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Low density polyethylene composites reinforced with Australian King Palm fibers: mechanical and thermal properties

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Abstract The aim of this work is to obtain and evaluate the mechanical and thermal properties of low Density Polyethylene (LDPE) composites reinforced with fibers from Australian King Palm fibers. *Raw* fibers were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) Spectroscopy. The chemical composition of the fibers was also evaluated. After characterizing the fibers were mixed into the LDPE, in proportions of 5, 10, 15 and 20% (wt/wt) using a thermokinetic mixer model MH-50H. Furthermore tensile, flexural and impact specimens were prepared for evaluation of mechanical properties. The composites were analyzed through SEM micrographs of fractured surfaces and thermal analysis. The results indicate that the reinforcement decreases the thermal stability of the composites, but caused an increase the mechanical properties of the composites. The composites reinforced with of raw fibers 20% (wt/wt) showed significant increase in the tensile strength, flexural and impact.

Keywords Palm fibers · LDPE · Composites · Mechanical properties · Thermal mechanical

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Introduction

Due to environmental concerns, new researches have been led to the use of sustainable materials. The most discussed sustainability parameters are related to the replacement of traditional materials by alternative ones. Thus, industries have invested in new techniques and technologies and also considered the environmental issue in their production strategies.

Thereby the interest in inserting natural fibers in polymeric matrices have caused deep impact on the point of view of reducing the need of materials from non sustainable sources, as well as environmental and economic [1–3]. Besides, the use of materials from sustainable sources has been studied due to the advantages they offer when compared to synthetic materials [4–6]. Natural fibers are advantageous due to their biodegradability, low density, low abrasion to equipment and comparable specific mechanical properties to glass fiber-reinforced composites [7].

An important factor which favors the use of natural fibers as sustainable input is the increasing perspective of power economy by reducing the weight of components as well as the aspects related to raw materials recovering and the re-use of materials in the end of products life cycle [8]. Besides, agro-industrial leavings are generated in large scale and the proposal of re-using them for example; the Australian Royal Palm is very interesting. The fiber of Australian Royal Palm presents advantages according to its abundance and cost once it is a palms industry byproduct. And as Brazil is responsible for supplying 95% of palm in external market, there was an increase in heart palm consumption which led to its disorderly extraction and to the extinction of palm native species.

To reduce predatory extraction and preserve native species, the growth of non-native species as the Australian King Palm (*Archontophoenix alexandrae*) [9] was begun. *A. alexandrae*, commonly known as King Palm, is a kind from *Aracaceae* family from Australia. The palm fiber can be extracted from several palm species. The *A. alexandrae* produces noble palm species [10].

From the cultivation, a lot of waste is generated. For each extracted palm, approximately 400 g of commercial palm is extracted and the waste generated consists of 80–90% of the palms total weight.

Despite these properties, incompatibility with non-polar matrices, moisture absorption, and vulnerability to thermal degradation are the main disadvantages for the use of natural fibers in composites [11]. For the reinforcement and matrix to act together in a specific application, interfacial contact must be proper [12]. Many works indicate superficial change in natural fibers to increase superficial energy, before being used as reinforcement of polymeric matrices aiming at improvement of compatibility between fiber and matrix [13]. The properties of composites also are influenced by the fiber architecture (aspect ratio and orientation of fibers) [14].

In this context, the aim of this work is to develop and evaluate the mechanical and thermal properties of the LDPE composites reinforced with fibers of Australia Royal Palm for Biosolvit company. LDPE have been widely used as matrix for obtaining composites reinforced with natural fibers: doum/LDPE [4], coconut/LDPE [15], sugarcane bagasse/LDPE [16], cotton/LDPE [17] among others.

Experimental

Materials

Fibers from Australian King Palm used were provided by Biosolvit company. These fibers were dried at 80 °C for 24 h. Firstly, the fibers were cut and dried in kiln at 60 °C until constant weight being sieved afterward in sieves of 10, 20 and 40 mesh. Low density polyethylene obtained from Braskem was used as matrix.

Fibers analysis

The palm fibers were characterized by XRD, SEM and FTIR Spectroscopy to evaluate the chemical, physical and morphological properties of fibers. It was also chemically characterized using analytical methodology of fibers from sugarcane bagasse validated by Gouveia et al. [18].

