

EFFECTS OF PIASSAVA FIBER INCORPORATION ON THE MORPHOLOGICAL, THERMAL AND VISCOELASTIC BEHAVIOR OF HDPE COMPOSITES

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Abstract

In the present work, the morphological, thermal and viscoelastic behavior of high density polyethylene (HDPE) matrix composites were investigated. HDPE reinforced with the piassava fiber weight fractions varying to 10 % to 40 % were prepared and characterized by means of scanning electron microscopy (SEM), differential scanning calorimetry analysis, thermogravimetric analysis (TG) and melt flow index (MFI) tests. The results showed that there were significant changes ($p < 0.05$) in surface morphology, melting enthalpy, crystallinity percentage variation and initial degradation temperature of the HDPE and HDPE/fiber composites content different piassava fractions. HDPE MFI values presented a significant reduction around 60 % due to piassava fiber incorporation, confirming that fiber addition significantly affects the dynamic viscoelastic melt.

Introduction

Studies on polymer composite materials through fiber reinforcement matrix were initially carried out with man-made fibers such as glass, aramid, carbon and others, because it satisfy the desired conditions, generally can withstand maximum load and transfer strength to the matrix constituent influencing and enhancing their properties. Lately the interest in fibers of vegetable origin for replacing man-made fibers has increased dramatically because vegetable fibers are available in abundant volume throughout the world, they are renewable and biodegradable. Other relevant factors are the low demand for energy and environmental impacts of these composite products compared with those usual [1, 2]. The effect of vegetable fibers content on the mechanical properties of polymer composites is of particular interest and significance. It is often observed that the increase in fiber content leads to an increase in the strength and modulus and also in the toughness if the matrix has low toughness [3]. Both thermoplastic and thermoset materials can be reinforced and made into composite materials, but composites with very short fibers tend to have thermoplastic matrices. The predominance of thermoplastics as matrices for very short-fiber composites is that thermoplastics often need the additional strength or additional stiffness gained from reinforcing with short fibers.

Nowadays, the techniques of polymeric composites such as extrusion, compression, rotational, and injection molding are applied into fiber in form of particles and short fiber-reinforced

composites processing. Injection molding is an important plastic processing method with the characteristic of rapid production rates. The composite material is heated and pumped into a permanent mold, where it takes shape and cools [4].

Regarding polymeric composites with vegetable fibers the major disadvantage is that they begin to degrade at temperatures that are concurrent with processing temperatures typically experienced by commodity thermoplastic polymers. Therefore, novel techniques processing or modification in current techniques must be employed to retain the intrinsic properties of the vegetable fibers and prevent their degradation [5, 6].

The high density polyethylene (HDPE) is an engineering thermoplastic used for several industrial applications due to low cost, desired mechanical properties and processing facility. The combination of vegetable fibers with thermoplastic matrix in general presents a considerable problem associated to incompatibility between the polar and hygroscopic fiber and the non-polar and hydrophobic matrix [7].

The melt flow index (MFI) is a measure of the plastic's ability to flow and it is inversely related to melt viscosity. MFI provides an indication of the polymer flow qualities. The MFI has been widely used at industry to characterize the flow properties of polymers due to simplicity and agility of the technique used in its determination. Melt flow index of a plastic decreases with increasing molecular weight and increases with decreasing molecular weight [8]. MFI is an indirect measurement of the molecular weight and structure of thermoplastic polymers it is an indicator of average molecular weight and is inversely related to it.

Many factors affect polymers' flow properties. Molecular weight distribution, the presence of comonomers, the degree of chain branching and crystallinity influence a polymer's MFI as well as heat transfer in polymer processing. In addition to its importance to thermoplastic polymers, the MFI of composites matrix thermoplastic is also important because the MFI indicates the relative ease with which these composites or thermoplastic matrix can be distributed during a compounding operation or in injection moulding machines. For this reason it was used in this study to compare the processing capabilities of the formed composites.

In general, a HDPE resin with a small MFI value has a high molecular weight and long molecular chain. The long molecular chain and high molecular weight help improve the interfacial adhesion between HDPE macromolecules by polymer chain entanglement. Furthermore, The HDPE resins with a long molecular chain and high molecular weight significantly enhance the absorption energy to the impact load with respect to the HDPE resins with a short molecular chain and low molecular weight, thus resulting in the improvement of the impact strength.

