

## Fracture and interlaminar properties of clay-modified epoxies and their glass reinforced laminates

Marino Quaresimin\*, Marco Salviato, Michele Zappalorto

*Department of Management and Engineering, University of Padova, Stradella San Nicola 3, 36100 Vicenza, Italy*

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### ABSTRACT

The present work illustrates the experimental results of a project aiming to assess the benefits deriving from the matrix nanomodification of composite laminates made by vacuum infusion of woven glass fabrics. The following properties have been investigated: mode I fracture toughness and crack propagation resistance for neat and clay-modified epoxy, interlaminar shear strength, mode I delamination resistance for base and clay-modified epoxy laminates.

Available results indicate a significant improvement in the fracture toughness and crack propagation threshold of clay-modified epoxy. However, due to the nanofiller morphology, the behaviour of clay-modified laminates is still almost comparable to that of the base laminates.

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### 1. Introduction

The chance to get substantial improvements of mechanical properties at low nanofiller volume fraction has arisen significant interest in the use of nanomodified epoxy resins.

It is well acknowledged that to achieve these results the nanofiller must be sufficiently dispersed and compatible with the epoxy resin. This requirement leads to a number of processing challenges, which depend on the adopted nanofiller.

As far as layered silicates are concerned, the dimensions of the clay platelets are of the order of microns in area, around 1 nm thick and arranged in stacks (tactoids). Complete exfoliation requires the separation of the tactoids from the primary particle, followed by the destruction of the order of the clay platelets within the tactoids.

In principle, a full exfoliation of the clay platelets will maximise the strength, modulus and toughness improvement [1,2]. However a balance between an exfoliated and intercalated structure might be preferable to maximise enhancements in the mentioned properties [3], intercalated tactoids promoting some toughening mechanisms such as crack deflection or crack pinning [4].

The weak out-of-plane inter-laminar properties of laminates are definitely those with the greatest potential and need to be improved. Indeed, for ternary laminates, matrix toughness improvement itself is the most interesting and promising result, the interlaminar fracture behaviour of traditional composites being a weak matrix dominated property.

Unluckily, the research performed to date, aimed at translating resin properties to the fibre reinforced composite, has met with changing fortunes. Rice et al. [5] reported a 12% improvement in modulus for aerospace composite materials at 2 wt.% of organosilicate, without improvements in other mechanical properties. Timmerman et al. [6], reported negligible improvements in mechanical properties of nanoclay composites compared to traditional composites. However, they reported a significant reduction in transversal microcracking during cryogenic cycling thus indicating the need for careful selection of

\* Corresponding author.

E-mail address: [marino.quaresimin@unipd.it](mailto:marino.quaresimin@unipd.it) (M. Quaresimin).

nanoclay concentration and surface modification. Becker et al. [7] have shown that improvements in crack opening fracture toughness can be achieved at low levels of clay addition. Quaresimin and Varley [8] reported “selective” improvements in toughness properties of carbon/clay-modified epoxy laminates due to the clay distributions: mode I toughness was slightly decreased while mode II slightly increased with respect to the values for neat epoxy laminates. The same behaviour was seen also for vapour grown carbon fibres (VGCF) modified laminates.

This paper presents the results of the ongoing studies carried out by the authors on the effect of nanomodification and its industrial potential by discussing the experimental results obtained on neat and nanomodified epoxy, as well as on neat and nanomodified epoxy laminates (ternary laminates).

After a brief description of the adopted materials and the manufacturing process, chosen for their industrial potential, we will present and discuss the experimental results obtained on nanomodified resins and laminates as well as investigations on the material morphology.

## 2. Materials

A DGEBA-based epoxy resin (EC157) from Elantas-Camattini was used as matrix polymer in this study. Due to a very low viscosity and long average pot life at 25 °C, it is especially suited for resin infusion techniques. In addition, an amminic hardener (W131) has been used. The fraction of this component has been the one suggested by the manufacturer for the neat epoxy (3:1) for each investigated nanofiller content.

The main mechanical properties of the adopted epoxy system, as specified by the supplier, are summarised in Table 1.

Nanomodification was achieved by using two different kind of commercial nanoclay, namely RXG7000<sup>®</sup> and Cloisite 30B<sup>®</sup> from Southern Clay Products (USA). They are surface modified lamellae of montmorillonite, 1 nm thick and with lateral dimensions from 70 to 150 nm according to the product data sheet supplied. The specific surfactants allow to improve the hydrophobicity of the clay. The surface of 30B lamellas is treated by a methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium salt while RXG7000 one by a dimethyl, hydrogenated tallow, 2-ethylhexyl quaternary ammonium salt.

Finally a twill glass fibre fabric VV-350T with generic sizing supplied by G. Angeloni S.r.l. has been used as reinforcement for neat and nanomodified epoxy laminates.

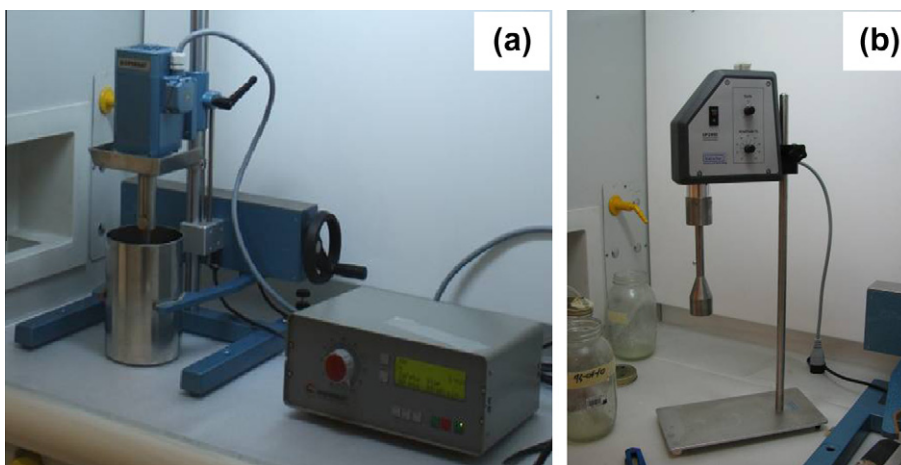
## 3. Nanocomposite and laminate manufacturing

The nanoclays were dispersed in the resin through a shear mixing (SM) process carried out with a DISPERMAT TU shear blender from VMA-Getzmann (see Fig. 1a).

