

## The dynamic-mechanical behavior of epoxy matrix composites reinforced with ramie fibers

Frederico Muylaert Margem<sup>I</sup>, Sergio Neves Monteiro<sup>I</sup>, Jarbas Bravo Neto<sup>I</sup>, Rubén Jesus Sánchez Rodríguez<sup>I</sup>, Bluma Guenther Soares<sup>II</sup>.

<sup>I</sup> State University of the Northern Rio de Janeiro, UENF, Advanced Materials Laboratory, LAMAV; Av. Alberto Lamego, 2000, 28013-602, Campos dos Goytacazes, RJ, Brazil.

e-mail: [fmargem@bol.com.br](mailto:fmargem@bol.com.br) ; [sergio.neves@ig.com.br](mailto:sergio.neves@ig.com.br) ; [babasneto@hotmail.com](mailto:babasneto@hotmail.com) ,

<sup>II</sup> Macromolecule Institute, IMA, Federal University of Rio de Janeiro, UFRJ, Brazil.

e-mail: [bluma@ima.ufrj.br](mailto:bluma@ima.ufrj.br)

### ABSTRACT

The exceptional tensile strength of ramie fiber has motivated investigations on its application as reinforcement in polymeric composites. In this study the temperature variation of the dynamic-mechanical parameters of epoxy matrix composites incorporated with up to 30% in volume of ramie fiber were investigated by DMA tests. The parameters were the storage modulus, loss modulus and tangent delta. The investigation was conducted in the temperature from 20 to 200°C in an equipment operating in its flexural mode at 1 Hz under nitrogen. The results showed that the incorporation of ramie fiber tends to increase the viscoelastic stiffness of the epoxy matrix. It was also observed sensible changes in the structure damping capacity when the fraction of fiber is increased in the composite. These results indicate that the segmental mobility of the epoxy chains is affected by interaction with ramie fibers in the composite.

**Keywords:** Ramie fiber, mechanical tests, composite.

### 1 INTRODUCTION

Natural fibers obtained from vegetables with a relatively large content of cellulose have been used since the beginning of humankind for making basic items such as baskets, rope and fabrics. Well known examples of these lignocellulosic fibers are the cotton, flax jute and hemp, especially used for cloth fabrication. A less known fiber of this kind is that extracted from the stem of the ramie plant (*Boehmeria nivea*), illustrated in Figure 1.



(a)



(b)

**Figure 1:** The ramie plant (a) and fibers extracted from the stem (b).

In comparison with other natural fibers, ramie has an exceptional strength [1] but its textile application has continuously been replaced by synthetic fibers, mainly in clothes. An economical motivation to revive the culture of ramie could eventually occur by finding possible engineering applications such as composite reinforcement. In fact, in recent years there has been a growing interest in substituting natural fibers for synthetic ones like the glass fibers, as composites reinforcement [2-7].

In the particular case of the ramie fibers, a limited number of works [8-13] has been so far dedicated to investigation on its use as reinforcement phase of polymer composites. Among these works, to the knowledge of the authors of the present work, just one evaluated the dynamic-mechanical behavior of ramie fibers reinforced polymer matrix composites [13]. It was found that the viscoelastic stiffness of the polyester matrix is increased with the amount of incorporated ramie fibers. To extend this investigation to another thermoset matrix, the present work conducted a preliminary investigation on the temperature dependence of the dynamical-mechanical parameters of epoxy composites reinforced with ramie fibers.

## 2 EXPERIMENTAL PROCEDURE

A lot of 5 kg of ramie fibers was commercially supplied by the Brazilian firm SISALSUL. The diameter and length were statistically characterized based, respectively, on profile projector and caliper measurement performed on 100 fibers randomly taken from the lot [13, 14]. The fiber length varied from 40 to 400 mm with a mean value of 158 mm, as can be seen in the Figure 2. The fiber diameter varied from 0.003 to 0.20 mm with a mean value of 0,011mm, also shown in Figure 2. Before using, the ramie fibers were cleaned and dried at 60°C for 24 hours.

