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EVALUATION OF THE DURABILITY PERFORMANCE OF GLASS-FIBER REINFORCEMENT EPOXY COMPOSITES EXPOSED TO ACCELERATED HIGROTHERMAL AGEING

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Abstract

Polymeric composite materials present modification of its physical and mechanical properties when exposed to aggressive environments (heat, humidity, ultraviolet radiation, etc.) and this is a serious concern for the manufacturers of composites. Unlike metallic materials knowledge about changes in the properties and characteristics due to degradation environments are still unknown. The level of deterioration depends on the environment and the period to which the material would be exposed. Degradation of polymeric composites can be physical or chemical. The physical degradation is characterized by the ability of the material returns to its original state after

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being exposed to a hygrothermal ageing after it returns to their original properties after drying. In this context, the aim of this work is to study the influence of accelerated hygrothermal ageing on glass/epoxy unidirectional composite two temperatures. The composites were molded by *resin transfer moulding* (RTM) with a fiber volume fraction (Vf) of 37% and characterized by water absorption, DMA, TGA and short-beam shear strength (at fiber orientation of 0º and 90º). Comparing water absorption at 50ºC and 80ºC, it was observed that only the last stabilized. The weight loss may be due to the dissolution of the fiber sizing or unreacted components of the matrix. In the short-beam strength testing, when comparing the samples exposed to 50ºC and 80ºC, it was observed the possible occurrence of physical degradation (plastification) of the first and second chemical (crosslink second of the matrix). The complexity of the ageing study of composite is due to the fact that a slight change in magnitude of any variable can produce very different results.

1. Introduction

There is still uncertainty regarding the properties of composite materials, not only for being a relatively new material compared to traditional ones, but also because there are few studies (Helbling et al. [7]; Kafodya et al. [8]) on the degradation of this material which are related to the actual environment and conditions to which the composite structure would be subjected. For example, the glass fiber composite can be applied from pool decks to boats or even wind turbine blades. The hydrolytic degradation is one of the most studied ageing process. There are reversible and irreversible changes of hydrolytic degradation. Plastification is a reversible phenomenon which disappears after drying and it may led to decrease of the thermomechanical properties of the composite (e.g., glass transition temperature) and induce plastic deformation (Ray [12]). Dissolution can be considered an irreversible phenomenon. Hydrolysis or micro-cracks (Apicella et al. [1]) occurs when there is a higher water absorption (which create greater tensions). Besides these, another irreversible effect is the creation of a second crosslinking step in the resin chains due to a specific type of hydrogen bond between resin and water molecule (Mouzakis et al. [10]). This depends on the chemical structure of the resin, the temperature and the total exposure time for the material in the water.

The amount of moisture absorbed by the matrix is different from that absorbed by the reinforcement. Moreover, the diffusion of moisture is a phenomenon dominated by the matrix. The moisture results in volumetric expansion between the matrix and the fibers, and thus allows the evolution of deformation fields and localized stresses in fibrous composites which weakens its mechanical performance (Ray [12]). Failure occurs in many cases in the interfacial region due to chemical and/or plasticizing reactions when water enter the interface (Apicella et al. [1]).

In this context, the aim of this study is to understand the behaviour of these composites by short-beam shear strength. Moreover, the thermal properties were evaluated by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) at one temperature above and one below the glass transition temperature of the matrix.

2. Materials and Methods

The materials used to produce the composites were: (i) unidirectional glass-fibre VEW 090/50 (E-Glass) fabric supplied by owens corning (aerial density: $450 g/m^2$); (ii) DGEBA (di-glycidyl ether of bisphenol A) epoxy resin (LY 1316) supplied by ARALSUL; and (iii) aromatic poliamine hardener (Aradur 2969) also supplied by ARALSUL.

