THERMO-MECHANICAL BEHAVIOR OF HDPE/SUGARCANE BAGASSE FIBER/ORGANOCLAY NANOCOMPOSITES

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Abstract

In recent years, studies have shown that the addition of natural fiber or proper filler is an effective strategy for achieving improved properties in polymer composites. Moreover, is especially important if such fibers are residues of agro-industrial processes. In this work, a promising technique to develop HDPE matrix nanocomposites by the addition of natural fibers and clay nanoparticles prepared by extrusion process is described. The HDPE with 20 % (w/w) of sugarcane bagasse fiber from agro-industrial residues and 3 % (w/w) of bentonite chocolate organophilic nanoclay (Brazilian smectitic organophilic clay) addition were obtained using a twin-screw extruder machine type. After extrusion process, the composites were characterized by tensile and flexural tests, SEM, Vicat and HDT tests. The MFI tests were determined to evaluate the effects of fiber and organoclay addition on dynamic viscoelastic melt of the HDPE. The results showed that the thermo-mechanical properties of nanocomposites obtained were superior to those of the pure HDPE.

Introduction

In recent years, studies have shown that the addition of natural fiber or proper filler (either organic or inorganic fillers) is an effective strategy for achieving improved morphology and mechanical properties in polymer composites. Moreover, is especially important if such fibers are residues of agro-industrial processes [1]. Sugarcane processing generates a large volume of residue called bagasse. Sugarcane bagasse fiber residues are widely produced in Latin America as by-products of the sugar and bioethanol industry [2, 3]. In 2009, the Brazil produced 612.21 million tons of the sugarcane, from which about 54 % was used to produce alcohol (bioethanol industry) and ca. 45 % was used to produce sugar. The Uruguay, in 2009, the sugarcane production reached the highest value of the decade, about 334.000 tons [4, 5].Disposal of bagasse is critical for both agriculture profitability and environmental protection. So, the use of annual growth agricultural crop such as sugarcane in Brazil and Uruguay has resulted in significant property advantages for use bagasse fiber residues in this country to produce polymer composites [6, 7]. It is estimated that the annual worldwide production of dry sugarcane bagasse fiber is about 54 million tons [3]. On the other hand, fiber reinforced polymer composites are

very attractive because of their ease of fabrication, economy and superior mechanical properties. Extrusion compounding and injection molding processes are frequently employed to make polymer composites [8].

Both thermoplastic and thermoset materials can be reinforced and made into composite materials, but composites with very short fibers tend to have thermoplastic matrices. This is because fibers must be able to go through small clearances, such as the gap between the extruder screw and the extruder wall or the gate that connects the mold cavity with the runner system in both injection molding and transfer molding when being extruded or injection molded. Moreover, thermoplastics often need the additional strength or additional stiffness gained from reinforcing with short fibers [9]. Recently, much effort has been made towards development of polymer-clay nanocomposites, and to understand the enhancement in properties upon addition and dispersion of organoclay in polymers [10, 11, 12]. High density polyethylene (HDPE) is a linear polymer with the chemical composition of polymethylene, (CH2)n, and is defined as a product of ethylene polymerization, with a density of 0.94 g/cm3 or higher. HDPE consumption continues to grow annually, with product substitution and potential new applications, increasing volume sales growth [13, 14]. The organophilic clays can have a high swelling in organic solvents and are widely used as rheological additives in paints, oil drilling fluids, in cosmetics and in industry in general. They are being used as nano fillers for polymer clay nanocomposites conferring high-level properties with additions of small amounts of filler [15].

The preparation of HDPE-clay nanocomposites remains a scientific challenge. Polyolefins are difficult to intercalate in the interlayer space of hydrophilic swelling clays without chemical modification of one of the two components. In order to solve the problem of the lack of interfacial adhesion between apolar HDPE and polar clays, the addition of polyethylene grafted with maleic anhydride to the polyethylene matrix has been proven to favor the intercalation/exfoliation process, with important improvements of the material stiffness, maintaining the ultimate stress and strain at an acceptable level [16].

