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On consideration the mode I fracture response of CFRP composite interleaved by composite nanofibers

F. Bovicelli, H. Saghafi, T. M. Brugo*, J. Belcari, A. Zucchelli, G. Minak

Dipartimento di Ingegneria Industriale, Alma Mater Studiorum Università di Bologna, Bologna 40125, Italy

Abstract

Inherent brittleness of epoxy in composite laminates restricted their application in many industries. Therefore, researchers are trying to decrease this shortage by interleaving electrospun nanofibers for toughening the matrix. In this research the influence of composite nanofibers on mode I fracture toughness of composite laminate is considered. For this aim, Polycaprolactone (PCL) and Nylon 6,6 nanofibers and their composition were interleaved in the mid-plane of unidirectional carbon/epoxy laminates. The results showed that PCL nanofibers did not have a positive effect on mode I energy release rate (GI) and Nylon 6,6 could increase it significantly, while the effect composite nanofibers is more than both of these nanofibers. For understanding more details and the role of nanofibers during the test, the crack path was investigated by optical microscope.

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Keywords: CFRP; Composite nanofibers; Fracture; Interleaving.

Nomenclature	
a	Crack length
B	Width of DCB specimen
C	Compliance
CFRP	Carbon fiber reinforced polymer

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*T.M.Brugo. Tel.: +39-051-20-9-0474; fax +39-051-20-9-0484.
E-mail address: tommasomaria.brugo@unibo.it

DCB	Double cantilever beam (test specimen for mode I fracture test)
F	Correction factor for large displacements
GI	Mode I energy release rate
GI_{MAX}	Maximum mode I energy release rate
L	Length
MBT	Modified Beam Theory
N	Correction factor for the stiffening caused by the metal blocks
P	Applied load
PCL	Polycaprolactone
PEK-C	Polyetherketone-cardo
PSF	Polysulfone
PVDF	Polyvinylideneuoride
t	Thickness
Greek symbols	
Δ	Correction factor for crack tip rotation and deflection
δ	Load displacement

1. Introduction

Developments in the use of polymeric composite laminates in many industries such as aerospace, automotive, marine application and etc have increased significantly over the last decade. It is because of the increased performance requirements in terms of stability and durability of these materials, and at the same time, a reduction in the cost of maintenance, operation and construction. Due to their nature, the most common failure mode of this high performance laminated material is delamination. Insufficient fracture toughness and delamination existence have been the main issues affecting the long-term reliability of thermosetting matrix composites. Many methods have been introduced for reducing this problem by Shu and Mai (1993); Tsai and Chen (2005); Ochoa and Chan (1989); Yadav et al. (2006); Wong et al. (2010); Howard et al. (1986), but it seems that toughening the matrix by thermoplastic polymers is one the best way. For this goal the modifier material which can be either particle, film or fiber interleaved between the composite layers. A homogeneous distribution of the particles is very complicated and can decrease the stiffness of the laminates (Akangah et al. (2010)). It is also shown that the efficiency of nanofibers is much more than films (Magniez et al. (2010) and Li et al. (2008)). Therefore study regarding the effect of nanofibers attract the attention of many researchers around the world.

Dzenis and Reneker (2001) firstly patented the use of nanofibers to reinforce carbon fiber composite laminate. In their patent authors showed that a reinforced laminate with electrospun nanofibrous mats placed at one or more ply interfaces can improve delamination resistance. Based on this research, some other topics introduced in which different kinds of polymers such as Nylon 6,6 (Palazzetti et al. (2012 and 2013), Polysulfone (PSF) (Li et al. (2008)), Polycaprolactone (PCL) (Zhang et al. (2012)), Polyvinylidene uoride (PVDF) (Magniez et al. (2010)), and polyetherketone-cardo (PEK-C) (Zhang et al. (2010)) used for toughening epoxy.

