

## ADDITION OF A BLOCK COPOLYMER INTO CARBON FIBERS/EPOXY COMPOSITES PROCESSED BY RTM: MICROSTRUCTURES AND MECHANICAL PROPERTIES

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### Abstract

The addition of a blend of phenoxy and a block copolymer (MAM) into a carbon fibers/epoxy composite processed by RTM leads to an important improvement of the mode I fracture toughness ( $G_{IC}$ ) as compared to phenoxy or MAM added individually. The explanation of the  $G_{IC}$  increase is based on a two-step study. The first step treats of the interdiffusion between a phenoxy/MAM filament and RTM6 resin. The second step deals with an observation of the microstructures of different phenoxy/MAM RTM panels. The results obtained during the present study seems to indicate that phenoxy and MAM have a synergistic effect on the out-of-plane fracture toughness of a RTM manufactured composite. It also seems that a critical range of concentration of the blend into the RTM6 resin leads to a microstructure gradient responsible of the  $G_{IC}$  increase.

### 1 Introduction

Since a few decades, composite materials based on carbon fabrics and epoxy resin are increasingly used for structural applications. Such composites exhibit excellent mechanical properties, low density, high thermal and chemical resistance. However, because of their high crosslinking density, they are characterized by a poor impact damage resistance. One of the common ways to improve their toughness consists in adding a ductile phase like a thermoplastic (e.g. phenoxy, polyethersulfone or polyamide) to the epoxy resin. Block copolymers containing an elastomer sequence in their molecular structure are also used (e.g. styrene-butadiene-methacrylate (SBM)<sup>1</sup> or methyl methacrylate-butyl acrylate-methyl methacrylate (MAM)<sup>2-4</sup>). Indeed, high improvement of fracture toughness of epoxy resin has been shown by a lot of studies with SBM. As MAM has only been little considered in epoxy resin, this block copolymer is investigated in this work.

However, it is well known that addition of a thermoplastic into epoxy resin dramatically increases its viscosity, even at low concentrations. This increase is an inconvenient for the production of composites using resin transfer molding (RTM). Therefore, in order to counteract this drawback, an alternative procedure for incorporation of MAM into the epoxy resin is proposed. This procedure is based on a concept exploiting a soluble thermoplastic (phenoxy) as carrier of additives like nanofillers (carbon nanotubes, clays,...)<sup>5</sup>. In that case,

the temperature program is adapted to promote dissolution and diffusion (swelling) of the thermoplastic into the RTM mold leading to a distribution as homogeneous as possible into the composite laminate.

The objective of this work is to show, as a first step, the influence of the addition of a phenoxy/MAM blend into a composite panel processed by RTM. As a second step, this study try to explain the reason why, depending of the generated microstructures, the blend can significantly improve fracture toughness more significantly than in panels with only phenoxy<sup>6</sup> or MAM in quite similar concentration. In order to reach these objectives, the study is based on a simplified system with a filament of phenoxy/MAM blend into RTM6 resin. Finally, observations are realized on RTM panels in order to correlate the microstructures and the fracture toughness.

## **2 Materials and testing methods**

Two tougheners are selected: a block copolymer and an amorphous thermoplastic. The block copolymer is a methyl methacrylate-butyl acrylate-methyl methacrylate (MAM) polymer (Nanostrength® M52 from Arkema) and the thermoplastic is poly hydroxylether of bisphenol A (phenoxy) (InChemRez® Phenoxy Resin PKHB from InChem Corporation). In order to stay below the phase inversion (30 wt.% MAM), a phenoxy/MAM blend 75/25 wt.% is produced by melt-processing (5 minutes at 150 rpm) in a DSM Xplore 15 ml micro-compounder at 220 °C. After the recirculation period, phenoxy, MAM or blend filaments of 100 µm were drawn with a DSM Xplore Spin Line and films of 40 µm and 80 µm were casted with a DSM Xplore Micro Film Device.

Simplified systems consisting in a filament of phenoxy, MAM or phenoxy/MAM blend placed into RMT6 resin between two glass slides were cured into a Mettler FP82HT hot stage monitored by a Mettler FP90 central processor. During the curing cycle, the samples were observed with an Olympus optical microscope.

