Accepted Manuscript

Fatigue behaviour of nanoclay reinforced epoxy resin composites

J.A.M. Ferreira, L.P. Borrego, J.D.M. Costa, C. Capela

PII:	S1359-8368(13)00151-0
DOI:	http://dx.doi.org/10.1016/j.compositesb.2013.04.003
Reference:	JCOMB 2331
To appear in:	*Composites: Part B*
Received Date:	27 November 2012
Revised Date:	19 February 2013
Accepted Date:	4 April 2013

FATIGUE BEHAVIOUR OF NANOCLAY REINFORCED EPOXY RESIN COMPOSITES

J.A.M. Ferreira [a,b], L. P. Borrego [a,c,*], J.D.M. Costa [a,b], C. Capela [a,d]

[a] CEMUC, University of Coimbra, Portugal

[b] Mechanical Engineering Department, University of Coimbra,
Rua Luís Reis Santos, Pinhal de Marrocos, 3030-788, Coimbra, Portugal

[c] Mechanical Engineering Department, ISEC, Polytechnic Institute of Coimbra,
Rua Pedro Nunes, 3030-199 Coimbra, Portugal

[d] Mechanical Engineering Department, ESTG, Polytechnic Institute of Leiria,
Morro do Lena - Alto Vieiro, 2400-901 Leiria, Portugal.

Keywords: A. Resins; A. Particle-reinforcement; B. Fatigue, B. Environmental degradation; nanocomposites.

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.

* Corresponding author. Tel.: +351 962560101; Fax: +351 239790331.
E-mail address: borrego@isec.pt (L.P. Borrego)

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]. B. Wang *et al.* [5] observed that the incorporation of nanoclay particles into epoxy resin improved the Young's modulus, but the tensile strength decreased slightly with the increase of the clay content. L. 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. L. 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, 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 to 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 3 wt% of nanoclay content.

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 hours. Then, the mixture was degassed under vacuum for 30 minutes, followed by the addition of the hardener agent. Finally, the mixture was stirred under vacuum for 10 minutes and put into the mould. The cure was vacuum moulded at room temperature during 6 hours and the post-cure was performed in an oven at 60ºC during 16 hours. Plates with a dimension of 100x100x4 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 2θ) were collected between 1.5º and 15º, at a scan rate of 2.5 º/min and with a step size of 0.02º. 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 6º, 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 Fig. 2b show 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 ºC) 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% nanoclay composites (as shown in Fig. 1 and Fig. 2a), an unequivocal improvement of tensile strength was to be expected. On the contrary, the static strength slightly decreased for both nanoclay filled composites. This behaviour is probably due to the presence of nanoclay aggregates as confirmed by SEM observations, which will be presented later on.

The fatigue results were analysed in terms of the stress range of the load cycle against the number of cycles to failure. Fig. 5 depicts the reinforcement content effect on the fatigue life. This figure clearly shows a tendency to a small decreasing of the fatigue strength with nanoclay content, reaching about 6% for the 3% wt nanofilled material. As mentioned previously, the presence of agglomerates, inhomogeneities and porosity points induce greater sensitivity to the initiation of fatigue cracks due to stress concentration in these regions, which may explain the observed opposite behaviour relatively to that generally reported in the literature, for example by Bellemare *et al* [12], for some other matrices and nanoparticles. Moreover, the analysis of the results indicated in Table 1 shows that the fatigue strength decreasing is related to the reduction of the static strength. In fact, the variation of the ratio between the fatigue strength for the life of 10^6 cycles and the static tensile strength is comprised only in the range 0.47-0.48 for the three materials analysed, suggesting that the fatigue failure mechanisms do not change.

The notch effect on the fatigue life is summarized in Fig. 6, in which the stress range is presented against the number of cycles to failure for smooth, as well as for central hole notched specimens with 3% wt of nanoclay content. The brittle behaviour of this nanocomposite potentiates the effect of the stress concentration caused by the presence of the hole notch, which reduces the fatigue strength approximately 40%.

The fatigue analysis of notched components is widely performed using the elastic factor of stress concentration k_t, defined by the following equation:

$$K_t = \frac{\sigma_{max}}{\sigma_{nom}} \tag{1}$$

where σ_{max} is the maximum stress around the notch and σ_{nom} is the nominal stress on the cross section (removing the hole area). The reduction in fatigue strength by the notch effect is usually quantified by the dynamic stress concentration factor, k_f, defined as the ratio between the fatigue strength (in terms of the stress amplitude) of a smooth specimen and the fatigue strength of a notched specimen, for a given fatigue life. The dynamic stress concentration factor, k_f, was calculated using the mean experimental S-N fatigue curves depicted in Fig. 6, respectively for smooth specimen and notched specimens. The values of the stress concentration elastic factor, k_t and the dynamic stress concentration factor, k_f, against the fatigue life are plotted in Fig. 7. This figure shows that, in spite of the brittle behaviour of the 3% nanoclay composites, k_f is much lower than k_t, being practically constant and independent of the fatigue life. Furthermore, only a slight and negligible increasing of k_f was observed for short lives. However, for longer lives the ratio k_f/ k_t is practically independent of the life, reaching the value of 0.725.