There are few studies about organoclays incoproration in natural fiber/polymer composites. The goal is to study the influence of the incorporation of a Brazilian organoclay in composites of high molecular weight polyethylene fiber and sugarcane bagasse.

Experiment/Methods

Materials

The materials used in this study were HDPE resin (HDPE JV060U – commercial grade by Braskem S/A), with MFI = 6.4 g/10 min at 190 0C/2.16 Kg, specific density = 0. 957 g/cm^3, HDPE grafted with maleic anhydride (1 wt %), sugarcane bagasse fiber from agro-industrial residues and bentonite chocolate organophilic nanoclay (Pegmatech Especialidades Tecnologicas Ltda.) as a powder with toluene swelling of 8 mL/g.

Sugarcane bagasse fibers Preparation

In order to remove the impurities, the sugarcane bagasse fiber residues were scraped, washed, and kept in distilled water for 24 h. The fiber was then dried at 80 ± 2 ºC for 24 h in an air-circulating oven. The dry fiber was reduced to fine powder, with particle sizes equal or smaller than 650 μm, by using knife mills, and dried again at 80 ± 2 ºC for 24 h to reduce the moisture content to less than 2 %.

Nanocomposites Preparation

The HDPE resin reinforced with 20 % sugarcane bagasse fiber and 3 % bentonite chocolate organophilic nanoclay and HDPE grafted with 1 % (w/w) maleic anhydride, was obtained using a twin-screw extruder machine "ZSK 18 MEGAlab extruder" made by Coperion Werner & Pfleiderer GmbH & Co. KG. The samples for thermo-mechanical tests and scanning electron microscopy (SEM) analyses were prepared using the injection molding machine made by Indústrias Romi S.A.

Nanocomposites Characterization

The following tests and analyses were performed to characterization of the HDPE and HDPE/Sugarcane bagasse fiber/bentonite chocolate organophilic nanocomposite, called HDPE and HDPE/Bagasse/Nanoclay, respectively.

Thermo-mechanical tests

The following thermo-mechanical tests were performed: the tensile tests according to ASTM D 638 [17] and the flexural tests were based on ASTM D 790 [18]; the Vicat softening temperature tests were done according to ASTM D 1525 [19] and those of heat distortion temperature (HDT) were based on ASTM D 648 [20]. Statistical analyses were conducted on the thermo-mechanical data to determine the significance of the differences between HDPE resin and HDPE/Bagasse/Nanoclay obtained. Five replicate samples were analyzed, and average and standard deviation were calculated to represent the data. In addition, significant differences between the HDPE and nanocomposite samples were determined by ANOVA assuming equal variance at a level of $p < 0.05$, using BioEstat software (version 5.0, 2007, Windows 95, Manaus, AM, Brazil).

Melt flow index (MFI) measurements

The MFI measurements were determined with a Microtest extruder plastometer (ASTM 1238-04) in the conditions specified for HDPE [25].

Scanning Electron Microscopy (SEM)

The scanning electron microscopy (SEM) analyses were carried out using a LX 30 (Philips).The samples were freeze-fractured under liquid nitrogen, and then the fractured surface was coated with a fine layer of gold and observed by scanning electron microscopy.

Results and Discussion

Thermo-mechanical tests

Figure 1 shows the results of the tensile strength at break tests for both, HDPE and HDPE/Bagasse/Nanoclay. These results shown in Figure 1 represent the mean values calculated from data obtained by tensile tests. The standard deviation for the results of the tensile strength was less than 10% for all tests. As it can be seen, there were significant increases ($p < 0.05$) of around 270 % in HDPE tensile strength at break due to sugarcane bagasse fiber and bentonite chocolate organophilic nanoclay addition.

