Article

Cellulose fiber-reinforced high-density polyethylene composites—Mechanical and thermal properties

Daniella R Mulinari[1], Herman JC Voorwald[2], Maria OH Cioffi[2] and Maria LCP da Silva[3]

Abstract

In this investigation, the thermal and mechanical properties of cellulose fibers from sugarcane bagasse reinforced with high density polyethylene composites were evaluated. Cellulose fibers were modified with hydrous Zr oxide to clean the fiber surface and improve the fibers–matrix adhesion. Composites were manufactured using a thermokinetic mixer process and the fiber content was responsible for 5, 10, 20, 30, and 40wt% in the composition. The chemical modification of the cellulose fibers with zirconium oxide was verified by FTIR analysis and the fibers' morphological aspects by SEM. After the chemical modification, the FTIR results showed reduction of OH bonds. SEM characterization showed that the modification changed the morphology of fibers. The results show that composites reinforced with modified cellulose fibers have an improvement in the thermal and mechanical properties, when compared to the non-cellulose fibers. In addition, an enhancement on the mechanical properties of composites was found, i.e. a gain of 122.4% compared to neat polymer at 40wt.% fiber loading in Young's modulus. The thermal properties show a slight decrease with increase of modified cellulose.

Introduction

Many questions on sustainable development have emerged due to the risk of exhaustion of non-renewable raw materials, and emissions of greenhouse gases. So, natural fibers have been evaluated as environment-friendly materials. Thus, the interest in composite materials reinforced with natural fibers increased considerably due to new environmental legislation and consumer pressure has forced manufacturing industries to search materials that can substitute conventional non-renewable materials such as glass and carbon fibers. In recent years, interest in natural fibers has increased worldwide due to their characteristics.[1–4]

Omrani et al.[5] reported on natural fiber-reinforced composites with special reference to the type of fibers, matrix polymers, treatment of fibers, and test parameters, and the results show that composites reinforced with natural fibers have an improvement in tribological properties and their properties are comparable with conventional fibers.

Barari et al.[6] studied that the plant-derived cellulose nano-fibers (CNFs)/bio-based epoxy composites were manufactured using the Liquid Composite Molding (LCM) process and the results indicated that the manufactured composites showed improved mechanical and tribological properties when compared to the pure epoxy samples. Brazil has a large range of natural resources, including natural fibers from several sources, such as banana, coconuts, sugarcane bagasse, cotton, sisal, and curaua.[7–9]

Natural fibers, compared with glass fibers, exhibit better specific mechanical properties, such as stiffness, impact resistance, flexibility and modulus.[10–12]

[1]Department of Mechanical and Energy, FAT/UERJ, Brazil
[2]Department of Materials and Technology, UNESP/FEG, Brazil
[3]Department of Chemical Engineering, EEL/USP, Brazil

Corresponding author:
Daniella R Mulinari, Department of Mechanical and Energy, FAT/UERJ, Resende/RJ, Brazil.
Email: dmulinari@hotmail.com.br

Other desirable properties, related to processing, include lower equipment abrasion and lower energy consumption. In addition, natural fibers are biodegradable and some can be produced on a large scale without displacement of other crops. For these reasons, natural fiber composites have been used in many applications such as architectural materials and in the automotive industry.[13]

However, they also present disadvantages such as incompatibility between fibers and polymer matrices, the tendency to form aggregates during processing, processing permissible temperature which does not collaborate to reinforce the polymer and the poor resistance to moisture, reducing the use of natural fibers as reinforcement in polymers. The incompatibility of components is responsible for poor thermal and mechanical properties.[14]

However, many studies have been aimed to improve the adhesion between fibers and matrix, such as bleaching, acetylation, etherification, estherification, alkali treatment and others.[15–19]

Another important point is the processing temperature, which must be maintained below 200°C to avoid negative influence on properties due to the natural fibers' degradation.[20] High density polyethylene, with melting point of about 120–140°C can be processed at temperatures in the range of 140–200°C.[21] The thermal dimensional stability of a material is a desirable property in many applications, especially when combining different materials.[22]

