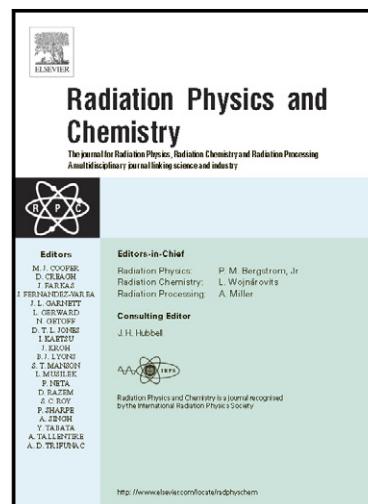


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BIODEGRADABILITY OF PP/HMSPP AND NATURAL AND SYNTHETIC POLYMERS BLENDS IN FUNCTION OF GAMMA IRRADIATION DEGRADATION

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ABSTRACT

Polymers are used for numerous applications in different industrial segments, generating enormous quantities of discarding in the environment. Polymeric materials composites account for an estimated from 20-30% total volume of solid waste. Polypropylene (PP) undergoes crosslinking and extensive main chain scissions when submitted to ionizing irradiation; as one of the most widely used linear hydrocarbon polymers, PP, made from cheap petrochemical feed stocks, shows easy processing leading it to a comprehensive list of finished products. Consequently, there is accumulation in the environment, at 25 million tons per year rate, since polymeric products are not easily consumed by microorganisms. PP polymers are very bio-resistant due to involvement of only carbon atoms in main chain with no hydrolysable functional group. Several possibilities have been considered to minimize the environmental impact caused by non-degradable plastics, subjecting them to: physical, chemical and biological degradation or combination of all these due to the presence of moisture, air, temperature, light, high energy radiation or microorganisms. There are three main classes of biodegradable polymers: synthetic polymers, natural polymers and blends of polymers in which one or more components are readily consumed by microorganisms. This work aims to biodegradability investigation of a PP/HMSPP (High Melt Strength Polypropylene) blended with sugarcane bagasse, PHB (Polyhydroxybutyrate) and PLA (Poly-Lactic Acid), both synthetic polymers, at a 10% level, subjected to gamma radiation at 50, 100, 150 and 200 kGy doses. Characterization will comprise IR, DSC, TGA, OIT and Laboratory Soil Burial Test (LSBT).

Keywords: polypropylene, gamma radiation, biodegradability, sugarcane bagasse, PLA, PHB.

1. Introduction

PP is a commodity plastic that accounts for more than 70% of total plastics market; immune to microbial degrading, polymeric materials remain in the soil and in landfills as a semi-permanent residue. Polymeric discard is one of the most challenging classes of waste to dispose (C. Longo et al, 2011). PP has its use restricted in certain

applications due to its low melting point and tendency to crack when stressed; crosslinking will add an important feature to the polymer, increasing its melt strength on heating (A. B. Lugão et al, 2003; A. G. Chmielewski et al, 2005). Due to its comprehensive use, PP and its derivatives are accumulating in the environment, since they are not easily degraded by microorganisms (J. Arutchelvi et al, 2008; Chandra et al, 1997; Y. Tokiwa et al, 2009).

Several possibilities have been considered to minimize the environmental impact caused by conventional polymers. Oxidation products of polyolefins are biodegradable, their molar masses are reduced, with further incorporation of polar, oxygen-containing groups such as acid, alcohol and ketone (Charlesby A. et al, 1960; Jakubowicz I. et al, 2003).

Enhancing biodegradation rate of recalcitrant polymers will be possible by modifying them or initiating a degradation process (Chiellini E. et al, 2003). Biodegradation can be viable by blending them with biodegradable natural polymers or with biodegradable synthetic polymers. The choice of PP and its amelioratives was due to their miscibility and compatibility with PLA, PHB and sugarcane bagasse; advantage from the production of miscible mixtures is based on one phase morphology and reproducibility of assessed properties (Doherty et al, 2011). Biodegradable polymer in a blend with a non-biodegradable polymer will act as an initiator for their oxidative degradation (Long Yuab et al, 2006; Ambika Arkatkar et al, 2009).

