Size limitations on achieving tough and healable fibre reinforced composites through the use of thermoplastic nanofibres

Amaël Cohades[1], Lode Daelemans[2], Charlie Ward[1], Timo Meireman[2], Wim Van Paepegem[2], Karen De Clerck[2], Véronique Michaud[1]

[1] Laboratory for Processing of Advanced Composites (LPAC), Institute of Materials (IMX), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

[2] Department of Materials, Textiles and Chemical Engineering (MATCH), Ghent University, Technologiepark 907, B-9052 Zwijnaarde, Belgium

Abstract
This research investigated a novel method to combine healing in epoxy matrix composites with interlaminar fracture toughness improvement. Polycaprolactone (PCL) electrospun nanofibrous veils were interleaved in glass fibre reinforced epoxy composites in order to assess the possibility to provide both toughening and healing at the same time. Mode I double cantilever beam testing revealed higher toughness (up to 48%) for the nanofibre enhanced composites as compared to pure epoxy composites. Crack surface analysis showed the presence of a fully phase-separated microstructure consisting of micronsized epoxy particles surrounded by a PCL matrix. The fine microstructure provided (i) microcracks bridging by the PCL and (ii) a tortuous crack path. A thermal treatment at 150 °C for 30 minutes was then applied on the specimens but no healing could be obtained due to two limiting factors: (i) the residual stresses in the nanofibres due to electrospinning which led to shrinkage during healing and thus limited the PCL expansion capacity; (ii) high PCL viscosity which prevented its flow in such a fine microstructure of epoxy interconnected particles at the time scale of the healing experiment. Modelling of the flow through the Carman-Kozeny equation provided hints to allow crack healing and high toughness properties.

1. Introduction

Fibre reinforced polymers (FRPs) are of utmost interest in many structural applications thanks to their high strength to weight ratio. However, their multilayer nature provides weaknesses at the inter-layer locations and results, during out-of-plane loading, in damage such as delamination and different forms of microcracking. This low tolerance to damage is particularly important when brittle thermoset matrices are used, leading to strict monitoring and maintenance schedules. Considerable research efforts have been carried out in the past years in trying to either (i) limit the growth of these damage induced cracks, or (ii) provide autonomic repair if needed.

One way of increasing damage tolerance in FRPs is to provide toughening. This has been achieved in the past decades by different methods such as rubber/thermoplastic toughening [1], addition of rigid nanoparticles [2] or using through-thickness reinforcements [3]. However, these also result in reduced in-plane properties, higher cost and weight, and increase the complexity of processing. One additional method, which raised much interest as it can tackle these drawbacks, consists in inserting thermoplastic electrospun nanofibre mats in between the FRP reinforcing plies prior to processing. Many studies in this field [4–13] elaborated on this concept. In particular, the toughening mechanism was explained through the study of glass/epoxy composites modified by nanofibres of poly(ε-caprolactone) (PCL) or polyamide 6 (PA6) (different nanofibre diameters and mats density) [6,12,13]. They showed that (i) the main toughening mechanism is through microcracks bridging by the nanofibres [12], (ii) nanofibres can decrease the rate of delamination by one order of magnitude under fatigue conditions [6] and (iii) the orientation of nanofibres plays a strong role as Mode II fracture toughness was increased 2-fold [13].

A. Cohades, L. Daelemans, C. Ward, T. Meireman, W. Van Paepegem, K. De Clerck, V. Michaud

Instead of providing toughening to FRPs to limit the growth of damage, research efforts have been also focused on integrating a self-healing functionality to polymeric thermoset matrices, so that internal damage can be repaired autonomously in FRPs. Two main strategies exist: (i) the use of extrinsic systems (capsules or vascules) into the thermoset matrix which can rupture and release a healing agent during crack propagation [14,15]; (ii) conferring to the matrix the intrinsic ability to heal through chemistry modification or by creating thermoset/thermoplastic blends [15,16]. Especially, creating immiscible blends between a thermoset matrix and a low melting point semicrystalline thermoplastic [17–20] demonstrated its interest for a viable use in FRPs and to overcome the need to develop a fully new matrix chemistry [20–24]. The healing principle relies on melting and volume expansion of the thermoplastic followed by melt flow into the damage volume and physical as well as possibly chemical phenomena once crack faces are in contact. Even though this healing approach requires external activation such as heat to trigger repair, it is repeatable and latent. Of particular interest for the present research are blends composed of a particulate thermoset phase embedded in a thermoplastic matrix [17,18] created through polymerization-induced phase separation. Indeed, blends of epoxy and 25 vol% PCL demonstrated recovery of Mode I crack opening in excess of 70% (after thermal mending at 150°C during 30 minutes) [17]. When further integrated into FRPs through conventional liquid composite moulding manufacturing process, those blends showed toughness, stiffness and compression strength recovery up to respectively 45%, 100% and 100% [23,24] while retaining strength and stiffness close to conventional epoxy FRPs. Toughness was however decreased by 40% as compared to the reference systems, which was explained by the blends morphology where PCL suffers from severe confinement between the epoxy particulate phase and thus cannot deform much before rupture. There is thus a need to tackle this lack of toughness in epoxy-PCL phase separated blends while keeping their healing ability in order to reach FRP healing systems that can be of interest both on damage prevention and repair ability.

