INFLUENCE OF LAURIC ACID ON THE THERMAL PROPERTIES IN THE RECYCLED POLYPROPYLENE/BAMBOO FIBER COMPOSITE

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Abstract
The global movement towards the use of natural, renewable, and biodegradable resources for the development of new materials has increased, highlighting the research on composites using vegetable fiber as reinforcement. Based on this search, this study aims to analyze the influence of lauric acid (LA) as a coupling agent in thermoplastic composites with recyclable polypropylene (PPr) matrix reinforced with bamboo fibers (FB) through thermal properties. The samples were characterized using thermogravimetry (TGA) and differential scanning calorimetry (DSC) techniques. The results showed that the use of lauric acid as a coupling agent promoted a greater fiber-matrix interaction and caused a positive influence on the thermal stability of the PPr/FB/LA composites. In conclusion, the use of carboxylic acids can be a sustainable option to replace the use of coupling agents of synthetic origin.
Keywords: *thermoplastic composites, polypropylene, bamboo fiber, lauric acid, injection molding.*

Introduction

Interest in obtaining sustainable materials has grown in recent years. In search of sustainability, interest in thermoplastic composites reinforced with fibers from renewable sources arose, specifically vegetable fibers. These fibers, also known as lignocellulosic fibers, when used as reinforcing agents, confer certain benefits such as low density, high specific strength, and high modulus [1]. Due to its promising properties, the development of products using thermoplastic composites is growing. Currently, these materials are found in several applications, such as aerospace, automotive, sports, architectural components, among others.

Among the various types of existing vegetable fibers, the bamboo of the species *Guadua angustifolia*, has been evidenced due to its physical-mechanical properties, large size and proven use in the industry. For the choice of thermoplastic matrix, the characteristics and ease of processing of recycled polypropylene (PPr) stand out among the several commonly used thermoplastic polymers. The polypropylene (PP) is a low-cost polymer, easily moldable, high chemical resistance, good mechanical resistance, and thermal stability [2]. These excellent combinations of properties allow for a wide variety of applications for this material.

Despite the advantages of using vegetable fibers as reinforcements, these have some limitations due to their lack, or weak, interfacial adhesion. This incompatibility, due to the difference in polarities between the polymeric matrix (non-polar) and the vegetable fiber (polar), can be improved by means of treatments (chemicals and/or physicals) on the surface of vegetable fibers or by the incorporation of compatibilizing agents in the fiber-matrix mixture [3]. In the research and development sector of composite materials, one of the most used additives for this purpose are the polyolefins functionalized with maleic anhydride, such as PP-g-MA. However, based on the idea of sustainability and the selection of materials from renewable sources, the use of organic acids

becomes attractive and innovative. According to studies [4], organic acids such as caproic, caprylic, capric and lauric acid are already being used as compatibilizing agents. To fulfill this function, in the present study, was opted to experiencing lauric acid; medium chain saturated fatty acid, present in palm kernel and coconut oils [5].

Therefore, the present study aims to evaluate the thermal properties of raw materials in their pure state (bamboo fiber, FB and PPr), as well as, of the composite material developed (PPr/FB) and the influence of the incorporation of lauric acid as a coupling agent (PPr/FB/LA).

Experimental
Materials
For the formulation of composites, was selected the recycled polypropylene (PPr) as a polymeric matrix, coming from soft drink bottle caps; bamboo fiber (FB) as a reinforcement and lauric acid (LA) as a coupling agent. The compositions, in percentage of mass, of the evaluated samples are specified in Table 1.

Table 1 – Formulation of samples.

Sample	PP (wt %)	FB (wt %)	LA (wt %)
PPr	100	-	-
PPr/FB	70	30	-
PPr/FB/LA	67	30	3

Then, the materials were mixed and homogenized in the HAAKE Rheomix OS Polylab chamber to obtain the composite material. This mixture underwent a process of reduction of granulometry and, later, the specimens were made by the injection molding process.