When semicrystalline thermoplastics polymers are used as matrix, the interfacial morphological features can be affected due to the direct influence of the fibers on the crystallization process [9, 10]. These featured changes can lead to variations on melting and crystallization temperatures or even on degree and type of crystallization, important factors to determinate the mechanical properties [11].

Thermal analysis is used to measure the thermal behavior of a composite material as a function of temperature. The processing temperature and other factors involved in the manufacturing of polymer composites are determined by their thermal characteristics. Differential scanning Calorimetry (DSC) is the simplest and most widely used thermal analysis technique. DSC can be used to measure the melting temperature (T_m), melting enthalpy (ΔH_m), glass transition temperature (T_g) and other thermal characteristics of polymer composites [12].

Piassava (*Attalea Funifera* Mart) is a Brazilian lignocellulosic fiber extracted from the leaves of a palm tree of natural occurrence in the Atlantic rain forest and its exploitation is an extractive activity that represents the main source of income to approximately 2000 small-scale farmers, processors and their families. The main use of these fibers is for industrial and domestic brooms,

industrial brushes, ropes, baskets, carpets and roofs. It is estimated that around 50% of the fiber is discarded during the cut, cleaning and baling and as residue by the transformation industries [13, 14]. Piassava fibers have been described as harder than other lignocelluloses fibers and have higher lignin content (around 48%) than any of the other common lignocellulosic fibers. Studies from Brazilian researchers have showed that the residues from piassava can be an important alternative to the reinforcement of thermoplastics and the production of composites with better thermal properties than original polymers [14, 15]. Moreover, the transformation of these residues in useful products, of high quality, with properties capable of competing with man-made fibers material prevents environmental pollution, which would be caused by throwing these materials in the environment without proper use. Earlier studies from our group have showed significant increases in tensile strength at break and flexural strength and module of HDPE due to piassava fiber addition, followed by electron-beam irradiation treatment. This studied indicated that piassava fiber reinforcement of HDPE could lead to the obtaining of composite materials with better thermo-mechanical properties than HDPE resin ones.

The objective of this study was to investigate the morphological, thermal and viscoelastic behavior of HDPE/Piassava fiber composites processed by extrusion and injection molding method.

Experimental

Materials

The materials used in this study were HDPE resin (HDPE JV060U – commercial grade by Braskem S/A), with MFI = 6.40 g/10 min at 190 °C/2.16 Kg, specific density = 0.951 g/cm³. Piassava fibers (*Attalea Funifera* Mart) residues disposed by some brooms and brushes manufacturers.

Preparation and Incorporation of Piassava fiber in HDPE resin

In order to eliminate impurities and waste fibers from palm fiber were washed and kept in distilled water for 24 h. The fiber was then dried at 80 ± 2 ° C for 24 h in circulating air oven. Piassava fiber residues were scraped, washed and kept in distilled water for 24 h. The fiber of palm fiber was reduced to fine powder with a particle size less than or equal to 250 µm by using ball mills and then was again dried at 80 ± 2 ° C for 24 h to reduce the moisture content of less than 2 %.

Preparation of composites was carried out in two steps. Firstly, the HDPE resin fiber reinforced piassava fiber 40 % (by weight) was obtained with an extrusion machine twin screw "extruder ZSK 18 Megalab" made by Coperion Werner & Pfleiderer GmbH & Co. KG. The compounded materials were passed through the different zones of the extruder and finally extruded. The extrudates coming out of the extruder were cooled down by using cold water for a better dimensional stability and wound up manually. Finally, the HDPE/Piassava fiber composite material (60:40 w/w) was pelletized by a pelletizer.

In the second step, part of the pelletized HDPE/Piassava fiber (60:40 w/w) were then dried at 80 ± 2 ° C for 24 h in circulating air over, fed into injection molding machine and specimens test samples were obtained. Part of the pelletized HDPE/Piassava fiber (60:40 w/w) and HDPE resin were mixed together to obtain composite with 10 % and 20 %, were then dried at 80 ± 2 ° C for 24 h in circulating air over and fed into injection molding machine to obtain specimens test samples composite containing 10 and 20 % (w/w) of the piassava fiber. The injection molding was carried out using a Sandreto 430/110 injection molding machine.

The barrel had a flat temperature profile with an injection pressure of 60 bar, holding pressure was kept at 40 bar, the total cycle time was approximately 19.5 s. The processing temperatures used for injection molded Composites goes up to 200°C.

