

Influence of Coupling Agent in Compatibility of Post-consumer HDPE in Thermoplastic Composites Reinforced with Eucalyptus Fiber

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This study investigates the feasibility of using recycled high density polyethylene (HDPE) and wood fiber from species *Eucalyptus grandis* (EU) to manufacture experimental composite panels. The use of maleated polyethylene as coupling agent (CA) improved the compatibility between the fiber and plastic matrix. The mechanical properties of the resultant composites were compared with polymer with and without compatibilizer. The influence of the coupling agent (CA) in the polymer matrices and composites were evaluated at different concentrations, checking the physical, mechanical and thermal properties of wood plastic composites (WPC). Results of mechanical, physical and thermal properties showed that concentration of 3% w/w CA in the polymer matrices was that which showed the best results, but in the composites properties were very similar in all formulations. Based on the findings in this work, it appears that recycled materials can be used to manufacture value-added panels without having any significant adverse influence on material properties.

Keywords: wood plastic composite, thermoplastic composite, HDPE, coupling agent, wood flour

1. Introduction

Nowadays much emphasis has been given to the preservation and conservation of the environment in order to ensure sustainable development. Among the various damages to the environment, one is related to the lignocellulosic and plastics wastes¹. The plastics waste generally takes a long time to undergo spontaneous degradation, and when burnt, can produce different degrees of toxicity². Therefore, there is a general tendency to use these polymers and lignocellulosic residues, considering the immense potential value of the processed materials and the implications of waste and pollution resulting from the non-use of such waste³.

The development of composites involving the use of lignocellulosic materials as reinforcements in polymeric matrices has grown recycled increasingly in response to environmental conservation, making more frequent in the polymer industry due to the lignocellulosic being renewable, inexpensive, biodegradable and non-toxic. Among the lignocellulosic materials most used for this purpose are sawdust, wood flour, plant fibers and agricultural and agroindustrial lignocellulosic waste⁴. Use of agro-waste materials as a reinforcement in the production of WPCs alleviate the shortage of wood resources, and can have the potential to start a natural fiber industry in countries where there are little or no wood resources⁵. Çöpür et al.⁶ also believe that agricultural byproducts are excellent alternative waste materials to substitute wood because they are plentiful, widespread, and easily available. Apart from their abundance and renewability, utilization of agricultural wastes can be advantageous to economy, environment, and technology.

However the preparation of such polymer composites with wood requires a good compatibility at the interface from polymeric matrix with the wood⁷. The main concern of obtaining reinforcements by incorporating wood fibers lies in the inherent incompatibility between the hydrophilic fibers and hydrophobic polymers, which results in a poor adhesion^{6,7}. Thus, some coupling agents have been used in the modification of fibers, to increase the interfacial adhesion between cellulosic reinforcement and polymeric matrix and thereby improve the mechanical properties of the polymeric composite⁸. The use of coupling agents is an efficient approach to improve the inter-phase compatibility of the composites⁹⁻¹¹. A coupling agent is a chemical that functions at the interface to create a chemical bridge between the reinforcement and the matrix¹². The agent improves the interfacial adhesion when one end of the molecule is tied to the reinforcement surface and the functionality at the other end reacts with the polymer phase. Copolymers containing maleic anhydride, such as maleated polypropylene (MAPP) or maleated polyethylene (MAPE), are the most commonly reported coupling agents used in wood plastic composites^{13,14}. The anhydride groups of the copolymers can react with the surface hydroxyl groups of wood, forming ester bonds. The other end of the copolymer entangles with the polymer matrix because of their similar polarities^{15,16}. Isocyanates have also been used as coupling agents in natural fiber reinforced polymer composites. Urethane links can be formed between the isocyanate functionality and the hydroxyl group of natural fibers¹⁷, consequently blocking the hygroscopic hydroxyl sites¹⁸. Silanes are recognized as efficient coupling agents as they can be hydrolyzed to

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expose the active silanol groups toward the hydroxyl groups of the wood, thereby reacting to form chemical bonding¹⁹.

The aim of this research was to improve the compatibility between HDPE matrix and wood sawdust and to develop WPC materials for structural applications, using post-consumer materials, aiming to reduce the environmental impact and add value to these new materials.

2. Materials and Methods

The materials used in this study were the following: post-consumer HDPE, provided from various packaging of cleaning products; eucalyptus flour (EU) of the species *Eucalyptus grandis* from the southern state of Rio Grande do Sul, Brazil; coupling agent (CA) – grafted polyethylene copolymer with 1% maleic anhydride (PEgMA) Fusabond E-528, melt flow index of 6.7 g/10 min and density of 0.922 g/cm³ from DuPont.

