Acoustic profilometry of interphases in epoxy due to segregation and diffusion using Brillouin microscopy

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Abstract. Reactive network forming polymer systems like epoxies are of huge technological interest because of their adhesive properties based on specific interactions with a large variety of materials. These specific interactions alter the morphology of the epoxy within areas determined by the correlation length of these interactions. The changed morphology leads to interphases with altered (mechanical) properties. Besides these surface-induced interphases, bulk interphases do occur due to segregation, crystallization, diffusion, etc. A new experimental technique to characterize such mechanical interphases is µ-Brillouin spectroscopy (µ-BS). With µ-BS, we studied interphases and their formation in epoxies due to segregation of the constituent components and due to selective diffusion of one component. In the latter case, we will demonstrate the influence of changing the boundary conditions of the diffusion process on the shape of the interphase.

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1. Introduction

Reactive polymers like epoxies are widely used to bond different kinds of materials together. In their initial mixed state, epoxies consist of a two-component liquid composed of a resin and a hardener. Depending on chemical composition of the hardener, the curing temperature and the mixing ratio of the resin and the hardener, the final cured state is either visco-elastic or glassy [1, 2]. The transformation from the initial liquid to the final polymer network is a complicated non-equilibrium process which may be accompanied by processes competing with homogeneous polymerization [3–5].

Among such competing processes (not in every case) are e.g. segregation, convection, heat fluxes, (rarely) crystallization of one chemical component or specific reactions between reactants and substrates. These processes result in morphological heterogeneities which depend on the curing time [6–8]. If the heterogeneous epoxy is divided into a rather homogeneous reference material and some regions deviating in their morphology from this reference state, the structurally deviating regions may be called interphases [9–12]. It is evident that such interphases may have an important impact on the average physical properties of the adhesive; this holds true especially for their mechanical properties. The existence of such interphases within the volume of epoxies was reported some time ago [9], but a lot of progress was achieved just recently [13–15]. Another type of interphase is created at the interface between a substrate and an epoxy. The chemical interaction between the adhesive and the substrate modifies the morphology of the adhesives in a thin layer close to the substrate [10]. The thicknesses of such chemical interphases are expected to be in the nanometre range. It was therefore exciting when interphases of about 100 µm thickness built up at the surfaces of different metal substrates were reported [14, 15]. These interphases were significantly altered in their mechanical properties compared to the related bulk properties and were therefore called mechanical interphases. It has been argued that these mechanical interphases could originate from mechanical stresses built up at the epoxy/metal interface due to the curing process [15].

The aim of the current paper is to demonstrate and to discuss the formation of interphases in epoxies different from those introduced above. Molecular segregation and diffusion through a boundary of the epoxy during the curing process are further important causes for the development of interphases and will be at the center of interest of this paper. The measurements are made with the recently developed technique of Brillouin microscopy (µ-Brillouin spectroscopy (µ-BS)) [16]. As a model substrate a non-adherent silicone rubber (‘Silgel 604’ from Wacker Silicone) is used.
2. Experimental details

The epoxy system investigated is composed of a resin diglycidylether of bisphenol A (DGEBA) and a hardener diethylene triamine (DETA) with a ratio of 100:14 mass parts. This reactive system is stirred at 55°C for 4 min in dry air and subsequently cooled down to ambient temperature. In order to obtain epoxy samples adequate for investigations of interphases by µ-BS, the epoxy is cured in different casting moulds (figures 1(a) and (b)) at 23°C for 48 h yielding samples with surfaces of optical quality. This curing procedure leads to an average chemical conversion of about 70% of the reactive groups (oxirane rings) of DGEBA in the undisturbed bulk. To achieve a chemical conversion of 100%, a post-curing step of 1 h at 120°C is necessary.

The casting moulds are made of Elastosil 604 from Wacker Silicone. The short name for this material is Silgel. Silgel is a completely transparent soft solid that does not adhere to other materials. Bringing Silgel in contact with pure DETA, Silgel swells and becomes opaque. This signifies that because of its large free volume Silgel can store a rather large amount of solvents like DETA. In contrast, the resin DGEBA does not swell Silgel. Consequently, Silgel provides a selective permeability for the resin and hardener. In order to modify the storage and transport properties of DETA in Silgel, casting moulds of different dimensions and wall thicknesses were prepared.

