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Interlaminar toughening of resin transfer moulded glass fibre epoxy laminates by polycaprolactone electrospun nanofibres

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ABSTRACT

Delamination and brittle matrix fracture has since long been a problem of fibre reinforced composites. This paper investigates if polycaprolactone (PCL) nanofibre nonwovens can increase the interlaminar fracture toughness of resin transfer moulded glass fibre/epoxy laminates, without causing problems during impregnation and without negatively affecting other (mechanical) properties.

The mode I fracture toughness was shown to be dependent on both the nanofibre content as well as on how the nanofibres were introduced into the laminates. Almost 100% improvement in fracture toughness could be achieved by electrospinning the PCL nanofibres on both sides of the glass fibre mats prior to impregnation. This led to a mode I fracture toughness of over 1200 J/m^2. Tensile and dynamic mechanical properties of the toughened laminates were not affected by the PCL nanofibres. It could be concluded that even state of the art infusion resins with a high intrinsic fracture toughness can benefit significantly from nanofibre toughening.

1. Introduction

Delamination and brittle matrix fracture has since long been a problem of fibre reinforced composites [1–3]. A lot of research has been devoted to prevent delamination by modifying the epoxy matrix, either by chemically modifying the resin and hardener components, e.g. by using dendritic hyper branched polymers [4], or by adding additional components to the epoxy resin, e.g. mixing in rubber particles or creating specific thermoplastic phase morphologies in the matrix [5–12]. Although creating a rubbery phase inside of the epoxy matrix often increases the fracture toughness of the laminates, this increase is often accompanied with a decrease in other mechanical properties such as stiffness and strength. In the research of Dadfar et al. the mode I interlaminar fracture toughness (G_{Ic}) of the glass epoxy laminates increased from 220 J/m^2 to about 500 J/m^2 whereas the elastic modulus and tensile strength went down from 28.4 GPa to 17.8 GPa and 584 MPa to 489 MPa respectively [12]. More recently, the effect of nanoparticles such as nanoclay, carbon nanotubes, nanowhiskers and vapour grown carbon nanofibres on the toughness of the epoxy matrix has been studied [13–15]. Although an increase in bulk fracture toughness could often be accomplished by adding these additional components to the epoxy matrix, the absolute increase in interlaminar fracture toughness of the composite laminates remains moderate at best [16–18]. For example, Arai et al. could improve the mode I initiation interlaminar fracture toughness ($G_{Ic,ini}$) of carbon fibre epoxy laminates from 200 J/m^2 to approximately 300 J/m^2 whereas the propagation fracture toughness (G_{Icprop}) increased form 500 J/m^2 to 650 J/m^2. Wang et al. obtained an increase in G_{IC} from 140 J/m^2 to 220 J/m^2 using nanowhiskers [17,18]. In addition, all the toughening systems mentioned above have two common disadvantages: (1) it is difficult to get a homogeneous dispersion of extra phases into the epoxy matrix and final laminate, and (2) the resin viscosity increases tremendously when these phases are mixed into the resin prior to moulding. These problems are of course very problematic for all infusion applications, such as resin transfer moulding (RTM).

Thermoplastic nanofibrous structures could offer a solution for the increased viscosity and the inhomogeneous dispersion, as nanofibre nonwovens can be readily deposited in between the primary reinforcing fibre layers prior to infusion. Thus, the viscosity of the epoxy resin is not affected. Although the idea of using electrospun nanofibres as a secondary reinforcement in composite

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structures has already been proposed by Dzenis and Reneker in 1999 [19], it is only since the last few years that the interlaminar toughening effects of thermoplastic nanofibres are being reported. Bilge et al. showed that P(St-co-GMA) nanofibrous interlayers can improve the open hole strength of carbon/epoxy laminates [20]. Palazetti et al. reported about the use of nylon 6.6 nanofibrous mats to increase the interlaminar properties and impact resistance of composites. The G_{Ic} increased from 473 J/m^2 to 496 J/m^2 [21,22]. Zhang et al. showed that G_{Ic} of a carbon fibre epoxy laminate could be increased from 175 J/m^2 to about 320 J/m^2 (depending on nanofibre diameter and interlayer thickness) using polyetherketone cardo nanofibres [23]. Li et al. used polysulfone (PSF) nanofibres to increase the G_{Ic} of carbon fibre epoxy laminates from 310 J/m^2 up to 870 J/m^2. Furthermore, it was shown that the use of PSF nanofibrous nonwovens leads to a more efficient toughening than the use of PSF films of equal weight [24].

All research papers mentioned above used prepreg material on which the nanofibres were deposited. Although prepreg materials are often used in industry, e.g. aerospace industry almost exclusively uses prepreg materials, resin infusion has substantially gained importance for the production of big composite parts such as windmill blades and yacht parts. Modern infusion moulded laminates make use of low viscosity and high toughness epoxy resins. The mode I interlaminar fracture toughness of these laminates is typically higher than 600 J/m^2. This fracture toughness is much higher than that of the prepreg materials studied so far in literature [20–24]. This paper aims to investigate if high toughness polycaprolactone (PCL) nanofibre nonwovens can increase the interlaminar fracture toughness of these infusion moulded laminates even more, without causing problems during infusion and without negatively affecting other (mechanical) properties of the laminates.