In present work was studied biodegradation of PP/HMSPP blended with sugarcane bagasse, PHB and PLA, all of them at 10% level, subjected to gamma radiation at 50, 100, 150 and 200 kGy.

2. Experimental

2.1 Materials

PP: PP-440K, Quattor, 3.5 g/10 minutes M.F.I.

HMSPP: PP samples previously kept in nylon bags, 48h under acetylene, Co⁶⁰ irradiated, room temperature, 12.5 kGy, 10 kGy⁻¹ radiation rate; pos-irradiation, samples air-forced oven annealed, 1 hour at 100°C, to eliminate remaining radicals (A. Adurafimihan Abiona et al, 2010).

Sugarcane bagasse: From Caçapava, São Paulo, running water washed; two months environment protected; 24 h, 60°C, air-forced oven. Grinded treated material kept for 4h at 60°C, sieve segregated in 355 µm meshes pan (Ricardo J. Brugnago et al, 2011).

PLA: Ingeo™ Biopolymer 3251D, designed for injection molding applications, NatureWorks®

PHB: PHB Biocycle®, PHB Industrial S/A.

2.2 Preparation of mixtures

A 50% PP/HMSPP mixture, compounded on a 3.1 L/D, 19/33 compression ratio twin-screw extruder (HAAKE Rheomex 332p), temperatures 170-200°C, 60 rpm. Pelletized extrudates used as basis (90%) for: **Bagasse in PP/HMSPP, PHB in PP/HMSPP and PLA in PP/HMSPP at 10% level.**

2.4 DSC

Thermal behavior by DSC Mettler Toledo, as per ASTM D3418-08, 5 to 9 mg, 25 to 300°C, 10°Cmin⁻¹.

2.5 TGA

Measurements of thermal stability (t_{onset} = initial thermal degradation and t_{endset} = final thermal degradation), in Mettler apparatus, as per ASTM E1641-07, 5 to 9 mg, 25 to 600°C, 10°Cmin⁻¹.

2.6 DSC-OIT

Oxidative Induction Time examined in Mettler apparatus, ASTM D3895-07, 5 to 9 mg sample, initial nitrogen purge for 5 minutes; heating cycle under 50 mLmin⁻¹ nitrogen from room temperature to 200°C, 20°Cmin⁻¹, 5 minutes, up to room temperature; change from Nitrogen to Oxygen, repeating the whole cycle. Initial breakdown of antioxidant protection accompanied by energy release with upward curve deflection from baseline, being OIT, period with none oxidation; results reported according to temperature/time pair (A. B. Lugão et al, 2002).

2.7 Laboratory Soil Burial Test

190°C compression molded 1 mm thick, 25 mm disks, buried with *inoculum* for gardening under (24°C ± 1°C/RH 80). Assessments in 1/2/4 months, thoroughly cleaned samples before dry weighing. Mass variation rate determined according to equation 1:

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

m_0 , initial mass sample at t_0 ; m_t mass at t , after soil burial (N. Lardjane et al, 2011; A. Shah, 2008).

2.8. Infrared Spectroscopy

IR spectra, ATR Nicolet 6700-FTIR spectrophotometer 64 scans, 4000 to 500 cm⁻¹.

3. Results and Discussion

3.1 Soil Burial Test

Non-irradiated samples did not show any mass loss, within 1 to 4 month burial period, excepting **Bagasse in PP/HMSPP**.