In this study, cellulose fibers from sugarcane bagasse modified with zirconium oxide and reinforced with high density polyethylene were selected to improve their thermal and mechanical properties. This type modification made in the cellulose fibers have also been used for specific applications such as: TiO_2 for bactericidal activities and reinforcement in polymers matrixes, ZrO_2 for retention and analysis of Cr(VI) and for adsorption of sulfate ions.[23–26]

Methods

Cellulose fibers from sugarcane bagasse were obtained according to Mulinari and Da Silva.[26] The length and diameter values are 100–500 μm and 10–30 μm, respectively.

The chemical structure of cellulose fibers and cellulose fibers modified with hydrous Zr oxide from sugarcane bagasse was evaluated by FTIR spectrophotometer (Perkin Elmer). The samples were prepared by mixing the materials and KBr in the proportion 1:200 (w/w). For all spectra, 16 scans were accumulated with a $4\,cm^{-1}$ resolution. SEM micrographs of non-modified and modified cellulose fibers were obtained using a JEOL JSM5310 field emission scanning electron microscope, operated at 15 kV. Prior to SEM evaluation, the specimen was coated using gold sputtering.

Composites preparation

Cellulose fibers from sugarcane bagasse modified and non-modified were mixed with the HDPE in a thermo-kinetic mixer, model MH-50H, with speed rate maintained at 5250 r/min, in which fibers were responsible for 5, 10, 20, 30, and 40 wt% in the composition. After the mixture, composites were dried and ground in mill. Composites and pure HDPE were placed in an injector camera at 165°C and $2°C\,min^{-1}$ heating rate in a required dimension pre-warm mold to obtain tensile specimens.

Mechanical properties

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 $2\,mm\,min^{-1}$ cross-head 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), and 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.

Thermogravimetric analysis (TGA and DSC)

Samples used for the thermogravimetric analysis were cut from the mixture materials in order to have a weight of 10 mg. Furthermore, specimens were dried in an oven for 1 h at 100°C. TGA was carried out using a SHIMADZU (TGA-50) instrument, in N_2 atmosphere at $10°C\,min^{-1}$ heating rate, from 30 to 650°C.

Results and discussion

Fibers analysis

Infrared spectra of cellulose fibers from sugarcane bagasse without and with modification are displayed in Figure 1.

Table 1 summarizes higher bands observed in the FTIR spectrum of cellulose fibers from sugarcane
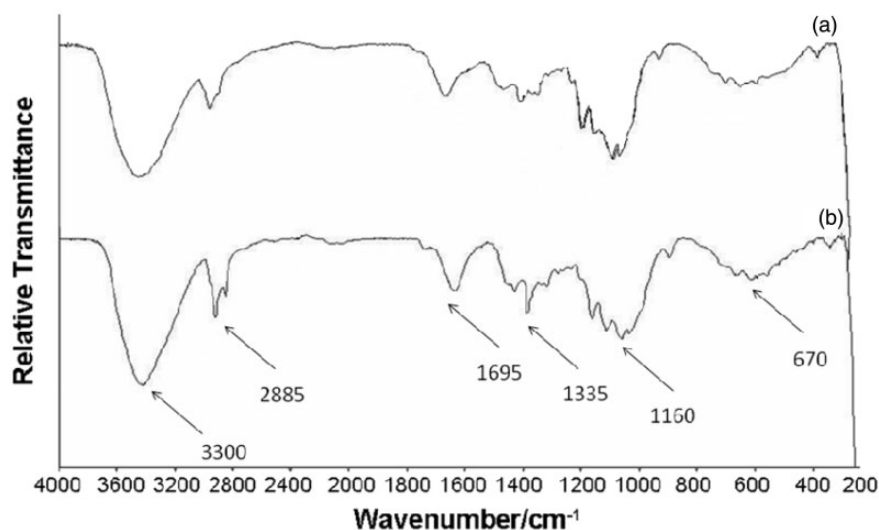
Figure 1. FTIR spectra of sugarcane bagasse (wavenumber 4000–400 cm^{-1}): non-modified cellulose (a) and modified cellulose fibers (b).