According to the literature each polymeric nanofibers has a specific benefit and each one is more effective either in mode I or mode II fracture (or perhaps is suitable for both modes but is not very effectiveness). For example Magniez et al. (2010) showed that PVDF is a good choice for increasing the fracture toughness in mode II, but decreased this parameter in mode I. Therefore in this paper the composite nanofibers are used to consider whether by interleaving two different polymers at the same, the benefits of the both can be transferred to the fracture behavior of composite laminates or not. For this aim, Nylon 6,6 and PCL nanofibers are used which both of them are suitable for toughening epoxy. The fracture tests conducted on mode I and for considering more details, the crack path is analyzed by optical microscope during the test.
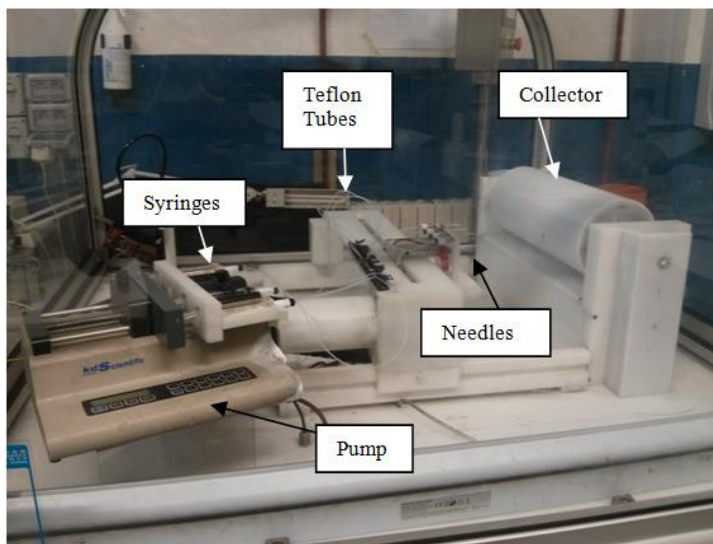
Fig. 1. Electrospinning machine used for producing nanofibers.

2. Experimental program

2.1. Producing nanofibers

Electrospinning process was used for producing nanofibers. The details about this method are reported in many papers presented before like Palazzetti et al. (2012). Polymeric solutions used for the electrospinning process were made dissolving the 14% wt of Nylon 6,6 (Zytel E53 NC010 provided from Dupont) in a solvent made 50:50 v/v by Formic Acid and Chloroform (Palazzetti et al. (2012)); PCL (Purchased from Sigma-Aldrich) solution was made by dissolving in Formic Acid/Acetic Acid solvent (60:40 v/v) in a polymer concentration of 15% w/v (Van Der Schueren et al. (2011)). The solutions were transferred into the syringes and then to an in-house electrospinning machine for producing nanofibers (Fig. 1). The machine consists of 4 needles, which each one was connected to one syringe by a Teflon tube. It should be mentioned that the nanofibers were collected on a paper and then transferred on the mid-plane of composite laminate.
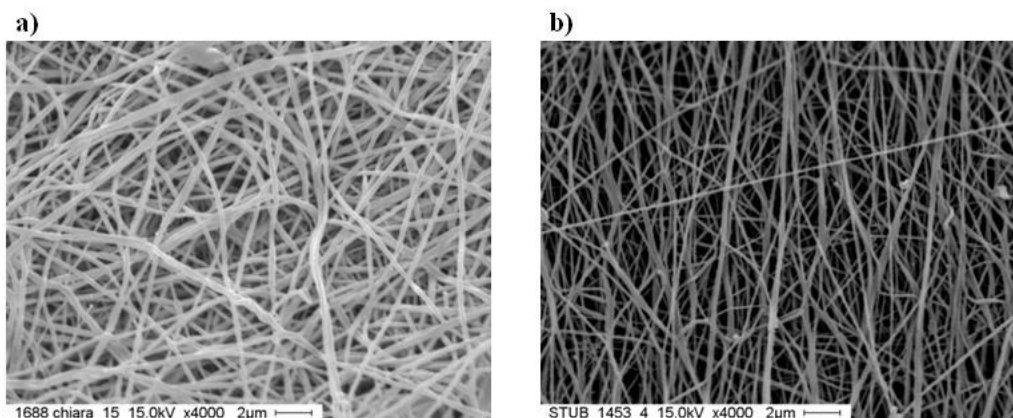

Fig. 2. Morphology of nanofibers (a) PCL; (b) Nylon 6,6.

