

Printability of HDPE/Natural Fiber Composites with High Content of Cellulosic Industrial Waste

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ABSTRACT

In this paper, a continuous polymeric matrix highly filled with fiber of sugarcane bagasse has been obtained and its feasibility as an ink-absorbing material has been evaluated. In order to study the effect of the amount of cellulose fiber on the surface printability, contact angle measurement using different liquids—water-based inks, ethanol and ink for ink-jet printers—and printing tests were performed on composites of high density polyethylene (HDPE) and sugarcane bagasse (SCB). The composites were processed in a Haake internal mixer, using the SCB without any previous chemical treatment or compatibilizer. The differential scanning calorimetry (DSC) and derivative thermogravimetry (TG/DTG) revealed an increase in the thermal stability and in the degree of crystallinity of the HDPE. The optical microscopy (OM) and scanning electron microscopy (SEM) showed that the cellulosic material was homogeneously embedded within the HDPE matrix. In order to assess the resistance of the composite sample to the pull strength of the printer, tensile tests were applied to the composites and the results were compared to known paper samples. The best result was achieved in the composite with the highest content of SCB, as well as the shortest drying time.

Keywords: Recycling, Composite, Printing Properties, HDPE, Sugarcane Bagasse

1. Introduction

Nowadays one of the major concerns of society is to preserve natural resources, because the awareness of its finitude. The search for sustainable solutions is visible in all sectors of economy [1]. Even raw materials from renewable font must have its levels of use reduced, since they make use of finite natural resources (fertilizers, water).

The use of polymeric materials has reduced the consumption of finite natural resources in many industrial applications [2]. The cellulose industry plays an important role in these sustainability matters, and is a sector of the productive chain that can be benefited by the use of polymeric materials. The use of thermoplastics in some commodities can reduce the necessary volume of cellulose in its composition, and even replace some established products—as paper, for instance, which already has a synthetic substitute for some printing applications.

Composite materials like plastic lumber [3], wood-plastic composites [4] and natural fiber reinforced composites [5] were developed intending to achieve more

sustainable solutions for the construction and reinforced plastics market. The proposition is, through the application of recycled plastics as raw material (raising its life-cycle and reducing its disposal in the environment), and using renewable-source reinforcing fillers, elaborate eco-friendly materials with wide application (as substitutes for some wood and automotive products). Cui *et al.* [6] studied the properties of wood fiber-reinforced recycled plastic composites manufactured from sawdust and post-consumer HDPE. It was observed that the incorporation of wood fibers results in higher melting and slower crystallization rate of the composites. Also its thermal and mechanical properties varied significantly according to plastic content, length of wood fiber and compatibilizer content of the composites.

Most of the existing plastic lumbers use recycled plastics only. Martins *et al.* [7], when studying mechanical properties of IMAWOOD® plastic lumber, inform its composition: LDPE/HDPE 3:1 blend, obtained from post-consumed plastic bags recovered from municipal dump. But they are designed to work mainly as structural parts, and its success as a commodity is attached to the effi-

ciency of the plastic waste selective collection.

The wood-plastic composites (WPC) have actually substituted some wood products (the medium density fiberboard—MDF—has overcome the traditional plywood boards in the Brazilian furniture market), but many compatibilizers and fiber treatments must be used in order to achieve the strong mechanical properties they need [8, 9]. And natural fiber reinforced composites (NFRC) intend to substitute inorganic for natural fiber reinforcing fillers [10], aiming to improve the properties of the neat polymer [11]. Singh *et al.* [12] developed jute fiber reinforced phenolic composite profiles as an alternative to wooden frames in buildings, intending to develop composites for structural applications. Most studies in the polyolefin/natural fibers composites area chemically treats the cellulosic fibers, to improve its adhesion and/or to bleach the fibers. Gwon *et al.* [13] studied the modification of wood fibers using alkali treatment and coupling agent reactions, mixed with polypropylene resin, concluding that the fiber treatments increased physical properties due to the introduction of compatible molecular structure onto the wood fiber surfaces.

