Integration of nylon electrospun nanofibers into structural epoxy adhesive joints

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Abstract. The fracture toughness is a key parameter in the development of bonded joints for several structural applications. Adhesives are commonly toughened with fillers or modifying the resin chemical composition. Many studies also suggest that resin toughening could be achieved through electrospun polymer nanomat. In previous works, the Authors proved that nylon nanomats can be used as an adhesive carrier and reinforcing web for the adhesive layer. This allowed developing a laboratory route to produce high-quality prepregs of electrospun nylon carrier using medium viscosity, two-component, unfilled epoxy adhesive. By applying the same methodology, in the present work, electrospun nylon prepregs were produced using a high strength and high toughness 2k structural epoxy adhesive to toughen the joint. The wet nano-reinforced strips were placed between S235 steel sandblasted adherents and oven-cured to obtain Double Cantilever Beam (DCB) joints. DCB tests have been performed to compare the mode-I fracture toughness with and without the nanofibrous mat. Unlike previous works with medium-low toughness epoxies, this time the fracture toughness is reduced after the integration of an electrospun nano-reinforcement. From the Scanning Electron Microscope (SEM) images it seems that the nanomat hinders the ductile failure mechanism which instead develops in the neat resin.

1. Introduction

Adhesive bonding is an attractive alternative to traditional joining methods, such as welding and mechanical fasteners [1]. Bonded joints guarantee high strength-to-weight ratio, uniform stress distribution, corrosion resistance, hydraulic sealing, thermal and electrical insulation, and dynamic damping [2,3]. These characteristics, together with the cost-effectiveness, have favoured the use of adhesives in several industrial sectors such as automotive, aerospace, and electronics.

Among the adhesives, epoxy resins are the most used, in particular for structural applications, as they have high modulus and breaking strength, low creep, and good performance at high temperatures [1–4]. However, they are brittle and can be toughened by modifying their chemical structure or introducing organic (rubber-like), inorganic (metal, ceramic) particles, or short fibers [5,6]. Rubber, for example, can be introduced in the form of already cross-linked [7,8] or core-shell particles [9]. Liquid rubber is also used as rubbery particles precipitate during the cross-linking process [8,10]. Nanoparticles improve strength, stiffness, and fracture resistance, although these strongly depend on production procedures and
parameters such as particle size, content, and interface reinforcement/matrix [6]. Carbon Nanotubes (CNTs) are widely used as fillers because they improve stiffness, strength, fracture toughness, and electrical conductivity [11–20]. Epoxy resin shear strength and fracture toughness are also enhanced by alumina nanospheres and nanorods [21]. Polymeric, composite, and ceramic ultra-thin nanofibers may significantly increase the interaction between the fibers and the matrix materials [22].

Similarly to bonded joints, the improvement of fracture toughness of epoxy resins is also crucial for composite materials. Several studies demonstrated that polymeric nanofibers between composite plies improve the mechanical properties of the laminate [23,24]. These electrospun nanomats activate a ply-to-ply bridging effect increasing the delamination strength and the fracture toughness of the laminate [25–32]. Mode I and Mode II of unidirectional (UD) carbon/epoxy composite laminates, could be improved by interleaving the laminates with lightweight thermoplastic nanofibrous veils [25]. Nylon 6,6 nanofibers, interleaved in the mid-plane of UD glass/epoxy laminate, improve both Mode I and Mode II fracture behaviour of the laminate [29]. The toughening effect of dissolvable thermoplastic interleaved in woven carbon/epoxy laminates has been demonstrated [30]. Nanofibers orientation distribution affects fracture toughness and delamination strength of UD composite, but always leading to an increase of fracture toughness due to crack bridging [31]. Fatigue delamination strength increases too [32].

It stands to reason that the integration of electrospun nanofibers into adhesive joints can lead to fracture toughness improvement, as happens for composite materials. In literature, there are only a few works that investigate the effect of electrospun nanofibers on adhesive joints [33–36]. These studies are mainly focused on medium-low fracture toughness epoxy resins. Razavi et al. [36] realized DCB tests with aluminum adherents and verified that the integration of polyacrylonitrile (PAN) nanofibers, directly electrospun into epoxy resin, double the values of fracture toughness of neat samples. Ekrem and Avci [33], on the other hand, found a two-fold increase in fracture toughness and a 13.5% improvement in shear strength of DCB and single lap joints bonded with epoxy resin and reinforced with polyvinyl alcohol (PVA) nanomat.

