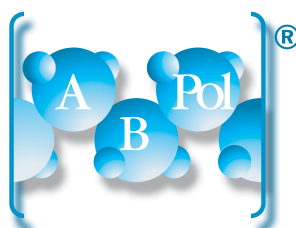


17º Congresso Brasileiro de Polímeros

29 de Outubro a 02 de Novembro de 2023

Joinville - SC

ANAIS



Associação Brasileira de Polímeros

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Dados Internacionais de Catalogação na Publicação (CIP)
(Câmara Brasileira do Livro, SP, Brasil)

Congresso Brasileiro de Polímeros (17. : 29 out. - 2
nov. 2023 : Joinville, SC)

Anais do 17° Congresso Brasileiro de Polímeros
[livro eletrônico] / organização Associação Brasileira
de Polímeros. -- Joinville, SC : Aptom Software, 2023.

PDF

Vários colaboradores.
ISBN 978-85-63273-55-0

1. Polímeros 2. Polímeros e polimerização
3. Química - Congressos I. Título.

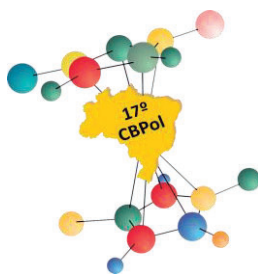
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CDD-540

Índices para catálogo sistemático:

1. Química : Congressos 540

Eliane de Freitas Leite - Bibliotecária - CRB 8/8415



INFLUENCE OF DIFFERENT ORGANIC ACIDS AS COUPLING AGENTS ON THE THERMAL PROPERTIES OF HDPE_{pc}/CURAUA FIBER COMPOSITE

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Abstract - The search for sustainable materials has led to the increased use of thermoplastic composites reinforced with fibers from renewable sources, mainly vegetable fibers. However, chemical treatments and coupling agents are often necessary to improve interfacial fiber-matrix adhesion due to these fibers' hydrophilic nature. Thus, one of the current challenges is to find a method to improve this adherence efficiently and sustainably. As an alternative, the present study aims to analyze the influence of different organic acids as a coupling agent in composites with post-consumer high-density polyethylene (HDPE_{pc}) matrix reinforced with curaua fiber (FC). The samples were characterized using thermogravimetric (TGA) and differential scanning calorimetry (DSC) techniques. The results showed that, like the effect observed with maleic anhydride grafted polyethylene (PEgAM), using organic acids improves the thermal stability of the HDPE_{pc}/30FC composites. Suggesting that using organic acids can be a viable alternative to chemical treatments and coupling agents of synthetic origin.

Keywords: *coupling agent, high-density polyethylene, curaua fiber, injection molding, thermoplastic composite.*

Introduction

The use of recycled materials and natural fibers in the production of composites has become increasingly common in recent years, aiming at environmental sustainability and cost reduction [1-3]. However, due to these fibers' hydrophilic nature, chemical and physical treatments and coupling agents are often necessary to improve adhesion between the natural fibers and the recycled polymeric matrix [4]. Thus, one of the current challenges of this process is to find a method to improve fiber-matrix adhesion efficiently and, at the same time, sustainably. Coupling agents of organic origin are being researched for their use as coupling agents in composites reinforced with vegetable fibers as an alternative to synthetic coupling agents to solve this problem [5-7]. Castro *et al.* used canola and castor oil as coupling agents in high-density biopolyethylene (HDBPE) composites reinforced with curaua fiber (FC). The authors reported that incorporating vegetable oils could be used to modify the properties of the fiber-matrix interfaces for materials prepared from hydrophilic fibers, such as lignocellulosic fibers, and hydrophobic matrices, such as HDBPE [5]. Poletto, Zattera, and Santana, in addition to maleic anhydride grafted polypropylene (PPgAM), used hexanoic (C6), octanoic (C8), decanoic (C10), and dodecanoic (C12) acids as coupling agents in recycled polypropylene (PPr) composites reinforced with wood flour. The authors observed that using organic acids improved interfacial adhesion and, consequently, improved the mechanical and thermal properties of the materials [6]. Lima used citric acid, lauric acid, palmitic acid, and PPgAM as coupling agents in PP/Bamboo Fiber composites. The author reported that among the organic acids, citric and palmitic acids showed similar behavior to PPgAM regarding the composite materials' mechanical, physical, and thermal properties [7].