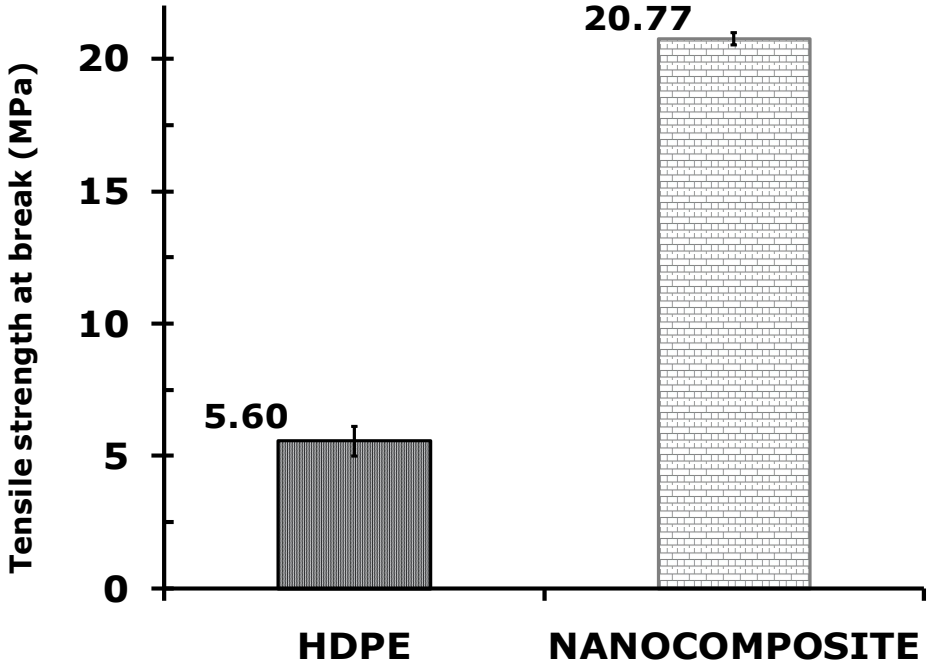

Figure 1. Tensile strength at break, for HDPE and HDPE/Bagasse/Nanoclay nanocomposite.

The flexural strength average values for both, HDPE and HDPE/Bagasse/Nanoclay, are given in Fig. 2. As it can be observed, the nanocomposite flexural strength was, significantly, ca. 18 % higher than for HDPE samples ($p < 0.05$).

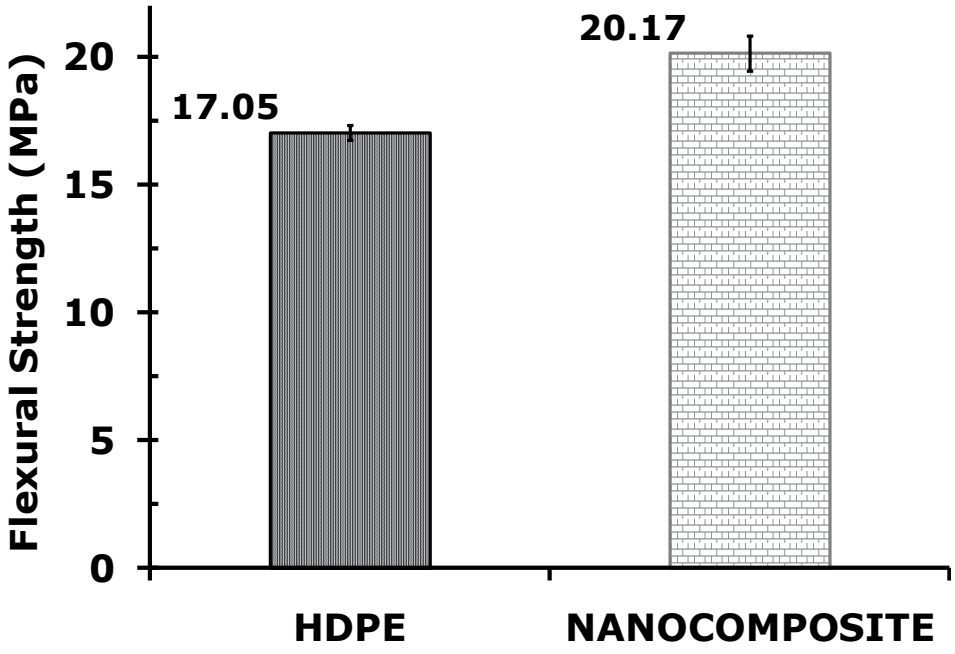

Figure 2. The flexural strength, for HDPE and HDPE/Bagasse/Nanoclay nanocomposite.

