COMPARATIVE STUDY OF EFFECT OF IONIZING RADIATION ON COMPOSITES OF WOOD FLOUR IN POLIETHYLENE AND POLYPROPILENE MATRIXES USING BARIUM TITANATE AS COUPLING AGENT

Leila Figueiredo de Miranda*
Jademir J. P. de Almeida**
Terezinha J. Masson***
Antônio Hortêncio Munhoz Júnior****
Nilson Casimiro Pereira*****
Leonardo Gondim de Andrade e Silva******

Abstract

This work deals with the effects of ionizing radiation on the properties of wood flour composites in polyethylene and polypropylene matrixes, using barium titanate as a coupling agent. The investigated compositions were carried out with polyethylene/wood flour with barium titanate and polypropylene/wood flour with barium tita-

* Universidade Presbiteriana Mackenzie (UPM).
** Universidade Presbiteriana Mackenzie (UPM).
*** Universidade Presbiteriana Mackenzie (UPM).
**** Universidade Presbiteriana Mackenzie (UPM).
***** Universidade Presbiteriana Mackenzie (UPM).
******Instituto de Pesquisas Energéticas e Nucleares (Ipen).

nate using different wood flour concentrations of 10% and 20wt%. For the polyethylene it was also studied the addition of 30wt% of wood flour. Subsequently, the samples were molded by injection, irradiated and submitted to thermal and mechanical tests. The mechanical properties (hardness, impact strength and melt flow index (MFI)), as well as the thermal properties (thermal distortion temperature and Vicat softening temperature) of the composites, non irradiated and irradiated were determined. The samples were irradiated in irradiation doses of 10 kGy and 20 kGy in an electron accelerator. For the polyethylene the samples were irradiated at 30 kGy also. Regarding the mechanical properties of non-irradiated samples, the incorporation of wood four to polyethylene, resulted in a decrease of impact strength, tensile strength and melt flow index, while increasing the hardness and HDT, showing that the wood flour is ineffective as reinforcement agent, but acts like a biodegradable filler. There is no change in Vicat softening temperature. In case of the irradiated samples, there was observed a reduction in the impact strength, tensile strength, HDT, and thermal distortion temperature while increasing the hardness and tensile strength. The Vicat softening temperature was unchanged. Regarding the mechanical properties of non-irradiated samples, the incorporation of wood flour to polypropylene, promotes a decrease of impact strength, melt flow index and an increase in hardness and tensile strength, showing that the wood flour acts like a reinforcement agent. In the same way as to the irradiated samples, it was observed a decrease in the impact strength, hardness and thermal distortion temperature and an increase in the tensile strength and Vicat softening temperature.

Keywords: Wood flour, barium titanate, ionizing radiation.

1 INTRODUCTION

The natural staple fibers application have been increasing as a reinforcement in polymers (thermosetting and thermoplastic) due its intrinsic properties, as good mechanical strength and low density. The fiber glass substitution by the natural staple fibers is disabled by economic reasons in many situations. However, the natural staple fibers offer several advantages as related to glass staple fibers: natural fibers are renewed resources and available in great amount, they are biodegradable; are less abrasive, more recyclable etc. The natural staple fibers can be subdivided due their origin, as vegetal, animal or mineral. The availability of great amounts of such staple fibers with well defined mechanical properties is generally the prerequisite for the successful use of these materials (BLEDZKI; GASSAN, 1999).

Reinforced thermoplastic polymers with natural staple fibers can be applied in different areas, like in the automotive industry, pickings even in the civil construction. The flour or wooden fiber as filler in thermoplastic have been used in the automotive industry since the decade of 70, as polypropylene composites with wooden flour, known in the market, as Woodstock®. These composites are extruded and plated in plates for internal covering of doors and trunk of vehicles in current use (VIANA; CORREA; RAZZINO, 2004).

The vegetal staple fibers are distinguished by the low cost, low density, processing flexibility, beyond being deriving of sources you renewed, available (many times as residues), biodegradables, fuels etc. (AQUINO; ALMEIDA; MONTEIRO, 2004).

