

INTERFACE DIFFUSION AND MORPHOLOGY OF AEROSPACE GRADE EPOXY CO-CURED WITH THERMOPLASTIC POLYMERS

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Abstract

Interfaces formed during the co-curing of an aerospace grade epoxy resin in contact with PEI, PES, and PSU surfaces are examined in this work. The interface found in each scenario is characterized by optical microscopy, and low voltage Scanning Electron Microscopy (SEM) using Energy-Dispersive X-ray spectroscopy (EDX) where applicable. Atomic Force Microscopy (AFM) in tapping mode is also used for high resolution imaging of the interface. The spatial resolution and limitations for each microanalysis technique are defined, and results are interpreted accordingly.

The morphology of each interface obtained is correlated with a thermodynamic approach based on the Hansen Solubility Parameter (HSP), which considers dispersion forces, polar forces, hydrogen bonding, and ionic forces between the two materials. The limitations of the HSP thermodynamic approach for this study are discussed.

Significant interdiffusion of more than 50 μm is found with PES, PEI and PSU. Nevertheless, a phase separation mechanism was evidenced only for PEI and PSU, and could

not be detected with PES. Larger interdiffusion was observed with PSU than PEI.

1 Introduction

High performance aerospace epoxy composite laminates largely consist of epoxy resin and carbon fibres. However these composites often include other organic materials, such as rubbers, other thermoset resins or thermoplastics, as part of the laminate. These can be in the form of coatings, particles, interleaves or inclusions [1-3], and are added for various reasons, including laminate surface protection, matrix toughening, or the incorporation of additional functionality into the laminate. Many organic materials including polyamides (PA), polyetherimides (PEI), polysulfones (PSU), polyethersulfones (PES), polyurethanes, and rubbers, can be found as part of “carbon-epoxy” composite laminates.

The interface mechanisms occurring between the reacting epoxy and these thermoplastics are very complex, and in some cases it is thought that the bond is enhanced by a degree of interdiffusion at the interface [4, 5]. More precisely, the adhesion strength at the interface, and the overall mechanical

performance of the final composite will primarily be dictated by the interface region of the two dissimilar materials [6, 7]. In order to predict the performance of the laminate in various situations, it is therefore valuable to understand the mechanisms occurring at the interface and characterize the morphology of such interface.

In the present study a selection of thermoplastics - PEI [4, 8], PSU [9-11], and PES [12, 13] - were chosen for their known compatibility with epoxy resins in order to offer a good range of compatible thermoplastics. The morphology of the interface formed between the thermoplastic and an aerospace grade epoxy resin co-cured in the presence of the thermoplastic is investigated through optical microscopy, SEM-EDX, and AFM. The interfacial measurements and morphologies observed in each scenario are correlated with the solubility parameters approach based on their thermodynamic affinities.

2 Experimental

2.1 Materials

The epoxy system used in this study is based on an aerospace grade epoxy system commonly used in prepregs. It contains three epoxy components: tetraglycidyl diaminodiphenyl methane (TGDDM) (Araldite MY721), diglycidyl ether of bisphenol F (Araldite GY281), and triglycidyl-p-aminophenol (Araldite MY0510) cured with diaminodiphenyl sulphone (DDS) (Aradur 976-1) hardener. All materials were supplied by Huntsman Advanced Materials (USA) and mixed according to the specified ratios.

The thermoplastic materials were all used in film form, with an identical thickness of 125 μm . The three amorphous thermoplastics selected are: polyetherimide (PEI) (Ultem® grade 1000), polysulfone (PSU) (Udel® grade P-1700), and polyethersulfone (PES) (Ultrason® grade E) obtained from CS Hyde. The glass transition temperatures (T_g) of PEI, PSU and PES are 214 °C, 182 °C and 217 °C, respectively. All values were measured by

Differential Scanning Calorimetry (DSC) according to ASTM D3418 standard.

2.2 Procedure

Co-cured epoxy/thermoplastic specimens were prepared by pouring the uncured (A-stage) epoxy mixture onto the thermoplastic film contained in a silicone rubber mould, and subsequently curing at 180°C under atmospheric pressure for 2 hours with a heating rate of 2°C/min. For each specimen a cross-section of the interface was taken, embedded and polished. These cross-sections were suitable for optical microscopy and Atomic Force Microscopy (AFM). For Scanning Electron Microscopy (SEM) the specimens were carbon coated with an approximate coating thickness of ~10 nm using a Quorumtech QT150-TES coater.