Based on the positive results observed with the use of oils and organic acids, it is certainly justifiable to carry out new studies that explore the use of different types of organic acids as coupling agents, highlighting citric acid ($C_6H_8O_7$), found naturally in many citrus fruits such as lemons, oranges, and tangerines; the malic acid ($C_4H_6O_5$), found naturally in various fruits, such as apples, pears, and grapes, and is also present in some plants and animals; the tartaric acid ($C_4H_6O_6$), who can be found naturally in many fruits, such as grapes, dates, and bananas, as well as some plants, such as tamarind; and the myristic acid ($C_{14}H_{28}O_2$), a saturated fatty acid, found naturally in many plants and animals, including nuts, seeds and vegetable oils [8, 9].

In short, organic acids are natural chemical compounds that can be found in various organic sources such as plants, fruits, flowers, and other living organisms [10]. These compounds can have a wide range of properties, including the ability to bind to other components, which makes them potential coupling agents in polymer matrix composites reinforced with plant fibers. Therefore, to replace the synthetic coupling agent, PEGAM, with an organic coupling agent, the present study aims to analyze the influence of different organic acids on compatibilized reinforced post-consumer high-density polyethylene (HDPEpc) composite materials with curaua fiber (FC).

Experimental

Materials

For the formulation of composites, was selected the post-consumer high-density polyethylene (HDPEpc) as a polymeric matrix, coming from jars/packaging of manipulated products; curaua fiber (FC) as reinforcement; maleic anhydride grafted polyethylene (PEGAM) as synthetic coupling agent. And to find an alternative for PEGAM were used as organic acids, citric acid (AC), malic acid (AMá), myristic acid (AMi), and tartaric acid (AT) from Êxodo Científica. The compositions, in percentage of mass, of the evaluated samples are specified in Table 1.

Table 1 – Samples' Formulation.

Sample	HDPEpc (%)	FC (%)	Coupling Agent (%)
HDPEpc	100	-	-
s/AA	70	30	-
PEGAM	67	30	3
AC	67	30	3
AMá	67	30	3
AMi	67	30	3
AT	67	30	3

Then, the materials were mixed and homogenized in the *HAAKE Rheomix OS PolyLab* mixing chamber to obtain the composite material. This mixture underwent a process of granulometry reduction, and later, the specimens were made by the injection molding process in a *Mini-Jet II* piston injector.

Characterization Methods

The thermal characterization of the samples was conducted 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 N₂ atmosphere (10 mL/min), as established in the ASTM E-1131 standard. And to obtain the melting temperatures and enthalpies of the samples, it was used DSC equipment, *Q20 - TA Instruments*, programmed in the temperature range of 25 to 200 °C with a heating/cooling ramp of 10 °C/min, under an N₂ atmosphere (50 mL/min), according to the ASTM D-3418 standard.

Results and Discussion

Thermogravimetric Analysis (TGA)

The TGA/DTG thermogravimetric analysis evaluated the samples' thermal stability and degradation. In Fig. 1 are presented the thermogravimetric curves (TGA) and the derived from thermogravimetric curves (DTG) of the samples analyzed.

