

THE EFFECT OF GAMMA-RADIATION ON BIODEGRADABILITY OF NATURAL FIBER/PP-HMSPP FOAMS: A STUDY OF THERMAL STABILITY AND BIODEGRADABILITY.

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ABSTRACT

This research was carried out to evaluate how gamma-radiation affected PP/HMSPP structural foams reinforced with sugarcane bagasse, in terms of thermal properties, biodegradability and infrared spectrum. Polymers are used in various applications and in different industrial areas providing enormous quantities of wastes in environment, contributing with 20 to 30% of total volume of solid residues. Besides, shortage of plastics resins obtained from oil and natural gas is addressing research and development toward alternative materials; environmental concerning in litter reduction is being directed to renewable polymers for manufacturing of polymeric foams. Biodegradable polymers, a new generation of polymers produced from various natural resources, environmentally safe and friendly, can contribute for pollution reduction, at a low cost. High density structural foams are specially used in civil construction, in replacement of metals, woods and concrete, but contribute for environmental pollution, due to components nature. In this study, it was incorporated sugarcane bagasse in PP/HMSPP polymeric matrix blends. Gamma radiation applied at 50, 100, 150, 200 and 500 kGy doses showed effective for biodegradability induction. TGA analyses pointed toward stability around 205°C; decomposition of both cellulose and hemicellulose took place at 310°C and above, whereas the degradation of reinforced fibers composites took place above 430°C. Infrared spectrum of foams were studied using FTIR, showing no sensitivity to the presence of C = C and C =O functional groups.

1. 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 are 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]. Many natural polymers are hydrophilic and some of them are water soluble. Water solubility raises degradability and increases the speed of degradation, in favor of biodegradation. They have good potential for use in waste management due to their biodegradability and their much lower production of ash during incineration [5].

Natural fibre reinforced polymer matrix composites have attracted great attention because of properties such as biodegradability, non-toxicity, low density, non-abrasiveness, eco-friendliness, cost-effectiveness and sustainability [6]. The main drawback of natural fibres is their hydrophilic nature, which lowers their compatibility with hydrophobic polymer matrices. The interfacial adhesion between natural fibres and polymer matrices has often been a vital issue in several different natural fibres reinforced polymer matrix composite systems; a strong bond in the interface is necessary to achieve high performances of composites. It has been established that the mechanical, thermal and acoustical performances of the composites depends not only on the properties of the principle components but also on the nature and strength of the interface. Therefore, a number of chemical and physical surface modification studies on a natural fibre have been crucial for understanding and enhancing the interfacial adhesion between the natural fibres and the polymer matrix, which further improve the composite performances [7]. An interface is formed if the fibre or matrix phases influence a region of the other phase in a manner that alters its chemical or physical structure; the interfacial properties can be improved by giving appropriate modifications to the components, which give rise to changes in physical and chemical interactions at the interface [8]. Surface modification typically involves: physical, chemical, mechanical and physical-chemical tests. Physical treatments include plasma, γ -radiation, among others. Characterization techniques are usually applied to assess the occurrence and the extent of the modification include Fourier transform infrared (FTIR); the main constituents of natural fibres are cellulose, hemicellulose, lignin, pectin, water soluble substances and waxes [9, 10]. 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. 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 ionizing radiation, in this case.

Samples prepared from a previously extruder homogeneized 50% blend PP and HMSPP (High Melt Strength Polypropylene), further admixed with sugarcane bagasse were extruded foamed by using CO₂ as PBA (Physical Blowing Agent), aiming to evaluations of thermo behavior as well FTIR essays. Biodegradability was investigated, before and after exposure of foams under gamma-radiation.

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 acetylene for 48 hours, were further gamma-irradiated, Co⁶⁰ source, JS 7500 and JS 9699, MDS Nordion, Canadá, at room temperature,

12.5 kGy dose and a 10 kGy h^{-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 [9].

2.1.3. Sugarcane bagasse

The material, from Caçapava, São Paulo, was previously washed in running water, dried at room temperature 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 $355 \mu\text{m}$ meshes. In present work it was used material retained in $355 \mu\text{m}$ meshes sieve [10].