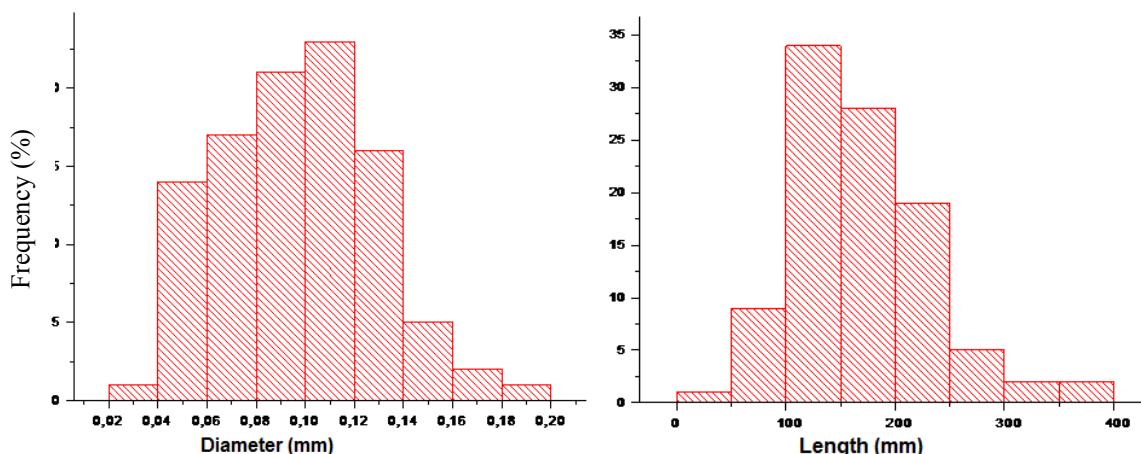


Figure 2: Statistical distribution of length and diameter of the lot of ramie fibers for this work.

Rectangular 50x13x5mm specimens were prepared for the dynamic-mechanical (DMA) tests. The preparation began by laying down continuous and aligned fibers, in separated volume fractions up to 30%, inside silicone molds. Still fluid epoxy resin type diglycidyl ether of the bisphenol-A (DGEBA), hardened with stoichiometric triethylene tetramine (TETA), was then placed onto the fibers. The liquid DGEBA was supplied by the Dow Chemical Co. (DER 331 374 g mol<sup>-1</sup>) and determined to have an equivalent weight epoxy group of 187.3 ± 1.1 g/equiv. These composite specimens were cured at room temperature for 24 hours. Figure 3 illustrates the aspect of the DMA specimens used in the present work.

Each composite specimen, including that for the pure DGEBA/TETA epoxy, was tested in a model Q 800 TA Instruments DMA equipment operating with its three points flexural mode at 1Hz of frequency, heating rate of 3°C/min. Curves for the storage modulus (E'), loss modulus (E'') and tangent delta (tan δ) were simultaneously registered. Two heating cycles were used for each sample. The sample was initially heated from 20 to 200°C and then cooled to room temperature before being immediately reheated to 200°C. The second scan was done at the latter heating rate.

Similar composite specimens with 122 x 25 x 10 mm were three points bend tested in a model 5582 Instron machine operating at a strain rate of 1.6 x 10<sup>-2</sup> s<sup>-1</sup> and 25°C with a span-to-depth ratio of 9. Fracture surfaces were analyzed by scanning electron microscopy, SEM, in a model JSM-6460 LV Jeol microscope operating with secondary electrons at 15 kV.