SEM micrographs were obtained through Hitachi-TM3000 Scanning Electron Microscope performing from 15 to 20 kV, using secondary electrons to obtain information of fibers morphology. The samples were fixed to a holder with double-side adhesive carbon tape and submitted to metallic recovering with gold.

Chemical structures of the fibers were evaluated by FTIR. The spectrum was obtained on an FTIR spectrophotometer (Perkin Elmer). The samples were prepared by mixing the material and KBr in a proportion of 1:200 (w/w). For each sample, 16 scans were accumulated with a 4 cm^{-1} resolution.

Crystallinity of the fibers was evaluated by XRD technique. X-ray diffractogram was obtained in a Shimadzu diffractometer, model XRD6000. The measuring conditions were: CuKa radiation with graphite monochromator, 40 kV voltage and 40 mA electric current. The patterns were obtained in 10°–50° 2θ angular intervals with 0.05° step and 1 s of counting time.

With the results obtained through the diffractometer it was possible to calculate the fiber crystallinity indexes using Eq. 1, defined by empirical method [19] that provides an estimated value:

$$I_c = \frac{I_{(002)} - I_{(am)}}{I_{(002)}} \times 100 \qquad (1)$$

in which: $I_c \rightarrow$ crystallinity index in percentage; $I_{(002)} \rightarrow$ peak of diffraction intensity which represents crystalline material close to $2\theta = 22°$; $I_{(am)} \rightarrow$ peak of diffraction intensity which represents amorphous material close to $2\theta = 16°$.

Preparation of composites

The fibers were mixed with the polymeric matrix (LDPE) in a thermokinetic mixer model MH-50H, with the speed rate at 5250 rpm (rotation achieved during the melting), in which fibers were responsible for 5–20 wt% of the composition. After mixing, composites were dried and ground in a mill model RONE. Then, fibers/PP composites were placed in an injector chamber model RAY RAM-model TSMP at

Table 1 Composition of the composites and pure LDPE

Samples	LDPE (wt%)	Fiber content (wt%)
LDPE	100	–
CP5%	95	5
CP10%	90	10
CP15%	85	15
CP20%	80	20

CP- palm fibers reinforced low density polyethylene composites

250 °C. The melted material was injected in required dimensions in a pre-warm mold to obtain tensile, flexural and impact specimens. The nomenclature and composition of samples tested are given in Table 1.

Mechanical tests

Composites were analyzed in an "EMIC" universal-testing machine (model DL10000) equipped with pneumatic claws. For tensile tests, five specimens of composites were analyzed, with dimensions in agreement with the ASTM D 638 standard: 19 mm width, 165 mm length and 3 mm thickness at 2 mm min^{-1} crosshead speed. In the flexural tests, a load was applied on the specimen at 1.3 mm min^{-1} crosshead motion rate. Five specimens were analyzed with dimensions in agreement with the ASTM D 790 standard: 25 mm width, 76 mm length and 3.2 mm thickness. The adopted flexural test was the 3-points method.

Impact test of the composites were analyzed in a "pantec" machine (model 30), five specimens of composites were analyzed, with dimensions in agreement with the ASTM D 6110 standard: 12 mm width, 55 mm length and 6 mm thickness.

The fractured composites were evaluated using scanning electron microscopy (SEM). The composites also were examined using an optical microscope equipped with a camera.

Thermogravimetric analysis (TGA)

Thermal stability of fibers and composites was performed on a Simultaneous Thermal Analyzer from Perkin Elmer under a flow of nitrogen. The temperature range selected was from 40 to 600 °C at a rate of 10 °C/min. For each sample, duplicate runs were done.

Results and discussion

The palm used as raw material was characterized for the chemical composition, and the results are given in Table 2. It was possible to evidence a superior cellulose contents in the fibers when compared to sugarcane bagasse, which favors the increase in strength of the composites, because the cellulose has the highest Young's modulus [20].