However, the adhesion between the hydrophobic matrix and the hydrophilic filler is weak, promoting a toughness reduction effect. The toughness of filled polymers can be improved in several ways: increasing the matrix toughness; optimizing the interface between the filler and the matrix through the use of coupling agents, compatibilizer, and sizes; optimizing the filler-related properties such as filler content, particle size, and dispersion; aspect ratio and orientation distributions also play a role in toughness of composites containing more fibrous materials (OKSMAN; CLEMONS, 1998).

The radiation can be used as an alternative in the development of new polymers and to improve the characteristics of polymer and composites. The ionizing radiation is a process capable of modifying the properties of a material, being a clean process because chemical agents are absent (CZVIKOVSZKY, 1996; ALBANO et al., 2001).

The coupling agent barium titanate (TiBa) was used in this study to provide better interaction of the wood flour and the polymeric matrix. Its structure allows chemical joints between the two interfaces, load and polymeric matrix improving the adhesion between them; the TiBa provides an even better dispersion of the load improving the mechanical properties (GARCIA, 1999).The main effects caused in polymers by the ionizing radiation are the main chain joint scission (degradation) and the generation of chemical links among polymeric molecules, known as crosslinking (O'DONNELL; SANGSTER, 1970).

During the crosslinking, there is an increase of the molecular weight, mechanical resistance, three-dimensional nets of the system, viscosity and the reduction of the solubility of the irradiated polymer and a change in the temperature of the vitreous transition in amorphous phase of the irradiated polymer. These changes also depend on the dose, dose rate, concentration, irradiation atmosphere among others. However, the susceptibility polymer to parameter changes depends on the type and size of the chains, as well as the polymer morphology (O'DONNELL; SANGSTER, 1970; LANDI; SILVA, 2003).

The objective of this work was to study the effects of ionizing radiation on the properties of wood flour composites in polyethylene and polypropylene matrixes, using barium titanate as a coupling agent.

2 EXPERIMENTAL

2.1 Materials

The polyethylene used in this work was LDPE LDPE with MFI = 3.45 g/10 min (190 ^{o}C/2.16 kg) and d = 0.9928 g/cm^3, made by Braskem S.A. (Brazil). The polypropylene used in this work was sort of SM 6100, with MFI = 11.81 g/10 min (230 ^{o}C/2,16 kg) and d = 0,905 g/cm^3, made by Quattor Petroquímica (Brazil). The wood flour was obtained from the sawdust and trituration of wood, specially the "Pinnus eliottis", better known as Pinus. The mesh provided by the "Pinhopó Madeira e Moagem Ltda" was the M-10050. The coupling agent used was the barium titanate type A, provided by Certronic Ind. e Com. Ltda.

2.2 Methods

The samples of composites were obtained with virgin LDPE, virgin PP, LDPE/wood flour and PP/woof flour. The samples containing wood flour were obtained with concentrations of 10 and 20wt% of the filler. For the polyethylene, samples containing 30wt% wood flour was also obtained. The filler was pre-treated with water and ethanol solution at 1wt% of TiBa. The materials were previously mixture in a calender and the samples were developed in a Torque Rheometer Haake, model

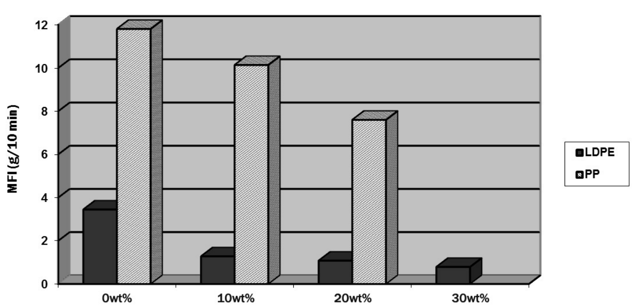
Rheocord 90, using an internal mixer Rheomix 600 as accessory. It was connected to a simple extrusion screw with the following temperatures in the heating zones: 160 ºC, 170 ºC, 185 ºC, 185 ºC.

