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Properties of Recycled High Density Polyethylene and Coffee Dregs Composites

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Abstract: Composites of recycled high density polyethylene (HDPE-R) and coffee dregs (COFD) were elaborated. The blends were made at the proportions of 100-0, 90-10, 80-20, 70-30, 60-40, 50-50 and 40-60% polymer-filler ratio. The materials were evaluated through scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetry/derivative thermogravimetry (TGA), and compressive resistance test. The compounding was done using a two-stage co-kneader system extruder, and then cylindrical specimens were injection molded. All composites had a fine dispersion of the COFD into the polymeric matrix. The composites degraded in two steps. The first one was in a temperature lower than the neat HDPE, but higher than the average processing temperature of the polymer. The melting temperature and the degree of crystallinity of the composites resulted similar to the neat HDPE ones. The compressive moduli of the composites resulted similar to the neat polymer one. The results show that these composites have interesting properties as a building material.

Keywords: *Composites, mechanical properties, thermal properties, recycling, HDPE.*

Introduction

Nowadays the development of polymeric substitutes to conventional materials has been pursued, due to the urgent need to develop sustainable industrial alternatives. Some authors of eco-economy have been dealing with this issue[1-3]. It is necessary to adapt the way of handling the finite natural resources, and plastics can be an interesting solution for that. Raw materials of polymeric composites are also a finite natural resource (petroleum). And environmental problems caused by plastics disposal are still without a solution compatible with the scale of the damages caused by them. Transforming large scale waste into a commodity product would deal both environmental and economical issues[4-6]. From this point of view, arose the idea of using recycled polymer and natural fibers waste to create a material for the construction industry. In literature, heavily filled natural fibers composites often show results of an increase on modulus proportional to the filler content[7-10]. This characteristic is not wanted in materials designed to work to tensile strain. But it is interesting for a material intended to resist to compressive efforts (e.g. concrete, clay). Compressive resistance in polymeric composites has not been widely studied yet. And the building materials field can bring up new possibilities for the sustainable use of post consumed plastics. The coffee dregs (COFD) are an organic waste present in large quantities at industrial and household waste, with no commercial destination. Using COFD as filler in a matrix of recycled high-density polyethylene (HDPE-R) is an attempt of transforming two waste materials into a new raw material for structural masonry bricks.

Then, the main goal of this study is to develop a composite of recycled high-density polyethylene (HDPE-R) filled with coffee dregs (COFD). This material should have enough mechanical properties to resist to compressive efforts. We investigated the morphology, thermal and mechanical properties of these materials. This study develops previous works[11], where it was studied thermal and mechanical properties of different types of coffee dregs over the properties of pure HDPE.

Materials and Methods

Materials

The materials used were recycled high-density polyethylene (HDPE-R), having 0.897 g.cm^{-3} density, and melt flow rate (MFR) of 0.3 g.10 min^{-1}. The density was measured according to ASTM D792 - 08 Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement - method B, on ethanol at 23°C; this density was tested 3 times, using 5 samples each time. The MFR was done using method A of ASTM D1238, 190°C, cut time 45 sec., melt time 240 sec, 2,16 kg load. HDPE-R was donated by COMBRARE Recycler (Brazil), in pellets. COFD was obtained through selective collection held at IMA-UFRJ facilities (Brazil).

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Composites and specimens preparation

Compounding and processing were performed at the thermoplastic processing unit of the Polymers Engineering department of University of Bayreuth at Hamburg, Germany. Materials were dried overnight in a vacuum oven at 80°C, and then compounded in a Buss® two-stage co-kneader system extruder, model MK 30-20, with air/water pelletizing system. The processing section used a 30 mm diameter screw, *L/D* ratio of 20 and screw speed of 330 rpm; The pressurizing section used a 40 mm diameter screw, *L/D* ratio of 6 and screw speed of 25 rpm. Processing parameters were: temperature profile in the processing section – 220,192, 190, 180, 179 and 178°C; temperature profile in the pressurizing section – 179°C. There was a 3 mm diameter die, with temperature of 260°C and pressure of 3.3 MPa. Extrusion process went to 60% of filler content. At this point, the material started to release smoke, indicating the COFD was already degrading. The blends were made at the proportions of 100-0, 90-10, 80-20, 70-30, 60-40, 50-50 and 40-60% polymer-filler ratio. Compounded materials were then injection molded into cylinders of 20 mm height and 10 mm diameter, using an Arburg All Rounder 420C 800-250 equipment. The processing parameters were: temperature profile of 230, 230, 210, 205 and 190 (nozzle) °C; clamping force of 80 kN; holding pressure of 240 MPa, mold temperature of 95°C; holding pressure time of 16s; closed mold time of 30 s; injection cycle time of 55s. The molten material was injected using 245 MPa pressure, and two speeds – first of 3 $cm^3.s^{-1}$ and second of 2 $cm^3.s^{-1}$. Composite 90-10 was not injected, nor tested for compressive resistance, because this amount (90-10) uses a very low percent of filler, and means no gain in terms of using an inert filler to spend less plastic and obtain similar mechanical results. Injection branches of cylinders were removed using a lathe EMCO Maximat V13.