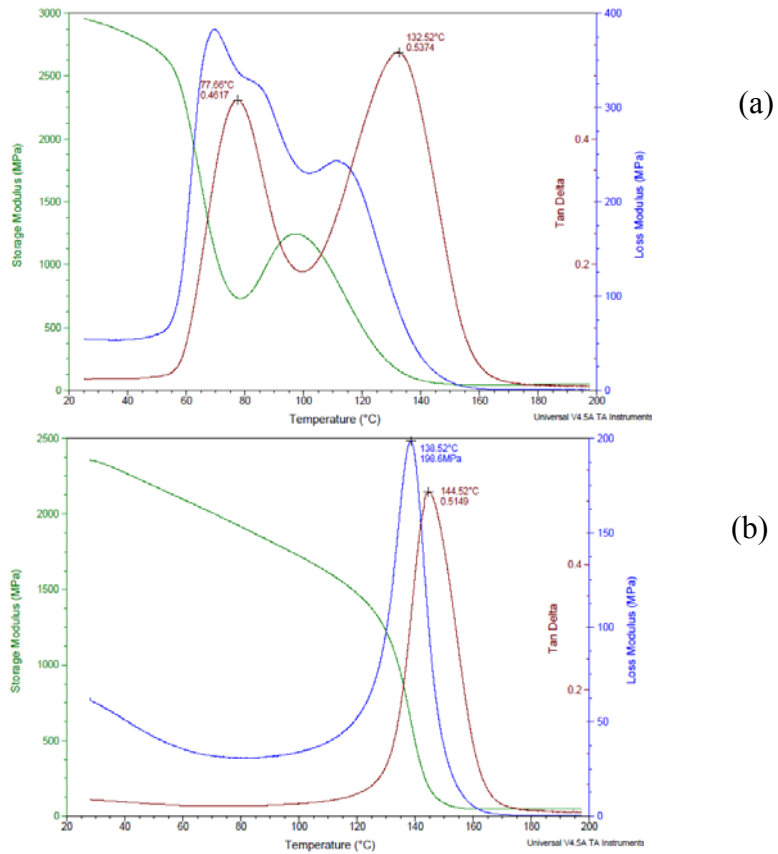
**Figure 3:** DMA specimens of DGEBA/TETA epoxy composites incorporated with different volume fractions of ramie fibers.

### 3 RESULTS AND DISCUSSION

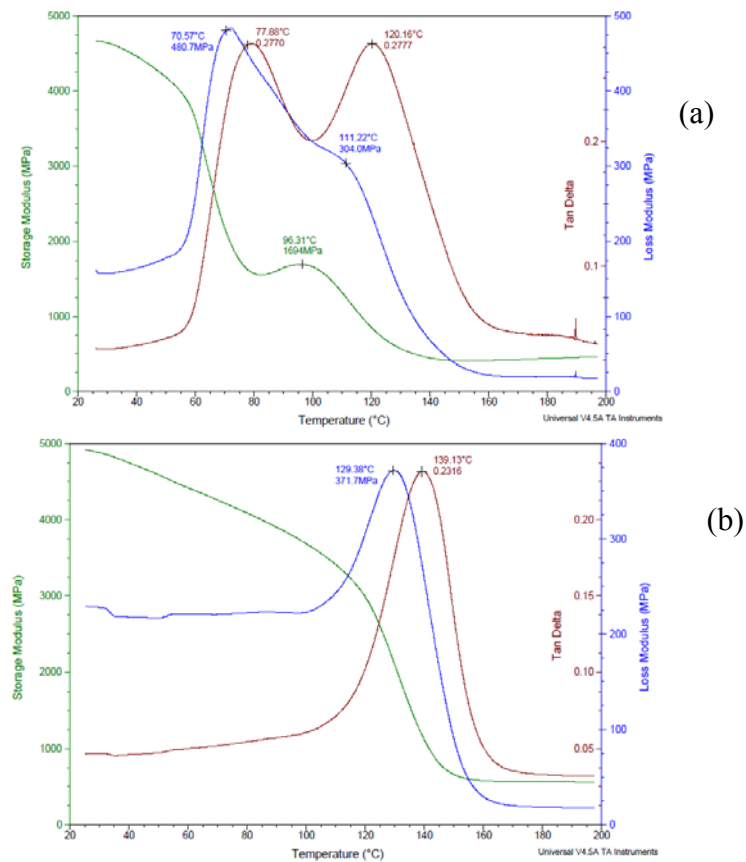
Figure 4 presents complete sets of DMA curves ( $E'$ ,  $E''$  and  $\tan \delta$ ) for the pure epoxy and Figure 5 for 30% ramie fibers composites specimens, both for a first and second heating scan. In these figures it should be noted that the first heating curves display a more complex behavior in their DMA spectrum. The first heating curve for the pure epoxy resin, Figure 4(a), and for the 30% ramie fiber composites, Figure 5(a) presents additional peaks and temperature displacement of the main DMA features as compared to the corresponding second heating curves, Figure 4(b) and 5(b). In the first heating, for instance, the storage modulus curve,  $E'$ , undergoes the characteristics steep decrease from 50 to 80°C followed by a broad peak around 100°C. The loss modulus,  $E''$ , shows an apparent superposition of three broad peaks between 50 and 140°C. The  $\tan \delta$  curves show two broad peaks at around 80 and 120°C. This behavior associated with broad peaks, non-existing in a second heating scan, is characteristic of incomplete crosslink process of epoxy formulations [15, 16].

