Thermal Analysis of Differential Scan-DSC Calorimetry for the Pure High-Density Polyethylene and Its Variables

Luiz Fábio de Oliveira Junior[1], Zarur Silvano[2], Pedro Martins Rocha[3]

[1]Student of Industrial Engineering, Faculdades Integradas de Cataguases-FIC/UNIS
[2] Specialist in Business Management, Faculdades Integradas de Cataguases -FIC
[3] Master in Materials Science and Technology,Universidade do Estado do Rio de Janeiro-UERJ
Cataguases/MG, Brazil

Abstract

he objective of the present work is to perform a thermal analysis of the high-density polyethylene (HDPE) material by means of a differential scanning calorimetry (DSC) equipment. In order to verify possible transformations in its molecular structure and change of phases present with the variation of temperature over time. The analysis was then carried out through 3 distinct cycles separated into 3 stages, the first of which the material will undergo a heating of the ambient temperature up to 178 ° C, at a rate of 10 ° C / min, the second stage a cooling from the temperature of 178 ° at a temperature of 43 °, with a rate of 10 ° / min, and the third stage the test body will undergo a new heating from 43 ° C to 184 ° C with a rate of 10 ° C / min. The results obtained from the thermograms for the five samples of the high-density polyethylene for the three required cycles, showed approximate values, with variations in centesimal scales that can be disregarded if we analyze the slight variations in the air pressure that the equipment can present. With this, it was possible to conclude the values of the parameters of the crystallization temperature (Tc), the percentage of crystallinity (% C), Melt Temperature (Tm) and melting enthalpy change (ΔHfm).

Keywords: *Analysis, Temperature, material, Parameters.*

I. INTRODUCTION

Reference [1], plastic is present in people's daily lives and their presence is frequent in the most diverse sectors and applications, be they basic products or those in which they require a little more technology to be manufactured.

Reference [2], Among the diversity of polymer elements, we highlight plastics. A macromolecular material consisting of polymers and additives in which they verify useful properties in the processing or applications. Additives are chemicals in which they add to the polymer to acquire specific properties or to facilitate their transformation, thereby facilitating their recycling or molding.

Reference [3], the polymer has two categories, thermosets, and thermoplastics in which they differ through their elasticity chains. The thermosets are plastics that in their chain of cross-links after the molding, are not able to be softened or remelted in another process, thus preventing re-machining. Since thermoplastics are elements that need heat to become flexible, their advantage is the ability to repeat in the heat or cooling cycle. We can consider as thermoplastics the High-Density Polyethylene (HDPE) the same is understood as thermoplastic for high resistance to chemicals and solvents but has a low permeability to gases and vapors. Its process requires conditions of high pressure and temperature, because of having the tendency to crystallize in its cooling phase during its molding.

With the objective of increasing the literary collection of thermal analysis of High-Density Polyethylene HDPE. The present study has as main objective to analyze parameters of the crystallization temperature (Tc),% of crystallinity, melting temperature (Tm) and variation of the enthalpy of fusion (), through an experiment performed by a DSC machine, and thermograms developed with the OriginLabTM software version 8.5.

In order to reach the results, the analyzed aspects were: Crystallization temperature (Tc): where the peak corresponding to the exothermic curve of the thermogram in the material cooling will be observed, Crystallinity percentage (% C): in which it will be obtained using equation (1) (Tm): obtained by the peak referring to the endothermic curve of the thermogram in the heating of the material and the Variation of the enthalpy of fusion (): Calculated by means of the equation (2), referring to the thermogram of heating the material.

II. LITERATURE REVISION

A. Plastic

Reference [4], the word plastic comes from Greek plastikó origin, has meant that which can be shaped. The elements denominated like plastics do not need to present the traces of this product, but they demonstrate priority in certain processes of its manufacture. The description for these so-called plastics materials is that they are artificial products,

blended through synthetic resins and that for some instant of their production assume a plastic state, to which they have been subjected to modifications, by means of solvents or heat, pressure or molds.

References [5], plastics are known as polymers, are formed from macromolecules made up of chains allocated in repetitions of low and simple basic units among covalent bonds called monomers, whose main chemical components are carbon and hydrogen atoms.