Figure 3 shows the results of the flexural module average data for both, HDPE and HDPE/Bagasse/Nanoclay. As it can be observed the flexural module of HDPE doubled, due to the incorporation of bagasse fibers and bentonite nanoclay.

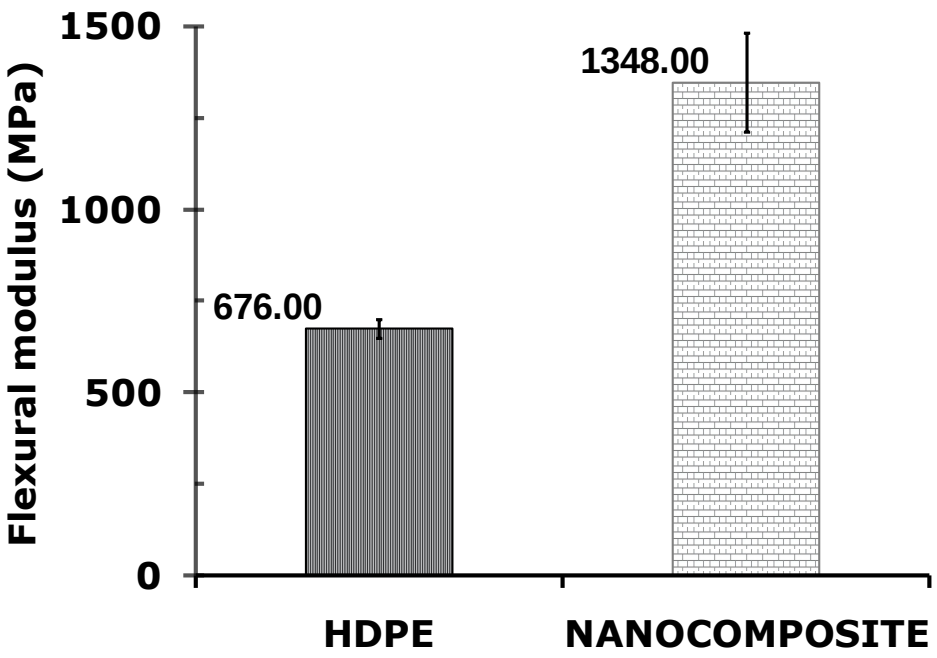

Figure 3. The flexural modulus, for HDPE and HDPE/Bagasse/Nanoclay nanocomposite.

In Figures 4 and 5, the heat distortion temperature (HDT) and Vicat testing results are presented, respectively, for both, HDPE and HDPE/Bagasse /Nanoclay. Figure 4 shows a gain of around 14 % concerning HDT of the nanocomposite in comparison with pure HDPE.