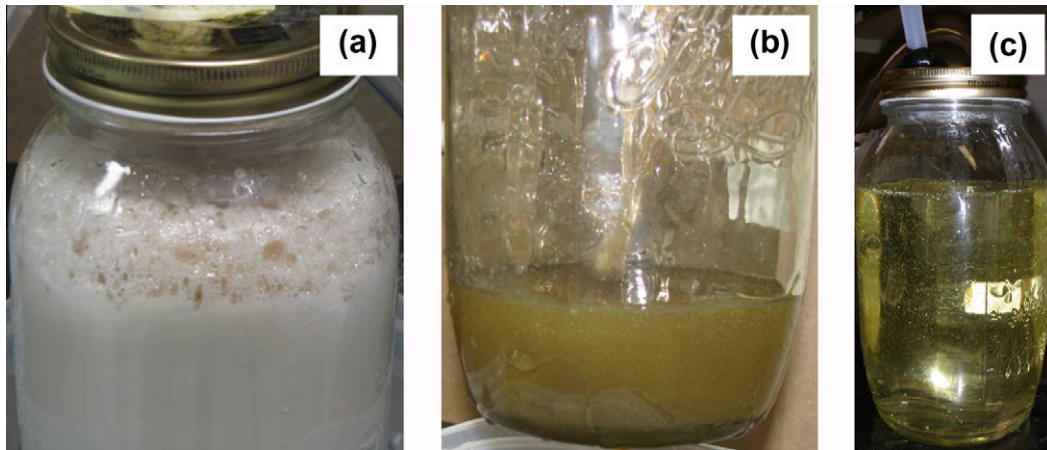
The nanoclays were added into the resin while mixing at an average rate of about 3500 rpm; this was kept on for about 1 h, in order to get an as good as possible distribution and dispersion of the nanofiller within the resin, promoting nanoclays intercalation/exfoliation and breaking of nanoclay clusters.

**Table 1**  
Properties of EC157/W131 epoxy system  
by Elantas-Camattini.

$E$	3.2–3.5 GPa
$\sigma_R$	68–76 MPa
$\epsilon_R$	6–8%



**Fig. 1.** Shear blender (a) and sonicator (b) used for material preparation.



**Fig. 2.** Nanomodified resin appearance; (a) after the shear mixing; (b) after 30 min degassing; and (c) at the end of degassing process.

To reach finer results, the obtained system was then sonicated by means of a HIELSCHER UP 200s SONICATOR (Fig. 1b). The sonication process was always operated at the maximum power amplitude of 200 W; conversely, various duty cycles (25%, 50%, and 75%) were chosen, in order to investigate the effect of this parameter on the fracture toughness.

The process was continued for about 40 min, until the hardener was added.

Finally, SM of the overall system followed for further 10 min, just to improve the resin–hardener mixing. During the entire process the resin has been cooled by an external bath suitable to avoid temperature rise and possible resin overheating.

As a major drawback of the shear mixing process, an amount of air was trapped making the obtained system foamy (Fig. 2a). Then, before moulding, an extensive degassing process was carried out in order to reduce the amount of trapped air and, consequently, to avoid the presence of voids in the matrix.

A low-vacuum pump has been used to induce a very low pressure in the resin's pot and to promote bubbles explosion. After 30 min most of air was released providing a brownish mixture (Fig. 2b). At the end of the degassing process, the modified resin was devoid of any bubble and translucent (Fig. 2c).

CT specimens were manufactured by simply pouring the resin into a silicone mould. The dimensions of the specimens were in agreement with the geometric specifications suggested by ASTM D 5045-99.

Laminates, instead, were fabricated by vacuum infusion of the degassed neat or nanomodified resin into a vacuum bag, where 16 layers of twill glass fabric were laid up. The resulting laminate thickness was about 4 mm and the volumetric fraction of fibres after infusion was about 53% as estimated by means of thermogravimetric analyses. The infusion system is shown in Fig. 3.

All the fabric layers were placed with their warp direction parallel to the longitudinal direction of the mould. A Teflon® film 50 µm thick has been used to create a pre-crack on the DCB specimens. Geometry and size of specimens were those suggested by ASTM D 5528-01.

Demoulding has been performed after complete curing at room temperature, followed by a post curing in a oven at a 60 °C temperature for 12 h.

#### 4. Morphological analysis

The morphology of the cured systems has been investigated using Scanning Electron Microscopy, in order to identify the presence of nanofiller agglomerates.

As an example, Figs. 4–6 report some SEM images for 1, 3 and 5 wt.% loaded resins showing a different morphology for 30B and RXG7000 nanocomposites. At 1 wt.% some traces of clay agglomeration are present for both the nanofillers even if it must be noticed that RXG7000 agglomerates are smaller (size about 15 µm) than 30B ones (size about 20 µm). Fig. 4a–d shows some example of the reported clay cluster. For higher contents, in the case of 30B, the dimensions of the agglomerates seems comparable to the ones reported for 1 wt.% even if their content is more elevated while, in the RXG7000 case, the dispersion of the clay seems good even at 5 wt.%. As a general trend for all the clay contents under investigation, RXG7000 seems to be better dispersed than 30B. A different morphology for 30B and RXG7000 nanoclays was expected as they differ for the organic modifier. Similar morphologies have been reported by other authors [9–12].

In order to further investigate the morphology of the nanocomposite systems, a XRD analysis has been carried out with the help of Dr. Andrea Dorigato (University of Trento, Italy). The results are summarised in Table 2 and the XRD patterns of the nanocomposites containing 1 and 3 wt.% of both 30B and RXG7000 clays are represented in Fig. 7. For the 1 and 3 wt.% 30B the reflection peaks are located at 2.62° (*d*-spacing: 33.7 Å) and at 2.57° (*d*-spacing: 34.3 Å) respectively. In the case of RXG7000, the reflection peaks of the 1 and 3 wt.% specimens are located at 3.00° (*d*-spacing: 29.4 Å) and 2.91° (*d*-spacing:

