MORPHOLOGICAL CHARACTERIZATION OF BENZOXAZINE RESINS USED FOR FST APPLICATIONS IN THE AIRCRAFT INDUSTRY

M.R. Gude[a*], A. Sanchez-Blazquez[b], R. Avila-Dominguez[b], F. Rodriguez-Lence[a]

[a]*Foundation for the Research, Development and Application of Composite Materials (FIDAMC), Av. Rita Levi Montalcini 29, 28906 Getafe, Spain*
[b]*Airbus Operations, Materials and Processes, Composite Technology, Av. John Lennon s/n, 28906 Getafe, Spain*
**maria.r.rodriguez@fidamc.es*

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Abstract
The morphology of two benzoxazine composites has been analyzed using the atomic force microscopy as the main experimental technique. These composites have been manufactured using two different technologies: autoclave and RTM. The prepreg resin for the composite cured in autoclave includes a thermoplastic in its formulation. The carbon fibre fabric for the textile and infusion composite manufactured by RTM is binder-coated, this binder is a thermoplastic polymer. In both cases, the presence of these additives originates complex and heterogeneous two-phase morphologies. The cure cycle evaluation has revealed that the two analyzed benzoxazine composites present robust morphology within and in the evaluated parameters of the outer limits of their respective industrial processing windows.

1. Introduction

Thermosetting polymers generally present a good combination of mechanical properties and thermal resistance. They show high design flexibility, allowing tailoring their final properties to a wide range of applications, such as matrix for composite materials in the aircraft industry.

Epoxy resins are the most common matrices for carbon fibre composites in structural applications. However, they cannot be used in aircraft components that must fulfill stringent fire-smoke-toxicity (FST) requirements [1]. Bismaleimides are currently the resins used in these applications, but they are expensive in terms of material and processing conditions (high temperature and long curing time) [2]. In the last years, an alternative resin for FST applications has been introduced for aeronautical applications: the benzoxazine resins. They fulfill stringent FST requirements and have cure temperature similar to that of epoxy resins, presenting also good mechanical properties and low cure shrinkage, among other advantageous properties [3, 4].

As other thermosetting resins, benzoxazines are usually modified by the addition of different additives. When the modifier is a polymer, either thermoplastic or elastomeric, it may be miscible or not-miscible in the benzoxazine resin. In addition, the solubility of the polymer in the resin may vary during cure, depending on several parameters such as heating rate, cure

temperature and time and intermediate dwells. As a consequence, the morphology may be influenced by the curing conditions. If the polymer is miscible in the cured resin, a homogeneous morphology with only one phase is obtained. However, if it is not completely miscible, complex morphologies with two or more different phases can be obtained. In this case, the morphological characterization implies the study of the different morphological features. Various morphological parameters, such as particle size, particle size distribution and matrix-to-particle adhesion, that may be influenced by the curing conditions, play an important role in the mechanical properties of the cured blends, in particular in the toughening effect.

The atomic force microscopy (AFM) technique has evolved into a useful and powerful tool for advanced characterization of materials. In this technique, the sample surface is scanned with a probe consisting of a sharp tip. In tapping mode, the tip scans the surface while oscillates at the resonant frequency of the cantilever. The changes in the phase of the oscillation motion depend on the sample stiffness. As a consequence, the resulting phase images are very useful for morphological analysis, as they allow the identification of components with different stiffness [5]. Although the assignment of colours to more/less stiff surfaces may change with the scanning parameters, the stiffer areas usually have a brighter colour in the phase image with the tapping conditions used in this case [3, 5].

In this work, the morphology of two carbon fibre/benzoxazine composites with thermoplastic polymers in their composition and cured with their respective nominal cure cycles has been analyzed. Once the different phases found in each case have been identified, laminates cured with different cycles within and in the outer limits of the industrial processing windows have been studied, in order to determine if the morphology is influenced by the cure cycle parameters. The main technique used for this cure cycle evaluation from the morphological point of view was the atomic force microscopy. Complementary experimental techniques used were optical microscopy, scanning electron microscopy (SEM) and infrared spectroscopy (FTIR).

2. Experimental

2.1 Materials

Two benzoxazine-based thermoset resins for two different composite manufacturing technologies (autoclave and RTM) have been evaluated.