HDPE plastic waste were pre-washing with water, following dried at room temperature for 24 hours. After, they were ground and crushed to size reduction in the form of flakes in a Retsch SM 200 knife mill. The wood flour (EU) passed by size separation in a sieves system with series of 32 and 16 Tyler mesh, and selected particle size of >250 and <500µm.

The formulation of the substrates was performed as shown in Table 1:

Mixtures were processed in a single screw extruder (L/D: 22), with the temperature profile of 170°-180°-190 °C, residence time of 80s and rotation of 65 rpm. HDPE with the coupling agent (CA) was first processed in the extruder in order to functionalizing the polyolefin, and after added sieved wood flour (30% w/w). After mixing by extrusion, samples were cropped in the shredder. The specimens for mechanical tests were prepared by injection molding (Mini Thermo Scientific Haake MiniJet II) at a temperature of 185 °C and pressure of 600 bar.

2.1. Characterization

2.1.1. Physical testing

Contact angle and surface energy

The contact angle measurements were made with Ramé-Hart goniometer (model 100-00), according to ASTM D 724-89. The liquids used for sessile drop test were deionized water and diiodomethane (CH₂I₂). For all samples were made

10 drops of each liquid, each drop image was measurement of angles using the SurfTens 3.0 software. The values obtained in the contact angle tests were used to calculate the surface energy to the samples. The calculation of the surface tension was carried out with the SurfTens 3.0 software.

2.1.2. Thermal testing

DSC

The temperatures, fusion and crystallization enthalpies and the degree of crystallinity of HDPE with different compositions from CA were evaluated using a differential exploratory calorimeter (DSC), from TA Instruments (Model Q-20). Samples were subjected to two stages of heating and one cooling, using a rate of 10 °C/min in a range 20-200 °C, according to ASTM D 3417. The percentage of crystallinity (% Xc) was calculated using the reference value of fusion enthalpy of the samples of 100% crystalline HDPE obtained from the literature^{10,11}. Crystallization time was obtained by calculating the cooling cycles observing the samples.

2.1.3. Mechanical tests

The tensile tests were performed on a Universal machine, model DL 2000 from EMIC, based on ISO 527-1 standard, using a load cell of 1000 N and the speed of separation of 2 mm/min, where were used eight specimens test.

2.1.4. Morphological tests

By SEM it is possible to observe the morphology of the polymer surface, orientation and possible changes made. This test was performed for analysis by scanning electron microscopy (SEM), using the JEOL JSM 6060 electron microscope, with a voltage of 10 kV and magnification of 80 times. The samples were manually cut, fixed on stubs with double sided tape and coated with gold. The images of the samples were obtained from the fracture surfaces after tensile test.

3. Results and Discussion

3.1. Physical properties

3.1.1. Contact angle and surface energy

The measurement of the contact angles of pure liquids, with known surface tension and hence surface tensions parameters, on a given solid surface is the common way of

Table 1. Formulation of compatibilized matrices and composites.

	Sample	Matrix	Filler	CA	% w/w CA
Compatibilized Matrices	1	HDPE	-	-	-
	2	HDPE	-	PEgMA	1
	3	HDPE	-	PEgMA	3
	4	HDPE	-	PEgMA	5
	5	HDPE	-	PEgMA	7
Compatibilized Composites	6	HDPE	EU	PEgMA	1
	7	HDPE	EU	PEgMA	3
	8	HDPE	EU	PEgMA	5
	9	HDPE	EU	PEgMA	7

obtaining the surface energy of the solid material²⁰. Figure 1 shows results of contact angles from HDPE, compatibilized HDPE matrices (HDPE/CA) and the compatibilized composites (HDPE/EU/CA).

The highest contact angles were obtained with water, whereas diiodomethane gave the lowest contact angles. The insertion of polar groups at the surface nonpolar polymer causes the contact angle decreases²⁰. Thus, there is a change of its hydrophobicity characteristics²⁰.

Results of the contact angle with water show that HDPE, being nonpolar polymer, exhibits high hydrophobicity, with values of contact angle above 80°. When incorporated the coupling agent (CA), contact angle values in composites decreases as there is an increased concentrations of CA, however showing a range of values very similar, between 60 and 70°, indicating a higher wettability and consequently improved adhesion. The decrease of the contact angle in this case indicated that the HDPE surface has become less hydrophobic, i.e., more wettable with the process and may thus lead to an increased interaction of the fibers for obtaining a good performance in the composites^{11,21}. For compatibilized matrices, there was also a slight improvement in wettability, although the contact angle values were almost equal. As an example the behavior of the liquid drop on the surface and its respective angles are shown in Figures 2a,b, presenting drops images on the HDPE and HDPE/CA 3% surface respectively.