Reference [6], polymeric monomers tend to be native or synthesized by means of atomic rearrangements, in which carbon and hydrogen chains are withdrawn from compounds having a high molecular weight of these atoms, and are then grouped as monomer chains. Natural gas and petroleum are the most viable means of synthetic polymer, but other methods of production are also used as wood, alcohol, coal and even CO_2, all of which are rich in the basic raw material of the monomers.

Reference [7], the characteristics presented to the polymer can be separated into two categories, being: thermosets and thermoplastics, in which they differ by the elasticity of their chains.

B. Thermoplastics and Thermoplastics.

Reference [3], thermosets present about 20% of the total consumed in the country, are plastics that, due to the formation of numerous cross-links in their chain, after the method and manufacturing (molding), are incapacitated to be softened and another subsequent process, preventing further machining of the material.

Reference [8], thermoplastics are elements that require heat to become flexible and, once cooled, acquire the geometric configuration in which they were molded. What makes this material malleable is the decrease in intermolecular forces caused by heating. The advantage of this material is the repeatability of the heating and cooling cycle.

Reference [9], due to its particularities, high-density polyethylene (HDPE), low-density polyethylene (LDPE), polystyrene (PS), polyamides (Nylon), among others, we can consider thermoplastics, high-density polyethylene (HDPE) served as an object of study for this article.

C. High-density polyethylene (HDPE).

Reference [9], the high-density polyethylene (HDPE), is understood to be a thermoplastic with high resistance to chemicals and solvents, yet it has a low permeability to gases and vapors. Reference [10], demonstrates in its study to be the polymer most used in the manufactures according to its high performance in relation to the mechanical and thermal resistance. Therefore, its process demands conditions that will be of high pressure and temperature, due to the fact that it has a great tendency to crystallize in its phase of cooling before its molding.

Reference [11], polyethylene is highly crystalline at a rate of 90% above, but has low branching, being a polymer of linear chains with side chains represented by 200 carbon atoms attached to its main chain, its temperature of crystalline melting approaches 132 ° C at a density between 0.95 and 0.97 g / cm 3, Figure 1.

Propriedades	Altamente Linear	Baixo grau de ramificações
Densidade, g/cm³	0,962 - 0,968	0,950 - 0,960
Índice de refração	1,54	1,53
Temperatura de fusão, ºC	128 - 135	125 - 132
Temperatura de fragilidade, ºC	-140 - -70	-140 - -70
Condutividade térmica, w/(m.k)	0,46 - 0,52	0,42 - 0,44
Calor de combustão, kJ/g	46	46
Constante dielétrica à 1 MHz	2,3 - 2,4	2,2 - 2,4
Resistividade superficial, Ω	10^ [15]	10^ [15]
Resistividade volumétrica, Ω.m	1017 - 1018	1017 - 1018
Resistência dielétrica, KV/mm	45 - 55	45 - 55
Ponto de escoamento, Mpa	28 - 40	25 - 35
Módulo de tração, Mpa	900 - 1200	800 - 900
Resistência à tração, Mpa	25 - 45	20 - 40
Alongamento, %		
No ponto de escoamento	5 - 8	10 - 12
No ponto de ruptura	50 - 900	50 - 1200
Dureza		
Brinell, Mpa	60 - 70	50 - 60
Rockwell	R55, D60 - D70	
Resistência ao cisalhamento, Mpa	20 - 38	20 - 36

Fig.1: Thermal, Physical, Electrical and Mechanical Properties of HDPE.

Their number average molecular weight is in the range of 50,000 to 250,000 [8,13], chain alignment and packaging are more efficient; its van der walls, act with more intensity and its melting point can occur in high temperatures when compared with other polymers of the family of polyethylenes.

[12], (HDPE) is a high-compaction linear polymer obtained through ethene media in a catalytic process called Ziegler Natta. In turn, polymerization tends to occur through three distinct phases: polymerization in solution, gaseous polymerization and suspension polymerization (slurry).

Reference [13], molecular weight, density, alignment, and packing factor do not significantly affect the electrical properties of high-density polyethylene (HDPE), but they do strongly affect its mechanical properties and the melting point of this polymer.