Composite panels (440x330x4.4mm) were produced by vacuum-assisted resin transfer molding (VARTM) with an Isojet piston using Hexflow RTM6 and HexForce® G0926 supplied by Hexcel Composites respectively as epoxy resin carbon fabrics and as reinforcement. The different RTM panels contain twelve layers of carbon fabrics (around 67 wt.%) with a quasi-isotropic [(+45/-45)/(0/90)]<sub>3</sub>S lay-up. A modified cure cycle of the RTM6 resin (1°C/min ramp from 80°C to 120°C, dwell of 30 minutes at 120°C, 1°C/min ramp from 120°C to 180°C followed by a 180°C isotherm for 2 hours) was applied. A first panel as reference with RTM6 resin (P1) and a second one with 4 wt.% of MAM previously dissolved into the resin (P2) were produced. Two additional panels were produced with phenoxy (P3) or phenoxy/MAM (P4) films of 40 µm placed between each carbon layer. Finally, two panels were produced with phenoxy (P5) or phenoxy/MAM (P6) films of 80 µm placed every two carbon layers. For P3 and P5, 20 wt.% phenoxy were reached in the RTM6 resin. For P4 and P6, 16 wt.% phenoxy and 4 wt.% MAM where reached. In each panel, a polyimide insert was placed in the preform mid-plane in order to initiate crack propagation during double cantilever beam (DCB) tests performed according to ASTM D5528-01. Samples were loaded in tensile mode using a Zwick Universal testing machine, at 1 mm/min.

The polished cross-sections of the RTM composite panels were examined by Scanning electron microscopy (SEM) using a LEO 982 (Zeiss) operating at 3 kV after etching (24 hours) of MAM and phenoxy respectively with toluene and tetrahydrofuran. The delaminated surfaces after DCB test where also observed by SEM with the same procedure and equipment.

