ASSESSMENT OF THE MECHANICAL PROPERTIES ON NANOCLAYED POLYMER BASED COMPOSITES

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ABSTRACT

Nanoscale reinforcement provides opportunities for enhancing polymer systems with unique properties and extended performance, leading, not only to an improvement in the mechanical and fatigue properties but also act as a barrier to slow water permeation. This paper presents the results of a current study concerned to the mechanical properties of a polypropylene binder resin enhanced by using nanoclay reinforcement. The study was centred on the potential benefits obtained by the addition of nanoclays on the stiffness, static and fatigue strength, absorbed impact energy and water absorption resistance. Specimens were produced by injection moulding process with up 3% in weight of nanoclay. Nanoclays improve bending stiffness and bending strength. The immersion in water during 40 days increases the stiffness more than 80% and the bending strength about 40% for all the material compositions. The nanoparticles did not affect significantly the impact energy absorbed and the immersion in water causes a reduction of at least 10%. The addition of 3% of nanoclay promotes a negative effect in G_c, while the water immersion improves significantly the strain energy release rate, particularly for nanoclay filled composites. All material configurations exhibit high cyclic creep showing a faster and intense stress release since the first cycles of fatigue. The 3% nanoclayed composite exhibits fatigue strength higher than the unfilled materials.

KEYWORDS: Nanocomposites, flexure properties, testing.

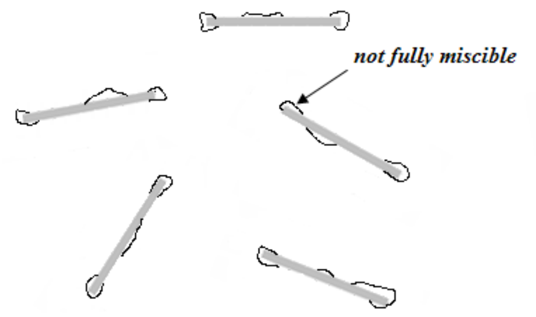
1. INTRODUCTION

Nanoclay are chemically modified clay where tiny nano level particles that when dispersed throughout a polymer matrix to give remarkably improvements in mechanical and physical properties even at low loading levels eg 1-6 % w/w [1-6].

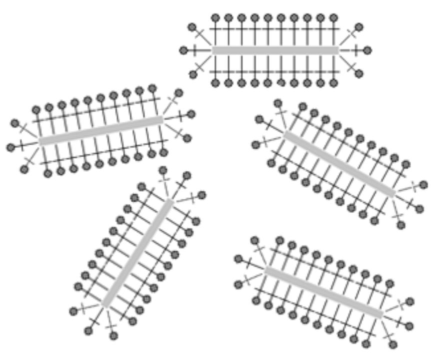
Unfortunately, dispersion is not easily achieved and the benefits claimed in the literature are, disappointingly, not often realized. It is reported in literature that the key to successful reinforcement with nanoclays is to ensure it completely exfoliates. For this purpose a special silane treatments were developed which radically out-performed commercially available gelcoats in terms of their blister resistance, hardness, stiffness, strength, toughness and fatigue life. Fig.1 shows schematically comparison of non treated and specially treated nano-particles so that they perfectly disperse through polymer matrix systems leading to exceptionally high levels of physical and chemical reinforcement. Studies of Yoshida et al [7] confirm the effectiveness of the silane coupling agent on the interface between silica particles and an epoxy resin. He found that the silane coupling agent has the effect of reducing the degradation of mechanical properties and the adhesiveness of the interface between the resin and silica particle and is satisfactory even after water absorption due to the deformation of a chemical bond.

As mentioned before, the effectiveness of nanoclayed composites increases with the better distribution of the clay in the polymer, being that one of the reasons for which it is not very popular to combine polypropylene (PP) with nanoparticles, once it presents a low rate of nanoparticles distribution onto the matrix. Naturally the PP presents a low compatibility during the mixture making poor distribution, but new techniques of mixture have been developed to improve exfoliation.

