Processing and Thermal Properties of Composites Based on Recycled PET, Sisal Fibers, and Renewable Plasticizers

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ABSTRACT: This investigation focuses on the preparation of bio-based composites from recycled poly (ethylene terephthalate) (PET) and sisal fibers (3 cm, 15 wt %), via thermopressing process. Plasticizers derived from renewable raw materials are used, namely, glycerol, tributyl citrate (TBC) and castor oil (CO), to decrease the melting point of the recycled PET ($T_m \sim 265°C$), which is sufficiently high to initiate the thermal decomposition of the lignocellulosic fiber. All used materials are characterized by thermogravimetric analysis and differential scanning calorimetry, and the composites are also characterized via dynamic mechanical thermal analysis. The storage modulus (30°C) and the tan δ peak values of CT [PET/sisal/TBC] indicate that TBC also acts as a compatibilizing agent at the interface fiber/PET, as well as a plasticizer. To compare different processing methods, rheometry/thermopressing and compression molding are used to prepare the recycled PET/sisal/glycerol/CO composites. These two different methods of processing show no significant influence on the thermal properties of these composites. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40386.

INTRODUCTION

The replacement of traditional materials, the processing methods of which are energy-intensive, by those from renewable/natural sources has attracted significant attention in recent decades.[1–4] Natural materials, such as lignocellulosic fibers, are important because they save energy during their processing, are derived from renewable sources and are biodegradable. These materials are carbon-neutral, which has a significantly positive impact on the atmospheric greenhouse effect and global warming.[5–7] Thus, the use of bio-based composite materials, such as polymeric composites reinforced by natural fibers, has emerged as one of the solutions to these complex environmental and sustainability problems.[8,9]

The demand for composites reinforced by lignocellulosic fibers, such as sisal fibers, has considerably increased in recent years.[2,10,11] This fiber is obtained from the leaves of the species *Agave sisalana* and is one of the major hard fibers produced throughout the world. Its production corresponds to approximately 70% of all commercial production of this type of fiber.[12]

Sisal was chosen for the present work because it has previously shown excellent properties as a reinforcement of polymeric matrices[13–15] and Brazil is the largest producer and exporter of sisal.[12]

Another challenge faced by modern society is the generation of urban waste, which is generated at a rate that outpaces the recycling rate. This fact reflects the current time of transition in the global economy; new economies are emerging, and their trade is intensifying.[16,17] In recent years, the amount of polymers disposed as urban solid waste has increased. This primarily consists of disposable packaging materials.[17,18] Due to their resistance to biodegradation and possible formation of toxic pollutants, the residues of polymeric materials represent a high risk to human health and the environment.[16,19,20]

The production of poly(ethylene terephthalate) (PET) corresponds to 5.9 wt % of the total amount of polymers produced in the world (9 wt % in Brazil), but represents approximately 20 wt % of the total amount of polymers present in urban solid waste.[18] This discrepancy can be explained by the final use of the polymer. While polymers such as polypropylene and polyvinyl chloride are mainly used as raw materials for the manufacture of long-life products by the consumer goods industry and civil construction, PET is widely used in short-life products, such as packaging.[18,21] Thus, the development of research that

leads to recycled PET-derived materials with favorable properties and prices, such as composites, is necessary. Brazil was the second largest PET recycler in the world, surpassed only by Japan.[22] In 2011, Brazil spent approximately 294 kton of packaging from post-consumer PET, representing 57.1% of the total of disposed packaging.[23]

Thus, sisal fiber was chosen in this article as reinforcing agent of composites prepared from recycled PET as a polymeric matrix in attempt to add value to lignocellulosic fibers and to recycled PET.

The processing of PET/lignocellulosic fibers composites is hindered by the thermal stability of the fibers. The melting temperature (T_m) of PET is approximately 265°C, which is sufficiently high to initiate the thermal decomposition of the fibers; hemicellulose decomposes above 200°C, followed by cellulose. Lignin decomposes above approximately 400°C, which is accompanied by the complete loss of the native structure of the fiber.[2,24] Thus, if the polymer coating is not sufficient to shift the decomposition of the fibers to higher temperatures, the addition of plasticizers is necessary to decrease the melting temperature of PET.[25–27]

Zou et al.[28] investigated the effect of the addition of plasticizers, such as glycerol and 2-phenyl phenol, at concentrations up to 10 wt % on the preparation of PET composites reinforced with cotton fibers. In this article, the authors reported that the addition of the plasticizers decreased the melting temperature of PET to 241°C, as indicated by differential scanning calorimetry (DSC) analysis.

Due to the presence of hydrophilic groups in lignocellulosic fibers and the hydrophobic characteristic of PET, the composites prepared from these components can show weak fiber–matrix adhesion at the interface.[29–31] A possible solution to this problem is the use of compatibilizing agents to increase the interfacial compatibility between natural fibers and the thermoplastic matrix and improve the mechanical performance of the composites.[32]

Corradini et al.[32] reported the addition of ethylene/n-butyl acrylate/glycidyl methacrylate and ethylene methyl acrylate as compatibilizing agents to recycled PET/sugarcane bagasse fiber composites. According to the authors, the use of both compatibilizing agents increased the interfacial adhesion of bagasse fibers/recycled PET, which was proven via torque rheometric measurements and dynamic mechanical thermal analysis (DMTA).

In the article, composites of recycled PET/sisal fibers were initially processed in a Haake torque rheometer with subsequent thermopressing at 260°C, but this method proved to be unsuitable because fiber decomposition was observed, i.e., the decomposition of the fibers was not delayed by the matrix coating. Consequently, different plasticizers derived from renewable sources, such as glycerol [Figure 1(a)], tributyl citrate [TBC, Figure 1(b)], and castor oil [CO, Figure 1(c)], were used to prepare recycled PET/sisal fiber composites in an attempt to decrease the melting temperature of the recycled PET (~265°C). Hydroxylated liquid polybutadiene [HLPB, Figure 1(d)] was used for comparison purposes.
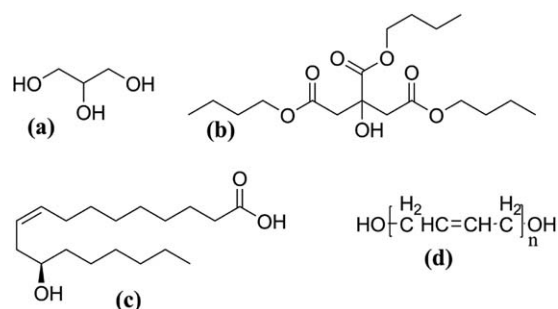

Figure 1. Structural formula of the plasticizers (a) glycerol; (b) tributyl citrate (TBC); (c) ricinoleic acid (major component of castor oil) (CO); (d) hydroxylated liquid polybutadiene (HLPB).

Chemical modifications in the polymer structure, such as grafting, can significantly increase the processing costs. Chemical modifications on the fiber's surface usually improve the fiber–matrix interactions. However, this approach can result in fibers with inferior mechanical properties (the reaction medium can be responsible for fiber deterioration).[33–35]

In this article, the previously mentioned plasticizers (Figure 1) were also chosen for their possible action as compatibilizing agents as an alternative to the chemical modification of the fibers to improve the compatibility between the fiber–matrix interface.

In general terms, the plasticizer processing parameters were exploited by mixing the components, followed by compression molding. The composition of the mixture and the processing parameters that led to the best set of results were considered for processing via torque rheometry/thermopressing. The thermal properties of the generated materials were evaluated.

