

MULTIFUNCTIONAL NANOCOMPOSITES WITH ENHANCED MECHANICAL AND ANTI-MICROBIAL PROPERTIES

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Abstract

The main aim of the present work is to investigate the possibility to obtain binary and ternary polymer nanocomposites with enhanced mechanical and anti-microbial properties. To this end a DGEBA-based epoxy resin has been loaded using montmorillonite clays and later used as matrix for glass fibre reinforced laminates. Both binary and ternary nanomodified specimens have been manufactured and subjected to mechanical testing. Moreover an accurate analysis of the effect of nanomodification on the biological activity has been carried out.

1. Introduction

The attractive combination of properties of epoxy resins (stiffness, strength, high heat distortion temperature, creep resistance, thermal and environmental stability) can be further improved and modulated by using the nanoclay/nanocomposite strategy [1]. Thus, the relatively easy synthetic procedures suitable to chemical modification allow in principle to introduce into the clay layers suitable cations able to confer new designed properties to the final nanocomposite. Most of the commercially available organoclays are produced by exchange of alkali or alkali earth cations in the interlayer space of clay mineral with ammonium salts, but other cations such as phosphonium, pyridinium and imminium have also been used to improve thermal stability. Combining epoxy resins and small quantities of nanoclays the mechanical [2], thermal [3], barrier [4] and anticorrosive [5] properties were highly improved compared to the neat epoxy resins. The aim of this work is to study the effect of the addition of the commercial nanoclay, Nanomer I.30E into the epoxy resin obtained by reaction of Elan-Tech EC157 with the polyamine Elan-tech W152LR and to verify the antimicrobial properties of the nanocomposite.

2. Materials and methods

In this work, a diglycidyl ether of bisphenol A (DGEBA, Elan.tech EC157) epoxy with the mixture of cycloaliphatic amines Elan-TechW 152 (supplied by Elantas) has been used as polymer matrix. Nanomer I.30E (montmorillonite clay with 25-30%wt octadecylamine surfactant, supplied by Aldrich) and a 350g/m² balanced twill glass fibres supplied by G.Angeloni were used as nanofiller and microsize reinforcement, respectively.

The presence of amine groups on the surfaces of the clays ensures compatibility between the

epoxy resin and the nanoreinforcement and, at the same time, add amine groups in excess with respect of the stoichiometric ratio.

Dog-Bone (DB) specimens and Compact Tension (CT) specimens have been manufactured with the nanomodified epoxy resin (Figure 1a-b), while Double Cantilever Beam (DCB) specimens as well as Interlaminar Shear Strength (ILSS) specimens have been obtained from the laminates.

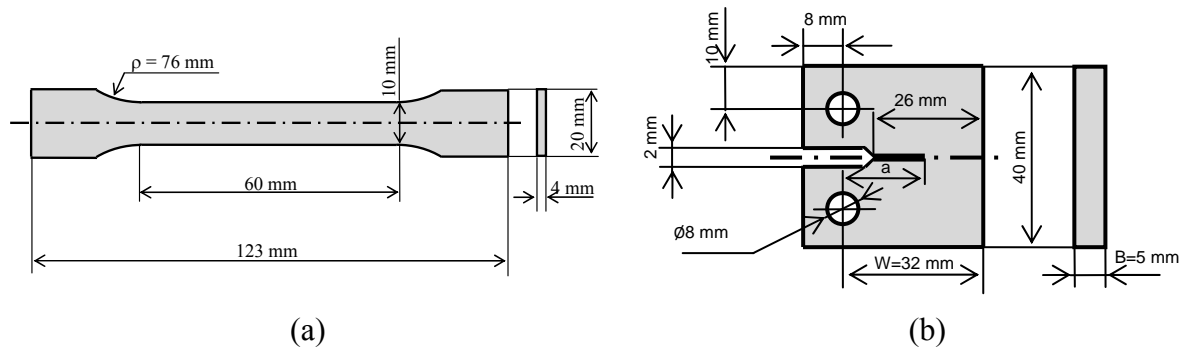


Figure 1. Geometries of the specimens used in testing neat and nanomodified resins.