The dynamic stress factor k_f and elastic stress concentration k_t are usually related by parameter q:

$$q = \frac{(K_f - 1)}{(K_t - 1)} \tag{2}$$

The presented results lead to a value of q = 0.54, indicating a relatively low notch sensitivity for lives above 10^5 cycles.

The morphologies of the fatigue fracture surfaces were analysed using a scanning electron microscope (SEM), Siemens XL 30. The samples were cleaned by ultrasound and coated with a thin layer of gold. The accelerating voltage used was 5 kV. Fig. 8a and Fig. 8b show typical scanning electron microscopy (SEM) observations of the fracture surfaces of the specimens reinforced with 3% wt of nanoclays, unnotched and hole notched, respectively. In Fig. 8a it can be observed a central region with about 1 mm diameter, where the fatigue crack was initiated and afterwards propagated until a brittle fracture occurs outside that region. This crack initiates emerging from the periphery of a nanoparticles agglomeration with approximately 100 micron, due to the correspondent stress concentration. Agglomerates of nanoparticles were also found by Bellemare *et al* [11] causing lower fatigue resistance. The presence of clay clusters can be responsible, not only by the decreasing of the fatigue strength, but also of the tensile and hardness of the nanocomposites. Lam *et al* [17] observed an increasing of the hardness with increasing nanoclay content up to an optimal limit. This behaviour is due to the size of the clusters, which increased with nanoclay content, reaching a crucial limit and therefore the reinforcing function of the nanoclays decreased. According to Srivastava *et al* [12], the cracks should initiate and propagate along the matrix inner intercalated layers. Therefore, the poor exfoliation observed in 3% nanoclay composites contributes to a reduction of the fatigue resistance. On the other hand, Wang *et al* [14] concluded that if there is a good dispersion/exfoliation of nanoclays into the matrix 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. 8b) shows that the fatigue crack was initiated and propagates from the hole, which is the region with the highest stresses in consequence of the stress concentration effect.

Water absorption of epoxy nanocomposites was performed according to ASTM D570-98 standard [18]. Two specimens with dimensions of 120×7.5×5 mm of each composition were tested. All specimens were initially dried at 50ºC during 24 hours, and then were weighted and immersed in distilled water at 20ºC. Periodically, the specimens were dried with filter paper, weighed immediately and then immersed again in water. The weights were evaluated on a balance with accuracy of 0.01 mg. The percentage gain, M_t of water at a given time, t, was calculated using the following expression:

$$M_t = \frac{W_t - W_0}{W_0} \times 100 \qquad (3)$$

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 by:

$$\frac{M_t}{M_\infty} = \frac{4}{h}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \qquad (4)$$

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

Fig. 9 shows the long term water absorption test results by plotting the water uptake along the immersed time. It must be noted that the absorption obtained in this work is lower than the absorption published in other investigations [19], which is attributed to the poor absorbent nature of the resin. It can be seen that the increasing of clay content also increased the water uptake, which contrast with some published works, but agrees with the behaviour observed by Wang *et al* [8]. One of the reasons for the actual behaviour can be related to 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 were calculated using Equation (4), and are indicated in Table 1. Each value presented is the average obtained from two specimens. The standard deviation of each value was very small. It can be concluded that the diffusivity slightly increases with the addition of nanoclays to the matrix, as expected after the results obtained for the weight gain.

Fig. 10a and Fig. 10b show the effect of the immersion in a tank with distilled water at 20 °C during 60 days on the S-N curves, for epoxy resin and 3% wt nanofilled composites, respectively. A similar influence of the long term immersion in water was observed on both material compositions, corresponding to a fatigue strength reduction of approximately 15%.

Moisture absorption in epoxy materials can lead to significant swelling of the polymer material, which can induce residual tensile stresses [20]. This stresses, as well as a significant degradation in the clay/resin interfaces adhesion, are the probable causes of the fatigue strength reduction.

4. Conclusions

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

- A small tendency to the decrease of fatigue strength with nanoclay content was observed, reaching about 6% for 3% wt of nanofiller, as consequence of some particle agglomerates, which promote easier fatigue crack initiation.

- Notch effect caused by central hole reduces the fatigue strength in order of 40%, which corresponds to a notch sensitivity factor, q = 0.54.

- For the 3% nanofilled material the immersion in water during 60 days caused a significant reduction in order of 15% of the fatigue strength.

