THERMOPLASTIC AS CARRIER OF NANOFILLERS INTO CARBON FIBRE – EPOXY RESIN COMPOSITES : INFLUENCE OF THERMOPLASTIC SOLUBILITY ON CARBON NANOTUBES DISTRIBUTION

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Abstract

The present work aims to evaluate the distribution of two selected thermoplastic (TP), phenoxy or polyethersulfone (PES), and non-functionalized Multi-Walled Carbon Nanotubes (MWCNTs) in the epoxy matrix of composite panels processed via Resin Transfer Moulding. The concept developed consider that nanocomposites made from a amorphous TP and filler can be dissolve by epoxy resin precursors, while the TP can act as carrier of fillers distribution toward the resin. The MWCNTs follow the thermoplastic diffusion. The impacts of the TP solubility and filler distribution on mechanical and physical properties of the resulting composites panels are investigated. Rather than phenoxy give a rise in the fracture toughness (G_{IC}) due to its better compatibility with epoxy precursors, PES seems to enhance fire properties of resulting composite laminates.

1 Introduction

With superior strength-to-weight ratio properties, composite materials are well established in many industries, especially in the aeronautic field. However, Carbon-Fibre Reinforced Thermoset (CFRT) composites still present drawbacks and many studies are focused on the improvement of physical and mechanical properties. Enhancement of performance like impact damage resistance, thermal and electrical conductivities can be achieved by adding various additives like thermoplastic (TP) or nanofillers directly in the polymer matrix. For example, improving the fracture toughness or impact damage resistance of epoxy resin or their composite laminates has been obtained by adding poly(ethersulfone) (PES) [1-3] or poly(hydroxyether of bisphenol A) (phenoxy) [4-6] as ductile phase. Alternatively, nanofillers such as carbon nanotubes have demonstrated improving significantly the mode I fracture toughness (G_{IC}) [7] and electrical conductivity of prepreg composites.

While *Resin Transfer Moulding* (RTM) seems to be a cost-effective alternative to prepreg-autoclave in order to produce high-quality composite parts, this process suffers from two major disadvantages when adding fillers or dissolved TP in the injected liquid resin. Significant increase of viscosity of such mixtures hinders injection and impregnation of dry preform. Moreover, a fillers filtering effect can occur when the resin flows through the carbon-fibre (CF) fabrics, consequently leading to a heterogeneous distribution.

A promising solution to such problems is proposed in the use of a concept exploiting nanofilled TP as carrier to introduce the fillers through a resin matrix. The resin precursors can act as solvent to dissolve the TP-based nanocomposites in view to release and distribute fillers in the resin. Nanofiller distribution depends on thermoplastic solubility according to the curing cycle applied during RTM process. Therefore, the TP solubility plays a major role in filler distribution. Dumont D. and co-workers have demonstrated it for phenoxy and PES having significantly different solubility within the precursors of epoxy resins [8]. The concept mentioned above has already demonstrated the toughening improvement of the resin, from incorporation of both additives, resulting in a microstructures gradient generated by reaction-induced phase separation (RIPS).

Regarding the solubility of the thermoplastic selected (phenoxy and PES), the present work aims to evaluate the distribution of both TP and non-functionalized Multi-Walled Carbon Nanotubes (MWCNTs) in the epoxy matrix of modified CFRT composite panels processed via RTM. The mechanical and physical properties of the resulting composites are confronted to the generated microstructures gradients, in the presence or not of the filler, in order to establish microstructures-properties relations.

The methodology involves first the production of MWCNTs-filled phenoxy or PES in order to generate the nanocomposites as pellets, filaments and films. Model systems consisting of binary and ternary blends based on phenoxy or PES, with MWCNTs or not, in RTM6, let to characterize the morphologies of the cured samples after RIPS. In parallel, the evaluation of dissolution and interdiffusion of pure TP and TP-based nanocomposites filaments into the selected epoxy resin are also studied. Then, TP or nanocomposites-modified RTM composite panels are produced via curing cycles allowing better dissolve interleaves. Finally, the mechanical and physical properties, as well as generated morphologies, are evaluated.

