THERMAL CARACTERIZATION BEHAVIOR OF EPOXY COMPOSITES REINFORCED RAMIE FIBERS[1]

Alice Barreto Bevitori[2]
Isabela Leão Amaral da Silva[2]
Frederico Muylaert Margem[3]
Renan Sopeletto Carreiro[4]
Sergio Neves Monteiro[5]
Veronica Calado[6]

Abstract

A natural fiber, extracted from the stems of the ramie plant is available in several regions around the world. Owing to its low cost and weight, it may be used in many applications, including engineering composites. In fact, epoxy composites reinforced with natural lignocellulosic fibers have attracted interest in several areas, especially engineering due to its low cost, besides being lighter. They can replace traditional composites such as fiber glass. The use of composites reinforced with ramie fibers above the ambient temperature has not been fully investigated. Therefore, the objective of this study was to evaluate the thermal behavior of epoxy composites reinforced with up to 30% by volume of ramie fibers. The analysis was conducted by thermogravimetric, TGA and DTG. The results show a sensible effect of the ramie fibers by reducing the thermal stability of the composites.

Key words: Thermal analysis; Epoxy composites; Ramie fibers.

CARACTERIZAÇÃO DO COMPORTAMENTO TÉRMICO DE COMPÓSITOS DE EPÓXI REFORÇADOS COM FIBRAS DE RAMI

Resumo

A fibra natural de rami, extraída do caule da planta de rami está disponível em diversas regiões, e devido seu baixo custo e peso, pode ser utilizada em muitas aplicações, incluindo compósitos de engenharia. De fato, compósitos de resina epóxi reforçados com fibras naturais lignocelulósicas vêm atraindo interesse em diversas áreas, especialmente a de engenharia devido seu baixo custo, além de ser mais leve, podendo substituir compósitos tradicionais, como a fibra de vidro. O uso destes compósitos reforçados com fibras de rami acima da temperatura ambiente ainda não foi completamente investigado. Portanto, o objetivo deste trabalho foi avaliar o comportamento térmico de compósitos de epóxi reforçados com até 30% em volume de fibras de rami. As análises realizadas foram termogravimétrica, TGA, bem como sua derivada. Os resultados mostram uma sensível influência das fibras de rami, reduzindo a estabilidade térmica dos compósitos.

Palavras-chave: Análises térmicas; Compósitos de epóxi; Fibras de rami.

---

[1] *Technical contribution to 67th ABM International Congress, July, 31th to August 3rd, 2012, Rio de Janeiro, RJ, Brazil.*

[2] *Msc, Doctor student, Laboratory of Advanced Materials (Lamav), Center of Science and Technology (CCT), State University of the Northern Rio de Janeiro (UENF), Brazil; alicebevitori@gmail.com.*

[3] *Post Doctoral Student, Lamav, UENF, Brazil.*

[4] *Technical, Lamav, CCT, UENF, Brazil.*

[5] *PhD, Professor, Lamav, CCT, UENF, Brazil.*

[6] *D.Sc. Professor, Chemistry School (EQ), Federal University of Rio de Janeiro (UFRJ), Brazil.*

1 INTRODUCTION

Since mid last century, polymeric composite materials have been replacing several conventional materials.(1) More recently, however, synthetic composites are losing their importance due to environmental and energy issues. Investigations are under way to find alternative solutions. For example, natural fiber composites used in substitution of non-recyclable and energy intensive glass fiber composites, known as “fiber glass”.(2-5) The main advantages of natural fiber reinforced composites are the lightness, low cost and flexible properties to attend the requirements of mechanical performance.(6) The use of natural fibers is also related to other technical benefits such as less abrasion to processing equipments and higher toughness.(3) It is also worth mentioning that the glass fiber not only poses a health risk when inhaled but is also associated with CO_2 emission during production and processing. None of these shortcomings apply to natural fibers, mainly the lignocellulosic fiber obtained from plants. Indeed, lignocellulosic fibers are biodegradable, renewable and neutral with respect to CO_2 emission, which is believed to be the main responsible for the earth greenhouse effect and global warming.(7) By contrast, lignocellulosic fibers present drawbacks including a relatively low thermal stability.