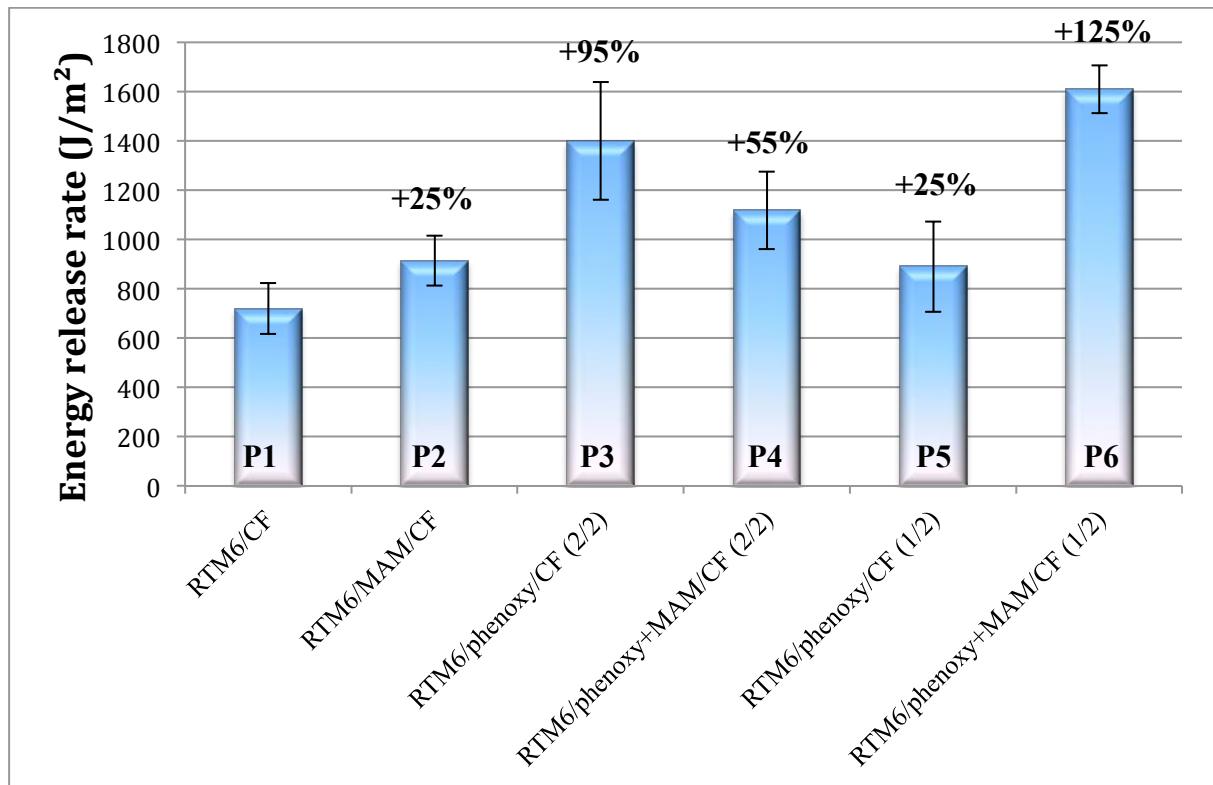
### 3 Results and discussion

When a filament or a film of thermoplastic is placed into an epoxy resin, it dissolves and diffuses leading to a concentration gradient and consequently to a microstructure gradient. Such a mechanism was previously explained by the diffusion of the RTM6 precursors into the thermoplastic leading to a swelling of the thermoplastic. In this part, the results of a study concerning the effect of these concentration and microstructure gradients on the toughness of different composite panels are presented. Panels with different layups and with different kind of films (phenoxy, MAM or blend) were produced. In order to explain the influence of the addition of phenoxy, MAM or phenoxy/MAM blend on the  $G_{IC}$  values, a simplified system with a filament placed into RTM6 resin was studied by optical microscopy and by infrared spectroscopy in a first time. Secondly, cross-sections of the RTM panels are examined by SEM and the microstructures are compared with those of the simplified systems. Finally, the delaminated surfaces after DCB measurements were also examined by SEM and compared with the previously observed microstructures.

#### 3.1 Mechanical measurements

As it was related in the experimental part, a first panel was produced as reference with RTM6 (P1) and a second one with 4 wt.% MAM previously dissolved into the resin (P2). Two additional panels were produced with phenoxy (P3) or phenoxy/MAM (P4) films of 40  $\mu\text{m}$  placed between each carbon layer. Two last panels were produced with phenoxy (P5) or phenoxy/MAM (P6) films of 80  $\mu\text{m}$  placed every two carbon layers. So, for the latter, there was no thermoplastic in the mid-plan before curing. It is expected that during the curing cycle, after dissolution, the thermoplastics will diffuse through the carbon fibers on the thickness of the panel and reach the mid-plan.

The failure propagation in the mid-plan of the six RTM panels was measured by DCB. The critical energy release rate ( $G_{IC}$ ) is presented on Figure 1 for these panels.