The electrospinning process was carried out under the following conditions: applied voltage 24-25 kV, feed rate 0.3 mL/h for Nylon 6,6 and 0.9 mL/h for PCL, distance between the needle tip and the collector 15 cm, at room temperature and relative humidity RH = 30-40%. Three different nanofiber mats were produced: 1- PCL nanofibrous mat, 2- Nylon 6,6 nanofibrous mat, and 3- composite nanofibrous mat (Nylon 6,6+PCL). The third one consists of 50% of Nylon 6,6 and 50% PCL. Since the feed rate of PCL is three times more than Nylon 6,6, two separated pumps were used and also three needles were applied for Nylon 6,6 and 1 needle for PCL. 8 ml of solution were electrospun for each mat and the final thickness was about 30±5μm. The average diameter of nanofibers in Nylon 6,6 and PCL were about 250 and 550nm, respectively. The morphology of nanofibers is illustrated in Fig. 2.

2.2. Specimen manufacturing and test setup

Double cantilever beam (DCB) specimens, for conducting mode I fracture tests, were produced by stacking 20 plies unidirectional prepreg (UG130 15K 505L Impregnatex provided by Angeloni Srl) on top of each other. Since the crack should propagate only between mid-layers of the laminate, the nanofibrous mat was placed between the tenth and the eleventh plies. For creating the initial crack a 15 μm Teflon sheet was placed in the same layer. After interleaving, the laminates were cured for 2 hours at 50°C and 1 hour at 130°C; then were cut in the following dimensions: t (thickness)=3.2±0.2mm, B (width)= 20±0.1mm, L (length)= 140mm, and a (initial crack length)= 50mm. It should be mentioned that for each nanomodified and virgin laminates three specimens were provided. The melting point of PCL and Nylon 6,6 is about 60°C and 250°C, respectively; therefore during the curing process the PCL was melt while the Nylon 6,6 protects its morphology. For conducting mode I fracture tests two blocks were attached to each specimen for applying the load. The fracture setup consists of a microscope to follow the crack propagation during the test. So, in this way the behavior of crack can be considered precisely.

The test setup and dimension of the specimens are according to ASTM D5528 and according to this standard the energy release rate for mode I fracture (GI) testing can be calculated from Modified Beam Theory (MBT) method,

$$GI = \frac{3P\delta}{2B(a+|\Delta|)} \times \frac{F}{N} \tag{1}$$

where P is the load, δ is the displacement, a is the crack length, F is a correction factor for large displacements, N is a correction factor for the stiffening caused by the metal blocks and Δ is a correction for crack tip rotation and deflection. Δ is determined from a linear regression analysis of $(C)^{1/3}$ versus a data, where C is the compliance (δ/P).

3. Results and discussion

The mode I fracture test results using DCB specimens are illustrated in Fig. 3. For better consideration, the behavior of fracture is divided in two stages: 1- initiation stage in which crack start to propagate 2- propagation stage. As seen in Fig. 3a, all samples have the same trend until the first force drop in which the crack start to propagate. Among the nanofibers, the crack in the PCL-modified laminates onset to propagate earlier than the virgin one, while Nylon 6,6 postpone it considerably. Therefore in the first stage the efficiency of Nylon 6,6 is much more than the PCL. On the other hand during propagation stage, the behavior of nanofibers changed completely. It means in this stage the force in PCL and Nylon 6,6-modified laminates increased and decreased, respectively compared to the virgin one. So each nanofiber has a specific benefit, therefore by mixing them the advantages of both can be obtained. As shown in the graph, Nylon 6,6 + PCL nanofibers could increase the force in both stages of initiation and propagation.

