Composites Science and Technology 136 (2016) 10–17

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Interlaminar toughening of resin transfer molded laminates by electrospun polycaprolactone structures: Effect of the interleave morphology

Sam van der Heijden [a], Lode Daelemans [a], Timo Meireman [a], Ives De Baere [b], Hubert Rahier [c], Wim Van Paepegem [b], Karen De Clerck [a, *]

[a] Ghent University, Department of Textiles, Technologiepark-Zwijnaarde 907, B-9052, Zwijnaarde, Belgium
[b] Ghent University, Department of Materials Science and Engineering, Technologiepark-Zwijnaarde 903, B-9052, Zwijnaarde, Belgium
[c] Vrije Universiteit Brussel, Department Materials and Chemistry, Pleinlaan 2, B-1050, Brussels, Belgium

A R T I C L E I N F O

Article history:
Received 17 June 2016
Received in revised form
7 September 2016
Accepted 19 September 2016
Available online 29 September 2016

Keywords:
Nano-structures
Resin transfer moulding (RTM)
Delamination

A B S T R A C T

Today, fiber reinforced polymer composites are a standard material in applications where a high stiffness and strength are required at minimal weight. Although fiber reinforced polymer composites show many advantages compared to other materials, delamination between reinforcing plies remains a major problem limiting further breakthrough. Previous work has shown that electrospun nanofibers can significantly improve the interlaminar fracture toughness of fiber reinforced composites thus preventing delaminations. In the present paper, the effect of the morphology of the toughening polymer is analyzed by incorporating different polycaprolactone structures in the interlaminar regions. Both Mode I and Mode II interlaminar facture toughness of composites containing five different electrospun morphologies - nanofibers, microfibers, microspheres, dense films, and PCL spray coated glass fibers - were evaluated. Analyzing the fracture behavior of the PCL toughened laminates ensures a better insight in the micromechanical fracture mechanisms behind the observed interlaminar fracture toughness and results in guidelines on the optimal interleave morphology. The results clearly demonstrate the distribution of PCL in the interlayer has a large effect on the crack path of the delamination and the resulting interlaminar fracture toughness. In order to improve the interlaminar fracture toughness in both Mode I as well as Mode II without adverse effects, porous PCL structures such as PCL nanofibers, microfibers, and microspheres are much more suitable than non-porous structures such as PCL films or spray-coated glass fibers. Among the porous structures, the nanofibers had an overall better performance with an increase in Mode I and Mode II interlaminar fracture toughness of about 60% and 80% respectively.

1. Introduction

Delamination and brittle matrix fracture have long been a problem of fiber reinforced composites. They are usually due to Mode I and Mode II loading conditions of cracks which are frequently encountered during realistic loading conditions such as impact or fatigue. Recently, the use of electrospun nanofibers has been proposed to toughen composites and prevent such delaminations. A relatively diverse set of polymer nanofibers has been studied in literature for the interlaminar toughening of epoxy composites. Examples include polysulfones (PSU), poly(ether ether ketone cardo) (PEK-C), poly(ε-caprolactone) (PCL), polyamides (PA), poly(vinylidene fluoride) (PVDF), polyacrylonitrile (PAN), polyamide-imide (PAI), poly(styrene-*co*-glycidyl methacrylate), and polyvinyl butyral (PVB) [1–12]. Such nanofibrous nonwovens can easily be placed between two reinforcing plies prior to composite production and result in a fine distribution of the nanoscaled phases of the chosen polymer in the surrounding epoxy phase. Hence, there is no need to disperse them into the resin as opposed to traditional toughening methods, which often involve mixing reactive rubbers or thermoplastic materials in the epoxy resin (followed by phase separation during curing) [13] or the more recently applied (functionalized) nanoparticles [14–17]. This is a major advantage for infusion applications, since mixing in any

* Corresponding author.
E-mail address: Karen.DeClerck@ugent.be (K. De Clerck).

http://dx.doi.org/10.1016/j.compscitech.2016.09.024

particle or thermoplastic material generally causes a large increase in viscosity.

