

Specific Influence of Polyethersulfone Functionalization on the Delamination Toughness of Modified Carbon Fiber Reinforced Polymer Processed by Resin Transfer Molding

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The specific influence of polyethersulfone (PES) end-functionalization with chlorine or hydroxyl end groups at same molar mass on PES-epoxy composites based on a high-performance tetra-epoxide with di-amine hardener resin (RTM6) is investigated in terms of morphology, thermal behavior, and toughness. A model study on PES filaments embedded in epoxy precursor is first performed to compare the interdiffusion and resulting morphology upon curing. PES-OH shows a larger interdiffusion distance compared to PES-Cl in the model systems and the laminates. This effect is more pronounced at high heating rate. Cross sections and fracture surfaces of composite panels are analyzed by scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) spectroscopy to establish the link between the microstructures and fracture mechanisms. The toughness of PES-OH-modified epoxy composites is doubled compared to unmodified reference panels, whereas the PES-Cl shows no improvement. The favorable influence of PES-OH is ascribed to enhanced miscibility, interfacial adhesion and morphology, resulting from the better affinity between hydroxyl-terminated PES and the epoxy-resin. POLYM. ENG. SCI., 00:000–000, 2019. © 2019 Society of Plastics Engineers

INTRODUCTION

Composite materials based on carbon fibers (CFs) and high-performance epoxy resins are increasingly used in high-end structural applications because of their excellent specific stiffness and strength as well as outstanding thermal and chemical resistance. However, they suffer from limited fracture toughness and impact damage resistance due to the high crosslinking density of the matrix. Amorphous, high glass-transition temperature (T_g), thermoplastics (TPs) are commonly used as tougheners for such resins [1–6]. Their effectiveness is controlled by the phase-separated morphology developing upon curing of the epoxy by the so-called reaction-induced phase separation. Ductile, dispersed TP domains provide resistance to crack propagation through various mechanisms such as crack path deflection or crack pinning [7, 8]. Poly-sulfones (PSFs) and polyethersulfones (PESs) are popular choices as tougheners for highly crosslinked epoxies. For a given, epoxy, the resulting phase separated morphology strongly depends on the exact chemical nature of the TP, its molar mass and the functional/reactive groups present along the chains or at the ends [9, 10].

A number of studies have been published, comparing the toughening of *unreinforced* epoxy resins by PSF and PES carrying functional groups to the toughening by corresponding unreactive or noninteracting TP references. However, the literature on the subject is not systematic nor are the findings fully consistent. A positive effect of TP functionality on toughness has, for instance, been reported by James et al. [11] and Hedrick et al. [12] for a phenolic terminated PSF oligomer incorporated in an epoxy resin (Epon 828) crosslinked by 4,4'-Diaminodiphenyl Sulfone (DDS) in the presence of tetramethylammonium hydroxide (TMAH) catalyst. Similarly, hydroxyl-terminated PSF was a better toughener for a Diglycidyl Ether of Bisphenol A (DGEBA) epoxy resin [13] than chlorine-terminated PSF. Rajasekaran et al. [14] incorporated a PES-OH/bis-maleimide hybrid with TMAH catalyst in an epoxy network based on DGEBA cured with diaminodiphenyl methane (DDM) and found a 68% improvement of G_{Ic} upon addition of 12 wt% PES-OH. On the contrary, Yoon et al. [15] observed a detrimental influence of reactive amino-terminated PES compared to that of a nonreactive PSF on the toughening of a DGEBA/DDS system. This seems to be generally the case when phase separation upon curing and the corresponding toughening mechanisms are prevented by excessive functional groups concentration, as observed for instance by Chen et al. [16] who compared the effect of standard and nitrated PEI on the interfacial bonding with a TGAP/DDS system.

The influence of high T_g PSF and PES on the toughness of laminated structural epoxy composites has similarly been reported in several articles. In particular, Yun et al. [17] studied the fracture toughness of composite panels based on carbon fibers (CFs) and epoxy resin toughened by PSF. TP films were inserted between the CFs layers pre-impregnated with DGEBA resin and DDS hardener. Double cantilever beam (DCB) tests showed a 270% improvement of G_{Ic} for a co-continuous microstructure. The final PSF concentration gradient resulting from the interdiffusion between the epoxy and TP was also measured by X-ray elemental analysis. An approximate interdiffusion distance of about 250 μm was found and a maximum PSF concentration of 21% was observed in the middle of the sample. Recently, Van Velthem et al. [18] examined the influence of epoxy-TP interdiffusion on the morphology and delamination toughness for two TP tougheners (PES and phenoxy) in a high-performance RTM6-based CFs composite processed by resin transfer molding (RTM). A 92% improvement of the interlaminar fracture toughness (G_{Ic}) was found for the phenoxy-RTM6 system as compared to that of the pure thermoset reference. On the other hand, PES had a detrimental effect on G_{Ic} . The authors hypothesized that the disappointing result for the PES-epoxy composite was due to the lack of reactivity between the epoxy resin and the chlorine-ended PES used in the study.

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Although the specific influence of PES or PSF functional groups on the toughness of *unreinforced* TP-epoxy systems has been extensively analyzed in a number of scientific publications as summarized earlier, the same is not true for the corresponding laminated composites, especially those containing interleaved TP films in the epoxy matrix (as opposed to homogenous TP-epoxy blends). In particular, for high-performance structural PES-toughened epoxies, the specific influence of TP end groups at identical chemistry and molar mass has, to the best of our knowledge, not yet been analyzed in depth. This is surprising, considering that a number of patents claim the advantage of PES/PSF functionalization and have resulted in the commercialization of toughened prepreps based on this observation. This realization has prompted us to thoroughly study the influence of end-group functionality while keeping all other parameters unchanged, that is, at identical PES concentration and molar mass on the morphology and the delamination toughness properties of PES-RTM6 systems processed by RTM. To this end, we first explore the experimental conditions for the microstructure formation via reaction-induced phase separation using simplified model systems consisting of reactive (OH end groups) or unreactive (Cl end groups) PES filaments in RTM6, by optical microscopy and Raman spectroscopy. In a second step, the results are transposed to RTM panels containing PES films interleaved between the CFs fabric. Scanning electron microscopy (SEM) observations of cross sections of the RTM panels reveal the TP distribution and the generated microstructures in the composites depending on the PES end-group functionalization. X-ray elemental analysis is further used to visualize the TP diffusion distance in the composite panel. DCB tests are performed to determine the delamination cracking resistance of the panels. Finally, the fracture surfaces are observed by SEM to analyze the corresponding failure mechanisms.

EXPERIMENTAL

Materials

The epoxy resin used in this work is HexFlow RTM6 [19] from Hexcel™, which is composed of a tetraepoxide resin (N, N, N', N' tetraglycidyl-4,4'-methylene dianiline [TGMDA]) and a blend of two

diamine hardeners (4,4'-methylenebis-(2-isopropyl-6-methyl)-aniline [MMIPA] and 4,4'-methylenebis-(2,6-diethyl)-aniline [MDEA]). This resin is specifically developed to fulfill the requirements of aerospace applications. The resin used for the dynamic mechanical analysis (DMA) experiments only contains one hardener (MDEA) but is otherwise identical. The CFs reinforcement is Hexforce™ G0926 [20] also from Hexcel™, with *Satin5* weave (375 g/m²). Two kinds of PES ($T_g = 220$ °C) with either hydroxyl end groups (PES-OH Radel® A105 NT [21]) or with chloride end groups (PES-Cl Veradel® A201 NT [22]) both supplied by Solvay Advanced Polymers are used in this study. Both PESs have similar molecular weights (around 35 kg/mol in PS equivalent measured by Gel Permeation Chromatography).

Manufacturing of Test Specimens

PES Filaments and Films. The PES materials previously dried at 80 °C during 24 h under vacuum are melt-processed at 340 °C in a DSM Xplore 15 mL micro-compounder. The mixing time is set to 5 min with the rotation speed of the co-rotating twin screws at 150 rpm. Subsequently, 100 µm diameter PES filaments and 100 µm PES films (used for model system study) and 40 µm thick PES films (used for composite structure) are produced using a DSM Xplore Fiber Spin Line and a DSM Xplore Micro Film Device, respectively.

Laminate Manufacturing. Twelve plies of CFs are stacked alternatively at +45°, 0°, −45°, and 90° to produce a quasi-isotropic preform. Between the fabrics, PES films (40–50 µm thick) are intercalated at every interlayer. The PES films thickness is informed by a previous study [18] and is selected to optimize the interdiffusion of the TP with RTM6. Moreover, a polyimide crack initiator having low affinity with RTM6 and easily forming a precrack with a known length during the DCB tests is inserted in the midplane along the panel edge. The stacking sequence is shown in Fig. 1.