Table 2 Chemical composition of palm fibers

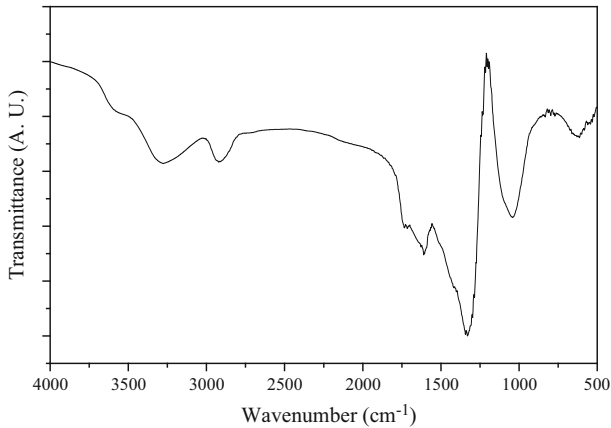| Chemical component (%)	Palm fiber	Sugarcane Bagasse fiber [20]
Cellulose	52.3 ± 0.6	47.4 ± 0.8
Hemicellulose	24.2 ± 0.5	25.1 ± 0.6
Lignin	21.5 ± 0.4	23.4 ± 0.2
Ashes	2.1 ± 0.1	3.3 ± 0.1
Process yied	100.1	100

Fig. 1 FTIR spectra of raw palm fibers

Figure 1 illustrates the FT-IR spectra obtained for raw palm fiber used in this work. The spectral profiles showing the characteristic peaks of lignin, hemicellulose, cellulose (strong wide band between 3610 and 3055 cm^{-1} assigned to O–H stretching vibrations of alcoholic an phenolic hydroxyl groups involved in hydrogen bonds and 2977–2830 cm^{-1} to C–H stretching vibration) and triglyceride [Ester carbonyl (C=O) functional group at 1735 cm^{-1} and Stretching vibration of the C–O ester group at 1172 cm^{-1}]. These absorptions are similar to sugarcane bagasse fibers [21, 22].

Figure 2 shows the diffractogram for the palm fiber; this fiber has characteristics of semicrystalline material. A major diffraction peak was observed for 2θ ranging between 22° and 23°, which corresponds to the cellulose crystallographic planes (0 0 2).

X-ray diffraction peaks for the material can be attributed to crystallinity scattering, whereas the diffuse background can be attributed to disordered regions. According to this method, fibers showed 29% of crystallinity. On analyzing the fibers crystallinity index, it could be observed as a lower value when compared to other fibers such as green coconut fibers and sugarcane bagasse fibers [23]. This occurred due to the presence of extracts on the fibers' surface. SEM technique and chemical characterization evidence the extracts' presence.
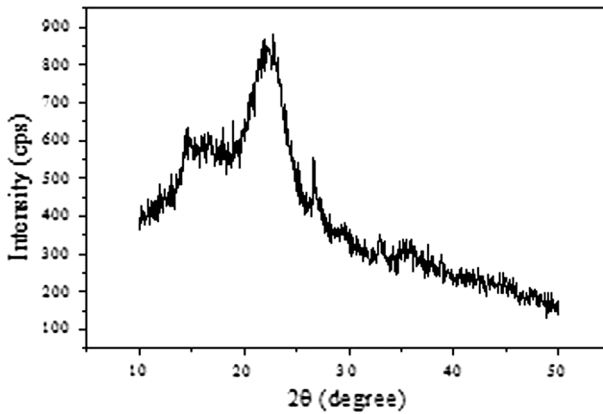
Fig. 2 XRD pattern of raw palm fibers

SEM micrographs of the palm fibers evidence cylindrical fragments and porous with smooth surfaces due to extractives presence, similar to some wax, which are present in the fibers in addition to amorphous contents as lignin and hemicelluloses (Fig. 3).

Besides, it was possible to observe the presence of pits disposed along the cell wall (Fig. 3d). These pits are responsible for transporting water and nutrients throughout various cells to the roots and leaves, and are hidden on the surface fibers [8]. The composites were obtained in different times of mix, due to fibers content. This difference can cause a break and thermal degradation of the fibers, and consequently affect the thermal and mechanical properties of the composites [23]. As the amount of reinforcement in the composite was varied, the visual appearance of the composite also showed this difference.

Mechanical properties of composites were made by three different tests: tensile, flexural and impact, which are shown in Table 3.

The tensile modulus of elasticity and strength of composites were influenced by the concentration of fibers. The tensile strength of the CP5% composites decreased compared to the LDPE pure because this fibers content was not sufficient to transfer the tensile applied at particles. CP20% composite showed more significant increase of tensile modulus compared to the others composites and LDPE pure with an increase of 215%, respectively. As expected, the concentration fibers reinforced in the matrix influenced in the tensile strength and in rigidity of the composites. Similar behavior was observed for Arrakhiz et al. [4] to evaluate the thermal and mechanical properties of doum fibers reinforcing with low density polyethylene (LDPE) composite.

