STRUCTURAL AND MICROMECHANICAL CHARACTERIZATION OF THE INTERPHASE REGION BETWEEN TWO THERMOSET RESINS

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Abstract
The local interactions at the interface between two thermoset resins are investigated using microscopic, chemical and micromechanical characterization techniques. The novelty of this work lies in the combination of physico-chemical measurement techniques to investigate polymer interfaces. The characterization techniques include scanning electron microscopy, Raman spectroscopy and nano-indentation. The results allow a quantitative analysis of the concentration profile in the interface region. The observation of the interfacial area by Transmission Electron Microscopy also highlights a gradient of morphological structure. This morphological gradient can be correlated to the concentration profile obtained by the other techniques. Based on the analyses, an estimated interphase length of 800 µm is found for the resins studied in this paper. The concentration gradient in resin/prepreg model systems could only be measured by energy dispersive X-ray microscopy. In this case, the length of the interphase was reduced to 500µm.

1. Introduction

Although all epoxy resins globally exhibit similar elastoplastic properties, the ability of the epoxy ring to react with a variety of substances gives the epoxy resins versatility in terms of modulus, thermal stability and electrical properties. Depending on the specific needs for certain physical and mechanical properties, combinations of choices of epoxy resin and curing agents can usually be formulated to meet specific requirements. Moreover, the interfaces between two epoxy resins can be tailored to respond to specific requirements with regards to gradient properties.

Understanding, characterizing and modeling the behavior of the interface region between two thermoset resins is of particular interest for the optimization of the SQ-RTM process[1] [1]. From a more fundamental viewpoint, a proper understanding of the properties of graded thermoset-thermoset interfaces is a challenging task, essential with respect to controlling the best conditions for making reliable systems.
The focus of this paper will therefore be the experimental determination of a concentration profile along the interface between two thermoset resins.

2. Experimental

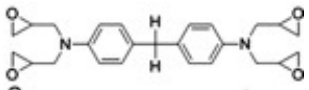
2.1 Materials

Although any couple of resins could be investigated with the techniques described hereafter, the resins used in this study were specifically selected because of their use in the SQ-RTM process. More specifically it consists of the aerospace graded 8552 epoxy produced by Hexcel and an injection resin, also provided by Hexcel (noted "Alpha resin" from here on). The alpha resin is composed of an epoxy resin based on an aromatic backbone, a curing agent containing chlorine groups and also contains spherical nanoparticles. With the SQ-RTM process in mind, the Alpha resin has been selected to have a low viscosity, a distinctive pink color and a cure kinetics that is close to the 8552 resin but formulated however with building blocks allowing differentiation from that 8552 resin. The characteristics and chemical structures for both resins are listed in table 1. [2]

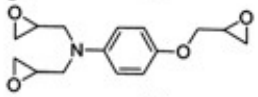
	8552 resin	*Alpha resin*
Epoxy component	TGMDA, TGAP	Aromatic backbone
Curing agent	DDS	Chlorine groups
Thermoplastic	PES (20%)	
Viscosity (Pa.s)	7,8 @ 120°C	0,07 @ 120°C
Gel time (min)	141 @ 120°C	440 @ 120°C

Annotations :

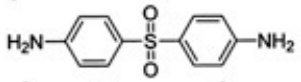
TGMDA : Tetraglycidyl methylenedianiline



TGAP : Triglycidyl-p-aminophenol



DDS 3,3 or 4,4 Diaminodiphenylsulfone



PES: Polyethersulfone

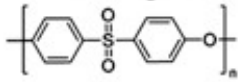


Table 1. Chemical formula for the resins at 120°C. This temperature corresponds to the injection temperature of the alpha resin.

[1] The challenge in the use of prepreg materials is to set up an adequate pressure within the mold to consolidate the layup and avoid porosity. This pressure is usually obtained by curing the part in an autoclave. For big parts, the costs of autoclave curing can rapidly escalate. In the case of the Same Qualified Resin Transfer Molding (SQ-RTM) process, the prepreg fabric is placed in a closed mould and an additional resin is injected through mold cavities strategically positioned around the perimeter in order to apply a hydrostatic pressure during the curing. The cure kinetics of the injected resin are carefully engineered to maintain the hydrostatic pressure until the gelation of the prepreg resin occurs.