All composite panels are manufactured using vacuum-assisted resin transfer molding process (VARTM) from Isojet. The preform is placed in the RTM sealed under a pressure of 9.5 bars. The resin

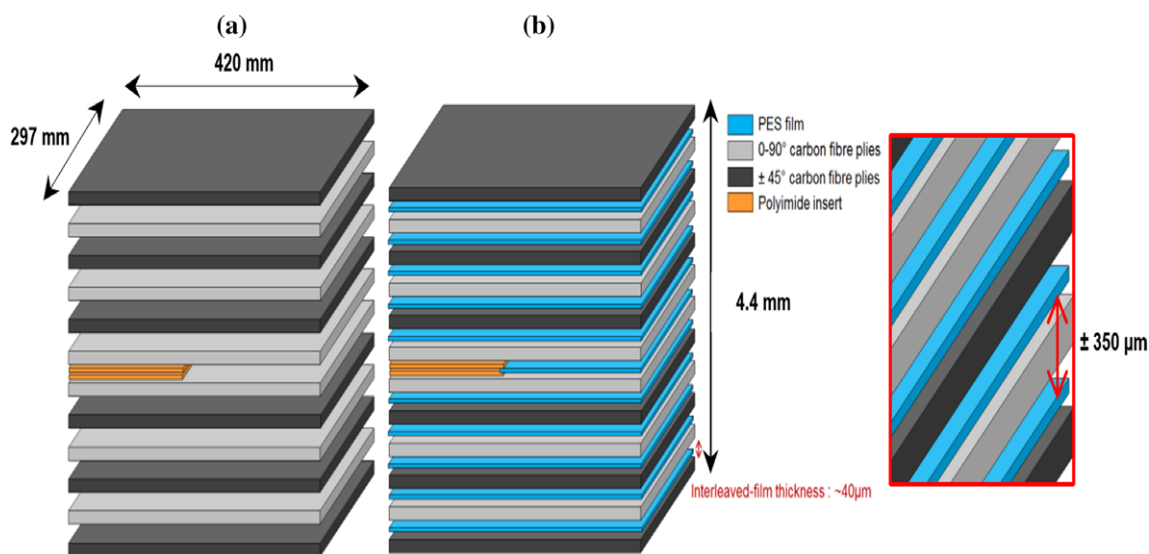


FIG. 1. Schematic of reinforcement structure stacking (quasi-isotropic) of (a) reference panel and (b) modified panels with 40 µm PES film. [Color figure can be viewed at wileyonlinelibrary.com]

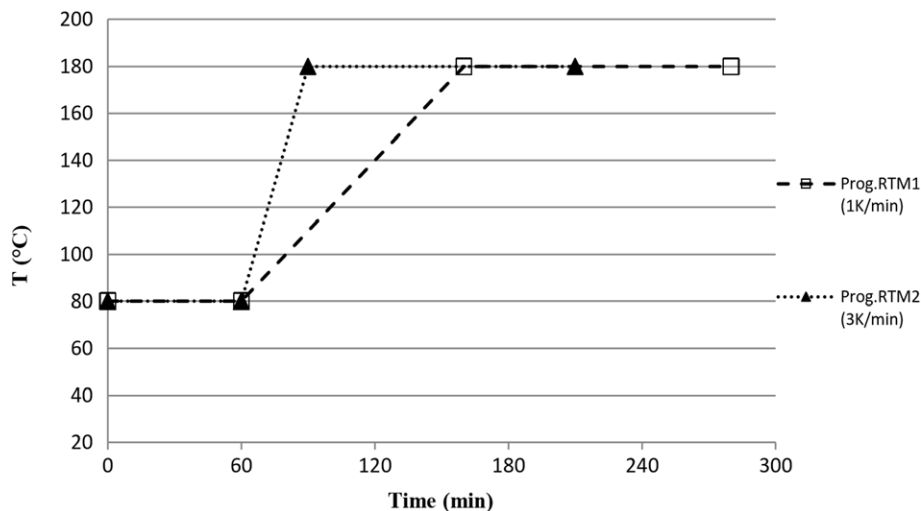


FIG. 2. Thermal curing profiles for RTM composite panels.

previously degassed at 80 °C during 30 min is introduced in the injection piston at 80 °C. An injection rate of 100 cm³/min is applied in the mold under vacuum of 10⁻⁴–10⁻⁵ bars. When the mold is filled, a pressure of 6.5 bars is maintained and the thermal curing program is applied. In this study, two different curing cycles, illustrated in Fig. 2, are investigated for the production of RTM panels. The fiber content of each panel is approximately 67 wt%, whereas PES TP concentration in the modified RTM6 is around 15 wt% (about 5 wt% of PES in the final composite). Prog.RTM1 comprises a 1 °C/min ramp from 80 °C to 180 °C for 2 h, whereas Prog.RTM2 is identical except for the heating ramp, which is set to 3 °C/min. The quality of the panels is analyzed with the help of an Ultrasonic

C-Scan non-destructive test (NDT). The results show no inclusions or apparent porosity.

Characterization Methods

Hot-Stage Optical Microscopy. An Olympus BX51 optical microscope equipped with a ColorviewI camera is used to observe the dissolution of PES filaments in the RTM6 epoxy resin under several thermal programs. Hot-stage microscopy is performed by observing a 100 ± 5 μm diameter filament embedded in the epoxy resin on a Mettler FP82HT hot stage monitored by a Mettler FP90 central processor connected to the microscope.

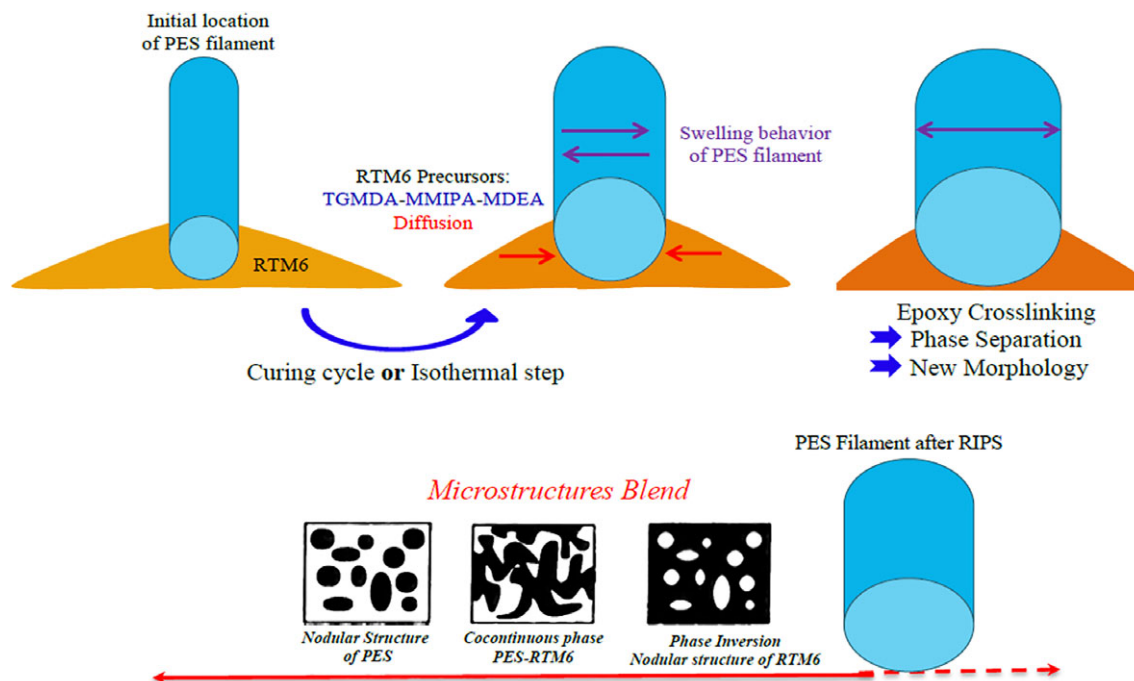


FIG. 3. Schematic representation of diffusion and swelling behavior of PES filament in RTM6 epoxy resin. [Color figure can be viewed at wileyonlinelibrary.com]

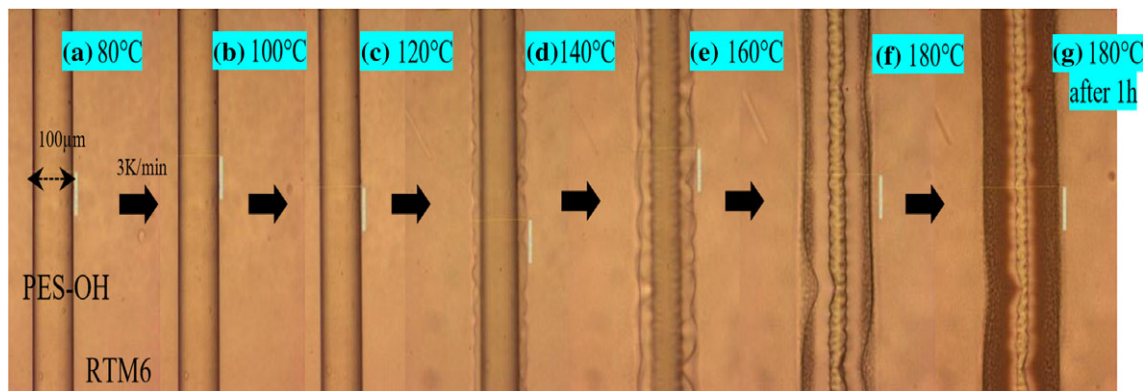


FIG. 4. Evolution of a PES-OH filament (initial diameter of 100 μm) in RTM6 resin observed by optical microscopy during thermal treatment (temperature ramp from 80 $^{\circ}\text{C}$ to 180 $^{\circ}\text{C}$ at 3 $^{\circ}\text{C}/\text{min}$). [Color figure can be viewed at wileyonlinelibrary.com]