The flexural strength and modulus of the composites were also influenced by concentration fibers inserted in the matrix when compared to pure LDPE. Figure 4 shows that increasing concentration fibers resulted in an increase in the Young's modulus in tensile and flexural compared to the pure LDPE, respectively. These properties have been attributed to interactions between the constituents of the material. Pöllänen et al. [25] also observed similar behavior to evaluate cellulose reinforced high density polyethylene composites.
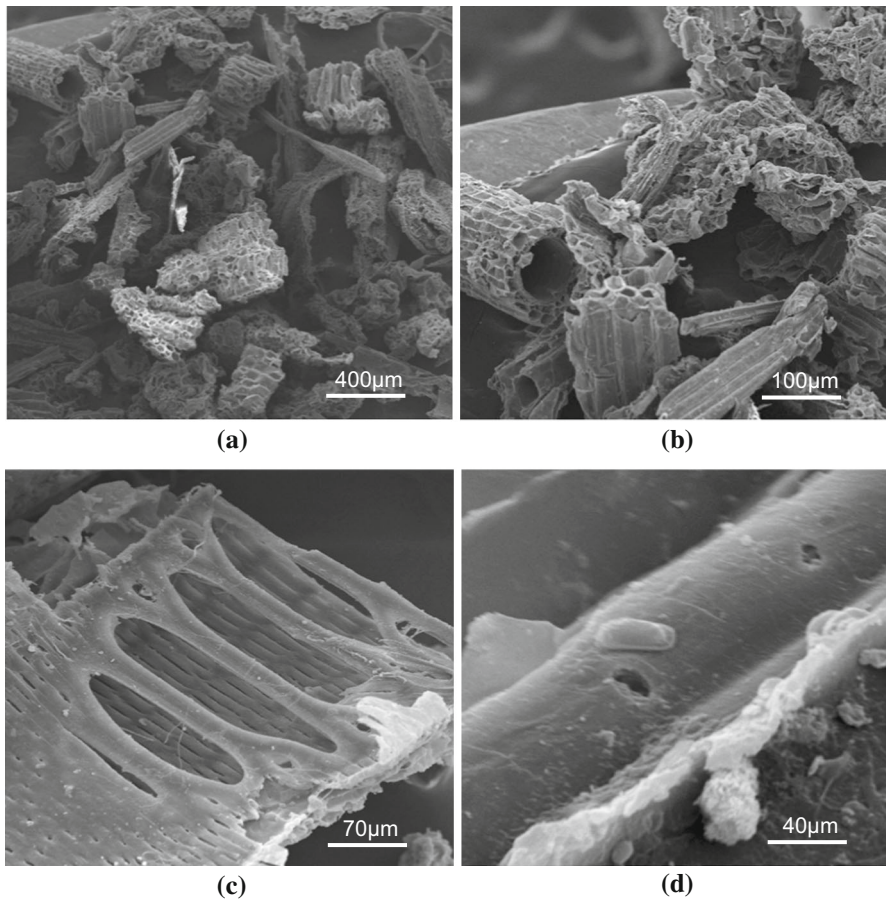
Fig. 3 SEM micrographs of *raw* palm fibers

Table 3 Mechanical properties of the composite materials

Samples	Elongation at break (%)	Tensile strength (MPa)	Tensile Modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (kJ m^{-2})
LDPE	70 ± 1.4	7.8 ± 0.2	63 ± 0.8	7.8 ± 0.5	92 ± 11.2	67 ± 11.2
CP5%	61 ± 0.3	7.6 ± 0.3	61 ± 0.3	7.5 ± 1.1	93.2 ± 23.4	69 ± 9.3
CP10%	69 ± 1.3	7.9 ± 0.4	69 ± 1.5	11 ± 1.1	171 ± 31.5	78 ± 1.1
CP15%	66 ± 1.1	9.1 ± 0.2	79 ± 1.2	16 ± 1.9	174 ± 17.2	88 ± 2.4
CP20%	26 ± 1.1	17.6 ± 0.7	198 ± 11.4	22.5 ± 1.2	226 ± 22.1	110.1 ± 1.9

