BIODEGRADABILITY AND MECHANICAL PROPERTIES OF SUGARCANE BAGASSE FILLED PP/HMSPP STRUCTURAL FOAMS BIOCOMPOSITES TREATED WITH GAMMA-IRRADIATION

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Abstract

In recent years, as a result of growing environmental awareness, natural polymers (starch, cellulose, chitin, sugarcane bagasse, sisal, etc…) have been increasingly used as reinforcing fillers in thermoplastic composite materials. Sugarcane bagasse was used as reinforcing filler, considering that Brazil is the largest world producer of this crop, with a 101 Mt main agro-industrial residue of sugarcane processing from 340 Mt of sugarcane. Bio-foams were compounded on a 3:1 L/D and 19/33 compression ratio extruder, by using CO_2 as PBA (Physical Blowing Agent), at 20 bar pressure. This study aims to investigate mechanical properties of PP/HMSPP-sugarcane bagasse 10, 15, 30 and 50% blends further gamma-irradiated at 50, 100, 150 and 200 kGy doses, by using a 5 kg load cell texturometer. Degradation essays will be investigated by DSC and TGA assessments. Biodegradability behavior will be indicated by Laboratory Soil Burial Test, for the time being based just in PP/HMSPP-sugarcane bagasse 10% sample. The main objective of this work is to support the application of bio-foams herein as environmentally friendly materials and reinforcing filler, keeping mechanicals properties in spite of gamma-irradiation doses imparted to them.

Introduction

Structural foams have a comprehensive application field, being used in order to improve appearance of insulation structures or to reduce costs involving materials, besides their applications in building and construction markets. Most thermoplastics can be extruded into structural foams; commercial activities have concentrated on the lower cost thermoplastic, such as Polypropylene (PP) [1].

Polypropylene (PP) is a commodity plastic that accounts for more than 70% of total plastics market; since polymeric materials are immune to microbial degrading, they remain in the soil and in landfills as a semi-permanent residue. Polymeric discard of PP and its derivatives/ameliorations, as well structural foams from them is, admittedly, one of the most challenging classes of waste to dispose of, in such a degree that their discarding is being blamed for shortening the life span of a sanitary landfill [2], [3], [4].

Samples prepared from a previously extruder homogeneized 50% blend PP and HMSPP (High Melt Strength Polypropylene), further admixtured with sugarcane bagasse were extruded foamed by using CO_2 as PBA, aiming to evaluations of mechanical tests and biodegradability, after exposed to gamma-irradiation.

Problem Statement

Biodegradation rate can be enhanced by foaming PP and its ameliorations/derivatives, with biodegradable natural polymers, such as sugarcane bagasse. Nevertheless, these *natural* structural foams should keep their original mechanical properties and simultaneously present an acceptable biodegradability, in spite of high energy (gamma-rays) and soil burial treatments.

Experimental

Materials

Polypropylene (PP)

PP-440K, from Quattor, 3.5 g/10 minutes Melt Flow Index.

HMSPP (High Melt Strength Polypropylene)

PP samples previously kept in nylon bags, under acethylene for 48 hours, were further gamma – irradiated, Co^{60} source, JS 7500 and JS 9699, MDS Nordion, Canadá, at room temperature, 12.5 kGy dose and a 10 $kGyh^{-1}$ estimate average for irradiation rate, monitoring via 4034 Harwell Red Perspex dosimeter. After irradiation, samples were air-forced oven annealed, 1 hour at 100^{o}C, in order to eliminate remaining radicals to accomplish termination reactions [5].

Sugarcane bagasse

The material, from Caçapava, São Paulo, was previously washed in running water, dried at ambient air and protected from environment, for two months. Then, it was kept in air-forced oven, at 60^{o}C, for 24 hours. Treated material was then grinded and kept for more 4 hours, at 60^{o}C, before sieve segregation in 355 µm meshes. In the present work it was used material retained in 355 µm meshes sieve [6].

Preparation of mixtures

PP/HMSPP 50% **(PP/HMSPP)**

A mixture containing 50% PP and 50% HMSPP was compounded on a 3.1 L/D and 19/33 compression ratio twin-screw extruder (HAAKE Rheomex 332p), at temperatures up to 200℃, 60 rpm. Homogeneized extrudate was used as basis for four admixtures: 10, 15, 30 and 50 % of sugarcane bagasse.

Foaming

All prepared samples were extruded foamed, within a 165 to 220^o C temperature range and using CO_2 as PBA, using a special screw for foaming and a 3x9 mm^2 rectangular die. Samples were collected directly from the die, squeezing them into homogeneous strips by means of a special device.