All measurements are performed by µ-BS, which allows for direct, contactless and non-destructive access to elastic interphases [16]. The spatial resolution is close to 1 µm. The spectrometer is a high-performance Sandercock Tandem Fabry–Pérot interferometer. We used the 90A scattering geometry as shown in figure 2. The shifting of the observed scattering volume is achieved either by shifting the whole sample, which changes the beam path of the laser inside the sample, or by rotating a glass plate that produces a parallel offset and shifts the scattering volume along a given beam path. The scattering volume has a lateral size of less than 30 µm. In 90A scattering geometry, the relationship between the measured phonon frequency and the...
longitudinal sound velocity is
\[ v = \frac{f^{90A} \cdot \lambda_0}{\sqrt{2}}, \]
where \( \lambda_0 = 532 \text{ nm} \) is the vacuum laser wavelength and \( f^{90A} \) is the frequency of the longitudinal phonon. Note that in 90A scattering geometry, this calculation does not depend on the refractive index \( n \) of the sample [17]. Since the local mass density of the sample is not known, only the sound velocities are given.

3. Results and discussion

One possibility for forming mechanical interphases in epoxies is by segregation of DETA in the epoxy bulk during the early stage of curing [18, 19]. In that case, the spatial distribution of DETA is altered, leading to concentration-dependent mechanical properties of the epoxy. Another possibility which yields mechanical interphases is based on the creation of concentration profiles in the epoxy due to diffusion of DETA across the epoxy/Silgel interface. In this latter case, DETA is removed from the epoxy and stored in the Silgel. The first and the second processes are not independent of each other since the state of demixing will influence the diffusion properties of DETA. The final spatial concentration distribution of DETA in the epoxy will determine the spatial dependence of the elastic properties within the epoxy sample: the lower the DETA concentration, the lower the resulting sound velocity. An excess of DETA, compared to the initial mixing ratio of 100:14, increases the sound velocity at least up to a mixing ratio of 100:18 [19].

In order to study the segregation properties of DETA in the bulk epoxy, a glass cuvette was filled with a freshly prepared DGEBA/DETA mixture. At the beginning, the material is
translucent; only some air bubbles, caused by the stirring of the sample, try to escape through the meniscus of the sample. After a short time of some minutes, new bubbles are formed preferentially at the bottom of the cuvette. These new bubbles rise in the upright standing cuvette and enrich in the upper part of the cuvette. It is likely that some of the bubbles escape across the meniscus of the sample. The process of formation and diffusion of these bubbles slows down with increasing curing time and stops at the end of curing, when the system undergoes a chemical glass transition. The final situation after curing at 23°C is shown in figure 3. In this figure, the epoxy-filled cuvette is in a lying position and the sample is illuminated by a laser beam ($\lambda = 532$ nm) penetrating the sample from the right through the bottom of the glass cuvette. The laser beam illuminates an ensemble of statistically distributed objects looking like bubbles. Obviously, these objects are not air bubbles; if they were air bubbles, the laser light would be much more scattered and reflected and would not, as it does, exit at the meniscus of the sample. It has been shown by means of $\mu$-Raman spectroscopy that the initially formed bubbles consist mainly of DETA [18]. These DETA bubbles ascend due to the fact that DETA has a lower mass density ($\rho = 0.95$ g cm$^{-3}$) than DGEBA ($\rho = 1.16$ g cm$^{-3}$). In order to study the mechanical nature of these ‘bubbles’, we have performed $\mu$-BS along the path of the laser beam within the cured epoxy.

Figure 4 shows the longitudinal sound velocity $v_L$ as measured by $\mu$-BS. In the course of these measurements, the scattering volume has been shifted according to figure 3 along the penetrating laser beam by moving the cuvette using a motor-driven translation stage. The measurements were made with a fully automated Brillouin spectrometer, which controlled all parameters including the position of the scattering volume. For time reasons, not the whole path was scanned but only a number of regions distributed along the path. In each region a scan with step width of slightly less than 20 $\mu$m was performed. As shown in figure 4, the average sound velocity increases slightly from the bottom of the cuvette to the top of the epoxy sample, suggesting an increased DETA concentration at the top of the sample compared to the bottom. Besides a slightly increased data scatter (about $\pm1\%$) there are no further indications of the apparent bubbles within the sample.