2.2. Mixtures preparation

2.2.1. PP/HMSPP 50% (PP/HMSPP)

A mixture containing 50% polypropylene (PP) and 50% high melt strength polypropylene (HMSPP) was compounded on a 3.1 L/D and 19/33 compression ratio twin-screw extruder (HAAKE Rheomex 332p), at temperature profile 175 to 200°C ; screw rotation speed was 60 rpm. Extrudates were not water quenched; they were wounded and cut off to pellets for subsequent measurements and used as basis for the following admixtures:

PP/HMSPP + 10%, 15%, 30% and 50% (w:w) of sugarcane bagasse.

The 4 admixtures were prepared in accordance with the procedure described for **PP/HMSPP 50%** above [11].

2.2.2. Foaming

All samples were extruded foamed, within a 165 to 220°C temperature range, using CO_2 as PBA (Physical Blowing Agent), special screw for foaming and a $3 \times 9 \text{ mm}^2$ rectangular die. Samples were collected directly from the die, squeezing them into homogeneous strips by means of a special device [12].

2.2.3. 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.

2.3. Methods

2.3.1. TGA-Thermal Gravimetric Analyses

TGA measures the amount and rate (velocity) of change in the mass of a sample in 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°C program, at a $10^\circ\text{C}/\text{min}$, in a nitrogen flow of 50 ml/min.

TGA was conducted on PP/HMSPP and its composites with sugarcane bagasse, irradiated and non-irradiated.

2.3.2. Laboratory Soil Burial Test

1 mm thick and 25 mm disk samples, produced by compression molding at 190° C and fast cooled 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° C ± 1° C/RH 80). The assessment was carried out after 1 (one) year 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 (mass loss) was determined in function of time following the equation 1:

$$T(\%) = \frac{m_0 - m_t}{m_0} \times 100 \quad (1)$$

Where m_0 is the initial mass sample at the time t_0 and m_t is the mass of the sample at the time t (after soil burial) [13, 14, 15].

2.3.3. Infrared Spectroscopy

Functional groups of composite materials were understood based on the data obtained from FTIR, within 4000 cm^{-1} to 400 cm^{-1} range, 64 scans, by using ATR Nicolet 6700-FTIR spectrophotometer. The FTIR was used to collect and understand the functional groups of the composite materials. Infrared spectrum was obtained through infrared software which presented information in transmittance mode.

3. RESULTS AND DISCUSSION

3.1. TGA-Thermal Gravimetric Analyses

The thermal characteristics of polypropylene based composites reinforced with natural fibres composites have been presented in Figures. Study of thermal degradation of natural fibres is important for the development of natural fibres reinforced polymer matrix composites, in both, service and manufacturing (extrusion, injection moulding, curing and compression moulding). The structural constituents of natural fibres such as cellulose, hemicellulose, and lignin are sensitive with different range of temperatures.

These fibres were exposed to intense heat during composite fabrication. Therefore, a thermal analysis study was conducted to determine the influence of fibres addition into polymer, on thermal stability of composites and to confirm possibility of degradation process during composite fabrication [16]

TGA was conducted on PP/HMSPP and its composites with sugarcane bagasse: non-irradiated for all sugarcane bagasse composites and irradiated just for 10% sugarcane bagasse composite. In Figures 1 and 2 are shown, respectively, behavior presented by them:

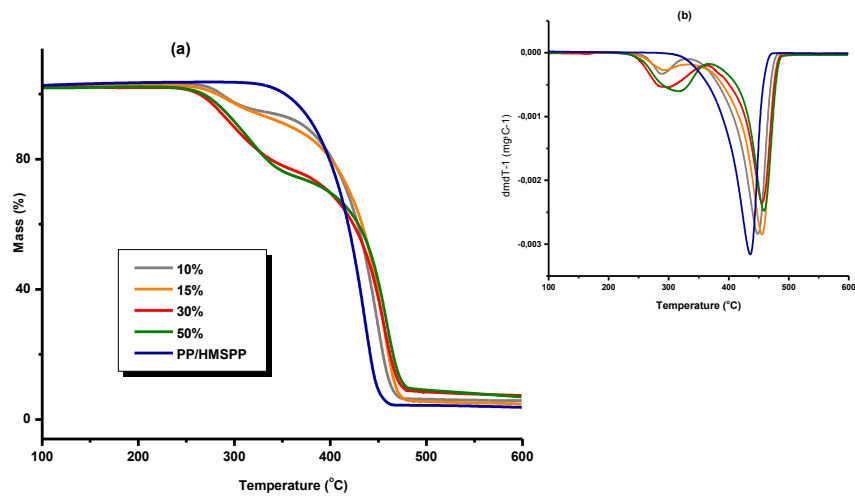


Figure 1: TG (a) and DTG (b) for non-irradiated PP/HMSPP and its composites with sugarcane bagasse