In previous works [37–39], the Authors studied the effect of the integration of nylon 6,6 electrospun nanofibers into 2k unfilled epoxy resin. In these works, they developed a laboratory route to produce high-quality prepregs and proved that the nanomat acts as a support for the adhesive layer and tends to improve the mechanical performance of the joints.

In the present work, electrospun nylon 6,6 nanomat prepregs have been produced applying the same methodology developed in the previous studies. A structural 2k epoxy resin, characterized by higher strength and fracture toughness compared to the ones employed in previous works, was used. Thixotropic agents were not added to the epoxy adhesive formulation to reduce viscosity and to improve the wetting of nanofibers without affecting the mechanical properties of the adhesive itself. The wet nanofibrous strips were placed between S235 steel adherents to obtain DCB bonded joints. DCB tests have been performed on both nano-reinforced and neat joints to compare the mode-I fracture toughness. SEM analysis were performed to investigate the failure mechanisms on the fracture surfaces. The aim is to evaluate the effect of the nylon nanomat in high-strength and high-toughness epoxy system and compare the results with those obtained in previous studies, in which medium-low toughness epoxies were used.

2. Experimental methodology

2.1. Nanofibrous mat production

The electrospun nylon 6,6 nanomat, named EM252, was produced following the procedure developed in the previous works [37–39]. A quantity of 13 %wt of 6,6 Zytel E53 NC010 (DuPont de Nemours Italiana S.r.l., Cernusco Sul Naviglio (MI), Italy) nylon pellets was dissolved in a 10:60:30 by volume trifluoracetic acid/formic acid/chloroform solution (Sigma Aldrich - Italy, Milan). The solution was put in a syringe and pushed into a needle, subjected to high voltage by a power supply. An electric field between the needle and the electrical ground was applied to induce an electrical charge on the surface
of the polymer solution. When the forces due to the electric field exceed the surface tension of the solution, a polymeric jet is ejected from the needle, the solvents evaporate instantly and the nylon polymerizes. A rotating drum is kept at zero potential to collect the accelerated and whirled filament randomly deposited, as shown in figure 1. The process parameters are summarized in table 1.

Figure 1. Electrospinning set-up.

Table 1. Electrospinning parameters.

| Production parameters               | Values     |
|-------------------------------------|------------|
| Flow rate                           | 0.70 mL/h  |
| Electric Potential                  | 25 kV      |
| Needle-collector distance           | 6.50 cm    |
| Needle inner diameter               | 0.51 mm    |
| Temperature                         | 24 °C      |
| Relative Humidity                   | 40 %       |
| Tangential speed of drum            | 400 mm/s   |

The nylon nanomat webs were collected in the form of a 400 × 300 mm² foil. The nanomat thickness was measured along the nanomat strip by a digital indicator (ALPA, Pontoglio (BS), Italy) with a preload of 0.65 N, resolution of 1 μm, the maximum error of 4 μm, and repeatability of 2 μm. Its value lies in the range between 120 to 160 μm. The nanofiber diameter, measured on the SEM image reported in figure 2, is assessed to be 150 ± 20 nm.

2.2. Steel S235 adherents
From a cold drawn bar of S235 steel, 14 adherents were machined to produce 3 DCB specimens defined as virgin (V, without nylon nanomat) and 4 DCB nano-reinforced specimens (N) with the nylon nanomat. The elastic modulus of the steel is assumed to be 210 GPa, while its yield strength 235 MPa. Perforated steel blocks were bonded to the adherents (one for each adherent), to fix the cured joints on the testing machine. The dimensions of the adherents and blocks are shown in figure 3.
The DCB dimensions are smaller compared to ASTM D3433 standards, to ensure the easy handling of the nanomat, especially after impregnation. Before bonding, the adherents were cleaned with acetone, sandblasted at 6 bar with quartz powders resulting in a roughness \( R_a = 3.9 \mu m \), and sonicated with acetone. This surface treatment is necessary to obtain clean surfaces and to ensure good adhesion between adherents and epoxy resin.