The lignocellulosic fiber extracted from the stem of the ramie plant (*Boehmeria nivea*) (Figure 1), is reported to reach tensile strength above 1,000 MPa.(8,9) However, information on the thermal behavior of polymer composites reinforced with ramie fibers are scarce.(10,11) Therefore, the objective of this work was to evaluate the thermogravimetric stability of epoxy matrix composites reinforced with different amounts of ramie fibers by means of TG and DTG analysis.

Figure 1. (a) The ramie plant; and (b) a bundle of ramie fibers.

2 MATERIALS AND METHODS

The ramie fibers investigated in the present work were supplied by the Brazilian firm Sisalsul. As the composite matrix, a type diglycidyl ether of the bisphenol A (DGEBA) epoxy resin hardened with 13 parts per hundred of triethylene tetramine (TETA) in stoichiometric proportions was used. The as received fibers were water cleaned and dried in a stove at 60°C for 24 hours. Composite with 0 vol%, 10 vol%, 20 vol% and 30 vol% of continuous and aligned ramie fibers were fabricated. This consisted of a careful initial accommodation of the fibers in a 5.5 mm in diameter and 20 mm long cylindrical mold. The still fluid DGEBA/TETA epoxy was then poured inside the mold and allowed to cure at room temperature for 24 hours. After extraction from the mold, the prepared composite was sectioned in thin discs with 2 mg of weight, which corresponds to approximately 1 mm in thickness. Individual discs, for each volume fraction of ramie fiber, were used as thermo gravimetric, TG/DTG, analysis sample. The analysis was carried out in a Perkin-Elmer equipment at a heating rate of 10°C/min under nitrogen atmosphere, from 25°C to 800°C.

3 RESULTS AND DISCUSSION

Figure 2 shows simultaneously the TG/DTG curves for the neat DGEBA/TETA epoxy obtained after room temperature curing for one day. In this figure one should note that the TG curve displays an almost horizontal first stage up to about 250°C associated with practically no weight loss. This is followed by a second stage up to about 500°C in association with a greater weight loss, above 90% of the total sample's weight. At even higher temperatures, from 500°C to 800°C, a third very slow declining weight loss corresponding to 8.3% of the sample is observed in Figure 2. The DTG curve displays only one symmetrical and uniform peak related to a maximum rate of weight loss at 399°C. Such a well defined peak is typical of pure polymeric resins that are also associated with a relatively small amount of high temperature residues.(12) In neat polymers, this unique DTG peak is related to the main thermal decomposition mechanism of macromolecular chain degradation or even depolymerization.(6,13)