Characterization Methods
The thermal characterization of the samples was carried out using the techniques of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). To perform the analysis related to the mass variation as a function of temperature, was used TGA equipment [Q50, TA Instruments] programmed in the temperature range of 25 to 1000 °C with a heating rate of 20 °C/min, under an N_2 atmosphere, as established in the ASTM E-1131 standard [6]. And, to obtain the melting temperatures and crystallization enthalpies of the samples, it was used DSC equipment programmed in the temperature range of 25 to 200 °C with a heating/cooling ramp of 10 °C/min, under an N_2 atmosphere, according to the ASTM D-3418 standard [7].

Results and Discussion
Thermogravimetric Analysis (TGA)
To evaluate the thermal stability and degradation of samples, the TGA/DTG thermogravimetric analysis was used. In Fig. 1 are presented the thermogravimetric curves (TGA) and the derived from thermogravimetric curves (DTG) of the samples FB, PPr, PPr/FB and PPr/FB/LA.

In this comparative analysis between the TGA curves (Fig. 1-a), it is observed that FB has four stages of mass loss, the first corresponds to moisture (due to its hydrophilic character), the second to hemicellulose, the third in greater mass proportion to cellulose and the fourth to lignin. On the other hand, for the injected PPr sample, only one stage of decomposition is observed, corresponding to the polymeric matrix.

For composites samples, it can be observed three stages of decomposition. The first stage occurs below 100 ºC, corresponding to a small loss of mass due to the moisture of the fibers. The second and third stage, between 250 and 375 ºC, where a shoulder and a maximum peak occurs, corresponds to the degradation of the fibers (hemicellulose and cellulose, respectively). In the

fourth stage, between 400 and 550 ºC, the greatest loss of mass occurs, corresponding to the decomposition of the polymer. And lastly, it follows a slow degradation, which may correspond to lignin and residues/ashes present in the samples.
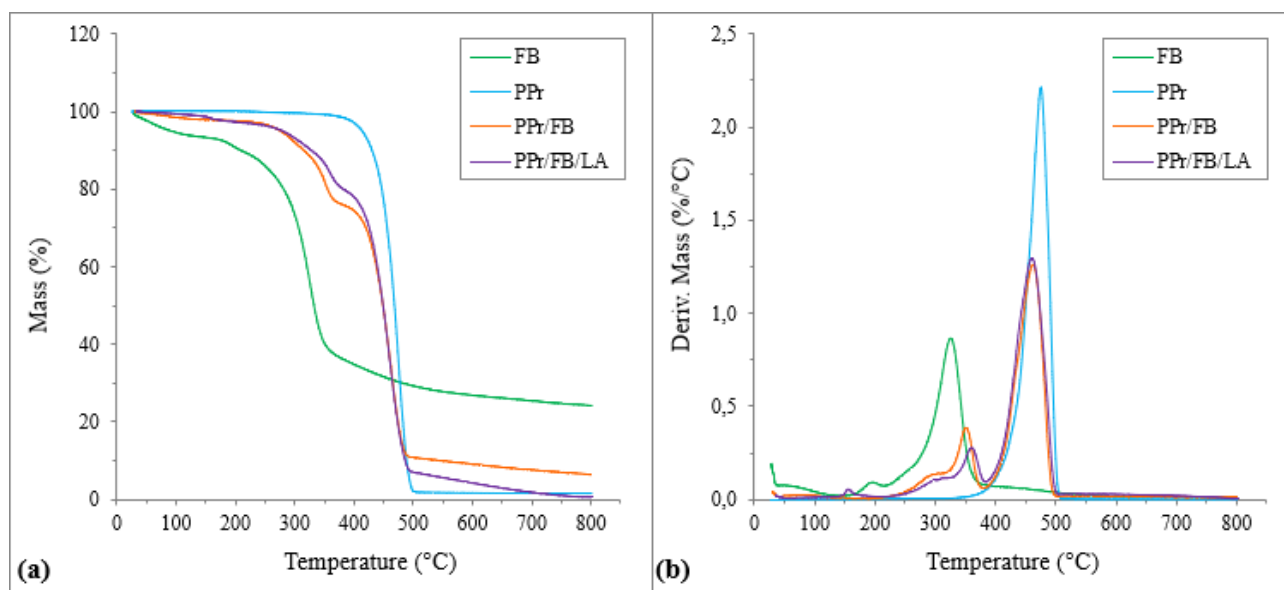