2.3. Resin system
Nylon nanomat prepreg was produced following the procedure developed in previous works for unfilled 2k epoxy adhesives characterized by medium viscosity [37–39]. The adhesive selected for this work is a 2k epoxy system named AS90/AW9, developed specifically for structural applications, supplied by Elantas (Elantas Europe S.r.l., Collecchio (PR), Italy). The supplier has removed the thixotropic agents from the resin to make it suitable for nanomat impregnation. In this way, epoxy viscosity was reduced without affecting the resin mechanical properties. The properties of the resin are summarized in table 2.

The resin was supplied in cartridges to avoid manual mixing and, therefore, air entrapment. An impregnation test was performed to verify the ability of the epoxy system to impregnate the nanomat properly. To this end, a nylon nanomat strip was placed on an epoxy resin layer. When the nanomat completely soaked up the resin, it was rolled between two calibrated and counter-rotating drums to remove excess adhesive. The obtained prepreg was embedded within two S235 steel supports and cured at 70 °C for 5 h. After nylon nanofibers dissolution in formic acid and surface polishing, the cross-section of the bonded joint was observed under SEM, as shown in figure 4. The fibers distribution into the adhesive layer appears uniform through the entire bondline, and no air bubbles were found. This preliminary test demonstrates that the resin is suitable for nanomat impregnation, allowing high-quality prepregs production.

2.4. DCB fabrication
Two series of DCB joints were produced to evaluate the effect of the nylon nanomat integration on the performance of the structural epoxy resin. The first series comprises 3 DCB virgin specimens, bonded with the neat adhesive, while the second one 4 nano-reinforced DCB specimens. The steel surfaces were prepared as previously described.

Regarding virgin specimens, two metal spacers, 150 µm thick, were placed both at the beginning and at the end of the DCB adherent, then a Teflon foil was cut and placed on the same steel substrate to obtain a 30 mm long defect. The adhesive was then spread on the surfaces to be bonded. The adherents
were consequently overlapped and bolted at the joint extremities, ensuring their correct positioning. The DCB joint was cured in an oven at 70 °C for 5 h. At the end of the curing cycle, the bolts were removed.

To manufacture the nano-reinforced DCB, it was first necessary to pre-crack the nylon nanomat, exfoliating it for a length of 30 mm in order to insert the Teflon sheet initial defect. The pre-cracked nanomat was then impregnated with the epoxy resin and gently squeezed throughout two calibrated and counter-rotating drum to remove the adhesive excess. The adherents surfaces were prepared as specified in subsection 2.2. The nanofibrous prepreg was then placed on the bonding surface of one steel supports. The second adherent was overlapped and bolted together with the first one. In this case, the bondline thickness is defined by the nanomat thickness. Again, after the same curing cycle of virgin specimens, bolts were removed.

Table 2. AS90/AW91 mechanical properties, supplied by Elantas.

| Property                                      | Units      | Value          |
|-----------------------------------------------|------------|----------------|
| Viscosity                                     | mPa*s      | 5000           |
| Gel Time                                      | h          | 5-6            |
| Cure cycle suggested by the supplier          | h          | 5              |
|                                               | °C         | 70             |
| Glass transition temperature (ASTM D 3418)    | °C         | 40-47          |
| after 24 h at RT                              |            |                |
| Flexural strength (ASTM D 790)                | MPa        | 70-80          |
| Strain at break (ASTM D 790)                  | %          | 4.5-7.5        |
| Flexural modulus (ASTM D 790)                 | MPa        | 2000-2500      |
| Tensile strength (ASTM D 638)                 | MPa        | 45-55          |
| Elongation at break (ASTM D 638)              | %          | 4.5-6.5        |
| Shear strength (ASTM D 1002) on AISI316,      | MPa        | 25.5-31.0      |
| cured 5h at 70°C                              |            |                |
| Peel strength (ASTM D 1876) on aluminum,      | N/cm       | 35-43          |
| cured 5h at 70°C                              |            |                |

(a) (b) (c)

Figure 4. SEM images of cross-section of nano-reinforced adhesive layer.
2.5. **DCB testing**

The tests were performed under displacement control, with constant crosshead speed. The servo-hydraulic testing machine used was a MTS 810, provided by a 3 kN load cell. A clip gage was used to measure the Crack Mouth Opening Displacement (CMOD) $\delta'$, reported in figure 5. The crack propagation was calculated by means of compliance measurements during the partial unloading of the test.