The prepreg has been manufactured using benzoxazine-based resin and standard modulus carbon fibre fabric. Prepreg composites have been cured in autoclave. The nominal cure cycle of this composite is 3 h at 185 ºC, with a heating rate of 1.8 ºC/min and a pressure of 6 bar. For the cure cycle evaluation, thirteen cure cycles have been evaluated, modifying the cure temperature from 175 to 200 ºC, the cure time from 2 to 9 h, the heating rate from 0.2 to 3.5 ºC/min and the pressure from 2 to 8.3 bar.

Textile and infusion composites have been manufactured by RTM using a benzoxazine resin and a binder-coated carbon fibre fabric. The nominal cure cycle is 3 h at 130 ºC plus 3 h at 185 ºC, with a heating rate of 1.8 ºC/min and a free stand post-cure at 200 ºC for 1 h. For the cure cycle evaluation, four cure cycles have been evaluated, modifying the cure temperature, heating rate and the intermediate dwell.

2.2 Experimental techniques

The AFM used was a Nanoscope Multimode microscope with a Nanoscope V controller (Digital Instruments®) and two different scanners: type E (maximum scan size: 10 x 10 µm) and type J (maximum scan size: 125 x 125 µm). All AFM analyses have been carried out in tapping mode using silicon tips with nominal resonance frequency of 320 kHz. Height and phase images were recorded simultaneously for each analyzed area. In order to get a sample surface as flat as possible, an ultramicrotome Leic Ultracut UC6 with diamond knife was used for sample preparation.

The morphological analysis by optical microscopy was performed on polished cross sections using a Nikon Elipse LV150 microscope.

A scanning electron microscope (SEM) EVO MA15 (Zeiss) equipped with chemical microanalysis by EDS (energy dispersive X-ray spectroscopy) INCA 330 (Oxford) was also used as a complementary morphology characterization technique for the prepreg composite.

In all cases, cross sections have been analyzed.

3. Results

3.1 Prepreg composite

The optical microscopy study of the prepreg composite cured with the nominal cycle reveals a heterogeneous two-phase morphology (Figure 1). For the identification of the phases in the different zones of the laminate, AFM and SEM have been used.

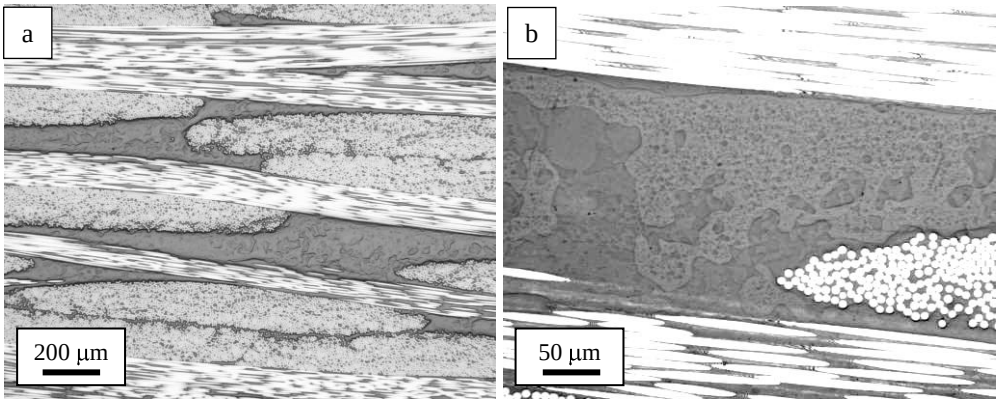

Figure 1. Optical micrographs of prepreg composite cured with nominal cycle: a) 50x, b) 200x.

First, the intra-ply zone has been analyzed. AFM micrographs of this zone are shown in Figure 2. A thermoset phase with nanoparticles (brilliant yellow particles in the phase image of Figure 2b) has been observed. The SEM micrograph (Figure 3) shows a homogeneous phase in the intra-ply zone. The results of the EDS microanalysis of this zone reveal the presence of silicon (Table 1). The nanoparticles contain this element, confirming their presence in the thermoset phase of the intra-ply zones.