2.3 Analysis

Scanning Electron Microscopy analysis was conducted using a JSM-6460 SEM (JEOL, Japan). Analysis was performed at 10 kV accelerating voltage and the observed probe resolution (or probe diameter) under these operating conditions was less than 50 nm. Care was taken to avoid the specimen damage often observed at 10 kV or higher on polymer materials, by operating a lower magnification and protecting the specimen with beam blanking between scans. Energy Dispersive X-ray (EDX) analysis was conducted across interfaces with a 25 % dead time using a JEOL minicup EDX detector. A 2.0 ms dwell time and a resolution of 512 pixels were used during line scans.

For Atomic Force Microscopy, a Veeco Multimode 6 AFM was used in tapping mode. For each scan, the height information, phase angle shift, and amplitude contrast were recorded. All images were recorded with a 512x512 pixels resolution using Bruker RTESPA silicon cantilevers with a spring constant $k=20-80$ N/m, frequency $f=299-368$ kHz and a nominal tip radius of 8 nm.

3 Results and discussion

3.1 Interface diffusion and morphology

Although interphase formation between two thermoplastics has been extensively studied [15-17], fewer studies exist on the interphase between thermoplastics and thermosets cured in their presence. It is expected that the formation of interphases in these materials involves other mechanisms than those found at thermoplastic-thermoplastic interfaces, since the reaction and diffusion of thermosetting monomers in presence of thermoplastics is fundamentally different [10]. Hence, the nature of these interfaces is better described through a series of mechanisms, which involve adsorption/wetability at first (strongly dependent on polymer compatibility), followed by interdiffusion, which can ultimately lead to the formation of a semi-interpenetrating polymer network (sIPN) or result in phase separation. The first mechanism is based on thermodynamics and defines whether different polymers are compatible by evaluating adhesive forces between them. It is the necessary thermodynamic condition for interphase formation.

In this study, the Hansen Solubility Parameter [14] is used to evaluate the compatibility of the selected thermoplastic films with the epoxy resin. The Hansen Solubility parameter is an extension of the work carried by Hildebrand and Scott [18, 19] and defines the cohesion energy of liquids with three different components: dispersion forces (δ_D) such as Van der Waals interactions; polar forces (δ_P); and hydrogen bond forces (δ_H). Therefore, using these three individual parameters, most chemical interactions except strong ionic forces become thermodynamically predictable. However ionic forces are mostly the domain of aqueous environments and are not found

relevant when investigating organic molecules [20]. The basic equation governing the assignment of Hansen solubility can be expressed as the sum of the Hansen δ_D (dispersion), δ_P (polar), and δ_H (hydrogen bond) components, as per equation below:

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (1)$$

Furthermore, Ra is defined as the distance in Hansen space between two materials based on their partial solubility parameter (equation 2), and the Relative Energy Difference (RED) number as the ratio Ra/R_o , as per equation 3. R_o is defined as the radius of interaction sphere in Hansen space for a given material.

$$Ra^2 = 4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2 \quad (2)$$

$$RED = Ra/R_o \quad (3)$$

A RED number of 0 is found for no energy difference (hence optimum compatibility); a RED number less than 1 indicates a high affinity; and numbers higher than one indicate that the two polymers are not soluble. Table 1 lists the Hansen solubility parameter components and R_o for each selected materials, and shows the calculated Ra and RED number for the selected thermoplastics compared to the epoxy resin. The solubility parameters of epoxy resin obtained from the literature [14] is based on a very similar formulation to the epoxy resin used in this study, both containing diglycidyl ether of bisphenol resin as their main component.

The Relative Energy Difference numbers obtained from the Hansen solubility parameters thus indicate that all three thermoplastics have a high compatibility with epoxy resin ($RED < 1$). These indicate that PES will be the most miscible with epoxy resin since PES has the lowest RED value among the studied polymers.