In the present work, we propose to interleave 20-25vol% of PCL nanofibres into woven glass fibre epoxy composites in order to reach phase separated microstructures as obtained in previous studies with epoxy-PCL blends for healing applications [17,23,24]. By keeping the cure kinetics close to the PCL melting point, we investigate the possibility to reach a biphasic matrix structure made of (i) phase separated morphology consisting of epoxy particles and a surrounding PCL matrix that can be efficient for crack healing and (ii) PCL nanofibres that are not affected during the curing process which can be efficient to provide toughening to the composite part. We first study this concept in resin model samples through thermal and microscopy analysis to assess the influence of nanofibres on the phase separation process. This concept is then applied to the production of FRPs through vacuum assisted resin infusion moulding and interlaminar toughness of the produced composites assessed through Mode I Double Cantilever Beam (DCB) experiments. The samples are finally subjected to a thermal cycle at 150 °C for 30 minutes to investigate their crack healing capacity.

2. Materials and methods

2.1. Materials
Nanofibre veils of PCL ($M_n \approx 80,000$ g/mol, *Sigma Aldrich*) of around 30 g/m^2 with a diameter of 345 ± 150 nm were produced through electrospinning following similar procedures as in [6,12,13]. Epikote MGS RIM 135 from *Hexion*, a commercial DGEBA resin with a molar mass per epoxide group of 166-185 g/eq was cured with RIMH 137 in a 100:30 weight ratio. The glass fibre reinforcement was a woven twill 2x2 E-glass fabric, with a nominal areal weight of 390 g/m^2, 6 end/cm for warp fibres and 6.7 picks/cm for weft fibres, fibre diameter of 9 μm, yarn thickness of 0.45 mm, warp tex of 68x5 and weft tex of 272, from *Suter-Kunststoffe AG*.

2.2. Samples Preparation
Four types of model samples made of nanofibres and epoxy resin with two different compositions (20 and 25 vol% of PCL nanofibres with respect to epoxy resin) and two curing conditions (60°C and 80 °C curing for 24h followed by a post-cure at 80 °C for 15h) were produced. Nanofibre rectangles of 12.5x35mm^2 were cut and disposed in the right concentration into silicon moulds of the same

A. Cohades, L. Daelemans, C. Ward, T. Meireman, W. Van Paepegem, K. De Clerck, V. Michaud

dimensions. The epoxy resin was then poured in between each nanofibre layer before letting the samples to cure.

Composite plates were processed by Vacuum Assisted Resin Infusion Moulding (VARIM) following a similar layout as described in [23,25] and stacking sequence of $[(+45/-45)/(0/90)]_{4s}$. 30 gsm nanofibre veils of dimensions 140x100 mm were cut and weighed before being placed in between each dry reinforcement layer using a template. Infusion was then performed with the epoxy resin at room temperature before placing the composite plate to cure at the desired temperature (room temperature, 60 or 80 °C) for 24h. Each composite plate underwent a post-curing treatment for 15h at 80°C. Process conditions, content, final fibre and nanofibre volume fractions are summarized in Table 1.

Table 1. Specimen designations, composition, curing conditions and the corresponding fibre volume fraction obtained after composite production as well as nanofibre (NF) volume fraction with respect to the matrix. Notice that every sample was post-cured at 80°C for 15h.

