Comparison of Thermal Properties in Composites of PHB Using Rice Husk Ash or Talc as Filler

Ivonete O. Barcellos[1], Leila Denise Alberti[2], Doris Zwicker Bucci[3],
Ricardo A.N. Ferreira[4]

[1,2,3]Departamento de Química, Universidade Regional de Blumenau-FURB, Blumenau, SC -Brazil.
*E-mail: iob@furb.br
[4]Centro de Desenvolvimento da Tecnologia Nuclear CDTN- UFMG, Belo Horizonte, MG- Brazil.

Abstract**—** *This study has been conducted in order to use rationally rice husk ash (RHA) since it is one of the most abundant industrial waste. With the purpose of comparing fillers, composites of PHB (polyhydroxybutyrate) with RHA and PHB with talc (TA), were obtain by twin-screw extrusion and injection molding techniques and characterized by the use of Laser Flash Method and Differential Scanning Calorimetry (DSC). The thermal conductivity value displayed by PHB polymer was 0.419* $W{\cdot}m^{-1}{\cdot}K^{-1}$ *while the composites values were slightly higher, due to the increasing content of the filler. PHB/RHA composite showed maximum values 0.456* $W{\cdot}m^{-1}{\cdot}K^{-1}$ *and, PHB/TA composite was 0.492* $W{\cdot}m^{-1}{\cdot}K^{-1}$*. As regards to the DSC it can be stated that the presence of filler does not change significantly the thermogram curve, as evidenced by the endothermic peak at 172.96°C, 173.61°C and 171.65°C to PHB, PHB/RHA (85/15) and PHB/TA (85/15), respectively. Fillers from waste contribute to sustainable materials.*

***Keywords—* PHB (polyhydroxybutyrate), Composites, Rice Husk Ash, Talc, Laser Flash Method.**

I. INTRODUCTION

Composites have gained more space in various industry segments mostly because these materials make possible a good synergy in the interaction between the different components forming it, resulting in a range of properties inherent to the material and more interesting economic and environmentally friendly than the original components [1-5].

PHB is a biodegradable and biocompatible thermoplastic polymer that can be produced by bacteria from carbohydrates in bioreactors [6]. Its mechanical properties are generally restricted to certain uses due to its fragility. Furthermore, PHB has a narrow processing window and thermal instability near 180 °C [7-10]. In order to be accepted on a large scale, it is evident the need for improvement of its properties and processability is necessary. This can be obtained by adding functional fillers.

Rice husk ash (RHA) is an abundant waste generated from drying rice operation in several countries [11]. The world rice production in the period of 2006 to 2007 was approximately 600 million tons. These represent a generation of 145 million tons of rice husk residue [12]. RHA contends a large amount of silica (SiO_2) at least 90% [13, 14]. Despite the great possibilities of using this residue [15], its main application remains as landfill, which is an unsatisfactory solution from both the environmental and economic points of view. Studies have been conducted in order to facilitate the RHA use in a more rational way [16-19]. The use of food waste in the production of bioplastic composite can be a good way to reduce cost of these polymers and the amount of residue to the environment [20].

The accurate determination of the thermal properties of a polymer is critical in many processes and engineering projects. Thermal conductivity is a property of transport that is directly linked to the rate of thermal energy transfer by diffusion through a material medium [21].The thermal diffusivity, in particular, is important in problems involving non-steady state, such as in heating and cooling a polymer and in applications involving thermal insulation. It is a fundamental processing property in injection molding process, for the determination of molding cycle time [22].

The aim of this present work is to prepare biodegradable composites that can be used as insulators for technological applications and more environmentally friendly, since it minimizes the problems due the tremendous amounts of plastic waste. For comparison purpose, composite specimens of poly (3-hydroxybutyrate) (PHB) using rice husk ash (RHA) as filler in different percentages were prepared, as well as the use of talc (TA) as conventional filler. They were obtained and evaluated through their thermal properties by Laser Flash Method and Differential Scanning Calorimetry (DSC). The physical-chemical, mechanical properties and biodegradability of PHB composites are presented in [2, 3].

II. MATERIALS AND METHODS

2.1 Materials

The materials to obtain the composites were the PHB, RHA and talc. PHB, with molecular weight of 115,000 g.mol^{-1}, was obtained from sugarcane fermentation, and supplied by PHB Industrial S/A (Serrana, SP, Brazil) registered under the brand name BIOCYCLE®. The batch used was FE-159: PHB with 3.14% of the nominal content of estradiol valerate and of 1000 μm granulometry (30-18 mesh) [15]. The rice husk ashes (RHA) of 149-297 μm granulometry (100-50 mesh) have been provided by Juriti Cooperative (Massaranduba-SC) and talc (TA) of particle size 75 μm (200 mesh) was also supplied by PHB Industrial S/A.