Table 1. Hansen solubility parameters for selected materials [14]

Material	δ_D	δ_P	δ_H	R_o	R_a	RED
Epoxy (based on diglycidyl ether of bisphenol resin)	18.1	11.4	9.0	9.1	-	-
PEI	19.6	7.6	9.0	6.0	4.84	0.80
PSU	16.0	6.0	6.6	9.0	7.24	0.80
PES	19.6	10.8	9.2	6.2	3.06	0.49

Preliminary analysis of the morphologies of the epoxy/thermoplastic interfaces was performed by optical microscopy as shown in Fig. 1. These images reveal that interdiffusion has occurred between epoxy and the amorphous thermoplastics PEI, PSU and PES on a micron level. This is in agreement with the literature, where interdiffused interfaces on the micron scale are commonly observed when epoxy systems are co-cured with amorphous thermoplastics, and interphase widths can vary from a few micrometres up to 300 μm [4, 5, 7, 9, 11, 21].

across the epoxy/PES interface and the absence of noticeable phase boundaries is suggesting that no phase separation has occurred. This behavior can be correlated with the solubility parameter, which reports the lowest *RED* number for the PES/epoxy, and consequently implies a high miscibility between the two materials.

The phase separation mechanism observed with epoxy cured in the presence of PEI and PSU was previously reported in interpenetrated structures [22]. In such structures, two main driving mechanisms are described: gelation and