In summary, this article was mainly motivated by (i) the higher generation rate of plastic packaging disposal compared to the material recycling rate, which highlights the need for applications of recycled PET, (ii) an increasing interest in the use of raw materials derived from renewable sources, such as the fibers and plasticizers considered herein, and (iii) the thermal properties of both the raw materials used herein and the final materials (composites), which are important for processing and defining possible applications of the final products.

The results showed that the T_m of the recycled PET decreased due to the presence of plasticizers, which also led to lower melting viscosities. Thus, the processing of the materials at temperatures below the melting point of the neat polymer prevented the thermal decomposition of sisal, and the decrease in the melt viscosity of PET increased the wettability of the fiber by the polymer. Hence, the materials were processed under considerably more favorable conditions compared to the processing conditions without plasticizers. The DMTA results indicated that TBC also acted as a compatibilizing agent, which suggested a higher affinity between the functional groups of its chemical structure and the groups present in the components of sisal fiber and PET, when compared with the other plasticizers.

EXPERIMENTAL

Materials

The recycled PET was kindly supplied by Gruppo Mossi & Ghi-solfi (M&G).

The sisal fibers used in this article were purchased from Sisal Sul Indústria e Comércio LTda. Before being used, the sisal fibers were treated under reflux with cyclohexane/ethanol (1 : 1, v : v) for 10 min (time interval determined in prior studies).[36,37] The fibers were then washed with water and dried in an air-circulated stove at 105ºC until a constant weight was reached. This pre-treatment aimed to eliminate the low molecular weight polar and apolar organic extractives.

Glycerol (99.5%, J. T. Baker) was used as received. The TBC plasticizer, trade name SCANDINOL SP-21, was kindly supplied by Scandiflex S/A. CO was purchased from A. Azevedo Indústria e Comércio de Óleos LTda. HLPB, trade name Liquiflex H, was kindly donated by Petroflex Ind. Com.

Methods

Preparation of Recycled PET Control Plaque (CTRPET) by Compression Molding. The recycled PET was obtained as a powder that resulted from cryogenic grinding in a mill with a vertical rotor and movable and fixed knives from Marconi, model MA048. The recycled PET powder, which was previously dried in an air-circulated stove at 160°C for 4 h, was poured into a portable mold with a capacity of approximately 350 g and dimensions of 300 × 140 × 5 mm that was previously covered with thin sheets of teflon.

The powder was then compression at a constant pressure of 38.08 Kgf cm^{-2} and the following temperature cycle: 80°C/10 min; 100°C/10 min; 200°C/20 min; 240°C/20 min; 260°C/1 h. These parameters were selected based on an initial exploration of the processing conditions.

Preparation of Composites by Compression Molding. For the compression molding of composites, sisal fibers (3 cm in length, 15 wt %, previously dried for 4 h in an air-circulated stove at 105°C to eliminate moisture[14]) were initially mixed with plasticizers. The percentage and fiber length were chosen based on previous studies,[35,38] in which these properties were varied to determine the best conditions for processing composites by compression molding. Based on the results of this article, higher percentages and other fiber lengths can be considered in the following steps.

A mechanical mixer (JVJ Company, Pardinho, São Paulo, Brazil) that contained a steel drum mixing chamber and forks was used to mix the materials and consequent impregnation of the fiber with polymers and/or plasticizers. The fibers were previously distributed between the forks and mixed with half of the total proposed quantity of plasticizer(s) for 3 min under continuous rotation (30 rpm). The time and rotation speed, which were chosen after various tests, were selected because they proved be suitable to impregnate the fibers with the plasticizers.

Subsequently, the fibers containing plasticizer(s) were mixed with the recycled PET powder (85 wt %), which was previously dried in an air-circulated stove at 160°C for 4 h, and mixed

Table 1. Compositions of Composites Processed Via Compression Molding

Code: composites	Composition
CG	Recycled PET/sisal fibers/glycerol
CT	Recycled PET/sisal fibers/TBC
CGT	Recycled PET/sisal fibers/glycerol/TBC
CGC	Recycled PET/sisal fibers/glycerol/CO
CGTC	Recycled PET/sisal fibers/glycerol/TBC/CO
CGTP	Recycled PET/sisal fibers/glycerol/TBC/HLPB

with the other half of the total proposed quantity of plasticizer(s). The mixture was then poured into the mold, which was previously covered with thin sheets of teflon. These steps were designed to yield a homogeneous distribution of the plasticizers between the recycled PET and sisal fibers during processing to favor their action as both plasticizers and fiber–matrix compatibilizing agents.

The composite was compression molded at a constant pressure of 38.08 Kgf cm^{-2} using the following temperature cycle: 100°C/15 min; 180°C/1 h 40 min; 200°C/1 h 40 min; 215°C/10 min; 225°C/35 min. This cycle was proven to be the optimal in a study that varied the pressure/time/temperature of each stage of the cycle.

Different compositions were explored for the preparation of the composites based on a fixed proportion of 15 wt % of sisal fibers mixed with 85 wt % of recycled PET with the addition of different types and mixtures of plasticizers.

The different compositions used for the preparation of composites via compression molding and their respective codes that are used hereafter are displayed in Table 1.

The percentages of plasticizers noted here correspond to nominal values because losses may occur during processing. These losses can primarily be attributed to volatilization at higher temperatures. However because the process was initiated with relatively high amounts of plasticizers, the final product retained a fraction of the added plasticizers. The loss of plasticizer via volatilization during polymer processing is virtually inherent to processes that use elevated temperatures.[39]

The composites CG and CT were prepared by adding 40 wt % of the plasticizers glycerol and TBC, respectively. CGT contained a mixture of 20% glycerol and 20% TBC, while CGC contained a mixture of 20% glycerol and 20% CO. The percentages of plasticizers noted here were relative to the mass of the recycled PET used.

The composite CGTC was prepared from a mixture of glycerol, TBC and CO. Twenty weight percent of the plasticizers glycerol and TBC were added each component relative to the mass of recycled PET used. Ten weight percent of CO was added relative to the total weight of recycled PET and other plasticizers used.

The composite CGTP was prepared from a mixture of glycerol, TBC, and HLPB. Glycerol and TBC were each added at a proportion of 20 wt % relative to the mass of recycled PET used. Fifteen weight percent of HLPB with respect to the total weight of recycled PET and other plasticizers added was used to prepare the composites.

Preparation of Composites by Torque Rheometer/Thermopressing. Initially, sisal fibers (5 mm of length, 15 wt %, previously dried in an air-circulated stove at 105°C for 4 h), recycled PET powder (85 wt %, previously dried in an air circulated stove at 160°C for 4 h), and 20 wt % of the plasticizers glycerol and CO each in relation to the mass of recycled PET used were mixed in a Haake torque rheometer equipped with a RHEOMIX 3000P mixing chamber with a capacity of 45 g at 225°C and 60 rpm for 5 min. Fifty grams of the recycled PET/ sisal fibers/glycerol/CO mixture were then placed between two sheets of Teflon, and the assembly was placed between two sheets of stainless steel on which an aluminum frame was placed to guarantee the regularity of the desired final thickness. The mixture was then thermopressed at 260°C for 3 min. The assembly was then maintained under forces of 0.5 ton, 1 ton, and 2 ton for an additional 1 min. The composite of recycled PET/sisal fibers/glycerol/CO (CHGC) was cooled to 60°C under a constant force of 2 ton and subsequently to room temperature, without additional force. The process parameters used in the torque rheometer and subsequent thermopressing were chosen after various tests. The fibers used in this case are shorter than those used in processing via compression molding (3 cm) because long fibers are broken during processing in a torque rheometer.

