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Effect of dwell stage in the cure cycle on toughening of epoxy using thermoplastic multilayers

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Abstract:

A second micro-phase (i.e. thermoplastic) can be added to epoxies to overcome their intrinsic brittleness. This addition of thermoplastics to epoxy resin results in reaction-induced phase separating morphologies in the micrometer range. In this paper, the influence of a two-dwell cure cycle on interphase formation, by hot stage microscopy experiments and final morphology, by scanning electron microscopy, of a poly(ether imide) (PEI) and high Tg epoxy system was investigated. The parameters changed in the cure cycle were the first dwell temperatures and first dwell times (up to the onset of phase separation (OPS) or up to the 80% degree of cure (80% DOC)). Especially at lower first dwell temperatures, the diffusion distance was higher in the OPS case compared to the 80% DOC case. This behavior was ascribed to the fact that, in the case of OPS, the epoxy polymer oligomers were still mobile and could diffuse further during the second dwell, while at 80% DOC, the epoxy cross-linked network was already bound but could still diffuse due to non-stoichiometric curing. The restricted mobility of the polymer chains for the 80% DOC case resulted in a larger part of a finer phase separated morphology, compared to the OPS case.

Keywords: Epoxy; Poly(ether imide) (PEI); Interphase formation; Curing cycle; Reaction induced phase separation

1. Introduction

Epoxies (EP) with high cross-linking densities are brittle and hence have a low fracture toughness. However, different methods are known to increase fracture toughness. Several approaches incorporate a second phase into the epoxy matrix, such as rubber, inorganic nanoparticles or thermoplastics [1]. In the case of thermoplastic (TP) tougheners, the second phase is created by diffusion and dissolution, followed by reaction induced phase separation, leading to a morphology in the micrometer range [2]. During the curing process, the liquid epoxy monomers diffuse into the glassy TP and partially swell or dissolve it, resulting in the diffusion of TP polymer chains into the epoxy resin. This inter-diffusion process tends to slow down and eventually stops after reaching the gel point due to the constrained mobility of the epoxy [3]. The inter-diffusion diffusion of the TS and TP components creates a concentration gradient in the interfacial region. The interfacial region, surrounded by the pure phases (epoxy and PEI), can be divided into three distinct regions, (1) infiltration layer, (2) gel layer, and (3) liquid layer. The liquid layer contains a diluted polymer solution with relatively free motions of entire polymer chains. The gel layer is a swollen polymer in a rubber-like state. In the infiltration layer, Fickian diffusion of the solvent molecules is observed. The epoxy penetration front between the gel and infiltration layer advances at a constant rate and this is usually referred to as case II diffusion

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[4]. The proceeding reaction between the epoxy co-monomers eventually results in a reaction-induced phase separation leading to a gradient morphology [4], where epoxy rich droplets can be observed, reducing in size towards the pure TP.

Curing of epoxy-based composites is typically done by performing two dwell cure cycles. In literature, the effect of cure cycle parameters such as cure temperature and time on the interphase formation, final morphology of EP and TP systems for single dwell cure cycles has been researched. Harismendy et al. [5] reported an increase in droplet size with the increasing cure temperature (140, 160, 180°C) for an epoxy/PEI system. Bian et al. [6] showed that both cure temperature and cure conversion of epoxy resin influences the morphology spectrum of a epoxy/PEI system. Previously, it was assumed that the diffusion process stops at the onset of phase separation for a single dwell cure cycle [4]. Recently, Voleppe et al. [7] reported that the penetration front of thermoset seemed to continue beyond phase separation for an epoxy and polyethersulfone (PES) system using a single dwell cure cycle.

The influence of the cure cycle with varying dwell time/degree of cure at the first dwell, on the interphase dimension and final morphology for Poly(ether imide) (PEI)/EP systems, is not well understood. PEI could be a potential modifier for epoxy resins for aerospace applications due to its high glass transition temperature (217°C), good miscibility due to its amorphous state and compatibility with epoxy systems, enhanced rigidity, and strength at higher temperatures [8]. The research presented in this work aims to understand the interphase formation and morphology, to attain the desired droplet size and interphase morphology for improved material toughness. This aim is achieved by analyzing the influence of dwell time by considering two main cases for each selected first dwell temperature (120-180˚C): (i) wait until the onset of phase separation (OPS) before increasing the temperature to 200°C (second dwell), (ii) wait until 80% degree of cure (80% DOC) before the second dwell.