The above mentioned specimens have been manufactured according to the following steps: (i) Nanoclays have been dispersed in the DGEBA resin by means of shear mixing and sonication. The shear mixing has been carried out with a DISPERMAT TU shear blender from VMA-Getzmann, at about 1800rpm for about 40 minutes. Then, the blend has been sonicated using a HIELSCHER UP 200S sonicator (amplitude 1 and duty cycle 1) for 10 minutes, in order to improve clay dispersion. After sonication, the hardener has been added and a further shear mixing at 300rpm for 5 minutes has been performed. The whole process has been carried out immersing the blend pot in icy cold water. (ii) In order to remove the air trapped within the blend as a consequence of the shear mixing, degassing has been carried out. To this end a low vacuum pump has been used to reach a relative pressure of -1 bar and, at the same time, mechanical shaking of the blend has been performed. After 30 minutes the composite has been poured in silicone moulds to manufacture binary nanocomposite samples. (iii) Glass fibre reinforced laminates have been produced by means of room temperature vacuum infusion of the nanomodified resin into a vacuum bag where 16 layers of glass fibre ply have been layered. An Aluminium film of 15 μ m has been used to create the pre-crack for the DCB specimens. (iv) After 3 days of curing at room temperature, demoulding of the specimens has been carried out. Finally, the specimens have been lapped and for CT specimens manual tapping has been carried out. Specimens have been manufactured at filler weight fraction of 0%, 1% and 3%.

3. Morphological and chemical characterization

The chemical characterization of the samples has been carried out through FTIR spectroscopy observing that the characteristic peaks of montmorillonite are too low to be identified (-OH stretching mode of Al-OH or Si-OH at 3626 cm^{-1} and the band associate with the bending in plane vibration of the -OH from water at 1634 cm^{-1}) (Figure 2).

At low magnification, TEM images show clusters of nanofiller-rich regions and resin-rich region. All TEM images at high magnification show that the gap between two adjacent platelets is about 2.0 nm, indicating that the nanocomposite has a partially intercalated structure (Figure 3).

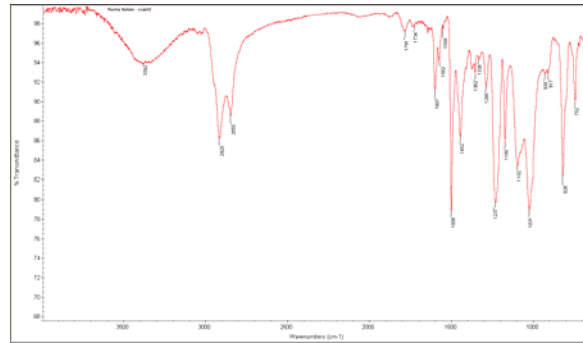


Figure 2: FTIR spectrum in ATR of a sample of epoxy resin containing 2% of I.30E

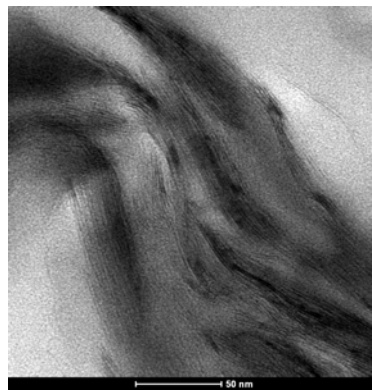


Figure 3: TEM micrograph for nanocomposite containing 3%wt of clay loading.

4. Mechanical testing and results

4.1. Testing Equipment

Tensile tests have been carried out on a MTS809 servo-hydraulic machine equipped with a 25kN load cell, in conjunction with a MTS632.29F-30 extensometer, for an accurate strain measurement. Fracture tests on the resins and interlaminar tests have been performed on a MTS858 servo-hydraulic machine equipped with a 2.5kN load cell.