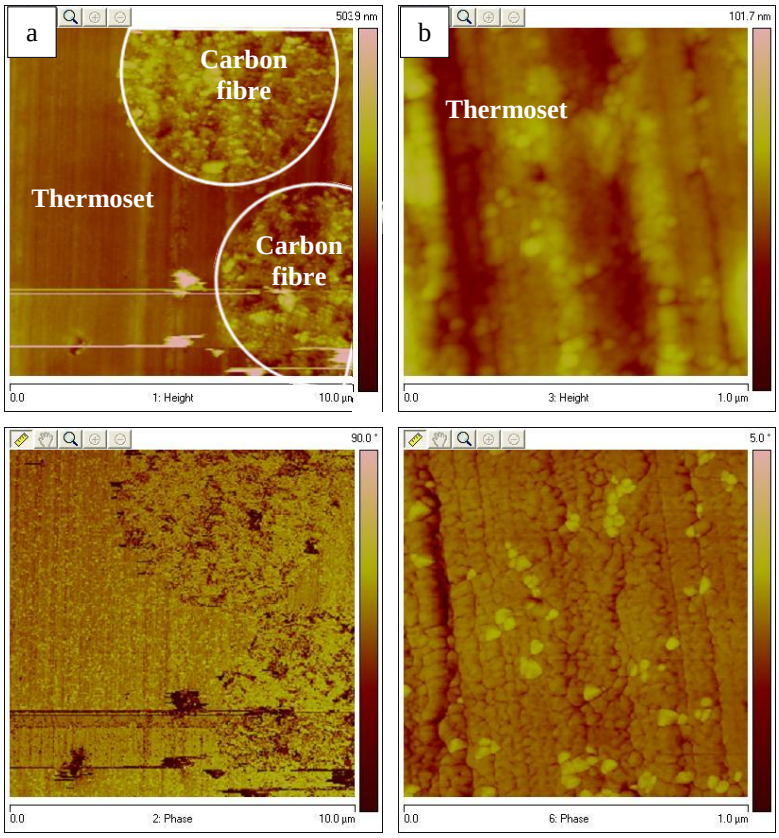

Figure 2. AFM micrographs of prepreg composite cured with nominal cycle, intra-ply zone: height (upper) and phase (lower) images.

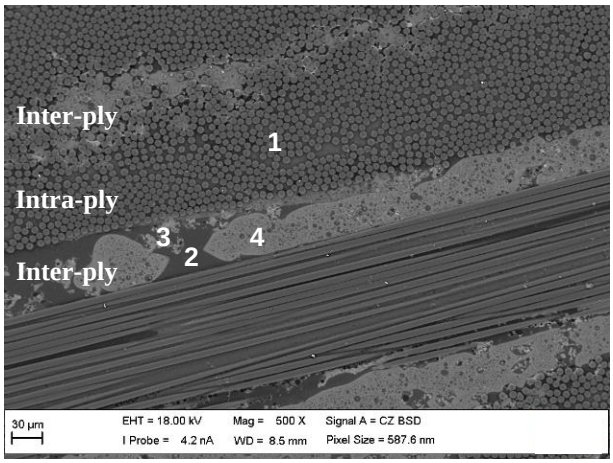

Figure 3. SEM micrograph of the prepreg laminate with nominal cure cycle.

Spectrum	C	O	Si	S
1	77.8	17.7	4.5	-
2	81.9	18.1	-	-
3	61.8	23.4	14.8	-
4	70.1	17.7	-	12.2

Table 1. EDS microanalysis (weight %) of the points selected in Figure 3.

In the inter-ply zones, the two different phases observed by optical microscopy have been analyzed by AFM (Figure 4). One of them is the same themoset phase (TS) with nanoparticles found in the intra-ply zones. The difference is that in this case the nanoparticles are heterogeneously distributed. This heterogeneous distribution can be observed in Figures 4a and 4c, where large thermoset domains present zones with and without nanoparticles. Also, the smaller spherical thermoset domains shown in Figure 4b do not have nanoparticles.

In the SEM micrograph (Figure 3), spectrum 2 corresponds to a zone of the thermoset phase without nanoparticles (no silicon has been detected in the EDS analysis) while spectrum 3 is thermoset resin with a high concentration of nanoparticles (higher silicon content than in the intra-ply zone).