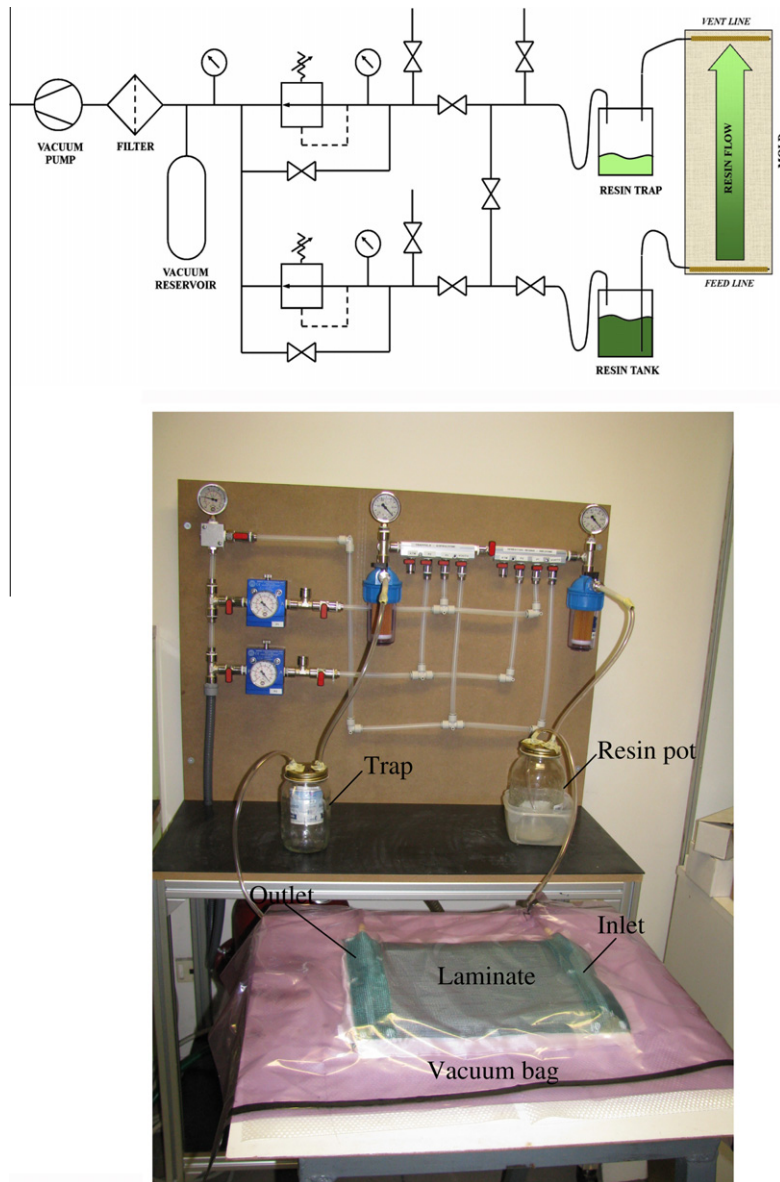


Fig. 3. Schematic representation (a) and picture (b) of the infusion system.

30.3 Å) respectively. Considering that both the organoclays are sold by the manufacturer with a  $d$ -spacing of about 18.5 Å, these values indicate a rather good degree of intercalation of the nanofiller.

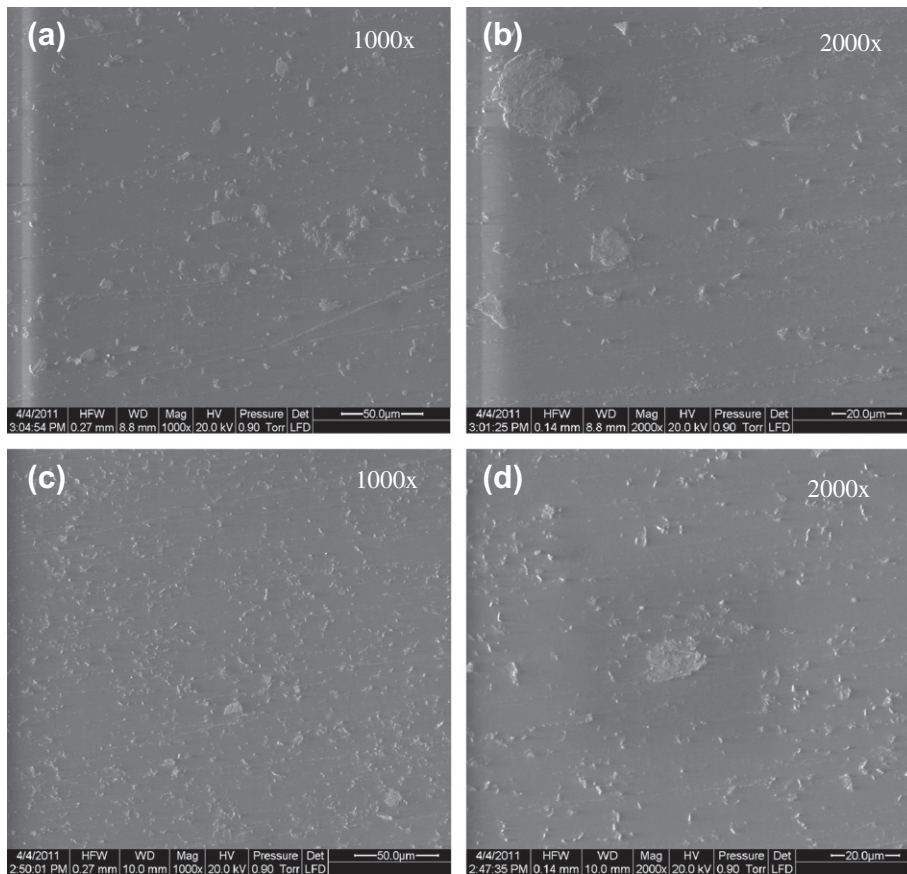
It is worth noting that the level of intercalation does not seem to be affected by the amount of organoclay either in the 30B or in the RXG7000 case. Moreover, the 30B shows a slightly more pronounced intercalation than the RXG7000 due to the greater hydrophilicity of its organo-modifier.

The results, on the one hand, indicate that a partial exfoliation and a good intercalation has been achieved with both the clays. On the other hand, the presence of large agglomerates does suggest the need of further investigations in order to optimise the manufacturing process and then, in turn, the material morphology.

A morphological analysis has been carried out also on nanomodified epoxy laminates with the aim to identify possible defects and voids due to the manufacturing process and to analyse the nanofiller dispersion within the laminate layers.

Optical microscopy images have been taken from the inlet and outlet of the infusion on both neat resin and nanomodified resin laminates revealing a good global quality and the absence of voids, as can be seen in Fig. 8a and b.

Some SEM images of 3 wt.% nanomodified laminates have also been taken (see Fig. 9), showing again the absence of voids and the emergence of clusters within the layers, whose size is comparable to that reported for the nanomodified resin at the same filler content.



**Fig. 4.** Scanning electron micrographs at different magnification of 1 wt.% clay-loaded resins. 30B nanoclays (a and b) and RXG7000 nanoclays (c and d).

In this situation it was considered non-essential to further investigate morphology using TEM analysis.

## 5. Experimental results and discussion

The experimental program included the following tests:

- tensile tests on the neat and nanomodified epoxy;
- mode I tests on the neat and nanomodified epoxy (CT specimens);
- mode I tests on neat and nanomodified epoxy laminates (DCB specimens);
- interlaminar shear tests on neat and nanomodified epoxy laminates;
- fatigue tests on the neat and nanomodified epoxy (CT specimens);
- preliminary fatigue tests on neat and nanomodified epoxy laminates (DCB specimens).

The experimental results for the neat and nanomodified epoxy and for the epoxy laminates are presented and discussed in the following sections.

All tests have been carried out by using a MTS 858 servo-hydraulic machine, equipped with a 1.5/15 kN load cell.

### 5.1. Nanomodified epoxy

#### 5.1.1. Tensile test

Tensile tests have been carried out on dog-bone specimens (dimensions:  $2 \times 15 \times 110$  mm) by using a crosshead speed equal to 2 mm/min. An MTS 632.29F-30 extensometer was used for accurate strain measurements and for tensile modulus calculation. Three specimens were tested for each material configuration. In all the performed tests failure took place in the centre of the specimen.