Acknowledgements

The authors gratefully acknowledge the Portuguese Foundation to Science and Technology for funding the work reported, Project nº PTDC/EME-PME/103622/2008 co-financed by FEDER, through the Operational Factors for Competitiveness Programme of QREN, with reference COMPETE: FCOMP-01-0124-FEDER-010249.

References

[1] Park JH, Jana SC. The relationship between nano- and micro-structures and mechanical properties in PMMA-epoxy-nanoclay composite. Polymer 2003;44(7):2091-2100.

[2] Zhou Y, Pervin, F, Biswas MA, Rangari VK, Jeelani S. Fabrication and characterization of montmorillonite clay-filled SC-15 epoxy. Materials Letters 2006;60(7):869-873.

[3] Ahmadi SJ, Huang YD, Li W. Review, synthesis routes, properties and future application of polymer-layered silicate nanocomposites. J. Mater. Sci. 2004;39:1919-1925.

[4] Shi H Z, Lan T, Pinnavaia T J. Interfacial effects on the reinforcement properties of polymer-organoclay nanocomposites. Chem. Mater. 1996;8:1584-1587.

[5] Wang B, Qi N, Gong W, Li XW, Zhen YP. Study of microstructure and mechanical properties for epoxy resin/montmorillonite nanocomposites by positron. Radiation Phys. Chem. 2007;76:146-149.

[6] Wang L, Wang K, Chen L, Zhang Y, He C. Preparation, morphology and thermal/mechanical properties of epoxy/nanoclay composite. Compos A 2006;37:1890-1896.

[7] Woong J. Boo, Luyi Sun, Jia Liu, Ehsan Moghbelli, Abraham Clearfield, Hung-Jue Sue, H. Pham, N. Verghese. Effect of nanoplatelet dispersion on mechanical behaviour of polymer nanocomposites. Journal of Polymer Science: Part B: Polymer Physics 2007;45:1459–1469.

[8] Wang L, Wang K, Chen L, He C. Hydrothermal effects on the thermomechanical properties of high performance epoxy/clay nanocomposites. Polymer Engineering and Science 2006;46(2):215–221.

[9] Liu X.H., Wu Q. J. Polyamide 66/clay nanocomposites via melt intercalation. Macromol. Mater. Eng. 2002;287:180-186.

[10] Becker O, Varley RJ, Simon GP. Thermal stability and water uptake of high performance epoxy layered silicate nanocomposites. European Polymer Journal 2004,40(1):187-195.

[11] Bellemare, Sim C., Martin N. Bureau, Johanne Denault, J. Ivan Dickson. Fatigue Crack Initiation and Propagation in Polyamide-6 and in Polyamide-6 Nanocomposites. Polimer Composites. 2004;433-441.

[12] Srivastava I, Koratkar N. Fatigue and Fracture Toughness of Epoxy Nanocomposites. JOM 2010; 50-57.

[13] Manjunath CM, Taylor AC, Kinloch AJ. The cyclic-fatigue behaviour of an epoxy polymer modified with micon-rubber and nano-silica particles. S. Sprenger 2009;4487-4490.

[14] Wang Gong-Tao, Hong-Yuan Liu, Nicolas Saintier, Yiu-Wing Mai. Cyclic fatigue of polymer nanocomposites. Engineering Failure Analysis 2009;2635-2645.

[15] Zhou Y, Pervin F, Jeelani S, Mallick PK. Improvement in mechanical properties of carbon fabric-epoxy composite using carbon nanofibers. J Mater Proc Technol 2008;198(1-3):445-453.

[16] ASTM D638-03. Standard test method for tensile properties of plastics. American Society for Testing and Materials. 2003.

[17] Lam, Chun-Ki, Cheung, Hoi-yan, Lau, Kin-tak, Zhou, Li-min, Ho, Man-wai, David Hui, D. Cluster size effect in hardness of nanoclay/epoxy composites. Composites: Part B 2005;36:263–269.

[18] ASTM D570-98. Standard test method for water absorption of plastics. American Society for Testing and Materials. 2010.

[19] Weiping L, Hoa SV, Pugh M. Water uptake of epoxy–clay nanocomposites: Experiments and model validation. Composites Science and Technology 2008;68:2066–2072.

[20] Loh WK, Crocombe AD, Abdel Wahab MM, Ashcroft IA. Modelling anomalous moisture uptake, swelling and thermal characteristics of a rubber toughened epoxy adhesive. International Journal of Adhesion and Adhesives 2005;25:1-12.

Table 1. Summary of the obtained properties.