The specimens were produced by RTM, maintaining constant Vf (37%). Firstly, a homogeneous mixture of resin and hardener was obtained using a mechanical stirrer followed by degassing the mixture in a vacuum oven (25°C/5min). After that, the glass/epoxy unidirectional composites (30 × 30 × 0.27cm), were moulded. Most samples were obtained by using a positive pressure of 1.34bar. The cure of the resins was carried out at room temperature for 24h followed by post-curing in an oven at 60°C for 4h.

The composite plates were exposed to accelerated hygrothermal ageing (immersion in distilled water at 50ºC and 80ºC in an air-circulation oven) for 5, 10, and 15 days, after the samples were cut according to the analyses.

The water absorption test was carried out with distilled water in a container inside an oven (according to ASTM D5229). Short beam shear test was performed according to ASTM D2344, using a span-to-depth ratio of 4:1 and test speed of 1.3mm.min^{-1}, in an INSTRON 3382 Universal machine (load cell of 100kN). Ten samples were tested for each family and the specimen length was 6 × thickness and width 4 × thickness. Samples were cut at the fiber orientations of 0º and 90º.

Thermogravimetric analysis (TGA) was carried out in a 2050 TGA V5.4A (TA Instruments). The samples were heated from 20 to 1000ºC at a heating rate of $20^{\circ}\text{C}\,\text{min}^{-1}$, under N_2 atmosphere, according to ASTM E1131. For the dynamic mechanical analysis (DMA), a thermal analyzer 2980 DMA V1.7B (TA Instruments) was used. Specimen dimensions were 35 × 17 × 2.6mm and the experimental conditions were: Single cantilever mode, strain amplitude of 0.1%, frequency of 1Hz, heating rate of $5^{\circ}\text{C}\,\text{min}^{-1}$ and temperature range from 25ºC to 200ºC, for this analysis the samples were also prepared according to the fiber orientation of 0º and 90º.

3. Results and Discussion

Figure 1 shows the rapid absorption in the early stages, which may be justified by the Fickian nature of the process, followed by an anomalous stage (slower) which diffusion is not controlled. This anomalous absorption behaviour has been explained in terms of polymeric relaxation and free volume in polymer (Sawpan et al. [13]). In this figure, it is also observed that there was a stabilizing water absorption only in the temperature of 80ºC, which can be explained by the fact that the moisture uptake by the composite is dependent on the temperature, relative humidity, exposure time, solvent/polymer interaction, filler content and mechanical load (De Kee and Lie [5]).

In Figure 1, it is observed that from the sixth day (for tests at 80ºC) there is a reduction in water uptake of the composite, which can be attributed to a double absorption process (quick) with accumulation of water in an internal pocket located in the fiber/matrix interface and discharge (slow) this pocket; but it can also refer to a phenomenon of adsorption/desorption (Upadhyay and Prucz [14]). Furthermore, according to Nakai et al. [11], there can be no dissolution of the matrix over time.