Specimen	Composition	Curing	V_f [%]	V_{NF} in matrix [%]
GF-Epoxy-RT	Pure epoxy	RT	49.4 ± 0.2	0
GF-Epoxy-NF-RT	30 gsm NF	RT	36.4 ± 3.4	11.9 ± 1.8
GF-Epoxy-NF-60	30 gsm NF	60 °C	46.9 ± 1.6	17.5 ± 0.9
GF-Epoxy-NF-80	30 gsm NF	80 °C	45.6 ± 2.1	17.8 ± 1.5

2.3. Morphological Characterisation

Cuts of the resin model samples were embedded in *Epofix* Resin, polished until 1 μm size diamond disc polishing, and observed with a reflexion optical microscope (*Olympus* BH-2). Fracture surface of the DCB specimens, coated with 10 nm of gold, were observed by scanning electron microscopy (SEM, *Philips* XLF-30 FEG).

2.4. Mode I Double Cantilver Beam testing

The fracture behaviour of the prepared samples was assessed in Mode I DCB following the ASTM standard D5528. For load introduction, aluminium blocks were glued on each side of the samples. Each sample underwent two loading-unloading cycles, the first one corresponded to the test of the *virgin* specimen, whereas the second applied to the *healed* specimens each after a thermal mending cycle of 30 minutes at 150 °C. In each cycle, loading was performed until displacement reached 30 mm before unloading at the same speed of 4 mm/min until the load reached zero. At least 5 tests were performed for each batch. During thermal mending, samples were left as unloaded, with only the crack faces imposed to be in contact at the location of the loading blocks, leading to a maximum crack thickness of nearly 100 μm, similar to our previous study [23].

3. Results and Discussion

3.1. Blends phase separation assessment

Four types of model samples made of 30 gsm PCL nanofibres and epoxy resin with two different compositions (20 and 25 vol% of PCL nanofibres) and two curing conditions (60 °C and 80 °C curing for 24h followed by a post-cure at 80 °C for 15h) were first processed to investigate the potential for a dual microstructure (phase separated as well as intact nanofibres). Immiscibility between the components is necessary in such blends [17] to obtain the biphasic phase separated structure, and further maintain structural integrity as well as healing; this can be assessed through thermal transitions determination. Differential Scanning Calorimetry experiments for the different blends after cure showed transition temperatures similar to those of the pure PCL nanofibres and pure epoxy, indicating a high degree of phase purity.

Cross sections of the four epoxy-PCL nanofibre specimens were further polished and observed by optical microscopy. Three distinct regions could be observed: (i) pure epoxy resin free of PCL; (ii) pure PCL nanofibres free of epoxy resin and (iii) phase separation between epoxy and PCL. The

A. Cohades, L. Daelemans, C. Ward, T. Meireman, W. Van Paepegem, K. De Clerck, V. Michaud

phase-separated region showed two phase-separated morphologies expected from previous studies [17,18]: epoxy particles in a PCL matrix and a domain like morphology (see Fig. 1). Epoxy particles are small and of around 1 μm diameter (smaller than the 20 μm ones in [17] for similar materials) due to the fast curing kinetics of the resin leading to a short time for nucleation and growth of the particles during phase separation. Overall, the obtained structure was not regular on the entire sample, demonstrating that epoxy resin could not dissolve all the nanofibres during the curing process, thus creating a gradient in PCL composition explaining the different phase separated morphologies. This resulting irregular morphology could be an asset for combined healing and toughness improved properties as it contains phase-separated regions for healing and nanofibres regions for toughening.
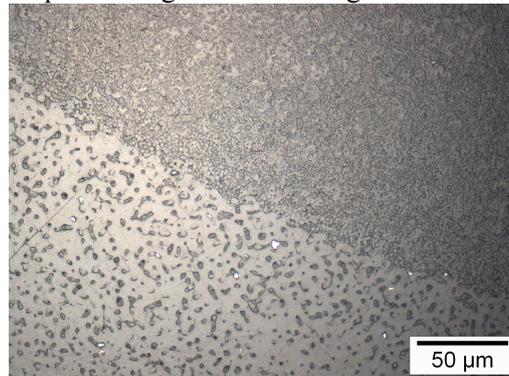
Figure 1. PCL nanofibres (20 vol%) in epoxy resin cured at 60 °C for 24h and post-cured for 15h at 80 °C showing the transition between two phase separated morphologies.