Relationships between adhesion strength and surface properties then provide a framework upon which adhesion

mechanisms are discussed. This knowledge is significant to understand the adhesion of complex heterogeneous multicomponent composites and also has direct applications for the wood plastic composites (WPC) industry. It was proposed by Wu²¹ and it is accepted widely that the intermolecular energy between two materials results from the summation of a dispersion component and a polar component. Since the surface free energy (or surface tension) is proportional to the intermolecular energy, the surface free energy itself can be considered as a sum of a dispersion component and a polar component²¹. According to Wu²¹ this method, known as harmonic mean may be successfully applied in the case of interaction between a polymer and a liquid either, as is the case studied in this work. Using two liquids with γ_{LV}^d and γ_{LV}^p known, can be determined γ_S^d and γ_S^p by means of contact angle measurements and using Equation 1. In general, Equation 1 is written in the algorithms of electronic measurement of contact angle and surface energy equipment.

$$\gamma_{LV} (\cos \theta + 1) = \frac{4 (\gamma_S^d \gamma_{LV}^d)}{\gamma_S^d + \gamma_{LV}^d} + \frac{4 (\gamma_S^p \gamma_{LV}^p)}{\gamma_S^p + \gamma_{LV}^p} \quad (1)$$

where: γ_{LV} = surface tension of the liquid, γ_S^d = dispersive component of solid surface, γ_{LV}^d = dispersive component of the surface liquid, γ_S^p = non-dispersive component (or polar) on the solid surface, γ_{LV}^p = non-dispersive component (or polar) of the surface liquid.

With results of contact angle from samples with water and diiodomethane are reached results of surface tension of the samples, as shown in Figure 3.

In this regard, for experimental results, incorporation of the coupling agent (CA) was efficient, leading to an increase in surface energy of the polymeric matrix and composites, which thus promoted better interaction of the polymeric matrix with wood waste (EU). Redighieri⁷ studied use of wood waste in the production of composites with recycled polyethylene, where polyethylene was functionalized with maleic anhydride (PE-g-MA) as coupling agent to provide better adhesion between the matrix and the dispersed phase. The results showed that treatment of the wood waste flour with PE-g-MA increased mechanical properties of the composite compared to composites containing untreated waste. The HDPE/EU/CA composites were those that

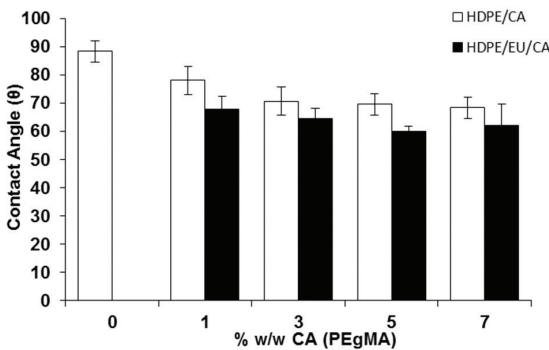


Figure 1. Contact angle of water on the samples surface.

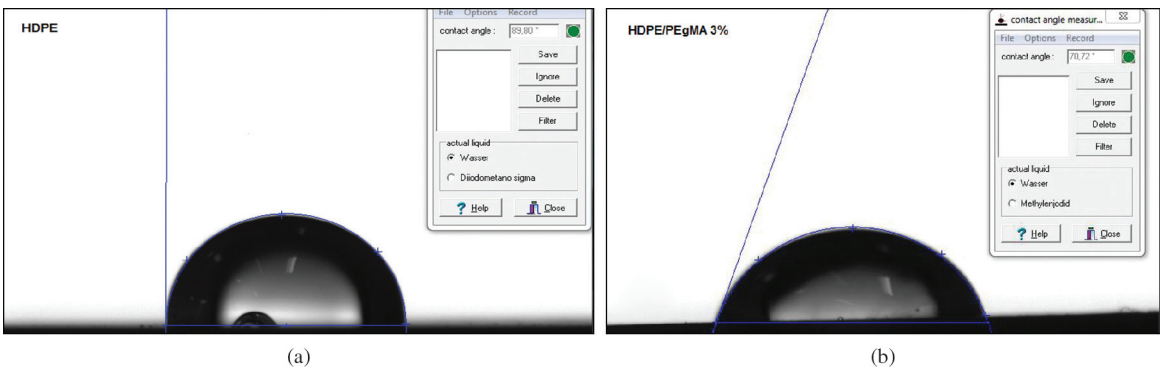


Figure 2. Image of the water drop profile on the surface of: (a) HDPE and (b) HDPE/CA 3%.

showed the best result, thus indicating a better adhesion between the phases.