Analyses

For this work some thermal and thermo-mechanical analyses and scanning electron microscopy analyses were performed to characterization of the HDPE and composites of HDPE with 10%, 20% and 40% of Piassava. Statistical analyses were conducted on the thermal and thermo-mechanical data to determine the significance of the differences between HDPE resin and HDPE/Piassava obtained. The differences between the results were then evaluated statistically by ANOVA using BioEstat software (version 5.0, 2007, Windows 95, Manaus, AM, Brazil). Significance was defined at $p < 0.05$.

Differential Scanning Calorimetry (DSC) The differential scanning Calorimetry (DSC) analyses were carried out using a DSC 50 (Shimadzu, Japan). DSC analyses of the materials were performed on four weighed samples with 5.0 ± 0.5 mg of the irradiated and non-irradiated materials. Samples were heated from 25 to 300 °C, at a heating rate of 5 °C/min (in a oxygen atmosphere).

Crystallinity was calculated from melting peak areas. The percentage of crystallinity (x_c) in a composite material was calculated by the equation 1 [10].

$$x_c = \frac{\Delta H_m \cdot 100}{\Delta H_m^0 \cdot w} \quad (1)$$

where :

ΔH_m^* is the melting enthalpy of the HDPE/Piassava sample

ΔH_m^0 is the initial melting enthalpy of the HDPE sample assuming 100% crystallinity, 290 J/g for HDPE

w is the polymer mass fraction in the composite

Thermogravimetric Analyses (TG) The thermogravimetric analyses (TG) were carried out using a TG 50 (Shimadzu, Japan). TG analyses of the materials were performed on three weighed samples with 7.0 ± 1.0 mg of the HDPE and HDPE composites irradiated and non-irradiated materials. Samples were heated from 25 to 500 °C, at a heating rate of 10 °C/min (in an oxygen atmosphere).

Melt flow index (MFI) measurements The MFI measurements were determined with a Microtest extruder plastometer (ASTM 1238-04) in the conditions specified for HDPE.

Scanning Electron Microscopy (SEM) The scanning electron microscopy (SEM) analyses were carried out using a LX 30 (Philips). The samples were cryofractured 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

Differential Scanning Calorimetry (DSC)

The results of the DSC analysis for enthalpy of fusion (ΔH_f) of the HDPE and HDPE/Piassava composites with 10, 20 and 40% of piassava fibers are given in Fig. 1. The results presented in Fig. 1 represent the average values calculated from the data obtained by DSC analysis. The standard deviation for DSC analysis was less than 10% for all tests. As it can be seen, there were significant gradient decrease ($p < 0.05$) between the HDPE and HDPE/Piassava composites ca. 8-30%, as can be see there was a gradient decrease with the increasing percentage of fiber in HDPE.

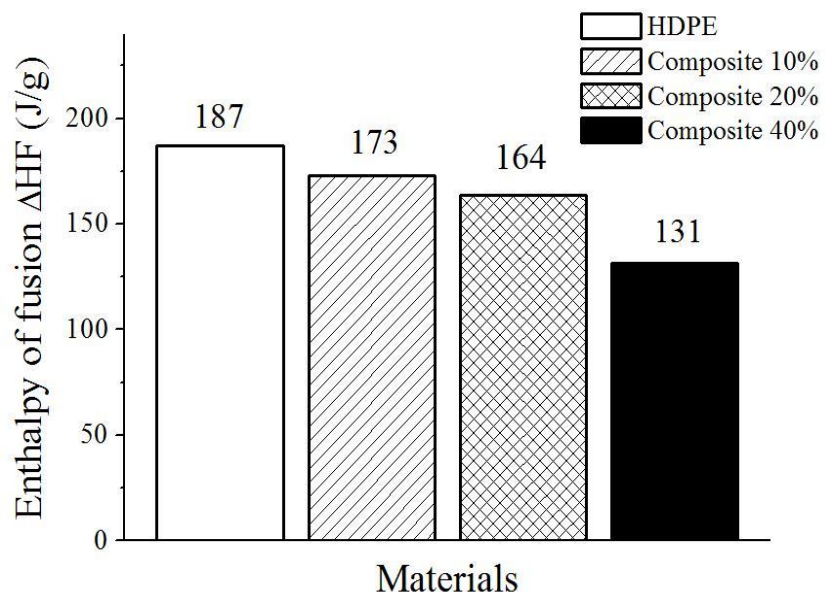


Figure 1 - Enthalpy of fusion for HDPE and HDPE/Piassava composites with 10 %, 20 % and 40% of piassava fibers.