The effect of the weight content of Cloisite 30B<sup>®</sup> nano-additives upon the nanocomposite tensile properties is shown in Fig. 10a–c.

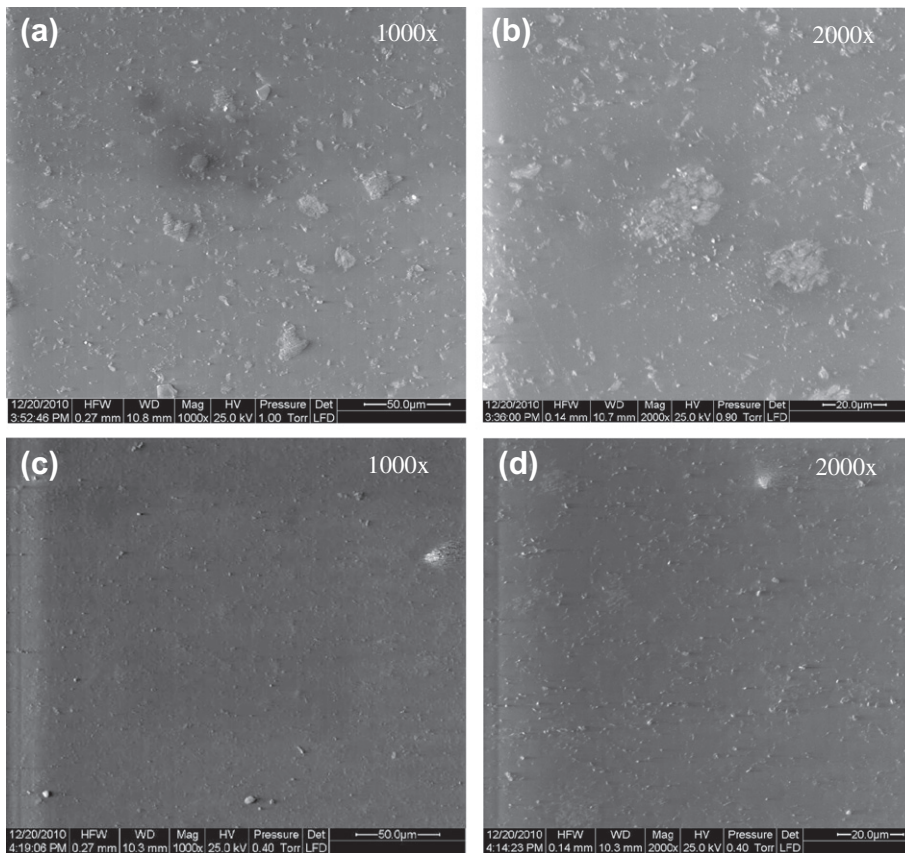


Fig. 5. Scanning electron micrographs at different magnification of 3 wt.% clay-loaded resins. 30B nanoclays (a and b) and RXG7000 nanoclays (c and d).

In particular Fig. 10a shows the tensile strength of the epoxy clays slightly decreasing with the increase of clay content; this result is in agreement with those of other researchers [13]. A similar trend is exhibited also by the strain-to-failure (see Fig. 10b).

It is the authors' opinion that this limited reduction of the tensile strength due to nanomodification is not significant, the improvement of the polymer fracture toughness, shown later, being much more important.

Conversely Fig. 10c shows that nanomodification resulted in a slight improvement of the elastic modulus of the modified resin with respect to the neat epoxy.

### 5.1.2. Fracture properties

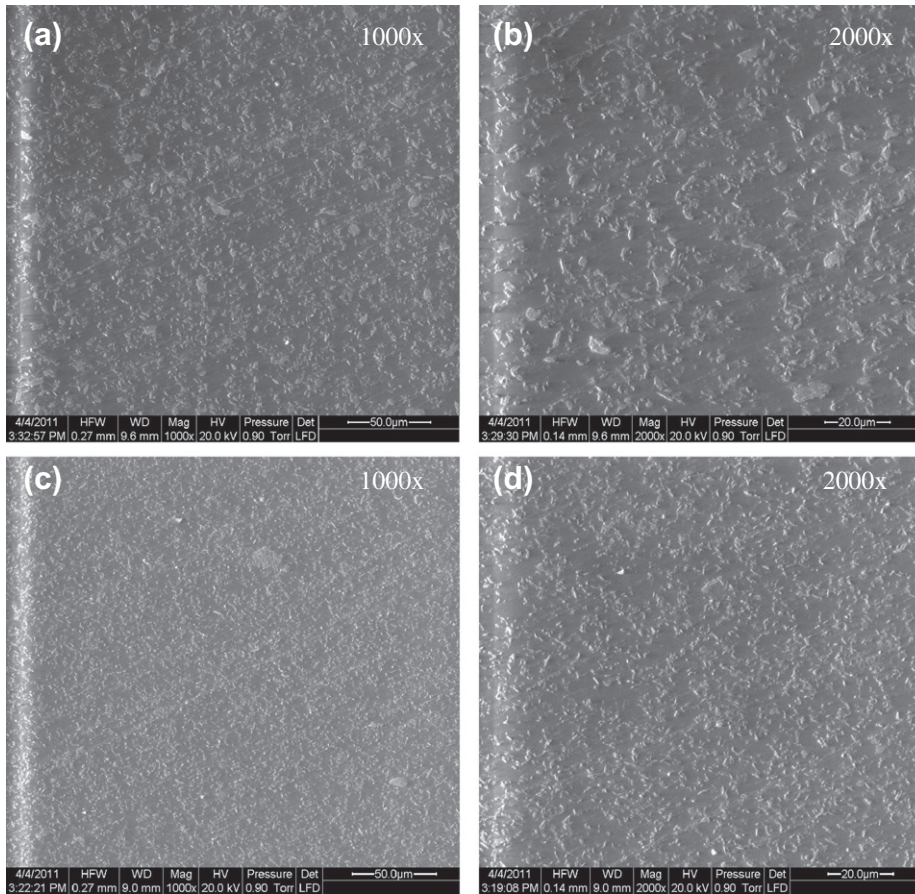
In principle, the overall macroscopic properties of nanocomposites may be substantially affected by the amount of nanofiller and by processing conditions, as well. Then, with the aim to capture both these effects, in the present work, a parametric study has been carried out, by comparing the effect of the sonication process for different content (wt.%) of nanofillers.

Fig. 11a and b shows the fracture toughness values versus the nanoclay content (wt.%) for 30B- and RXG7000 nanomodified resin, with respect to the neat resin value. Experimental results exhibit a peak value of the fracture toughness for 1 wt.% of both nanofillers, independently whether sonicated or not. In particular 30B nanomodified resin exhibits the highest fracture toughness, about a 40% higher than that of the neat resin. For higher nanofiller content, the 30B nanomodified resin is monotonically decreasing, while RXG7000 toughness increases again after 3 wt.%.

