Effect of mixing sequence on the curing of amine-hardened epoxy/alumina nanocomposites as assessed by optical refractometry

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Abstract. High performance refractometry has been proven to be a useful tool to elucidate the isothermal curing process of nanocomposites. As a model system an amine-hardening epoxy filled with non-surface-treated alumina nanoparticles was selected. The tremendous resolution of this experimental technique is used to study morphological changes within nanocomposites via the refractive index. It is shown that these morphological changes are not simply due to the curing process but also depend on the sequence of mixing the nanoparticles either first into the resin or first into the hardener. Independent of the resin/hardener composition, the type of the mixing sequence discriminates systematically between two distinct refractive index curves produced by the curing process. The difference between the two refractive index curves increases monotonically with curing time, which underlines the importance of the initial molecular environment of the nanoparticles.

Keywords: nanocomposites, mixing sequence, optical properties, epoxies

1. Introduction

The interest in thermoset-based nanocomposites stems first of all from experimental evidences that due to chemical and/or physical interactions between the surfaces of the nanoparticles and the thermoset the physical properties of the composite are often more affected than predicted by a simple mixing rule applied to the properties of the related constituents [1–9]. It is supposed that the existence of specific interactions between the nanoparticles and the constituents of a thermoset will influence the curing process. Therefore the sequence of mixing the nanopowder first into the resin or first into the hardener may influence the physical properties of the final cured nanocomposite. The importance of this mixing sequence for the morphology and

consequently for the phenomenological properties of the molecular network is the main interest of this paper.

The thermoset chosen is an amine-hardening epoxy. As suitable nanoparticles we selected alumina powder produced by industry. As nanoparticles we denote here particles with lateral dimensions smaller than 1 μm (see below). Because of the technical importance an almost stoichiometric resin/hardener composition was chosen as model thermoset. In order to deepen the physical understanding of the role of the mixing sequence several under-stoichiometric compositions are investigated.

Because of its tremendous resolution high performance optical refractometry is chosen as a rather

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unconventional experimental technique to study temporal evolutions of structure-property relations during the isothermal curing process of epoxy-based nanocomposites as a function of the mixing sequence. The experimental data will be discussed on the base of the Lorentz-Lorenz relation.

2. Experimental

2.1. The constituents

In order to investigate the influence of the mixing sequence on the refractive index properties of epoxy-based nanocomposites the following three constituents were chosen:

- i. as a hardener (*H*) we selected diethylene tri-amine (DETA) (epoxy equivalent weight: 20.64 g/eq) from Fluka Chemie GmbH, Buchs, Switzerland. The DETA molecules possess three reactive amine groups. The refractive index was determined to be $n_D^{298\text{ K}} = 1.4846 \pm 10^{-4}$.
- ii. as resin (*R*) diglycidyl ether of bisphenol A (DGEBA) DER 331 (epoxy equivalent weight: 182–192 g/eq) from DOW Europe GmbH, Stade, Germany was chosen. This resin contains a small amount of dimers and trimers in order to hinder the crystallization of the DGEBA monomers, although even monodisperse DGEBA (melting temperature $T_m = 315\text{ K}$) can easily be supercooled. The refractive index was measured to be $n_D^{298\text{ K}} = 1.5712 \pm 2 \cdot 10^{-4}$.
- iii. as nanoparticles (*N*) alumina Aerioxide® Alu C from Evonik industries AG, Hanau, Germany was selected. These alumina nanoparticles were chosen because they are not surface-treated and they yield improved mechanical properties in epoxy nanocomposites [1]. Finally these nanoparticles are available in sufficient quantities. The primary particles have an average diameter of 13 nm and agglomerate in clusters with diameters below 300 nm (as determined by dynamic light scattering). The refractive index of the nanoparticles was estimated from crystal data [10] to 1.76 at 298 K. As for all stiff crystalline materials, away from structural phase transitions, the refractive index of the alumina particles changes little with temperature and pressure. We suppose that the surfaces of the

alumina nanoparticles are contaminated at least with water.