Characterizations

Sisal Fibers. The moisture content of the fibers was determined according to ABNT NBR9656 (Brazilian Technical Standards Association) by calculating the percentage difference between the initial sample weight and that after the drying process in an air-circulated stove at 105°C for 4 h.

The ash content of the fibers was determined according to TAPPI T211 from the percentage difference between the initial dried sample weight and that after calcination at 800°C for 4 h.

The Klason lignin content was determined according to TAPPI T13M-54. This method is based on the acid hydrolysis of the polysaccharides (cellulose and hemicellulose), subsequent separation and gravimetric determination of lignin insoluble in sulfuric acid (72%, Synth).

The holocellulose content (cellulose + hemicellulose) was determined according to TAPPI T19M-54 via the selective degradation of lignin using sodium hypochlorite (J. T. Baker) at 70°C. The content of cellulose was determined via the selective degradation of hemicellulose using sodium hydroxide (17.5%, Synth) at room temperature. The hemicellulose content was determined by the difference between the content of holocellulose and cellulose.

The samples were initially dried in an air-circulated stove at 105°C for a period of 4 h for all previously mentioned analyses with the exception of the moisture content analysis of the sisal

fibers. The analyses were performed in triplicate, and the average values are presented in the next section.

The crystallinity index (I_c) of the cellulose present in the sisal fibers was determined by X-ray diffraction. A RIGAKU Rotaflex model Ru-200B diffractometer operating at 40 kV, 2 mA, and λ (Cu Kα) = 1.5406 Å was used in this process. The I_c was calculated using the Buschle-Diller and Zeronian[40] equation:

$$I_c = 1 - \frac{I_1}{I_2} \tag{1}$$

where I_1 is the intensity of the minimum diffraction, which is related to a non-crystalline region ($18° < 2\theta < 19°$) and I_2 is the intensity of the maximum diffraction, which is related to the crystalline region ($22° < 2\theta < 23°$).

Thermogravimetric analyses (TGA) of sisal fibers were performed using the Shimadzu equipment, model TGA-50TA. The samples (8–10 mg) were placed in a platinum pan and heated from 25°C to 800°C (at 10°C min^{-1}) in a nitrogen and synthetic air atmosphere (flow of 50 mL min^{-1}).

The DSC analyses of sisal fibers were performed using the Shimadzu equipment, model DSC-50. The samples (6–8 mg) were placed in an aluminum seal pan and heated from 25°C to 400°C (at 10°C min^{-1}) in a nitrogen and synthetic air atmosphere (flow of 50 mL min^{-1}).

Recycled PET and Plasticizers. The TGA and DSC analyses of recycled PET and plasticizers were performed under the same conditions described previously. For the recycled PET sample, the TGA and DSC analyses were also performed in a synthetic air atmosphere (under the same conditions that were previously described).

The melt flow index (MFI) of the recycled PET powder (160°C and 2.16 Kg) was determined using a Davenport plastometer (Harts, England) according to ASTM D-1238. The analysis was performed in triplicate.

Recycled PET Control Plaque and Composites. Recycled PET Control Plaque (CTRPET) and composites were characterized via TGA and DSC analyses under the same conditions described previously.

The DMTA was performed using a DMA thermal analyzer, model Q800 from TA Instruments. The equipment was used in flexural mode at an oscillation amplitude of 20 μm, frequency of 1 Hz and heating rate of 2°C min^{-1} over a temperature range 30–200°C. The composite samples were 64 mm in length $\times$ 12 mm in width $\times$ 3.2 mm in thickness.

RESULTS AND DISCUSSION

Characterization of the Sisal Fibers

Figure 2 shows the results of the characterization of the sisal fibers.

These results agree with those found in the literature for sisal fibers (9–11% lignin content; 50–65% cellulose content; 20–35% hemicellulose content; 60–62% for the crystallinity index).[2,37,41] The moisture and ash contents (inorganic components such as calcium, sodium, potassium, and silica attached
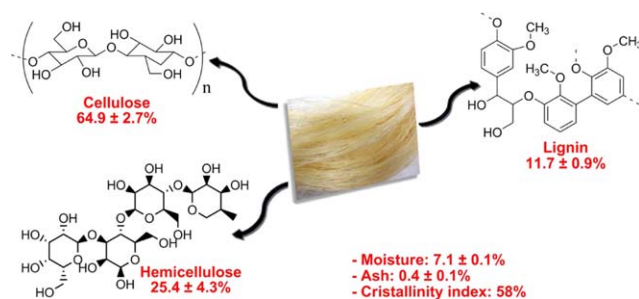
Figure 2. Sisal fibers: composition and properties. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the fibers in the form of salts) obtained in the article also agree with the values reported in the literature (6–11% moisture content; 0.6–1.1% ash content).[42–44]

Factors, such as the origin of the plant, age, climatic conditions to which the plant was submitted, extraction, and purification processes, can influence the fiber structure as well as the chemical composition of the sisal.[42]

Figure 3 shows the DSC, TG, and dTG curves of the sisal fiber.

Figure 3(a) shows an endothermic event related to the vaporization of the water present on the surface and interstitial sites of the fiber at approximately 80°C.[24,37] The low intensity peak at approximately 300°C is likely related to the exothermic decomposition of hemicellulose. The peak observed at approximately 370°C corresponds to the exothermic decomposition of cellulose, starting with dehydration and depolymerization and leading to the release of volatile products, such as carbon dioxide and monoxide.[37,45–47]

Above 400°C, the thermal decomposition of lignin resulted in the low intensity and large peak in this temperature range [Figure 3(a)]. The low intensity is attributed to the low lignin content in the sisal fiber (~12%, Figure 2). The decomposition reactions are exothermic, and the release of volatile products resulting from the decomposition is an endothermic event. Thus, the peaks observed can be both exothermic or endother-

mic, depending on the balance between the decomposition reaction/release of volatile products.[34] All peaks in Figure 3(a) were exothermic.

The sisal fiber was also analyzed under an atmosphere of synthetic air (figure not shown) for comparison purposes. The DSC curve obtained exhibited thermal events similar to the ones obtained under an atmosphere of nitrogen [Figure 3(a)]. The exothermic peaks related to the thermal decomposition of cellulose and lignin at approximately 350°C and approximately 370°C, respectively, had shifted to lower temperatures compared to the peaks presented by the DSC curve in Figure 3(a) (~370°C and ~420°C, respectively). The peak related to the decomposition of hemicellulose remained at approximately 300°C, i.e., the starting temperature of fiber decomposition was not changed when DSC was carried out under an air atmosphere.