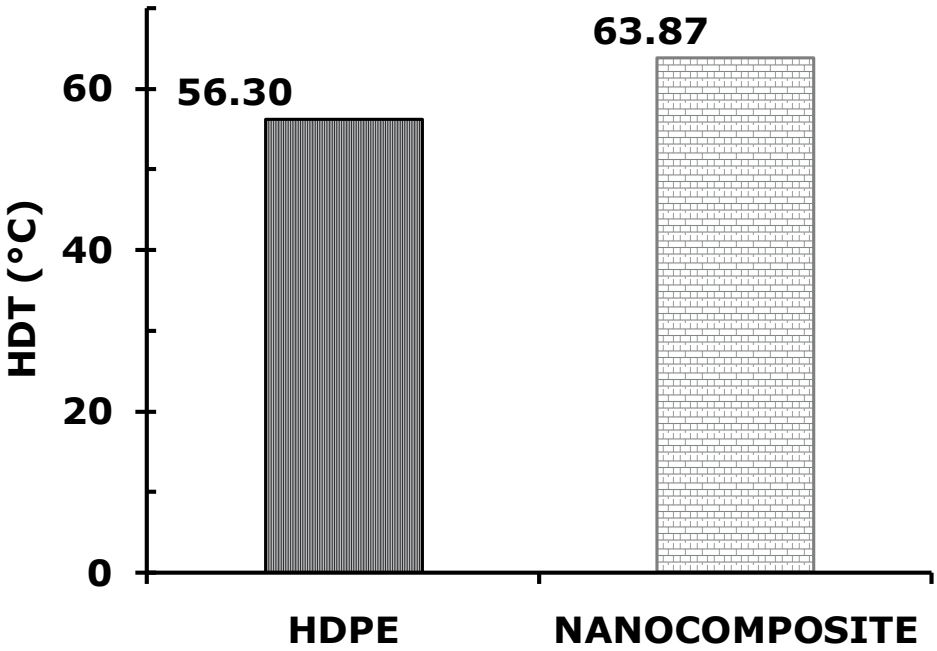

Figure 4. HDT, for HDPE and HDPE/Bagasse/Nanoclay nanocomposite.

On the other hand, no significant changes, only a slight drop, in Vicat HDPE were observed after the obtaining of HDPE/Bagasse/Nanoclay Fig. 5.

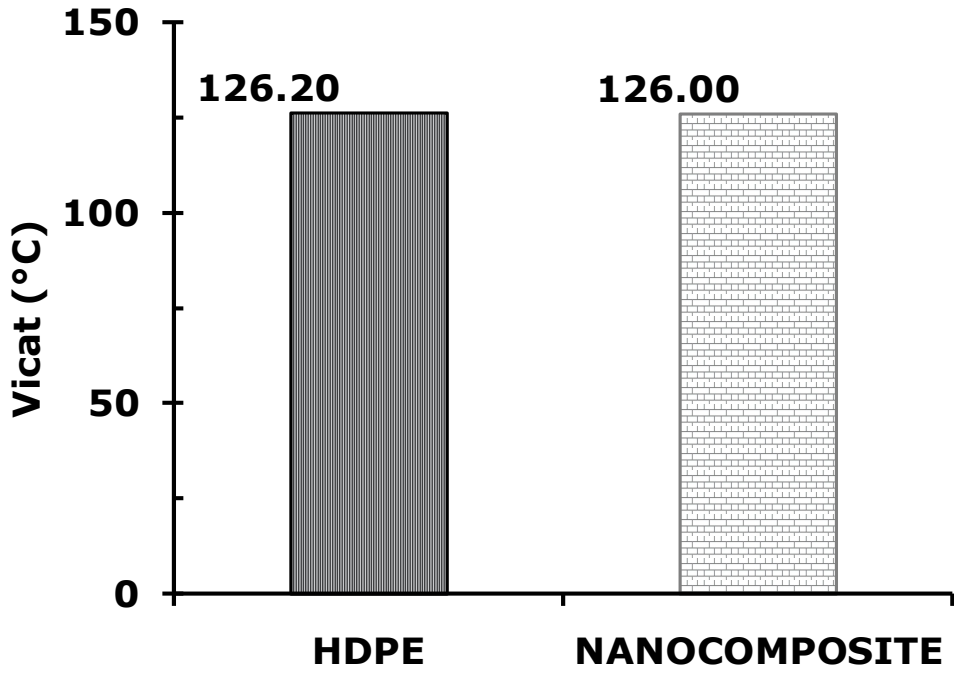

Figure 5. Vicat for HDPE and HDPE/Bagasse/Nanoclay nanocomposite.

Melt flow index (MFI) measurements

The results for the MFI measurements of both, HDPE and HDPE/Bagasse/Nanoclay are showed in Fig. 6.

