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BIODEGRADABILITY AND MECHANICAL PROPERTIES OF PP/HMSPP AND NATURAL POLYMERS BIO-COMPOSITES IN FUNCTION OF GAMMA-IRRADIATION

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ABSTRACT

PP, expressed as C_nH_{2n}, is one of the most widely used linear hydrocarbon polymers; its versatility arises from the fact that it is made from cheap petrochemical feed stocks through efficient catalytic polymerization process and easy processing to various products. Thus, enormous production and utilization of polymers, in general, lead to their accumulation in the environment, since they are not easily degraded by microorganisms, presenting a serious source of pollution affecting both flora and fauna. These polymers are very bio-resistant due to the involvement of only carbon atoms in main chain with no hydrolysable functional group. Non-degradable plastics accumulate in the environment at a rate of 25 million tons per year. In recent years, as a result of growing environmental awareness, natural polymers 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-composites were compounded on a twin-screw extruder and samples collected directly from the die. This study aims to investigate mechanical properties of PP/HMSPP-sugarcane bagasse 10, 15, 30 and 50% blends gamma-irradiated at 50, 100, 150 and 200 kGy doses. Degradation essays will comprise DSC and TGA tests and biodegradability behavior will be indicated by Laboratory Soil Burial Test. The main objective of this work is to support the application of these composites as environmentally friendly materials, without prejudicing mechanicals properties, in spite of applied gamma-irradiation.

1. INTRODUCTION

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, 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 [1], [2],

Thus, due to its comprehensive use, in a great variety of applications, the accumulation of polyolefins, specially PP and its derivatives/ameliorations, is leading to their accumulation in the environment, since they are not easily degraded by microorganisms and presenting a serious source of pollution affecting both flora and fauna.

Several possibilities have been considered to minimize the environmental impact caused by the use of conventional polymers. Polymeric materials can undergo physical, chemical, and biological degradation or combination of all these due to the presence of moisture, air,

temperature, light (photo-degradation), high energy radiation (UV, gamma radiation) or microorganisms (bacteria or fungi) [3], [4].

Efforts have been made to enhance the rate of biodegradation of these recalcitrant polymers by modifying them or initiating the degradation process by generating free radicals etc. The rate of the biodegradation can be enhanced by blending them with biodegradable natural polymers-sugarcane bagasse. The presence of any biodegradable polymer as a blend will affect the behavior of the polyolefins and will act as an initiator for their oxidative degradation by heat, light, ionizing radiation and microbes

The purpose of this paper is studying the behavior of PP/HMSPP sugarcane bagasse reinforced at 10, 15, 30 and 50% level, further subjected to gamma-irradiation at 50, 100, 150 and 200 kGy, in relation to their mechanical properties and contribution as an environmental friendly material.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Polypropylene (PP)

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

2.1.2. 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°C, in order to eliminate remaining radicals to accomplish termination reactions [5].

2.1.3. 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°C, for 24 hours. Treated material was then grinded and kept for more 4 hours, at 60°C, before sieve segregation in 355 µm meshes. In the present work it was used material retained in 355 µm meshes sieve [6].

2.2. Mixtures preparation

2.2.1. 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°C, 60 rpm. Homogeneized extrudate was used as basis for four admixtures: 10, 15, 30 and 50 % of sugarcane bagasse.

2.3. Methods

2.3.1. 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.

2.3.2. 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.

2.3.3. 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.

2.3.4. 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].

3. RESULTS AND DISCUSSION

3.1. DSC-Evaluations

PP/HMSPP natural basis and 10% bagasse in PP/HMSPP samples irradiated at 50, 100, 150 and 200 kGy 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 100, 150 and 200 kGy doses. Irradiated 10% bagasse in PP/HMSPP showed T_m and crystallinity proportionally inverse to gamma-irradiation. Results are summarized in Table 1:

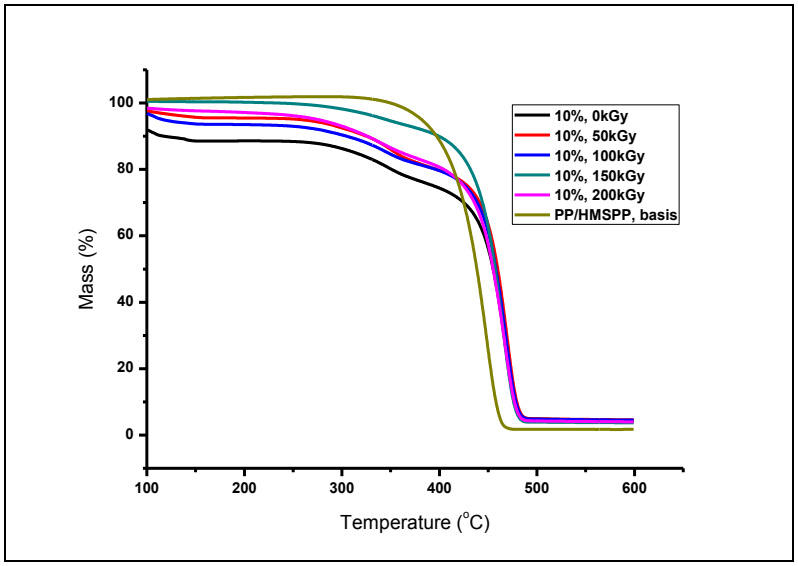
Table 1: Melting temperature (T_m)and crystallinity(W) of non-irradiated and irradiated samples.