The samples were irradiated at 0, 10 and 20 kGy in an electron accelerator JOB 188 (Dynamitron), energy 1.5 MeV was used. For the PE samples the 30 kGy irradiation was also used. The properties of the samples non-irradiated and irradiated were determined according to the standard ASTM tests. These samples are (will) to be used in the mechanical tests (tensile strength, impact strength and hardness), Vicat softening temperature and HDT. The samples were characterized by means of the following tests: Melt Index Flow (ASTM D-1238: 180 ºC; 5000 g of weight; permanence time of 240 s; cutting time of 10 s); Tensile Strength (ASTM D-638-94); Impact Izod Strength (ASTM D-256); Hardness Shore (D–ASTM D785); Thermal Distortion Temperature-HDT (ASTM D-648) (0.237 kg); Vicat softening temperature ASTM D1525 – 07.

3 RESULTS AND DISCUSSION

3.1 Melt index flow

The wood flour addition effect in the melt index flow of the obtained no irradiated composites is shown in the Graphic 1.



Graphic 1 Melt index flow for LDPE, PP, LDPE/wood flour and PP/wood flour samples.

Source: Elaborate by the authors.

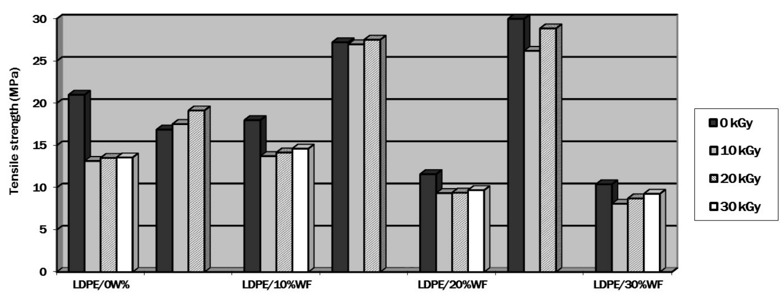
The results show that:

- The melt index flow of LDPE decreases with the increase of wood flour concentration. This decrease is of 63%, 69% and 78% to wood flour concentration of 10, 20 and 30wt%, respectively.

- The melt index flow of PP decreases with the increase of wood flour concentration. This decrease is of 14.1% and 35.5% to wood flour concentration of 10 and 20wt%, respectively.
- The wood flour presence makes the processing of composites difficult for both matrixes (LDPE and PP). The wood flour influence in the melt index flow is more effective in the LDPE than in the PP.

3.2 Tensile strength

The tensile strength was determined for pure LDPE, pure PP, LDPE/wood flour and PP/wood flour composites irradiated and no irradiated. The Graphic 2 present the results of tensile strength for studied composites.



Graphic 2 Tensile Strength of LDPE, PP, LDPE/wood flour and PP/wood flour samples

Source: Elaborate by the authors.

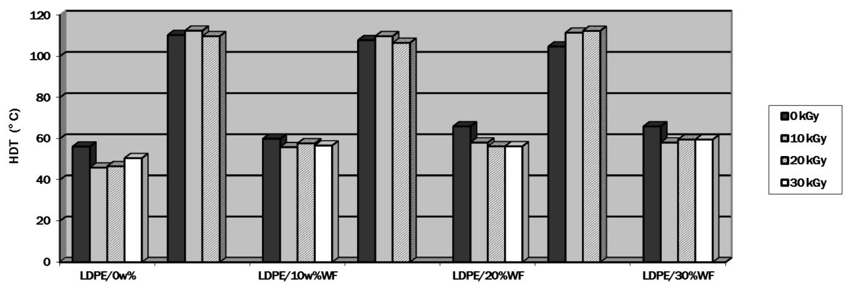
The results show that:

- For LDPE the tensile strength decreases with the increase of wood flour concentration in the composites. For LDPE the filler is acting as no reinforcement filler; in this polymer it was observed that samples containing 30wt% wood flour present a small decrease as related to the samples containing 20wt% wood flour.
- For PP the tensile strength increases with the increase of wood flour concentration in the composites. For PP the filler is acting as reinforcement filler.
- There is a greater interaction of the PP matrix than the LDPE matrix.
- For irradiated samples (LDPE and PP), to same wood flour concentration the tensile strength increase with the irradiation dose.
- For LDPE, comparing the irradiated samples it was observed that there is an increase in the tensile strength of samples containing 10wt% of wood flour. For the samples containing 20 and 30wt% wood flour there is a decrease in the tensile strength.

- For PP, comparing the irradiated samples it was observed that there is a decrease in the tensile strength of samples containing 10wt% of wood flour. For the samples containing 20wt% wood flour there is an increase in the tensile strength.
- The radiation action is more effective in the PP matrix.

