EFFECT OF FIBERS ALKALI TREATMENT ON THERMAL BEHAVIOUR OF CURAUÁ/ POLYESTER COMPOSITES

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Abstract:

The interaction between natural fibers and polymeric matrices can be the main disadvantage to expansion of natural fibers in industry application. Alkali treatments are usually applied on natural fibers to remove the lignin and extractives improving the adhesion between the reinforcement and matrix, and consequently, the thermal properties. The curauá, a typical plant from Amazon region, becomes very attractive since it presents high cellulose content, low density, and high strength. The primary objective of this work is to evaluate the thermal behavior and cure parameters of the curauá/ polyester composites through thermal analysis. The untreated curauá fibers and alkali treated by solutions of KOH 10% (w/v) or NaOH 5% (w/v) were mixed to polyester resin and a hardener (2 phr). Further, the curauá/ polyester composites were fabricated by hand lay-up method with fiber fraction of 10 or 20 wt% and cured for 24 hours. Thermogravimetry and its derivative curves (TG-DTG) and differential scanning calorimetry (DSC) analysis were used to determine composites thermal behavior as well its glass transition temperature (T_g). TG-DTG analysis revealed that the curauá treated with NaOH 20 wt%/ polyester composite presented the higher thermal stability compared to the neat matrix and other composites. Besides, the composites with both treated fibers presented higher T_g than the neat matrix, increasing with fiber content. The composite reinforced with curauá treated with NaOH 10 wt% shows the higher change in T_g, increasing to 11.3 °C. The DSC analysis showed that the second exothermic peak that appears in the curves is associated with the cure of composite between 117-119 °C. Finally, the composites with fibers treated with alkaline presented better thermal stability than composite reinforced with untreated fibers.

Keywords: Curauá fibers, polyester, composite, thermal properties.

1. INTRODUCTION

In recent years, the increasing interest of the industry in the use of natural fibers such as sisal, curauá, rami and buriti to replace synthetic fibers in polymeric composites has demanded

studies on the performance of these materials. Natural fibers have been increasingly applied in polymeric composites due to its lower density and costs, and good mechanical strength concerning synthetic fibers [1-2]. The use of natural fibers as on the field of composites has become vital since they are renewable and biodegradable, as well as causing a lower risk to human health [2].

The curauá plant (*Ananas erectifolius*) is cultivated in the northern of Brazil, and its average chemical composition is 62% cellulose, 15% hemicellulose, 7% lignin and 0.9% ash [3]. The curauá fibers are extracted from their leaves and exposed to air to dry. Because of their excellent mechanical properties, curauá fibers are widely used as reinforcement of polymeric composites [3-5].

Achieving a fiber/matrix adhesion, the natural fibers are usually exposed to a chemical treatment to increase the fiber contact region with a polymer. Alkali, silane, acetylation, and benzoylation can be mentioned as chemical reagents most used to treat the surface of the natural fibers [6-7]. This increase in adhesion occurs due to the modification of the fiber structure and chemical composition. As a result, the hydrophilic nature of fiber is reduced, and its compatibility with the matrix increases once the surface roughness of the fiber also increases [5-7].

A wide variety of products to produce polymeric composites is commercially available, and the polyester resin is applied as the main material [9-10]. The polyester resin is a polymer matrix widely used by industry. The resin presents many attractive properties, such as excellent impact resistance, good adhesion properties and resistance to chemical corrosion [10]. The high crosslinking density, in which the binding of the macromolecules occurs, makes the polyester resins high thermally stable and mechanically harder. However, despite these advantageous properties, thermosetting resins are brittle and more predisposed to mechanical failure [12].

Thermogravimetry analyses (TG) is an important technique that is used to understand degradation that occurs in composite materials with the increase of temperature (TG), as well as to evaluate the thermal stability of materials. Its derivative thermogravimetric curves (DTG) provides data indicating the temperature at which specific thermal events occur and show the materials stages of degradation [12-13].

Another technique used to analyse the thermal behavior of composites is the differential calorimetry scanning (DSC), on this technique the physical property measured is the temperature difference between the sample and the reference material, as both are subjected to the same controlled variation of temperature. By this method it is possible to study the curing reaction in composites of thermosetting polymers, thus, determining the temperature at which the polymer curing takes place [14-15].