The results of the crystallinity percentage for HDPE and HDPE/Piassava composites with 10, 20 and 40% of piassava fibers are represented in figure 2. As it can be seen, the crystallinity percentage showed a gradient increase up to 75.5 (for HDPE/Piassava 40%) which means a difference of 11% of increase when compared with HDPE.

These results are very important because the increase in HDPE/Piassava crystallinity reduces the mobility of the amorphous chains leading to more efficient molecular orientation, and gain on some mechanical properties. [16].

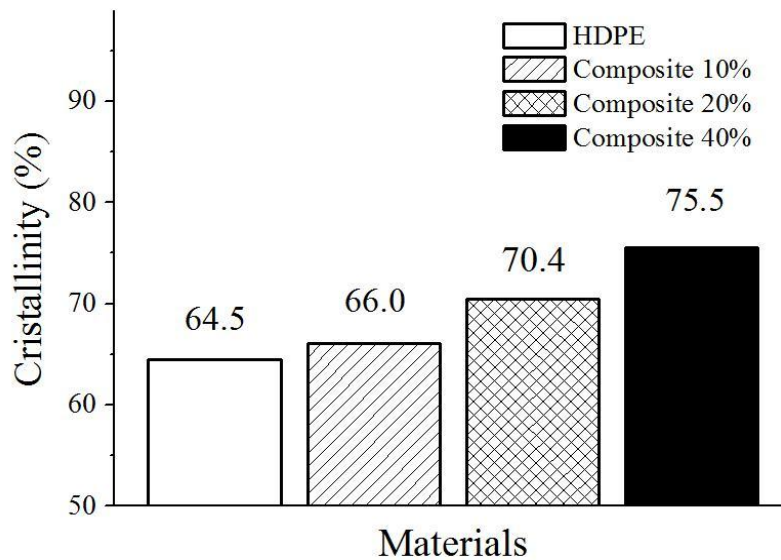


Figure 2 - Crystallinity for HDPE and HDPE/Piassava composites with 10 %, 20 % and 40% of piassava fibers.

Thermogravimetric Analyses (TG)

The results of the thermogravimetric analyses (TG) are presented in Table 1. It showed the incorporation of piassava fibers in HDPE resin for the initial degradation temperature and weight loss. The results presented in Table 1 represent the average values calculated from the data obtained by TG analysis. The standard deviation for TG analysis was less than 10% for all tests. As it can be seen, there were significant differences ($p < 0.05$) in the initial degradation temperature and weight loss for all HDPE/Piassava composites when compared to HDPE. With relation to weight loss, after the samples heating up to 500 °C, Table 1 showed that there was significant decrease, about 10 %, for HDPE/Piassava 10% compared with other materials ($p < 0.05$). This result suggests that composites from injection reprocessing tend the more thermal degradation than that from the extrusion process, followed by injection; it's possible that reprocessing causes a slight degradation in material.

Table 1 Initial Decomposition Temperature and Total Weight Loss for HDPE and HDPE/Piassava Composites Materials

Material	Initial Degradation Temperature (°C)	Statistic Differences ($p < 0.05$)	Total Weight Loss (%)	Temperature Differences ^(a) (%)
HDPE	414.76		93.04	-
HDPE/Piassava 10%	377.50	s ^(b)	83.67	8.98
HDPE/Piassava 20%	376.88	s ^(b)	91.59	9.13
HDPE/Piassava 40%	381.33	s ^(b)	97.96	8.06

^(a) percentage variation of initial degradation temperature between HDPE and HDPE/Piassava composite; (b) Significant differences.

Melt flow index (MFI) measurements

The results of MFI measurements for HDPE and HDPE/Piassava composites with 10, 20 and 40% of piassava fibers are represented in figure 3.