SEM Coupled with EDX Spectroscopy. Specimens for energy dispersive X-ray (EDX) analysis are mounted on stubs and coated with a 8 nm chromium layer (Cressington sputter 208HR) to create a thin conductive layer, minimizing degradation and drift due to thermal expansion. SEM and SEM-EDX analyses are performed on polished surfaces in a Jeol FEG SEM 7600F equipped with an EDX system (Jeol JSM2300) operating at 15 keV with a working distance of 8 mm. The acquisition time for chemical spectra is 300 s with a probe current of 1 nA. The quantitative analyses of atomic elements are done with the integrated software Analysis Station. A two-step analysis procedure is applied to obtain quantitatively reliable results for the element profiles over the entire cross sections: (1) the subtraction of bremsstrahlung done with the classical “Top Hat Filter” method [23–25] and (2) the quantification of area under each atomic peak determined by the ϕ (ρz) model [26, 27].

DCB Test. The Mode I interlaminar fracture toughness (G_{IC}) is measured using the DCB test configuration according to the standard ASTM D5528-01 [28]. The specimen geometry consists of a rectangular beam with dimensions 150 $\times$ 25 $\times$ 4.4 mm. The

precrack length produced by the polyimide film insert is 50 mm (see Section Manufacturing of Test Specimens). The sample is loaded using a Zwick universal testing machine at a constant cross-head speed of 1 mm/min. Crack growth is determined using a magnifying lens and load/displacement measurements at corresponding crack length are recorded. Moreover, the fracture surfaces were also examined by SEM after sputtering 8 nm of chromium in a Cressington 280HR deposition equipment.

Dynamic Mechanical Analysis. The T_g , defined as the maximum of the tangent delta peak values, of PES-Cl and PES-OH films as well as reference and modified epoxy resin specimens were determined using a dynamic mechanical analyzer DMTA/SD-TA861e from Mettler Toledo. Rectangular specimens of 9 $\times$ 4 mm size were heated from 30 $^{\circ}$ to 300 $^{\circ}\text{C}$ at 3 $^{\circ}\text{C}/\text{min}$ and analyzed at a frequency of 1 Hz in a tensile deformation mode.

Background on T_p Filaments Dissolution in the Epoxy Resin

The toughening concept used in this work takes advantage of the presence in the mold before resin injection of TP films purposely intercalated between the plies of the *CF* preform. It hence

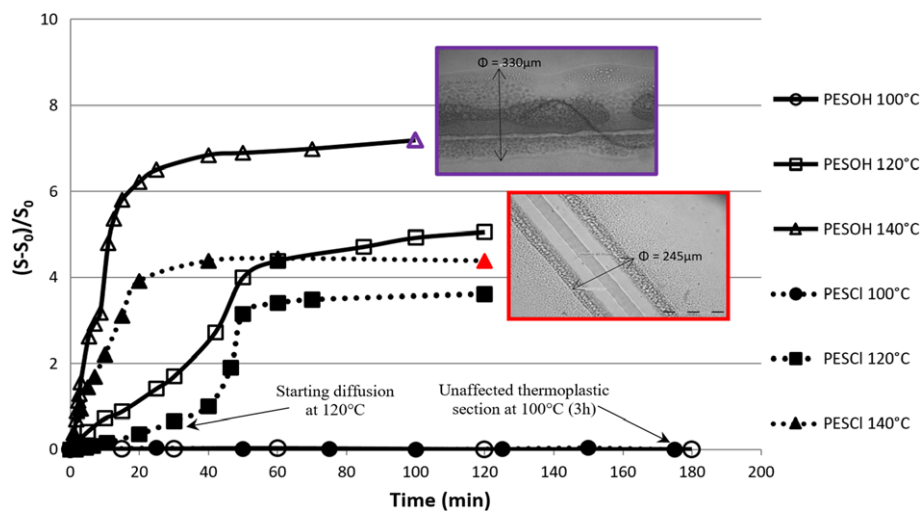


FIG. 5. Evolution of relative section of PES filaments (PES-OH and PES-Cl) as a function of time at different isothermal treatments (100, 120, and 140 $^{\circ}\text{C}$). [Color figure can be viewed at wileyonlinelibrary.com]

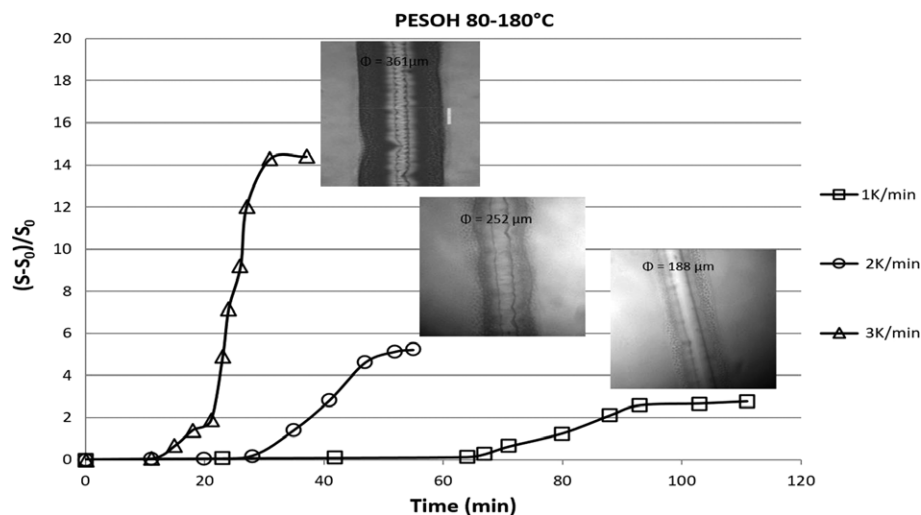


FIG. 6. Influence of heating rate on diffusion distance of the PES-OH filament in RTM6 epoxy resin.

critically depends on the control of the interdiffusion between the TP and the epoxy precursors during the curing program. This strategy avoids mold filling issues related to the high viscosity of the epoxy resin if it is premixed with the TP. On the one hand, the TP must remain insoluble in the epoxy resin during the mold filling stage to avoid TP flushing by the resin flow. On the other hand, rapid TP dissolution in the epoxy resin must be achieved once the mold is completely filled and the preform is impregnated by the low viscosity resin. A compromise between the diffusion kinetics of the resin precursors into the TP and the cure reaction kinetics must be found by applying an adapted temperature profile. Indeed, crosslinking progressively slows down diffusion and essentially stops it at the gel point. The diffusion coefficients of the TP and of large epoxy oligomers are orders of magnitude lower than those of the resin monomers [18, 29]. Hence, we mainly observe a swelling of the TP by the epoxy monomers. Theoretical diffusivity models [30, 31] describe this competition between the mutual diffusion process and the crosslinking reaction. In addition to the epoxy network formation that reduces mobility of the diffusing molecules,

the dissolution process is also progressively inhibited by the reduction of the concentration gradient at the resin-TP interface. To conveniently study the interdiffusion, an experimental system based on a single TP filament placed in a RTM6 resin droplet is used. The schematic interdiffusion behavior of a 100 μm diameter PES filament in RTM6 resin and the possible microstructures that can be generated after reaction-induced phase separation are illustrated in Fig. 3.