2.2 Sample Preparation

Different types of simplified samples mimicking either resin-resin or resin-prepreg interface phenomena were produced in recipients according to figure 1. The samples were cured in a pressurized HP-DSC oven applying the same pressure and temperature conditions as applied during the industrial scale curing process. The cured samples were cut and embedded in mounting resin before polishing the cross sectional area up to 1 µm surface roughness.

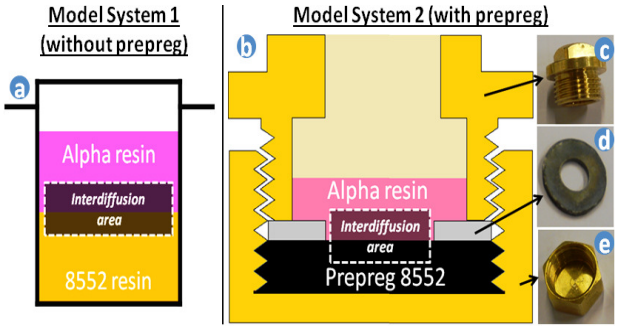


Figure 1. Schematic view of the DSC pan cross-section containing the resin/resin model system (a) Schematic view of the mold cross-section containing the resin/prepreg model system (b) and photos of the mold elements: the perforated 3/8' brass plug (c), the metallic washer (d) and the 3/8' brass compression cap (e).

2.3 Interface characterization

2.3.1 Raman spectroscopy coupled with chemometrics: The concentration gradient of the model system was determined using Raman spectroscopy by following the evolution of the spectra in the interface region with a resolution of 1 µm³. In order to determine the concentration profile at the interface between the two resins, a Raman mapping (measurements taken at regular steps) was performed over a distance of 2 mm perpendicular to the interface. The concentration of the respective resins could be followed through strong characteristic distinguishable peaks in the Raman spectrum. For the 8552 resin, the sulfone function which is characterized by an intense Raman spectral band centered at 1149 cm^{-1} due to the symmetric stretching vibration of the sulfone groups was selected. The alpha resin was traced by means of an aromatic group at 1387 cm^{-1} due to the ring vibration of the di-substituted aromatic groups. The Raman spectra of both pure cured resins are shown in figure 2.

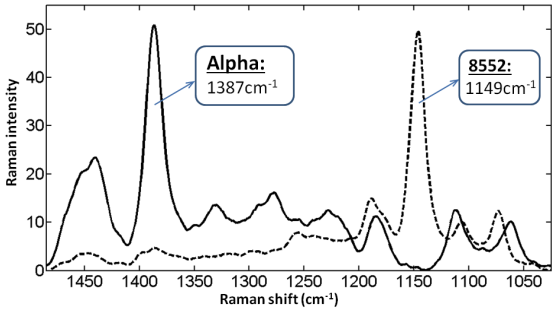


Figure 2. Raman spectra of both pure cured 8552 and Alpha resins with their own characteristic peaks.

The exact concentration of the 8552 resin was determined using a quantification model based on chemometrics. The Raman spectra of manually mixed calibration samples containing different ratios of both resins were used to generate this model.

2.3.2 X-Ray spectrometry (EDX): The presence of carbon fibers in the composite samples would completely saturate the signal obtained by Raman spectroscopy and could even lead to the burning of the sample. Therefore, model systems with carbon fibers were characterized by SEM-EDX. An EDX analysis was performed by tracing sulfur elements from the 8552 prepreg and chlorine elements from the Alpha resin. Similarly to the methodology used for the Raman spectroscopy, a mapping was performed perpendicular to the interface. Specimens for EDX (Energy Dispersive X-ray Spectrometry analysis) were coated with a 8 nm chromium layer in order to create a thin conductive layer which minimizes degradation and drift due to thermal expansion. The resolution of the EDX is about 0.5 µm [3].

2.3.3 *Transmission electron microscope (TEM)*: The gradient of the morphological structure was observed by TEM. The specimen were produced from the initial samples by cutting, transverse to the interface, layers with a thickness of about 95 nm. Figure 3 shows the morphology of both bulk resin samples.