Samples of weight, low molecular weight, density and alignment of the non-efficient chains are fragile, have low impact strengths, breaking through tensile tests showing low deformations, without the development of "neck". The same for the melting point, decreasing its temperature range in relation to the low packing factor (HDPE) samples, in addition to non-efficient chain alignment orientations. Mechanical and electrical characteristics of high-density polyethylene (HDPE) are presented in table 1. One factor that affects its mechanical properties is the branching content, in which, it tends to reduce

crystallinity, altering its elongation at rupture and consequently a reduction in its tensile strength. [13]

D. Thermal Analysis and Differential Exploration Calorimetry (DSC).

Thermal analysis is a commonly used method when analyzing the characteristics of polymeric materials. Through this method it is possible to verify the melting points, boiling,% crystallization, glass transition, heat flow among others fewer visas for analysis of plastics. [14]

The use of Differential Exploration Calorimetry (DSC) as a thermal analysis method is the most favorable for specimens considered as plastic. In this experimental mechanism, the heat flux between a substance and a reference material is analyzed as a function of a heating or cooling under certain atmospheres. Recently, many thermal analysis papers have been published in the field of polymers, thus the polymer industries are increasingly demonstrating an interest in this type of experiment. [15]

The DSC is considered a thermal analysis equipment in which it is possible to analyze the enthalpy changes performed by heating and cooling the samples by means of two different processes, with power compensation and with heat flow. [16]

1) DSC with Power Compensation: Arrangement in which the reference and sample are maintained at the same temperature, through individual electric heaters. The power dissipated by the heaters is related to the energy involved in the endothermic or exothermic process. [14]

2) DSC with Heat Flow: the Simplest arrangement is one in which the sample and the reference, contained in their respective sample holders, are placed on a metal disc. The heat exchange between the oven and the sample preferably takes place by the. [14]

III. METHODOLOGY

For the elaboration of the present scientific article, articles researched in Google Scholar, in the Scielo and sites linked to the subjects of thermal analysis were used, giving focus to the Differential-DSC Exploration Calorimetry of High-Density Polyethylene HDPE. And through the previous studies carried out in the research laboratory of UERJ-RJ, the present experiment had the parameter to be able to allocate the ideal temperatures to notice the points in which the study intends to analyze.

By the analysis of the Differential-DSC Exploration Calorimetry of High-Density Polyethylene (HDPE). The present scientific article will obtain quantitative results generating data in relation to the points to be analyzed.

A. Experimental

1) Thermal Analysis: The residues of high-density polyethylene (HDPE) in its pure form. They were used in the function of the quantitative of analyzes in the study laboratory located in the Polytechnic Institute of the State of Rio de Janeiro, in which the city of Nova Friburgo belongs to RJ.

The selection was done by 5 units of 20 mg of the component in the form of pallets, each unit was allocated inside an alumina crucible under the air atmosphere in order to initiate the Analysis of Differential Exploration Calorimetry (DSC), through the equipment Perkin Elmer Model STA-6000, Simultaneous Thermal Analyzer.

The choice of five HDPE units was based on the literature, and through experiments in the biomaterials laboratory located in the polytechnic institute of Rio de Janeiro, which showed little variation in the established criteria and therefore little amplitude of results.

The following analysis was performed on 3 distinct cycles, which: a) The first step was to warm the sample from room temperature to 178 ° C at a rate of 10 ° C / min; b) The second step was represented by a cooling from the temperature of 178 ° C to a temperature of 43 ° C, with a rate of 10 ° C / min; c) In the third stage, the heating occurred from 43 ° C to 184 ° C with a rate of 10 ° C / min.

The parameters prescribed in the analysis were the crystallization temperature (Tc) obtained in the sample cooling, the melting temperature (Tm) observed in the third stage, by means of the second heating, enthalpy of crystallization (ΔHc) calculated by means of the area under the peak exotherm generated by the thermogram and the melting enthalpy (ΔHc) calculated from the area of the melting peak of the thermogram. The thermograms for the study of the present analyzes were obtained through the Software program OriginLabTM, version 8.5.