4.2. Tensile Tests

Tensile tests on DB specimens have been carried out with the aim to determine the failure stress, σ_R , the elastic modulus, E and the strain to failure, ϵ_R of the neat and nanomodified epoxy resin. The specimen geometry complies with the ASTM D638-10 suggestions and tests have been carried out with crosshead speed equal to 2 mm/min. For each material configuration, at least three specimens have been tested. In all the performed tests failure took place in the gauge length of the specimen.

The effect of the weight content of silica nanoparticles upon the nanocomposite tensile properties is shown in Figure 4. It appears clear that the nanomodification of the epoxy resin results in a reduction of the mechanical properties considered. Nevertheless these trends are in accordance with experimental tests performed in similar nanomodified epoxies with exact stoichiometric ratio [2,6-8].

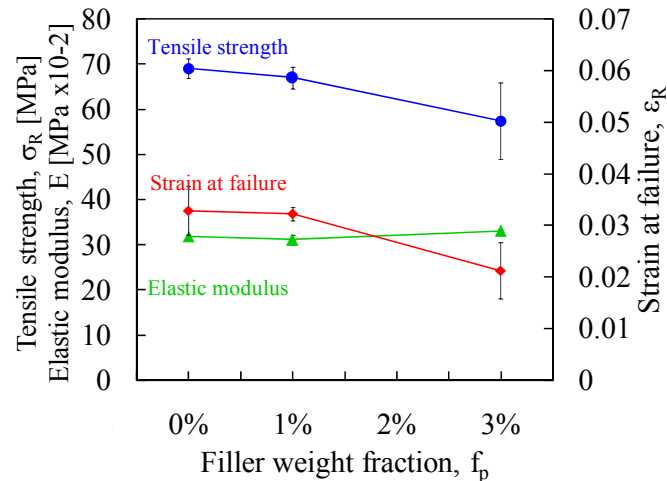


Figure 4. Effect of the nanomodification of the epoxy resin evaluated from tensile tests.

4.3. Mode I Fracture Tests

Fracture tests have been carried out on CT specimens according to the ASTM D5045-99 suggestions. Pre-cracking of the specimens has been performed by manual tapping and at least 3 values for each material have been obtained. Mode I fracture toughness has been computed from the following expression:

$$K_{Ic} = \frac{P_{cr}}{B W^{0.5}} f\left(\frac{a}{W}\right) \quad (1)$$

where P_{cr} is the fracture load, a is the crack length, B the specimen thickness and W is the ligament (Figure 1b). The suggested expression for $f(a/W)$, valid for $0.2 < \frac{a}{W} < 0.8$, is:

$$f\left(\frac{a}{W}\right) = \frac{\left(2 + \frac{a}{W}\right) \left[0.886 + 4.64 \frac{a}{W} - 13.32 \left(\frac{a}{W}\right)^2 + 14.72 \left(\frac{a}{W}\right)^3 - 5.6 \left(\frac{a}{W}\right)^4\right]}{\left(1 - \frac{a}{W}\right)^{1.5}} \quad (2)$$

The experimental results in term of K_{Ic} have been computed applying Eq. (1) and have been reported in Figure 5. Differently from tensile properties, the mode I fracture toughness of the epoxy resin has been enhanced by nanomodification: the K_{Ic} of $0.96 \text{ MPa m}^{0.5}$ of the neat-epoxy is increased to $1.23 \text{ MPa m}^{0.5}$ (about +20%) with a filler weight fraction of 3% of nanoclay, despite the unbalanced stoichiometric ratio.

4.4. Interlaminar Tests

In order to evaluate the laminate interlaminar properties, tests on ILSS as well as DCB specimens have been performed. DCB tests have been carried out following the guidelines reported in ASTM D5528. For each composite 5 specimens have been tested and the crack propagation has been monitored by means of a travelling stereoscope. The crosshead speed has been set at 0.5mm/min. The resulting strain energy release rate, G_{Ic} , has been evaluated by means of the modified compliance calibration method (MCC) and the initiation values have been measured according to the 5% offset method. The results are reported in Figures 6 and 7 where it is evident that the R-curves exhibit a substantial constancy, independently of the

filler weight fraction, both in terms of crack propagation and initiation.