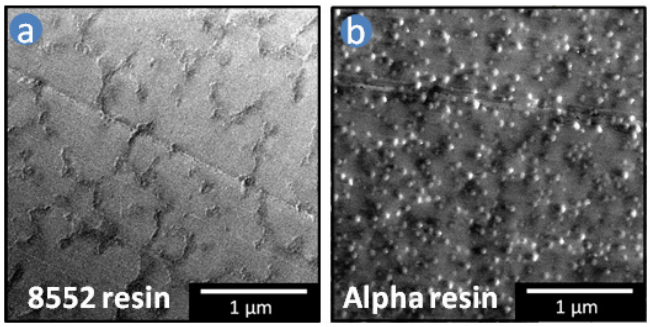


Figure 3. TEM micrographs of 8552 resin (a) and Alpha resin (b)

2.3.4 *Nano-indentation*: Nano-indentation was used to determine the local modulus of the resin along the interface. This method has already been used to measure the Young's modulus of the two neat resins in an infusion-prepreg system [4]. A flat punch tip with a diameter of 23.65µm was used at room temperature. The measured modulus of the bulk resin was in good agreement with macroscopic compression tests. The 5 sets of 18 indents were used to map a wide area across the interface. To insure a proper indentation in a material with 1µm surface roughness with the flat punch tip the indentation depth needs to be at least 3µm. The spacing between the indents however has to be at least 30 times the indentation depth to avoid the influence of the plastically deformed zones from the previous indents. Therefore, when choosing the indent locations perpendicular to the interface, the resolution of the nano-indentation experiment in this study was of 100µm.

3. Results and discussion

3.1 Pysico-chemical measurements

An interphase distance of 700-900 µm is estimated with the Raman spectroscopy[2]. Measurements by EDX and nano-indentation show similar results for samples without carbon fiber (figures 4, 5a, 5c & 6). All the measurements indicate a gradual S-shaped concentration gradient typical of Fickian diffusion. It is not evident to determine if this profile is really the result of an (inter)diffusion process or barely the consequence of viscous flow. The viscosity being directly related to the cure cycle, more research is currently being conducted to determine its influence on the concentration gradient along the interphase.

Moreover, for the neat resin samples without fibers, there is no reference state of the concentration profile at the start of the cure. It is therefore difficult to draw conclusions as to which resin preferentially migrates into the other.

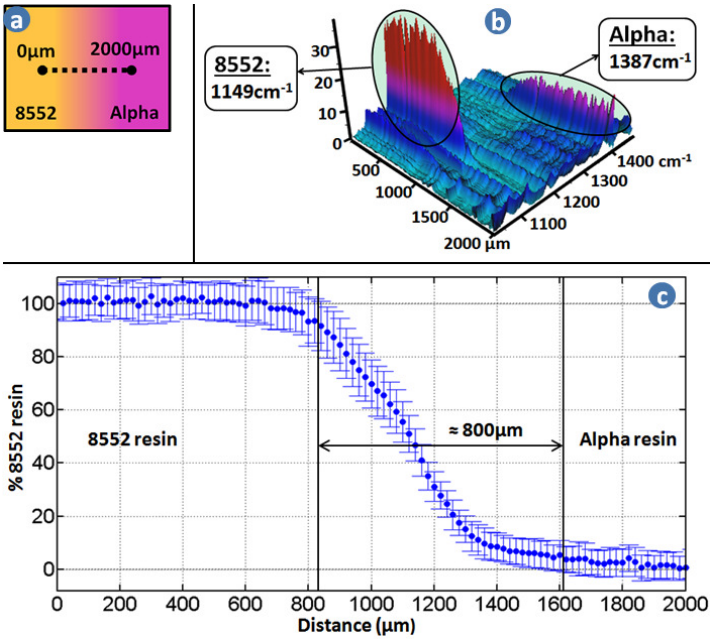


Figure 4. (a) provides a schematic representation of the analyzed surface of a cured sample. The Raman mapping was performed over a distance equal to 2000 µm along the dotted line perpendicular to the interphase. A three-dimensional representation of the Raman spectra from the mapping is shown in Figure 3 (b). Qualitatively, the interphase length corresponds to the area of the decreasing sulfone peak accompanied with an increasing aromatic peak.