2. Materials and methods

2.1. Materials

All composite laminates were reinforced with unidirectional E-glass fabric (Roviglas R17/475). The reinforcement had a weight of 475 g/m^2 in the fibre direction and a weight of 17 g/m^2 in the perpendicular direction.

The epoxy resin was composed of EPIKOTE resin MGS RIMR 135 with EPIKURE curing agent MGS RIMH 137 (Momentive). This is an infusion resin designed for windmill applications and it has a low viscosity and a high toughness.

Polycaprolactone pellets and solvents 98 v% formic acid and 99.8 v% acetic acid were supplied by Sigma–Aldrich and used as received.

2.2. Electrospinning

Prior to electrospinning, an appropriate solvent system was selected to allow for the production of nanofibre nonwovens in a stable and reproducible way. Furthermore the toxicity of the solvent system should be low, in order to make the system relevant for industrial application.

PCL can be electrospun in a stable and reproducible manner from a 1:1 formic acid/acetic acid solution which has a relatively low toxicity [25,26]. Therefore, 14 wt% of PCL was dissolved in a 1:1 solution of formic acid and acetic acid. To obtain large uniform nanofibrous nonwovens, the nanofibres were produced using a multi-nozzle electrospinning set-up. This multi-nozzle method, an in house developed technology [22], diverges from a mono-nozzle set-up mainly by the number of nozzles, the general methodology itself is identical. It consists out of 32 nozzles, each fed by 16 syringes. The nozzles are placed in 4 alternating rows which have a movement in the transverse direction to ensure uniform deposition of nanofibres. In the meantime, a grounded collector is moving in the longitudinal or production direction. The speed of the ground-collector is adjusted to obtain the required areal density of the nanofibrous nonwovens. All nanofibrous nonwovens were spun in a conditioned room at 23 ± 2 °C and 50 ± 5% RH. The tip-to-collector distance was 12.5 cm and the flow rate was set at 1 ml/h (per nozzle). The voltage was set between 20 kV and 25 kV until a stable process was achieved. Nanofibrous structures were both produced as stand-alone structures as well as deposited structures. The stand-alone nanofibrous nonwovens were electrospun on an aluminium foil, and were peeled off afterwards. The deposited structures were directly electrospun onto glass fibre mats. In both cases the fibre diameter of the nanofibrous structures was 400 ± 100 nm.

2.3. Vacuum assisted resin transfer moulding and preparation of PCL toughened laminates

The composite laminates were manufactured by vacuum assisted resin transfer moulding (VARTM). The glass fibre mats were stacked into a steel mould, either in a $[0°]_8$ or in a $[0°/90°]_{2s}$ configuration. All laminates consisted out of 8 layers of glass fibres and had a total thickness of 3 ± 0.1 mm. Three different configurations were used to introduce the nanofibres into the laminates. In addition to these three configurations, reference samples were produced containing only glass fibres.

In the first configuration a single layer of nanofibres was directly electrospun on one side of the glass fibre mats. These mats are stacked on top of each other. Hence, the interlayer of two neighbouring plies contains a single layer of nanofibre nonwoven. This configuration will be referred to as the single layer deposited configuration (SLD).

The second configuration, referred to as the double layer deposited configuration (DLD), consists out of one layer of nanofibres electrospun on each side of the glassfibre mats. Therefore, the interlayer of two neighbouring plies contained two layers of nanofibres on top of each other.

The third configuration was named the interlayered configuration (IL). This configuration consists of standalone nanofibre nonwovens placed in between the glass fibre mats. Therefore, the interlayer contains one layer of nanofibrous nonwoven, but that layer is not directly electrospun onto the glass fibre mats.

The samples prepared for the tensile tests contained nanofibrous nonwoven, according to the above configurations, in each interlayer. For the double cantilever beam samples (DCB), the nanofibrous nonwoven was incorporated in the tested interlayer.

Prior to infusion, the resin and hardener were mixed in a 100:30 mass ratio. A mechanical stirrer was used to ensure good mixing of resin and hardener. After mixing, the epoxy resin was placed under vacuum for 15 min to remove any air introduced during mixing.

After injection, the glass–epoxy laminate is first cured at room temperature for 24 h and then post-cured for 15 h at 80 °C. It should be noted that although the temperature in the post curing step is above the melting region of PCL (approximately at 60 °C) the curing at room temperature is well below the melting region [27].

2.4. Characterisation

Scanning electron microscopy (SEM, Joel Quanta 200 F FE-SEM) was used to investigate the fibre diameter of the electrospun nanofibres as well as the delamination fracture surface of the laminates. Prior to the SEM-measurements, the specimens were coated by a gold sputter coater (Balzers Union SCD 030). An optical microscope, an Olympus BX51 with an Olympus UC30 camera, was used to visualise delamination cracks in the cross section of the composite