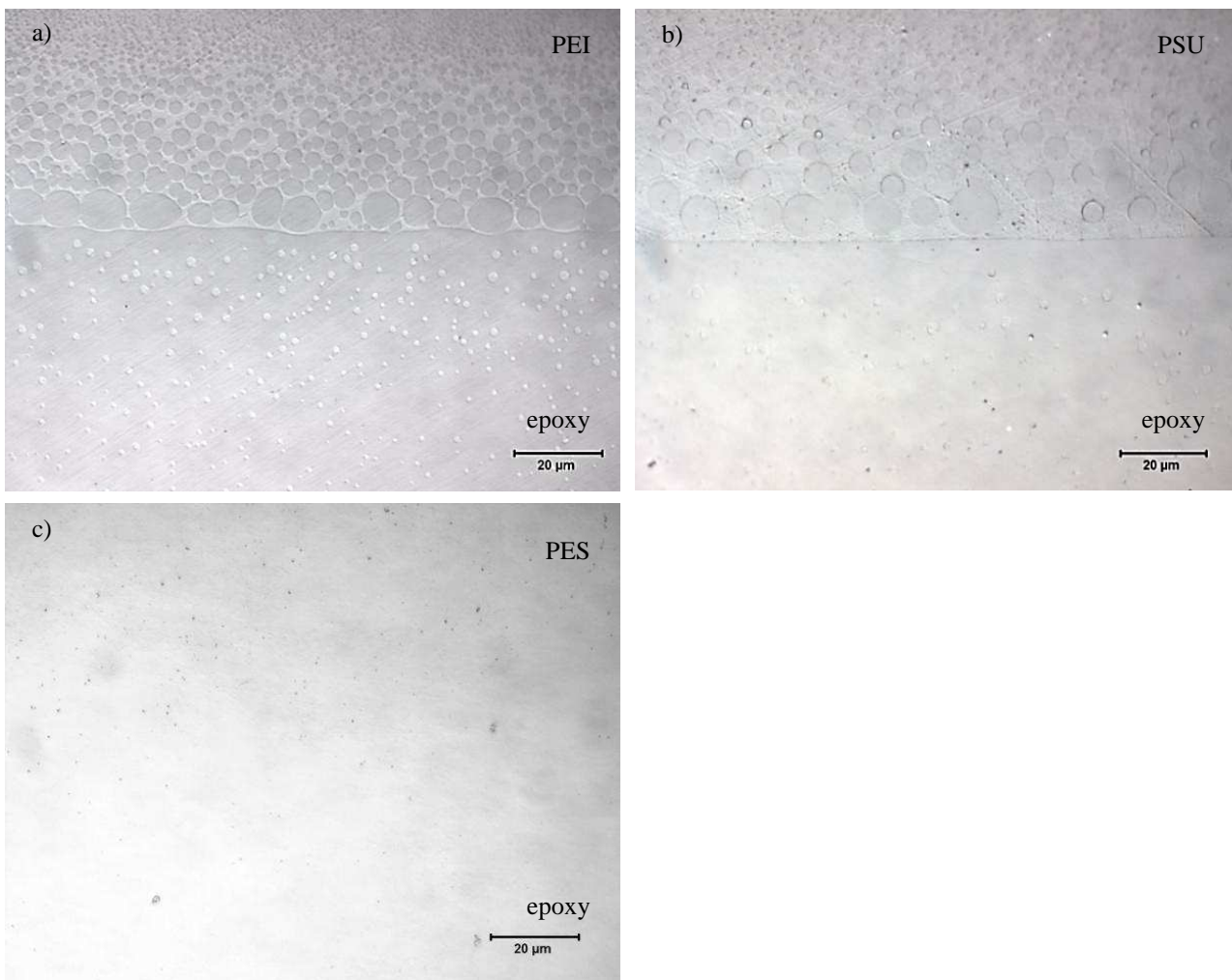


Fig. 1. Optical micrographs, showing the interface morphology between epoxy resin co-cured with a) PEI, b) PSU, and c) PES.

However, further observation of the interdiffusion morphologies reveal that, in the case of PEI and PSU, phase separation has occurred. Conversely, the gradual transition

phase separation. In the epoxy resin, gelation occurs at a sufficient degree of cross-linking where the polymer networks starts behaving as a gel, and prevents any further diffusion or phase

separation mechanisms. Phase separation is driven by interactions between macromolecules and by the cross-linking reaction of the thermoset. In polymer blends, it is reported [22] that, if phase separation occurs before gelation, the phase domain sizes will tend to be large. When gelation finally occurs, it will tend to keep the domains apart. Conversely, if gelation happens first, the presence of cross-links will tend to keep the domains much smaller. However in this study, the phase size is found to decrease when it is formed further away from the interface. This can be attributed not only to a different gelation point, and a different cross-linking rate of the epoxy as the concentration varies across the interface, but also to a variation in the degree of swelling of the thermoplastic. Hence, the morphology of the interface is dependent on the nature of the thermoplastic and on the epoxy curing reaction, which in turn is dictated by the cure cycle. The effect of the cure cycle on the morphology of the interface with PEI has been previously investigated[4].

The interdiffusion widths observed with PEI and PSU are measured in Fig. 2. It is found that the epoxy diffuses up to $\sim 53 \mu\text{m}$ in PEI and $\sim 67 \mu\text{m}$ in PSU. In both cases, the epoxy phases are measured to start consistently from $9 \mu\text{m}$ in diameter and gradually decrease to substantially smaller phases on the nanometer scale. Thermoplastic phases are also found in the epoxy resin over a larger distance ($\sim 114 \mu\text{m}$ for PEI and $\sim 118 \mu\text{m}$ for PSU), with phase sizes starting from $2 \mu\text{m}$ in diameter. The PES interface morphology is investigated, via SEM-EDX, in the following section.