None of these cited composites—plastic lumber, WPC and NFRC—have been elaborated just to gather the cellulosic filler with polymer, neither dealing with poor adhesion between polymer and filler, nor aiming to improve mechanical properties. But the development of such material would be an interesting application to cellulosic filler in a polymeric composite, and could lead to a sustainable material for the printing industry, and reduce the consumption of cellulosic pulp in several know applications.

Therefore, the idea of this work is to create a sustainable material making use of the polarity of cellulose as vehicle for receiving and retaining ink, in order to obtain a continuous polymeric matrix highly filled with fiber of sugarcane bagasse and to evaluate its feasibility as an ink-absorbing material. The goal of the experiment was to achieve simple blends, with few components.

As this work focus on the environmental aspects of the experiment, it was decided not to bleach the SCB fibers, to preserve its natural polarity and to avoid the generation of pollutant effluents (chlorine and hydrogen peroxide based). At first, the idea was to use recycled HDPE, but the difficulties in dealing with a heterogeneous material, associated with raw filler, lead to the use of virgin HDPE instead of the recycled polymer.

2. Experimental

2.1. Materials

The materials were high density polyethylene (HDPE) named Petrochem HC 7260—density equal $0.958 \text{ g}\cdot\text{cm}^{-3}$;

melt flow rate (MFR) equal $8\text{g}\cdot 10 \text{ min}^{-1}$ —supplied by Ipiranga Petroquímica, and sugarcane bagasse (SCB) waste from HC Sucroquímica sugarcane plant (Campos dos Goytacazes, RJ, Brasil).

The latter was used without any previous chemical treatment, and then grinded and sifted using a sieve with 40 mesh, according to the ISO 3301. The SCB fiber that passed through the sieve was used in the composite. Before the composite preparation, both materials were dried in an oven, at 105°C , for 2 hours.

2.2. Composite and Specimen Preparation

Composites of HDPE/SCB were prepared varying the SCB content from 0 to 70 wt%—named 100/0, 80/20, 50/50 and 30/70—in a Haake internal mixer, at 180°C , 60 rpm, for 10 minutes. After that, the material was compression molded as a plate of 1 mm thickness, in a hydraulic press at 200°C , 10,000 psi, for 5 minutes, being subsequently cooled in another hydraulic press, at 25°C , 430 psi, for 5 minutes.

2.3. Optical Microscopy and SEM Analysis

The morphology of the materials was noticed by usual techniques. Optical microscopy (OM) observation was performed with an Olympus stereo microscope, model SZH10, equipped with a Nikon Coolpix 5400 digital camera attached.

Triturated SCB, processed HDPE and the three composites were analyzed. Scanning electron microscopy (SEM) was performed using a Fei Company microscope model Quanta 200, using specimens coated with 300 nm gold particles (Au) applied by JEOL equipment model JFC 1500. Cryogenically fractured transversal sections and surfaces of the samples were assessed.

2.4. Differential Scanning Calorimeter (DSC)

The differential scanning calorimetry (DSC) was done using a TA equipment model TA Q1000. Three thermal cycles were performed. In first one, the sample was heated from 0°C to 200°C , at heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$, under nitrogen atmosphere. In order to eliminate the thermal history, it was left at 200°C for 2 minutes. The second one was a cooling cycle from 200°C up to 0°C , at $10^\circ\text{C}\cdot\text{min}^{-1}$. At the third cycle, the same temperature range and heating rate of the first cycle were applied.

The crystalline melting temperature (T_m) and the degree of crystallinity (X_c) of the HDPE were obtained considering the second heating cycle curves. The X_c was determined based on the ratio between the ΔH of the HDPE in the composite and the ΔH of the 100% crystalline HDPE (290 J/g), adjusted according to the percentage of the polyolefin in the composite.

2.5. Thermogravimetry

Thermogravimetry/derivative thermogravimetry (TG/DTG) was performed in a TA model Q500 equipment, from 30°C to 700°C, at heating ratio of 10°C·min⁻¹, in a nitrogen atmosphere. The weight loss, initial and final degradation temperatures— T_{onset} , T_{final} respectively—were evaluated.