The percent crystallization of each sample was established in figure 2.

$$\% \text{ Cristalinidade} = \frac{\Delta Hf_A}{\Delta Hf_A \ 100\% \ \text{cristalino}} \times 100$$

Fig. 2: the Formula for calculation of crystallinity.

(ΔHf) is the melting enthalpy change of the sample whose crystallinity percentage is unknown and (ΔHf) 100% crystalline is the change in the melting enthalpy of the 100% crystalline sample, whose values are found in the literature. [17]

The melting enthalpy change (ΔHf) of each sample was calculated by means of figure 3.

$$m. \Delta Hf = K. A$$

Fig. 3: the Formula for calculation of enthalpy.

If m is the mass of the sample, A is the area of the peak and K is a proportionality constant established

through the mass and the (ΔHf) of the standard sample, in which the value is tabulated. [18]

After stipulating the parameters of the (DSC) for each individual sample, an average of the results was linked and then the production of the thermogram for any related analyzes.

IV.RESULTS AND DISCUSSIONS

The results of the parameters obtained from the thermograms for the five samples (quintuplets) of the high density polyethylene (HDPE) for the three required cycles, showed approximate values, with variations only in centesimal scales, which can be disregarded if we analyze the slight variations the Perkin Elmer, Model STA-6000, differential scanning calorimetry (DSC), simultaneous Thermal Analyzer. Consequently, as it appears in the literature only the decimal values with equality

for five samples were used to make the thermograms.

Reference [19], the polymer matrices generally have a low strength and low melting point.

The thermogram was performed using the analysis of the samples of 20 mg of High-Density

Polyethylene (HDPE), through the analysis of Differential Exploration Calorimetry (DSC), for the second cycle, in which a cooling takes place, is represented by figure 4.

An exothermic peak with the onset at 120.16 ° C can be seen in figure 4, having a peak of variation at 113.59 ° C with a temperature of 75.75 ° C. Such an exothermic curve of pure (HDPE) tends to be a crystallization process, since the obtained points are approximated to the values related to the exothermic curves of crystallization for the material.

According to a study on pure HDPE residues in colorless form, 20mg to 25mg of the product was used for analysis using differential scanning calorimetry (DSC) under air atmosphere, [20]. A cooling rate of 10 ° C / min ranging from 210 ° C to room temperature. Their study obtained as the conclusion a peak in its crystallization temperature of 110,7ºC.
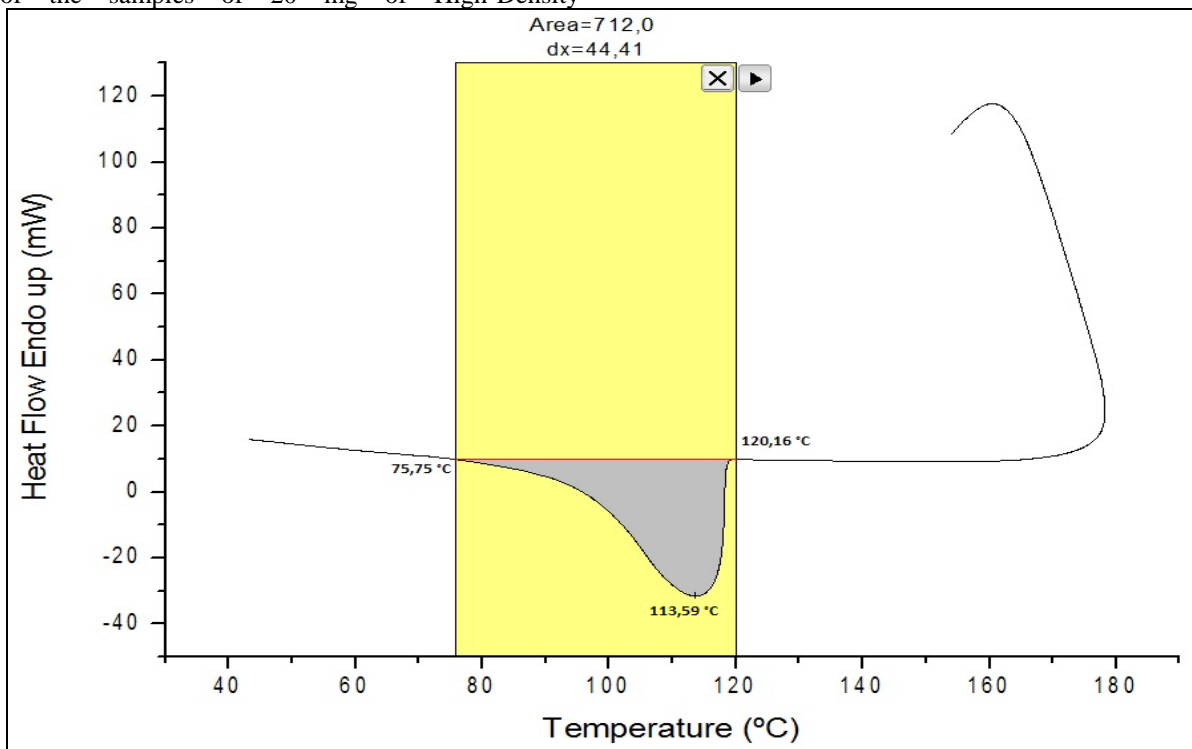