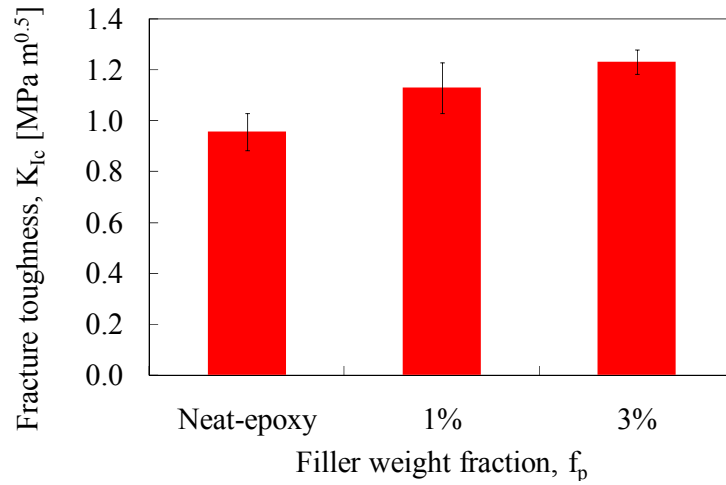


Figure 5. Effect of the nanomodification of the epoxy resin evaluated from CT tests.

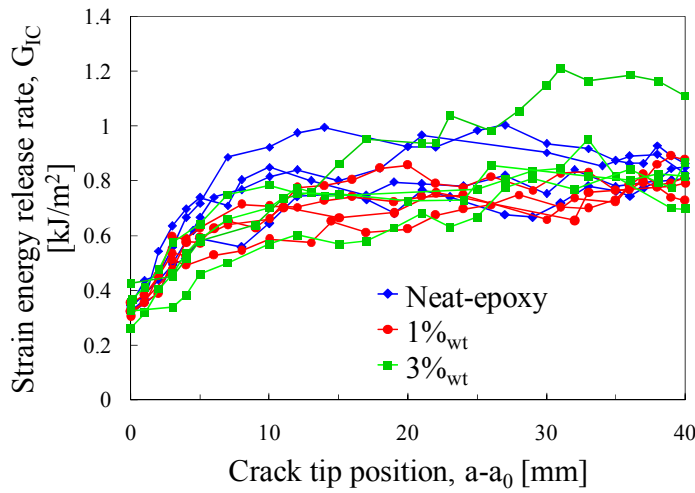


Figure 6. R-curves obtained from the DCB tests.

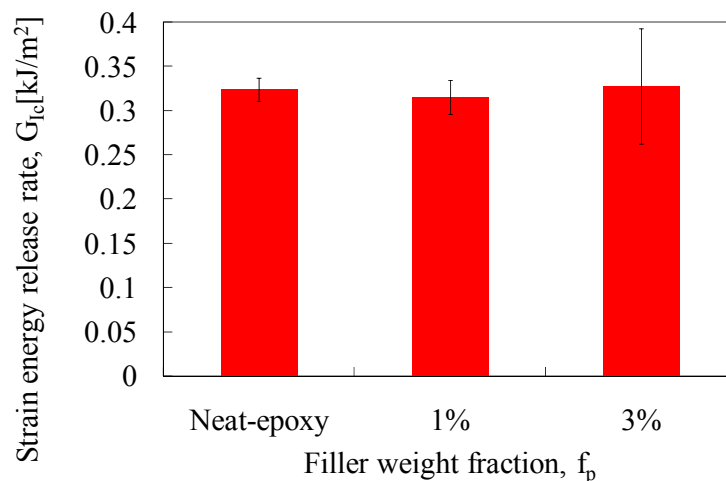


Figure 7. Initiation values of the R-curves reported in Figure 6.