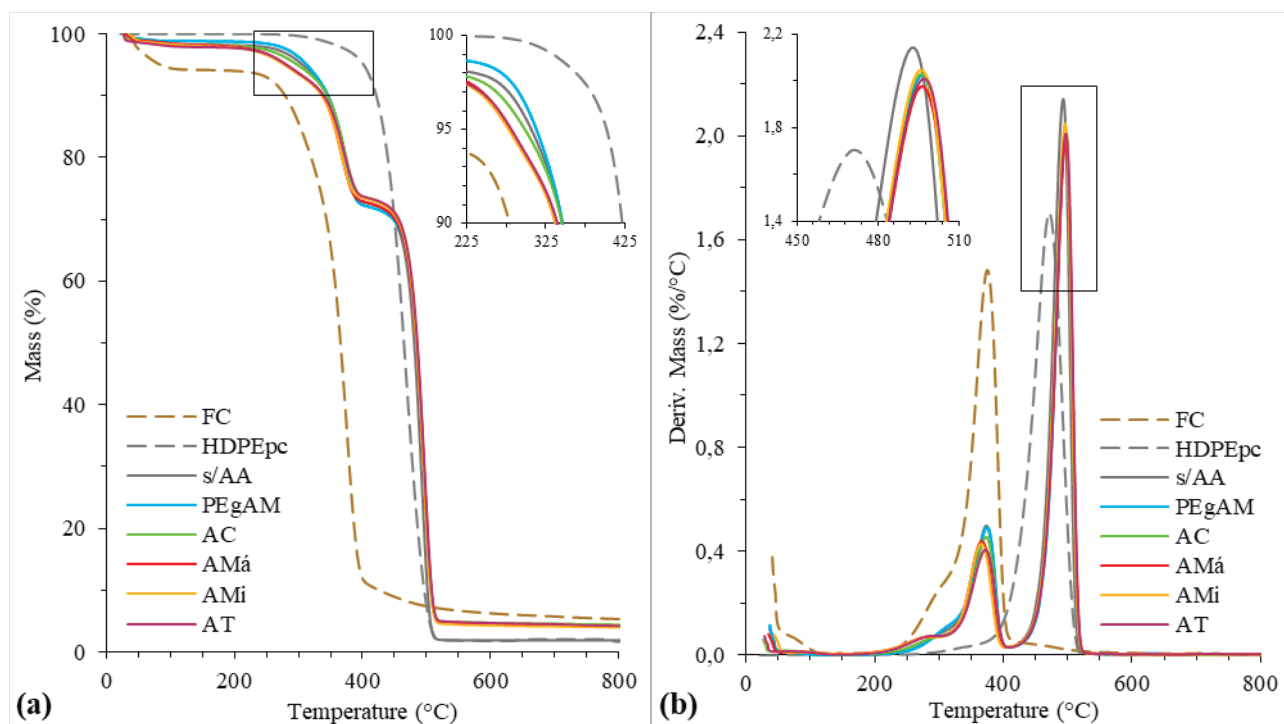


Figure 1 – Curves of the analyzed samples: (a) TGA and (b) DTG.

In Fig. 1-a, it is observed that the FC has three stages of mass loss, the first corresponds to moisture and some low molecular weight extractives present in plant fibers, the second to hemicellulose and to cellulose (in a more significant proportion of mass) and the third to lignin. In counterpart, for the injected HDPEpc sample, only one stage of decomposition is observed, corresponding to the polymeric matrix. In turn, two principal decomposition stages can be observed for samples of composite materials. The first stage, between 250 and 400 °C, where a shoulder and a maximum peak occur, corresponds to fiber degradation (hemicellulose and cellulose, respectively). In the second stage, between 425 and 525 °C, the most significant loss of mass occurs, corresponding to the decomposition of the polymer. Moreover, lastly, it follows a slow degradation, which may correspond to lignin and residues/ashes present in the samples.

In Fig. 1-b, the DTG curves complement and confirm the information obtained from the TGA curves. In the composites, one shoulder and two peaks can be observed, with the shoulder and the peak having the lowest intensity (between 250 and 400 °C) corresponding to the components of the curaua fiber and the highest intensity peak (between 425 and 525 °C), corresponding to the polymeric matrix, HDPEpc.

As shown in the approximation of Fig. 1-a, initially, the PEGAM and s/AA samples showed greater thermal resistance, which may be due to the influence of impurities and other extractives more resistant to decomposition present in these samples. However, after a 10% mass loss, the AC composite acquired a thermal resistance analogous to the PEGAM sample. Other authors observed similar behavior, suggesting that the composites coupled with citric acid have a more significant interfacial interaction due to the reaction of the functional groups of citric acid and the hydrophilic groups on the surface of the curaua fiber [7]. The results obtained through the analysis of the TGA/DTG curves of the samples are shown in Table 2.

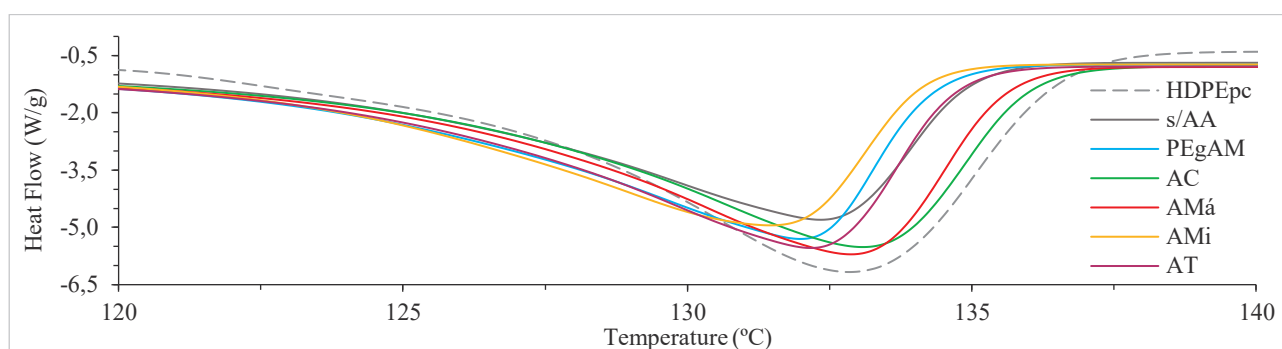
Table 2 – Results of the analyzed samples' thermal properties (TGA/DTG).