The maximum value for 30B clay is about 10% higher than the RXG7000 one, either for sonicated or non-sonicated specimens. Surprisingly, the sonicated specimens show lower  $K_{IC}$  values, except for 5 wt.% RXG7000.

Usually, sonication is reported to improve properties of nanocomposites, however, opposite indications, in agreement with the results presented here, were reported in [14]. This suggested us to carry out a deeper analysis to investigate the effect of sonication in terms of duty cycle or, equivalently, in terms of effective sonication time. Fig. 12 shows that there is a detrimental effect of a duty cycle percentage increase on the measured fracture toughness, thus suggesting sonication could penalise the nanocomposite overall properties.

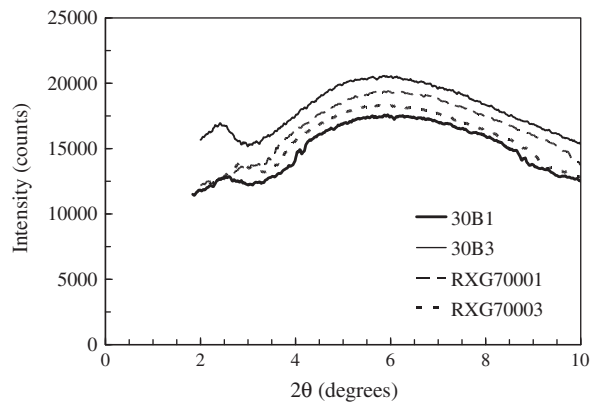
On the other hand, XRD analyses carried out on sonicated and non-sonicated specimens showed the same  $d$ -spacing values of about 33 Å, revealing that this parameter, representative of the overall morphology, was not influenced by sonication. This apparently opposite trend, does suggest that some further investigations are needed, in order to better clarify the actual effect of the sonication process, both on the material morphology and on the overall strength properties.



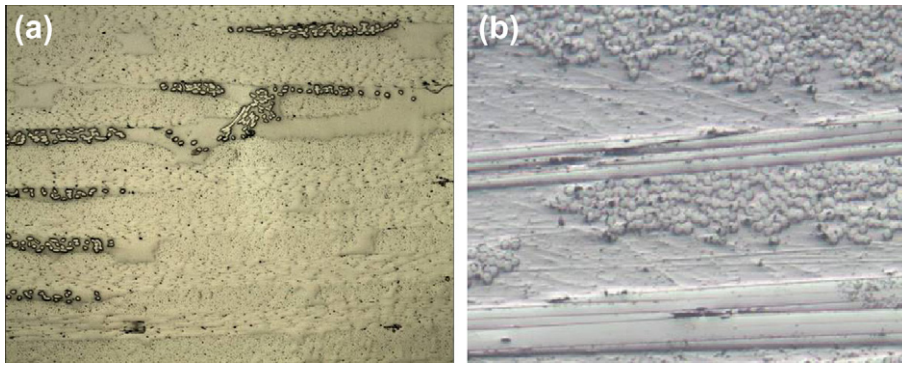
**Fig. 6.** Scanning electron micrographs at different magnification of 5 wt.% clay-loaded resins. 30B nanoclays (a and b) and RXG7000 nanoclays (c and d).

**Table 2**  
*d*-Spacing for different clays and weight contents.

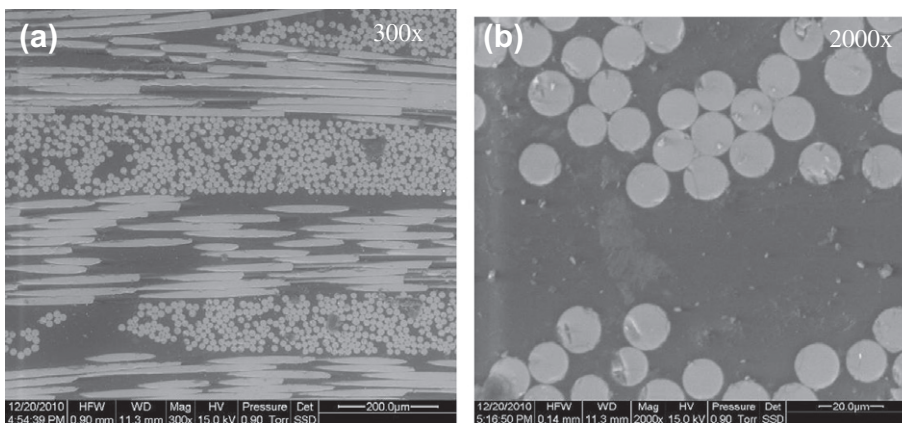
Specimen	$2\theta$ ( $^{\circ}$ )	$d$ ( $\text{\AA}$ )
30B 1 wt.%	2.62	33.7
30B 3 wt.%	2.57	34.3
RXG7000 1 wt.%	3.00	29.4
RXG7000 3 wt.%	2.91	30.3



**Fig. 7.** XRD patterns of nanocomposites containing different clay concentrations.



**Fig. 8.** Micrographs of a typical neat epoxy laminate produced by vacuum infusion revealing a good overall quality and the absence of voids either in the inlet (a) or in the outlet (b) of the infusion.



**Fig. 9.** Scanning electron micrographs of a typical 3 wt.% epoxy laminate produced by vacuum infusion revealing a good overall quality and the absence of voids. The figures confirm the presence of agglomerates (size comparable to those identified in nanomodified resins).

### 5.1.3. Fatigue test results

Mode I fatigue tests on CT samples have also been carried out. Fatigue tests were performed according to procedures reported in the ASTM E 647-00. CT specimens (width 33 mm and thickness 5 mm) were pre-cracked by manual tapping using a razor blade. The length of the pre-crack was about 2 mm.

Tests were characterised by a nominal load ratio  $R = F_{\min}/F_{\max}$ , equal to 0.1, with a frequency of 20 Hz.

The crack tip area was magnified by means of a travelling microscope and then captured by means of a digital camera and an in-house-developed acquisition and analysis software (LabVIEW® environment). The crack growth was regularly detected and the crack length as a function of the number of cycles was reported. Fig. 13 shows a typical  $a-N$  curve obtained.

The incremental polynomial method was implemented according to ASTM E 647-00 and used to evaluate the crack growth rate  $da/dN$ .

In some cases the  $\Delta K$  value chosen for the beginning of the test was such that the crack was already in the Paris regime, where the crack growth rate linearly increases with  $\Delta K$ . Thus, the crack propagation threshold could not always be clearly detected.

Representative results, reported in Fig. 14, show that the highest threshold value is exhibited by 1 wt.% 30B nanomodified epoxy CT specimens, with a threshold value about 35% higher than that of the neat resin. The better performances at low clay content suggest a more uniform and less agglomerated morphology for the 1 wt.% nanocomposites.