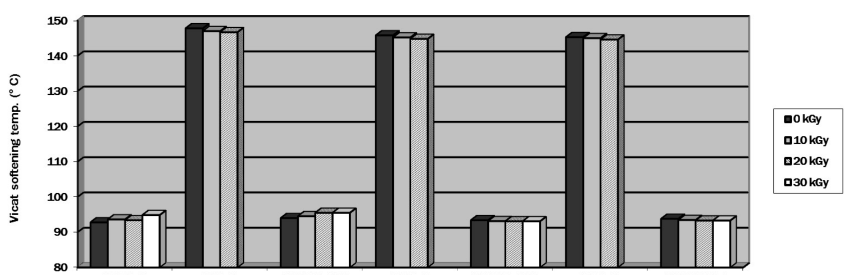
3.3 HDT and Vicat softening temperature

The Graphics 3 and 4 present the results of HDT and vicat softening temperature for the studied composites.



Graphic 3 HDT of LDPE, PP, LDPE/wood flour and PP/wood flour samples.

Source: Elaborate by the authors.



Graphic 4 Vicat softening temperature of LDPE, PP, LDPE/wood flour and PP/wood flour samples.

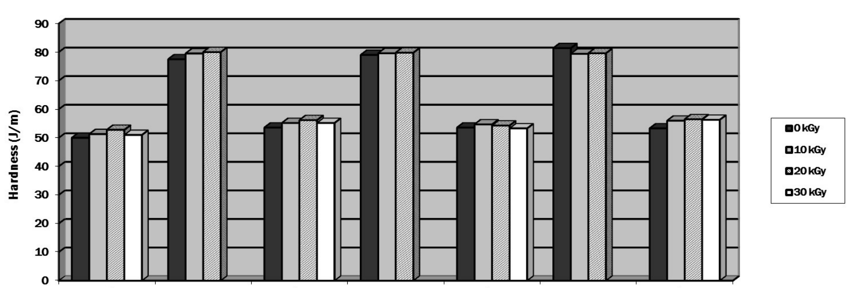
Source: Elaborate by the authors.

- Analyzing the values of Graphic 3, it can be observed that the value obtained for HDT of LDPE samples containing 10wt% of wood flour is approximately 10% greater than the value obtained for pure LDPE and for the samples containing 20 and 30wt% of wood flour is approximately 18% greater than the value obtained for the pure LDPE.

- For PP samples containing 10wt% of wood flour is approximately 2.3% smaller than the value obtained for pure PP and for the samples containing 20wt% of wood flour is approximately the same of the samples containing 10wt% of wood flour.
- The wood flour presence exerts greater influence in HDT of the composites contends LDPE.
- It can be observed that the value obtained for the HDT for the irradiated LDPE matrix samples is smaller than that of no irradiated samples.
- For PP matrix composites, the HDT for the irradiated samples is greater than the no irradiated samples. The radiation improves the thermal stability of the PP matrix composites.
- By Graphic 4 it can be observed that for LDPE composites, the wood flour addition increase slightly the Vicat softening point. The Vicat softening point values to the samples containing wood flour is practically the same.
- There is an increase in the Vicat softening point of the samples with pure LDPE and LDPE with 10wt% of wood flour. The irradiated samples containing 20 and 30wt% of wood flour present Vicat softening point values smaller than the ones no irradiated.
- For PP samples can be observed that the wood flour addition slightly decrease the Vicat softening point. The Vicat softening point values to the samples containing wood flour is practically the same.
- The Vicat softening point values of irradiated and no irradiated samples containing wood flour is practically the same for all composites studied.

3.4 Hardness

The Graphic 5 presents the results of hardness for studied composites.



Graphic 5 Hardness shore D of the LDPE, PP, LDPE/wood flour and PP/wood flour samples.

Source: Elaborate by the authors.

The results indicate that:

- The values of hardness increase with the addition of wood flour.
- For LDPE composites, the increase is of 6.6% for all samples containing wood flour.
- For PP composites, the increase is of 2% for samples containing 10wt% of wood flour and of 5% for samples containing 20 wt% of wood flour.
- For LDPE composites, there is an increase in the hardness with the dose increase until 20 kGy dose. For the 30 kGy dose occurs a decrease, but this value is greater than the no irradiated samples.
- For PP composites, there is an increase in the hardness for 10 kGy dose and a decrease for 20 kGy dose. These variations are very small.