This paper presents the results of a current study concerned to the mechanical properties of a polypropylene binder resin enhanced by using nanoclay reinforcement. The study was centred on the potential benefits obtained by the addition of nanoclays on the stiffness, static and fatigue strength, the absorbed impact energy and water absorption resistance and . Composites sheets were produced by injection moulding process with up to 3% in nanoclay weight.



Without Treatment



With Treatment

Figure 1. Exfoliates and distributes created by special silane treatment.

2. MATERIALS PROCESSING AND TESTING

Five material formulations were manufactured as summarized in Table 1. Specimens were produced by injection moulding process with 60x10x4 mm^3. 1% w/w pure liquid paraffin (Boots Brand) was added to PP powder along with up to 3% w/w of nanoclays and then stir mixed before injection moulding (PPA3). For PPB3, the liquid paraffin containing small percentage of nanoclays. For PPA and PPB compositions the same procedure was done but without adding nanoclay.

The bending and the strain energy release rate tests were performed in three-point bending loading with a span of 40 mm, by using a Shimadzu AG-10 universal testing machine, equipped with a 5kN load cell and TRAPEZIUM software, at a displacement rate of 1 mm/min. Fatigue tests were performed in three points bending using an imposed displacement electromechanical machine at 10 Hz frequency. All tests were carried out at room temperature.

Table 1. Summary of the specimen's configuration

Code	Composition
PP	Polypropylene
PPA	Polypropylene and paraffin (1% w/w pure liquid paraffin)
PPB	Polypropylene and paraffin (1% w/w pure liquid paraffin containing small percentage of nanoclays)
PPA3	3 % of nanoclays added to polypropylene and paraffin (1% w/w pure liquid paraffin)
PPB3	3 % of nanoclays added to polypropylene and paraffin (1% w/w pure liquid paraffin containing small percentage of nanoclays)

The nominal bending stress (σ) was calculated using:

$$\sigma = \frac{3PL}{2bh^2} \tag{1}$$

being P the load, L the span length, b the width and h the thickness of the specimen.

Bending strength was obtained using peak load in equation (1), while the stiffness modulus was calculated by the linear elastic bending beams theory relationship

$$E = \frac{\Delta P \cdot L^3}{48\Delta u \cdot I} \tag{2}$$

where: I is the inertia moment of the transverse section and ΔP and Δu are, respectively, the load range and flexural displacement range at middle span for an interval in the linear region of load versus displacement plot.

Charpy impact tests were performed using rectangular 10x4 mm^2 notched specimens, according to ASTM D 6110-97. A 2 mm deep sharp notch with 45º flank angle was machined in each specimen. Afterwards, the tests were carried out on a Ceast 6548/000 pendulum with 50 mm span and an impactor of 2 J. The absorbed energy was directly measured by machine software. The displayed value is obtained from the difference of potential energy between the starting and after-impact highest position of the pendulum.

Water absorption was obtained using the next procedure: the samples are placed in an oven at 80 ºC for 2 hours, cooled and weighted in order to obtain the dry weight (DW), afterwards, the samples are immersed in water and periodically weighted to obtain the current wet weight (CWW). The water absorption in weight percentage (W%) was calculated from equation (3)

$$W\% = \frac{CWW - DW}{DW} x100 \qquad (3)$$

Figure 2 shows the water absorption curves for three material configurations. All these configurations show very small water absorption up to 650 hours. However, for the paraffin additive materials (PPB) and the nanoclay filled configuration (PPB3) lower water absorption was obtained with a tendency to stabilization after only few hours.