Material	Epoxy matrix	1% Nanofilled composite	3% Nanofilled composite
Tensile strength [MPa]	68.3±1.7	65.1±0.6	64.8±0.5
Fatigue strength at 10^6 cycles [MPa]	32.7	31.2	30.5
Diffusivity ($\times 10^7$) [mm^2/s]	7.057	7.138	7.204

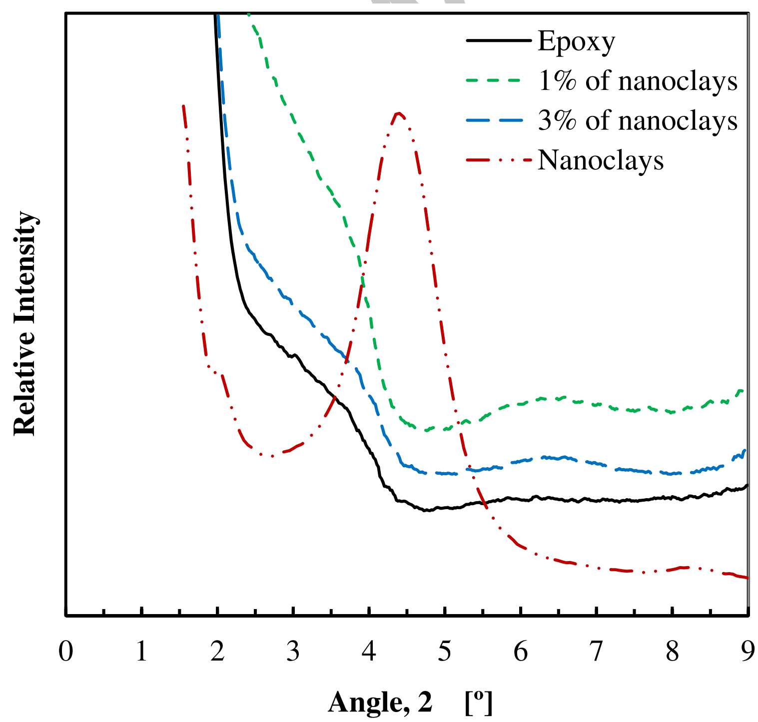


Fig. 1. XRD patterns.