2 Material and experimental procedures

Phenoxy InChemRez® PKHB (T_g ~85°C, InChem Corp.), PES-Cl Radel® A200NT (T_g ~220°C, Solvay Advanced Polymers) and Nanocyl™NC7000 MWCNTs (Nanocyl sa.) are selected materials as reinforcement for HexFlow®RTM6 epoxy resin (Hexcel Corp.).

Phenoxy and PES nanocomposites are produced by melt compounding (high-shear extrusion) to disperse homogenously 1 or 3wt.% MWCNTs. Ultrathin sections (~70 nm in thickness) are cut at room temperature with a Reichert Microtome equipped with a diamond blade and collected on on 300 mesh copper grid. Observation of the nanofiller dispersion is performed by transmission electron microscopy (TEM) using Leo922 (Jeol), operating at 200kV. Pure TP and nanocomposites are subsequently melted in a DSM Xplore 15 ml micro-compounder (220 °C for phenoxy, 350°C for PES) and then drawn as filaments (~100 µm diameter) or casted as films (~40 µm thick) using DSM Xplore Spin Line or Micro Film Device.

Pure phenoxy, pure PES and their corresponding MWCNTs nanocomposites are mixed with RTM6 resin to prepare homogenous binary and ternary blends, cured after solvent removal. Etching of their TP phase is performed for 24 hours (tetrahydrofuran for phenoxy, methylene choride for PES). Scanning electron microscopy (SEM) operated at 3 kV on a Leo982 FE-SEM (Zeiss), and TEM (microtome cut thickness : ~100 nm) are then used to observe the TP-resin microstructures and nanofillers distribution.

Thermal dissolution of pure and nanofilled phenoxy or PES filaments into RTM6 resin, is performed using a Mettler FP82HT hot stage monitored by a Mettler FP90 central processor. The process is continuously recorded using an Olympus BX51 optical microscope equipped with a ColorviewI camera, until RIPS and gelation of the resin. In order to determine the TP and fillers concentration profiles resulting from the dissolution and diffusion in RTM6, the cured samples are analyzed by a DXR Raman spectrophotometer (ThermoScientific, 780nm laser) by scanning perpendicularly to the initial filament direction each 10 μm. Surface of MWCNTs, PES or phenoxy bands (respectively at 1310, 1148 and 1111 cm^{-1}) are integrated to plot concentration profiles as a function of diffusion distance from the initial position.

Composite panels (420 mm x 300 mm x 4.4 mm) are produced by vacuum-assisted RTM (piston from Isojet Équipements), using HexFlow®RTM6 (Hexcel Corp.) as matrix and twelve layers of HexForce® G0926 CF fabrics (Hexcel Corp.) as woven reinforcement with quasi-isotropic $[(\pm45°)/(0/90°)]_{3S}$ lay-up. Except for the reference composite containing only the resin RTM6 as matrix, others panels contain films of pure or MWCNTs-filled phenoxy or PES inserted between each carbon fabric layer. Polyimide inserts are placed in the preform mid-plane in order to initiate crack propagation for mechanical testing. A typical cure cycle of RTM6 consisting of a 1 K/min ramp from 80°C to 180°C followed by a 180°C isothermal step for 2 hours is modified with an intermediate isotherm of 30 minutes at 120°C favouring thermal dissolution and interdiffusion of phenoxy in RTM6 before crosslinking. To cure the panels with PES films, the dynamic ramp is fixed to 3 K/min, expecting to obtain larger domains of TP rich-phase in epoxy resin [9], before an identical isothermal step at 180°C. The presence of porosity is controlled by ultra-sonic non-destructive testing (NDT) "C-Scan".