ILSS tests have been carried out according to the ASTM D2344 suggestions. The crosshead speed has been set at 1mm/min and five specimens have been tested for each material configuration. During the tests all specimens have failed by delamination. The results are reported in Figure 8 where it is evident that the interlaminar shear strength shows a slight

reduction with the increase of the nanoclay content.

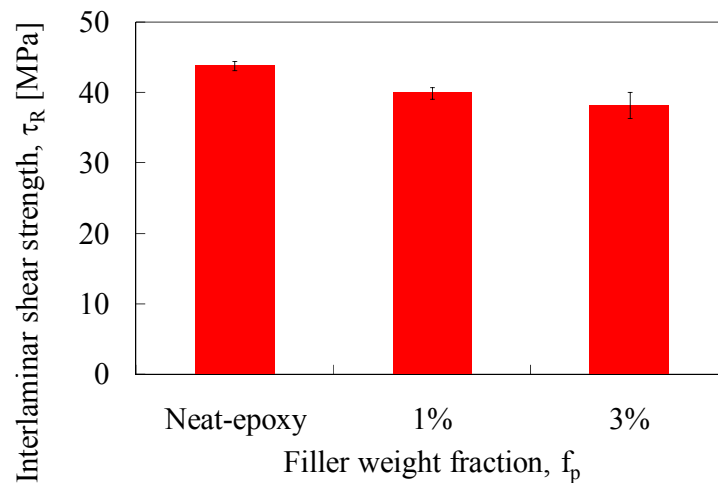


Figure 8. Laminate interlaminar shear strength obtained from ILSS tests.

5. Biological activity

The antibacterial activity of the surface were tested against *E.coli* ATCC 8739, selected as an example of gram-negative bacteria. The tested samples were submitted for 24 h to a sterilizing UV irradiation, coated with 100 μ L of bacteria in a triptone soy broth suspension (pH 6.6) (1:500) and incubated for 2 and 24h at 35°C. The bacteria were recovered by adding 10mL of soybean casein digest with lecithin and polysorbate neutralizer broth (SCDLP: 17.0g of casein peptone, 3.0g of soybean peptone, 5.0 of sodium chloride, 2.5g of sodium hydrogen phosphate, 2.5g of D-glucose, 1.0g of lecithine and 7.0g of Tween in 1000mL of deionized water) according to ISO 22196. The viable bacteria were enumerated by performing successive 10-fold serial dilutions in phosphate buffered physiological saline (34g/l di KH_2PO_4 diluted 1:800 in physiological solution) of the 10mL suspension recovered from the test specimen. Samples of 1 mL of each dilution were put into sterilized Petri dishes, together with 15mL of a plate count agar. The suspensions were gently swirled to disperse the bacteria and incubated at 35°C for 48h. All the platings were performed in duplicate. After incubation, the number of colonies of each dilution was counted and the mean values of the counts below 300 CFU/mL were reported. The data have been compared with reference samples.

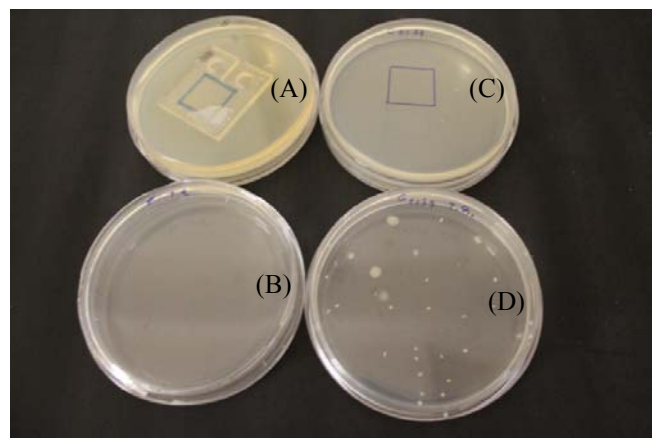


Figure 8: Antimicrobial effect of the nanocomposite containing 3% of clay on *Escherichia coli*. (A) Sample, before. (B) Sample, after. (C) Reference, before. (D) Reference, after.