The other phase found in the inter-ply zones is a thermoplastic polymer (TP). The point 4 in the SEM micrograph corresponds to this phase. In addition to carbon and oxygen, the EDS spectrum contains sulfur, that is a chemical element characteristic of this thermoplastic polymer included in the resin formulation. The absence of sulfur in the spectrums 1, 2 and 3 confirms that there is there is not thermoplastic dissolved in the thermoset phase.

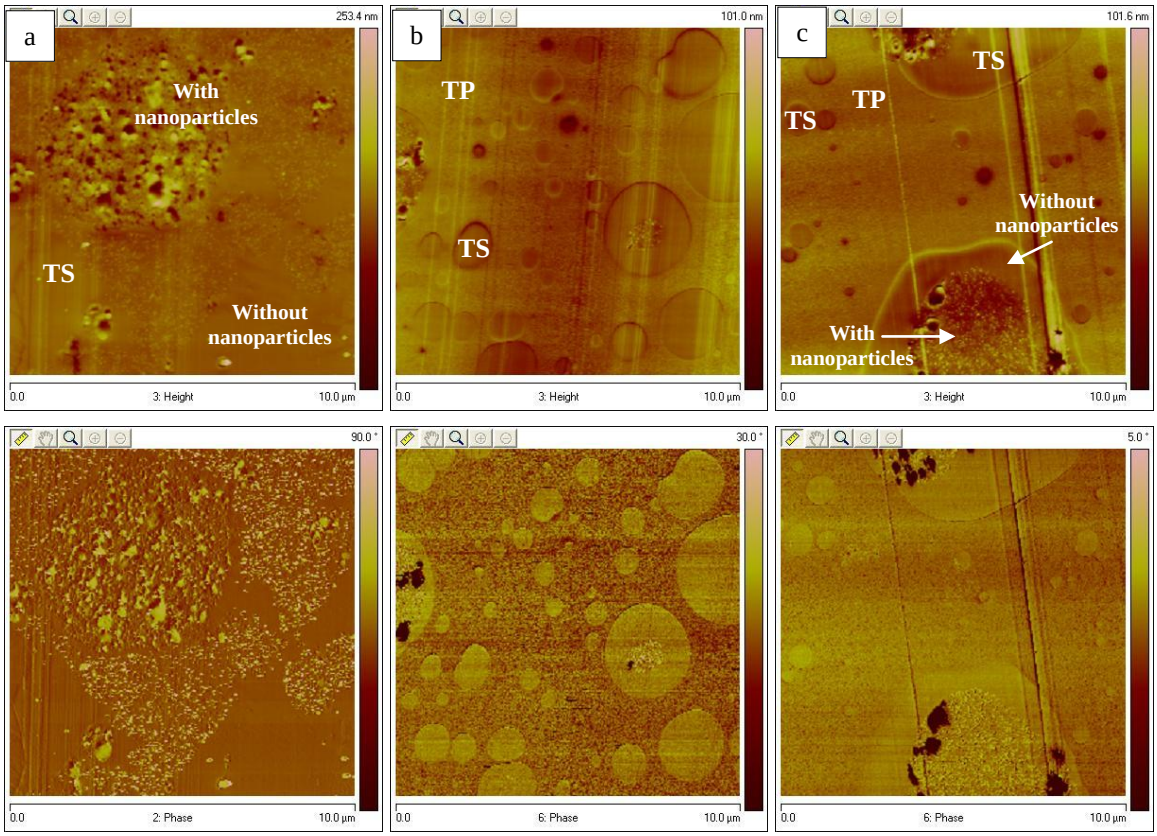

Figure 4. AFM micrographs of prepreg composite cured with nominal cure cycle, resin-rich zone: height (upper) and phase (lower) images.

For the cure cycle evaluation of the prepreg composite from the morphological point of view, samples cured with different cycles have been analyzed by optical microscopy and AFM. The same morphology has been found independently on the cure cycle, proving that this benzoxazine composite presents a robust morphology. As an example, optical micrographs of the inter-ply zone of laminates with three different cure cycles are shown in Figure 5.