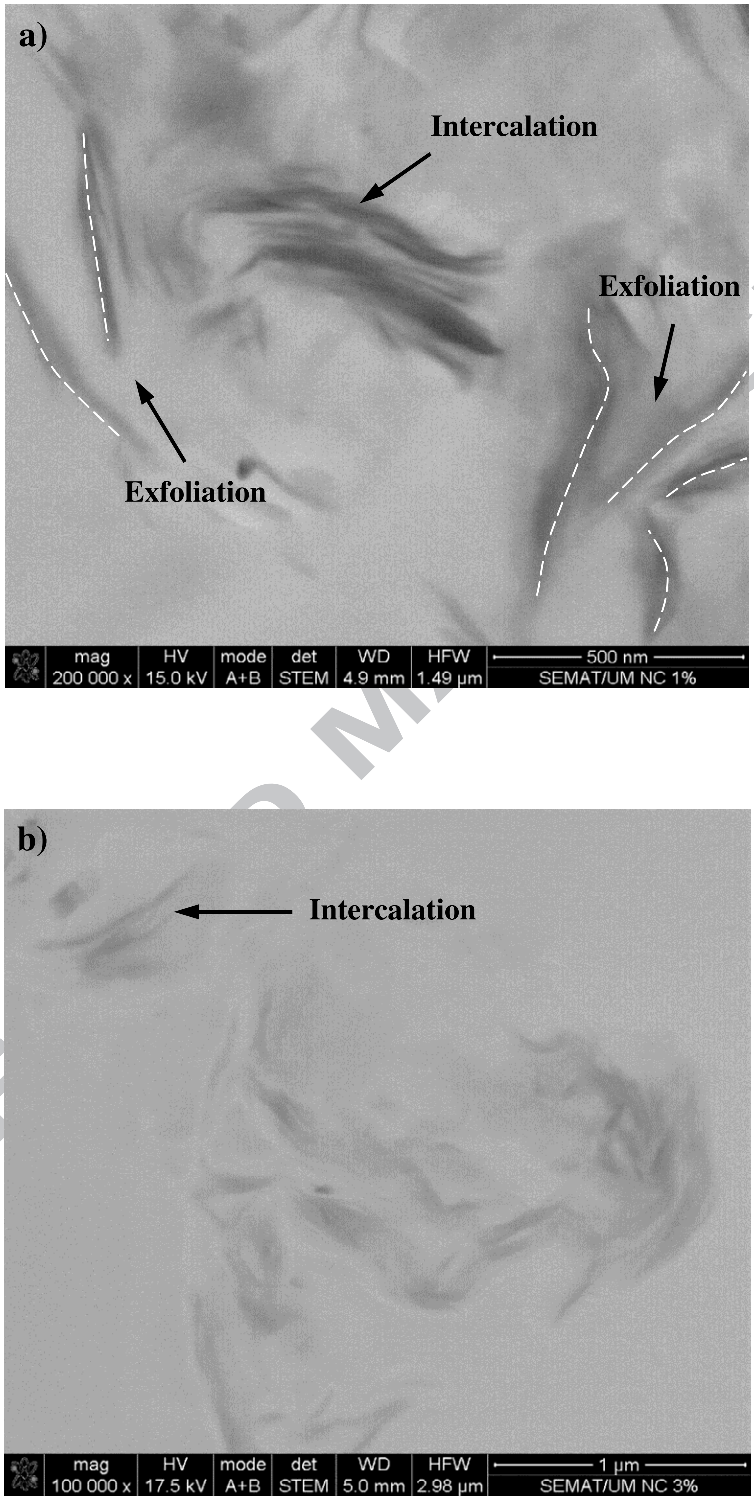


Fig. 2. TEM observations: a) 1% nanoclay; b) 3% nanoclay.

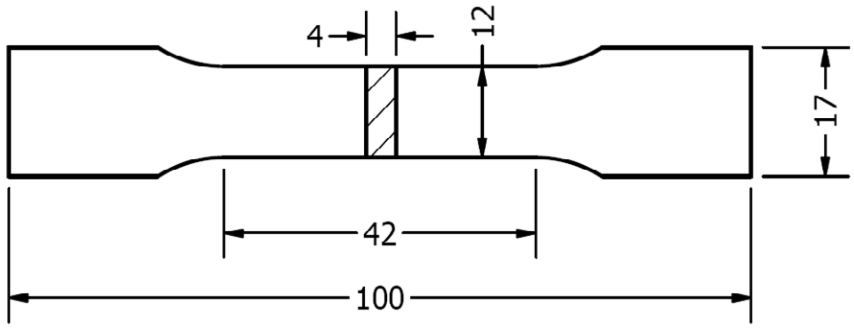


Fig. 3. Specimen geometry (dimensions in mm).

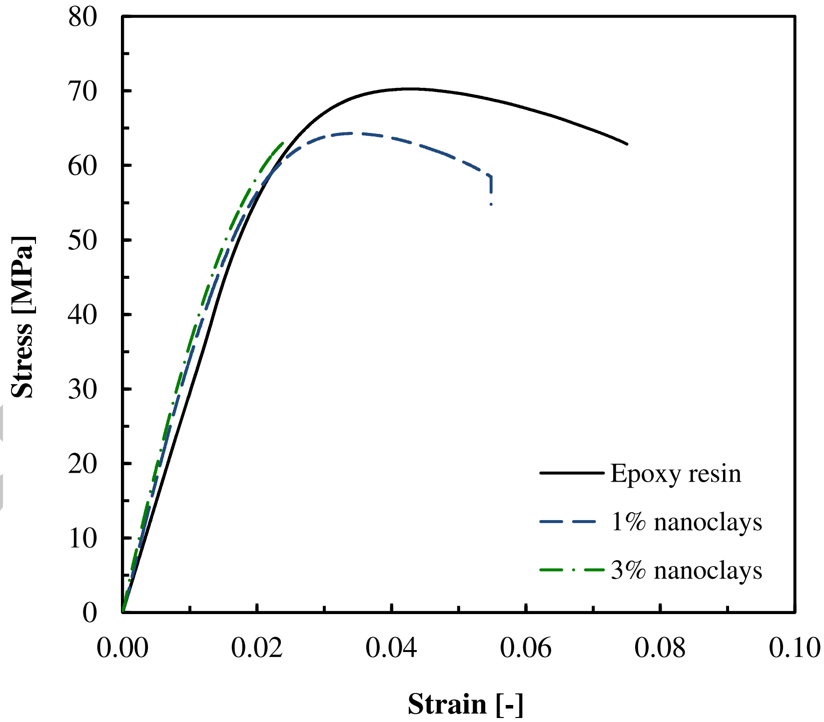


Fig. 4. Typical stress-strain curves.