In the presence of carbon fibers, the interphase length is reduced down to 500 µm (figure 5) and is of the same order of magnitude as the interdiffusion distance described in combined infusion-prepreg systems [4]. It is believed that this decrease is an effect of the preform permeability. In the presence of the carbon fibers, the 8552 resin penetrates to about 150µm in the Alpha resin. The total interphase region being 500µm wide, it thus seems that the Alpha resin penetrates the 8552 more even though the fibers probably hinder the transport phenomena.

[2] For all measurements, the 8552 resin concentration was defined as [100 x A/ (A + B)] where A and B indicates the signal measured for resins 8552 and Alpha respectively.

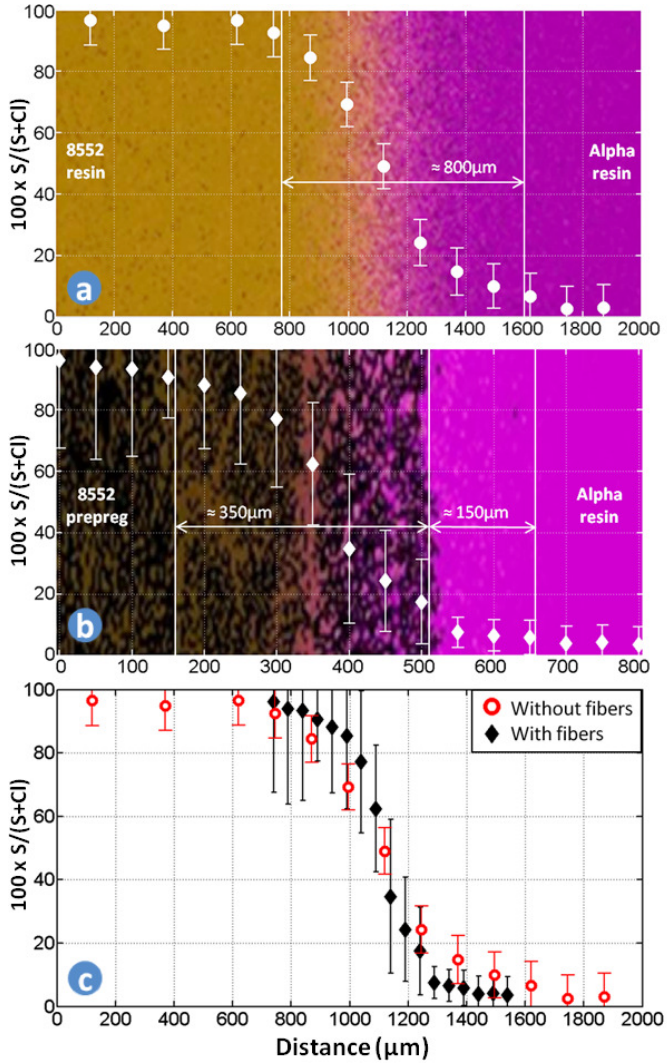


Figure 5. (a) and (b) sulfur (yellow) and chlorine (purple) SEM-EDX maps in the interphase region, without and with carbon fibers respectively, with their associated concentration gradient. (c) Percentage of sulfur atoms from 8552 resin with its standard error at the interface in the presence and in the absence of carbon fibers.

It is important to bear in mind the initial low viscosity and slow crosslinking kinetics of the Alpha resin with respect to the 8552 resin. The low-viscosity Alpha resin is believed to swell the 8552 resin before crosslinking hence reducing the local fiber volume fraction of the outermost plies. So far, no technique has been found to accurately determine the local (ply per ply) fiber volume fraction but this topic will be addressed in further research.

3. 2 Microscopic imaging

The investigation of the microstructure gradient across the interface is another way to estimate the concentration gradient. First, TEM micrographs of the 8552 and Alpha resins were taken. The microstructures of these pure resins were considered as the boundaries of the interphase zone. The 8552 epoxy resin which contains 20%wt PES exhibits a morphology close to co-continuity as observed in the TEM micrograph presented in figure 3 (a) A homogeneous distribution of individual spherical nano-inclusions of about 50 nm diameter size is clearly visible in the TEM morphology of the Alpha resin as shown in figure 3 (b).

The morphology observed in the region of high 8552 concentration in figure 6 is exactly the same as for the pure 8552 resin (see figure 3 (a)). It evolves progressively from co-continuity to dispersed thermoplastic nodules in a continuous epoxy resin-rich phase as seen in the TEM micrographs of figure 6. The distribution of nanoparticles observed in figure 6 is similar to that of the pure Alpha resin (see figure 3 (b)). The microstructure gradient develops over a distance estimated between 450 and 750 µm, close to the value obtained by Raman spectroscopy.