After specimens cutting of panels, some mechanical and physical properties are measured :

1. Impact damage resistance by Compression after Impact (CAI) according to AITM 1.0010. CAI specimens are cut to 100 x 150 mm size and impacted at 30 J using an Instron Dynatup 9250HV impactor. Damaged area is determined with an ultrasonic C-scan. The specimens CAI is measured in a Zwick Z250 with a load cell of 250 kN.
2. G_{IC} fracture toughness by Double-Cantilever Beam (DCB) following ASTM D5528-01. Specimens (dimensions : 25 x 150 mm) are loaded in tensile mode using a Zwick Universal testing machine, at 1 mm/min.
3. Heat and fire resistance using cone calorimeter were carried out using a FFT (Fire Testing Technology) Mass Loss Calorimeter. The specimens (100 x 100 mm) are irradiated in a horizontal position by applying a 50 kW/m^2 external heat flux.

Polished cross sections of the composite panels and fracture surfaces from DCB samples are coated with 8 nm of chromium by sputtering (Cressington 280HR), before being examined by SEM in order to observe the TP-resin microstructure gradients and the MWCNTs distribution.

3 Results and discussion

*3.1 Binary & ternary blends – Microstructures of polymer alloys and fillers location*

Binary polymer alloys prepared from phenoxy (Figure 1 **a-c**) or PES (Figure 1 **d-e**) at different concentrations into RTM6 resin allow to show clearly a TP concentration-dependent microstructures, resulting of RIPS. Thermoplastic nodular microstructures are observed for 20wt.% of phenoxy (Figure 1 **a**) and 10wt.% of PES (Figure 1 **d**), while the incorporation of 40 and 20wt.% of phenoxy and PES in RTM6 respectively (Figure 1 **c** and **f**) show reaching their phase-inverted morphologies. Moreover, the phenoxy addition in the epoxy resin generates, after phase inversion, microstructures with much smaller nodules than for PES. This behaviour is probably due to a greater affinity of the RTM6 resin precursors for phenoxy.

In prospect of the RTM panels production with TP interleaves, the phase inversion has to remain limited in the interlaminar region in order to preserve thermomechanical and chemical properties of the thermoset network. A co-continuous microstructure (Figure 1 **b** and **e**) seems to be a more effective morphology for G_{IC} improvement. The final average TP content is fixed around 15wt.% of the RTM panel matrix for both pure and nanofilled TP polymers.
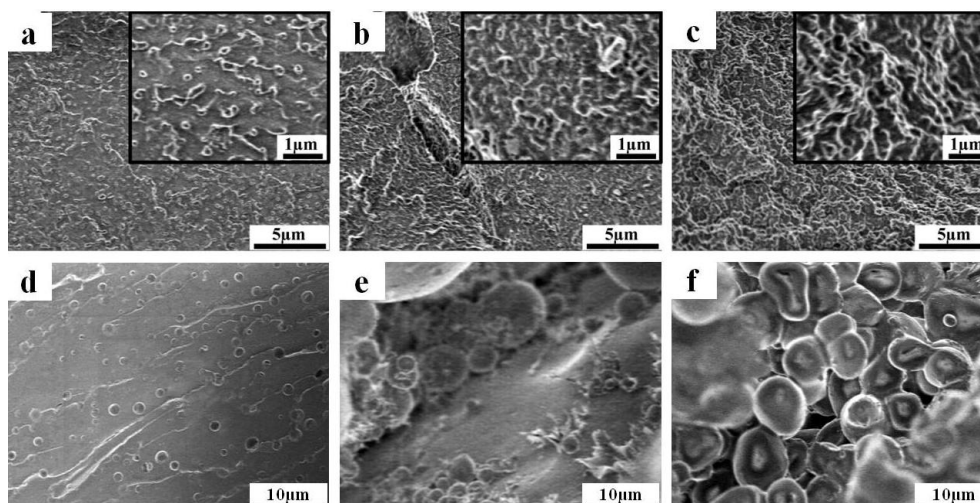
Figures 1. SEM micrographs of etched fracture surface of resulting microstructures in binary blends of RTM6 resin including (**a**) 20, (**b**) 30 and (**c**) 40wt.% of phenoxy or (**d**) 10, (**e**) 15 and (**f**) 20wt.% of PES.