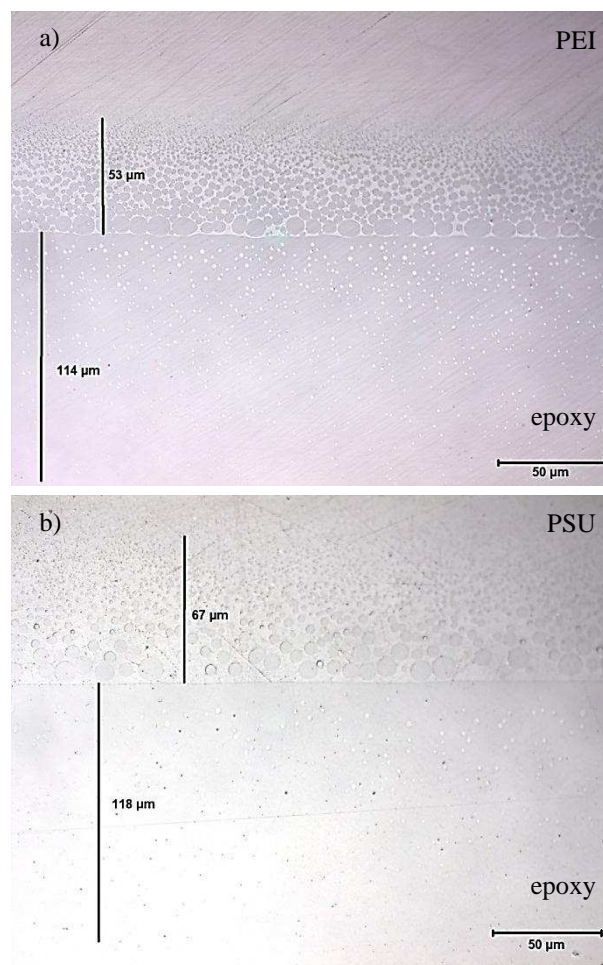


Fig. 2. Measurements of interdiffused interfaces between epoxy co-cured in the presence of a) PEI, and b) PSU. There is more diffusion of epoxy into PSU ($67 \mu\text{m}$) than PEI ($53 \mu\text{m}$).

3.2 SEM-EDX analysis

SEM-EDX provides data on chemical composition, by analyzing characteristic X-rays generated as a result of transitions between inner atomic electron energy levels of a specific element. In this study, an EDX line analysis was performed across the PES/epoxy interface by tracing the sulfur element, to investigate the extent of interdiffusion during the co-curing process.

Prior to performing the EDX study, the electron scattering in our specimen was simulated using the Monte Carlo Simulation software CASINO version 2.4.8 [23], in order to evaluate the spatial resolution under our operating conditions, defined by the X-ray generation volume. This volume represents the

region underneath the surface of the specimen from which X-rays are generated, and is known to be significantly larger than the incident electron beam diameter. It varies with accelerating voltage, beam diameter, and atomic number of the trace element [24]. The specimen was modeled as a 1 mm substrate (PES and epoxy with densities of 1.37 g/cm³ and 1.28 g/cm³ respectively) covered by a 10 nm carbon layer (coating). Simulation parameters were set to 100,000 electrons, 10 kV acceleration voltage, and a 50 nm beam diameter. The CASINO physical models used were *Mott by Interpolation* for cross-sections [25], and the *Random Number Generator* of Press et al [26].

The simulation results indicate that the X-ray generation volume is largest in the epoxy resin and has a diameter of ~500 nm. This is shown in Fig. 3 (b), in which the volume is delimited by electrons having a sufficient energy to generate X-rays from the sulfur atoms, also known as the K α for Sulfur (2.3 kV). Fig. 3 (a) shows the electron trajectories in the epoxy materials for illustrative purposes. The simulation results above thus indicate that the EDX analysis in this work is conducted with a spatial resolution of approximately 0.5 μ m.

The EDX line analysis of the PES/epoxy interface is shown in Fig. 4. The sulfur element is chosen as a trace element during the EDX analysis since it is present in PES. However, it should be noted that sulfur is also present in the epoxy resin in much smaller quantities due to the DDS hardener, which explains why the Sulfur K α intensity in the epoxy does not return to the noise level, as seen in the first ~20 μ m of the line analysis (which correspond to an area outside of the specimen). Interdiffusion of PES and epoxy is observed to extend over a distance of ~150 μ m. Hence, PES shows a larger interdiffusion region than PEI and PSU (~53 μ m and ~67 μ m, respectively) without the presence of phase separation mechanisms, as seen in Fig. 1 c). This result is expected considering the higher compatibility with epoxy resin, which was indicated with the lower *RED* value for PES in Table 1.