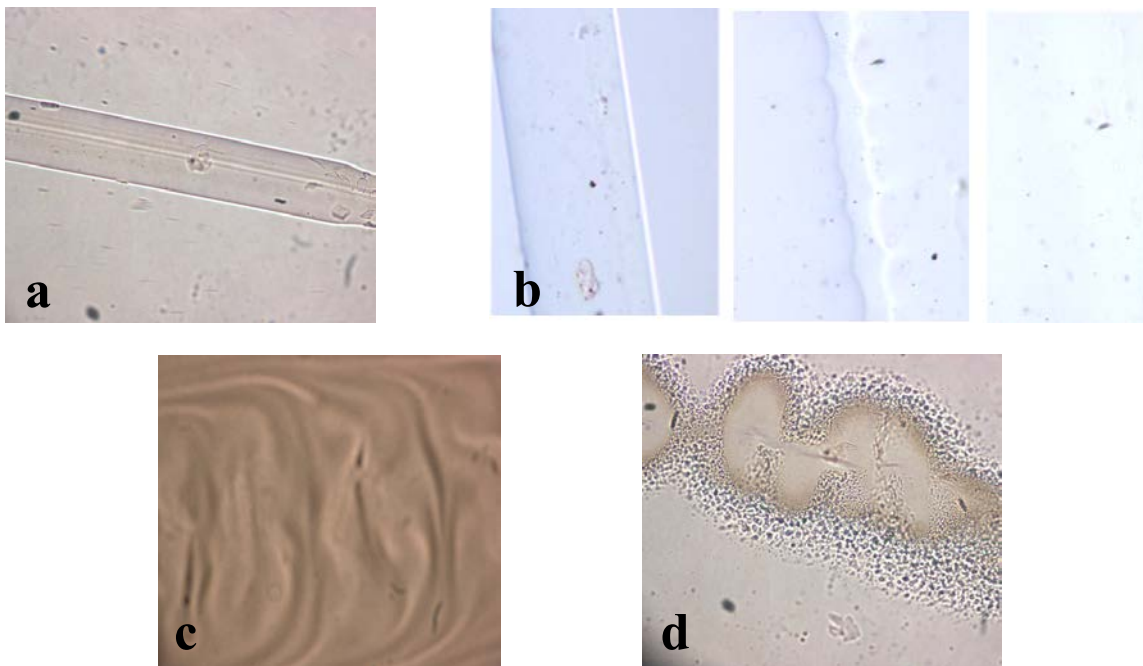
**Figure 1.** Fracture toughness ( $G_{IC}$ ) of RTM panels (a) without thermoplastic films (P1); (b) 4 wt.% MAM injected with the resin (P2); (c) 40  $\mu\text{m}$ -thick phenoxy films between every carbon layers (P3); (d) 40  $\mu\text{m}$ -thick phenoxy/MAM blend films between every carbon layers (P4); (e) 80  $\mu\text{m}$  thick films of phenoxy every two carbon layers (P5) and (f) 80  $\mu\text{m}$  thick films of phenoxy/MAM blend films every two carbon layers (P6).

With an addition of MAM (P2), the  $G_{IC}$  increases by 25%. With an incorporation of phenoxy,  $G_{IC}$  is improved by 95% for panel P3 and 25% for panel P5. With the phenoxy/MAM blend, an improvement of 55% is obtained for panel P4 and 125% for panel P6. Due to the layup, the thermoplastic concentration in the mid-plane of panel P3 and panel P5 is totally different with a higher concentration for P3. The same layup is used with panel P4 and panel P6, so higher value of  $G_{IC}$  was expected for panel P4 in place of panel P6. The toughness of panel P6 is better than panel P4 but is also better than all the other panels.

### 3.2 Dissolution of filaments into RTM6 resin

The dissolution of thermoplastic filaments (MAM, phenoxy and phenoxy/MAM blend) in the precursors of the RTM6 resin and their diffusion into the filaments are studied and the generated microstructures are observed.

A filament of phenoxy, MAM or phenoxy/MAM blend was placed into a droplet of RTM6 resin (Figure 2). The RTM temperature program was applied to the sample and the diffusion distance was measured after the reaction induced phase separation (RIPS).



**Figure 2.** Optical microscopy images of a filament of (a) phenoxy/MAM blend into RTM6 resin before dissolution; (b) phenoxy during dissolution and after phase separation; (c) MAM after dissolution and phase separation; (d) phenoxy/MAM blend after dissolution and phase separation.

