PHYSICAL PROPERTIES OF PARTIALLY CROSS-LINKED RTM6 EPOXY RESIN

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Abstract
Density and hardness of partially and completely cross-linked RTM6 epoxy resin samples in the glassy state were analyzed as function of curing degree and curing history. The density of the partially cured samples decreases with increasing curing degree and shows a discontinuity in the so called transition region, which is related to the transition from rubber to glassy state during cross-linking. In contrast, hardness values are not sensitive to this transition and only show marginal variations as function of curing degree. To investigate the influence of curing history, all partially cured samples are submitted to a second, final curing cycle to achieve complete cross-linking. A significant reduction of density of all finally cured samples is found.

1. Introduction

Tetra-functional epoxy resins are characterized by excellent material properties and are widely used in aerospace industry for production of advanced composite materials, primarily carbon fiber reinforced polymers (CFRP).[1,2] After infiltration of the dry fiber fabric, the thermosetting polymer is cross-linked in a thermal curing process. The reactivity of the completely cross-linked epoxy resin is very low. Partial cross-linking maintains a particular rest reactivity of the resin and opens new options for CFRP production. For example a joining of partially cured and fresh resin systems can be realized, which allows an increased level of integral construction of CFRP components.[3] A subsequent final curing cycle guarantees the complete cross-linking of the new component.

For a given chemical composition, the material properties of a cross-linked resin are determined in particular by the curing parameters, namely the curing temperatures, heating rates and curing durations.[4] During the curing process a chemical reaction between epoxy groups and reactive groups of the hardener takes place, which results in an increasing cross-linking density of the polymer and the subsequent transitions from liquid through rubber to glassy state.[5] Annealing of a glassy polymer at temperatures below its glass transition temperature, results in physical ageing processes due to structural relaxations.[6,7,8] Therefore, cross-linking density, molecular arrangement and physical state of the cured resin depend sensitively on the curing parameters. To consider variations of existing curing cycles, knowledge of the relation between basic material properties and the curing history of partially and completely cross-linked epoxy resins is of interest and subject to actual research activities.[4,8,9,10,11,12] In epoxy resins with functionality higher than two a three

dimensional network forms during curing. A decrease of density and modulus with increasing cross-linking of the polymer chains is observed in the glassy state (above the gelation point).[8,13] Generally, relaxation processes due to physical ageing of the glassy epoxy resin result in an increase of density, modulus and hardness.[6,7,14,15] For several amorphous polymers a linear correlation of modulus, glass transition temperature and hardness is found.[15,16]

In the actual work, the density and hardness of partially and completely cross-linked tetra-functional epoxy resin samples are investigated as function of curing degree and curing history. Of particular interest are initial curing degrees within the so called transition region, where an abrupt increase of density and modulus was found.[17] To investigate the influence of the curing history, the partially cross-linked samples are submitted to a second, final curing cycle to achieve complete cross-linking. Density and hardness of the finally cured samples are measured and compared to the values after single cure. To determine the hardness the micromechanical method of nanoindentation is used.

2. Experimental

1.1. Preparation of partially and completely cross-linked epoxy resin samples

All resin samples discussed in this work are manufactured of the mono-component epoxy resin system HexFlow ® RTM6 distributed by the Hexcel Corporation.[18] It is composed of the tetra-functional epoxy resin Tetraglycidyl Methylene Dianiline (TGMDA) and the hardeners 4,4'-Methylenebis(2,6-diethylaniline) (MDEA) and 4,4'-Methyylenebis(2-Isopropyl-6-methylaniline) (M-MIPA).
Modified curing cycles are used to obtain resin samples with defined partial curing degrees, 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 cross-linked sample with a curing degree of nearly 100% the resin is cured subsequently for 2.5 hours 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 an isothermal heat treatment at a reduced temperature of 135°C. The different curing degrees result from different durations of these isothermal heating cycles and are measured by differential scanning calorimetry.[17] For final curing, the partially cross-linked samples are submitted to a second curing cycle at 180°C for 2.5 hours. This second curing step transforms the partially cross-linked resin, e.g. with a curing degree of 60%, to a fully cross-linked resin further nominated as "60/100". Partially/finally cured samples with other initial curing degrees are named equivalently.

1.2. Micromechanical testing and density

Hardness of the partly and completely cross-linked epoxy resin samples was 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.[19,20,21]
The nanoindentation measurements were performed with a NanoTest 600 nanoindenter (Micromaterials Ltd.) and a Berkovich geometry indenter. The load controlled mode was used with loading and unloading rates of 2mN/sec. In all measurements a dwell time of 5sec 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, the unloading curve was fitted with a power law between $0.8 \cdot F_{max}$ and F_{max}. Average modulus values were obtained by investigation of several comparable resin regions. All average values are calculated from more than nine individual values. The measurements were performed on plane surfaces of the polymer samples, which were prepared by a grinding and polishing process of the fresh resin sample.
Density of the polymer samples of different curing degrees is measured with a helium pycnometer AccuPyc II 1340 (Micromeritics). For each curing degree and ageing period at least three resin samples were analyzed.