By contrast, the second heating shows  $E'$  curves without any additional peak after the steep decrease, which occurs at comparatively higher temperature from 120 to 140°C. The  $E''$  and  $\tan \delta$  curves after the second heating display better defined peaks associated with glass transition at higher temperatures, which is an indication that the epoxy matrix achieved a greater density of crosslink. For this reason, only results corresponding to a second heating scan up to 200°C, corresponding to almost completely cured epoxy matrix samples, will be considered for discussion in the present work.

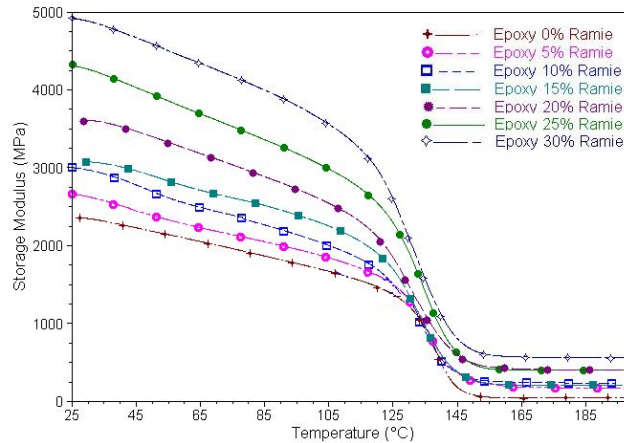
Figure 6 compares the variation of the storage modulus,  $E'$ , for the different composites investigated, as a function of the temperature. The curves in this figure revealed that the incorporation of ramie fiber sensibly increase the value of  $E'$ . In fact at 25°C,  $E'$  for pure epoxy is around 2.3 GPa and for 30% fiber composite is around 4.9 GPa. This means that the ramie fibers increase the epoxy matrix capacity to support mechanical constraints with recoverable viscoelastic deformation. In particular the composite stiffness is substantially increased with ramie fiber incorporation, which is also comparable to a result found in quasi-static tensile tests for similar composites at 25°C as shown in Figure 7.



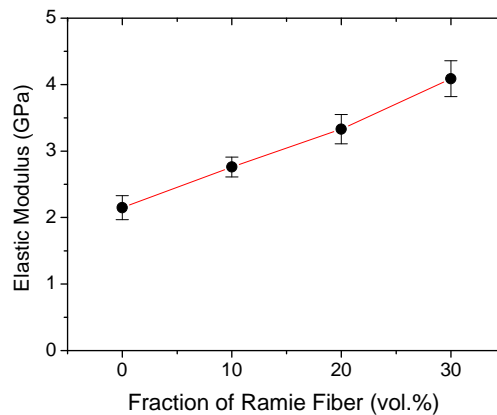
**Figure 4:** DMA  $E'$ ,  $E''$  and  $\tan \delta$  curves for samples of pure epoxy (0% ramie fibers) (a) first test and (b) second test.



**Figure 5:** DMA  $E'$ ,  $E''$  and  $\tan \delta$  curves for samples of epoxy with 30% ramie fibers: (c) first test and (d) second test.



**Figure 6:** Variation of the storage modulus with the temperature for the pure epoxy and the composites reinforced with different volume fractions of ramie fibers.



**Figure 7:** Variation of the quasi-static elastic modulus with the amount of ramie fiber in the epoxy matrix composites.

For polyester matrix composites reinforced with ramie fibers, the inverse behavior occurs [11]. The reason for these distinct DMA results is still not clear. However, the possibility of different interfacial strengths in ramie fibers interaction with polyester [11] or epoxy (present work) could provide an explanation. The degree of fibers adhesion affects the mobility of the epoxy molecular chains and hence its temperature transition to an amorphous structure. This will be analyzed further in the present work.