The TG curve for the sisal fiber [Figure 3(b)] indicated that approximately 1% of the mass was lost up to a temperature of 105°C, which corresponded to the water loss (moisture absorbed/adsorbed by the fiber). Most of the water molecules are bound to hemicellulose chains because they are present in the non-crystalline regions of the fiber.[37,44]

Between 160°C and 245°C [Figure 3(b)], the sisal fibers experienced a mass loss of 2%, which can be related to the loss of structural water from the fiber, i.e., the water strongly adsorbed to the fiber. From 245°C to approximately 420°C, the weight loss was maximized (55%) due to the thermal decomposition of the sisal fiber, starting with the decomposition of hemicellulose followed by cellulose.[35,42] According to the dTG curve, the intense peak that characterizes the decomposition of the fiber components has a maximum at 350°C (T_d), which is related to the maximum decomposition temperature (T_d) of the fiber. In the dTG curve, the decomposition of hemicellulose was fully incorporated into the peak of the cellulose decomposition because this peak did not show a shoulder. The sample could be considered stable until 245°C because the low mass loss was not a consequence of thermal decomposition below this temperature.
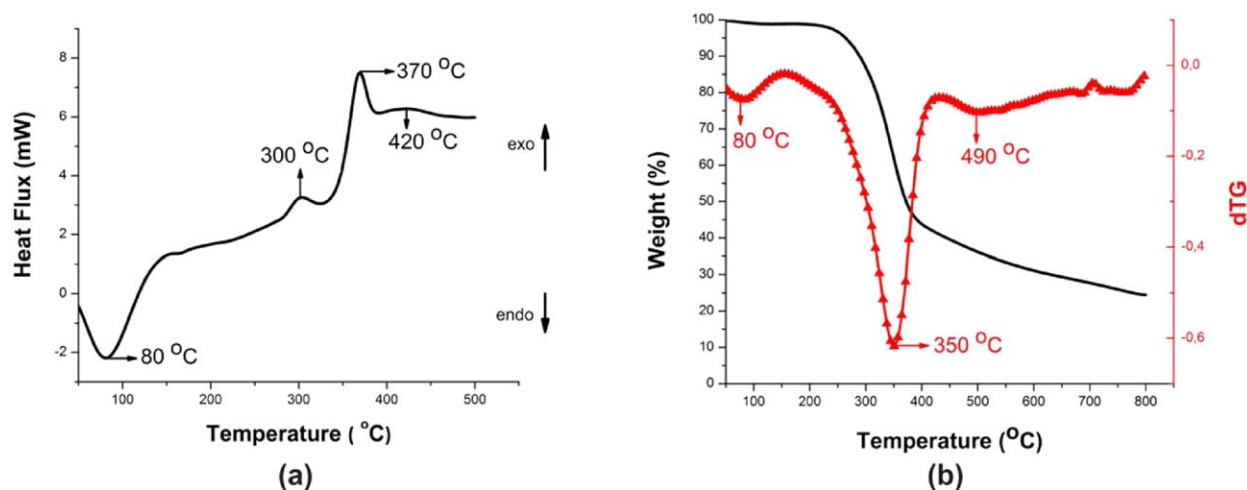

Figure 3. Curves (a) DSC and (b) TG and dTG of the sisal fiber (N_2 atmosphere 50 mL min^{-1} and heating rate of 10°C min^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

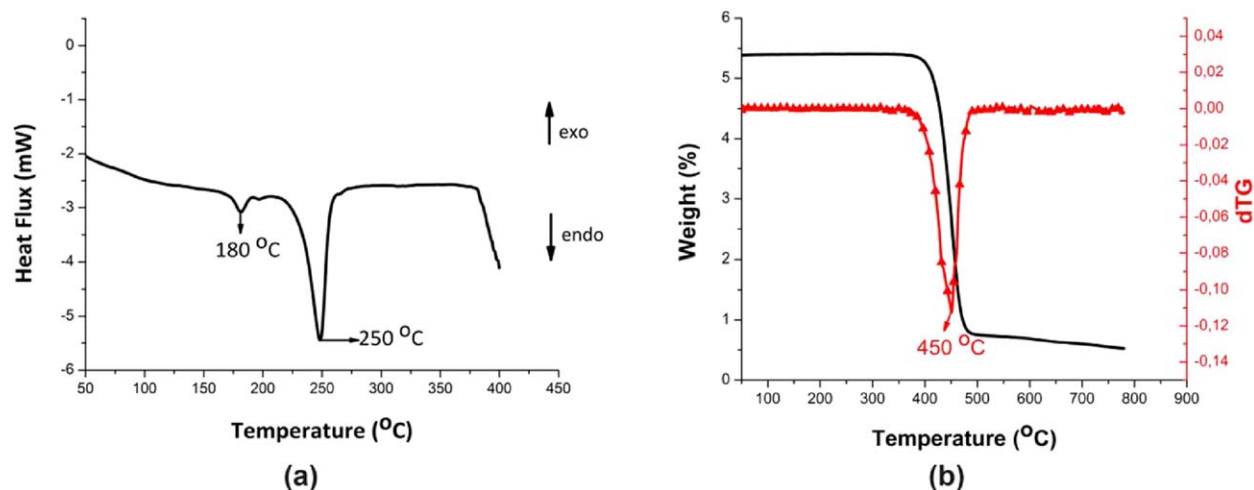**Figure 4.** Curves (a) DSC and (b) TG and dTG of the recycled PET (N_2 atmosphere 50 mL min^{-1} and heating rate of 10°C min^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The low intensity, large peak after 450°C [Figure 3(b)] corresponds to the protolignin (native lignin) bond breaking.[35,42,48] Due to its aromatic structure, lignin is highly thermally stable compared to other sisal components, such as cellulose.[48] The thermal decomposition of the fiber components was observed in the same temperature ranges in the corresponding TG and DSC curves (Figure 3).

The dTG curve for the sisal fiber obtained in atmosphere of synthetic air (figure not shown) showed a shift in the T_d from 350°C [under atmosphere of nitrogen, Figure 3(b)] to 340°C. Similar to the dTG curve obtained under a nitrogen atmosphere, the decomposition of hemicellulose was incorporated into the cellulose peak. According to the TG curve (figure not shown), the fibers could be considered thermally stable up to approximately 245°C under an air atmosphere, which approximated the results obtained under a nitrogen atmosphere.

Characterization of Recycled PET

To investigate the possible effects of the recycling process on the average molar mass of the recycled PET, this polymer was characterized by the MFI. The recycled PET sample had a MFI of 36.4 g (10 min)$^{-1}$, which is consistent with values found in the literature for recycled PET.[49]

Mancini et al.[49] analyzed the influence of the type and number of recycling cycles on the MFI of PET. This article showed that the PET MFI positively correlates with the mechanical recycling number. Thus, the MFI obtained for virgin PET was 16 g (10 min)$^{-1}$, and increasing the recycling number (5 in total) increased this value to approximately 400 g (10 min)$^{-1}$, which is approximately 20 times higher. The increase in the MFI is a consequence of a decrease in the polymer viscosity, which indicates a decrease of its average molar mass as a function of the increase of the recycling number. This behavior was confirmed by the increase of the concentration of carboxylic terminal groups in the PET.[49] The increased presence of –COOH terminal groups indicates a high presence of small chains, which allows the small chains to slide between longer ones (in the molten state) and the material to flow more easily.[50] The lower

MFI of recycled PET compared to the virgin PET favors the wetting of the fiber by the polymer during the preparation of composites, which usually improves the fiber–polymer interface.

The recycled PET used in the article was obtained from the mechanical recycling of colorless PET bottles. Thus, the MFI value obtained for this polymer indicates that this material has suffered a partial degradation of polymer chains, with consequent reductions of its viscosity and increase of its MFI compared to the virgin PET used in this type of application.[49]

Figure 4 shows the DSC, TG, and dTG curves for the recycled PET used in the article. The low intensity peaks near 180°C and 250°C [Figure 4(a)] were attributed to the endothermic event of melting. The peak near 180°C is due to the fusion of the crystal fraction formed from chains with smaller average molar masses.[51]

DSC analysis could not detect the glass transition temperature (T_g) of the recycled PET, which normally occurs near 80°C.[51] This transition is detected by a deviation in the baseline in the DSC curve, which is not always easily identified.

The DSC curve of the recycled PET analyzed under an atmosphere of synthetic air (figure not shown) showed the same thermal events observed under an atmosphere of nitrogen, with peaks at approximately the same temperature ranges [Figure 4(a)].