The objective of this work is to evaluate the thermal behavior of the curauá/ polyester composites, using the polyester resin as a matrix and the curauá fibers as reinforcement, comparing the treated fibers with different alkali to untreated curauá fibers. This comparison will allow a better understanding how the treatment and the fiber content will affect the thermal behavior.

2. EXPERIMENTAL

2.1 Materials

The curauá fibers used in work originated from Santarém - PA and were supplied by CEAPAC. The fibers were available untreated and long, with an average length of 80 cm. The AZ 14.0 infusion polyester resin of the E-composites brand was used as the polymer matrix with the Demelox 14.0 catalyst, both from *DML Produtos Químicos*.

2.2 Fibers chemical modification

The curauá fibers cut to a length of (5-6 cm) were submitted to two different alkali treatments. In the first treatment, the fibers were mercerized in a solution of sodium hydroxide 5% (w/ v) at ratio of 10: 1 (solution: fiber), at a temperature of 50 °C for 2 h under manual stirring. Finally, the fibers were washed with distilled water until neutralized pH, dried at room temperature for 48 h and in an oven for 24 h at 60 °C.

On the second treatment, the fibers were soaked at distilled water in a ratio of 10: 1 (water/ fiber) for 1 h at room temperature and then filtered. The fibers were immersed in a solution of potassium hydroxide 10% (w/ v). The mixture was mechanically stirred at a speed of 50 rpm and orbital agitation of 150 rpm simultaneously for 3 h at room temperature. Subsequently, the fibers were washed with distilled water until pH neutralized, dried at room temperature for 48 h and in an oven for 24 h at 60 °C.

2.3 Preparation of composites

The composites developed in this study were manufactured using the hand lay-up method. The polyester resin was forced through the fibers blankets by a hand roller. The composites with 3 x 5 x 0.2 cm dimensions was cured at room temperature for 24 h.

2.4 Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

The samples were analysed in a simultaneous (TGA-DSC) thermal analyser Q600 SDT equipment (TA Instruments, USA) under an inert atmosphere of nitrogen with a flow rate of 50 mL/min. The samples with 10 ± 0.5 mg were deposited in an alumina pan. The analyses were carried out under a heating rate of 5 °C/ min from 25 to 600 °C (fibers) and 25 to 300 °C (composites).

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric Analyses

Figure 1 shows the thermal degradation curves of the untreated or treated curauá fibers, from the TG-DTG analysis. The thermal behavior of fibers is similar to each other, with a slight thermal stability for NaOH treated fibers. The thermal stability was found at the temperature range between 265 and 273 °C. Residues resulting from the fiber analysis (maximum TGA temperature of 600 °C) were around 12% - 15%. The residues content increases according to the treatments. The free ends of cellulose chains decompose at low temperature, increasing cellulose crystallinity and carbon ratio, resulting in waste content increases at the end of analysis [8, 19].