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This result is interpreted by initially formed DETA bubbles due to segregation of DETA at ambient temperature. Then, the slow diffusion of these bubbles to the top of the sample implies a net flow of DETA to the top of the cuvette and thus an increase of DETA concentration in that part of the cuvette. Since the segregation tendency competes with the curing process and since the DETA bubbles can hardly escape from the sample, DGEBA molecules diffuse into the bubbles and the curing takes place also in these parts of the sample. At the end of the curing process, the epoxy sample has become almost homogeneous. This is exactly what the $\mu$-BS data display: the slightly increased scatter of the elastic data reflects small deviations from the average sound velocity of the undisturbed bulk material. This explains also the rather small elastic laser light scattering. As a result, the optically evident bubbles are reminiscent of the DETA segregation in the early stage of the curing process.

Whether additional mechanical interphases exist in the vicinity of the glass windows has not been studied. Because of interphases found in epoxies cured between glass slides it is likely that such interphases also exist within the epoxy near the cuvette walls. Because of the roughness of the meniscus, the mechanical interphase at the sample boundary with air could not be studied.

The second objective of this work is to study the influence of an interface with selective permeability between the sample and the sample holder (cuvette) on the formation of interphases during the curing process. As a suitable material, the silicone rubber Silgel is used. Taking into account that pure DETA swells Silgel on the one hand and that DETA tends to demix at least in the initial states of the curing process, diffusion of DETA across the epoxy/Silgel interface is expected provided the difference of chemical potentials of all chemical partners is in favor of this phase separation.

For a first measurement, an epoxy sample of dimensions $10 \times 10 \times 0.6$ mm$^3$ was prepared in a flat-lying casting mould according to figure 1(a). Having cured this sample at ambient temperature for more than 20 h and subsequently post-cured at $120^\circ$C for 1 h, $\mu$-BS was performed on the sample. For this purpose, the scattering volume was shifted across the thickness of the sample from one surface to the other (bottom to top) according to figure 2. The result of this investigation is shown in figure 5. The hypersonic velocity strongly depends on the position of the scattering volume between the top and bottom surfaces of the sample. The
Figure 5. Sound velocity profile of a 600 µm thick epoxy plate, having been prepared in a flat-lying Silgel cuvette according to figure 1(a). Wall thickness of the cuvette was about 1 mm.

sound velocity as a function of the spatial coordinate is W-shaped and asymmetric with respect to the center plane parallel to the large surfaces of the sample. The asymmetry is attributed to some loss of DETA through the Silgel lid closing the top of the casting mould. Consequently, the sound velocity is found to be larger at the bottom of the sample where the average DETA concentration was probably greater during the curing process compared to the top of the mould. As epoxy does not adhere to Silgel, mechanical stresses cannot be involved in the formation of this sound velocity profile.

The W-shaped sound velocity profile in figure 5 is explained as follows (figure 6): after filling the casting mould with the fresh and fluid epoxy sample, DETA diffuses across the Silgel interface and is stored within the Silgel. A concentration gradient with a maximum of DETA in the middle of the sample is established (figure 6(a)). Simultaneously, the curing process proceeds and diminishes the concentration of DETA in the epoxy. At this stage of the curing process, the spatial sound velocity distribution is expected to mirror the more \( \Lambda \)-like profile of the DETA concentration having its maximum in the middle of the sample. At some point in time the DETA concentration within the Silgel interface exceeds that within the adjacent epoxy. As a consequence, DETA flows back through the Silgel/epoxy interface into the epoxy and permits in the near-interface regions a further formation of network links within the epoxy, which in turn explains the increase of the sound velocity close to the interfaces of the epoxy sample. The diffusion of DETA back into the epoxy is of course hindered by the epoxy network which has formed in the meantime, so that the maximum diffusion length is reduced.

The plateau in figure 5 corresponds quite well to the sound velocity of the undisturbed bulk of a post-cured sample. Accordingly, a regime of about 200 µm adjacent to each interface has to be called an interphase, as the properties are altered compared to the bulk. But attention should be paid to the fact that even in the plateau region some DETA could have disappeared. As the post-curing leads to the greatest possible chemical conversion, it is evident that even at the minima \( (v = 2935 \text{ m s}^{-1}) \) there is more DETA than is necessary to achieve the bulk sound velocity for curing at ambient temperature \( (v = 2845 \text{ m s}^{-1}) \) but lower than 100:14. However,
Figure 6. Schematic drawing of the influence of the diffusion processes and the chemical reactions on the concentration of DETA at the beginning (a) and at a later point in time (b) of the cross-linking reaction.

the sound velocity value of 3022 m s\(^{-1}\) at the bottom of the sample indicates that here the DETA concentration is even increased compared to the bulk mixing ratio, which in turn leads to a stiffening of the network.