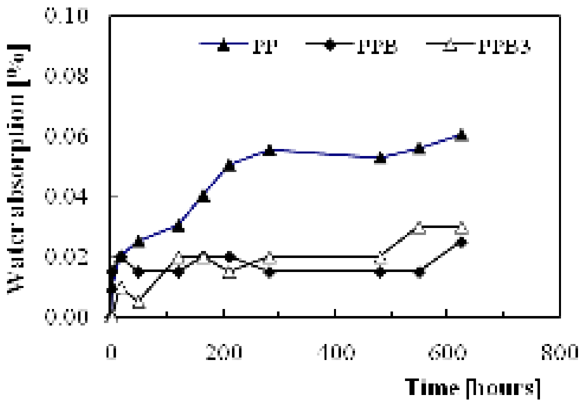


Figure 2. Water absorption curves.

3. RESULTS AND DISCUSSION

3.1. Bending tests

Figure 3 shows typical bending stress versus transversal displacement for three material compositions. The three curves are closed, pointing to a small influence of the filler and additive on stiffness and maximum stress, in spite of a tendency to the improvement in both properties by the nanoclays addition. All compositions exhibit a nonlinear behavior even for low stress level with a high plasticity.

Figure 4 shows the average values of the bending strength obtained for dry specimens and specimens immersed during 40 days in water at 20 ºC. Materials filled by nanoclays exhibit only a slight tendency to increase bending strength. However, surprisingly the immersion in water causes a benefit effect about 40% in all the five material compositions. A benefit in stiffness and strength were also obtained by L. Sobrinho et al. [8], in a vinyl ester resin system that initially presented ductile behavior and modified to brittle after 16 days of hygrothermal ageing at 60 °C due to the increase of crosslink.

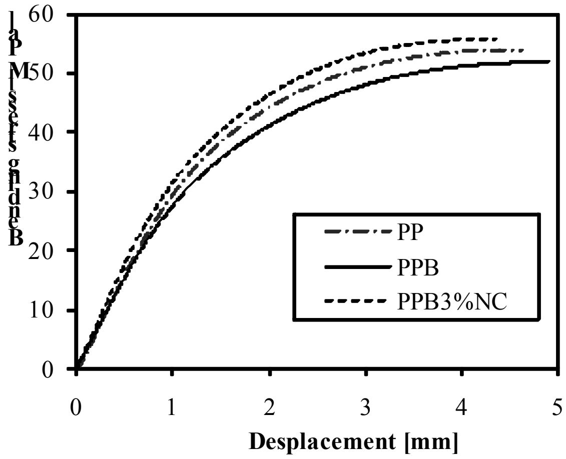


Figure 3. Comparison of stress-displacement curves for nanoclayed and unfilled materials.

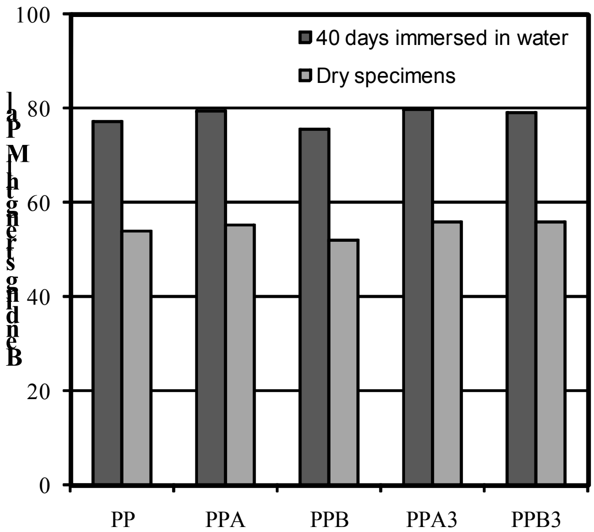


Figure 4.Average bending strength: influence of the material composition and water exposure.