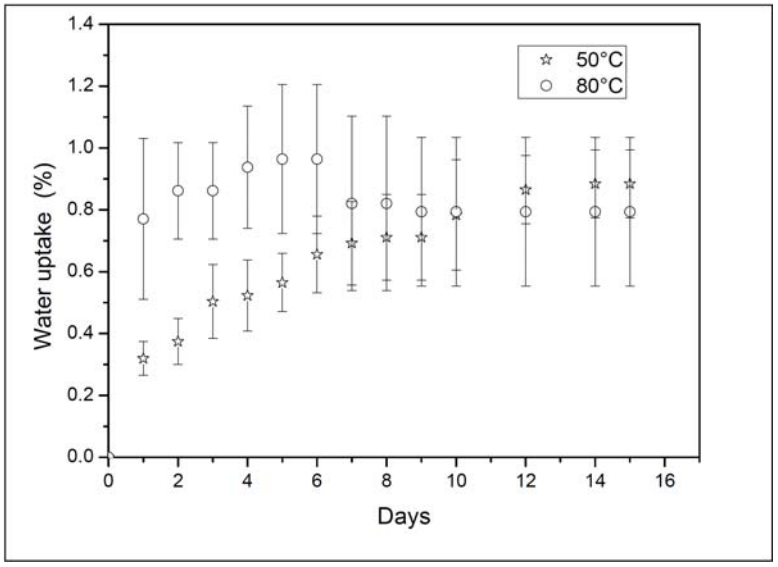
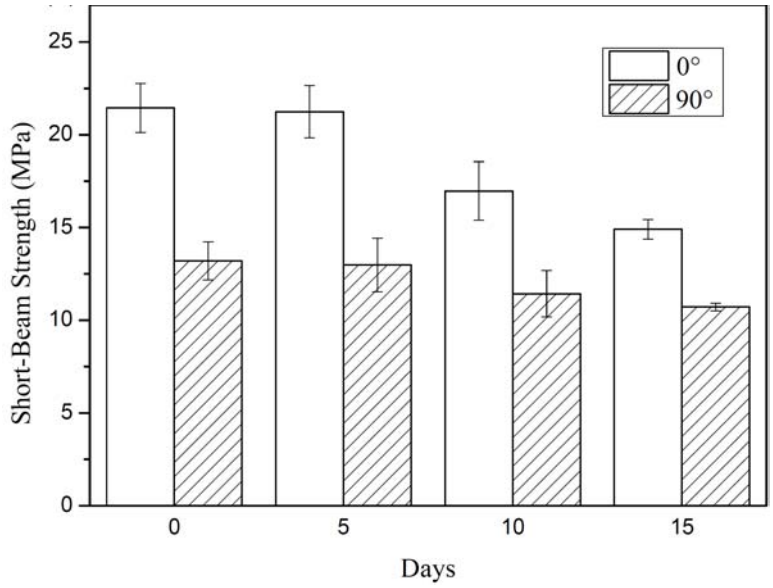
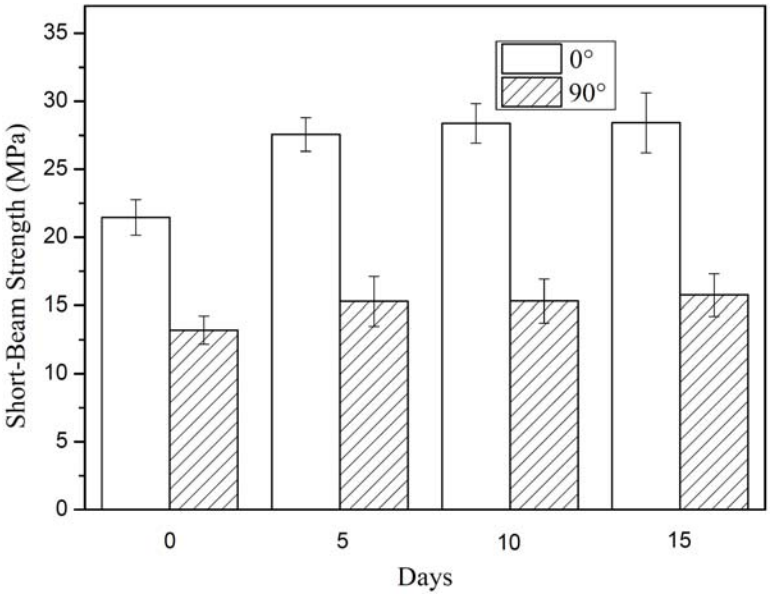


Figure 1. Analysis of the water uptake at 50ºC and 80ºC.

Figure 2 shows the mean values of short-beam shear strength of composite aged at 50ºC and 80ºC. The off-plane shear strength is dependent primarily of properties of the polymeric matrix and interfacial adhesion fiber/matrix as can be seen by the short-beam shear test. Thus, for the samples with fiber orientation of 90º it was observed a variation that can be attributed to the polymeric matrix being plasticed, since the orientation arrangement of the fibers reduces the shear strength. However, in the case of the samples with fibers oriented at 0º, there was a combination of the loss of fiber/matrix adhesion with the plasticizing of the matrix (Barjasteh and Nutt [3]).