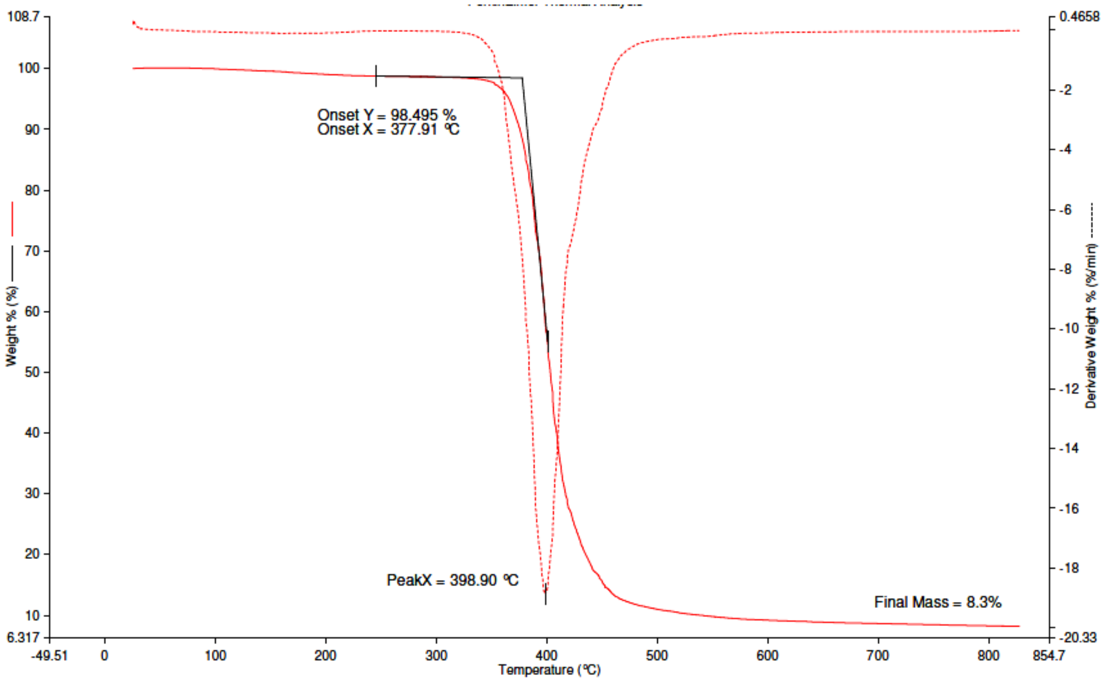

Figure 2. TG/DTG curves of the neat DGEBA/TETA epoxy.

The thermo gravimetric parameters obtained from the TG/DTG curves in Figure 2 are presented in Table 1.

Table 1. Thermo gravimetric parameters of the neat DGEBA/TETA epoxy and related composites with up to 30 vol% of ramie fibers

Sample	Initial peak (^oC)	Onset of the second stage (^oC)	Shoulder peak in second stage (^oC)	Main peak in second stage (^oC)	Final residue (%)
Neat DGEBA/TETA epoxy	-	378	-	399	8.3
Epoxy – 10 vol% ramie fiber	75	326	357/388	410	14.1
Epoxy – 20 vol% ramie fiber	64	328	360	419	14.2
Epoxy – 30 vol% ramiefiber	82	323	356	417	16.9

Figures 3 to 5 show, simultaneously, the TG and DTG curves for the DGEBA/TETA epoxy matrix composites reinforced with 10 vol%, 20 vol% and 30 vol% of ramie fibers, respectively. The main thermogravimetric parameters obtained from these curves are also listed in Table 1. The results presented in Figures 3 to 5, jointly with the values in Table 1, reveal sensible differences with respect to corresponding results in Figure 2 for the DGEBA/TETA epoxy, which serves as composite matrix. Different than the pure epoxy, the first stage in the composites, up to 250°C, exhibits small peaks between 64°C and 82°C, in association with an appreciable weight loss increasing from 3.3% to 6.9% with the amount of ramie fiber. These initial peaks at lower temperatures are characteristics of natural fiber reinforced polymer composites and attributed to the release of water adsorbed on the surface of all lignocellulosic fibers.(14-18) Although small, these initial peaks could be considered as a first limit for the thermal stability of lignocellulosic fiber reinforced polymer composites, particularly those of ramie fiber in epoxy matrix.