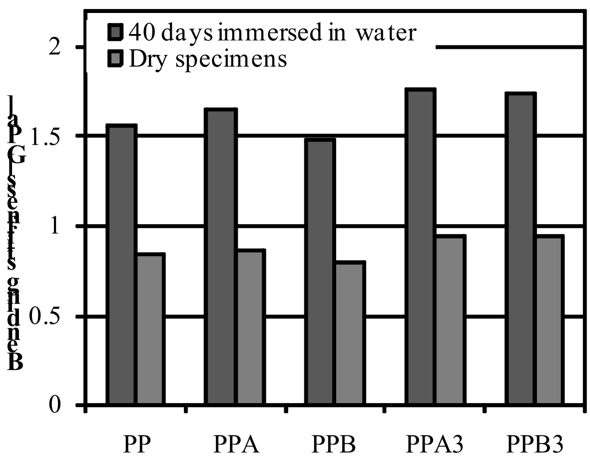


Figure 5.Average bending stiffness: influence of the material composition and water exposure

This is in agreement with the results obtained in this work for bending stiffness and shown in Figure 5 in terms of average values. Materials filled by nanoclays exhibit bending stiffness about 12% higher than unfilled materials. The immersion in water during 40 days increases the stiffness more than 80% for all the five material compositions.

3.2. Impact energy

The results of absorbed impact energy are presented in Fig. 6 in terms of the average value obtained from at least four tests for each test condition. The figure shows the results obtained for all the five configurations studied, using specimens stored in dry air and specimens immersed in water during 40 days. The results show a significant spread, but nevertheless it can be concluded that the filling of nanoparticles did not significantly affect the impact energy absorbed. In addition the immersion in water causes a reduction of the impact energy of at least 10%, confirming the embrittlement of the material previously observed.

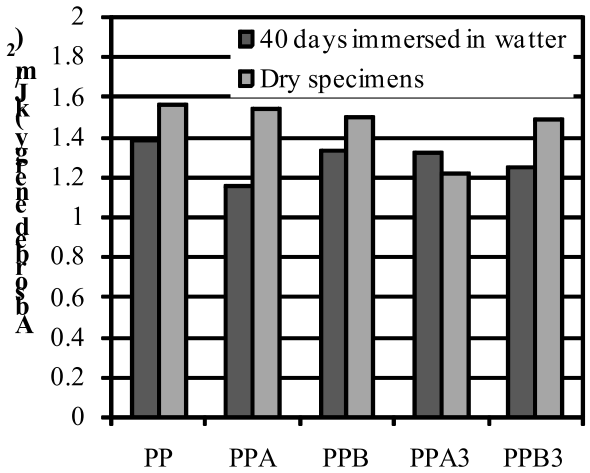


Figure 6. Absorbed impact energy: influence of the material composition and water exposure.

3.3. Strain energy release rate results

The strain energy release rate tests were carried out according ASTM D 5045-96 standard [9]. The average values obtained on dry specimens and on specimens immersed in water during forty days are presented in Figure 7.

For dry specimens a negligible influence of paraffin addition was observed. However, the addition of 3% of nanoclays promotes a negative effect that causes a decrease in G_c of about 20%. The water immersion improves significantly the strain energy release rate, particularly for nanoclay filled composites for which the average increase was over 50%.

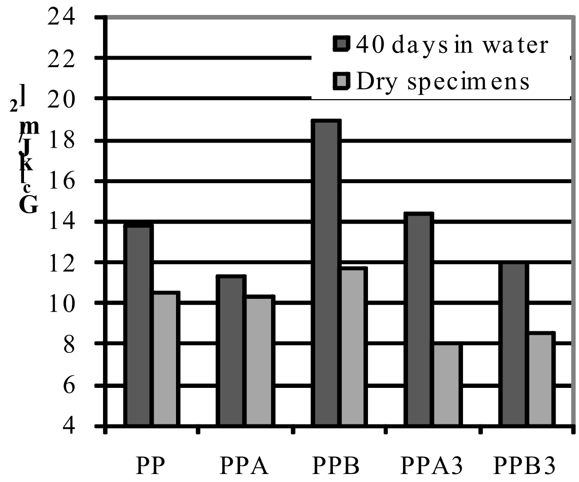


Figure 7.Average strain energy release rate: influence of the material composition and water exposure.