In Fig. 3b is shown GI and its variation during crack propagation. Almost for all laminates the GI is minimum at the start of propagation and after that it increased significantly. So the variation is very high in the onset of the second stage, but after that the changes of GI during the propagation is less, i.e. between 600 to 800J/m^2. As seen, initiation GI belongs to PCL modified-laminate which is less even than the reference, but Nylon 6,6 and PCL/Nylon 6,6 modified laminates have almost the same amount of GI and much more than the virgin composite. In the propagation stage the effect of Nylon 6,6 is very weak and its behavior is like the virgin specimen, while the PCL and mixed ones are more efficient.
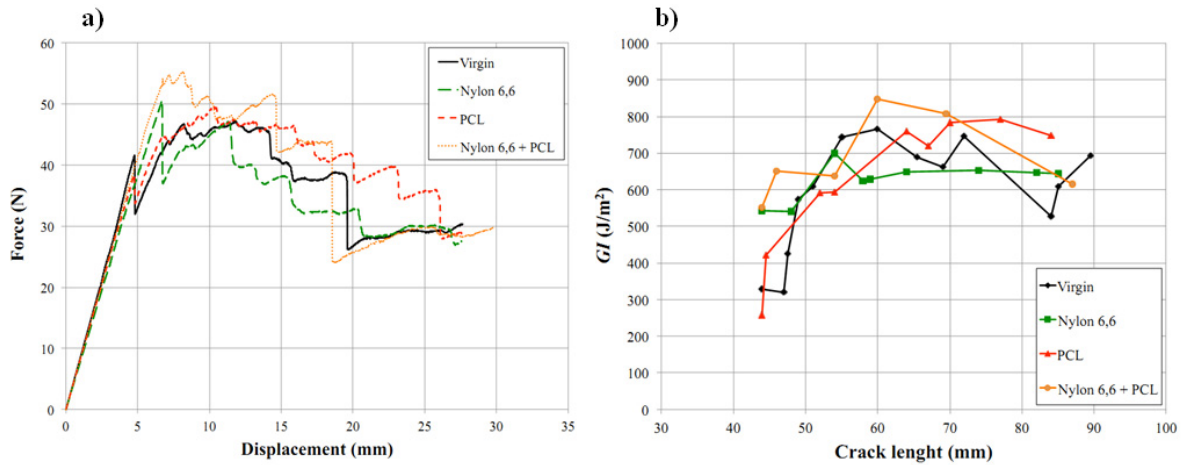
Fig. 3. Mode I fracture test results for virgin and modified specimens:
(a) force versus displacement; (b) *GI* during crack propagation.

Table 1. The details of all fracture parameters.

	F_{MAX} (N)		*GI*-Initiation (J/mm^2)		*GI*-Propagation (J/mm^2)		GI_{MAX} (J/mm^2)	
	Mean	Var. (%)	Mean	Var. (%)	Mean	Var. (%)	Mean	Var. (%)
Virgin	45.1 ± 1.8	----	328 ± 39	----	688 ± 52	----	761 ± 8	----
Nylon 6,6	49.0 ± 4.0	+ 8.5	504 ± 61	+ 53.6	665 ±57	- 3.4	692 ± 36	- 9.0
PCL	51.1 ± 2.6	+ 11.1	318 ± 72	- 3.2	765 ± 44	+ 11.2	803 ± 22	+ 5.5
Nylon 6,6 + PCL	55.0 ± 0.4	+ 21.7	540 ± 75	+ 64.9	796 ±32	+ 15.8	836 ± 34	+ 9.8