Gamma-irradiation treatment

Foamed PP/HMSPP and its compositions with sugarcane bagasse at 10, 15, 30 and 50% were further gamma-irradiated within 50, 100, 150 and 200 kGy doses.

DSC-Differential Scanning Calorimetry

Samples thermal behavior was examined in a DSC Mettler Toledo apparatus, according to ASTM D3418-08 – Standard Test method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry, by using 5 – 9 mg of sample, within a 25 to 300 ^{o}C program, at a 10^{o}C/min, in a nitrogen flow of 50 ml/min.

TGA-Thermal Gravimetric Analyses

TGA provides complimentary and supplementary characterization information to DSC, by measuring the amount and rate (velocity) of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. Measurements are used primarily to determine the thermal and/or oxidative stabilities of materials as well as their compositional properties. The technique can analyze materials that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatiles (such as moisture). TGA in pellets samples were performed using a DSC Mettler Toledo apparatus, according to ASTM E1641-07 – Standard Test method for Decomposition Kinetics by Thermogravimetry, by using 5 – 9 mg of sample, within a 25 to 600 ^{o}C program, at a 10^{o}C/min, in a nitrogen flow of 50 ml/min.

Texturometer

Mechanical testing was performed on a TA-Hdi (Stable Micro Systems Texture Analyser) texturometer using a load cell of 5 kg, and operating at a deformation rate of 0.5 m/s. The tensile tests were performed under ambient conditions.

Laboratory Soil Burial Test

1 mm thick and 25 mm disk samples, produced by compression molding at 190^o C and fast cool in a water bath, were buried inside 1,000 ml glass beakers, containing specific inoculum for gardening. Beakers were kept under specific conditions of temperature and humidity (24^o C ± 1^o C/RH 80). The assessment was carried out at 1, 2 and 4 months of exposure in soil, with samples perfectly and carefully cleaned with a brush and a soft towel, before dry weighing in an analytical digital balance, model BP210D, Sartorius AG, RFA. The rate of variation of the mass was determined as a function of time following the equation 1:

$$T(\%) = \frac{mo - mt}{mo} \times 100 \quad (1)$$

where m_o, is the initial mass sample at the time t_o and m_t, is the mass of the sample at the time t (after soil burial) [7], [8], [9].

Results and discussion

DSC-Evaluations

In DSC experiment all samples were heated beyond the melting temperature and cooled back to room temperature, before the second run test (second scanning). A higher melting temperature (T_m) is associated to a higher sample thermal stability [10] Irradiated PP/HMSPP showed a higher and almost the same crystallinity for 50, 100, 150 and 200 kGy doses; irradiated 10% bagasse in PP/HMSPP showed a lower crystallinity range when compared to natural irradiated basis. In Tables 1 and 2 are summarized their behavior:

Table 1: Irradiated PP/HMSPP basis

Sample	0 kGy	50 kGy	100 kGy	150 kGy	200 kGy
T_m (^{o}C)	168.6	162.4	159.1	157.3	156.5
Crystallinity (%)	42.3	46.5	52.9	52.0	51.6

Table 2: Irradiated 10% bagasse in PP/HMSPP

Sample	0 kGy	50 kGy	100 kGy	150 kGy	200 kGy
T_m (°C)	160.9	157.3	152.1	150.3	149.7
Crystallinity (%)	30.3	29.8	27.6	27.4	26.9

TGA-Evaluations

10% bagasse in PP/HMSPP, within a gamma-irradiation range from 0 to 200 kGy was analyzed against a natural pristine basis. For bagasse compounded samples, main two-stage mass loss was observed: the first one with a small hump in the temperature range from 250 to 370°C, characteristic of low molecular weight components, such as hemicellulose and the second one, in the range of 370 and 500°C, corresponding to the thermal degradation of cellulose [11], [12]. PP/HMSPP non-irradiated, showed an initial temperature of mass loss (t_{onset}) at 380° C, according to shown in Figure 1:

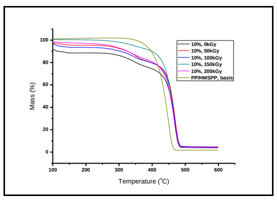

Figure 1: Thermal behavior of bagasse compounded samples.