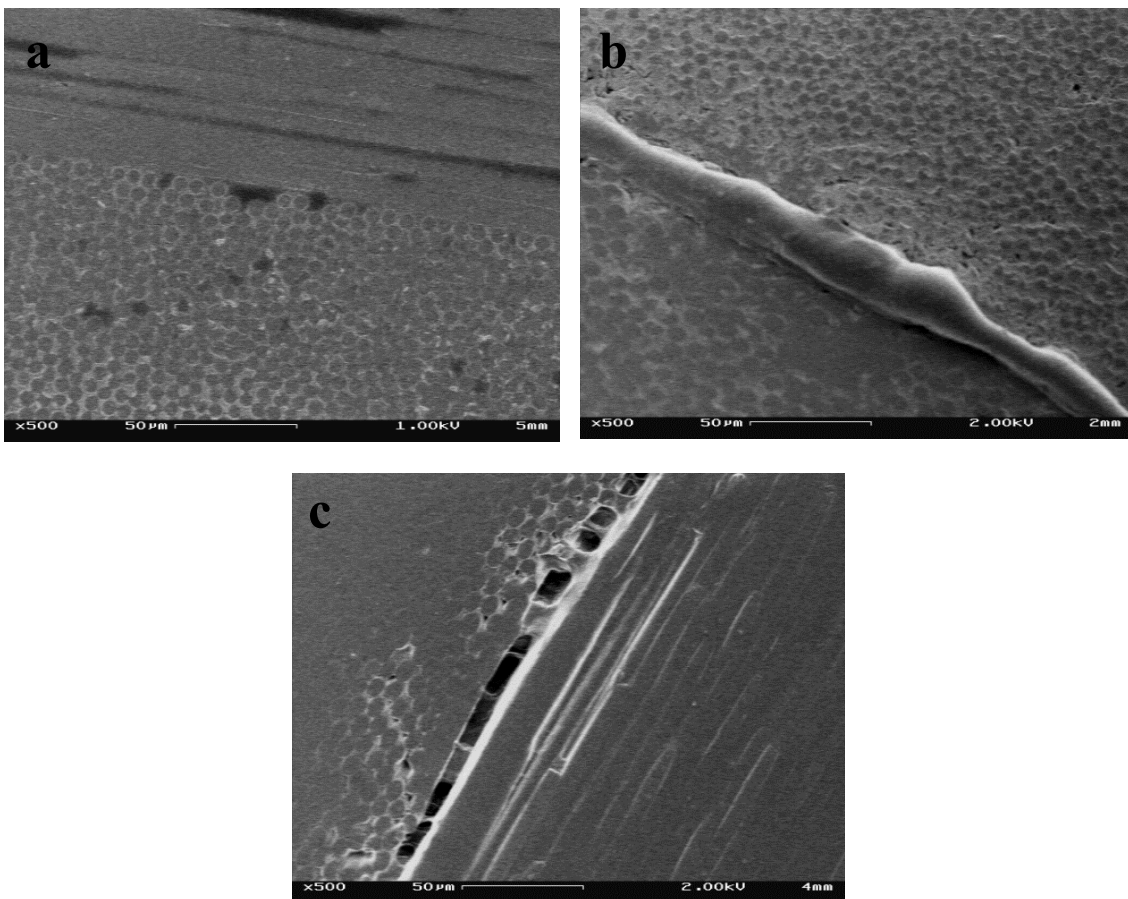
Filaments of phenoxy, MAM or phenoxy/MAM blend of 100 $\mu\text{m}$  diameter diffuse respectively on distances of 800, 2000 and 1300 $\mu\text{m}$ . For phenoxy or MAM alone, a linear diffusion front can be observed without any microstructures but small nodules can only be detected around the phenoxy/MAM filament. In order to correlate the microstructure gradient and the

concentrations, a mapping was performed by FTIR spectroscopy and profiles were evaluated using an isolated signal around  $1730\text{ cm}^{-1}$ . The diffusion distance of the MAM determined by FTIR spectroscopy and with optical microscopy are almost identical. A Gaussian distribution of the concentration is obtained. This result means that the small nodules are only observed in the areas where the MAM concentration is the lowest.

### 3.3 Microstructures of RTM panels

Due to the swelling distances of the different thermoplastics (between  $800$  and  $2000\text{ }\mu\text{m}$ ), and the interlayer spaces ( $370\text{ }\mu\text{m}$ ) in the RTM panels, a diffusion of the thermoplastic films through the fibers up to the mid-plane of the RTM panel can be expected for panels P5 and P6.