Samples compounded with PP/HMSPP matrix, irradiated from 50 to 200 kGy did not present any mass loss within 1 to 4 months soil buried, excepting **Bagasse in PP/HMSPP**; even at 500 kGy, natural **PP/HMSPP, PHB in PP/HMSPP and PLA in**

PP/HMSPP presented negligible values for mass loss due to water penetration in their visually damaged surfaces, according shown in Table 1:

[Insert Table 1]

PLA in PP/HMSPP showed a much higher mass loss variation, when compared to natural matrix and **PHB in PP/HMSPP**.

Water uptake in irradiated **Bagasse >355 μ m in PP/HMSPP** occurred due to additives migration through cracks in degraded surface by gamma-irradiation (H. Kim et al, 2006). Water uptake level increased in function of degradation time due to a higher surface permeability (H. S. Azevedo et al, 2004).

3.2. DSC

Non-irradiated PP/HMSPP, natural polymer (sugarcane bagasse) and synthetic polymers (PHB and PLA) samples, after evaluations, presented a similar behavior in terms of T_m (melting point) and W (crystallinity), excepting both PHB, with a high degree of crystallinity and sugarcane bagasse, with a very high result for T_m , due to its peculiar composition: cellulose-46.6%, hemicelluloses-25.2% and lignin- 20.7% (Taupier et al, 1999).

After being compounded with PP/HMSPP matrix, PHB, PLA and bagasse >355 μ m, at 10% level, were individually irradiated; results obtained are shown in Table 2:

[Insert Table 2]

Variations for W and T_m were within expected values and apparently showed that gamma-irradiation did not impart considerable effects on samples evaluated.

3.3. TGA

A summary of behavior presented by natural PP/HMSPP matrix, PHB, PLA and Bagasse >355 μ m is shown in Figure 1:

[Insert Figure 1]

T_{onset} values for PP/HMSPP, PHB and PLA occurred in a single stage, at 350°C, 300°C and 400°C, respectively. Bagasse >355 μm showed two mass loss stage, the first one with a small hump within 250–370°C range, characteristic of low molecular weight components, such as hemicellulose, and the second one within 370–500°C range, due to the thermal degradation of cellulose (N. Vogelsager Jr et al, 2004).

After being 10% compounded with PP/HMSPP, PHB, PLA and bagasse >355 μm , samples were individually irradiated at: 50, 100, 150 and 200 kGy; both PHB and PLA in PP/HMSPP as well natural matrix PP/HMSPP kept same values for t_{onset} and t_{endset} , before radiation.

All **Bagasse in PP/HMSPP**, non-irradiated and irradiated, presented a similar thermal behavior, with t_{onset} around 410°C, indicating a final mixture more thermal resistant, in spite of imparted gamma irradiation doses, as can be shown in Figure 2:

[Insert Figure 2]

3.4 DSC – OIT

Induction time values obtained for all samples, as well their respective temperatures did not show a considerable difference among them.

Oxidation temperature for all assessed samples varied from 197 (PP/HMSPP and PLA in PP/HMSPP) to 200°C (PHB in PP/HMSPP and PLA in PP/HMSPP); OIT for all non-irradiated samples, from 0.5 min (PP/HMSPP, PHB in PP/HMSPP and Bagasse in PP/HMSPP) to 0.9 min (PLA in PP/HMSPP).

The radiation process increased only OIT of assessed samples, oxidation temperature remaining stable; the highest value (1.6 minutes) for PP/HMSPP, PHB in PP/HMSPP and Bagasse in PP/HMSPP) and the lowest one (0.8 min) for PLA in PP/HMSPP.

3.5. Infrared Spectroscopy

FTIR-ATR was used herein to identify functional groups that emerged in the samples, with interest mainly 1600 cm^{-1} centered. Behavior presented by samples before gamma-irradiation and soil burial is shown in Figure 3.