The TG curve [Figure 4(b)] exhibited a single stage of mass loss from 365°C to 500°C, which was related to the decomposition of recycled PET (mass loss of approximately 80%). The maximum decomposition temperature (T_d) was observed at 450°C, which was considerably higher than the T_d of the sisal fiber [350°C, Figure 3(b)]. Figure 4(b) shows that the recycled PET was thermally stable until approximately 367°C, i.e., 120°C above its melting temperature.

Unlike the TG and dTG curves for the recycled PET obtained under an atmosphere of nitrogen [Figure 4(b)], the curves obtained under an atmosphere of synthetic air (figure not shown) showed two stages of mass loss. The first stage was

observed between 290°C and 500°C (intense peak with mass loss of approximately 85%, T_d of 440°C). The first stage can be attributed to oxidative events, which is favored in the presence of air. The second stage was observed between 500°C and 630°C (low intensity peak with mass loss of approximately 10%, T_d of 570°C). Thus, the recycled PET was thermally stable in synthetic air below approximately 290°C, which was significantly lower than the thermal stability of this polymer under an atmosphere of nitrogen [~367°C, Figure 4(b)]. However, the processing temperature of the composites remained dependent on the thermal decomposition of the fiber, which was stable up to approximately 245°C.

Characterization of Plasticizers

Figure 5 presents the DSC, TG, and dTG curves for the plasticizers glycerol, CO, HLPB, and TBC.

The glycerol DSC curve [Figure 5(a)] showed an intense peak near 290°C related to the endothermic volatilization of this plasticizer, which has a boiling point at the same temperature. The DSC curve of CO shows two endothermic peaks [Figure 5(b)], a low intensity peak near 347°C and an intense peak near 389°C. These peaks are related to the volatilization/decomposition of fatty acid esters that comprise the CO. The main component of CO, the ricinoleic acid methyl ester, was likely responsible for the intense peak near 389°C in the DSC curve.[52] The thermal decomposition of HLPB led to a large and intense exothermic peak near 380°C in its DSC curve [Figure 5(c)].

The DSC curve of TBC [Figure 5(d)] showed an intense peak near 230°C, which was likely due to its endothermic volatilization because this plasticizer has a boiling point near 234°C. Notably, the experimental conditions in which the boiling points are determined are usually different from those of DSC analysis, which can lead to some differences between the values found here and those found in the literature.

The dTG curve of glycerol [Figure 5(a)] showed one intense peak with maximum at 210°C (T_d), which can be attributed to its volatilization at a lower temperature than that detected by the DSC curve [290°C, Figure 5(a)]. The TG curve [Figure 5(a)] shows that the weight loss in the temperature range that included T_d was 98.6%.

The dTG curve for CO [Figure 5(b)] showed two stages of weight loss related to the decomposition of fatty acid esters, which was predominated by ricinoleic acid. The first stage is characterized by an intense peak between 200°C and 428°C, with a maximum at 380°C and weight loss of approximately 74%, which can be attributed to the volatilization/decomposition of ricinoleic acid.[53,54] The second stage is characterized by a low intensity peak between 428°C and 530°C, with a maximum at 455°C and a weight loss of approximately 22%.

The TG and dTG curves for HLPB [Figure 5(c)] indicated that this material was thermally stable up to 300°C. Above this temperature, the decomposition of the rubber begins as indicated by a peak between 300°C and 452°C, with a maximum at 447°C and a weight loss of approximately 25%. The second peak was observed between 452°C and 519°C, with a maximum at 480°C and a weight loss of approximately 73%. The TG and

dTG curves for TBC [Figure 5(d)] showed a single stage of significant weight loss between 126°C and 280°C, with a maximum at 248°C, which was attributed to the volatilization of this plasticizer (with a weight loss of approximately 99%).

Characterization of Composites (see TABLE 1 for codes)

The composites were analyzed under only a nitrogen atmosphere (DSC, TGA) given that their main components (sisal fiber and recycled PET) had already been analyzed under air atmosphere. Furthermore, the composite PET/sisal fiber is not shown here because the PET melts at a temperature that is high enough to thermally decompose the fibers in the absence of plasticizers, as mentioned above.

Figure 6(a) depicted the DSC curves of CTRPET and of the composites CG, CT, CGT, CGTC, and CGTP.

The DSC curve of CTRPET [Figure 6(a)] showed a low intensity peak near 250°C and an intense peak near 260°C; both peaks were attributed to the endothermic melting of the material. The lowest melting temperature, 250°C, corresponds to the crystalline domains formed from lower molar mass polymer chains. The comparison of the DSC curve of the molded [CTRPET, Figure 6(a)] and the powder recycled PET [Figure 4(a)] shows that the powder melted at lower temperatures (near 180°C, low intensity peak, and 250°C, intense peak). This shift in the temperature was likely due to the powdered state of the recycled PET sample, whereas the CTRPET corresponded to small fragments obtained from its cryogenic grinding process. The higher surface area of the recycled PET powder could have facilitated its melting compared to the fragments of CTRPET, which had a lower surface area. In addition, the compression molding process can rearrange the chains of the molten recycled PET, which may have led to the formation of a higher proportion of crystalline domains from chains with higher average molar mass.

The peaks related to the endothermic melting of CT (between 232°C and 248°C) [Figure 6(a)] were observed in regions of lower temperature compared to CTRPET (approximately 260°C). The plasticizer TBC was less effective in reducing the T_m of PET compared to the mixture glycerol/TBC used to form CGT, which was indicated by the peaks near 160°C and 230°C in DSC curve of CGT [Figure 6(a)] related to the melting of the polymeric matrix. These peaks occurred at even lower temperatures than those yielded by the powder recycled PET [Figure 4(a)].

The DSC curves for the composites CG, CGTC, CGTP [Figure 6(a)], and CGC (figure not shown) showed a single and intense peak related to the endothermic melting. These peaks were observed in a lower temperature region (near 235°C) compared to both the CTRPET and the powder recycled PET [Figure 4(a)].

The DSC curve of CGT [Figure 6(a)] shows a low intensity peak near 300°C, which may be attributed to the volatilization of glycerol (boiling point approximately 290°C).