Thermal analysis (thermogravimetry – TGA – and differential scanning calorimetry – DSC) were done using cut pellets. Thin films were compression molded in order to perform optical (OM) and scanning electron microscopy (SEM). They were done using a heated press at 190°C, at 3 MPa, for 5 minutes, and then cooled in a press at 25°C, at 3 MPa, for 5 minutes.

Thermogravimetry - TGA

Thermogravimetry was performed using a Metler-Toledo equipment TGA/SDTA 851e model. Temperature range was from 25 to 800°C, at a heating rate of 10°C. min^{-1}, under nitrogen atmosphere. It was measured the mass loss, initial (T_{onset}), maximum (T_{max}) and final (T_{final}) degradation temperatures..

Differential scanning calorimetry

The differential scanning calorimetry was performed using a Metler-Toledo equipment DSC/SDTA 821e model. The samples were analyzed under nitrogen atmosphere, according to the following cycles: in the first cycle the sample was heated from 20 to 200°C, at a heating rate of 10°C.min^{-1}, leaving the material at 200°C for 2 minutes; the second cycle was done using a cooling rate of 10°C.min^{-1}, until 20°C; in the third cycle the sample was heated from 20 to 200°C, at a heating rate of 10°C.min^{-1}. The crystalline melting temperature (T_m) and the degree of crystallinity (X_c) of the HDPE were obtained considering the second heating curves. The X_c was determined based on the ratio between the melting enthalpy (ΔH_m) of the HDPE in the composite and the 100% crystalline HDPE (293 $J.g^{-1}$), adjusted according to the content of polyolefin in the composite.

Scanning electron microscopy (SEM)

Scanning electron microscopy was performed over the cross section of cryogenically fractured samples, using a scanning electron microscope Jeol model JSM-6510. The samples were previously metalized with a 300 nm layer of gold.

Compressive resistance

Compressive resistance test was performed according to ASTM D 695, in a Zwick universal tester 1485 model, using a 250 kN load cell, test speed of 1,3 mm.min^{-1}, till 60% deformation. This test was held at New Materials Center of Bayreuth, at Bayreuth, Germany.

Results and Discussion

Regarding to TGA results, observing the superposition of the curves (Figure 1), a first step of degradation appeared around 250°C, followed by another step around 350°C - slightly lower than the typical onset of HDPE[12,13]. Behavior of 50-50 resembles 60-40 one, as well as 70-30 does to 80-20 composite. The residue content rose proportionally to the raise of COFD volume. Even for the 40-60 composite, the presence of COFD did not cause degradation of the material in the temperature range commonly used for thermoforming HDPE articles (180-200°C).

DSC curves (Figure 2) revealed that there was another material mixed with the HDPE-R. The peak aspect and temperature is similar to polypropylene – PP ones, as seen in literature[14,15], around 160°C. There was no significant variation in the T_m of the HDPE-R in the composites.

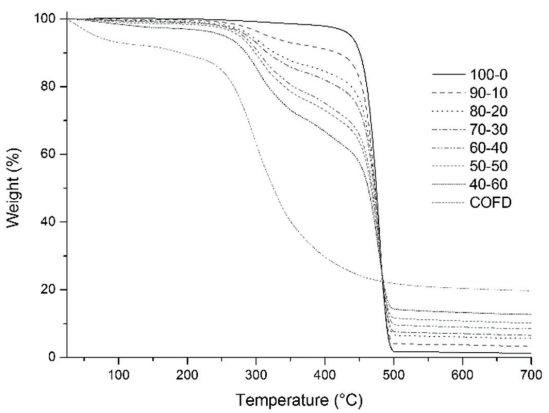

Figure 1. Superposition of TGA curves of the composites.