3.2. Fracture and healing properties of PCL enhanced composites

Nanofibres were further interleaved in FRPs at a theoretical composition of 20vol% with respect to the epoxy matrix and cured at three different temperatures: room temperature, 60 °C and 80 °C. A reference composite plate was manufactured without any nanofibres and cured at room temperature. In Table 1 gives the overall fibre volume fractions and nanofibre volume fractions with respect to the resin for each cured composite plate. While for the reference composite plate, the fibre volume fraction was close to the theoretical value (i.e. 50%), it varied for the other systems containing nanofibres because these blocked nesting of the reinforcement layers during compaction under vacuum prior to infusion, thus increasing the overall thickness of the specimens. For the nanofibre enhanced composites cured at room temperature, this effect was high as the PCL could not melt during the curing process. For the composites cured at 60 °C and 80 °C, this effect was reduced as PCL nanofibres partly melted during the curing process. This behaviour not only influenced the volume fraction of fibres, but also the nanofibre volume fraction with respect to the epoxy resin. At room temperature, the nanofibre volume fraction with respect to the epoxy matrix was of only 12% (whereas it was theoretically calculated as 20%) as the veils prevented nesting between the layers. For the composites cured at 60 °C and 80 °C, the nanofibre volume fraction with respect to the epoxy resin was of 18%, not differing much from the targeted value as the veils partly melted during the curing process, which allowed better nesting between the glass reinforcement layers.

Fig. 2 shows fracture toughness mean values for the processed composites. Toughness values for the reference pure epoxy composite (i.e. *GF-Epoxy-RT*) are similar to previous studies on the same woven reinforcements [23,25], although slightly higher due to the high intrinsic toughness of the epoxy resin used in this work[12]. When integrating nanofibres in between each FRP layer, toughness values were increased between 43 and 48% depending on the system. For the composites cured at room temperature (i.e. *GF-Epoxy-RT*), this toughness increase is related to microcracks bridging by the nanofibres, similar to the work of Daelemans *et al.* [12]. Furthermore, toughness was also increased in systems cured at higher temperature (i.e. *GF-Epoxy-NF-60* and *GF-Epoxy-NF-80*) where the nanofibres should have dissolved into epoxy resin before being phase separated during cure. Crack surface analysis further showed that room temperature curing allowed keeping the nanofibres fibrous structure intact, in accordance with [12], thus explained the increase in fracture toughness mean

A. Cohades, L. Daelemans, C. Ward, T. Meireman, W. Van Paepegem, K. De Clerck, V. Michaud

values. For composites cured at 60°C, the targeted phase separated morphology was observed, with epoxy particles of around 1 μm diameter. For composites cured at 80°C, a domain like morphology (also of characteristic size in the range of the micron) was however mostly observed and explained by the higher curing temperature that dissolved more PCL which could diffuse and provide an overall constant concentration of PCL corresponding to the concentration providing this morphology. The increase of mean fracture toughness values for the phase separated structures was attributed to the fine microstructure obtained, providing microcracks bridging by the PCL.
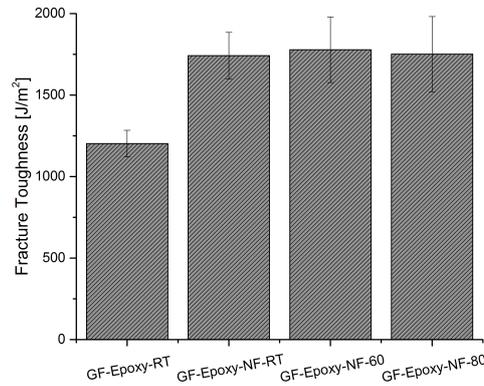
Figure 2: Fracture toughness for the different assessed composites. See Error! Reference source not found. for details on samples naming.

Damaged samples were then clamped at the loading blocks and healed at 150°C for 30 minutes. For every sample, the loading part of the healed cycle followed exactly the unloading part of the virgin cycle during DCB testing demonstrating that no crack healing could take place within the nanofibre enhanced composites.

To understand the inability of the samples to heal the propagated cracks, observations of the fracture plane after healing were performed. The analysis was restricted to samples cured at 60 °C as these contained the phase-separated microstructure most favourable for healing applications (i.e. epoxy particles in a PCL matrix) as determined in [17,23]. Fig. 3 shows the healed fracture surface of a nanofibre enhanced composite sample cured at 60°C (i.e. *GF-Epoxy-NF-60*). The phase-separated morphology consisting of epoxy particles with a surrounding PCL matrix is well observed. As for healed fracture surfaces seen in [23], some bleeding of the PCL was observed as expected. However, the bleeding amount was low, not present on the entire fracture plane and restricted to only few microns thick whereas it is expected from [23] that in such samples, the PCL volume should lead to an expansion of nearly 36 μm.