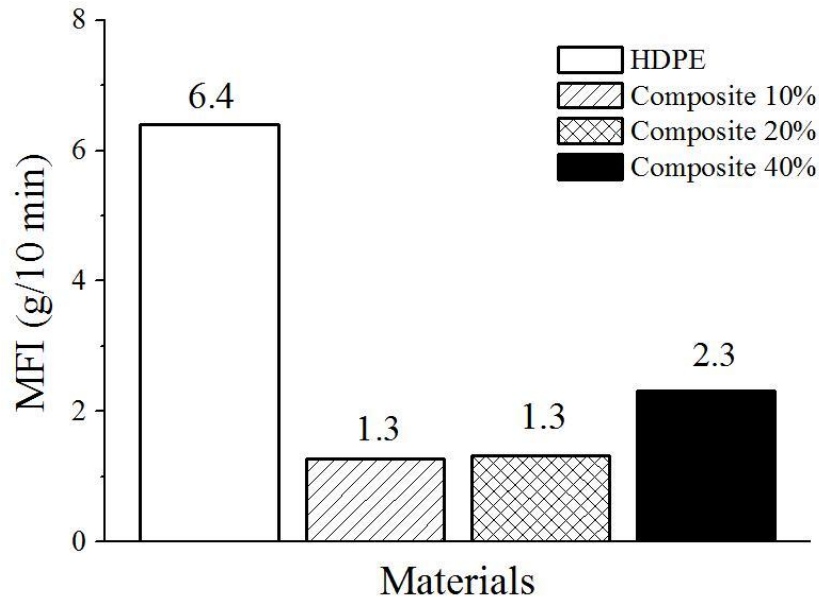


Figure 3 - MFI results for HDPE, and HDPE/Piassava composites with 10 %, 20 % and 40% of piassava fibers.

Figure 3 shows a significant reduction of the composites melt flow index compared with HDPE. The HDPE/Piassava 40% MFI presented a decrease around 64 % that may be attributed the piassava fibers incorporation in HDPE. However, this Fig. shows a reduction of around 75 %, for HDPE/Piassava 10 and 20% due to piassava fiber incorporation plus injection reprocessing. These results indicate that piassava fiber incorporation affects the dynamic viscoelastic melt, reducing molecular mobility and causing a decrease in fluidity.

Scanning Electron Microscopy (SEM)

SEM micrographs for HDPE and HDPE/Piassava composites with 10, 20 and 40% of piassava fibers are showed in Fig.4. The Fig. 4(A) is the SEM micrographs of the HDPE. The SEM micrographs of the HDPE/Piassava with 10, 20 and 40% of piassava fibers are presented in Fig. 4(B), 4(C) and 4(D) respectively. Comparing Fig. 4(A) with Fig. 4(B)-4(D), it can be seen that there is a large difference between the crystalline phases for HDPE reinforced with 0 – 40 % of the piassava fibers. It means that the order of macromolecules arrangement of HDPE was changed by piassava incorporation and processing method. From the micrographs showed in Fig. 4(B)-4(D) it undoubted appears that there is two phases, one due to presence of the irregular form particles from the piassava as a dispersed phase distributed on a continuous phase, which is the HDPE phase. Micrographs shows homogeneous distribution of fiber particles in the matrix and polymer-rich surfaces in injection reprocessing samples, whereas exposed fiber ends, some fiber aggregates and several voids are seen at surface of HDPE/Piassava 40 % samples. Fig. 4(B) shows a very brittle surface with cavities containing piassava particles in the HDPE phase and few empty cavities. The Fig. 4(D) seems to present several empty cavities (probably due to pull-out) and shows a large number of cavities containing piassava particles in the HDPE phase and some piassava fiber aggregate In contrast, the HDPE/Piassava 20% (Fig. 4(C)) the micrograph

show a smoother surface and no distinct interspaces between the phases indicating a better interfacial adhesion between phases than the others composites studied. These structural differences suggest that the mechanical and physical behaviors of HDPE, HDPE/Piassava 40 %, and HDPE/Piassava (10%, 20%) from injection reprocessing are differ.

