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Multifunctional polymer nanocomposites with enhanced mechanical and anti-microbial properties

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The paper reports the results of a project aiming to obtain multifunctional binary and ternary polymer nanocomposites with enhanced mechanical and anti-microbial properties. To this end a DGEBA-based epoxy resin is loaded using montmorillonite clays and later used as matrix for glass fibre reinforced laminates. Both binary and ternary nanomodified specimens are manufactured and subjected to mechanical testing. An accurate analysis of the effect of nanomodification on the biological activity is carried out as well.

1. Introduction

The most recent advancements in polymer and composite science and technology allow the design of materials and structures at the nanometer scale, resulting in exciting accomplishments in the development of multi-functional materials with enhanced physical and mechanical properties for several fields of application [1–8].

Thanks to the complex physical interactions among constituents occurring at the atomic level, nanomodified polymers are provided with exceptionally enhanced properties even at low filler concentrations, making polymer nanocomposites a unique vector for functional properties.

Within this context, clay based nanocomposites are very promising new materials from the perspective of achieving high performances at a relative low cost. Nanoclays are silicate platelets with about 1 nm of thickness and disposed in tactoids; commonly, a hybrid exfoliated and intercalated structure represents a trade-off between the capacity of obtaining the desired property enhancements and manufacturing complexity [9–16]. A complete exfoliation is, indeed, complicated to be obtained since it requires the separation of the platelets from the primary tactoids.

Due to their very high aspect ratio, nanoclay platelets are suitable to improve the tensile elastic modulus of polymeric systems [9–11], the matrix fracture toughness [16,17] and, in principle, the strength, even if conflicting results have been reported [12–16].

As far as the possibility to transfer the improvements obtainable in the mechanical properties of binary nanocomposites to ternary fibre reinforced nanocomposites is concerned, the results reported up to now in the literature do not show a unique trend. Encouraging results were obtained by Becker et al. [18], who documented improvements in crack opening fracture toughness with low levels of clay addition and by Quaresimin and Varley [19], who reported "selective" improvements in the mode II toughness properties of carbon/clay-modified epoxy laminates. Differently, the investigations carried out by Timmerman et al. [20] and Quaresimin et al. [16] showed only limited improvements in the mechanical properties of clay modified composites compared to those produced with unmodified resins.

When using adequate surfactants, polymer loading through montmorillonite (MMT) nanoclays also offers exceptional improvements of anti-microbial properties [21–23], assisting in the achievement of self-decontaminating surfaces which are highly desirable for many fields of application, such as composite parts in the medical field (external prostheses or sterilised equipments and tables).

Quaternary ammonium compounds (QACs) have great antibacterial activity thanks to the positive charge of the amine

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which is attracted and interact with the negatively charged cell surfaces of bacteria [24,25]. The concept of polymeric spacer is commonly used when describing QACs activity: more precisely, the agent is supposed to adsorb and penetrate into the bacterial cell thanks to a sufficiently long alkyl chain which should allow it to reach gradually the cytoplasmic membrane and kill the bacteria by destabilizing and destroying the phospholipid bilayer.

An alternative mechanism proposed to explain the antimicrobial activity of these compounds is known as the contact-killing via the phospholipid sponge effect which consist of an absorption and removal of such negative molecules from cell membranes thus leading bacteria to death [24–27].

This concept is reconsidered in this work, where the preliminary results of a project aimed at designing, manufacturing and testing advanced multifunctional polymer nanocomposites with enhanced mechanical and anti-microbial properties are presented. In more details, binary and ternary nanocomposite specimens are manufactured using a DGEBA-resin reinforced with octadecylamine surface-modified montmorillonite (MMT). By one side, this particular functionalisation is proved to be very effective in terms of anti-microbial properties. On the other side clay-loading assists in the improvement of the polymer toughness. Eventually, the capability of translating the improved resin properties to the fibre reinforced composite is studied as well.

2. Materials and specimens manufacturing

In this work, a diglycidyl ether of bisphenol A (DGEBA, Elan-tech EC157) epoxy with the mixture of cycloapliphatic amines Elan-Tech W152LR (supplied by Elantas) was used as polymer matrix. Nanomer I.30E (montmorillonite clay with 25–30% wt octadecylamine surfactant, supplied by Sigma–Aldrich) and a 350 g/m^2 balanced twill of glass fibres supplied by G. Angeloni were used as nanofiller and microsize reinforcement, respectively.