2.6. Contact Angle

The measurement of contact angle was performed in a Ramé-Hart N.R.L goniometer, model 100 - 00, using RHI 2001 Imaging Software. It measures the angle between a plane tangent to a drop of liquid over a solid surface, and the plane of this surface. Four liquids were used: distilled water (DW), ethanol (EOH), mixture DW/EOH and ink-jet ink (IJI).

2.7. Printing Test

Printing tests were done using a Cannon printer, model MP 160. Samples of 110 × 110 × 0.5 mm of each composite were attached to a sheet of A4 paper. Text, color and black-and-white drawings were printed onto the composites surface, and pictures were taken after the drying time. The photographs were taken with a Canon EOS XT 350D digital camera, 35 - 80 mm lens.

2.8. Tensile-Strain Test

The tensile test was performed in an Instron tester model 5569, according to the ASTM D 882, using a load cell of 10 kN, test speed of 25 mm/min., and rectangular specimen of 10 × 100 mm. The test was also carried out over known paper samples (board and kraft), to compare the results. The Young modulus, the stress and elongation at yield, the stress and elongation at break were evaluated. The results consider the mean of 5 specimens of each sample.

3. Results and Discussion

The distribution of fiber length revealed that 77% of the ground SCB has passed through the 20 mesh sieve. In this fraction, the higher portion—36%—passed through the 100 mesh sieve. Since smaller fibers present a better dispersion into the polymeric matrix, it was decided to use all the material that passed through the 40 mesh sieve (around 1 mm to lower fiber lengths), corresponding to 66% of the triturated SCB. The ratios between fines/HDPE percentages in the composites were calculated, in order to evaluate the influence of the fines in the properties of the composites—0.14 for the 80 - 20, 0.55 for the 50 - 50 and 1.28 for the 30 - 70 composite.

3.1. Optical Microscopy and SEM Analysis

The OM and SEM photomicrographies of the composites (**Figures 1-2**) revealed fine dispersion between polymer

and filler. Comparing the particle size of the triturated filler to those of the composites shows that some shearing occurred during the processing in the Haake mixer.

The good interaction between the two materials may have come from the variety of sizes of the ground SCB particles, which included a lot of fines. Also the presence of lignin may have worked as a compatibilizing agent in the composites, as seen in some studies [4,14]. The SEM revealed that the SCB particles were completely encapsulated by the HDPE, even in the 30 - 70 composite. It also confirms fine dispersion between the materials.

3.2. Differential Scanning Calorimetry

The DSC curves are shown in **Figure 3**, and the results of the composites and its parent materials are in **Table 1**. The SCB curve presented an intense peak at the first heating cycle—between 50°C - 170°C (maximum value was around 120°C), ascribed to the loss of moisture—which disappeared in the second heating cycle. For the composites, considering the second heating cycle, no variation was observed in the T_m of the HDPE (132°C), denoting that the average size of the crystals did not change. At all the heating cycles, there was a raise in the X_c depending on the content of SCB in the composites.

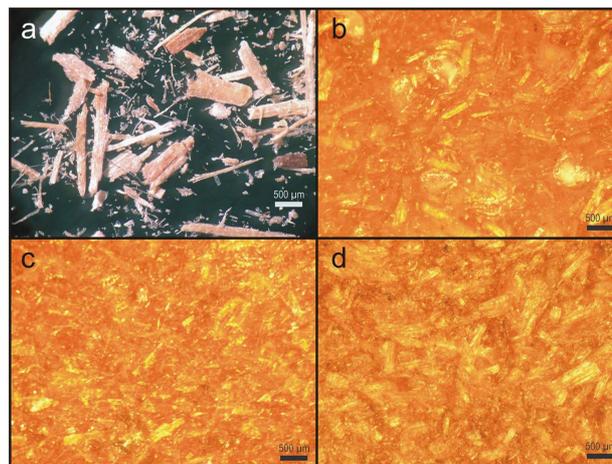


Figure 1. OM photomicrographies of the materials: (a) ground SCB, (b) 80 - 20 composite, (c) 50 - 50 composite and (d) 30 - 70 composite.

Table 1. Melting temperature and degree of crystallinity of the composites.