Similar results were observed in the impact strength, because the fibers' content reinforced in the matrix increased the absorbed energy due to energy dissipation mechanism. When a stress is applied to a polymer, a part of the energy is dissipated
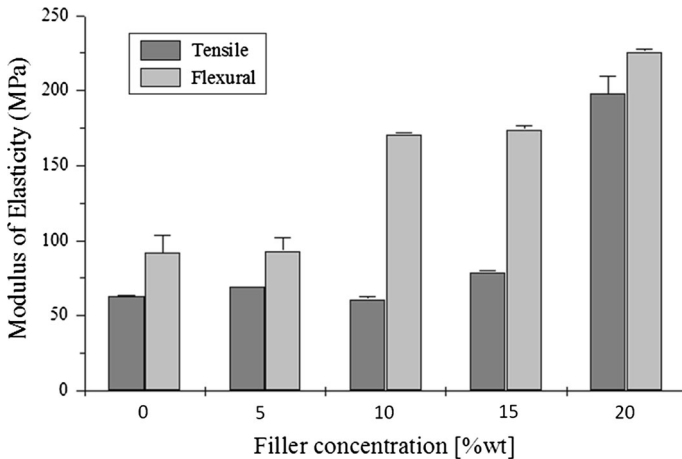
Fig. 4 Tensile and flexural modulus of elasticity of composites with different concentration of fibers

by the movements of chains—viscous flow. These effects are time (or speed or frequency) and temperature dependent—time/temperature superposition principle. Energy dissipation is mainly governed by adhesive viscoelastic properties. The different sources of energy dissipation in fiber-reinforced composites are: viscoelastic nature of matrix and/or fiber materials, damping due to interphase, damping due to damage, viscoplastic damping and thermoelastic damping. It is well known that the toughness of a material is directly dependent on the energy dissipation [24]. The fibers were pulled out from the matrix and dissipated energy during mechanical friction process. Figure 5 shows the fracture of composites after tests, where it could be seen a fiber distribution uniformity in the matrix, broken fibers along the matrix and fibers pulled out, characterizing fragile breakage mechanism.

TGA curves of fibers (Fig. 5) indicate two degradation stages; the first occurred between 200 and 300 °C and it is related to materials thermal degradation and the second stage occurred between 300 and 500 °C which corresponds to the materials full decomposition. Under 100 °C the fiber mass loss is associated to fibers humidity. The degradation of hemicellulose occurred between 200 and 300 °C and the degradation of cellulose and lignin occurs with significant mass loss above 300 °C [20]. Panaitescu et al. [26] evidenced also a broad peak related to pectin and hemicellulose degradation in the range from about 200 to 300 °C in polypropylene composites reinforced with hemp fibers. The degradation of cellulose started later than that of hemicellulose, close to 300 °C, since cellulose is mostly crystalline and more energy is necessary for its degradation.

TGA curves of pure LDPE and composites presented different behaviors. Degradation process of pure LDPE occurred in one stage whereas for composites it occurred in two stages. The first corresponds to fibers decomposition and the second is related to the matrix decomposition. It is noticed that when a larger amount of reinforcement is inserted in the matrix, there is a slight decrease of thermal stability
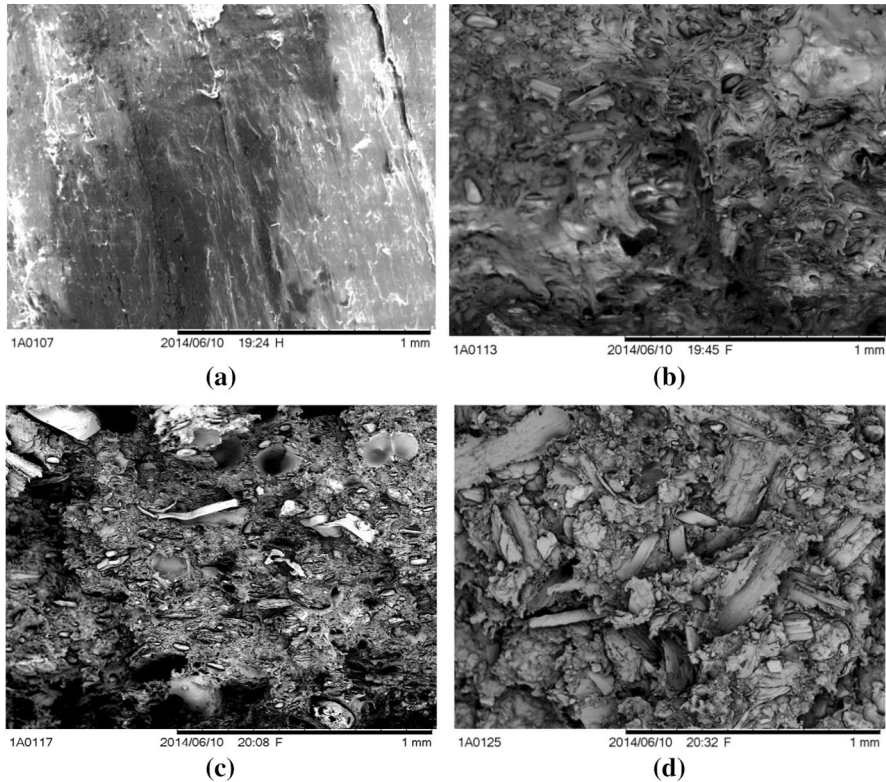
Fig. 5 SEM micrographs of composites with magnification of ×100: CP5% (**a**), CP10% (**b**), CP15% (**c**) and CP20% (**d**)