On the other hand, it can be observed that clay loading results in an improved crack propagation resistance. Again, this behaviour could be due to the presence of slightly larger agglomerates with respect to the more finely dispersed clays, inducing a more significant crack path deflection and thus resulting in a higher resistance to crack propagation.

A part from these speculations, generally speaking it can be said that all nanomodified epoxy CT specimens exhibit improved fatigue behaviour with respect to the neat resin. The same behaviour was reported also for other nanomodified systems [15].



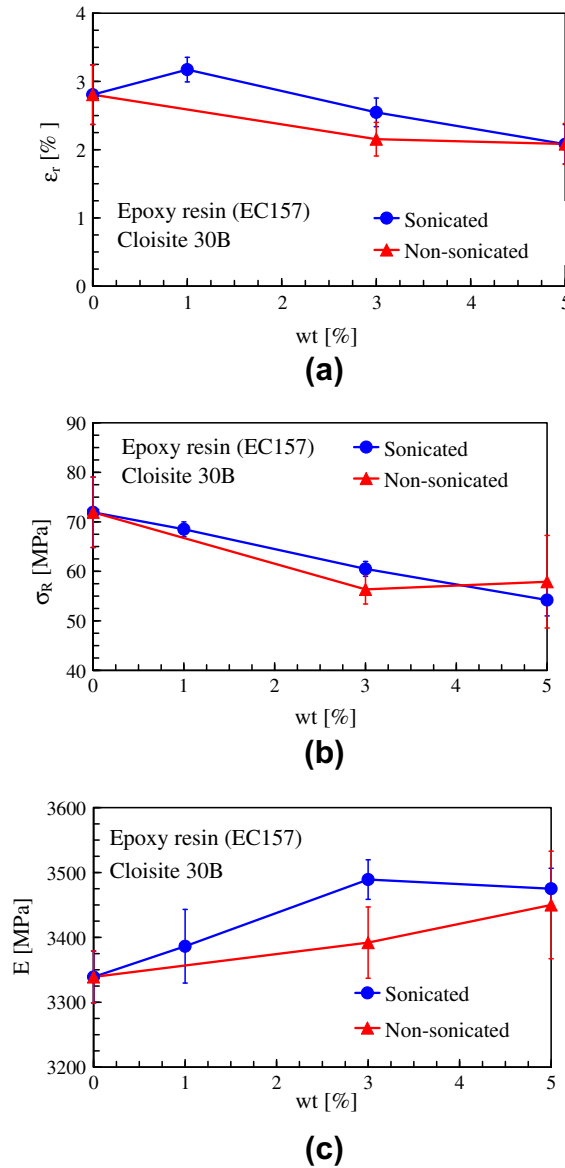


Fig. 10. Results of tensile tests on neat and nanomodified epoxy resin.

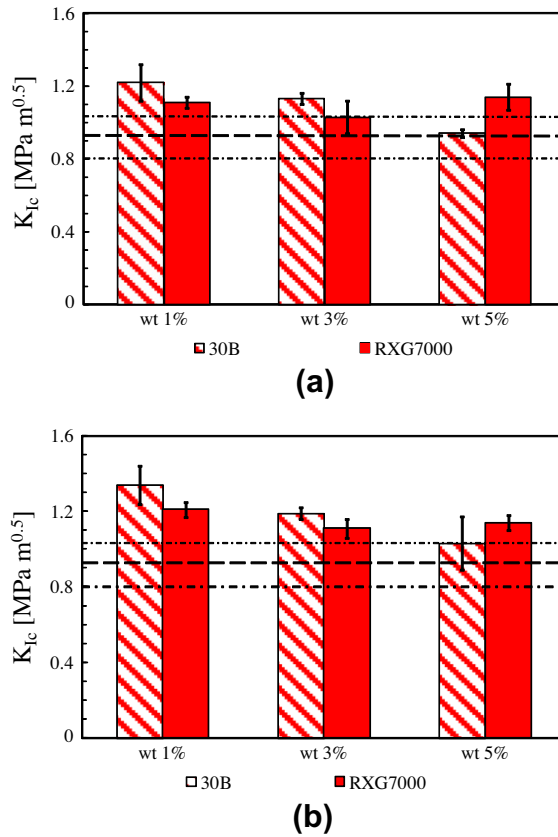
## 5.2. Clay modified epoxy laminates

### 5.2.1. Fracture properties

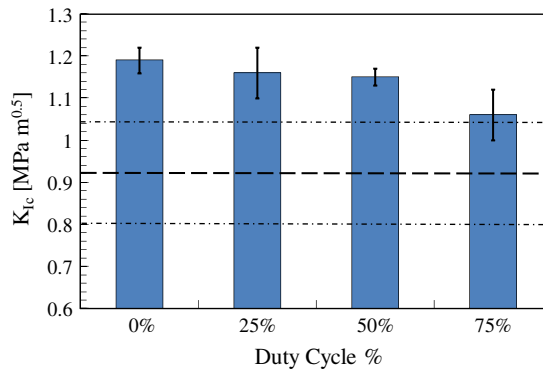
The manufacturing of vacuum infused nanomodified glass epoxy laminates is a solution of potential industrial interest provided, of course, that a suitable compromise between production costs and performances enhancement is achieved.

For ternary laminates, matrix toughness improvement itself is the most interesting and promising result, the interlaminar fracture behaviour of traditional composites being a weak matrix dominated property. In the previous section it has been proved that 30B nanomodified epoxy resin exhibits higher fracture properties with respect to both the neat resin and to RXG7000 nanomodified epoxy resin. Research activities on laminates have been then mainly focused on 30B clay modified epoxy laminates. Tests have been carried out to evaluate the laminate interlaminar properties, by means of interlaminar shear (ILSS) tests, and mode I interlaminar fracture toughness with DCB quasi-static tests.

ILSS tests have been carried out, according to ASTM D2344. The crosshead speed was set at 1 mm/min and three specimens were tested for each material configuration. The specimen thickness was 4 mm and the span was 16 mm. During the interlaminar shear tests all the specimens failed by delamination.



**Fig. 11.** Fracture toughness versus nanoclay content (wt.%) for 30B and RXG7000 modified resin sonicated (a) and non-sonicated (b) specimens. (Three tests per condition. The scatter band of the values for neat epoxy is given by the dashed lines.)



**Fig. 12.** Fracture toughness versus duty cycle % for 3 wt.% 30B specimens and comparison with neat resin. 0% duty cycle stands for no sonication. (Three tests per condition. The scatter band of the values for neat epoxy is given by the dashed lines.)

Fig. 15 shows a comparison between interlaminar shear strength of the neat, 1 wt.% and 3 wt.% 30B nanomodified epoxy laminates and 3 wt.% RXG7000 nanomodified epoxy laminates. If one considers the actual scatter of the data it can be seen that 3 wt.% 30B laminates exhibit a slightly improved interlaminar shear strength, while RXG7000 laminates does not exhibit a significant increment.