RESULTS AND DISCUSSION

Influence of Thermal Treatment on PES Filament Swelling in RTM6 Epoxy Resin

The swelling kinetics of a PES filament in a RTM6 droplet is studied for various thermal programs. Optical microscopy images taken during a constant heating rate ramp from 80 °C to 180 °C at 3 °C/min show the progressive swelling of the filament (Fig. 4). This can be inferred from the reduction of the unswollen TP diameter and the corresponding increase of a gel layer (involving TP and epoxy monomers), which are observed at 140 °C and

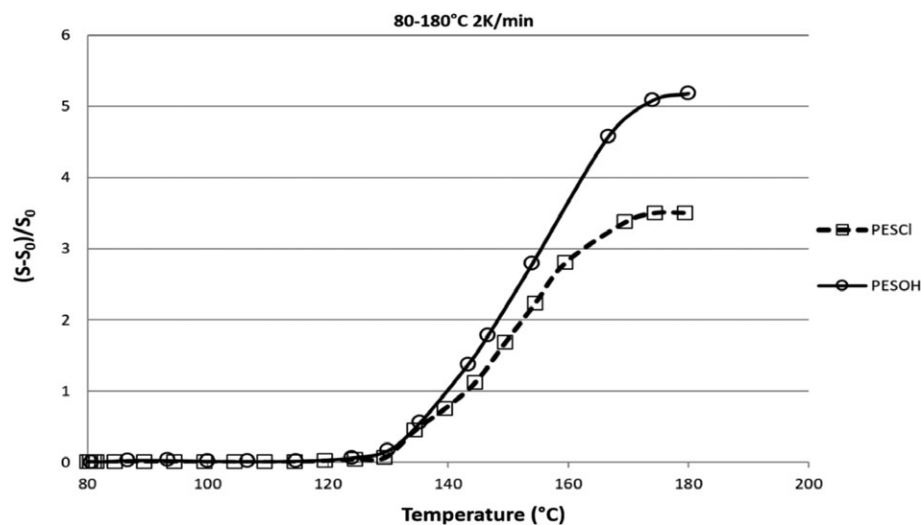


FIG. 7. Influence of the PES functionalizations on the diffusion distance in RTM6 epoxy resin at 2 K/min from 80 °C to 180 °C.

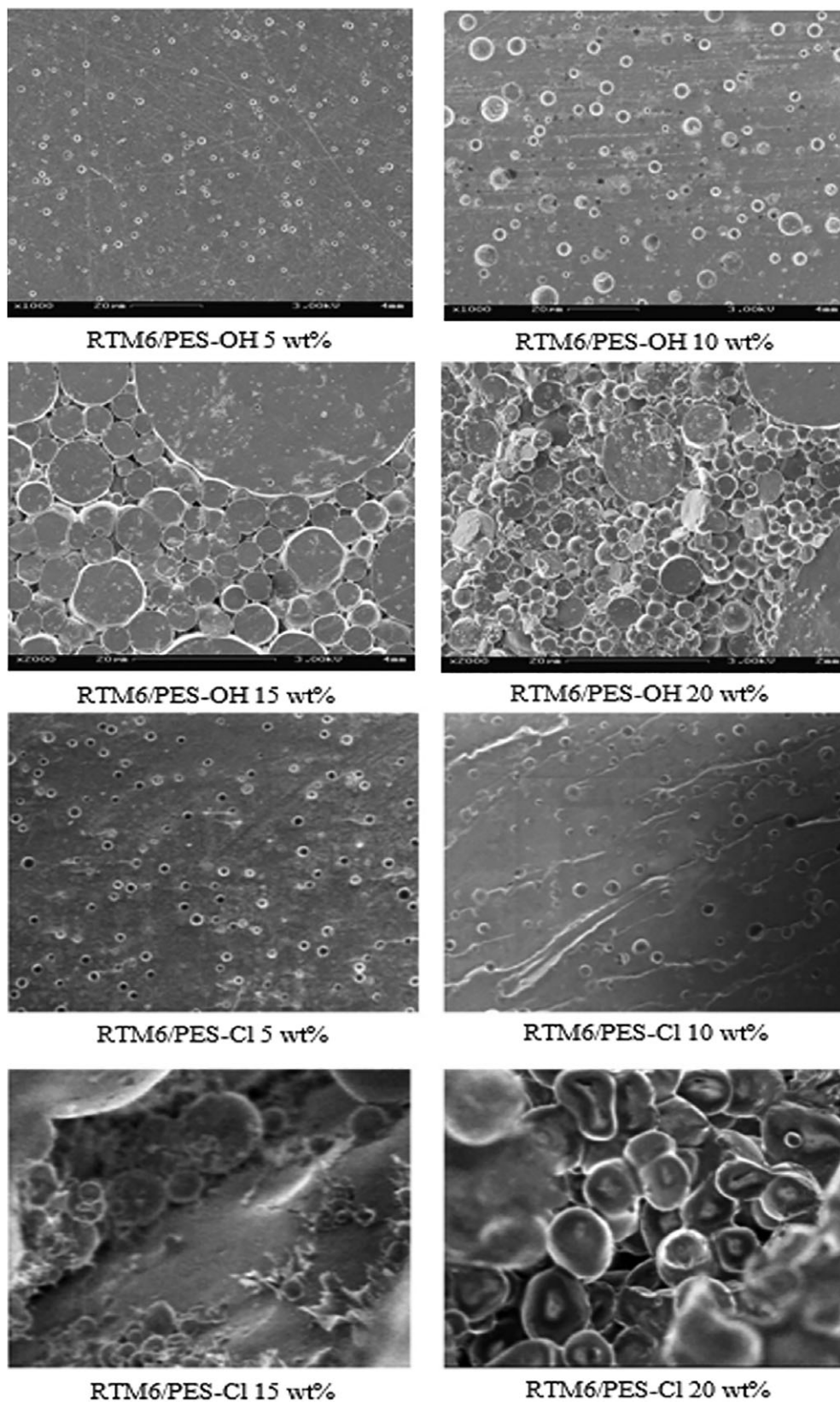


FIG. 8. SEM micrographs of model systems (binary blends RTM6/PES-OH and RTM6/PES-Cl) after solvent etching.

above (Fig. 4d). The unmodified TP core diameter decreases quite regularly during the thermal treatment. At later stages, as the program continues and the curing reaction proceeds, phase separation

is initiated and becomes progressively detectable. Indeed, differences between the refractive indices of the phases produce observable interfaces. The residual core of the original PES filament in

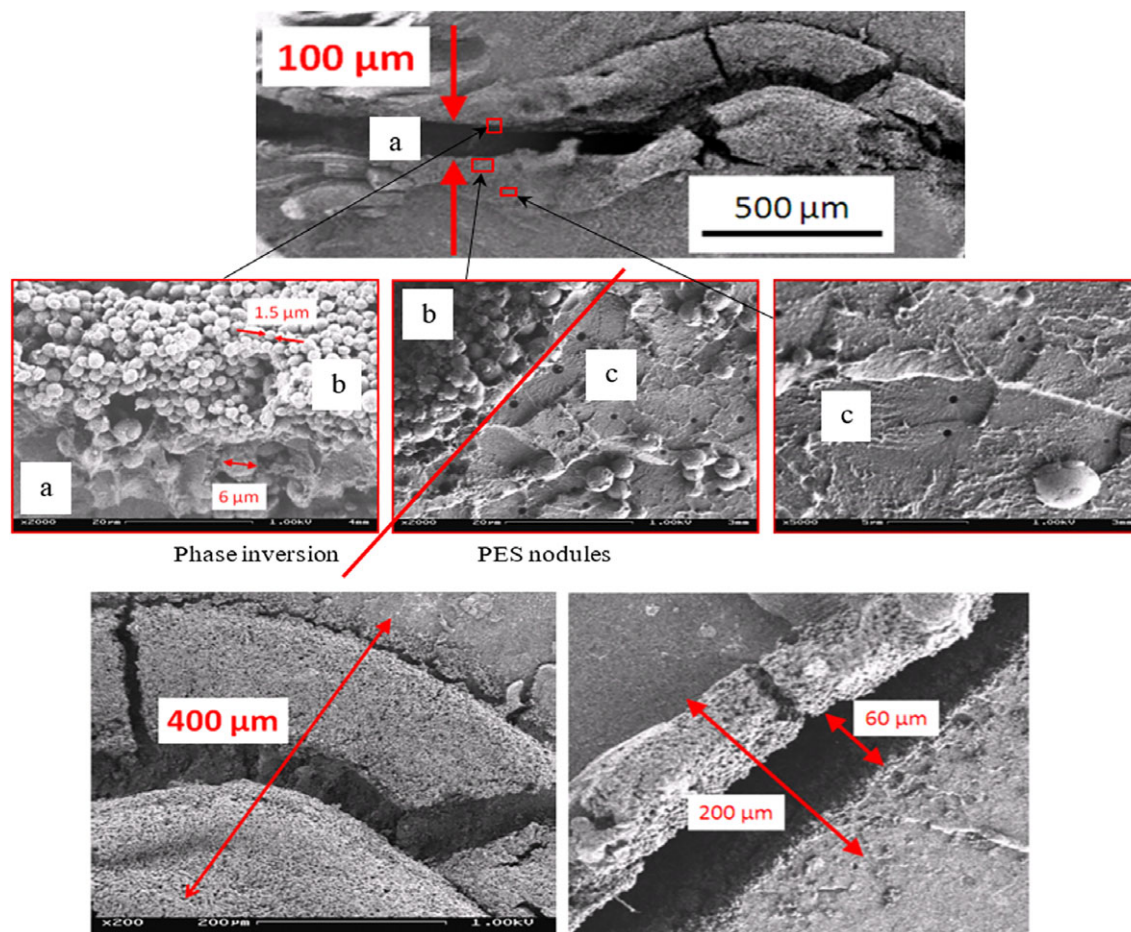


FIG. 9. SEM images of generated microstructures after dissolution/diffusion of a PES-Cl film in RTM6 epoxy resin at 140 °C for 90 min: (a) PES initial location, (b) phase inversion zone, (c) nodular PES area, and (d) at high magnification. [Color figure can be viewed at wileyonlinelibrary.com]

RTM6 resin cured at 180 °C is observed in Fig. 4f, which also shows the microstructure gradient resulting from reaction induced phase separation. The vanishing molecular mobility at gel time is responsible for incomplete swelling of the PES-OH filament.