Table 1. Infrared main transitions for sugarcane bagasse.

Wavenumber (cm^{-1})	Vibration	Source
3300	O–H linked shearing	Polysaccharides
2885	C–H symmetrical stretching	Polysaccharides
1650-1630	OH (water)	Water
1335	C–O aromatic ring	Cellulose
1162	C–O–C asymmetrical stretching	Cellulose
670	C–OH out-of-plane bending	Cellulose

bagasse and their assignments to chemical group vibrations and molecules.

The most visible differences between the spectra of non-modified cellulose fibers and Cell/ZrO$_2$.nH$_2$O are the modifications of the signal at 2885 cm^{-1} and 1732 cm^{-1}, characteristics of the stretching of symmetrical CH groups and stretching of unconjugated CO groups present in polysaccharides and xylans. Considering the first region, the ratio between intensity of the C–H stretching band ($\sim$2900 cm^{-1}) is lower in the spectrum of the Cell/ZrO$_2$.nH$_2$O material than that observed for the non-modified cellulose fibers. On the other hand, at the second region it may be observed modifications, especially in the ratio between the intensities of the C=O stretching band ($\sim$1730 cm^{-1}).

The SEM evaluations were applied for cellulose fiber characterization before and after chemical modification with hydrous zirconium oxide. Cellulose fibers are shown in Figure 2(a), which evidence fibers of flattened forms and different sizes. The length and diameter values are 100–500 μm and 10–30 μm, respectively. In the modification of fibers, it is noted a large area and roughness on the surface according to Figure 3.

Thermogravimetry analysis

The thermogravimetric results of HDPE, and modified and non-modified cellulose fibers show distinct process of weight loss occurring at different temperatures. Figures 4 to 6 show TGA curves of HDPE, modified and non-modified cellulose fibers, and cellulose fibers/HDPE composites (5 and 40 wt%). For HDPE, there is only one-step decomposition process, while the cellulose fibers and composites show two-step processes.

From the TGA curves, it is possible to observe the starting of modified and non-modified cellulose fibers' weight loss at 300°C (Figure 4). The first process of weight loss of the modified and non-modified cellulose fibers is attributed to thermal degradation of fibers. The next weight loss is associated to decomposition of the α-cellulose present in the fibers. Araújo et al.[20] observed similar behavior with the curaua fibers.

HDPE started decomposition at about 430°C, which was higher in comparison to fibers, Figure 4. On the other hand, composites presented intermediary thermal stability between fibers and matrix, showing synergistic interactions. The addition of fibers decreased the thermal stability of the composites, Figures 5 and 6.

Table 2 shows the weight loss and degradation temperature peak of composites, HDPE, and modified and non-modified cellulose fibers.

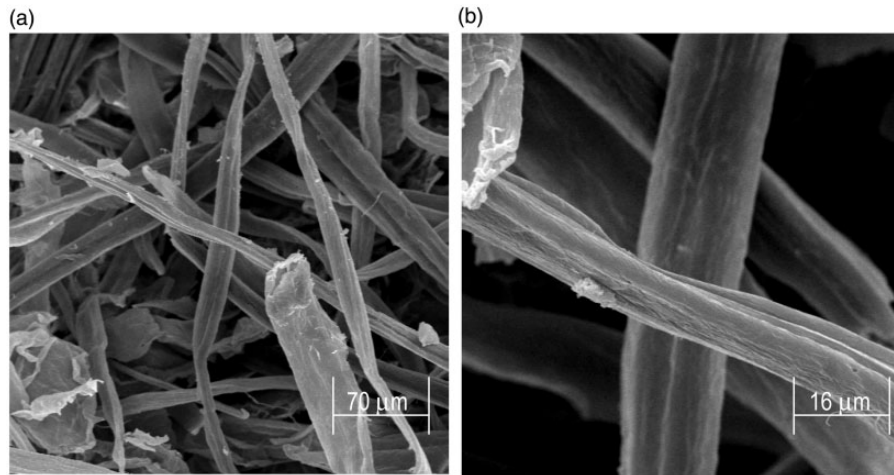Table 2 shows that all the composites have lost less than 10% of their weight up to 270°C, which is