2.2 Methods

2.2.1 Preparation of composites specimens

Composites were prepared in the Laboratory of Biodegradable Polymers-UFSCAR- *Universidade Federal de São Carlos*. The proportions of filler by weight in the PHB polymeric matrix was 5%, 10%, 15% of both, rice husk ash (RHA) and Talc (TA) The composites were extruded in a co-rotating twin screw, 30:40 DRC model IF, brand IMACOM, thread 30mm, L/D 40. After extrusion, pellets were dried in circulating air oven at 60ºC for a period of 24 hours, further being injected in molded specimens by a Romi Pratica 130, injection-molding machine. The extrusion and injection conditions adapted are presented in Alberti et al [15].

2.2.2 Determination of thermophysical properties

Ten measurements in diameter and thickness on each specimen were performing to determine the mean values using a micrometer with 1 μm resolution. For mass, ten measurements for each specimen using an analytical balance with resolution of 10^{-4}g were performed. The densities ρ were determined geometrically employing the equation (1): $\rho = 4.m / (\pi.d^2.L)$ for calculation, where *m* is the mean mass, *d* is the mean diameter and *L* the mean thickness of the sample.

Five measurements at room temperature were performed for each specimen to determine the thermal diffusivity α and specific heat *Cp*, using the Laser Flash method [23] and according to ASTM-E-1461-07 [24].

Measurements were carried out in the LMPT - *Laboratório de Medição de Propriedades Termofísicas de Combustíveis Nucleares e Materiais* of CDTN - *Centro de Desenvolvimento da Tecnologia Nuclear*. The system of LMPT uses a sealed CO_2 laser, supplied by the company Bioluz, which has the maximum power of 100 W.

The flash duration was fixed at 15 ms and the laser power at 93 W. The thermal diffusivity α was calculated by equation 2:

$$\alpha = 1.37L^2/\pi^2.t_{1/2} \tag{2}$$

where:

α = thermal difusivity [$m^2 \cdot s^{-1}$];

L = sample thickness [m];

$t_{1/2}$ = half-excursion time [s].

The specific heat capacity *Cp* [$J \cdot kg^{-1}K^{-1}$] was calculated according to equation (3) below:

$$Cp = Q/\rho.L(T_M - T_i) \tag{3}$$

where:

Q = amount of heat absorbed in the face area of the sample [$J \cdot m^{-2}$]

ρ = sample density [$kg \cdot m^{-3}$]

L = sample thickness [m]

T_i = sample initial temperature [K];

T_M = maximum temperature reached on the opposite face of the sample [K].

For Cp value calculation of each specimen, it was necessary to obtain the Q value. A standard sample of 9606 Piroceramic supplied by Netzsch Company was used. Five measurements in triplicate were performed to obtain Q, with the same parameters used in the specimens' measurements, i.e. flash duration of 15 ms and laser power of 93 W.

The thermal conductivity k was calculated by the product of thermal diffusivity, specific heat and density, in accordance with equation (4) below:

$$k = \alpha.\rho.C_p \tag{4}$$

2.2.3 Thermal analysis

The thermograms where obtained by differential scanning calorimeter (DSC), using the equipment DSC Q2000, TA Instruments, under the following conditions: The samples (10 mg) were heated up to 250 ºC at rate of 20 ºC/min, and kept at this temperature for 10 minutes to erase its previous thermal history. Then the samples were cooled at 10 ºC/min down to 25ºC and heated again, until their complete melting at 10 ºC/min. The reported thermal properties were taken during the cooling and the second heating cycles. All the measurements were made under nitrogen flow.

III. RESULTS AND DISCUSSIONS

Table 1 shows the results of the analyses of thermal diffusivity, density, specific heat and thermal conductivity for composites with various fillers contents.