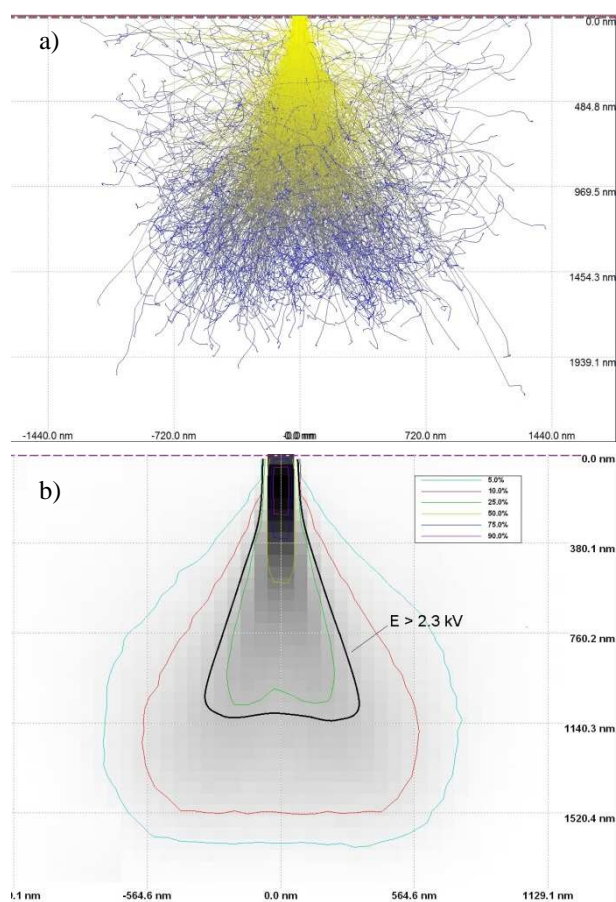


Fig. 3. CASINO simulation of a 10 kV electron beam in epoxy resin, showing (a) electron trajectories and (b) electron energy distribution in epoxy resin.

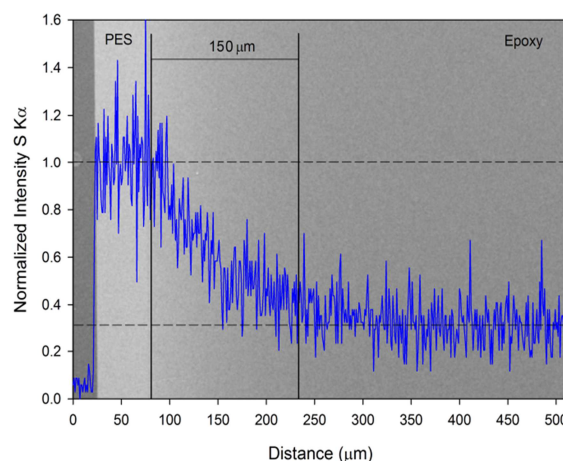


Fig. 4. Normalized Sulfur K α X-ray intensity across the PES/epoxy interface (note that the first 20 μ m are outside the specimen).

3.3 Atomic Force microscopy

Atomic Force Microscopy in tapping mode was used in this section to obtain a higher resolution image of the interface morphology, by generating height contrast and phase angle shift images. The first imaging technique reveals topographical information about the specimen, while the latter provides qualitative information related to hardness and viscoelastic behavior of the material [4]. With phase imaging, harder and less viscoelastic material will appear brighter (a larger phase shift angle) whereas softer and more viscoelastic materials will appear darker (a smaller phase shift angle) [27].

Fig. 5 shows AFM imaging of a PEI/epoxy interface. The high resolution of AFM (a few tens of nanometers) allows smaller phases to be detected, leading to a new measurement of the interdiffusion width of $\sim 56 \mu\text{m}$. This, however, represents a variation from the initial

measurement obtained through optical microscopy of less than 5%, and simply confirms these measurements.

4 Conclusion

Morphological and quantitative analyses of interfaces formed between epoxy and several thermoplastic was carried out through optical microscopy, SEM-EDX, and AFM. All three thermoplastics exhibited a high compatibility with epoxy resin. Interdiffusion in the order of $50 - 70 \mu\text{m}$ was observed for PEI and PSU, however this was coupled with phase separation phenomena. These measurements were verified with those taken by AFM, and found to be within 5%. The size of the phases formed varies across the interface and is believed to be dictated by the epoxy curing kinetics and the curing cycle.