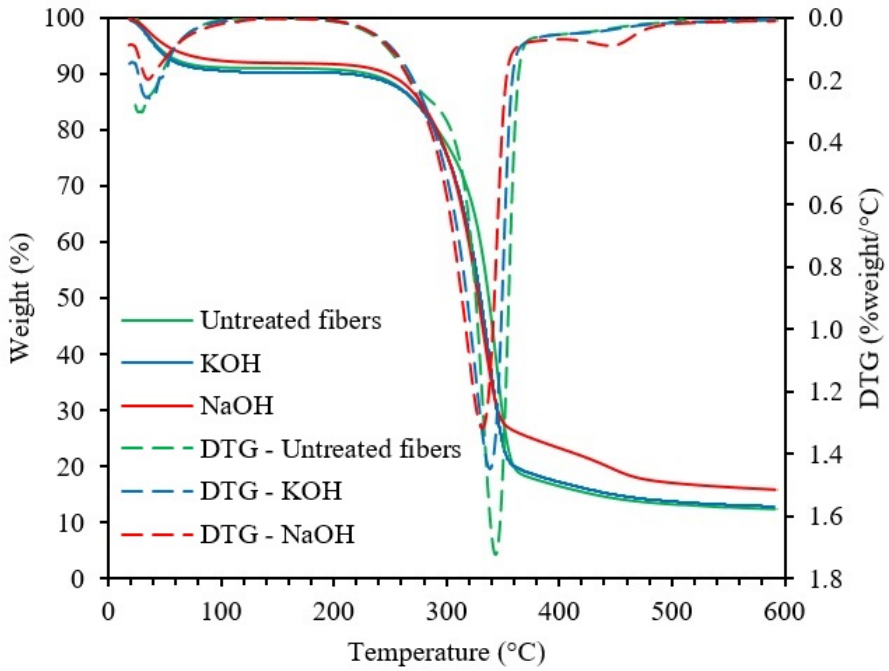

Figure 1: TG and DTG curves for untreated and treated curauá fibers

The DTG curves observed in Figure 1, presented two degradation peaks. The first peak corresponds to the moisture loss of fibers that can be observed at 100 ºC [17]. The second peak that occurs between 270 - 380 °C is attributed to the degradation of cellulose and hemicellulose [17]. The DTG curves also show that the untreated fibers present the maximum decomposition temperature, with T_{peak} around 343 °C and T_{onset} at 268 °C. The fibers treated with NaOH shows T_{peak} at 331 °C and T_{onset} at 273 °C, and the fibers treated with KOH shows T_{peak} of decomposition occurs at 338 °C and T_{onset} at 264 °C.

Table 1 shows the data from the TG-DTG curves for the curauá/ polyester composites. The composites treated with alkali presented the highest thermal stability compared to untreated fibers composites and polyester resin cured. The thermal stability of the composites was found at the temperature range between 251-254 °C.

Table 1: TG and DTG data of the curauá/ polyester composites

Sample	Moisture (%)	T_{onset} (°C)	The residue at 300 °C (%)
Untreated curauá 10 wt%/ polyester	2.97	247.86	81.36
Untreated curauá 20 wt%/ polyester	3.06	247.79	83.19
Curauá treated with KOH 10 wt%/ polyester	3.06	254.23	80.50
Curauá treated with KOH 20 wt%/ polyester	2.90	251.43	80.61
Curauá treated with NaOH 10 wt%/ polyester	2.97	251.95	79.88
Curauá treated with NaOH 20 wt%/ polyester	4.53	254.93	76.53
Polyester resin cured	-	228.17	81.75

3.2 Differential Scanning Calorimetry Analyses

Figure 2 presents the DSC curves of the curauá/ polyester composites. DSC analyses permit to find the glass transition temperature (T_g) and cure behavior of the composite as a function of treatment and fiber content.