The antimicrobial activity of the nanocomposite containing 2% of clay was established by comparing the initial number of CFU of E.coli to the final number of bacterial colonies after contact. The antibacterial activity (Figure 8) was very high (log kill > 1.5; Table 1). Also in the case of laminates, the presence of the nanoclay induces antimicrobial activity (Figure 9 and Table 2).

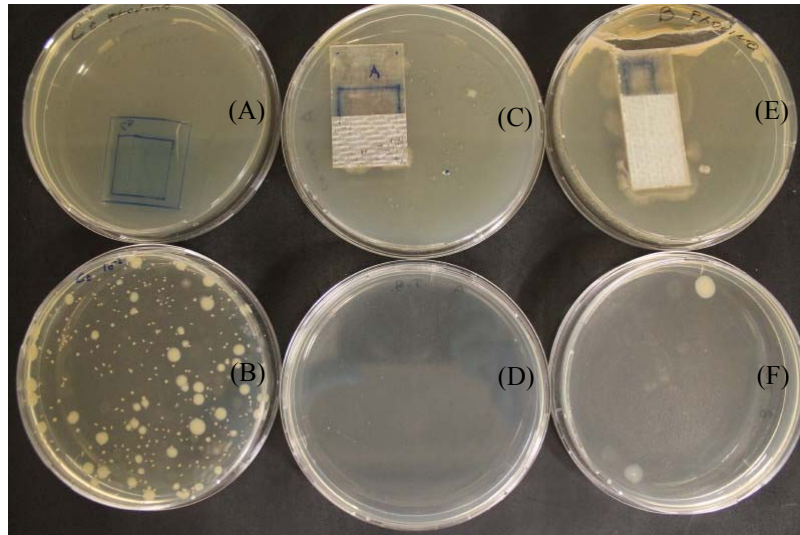


Figure 9: Antimicrobial effect of the laminates on Escherichia coli. (A) Reference, before. (B) Reference, after. (C) Laminate 3%, before. (D) Laminate 3%, after. (E) Laminate neat, before. (F) Laminate neat, after.

	UFC/100µl /4cm ²	LogUFC/100µl /4cm ²	UFC/cm ²	LogUFC/cm ²	Antimicrobial activity logC _{t=2} -logp _{t=2}
Test Suspension	2.13 x 10 ⁶	6.33	5.33x10 ⁵	5,73	
Reference (t = 0)	1.71x10 ⁶	6.23	4.28x10 ⁵	5,63	
Reference (t = 24ore)	3.15,0x10 ²	2.50	7.88x10 ¹	1.90	
Nanocomposite	<10	<1	< 2.5	< 0.40	>1.5

Table 1. Antimicrobial activity of nanocomposite containing 3% of clay.

	UFC/100µl /4cm ²	LogUFC/100µl /4cm ²	UFC/cm ²	LogUFC/cm ²	Antimicrobial activity logC _{t=2} -logp _{t=2}
Test Suspension	3,8 x 10 ⁵	5,6	1,4x10 ⁵	5,73	
Reference (t = 0)	3,8x10 ⁵	5,6	1,4x10 ⁵	5,63	
Reference (t = 2ore)	4,0x10 ⁴	4,6	1,0x10 ⁴	4,0	
Laminate 3%	<10	<1	<0,3	0	4,0
Laminate neat	25	1,4	6,3	0,8	3,2

Table 2. Antimicrobial activity of laminates

6. Conclusions

In this work the possibility to obtain binary and ternary polymer nanocomposites with enhanced mechanical and anti-microbial properties has been investigated. To this end a DGEBA-based epoxy resin has been loaded using montmorillonite clays and later used as matrix for glass reinforced laminates. Both binary and ternary nanomodified specimens have been manufactured and subjected to mechanical testing. Moreover an accurate analysis of the effect of nanomodification on the biological activity has been carried out.

The results indicate that the nanomodified laminates are characterised by mechanical properties almost comparable to those of the base laminates; conversely the antimicrobial properties are substantially improved by nanomodification.

Acknowledgments

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