Figure 5 compares the evolution of the relative cross-sectional area ($\frac{\pi d^2}{4}$) of PES filaments (PES-OH and PES-Cl) as a function of time for different isothermal treatments (100, 120, and 140 °C). PES is almost insoluble in RTM6 resin at 100 °C, as confirmed by the essentially unaffected TP diameter after resin gelation. The swelling of PES filaments is only initiated at 120 °C but slowly and limited (80–100 min) because of the increasing molecular weight of the resin, which prevents further diffusion of the reactive resin precursors. Faster filament swelling can be achieved by increasing the temperature to 140 °C although the corresponding gel time (~40 min) and consequently the time window for dissolution is limited. PES-OH swells faster and over a larger distance compared to PES-Cl for all isothermal treatments. This different swelling characteristic can be related to the better affinity of PES-OH with the RTM6 precursors because the two TP have similar molecular weights (see Experimental Section). The swelling kinetics of the filaments is not investigated at temperatures higher than 150 °C because the balance between diffusion and curing rates becomes unfavorable, therefore reducing the corresponding RTM processing window.

Similarly to isothermal diffusion programs, temperature ramps lead to a partial dissolution of the PES filament in RTM6 as well. The residual PES glassy core can be controlled by the applied heating rate as shown in Fig. 6. The best balance is achieved for a 3 K/min heating ramp from 80 °C to 180 °C, leading to the largest decrease in the filament core, with only some residual spots of the original filament remaining.

The influence of PES functionalization on the interdiffusion distance at a heating rate of 2 K/min is also investigated (Fig. 7). Results show a broader swelling front in case of PES-OH presumably due to the presence of the hydroxyl end groups increasing the affinity with RTM6 precursors.

Blend Morphologies

Blends based on RTM6 epoxy resin with different concentrations of PES (5, 10, 15, and 20 wt%) are cured and the resulting reaction-induced phase separated microstructures are examined by SEM after solvent etching with methylene chloride, which removes the PES phase. The pictures reveal a spectrum of morphologies, ranging from a continuous epoxy-rich phase with dispersed PES nodules to a phase-inverted microstructure as shown in Fig. 8.

When the PES-OH concentration increases from 5 wt% to 10 wt%, the TP appears as a nodular phase dispersed in the

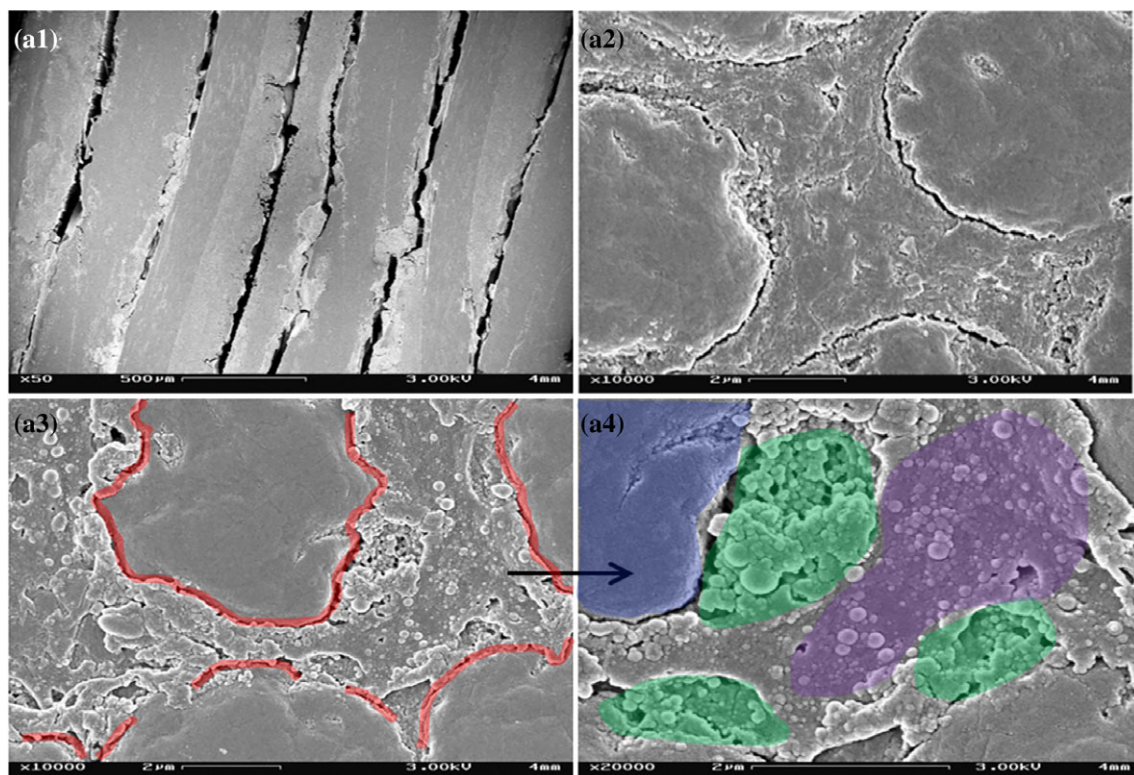


FIG. 10. SEM images of RTM6/PES-Cl cross-sectional panel zones (3 K/min) after solvent etching, (a1): General view, (a2) presence of cavities, and (a3, a4): presence of microstructure gradient, in blue: the carbon fibers, in red: holes produced after PES-Cl extraction (PES-Cl rich phase before etching), in green: Co-continuous zones and in purple: PES-Cl nodules dispersed in epoxy matrix. [Color figure can be viewed at wileyonlinelibrary.com]

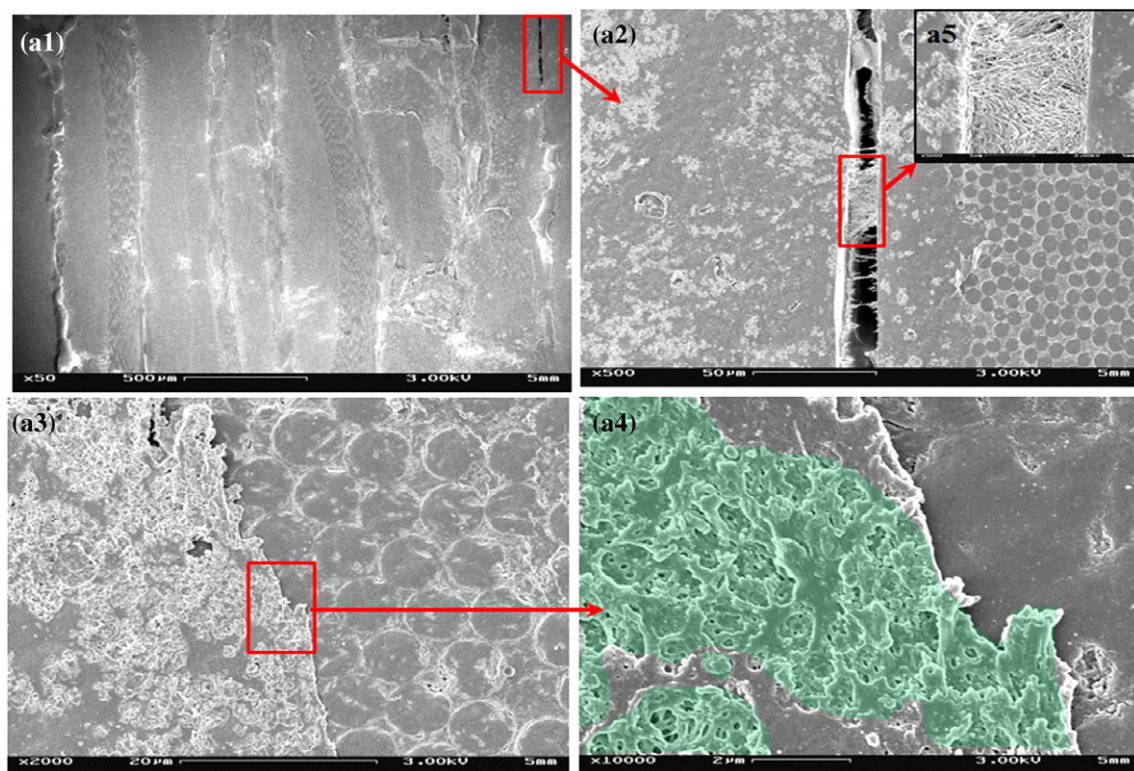


FIG. 11. SEM images of RTM6/PES-OH panel section zones (3 K/min) after solvent etching, (a1): General view, (a2 and a5): bridging between two plies of carbon fibers, (a3 and a4): lack of presence of microstructure gradient and the presence of a co-continuous phase. [Color figure can be viewed at wileyonlinelibrary.com]