3.5 Impact strength izod

The Table 1 presents the results of impact strength for studied composites.

TABLE 1

Results to impact strength for studied composites

Irradiation dose (kGy)	Composites (wt%) LDPE/ 0%WF	PP/ 0%WF	LDPE/ 10wt%WF	PP/ 10wt%WF	LDPE/ 20wt%WF	PP/ 20wt%WF	LDPE/ 30wt%WF
	Impact strength (J/m)						
0	Non-Break	33.78	Non-Break	28.80	239.73 (Partial)	20.43	Non-Break
10	Non-Break	24.60	Non-Break	23.43	233.14	23.33	Non-Break
20	239.73	18.37	233.14	17.85	259.91	17.73	268.00
30	207.74	-	250.00	-	Non-Break	-	Non-Break

Source: Elaborate by the authors.

The results show that:

- The impact strength decrease with addition of wood flour in the composites. This decrease is proportional to the wood flour concentration.
- For LDPE composites, for the same wood flour concentration the impact strength increases with the increase of the radiation dose.
- The results show that the wood flour contributes as a toughening agent for the LDPE composites with the increase of the radiation dose.
- For PP composites, for the same wood flour concentration the impact strength decrease with the increase of the radiation dose.
- The results show that the wood flour contributes as a nucleating agent for the PP composites.

4 CONCLUSION

By means of the results it can be concluded that:

- The presence of wood flour decreased the melt flow index and *makes the composites processing rather difficult*.
- For LDPE, the wood flour is ineffective as reinforcement agent having as principal effects the enhancement of the compound biodegradation. The filler is a biodegradable material.
- For PP the filler is acting as reinforcement filler.
- There is a greater interaction of the PP matrix than the LDPE matrix.
- For irradiated samples (LDPE and PP), to same wood flour concentration the tensile strength increase with the irradiation dose.
- For LDPE, comparing the irradiated samples it was observed that there is an increase in the tensile strength of samples containing 10wt% of wood flour. For the samples containing 20wt% wood flour there is a decrease in the tensile strength.
- For PP, comparing the irradiated samples it was observed that there is a decrease in the tensile strength of samples containing 10wt% of wood flour. For the samples containing 20wt% wood flour there is an increase in the tensile strength.
- The presence of wood flour increases the HDT of LDPE composites and decreases the HDT of PP composites. The wood flour presence exerts greater influence in HDT of the composites contends LDPE.
- The radiation improves the thermal stability of the LDPE matrix composites and get worse the thermal stability of the PP matrix composites.
- The thermal stability of the irradiated composites is smaller than the no irradiated composites.
- The values of hardness increase with the addition of wood flour in the composites.
- For LDPE composites, there is an increase in the hardness with the increase of the radiation dose until 20 kGy. It was observed a decrease in the hardness for the samples irradiated ar 30 kGy.
- For PP composites, there is an increase in the hardness for 10 kGy dose and a decrease for 20 kGy dose. These variations are very small.
- For LDPE composites, the wood flour addition toughens the material contributing to increase of the impact strength. There was an increase in the hardness

for the irradiated composites up to 20 kGy. For the 30 kGy occurred a decrease, but this value is greater than the non irradiated samples.

For PP composites, the wood flour addition increases the cristalinity and decrease the impact strength.

ESTUDO COMPARATIVO DO EFEITO DA RADIAÇÃO IONIZANTE EM COMPÓSITOS DE FARINHA DE MADEIRA EM MATRIZES DE POLIETILENO E POLIPROPILENO, USANDO TITANATO DE BÁRIO COMO AGENTE DE ACOPLAGEM