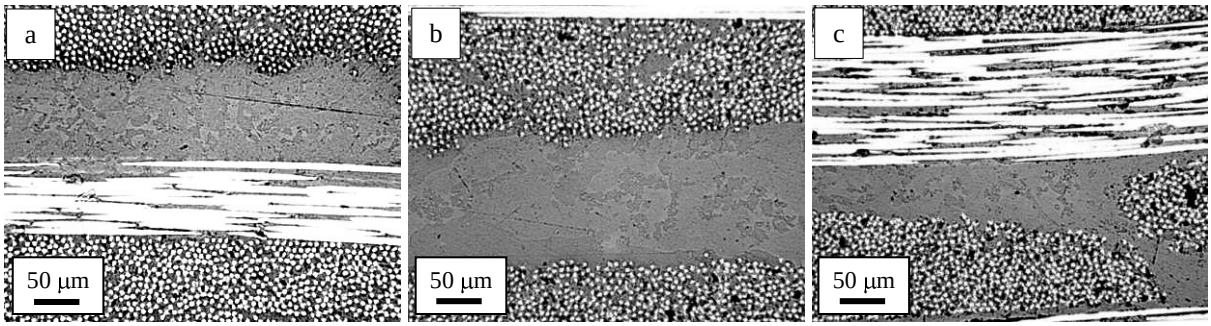

Figure 5. Optical micrographs of prepreg composites with different cure cycles: a) 175ºC/2h 50min, b) 195ºC/ 3h 10min, c) 200ºC/2h.

3.2 Textile and infusion composite

The infusion benzoxazine resin presents a homogeneous one-phase morphology. The presence of a thermoplastic binder in the carbon fibre fabric used for the textile and infusion composites originates a heterogeneous two-phase morphology, as it can be observed in Figure 6a. As it was previously observed in the prepreg composite, in the intra-ply zones there is a thermoset phase (Figure 6b). The difference with the prepreg composite is that the textile and infusion composite does not include nanoparticles in its formulation. The thermoplastic binder (TP) has been found in the inter-ply zones. Here, the thermoset and thermoplastic phases are heterogeneously distributed, as it can be observed in Figures 6a, 6c and 6d.