10% Bagasse in PP/HMSPP	T_m (^oC)	W (%)	PP/HMSPP	T_m (^oC)	W^* (%)
0kGy	160.9	30.3	**0 kGy**	168.6	42.3
50kGy	157.3	32.6	**50 kGy**	162.4	36.5
100kGy	152.1	27.6	**100kGy**	159.1	52.9
150kGy	150.3	27.7	**150kGy**	157.3	52.0
200kGy	154.0	26.9	**200kGy**	156.5	51.6

3.2. TGA – Evaluations

10% bagasse in PP/HMSPP, within a gamma-irradiation range from 0 to 200 kGy was analyzed against a natural pristine basis (PP/HMSPP). 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^{o}C, characteristic of low molecular weight components, such as hemicellulose and the second one, in the range of 370 and 500^{o}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^o C, according shown in Figure 1:

Figure 1: Thermal behavior of bagasse compounded samples.



3.3. Laboratory Soil Burial Analyses

10% bagasse in PP/HMSPP and PP/HMSPP basis 0, 50, 100, 150 and 200 kGy samples 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. In Table 2 it is shown their behavior:

Table 2: Mass variation index.

Time (month)	**PP / HMSPP basis**	**Bagasse >355µm in PP / HMSPP**				
	(kGy)	**(kGy)**				
	200	**0**	**50**	**100**	**150**	**200**
1	0.16	6.41	-1.84	-0.51	-0.47	3.15
2	0.75	10.84	-1.95	1.07	0.17	9.38
4	0.75	13.42	-0.27	3.50	2.00	9.38

3.4. 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 typical stress–strain curves.

PP/HMSPP natural basis suffered a drastic reduction in its tension/strain values when subjected to gamma-irradiation doses, according shown in Figure 2. This behavior was not observed in both non-irradiated and irradiated bagasse compounded samples: non-irradiated samples showed a smooth reduction in both yield strength and elongation at yield in function of a raise in bagasse contents and irradiated ones experienced almost the same stress/strain pair reduction for all irradiation gamma doses. In Figures 3, 4, 5 and 6 is shown the behavior of each bagasse compounded sample in function of gamma-irradiation:

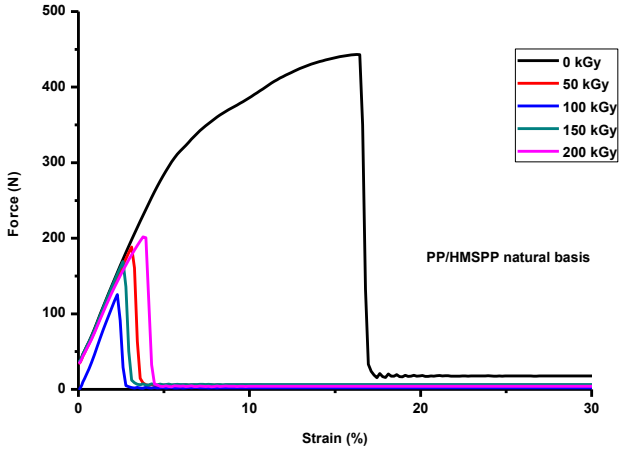


Figure 2: Mechanical behavior of PP/HMSPP natural basis, in function of gamma-irradiation.

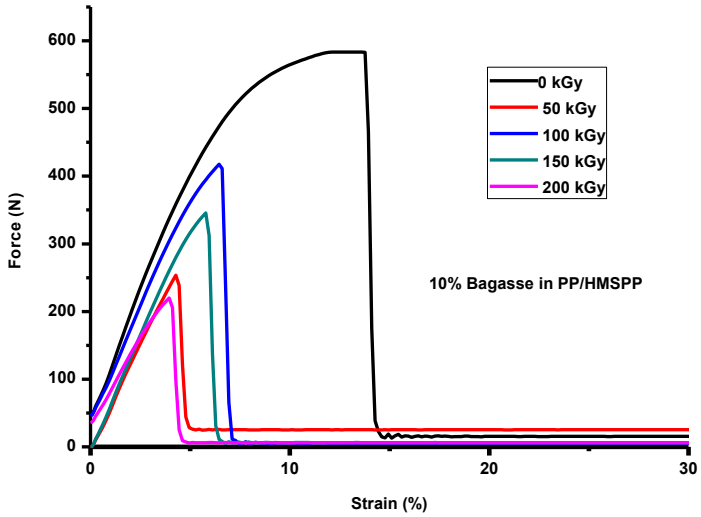


Figure 3: Mechanical behavior of 10% sugarcane bagasse in PP/HMSPP, in function of gamma-irradiation.