3.2. Thermal properties

3.2.1. DSC

The DSC analyzes were performed only in the compatibilized matrix with CA in order to verify thermal properties with different concentrations of coupling agent and thus set the optimal concentration to be used for the manufacture of wood plastic composites (WPC). Table 2 indicates the results of DSC analysis, which shows the values of temperature, fusion and crystallization enthalpy, crystallization time and crystallinity of HDPE samples without and with coupling agent (HDPE/CA).

The CA variation caused no significant changes in the thermal properties of compatibilized HDPE (T_f , T_c). However, according to Lu et al.²², and Liang et al.²³, there is an optimum concentration of these agents to promote better adhesion between the matrix and the dispersed phase and consequently, that the composites show improvement in their properties.

Regarding the change of enthalpy (ΔH), there are differences between all samples, and there was a decrease in both the enthalpy of fusion (ΔH_f) as the crystallization enthalpy (ΔH_c) relative to the compatibilized HDPE samples. However it is observed that HDPE sample with 3% w/w of CA showed opposite behavior to the other, with higher values of ΔH_f the first and second heating, so as ΔH_c . This sample was analyzed again to confirm the result, which confirmed this behavior. The HDPE/CA 3% w/w

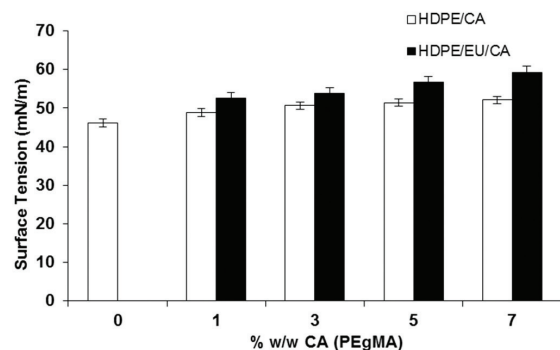


Figure 3. Surface tension of HDPE matrices and its composites.

when subjected to the second heating cycle reorganized its structure and showed a variation of enthalpy (ΔH) higher than that in the first heating. Compatibilized HDPE also had lower crystallinity index than the pure HDPE, with the exception also of the HDPE/CA sample (3% w/w).

In general, coupling agent in the HDPE/CA 3% showed a tendency to act as a nucleating agent, ie, make the polymer can achieve at times smaller, a larger proportion of crystalline material²⁴⁻²⁶. At the beginning of crystallization of the composites there is formation of larger crystals, which accelerates the crystallization^{27,11}. At the end of the process, these crystals hinder the arrangement of smaller chains, causing an increase in the crystallization total time (t_c). From the data obtained, HDPE/CA 3% showed higher X_c and lower t_c than the other samples, being chosen so this concentration of coupling agent (CA). The result of the higher degree of crystallinity indicates the best performance of this formulation. For this reason and also for economic reasons, taking into account the “cost x properties” shown in the tests, the concentration of 3% w/w of CA was determined as the most appropriate concentration.

3.3. Mechanical properties

Table 3 shows results of tensile strength of post-consumer HDPE matrices with the coupling agent (HDPE/CA) and compatibilized composites (HDPE/EU/CA).

Among the compatibilized composites, those who presented the best results were those with levels of 3 and 7% CA, respectively, with tensile strength values similar, being the composite with 3% CA had the highest value. However, the differences between all coupled composites were not so significant.

In general, composites where was added the coupling agent (CA) showed clearly increased stiffness and mechanical strength in comparison with the compatibilized HDPE matrices.

HDPE is a highly tenacious matrix, ie, is able to undergo a high degree of deformation before breaking, but has low tensile strength and low modulus of elasticity. It is observed for the results of composites that wood fiber was able to promote the effect of reinforcement in matrix thermoplastic, increasing tensile strength and elasticity modulus (Table 3).

Increases in tensile strength observed in compatibilized composites indicate improved transfer tensile from matrix for cellulosic reinforcement in interface resulting in a probable occurrence of mechanical anchoring or chemical

Table 2. Thermal behavior of HDPE without and with different concentrations from CA.