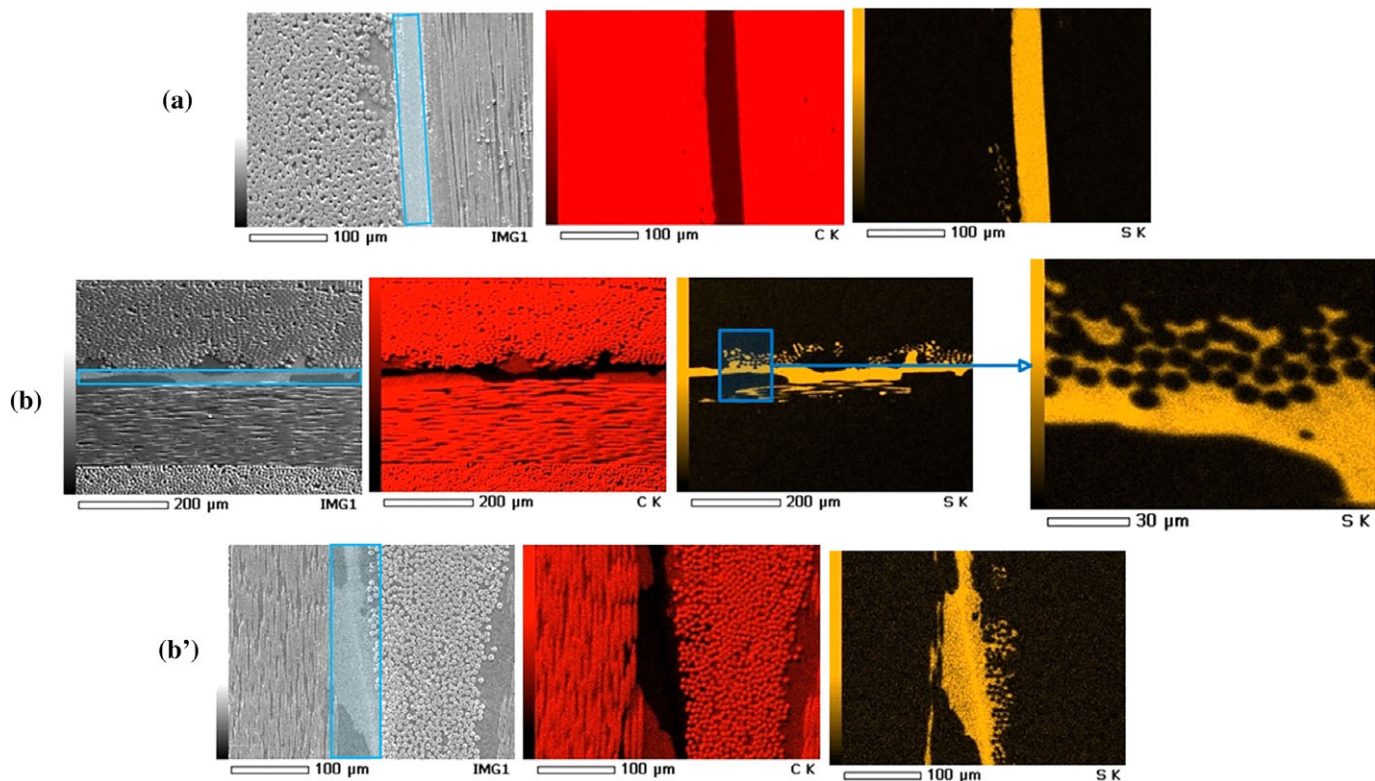


FIG. 12. SEM/EDX images of (a): PES-Cl composite panel section (carbon and sulfur elements) and (b and b'): PES-OH composite panel section (carbon and sulfur elements). [Color figure can be viewed at wileyonlinelibrary.com]

epoxy-rich matrix. The nodules areal density does not change, but the mean size of the nodules increases from 1–2 μm to 2–5 μm . The nodules are spherical with relatively homogenous size. Phase inversion is observed at a concentration of 15 wt%. RTM6 nodules with a broad size distribution (2–50 μm) are dispersed in a continuous PES-rich phase (which has been etched away), being continuous in some places, while in others, still separated by PES ligaments. At a concentration of 20 wt%, the distribution size of the epoxy nodules is bimodal, with a first class of sizes of diameter below 10 μm and a second class with diameter larger than 20 μm .

In the case of PES-Cl, the presence of 2–3 μm -sized nodules is already observed at a concentration of 5 wt%. At 10 wt% PES, the nodules are larger with a 3–4 μm size. The co-continuous phase observed at 15 wt% PES reveals RTM6 nodules with dimension up to 10 μm appearing more disconnected (wider PES ligaments) when compared to the PES-OH case. At 20 wt% PES, the size of the nodules is about 10–15 μm and the onset of phase inversion is clear. The same morphologies are observed in both conditions, meaning that PES functionalization does not drastically alter the mechanisms of phase separation in the model systems, but phase separation occurs earlier for PES-Cl and the size

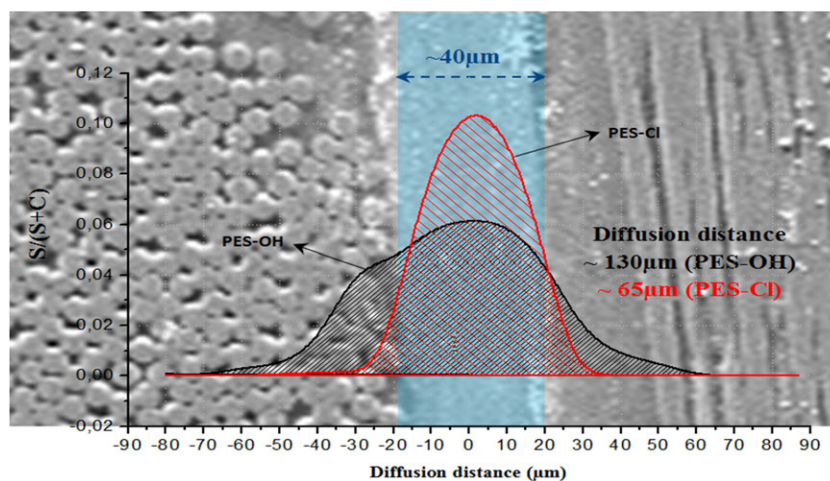


FIG. 13. SEM/EDX quantitative profile for both composite panels. [Color figure can be viewed at wileyonlinelibrary.com]

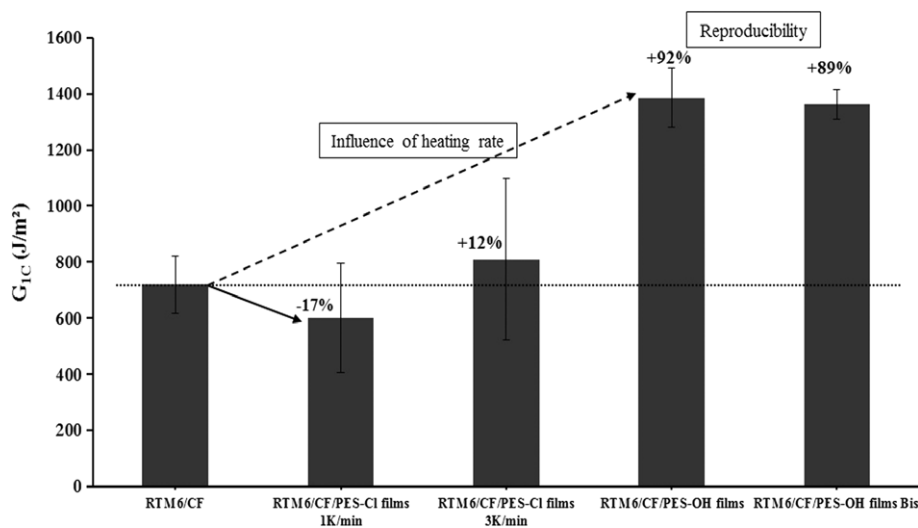


FIG. 14. Critical energy release rate required for mode I crack propagation (G_{IC}) of the reference and modified composite panels containing either PES-Cl or PES-OH thermoplastic films (40 μm thick).

of the nodular phase is larger, indicating a weaker miscibility with RTM6 epoxy.

Film-Based Model Systems

Interdiffusion between the TP and the epoxy must be considered in more detail for the transposition of the model TP-epoxy systems to real composites. As our strategy is to interleave TP films between the CF plies in the mold, we next study the structure of a TP film embedded in the epoxy. The goal is to predict the residual composition gradient frozen in the polymer blend after curing to orient the choice of TP layouts adapted for the RTM process.