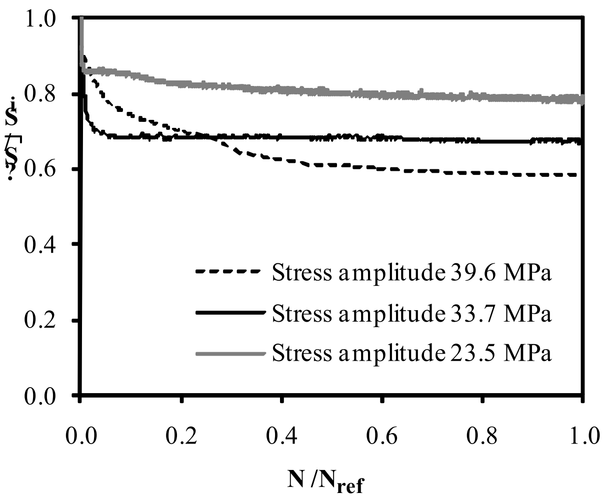
3.4. Fatigue behavior at constant displacement cycles

During fatigue tests the maximum and minimum peak loads were monitored at each cycle. Figures 7a) and b) show the evolution of the normalized stress amplitude versus the normalized number of cycles, where: ΔS is the current stress range, ΔS_i is the initial stress range, N is the current number of cycles and N_{ref} is the failure number of cycles corresponding to 50% decay in maximum stress.

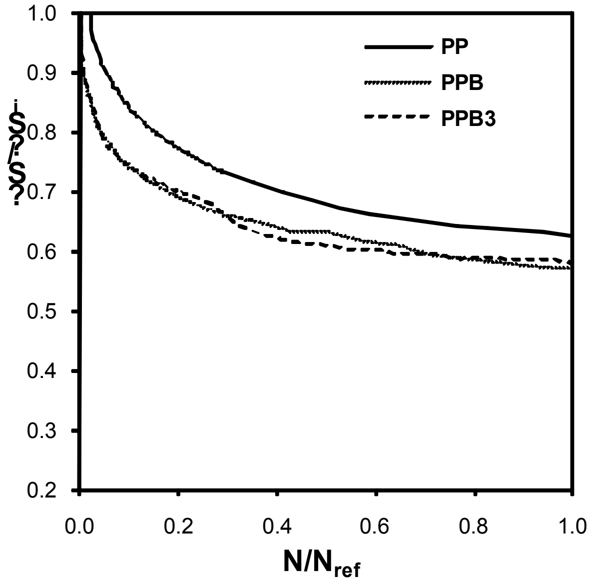
Fig. 7a) shows the influence of the stress level for PPB3 composite while Fig. 7b) shows the influence of the material for 39.6 MPa initial stress amplitude. Matrix resin (PP), PP and paraffin material and 3% nanoclayed composite material exhibit high cyclic creep. The stress release is faster and more intense for higher initial stress levels and also for nanoclayed composites when compared with matrix resin.

Figures 8a) and b) show the initial stress amplitude versus the number of cycles to failure, where the failure is defined for different values on maximum stress decay: 20%, 30%, 40% and 50%. These figures present the results for PPB and PPB3, respectively. For both materials the results show a stress relieve, occurring a decay on maximum stress more than 30% even for low number of cycles.

The performance of the materials in terms of fatigue strength is compared in Fig. 9, where the initial stress range is plotted against the number of cycles for 50% of decay on maximum stress. For this failure criterion the nanoclayed composite PPB3 exhibits a fatigue strength about 10% higher than the paraffin containing small percentage of nanoclays (PPB material) and 20% higher than the PP matrix.



a)