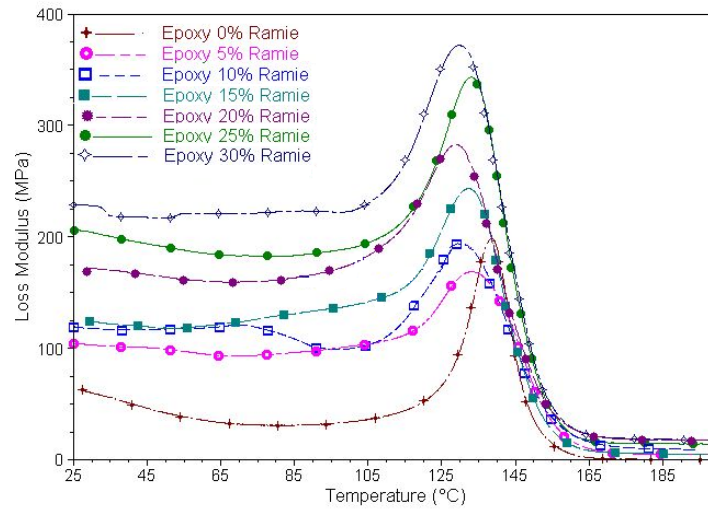
Figure 8 depicts the variation of the loss modulus,  $E''$ , for the different composites investigated, as a function of the temperature. All  $E''$  curves in this figure show broad peaks with distinct amplitude and temperatures positions, as compared to the pure epoxy peak. These can be associated with the  $\alpha$  peak and suggests a more complex structural relaxation behavior by the composites. According to Mohanty *et al.* [14], this relaxation is attributed to the chain mobility of the polymeric matrix.

It should be noticed in Figure 8 that the all composite peaks are displaced to lower temperatures in comparison to the pure epoxy peaks. This is possibly due to an increase in the flexibility of the epoxy chains caused by the incorporation of ramie fibers. Once again, a low interfacial strength could permit the chains to move without much restriction at the contact with the ramie fibers. On the contrary, the peaks of  $E''$  for the polyester composites [11] are displaced to higher temperatures indicating a reduction in the chain flexibility.

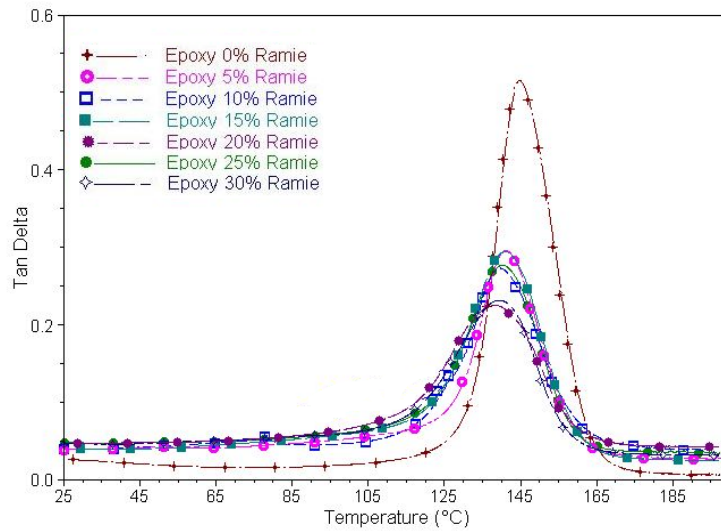
Figure 9 compares the temperature dependence of the dumping spectrum associated with the  $\tan \delta$  for the different composites investigated. In this figure one should notice the characteristic peaks associated with the upper temperature limit of the glass transition temperature,  $T_g$ . In fact,  $\tan \delta$  also indicates the composite damping capacity [14], which has a maximum value at the amorphous transition.