HDPE/SCB composite	T_m (°C)	T_c (°C)	X_c (%)
100 - 0	132	120	66
80 - 20	132	119	84
50 - 50	132	121	68
30 - 70	132	120	83

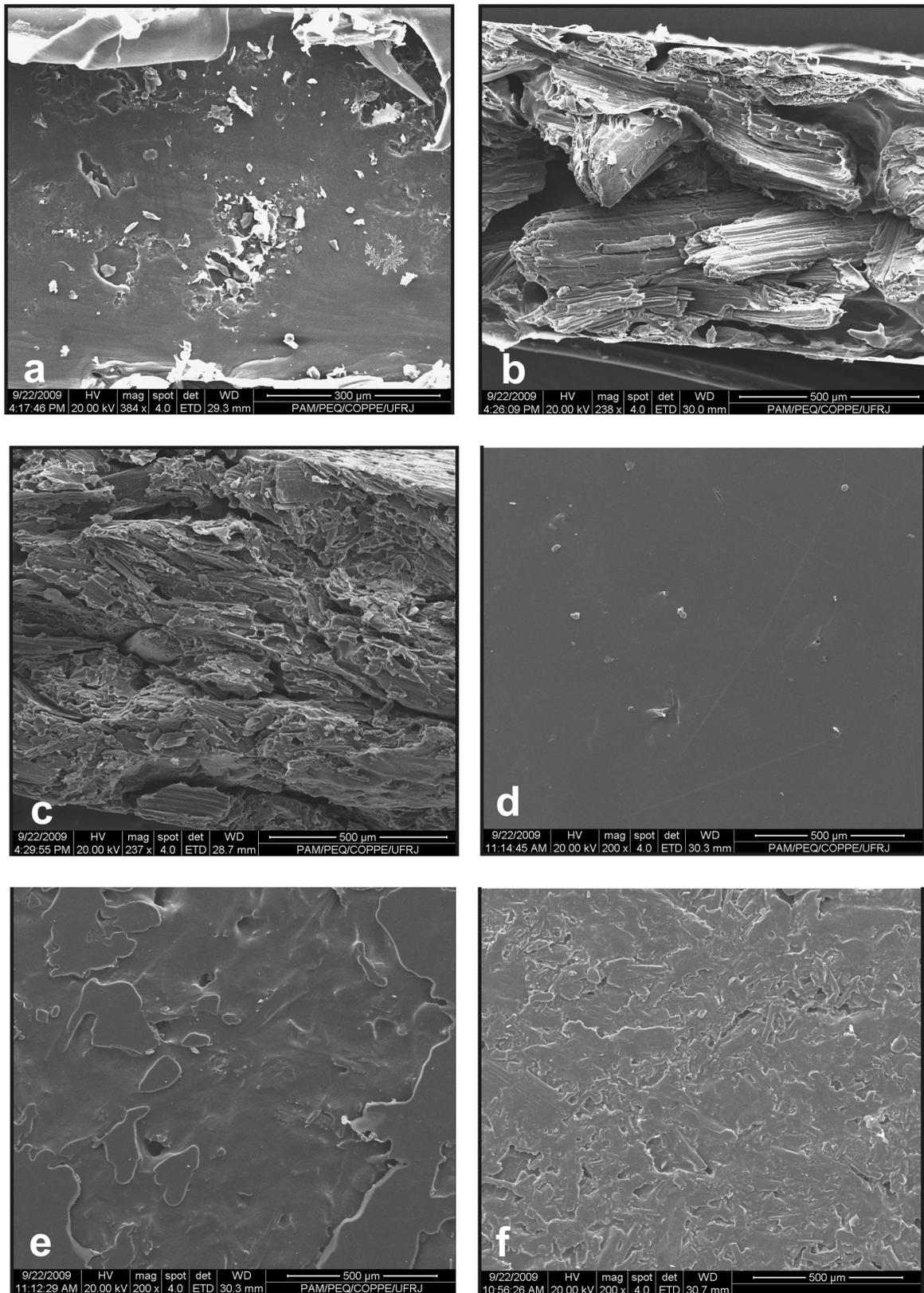


Figure 2. SEM photomicrographies of the materials: 80 - 20 composite (a) section and (d) surface, 50 - 50 composite (b) section and (e) surface, and 30 - 70 composite (c) section and (f) surface.