(a)



(b)

Figure 2. Short-beam strength of aged composites at (a) 50°C and (b) 80°C.

Barjasteh and Nutt [3] studied the hygrothermal ageing (60ºC/85% R.H.) of hybrids rods of glass/carbon/epoxy being the carbon fiber the core material aged for 4 months and they also observed a decrease in short-beam strength with time which was mainly coming from the matrix plasticizing. This justification was the reason for not finding in sections polished of composite loss of adhesion fiber/matrix and microcracks in the matrix (Barjasteh and Nutt [3]), this probably because it used a soft environment and other type of material when compared used in this work. Figure 2(b) shown average values of short-beam shear strength (off-plane) for composites aged at 80ºC. Unlike Figure 2(a), the sample aged showed an tendency increasing in short-beam strength which can be a characteristic of the second crosslinking of the polymer matrix which would characterize a chemical degradation.

In the TGA, as shown in Figure 3, the first stage of the curve of the materials subjected to ageing refers to loss of moisture (5% by mass). The next stage at a temperature of about 450ºC is the degradation of the composite matrix. TGA analysis basically report the decomposition temperature of the material (in this case), the ageing conditions of the composite does not influence the residual mass percent, however a discrepancy between the analyzed samples has been found, which can be explained by the fact to be a material composed of two phases and the amount of mass used in this analysis is on the order of 20mg.

Thus, for explaining this difference, the composite was put in a muffle and the samples were burned at a temperature of 600ºC for 4 hours. From that, at the end, only glass fiber was left and the mass fraction of glass fiber was similar according to the results in Table 1.

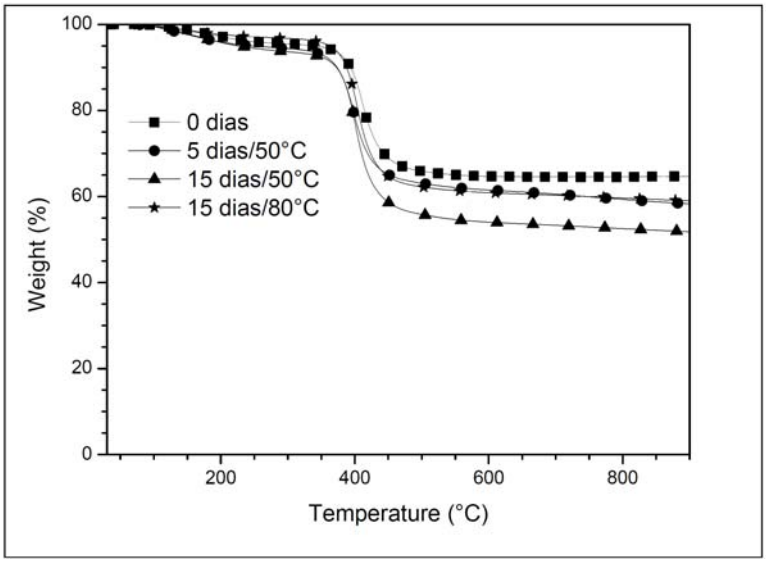


Figure 3. Thermogravimetric analysis of the composites.

Table 1. Mass percentage of the composites

Mass percentage		**50ºC**			**80ºC**		
	0 days	5 days	10 days	15 days	5 days	10 days	15 days
	49	48	45	43	48	57	49

In the TGA curve (Figure 4) comparing the resin without/with ageing for 15 days at 80ºC, it is observed that the last showed no tendency to stabilize in the analyzed rage of temperatures. It was expected that this water uptake in this time/temperature should have caused the formation of microcracks in the resin (Wolfrum et al. [15]) where the water was located and would have taken longer times to stabilize the curve compared to 0 days resin.