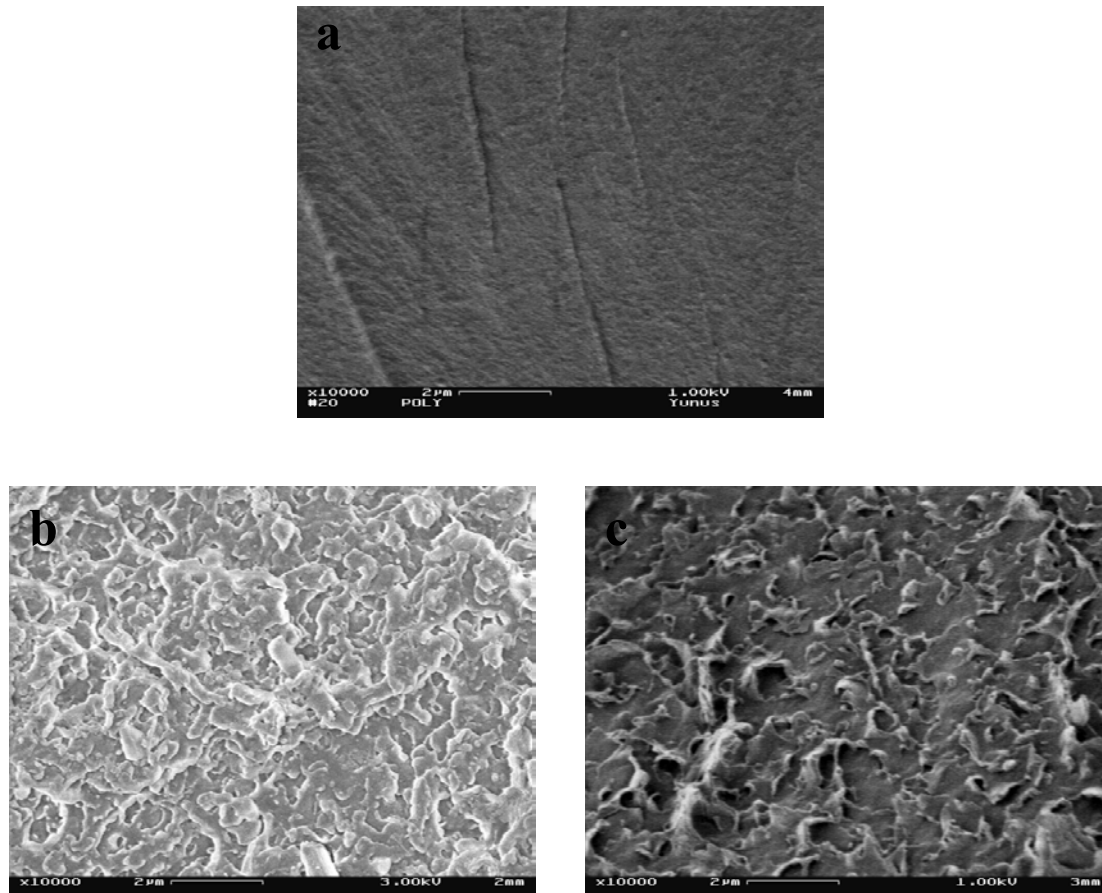
To confirm this hypothesis, the cross-section of panel P6 is analysed by scanning electron microscopy (Figure 3). In order to reveal the microstructures, after a polishing step, a selective etching was performed on the sample with toluene to dissolve the MAM copolymer on the one hand and on the other hand a complete etching with THF was performed to dissolve the MAM and the phenoxy polymers.



**Figure 3.** SEM micrographs of panel P6 cross-section (with phenoxy/MAM blend films every two carbon layers) (a) without etching; (b) with a toluene etching and (c) with a THF etching.

The microstructures observed after etching are quite similar to the ones previously observed after dissolution of a phenoxy/MAM filament. The micrographs show a diffusion of the thermoplastic through the carbon fibers with a concentration gradient. Furthermore, on the initial location of the phenoxy/MAM film, the continuous phase is phenoxy. Cavities can be observed around the film on the Figure 2b (with a selective etching with toluene).

After DCB measurements, the delaminated surfaces of the different samples were also examined by SEM (Figure 4).



**Figure 4.** SEM images of the delaminated surfaces after DCB measurement on the samples (a) without thermoplastic films (P1) (b) with 40 µm-thick phenoxy/MAM blend films between every carbon layers (P4) (c) with 80 µm thick-films of phenoxy/MAM blend films every two carbon layers (P6).