This lack of healing was attributed to two limiting elements: (i) residual stresses due to nanofibre stretching during processing which provided some shrinkage during healing and thus limited the full PCL expansion capacity; (ii) high PCL viscosity which prevented its flow in such a fine microstructure of epoxy interconnected particles. The second point was highighlited as the main cause for this absence of PCL bleeding in the crack plane and was further modelled considering that within phase separated structures consisting of epoxy particles with a surrounding thermoplastic (i.e. PCL) matrix, the thermoplastic flow when heating the structure is similar to the flow of any liquid within a porous media and is thus dependent on the capillary pressure as well as the required pressure for the liquid to flow within the media. The driving force is thus the pressure generated by the PCL expansion during heating at 150 °C. This last was determined to be 184 MPa at most, calculated through the PCL volume expansion at 150 °C (14% in the present case) and the liquid bulk modulus at the same temperature (1.31 GPa in the present case). Detailed calculations of the PCL expansive pressure and the PCL bulk modulus in the liquid state are provided in [18,26]. Considering that flow takes place in a network of epoxy particles with 1 μm diameter, the capillary pressure reaches around 100 kPa

A. Cohades, L. Daelemans, C. Ward, T. Meireman, W. Van Paepegem, K. De Clerck, V. Michaud

(calculated from the *Young-Laplace* equation considering PCL surface tension of around 30 mN/m). As PCL melting is generating a relatively large pressure (184 MPa), the capillary pressure is thus not limiting for the PCL to flow within the studied phase separated network. The second possible limiting parameter for PCL bleeding is the pressure required for its flow within the phase separated structure. The time t for the PCL to flow from under a pressure drop ΔP is given by the *Carman-Kozeny* equation, considering flow in a porous structure made of particles of a given diameter D:

$$t = \frac{150\eta(1-\varepsilon)^2 L^2}{\Delta P \Phi^2 D^2 \varepsilon^2} \tag{1}$$

where η is the PCL viscosity, ε the porosity, L the channel length, ΔP the pressure drop over the porous medium (taken as 184 MPa), Φ the sphericity and D the particle diameter. Considering the case studied here of a 5 mm thick DCB sample with a propagated crack in the middle, the channel length L is assumed to be 2.5 mm. The sphericity Φ of the epoxy particles can be assumed to 1. Porosity ε is further calculated as 20.7% based on the weight fractions (20.1% of PCL for the composites with 60 gsm PCL nanofibres) and densities of epoxy and PCL. The PCL viscosity was measured by rheological experiment in flow (plate rheometer AR 2000 from *TA Instrument*) at a frequency of 1 s^{-1} and at 150 °C, and provided a value of 4819 Pa·s. The PCL flow within such a porous network strongly depends on the particle diameter, especially at low particle size. Indeed, considering the systems studied (with particles diameter of 1 μm), the time for the PCL to flow through half of the sample thickness is of around 100 hours, which is far more than the 30 minutes thermal treatment applied for healing. The lack of bleeding (and thus of crack healing) observed during the present study is thus explained by the long time required for the PCL to flow through the network of epoxy particles. Increasing the particle size would allow higher amount of healing, decreasing to 6 minutes at 30 μm diameter. For the case of the systems studied in ref. [17,23], the lower molecular weight PCL had a much lower viscosity (40 Pa·s), which further decreased the overall flow time (calculated by Eq. 1). In those systems, crack healing was thus possible thanks to PCL bleeding. Considering the fact that toughness of the systems was reduced (see [17,23]) with epoxy particles of around 20 μm diameter, whereas in the present case, a fine microstructure (i.e. particle of around 1 μm diameter) provided an increased toughness, using a lower molecular weight PCL in FRPs with a fine microstructure (through the use of PCL nanofibres) would thus be a way to provide toughness as well as healing to a crack. However, the production of PCL nanofibres with a lower molecular weight is difficult to achieve due to the need of higher thermoplastic viscosity for the electrospinning process to work.
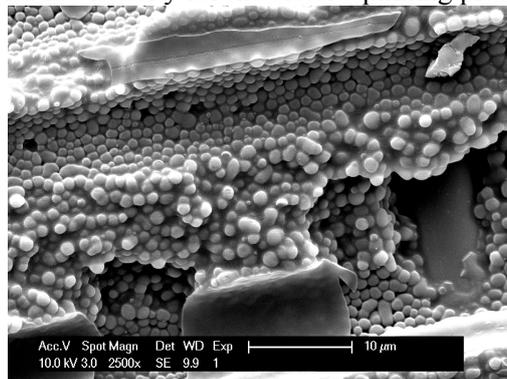
Figure 3: Healed fracture surface of composite containing nanofibres and cured at 60 °C (i.e. *GF-Epoxy-NF-60*) showing the phase separated morphology of epoxy particles with a surrounding matrix.