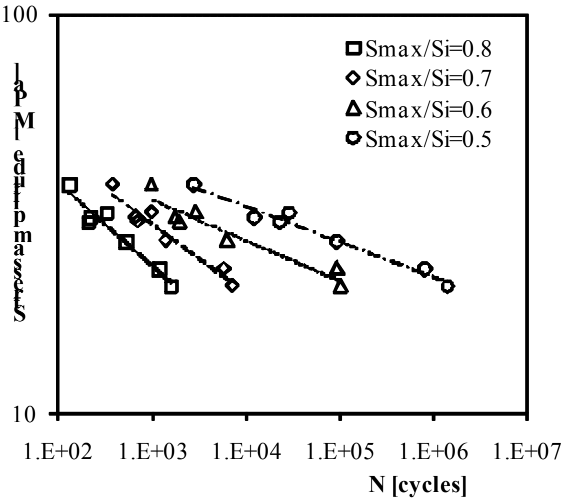
b)

Figure 7. Evolution of the stress amplitude versus the number of cycles: a) PPB3 and various stress levels; b) Different materials and initial stress amplitude 39.6 MPa.

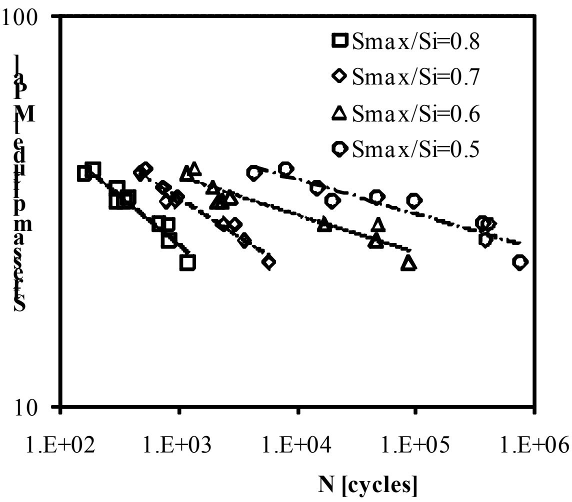
4. CONCLUSIONS

The effect of the nanoclay addition in polypropylene matrix on the stiffness, static and fatigue strength, absorbed impact energy and water absorption resistance was studied and the main conclusions are:

- Nanoclayed composites exhibit bending stiffness about 12% higher than the unfilled materials and only a slight increase on bending strength. The immersion in water during 40 days increases the stiffness more than 80% and the bending strength about 40% in all the five material compositions.



a)



b)

Figure 8. Initial stress range versus number of cycles curves for various maximum stress decay: a) PPB; b) PPB3.

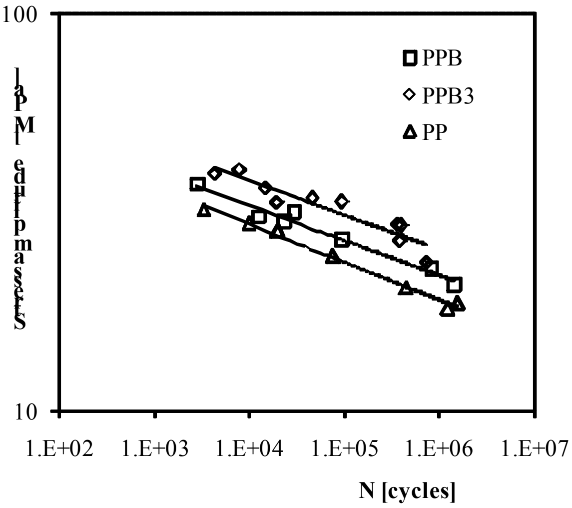


Figure 9. Initial stress range versus number of cycles curves for 50% of maximum stress decay; comparison of the materials.

- The nanoparticles did not affect significantly the impact energy absorbed while the immersion in water causes a reduction of at least 10%, due to an embrittlement of the material.

- The addition of 3% in nanoclays promotes a negative effect that causes a decrease in G_c about 20%. The water immersion improves significantly the strain energy release rate, particularly for nanoclay filled composites for which the average value increases over than 50%.

-The five material compositions exhibit high cyclic creep, showing a fast and intense stress release. For a failure criterion corresponding to 50% on the decay of maximum stress, the nanoclayed composite PPB3 exhibits a fatigue strength about 10% higher than the paraffin containing small percentage of nanoclays PPB material and 20% higher than the PP matrix.

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