In ternary model systems, it is observed that the location of the MWCNTs depends of the TP used. After dissolution of nanocomposites in epoxy resin, the fillers are mainly localized in epoxy-rich phases for RTM6-20wt.% [phenoxy-3wt.%MWCNTs] (Figure 2 **a**), while they are essentially situated in TP-rich phase for RTM6-10wt.% [PES-3wt.%MWCNTs] (Figure 2 **b**).
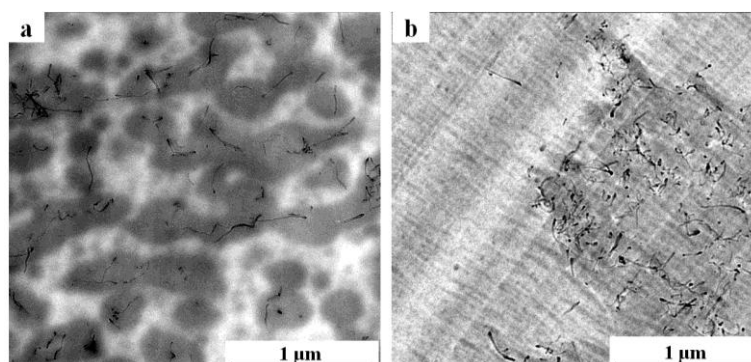
Figures 2. TEM micrographs of RTM6 with (**a**) 20 wt.% of [phenoxy-MWCNTs] and (**b**) 10 wt.% of [PES-MWCNTs] nanocomposites after RIPS and curing at 120°C.

Fillers displacement from phenoxy to epoxy may lie in a "phenoxy chains desorption - RTM6 precursor adsorption" mechanism on filler surfaces before the phase separation. The last mechanism is not expected for the other blend due to a better affinity of MWCNTs for the PES and/or a poor efficiency of RTM6 precursors to swell-dissolve the PES nanocomposite.