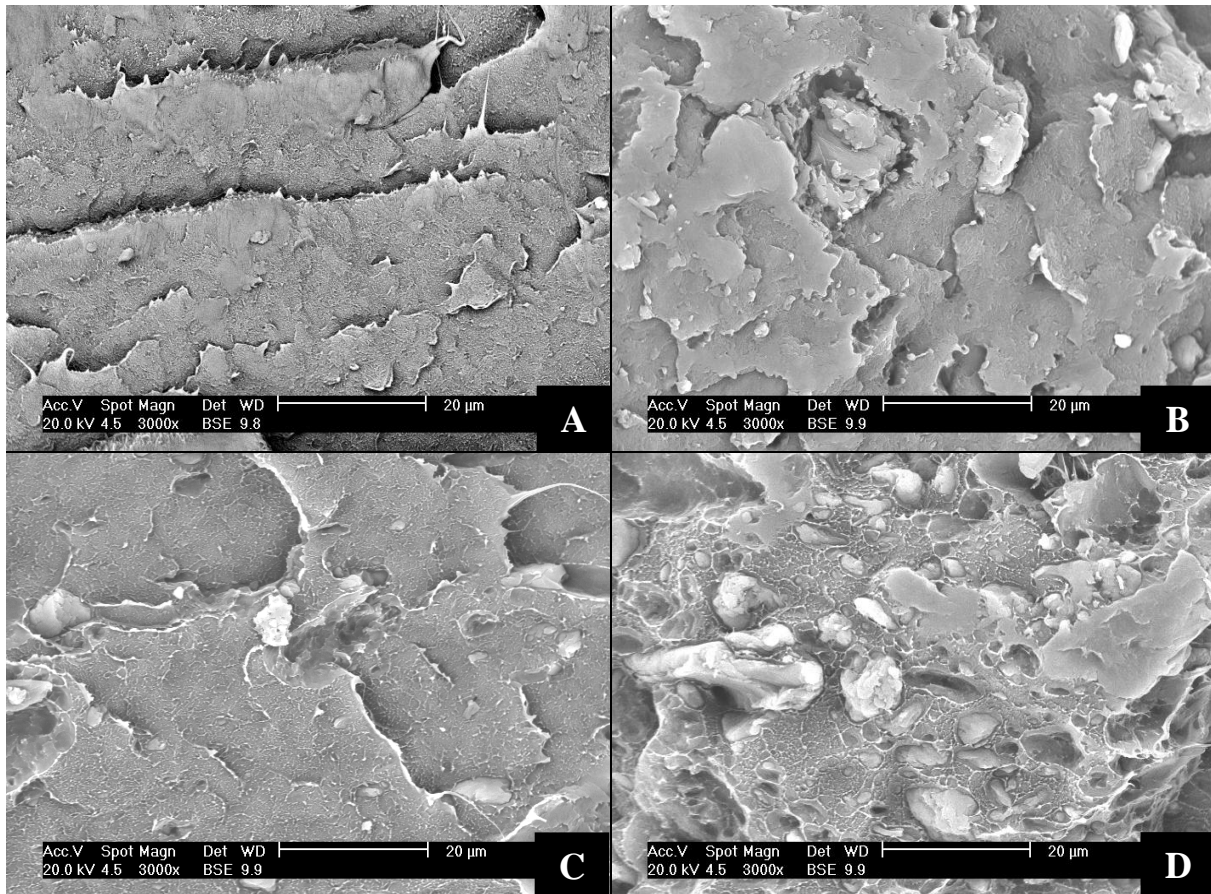


Figure 4. Scanning Electron Microscopy (SEM) micrographs of cryofractured surfaces of HDPE and HDPE/Piassava composites. Fig. 4(A) HDPE; Fig. 4(B) HDPE/Piassava 10%; Fig. 4(C) HDPE/Piassava 20%; Fig. 4(D) HDPE/Piassava 40%.

Conclusions

The objective of the present study was to investigate the morphological, thermal and viscoelastic behavior of HDPE/Piassava fiber composites processed by extrusion and injection molding method. The HDPE/Piassava presented a slight gain of crystallinity by 2-11 % and a loss of initial degradation temperature ca. 9 % with relation the HDPE resin. This result suggests that composites from injection reprocessing tend the more thermal degradation than that from the extrusion process, followed by injection; it's possible that reprocessing causes a slight degradation in material. The incorporation of piassava fiber promoted a significant reduction in MFI of the HDPE indicating an increase in the viscosity, reducing molecular mobility and causing a decrease in composite fluidity. The HDPE and HDPE/Piassava 20 % micrographs revealed rough, dense and compact cryofractured surface morphologies, but HDPE exhibited a slightly smoother surface than HDPE/Piassava composites. The results showed that there was a large difference between the crystalline form of the HDPE and HDPE/Piassava. It means that the order of macromolecules arrangement of HDPE was changed by piassava incorporation and

injection reprocessing. The HDPE/Piassava micrographs presented two phases, one due to presence of the irregular form particles from the piassava as a dispersed phase distributed on a continuous HDPE phase. The SEM micrographs indicated a better interfacial adhesion between piassava fiber and HDPE for HDPE/Piassava 20 %. These results are very important, since that could lead to the obtaining of materials with better properties than the original HDPE resin.