2. Methodology

2.1 Materials

A blend of TGMAP (Araldite MY 0610 CH), and bisphenol-F epoxy resin monomer (DGEBF, Araldite PY 306 CH) was used as the epoxy resin, while DDS (Aradur 9719-1) was used as a hardener, all supplied by Huntsman, Switzerland. The epoxy system is characteristic for aerospace composites prepregs with a cure temperature of 180°C. 60 µm thermoplastic PEI films (Ultem 1000) were provided by SABIC, Saudi Arabia.

2.2 Cure Cycle

To study the effect of first dwell time and temperature of two-dwell cure cycles, the first dwell times and temperatures (t_{dwell} and T_{dwell} resp.) were varied while the second dwell was kept constant during the experiments: 200°C for 20 min to reach full cure (Figure 1). The selection of the dwell temperatures and times was based on the cure kinetics model of the epoxy system

[2]. Two different first dwell times (t_{dwell}) corresponding to (1) onset of phase separation (OPS) and (2) 80% degree of cure (80%DOC), were selected for each investigated first dwell temperature: 120°C, 140°C, 160°C, or 180°C.

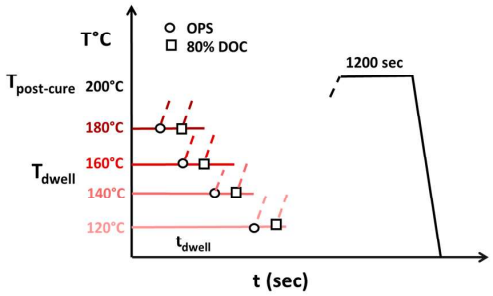

Figure 1. Representative two-dwell cure cycle used for experiments with variable first dwell time and temperature [9].

2.3 Hot stage experiments

Hot stage microscopic analysis was performed to observe the epoxy/PEI interphase formation during the cure cycle. The experimental setup used for hot stage analysis was described by [2]. A PEI film having 2-3 mm wide central slit was sandwiched between two cover glasses and was placed on a temperature-controlled microscope stage THMS600 (Linkam Scientific, UK). The reactive liquid epoxy was then injected into the slit region, where the resin drop immediately reached the specimen temperature by having contact with the hot stage and filled the slit by capillary forces. Upon resin contact with the hot stage, the selected cure cycle was started. An optical microscope (Keyence VHX-2000) was used to attain 30-second interval time-lapse allowing to observe the region of the epoxy/PEI interface.

2.4 Optical interphase analysis

To study the interphase and the morphology of the cured samples, scanning electron microscopy (SEM) (JEOL JSM-7500F, Germany), see Fig. 2a, and confocal laser scanning microscopy (CLSM) (Keyence 3D, VK-X1000) were used. Samples were first embedded in a fast-cure epoxy resin, then grinded and polished after which they were etched with N-Methyl-2-pyrrolidone for qualitative observation of the interphase morphologies.

2.5 Image Analysis

The micrographs obtained with SEM were further used to quantify the droplet sizes and their distribution. To obtain the droplet sizes from the images, the multi-stage thresholding and marker-based watershed image segmentation procedure was used using Weka - a machine learning segmentation tool in ImageJ. The Python packages (Scikit-Image, SciPy, Numpy, and matplotlib) and blob detection within OpenCV were used to calculate the droplet size across the interphase region (Fig. 2c).

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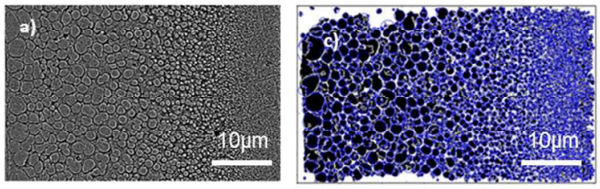

Figure 2. a) SEM image of sample at 180°C, c) blob detection from segmented image [9]

3. Results

3.1 Interphase formation

In Figure 3, the micrographs of a sample with a first dwell at 180°C for two different first dwell times are shown, at different stages during the cure cycle. Fig. 3a shows the presence of (1) a penetration front of epoxy in the PEI film, (2) a darker region close to the penetration front, consisting of swollen thermoplastic resulting from the dissolution of the epoxy monomers (i.e. gel layer) and (3) a clear interface between the gel layer and epoxy (PEI front), indicating the onset of phase separation [2]. Fig. 3a-c presents the evolution of the interphase region when the second dwell is started at the time of onset of phase separation (OPS case). It can be seen that both the epoxy and PEI front progress significantly over time during the second dwell, even beyond the onset of phase separation. Fig. 3d-f shows the evolution of the interphase region when the second dwell started after achieving 80% degree of cure (80% DOC case): in Figure 3d, the onset of phase separation is shown and in 3e-f the progression of the diffusion front, which is small compared to Figure 3b-c.