Table 1 shows that T_m peaks resulted also similar, but with the ΔH lower (from 12 to 59%) than the HDPE-R one. This points out an interference of the COFD in the crystalline packing of the polymer. The increase of 14% on X_c of the 50-50 may be due to an experimental error, since the rest of the composites showed only a slight variation on this parameter.

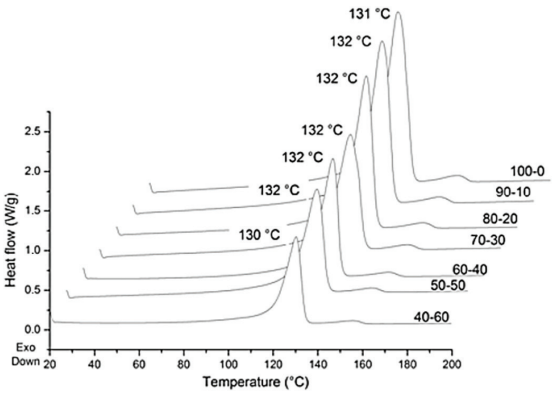

Figure 2. Superposition of DSC curves of the composites.

The SEM analysis (Figure 3) showed a fine dispersion of the COFD within the HDPE-R. This behavior was seen in a previous study[11]. From the 90-10 to the 60-40 composites, it is difficult to identify the filler within the polymeric matrix. The 50-50 and 40-60 ones formed an uniform structure, where polymer and filler only can be identified on higher magnifications. Some foaming has occurred in the HDPE-R. Increasing the magnification, one can see the retained portions of the molten HDPE-R in the COFD voids (Figure 4).

On the HDPE-R images (Figure 5) some other material seems to be mixed with the polymer. In literature[16] there

Table 1. Crystalline melting temperature (T_m), fusion enthalpy (ΔH), degree of crystallinity (X_c), percentual variation ($\Delta\%$) of ΔH and X_c of the composites.

Material	T_m (°C)	ΔH (J.g^{-1})	T_c (°C)	X_c
100-0	131	169	118	58%
90-10	132	150	118	57%
80-20	132	134	118	57%
70-30	132	117	117	57%
60-40	132	100	117	57%
50-50	132	97	116	66%
40-60	130	70	117	59%

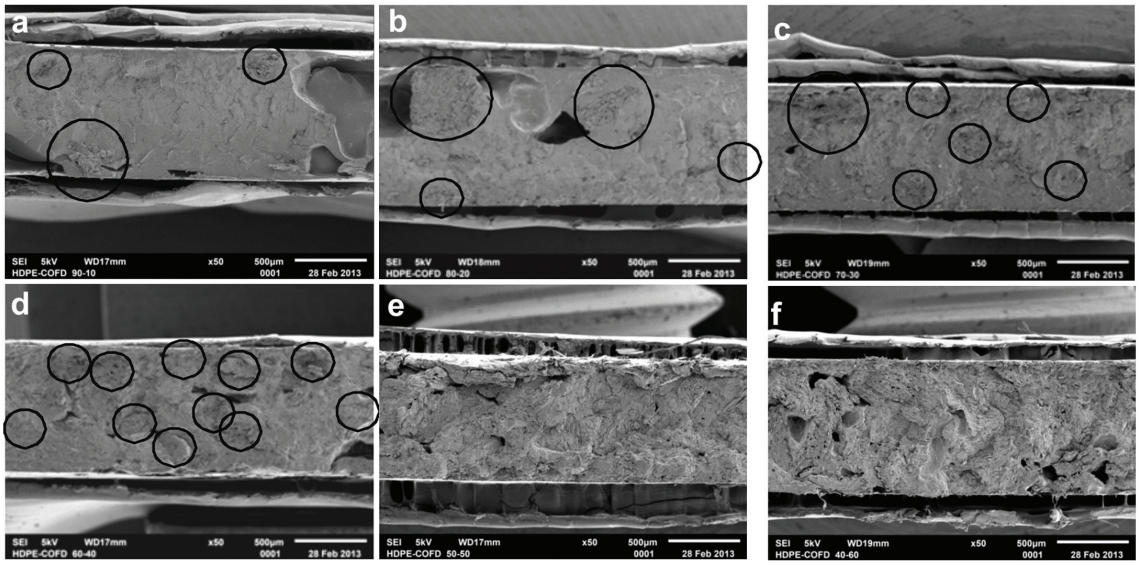

Figure 3. SEM images of composites 90-10 (a), 80-20 (b), 70-30 (c), 60-40 (d), 50-50 (e) and 40-60 (f) magnified 50 times; filler highlighted in black circles.