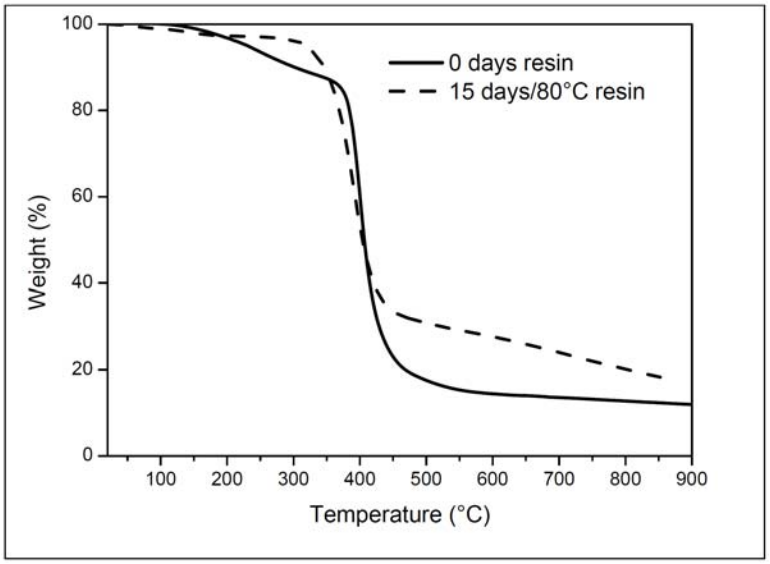


Figure 4. Thermogravimetric analysis of the resin without ageing and aged at 80ºC.

Through results DMA analysis presented in the Figures 5-6, it can be seen the curve of the storage modulus (E') from which it is possible to obtain valuable information about the material stiffness. This property is very sensitive to structural changes such as the polymeric matrix molecular weight, the crosslinking density and fiber/matrix adhesion; Loss modulus (E'') (Figures 7 and 8) is a measure of the energy dissipated or lost as heat. This property indicates the viscoelastic behaviour of the resin, and is more sensitive to molecular motions. From it, we obtain E'' peak which characterizes the degree of crosslinking, degradation and thermal stability; Damping factor (Tan Delta) (Figures 9 and 10) is sensitive to structural changes that occur at the molecular level during ageing process. The maximum in the curve of tan delta indicates a relaxation process that is related to the movement of small groups or chains of molecules within the polymer structure, which are initially frozen: Generally, an increase in this peak is related to a higher degree of molecular mobility (Sawpan et al. [13]).

Through Figures 5 and 6, it can be observed a big difference between E' in the glassy region, obtained for composites oriented at 0º and 90º. This is due to the fact this test is punctual and the energy propagation occurs preferentially toward support. For this reason is expected that the composite with fiber orientation at 0º presents a greater difficulty in propagating this energy due to higher fiber stiffness than the 90º that have alternating regions between fiber and matrix justifying further values higher E' for the composite to 0º.

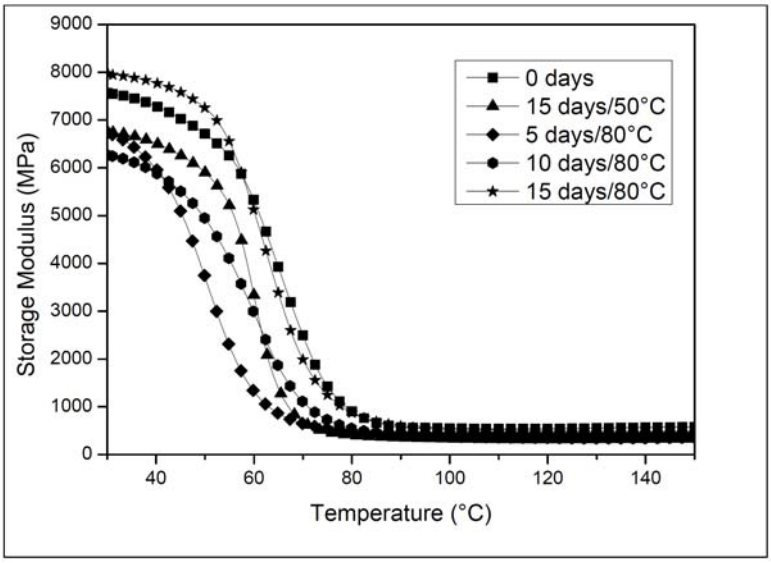


Figure 5. Storage modulus of the samples oriented at 0º.