The DSC curves of CG, CGT, CGTC, CGTP [Figure 6(a)], and CGC (figure not shown) showed peaks between 370°C and 390°C, which are related to the exothermic decomposition of the sisal fiber. This decomposition was likely the result of
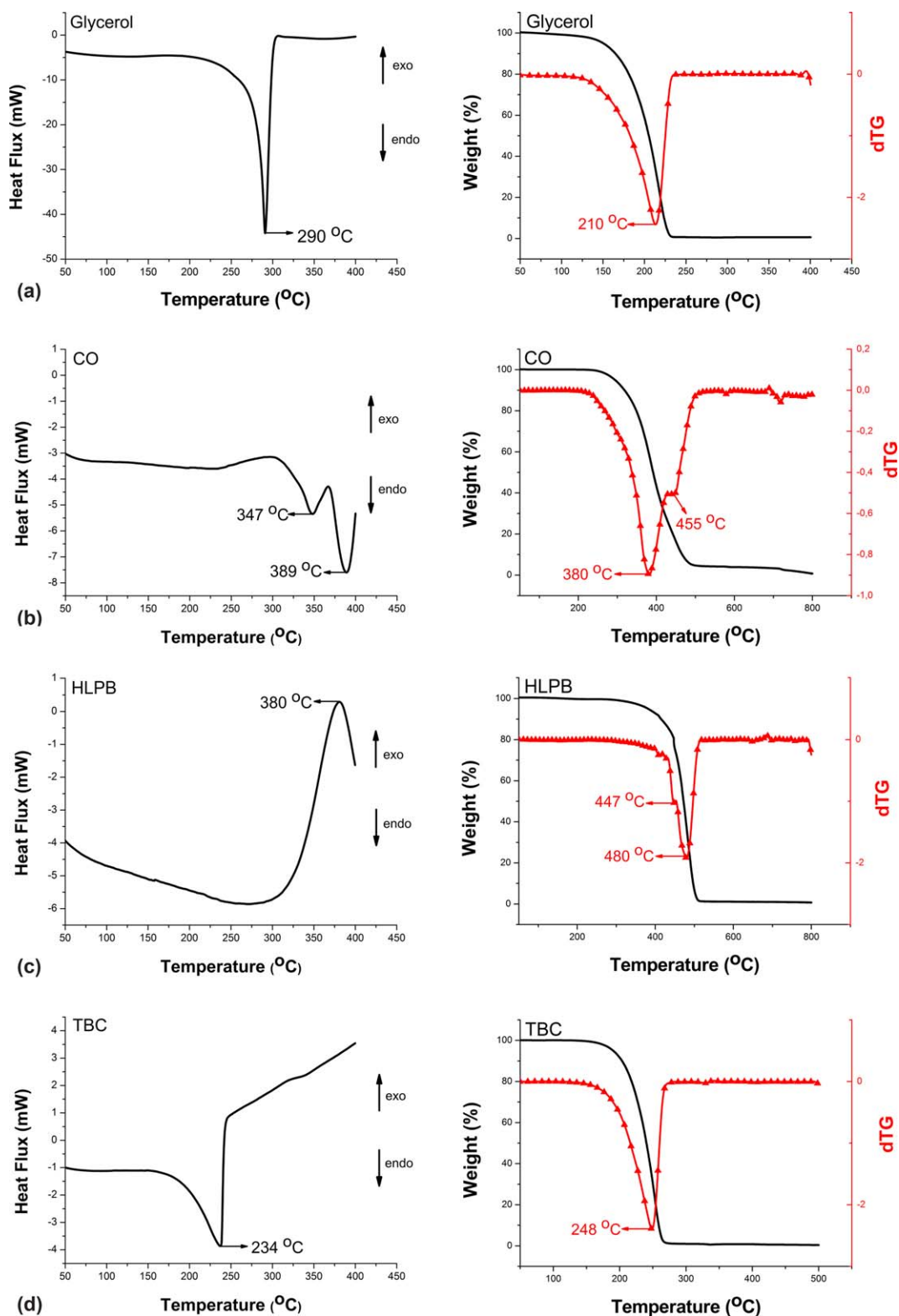
Figure 5. DSC, TG, and dTG curves of the plasticizers (a) Glycerol; (b) CO; (c) HLPB, and (d) TBC (N$_2$ atmosphere 50 mL min^{-1} and heating rate of 10°C min^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decomposition of cellulose, which is the major component of the fiber. In the DSC curve of sisal fiber, the decomposition of cellulose is characterized by a peak around 370°C [Figure 3(a)].

A powdered PET was mixed with the plasticizers and sisal fibers to prepare the composites (see Experimental). Therefore, the powdered PET melted at a temperature during the processing
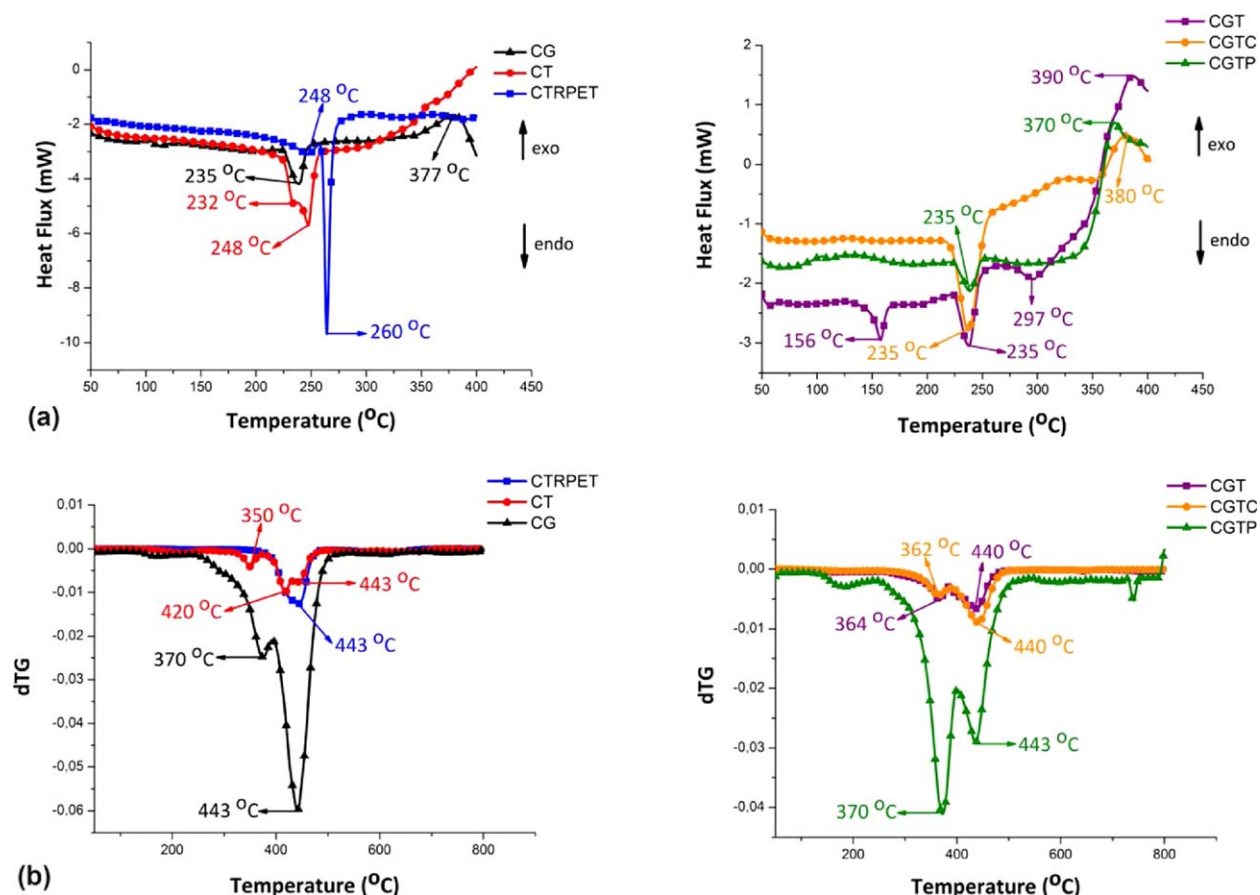
Figure 6. Curves (a) DSC and (b) dTG of CTRPET, CG, CT, CGT, CGTC, and CGTP (N_2 atmosphere 50 mL min^{-1} and heating rate of 10°C min^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that was lower than those detected for the materials consolidated as composites, which were analyzed as fragments during the DSC/TGA analyses, as previously mentioned.

The dTG curve of CTRPET [Figure 6(b)] showed a single and intense peak of decomposition near 440°C. The dTG curves of the composites CG, CGT, CGTC, CGTP (Figure 7), and CGC (figure not shown) showed two stages of weight loss between 360°C and 450°C. The composite CT showed [Figure 6(b)] three stages of weight loss between 350°C and 450°C in its dTG curve. The decomposition peaks presented by CTRPET and its composites ranged from 420°C to 450°C and were related to the decomposition of recycled PET. In the dTG curve of the composites, the peaks between 350°C and 370°C can be attributed to the decomposition of the sisal fiber, which mainly consisted of the decomposition of cellulose [Figure 3(b)].