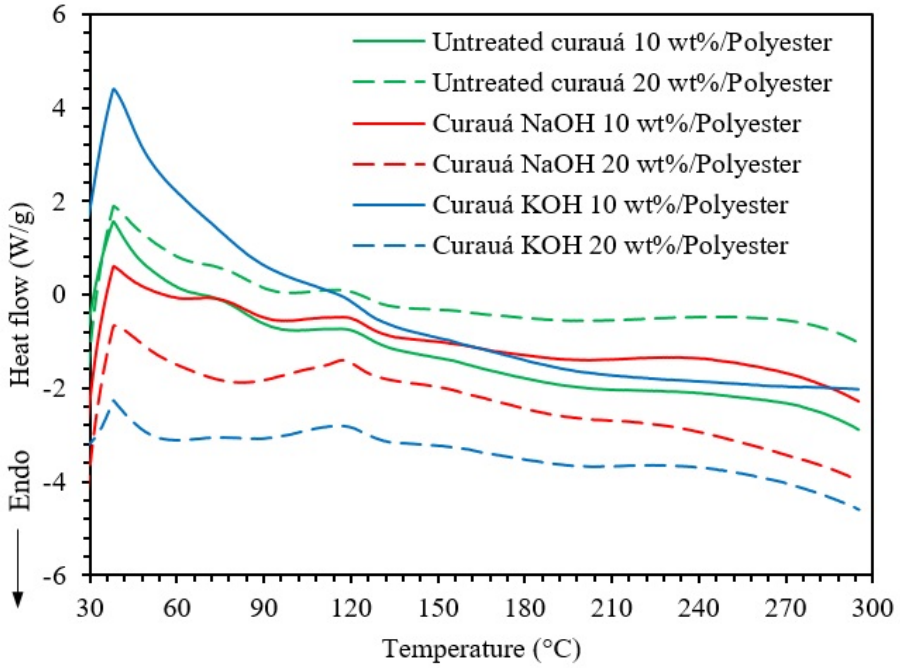

Figure 2: DSC data of the curauá/ polyester composites

Table 2 shows the data from the DSC curves of curauá/ polyester composites. The untreated curauá 10 wt%/ polyester composite showed the residual cure exothermic peak around 118 °C with *ΔH* of 3.19 J/g, while the curauá treated with KOH 20 wt%/ polyester presented the cure temperature at 116 ° C with enthalpy involved in this process of 6.80 J/g. The enthalpy involved in the curing process for alkali-treated composites increased compared to untreated fiber composites. This means that the higher the enthalpy energy could be given for the fiber/ matrix interaction [18].

Table 2: DSC data of the curauá/ polyester composites

Sample	T_g (°C)	T_{peak} cure (°C)	ΔH (J/g)
Untreated curauá 10 wt%/ polyester	91.44	118.69	3.19
Untreated curauá 20 wt%/ polyester	89.80	118.11	3.37
Curauá treated with KOH 10 wt%/ polyester	86.31	117.59	1.84
Curauá treated with KOH 20 wt%/ polyester	83.97	116.62	6.80
Curauá treated with NaOH 10 wt%/ polyester	90.62	119.03	4.44
Curauá treated with NaOH 20 wt%/ polyester	89.47	117.17	6.76
Polyester resin cured	79.32	118.18	3.06

According to the data obtained for enthalpy, the increase of fiber content on the composites decreases the T_{peak} cure of the material. The composites with 20 wt% fiber contents presented the highest enthalpy register on the residual cure stage, in this case, the material needed more energy to move. This is related to the presence of curauá fiber in composites. The bonds between the cellulose chains from fibers tend to increase the enthalpy values [18,19].

It was observed that there was an increase of T_g of composites concerning the T_g of the cured polyester. The increase in T_g is related to a reduction in molecular chain mobility and the increase in the formation of more efficient crosslinks. This phenomen reduces the volume of disordered molecular packaging, in this way, the increases in T_g occurs [20]. It is also noted

that the composites with a lower content of fiber present the highest T_g. This is because the composites with lower fiber content have more resin and less crosslinks mobility, then a higher T_g is required for changes in the molecular structure of the composites [21]. The curing temperature of composites remained practically constant compared to the curing temperature of the polyester.

4. CONCLUSIONS

The alkaline chemical modifications promoted in the curauá fibers a best thermal stability for curauá fibers. The composites reinforced with NaOH and KOH treated fibers were also the most thermally stable when compared to composites untreated fibers. Noted that the T_g of the composites increased comparing to the polyester resin, which implies that a higher T_g is required to cause modification of the composite structure. Consequently, it was concluded that the alkali treatment is effective for curauá fiber to promote thermal stability increase in polymeric composites.

5. ACKNOWLEDGMENTS

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6. REFERENCES

[1] Barreto, A. C. H., Rosa, D. S., Fechine, P. B. A., Mazzetto, S. E., ' Properties of sisal fibers treated by alkali solution and their application into cardanol-based biocomposites', *Composites Part A: Applied Science and Manufacturing.* **42** (2011) 492-500.

[2] Lavoratti, A., Romanzini, D., Amico, S.C., Zattera, A.J., 'Influence of fiber treatment on the characteristics of buriti and ramie polyester composites'. *Polymers & Polymer Composites*. **25** (4) (2017) 247-256.

[3] Spinacé, M. A.S., Lambert, C. S., Fermoselli, K. K.G., De Paoli, M.A.,'Curaua fiber reinforced high-density polyethylene composites: effect of impact modifier and fiber loading',*Carbohydrate Polymers Journal* **77** (2009) 47.

[4] Morais, J. A., Gadioli, R., De Paoli, M. A., 'Recycled polypropylene reinforced with curaua fibers by extrusion', *Journal of Applied Polymer Science*. **26** (2) (2016) 115-122.