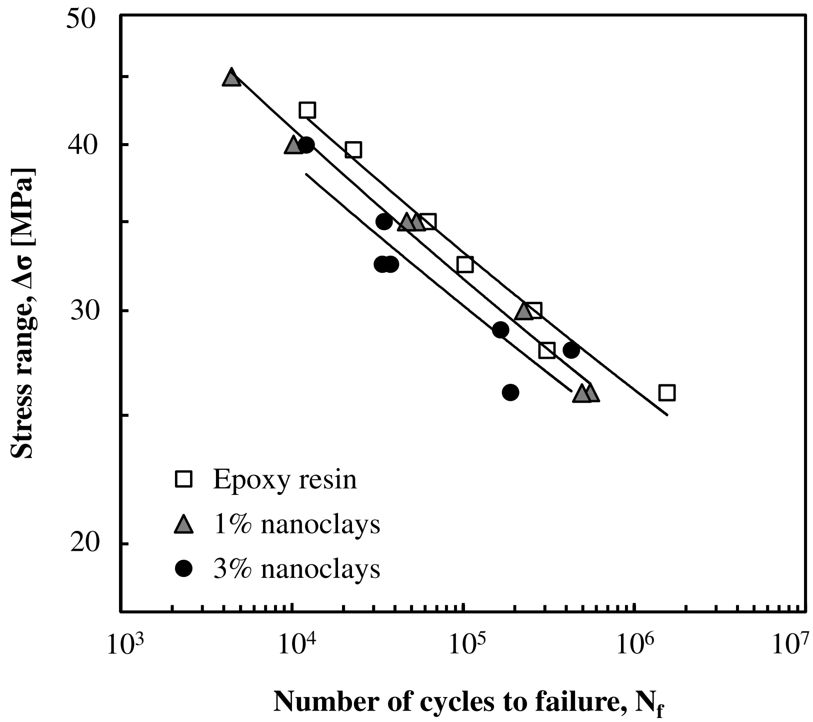


Fig. 5. Effect of filler content on S-N fatigue curves.

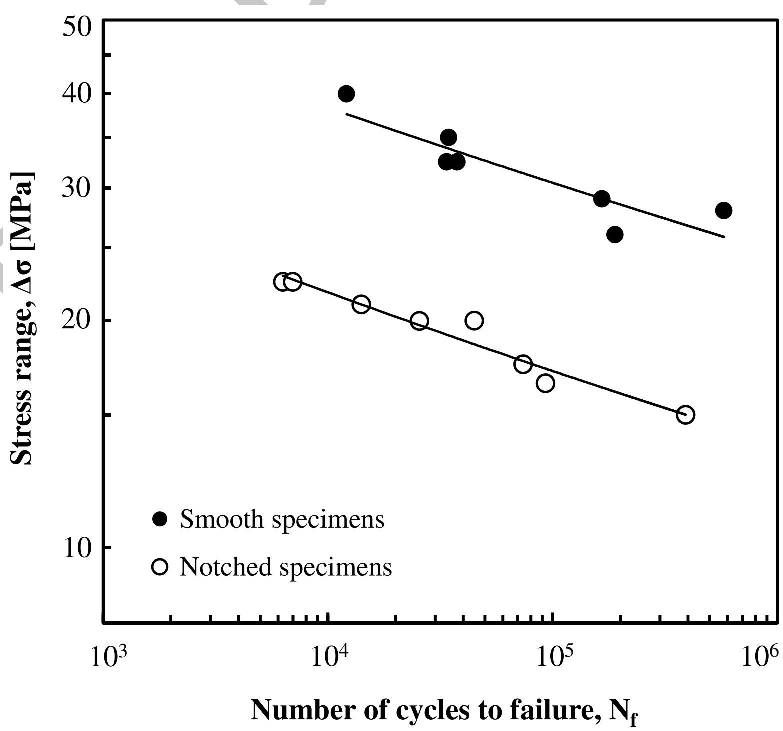


Fig. 6. Notch effect on S-N fatigue curves.

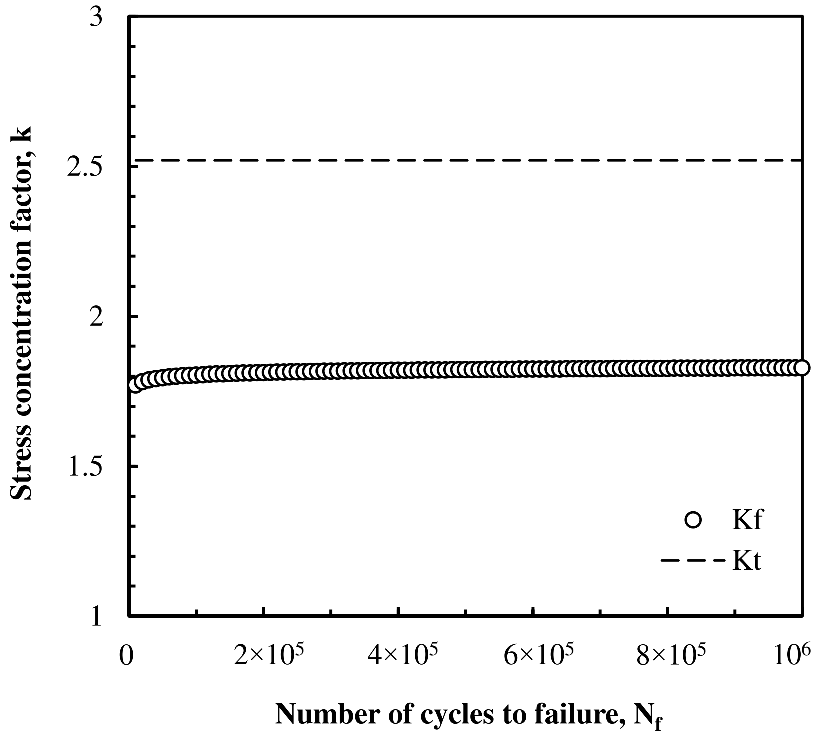
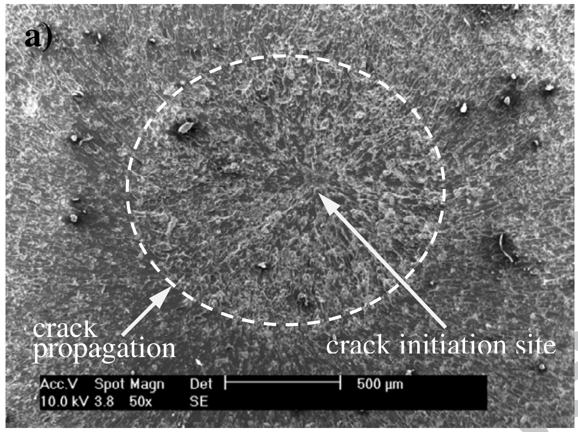