Fig. 4: Termograma da análise registrada pelo (DSC) para o resfriamento do (PEAD) puro.

Reference [21] differential scanning calorimetry (DSC) was also used for the characterization of an HDPE, for the experiment was selected from 20 to 25mg of the product in commercial form, using porcelain crucibles under an air atmosphere. With a sample cooling of 210 ° C at room temperature at a rate of 10 ° C / min the analysis found a peak at the crystallization temperature at 114.5 ° C. The

percentage of crystallinity for pure HDPE through the use of equation (1) was 55.46%, which is in accordance with the percentage of crystallinity for pure HDPE found in the literature. In the article by Costa et al. (2014), 20 to 25mg of HDPE was used for the calculation, resulting in 56.8% of percentage crystallinity.

Reference [21], for 20 to 25mg of commercial HDPE, a crystallinity rate of 57.1% was established at a rate of 10 ° C / min. For enthalpy of crystallization, which was determined by equation (2), the value obtained was 160 J / g. the Value in which it conforms to the values found in the literature. Reference [21], for 20 to 25mg obtained was 166.4 J / g enthalpy of crystallization.

Figure 5 shows a heating thermogram for the pure HDPE, whose graph shows an endothermic curve that starts at a temperature of 100.36 ° C. When compared with the studies related in the literature, the present endothermic curve tends to be the enthalpy of melting of the material.

Reference [23], an (HDPE) blended with composition of ternary blends in a composition of 25% was used, the endothermic curve was given by heating in the DSC at a rate of 10 ° C under an inert atmosphere, resulting in a peak at the enthalpy of 134.7 ° C. Reference [24] - [21], under the same experimental conditions of the current work resulted in a peak in the melting enthalpy of 131 ° C and 130.60 ° C respectively.

Calculated by equation 2, the enthalpy change found for pure HDPE in the present study was 162.49 J / g, and this value is approximated to the values found in the literature.