The presence of amine groups with carbon chains on clay surfaces ensures compatibility between the epoxy resin and the nanoreinforcement and, at the same time, add amine groups in excess with respect to the stoichiometric ratio, giving a contribution to the development of anti-microbial properties. Indeed, Kubo et al. [22] reported how amine groups are capable to modify the pH of the material and might affect antibacterial activities.

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

The above mentioned samples were manufactured according to the following steps:

1. Nanoclays were dispersed in the DGEBA resin by means of shear mixing and sonication. The shear mixing was carried out with a DISPERMAT TU shear blender from VMA-Getzmann with a 70 mm diameter blade (about 1800 rpm for 40 min). Then, the blend was sonicated with a HIELSCHER UP 200S sonicator using a 40 mm diameter sonotrode (amplitude 160 W and duty cycle 1) for 10 min, in order to improve the clay dispersion. After the sonication, the hardener was added and a further shear mixing at 300 rpm for 5 min was performed.
2. Degassing was carried out for removing the air trapped within the blend as a consequence of the shear mixing. To this end a low vacuum pump was used to reach a low pressure within the resin pot and, at the same time, mechanical shaking of the blend was performed. After 30 min the composite was poured in silicone moulds to manufacture binary nanocomposite samples.
3. Differently, glass fibre reinforced laminates were produced by means of room temperature vacuum infusion of the nanomodified resin into a vacuum bag where 16 layers of glass fibre ply were layered. An Aluminium film 15 μm thick was used to create the pre-crack for the DCB specimens.
4. After 3 days of curing at room temperature, demoulding of the specimens was carried out. Finally, the specimens were polished and for CT specimens manual tapping was carried out. Filler weight fractions of 1% and 3% have been used to modify the polymer resin.

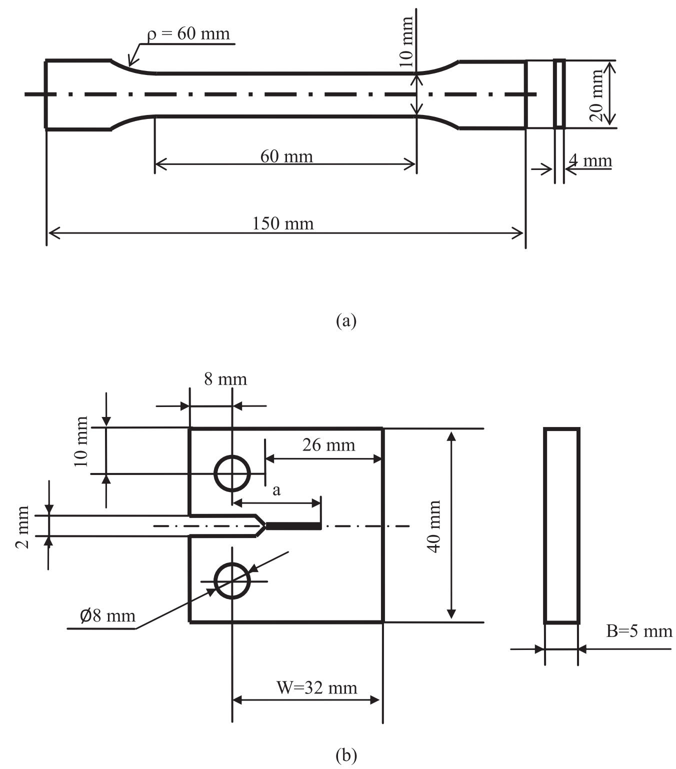

Fig. 1. (a) A Dog-Bone (DB) specimen and (b) a Compact Tension (CT) specimen used in the mechanical tests.

3. Binary nanocomposites

3.1. Morphological and chemical characterization

A chemical characterization of the samples made of nanomodified polymer was carried out through FTIR spectroscopy using a thermo electron Nicolet Nexus 5700 with smart performer single-bounce ATR accessory. Results shown in Fig. 2 make it evident that the characteristic peaks of montmorillonite were 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}).

Moreover, high magnification TEM images showed a partially intercalated structure for the nanoclay (Fig. 3).

ESEM analyses were also carried out by means of a Quanta200 FEI on sample surfaces (Fig. 4); the results suggest that montmorillonite inclusions were deep inside the matrix, the surface being essentially clay-free. Moreover, a non-homogeneous distribution of the clay was evident in the case of 3% wt (see Fig. 4b).