2.2. Samples and sample preparation

The choice of the sample compositions was made on the base of the following four arguments:

- i. the influence of the mixing sequence on technically relevant compositions. From the stoichiometric point of view the best choice would be a resin/hardener mass ratio of about *R/H* (100/11). The present study is based mainly on the slightly over-stoichiometric *R/H* (100/14) system, which shows the biggest tensile shear strength during fracture experiments performed on different epoxy mixtures glued on native aluminium [11]. This composition is known to undergo a chemical glass transition at ambient temperature which restricts the chemical conversion of DGEBA's oxirane rings as measured by infrared spectroscopy to about 70%.
- ii. After a curing time of more than two hours, the epoxy *R/H* (100/14) adheres perfectly on the prism of the refractometer. In order to avoid destruction of the refractometer, the curing behaviour of epoxy *R/H* (100/14) can be followed only during this chemical reaction time.
- iii. In order to overcome the shortcomings of ii. and to get insight in the influence of the mixing sequence on the final properties of adhesives (in the sense that all possible chemical reactions have taken place) the following under-stoichiometric sample compositions were selected: *R/H* (100/7), (100/3), (100/2) and (100/1).
- iv. Pre-investigations have shown that at maximum a mass ratio of hardener/nanoparticles *H/N* (2/1) is possible. To make the effect of the nanoparticles as visible as possible concerning the mixing sequence for a given *R/H* composition, the amount of nanoparticles for the selected *R/H* compositions was chosen to be always maximal with respect to the amount of hardener (i.e. *H/N* (2/1)).

To definitely avoid DGEBA monomer crystals the resin is heated for 15 minutes above the melting temperature $T_m = 315\text{ K}$ [12] and then cooled to ambient temperature. The whole preparation takes place under normal room temperature and atmosphere conditions. The realisation of different mix-

ing sequences is achieved by stirring the alumina nanoparticles by hand for five minutes alternatively into the resin ($\rightarrow (R/N)$) or into the hardener ($\rightarrow (H/N)$) yielding the primary suspension. The lacking hardener respectively resin is mixed subsequently by hand for five minutes into this suspension. Typical sample masses amount to 6 to 8 grams. The time of adding the resin or the hardener to the primary suspension is always taken as the start of the chemical crosslinking. The crosslinking is performed isothermally at 298 K.

2.3. Experimental technique

2.3.1. Theoretical background

In this work high performance optical refractometry is used as a sensitive tool to probe the refractive index of isotropic materials at a wavelength of 589 nm. Based on the mean field theory developed by Clausius-Mosotti and Lorentz-Lorenz [13–16], the Lorentz-Lorenz equation (1) relates for non-interacting molecular systems the refractive index n_D to the mass density ρ :

$$\frac{n_D^2 - 1}{n_D^2 + 2} = r \cdot \rho \quad (1)$$

The specific refractivity r is defined by Equation (2):

$$r = \frac{N_A \alpha}{M_w 3\epsilon_0} \quad (2)$$

where N_A is the Avogadro number, M_w the molecular mass, ϵ_0 the vacuum permittivity and α the locally averaged molecular polarisability. At the related frequencies ($\sim 5 \cdot 10^{14}$ Hz) the molecular polarisability is purely electronic in origin. Considering non-interacting small molecules the specific refractivity appears as a constant. In this case the mass density ρ is directly proportional to the refractive index n_D , thus coupling optical properties to the packing of molecules. Equation (2) becomes meaningless for fully cured polymer networks since N_A and M_w are badly defined quantities. Therefore the proportionality discussed above is no more expected for thermosets.

Astonishingly, the Lorentz-Lorenz relation has been experimentally verified to be applicable to many classes of materials under different thermo-

dynamic conditions, including isothermal curing of adhesives [17, 18]. In other words, the specific refractivity remains almost constant even in the case of molecular network formation in polymers. In this case the polarisability α is understood as a locally averaged quantity. ‘Local’ means in this context small in comparison to the wavelength of light, but large enough to get rid of the tensor properties of the molecular segments of polymers. As a result within the mean field approximation changes of the refractive index reflect variations of the molecular morphology either by changes of density or by small changes of the specific refractivity. From this discussion it is clear that optical refractometry gives no information on the discrete microscopic molecular structure but only on the average morphological properties in so far as they affect the optical polarisability or density. In this sense the refractive index is a highly sensitive tool to detect variations of the average molecular architecture [15, 16].

Beside the mean field approximation a spatial averaging takes place on the prism of the refractometer. For our instrument, the refractive indices are averaged over sample volumes of about $(5 \times 5 \times 0.5 \cdot 10^{-3})$ mm³. Moreover, because of the high probe frequencies (10^{14} – 10^{15} Hz) optical refractometry is not affected by relaxation processes which often hide information about quasi-static properties of the studied material while using experimental techniques with lower probe frequencies.

