ASSESSMENT OF THE FATIGUE BEHAVIOUR ON NANOFILLED EPOXY 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 last year's concerning the enhancement of the mechanical properties of nanoparticle filled polymers, but only a reduced number of studies were done about the fatigue behaviour of this type of materials. This paper studies the influence of nanoclay filling 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 controlled by X-ray Diffraction (XRD) and transmission electron microscopy (TEM). Fatigue strength was reduced by the nanoclay adding. Fatigue life of nanoclay filled composites was significantly reduced by the notch effect and by the long-time immersion in water.

1 Introduction

The polymer reinforced nanocomposites have been widely investigated during last year's. Generally, literature reports indicate significant improvements in mechanical, thermal and physical properties in comparison with the neat resin [1-3], even for low nanoparticle loading. Montmorillonite (MMT) clay is the most used for preparing polymer nanocomposites in consequence of its high aspect ratio and economic advantages [4]. However, the benefit obtained by the addition of nanoclays shows no apparent consensus. For example, Wang *et al* [5] concluded that the incorporation of clay into epoxy resin improves the Young's modulus, but the tensile strength decreased slightly with the increase of the clay content. Wang *et al* [6] obtained a linear increase of the Young´s modulus. However, the tensile strength increased up to content of 2 wt%, and afterwards dropped with the filler percentage. These results were explained by the heterogeneity of the density of the samples and by the presence of air bubbles trapped during the sample preparation, which may increase with the clay content. The analysis of reported literature indicates that the main factor which determines the enhancement of the mechanical properties is the degree of dispersion and exfoliation of nanoclays in the polymer matrix. Moreover, it is well recognized the technical difficulties and the cost involved for achieving full exfoliation. Woong *et al* [7] have performed a comprehensive study to determine the clay dispersion influence on the mechanical properties, in order to determine possible negative effects of a certain degree of intercalation or nanoaggregation in the polymer nanocomposite on its mechanical properties and fracture toughness.

Despite the numerous research works about the mechanical behaviour of nanoreinforced composites, a relatively scarce number of studies on the fatigue behaviour are found in the literature. Bellemare *et al* [8] studied the behaviour of polyamide-6 reinforced with nanoclays. They obtained an increase in fatigue life as result of increased intrinsic resistance to the initiation of cracks in the material, which is favoured by the effect of increasing the modulus of elasticity caused by the particles and the consequent reduction in the amplitude of deformation of the macromolecules during cyclic loading. The nanoparticles increase the stiffness of the material, but on the other hand can act as critical points of initiation of fatigue cracks. Recently, Wang *et al* [9] achieved a significant improvement concerning the resistance to the initiation of fatigue cracks by the incorporation of silica nanoparticles. Improvements in tension–tension fatigue lives were also obtained by Zhou *et al* [10] using carbon nanofibers as a reinforcement of epoxy/carbon composites.

The main objective of this work was to study the influence of the nanoclay content on the fatigue strength. Also the effects of notch hole and water uptake on the fatigue life are studied for the case of 3 wt% nanoclay composites.

2 Materials and testing

Three batches of materials were studied, namely epoxy matrix resin and composites with 1% and 3% wt of filler content. The organo-montmorillonite, Nanomer I30 E, commercially available surface modified with an octadeyl amine modified, provided by Nanocor Inc and produced to be easily dispersed into epoxy resin was used. 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 has good waterproof and adhesion properties and it is commonly used in shipbuilding and aerospace industries.

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 during 30 minutes and afterwards, the hardener agent was added. Finally, the mixture was stirred under vacuum for 10 minutes and placed into the mould. The cure was vacuum molded at room temperature during 6 h and the post-cure was performed in an oven at 60ºC during 16 hours. The tested specimens were machined from the moulded plates.

The nanocomposite plates were controlled 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 2θ) were collected between 1.5º and 15º at scan rate of 2.5 º/min with a step size of 0.02º. Figure 1 shows the scattering patterns of nanoclays, neat epoxy and nanocomposites. It is possible to identify the peak that corresponds to basal spacing of nanoclays which is located near 4.5°. Analysing the spectra of nanocomposites and comparing them with the spectrum of pure resin is visible an increase in the basal spacing, but without the presence of peaks, indicating that the particles are intercalated into the resin. There is a slight shoulder in intensity at about 6º, more pronounced in 3 wt% which suggests the presence of some aggregates of nanoclays within the matrix, as effectively seen later by SEM fracture surface analysis.