It is well known that for thermoplastic and rubber toughening by phase separation, the final phase separated morphology of the thermoplastic/rubber phase has a major influence on the fracture toughness of the epoxy matrix [18–20]. As such also the morphology of the electrospun structure might affect the interlaminar fracture toughness of nanofiber toughened laminates. In the present paper, we will investigate this effect by interleaving different electrospun PCL structures into resin transfer molded glass epoxy laminates to increase their fracture toughness. The study of PCL is especially relevant since some of the highest increases in interlaminar fracture toughness have been obtained using PCL nanofibers [6,21,22]. Both the Mode I as well as the Mode II fracture toughness of five different electrospun morphologies, i.e. nanofibers, microfibers, microspheres, films and spray coated PCL, are evaluated. Throughout this paper special emphasis will be given to analyzing the effect of the electrospun morphology on the interlaminar crack path. Since recent work by the authors showed that in a nanofiber interleaved composite laminate, the macroscopic crack path of the delamination can be influenced by numerous parameters such as the delamination mode, the nanofibrous veil areal density, reinforcing ply architecture, the interleaving method and mechanical properties of the nanofibers [23]. Hence, extensive microcopy analysis of the interlaminar crack path will provide better insight in the micromechanical fracture mechanisms behind the observed interlaminar fracture toughness.

2. Materials and methods

2.1. Materials

All composite laminates were reinforced with unidirectional E-glass fabric with an areal density of 500 g/m^2, UDO ES500 manufactured by SGL Group. 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 was supplied by scientific polymer products. The solvents 98 v% formic acid and 99.8 v% acetic acid were supplied by Sigma–Aldrich and used as received.

2.2. Electrospun structures

All electrospun structures where prepared on an in-house developed nozzle based electrospinning machine. The required amount of PCL was dissolved into a mixture of acetic acid (70 v%) and formic acid (30 v%). The electrospinning parameters are summarized in Table 1. Except for the PCL films, all of these structures were deposited directly on top of the unidirectional glass fiber fabrics and had an areal density of 5 g/m^2. The PCL films were produced using the same parameters as spray coated glass fibers, with the exception that the PCL was first electro sprayed onto aluminum foil and subsequently peeled off once all the solvent had vaporized, whereas in case of the spray coated structure, the PCL was sprayed directly onto the unidirectional glass fiber fabrics. The PCL films had an areal density of 5 g/m^2 or 10 g/m^2 depending on whether a double or single film configuration was used.

2.3. Laminate production

The composite laminates were manufactured by vacuum assisted resin transfer molding (VARTM). The unidirectional glass fiber fabrics (areal density 500 g/m^2) were stacked into a steel mold in a $[0°]_8$ configuration. All glass epoxy laminates had a nominal thickness of 3 ± 0.1 mm. Electrospun PCL structures as well as an initiation film are located in the middle interlaminar region between the two middle reinforcing glass fiber plies. Except for the PCL films, the electrospun structures were introduced using a double layer deposited configuration, as described in our previous work [24]. The PCL films were simply placed between the two middle glass fiber plies, where for the single film configuration the initiation film was placed on top of the PCL film and for the double PCL film configuration the initiation film was placed in between both PCL films. After infusion, the laminates were cured at room temperature for 24 h, followed by a post-cure at 80 °C for 15 h according to the manufacturer's recommended cure cycle. Although the post-curing temperature is above the melting temperature of PCL, our previous work has shown that the electrospun morphology of the PCL will be largely maintained after curing. After the room temperature curing step the PCL phase is already entrapped into the solid, cross-linked, epoxy network [23,25].

2.4. Tensile properties of PCL

The tensile properties of bulk PCL were measured on PCL films according to ASTM D 882. Films were used as an approximation of the properties of the PCL in the composite (after curing). It should be noted that PCL fibers might have different tensile properties due to the polymer orientation introduced by the electrospinning process [26]. However, such polymer orientations will be partially lost in the final composite since it is post-cured above the melting temperature of PCL.

2.5. Interlaminar fracture toughness

The Mode II interlaminar fracture toughness (G_{IIc}) of the laminates was determined by End Notched Flexure (ENF) experiments, according to a previously reported procedure [27–29]. The Mode I interlaminar fracture toughness (G_{Ic}) of the laminates was determined using the Double Cantilever Beam (DCB) method according to ASTM D5528. Samples were prepared according to a previously reported procedure [9]. At least three specimens were tested for each configuration.

3. Results and discussion

3.1. Morphology and tensile properties of electrospun structures

By modifying the electrospinning parameters (section 2.1), PCL

Table 1
Electrospinning parameters used to obtain different morphologies.

	Voltage (kV)	Tip to collector distance (cm)	Flow rate (ml/h)	Substrate on collector	PCL in AA/FA mixture (wt %)
Nanofibers	24	23	2	Glass fibers	23
Microfibers	12	26	10	Glass fibers	37
Microspheres	45	34	2	Glass fibers	5
Films	11	6	2	Al Foil	5
Spray Coated	12	6	2	Glass fibers	5