Laboratory Soil Burial Analyses

10% bagasse in PP/HMSPP and PP/HMSPP basis were kept soil buried within a 1-4 month period. Except for 200 kGy dosis, natural basis showed none mass loss variation. Irradiated 10% bagasse in PP/HMSPP showed an atypical behavior: soil buried samples presented an increase in weighed mass pointing toward water penetration in them; lower masses variation for 200 kGy, when compared to those ones for 0 kGy, confirmed the water penetration effect in a visually damaged surface prejudiced by gamma irradiation. Tables 3 and 4 show their behavior:

Table 3: Mass Variation (%) for irradiated PP/HMSPP basis.

Time (month)	0 kGy	50 kGy	100 kGy	150 kGy	200 kGy
1	-	-	-	-	0.16
2	-	-	-	-	0.75
4	-	-	-	-	0.75

Table 4: Mass Variation (%) for irradiated 10% bagasse inPP/HMSPP.

Time (month)	0 kGy	50 kGy	100 kGy	150 kGy	200 kGy
1	6.41	-1.84	-0.51	-0.47	3.15
2	10.84	-1.95	1.07	0.17	9.38
4	13.42	-0.27	3.50	2.00	9.38

Mechanical assessments via texturometer

The effect of gamma-irradiation on samples was investigated up to their failure. Tensile strength indicated by the force exerted on samples under tension, were determined from the typical stress–strain curve and increased in function of sugarcane bagasse contents, as shown in Figure 2, for non-irradiated samples; only exception registered for 50% bagasse in PP/HMSPP sample. Additionally, the presence of cellulose fibers caused a considerable decrease in the elongation at break, in all compounded samples.

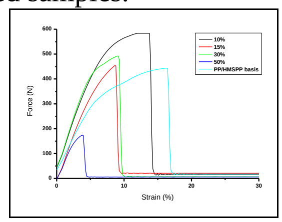

Figure 2: Mechanical behavior of non-irradiated samples.

PP/HMSPP natural basis suffered a considerable reduction in its tension/strain values when subjected to gamma-irradiation doses; figures 3, 4, 5 and 6 showed for all bagasse compounded samples lower values for stress/strain pair, even though higher than those ones obtained for irradiated natural basis.

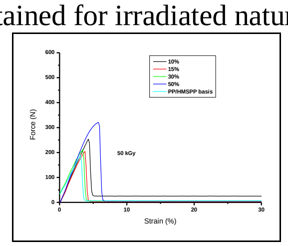

Figure 3: Mechanical evaluations for bagasse compounded samples, 50 kGy irradiated.

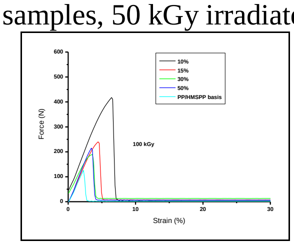

Figure 4: Mechanical evaluations for bagasse compounded samples, 100 kGy irradiated.

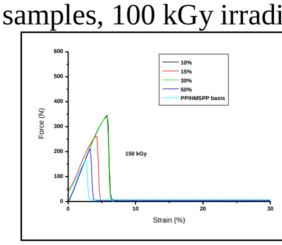

Figure 5: Mechanical evaluations for bagasse compounded samples, 150 kGy irradiated.

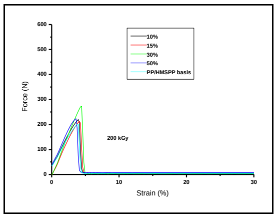

Figure 6: Mechanical evaluations for bagasse compounded samples, 200 kGy irradiated.

Summary and Conclusions

Results presented herein suggested that it is possible to blend the non-degradable Polypropylene and its derivatives/amelioration with Sugarcane Bagasse in order to improve its biodegradability. The extremely hydrophobic property of plastic-based materials contributes to make them non-biodegradable. In addition, structural foams from them are formed by closed cells, with their inner surfaces unexposed to microbes or enzymes, and consequently, non-favorable to biodegradation. Cellulose contained in sugarcane bagasse (32-34%) is responsible by its hydrophilic characteristic; extensive water uptake behavior, as shown in soil burial assessments, encouraged the growth of soil microorganisms, favoring the biodegradation.

High T_{onset} and T_{endset} shown by TGA analyses indicated that PP/sugarcane bagasse compounds were thermally stable around 275°C, which foster its thermal compatibility with Polypropylene and its derivatives/amelioration.

Low crystallinity presented by PP/sugarcane compounds, from DSC investigations, induces the occurrence of biodegradation in amorphous regions.

Mechanical essays accomplished in structural foams comprising 10, 15, 30 and 50% of sugarcane Bagasse in PP/HMSPP recommend the use of sugarcane bagasse as a biodegradable filler in polymeric materials to minimize environmental pollution and to act as a strong reinforcing filler, simultaneously.

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