Figure 1 – Curves of the analyzed samples: (a) TGA and (b) DTG.

Fig. 1-b, the DTG curves complement and confirm the information obtained in the TGA curves. In these curves, it can be observed a peak temperature with maximum decomposition rate, corresponding to the PPr. Already the composites feature a shoulder and two peaks, being the shoulder and the peak of lesser intensity (300 - 400 ºC) corresponding to the FB components and the highest intensity peak (400 - 500 ºC), corresponding to the polymeric matrix (PPr). The results obtained through the analysis of the TGA/DTG curves of the samples are found in Table 2, where "T_p" is peak temperature of each decomposition stage.

Table 2 – Results of the thermal properties (TGA/DTG) of the analyzed samples.

Sample	TGA				DTG			
	T (°C) 10% wt	PP (%)	FB* (%)	Ash (%)	1st T_p (°C)	2nd T_p (°C)	3rd T_p (°C)	4th T_p (°C)
FB	208.80	-	75.80	24.20	65.79	193.30	325.75	534.12
PPr	430.50	98.40	-	1.60	-	-	-	475.50
PPr/FB	315.20	65.33	28.22	6.44	80.37	285.84	351.91	462.23
PPr/FB/LA	328.00	72.88	26.32	0.55	156.07	298.16	361.16	460.84

* included the loss of moisture mass and fiber extractives.

Differential Scanning Calorimetry (DSC)

According to Canevarolo [8], the monitoring of the melting process allows the study of a series of phenomena related to the structure and properties of polymers, such as the identification of mixtures. To perform the identification of the polymeric matrices that make up a sample from recycling, must be made a comparison of the melting temperature peaks obtained through the second scan by DSC with the T_f values obtained in the literature for thermoplastic polymers. Thus, for the present study, the thermal analysis by DSC was performed through three scans, where the first heating aims to eliminate the previous thermal history of the samples, followed by a cooling to obtain crystallization temperature data (T_c) and the second heating to obtain the melting temperature

data (T_f) and melting enthalpy (ΔH_f) the samples. Fig. 2 shows the comparative DSC curves of the PPr, PPr/FB e PPr/FB/LA samples.
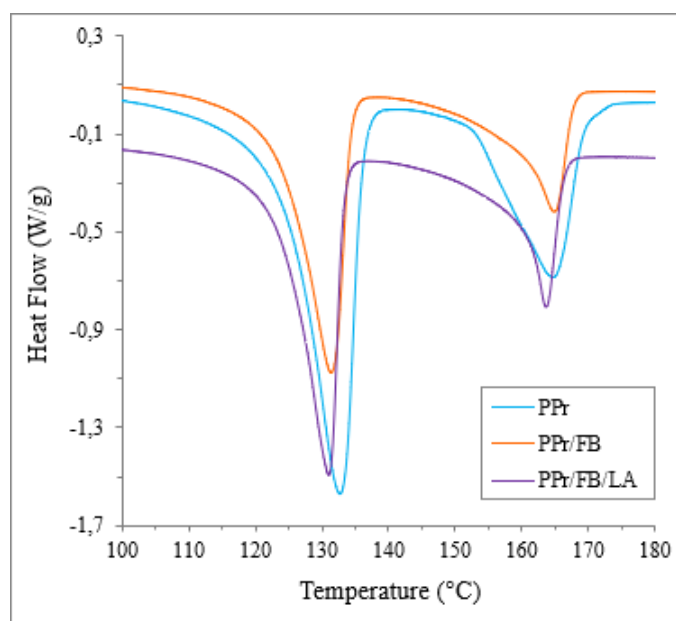

Figure 2 – 2nd heating curves of the samples analyzed using the DSC technique.