DCB quasi-static tests have been carried out, according to ASTM D5528. Three double cantilever beam (DCB) specimens for each material configuration were tested; the crack propagation was monitored by using a travelling microscope.

The crosshead speed was set at 0.5 mm/min. The reported  $G_{Ic}$  values were calculated using the compliance calibration method (MCC) and the initiation values were determined by visual observation.

Test results, shown in Fig. 16, allow us to draw the following conclusions:

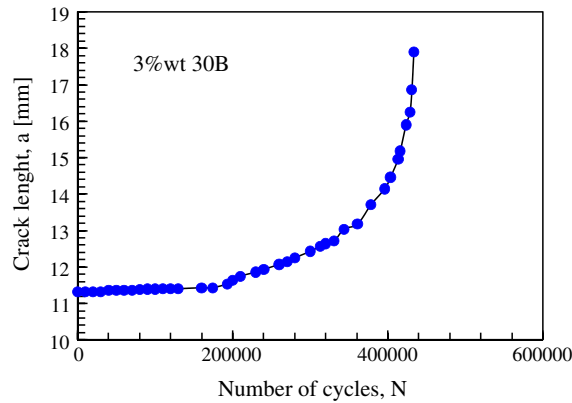


Fig. 13. Crack growth for a 3 wt.% 30B loaded CT specimen.

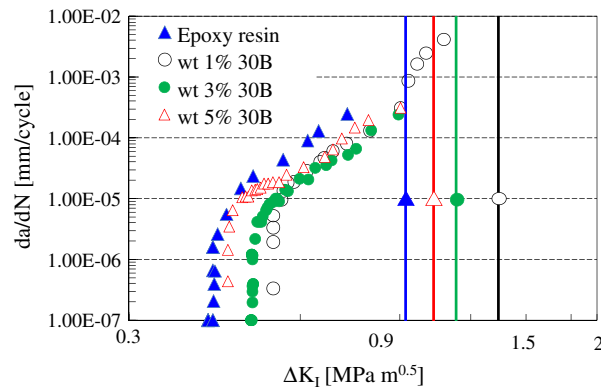


Fig. 14. Comparison of the Paris curves for the neat and nanomodified epoxy CT specimens. Vertical lines correspond to the static fracture toughness,  $K_{IC}$ .

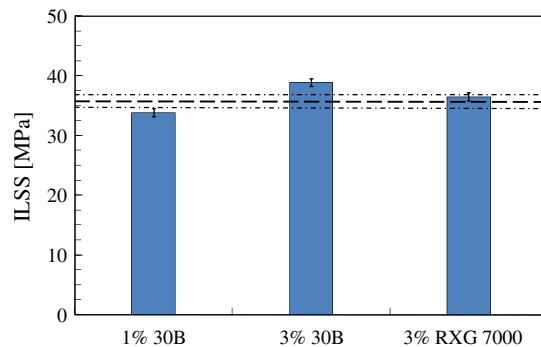


Fig. 15. Comparison of interlaminar shear properties for neat and nanomodified epoxy laminates (the scatter band for neat epoxy laminates is given by the dashed lines).

- Concerning the initiation values, there is no evident effect due to the nanoclay addition.
- Differently, a limited decrease is noticed for the propagation values in the case of nanomodified epoxy laminates. In more details, 1 wt.% seems to provide the lowest result, although it was the best percentage in the nanomodified epoxy system. The decrease is not significantly pronounced and further tests might be needed in order to clarify the obtained behaviour.

### 5.2.2. Fatigue test results

Besides the above described static tests, mode I fatigue tests on laminates have also been carried out, with a load ratio  $R = 0.1$ . Crack opening was monitored by means of the displacement transducer of the testing machine and the crack length was measured by means of a travelling optical microscope with a magnification of  $40\times$ . Preliminary results are shown in

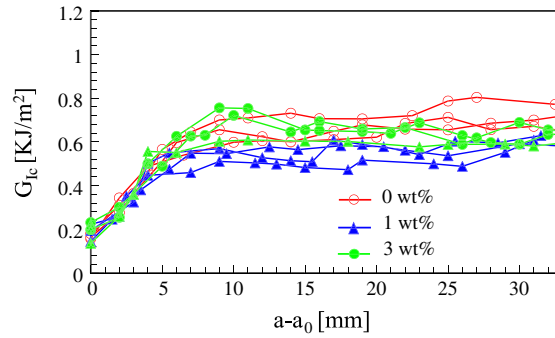


Fig. 16. R-curves for neat and nanomodified epoxy laminate DCB specimens (30B only).

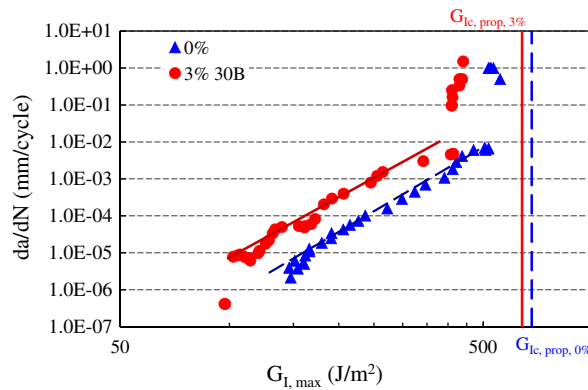


Fig. 17. Comparison between the Paris curves for a neat and 3 wt.% nanomodified epoxy laminate.

Fig. 17. 3 wt.% 30B nanomodified epoxy laminates exhibit a worse behaviour, both in terms of propagation and of threshold value. However, only few tests have been carried out so far and this does not allow us to draw any significant conclusion in this direction.

### 5.2.3. Fracture surface analyses

As an attempt to understand the reason for the above reported results, namely a comparable fracture toughness of the nanomodified epoxy laminates with respect to that of the neat ones and the worse behaviour under cyclic loading, SEM images of the fracture surfaces were taken.