In the study by Moreira da Costa (2016) for a commercial HDPE, under a heating rate of 10 ° C / min, obtained a melting enthalpy variation of 167.4 J / g. Using an HDPE also pure under the same experimental conditions of the present study, Costa et al. (2014) found a melting enthalpy for the material of 166.4 J / g.
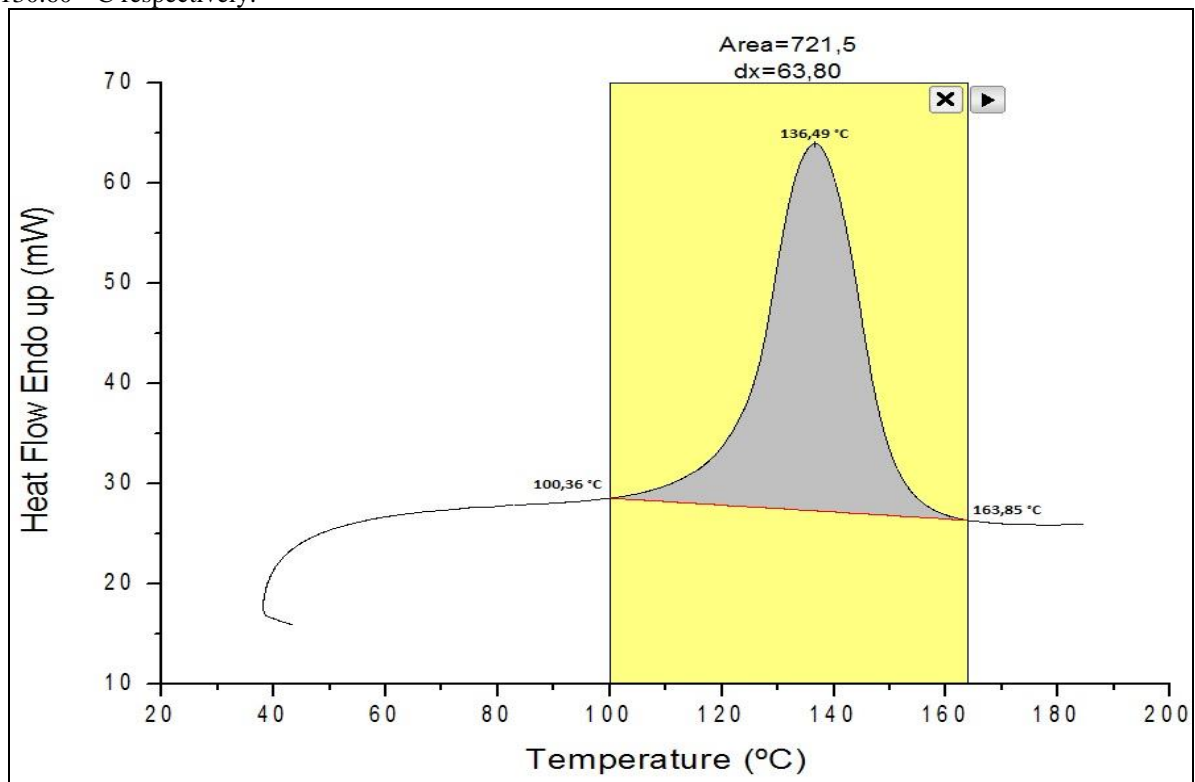

Fig. 5: Heating thermogram for pure HDPE.

V. CONCLUSION

It was possible to conclude the values of the parameters of the crystallization temperature (Tc), the percentage of crystallinity (% C), temperature of crystallinity (Tc) melting (Tm) and melting enthalpy variation (ΔHf_m).

The analysis of the thermogram curve in the cooling allowed to find a crystallization range of 120.16 to 75.75 C, with a maximum peak of 113.59.

By means of equations 1 and 2, it was possible to find a% crystallinity of 55.46% and a melting enthalpy variation of 160 J / g. The thermogram curve on material heating determined a melting temperature range of 136.49 to 163.85 ° C, with a peak at 136.49 ° C.

The values found for the four parameters resemble those of pure, commercial and white HDPE under the same assay conditions present in the literature. Due to the small temperature range

worked in the present study, it was not possible to observe other phenomena in the heating and cooling stages of the material, similar to that found in the literature.

REFERENCES

[1] DE OLIVEIRA, Matheus Silva; DA SILVA, Devanildo Braz. Aplicação da Curva ABC para Definição dos Itens de Maior Relevância na Composição da Receita de Vendas em uma Empresa do Segmento de Reciclagem de Materiais em Campo Grande/MS. ANAIS-ENCONTRO CIENTÍFICO DE ADMINISTRAÇÃO, ECONOMIA E CONTABILIDADE, v. 1, r. 1,2016

[2] DA SILVA OZÓRIO, Maiza et al. Promovendo a conscientização ambiental: resultados de uma pesquisa realizada com alunos do ensino médio sobre polímeros, plásticos e processos de reciclagem. Revista Brasileira de Educação Ambiental (RevBEA), v. 10, n. 2, p. 11-24, 2015.