Comparing the delaminated surfaces, the reference panel (P1) presents a smooth surface and the panels P4 and P6 a rough surface with two different microstructures. The delaminated surfaces of the samples with the phenoxy/MAM blend every layer (P4) and every two layers (P6) are completely different. The panel P6 image (Figure 4c), show a diffusion of the thermoplastic through the fibers increasing the toughness in the mid-plan. For the panel P5, some empty nodules which can be removed by etching with toluene are observed on the complete surface.

### 3.4 Discussion

A nodular microstructure can only be observed for the phenoxy/MAM blend filament into the resin where the thermoplastic concentration is the lowest. The same microstructure is observed on the cross-section of the P6 panel and finally on the delaminated surface after DCD measurement. Panel P4 presents a high thermoplastic concentration in the mid-plan. Identified as a phenoxy continuous phase in Figure 3b and confirmed in figure 4b. Panel P6 presents a low thermoplastic concentration in the mid-plan and a nodular microstructure (Figure 4c) corresponding to the surrounding nodules in Figure 2d.

As it is possible to dissolve these nodules with a selective etching of the MAM, it seems that they are composed of pure MAM or shells of MAM containing phenoxy. While the highest phenoxy concentration possible is required to improve toughness of composite panels, only a small amount of blend is sufficient with an adequate microstructure.

#### 4 Conclusions

A significant improvement of the toughness is observed with an addition of MAM, phenoxy or phenoxy/MAM as interleaves between the carbon fabrics of RTM panels based on an RTM6 resin matrix. The higher improvement is observed for the panel P6 with phenoxy/MAM films every two carbon layers. By comparing panels with phenoxy/MAM films every carbon layers (P4) to panel P6, it appears that the higher improvement is reached with the lowest thermoplastic concentration in the interlayer where the DCB test is performed. The diffusion of a Phenoxy/MAM filament into the RTM6 leads to a Gaussian distribution of the concentration and to a microstructures gradient. The diffusion of a phenoxy/MAM film through the carbon fabrics when it is used as interleave in a composite is also demonstrated and the same microstructures than for the filament are generated. The nodular microstructure, defined as pure MAM or MAM shells containing phenoxy nodules, is only observed where the thermoplastic concentration is the lowest.

As expected, the delaminated surfaces exhibit a thermoplastic continuous phase for panel P4 and a nodular phase for panel presenting a lower concentration of blend (P6). For pure phenoxy, the continuous phase generated by a high thermoplastic concentration is preferred to improve the toughness while only a small amount of the phenoxy/MAM blend leading to a nodular microstructure seems to induce the best results.

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#### References

- [1] Ritzenthaler S., Court F., Girard-Reydet E., Leibler L. and, Pascault J. P. ABC triblock copolymers/epoxy-diamine blends. 2. Parameters controlling the morphologies and properties. *Macromolecules*. **36 (1)**, 118-126 (2003).
- [2] Pascault J.-P. *Thermoplastic – Thermoset blends* in “Proceeding of *Baekeland 2007: Thermosets, 100 years after Bakelite*, Ghent, Belgium, (2007).
- [3] Fabris F.-W. *Modification of the RTM6 epoxy system with block-copolymer MAM and its use in carbon fibre reinforced composites* in “Proceeding of *Baekeland 2007: Thermosets, 100 years after Bakelite*, Ghent, Belgium, (2007).
- [4] Gerard J.F., *Nanostructured thermosets - From Organic-Inorganic Block Copolymers to Supramolecular Units as Nanostructuring Blocks* in “Proceeding of *thermoset 2011*, Berlin, Germany, (2011).
- [5] Henry E., Berben R., Cordenier F., Dumont D., Slavovs M., Van Velthem P., Daoust D. *Toward a new generation of aeronautic composite materials using nanofilled thermoplastic as reinforcement* in “Proceeding of *thermoset 2011*, Berlin, Germany, (2011).
- [6] Beier U., Sandler J. K. W., Altstaedt V., Spanner H., Weimer C. Mechanical performance of carbon fibre-reinforced composites based on stitched and bindered

performs. *Composites, Part A: Applied Science and Manufacturing*, **40A (11)**, 1756-1763 (2009).