Fig. 7. Variation of stress concentration factors with fatigue life.



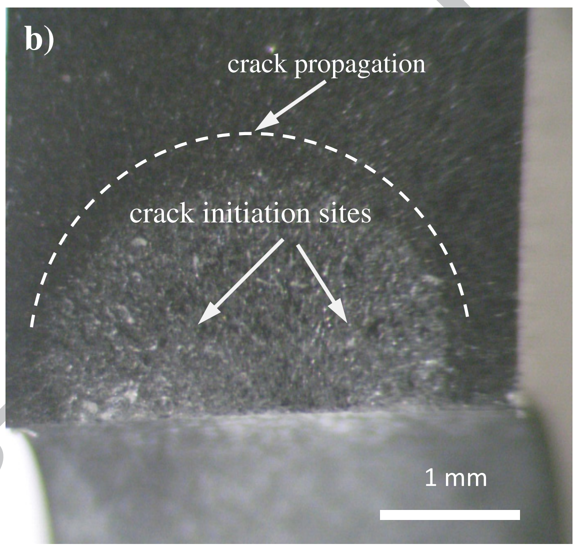


Fig. 8. SEM observations of fatigue fracture surface for 3 wt%: a) Smooth specimen; b) Notched specimen.

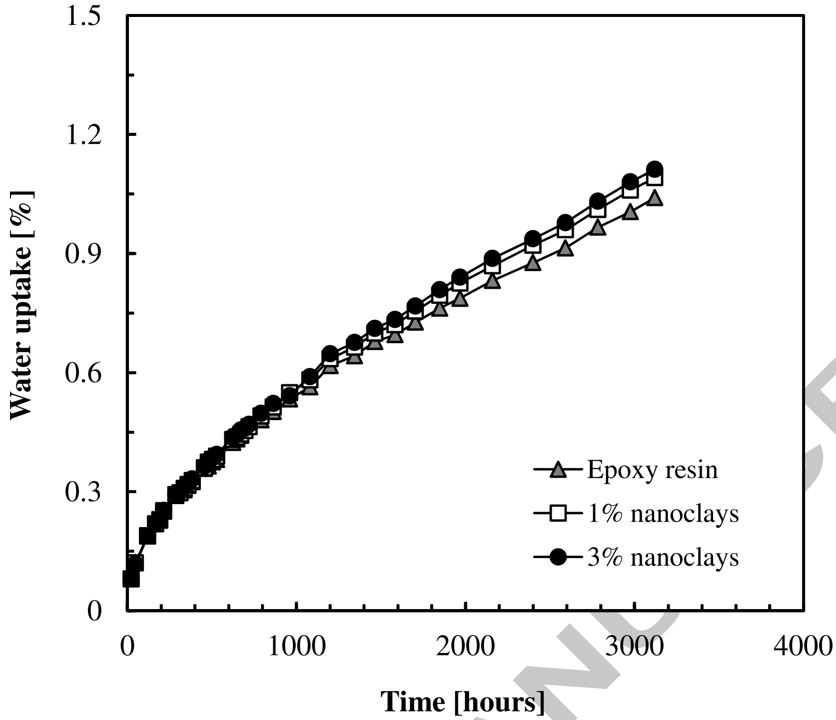


Fig. 9. Water uptake against the immersed time.