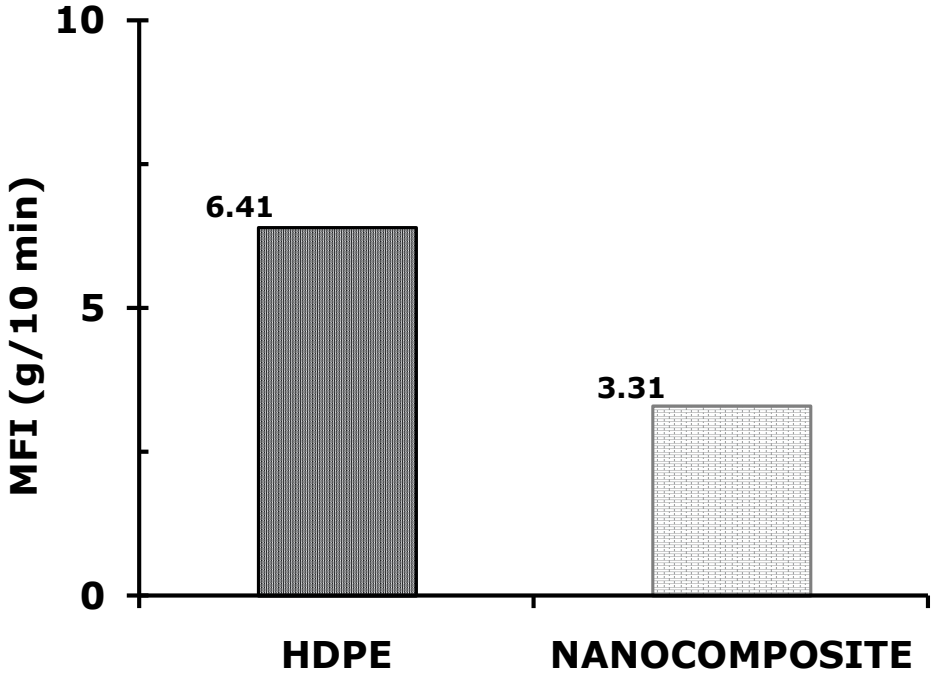

Figure 6. MFI measurements for HDPE and HDPE/Bagasse/Nanoclay nanocomposite.

Figure 6 shows that the incorporation of sugarcane bagasse fiber and bentonite chocolate organophilic nanoclay promoted a significant reduction of around 50 % in melt flow index of the HDPE, which decreased from 6.41 g/10 min at 190 0C/2.16 Kg to 3.31 g/10min at 190 ^{0}C/2.16 Kg. These results indicate an increase in the viscosity and show that fiber and nanoclay addition affects the dynamic viscoelastic melting, reducing molecular mobility and causing a decrease in nanocomposite fluidity.

Scanning Electron Microscopy (SEM)

SEM micrographs for HDPE resin and HDPE/Bagasse/Nanoclay are shown in Fig.7. This Figure compares the SEM micrographs of the HDPE and nanocomposite surfaces; magnification 1000 X and 3000 X.