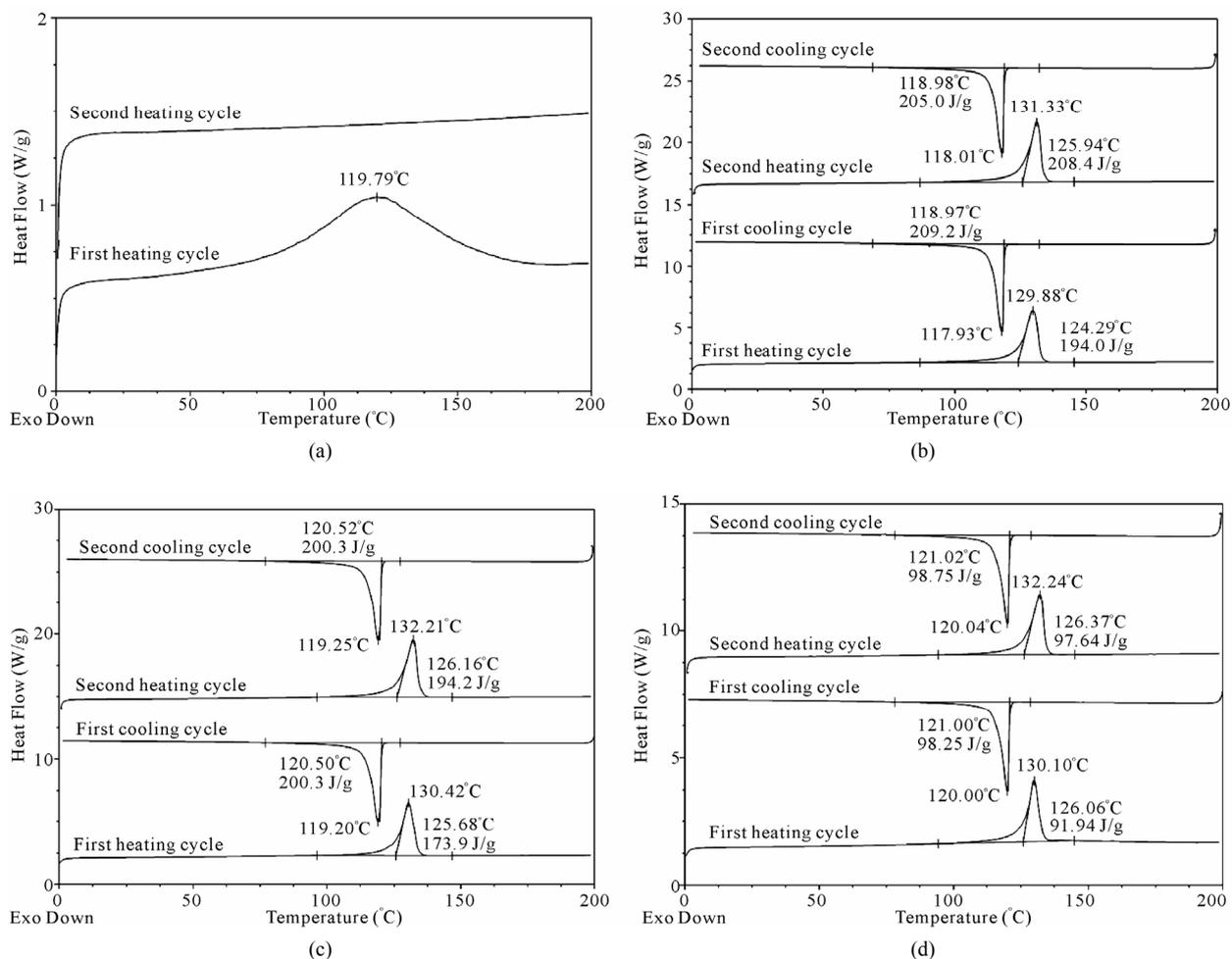


Figure 3. DSC curves of the materials: (a) SCB, (b) 80 - 20 composite, (c) 50 - 50 composite and (d) 30 - 70 composite.