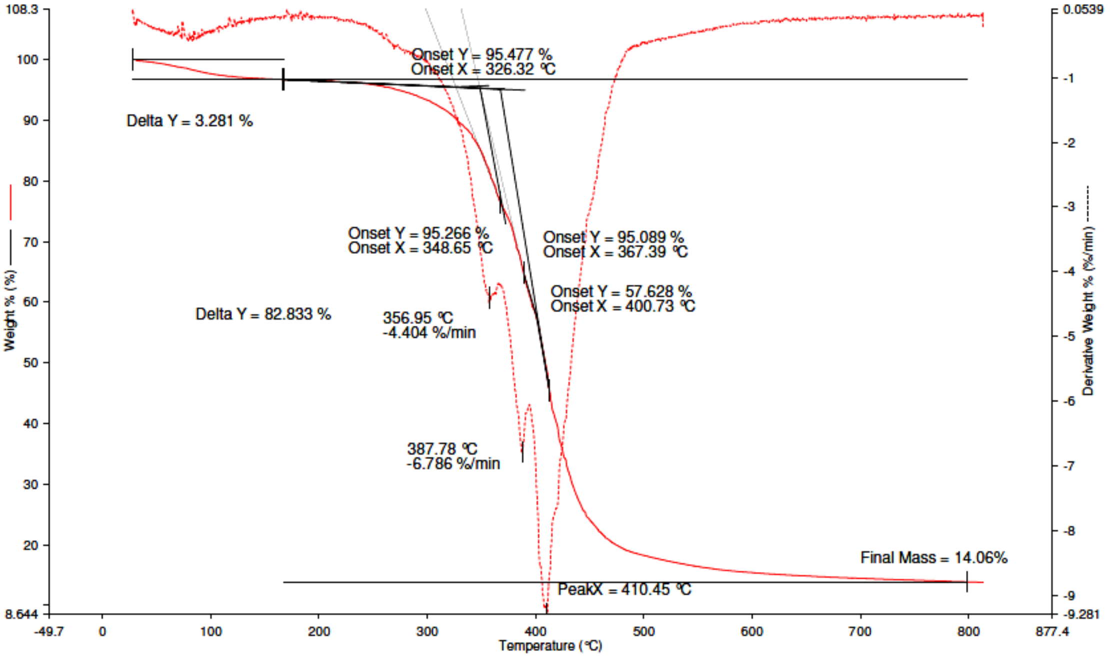

Figure 3. TG/DTG curves for DGEBA/TETA epoxy composites reinforced with 10 vol% of ramie fibers.

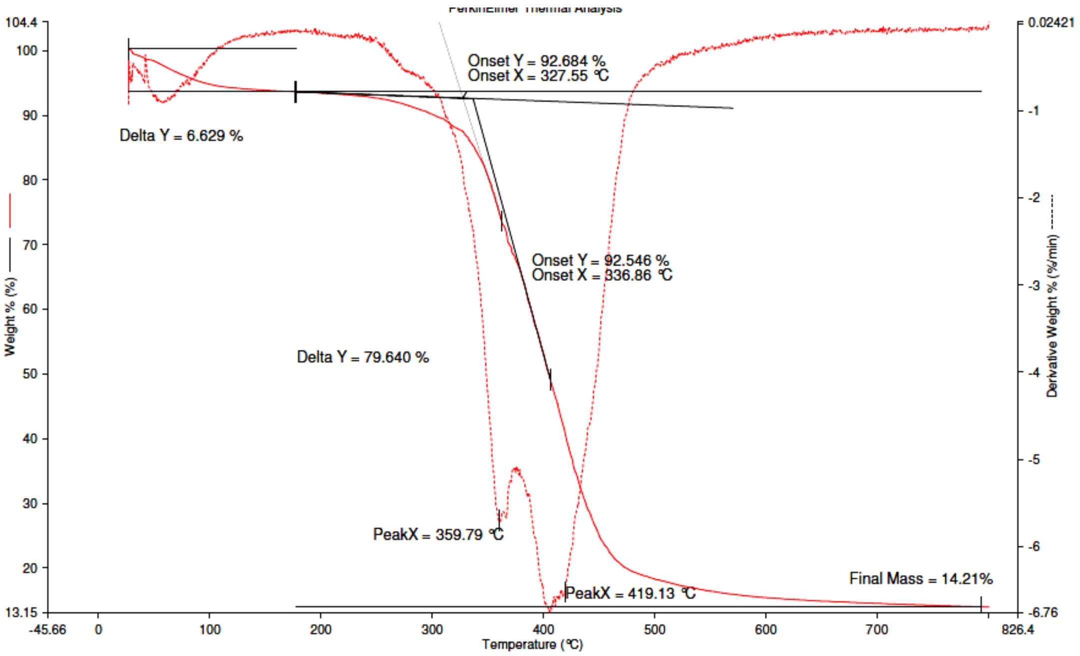

Figure 4. TG/DTG curves for DGEBA/TETA epoxy composites reinforced with 20 vol% of ramie fibers.