[Insert Figure 3]

PLA in PP/HMSPP presented a well defined peak for carbonyl, able to initiate the biodegradation process. Samples were then soil buried for three months and irradiated from 0 to 200 kGy. EIV assessments showed similar behavior among samples and compatible with that one shown in Figure 3, proportional raise in all peaks centered at 1600 cm^{-1} . The intensity of this peak increases in function of dosage level and oxidation can take place after gamma irradiation, making the polymer less potent to microbial attack, due to a decrease in its hydrophobicity. A higher dose (500 kGy) was applied to the samples and after a three months burial period EIV investigation is presented in Figure 4.

[Insert Figure 4]

PHB in PP/HMSPP, PLA in PP/HMSPP and PP/HMSPP showed a well defined peak at 1600 cm^{-1} , respectively; just **PLA in PP/HMSPP**, presented a peak at 1730 cm^{-1} , assigned to PLA ester family (Dipak Sinha, 2012).

4. Conclusions

Natural PP/HMSPP matrix for samples was not affected by soil burial investigations; even gamma-irradiated, mass loss variation was negligible. After irradiation, synthetic polymers presented slightly higher results for mass loss, especially **PLA in PP/HMSPP**. Natural polymer (**Bagasse >355 μm**), before irradiation, showed a mass loss variation around 13%, after 4 month soil burial. Nevertheless, when irradiated, these samples suffered cracks and holes in their surfaces, inducing water uptake, as a signal of hydrophilicity, facilitating the entrance of soil microorganisms, due to material

degradation. A precise mass loss determination was prejudiced, but, even though, the biodegradation complex process was triggered.

Infra-red determinations provided just “signals” of biodegradation, considering carbonyl peaks 1600 cm^{-1} centered. OIT investigation failed in giving subsidies for biodegradation. Crystallinity and melting point, as well thermal behavior obtained for all samples were within expectations, showing a complete miscibility between PP/HMSPP and PHB, PLA and Bagasse blends.

In summary, natural and synthetic polymers added to natural matrix PP/HMSPP at a 10% level, was enough just to provide initial blends biodegradation; so, higher contents ($\geq 30\%$) should be used in future work, aiming to an effective biodegradation.

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Figure 1: TGA curves for individual samples.

Figure 2: TGA curves presented by Bagasse > 355µm/PP HMSPP blends.

Figure 3: Samples before burying and gamma-irradiating.

Figure 4: Samples irradiated at 500 kGy after 3 month-burying.

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Table 1: Mass variation index.

Table 2: Melting temperature (T_m) and Crystallinity (W) of non-irradiated and irradiated samples.

Tables

Table 1

Time (month)	Bagasse >355 μ m in PP / HMSPP	PP / HMSPP (kGy)		PHB in PP / HMSPP (kGy)		PLA in PP / HMSPP (kGy)		Bagasse >355 μ m in PP / HMSPP (kGy)				
		200	500	200	500	200	500	50	100	150	200	500
		1	6.41	0.16	----	0.91	----	1.78	----	-1.84	-0.51	-0.47
2	10.84	0.75	----	0.93	----	4.96	----	-1.95	1.07	0.17	9.38	---
4	13.42	0.75	0.50	1.04	3.40	5.01	0.03	-0.27	3.50	2.00	9.38	4.81

Painted values indicate increase in samples mass due to water uptake

Table 2:

PHB 10%	T _m (°C)	W (%)	PLA 10%	T _m (°C)	W (%)	Bagasse 10%	T _m (°C)	W (%)	PP/HMSPP	T _m (°C)	W*
0kGy	168.3	40.0	0kGy	168.2	38.7	0kGy	160.9	30.3	0 kGy	168.6	42.3
50kGy	165.6	43.2	50kGy	165.1	39.6	50kGy	157.3	32.6	50 kGy	162.4	36.5
100kGy	161.2	40.2	100kGy	164.0	36.7	100kGy	152.1	27.6	100kGy	159.1	52.9
150kGy	163.0	39.0	150kGy	160.4	37.6	150kGy	150.3	27.7	150kGy	157.3	52.0
200kGy	157.0	41.3	200kGy	160.1	38.2	200kGy	154.0	26.9	200kGy	156.5	51.6
500kGy	161.3	42.7	500kGy	162.0	40.5	500kGy	156.9	28.9	500kGy	151.8	46.0
PHB	171.2	68.0	PLA	155.1	37.0	Bagasse	350.0	40.0	---	---	---