Sample	TGA					DTG	
	T (°C) 5%wt	T (°C) 10%wt	HDPEpc (%)	FC* (%)	Ash (%)	1st T _p (°C)	2st T _p (°C)
FC	84.47	279.14	-	95.03	4.97	375.30	-
HDPEpc	401.63	421.42	98.12	-	1.88	-	471.35
s/AA	306.52	345.30	70.94	27.16	1.90	373.85	493.01
PEgAM	313.05	345.94	68.50	27.69	3.81	374.81	496.48
AC	298.43	345.43	69.66	26.35	3.99	373.18	496.03
AMá	280.39	337.60	69.09	27.08	3.83	366.61	496.54
AMi	278.02	336.94	69.72	26.50	3.78	365.80	496.08
AT	281.31	339.54	69.77	26.27	3.96	372.04	497.26

* Included the loss of moisture mass and fiber extractives.

Differential Scanning Calorimetry (DSC)

To evaluate the thermal behavior and the effect of different coupling agents us the composite materials (HDPEpc/30FC), a thermal analysis by DSC was conducted through three scans. Fig. 2 shows the curves obtained through the second heating of the DSC technique.

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

In Fig. 2, it can be observed that the composites' melting peaks are less intense than the peak of HDPEpc, suggesting that the fiber may be affecting the crystallization of the composite material. This could be due to several factors, including the size, shape, and orientation of the fibers, as well as their interaction with the polymeric matrix. These results corroborate previous studies, which indicated that the presence of FC can hinder the crystallization of the composite material, reducing the mobility of the polymeric chains in the region close to the fibers [11]. Data obtained through the DSC curves were used to calculate the degree of crystallinity of the samples with Eq. 1.

$$X_c = \frac{\Delta H_m}{(\Delta H_m^0 \times W)} \times 100\% \quad (1)$$

Where (X_c) is the crystallinity index; (ΔH_m) is the melting enthalpy of the sample; (ΔH_m⁰) is the melting enthalpy of the PEAD, hypothetically, 100% crystalline. In literature [12], the most frequent value found for the melting enthalpy of HDPE is 293 J/g; and (W) is the mass fraction of the polymers in each sample.

As shown in Table 3, the s/AA sample has a low degree of crystallinity, 67.33%, when compared to the other analyzed composites. However, it is noted that there was an increase in the degree of crystallinity of the AC and AMá samples, indicating an improvement in the fiber-matrix interaction, where the composites were compatibilized with organic acids that also can act as a flow agent [7]. Furthermore, when compared to the s/AA composite, the addition of coupling agents in the

HDPEpc/30FC composites caused an increase in the enthalpy of fusion, highlighting AMá. This higher energy required for melting to occur suggests that the addition of organic acids provides better adhesion between the phase fiber-matrix of the composite material. This is because when a material melts, it is necessary to provide energy for the molecules to separate and for the material to change phase. If there is a strong interaction between the phases because of using a coupling agent, this required energy may be greater [13].

Table 3 – Melting temperature (T_m), melting enthalpy (ΔH_m), and degree of crystallinity (X_c) of the samples.

Sample	T_m (°C)	ΔH_m (J/g)	X_c (%)
HDPEpc	132.87	241.40	87.55
s/AA	132.39	138.10	67.33
PEgAM	132.00	152.00	77.43
AC	133.09	162.60	82.83
AMá	132.88	167.80	85.48
AMi	131.46	148.40	75.59
AT	132.16	159.10	81.05

Conclusions

Based on the results obtained in the present study, it can be concluded that incorporating organic acids into the composite materials was beneficial for the thermal stability and the degree of crystallinity of the materials, as well as the addition of the synthetic coupling agent, PEGAM. Thus, it is evident that using organic acids can be a viable and sustainable alternative to chemical treatments and coupling agents of synthetic origin. Furthermore, using a recycled polymeric matrix combined with reinforcement and compatibilizer of natural origin appears as an excellent option to produce environmentally sustainable materials.

Acknowledgements

We are grateful to the Laboratory of Polymeric Materials (LaPol) of UFRGS, CAPES, and CAPES PROEX for all the support for elaborating this research.

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