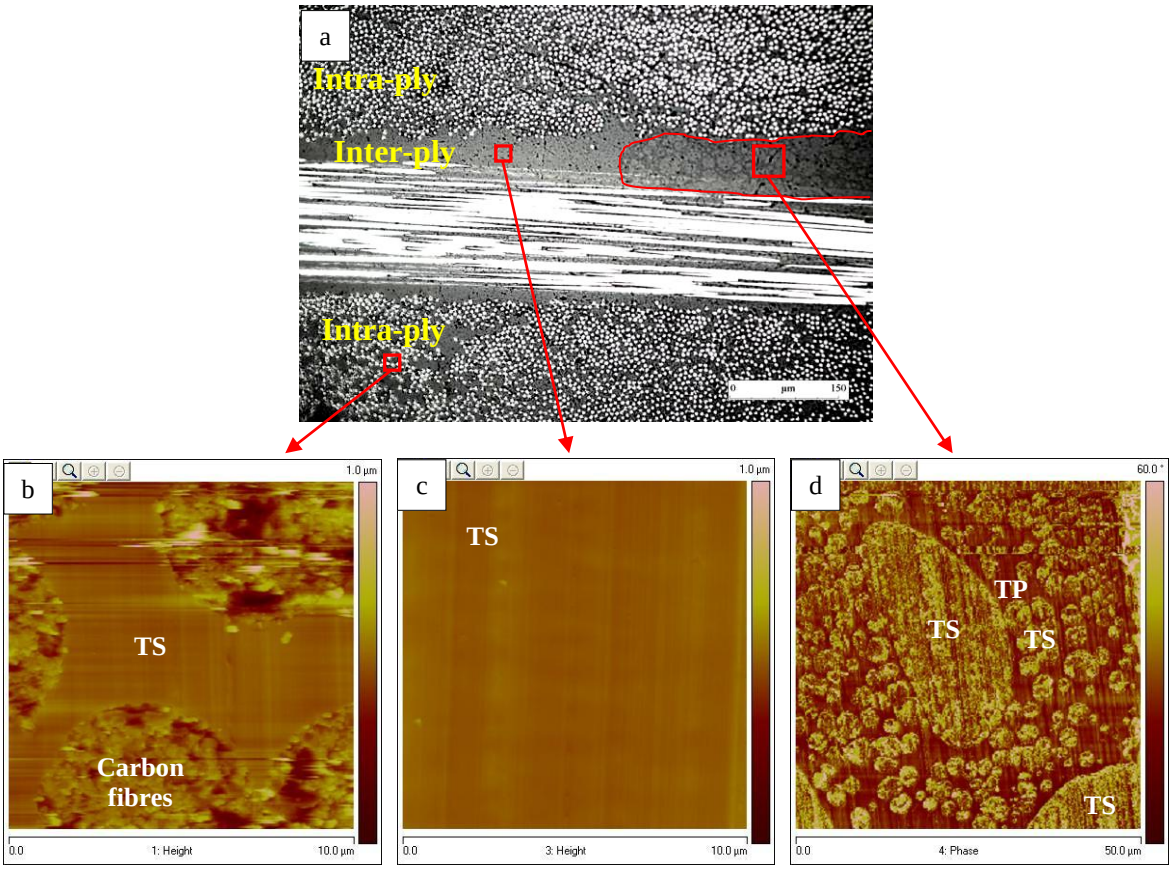

Figure 6. Optical and AFM micrographs of the textile and infusion composite cured with nominal cycle.

For the cure cycle evaluation, four textile and infusion panels with different cure cycles have been analyzed. The same two-phase morphology has been observed in all of them using

optical microscopy and AFM. As an example, Figure 7 shows AFM micrographs of three panels with different cure cycles. It has been found that this material presents a robust morphology.

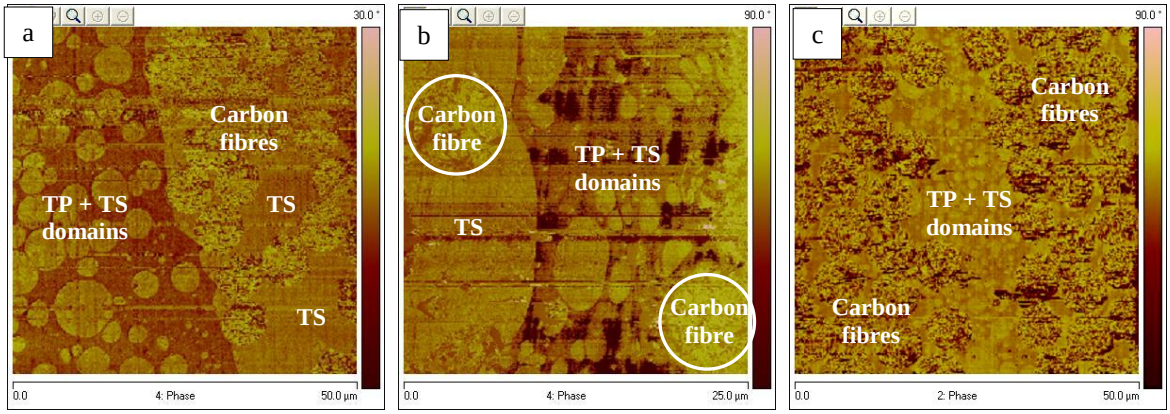

Figure 7. AFM micrographs of textile and infusion composites with different cure cycles: a) cure temperature 160 ºC, b) heating rate 0.2 ºC/min without dwell, c) heating rate 3.5 ºC/min, cure temperature 200 ºC without dwell.

4. Conclusions

The two analyzed benzoxazine-based composite materials present heterogeneous two-phase morphology due to the presence of thermoplastic additives (included in the resin formulation in the case of the prepreg resin and the binder in the textile and infusion composite).

The same phase distribution has been found in both cases: thermoset phase in the intra-ply zones and thermoset and thermoplastic phases heterogeneously distributed in the inter-ply zones. The only difference is that the prepreg composite includes nanoparticles in its formulation. They are homogeneously distributed in the intra-ply and heterogeneously distributed in the inter-ply zones.

The two benzoxazine-based composites present robust morphology within their respective industrial processing windows. The parameters evaluated in the outer limits of these processing windows also reveal robust morphology.

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