For better analyzing the data and the effect of nanofibers, all fracture parameters were summarized in Table 1. Generally, at first glance, in all parameters by mixing the PCL and Nylon 6,6 the fracture behavior of CFRP increased. Regarding maximum force, F_{MAX}, during the test, PCL showed better result than the Nylon 6,6, but by mixing these two the improvement was about doubled (PCL increased maximum force 11% and mixed one 21%). As mentioned before, at the start of crack propagation the effectiveness of PCL was very weak while Nylon 6,6 could increase *GI* about 53.6%, but by applying composite nanofibers the improvement increased more to 64.9%. The effect of nanofibers on *GI* is completely different during the crack propagation: some times more than virgin laminate and some times less, but in average the behavior of PCL and Nylon 6,6 was turned and this stage PCL is better with 11.2% of increase. In this stage again the mixed nanofiber increased the fracture toughness more than individual ones (+15.8%). As shown in the Fig. 3b, *GI* is varied during the test, so the last column of the table presented the maximum *GI* obtained for each nanofibers. This parameter decreased by applying Nylon 6,6, while PCL and composite nanofibers could enhanced it with 5.5% and 9.8%, respectively.

According to the results mentioned in the last paragraph, the Nylon 6,6 is suitable in crack initiation but not in the propagation stage. Therefore, to find out the reason, the crack path was investigated by a micrograph analysis (Fig. 4). As seen in Fig. 4a in the initiation stage the crack is exactly in the layer that nanofiber exists and propagate through them. The observation showed that this behavior continued for 5mm, but then the crack deviated to adjacent layer (Fig. 4b). Crack propagation in this layer leads to the same toughness for the Nylon 6,6-modified and the virgin laminates in this stage, because the adjacent layer is not reinforced by nanofibers.

By adding PCL to Nylon 6,6 nanofibers the problem mentioned was reduced, which is confirmed by the data presented in Table 1.
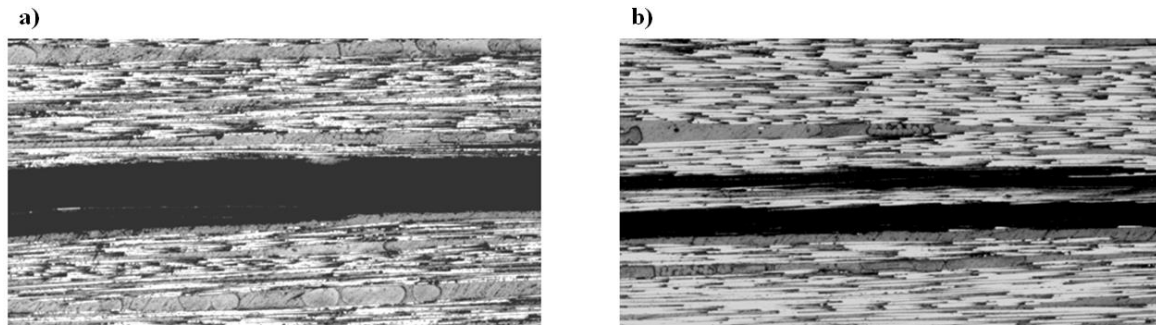
a)

b)

Fig. 4. Optical pictures of the crack path in Nylon 6,6 interleaved laminate: (a) initiation stage; (b) propagation stage.

4. Conclusions

In this study the mode I fracture behavior of nanofiber-modified and virgin CFRP laminates was investigated. Three different nanofibrous mats were produced by electrospinning method: Nylon 6,6, PCL and their mixture. It is shown that each of individual nanofibers, Nylon 6,6 and PCL, have opposite advantages. It means Nylon 6,6 can improve toughness in crack initiation, whereas PCL is suitable during crack propagation. On the basis of these results these two types of nanofibers were combined for applying the advantages of the both. The experimental results showed that while Nylon 6,6 and PCL increased and decreased the fracture toughness +53% and -3%, respectively, the mixed one improved it 65% in initiation stage. In propagation this phenomenon is completely inverse: the weakness of the Nylon 6,6 (-3%) was compensated by PCL (+11%) obtaining at the end for the mixed one +15% enhancement. It is also shown by micrograph analysis that the shortage of the Nylon 6,6 in propagation stage was because of deviating crack to non-modified layer.

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