Analyzing the graph (Fig. 2) it is possible to observe that, for all samples, there are two melting peaks. According to the melting temperature reference values of the thermoplastic polymers [8], it can be inferred that the first endothermic event (131.7 ºC) corresponds to the melting of high-density polyethylene (HDPE) and the second endothermic event (164.4 ºC) the melting of polypropylene (PP). That is, the appearance of two melting peaks in the curves of all samples is an indicative that the recycled polymer matrix (PPr) is, in reality, a PP/HDPE blend; probably not all caps collected were made of PP.

In that case, it is necessary to determine the content of each of the phases of the polymers that make up the PPr sample to subsequently determine the degree of crystallinity of the samples. Thus, considering the reference value of the melting enthalpy of pure polymers it is possible to calculate the content of the polymer phase in each mixture using the Eq. 1. And, through Eq. 2, to determine crystallinity index of the samples.

$$\%Pol = \Delta H_f / \Delta H_{Pol} * 100\% \tag{1}$$

where, [% Pol] is polymer content (PP or HDPE); [ΔH_f] is melting enthalpy of the polymer in the sample; and [ΔH_{Pol}] is melting enthalpy of the pure polymer.

$$X_c = \Delta H_f / (W * \Delta H_f^o) * 100\% \tag{2}$$

where, [X_c] is crystallinity index; [ΔH_f] is melting enthalpy of the sample; [ΔH_f^o] is melting enthalpy of the PP, hypothetically, 100% crystalline. In literature [8], the most frequent value found for the melting enthalpy of PP is 209 J/g and of HDPE 293 J/g; and [W] is mass fraction of the polymers in each sample.

The results obtained through DSC analysis and calculation the degree of crystallinity of the samples, are presented in Table 3. As expected, there was no significant difference (± 1ºC) in the melting temperatures of the samples, but it was verified a variation in their enthalpies.

Table 3 – Melting temperature, melting enthalpy and degree of crystallinity of the samples.

Sample	1st Endothermic Event - HDPE				2nd Endothermic Event - PP			
	HDPE (%)	T_f (°C)	ΔH_f (J/g)	X_c (%)	PP (%)	T_f (°C)	ΔH_f (J/g)	X_c (%)
PPr	44.57	132.69	87.53	67.03	55.43	164.75	45.31	39.11
PPr/FB	32.37	131.37	55.34	58.35	37.63	164.93	26.78	34.05
PPr/FB/LA	30.86	131.01	56.90	62.93	36.14	163.64	27.74	36.73

According to studies [9], this reduction in the value of the melting enthalpy of composite materials may be related to the presence of the vegetable load, because the fibers make it difficult to packaging macromolecules. Fig. 2, it is also possible to observe that the melting peaks corresponding to the PP of composites are wider and less intense when compared to that of pure polymer, corroborating with the studies that indicate that the fiber hinders the crystallization of the composite material. However, when adding lauric acid, the fiber-matrix interaction is increased, and consequently, there is an increase in the degree of crystallinity of the PPr/FB/LA composite, as shown in Table 3.

Conclusions

Based on the results obtained in the present study, it can be concluded that the incorporation of lauric acid to the composites provided an increase in the degree of crystallinity and, therefore, a greater thermal stability. Thus, it is evident that the use of a polymeric matrix from recycling, as well as the reinforcement and compatibilizing agent of natural origin, presents itself as a good alternative for obtaining new sustainable and eco-friendly materials.

Acknowledgements

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