![Figure 5. SEM images of cross-section of nano-reinforced adhesive layer.](image)

The fracture toughness was calculated using Krenk’s model [40], represented by equation (1). The equation was corrected considering the distance $g$ of the CMOD measurement point from the load axis and the effect of shear (the last term in equation (1)). Before the tests, pre-cracking was carried out at 5 Hz under load control to obtain the initial crack propagation of 5 mm.

$$\delta' = 2 \left[ \frac{2\lambda_a}{k} (1+\lambda_a) + \frac{(2\lambda_a^2)}{k} (1+2\lambda_a) + \frac{a^3}{3EJ} + \frac{g a^2}{2EJ} \right]$$

(1)

The parameters $\lambda_a$ and $k$ are reported in equations (2) and (3):

$$\lambda_a = \left( \frac{6}{h^3 t E(1-\nu_a^2)} \right)^{1/4}$$

(2)

$$k = \frac{2E_a b}{t (1-\nu_a^2)}$$

(3)

The strain energy release rate $G$ is defined as:

$$G = \frac{(Pa)^2}{bEJ} \left( 1 + \frac{1}{\lambda_a a} \right)^2$$

(4)

The value of $\nu_a$ was considered equal to 0.4 as common for epoxies. Since the elastic modulus of nylon 6,6 is approximatively the same of the epoxy resin, also the Young’s modulus of the nanomat prepreg can be considered approximately the same of the neat adhesive. The obtained bondline thickness is in the range 150÷200 μm for both virgin and nano-reinforced joints.

3. **Results**

The DCB test results are summarized in figure 6a, where the load against CMOD is reported for both a virgin (V) and a nano-reinforced (N) specimens taken as representative. figure 6b shows the $R$-curves for each tested specimen. Dashed curves represent the results of the nano-reinforced joints, while solid curves refer to the virgin ones. The black markers of figure 6b refer to the $G_{IC}$ values considered to calculate the fracture toughness mean value during the steady-state crack propagation phase for each DCB series. The grey markers, instead, represent the values excluded from the calculation. Virgin joints have an average $G_{IC}$ value of $1.05 \pm 0.28$ N/mm, while for the nano-reinforced joints this value is equal to $0.38 \pm 0.07$ N/mm.
Figure 6. (a) Load against CMOD ($\delta'$) for both a virgin (V) and a nano-reinforced (N) specimens taken as representative. (b) $R$-curves for all the tested specimens. Solid lines refer to virgin specimens, while dashed lines refer to nano-reinforced ones. The black markers of the $R$-curves graph indicate the $G_{IC}$ values considered for the steady-state fracture toughness average value calculation, whilst the gray ones the excluded values.

From the present experiments, the nanofibrous reinforcement seems to yield a detrimental effect on the fracture toughness of high strength and high toughness structural adhesive. Nano-reinforced DCB $R$-curves show low initial $G_{IC}$ values, which increases before stabilizing during crack propagation. The $R$-curves becomes flat for almost all the N specimens after the $\Delta a$ range 10÷20 mm. Virgin DCB specimens reveal higher $G_{IC}$ values, despite their $R$-curve behaviour is more scattered respect to the nano-reinforced ones. For the N specimens, the $G_{IC}$ value increases approximately three times when it becomes stationary. While, the fracture toughness of the neat adhesive increases only two times compared to the initial $G_{IC}$ values, although with higher absolute values. In particular, the nano-reinforced specimens showed a 64 % fracture toughness reduction compared to the virgin ones.