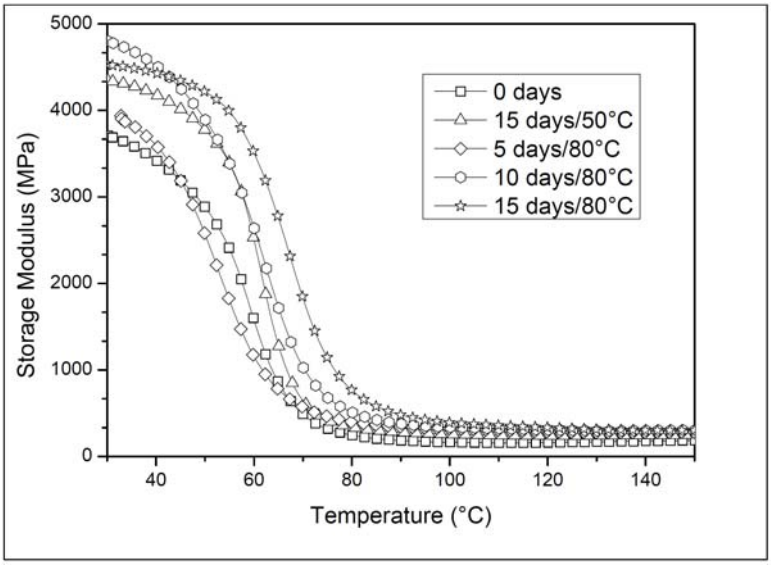


Figure 6. Storage modulus of the samples oriented at 90º.

In Figures 5 and 6, comparing the composite oriented at 0º with the oriented at 90º it can be seen that among the aged composites there are two factors of major influence: the first the loss of interfacial adhesion that can be observed through the decrease in E' in the glassy region to samples 15 days/50ºC, 5 days/80ºC, and 10 days/80ºC, the second factor is the crosslinking of the polymeric matrix, which can be observed in the sample 15 days/80ºC by increasing E' in the vitreous region to compare this with the composite without ageing. In the samples at 90º, there was a single predominant factor that refers to the second cross-linking as can be observed comparing all samples.

Analyzing E'' (Figures 7 and 8) for composites oriented at 0º and 90º, were obtained values lower for the composite without ageing. Among them the 90° have the lower value. This property is related to the degree to which a polymeric chain can move in relation to one another and therefore is expected to increase since the intramolecular or intermolecular bond is broken (Sawpan et al. [13]), which also explains

the greater dispersion between results of samples aged 0º which is more dependent on the fiber/matrix adhesion in loading. In addition, the water absorption of the composite induces dissolution of the components of higher mobility, in other words, those of low molecular weight. Also, another factor that can happen is the plasticizing observed in both (0º and 90º) (Botelho et al. [4]; Apicella et al. [2]).