This increase in the X_c , associated with no variation in the T_c , may be due to some transcrystallization. Commonly, after melting, the bulk molten of a semicrystalline polymer can recrystallize under cooling. It takes place under homogeneous nucleation, and where the amount of the crystalline portion has the same order of magnitude as the initial material. Concerning to the composites, transcrystallization is a special case of crystallization where a heterogeneous nucleation is feasible along a fiber surface. The transcrystallization is a function of nucleating activity of the fiber surface and crystallization kinetics of the resin matrix [15]. Also, this phenomenon was described by Na *et al.* [16], when performing morphological investigations of an isotactic polypropylene matrix induced by synthetic fibres.

3.3. Thermogravimetry

Table 2 lists the initial and final degradation temperatures (T_{onset} and T_{final} , respectively), the maximum degradation temperature (T_{max}) and the amount of remaining

residue of the parent materials and the composites. The HDPE curve (Figure 4(a)), as expected, showed a single step degradation, and the entire sample burned, leaving no residue. The SCB and 30/70 composite curves are shown in Figures 4(b) and 4(e). The SCB presented three different steps of weight loss. The first one is probably due to loss of moisture. At the second stage, the ascending part of the derivative thermogravimetry (DTG) curve presented a shoulder and a peak—highlighted in a

Table 2. T_{onset} , T_{final} and T_{max} of the materials.

HDPE/SCB Composite	T_{onset} (°C)	T_{final} (°C)	T_{max} (°C)	Residue (%)
100/0	433	500	461	-
80/20	307/459	500	354/478	-
50/50	303/444	550	349/472	3
30/70	258/448	550	295/351/472	10
SCB	292	575	344/496	2