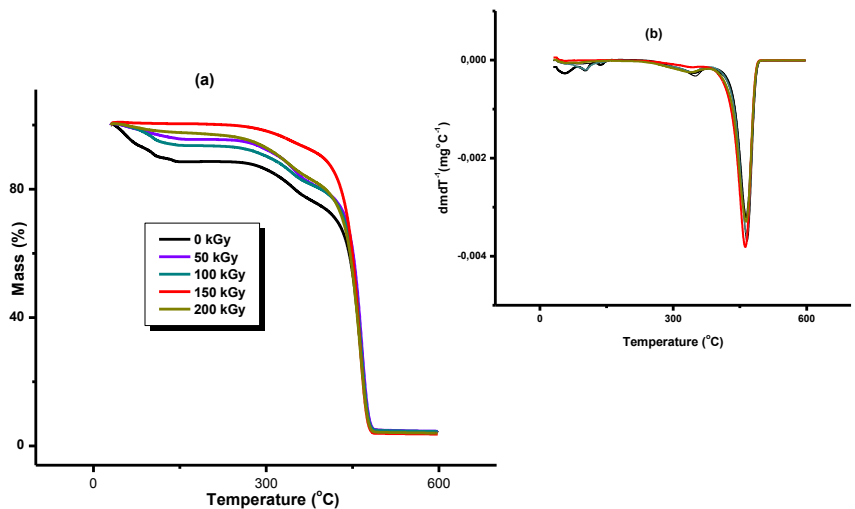


Figure 2: TG (a) and DTG (b) for irradiated mixture of sugarcane bagasse 10% in PP/HMSPP.

In Figure 1, initial thermal decomposition (t_{onset}) for PP/HMSPP basis showed typical expected value: near 350° C [14]. In sugarcane compositions, the mass loss that takes place up to 100°C may be associated with water loss caused by moisture vaporization previously present in fibres [16]. The total elimination of water is made difficult by the hydrophilic nature of the fibres, which present structural bound water molecules. While the decomposition of lignin was only just initiated, decomposition of other fibre components, such as waxes, glycosidics and pectin took place at this lower temperature range of 110 – 220°C [17]. Degradation of fibres does not occur until 250°C. Fibres show a considerable

mass loss due to decomposition of both cellulose and hemicellulose in the fibres from temperatures 330°C and above. Above 400°C, degradation of fibres can be seen as a result of the break of bonds of the proto-lignin [18]. Lignin decomposes slower than cellulose and hemicellulose components, over a broad temperature range of 200 – 500°C [19]. Thermal degradation and mode of decomposition under the influence of heat is highly recommended for the optimization of process parameters during fabrication of natural fibres reinforced polymer matrix composites [19]. In summary, initial degradation temperature (t_{onset}) for sugarcane bagasse compounds was slighter superior to that one found for polymeric base PP/HMSPP: 420°C [14].

In Figure 2 a higher water loss was verified for non-irradiated sample while for 50 to 200 kGy irradiated 10% sugarcane bagasse composite water contents was drastically reduced. Initial degradation temperature t_{onset} was almost the same for all samples (460° C) and curve slope changed from soft to upright at final degradation above 460°C.

3.2 Laboratory Soil Burial Test

Sugarcane bagasse composites 10%, 15%, 30% and 50% in PP/HMSPP showed after 1 (one) year of soil burial a mass loss of 26%, in average, according to Table 1:

Table 1: Mass loss variation (%) for non-irradiated 10, 15, 30 and 50% sugarcane bagasse in PP/HMSPP foams, after 1 (one) year of soil burial.

	<i>Sugarcane bagasse in PP/HMSPP</i>
%	
10%	21.3
15%	22.5
30%	29.2
50%	32.4

According to values listed in Table 1, sugarcane bagasse highly contributed for mass loss of samples and consequently, for their partial biodegradation, based in reference value obtained for PP/HMSPP base that, even subjected to 500 kGy, showed after one year of soil burial a mass loss of 1.9% [14].