3. Experimental results and discussion

In the following the density and hardness values of partially and completely cross-linked RTM6 epoxy resin samples as function of curing degree are presented. Besides, the influence of a second, final curing cycle on the resin properties is investigated.

3.1. Density of partially and finally cross-linked epoxy resin

During cross-linking of thermosetting network polymers density changes occur, which are caused by different, partly opposing effects. First, the increase of the covalent bond fraction causes a densification of the polymer with conversion. Secondly, the more and more restricted packing of polymer chains due to network formation results in a decrease of density with increasing cross-linking degree.[8,10] Besides, curing of a glassy material at temperatures below the glass transition temperature results in physical ageing induced structural relaxation processes and a densification.[6,7,14] The density of the resulting glassy thermoset as function of curing degree is determined by the individual contributions of the described effects, which in turn are effected by the chemical structure of polymer and hardener and the processing conditions.
As shown in our previous work, the density values of partially cured RTM6 epoxy resin samples vary significantly as function of curing degree.[17]
During the isothermal curing treatment a transition from rubber to glassy state takes place. 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. Here, the 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 step-like increase of density in the transition region. The density of the partially and completely cross-linked resin samples as function of curing degree is shown in Figure 1. Also the transition region is indicated in the figure.

All partially cross-linked resin samples are submitted to a second, final curing cycle at a temperature of 180°C. As shown in our previous work, the final curing cycle results in further cross-linking of all resin samples and the correspondent increase of curing degree and glass transition temperature.[17] The density values of all partially/finally cured samples are included in Figure 1. It has to be noted that the density values of the partially/finally cured samples are shown as function of their initial curing degree. Therefore, they are positioned at

the same initial curing degree as the density values of the corresponding partially cured sample.

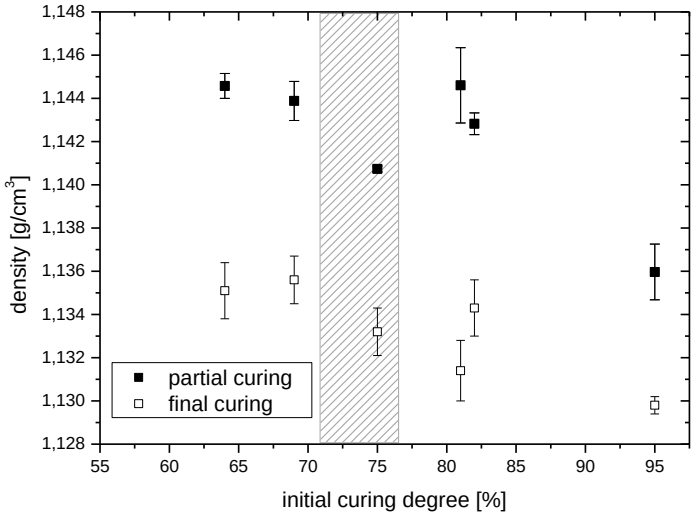

Figure 1. Density of partially and partially/finally cured epoxy resin samples as function of initial curing degree.

After final curing treatment, a decrease of density is observed for all partially/finally cured resin samples. The density values even are below that of the completely cured sample after single cure. The final heat treatment, performed at a curing temperature higher than the glass transition temperatures of the partially cross-linked samples, results in further cross-linking of the polymer and the correspondent reduction of density.[4,17] Independent from the initial partial curing degree a similar reduction of density is observed after final curing.
The step-like discontinuity observed for the partially cross-linked samples still is weakly observable for the partially/finally cured samples. This is in contrast to our correspondent modulus measurements after final cure, which show no discontinuity.[17]
For the partially/finally cured samples (64/100) and (69/100) a quite good agreement of the densities with that of the completely cured sample after single cure can be stated. This can be important for application of partially cross-linked epoxy resins, as the partial/final curing treatment guarantees densities similar to that of a conventional single curing step. Only small mismatch of material properties is expected for samples with different heating histories, e.g. for joining of partially/finally and fully cured resin regions.

For the completely cross-linked sample also a decrease of density is observed after the final curing treatment. However, the density reduction is smaller than that of the partially/finally cured samples. Here, two opposing effects occur. On the one hand, the increasing cross-linking of the polymer results in a reduction of density. On the other hand, an annealing treatment occurs, as the glass transition temperature of 209°C lies above the curing temperature of 180°C.[17] This heat treatment at $T_c<T_g$ results in physical ageing induced structural relaxation processes, which create an increase of density. The contributions of these two opposing effects result in the observed, smaller density reduction.
The decrease of density of the completely cured sample after final curing treatment is in contrast to our modulus measurements. The modulus of the finally cured (95/100) sample is clearly higher than that of the completely cured sample after single cure.[17] This missing direct correlation of density and modulus values can be caused by the different probing depths of the used methods. Density measurements average over the whole sample, and, therefore, result in bulk material properties. In contrast, the micromechanical testing by nanoindentation

is a strongly surface sensitive measurement. For the partially cured resin samples it has been shown, that no difference between micromechanical surface moduli and bulk sensitive macromechanical moduli exists. A very good agreement was found.[17] For the partially/finally cured resin samples no macromechanical testing was performed so far. Possibly an increased surface stiffness is created by the final heat treatment, which creates a deviation of surface modulus from the bulk density measurements.