4. Conculsions

This research investigated a novel method to combine healing in epoxy matrix composites with interlaminar fracture toughness improvement. PCL electrospun nanofibrous veils were interleaved in glass fibre reinforced epoxy composites in order to assess the possibility to provide both toughening and healing at the same time. Resin model samples were first produced and cured at 60 °C to obtain a combined microstructure consisting of phase-separated regions (epoxy particles surrounded by a PCL matrix) ideal for crack healing as well as retaining intact nanofibres ideal for interlaminar toughening.

A. Cohades, L. Daelemans, C. Ward, T. Meireman, W. Van Paepegem, K. De Clerck, V. Michaud

Glass fibre reinforced epoxy composites interleaved with PCL nanofibres were further successfully produced by vacuum assisted resin infusion moulding with a slightly lower fibre volume fraction (40%) than expected due to the use of nanofibres which prevented compaction and nesting of the glass fibre reinforcement. Mode I DCB testing revealed higher toughness (up to 48%) for the nanofibre enhanced composites as compared to pure epoxy composites. Crack surface analysis further showed the presence of a fully phase-separated microstructure consisting of epoxy particles surrounded by a PCL matrix. Due to the interplay between reaction kinetics and PCL diffusion with the resin used, the epoxy particles were small (1 μm diameter), leading to increased toughness of the produced specimens. The fine microstructure provided (i) microcracks bridging by the PCL and (ii) a tortuous crack path. A thermal treatment at 150 °C for 30 minutes was then applied on the specimens to assess the capacity of the PCL to bleed, flow and bridge the crack faces, thus healing the crack. However, no healing could be obtained due to two limiting factors: (i) the residual stresses in the nanofibres due to electrospinning which led to shrinkage during healing and thus limited the PCL expansion capacity; (ii) high PCL viscosity which prevented its flow in such a fine microstructure of epoxy interconnected particles at the time scale of the healing experiment. Modelling of the flow through the Carman-Kozeny equation demonstrated that the use of a lower viscosity PCL under the form of this nanofibres, should allow crack healing and high toughness properties.

References
[1]   Xu F, Du XS, Liu HY, Guo WG, Mai YW. Temperature effect on nano-rubber toughening in epoxy and epoxy/carbon fiber laminated composites. Compos Part B Eng 2016;95:423–32.
[2]   Chandrasekaran S, Sato N, Tölle F, Mülhaupt R, Fiedler B, Schulte K. Fracture toughness and failure mechanism of graphene based epoxy composites. Compos Sci Technol 2014;97:90–9.
[3]   Tan KT, Watanabe N, Iwahori Y. X-ray radiography and micro-computed tomography examination of damage characteristics in stitched composites subjected to impact loading. Compos Part B Eng 2011;42:874–84.
[4]   Dzenis YA, Reneker DH. Delamination resistant composites prepared by small diameter fiber reinforcement at ply interfaces. United States Patent 6265333, 2001.
[5]   Kim J, Reneker DH. Mechanical properties of composites using ultrafine electrospun fibers. Polym Compos 1999;20:124–31.
[6]   Daelemans L, van der Heijden S, De Baere I, Rahier H, Van Paepegem W, De Clerck K. Improved fatigue delamination behaviour of composite laminates with electrospun thermoplastic nanofibrous interleaves using the Central Cut-Ply method. Compos Part A Appl Sci Manuf 2017;94:10–20.
[7]   van der Heijden S, Daelemans L, De Bruycker K, Simal R, De Baere I, Van Paepegem W, et al. Novel composite materials with tunable delamination resistance using functionalizable electrospun SBS fibers. Compos Struct 2017;159:12–20.
[8]   Beckermann GW, Pickering KL. Mode I and Mode II interlaminar fracture toughness of composite laminates interleaved with electrospun nanofibre veils. Compos Part A Appl Sci Manuf 2015;72:11–21.
[9]   Nash NH, Ray D, Young TM, Stanley WF. The influence of hydrothermal conditioning on the Mode-I, thermal and flexural properties of Carbon/Benzoxazine composites with a thermoplastic toughening interlayer. Compos Part A Appl Sci Manuf 2015;76:135–44.
[10]   Li G, Li P, Zhang C, Yu Y, Liu H, Zhang S, et al. Inhomogeneous toughening of carbon fiber/epoxy composite using electrospun polysulfone nanofibrous membranes by in situ phase separation. Compos Sci Technol 2008;68:987–94.
[11]   Magniez K, Chaffraix T, Fox B. Toughening of a Carbon-Fibre Composite Using Electrospun