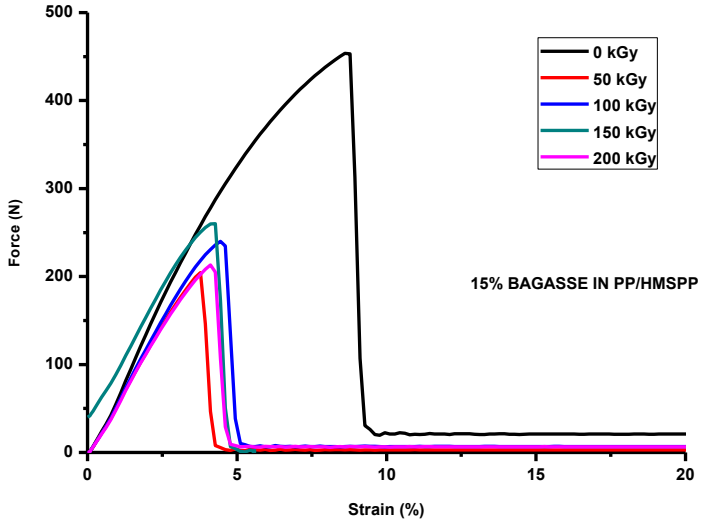


Figure 4: Mechanical behavior of 15% sugarcane bagasse in PP/HMSPP, in function of gamma-irradiation.

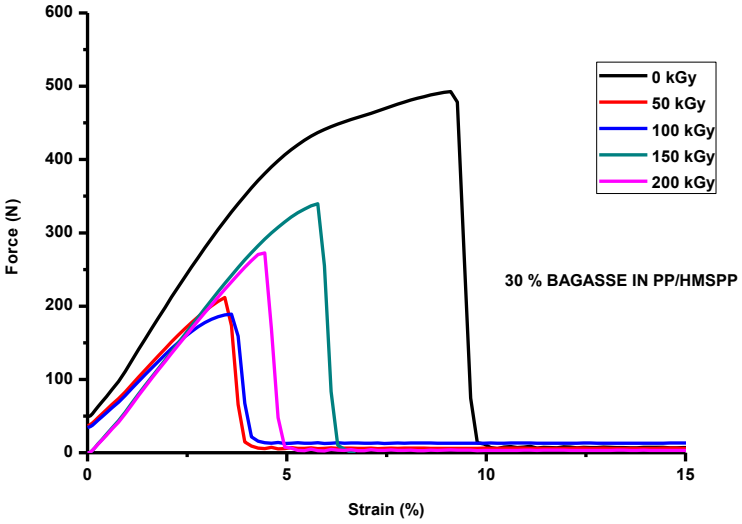


Figure 5: Mechanical behavior of 30% sugarcane bagasse in PP/HMSPP, in function of gamma-irradiation.

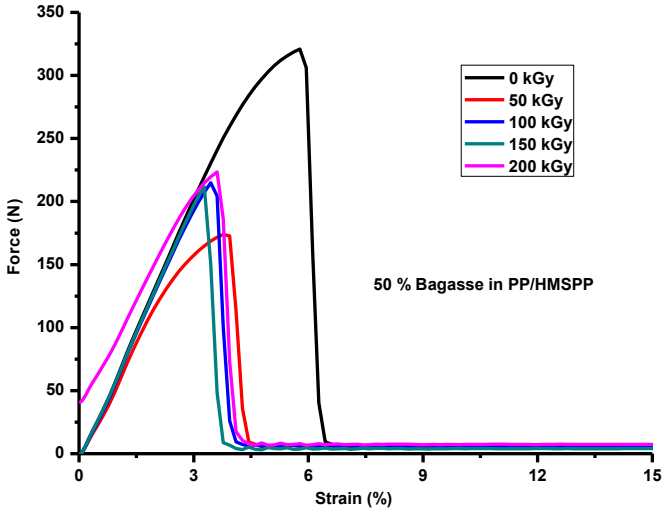


Figure 6: Mechanical behavior of 50% sugarcane bagasse in PP/HMSPP, in function of gamma-irradiation.

4. CONCLUSIONS

The extremely hydrophobic property of plastic-based materials contributes to make them non-biodegradable; 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. 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^{o}C, which foster its thermal compatibility with Polypropylene and its derivatives.

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 showed a lower influence imparted by gamma-irradiation, when compared with natural PP/HMSPP basis. Even lower results shown by elongation at yield are within indicated range for a typical ductile polymer: 5 – 10% strain and do not compromise the use of sugarcane bagasse as reinforcing filler.

Sugarcane bagasse can be recommended as a biodegradable filler in polymeric materials, based in 10% sugarcane bagasse in PP/HMSPP, non-irradiated and irradiated samples; 15%, 30% and 50% sugarcane bagasse in PP/HMSPP, non-irradiated and irradiated samples will be investigated in future work, just to confirm biodegradability activity.

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