2.3.2. The refractometer

A modified high performance refractometer (Abbe-mat) from Anton Paar OptoTec, Seelze, Germany is used to investigate the refractive index of epoxy/alumina nanocomposites. A light source with a wavelength of 589 nm is used (sodium D line). The modification of the refractometer consists in a better temperature stabilisation of its detection system, the electronics and the sample. The resolution of the Abbe-mat is about 10^{-6} , the absolute accuracy about 10^{-5} . The curing measurements are performed at (298 ± 0.01) K. Data recording is performed under the control of a LabView software developed to control and to record all relevant system parameters in the course of the isothermal measurements.

Figure 1. Isothermal temporal evolution at 298 K of the refractive index of the hardener (black curve), the alumina filled hardener H/N (2/1) (red curve) and the alumina filled resin R/N (4/1) (blue curve). The filled samples are measured after freshly stirring them.

3. Results and discussion

The basis for the current work is the expectation that there exist different interactions between the alumina nanoparticles and the hardener on one hand, and between the nanoparticles and the resin on the other. These differences are evidenced in Figure 1 by refractive index measurements performed on the primary suspensions H/N (2/1) and R/N (4/1). The mass concentrations (2/1) and (4/1) correspond to the composition related maximum concentration of alumina nanoparticles. During the preparation of the primary suspensions H/N (2/1) significant thixotropy is observed, which is not noticed in case of the filled resin R/N (4/1). This thixotropy of the nanoparticle filled hardener is synonymous to an increased viscosity of this sample after temporal relaxation of the material. This increase of the shear viscosity could be accompanied by a densification. According to Figure 1 the refractive index of the nanoparticle filled hardener relaxes during more than 14 hours after the mixing (order of magnitude: 10^{-2}), whereas the refractive index variation of the pure hardener is insignificant. Using Equation (1) this refractive index increase corresponds to a mass densification of about 1% for the nanoparticle filled hardener. The temporal refractive index changes of the filled resin are also completely negligible in comparison to that of the filled hardener. This confirms distinct interaction forces between the resin and the hardener molecules with the nanoparticles' surfaces.

As the hardener and the resin behave differently in presence of the nanoparticles, the question arises whether these different interaction forces play still a significant role while adding the missing reactant necessary to start the curing. Considering the starting conditions (different attraction forces between nanoparticles and the resin respectively the hardener, strong mixing of the missing reactant with the primary suspensions) leads us to the following hypotheses:

- no differences in the refractive indices during the whole curing process,
- differences in the refractive indices at the beginning which are removed from the material in the course of curing or,
- differences in the refractive indices at the beginning which are partly maintained after curing.

At first, the curing behaviour of the nanocomposites based on the slightly over-stoichiometric epoxy R/H (100/14) is studied. A reliable interpretation of refractive index data needs a precise idea of the influence of errors performed during the sample preparation on the repeat accuracy. Therefore the pure over-stoichiometric epoxy R/H (100/14) and the nanocomposites based on the filled resin $R/N/H$ (100/7/14) respectively on the filled hardener $H/N/R$ (14/7/100) (mass ratios) are prepared independently at least three times and investigated as long as they are not too sticky. For the sake of clarity, only two curves are shown in Figure 2 for each type of sample. According to this figure the repeating accuracy (see grey curves) is convincing for

Figure 2. Temporal evolution of the refractive indices for R/H (100/14), for $R/N/H$ (100/7/14) and $H/N/R$ (14/7/100) during the curing at 298 K. For each kind of epoxy two measured curves are shown (the grey curves indicate the repeat accuracy).

each mixing sequence. Taking into account the high resolution of the refractometer the shift in the absolute refractive index values of the three groups of curves is reliable.

Considering the high refractive index of the alumina nanoparticles ($n_D = 1.76$) and assuming a simple mixing rule between the resin's, the hardener's and the nanoparticles' refractive indices, it seems reasonable that the nanocomposites show higher values than the pure epoxy during curing. Remarkably, during the whole time of the experiments remains a refractive index difference of $\Delta n_D \sim 10^{-3}$ for the two nanocomposites having the same composition. The fact that Δn_D exists at the start confirms the important role of the initial distribution of the three constituents. Within the measured time interval the three types of curves are shifted vertically against each other, but the time evolution is similar. The latter result confirms that the time evolution of the refractive indices stems from the curing of the epoxy. However, the observed time interval of curing is too short to extrapolate to the final state of isothermal curing.

Preliminary transmission electron microscope (TEM) measurements show that the nanoparticles in *H/N/R*-samples are more clustered than in *R/N/H*-samples. It should be stressed that TEM measurements do not distinguish between compact alumina aggregates and agglomerates of alumina particles glued together by a thin epoxy layer. Clouds of alumina particles covered with epoxy would behave optically more similar to a well-dispersed nanocomposite than to compact alumina clusters.