Figure 2. Morphology of cellulose fibers non-modified: (a) 500× and (b) 2000×.
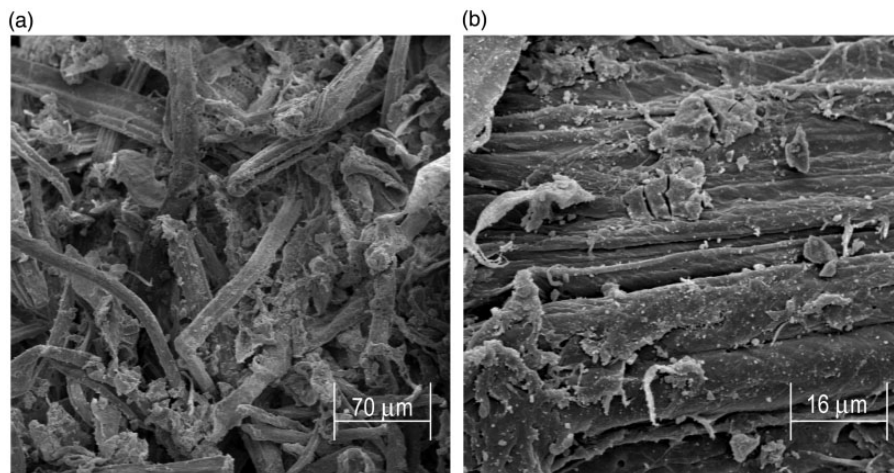

Figure 3. Morphology of cellulose fibers modified: (a) 500× and (b) 2000×.

sufficient for their melt processing. It is worth noting that about 8% of this weight loss was released up to 100°C, representing the adsorbed water. The small differences detected above 300°C (see detail in Figures 5 and 6) can be correlated with the thermal stability of the fibers. Thus, reinforcement decreases the thermal stability of the composite.

It is also observed that high density polyethylene practically did not lose weight at 400°C; however, from 450°C on, the weight loss was fast and accentuated, resulting in minimum residue. HDPE started decomposition at about 434°C (indicates the degradation of saturated and unsaturated carbon atoms in high density polyethylene), which was higher than that for fibers. In this same temperature around, the addition of fibers decreased the thermal stability of the composite, but modified cellulose

fiber-reinforced HDPE composites presented higher thermal stability than the non-modified cellulose fiber-reinforced HDPE composites (at 400°C). One explanation for this fact is that the modified cellulose fiber-reinforced HDPE composites presented more interfacial interaction due to modification on the fibers surfaces. The modified cellulose fibers with hydrous zirconium oxide can be described by equation (1)

$$mCellOH + MX_n \rightarrow (CellO)_m MX_{n-m} + mHX \quad (1)$$

where MX_n is an active metal compound and CellOH corresponds to the hydroxyls groups.