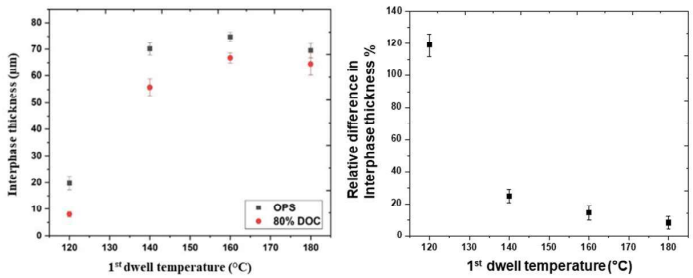

Figure 4. (left) final interphase thickness against first dwell cure temperature at different first dwell times. (right) Relative difference in final interphase thickness between OPS and 80% DOC first dwell times as a function of first dwell temperature [9].

In Figure 4 (left), the interphase thickness as a function of first dwell temperature is shown for both the OPS and 80% DOC case. The interphase thickness increases with first dwell temperature until 160°C for both cases, after which it slightly decreases for a first dwell temperature of 180°C. To evaluate the effect of both first dwell cure temperature and time on the interphase formation, the relative difference in interphase thickness between the two cases (OPS and 80% DOC) is plotted as a function of first dwell temperature, see Figure 4

(right), with 80% DOC as a reference. The results show that the relative difference in interphase thickness is higher at lower first dwell cure temperatures, that is ≤ 140°C.

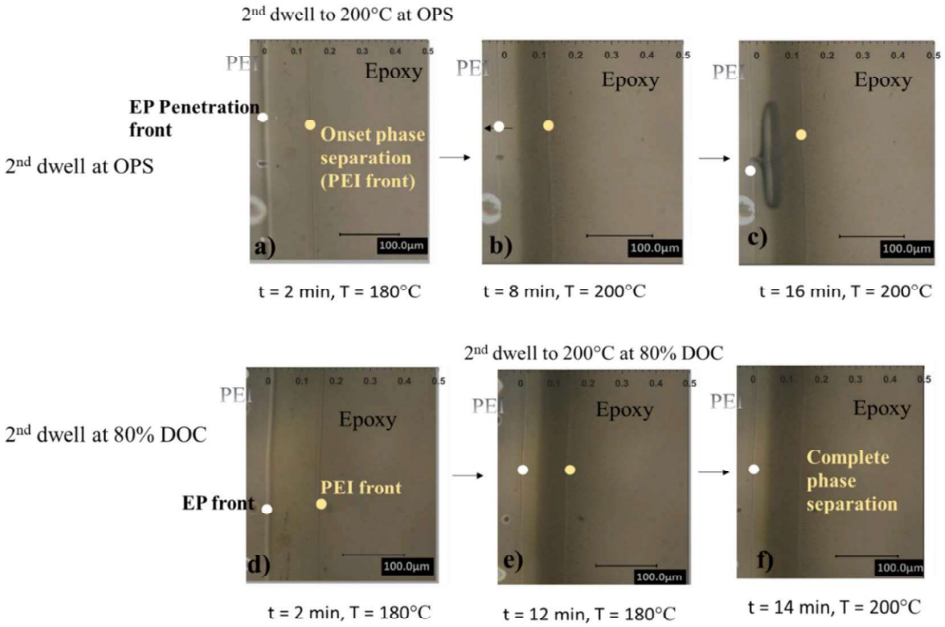

Figure 3. Optical micrographs for 180°C first dwell temperature; a) second dwell started just after OPS b, c) showing change in position of EP and PEI front through pointer. d,f) second dwell started after 80 % DOC (d) OPS, (e,f). showing change in position of EP and PEI front through pointer (the 0 mark is the initial interface between PEI and EP, the scale is in mm) [9].