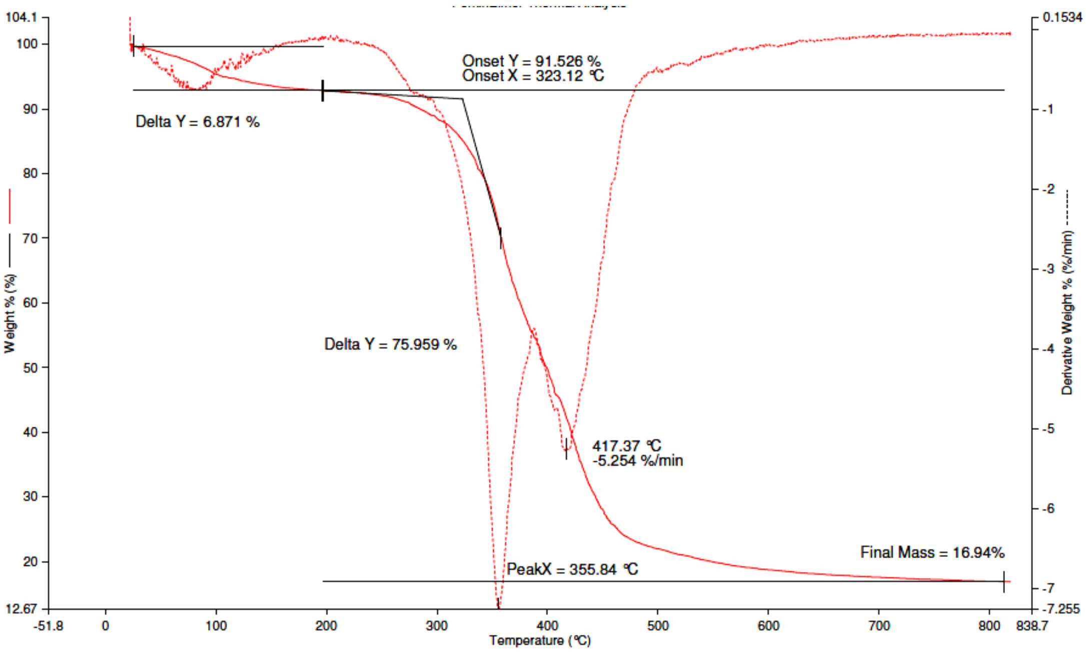

Figure 5. TG/DTG curves for DGEBA/TETA epoxy composites reinforced with 30 vol% of ramie fibers.

Another relevant difference between the neat epoxy and the composites refers to the onset of the second TG stage associated with the greater weight loss, up to around 500°C. As presented in Table 1, this onset for the neat epoxy occurs at 378°C, which is a temperature significantly above those, 323°C-328°C, for the composites. Similar behavior was reported by Yu, Li and Ren(11) for polyacid lactic matrix composites reinforced with short-cut ramie fibers. The reason for this reduction in the second stage onset temperature, which is technically accepted as the composite limit of stability, is ascribed to the process of ramie fiber thermal decomposition. In fact, as any lignocellulosic fiber, the ramie begins its thermal decomposition by the lignin at temperatures as low as 220°C.(18) At approximately 300°C-400°C, this decomposition is maximized. It is then suggested that the ramie fiber lignin degradation be the responsible for the composite thermal stability limit. In other words, the stability limit of ramie fiber reinforced DGEBA/TETA epoxy composites be given by the onset temperature of the second TG stage as listed in Table 1.