The specimens used for tensile static and fatigue tests were machined with a dog bone shape with the dimensions indicated in Fig. 2. Fatigue tests to study the notch sensibility 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, conducted according to the specification ASTM D2344, were performed to determine the tensile strength. An extensometer with gauge length of 25 mm 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. Axial strength was obtained as nominal stress for the maximum axial load.

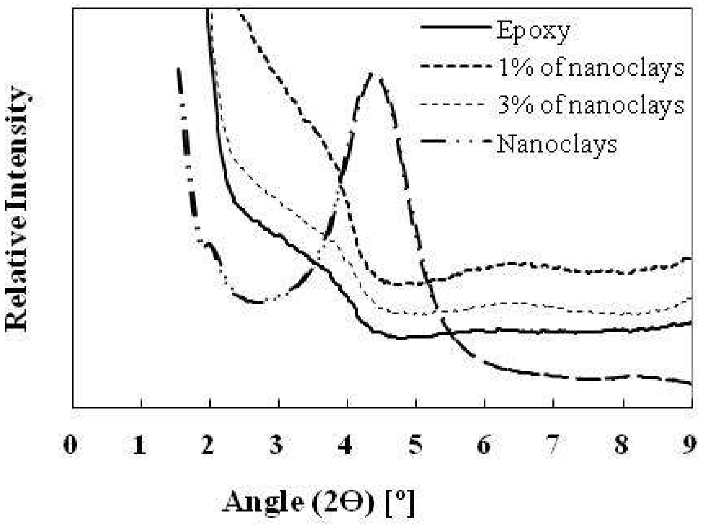

Figure 1. XRD patterns.

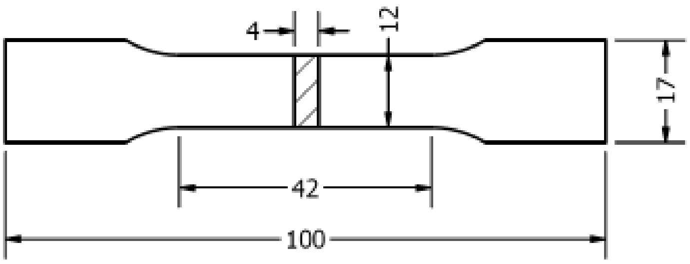

Figure 2. Specimen geometry (dimensions in mm).

The tensile fatigue tests were carried out under constant amplitude loading in 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 surface of the specimen was monitored at the middle point of the specimens, using type K thermocouples. Only a negligible increase of the temperature was observed.

2 Results and discussion

The fatigue results were analysis in terms of the stress range of the load cycle against the number of cycles to failure. Fig. 3 shows the effect of the filler content on the fatigue life. It was observed a tendency, not very marked, to decrease the fatigue strength with the nanoclay content, probably caused by the presence of agglomerates, which favour the initiation of fatigue cracks due to increased stress concentration in these regions. This may explain the opposite behaviour to that reported in the literature, for example by Bellemare et al [8], for other matrices.

The notch effect on the fatigue life is summarized in Fig. 4. This Figure shows the results of the stress range against the number of cycles to failure for smooth specimens and for central hole notched specimens, for 3% wt of nanoclay composite. The presence of the hole notch reduces the fatigue strength approximately 40%, as consequence of the brittle behaviour of this nanocomposite. The reduction in fatigue strength by the notch effect is usually quantified by the dynamic stress concentration factor, k_f, defined as the fatigue strength (in terms of the stress amplitude) of a smooth specimen divided by the fatigue strength of a notched specimen, for a given fatigue life. It was observed that the k_f factor is practically constant, and only a slight and negligible increase was observed for short lives. For longer lives, k_f is practically insensitive to the fatigue life reaching the value of about 1.8.