in the composite, as expected. Figure 6 evidences the peak temperatures of the composites which show that reinforcement decreases the thermal stability of the material.

Table 4 evidences that all the composites have lost less than 10% of their weight up to 230 °C, which is sufficient for their melt processing. It is worth noting that about 6% of this weight loss was released up to 100 °C, representing the absorbed water. The small differences detected above 270 °C (see detail in Fig. 5) can be correlated with the thermal stability of the fibers. Thus, reinforcement decreases the thermal stability of the composite.

Conclusion

Palm fiber-reinforced low density polyethylene (LDPE) composites which can be used in several applications (mechanical part, fiber panel, etc.) were manufactured by a thermokinetic mixer followed by injection molding. This study showed that the in natural palm fibers is an interesting reinforcement for the fabrication of composite materials, because it was not necessary to perform surface treatment to
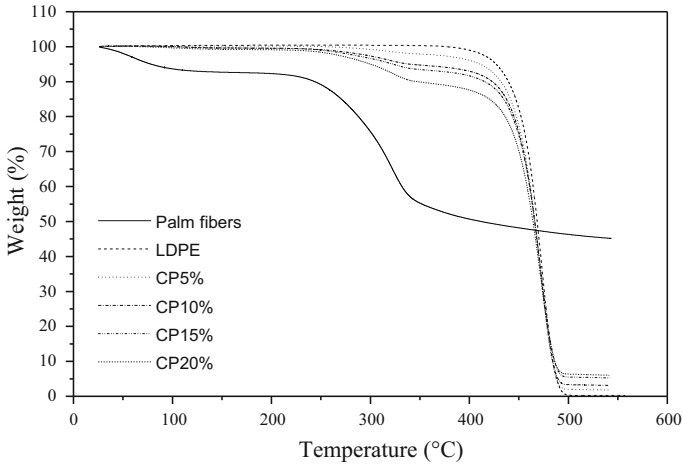
Fig. 6 TGA curves of the materials

Table 4 Mass loss at different temperatures and degradation peaks for pure LDPE and composite fibers

Samples	Mass loss (%)						Degradation temperature (°C)	
	100 °C	200 °C	300 °C	400 °C	450 °C	500 °C		
LDPE	0.1	0.1	0.1	1.0	17.7	99.6	–	423.7
Fiber	6.4	7.7	24.3	49.3	51.8	53.7	238.6	342.9
CP5%	0.1	0.1	0.8	3.9	22.5	98.0	284.5	425.4
CP10%	0.1	0.5	2.7	7.0	24.5	96.7	279.1	436.5
CP15%	0.1	0.4	3.4	8.3	25.4	94.5	313.2	433.5
CP20%	0.4	0.9	5.0	12.4	29.8	93.6	338.2	440.6

improve the interaction between fiber and matrix. The results demonstrated that the content of reinforcement inserted in the LDPE matrix influenced the mechanical and thermal properties, causing a greater stiffness and a decrease in the thermal stability.

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