In order to test the influence of the cluster size of nanoparticles on the refractive index we have compared the refractive index of an alumina filled DGEBA DER 331 resin prepared by a mechanical dispersion technique (mean alumina cluster size: below 50 nm) [1] to that of hand-mixed alumina filled resin (mean alumina cluster size: below 300 nm). Astonishingly, both preparation techniques lead to samples showing within the margin of error the same refractive indices. The same agreement is found during the curing of such differently prepared composites by adding the same amount of hardener. Taking into account the high sensitivity of our refractometer this unexpected result seems to be due to a rather small dependence of the refractive index on the size of the alumina

clusters, provided the total amount of nanoparticles remains constant. We therefore conclude that the observed changes in the refractive indices (related to the mixing sequence) are due to morphological changes in the polymer rather than to different cluster sizes of the alumina particles.

Without destroying the refractometer we have no access to the refractive indices in the further course of curing of the adhesives presented in Figure 2. In other words, the nanocomposites get really sticky during room temperature curing and even undergo glass transitions. The interesting information about the evolution of the refractive indices for different mixing sequences in the full course of curing up to the depletion of all amine groups can be obtained only for significantly under-stoichiometric compositions.

Four types of nanocomposites with different (under-stoichiometric) *R/H*-compositions, varying between (100/1) and (100/7) are investigated (see Figure 3). The almost horizontal time evolution of the refractive index after 10 h for the nanocomposites with the *R/H*-composition of (100/1) and (100/2) shows that the whole chemical crosslinking can be studied for these materials.

Applying a simple linear mixing rule to the refractive indices of the three constituents, the initial refractive indices of the nanocomposites (at $t = 0$ h) were estimated. Astonishingly, the estimated values are in agreement with the measured data within 1%.

Figure 3. Influence of the mixing sequence (red or black lines) on the time evolution of the refractive index during the curing at 298 K of four kinds of nanocomposites: mass ratios for the constituents of samples (1): *R/N/H* (100/0.5/1); (2): *R/N/H* (100/1/2); (3): *R/N/H* (100/1.5/3) and (7): *R/N/H* (100/3.5/7).

The time evolution of the refractive indices shown in Figure 3 is in line with the results given in Figure 2: The refractive indices of the *R/N/H*-samples exceed those of the *H/N/R*-samples, even after long curing times when the chemical reaction has almost stopped due to the depletion of the amine groups. As a result, for a given hardener concentration the spread between corresponding curves increases with time. This contradicts the aforementioned hypotheses i. to iii.

Decreasing the hardener concentration, a decreasing spread is observed for a given curing time as also less nanoparticles are present. From our point of view it is really astonishing that even for the nanocomposites (100/0.5/1) and (1/0.5/100) a significant Δn_D is preserved in the long time limit. Consequently, as a function of curing time *R/N/H*- and *H/N/R*-samples do not develop the same morphology although they have the same global composition. The differences in the morphology between both kinds of mixing sequences tend to increase with curing time. As already mentioned, these differences stem from the polymer and not from the nanoparticles nor from the cluster sizes, but both take of course influence on the morphology of the polymer.

At least in principle the observed differences in molecular morphology evolution may be attributed to different curing rates. However, it is hard to understand why these hypothetical differences in reaction rate (as deduced from the refractive index) should be the largest in the almost finished curing regime. For the *R/N/H* (100/0.5/1) and *H/N/R* (1/0.5/100) samples the horizontal shift at the end of both curves would exceed eight hours as indicated by the blue dashed line. If a hindering of the chemical reactions can be excluded, it is likely that the constituting sequence is decisive for the related molecular morphologies in the course of the whole curing process. Accordingly the different morphologies are not temporary in nature but permanent.

The above discussed influence of the mixing sequence on the optical properties of epoxy/alumina nanocomposites has recently been observed also for a two component silicone rubber filled with alumina nanoparticles. The effect of the mixing sequence on the refractive index turns out to be even more pronounced.

4. Conclusions

High performance refractive index experiments have been performed during the isothermal curing of epoxy/alumina nanocomposites in order to investigate the role of the mixing sequence of the constituents. The results clearly show that the constituting sequence of DGEBA, DETA and alumina nanoparticles has an impact on the optical properties of the composites. As the optical polarisability of the nanoparticles is not expected to change during the curing process, the different temporal behaviour of the refractive index for several mixing sequences is indicative for different morphological evolutions in the course of curing.

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