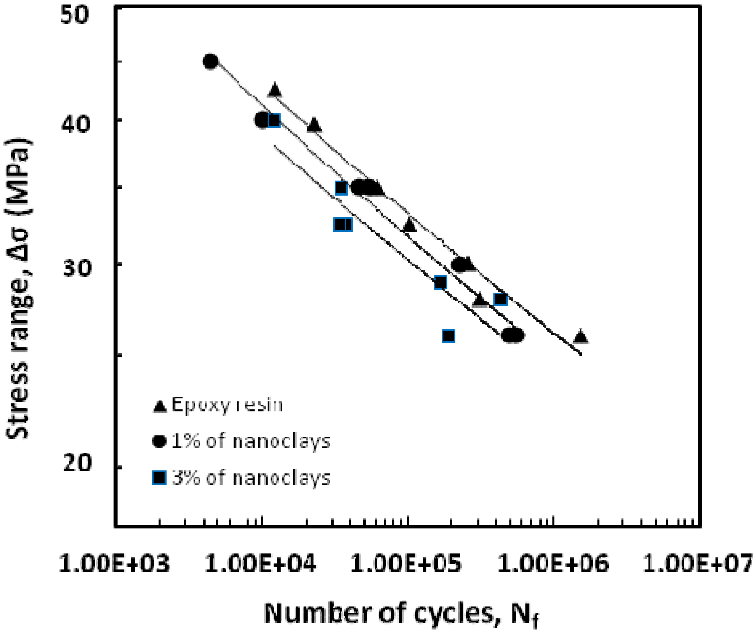

Figure 3. Effect of filler content on S-N fatigue curves.

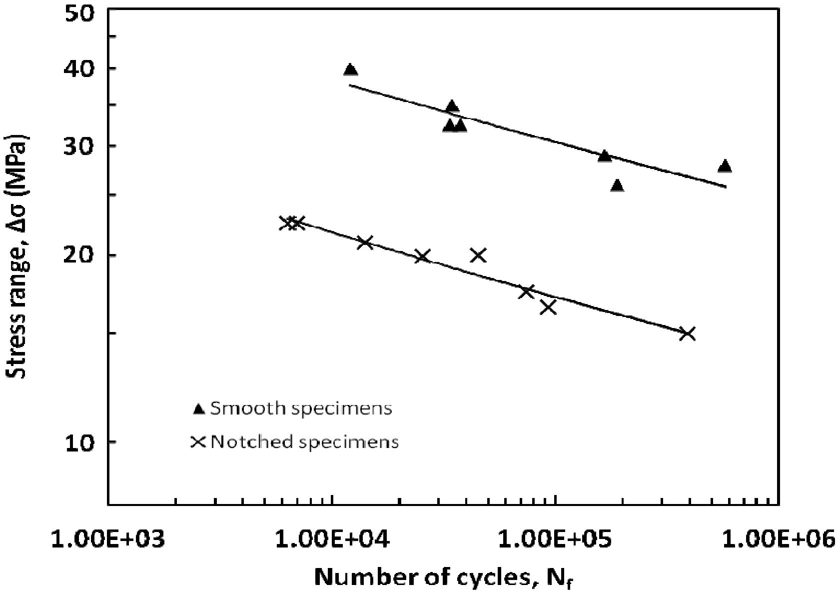

Figure 4. Notch effect on S-N curves.

The morphologies of the fracture surface of the fatigue specimens were analysed using a scanning electron microscope (SEM), Siemens XL 30. Fig. 5a) and b) shows observations of the fracture surfaces of the specimens reinforced with nanoclays 3%, unnotched and hole notched, respectively. Fig. 5a) shows a central region with about 1 mm diameter, from which the fatigue crack was initiated and propagated until brittle fracture occurs outer of this region. There is crack propagation emerging from the periphery of a cluster of nanoparticles with approximately 100 micron, caused by the respective stress concentration. These agglomerates were also found by Bellemare *et al* [8] causing lower fatigue resistance. On the other hand, Wang *et al* [9] concluded that if a good dispersion/exfoliation of nanoclays into the matrix was achieved, cracks should start in the side contours of the sample, which are the highest stress concentration areas. As expected the analysis of the fracture surfaces of notched specimens (Fig. 5b) shows that the fatigue crack initiates at the hole, which is the region with highest stresses in consequence of the stress concentration effect.