[5] Nacas, A. M., Silva, R.L., De Paoli, M. A., Spinacé, M.A. S., 'Polypropylene composite reinforced with fibrillated curaua fiber and using maleic anhydride as coupling agent'. *Journal of Applied Polymer Science.* **113** (44913) (2017) 1-8.

[6**]** Kabir, M.M., Wang, H., Lau, K.T., Cardona, F., 'Chemical treatments on plant-based natural fibre reinforced polymer composites: an overview', *Composites Part B: Engineering*. **43** (2012) 2883-2992.

[7] Nimanpure, S., Hashmi, S.A.R., Kumar, R., Bhargaw, H.N., Kumar, R., Nair, P., Naik, A., 'Mechanical, electrical, and thermal analysis of sisal fibril/kenaf fiber hybrid polyester composites', *Polymer Composites*. (2017) 1-13.

[8] Harnnecker, F., Rosa, D.S., Lenz, D. M., 'Biodegradable polyester-based blend reinforced with curauá fiber: thermal, mechanical and biodegradation behaviour', *Journal of Polymers and the Environment.* **20** (2012) 237–244.

[9] Rossi, G., Giannakopoulos, I., Monticelli, L., Rostedt, N. K. J., Puisto, S.R., Lowe, C., Taylor,A. C., Vattulainen, I., T.A. Nissila., 'A martini coarse-grainedmodel of a thermoset polyester coating', *Macromolecules.* **44** (2011) 6198–6208.

[10] Wang, B., Qian,T., Zhanga, Q., Zhana, X., Chen, F., 'Heat resistance and surface properties of polyester resin modified with fluorosilicone', *Surface & Coatings Technology.* **304** (2016) 31–39.

[11] He, S., Petkovich, N. D., Liu, K., Qian, Y., Macosko, C. W., Stein, A,'Unsaturated polyester resin toughening with very low loadings of GO derivatives', *Polymer*. **110** (2017) 149-157.

[12] Mothé, C.G., Araújo C.R., 'Properties of polyurethane elastomers and composites by thermal analysis', *Thermochimica Acta*. **14** (2000) 357-358

[13] Jayaraman, K., Kok, M. V., Gokalp, I., 'Thermogravimetric and mass spectrometric (TG-MS) analysis and kinetics of coal-biomass blends', *Renewable Energy.* **101** (2017) 293-300.

[14] Kazilas, M. C., Partridge, I. K., 'Exploring equivalence of information from dielectric and calorimetric measurements of thermoset cure a model for the relationship between curing temperature, degree of cure and electrical impedance', *Polymer*. **46** (2005) 5868–5878.
[15] Papadopoulos, E., Markovic, M.G., Clarke, S., 'A Thermal and rheological investigation during the complex cure of a two-component thermoset polyurethane', *Journal of Applied Polymer Science*. **114** (2009) 3802–3810.
[16] Roman, M., Winter, W. T., 'Effect of sulfate groups from sulfuric acid hydrolysis on the thermal degradation behavior of bacterial cellulose', *Biomacromolecules.* (5) (2004) 1671-1677.
[17] Monteiro, S. N., Calado, V., Rodriguez, R. J.S., Margem, F. M., 'Thermogravimetric stability of polymer composites reinforced with less common lignocellulosic fibers', *Journal of Materials Research and Technology*. **1** (2) (2012) 117-126.
[18] Song, W., Zhao, F., Yu, X., Wang, C., Wei, W., Zhang, S., 'Interfacial characterization and optimal preparation of novel bamboo plastic composite engineering materials', *BioResources.* **10** (3) (2015) 5049-5070.
[19] Saw, S.K., Datta, C., 'Thermomechanical properties of jute/bagasse hybrid fibre reinforced epoxy thermoset composites', *BioResources* **4** (4) (2009) 1455-1476.
[20] Boey, F. Y. C., Lee, T. H., Sullivan, P. L., 'High-pressure autoclave curing for a thermoset composite: effect on the glass transition temperature', *Journal of Materials Science*. **29** (1994) 5985-5989.
[21] Bachtiar, D., Sapuan, S. M., Abdan, K., Zaman, K., 'The flexural, impact and thermal properties of untreated short sugar palm fihre reinforced high impact polystyrene (HIPS) composites', *Polymers & Polymer Composites*. **20** (5) (2012) 493-502.