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# Fatigue behaviour of nanoclay reinforced epoxy resin composites

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ABSTRACT

Nanoparticle filling is a feasible way to increase the mechanical properties of polymer matrices. Abundant research work has been published in the last number of years concerning the enhancement of the mechanical properties of nanoparticle filled polymers, but only a reduced number of studies have been done focusing on the fatigue behaviour. This work analyses the influence of nanoclay reinforcement and water presence on the fatigue behaviour of epoxy matrices. The nanoparticles were dispersed into the epoxy resin using a direct mixing method. The dispersion and exfoliation of nanoparticles was characterised by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Fatigue strength decreased with the nanoclay incorporation into the matrix. Fatigue life of nanoclay filled composites was significantly reduced by the notch effect and by the immersion in water.

## 1. Introduction

Nanoparticle-reinforced polymer composites have been widely investigated, indicating significant improvements in mechanical, thermal and physical properties in comparison with the neat resin. The beneficial effect obtained by using nanoclay reinforcement has been observed, even for low nanoclay content, e.g. [1–3]. Montmorillonite (MMT) clay is the most widely used material for preparing polymer nanocomposites due to of its high aspect ratio and economic advantages [4]. Wang et al. [5] observed that the incorporation of nanoclay particles into epoxy resin improved Young's modulus, but the tensile strength decreased slightly with the increase of the clay content. Wang et al. [6] also obtained a linear increase of the Young's modulus with the nanoclay percentage. However, the tensile strength only increased up to 2 wt.% nanoclay content and dropped with increasing nanoparticle percentage. These results were explained by the density heterogeneity due to the presence of air bubbles trapped during the sample preparation which may increase with the clay content.

The dispersion degree of nanoclays into the polymer nanocomposites aims to enhance the mechanical properties, however it is well recognized the technical difficulties and the cost involved for achieving full exfoliation. Woong et al. [7] performed a systematic study to determine the influence of clay dispersion on the mechanical properties, obtaining a negative effect of certain degree of intercalation or nanoaggregation in the polymer nanocomposites on the mechanical properties, including the fracture toughness. Moreover, not only the amount of clay but also the type of epoxy resin and the technique used to prepare the samples play key roles on the mechanical properties of the obtained nanocomposites.

The permeability can decrease substantially by using nanoclay filling into polymer matrices, which can be an advantage of polymer–clay nanocomposites. However, in the case of epoxy matrices, results do not always show clear advantages. Wang et al. [8] analysed the water absorption of neat epoxy and of nanocomposites with 2.5 wt.% nanoclays, obtaining a 0.65% higher saturating point in the nanocomposites in comparison to the neat epoxy. The difference between the results obtained in other researches [9,10] is justified by the clay surface silane treatment, which is less hydrophobic than the alkyl-ammonium salts usually used.

Despite the numerous researches about the mechanical behaviour of nanoreinforced composites, a relatively scarce number of studies on the fatigue behaviour can be found in the literature. Bellemare et al. [11] studied the mechanical behaviour of polyamide-6 reinforced with nanoclays. An increase in fatigue life was observed as result of the increased intrinsic resistance to the initiation of cracks in the nanocomposite material. This behaviour was favoured by the effect of increasing the elasticity modulus caused by the particles, which lead to the consequent reduction in the deformation amplitude of the macromolecules during cyclic loading. The nanoparticles increase the stiffness of the material,

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but simultaneously can act as critical points for fatigue crack initiation.

Recently Koratkar and Srivastava [12], Manjunatha et al. [13] and Wang et al. [14] also studied the influence of the nanoparticle content in the fatigue strength. Manjunatha et al. [13] analysed the influence of the addition of rubber and silica nanoparticles. The addition of 10% of silica nanoparticles improved 3–4 times the fatigue life in comparison with the neat resin. Wang et al. [14] also achieved significant improvement concerning the resistance to the initiation of fatigue cracks. The incorporation of 2 and 6 wt.% silica nanoparticles improved fatigue life in the order of 145% and 56%, respectively. Improvements in tension–tension fatigue lives were also obtained by Zhou et al. [15] using carbon nanofibers as reinforcement of epoxy/carbon composites.

The main objective of this work was to study the influence of the nanoclay content on the fatigue strength of epoxy resin composites. Also, the effects of notch hole and water uptake on the fatigue life are analysed for the nanocomposites with wt.% of nanoclay content.

