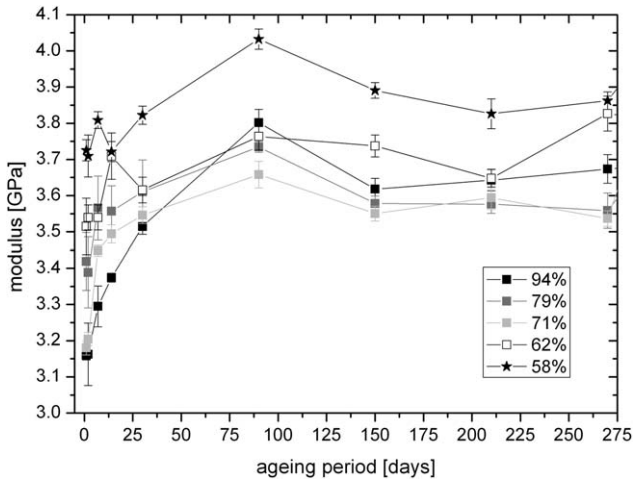

Figure 7. Micromechanical modulus of partially and completely crosslinked resin samples as function of aging period.

the glassy sample during isothermal curing.[17] With increasing aging time the modulus value increases up to a maximum value of 3.80 ± 0.036 GPa after 90 days. The reason for the observed maximum, which also is observed for the other samples, is not clear yet. For longer aging times, the modulus first slightly decreases and then saturates for aging times above 150 days. Here a steady state of the system near equilibrium is achieved. The corresponding average modulus value (averaged over the aging times of 210 and 270 days), in the following called steady state modulus, amounts to 3.66 ± 0.034 GPa. The modulus increase starting from the freshly cured resin to the aged steady state amounts to 16%. Further crosslinking or a degradation of the polymer due to water absorption would result in a reduction of modulus, in contrast to our results. As shown above, the relevant time scale of postcuring effects is 30 days, while the modulus changes are on a time scale of 150 days. Therefore, the results confirm the assumption of negligible postcuring and water absorption effects. In addition, the results are in agreement with literature, where physical aging induced modulus increases of similar orders of magnitude are reported for epoxy resin systems.[3,32–34]

Also all other samples of varying initial curing degree shown in Figure 7 exhibit an increase of micromechanical modulus with increasing period of aging. After 90 days of aging, all samples reach their maximal modulus values. For aging periods longer than 150 days the moduli of all samples achieve a near-equilibrium value. The time scales relevant for physical aging processes of RTM6 epoxy resin as characterized by modulus changes thus are independent of the curing degree of the resin. The values of the fresh resin vary between 3.16 and 3.73 GPa and differ by 18%. The steady state moduli vary between 3.57 and 3.84 GPa and differ by only 8%. The high modulus variances of resins with different curing degrees thus are typical for resins directly after cure and diminish with increasing aging time.

To evaluate the degree of aging of the presented partially and fully cured samples, relative modulus increases are of interest. The relative modulus after an aging period t is defined as the

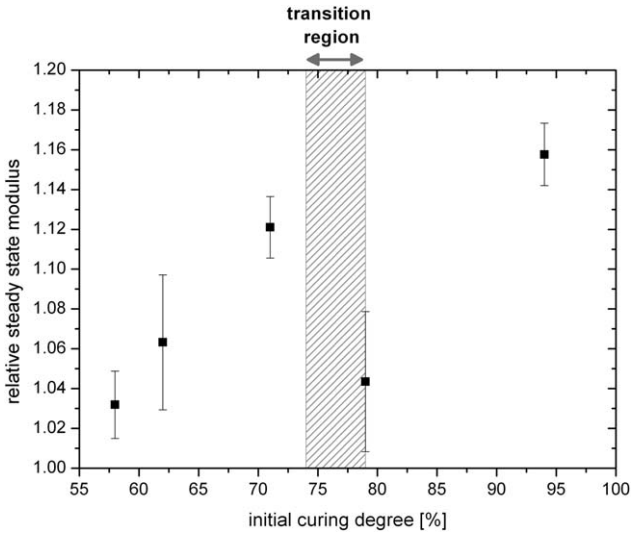

Figure 8. Relative steady state modulus of partially and completely crosslinked resin samples as function of the initial curing degree.

modulus after period t divided by the modulus of the fresh resin sample.

To quantify the influence of the curing degree on the degree of aging, the relative steady state moduli are compared for all investigated initial curing degrees, as shown in Figure 8. The relative steady state modulus is a measure of the modulus changes due to physical aging. A freshly cured sample will have a value of one. An aged sample with a high degree of structural relaxations and thus a high increase of modulus will have a value clearly above one. In Figure 8 also the transition region is marked, which is characterized by a step-like increase of density and modulus of the fresh resin samples.[17]

The relative steady state moduli as function of the initial curing degree also show a step-like discontinuity in the transition region.