Resumo

Este trabalho trata dos efeitos da radiação ionizante sobre as propriedades de compósitos de farinha de madeira em polietileno e polipropileno matrizes, usando titanato de bário como agente de ligação. As composições investigadas foram realizadas com polietileno/farinha de madeira com titanato de bário e polipropileno/farinha de madeira com titanato de bário, utilizando concentrações diferentes de madeira de farinha de 10% e 20wt%. Com relação ao polietileno, estudou-se também a adição de 30wt% de farinha de madeira. Posteriormente, as amostras foram moldadas por injeção, irradiadas e submetidas a testes térmicos e mecânicos. Determinaram-se as propriedades mecânicas (dureza, resistência ao impacto e índice de fluidez (MFI)), bem como as propriedades térmicas (temperatura de distorção térmica e temperatura Vicat amolecimento) dos compósitos, não irradiados e irradiados. As amostras foram irradiadas em doses de irradiação de 10 kGy e 20 kGy em um acelerador de elétrons. Para o polietileno, as amostras foram irradiadas com 30 kGy. Sobre as propriedades mecânicas de amostras não irradiadas, a incorporação de madeira de quatro ao polietileno resultou em uma diminuição da resistência ao impacto, da resistência à tração e do índice de fluidez, aumentando a dureza e HDT, o que significa que a farinha de madeira é ineficaz como agente de reforço, mas age como um filler biodegradável. Não há mudança na temperatura de amolecimento Vicat. No caso das amostras irradiadas, não foi observada redução na resistência ao impacto, resistência à tração, HDT, e térmica de temperatura de distorção, aumentando a dureza e resistência à tração. A temperatura de amolecimento Vicat não foi alterada. Sobre as propriedades mecânicas de amostras não irradiadas, a incorporação de farinha de madeira ao polipropileno promove uma diminuição da resistência ao impacto e do índice de fluidez, e um aumento na dureza e resistência à tração, mostrando que a farinha de madeira funciona como um agente de reforço. Da mesma forma como para as amostras irradiadas, observou-se uma diminuição na dureza do impacto, força e temperatura de distorção térmica, e um aumento na resistência à tração e temperatura de amolecimento Vicat.

Palavras-chave: Pó madeira, titanato de bário, radiação ionizante.

REFERENCES

ALBANO, C. et al. Mathematical analysis of the mechanical behavior of ^{60}Co-irradiated polyolefin blends with and without woodflour. *Polymer Degradation and Stability*, v. 73, n. 1, p. 39-45, 2001.

AQUINO, E. M.; ALMEIDA, J. R. M.; MONTEIRO, S. N. Comportamento mecânico e morfologia de fratura do compósito piaçava/resina poliéster. In: CONGRESSO BRASILEIRO DE ENGENHARIA E CIÊNCIA DOS MATERIAIS, 16., 2004, Porto Alegre. *Anais*... Porto Alegre: Metallum Eventos Técnicos e Científicos, 2004.

BLEDZKI, A. K.; GASSAN, J. Composites reinforced with cellulose based fibers. *Prog. Polym. Sci.*, v. 24, n. 2, p. 221-274, 1999.

CZVIKOVSZKY, T. Electron-beam processing of wood fiber reinforced polypropylene. *Radiat. Phys. Chem.*, v. 47, n. 3, p. 425-430, 1996.

GARCIA, J. R. Efeitos dos agentes de acoplagem na processabilidade e nas propriedades mecânicas do polipropileno reforçado com wollastonita. 1999. Tese (Doutorado)–Universidade Presbiteriana Mackenzie, São Paulo, 1999.

LANDI, T. R. L.; SILVA, L. G. A. Estudo do efeito da radiação ionizante com feixe de elétrons sobre o terpolímero acrilonitrila butadieno estireno – ABS. *Revista Mackenzie de Engenharia e Computação*, São Paulo, v. 4, n. 4, p. 107-117, 2003.

O'DONNELL, J. H.; SANGSTER, D. F. *Principles of radiation chemistry*. New York: Arnold E., 1970.

OKSMAN, K.; CLEMONS, C. Mechanical properties and morphology of impact modified polypropylene-wood flour composites. *Journal of Applied Polymer Science*, v. 67, n. 9, p. 1503-1513, 1998.

VIANA, W. L.; CORREA, C. A.; RAZZINO, C. Efeito dos tipos de poliestireno de alto impacto nas propriedades de compósitos termoplásticos com farinha de resíduo de madeira. *Polímeros*: ciência e tecnologia, v. 14, n. 5, p. 339-348, 2004.

Contato

Leila Figueiredo de Miranda
e-mail: lfmiranda@sti.com.br