Hydrolysis leads to the formation of oxide monolayer, where the metals are incorporated to the surface through CellO–M bond. The hydrolysis reaction is
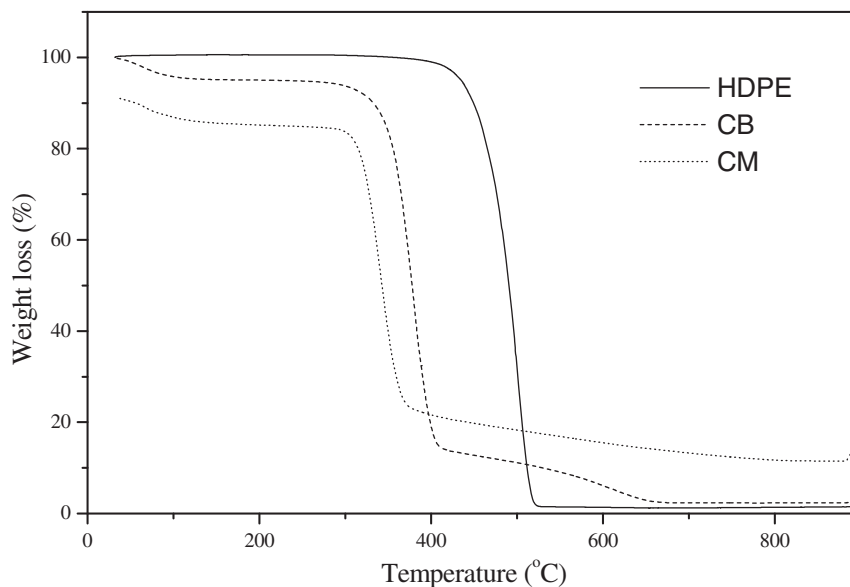
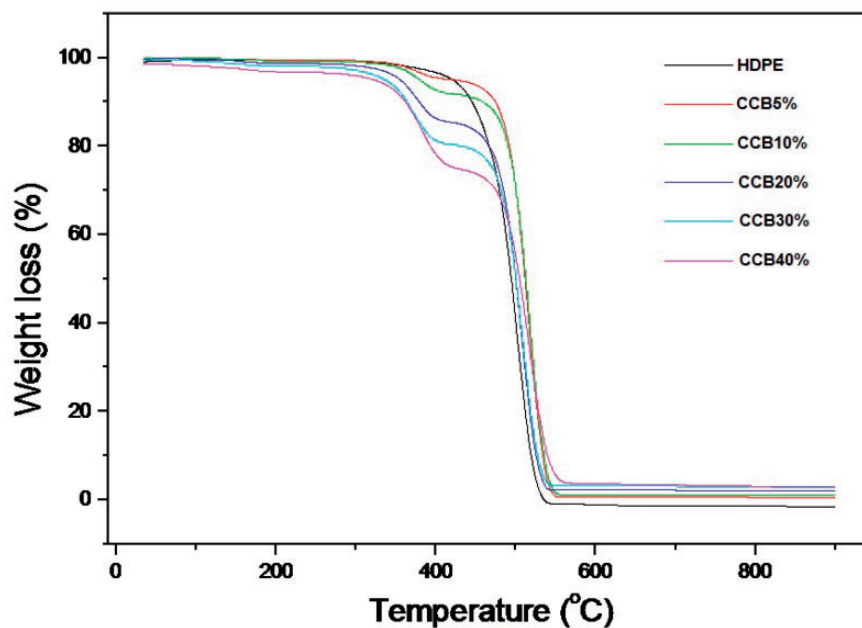**Figure 4.** TGA curves of HDPE and cellulose fibers non-modified (CB) and cellulose fibers modified (CM).

Figure 5. TGA curves of HDPE and CB composites.

shown in equation (2).

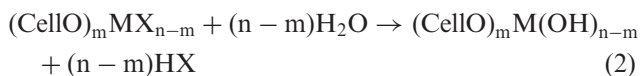$$(CellO)_m MX_{n-m} + (n-m)H_2O \rightarrow (CellO)_m M(OH)_{n-m} + (n-m)HX \quad (2)$$

Figure 7 shows the schematic reaction representation of the Lewis acid with the cellulose.[26] The reaction is carried out under anhydrous conditions in the first step because it is supposed that primarily a donor-acceptor bond is formed between $ZrO_2.nH_2O$ and the oxygen of the C^1–O–C^5 and C^1–O–C^4 bonds. The attack to the former oxide bond leads to a ring opening and provides a molecule rupture process in order to form micro fibers. Ammonium solution is a required mean to promote the chemical link of metallic oxide with fibers surfaces.