3.2 Dissolution-diffusion of pure TP and TP-based nanocomposites filaments in RTM6 resin

Exploiting the concept using thermoplastics for MWCNTs dispersion in RTM composites requires phenoxy and PES dissolution and further distribution in RTM6 resin, before gelation. The selection of an adequate temperature profile is thus primordial and will be established from a model system described below. Composition profiles induced in model systems consisting in a unfilled 100 µm diameter phenoxy and PES filament exposed to an isothermal treatment at 120°C into RTM6 resin (gel time > 240 minutes) are compared in Figure 3.
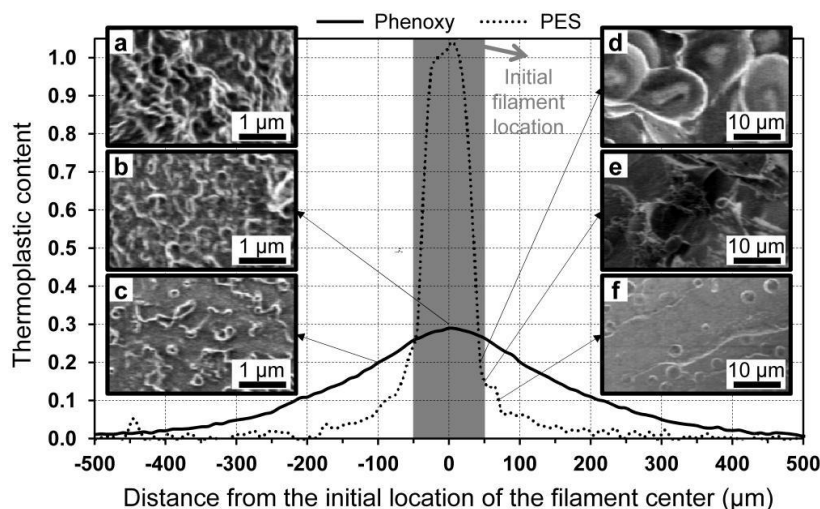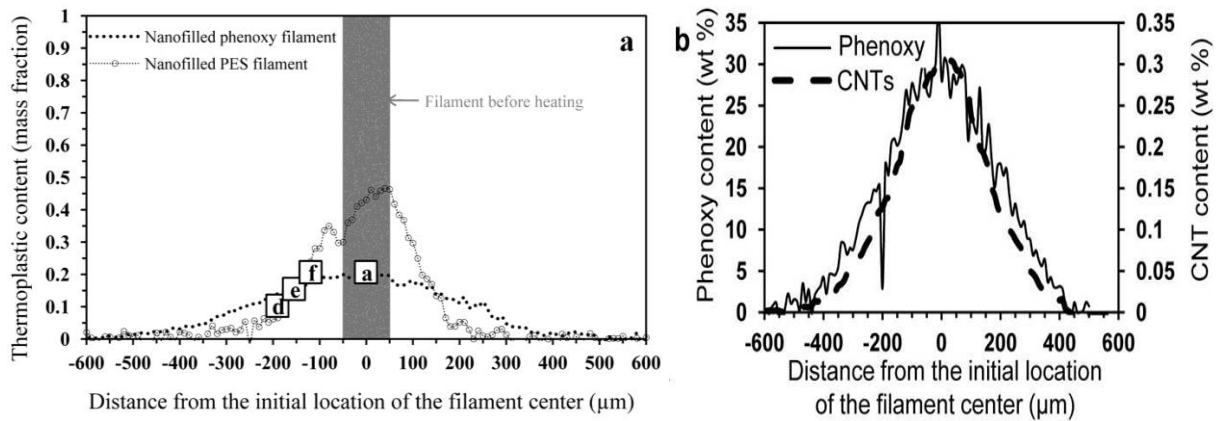

Figure 3. PES and phenoxy concentration profiles in RTM6 resin determined by Raman spectroscopy after a 120 °C isotherm applied to a 100 µm diameter filament and blend microstructures corresponding to local compositions: (a) 20 wt.%, (b) 30 wt.% and (c) 40 wt.% phenoxy; (d) 10 wt.%, (e) 15 wt.% and (f) 20 wt.% PES.

At this temperature, the inner core of the PES filament remains unaffected by the RTM6 resin precursors and a poor distribution of the PES macromolecules is achieved (up to 200 µm). In opposite, suitable dissolution is observed for phenoxy, allowing a larger diffusion until 400 µm from initial location. This improved swelling occurs thanks to favourable diffusion of the epoxyde and diamine precursors through the chains of this lower T_g thermoplastic [8]. The phenoxy distribution leads to a lower local phenoxy concentration in RTM6 resin and more homogeneous microstructure on the entire diffusion domain than PES case.

Similar diffusion distances are obtained for the nanocomposite filaments with 1wt.% MWCNTs (Figure 4 **a** and **b**). The distribution profiles reveal similar distances of diffusion (up to 400 µm) for MWCNTs independently of the carrying TP, confirming that nanofiller distribution will depend on thermoplastic solubility into the epoxy resin.

Figures 4. Concentration profiles of (**a**) 1wt.% MWCNTs-filled phenoxy and PES, or (**b**) phenoxy and CNTs, determinate by Raman spectroscopy for a 100 µm diameter filament after interdiffusion at 120°C in RTM6 resin.

3.3 TP-modified RTM composite panels – Mechanical properties and their resulting morphologies

From defined RTM temperature profiles and preform structure lay-up, five composites panels including pure TP (phenoxy or PES) or nanocomposites (TP filled with 3wt.% CNTs) interleaves in order to have around a 15% TP-modified RTM6 epoxy matrix, are produced.