Figures

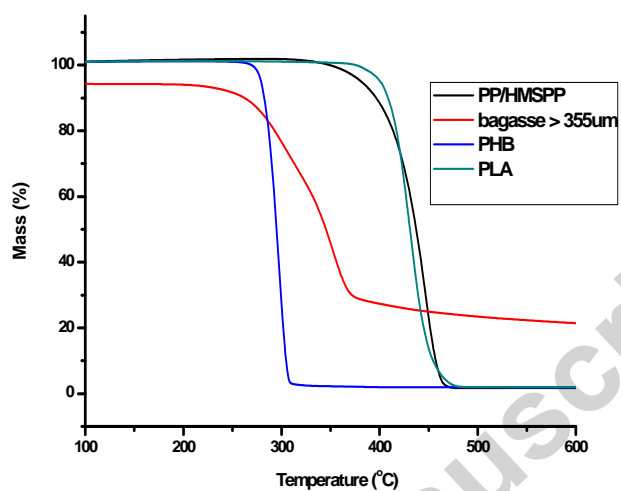


Figure 1

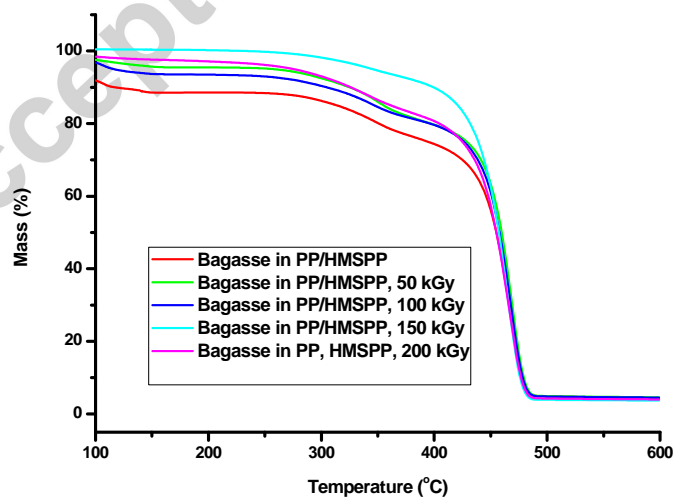


Figure 2

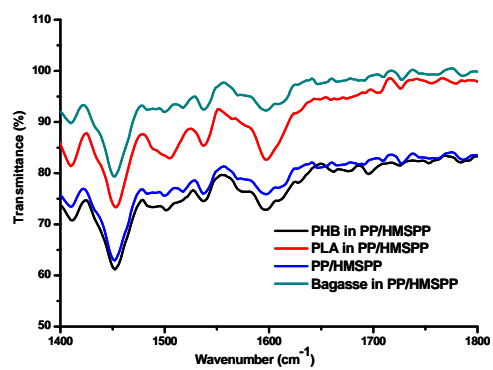


Figure 3

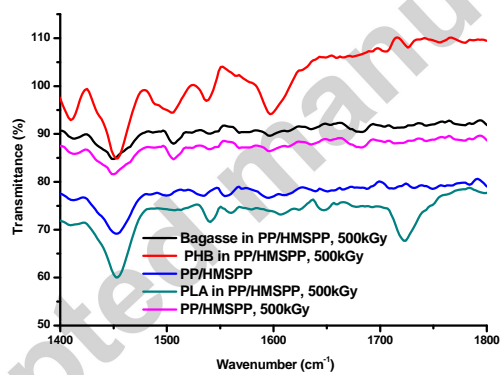


Figure 4