The generated microstructures observed on a 100 μm thick PES-Cl film embedded in RTM6, after interdiffusion at 140 $^{\circ}\text{C}$ for 90 min and after solvent etching, are illustrated in Fig. 9. The etched away PES rich-zone close to the original TP film location, a phase inversion zone and a nodular PES area are observed in Fig. 9a–c, respectively, as the distance from the TP film increases. The examination of these morphologies shows an incomplete dissolution of the PES film over a distance of 130 μm after PES swelling by the RTM6 precursors. As previously described, the diffusion distance or swelling behavior of PES in RTM6 resin depends on the applied thermal profiles, whereas the overall shape of the microstructure gradient is not affected.

The interdiffusion distance and the microstructure evolution can be observed at high magnification as a function of the local concentration (Fig. 9d). The entire range of microstructures can be easily seen. The decrease in the size of the nodules and the phase inversion can be simultaneously observed. The interdiffusion distance is twice as large, which could be due to some movement of the film during curing or to the curved shape of the film.

Morphological Characterization of Panel Cross Sections before Mechanical Tests

The morphological characterization of a RTM6/PES-Cl panel cross sections after solvent etching shows the presence of large cavities corresponding to etched away PES-rich zones, at the original TP film location (Fig. 10a1). The width of the cavities

corresponds to the initial TP thickness (50 μm) as shown for the model system (Fig. 9a). The presence of additional cavities (Fig. 10a2 and red part in Fig. 10a3) observed near the CFs could be explained by the preferential affinity of PES-Cl for CFs. Moreover, Fig. 10a4 shows a co-continuous phase (highlighted in green near the CFs that highlighted in blue), whereas, when moving away from the CF, a PES-Cl nodular dispersion is observed inside the epoxy (highlighted in purple).

In the PES-OH composite (Fig. 11a1), the cavities corresponding to the original location of the TP films are discontinuous and their width is much smaller than in the RTM6/PES-Cl panel (see comparison between Fig. 10a1 with Fig. 11a1). Epoxy-rich bridges between plies of CFs are observed close to the initial film location in the PES-OH composite (Figs. 11a2 and 11a5) as opposed to the PES-Cl composite (Fig. 10a1). Finally, a microstructure gradient is not observed around CFs for the PES-OH composite, as opposed to the PES-Cl composite (see the comparison between Fig. 11a3 and Fig. 11a4 and Fig. 10a3 and Fig. 10a4), indicating no preferential affinity for CF in the former case. The major differences observed between the PES-OH and PES-Cl cases cannot be explained by mobility differences between the two PES because the molecular weight of the two polymers is comparable. Hence, they clearly reflect a better affinity and resulting interdiffusion of PES-OH with RTM6. Although it cannot be excluded that the higher polarity of OH end groups compared to Cl ones plays a role, a chemical coupling between the epoxy and PES-OH during the curing reaction is probably the main explanation for the differences. It has indeed been demonstrated that the hydroxyl groups of PES-OH can react with epoxide groups of RTM6 by etherification, leading to strong cohesion between the components [8, 11]. Such reaction occurring before phase separation will generate an PES-epoxy copolymer, which will increase the miscibility between the two components, and hence the driving force for interdiffusion, as well as reinforce the interfaces after phase separation.

SEM coupled with EDX is performed to better visualize the interdiffusion patterns in the composite panels and to understand the relationship between the morphology and the mechanical properties. The sulfur atom present in PES can be detected by

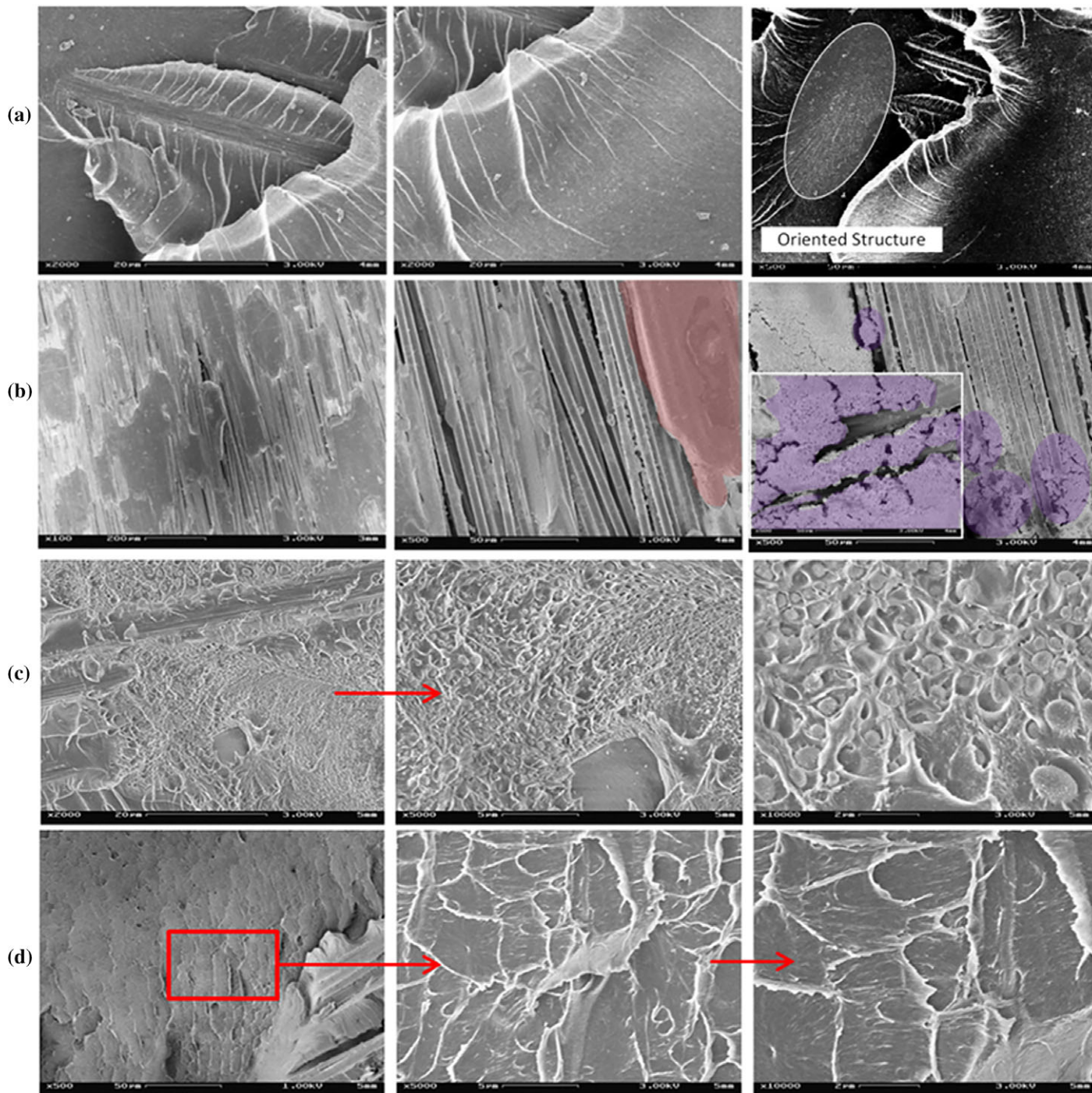


FIG. 15. SEM fracture surfaces images of (a) reference panel, (b) PES-Cl composite panel, (c) and (d) PES-OH composite panel. [Color figure can be viewed at wileyonlinelibrary.com]

EDX, to follow the TP diffusion distance and to evaluate the hindrance caused by the presence of the *CF* reinforcements.

Figure 12 presents SEM/EDX images of RTM6/PES-Cl and RTM6/PES-OH panel cross sections. A conventional SEM picture is added on the left side of the figure. The color is directly related to the atomic concentration, the carbon and sulfur signals from SEM/EDX being identified as red and yellow, respectively. The diffusion distance of PES-OH (Fig. 12b and b') through the *CF*s is larger than for the PES-Cl one (Fig. 12a). This has

been confirmed by establishing a quantitative profile based on the sulfur/(carbon + sulfur) ratio (Fig. 13).

Figure 13 shows that the diffusion distance in the PES-OH panel (around 130 μm) is twice as large as in the PES-Cl one (around 60 μm) despite similar molecular weights. This is in agreement with the above results. However, the diffusion distance obtained for the PES-OH panel is shorter than in the model system (without *CF*s), due to the presence of the *CF*s acting as a diffusion barrier.