The SEM-EDX profile from figure 5 (a) was compared to the Raman and nano-indentation profiles from by arbitrarily superimposing the points at 50% from the SEM-EDX and Raman profiles. The TEM micrographs were added by associating each micrograph to its estimated PES concentration calculated above.

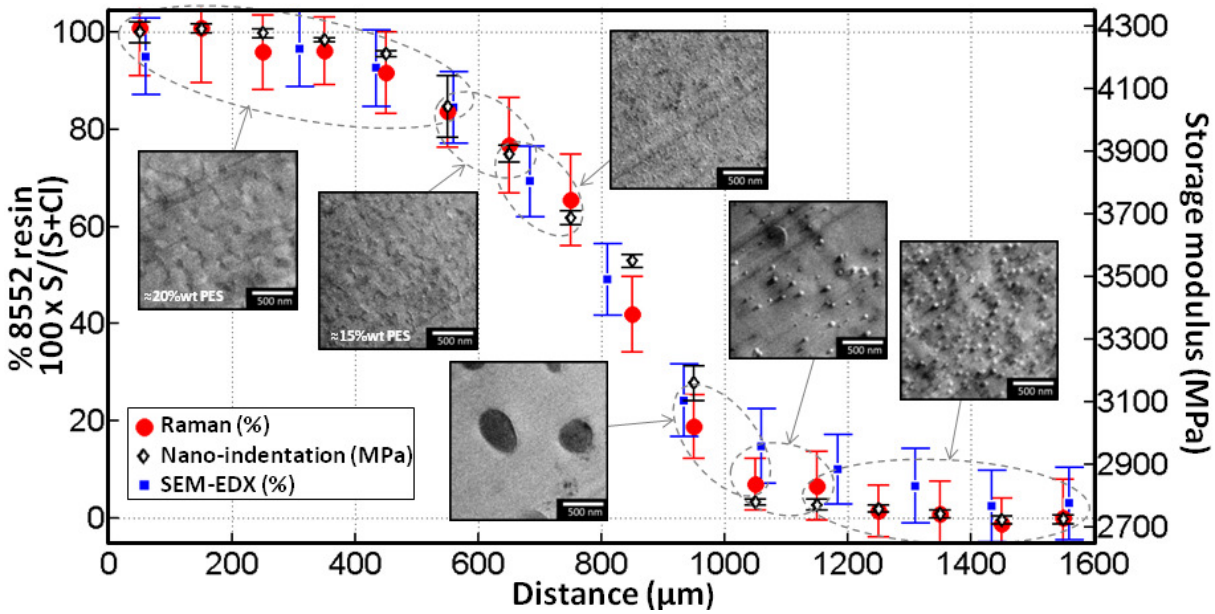


Figure 6. Comparison of Raman, SEM-EDX and nano-indentation profiles for an 8552-Alpha resins sample with the associated TEM microstructures

4. Conclusions

The concentration gradient between two different thermoset resins was quantified using Raman spectroscopy coupled with chemometrics, X-ray spectrometry using scanning electron microscopy, transmission electron microscopy and nano-indentation. The repeatability of the interphase length and of the properties gradient measured by all techniques validates the accuracy of each of these techniques.

The EDX technique allowed the analysis of samples with carbon fibers and showed that the fibers act as a diffusion barrier that shortens the length of the interphase with about 200 µm with respect to the bulk samples for the 8552-Alpha couple.

The novelty of this research lies in the combination of physico-chemical measurement techniques that can be used to investigate polymer interfaces. These techniques create a robust experimental framework for future research needed to better understand the topic of concentration gradients between thermoset polymers.

The nano-indentation technique will be further developed. On the one hand the equipment will be pushed to perform accurate measurements at temperatures above Tg. This way the local rubbery modulus, which directly relates to the crosslink density, can be measured.
On the other hand, an image correlation method is being developed to predict the constraining effect of the fibers during nano-indentation of the resin in the presence of fibers.
The preliminary tests show promising results, but the testing procedures still need more refinement.

5. Acknowledgments

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6. References

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