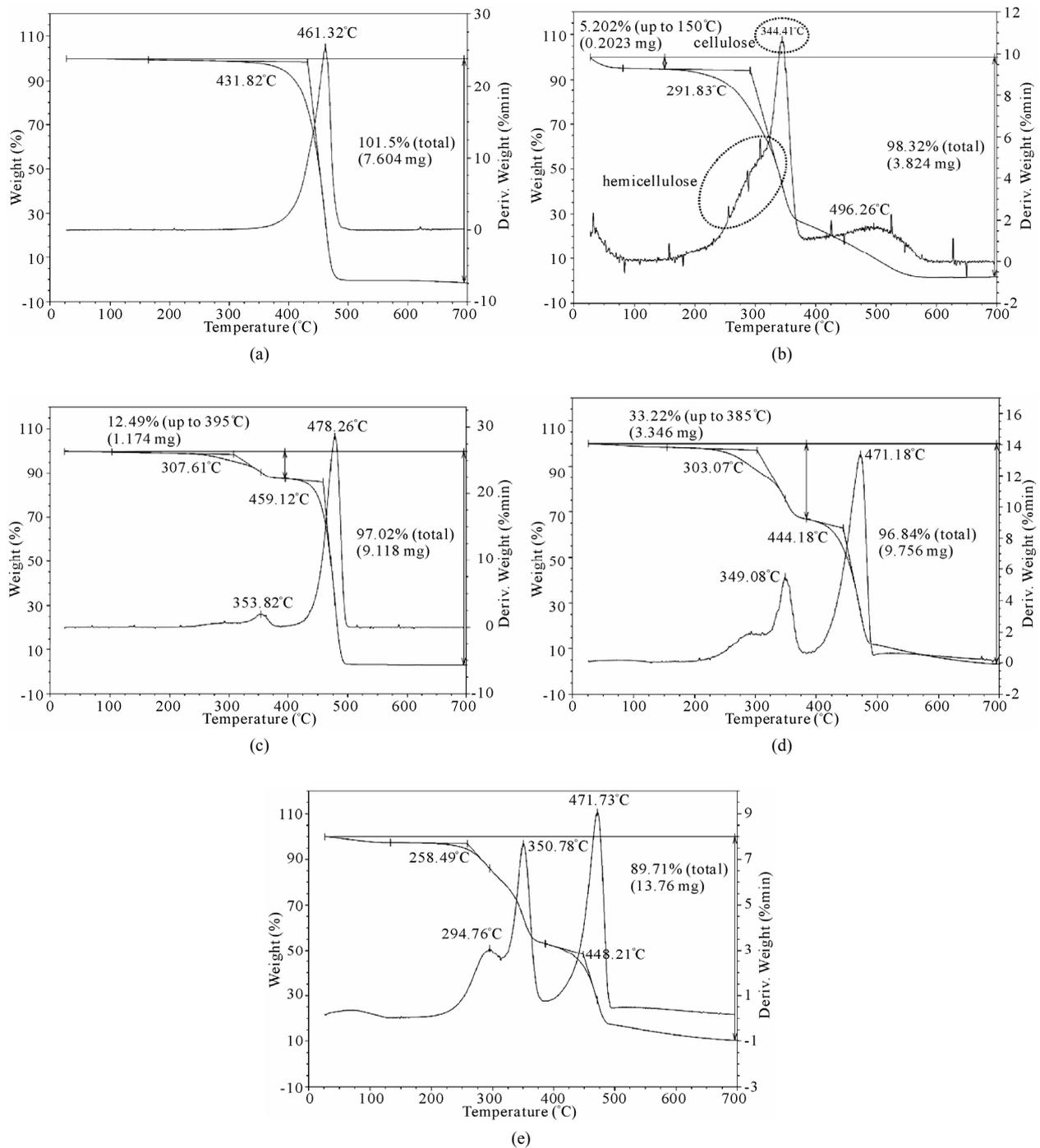


Figure 4. TG/DTG degradation curves of the materials: (a) HDPR, (b) SCB, (c) 80 - 20 composite and (d) 50 - 50 composite; (e) 30 - 70 composite.

dot circle—asccribed to the burn of hemicellulose and cellulose, respectively. And the third step was attributed to the degradation of lignin.

The weight loss curves of the composites showed burn steps similar to the parent materials. There was mutual influence in the thermal parameters considered in this

study. The T_{onset} , T_{final} and T_{max} temperatures of the HDPE were shifted to higher values, indicating a raise in its thermal stability due to the presence of the SCB.

Concerning to the 30 - 70 composite, there was a change in the burn profile of the SCB. What first seem to be a shoulder and a peak on the SCB thermogram, turned

into two well-defined peaks ($T_{\max} = 295$ and 351°C). The amount of residue increased as the content of SCB in the composite raised.

3.4. Contact Angle

Contact angle test results for the four liquids (DW, EOH, DW/EOH and IJI) are shown in **Table 3**. **Figure 5** graphically shows an overall comparison. The composites presented high repellency to DW (water). The 100 - 0 composite presented nearly no variation to the three other liquids. The addition of 20%, 50% and 70% of SCB influenced the results for EOH, DW/EOH and IJI contact angles.

Concerning to DW/EOH and IJI contact angle values, the composites showed a similar behavior. For EOH, there is a linear decrease of the contact angle depending on the SCB content. The results clearly show that the increase of the SCB content in the composites raises the absorption efficiency of the tested liquids.

3.5. Printing Test

The composite sheets were cleaned with ethyl alcohol before being printed, having no other surface treatment. The printing tests (**Figure 6**, Online Resource 1) showed the composites' capability of absorbing inkjet ink. It took from 6 to 24 hours for the ink to completely dry on the other composites, and the 80 - 20 composite was unable to retain it at all.

Observing the 80 - 20 and 50 - 50 printing tests, one

can see the ink had formed drops that did not spread on the sheet surface, resulting in a blurred, non-graphic quality, which was easily smudged. On the 30 - 70 composite the ink was completely dried and partially absorbed within a reasonable time (about 1 hour). The quality of the printing improved as the cellulose content in the composite raised.