From DCB tests, interlaminar G_{IC} is determined and the results show a positive rise of crack propagation energy (+88%) for the "RTM6-CF with phenoxy films" panel (Figure 5). On the contrary, PES films seem to slightly decrease interlaminar fracture toughness (-8%).
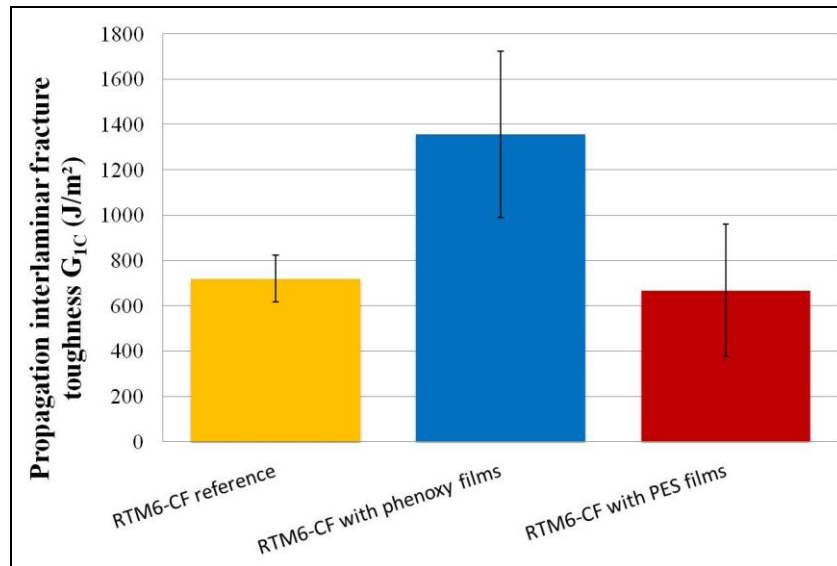

***Figure 5.** Propagation fracture toughness in mode I (G_{IC}) from DCB measurements of the reference and the pure TP interleaves CFRT composite panels produced.*

The morphological inspection on DCB specimen fracture surfaces shows, in accord with the observations on the model systems, that for phenoxy (Figure 6 **a**) a more rough microstructures than for the PES (Figure 6 **b**) corrobotates the G_{IC} results, due to probable better interdiffusion of phenoxy-resin precursors.
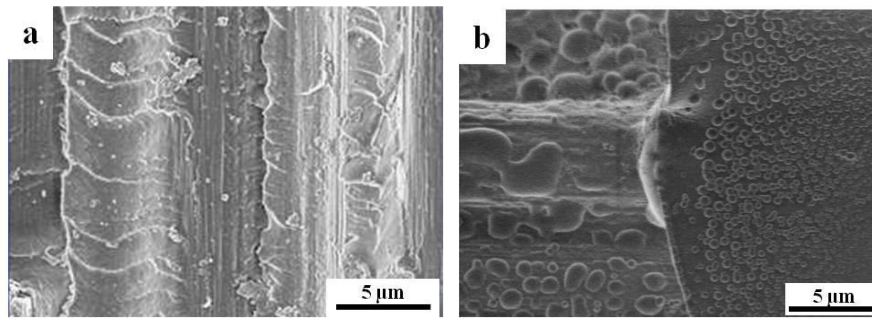
Figures 6. SEM micrographs of DCB specimen fracture surface of RTM6-CF composite panels (**a**) with phenoxy films or (**b**) with PES films showing clear differences in morphologies.