To better understand the phenomena that act in the nano-reinforced adhesive, SEM analyses were carried out on the fracture surfaces of both V and N tested DCB specimens. The fracture surfaces of virgin DCB were mainly cohesive, while they look mixed for the nano-reinforced ones. In figure 7 are reported the fracture surfaces of V2 and N4 samples, whose $P-\delta'$ curves are reported in figure 6. As shown in figure 8a, fracture surfaces of the V2 sample reveal the presence of micro-dimples into the adhesive layer, which proves that ductile fracture mechanisms occurred in the neat resin.

This morphology was not observed in nano-reinforced specimens. The SEM image of figure 8b of N1 sample shows a brittle fracture surface, with no presence of microcavities and no areas with fiber bridging. Compared to N1 sample, the N4 one was also analysed (figure 8c) and no significant differences were found, showing comparable $G_{IC}$ values in the investigated area, i.e. for $\Delta a$ values between 40÷50 mm. From the SEM images of N samples, it appears that nanomat exfoliation occurs without fiber pull-out, representing a preferential fracture zone inside the adhesive layer. The absence of micro-dimples underlines that the adhesive did not deform and fail in a ductile way, resulting in a fracture energy reduction compared to virgin samples.
4. Conclusions
In the present work, electrospun nylon 6,6 prepregs were produced using a high strength and high toughness 2k structural epoxy resin to toughen adhesive joints. DCB virgin and nano-reinforced specimens were produced to compare the fracture toughness values.

Unlike medium-low toughness epoxies, DCB tests show that the electrospun nanomat seems to yield a detrimental effect on the fracture toughness of a high-performance structural adhesive. The integration of the nylon nanofibrous prepreg caused a $G_{IC}$ reduction of the 64% respect to the neat adhesive.

To better understand the phenomena that act in the nano-reinforced adhesive, SEM analyses were carried out on the fracture surfaces of both virgin and nano-reinforced tested DCB specimens. The fracture surfaces of virgin DCB were mainly cohesive, while they look mixed for the nano-reinforced ones. Virgin specimens are characterized by the presence of micro-dimples, caused by ductile fracture mechanisms. Contrarily, the nano-reinforced specimens show brittle fracture surfaces, with no microcavities. Their SEM analyses do not reveal areas characterized by fiber bridging. Instead, it appears that nanomat exfoliation occurs, representing a preferential fracture zone inside the adhesive layer. The nanomat seems therefore to hinder the ductile deformation mechanisms of the adhesive without adding other toughening mechanisms or even giving a preferential way to the crack because of its tendency to exfoliate, causing an absorbed energy reduction compared to virgin samples. This is also confirmed by the absence of micro-dimples.

This peculiar behaviour, not detected with medium-low toughness epoxies were the nanomat improved someway the fracture toughness, could also depend on the nanomat thickness. A lower thickness could reduce the exfoliation risk, ensuring also tighter control over the adhesive bondline.

Figure 7. Fracture surfaces of (a) virgin V2 and (b) nano-reinforced N4 DCB samples.

Figure 8. SEM images of fracture surfaces of (a) V2, (b) N1, and (c) N4 samples.
Also the adhesion at the interface between the epoxy resin and the nanofibers can play a role in determining whether the final result is good or not, especially if a high toughness epoxy is used.

Therefore, before coming to a definitive conclusion about the effect of nylon 6,6 nanofibers, further tests are foreseen with a lower nanomat thickness and by optimizing the solvent system for the electrospinning polymeric solution. Moreover, plasma treatment is planned to improve the adhesion at the interface between the epoxy resin and the nanofibers, without compromising their wettability.

**Nomenclature**

- \( a \) crack length
- \( A \) cross section of the adherent
- \( b \) width of the specimen
- \( g \) distance from load axis of CMOD measurement point
- \( E \) Young’s modulus of the adherent
- \( E_a \) Young’s modulus of the adhesive
- \( G_{Ic} \) fracture toughness
- \( h \) thickness of the adherent
- \( J \) area moment of inertia of the adherent
- \( k \) elastic foundation stiffness [53]
- \( P \) force
- \( t \) thickness of the bonding interface
- \( \delta' \) Crack Mouth Opening Displacement (CMOD)
- \( \lambda_a \) length scale of the stress distribution in a DCB joint
- \( \nu_a \) Poisson’s coefficient of the adhesive

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