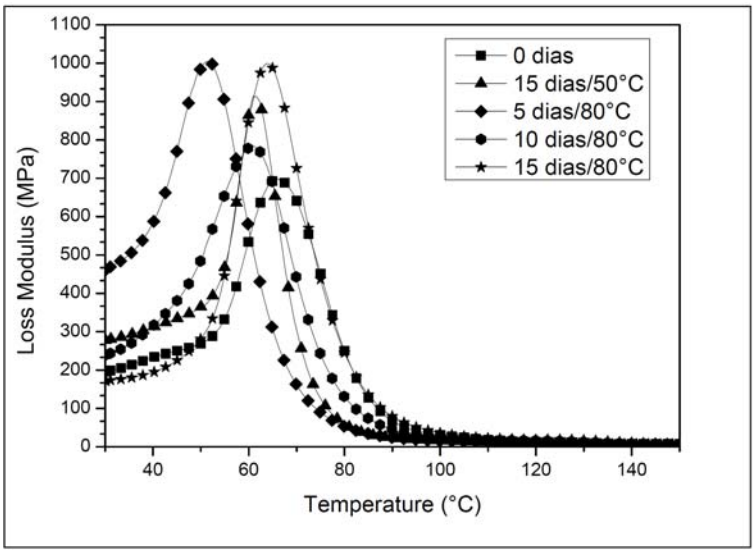


Figure 7. Loss modulus of the samples oriented at 0º.

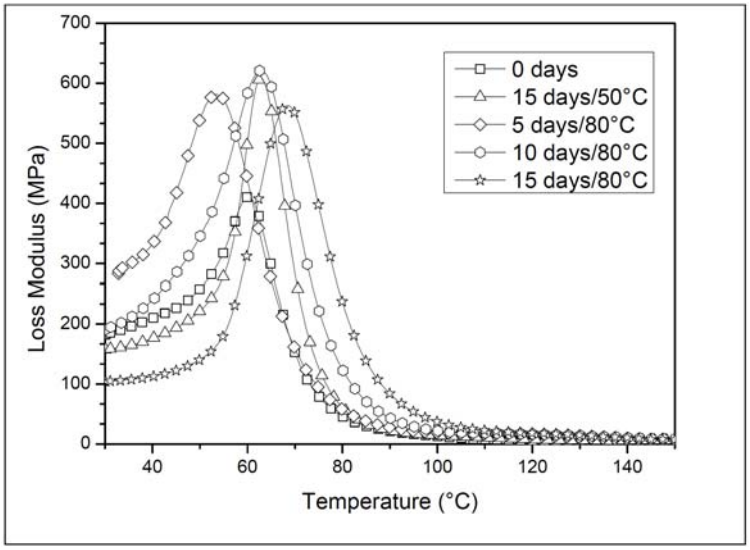


Figure 8. Loss modulus of the samples oriented at 90°.

Through Figures 9 and 10, it can be seen that composite without ageing shows the lowest peak of tan delta (damping factor), which is related to deterioration and absence of polymeric chain mobility induced by hygrothermal ageing. When moisture is absorbed by the polymeric composite by diffusion, the presence of micro-structural voids and physicochemical nature of the resin causes generally distribution of moisture localized, this is, not uniform. Therefore, these effects form a number of localized phases due to moisture absorption and each phase has a T_g located, and it extends the region of glassy transition relative to materials without ageing (Khan et al. [9]).

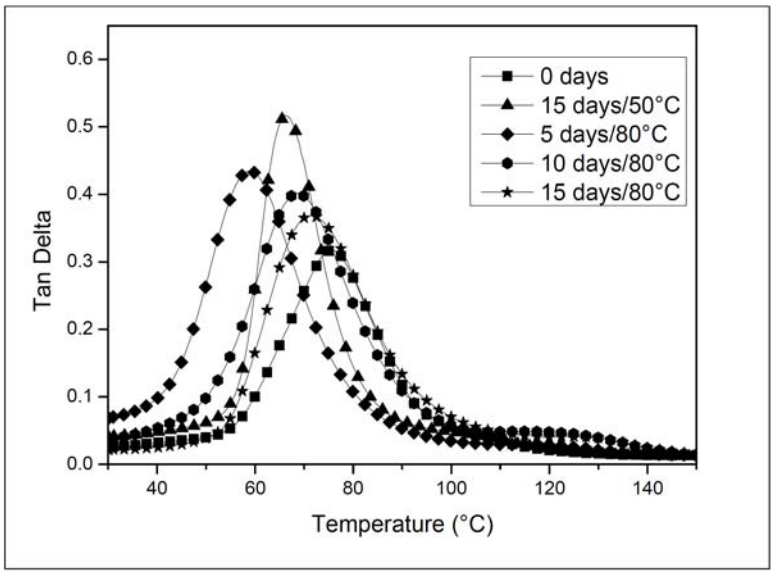


Figure 9. Damping factor of the samples oriented at 0º.