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References

1. Joseph, P.V., Joseph, K., Thomas, S., Effect of processing variables on the mechanical properties of sisal-fiber-reinforced polypropylene composites. *Composites Science and Technology* v. 59, p.1625-1640, 1999.
2. Panthapulakkal, S.; Sain, M. Agro-residue reinforced high-density polyethylene composites: Fiber characterization and analysis of composite properties. *Composites: Part A*, v. 38, p.1445–1454, 2007.
3. Santos, P.; Pezzin, S.H. Mechanical properties of polypropylene reinforced with recycled-pet fibers. *Journal of Materials Processing Technology* p.143–144 (2003).
4. Xue Li, Lope G. Tabil, Satyanarayan Panigrahi, William J. Crerar. Processing Flax Fiber-reinforced Polymer Composites by Injection Molding, *Proceedings of the CSAE/SCGR 2005 Meeting Winnipeg, Manitoba - June 26 - 29, 2005, Winnipeg, Manitoba, Canada*. In: <http://www.bioeng.ca/pdfs/meeting-papers/2005/CSAE%20papers/05-033.pdf> Accessed on June 01, (2010).
5. Swanda. D.-"The reactive extrusion of polypropylene". Master of Applied Science Thesis. Dept. of Chem. Eng. and Appl. Chem., Univ. of Toronto (1987).
6. Barone, J.R.; Schmidt, W. F.; Liebner, C.F.E. Compounding and molding of polyethylene composites reinforced with keratin feather fiber. *Composites Science and Technology*, v. 65 p. 683–692, 2005.
7. Li Y, Hu C, Yu Y. Interfacial studies of sisal fiber reinforced high density polyethylene (HDPE) composites. *Composites A* v.39 p.570–578, 2008.
8. LU J.Z; WU, Q.; NEGULESCU I.I.; CHEN, Y. The influences of fiber feature and polymer melt index on mechanical properties of sugarcane fiber/polymer composites. *J Appl Polym Sci*, v.102, p.5607–5619 (2006).
9. J.W. Gillespie, JR. , T.J. Chapman. The Influence of Residual Stresses on Mode I Interlaminar Fracture of Thermoplastic Composites. *Journal of Thermoplastic Composite Materials*, April 1993; vol. 6, 2: pp. 160-174.

10. Sirisinha, K., Meksawat, D., 2004. Comparison in process-ability and mechanical and thermal properties of ethylene–octene copolymer crosslinked by different techniques. *J. Appl. Polym. Sci.* 93 (3), 1179–1185.

11. P. Gañán, I. Mondragon. Thermal and degradation behavior of fique fiber reinforced thermoplastic matrix composites. *Journal of Thermal Analysis and Calorimetry*, Vol. 73 (2003) 783.795

12. Han-Seung Yang; Douglas J. Gardner; Hyun-Joong Kim Viscoelastic and thermal analysis of lignocellulosic material filled polypropylene bio-composites. *Journal of Thermal Analysis and Calorimetry*, Vol. 98 (2009) 553-558.

13. Moura, E.A.B.; Nogueira, B.R.; Ortiz, A.V. “Changes in Physicochemical, Morphological and Thermal Properties of Electron-Beam Irradiated Ethylene–Vinyl Alcohol Copolymer (EVOH) as a Function of Radiation Dose” - International Topical Meeting on Nuclear Research Applications and Utilization of Accelerators, Proceedings Series, IAEA – International Atomic Energy Agency, May, 2009. In: http://www-pub.iaea.org/MTCD/publications/PDF/P1433_CD/datasets/abstracts/sm_eb-16.html>

14. Aquino, R.C.M.P; d’Almeida, J.R.M & Monteiro, S.N. – “Propriedades de compósitos de piaçava com matriz polimérica”, in: 55o Congresso Anual da ABM, p. 2898, Rio de Janeiro, RJ (2000)

15. Bonelli, C.M.C.; Elzubair, A.; Suarez, J.C.M.; Mano, E.B. Comportamento térmico, mecânico e morfológico de compósitos de polietileno de alta densidade reciclado com fibra de piaçava. *Polímeros: Ciência e Tecnologia*, vol.15, n.4, p. 256-260, 2005.

16. KUCUKPINAR, E.; DORUKER, P., “Effect of absorbed water on oxygen transport in EVOH matrices. A molecular dynamics study”, *Polymer*, v. 45 p.3555–3564, 2004.