In particular, it is worth mentioning that a recent work on the thermal analysis of isolated ramie fibers(19) revealed initial peaks of water release around 60°C. Furthermore, in the isolated ramie fiber the onset of thermal decomposition occurs at about 290°C owing to the degradation of lignin and hemicellulose. In addition the authors(19) reported main peaks around 325°C that were assigned to cellulose degradation. These previous results showed that the isolated ramie fiber is less thermally resistant than both the DGEBA/TETA epoxy and related composites given in Table 1.

One more significant thermogravimetric aspect of the composites shown in Figures 3 to 5 that needs to be discussed is the existence of shoulder peaks in the DTG curves. These shoulder peaks are also observed in other lignocellulosic fiber composites(16,20) and attributed to the degradation of the fiber constituents specially the hemicellulose and cellulose.(6,18) Here it is worth noticing that the 10 vol% ramie fiber composite, Figure 3 displays two distinct shoulder peaks in its DTG curve. The first peak at 357°C might be assigned to the thermal decomposition of hemicellulose. Similar peaks at 360°C and 356°C are also observed in Figures 4 and 5 for the 20% and 30% ramie fibers composites, respectively. By contrast, a second shoulder peak at 388°C in Figure 3 for the 10% ramie fiber composite, probably due to cellulose decomposition, is not verified in the other DTG curves for 20 vol% and 30 vol% ramie fiber composites shown in Figures 4 and 5, respectively.

A main DTG peak is observed not only for the neat epoxy, at 399°C in Figure 2, but also at higher temperatures 410°C-419°C for the composites in Figures 3 to 6. This main peak associated with the epoxy decomposition, is apparently affected by the presence of ramie fibers. It is proposed that the fiber cellulose macromolecules interact with those of the epoxy and increase the thermal stability of the composite. This behavior has not yet been reported in the literature and deserves to be deepened.

As a last point to be discussed, the introduction of ramie fibers, as presented in Table 1, increased the amount of high temperature from 8.3%, in the neat epoxy (Figure 2), to 14.1%-16.9% in the composites, (Figures 3 to 5). This can be ascribed to the participation of carbonaceous matter and tar/char, predominantly formed during the pyrolysis process of the ramie fiber.(6,18) This also results in lesser weight loss in the second thermogravimetric stage of the composites.

4 CONCLUSIONS

- Composites with stoichiometric DGEBA/TETA epoxy matrix reinforced with up to 30 vol% of ramie fibers display sensible changes in the thermal behavior evaluated by thermo gravimetric, TG/DTG, analysis;
- the incorporation of ramie fibers causes a decrease in the composite onset temperature, which characterizes the beginning of a second stage of greater weight loss, as compared to the neat epoxy, owing to the degradation of the ramie fiber;
- in the composites, but not in the neat epoxy, initial DTG peaks were observed around 64°C-82°C due to water release form the ramie fibers;

- the main DTG peak around 400°C for the neat epoxy, which can be assigned to the degradation of the macromolecular chain, is slightly displaced to 410°C-417°C as a consequence of ramie fiber/epoxy matrix interaction;
- shoulder peaks only observed in the composites were attributed to hemicellulose and cellulose contained in the ramie fibers;
- the final thermal degradation residue increases in proportion with the amount of ramie fiber due to the greater formation of carbonaceous matter and tar.

Acknowledgements

The authors thank the support to this investigation provided by the Brazilian agencies: CNPQ, Capes and Faperj. It is also acknowledge the technical contribution to the experimental work by Rosana Gouvêa Maurício of the Ladeq/UFRJ.