TABLE 1
THERMOPHYSICAL PROPERTIES OF SPECIMENS

Specimens	Filler contents	Thermal Difusivity $^{s.d}$	Density $^{s.d}$	Specific Heat $^{s.d}$	Thermal Conductivity $^{s.d}$
	wt%	$*10^6 m^2 \cdot s^{-1}$	$kg \cdot m^{-3}$	$J \cdot kg^{-1} \cdot K^{-1}$	$W \cdot m^{-1} \cdot K^{-1}$
PHB	0	$0.178^{0.002}$	$1212.9^{9.6}$	$1946.8^{200.3}$	$0.419^{0.037}$
PHB/RHA	5	$0.188^{0.003}$	$1237.1^{4.9}$	$1911.8^{126.7}$	$0.444^{0.025}$
PHB/RHA	10	$0.180^{0.004}$	$1266.9^{2.8}$	$1965.6^{45.5}$	$0.447^{0.013}$
PHB/RHA	15	$0.198^{0.002}$	$1291.1^{4.8}$	$1786.8^{44.9}$	$0.456^{0.006}$
PHB/TA	5	$0.169^{0.008}$	$1249.1^{5.5}$	$2160.7^{159.6}$	$0.456^{0.036}$
PHB/TA	10	$0.185^{0.004}$	$1284.3^{8.5}$	$2035.6^{77.7}$	$0.484^{0.011}$
PHB/TA	15	$0.182^{0.010}$	$1310.7^{34.2}$	$2066.5^{41.5}$	$0.492^{0.005}$

s.d. Standard deviation of experimental measurements

According to Fig. 1, regarding to the pure polymer, there is a slight growth in the composites density, which is proportional to the increase in the percentage of filler. The growth of density, with the highest content of filler, did not exceed 6.45% for composites of PHB/RHA and 8.06% for the composites of PHB/TA, which does not compromise the material performance [2]. Inert inorganic fillers are often added to foam formulation to increase density, sound attenuation as load bearing [25]. It is also quite common to find that the foam density increases with filler contents since the effect of adding a denser material (filler) to the foam could prevail over the other effects [26]. This is an important result for materials selection, because the search of materials with good strength and low density is even greater nowadays. This is a decisive factor when choosing materials for specific applications [27], and in this case, composites with RHA are closer to the conventional TA fillers.

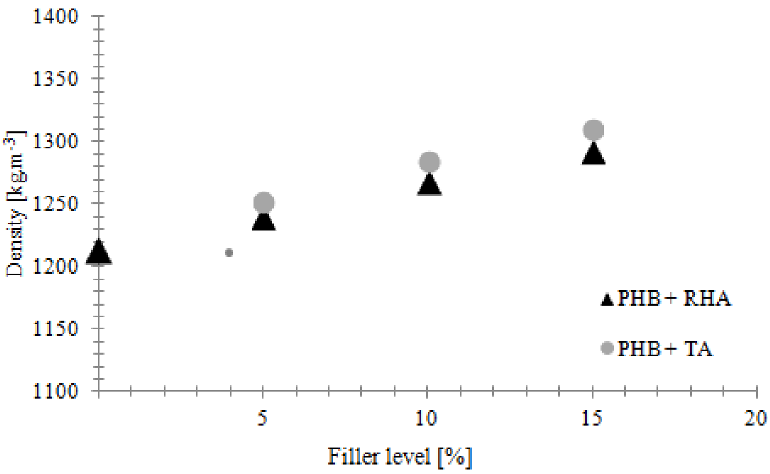


FIGURE 1. SPECIMENS' DENSITY GROWTH BY INCREASING FILLER CONTENT

Thermal conductivity is the important property that governs insulation application of one material. Fig. 2 shows a behavior of thermal conductivity in function of filler content since a slight rise in thermal conductivity is observed due to the increase of filler content, being slightly more pronounced for talc between 0.45-0.49 $Wm^{-1}K^{-1}$, while for RHA between 0,44 and 0,45 $Wm^{-1}K^{-1}$, probably due to the smaller particle size of this filler, allowing greater diffusibility. Values between 0.44 and 0.51 $Wm^{-1}K^{-1}$ for polyurethane (PU) with RHA [12] were found in related literature. Da Silva et al in their study on synthesis and physical chemical characterization of PU foams reinforced with rice husk ash, observed decreases of density and an increase of thermal conductivity with contents of RHA. Whenever there is a higher concentration of reinforcement, this interference occurs with more intensity. This explanation might be applied to the present case [12].