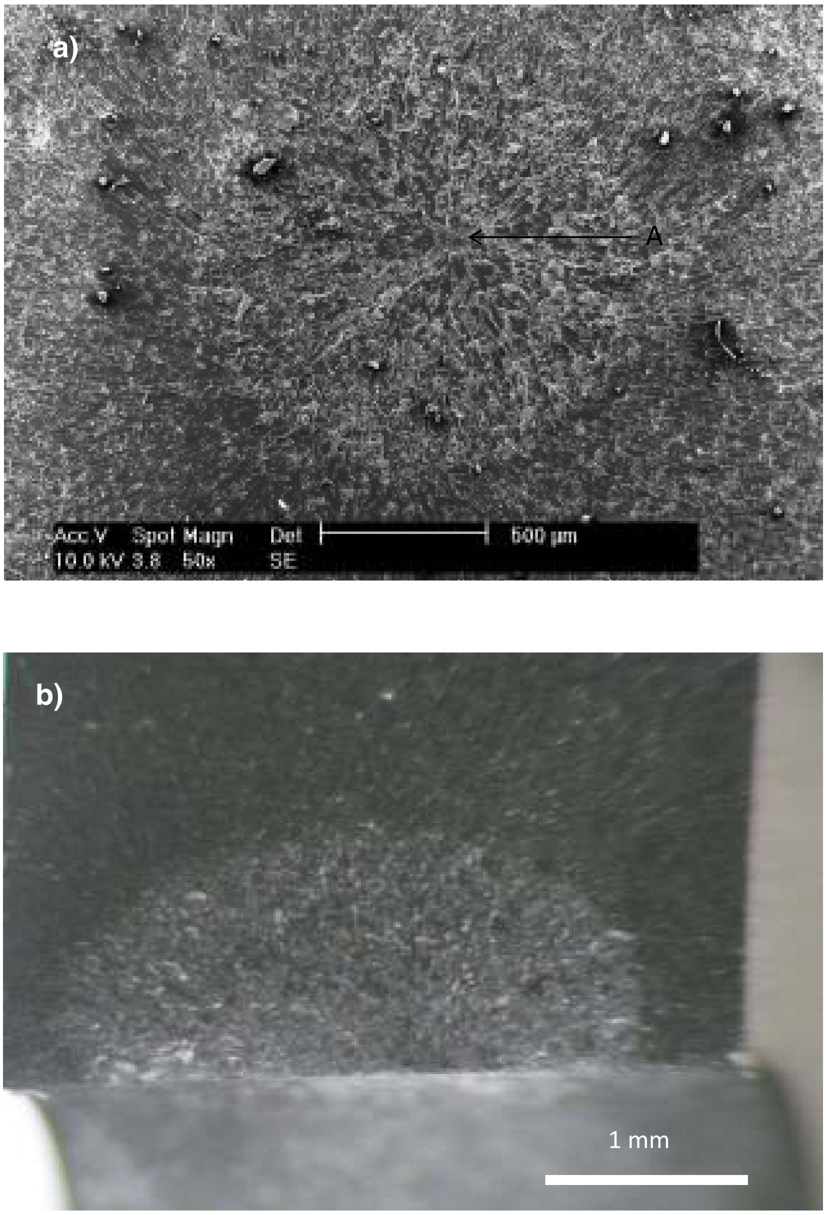

Figure 5. SEM observations of fatigue surface fracture. a) Smooth specimen; b) Notched specimen.

Water absorption was performed according to ASTM D570-98 standard. The percentage gain of water at a given time t, Mt, was calculated using the following expression:

$$M_t = \frac{W_t - W_0}{W_0} x100 \tag{1}$$

where W_0 is the weight of dried material and W_t the weight of materials after exposure to water absorption at time *t*.

The water diffusivity *D*, was calculated accordingly to the following equation:

$$\frac{M_t}{M_\infty} = \frac{4}{h}\left(\frac{D.t}{\pi}\right)^{\frac{1}{2}} \tag{2}$$

where M_∞ is the mass gain at the equilibrium state and *h* is the thickness of the sample.

The obtained absorption is lower than the absorption reported in other studies. This is due to the poor absorbent nature of the resin used, developed particularly to acquire impermeability. The increasing of clays load also increases the water uptake in accordance with Wang *et al* [11]. One of the reasons for the actual behaviour can be the fact that the addition of nanoclays into the matrix may induce the diffusion of water due to the formation of defects in the material. The diffusion coefficients of different materials, calculated using equation (2), are plotted in Figure 6. It is clearly observed that the diffusivity increases with the loading of nanoclays to the matrix, as expected after the results obtained for the weight gain.