The composites CG, CT, CGT, CGTC, CGTP [Figure 6(b)], and CGC (figure not shown) showed a lower thermal stability than CTRPET. This difference was attributed to the presence of sisal fibers in the CTRPET composites. The decomposition started near 240°C–250°C for the composites and near 340°C for CTRPET [Figure 6(b)].

The CTRPET and composites were analyzed via DMTA (Figure 7). The results obtained for the composites reflected not only the characteristics of the matrix and fiber used but also other

factors, such as the plasticizers used in the material. At the molecular level, the PET chains present in a given layer may be interacting with the apolar domains of both the fibers and plasticizer at the interface, which in turn may be interacting amongst themselves. These differences may modify the mobility of the polymer chains and thus the properties evaluated via DMTA.[35,55]

The storage moduli (E', 30°C) of the composites were lower than those of the neat polymer, CTRPET [Figure 7(a)]. This result indicated that the incorporation of the fibers and the various types and/or mixtures of plasticizers in the polymer matrix decreased the stiffness of composites compared to CTRPET, i.e., the effect of the plasticizer exceeded the possible effect of the presence of the fibers, which usually increase the rigidity of the composite compared to the neat polymer. The plasticizers can decrease the material stiffness due to a reduction of the intermolecular interactions between the polymer chains, which facilitates the movement of their segments.[56] This result indicated that the incorporation of the fibers and the various types and/or mixtures of the plasticizers in the polymer matrix resulted in composites that were less stiff than CTRPET. The plasticizers can decrease the materials stiffness due to a reduction of the intermolecular interactions between the polymer chains, which facilitates the movement of their segments.[56]
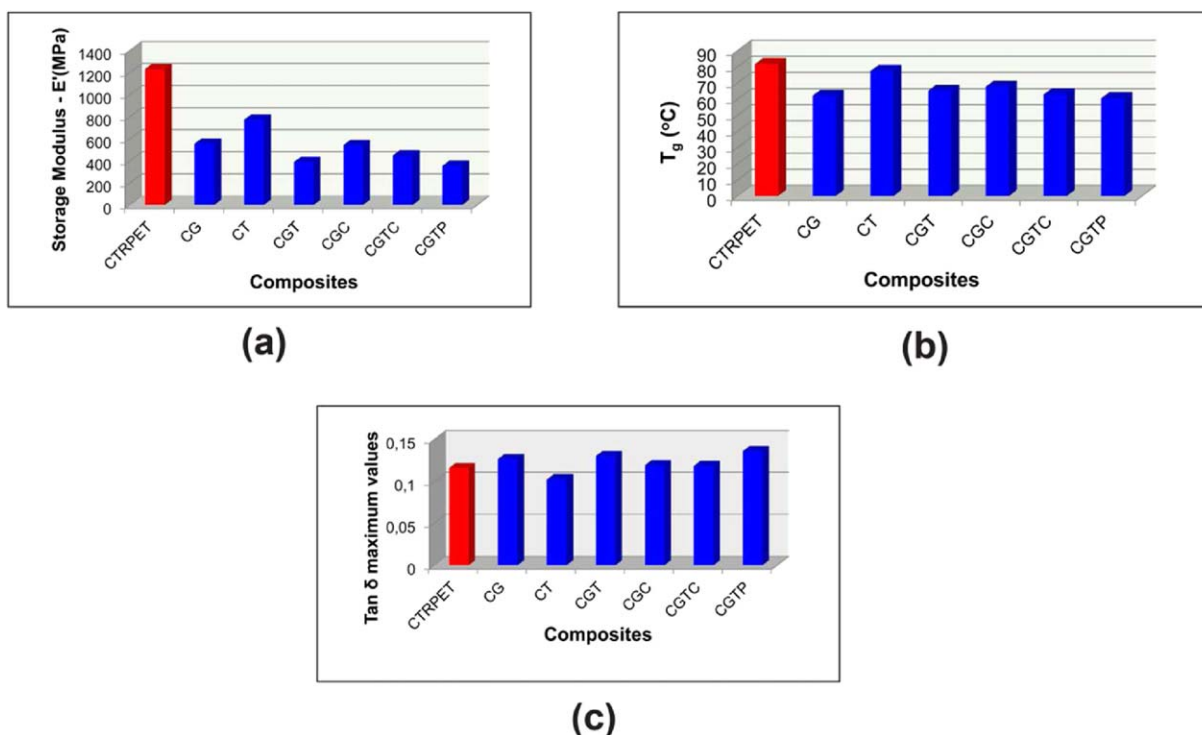
Figure 7. CTRPET and composites (a) Storage Modulus (30°C) and (b) glass transition temperature (T_g), and (c) tan δ maximum value. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Among the composites, CT showed the highest storage modulus, which can be attributed to the favorable interaction of the TBC with the recycled PET and sisal fibers (Figure 8). This interaction can decrease the mobility of the segments of the polymer chains, which in turn would indicate that the plasticizer also acted as a compatibilizer.

Figure 7(a) shows that the CGTP exhibited one of the lowest storage moduli among the other composites. This finding can be explained by the presence of an elastomeric component, in this case the HLPB (15 wt % relative to the mass of recycled PET/other plasticizers added), which reduced the stiffness of the composite.[36]

The damping measurement (tan δ, curves not shown) expresses the ability of a material to convert mechanical energy, and its maximum value is associated with the glass transition temperature (T_g). The values of glass transition temperature (T_g) of CTRPET and the composites obtained from the maximum of the tan δ vs. temperature curves are shown in Figure 7(b).

Figure 7(b) shows a decrease in the T_g values of the composites compared to CTRPET. The T_g at 82°C for CTRPET is consistent with the values reported in the literature for virgin PET and recycled PET (T_g between 70°C and 80°C).[32,57] The presence of plasticizers between the chains reduces the intensity of intermolecular interactions between their segments and increases their mobility, which decreases the T_g of the polymer matrix. This effect is well known. The differences in the decrease of the T_g values for the composites compared to CTRPET can be attributed to the use of different types/mixtures of plasticizers during the preparation of the composites.

All composites that contained glycerol exhibited lower T_g values than CT [Figure 7(b)]. These results indicated that the presence of a small molecule such as glycerol, even when mixed with larger molecules, such as CO and TBC, led to a stronger plasticizing effect. The interaction of segments of polymer chains with fibers at the composite interface interferes with the tan δ peak height. As a consequence of decreasing the movement of the chain segments, less energy can be dissipated, which in turn can decrease the magnitude of the damping peak compared to the neat polymer. The intensity of the interactions at the interface positively correlates with the decrease in the tan δ peak height. Thus, the height of tan δ peak may be correlated with the quality of the interface in composites.[58,59] The effect on the
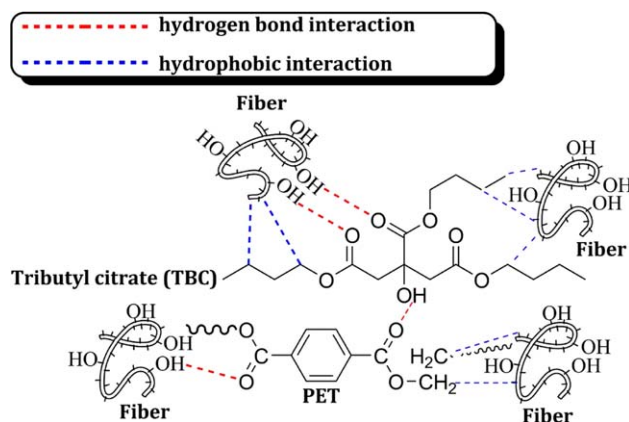