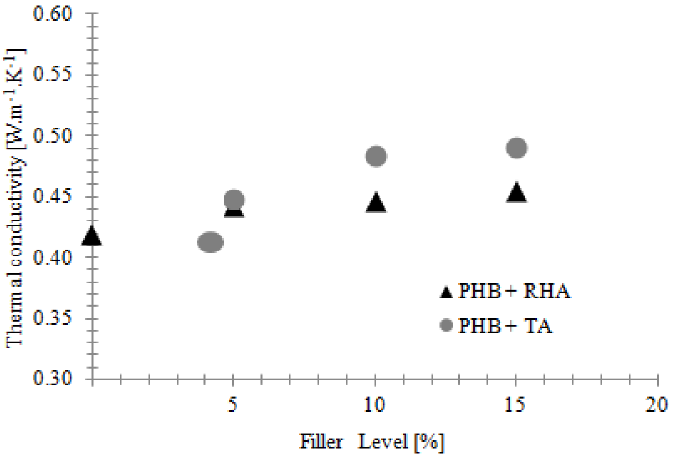
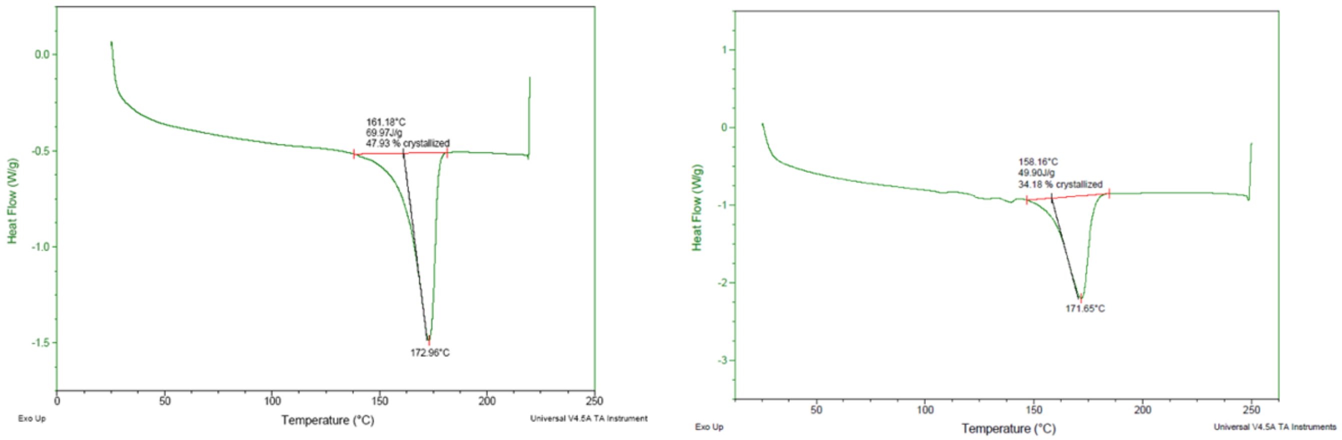


FIGURE 2. THERMAL CONDUCTIVITY OF THE SPECIMENS AS FUNCTION OF FILLER ADDITION

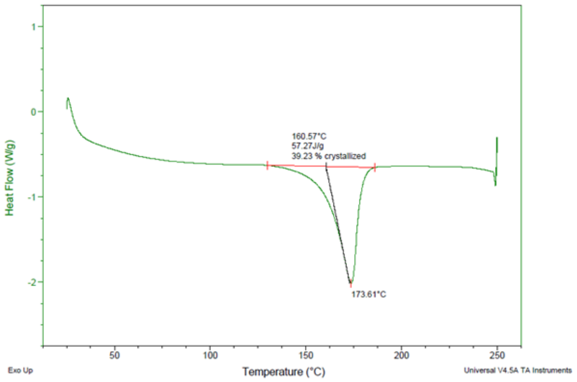
A previous study also showed [28] that the percentage of incorporated sludge in composites matrix of polyester resin, glass fibers, chrysotile fibers is proportional to the thermal conductivity of the materials, as well as the thermal stability of the polyester matrix were not affected.

With respect to the thermal analysis by DSC, curves of the PHB homopolymer and composites PHB/RHA and PHB/TA are shown in Fig.3. The presence of RHA and TA fillers unaffected the thermogram curve showing a single endothermic peak at 172.96 °C, 173.61 °C and 171.65°C for the PHB100%, PHB/RHA (85/15) and PHB/TA (85/15), respectively. This is similar to the results suggested by Goldbole et al [29], with no significant shift in the melting point being observed to the blend PHB-starch which ranged between 168-165 ºC, suggesting in this case no interaction between the PHB matrix and starch.