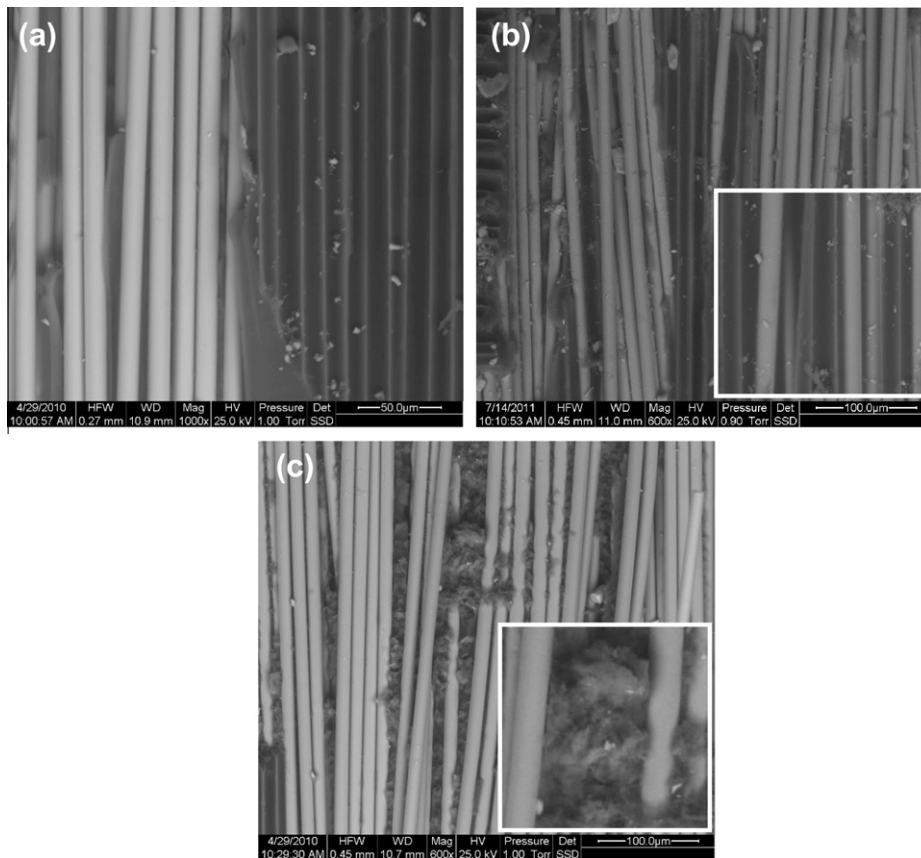
Fig. 18a shows a typical fracture surface for a neat resin laminate. The SEM image clearly shows a brittle fracture occurring at the matrix–fibre interface: the fibres appear very clean and no evident matrix damage has taken place. A similar situation is present in the fracture surface of 1 wt.% 30B laminates (see Fig. 18b).

Differently, Fig. 18c shows the fracture surface of a 30B 3 wt.% nanomodified epoxy laminate. Even if the governing mechanism seems to be, again, matrix–fibre interface failure, there is a different morphology of the matrix failure surface. These differences suggest an improved local energy dissipation for the nanomodified laminates. However this conclusion is not supported by the experimental results reported in the previous section, which do not show any increment in the fracture toughness due to the nanomodification of the matrix.

The improved matrix damage could be promoted by the clay presence and by the lower degree of cross-linking caused by the interactions between the nanoclays and the matrix [16]. However, a possible, local deformation of the matrix does not necessarily correspond to an increased interlaminar fracture strength. In facts, the dominant mechanism is proved to be matrix–fibre interface failure, so that the deformation of the matrix would not be as important as the interface toughness which, on the other hand, could be negatively affected by nanoclay addition.

## 6. Discussion

In this work we have presented the results of the ongoing studies carried out by the authors on the effect of nanomodification and its industrial potential by discussing the experimental results obtained on neat and nanomodified epoxy, as well as on neat and nanomodified epoxy laminates (ternary laminates).



**Fig. 18.** SEM images of fracture surfaces after DCB test for neat resin laminate, (a) and nanomodified epoxy laminate for different nanoclay loadings: 1 wt.% 30B (b) and 3 wt.% 30B (c).

As far as the nanomodified epoxy is concerned, the morphological analyses have made it evident the presence of clay agglomerates at least in the 30B case.

By the one hand, this result does suggest that some further investigations are needed, in order to optimise the manufacturing process, and then, in turn, the material morphology.

On the other hand experimental results provided in Section 5.1 show that nanomodification of the resin results in improved fracture toughness, of about 40%, and an ameliorated fatigue behaviour, with a threshold value for the 1 wt.% 30B loaded epoxy about 35% higher than that of the neat resin. Therefore a finer distribution of at least intercalated clays must be present since the improvement in properties cannot be explained by assuming only micrometric size reinforcement at so low volume fraction.

The overall behaviour can be explained by arguing that even if, in principle, a full exfoliation of the clay platelets should maximise toughness improvements, sometimes a balance between an exfoliated and intercalated structure might be preferable as shown in Ref. [3]. Indeed, the presence of intercalated tactoids might promote toughening mechanisms such as crack deflection or crack pinning, which could not take place, by nature, at the very nanoscale.

Different from the clay-loaded epoxy, the effect of resin nanomodification on behaviour of clay-modified laminates was found to be weak, the results being almost comparable to or even worse than those for that of the neat epoxy laminates.

If, by one side, micrographics on both neat resin and nanomodified resin laminates revealed a good global quality and the absence of any void (Fig. 8), the SEM images taken on 3 wt.% nanomodified laminates (Fig. 9) show again the presence of clusters within the layers, whose size is comparable to that reported for the nanomodified resin at the same filler content.

The SEM analysis on the fracture surfaces of a neat resin laminate (Fig. 18a) and nanomodified laminates 1 wt.% 30B (Fig. 18b) show a brittle fracture occurring at the matrix–fibre interface. A similar behaviour is exhibited by the 30B 3 wt.% nanomodified epoxy laminate (Fig. 18c), where a different morphology of the matrix failure surface is also evident, suggesting an improved local energy dissipation.

The limited nanomodification-induced improvements of laminates properties could then be explained by the argument that the dominant fracture mechanism is matrix–fibre interface failure and that the interface toughness could be negatively affected by nanoclay addition.

For this reason future efforts should be made with the aim to improve the interface toughness.

In the authors' opinion this target can be achieved either through the optimisation of the dispersion process, to obtain a better dispersion and distribution of the nanofiller within the matrix, or improving fibre seizing. With particular reference to the last mentioned approach, the authors are investigating the chance to destroy the seizing on commercial fibres and to prepare an ad hoc seizing, which maximizes fibre–matrix adhesion. Preliminary results in this direction are very promising.

Differently, in order to detect the increasing improvements of nanofiller dispersion and distribution, it will necessary to carry out an extensive TEM investigation.

## 7. Conclusions

The preliminary experimental results of a project aiming to assess the benefits deriving from the matrix nanomodification of composite laminates made by vacuum infusion on woven glass fabrics have been presented.

The experimental program was aimed at investigating the following properties: mode I fracture toughness and crack propagation resistance for neat and clay-modified epoxy (CT test), interlaminar shear strength (ILSS test), delamination threshold and delamination resistance for base and clay-modified epoxy laminates (fatigue and quasi-static DCB test).

Available results indicate significant improvements in the fracture toughness and crack propagation threshold of clay modified epoxy.

On the other hand, the behaviour of clay-modified laminates is almost comparable to that of the neat epoxy laminates. This is assumed to be related to the nanofiller morphology and to the main failure mechanism in the laminates which was observed to be matrix–fibre interface failure.

In this situation, benefits deriving from matrix improved properties cannot be fully exploited.

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