Mechanical properties

The addition of cellulose fibers (modified and non-modified) to the HDPE matrix resulted in
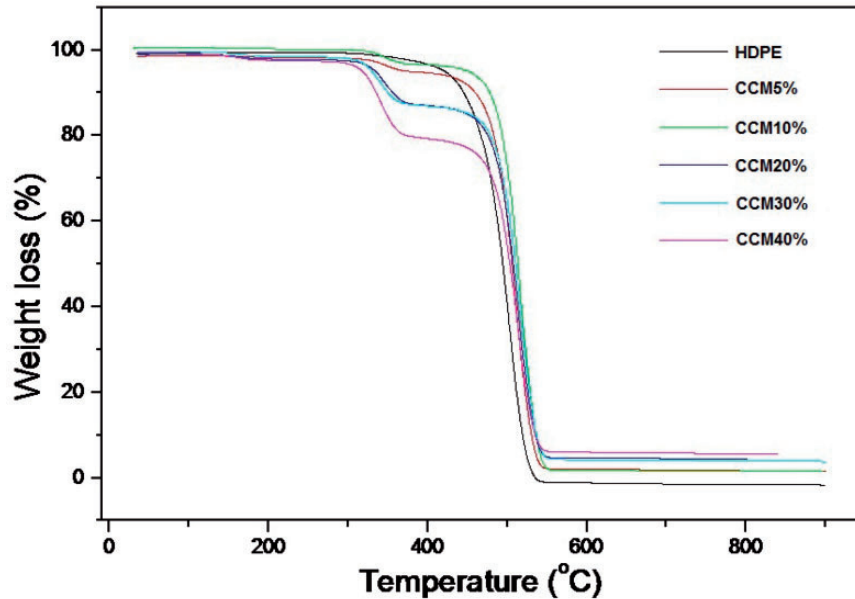
Figure 6. TGA curves of HDPE and CM composites.

Table 2. Thermal properties of the materials.

Samples	Weight loss (%)						Degradation temperature (°C)
	100°C	200°C	300°C	400°C	500°C	600°C	
HDPE	0.65	0.65	0.74	3.33	59.7	98.7	–	434
CB	4.3	5.1	6.4	81.2	88.9	93.9	–	335
CM	13.1	14.8	16.3	78.4	81.7	84.5	–	312
CCB5%	0.0	0.5	0.6	4.3	26.7	99.4	365.0	476.0
CCB10%	0.2	0.65	1.0	7.6	33.4	98.8	376.8	513.7
CCB20%	0.3	1.2	1.8	13.4	43.9	97.8	379.3	510.3
CCB30%	0.6	1.8	2.7	18.4	45.2	96.8	375.6	511.2
CCB40%	1.9	3.2	4.2	22.8	49.1	96.4	377.7	512.7
CCM5%	1.3	1.7	19	5.3	39.8	98.0	347.1	510.4
CCM10%	0.8	1.0	1.2	4.7	28.2	98.2	345.2	516.6
CCM20%	1.05	2.1	2.5	13.0	39.1	95.3	346.4	513.4
CCM30%	0.5	1.5	2.0	13.1	35.4	95.7	339.3	515.5
CCM40%	0.8	2.4	3.2	20.7	45.6	94.0	340.0	511.8

CB, cellulose fibers non-modified; CM, cellulose fibers modified; CCB%, HDPE composites reinforced with cellulose fibers non-modified %wt; CCM%, HDPE composites reinforced with cellulose fibers modified %wt.

changes of the mechanical properties, which are shown in Table 3.

The increase in the fiber content from 0 to 40 wt.% resulted in a twofold increase in the Young's modulus, from 732.5 MPa of neat HDPE to 1629 MPa when 40 wt.% fiber is added. A significant increase in the modulus can be observed with increasing fibers content.[25] Cellulose fibers modified may exhibit greater interactions with the polymer matrix, resulting in a good dispersion in the composite. This fact occurred due to modification of the fibers, which decreases the effective interfacial tension between fibers and the polymer chains leading to better interaction and properties.