On the other hand, the thermal stability is higher for composites at 250 °C. Luyt et al [4] observed in polypropylene (PP) and nanostructure wollastonite filler, that the melting peak temperature of composites were unaffected by the presences of the filler. However, the thermal stability of composite is higher than that of the pure PP.



(A) PHB 100 % **(B) PHB/TA (85%/15 %)**



(C) RHA (85%/15%)

FIGURE 3 – DSC THERMOGRAM OF SPECIMENS OF PHB AND PHB COMPOSITES.

IV. CONCLUSION

Composites of PHB/RHA and PHB/TA were obtained with different fillers contents by extrusion and injection molding techniques. The melting temperature of the composites did not change significantly if compared to the pure PHB, and the composites with RHA showed values closer to PHB in DSC analysis. The thermoanalysis showed no indication of any interaction between the polymer and the filler, but a high thermal stability for composites. The pure PHB presented thermal conductivity of about 0.419 W $m^{-1}.K^{-1}$, the composites PHB/RHA increasing thermal conductivities in the range between 0.444 W $m^{-1}.K^{-1}$ and 0.456 W $m^{-1}.K^{-1}$, and the composites PHB/TA thermal conductivities in the range of 0.456 W $m^{-1}K^{-1}$ to 0.492 W $m^{-1}.K^{-1}$, depending on the content of filler addition. The RHA with applications until 15wt% can be used as filler in composites of PHB. Because its influence on the properties examined is not significant, suggesting a better performance as thermal insulation if compared to conventional mineral fillers for polymers as talc. In this case, RHA as a natural filler represents a new category of green material, could be a good alternative under technical and sustainable points of view, since this is one waste, which is abundantly available in the world.

ACKNOWLEDGEMENTS

The authors would thank PHB Industrial S/A and Juriti Cooperative (Massaranduba-SC) for the donation of the materials, also the Laboratory of Biodegradable Polymers/UFSCAR, and with the support and the collaboration of Professor José A. M. Agnelli.

REFERENCES

[1] A. Casarin, E.R. Gomes, M.R. Soares, M.C. Fredel, H.A. Al-Qureshi, ‘Análise micromecânica dos compósitos com fibras curtas e partículas”. Revista Matéria, vol.12, pp.408-409, 2007.

[2] L.D. Alberti, O.F. Souza, D. Z. Bucci, I.O. Barcellos, “Study on Physical and Mechanical Properties of PHB with Rice Hull Ash”, Mater. Science Forum vol. 775-776 pp.557-561, January,2014. Retrieved from http://dx.doi.org/10.4028/www.scientific.net/MSF.775-776.557.

[3] A. P. W.Boitt, I. O.Barcellos , L.D.Alberti, D. Z Bucci, Evaluation of the Influence of the Use of Waste from the Processing of Rice in Physicochemical Properties and Biodegradability of PHB in Composites, *Polímeros: Ciência e Tecnologia*, vol.24, pp.640-645,December 2014. Retrieved from http://dx.doi.org/10.1590/0104-1428.1593.

[4] Luyt, A.S., Dramicanin, M.D., Antic, Djokovic, Z. V. (2009). Morphology mechanical and thermal properties of composites of polypropylene and nanostructured wollastorite filler, *Polymer Testing 28(3)*, 348-356.

[5] Caraschi, J.C., Ramos, U.M. Compósitos biodegradáveis de Polihidroxibutirato(PHB) reforçado com farinha de madeira: propriedades e degradação, *Acta Science Technolo*gy 24 (2002)1609-1614. Retrieved from http://periodicos.uem.br/ojs/index.php/ActaSciTechnol/article/view/2475/1555.

[6] Lenz, R.W., Marchessault, R.H. (2005). Bacterial Polyesters: Biosynthesis Biodegradable Plastics and Biotechnology. *Biomacromolecules*, 61-68.

[7] Lemoine, M.A. Inst. Plast. In: Scott, G., Gillead. D. (1995), *Degradable Polymers*, Chapmam and Hall, London, pp. 271.

[8] Gregorova, A., Wimmer, R. M., Hrabalova, Koller, M. Ters, T. and Mundigler, N. (2009). Effect of surface modification of beech wood flour on mechanical and thermal properties of poly (3-hydroxybutyrate)/wood flour composites. *Holzforsch*, 63, 565-570.