3.2 Morphological analysis

For most cases studied, an epoxy/PEI biphasic region separated by a distinct interface of pure epoxy (left) and pure PEI (right) was observed, see Figure 5a and 5c-f. Close to the pure epoxy interface, the epoxy/PEI biphasic morphology was described by epoxy-rich droplets dispersed in a PEI matrix, i.e. phase-inverted morphology [2]. The phase inversion occurs due to a viscoelastic phase separation phenomenon, also observed for other epoxy/thermoplastic blends [10]. The epoxy droplet size and frequency is shown as a function of the position along the interphase in Fig. 5 for the different cure cycles. The size of these epoxy droplets was observed to decrease gradually towards the pure PEI region, due to the increase in PEI content. The droplet size close to the epoxy interface increased as a function of first dwell cure temperature until 160°C. Additionally, the frequency of smaller droplets was higher in the case of 80% DOC as compared to the OPS (see for instance Fig. 5e and 5f).At a first dwell temperature of 120°C, with 80% DOC, (Fig. 5b), no gradient morphology was observed but rather a narrow droplet size distribution.

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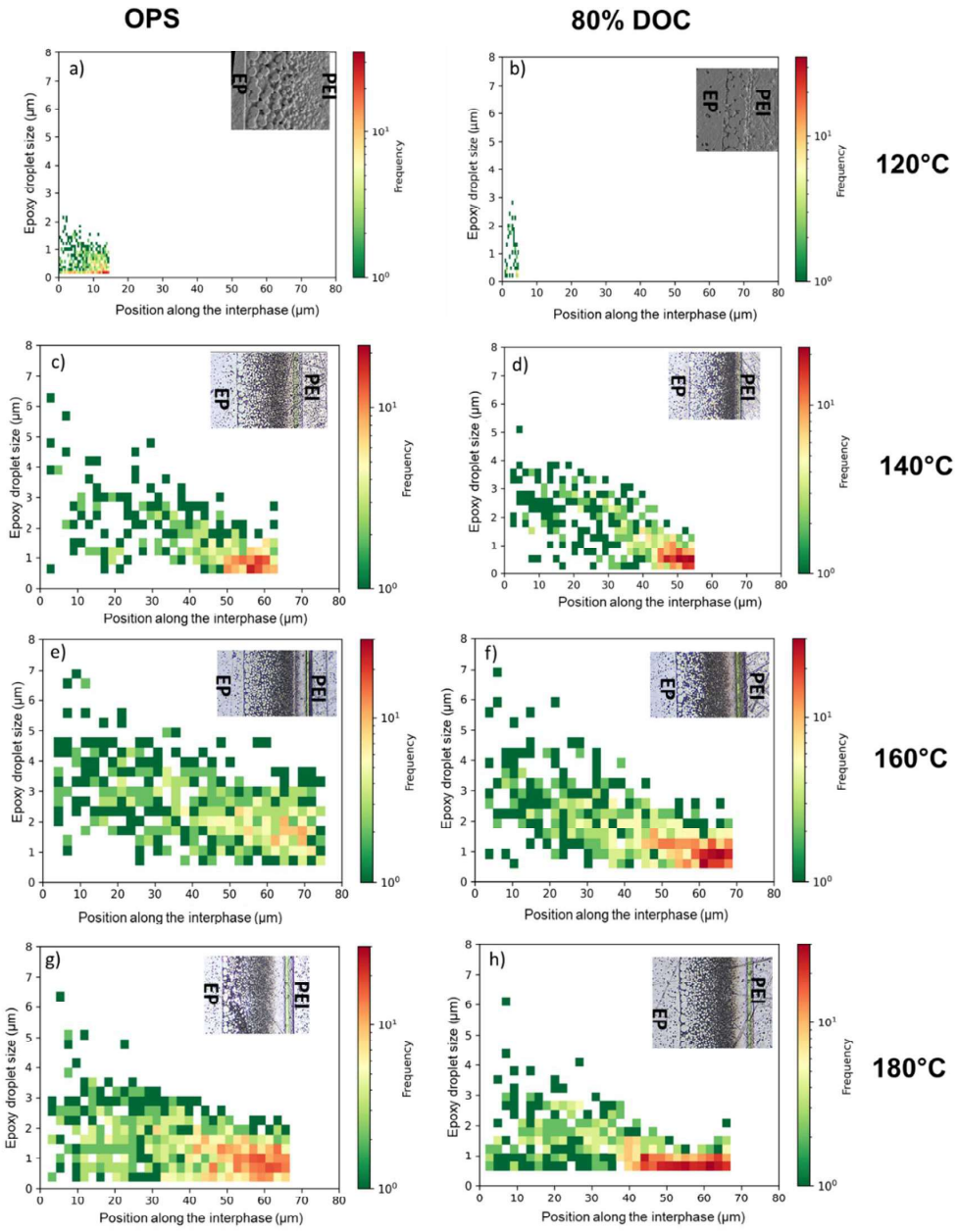

Figure 5. The epoxy droplet size histograms plotted as a function of position along the interphase (0 = pure EP) for samples cured until OPS or 80% DOC at different first T_{dwell} [9].