At low curing degrees, far below the transition region, the relative steady state modulus is near one. Here, at the end of curing the resin is in the rubber state and the glass transition temperature is quite low.[17] While cooling down to room temperature after the curing process the sample mostly remains in the equilibrium rubber state, where the specific volume decreases linearly as function of the temperature and a corresponding densification occurs. Only after the system crosses the glass transition temperature, a deviation from this linear behavior is found and the densification slows down significantly.[3,8,22] A low glass transition temperature therefore results in a high packing density and a final glassy state close to equilibrium.[22] Correspondingly, during the room temperature aging period only minor structural relaxation processes occur. The long term aging induced density and modulus changes (see Figures 5 and 6) are small and the relative steady state modulus is nearly one.

With increasing curing degree, but still below the transition region, the relative steady state modulus increases. This is caused by the increase of the glass transition temperature with increasing curing degree,[17] which results in a glassy state further away from equilibrium.[22] During the room temperature aging period correspondingly more structural rearrangements take place, resulting in an increase of the relative steady state modulus. Accordingly, also the long term aging induced increase of density and modulus rises in this region of curing degrees (see Figures 5 and 6).

In the transition region a jump to very small relative steady state moduli near one takes place. Here, due to the crossing of glass transition temperature and curing temperature, an annealing treatment of the now glassy sample starts already during curing, which allows structural relaxation processes to occur. As the annealing takes place at temperatures near T_g, equilibrium is achieved rapidly.[5,7,8] Therefore, the sample is already in an aged state with high packing density immediately after curing. During the room temperature aging period only minor further structural rearrangements occur. Therefore, long term aging results in only small increases of the modulus for curing degrees directly above the transition region (see Figure 6). Density values in Figure 5 show no increase at all directly above the transition region.

The sample with a curing degree of 94% has to be discussed separately, as it is cured at higher temperatures than the other samples. Due to the faster crosslinking reaction, the higher crosslinking degree and the possibly different network structure a direct comparison to the samples cured at lower temperatures is not possible. Due to the different network structure the relaxation processes may differ. Nevertheless, here also an annealing takes place during curing in the glassy state. However, due to the higher difference between T_g and curing temperature the 94% sample is further away from equilibrium than samples with curing degrees in the transition region. Therefore, the physical aging effects during the room temperature aging period are high, which results in a high relative steady state modulus and a strong increase of density and modulus after long term aging (Figures 5 and 6).

The results confirm that the discontinuity in the material properties of the fresh partially cured epoxy resin samples is reflected in the physical aging behavior. The degree of volumetric physical aging, characterized by the relative steady state modulus of the aged samples, is dominated by the curing history and the resulting physical properties of the freshly cured epoxy resin samples. A control of physical aging behavior of RTM6 epoxy resin thus is possible via choice of suitable curing conditions.

Long-Term Aging of Epoxy Resin Samples: Surface and Volume Effects

Aging effects are not only observed for the bulk properties, but also the polymer surface undergoes aging induced material changes. Chemical and/or hydrothermal aging of the surface layer is accelerated by the direct contact to environmental conditions. In addition, the changed molecular mobility and configuration of the polymer chains at the surface influence the packing density and the configurational entropy and result in an increased surface density and modulus.[18] Aging of polymer samples at ambient conditions does not allow a clear separation of these different influence factors. However, room temperature aging, low humidity and missing irradiation lead to the

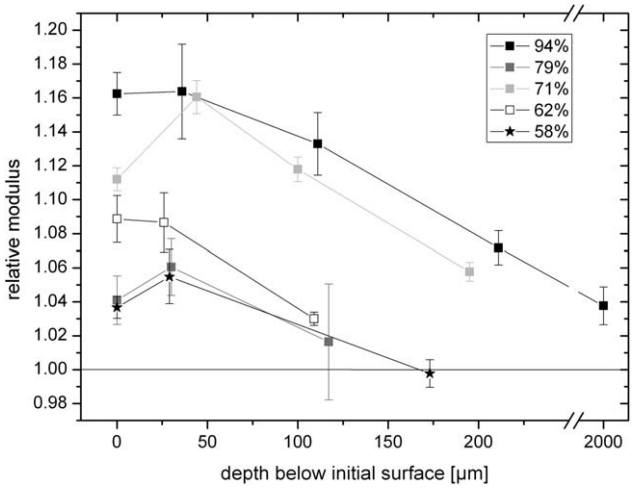

Figure 9. Relative moduli of partially and completely cured resin samples as function of depth below the initial, aged surface.

expectation, that chemical and hydro-thermal aging are negligible compared to physical aging. The latter is expected to increase surface density and modulus. For a similar TGMDA based epoxy resin system aged at ambient conditions an increase in surface modulus of about 12% is reported.[35] Also on long term aged commercial aerospace composite samples based on TGMDA a stiffening of the surface layer is detected.[36]

To investigate the impact of surface aging, the micromechanical moduli of the partially and the completely crosslinked epoxy resin samples are determined as function of the distance to the initial, aged surface. To this end a subsequent abrasion of the surface layer of the same sample and micromechanical analysis of the resulting surfaces is performed. As micromechanical testing by nanoindentation probes the surface properties of the sample up to a depth of a few micrometers, it is a very valuable tool for our investigation. Samples of the same curing degrees as above are aged for 270 days and thus are in their steady state. In Figure 9, the relative micromechanical moduli of the partially and completely cured samples, as defined above, are shown as function of the depth below the initial surface.