[9] Erceg, M., KovacÏicÂ T. and Sanja P. (2010). Isothermal degradation of poly (3-hydroxybutyrate)/organically modified montmorillonite nanocomposites. *Polymer Composite*, 31, 272-278.

[10] Prasad, D.S., Krishna, A. R. (2012). Tribological Properties of A356.2/RHA Composites. *Journal of Materials Science and Technology*. 28, 367-372.

[11] Da Silva, Mosiewicks,V. R. Yoshide, M.A. Da Silva, M.C. Stefani,P.M. and Marcovichi, N.B. (2013). Polyurethane foams base on modified tung oil and reinforced with rice husk ash: Synthesis and Physical chemical characterization. *Polymer Testing*, 32, 438-445.

[12] Della, et al., V. P. (2001). Caracterização de cinza de casca de arroz para uso como matéria-prima na fabricação de refratários de sílica. *Química Nova*, 24(6), 778-782.

[13] Angel, J. D M et al**.** (2009). Caracterização de cinza obtida por combustão de casca de arroz em reator de leito fluidizado. *Química Nova*, 32110-1114. Retrieved from http://www.scielo.br/pdf/qn/v32n5/v32n5a06.pdf

[14] Alberti, L. D., Bucci, D.Z., Barcellos, I.O.(2013). *Propriedades Físico-químicas e Mecânicas de Compósitos de Poli(hidroxibutirato) PHB. (*Dissertação de Mestrado). Universidade Regional de Blumenau, Brazil. Retrieved from http://www.bc.furb.br/docs/DS/2013/352555_1_1.PDF

[15] Premalal, H.G. B. et al. (2002) Comparison of the mechanical properties of rice husk powder filled polypropylene composites with talc filled polypropylene composites. *Polym. Test.*, (21) 833-839.

[16] Alberti, L.D., Gavronski, S., Lovatel, A., Barcellos. I.O. (2012). Utilização em compósitos de resíduo gerado na produção de energia a partir da queima da casca de arroz, *Revista Sodebras*, 8431-36. Retrieved from http://www.sodebras.com.br/edicoes/N84.pdf

[17] Chiarello, L.M., Blosfeld, A.M., Giovanella, R.F. Barcellos, I.O. (2008). Tingimento de tecidos de algodão com soluções de corantes reativos tratados com cinza de casca de arroz. *Quím. Têxt.*, 9154-9166.

[18] Ferro, N.P. Silva, L.G. A. (2007). Uso da Cinza de Casca de Arroz como carga em matrizes de poliamida 6 e Poliamida 6,6, Polímeros: *Ciência e Tecnologia*,17240-17243.

[19] Koller, M. (2014).Polyhydroxyalcanoates for Food Packaging, *Appl. Food Biotech.*, 11-13.

[20] Incropera, F. P. et al. (2007). *Fundamentals of Heat and Mass Transfer***,** 7th. ed. John Wiley & Sons.

[21] Santos, W.N., Gregório, R.F. e Mummery, P. (2003). Propriedades térmicas de polímeros por métodos transientes de troca de calor, *Polímeros: Ciência e Tecnologia*;13265-13269. Retrieved from http://www.redalyc.org/pdf/470/47013410.pdf

[22] W. J. Parker, R. J. Jenkins, C. P Butler, G. L. Abbott, (1961). Flash Method of Determining. *J. Appl. Phys.*, 32, 1679-1684.

[23] ASTM-E-1461-07. Standard test method for thermal diffusivity of solids by the flash method. Annual book of ASTM standards, ASTM 14.02. 1992. p.1-11.

[24] Katz, H.S., Milewski. J. (1987). *Handbook of fillers for Plastics*.Van Nostrand, Reinholde,

[25] Thirumal, M., Singhe, N.K. Khastgin, D., Manjunath,Y.P. (2010) Halogen free flame retardant rigid polyurethane foams: Effect of alumina trihydrate and triphenylphosphate on the properties of polyurethane foams, *J. Appl. Polym. Sc.*, 116, 2260-2268.

[26] Godlewaki, R.E. et al. (1989). *Agents in thermoplastic polymers additives*. 1st ed. Marcel Dekker Inc.

[27] Barcellos, I. O., Souza, A. C. e Selke, A. E. (2009*)*. Incorporação de lodo industrial em compósitos de resina poliéster. *Polímeros,* 19155- 19159.

[28] Goldbole, S. et al. (2003). Preparation and characterization of biodegradable poly-3-hydroxybutyrate starch blend films. *Bioresource Technol.*, 8633-8637.