10, 15, 30 and 50% sugarcane bagasse foams irradiated samples showed after 12 months soil burial for final mass values higher than those ones for initial mass, according to calculations using equation 1. This is explained by surface erosion caused by gamma radiation that favored water absorption through damaged surface (water uptake). Even impossible to accurately quantify mass variation due to water absorption (water uptake), sugarcane bagasse foams will be subjected to partial biodegradation due to microorganisms action caused by water inlet.

3.3 Infrared Spectrum Analyses

One of the factors that affect the property enhancement of natural fibre reinforced composites is the interaction between the fibre and polymer. FTIR analysis gives the insight about the interactions between the fibre and polymer. FTIR spectra of PP/fibres composites were presented in the mid infrared region $4000 - 400\text{cm}^{-1}$. The four regions are X-H stretching region ($4000 - 2500\text{cm}^{-1}$), the triple-bond region ($2500 - 2000\text{cm}^{-1}$), the double bond region ($2000 - 1500\text{cm}^{-1}$) and the fingerprint region ($1500 - 600\text{cm}^{-1}$) [20]. The major vibrations in the $4000 - 2500\text{cm}^{-1}$ region are generally due to O-H, C-H and N-H stretching. The principal band in the $2000 - 1500\text{cm}^{-1}$ region is due to C=C and C=O stretching. The spectrum can be regarded as a fingerprint of the molecules in this region $1500 - 650\text{cm}^{-1}$, which is referred to as the fingerprint region [21]. The FTIR spectrum of the studied polypropylene/natural fibre composites showed various bands at aliphatic hydrocarbon. Identification of spectral lines reveals hydrogen bonded stretching bands on OH groups in the region 3400 cm^{-1} and in the region of $1030 - 1150\text{ cm}^{-1}$.

In Figure 3 it is shown FTIR for 10% sugarcane bagasse in PP/HMSPP subjected to gamma radiation before soil burial:

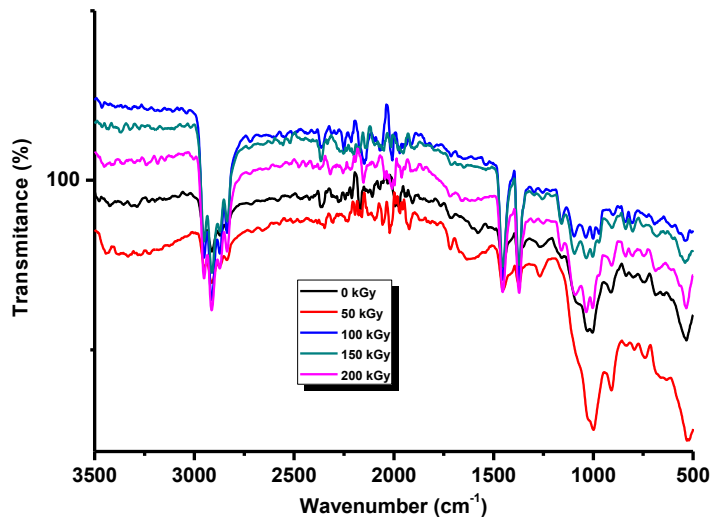


Figure 3: FTIR spectra for sugarcane bagasse foam 10% in PP/HMSPP subjected to gamma radiation at 50, 100, 150 and 200 kGy.

FTIR was not accomplished in soil buried samples after one year due to samples deterioration caused by water uptake.

3. CONCLUSIONS

Sugarcane bagasse/PP-HMSPP composites showed a higher thermal stability due to the increased fibre matrix interaction. Irradiated 10% sugarcane bagasse composite presented a drastic water reduction due to gamma radiation imparted on it and kept final degradation temperature around 460°C . Irradiated sugarcane bagasse compositions showed an atypical behavior: soil buried samples presented an increase in weighed mass pointing toward water penetration in them (water uptake) through eroded surface. Even impossible to accurately quantify mass loss in irradiated foams, the water uptake phenomenon will contribute for biodegradation due to micro-organisms action.

FTIR investigations did not contribute for foams biodegradability evaluation in irradiated foams considering the impossibility of analyzing deteriorated buried specimens. FTIR graph presented for 10% sugarcane bagasse in PP/HMSPP just depicts normal bands present in sugarcane bagasse fibers.

ACKNOWLEDGMENTS

The authors would like to thank Embrarad/CBE for irradiation process; Quattor, and IPEN/CNEN-SP for financial support.

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