In Figure 9 it can also be seen that the composites present lower amplitude peaks as compared to the pure epoxy as the volume fraction of ramie fibers increases. Moreover, these peaks are displaced toward lower temperatures. This suggests, as also found with  $E''$  in Figure 8, that the incorporation of ramie fibers increases the mobility of the epoxy chains. As a consequence, the transition from glassy to rubbery state could occur at lower temperature. An inverse situation was found for the polyester composites [11], in which

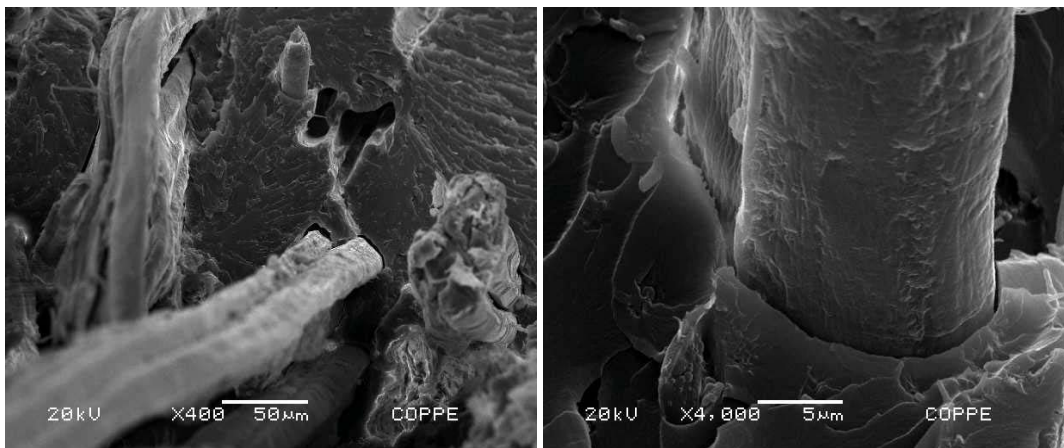
the composite tan  $\delta$  peaks are displaced toward higher temperatures indicating a reduction in the epoxy chain mobility.



**Figure 8:** Variation of the loss modulus with the temperature for the pure epoxy and the composites reinforced with different volume fraction of ramie fibers.



**Figure 9:** Temperature dependence of tan  $\delta$  for the pure epoxy, and the composites reinforced with different volume fraction of ramie fibers.



**Figure 10:** SEM fractographs of ramie fiber reinforced epoxy composites; (a) 20%v. general view of fibers and holes; (b) 10%v. detail of a fiber/matrix interface initial process of debonding.

A comparison between DMA results of ramie fiber composites with polyester matrix [11] and epoxy matrix in the present work indicate that the interfacial strength could play a major role in the explanation of this contradictory behavior. It is suggested that ramie fibers have a superior adherence to the polyester matrix but a weak adhesion to the epoxy matrix. To investigate this possible condition, the fracture surface of bend ruptured ramie fiber reinforced epoxy composites was analyzed by SEM. Typical examples are shown in Figure 10 for composites with different volume fractions of ramie fibers.

Finally, it is proposed that the lignocellulosic fiber, having hydroxylic, carboxylic and phenolic groups, provides ample scope for an anchorage of epoxy resin segments since some of these groups could be present at the fiber surface. The cellulosic, hemicellulosic and lignin constituents in the natural fiber, which by itself is a natural composite, become integral parts of the amine cured epoxy network. As a consequence, the overall modification of the fiber/epoxy interface and of the interfacial region at the matrix is such that the fiber reinforced epoxy network composite, with 30% of volume fraction, shows nearly comparable values for loss modulus and glass transition temperature. This also reveals a reinforcing role of the ramie fibers in the form relatively higher values for the storage modulus.

#### 4 CONCLUSIONS

DGEBA/TETA epoxy composites present an increase in viscoelastic stiffness, measured by the DMA storage modulus,  $E'$ , with the volume fraction of continuous and aligned ramie fibers. This corroborates quasi-static stiffness results obtained for similar composites in flexural tests.

The onset of epoxy matrix abrupt softening in  $E'$  as well as the  $\alpha$  peaks in the  $E''$  and the upper Tg peaks in  $\tan \delta$  are slightly displaced toward lower temperature with incorporation of ramie fibers.

It is suggested that these displacements are associated with an increase in the flexibility of the epoxy chains and could be a consequence of low interfacial strength permitting these chains to move without much restriction at the contact with the ramie fibers.

SEM fractograph analysis showed evidences of weak adhesion between the ramie fiber and the epoxy matrix, which indicates a low interfacial shear stress.