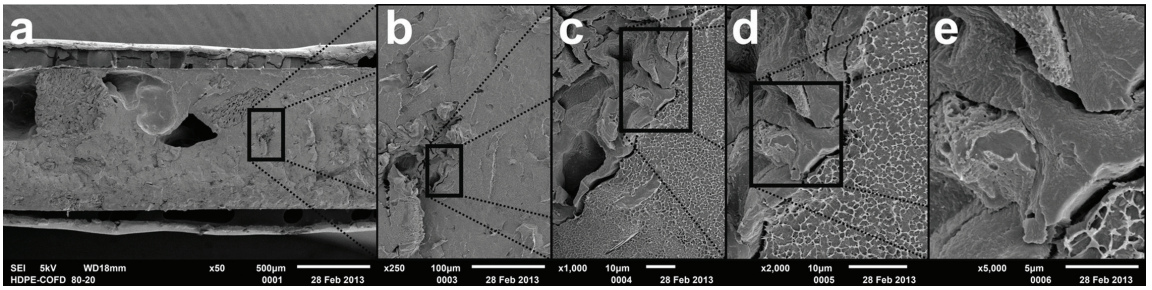

Figure 4. SEM images of composite 80-20 magnified 50x(a), 250x (b), 1,000x (c), 2,000x (d) and 5,000x (e).

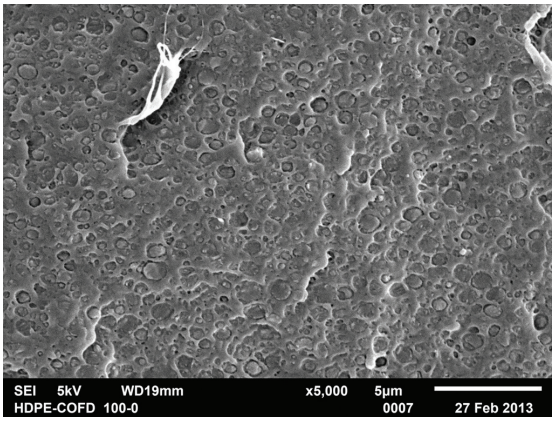

Figure 5. SEM images of HDPE-R magnified 5,000x.

Table 2. Compressive moduli of the composites.

Material	E_c (MPa)	SD (Mpa)	$\Delta\%$ E_c
100-0	844	36	-
80-20	655	37	–22%
70-30	803	46	–5%
60-40	754	23	–11%
50-50	749	31	–11%
40-60	596	38	–29%

Figure 6. Compressed specimens of 100-0 composite.

are similar images, for HDPE/PP blends. This SEM image and the peak around 160°C on DSC curves indicate that this recycled HDPE may have some PP blended.

There was a decrease in the compressive modulus of the 80-20 composite. Then, the 70-30 showed a modulus very close to HDPE-R one (Table 2). 60-40 and 50-50 had a decrease of 11%, and the 40-60 has 29%, the highest reduction. Some specimens had voids inside, probably due to some gas released during the injection molding process. This could be noticed by the irregular shape of the cylinders after the test (Figure 6).

Conclusions

Despite the appearance of a first stage of degradation, the composites showed thermal resistance similar to that of HDPE-R in the second step of degradation. The pairs of composites 50-50/60-40 and 70-30/80-20 degraded in a similar manner. There was an increase in the residue content proportional to the increase of filler in the composites. DSC curves confirmed the presence of another polymer in the HDPE-R – probably PP – due to a second peak on the curve, near to 160°C. The T_m of the composites was almost the same of HDPE-R. There was a progressive reduction on the X_c of the polymer, ascribed to uncrystallized portions of HDPE-R retained amongst the voids of COFD. It might have hindered the diffusion of the molecules to the centers of crystallization. The crystallization temperature (T_c) of the composite remained practically the same of the HDPE-R, except for the 50-50 one.

The study indicates that coffee dregs are an interesting filler for polymeric composites. Besides not needing any soluble extraction and particle size reduction process, as seen in previous study[11], the composite with 30% filler resulted in nearly the same compressive resistance of neat polymer. It is a significant economy of polymer in the composite, and could be a key factor for choosing this fiber waste as filler for polymeric composites.

Acknowledgments

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