Observation of cross-section polished surface of the phenoxy-MWCNTs modified RTM composite panel evidences that interdiffusion between phenoxy and the resin precursors taking place during the initial stages of the curing cycle, allowing slight release of MWCNTs in the RTM6 matrix (Figure 7 **a**). However, further distribution domain of MWCNTs as large as in model system (400 μm, Figure 4 **b**) is not reached in RTM panel, due to a barrier effect of fibrous carbon reinforcement hindering the diffusion of fillers inside the intralaminar region (Figure 7 **b**).
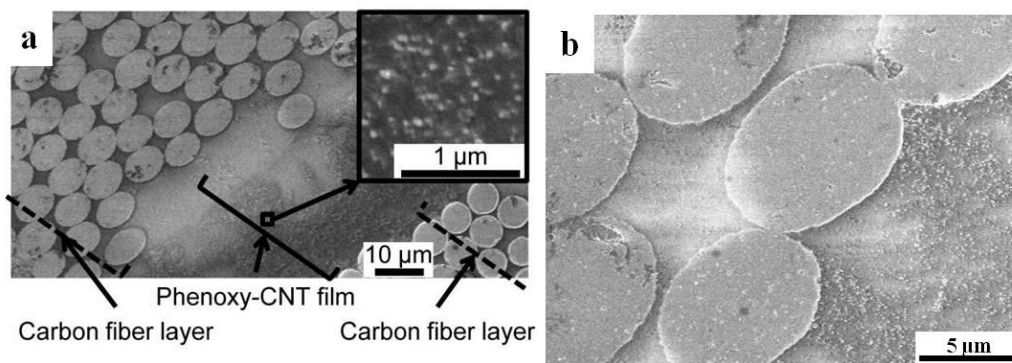
Figures 7. SEM micrograph of the cross-section of the composite panel with films of phenoxy-3wt.%MWCNTs (**a**) in an interlaminar region and (**b**) at the border of a CF fabric and the interlaminar region.

Impact and CAI investigation on panels don't lead to clear property enhancements.

3.4 Pure TP and nanocomposites-modified RTM composite panels – Fire properties

Using a cone calorimeter with a 50 kJ/m² heat flow, the fire properties of the interleaved pure or CNTs-filled phenoxy and PES films composite panels are evaluated by recording the heat released rate (HRR) and the weight loss as a function of time. In Table X, the maximum recorded HRR (peak HRR) and the total heat release (total HR) are shown and compared (reproducibility within variation less than 10 %.).

RTM panel	Peak HRR [kW/m²]	Total HR [MJ/m²]
RTM6-CF reference	112	39
RTM6-CF with phenoxy films	105	36
RTM6-CF with phenoxy-3wt.% MWCNTs films	95	28
RTM6-CF with PES films	78	31
RTM6-CF with PES-3wt.% MWCNTs films	85	27

Table 1. Fire properties of interleaved pure or CNTs-filled phenoxy and PES films composite panels.

It is shown that incorporation of PES films have a significant reduction of the peak HRR (-30%), with no clear impact of MWCNTs. Similar observations are discussed by Biswas B. in the reference [10]. However, these fillers seem to get an interesting potential for total heat released decrease, not explain at the moment.

4 Conclusions

Phenoxy demonstrates several advantages for an exploitation as carrier to disperse CNTs into the matrix of composites processed by RTM as compared to another amorphous thermoplastic like PES. Firstly, a better distribution of phenoxy is observed into RTM6 resin. Secondly, since phase separation takes place at higher phenoxy concentration in the RTM6 resin-phenoxy blend, larger phenoxy amounts can be added to the composite matrix while conserving a continuous epoxy resin phase. Finally, toughening of composites interleaved with phenoxy films is evidenced unlike with PES films. Therefore, phenoxy demonstrates an interesting potential to disperse CNTs in composite matrices by inserting nanocomposite films in the preform with a resulting CNT distribution depending on phenoxy swelling by the resin precursors during heating. While the limited CNT amount has no additionnal effect on G_{IC}, other properties could be influenced as fire resistance. Moreover, the concept using phenoxy as carrier could be tested with higher CNT contents or transposed to other fillers.

Acknowledgement

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