#### 5 ACKNOWLEDGEMENTS

The authors thank the support to this investigation by the Brazilian agencies: CNPq, CAPES, FAPERJ and TECNORTE/FENORTE. It is also acknowledged the permission to the use of the SEM microscope by the PEMM from COPPE/UFRJ.

#### 6 REFERENCES

- [1] SATYANARAYANA, K.G., GUIMARÃES, J.L., WYPYCH, F., “Studies on lignocellulosic fibers of Brazil. Part I: Source, production, morphology, properties and applications”, *Composites: Part A*, v. 38, pp. 1694-1709, 2007.
- [2] BLEDZKI, A.K., GASSAN, J., “Composites reinforced with cellulose- based fibers”, *Progress in Polymer Science*, v. 4, pp. 221-274, 1999.
- [3] NABI, SAHED, D., JOG, J.P., “Natural fiber polymer composites: a review”, *Advances in Polymer Technology*, v. 18, pp. 221-274, 1999.
- [4] MOHANTY, A.K., MISRA, M., HINRICHSEN, G., “Biofibers, biodegradable polymers and biocomposites: an overview”, *Macromolecular Materials and Engineering*, v. 276/277, pp. 1-24, 2000.
- [5] EICHHORN, S.J., BAILLIE, C.A., ZAFEIROPOULOS, N., MWAKAMBO, L.Y., ANSELL, M.P., DUFRESNE, A., “Review of current international research into cellulosic fibres and composites”, *Journal of Materials Science*, v. 36, pp. 2107-2113, 2001.
- [6] WAMBUA, P., IVENS, J., VERPOEST, I., *The Composites Science and Technology*, v. 63, pp. 1259, New York Journal, NY, USA, 2003.
- [7] SHIHONG, L., BENLIAN, Z., QIYUN, Z., XIANRONG, B., “A new kind of super-hybrid composite material for civil use - ramie fibre/Al”, *Composites*, v. 25, pp. 225-228, 1994.

- [8] PARK, J.M., SON, T.Q., JUNG, J. G., HWANG, B.S., “Interfacial evaluation of single ramie and kenaf fiber/epoxy resin composites using micromechanical test and non-destructive acoustic emission”, *Composite Interfaces*, 13, pp. 105-129, 2006.
- [9] NAM, S., NETRAVALI, A.N., “Green composites I – Physical properties of ramie fibers for environment-friendly green composites”, *Fibers and Polymers*, v. 7, pp. 372-379, 2006.
- [10] NAM, S., NETRAVALI, A.N., “Green composites. II - Environment-friendly, biodegradable composites using ramie fibers and soy protein concentrate (SPC) resin”, *Fibers and Polymers*, 7, pp. 380-388, 2006.
- [11] KISHI, H., FUJITA, A., “Wood-based epoxy resins and the ramie fiber reinforced composites”, *Environmental Engineering and Management Journal*, 7, pp. 517-523, 2008.
- [12] KALIA, S., KAITH, B.S., KAUR, I., “Pre-treatments of natural fibers and their application as reinforcing material in polymer composites – A review”, *Polymer Engineering and Science*, v. 49, pp. 1253-1272, 2009.
- [13] MONTEIRO, S.N., MARGEM, F.M., RODRIGUEZ, R.J.S., SOUZA, D., “Dynamic mechanical behavior of ramie fiber reinforced polyester matrix composites”, In: Proceedings of the 63rd International Congress of the Brazilian Association for Metallurgy and Materials - ABM (Santos, SP, Brazil), pp. 1-10, July, 2008.
- [14] MOHANTY, S., VERMA, S.K., NAYAK, S. K., “Dynamical Mechanical and thermal properties of mape treated jute/HDPE composites”, *Composites Science and Technologies*, v. 66, pp. 538-547, 2006.
- [15] STARK, W., GOERING, H., MICHEL, U., BAYERL, H., “Online monitoring of thermoset post-curing by dynamic mechanical thermal analysis DMTA”, *Polymer Testing*, v. 28, pp. 561-566, 2009.
- [16] GARCIA, F.G., SOARES, B.G., PITA, V.J.R.R., SANCHEZ, R., RIEUMONT, J., “Mechanical Properties of Epoxy Networks Based on DGEBA and Aliphatic Amines”, *Journal of Applied Polymer Science*, 106, pp. 2047–2055, 2007.