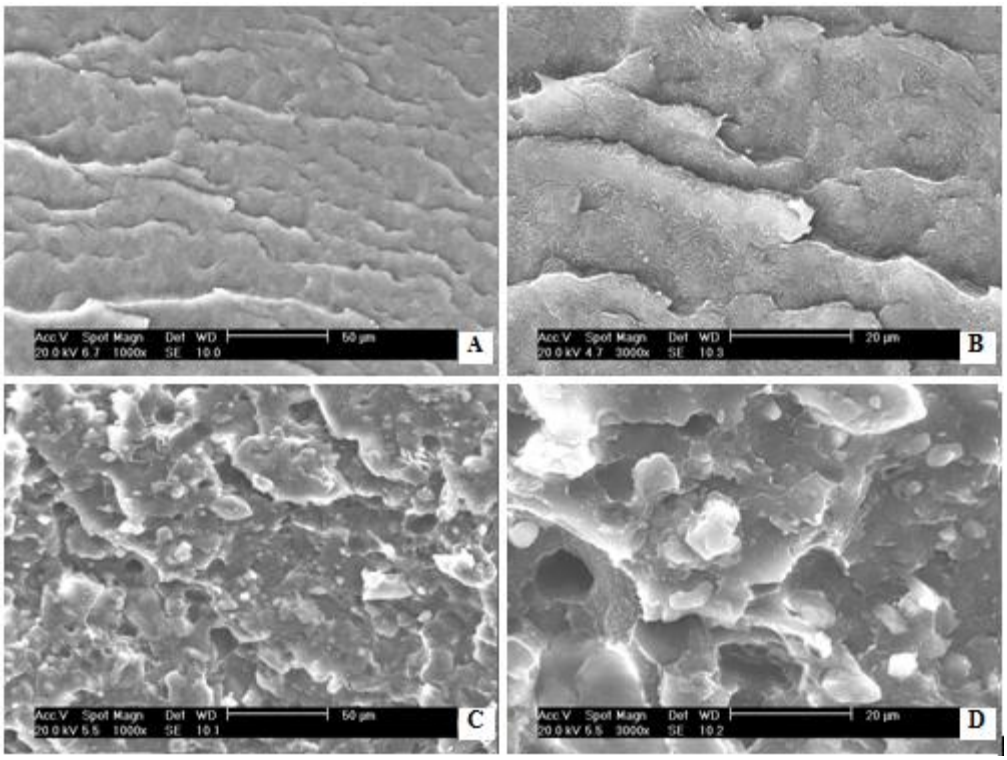

Figure 7. Scanning Electron Microscopy (SEM) surfaces micrographs. (A) HDPE resin, 1000 X; (B) HDPE resin, 3000 X; (C) HDPE/Bagasse/Nanoclay nanocomposite 1000 X and (D) HDPE/Bagasse/Nanoclay nanocomposite 3000 X.

SEM study shows that there was a large difference between the surface morphologies of the HDPE resin and HDPE/Bagasse/Nanoclay nanocomposite (Fig.7). SEM micrographs of the HDPE in Fig. 7(A)-(B) revealed rough, dense and compact cryofractured surface morphologies. On the other hand, in the micrographs of the nanocomposite, Fig. 7(C)-(D), there seemed to be two phases, one due to the presence of the irregular shaped particles from the bagasse fiber and nanoclay as a dispersed phase distributed on a continuous phase, which is the HDPE matrix phase. The distribution and compatibility between the fillers and the matrix could be observed in Fig. 7(C)-(D). The presence of several and large cavities is clearly visible in these Figures. It seems that the level of interfacial bonding between the bagasse fibers and the matrix is weaker than the nanoclay-matrix bonding, and when stress is applied it causes the fibers to be pulled out from the matrix easily leaving gaping holes behind. Therefore nanoclay might have contributed

more to the improvement of the thermo-mechanical properties of the nanocomposite than the bagasse fiber.

Conclusions

Based on the results of this study the following conclusions can be drawn:

1. Thermo-mechanical behavior of HDPE/Sugarcane bagasse fiber/bentonite chocolate organophilic nanocomposite obtained was superior to that of the pure HDPE.
2. The incorporation of sugarcane bagasse fiber and bentonite chocolate organophilic nanoclay promoted a significant reduction in MFI of the HDPE indicating an increase in the viscosity, reducing molecular mobility and causing a decrease in nanocomposite fluidity.
3. SEM study showed that there are distinct cavities between the matrix and the fillers. It seems that the level of interfacial bonding between the bagasse fibers and the matrix is weaker than the nanoclay-matrix bonding, and when stress is applied it causes the fibers to be pulled out from the matrix easily leaving gaping holes behind. Therefore nanoclay might have contributed more to the improvement of the thermo-mechanical properties of the nanocomposite than the bagasse fiber, since the addition of polyethylene grafted with maleic anhydride to the polyethylene matrix can have favored the intercalation/exfoliation process and contributed to the improvement of thermo-mechanical properties.

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