REFERENCES

1 CHAWLA, K.K. Composite Materials, New York: Springer–Verlag, (1993).
2 MONTEIRO, S.N., LOPES, F.P.D., FERREIRA, A.S., NASCIMENTO, D.C.O. Natural fiber polymer matrix composites: cheaper, tougher and environmentally friendly, *JOM*, 61 (2009) 17-22.
3 WAMBUA, P., IVENS, I., VERPOEST, I. “Natural fibers: can they replace glass and fiber reinforced plastics?”, *Composites Science and Technology*, 63 (2003) 1259 – 1264.
4 CROCKER, J., “Natural materials innovative natural composites”. Materials Technology, 2-3 (2008) 174-178.
5 MOHANTY, A.K., MISRA, M., HINRICHSEN, G., “Biofibers, biodegradable polymers and biocomposites: an overview”, *Macromolecular Mat. and Engineering*, 276/277 (2000), 1-24.
6 NABI SAHED, D., JOG, J.P. Natural fiber polymer composites: a review, *Advances in Polymer Technol*., 18 (1999), 221-274.
7 GORE, A., “An Inconvenient Truth. The Planetary Emergency of Global Warming and What We Can do About It”. Emmaus, Pennsylvania, USA: Rodale Press, 2006.
8 MONTEIRO, S. N., SATYANARAYANA, K. G., LOPES, F. P. D., High strength natural fibers for improved polymer matrix composites, *Materials Science Forum*, 638-642 (2010) 961-966.
9 MONTEIRO, S. N., LOPES, F. P. D., BARBOSA, A. P., BEVITORI, A. B., DA SILVA, I. L. A., DA COSTA, L. L., Natural lignocellulosic fibers as engineering materials – An overview, *Metallurgical and Mater. Trans A*, 42A (2011) 2963-2974.
10 LU, Y. WENG, L., CAO, X., Morphological, thermal and mechanical properties of ramie crystallites-reinforced plasticized starch biocomposites, *Carbohydrate Polym*., 63 (2006) 198-204.
11 YU, T., LI, Y., REN, J., Preparation and properties of short natural fiber reinforced poly(latic acid) composites. *Trans. Nonferrous Me. Soc. China*, 19 (2009) s651-s655.
12 MCNEIL, editor, Comprehensive Polymer Science, vol. 5, cap. 15, Pergamon Press, New York, 1989.
13 JOSEPH, P. V., JOSEPH, K., THOMAS, S., PILLAI, C. K. S., PRASAD, V. S., GROENINCKX, G., SARKISSOVA, M., The thermal and crystallization studies of short sisal fiber reinforced polypropylene composites. *Composites Part A*, 34 (2003) 253-266.
14 SGRICCIA, N., HAWLEY, M. C., Thermal, morphological, and electrical characterization of microwave processed natural fiber composites. *Compos. Sci. Technol.* 67 (2007) 1986-1991.
15 MOTHÉ, C. G., DE ARAUJO, C. R., Thermal and mechanical characterization of polyuretane cmposites with curaua fibers, *Polímeros: Ciência e Tecnologia* 14(4) (2004) 274-288.

16 FERREIRA, A. S., RODRIGUEZ, R. J. S., LOPES, F. P. D., MONTEIRO, S. N., Thermal analysis of curaua fiber reinforced polyester matrix composites. In: Characterization of Minerals, Metals and Materials Symposium – TMS Conference (TMS 2010), Seattle, WA, EUA, March 2010, p. 1-7.
17 MWAIKAMBO, L. Y., MARTUSCELLI, E., AVELLA, M., Kapok/cotton fabric-polypropylene composites. *Polym. Testing*, 19(8) (2000) 905-918.
18 NGUYEN, T., ZAVARIN, E., BARRAL, E. M., Thermal analysis of lignocellulosic material. Part I – Unmodified materials. *J. Macromol. Sci. – Rev. Macromol*. Chem. C 20 (1981) 1-65.
19 RODRIGUEZ, R. J. S., BEVITORI, A. B., SILVA, I. L. A., LOPES, F. P. D., MONTEIRO, S. N., Thermal analysis characterization of ramie fibers with different diameters. In: Characterization of Minerals, Metals and Materials Symposium – TMS Conference (TMS 2011), San Diego, CA, EUA, March 2001, pp. 1-6.
20 GAÑAN, P., MONDRAGON, I., Thermal and degradation behavior of fique fiber reinforced thermoplastic matrix composites. *J. Therm. Anal Cal.* 73(3) (2003) 783-795.