Figure 8. TBC/PET/fiber interactions (CT composite). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
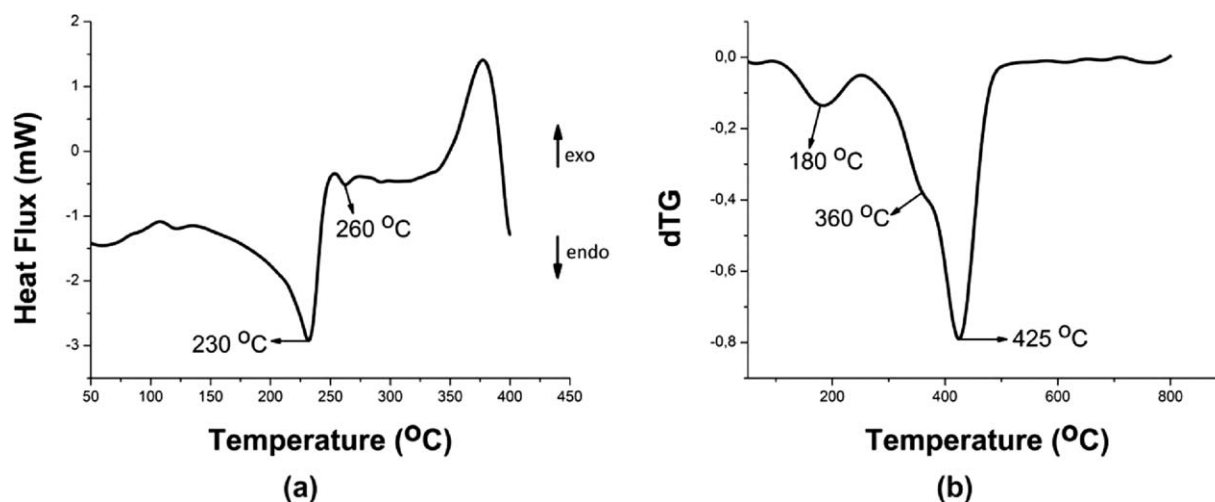
Figure 9. CHGC curves (a) DSC and (b) dTG (N$_2$ atmosphere 50 mL min^{-1} and heating rate of 10°C min^{-1}).

height of the damping peak depends on the fiber content used in the preparation of the composite.[60,61]

In this article, the fiber content was not high (15 wt %), which is reflected in Figure 7(c). With the exception of CT, all composites exhibited a damping peak close to or even superior to that of the neat polymer. This finding indicated that the expected decrease in the tan δ peak height due to the interactions at the interface was balanced or even overcome by the plasticizing effect, which increases the mobility of the segments of the polymer chains. If the mobility of the segments increases, more energy can be dissipated, which increases the magnitude of the damping peak. For these composites, the action of the plasticizer as a compatibilizing agent was not clearly evident. However, the results obtained allow the adjustment of the conditions to prepare composites with a higher fiber content.

The addition of TBC decreased the T_m of PET (CT, 232°C–248°C) compared to CTRPET (260°C) due to its action as a plasticizer. However, among the composites, the T_g of the CT composite (recycled PET/sisal/TBC, 77°C), was closest to that of the CTRPET T_g (82°C) [Figure 7(b)]. This result agrees with the higher stiffness of this composite compared to the other materials [Figure 7(a)]. The stronger interactions between the segments of PET chains/TBC/sisal fibers (Figure 8) decreased the mobility of the segments at the interface, which shifted the T_g to higher values when compared to the other composites. Additionally, this decrease in the mobility of the segments due to the presence of TBC decreased the damping peak of CT compared to the neat polymer (CTRPET), as shown in Figure 7(c).These results indicated that this plasticizer also acted as a compatibilizer.

After the exploration of the processing parameters via compression molding, torque rheometry/thermopressing was chosen to prepare the composites based on recycled PET/sisal fibers/plasticizers to verify the feasibility of faster processing. This process restricts the length of the fibers. Thus, fibers that were 5 mm in length were used in this article.

The goal of this step was to prepare only one composite to compare the properties of the composites prepared from two different processes (torque rheometry/thermopressing and compression molding). In this context, only the post-processing mixture of recycled PET/sisal fibers/glycerol/CO was chosen for further thermopressing and characterization.

The DSC and dTG curves for the composite CHGC are presented in Figure 9.

The DSC curve of the composite CHGC [Figure 9(a)] shows peaks between 230°C and 260°C, which were related to the endothermic melting. Near 380°C, the curve showed an exothermic peak, which can be attributed to the exothermic decomposition of cellulose. This decomposition results a decomposition peak in DSC curve of fibers near 370°C [Figure 3(a)], as previously mentioned. The composite CGC (processed via compression molding) that had the same composition as the CHGC showed on its DSC curve the same thermal events presented by the CHGC at similar temperature values (figure not shown).

The dTG curve of the composite CHGC [Figure 9(b)] showed two stages of mass loss. The first stage of mass loss near 180°C can be attributed to plasticizer volatilization. The other stage of mass loss near 420°C was likely related to the decomposition of recycled PET. A "shoulder" can also be observed near 360°C, which may be attributed to thermal decomposition of sisal fibers [Figure 3(b)]. The different processing methods used to generate the identically composed CHGC and CGC (i.e., torque rheometry/thermopressing and compression molding, respectively) did not significantly affect the thermal properties of the materials. The dTG curve for CGC (figure not shown) showed the same stages of mass loss in temperature regions similar to those observed for CHGC. The thermal decomposition of CHGC began near 270°C and near 260°C for the composite CGC.

The DMTA results (curves not shown) indicated that CHGC showed a T_g of approximately 63°C. This value is relatively close to the T_g obtained for the composite CGC [approximately

68°C, Figure 7(b)], which has the same composition as CHGC but was processed via compression molding.

The composites that had the same composition but were processed via different techniques and using different fiber lengths (5 mm and 3 mm, respectively), i.e., CHGC and CGC, also showed similar storage moduli at 30°C. Specifically, CHGC had a storage modulus of 502.1 MPa and CGC had a storage modulus of 540.9 MPa [Figure 7(a)].

CONCLUSIONS

The different types and/or mixtures of plasticizers used in this article decreased the T_m of the recycled PET, which facilitated the processing of the materials at temperatures below the melting point of the neat polymer. Without the use of plasticizers, this temperature is high enough to lead to significant decomposition of the lignocellulosic fiber (sisal, in the article). Additionally, the decrease in the melt viscosity of PET, which resulted from the presence of plasticizers, increased the wettability of the fiber by the polymer. This effect in turn increased the protection of the fiber against thermal decomposition because they were more efficiently covered by polymer during processing. These factors enabled the preparation of composites that did not indicate thermal decomposition of the fiber, such as that observed during processing without plasticizer.

The storage modulus (30°C), T_g and damping peak values of CT indicated that TBC also acted as a compatibilizer as well as a plasticizer. In other composites, the plasticizing action was more evident due to the presence of a small molecule (glycerol).

The different processing techniques (rheometry/thermopressing and compression molding), which were used to prepare the composites with the same composition and different sisal fibers lengths, did not significantly influence the thermal properties of these materials.

Composites were prepared from a recycled polymer available in many parts of the world and from other components derived from renewable sources, namely, sisal fibers and the plasticizers considered in this article. This approach meets the environmental expectations of global society. The materials described in this article have potential for various applications, such as nonstructural parts of automotive vehicles and civil construction, among other possibilities.

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