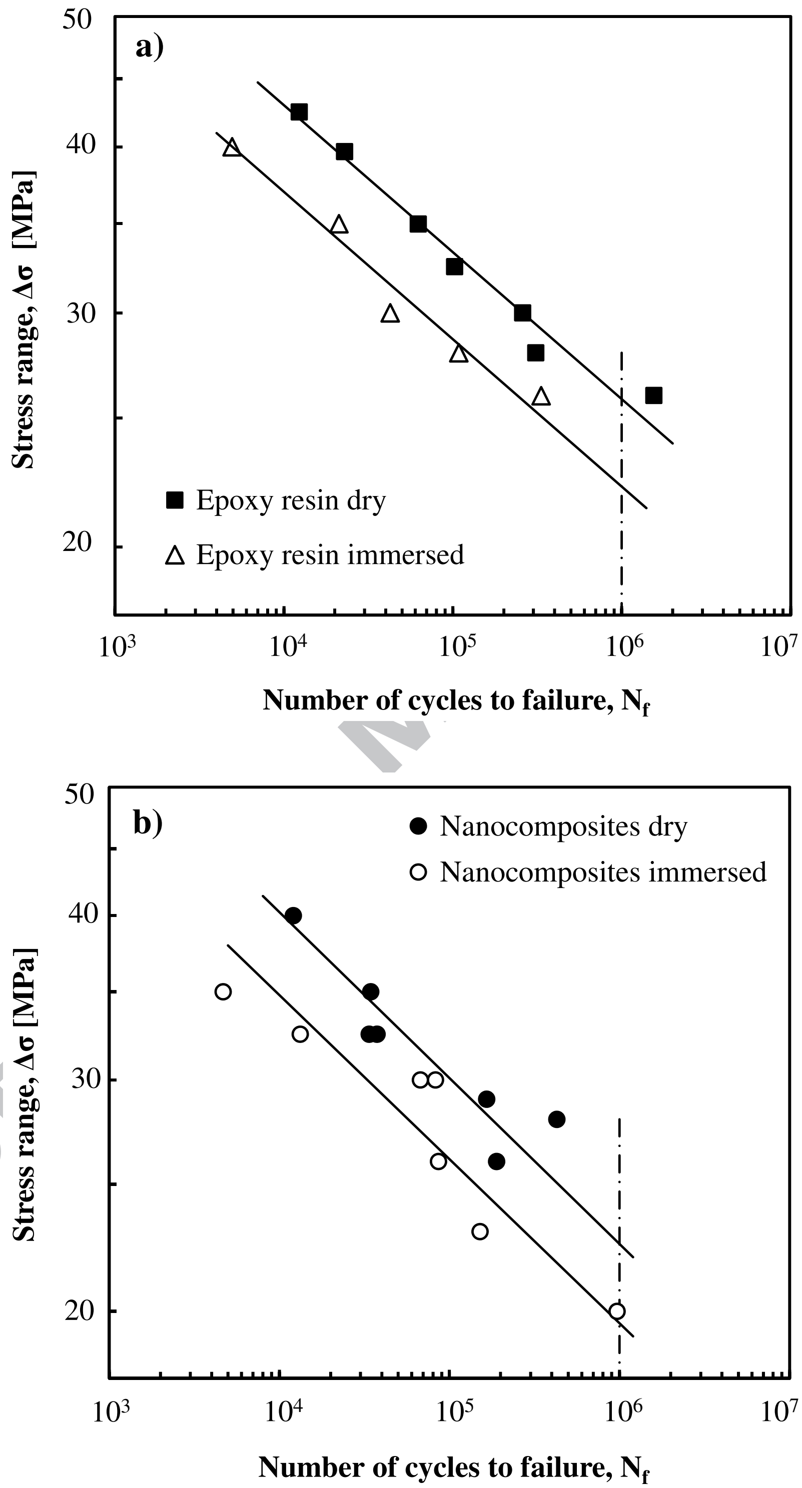


Fig. 10. Effect of water immersion on S-N fatigue curves. a) Epoxy matrix; b) 3% reinforced composites.

Table Captions

Table 1. Summary of the obtained properties.

Figure Captions

Fig. 1. XRD patterns.

Fig. 2. TEM observations: a) 1% nanoclay; b) 3% nanoclay.

Fig. 3. Specimen geometry (dimensions in mm).

Fig. 4. Typical stress-strain curves.

Fig. 5. Effect of filler content on S-N fatigue curves.

Fig. 6. Notch effect on S-N fatigue curves.

Fig. 7. Variation of stress concentration factors with fatigue life.

Fig. 8. SEM observations of fatigue fracture surface for 3 wt%: a) Smooth specimen; b) Notched specimen.

Fig. 9. Water uptake against the immersed time.

Fig. 10. Effect of water immersion on S-N fatigue curves. a) Epoxy matrix; b) 3% reinforced composites.