Poly(Hydroxyether of Bisphenol A) Nanofibrous Membranes Through Inverse Phase Separation and Inter-Domain Etherification. Materials (Basel) 2011;4:1967–84.

[12]   Daelemans L, Van Der Heijden S, De Baere I, Rahier H, Van Paepegem W, De Clerck K. Damage-Resistant Composites Using Electrospun Nanofibers: A Multiscale Analysis of the Toughening Mechanisms. ACS Appl Mater Interfaces 2016;8:11806–18.

[13]   Daelemans L, van der Heijden S, De Baere I, Rahier H, Van Paepegem W, De Clerck K. Using aligned nanofibres for identifying the toughening micromechanisms in nanofibre interleaved laminates. Compos Sci Technol 2016;124:17–26.

[14]   Blaiszik BJ, Kramer SLB, Olugebefola SC, Moore JS, Sottos NR, White SR. Self-Healing Polymers and Composites. Annu Rev Mater Res 2010;40:179–211.

[15]   Wu DY, Meure S, Solomon D. Self-healing polymeric materials: A review of recent developments. Prog Polym Sci 2008;33:479–522.

[16]   Garcia SJ. Effect of polymer architecture on the intrinsic self-healing character of polymers. Eur Polym J 2014;53:118–25.

[17]   Cohades A, Manfredi E, Plummer J-C, Michaud V. Thermal mending in immiscible poly(ε-caprolactone)/epoxy blends. Eur Polym J 2016;81:114–28.

[18]   Luo X, Ou R, Eberly DE, Singhal A, Viratyaporn W, Mather PT. A thermoplastic/thermoset blend exhibiting thermal mending and reversible adhesion. ACS Appl Mater Interfaces 2009;1:612–20.

[19]   Meure S, Wu DY, Furman S. Polyethylene-co-methacrylic acid healing agents for mendable epoxy resins. Acta Mater 2009;57:4312–20.

[20]   Pingkarawat K, Bhat T, Craze DA, Wang CH, Varley RJ, Mouritz AP. Healing of carbon fibre–epoxy composites using thermoplastic additives. Polym Chem 2013;4:5007.

[21]   Wang CH, Sidhu K, Yang T, Zhang J, Shanks R. Interlayer self-healing and toughening of carbon fibre/epoxy composites using copolymer films. Compos Part A Appl Sci Manuf 2012;43:512–8.

[22]   Pingkarawat K, Mouritz AP. Stitched mendable composites: Balancing healing performance against mechanical performance. Compos Struct 2015;123:54–64.

[23]   Cohades A, Michaud V. Thermal mending in E-glass reinforced Poly(ε-caprolactone)/epoxy blends. Compos Part A Appl Sci Manuf 2017;99:129–38.

[24]   Cohades A, Michaud V. Damage recovery after impact in E-glass reinforced Poly(ε-caprolactone)/epoxy blends. Compos Struct 2017;180:439–47.

[25]   Manfredi E, Cohades A, Richard I, Michaud V. Assessment of solvent capsule-based self-healing for woven E-glass fibre-reinforced polymers. Smart Mater Struct 2015;24:1–11.

[26]   Rodgers PA. Pressure-Volume-Temperature Relationships for Polymeric Liquids: A review of Equations of State and Their Characterisitc Parameters for 56 Polymers. J Appl Polym Sci 1993;48:1031–80.

A. Cohades, L. Daelemans, C. Ward, T. Meireman, W. Van Paepegem, K. De Clerck, V. Michaud