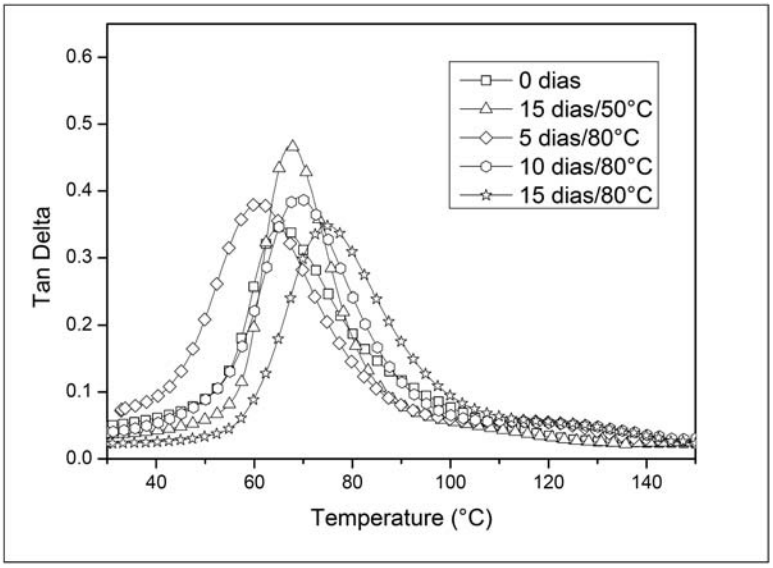


Figure 10. Damping factor of the samples oriented at 90º.

The T_g of the composite (Table 2) was defined by the peak of tan delta, because the samples that have undergone hygrothermal ageing have a moisture concentration gradient on the T_g region and a corresponding temperature distribution which is dependent on the molecular relaxation time, the which should affect the data DMA. As it can be observed from Table 2 the aged composites exhibit T_g values between no ageing composites. The composite with the fibers oriented at 0^o has greater T_g values, because in this case, the fibers are oriented in the direction of loading difficulting the mobility of the system (reinforcement + matrix), considering that there is a good fiber/matrix adhesion. In the case, of fibers oriented at 90^o has the direction loading opposite to the composite fibers oriented in 0^o, thus the properties of the matrix is that influence this case, and this can be observed with exception of sample 5 days of ageing, the others showed the values T_g higher than reference sample which may be related to the extraction of soluble in the polymeric matrix (Faguaga et al. [6]). However, the samples aged in the same conditions, only changing the orientation showed similar values may have been influenced both by resin plasticizing and by second crosslinking in ageing condition more severe.

Table 2. Values T_g for the composites obtained through the peak of the Tan Delta curve

	0º	**90º**
0 days	76ºC	65ºC
15 days/50ºC	66ºC	68ºC
5 days/80ºC	59ºC	61ºC
10 days/80ºC	69ºC	69ºC
15 days/80ºC	72ºC	75ºC

4. Conclusion

In the water absorption test was find a period of stabilization only for immersed sample at 80ºC. TGA analysis showed a mass percentage of fiber equivalent between the composites this study.

In short-beam shear test, it was observed an opposite trend for the two temperatures used in this work with time, which suggests that at 50ºC occurred a physical degradation and at 80ºC occurred chemical degradation.

The dynamic mechanical analysis showed clearly a change in the storage and loss modulus of samples with and without hygrothermal ageing, which may be due to the smaller relaxation time of the polymeric matrix, by reduce of the glassy transition temperature of the composite due to water absorption of composites except for the sample aged 15 days /80ºC so it is possible have occurred chemical degradation. Due to fact hygrothermal ageing cause several factors in the matrix and interface there is not a trend of increase or reduction to compare T_g of this composites.

The work with these two temperatures showed an influence significative despite the small gradient between them in properties studied.

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