It is worth noting that the final interphase profile strongly depends on geometrical factors of the Silgel cuvette including its wall thickness. It is of great importance that the volume of the Silgel defines the storage capacity for DETA, whereas the spatial distribution of the Silgel cuvette with respect to the geometry of the epoxy sample determines the time constant in order to equilibrate the DETA concentration.

Figure 7 shows the \(\mu\)-BS measurements across (the thickness of) a much thicker epoxy sample prepared in an upright-standing Silgel cuvette with three times thicker walls. This sample has only undergone curing at ambient temperature. As a matter of fact the large asymmetry between the sound velocities at the two interfaces has disappeared, which can be attributed to the fact that the cuvette was standing upright. In addition, the \(W\)-shaped sound velocity profile is much less pronounced, but the distance of the minima from the interfaces of up to 1 mm is much longer. The shallow minima can be explained in two ways. Firstly, the curing at ambient temperature stops at the occurrence of the chemical glass transition which depends again on the DETA concentration and so do the resulting sound velocities. But as long as there is enough DETA to reach the chemical glass transition the differences in the sound velocity are not enormous. The post-curing would lead to bigger differences as it maximizes...
the cross-linking potential. Secondly, the larger wall thickness of the Silgel cuvette smoothes the concentration profile due to its bigger storage capacity and the longer diffusion distances. In any case the positive deviation of the sound velocity at the interfaces signifies a slightly higher DETA concentration than 100:13, since the plateau fits the nominal bulk sound velocity of $v = 2845$ m s$^{-1}$. A DGEBA:DETA ratio of 100:18 leads to a sound velocity increase of about 1.3% compared to 100:14 after curing at ambient temperature for 72 h. Consequently, the DETA enrichment at the interfaces of this sample seems to reach roughly 100:18, which means an increase of up to 29%.

In other words, the polymerization of the epoxy is too fast in comparison to the back-diffusion of DETA. In favor of this argument is also the fact that the maxima of the W-like sound velocity profile is slightly distant from the interfaces of the sample.

The $\mu$-BS measurements discussed so far were made after having cured the samples. At this time, we were not sure whether this technique would be able to resolve the evolution of the sound velocity as a function of time and, simultaneously, as a function of the space coordinate. Such a measurement suffers particularly from the defect that every recording of the Brillouin spectrum needs at least about 2 min. During the recording of the spectrum, the curing process proceeds. In order to record the spatial profile almost simultaneously, only a few different spatial positions can be analyzed at the ‘same’ time. Figure 8 shows the temporal and spatial evolution of the sound velocity of an epoxy sample during the curing process at ambient temperature. The sound velocity measurements were performed at $d = 0$, 200 and 400 $\mu$m from one of the two interfaces. It turns out that the evolution of sound velocity is fastest at a distance of 400 $\mu$m and slowest at a distance of 200 $\mu$m. The interface itself ($d = 0$ $\mu$m) takes an intermediate position. Taking into account that the start of the $\mu$-BS measurement is delayed by at least 20 min in comparison to the preparation of the sample, the sound velocity curves are probably indicative of a state where DETA has already been stored in the Silgel and is flowing back to the epoxy. Extended measurements are under way.
Figure 8. Temporal development of the sound velocity during the cross-linking reaction of epoxy in a Silgel cuvette, measured at three distances $d$ to the Silgel–epoxy interface. (A 1 mm thick epoxy plate, cured standing in a Silgel cuvette, was used.) The wall thickness of the cuvette was about 2 mm.

4. Conclusion

Space and time-resolving Brillouin measurements have been performed on epoxy samples. It has been shown that segregation as well as transport by diffusion through the sample boundary during the curing process can produce extended and pronounced mechanical interphases. These interphases can be resolved by a new $\mu$-Brillouin technique. The combination of time and space-resolving BS is even able to resolve the temporal evolution of the spatial profile of mechanical interphases.

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