All samples show a decrease of relative moduli with increasing distance to the initial polymer surface. As the different curing degrees exhibit different aging behavior and thus different relative moduli after the aging period of 270 days, the starting values at zero depth differ. One can distinguish two different kinds of behaviors. One group of samples, namely the curing degrees 58%, 62 and 79%, starts with relative moduli between 1.02 and 1.1. With increasing distance to the initial sample surface these relative moduli first slightly increase up to a depth of about 30 µm. Then they gradually decrease and reach one at a depth between 150 and 200 µm. Here the polymer exhibits the modulus value of a fresh, unaged resin sample. Thus, in the bulk material no physical aging induced modulus changes are expected, which is in agreement with literature data.[36] The aging induced modulus increase is concentrated at a surface region of about 150 µm thickness.

The second group of samples; namely, the curing degrees 71 and 94%, start with higher relative moduli between 1.1 and 1.2. Again, with increasing distance to the initial surface the relative moduli slightly increase up to a depth of about 30 µm. With further increase of depth a decrease of the relative moduli is found. The strongest decrease occurs in a region of about 150 µm below the surface. However, the modulus values of these samples never reach one. For the completely cured resin sample even at a depth of 2 mm below the sample surface, i.e., in the bulk material, a slightly increased relative modulus of 1.04 is observed. It should be noted that the aging induced increase of the surface modulus with 16% is much higher than that of the bulk modulus with 4%.

The results clearly indicate a significant degree of surface aging of all partially and completely cured RTM6 resin samples, which is characterized by an increase of stiffness of the surface region. An increase of surface modulus between 6 and 16% is observed. As described above, this modulus increase probably is caused by a densification of the surface area due to volumetric physical aging processes. This is in good agreement with literature.[20,35,36] The increase of surface stiffness of partially and completely cured, aged RTM6 epoxy resin samples is highly relevant for all surface sensitive technical applications, e.g., joining of CFRP components or functionalization of polymer surfaces, and has to be considered for each specific processing route.

The physical aging induced increase of surface stiffness results in differences between bulk and surface material properties of all partially and completely cured RTM6 epoxy resin samples. This has to be considered comparing surface or bulk sensitive measurement. Density measurements average over the whole sample and, therefore, result in small aging induced changes due to the small densification of the center of the sample. In contrast, surface sensitive methods like nanoindentation detect a stronger ageing effect. The results explain the relatively small aging induced density increases and the high micromechanical modulus increases presented in the previous chapter. Since aging affects surface layers up to different depths for different partial curing degrees, a direct correlation of density and micromechanical modulus of aged samples is not possible.

CONCLUSION

Glassy epoxy resin systems are in a thermodynamic disequilibrium state and will experience material changes due to aging processes over an extended period of time. Knowledge of these aging induced changes of material properties is essential for technical applications of epoxy resins requiring long term stability, e.g., for structural CFRP airplane components. Also for partially cured epoxy resin parts, which constitute a promising route for production of CFRP components with high integration level, the influence of ageing processes is of high interest. To this objective the aging induced changes of curing degree, glass transition temperature, density, and micromechanical modulus of partially and completely cured RTM6 epoxy resin samples were investigated as function of aging period, initial curing degree or depth below the surface. Aging was performed at ambient conditions, minimizing effects of chemical and

hydro-thermal aging and emphasizing the influence of physical aging processes.

As expected for volumetric physical aging, density and modulus increase with increasing aging period. The relevant time scales are independent of the curing degree and amount to at least 150 days to reach a steady state. For all curing degrees a difference between bulk and surface aging is detected, which results in an increased surface modulus. As function of the initial curing degree the relative steady state modulus, which is a measure of the degree of aging induced modulus changes, exhibits a step-like decrease in the so-called transition region. For curing degrees directly below the transition region and for completely cured resin samples high physical aging effects are observed, which affect the whole sample. Here the resulting changes of material properties of up to 16% are substantial and have to be taken into account for technical applications, e.g., the storing of partially cured CFRP components. For low curing degrees and curing degrees directly above the transition region low physical aging induced changes are observed, which are restricted to a surface region with a thickness of about 150 µm. The role in technical applications is expected to be small.

The results demonstrate the importance of physical aging processes on the physical properties of partially and completely cured RTM6 epoxy resin samples and the high impact of the curing history on the effect of physical aging. A defined production of materials with low sensitivity to physical aging processes is possible and offers high potential for the development of new CFRP processing routes.

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