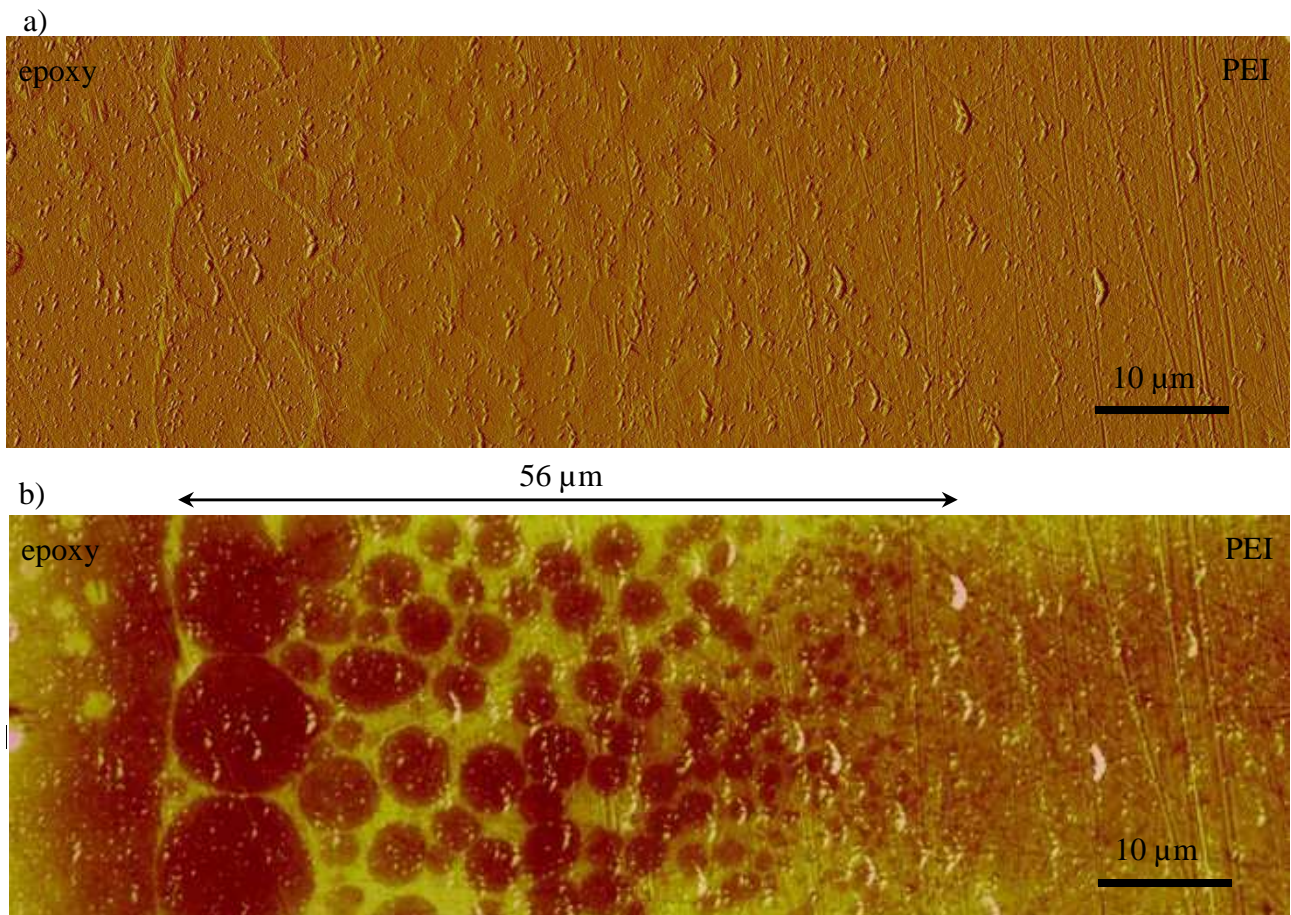


Fig. 5. AFM images a) phase image and b) height image of PEI/epoxy interface, showing an interdiffused region with phase separation.

The interdiffusion mechanism with PES did not result in phase separation and the interdiffusion depth was in the range of 150 μm as detected by SEM-EDX. The absence of phase separation was an indication of excellent thermodynamic compatibility with epoxy resin and is in agreement with the solubility parameter predictions.

The solubility parameter approach was found to be a useful tool for predicting polymer compatibility with epoxy resin and was verified with amorphous thermoplastics. Nevertheless, the solubility parameter is mainly suitable for non-reactive thermodynamic systems, and does not consider the epoxy curing reaction (i.e.: it uses the solubility of each individual epoxy component prior to cross-linking). This can be considered as an area of strong interest for gaining a better understanding of interphase formation between epoxies and thermoplastics.

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