Another result that is observed is the progressive decrease in elongation at break of composites compared to pure HDPE. This decrease on the elongation may be attributed to a reduction in deformability of the rigid interface between fibers and matrix.[25]
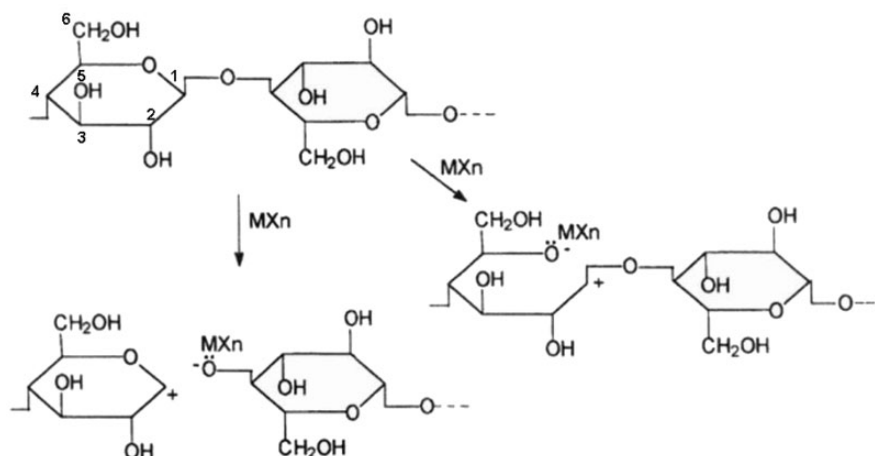
Figure 7. Reaction of the Lewis acid with cellulose and formation of the donor-acceptor bond.[27]

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})
HDPE	8.9 ± 0.8	15.7 ± 1.1	732.5 ± 90.6	18.6 ± 0.2	794 ± 17	38.9 ± 0.5
CCB5%	5.4 ± 0.4	16.2 ± 0.7	942.5 ± 98.6	18.8 ± 0.4	1002 ± 32	45.9 ± 0.1
CCB10%	5.5 ± 0.2	15.6 ± 0.3	897 ± 27.5	20.1 ± 0.7	1107 ± 35	46.5 ± 0.1
CCB20%	5.7 ± 0.3	15.8 ± 0.3	1141 ± 62.5	20.4 ± 0.3	1087 ± 37	48.0 ± 0.2
CCB30%	6.0 ± 0.7	16.7 ± 0.8	1156 ± 178	21.9 ± 1.4	1176 ± 65	49.0 ± 0.3
CCB40%	5.7 ± 0.5	16.8 ± 1.3	1217 ± 191	22.1 ± 1.0	1238 ± 50	50.6 ± 0.1
CCM5%	7.2 ± 0.1	20.8 ± 0.4	1178 ± 25	18.8 ± 0.7	1294 ± 94	48.1 ± 0.7
CCM10%	7.4 ± 0.4	21.9 ± 0.6	1238.5 ± 41	22.1 ± 0.5	1244 ± 21	50.0 ± 0.1
CCM20%	6.5 ± 0.2	20.9 ± 0.4	1306 ± 27	21.3 ± 0.5	1241 ± 40	51.6 ± 0.1
CCM30%	5.5 ± 0.2	19.9 ± 0.4	1490 ± 71	23.2 ± 0.1	1303 ± 30	52.4 ± 0.1
CCM40%	5.9 ± 0.4	23.2 ± 0.6	1629 ± 109	23.1 ± 1.7	1304 ± 97	53.5 ± 0.1

CCB%, HDPE composites reinforced with cellulose fibers non-modified %wt; CCM%, HDPE composites reinforced with cellulose fibers modified %wt.

Similar behavior was described by Arrakhiz et al.[28] to evaluate the mechanical and thermal properties of Pine cone fiber-reinforced compatibilized polypropylene.

Flexural properties of the composites were also influenced by amount of reinforcement embedded in the matrix. It was noted that the content of fibers reinforced in the matrix influenced the flexural strength and modulus when compared to pure HDPE, respectively. The flexural modulus of composites also increased from 0 wt.% to 40 wt.% fiber mass content. This increase may be explained by a better fibers–matrix interaction under the compressive stresses during bending, developed in the transverse section of the flexural specimens for whatever the surface condition of the fibers.[29] In this work, 30 wt.% cellulose fibers-modified reinforced HDPE matrix was the optimum percentage to make the best flexural modulus.