Sample	DSC								
	1° Heating			Cooling			2° Heating		
	T_f (°C)	ΔH_f (J/g)	X_c (%)	T_c (°C)	ΔH_c (J/g)	t_c (min)	T_f (°C)	ΔH_f (J/g)	X_c (%)
HDPE	130.3	164	56	118.8	194	5.8	132.8	197	68
HDPE/CA 1%	131.0	160	55	118.0	176	6.0	133.0	177	61
HDPE/CA 3%	131.5	194	67	118.9	201	5.5	132.8	208	72
HDPE/CA 5%	131.3	129	44	117.8	150	6.0	132.9	148	51
HDPE/CA 7%	130.0	135	46	118.9	144	5.5	131.5	152	52

ΔH_f - enthalpy of fusion, T_f - melting temperature; X_c - crystallinity index; ΔH_c - enthalpy of crystallization, T_c - crystallization temperature; t_c - crystallization time.

interactions between the anhydride groups and the hydroxyls of cellulose in polymer-wood interface²⁸⁻³⁰.

Regarding the modulus of elasticity, HDPE without treatment with CA showed a higher modulus than

Table 3. Tensile strength at break of HDPE, compatibilized HDPE matrices and composites.

Samples	Mechanical Properties	
	Tensile Test	
	Tensile Strength at rupture (MPa)	Modulus of Young (MPa)
HDPE	33 ± 1,5	520 ± 57
HDPE/CA 1%	28 ± 2,5	372 ± 77
HDPE/CA 3%	31 ± 3,2	360 ± 70
HDPE/CA 5%	29 ± 1,7	475 ± 78
HDPE/CA 7%	29 ± 1,3	337 ± 55
HDPE/EU/CA 1%	35 ± 1,8	596 ± 55
HDPE/EU/CA 3%	40 ± 2,4	651 ± 45
HDPE/EU/CA 5%	36 ± 1,2	695 ± 54
HDPE/EU/CA 7%	39 ± 1,8	650 ± 71

those compatibilized, but smaller modulus compared to composites of HDPE/EU/CA. Among the compatibilized composites, all showed similar results. Across the statistical analysis, it was found that there was no significant difference between all the composites. Thus, for results of the mechanical properties of tensile strength and the modulus of elasticity, in general the HDPE-EU composites with coupling agent (CA) had higher result compared to HDPE and compatibilized HDPE matrices.

3.4. Morphological Properties

By scanning electron microscopy was possible to evaluate the efficiency of the dispersion of the cellulosic filler in the thermoplastic matrix and the capacity of wetting the surface fiber for thermoplastic matrix as a way to evaluate the efficiency of coupling agent^{31,32}. Aspects related with wettability and level of fiber-matrix interfacial adhesion can be observed in the micrographs presented.

Figure 4a shows the micrograph of the fracture surface after the tensile test of HDPE/EU/CA 1% composite, where there is the presence of various structures like fibrils, characteristics for polymeric matrix, and some holes promoted by removal of the filler, which indicates that there