4. Discussion

Figure 3 showed higher diffusion distances in the OPS case which may be attributed to the fact that the gel point was not attained in the OPS case resulting in a higher diffusivity. The degree of cure ranged from 0.15 to 0.36 for the OPS cases while the gelation point was estimated to

be at a degree of cure of 0.43 (based on Flory–Stockmayer). Therefore the epoxy polymer chains are still in a mobile state and can diffuse further during the second dwell phase [6]. At 80% DOC however, the degree of cure was beyond gelation, and therefore the epoxy network should be completely bound due to infinite molecular weight. Nonetheless a considerable diffusion distance was still observed for the 80% DOC case. Due to the different diffusion speeds of three constituents of the epoxy system, demixing and/or non-stoichiometric curing may take place, which was more prominent at higher first dwell temperatures. This could imply that at the diffusion front, the reaction rates predicted from the reaction kinetic model are inaccurate: a slower reaction between epoxy monomers seems to take place, resulting in a longer mobility and diffusion time, even after achieving the nominal gel point.

An increase in interphase thickness with increasing first dwell temperature (Fig. 4 left) can be explained by the competition between the rate of phase separation and curing rate. When the phase separation rate is higher than the curing rate, the interphase thickness is primarily controlled by the rate of phase separation (i.e. first dwell temperatures ≤ 160°C) and vice versa for first dwell temperature greater than 160°C [2]. A similar trend of increase and then decrease in interphase thickness as a function of increasing first dwell temperature was observed for DGEBA epoxy toughened with polysiloxanes [11]. The authors attributed this behavior to the chemical reaction, coalescence, and inter-diffusion of DGEBA and polysiloxanes. The high relative difference in interphase thickness between OPS and 80% DOC (Fig. 4 right) at lower first dwell temperature shows the higher diffusion/dissolution of polymeric chains by starting second dwell at OPS for lower first dwell temperatures. These results indicate that, both first dwell temperature and time (i.e. OPS and 80% DOC) influence the interphase thickness, especially at lower first dwell temperatures.

When looking at the morphology, influence of both first dwell temperature and time was seen. The absence of gradient morphology at 120°C (Fig. 5b) suggests that there is no concentration gradient, indicating the occurrence of case II diffusion for shorter diffusion lengths. At higher first dwell temperatures, a clear concentration gradient was seen (Fig. 5c-f), indicating a mixed-mode between case I and case II diffusion. The droplet size in the vicinity of pure epoxy increased for increasing first dwell temperatures until 160°C (Fig. 5), possibly caused by higher mobility of polymeric chains at the start of the second dwell, favoring a longer growth phase after nucleation. The frequency of smaller droplets increased in the case of 80% DOC (compared to OPS), which may be linked to the restricted mobility of the polymer chains after gelation, eventually preventing growth of particles and resulting in smaller droplets [9]. This hypothesis was further verified by the absence of smaller droplets at 120°C for 80% DOC case.

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5. Conclusions

The main objective of this work was to study the effect of dwell time and temperature in the first dwell on the droplet size formation and interphase morphology. Hot stage microscopy experiments showed that the epoxy and PEI diffusion fronts continued to progress, even after the onset of phase separation. The diffusion distance was higher in the case of OPS, compared to the 80% DOC case, especially at lower first dwell temperatures, resulting in a larger interphase region. The interphase thickness increased with first dwell temperature until 160˚C for both cases, after which it slightly decreased for a first dwell temperature of 180˚C. Furthermore, the size of bigger droplets near the pure epoxy region was mainly controlled by dwell temperature, while the frequency of smaller droplets was controlled by dwell time. A higher interphase thickness was obtained for the OPS case while a larger number of smaller particles were observed for 80% DOC. Therefore, the influence of both interphase thickness and droplet size on fracture toughness will be investigated in the future. This work highlights the importance of the curing process beyond phase separation to control interphase dimension and morphology.

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