It was observed similar results in impact tests. The insertion of fibers in the matrix caused an increase in the absorbed energy and consequently in the strength due to energy dissipation mechanism. This is probably due to the brittle behavior of fibers which limits the plasticity behavior of the composites compared to the neat polymer matrix.[27] The fibers were pulled out from the matrix and dissipated energy during the mechanical friction process. Figure 8 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 (Figure 8(a) and (c) for non-modified), characterizing fragile breakage mechanism. Thus, from Figure 8(b) and (d) it was found that
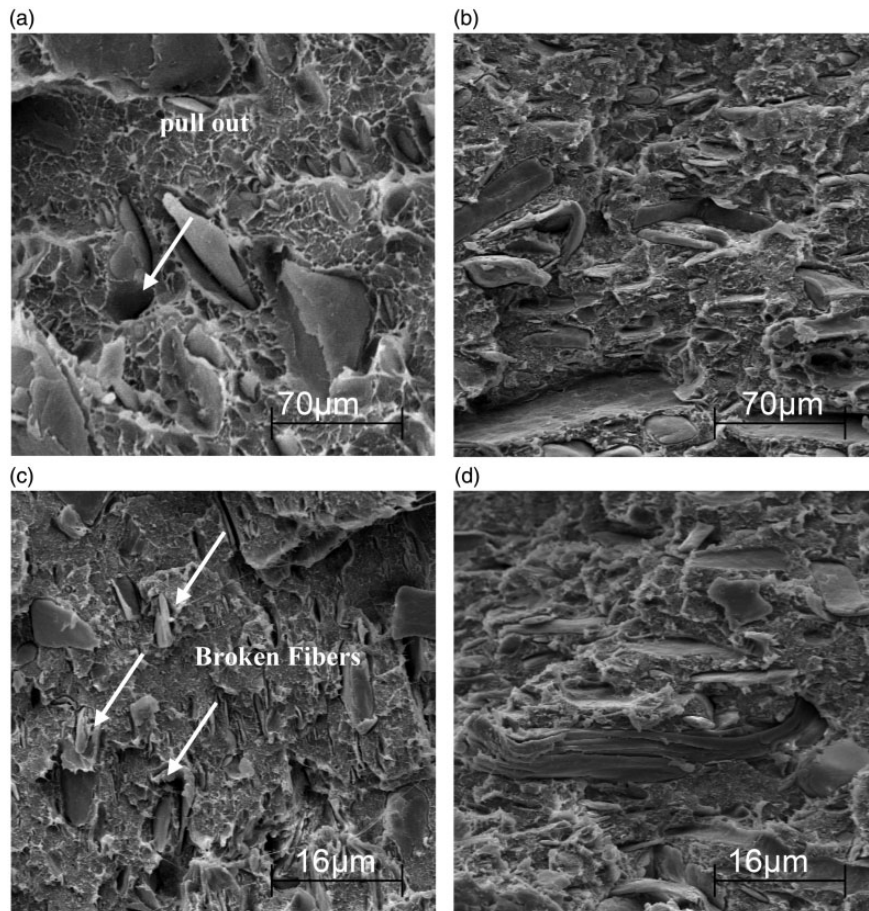
Figure 8. SEM of the composites after impact tests: (a) CB 30%; (b) CM 30%; (c) CB 40%; and (d) CM 40%.

the modified cellulose fibers facilitated diffusion matrix to the interior of the fiber, increasing the impact resistance.

Conclusions

The objective of this study was to evaluate the benefits of reinforcing high density polyethylene with cellulose fibers modified with zirconium from sugarcane bagasse. The effect of zirconium oxide on cellulose fibers from sugarcane bagasse was confirmed by FTIR analysis and SEM. After the chemical modification, the FTIR results showed reduction of OH bonds. SEM characterization showed that the modification changed the morphology of fibers. The modification on cellulose fibers surfaces and composition affected the thermal stability and mechanical properties of the composites.

Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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