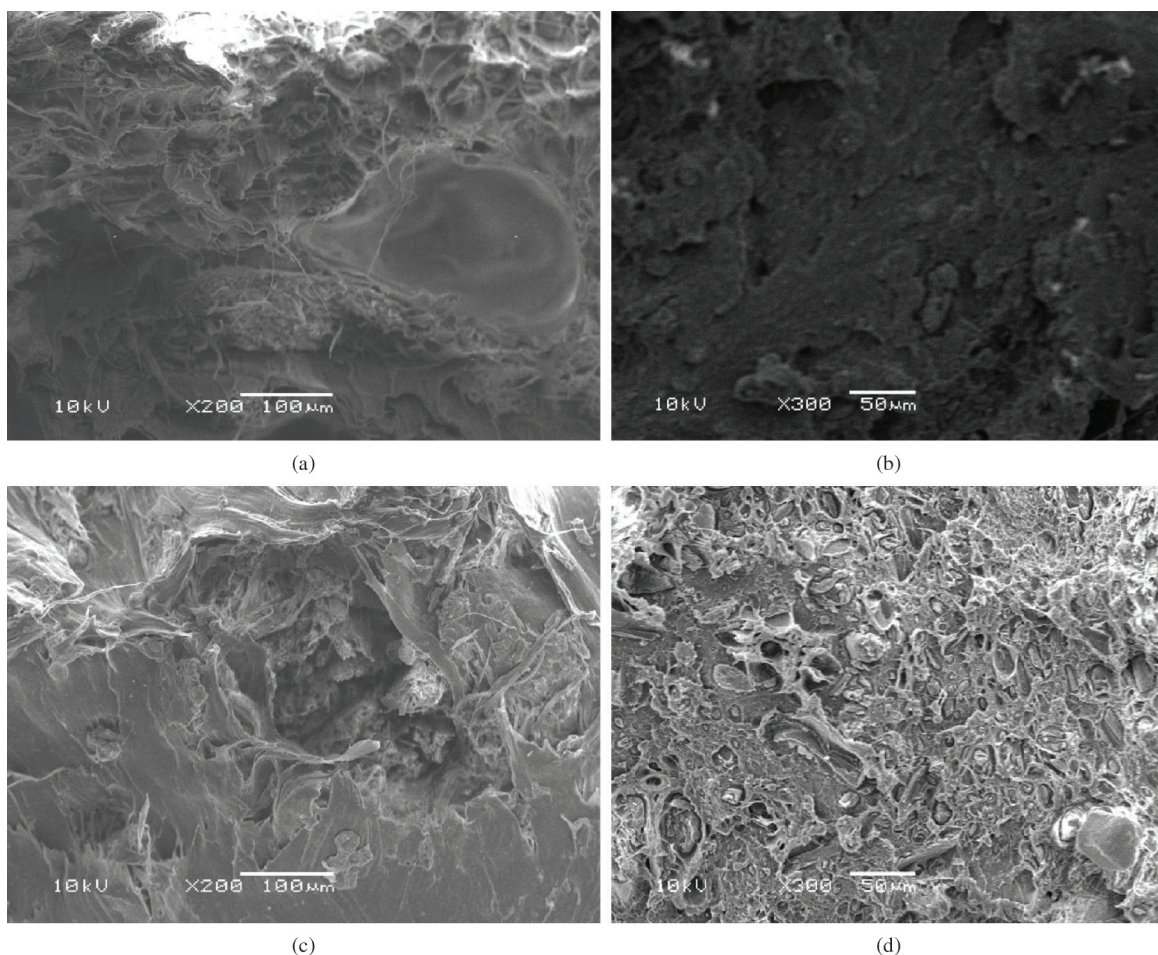


Figure 4. SEM micrographs of fracture surfaces of HDPE/EU/CA 1% (a), HDPE/EU/CA 3% (b), HDPE/EU/CA 5% (c) and HDPE/EU/CA 7% (d) composites.

is a poor interaction between fiber and polymeric matrix³³. In the Figure 4b is a micrograph of the fracture surface from HDPE/EU/CA 3% composite where can be seen that there are several particles of fiber presents, some that are not fully adhered to the polymeric matrix, and smaller ones are fully adhered, demonstrating a good compatibility between the two phases^{34,35}. Also presents some gaps in its structure, however the composite is more homogeneous, where the filler particles are better attached to the HDPE matrix, indicating that the CA has acted positively on the interfacial adhesion of the polymeric matrix with reinforcement^{36,37}, which can be also indicated by the results of tensile strength the composites.

The SEM micrographs of fracture surface from HDPE/EU/CA 5% (c) and HDPE/EU/CA 7% (d) composites also showed structures like fibrils, characteristics for polymeric matrix, and also some holes, but showing a good compatibility between matrix and reinforcement, however it was find a lower interaction between polymer matrix and the fiber in relation to HDPE/EU/CA 3%.

Images shown clearly that the coupling agent (CA) provides an improved interfacial adhesion between the cellulosic fiber and thermoplastic matrix independent of wood size. The images confirm the results obtained in mechanical tests where the compatibilized samples showed an increase of strength in relation to the non-compatibilized compositions.

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4. Conclusions

After analyzing the physical, mechanical, thermal and morphological properties, concentration of 3% w/w CA was more suitable for the production of materials, especially by DSC results that showed the most interesting characteristics make this concentration to be applied to the composites.

All composites treated with coupling agents showed a better thermal stability when compared to compatibilized HDPE matrices. The results observed by the contact angle with the surface and morphological properties show an improvement in interfacial adhesion between the components of the composites (HDPE/EU/CA) when it is used the maleic anhydride as coupling agent, corroborating with the performance obtained in mechanics tests. The result of the physical and mechanical properties in general indicates that the use of recycled polyolefins is a viable alternative for the production of new materials and can therefore be used in many new applications, even in construction, thus contributing to reduction in impacts to the environment and enabling new sustainable alternatives.

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