3.2. Hardness of partially and finally cross-linked epoxy resin

Micromechanical hardness is closely connected to structural properties of glassy polymers. A direct correlation to the glass transition temperature and the packing density is described in literature. Also a relation to the modulus is reported.[15,16] For epoxy resins a qualitative agreement of micromechanical hardness and modulus is shown for photo-oxidation experiments.[22] Therefore, hardness measurements are a valuable tool for further investigation of structural changes of partially and completely cross-linked epoxy resin samples and should give complementary results to density and modulus measurements. In Figure 2 the hardness values of the partially and partially/finally cured resin samples are shown as function of curing degree. Also the transition region is marked.

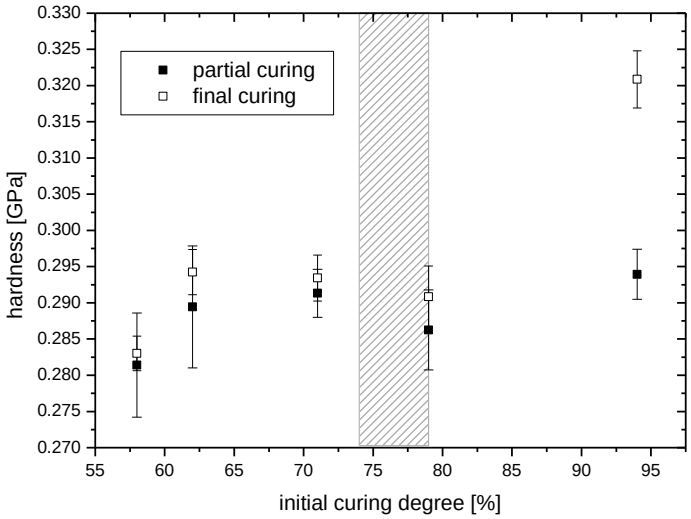

Figure 2. Hardness of partially and partially/finally cured epoxy resin samples as function of initial curing degree.

In contrast to the density values shown in Figure 1 and the modulus values presented in Ref.[17], no significant changes of hardness of the partially cured samples are observed as function of curing degree. In particular, no discontinuity is found in the transition region. No direct correlation of hardness to the already investigated quantities, namely density and modulus, can be stated. The reason of the missing correlation is not clear so far.
After final curing treatment, the partially/finally cured resin samples show a marginal increase of hardness. Here, also, a discrepancy to density and modulus results has to be stated, which both show a decrease after final curing. No significant variation of hardness of the partially/finally cured samples as function of initial curing degree is found. A good agreement of hardness of the (62/100) and (71/100) samples with that of the completely cured resin sample is found, which could be advantageous for applications of partially cured samples.

For the completely cured sample a clear increase of hardness is observed after final curing. The hardness of the (95/100) sample with 0.321GPa±0.0040GPa is about 9% higher than the hardness of the completely cured sample after single cure. This result is in agreement with micromechanical modulus measurements, where also a significant increase of modulus of about 8% is observed for the (95/100) sample.[17] However, the density values do not show a correspondent increase. Probably surface hardening effects during final heat treatment influence the surface sensitive hardness measurements, as already described for the modulus investigation.

3. Summary

Partial cross-linking of epoxy resins marks a promising way for new curing and processing routes for CFRP production. A particular chemical reactivity of the polymer is retained, which in a subsequent processing step can be used, e.g. for joining of CFRP parts. A second final curing step guarantees the complete cross-linking of the resin.
To develop specifically adapted curing cycles for different applications, knowledge of the relation between basic physical properties and the curing history is essential. With this objective the investigation of density and hardness of partially and finally cured RTM6 epoxy resin samples in the glassy state was performed. The density of the partially cured samples decreases with increasing curing degree and shows a discontinuity in the so called transition region, which is related to the transition from rubber to glassy state during cross-linking. Hardness values, in contrast, are not sensitive to this transition and show only minimal variations as function of curing degree.
After the second, final curing cycle a significant reduction of density of all partially/finally cured samples is found, which is created by the further cross-linking of the resin and the more restricted packing of the polymer chains. The density values are even smaller than that of the completely cured sample after single curing. Hardness values, in contrast, show a slight increase for all partially/finally samples. For the (95/100) sample even a strong increase of hardness is found. Possibly surface hardening effects are relevant for the finally cured samples, which affect the surface sensitive nanoindentation measurement and prevent a direct correlation of hardness and density results.
For some initial partial curing degrees a good agreement of density and hardness of the partially/finally cured samples and the completely cross-linked sample exists. This could be advantageous for different applications, e.g. the joining of partially cured and fresh resin parts, as the mismatch of material properties between the joined components is expected to be small.

The results demonstrate the impact of thermal history on basic physical properties of a tetra-functional epoxy resins system and the potential applications of partially cross-linked epoxy resin systems.

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