3.6. Tensile-Strain Test

The tensile test provided by the Young modulus, tensile stress at maximum load, tensile strain at maximum load, stress at break and strain at break, and the results are shown in **Table 4**. The Young modulus decreases with lower amounts of SCB filler, but for the 50 - 50 and 30 - 70 composites it reaches a value close to neat HDPE. The increase of the amount of filler decreases the tensile stress, tensile strain, break strength and break elongation values, as seen by Mulinari *et al.* [17] when studying sugarcane bagasse/HDPE composites obtained by extrusion. The moduli of the plastic materials are inferior to those of commercial paper, but the elongation of the 80 - 20 composite is similar.

4. Conclusions

These results show that the association of trituated SCB with a polymeric matrix brings up fine results in terms of printability, thermal and mechanical properties. In general, the developed materials seem to fit the purpose of aggregating cellulosic industrial waste using a polyole-

Table 3. Contact angles for the materials.

Composite HDPE/SCB	Liquids			
	DI water	Ethanol	DI water/ethanol mix 50 - 50%	Inkjet ink
100 - 0	75 ± 13	23 ± 7	23 ± 7	20 ± 4
80 - 20	61 ± 12	20 ± 2	37 ± 4	25 ± 5
50 - 50	71 ± 11	12 ± 4	46 ± 4	31 ± 6
30 - 70	77 ± 12	8 ± 3	42 ± 8	26 ± 7

Table 4. Tensile parameters.

Material	Young modulus (MPa)	Stress at Maximum Load (MPa)	Elongation at Maximum Load (%)	Stress at break (MPa)	Elongation at break (%)
HDPE	590 ± 54	24.1 ± 1.6	14.1 ± 1.7	19.3 ± 1.3	24.2 ± 8.0
80% - 20%	356 ± 19	7.7 ± 0.8	3.1 ± 0.4	6.1 ± 0.6	3.6 ± 0.5
50% - 50%	512 ± 128	4.4 ± 1.7	1.2 ± 0.3	3.5 ± 1.4	1.4 ± 0.3
30% - 70%	588 ± 133	3.0 ± 0.8	0.9 ± 0.1	2.4 ± 0.6	1.0 ± 0.1
Board paper	1568 ± 87	22.6 ± 1.1	2.6 ± 0.2	22.4 ± 1.0	2.6 ± 0.2
Kraft paper	2218 ± 195	67.1 ± 4.3	4.5 ± 0.2	66.4 ± 4.2	4.5 ± 0.2

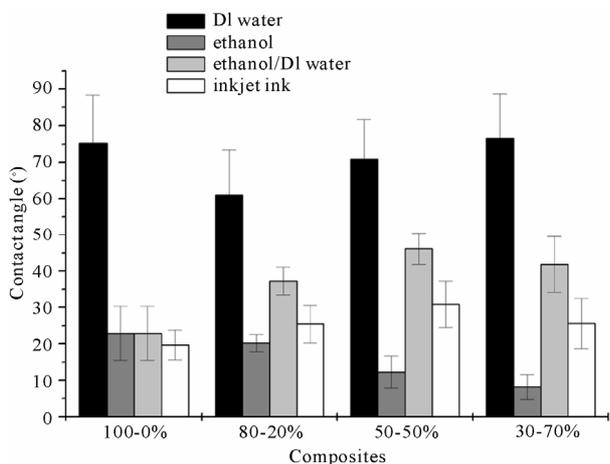


Figure 5. Comparative graphic contact angle x solids.

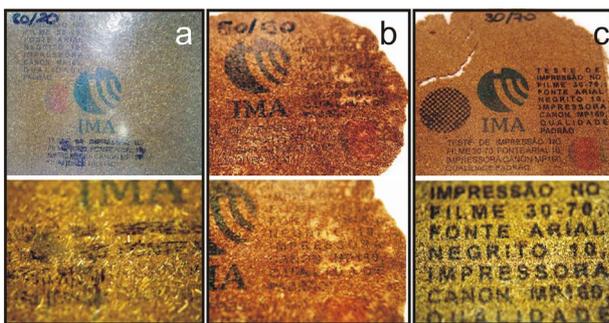


Figure 6. Printing test of the composites: (a) 80 - 20 composite, (b) 50 - 50 composite and (c) 30 - 70 composite.

finic matrix, in order to create a printing surface through a simple, low cost and eco-friendly composite.

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