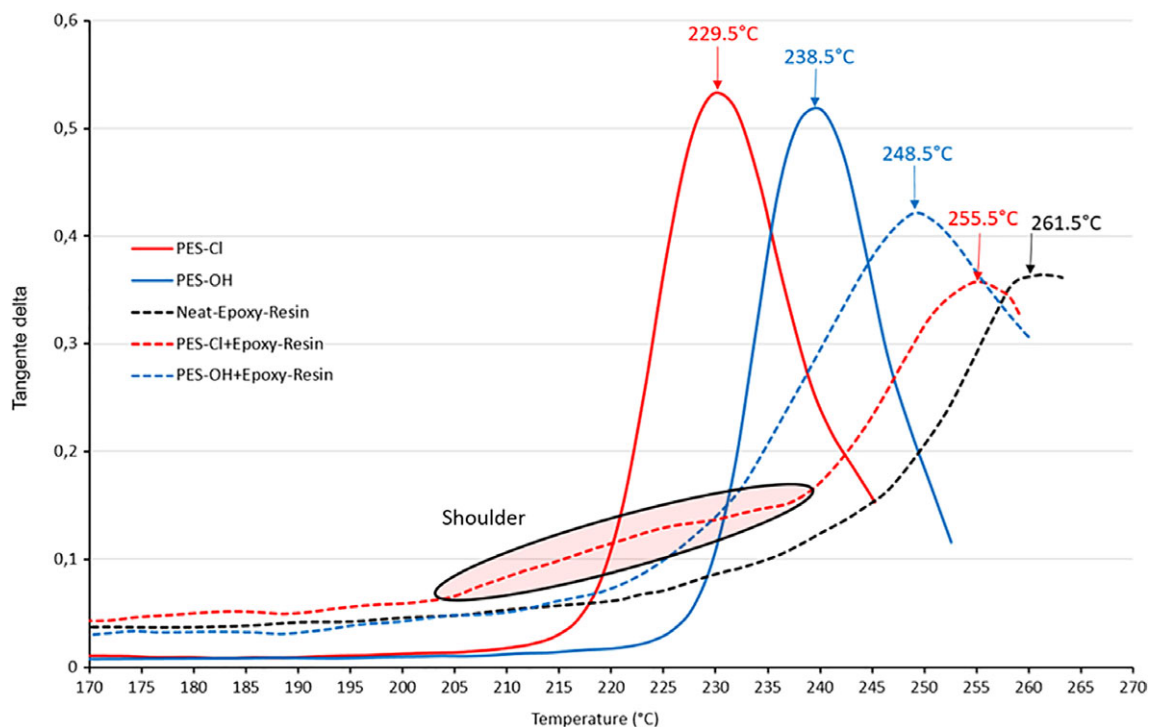


FIG. 16. Tangent delta peaks of various studied systems in the vicinity of the glass transition. [Color figure can be viewed at wileyonlinelibrary.com]

Fracture Toughness Measurements on Composite Panels

Figure 14 gathers the mode I critical interlaminar energy release rate (G_{Ic}) measured on the reference and modified composite panels by the DCB test configuration. For the PES-Cl-modified panel cured at a heating rate of 1 K/min, the energy release rate required for crack extension decreases by 17% when compared to the reference panel. However, the G_{Ic} value is slightly enhanced by 12% when using a faster temperature curing ramp (3 K/min), but this result lies within the standard deviation. The lack of improvement is attributable to the poor affinity between PES-Cl and the epoxy matrix, leading to a narrow TP diffusion profile as shown in Fig. 13. On the contrary, a very significant improvement of G_{Ic} (around 90%) is obtained with the PES-OH-modified system (cured at 3 K/min), which is most probably due to the broader interdiffusion, the origin of which has been discussed earlier. A reproducibility test on a second PES-OH panel has confirmed the same G_{Ic} improvement.

The fracture surface of the reference panel after DCB testing (Fig. 15a) exhibits riverlines and smooth oriented textures, which indicate a relatively brittle behavior.

The fracture surfaces of the PES-Cl panel reveal uncoated (debonded) CFs and the presence of large smooth areas of brittle resin devoid of TP (Fig. 15b). A small microstructure gradient is observed around the CFs close to the original TP film location. The low adhesion between the resin and the CFs on the one hand and the presence of undissolved PES-Cl on the other constitute direct explanations for the observed low crack propagation resistance.

The disappointing G_{Ic} value of the PES-Cl-reinforced panels can hence be associated with the poor interfacial adhesion and limited interdiffusion between the different composite components,

which easily generate damage sites along the interfaces, hence limiting the resistance to cracking.

The fracture surface of the PES-OH panel is drastically different: it shows extensive resin fibrillation (Fig. 15c) due to strong chemical adhesion between the PES-OH nodules and the epoxy matrix. The fracture behavior is now much more ductile. Newman and Strella [32] have developed a rational hypothesis for the improved toughness of rubber-modified glassy polymers as defined by the energy to rupture in a tensile measurement. It is shown that a triaxial stress field in the environment of the dispersed particles causes an increase in free volume sufficient to lower the local T_g of the matrix adjacent to the rubber particles, which helps the initiation of cold drawing and provides the rubber with sufficient breaking stress to prevent premature crack propagation. In the PES-OH panel, plastic deformation of the epoxy resin matrix is observed (Fig. 15d) in resin-rich zone close to the PES-OH nodules and around CF leads to a rough surface aspect. The presence of the PES-OH nodules favors extensive plastic deformation while not introducing any weak spots for easy damage initiation.

Dynamic Mechanical Measurements

To help clarify the origin of the better performance of PES-OH-based systems, DMA analyses have been performed. Figure 16 shows tangent delta as a function of temperature for neat PES with chlorine and hydroxyl end groups, the neat fully cured epoxy resin and the blends of epoxy/PES-Cl and epoxy/PES-OH at 10 wt% PES concentration. The graph shows that the T_g of PES-OH identified by the maximum of tangent delta (238.5 °C) is higher than the T_g of PES-Cl (229.5 °C) at the same molar mass. This can be explained by the influence of the

hydroxyl ends groups, which generate strong hydrogen bonds with the sulfone groups, effectively reducing chain mobility, and this effect is absent in PES-Cl. The tangent delta maximum of the fully cured neat epoxy resin is at 261.5 °C and the peak is much broader than the neat PES peak, reflecting a slight heterogeneity of crosslinking density, as already observed by Bahrami et al [33]. For the PES-Cl/RTM6 blend, we observe a main peak with a maximum at 255.5 °C preceded by a broad, low but distinct shoulder around ~225 °C. In the case of the PES-OH RTM6 blend, we observe a single but extremely broad peak with a maximum at 248.5 °C. Furthermore, we know from morphological analysis that both blends are phase separated, the morphology of the PES-OH blend being finer than of the PES-Cl one. The only logical explanation for these complex features is a partial intermiscibility between PES and the cured epoxy, strongly dependent on the nature of the PES end groups, with PES-OH being more miscible than PES-Cl in the epoxy-rich phase. Indeed, at 10% PES concentration, a distinct DMA signature of the PES-rich phase is still visible for the PES-Cl blend, whereas it is hidden in the very broad epoxy peak for the PES-OH blend. The location of the PES shoulder close to the neat PES T_g in the PES-Cl blend suggests there is very little epoxy dissolved in the PES-rich phase of that blend. The absence of a visible shoulder and the lower T_g of the epoxy-rich phase in the PES-OH blend suggest stronger intermiscibility in that system. It is well known that higher intermiscibility leads to a wider interfacial thickness in phase-separated polymer blends through the classical Helfand–Tagami relationships [34]. A wider interface in turn leads to stronger interfacial cohesion (chiefly through entanglements). Although a straightforward comparison between the T_g s of the neat and blended systems is rendered imprecise by subtle effects of local stoichiometry imbalance that might arise in the blends from diffusion rate differences between the epoxy precursor and hardener, leading to a lower T_g than expected, the picture presented by the DMA results is clear.

The higher TP-TS intermiscibility observed for the PES-OH epoxy system after curing is probably true even in the absence of any cross-reaction, as suggested by the better diffusion of RTM6 precursor in PES-OH versus PES-Cl already observed at low temperature in the model systems. This does not exclude an additional influence of PES-epoxy copolymer, which can be generated by interfacial or bulk reaction between the PES-OH end groups and the epoxy precursor, but our results are not providing information in this direction. This has to be left to a future work.

CONCLUSION

This study has addressed the specific influence of PES functionalization at fixed molar mass on its toughening potential for high-performance epoxy composites based on an important example (RTM6). The differences in toughening have been clearly related to the diffusion behavior and the resulting phase-separated morphologies as a function of the functionalization, with the help of model systems and DMA experiments. PES-OH filaments in RTM6 droplets (model systems) swell more than PES-Cl, due to the presence of hydroxyl end groups, reflecting an increased affinity of the latter with the multicomponent epoxy precursors. The morphological characterization

of RTM6/PES blends and composites highlights the resulting positive influence of the OH end groups on PES (at same molar mass). A quantitative estimate obtained by SEM/EDX analysis shows twice as large a diffusion distance in the case of PES-OH (around 130 μm) as compared to PES-Cl (around 60 μm). This in turn leads to higher toughness for the PES-OH-based composite (doubling of G_{Ic}) as compared to no improvement for PES-Cl. DMA analysis clearly points to improved intermiscibility and the resulting stronger interface between PES-OH and RTM6 as a significant contribution to the improved toughness, although our results do not provide information on the potential additional contribution of PES-epoxy copolymer reactively generated during the cure program.

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