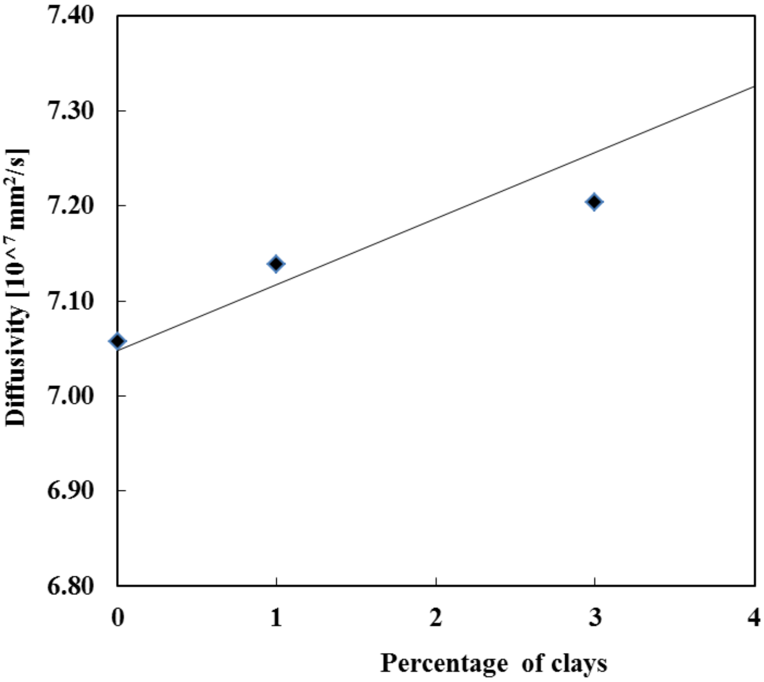

Figure 6. Moisture diffusivity against nanoclay content.

Fig. 7 shows the effect of the immersion in water, at room temperature (20±2ºC) during 60 days, on the S-N curves for 3% wt nanofilled composites. The long term immersion in water causes a significant material degradation, corresponding to a reduction of approximately 15% in the fatigue strength.

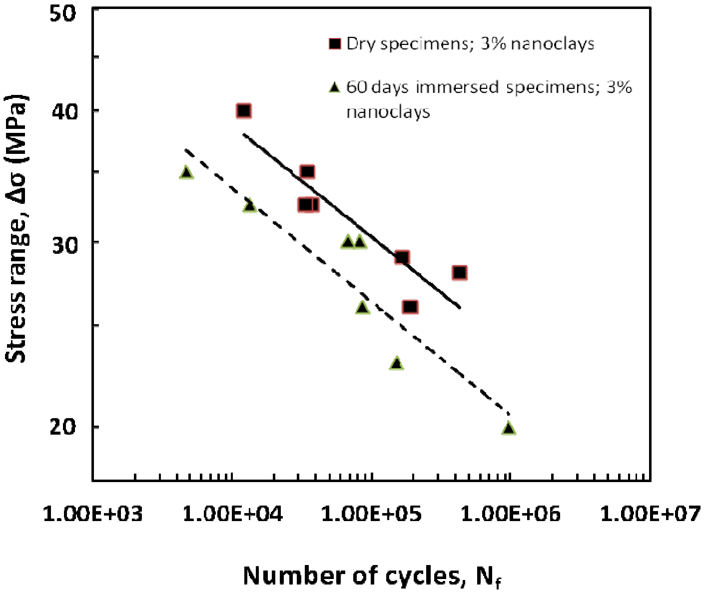

Figure 7. Effect of water immersion on 3% wt nanofilled composites.

CONCLUSIONS

This paper studied the influence of nanoclay content, the notch effect and water uptake on the fatigue life epoxy resin filled up to 3 wt% of nanoclay. The main conclusions are:

- A tendency to decrease the fatigue strength with the nanoclay content was observed, as consequence of the agglomerates, which promote fatigue crack initiation.
- The 3% filled composites hole notched specimens presented a decrease of approximately 40% of the fatigue strength in comparison to the unnotched specimens.
- For the 3% nanofilled material, the immersion in water during 60 days caused a reduction of approximately 15% on the fatigue strength.

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