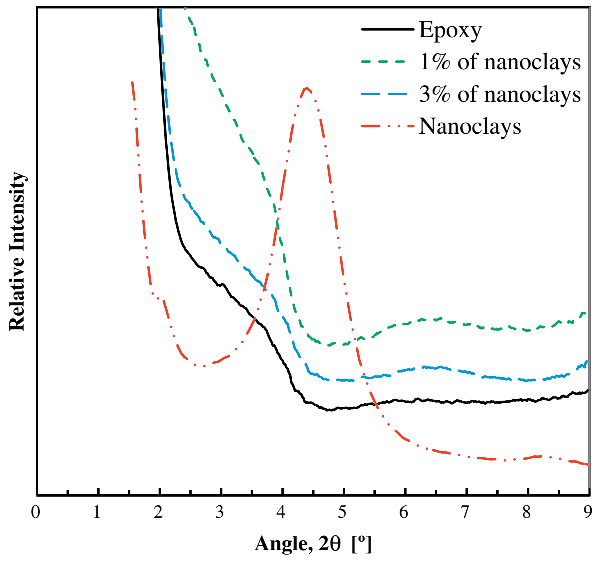

**Fig. 1.** XRD patterns.

## 2. Materials and procedure

Three materials were studied, namely, control epoxy matrix resin and composites with 1% and 3 wt.% of nanoparticle content. The nanoclay used in the present work was the commercially available organo-montmorillonite, Nanomer I30 E, with the surface modified with an octadeyl amine modified, provided by Nanocor Inc. and produced to be easily dispersed into epoxy resins. The epoxy resin was the SR 1500, formulated by bisphenol A and F, and it was combined with the hardener SD 2503, both supplied by Sicomin. This epoxy system presents good waterproof and adhesion properties and it is commonly used in shipbuilding and in the aerospace industry.

The desired amount of clays was dispersed into the epoxy resin using a high rotation technique (8000 rpm) during 2 h. Then, the mixture was degassed under vacuum for 30 min, followed by the addition of the hardener agent. Finally, the mixture was stirred under vacuum for 10 min and put into the mould. The cure was vacuum moulded at room temperature during 6 h and the post-cure was performed in an oven at 60 °C during 16 h. Plates with a dimension of 100 × 100 × 4 mm were moulded, from which the specimens were machined with the desired dimensions.

The nanocomposite plates were monitored in terms of dispersion and exfoliation using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

X-ray diffraction analysis was performed using a Seifert 3000 XPS generator with Cr radiation operated at 40 kV and 30 mA. The diffraction patterns (Bragg angle $2\theta$) were collected between 1.5° and 15°, at a scan rate of 2.5°/min and with a step size of 0.02°. Fig. 1 shows the scattering patterns of nanoclays, neat epoxy and nanocomposites. It is possible to identify the peak that corresponds to the basal spacing of nanoclays, which is located near 4.5°. Analysing the spectra of nanocomposites and performing a comparison with the spectrum of pure resin, an increase in basal spacing is clearly visible, but without the presence of peaks, indicating that the particles are intercalated into the resin. There is a slight intensity shoulder at about 6°, more pronounced in 3 wt.%, which may suggest the presence of some aggregates of nanoclays within the matrix, as will be seen later on after presenting the SEM fatigue fracture surface analysis.

Samples were prepared in an ultramicrotome for ultrathin sectioning EM FCS, Leica Company. Morphological analyses were realized in an Ultra-high resolution Field Emission Gun Scanning Electron Microscopy (FEG-SEM), NOVA 200 Nano SEM, FEI Company, using a Scanning Transmission Electron Microscopy (STEM) detector and an acceleration voltage between 15 and 18.4 kV to obtain the micrographs. Fig. 2a and b shows two of these observations for 1% and 3% nanoclay composites, respectively. Good dispersion, intercalation and clay exfoliation was observed in Fig. 2a for 1% nanoclay, while in Fig. 2b exfoliation is not evident and only clay intercalation was clearly observed. Furthermore, clay dispersion was not well achieved.

Tensile static and fatigue tests were performed using specimens machined with a dog bone shape with the dimensions indicated in Fig. 3. Fatigue tests to study the notch sensitivity effect were performed using parallelepiped specimens with 15 mm width and 4 mm thickness containing a transverse central hole with 3 mm diameter.

Tensile tests were performed according to the ASTM D638-03 [16] specification in order to determine the tensile strength. An extensometer with 25 mm of gauge length was attached to the specimen in order to monitor the axial displacement during loading. The tested were carried out using a Shimadzu SLBL-5kN testing machine. The axial strength was obtained as nominal stress for the maximum axial load. Four tests were performed for each material.

The tensile fatigue tests were carried out at constant amplitude loading using a servo hydraulic Instron testing machine using a sinusoidal wave load with a load ratio $R = 0.05$ and a frequency of 12 Hz. All tests were carried out at room temperature. The temperature rise at the specimen surface was monitored at the middle point of the specimens using type $K$ thermocouples. Only a small increase of temperature (less than 15 °C) was observed.

## 3. Results and discussion

Fig. 4 shows the typical tensile stress versus strain curves obtained for neat resin and for filled composites. The analysis of these results shows that the nanoclay filling increases the tensile stiffness, but simultaneously the strength (stress at peak load) decreases. The presence of nanoparticles also reduces the strain at failure, indicating a significant trend to embrittlement of the material. The tensile strength was calculated by dividing the peak load by the cross section area. Table 1 summarizes the average and standard deviation values of the tensile strength obtained from four tests performed for each material. Taking into account the good dispersion with clay exfoliation achieved at least for 1%