[3] Pires, Prestes, and Pamela Galera. "Adição de resíduo termofixo em matriz de polipropileno reciclado: análise de propriedades térmicas e mecânicas." (2017).

[4] Candian, Lívia Matheus. "Estudo do polietileno de alta densidade reciclado para uso em elementos estruturais." São Carlos (2007).

[5] De Paoli, Marco Aurelio. "Degradação e estabilização de polímeros." (2009).

[6] DE TITÂNIO, PARTÍCULAS DE DIÓXIDO. ANÁLISES TERMO MECÂNICAS DE NANO. 2015.

[7] Pauleski, Dalva Teresinha. "Características de compósitos manufaturados com polietileno de alta densidade (PEAD) e diferentes proporções de casca de arroz e partículas de madeira." (2005).

[8] Coelho, Marilia Botelho. "Compósitos de polietileno de ultra alto peso molecular (PEUAPM) com casca de arroz." (2016).

[9] Pauleski, Dalva Teresinha, et al. "Características de compósitos laminados manufaturados com polietileno de alta densidade (PEAD) e diferentes proporções de casca de arroz e partículas de madeira." Ciência Florestal 17.2 (2007).

[10] Munaro, Marilda. "Desenvolvimento de blendas de polietileno com desempenho aperfeiçoado para utilização no setor elétrico." (2007).

[11] SOARES, Alexandre R. et al. Nanocompósito de matriz polimérica termoplástica de polietileno de alta densidade com adição de nanocargas com expansão térmica baixa de Al2 Mo3 O12. Cadernos UniFOA, v. 8, n. 1 (Esp.), p. 67-85, 2017.

[12] Araújo, Joyce. Compósito de polietileno de alta densidade reforçados com fribra de curauá obtidos por extrusão e injeção. 153f. Dissertação (mestrado). Departamento de química inorgânica, Universidade Estadual de Campinas – UNICAMP, 2009.

[13] COUTINHO, F, M ,B; MELO, I, L; MARIA, L, C, S. Polietileno: principais tipos, propriedades e aplicações. Revista polímeros: ciência e tecnologia, Rio de Janeiro, v. 13, n. 1, 2003.

[14] DENARI, Gabriela Bueno; CAVALHEIRO, E. T. G. Princípios e aplicações de análise térmica. São Carlos: IQSC, 2012.

[15] OLIVEIRA, Marcelo Antonio et al. Análise térmica aplicada a fármacos e formulações farmacêuticas na indústria farmacêutica. Química Nova, v. 34, n. 7, p. 1224-1230, 2011.

[16] Bernal, Cláudia, et al. "Influência de alguns parâmetros experimentais nos resultados de análises calorimétricas diferenciais-DSC." Química Nova 25.5 (2002): 849-855.

[17] LÍBANO, E. V. D. G., Leila LY Visconte, and E. B. A. V. Pacheco. "Propriedades térmicas de compósitos de polipropileno e bentonita organofílica." Polímeros 22.5 (2012): 430-435.

[18] LUCAS, F, E, Soares. Caracterização de polímeros: determinação de peso molecular e análise térmica. Rio de Janeiro: E-papers, 2001.

[19] PADILHA, Angelo Fernando. Microestrutura e Propriedades. São Paulo: Hemus, 1997.

[20] MOREIRA DA COSTA, Helson et al. Análise térmica e propriedades mecânicas de resíduos de polietileno de alta densidade (PEAD). Polímeros: Ciência e Tecnologia, v. 26, 2016.

[21] COSTA, H, M; LESSA, M, C, A, M, D; RAMOS, V, D. Cinética de cristalização não-isotérmica de resíduos de polietileno de alta densidade (PEAD). Revista polímeros, Nova Friburgo, v. 24, n. 4, 2014

[22] DA COSTA, Helson Moreira et al. Análise térmica e propriedades mecânicas de resíduos de polietileno de alta densidade (PEAD) Thermal analysis and mechanical properties of high-density polyethylene (HDPE) scraps. Polímeros: Ciência e Tecnologia, v. 26, p. 75-81, 2016.

[23] LUNA, Carlos Bruno Barreto et al. Desenvolvimento de blendas poliméricas visando à tenacificação dos polímeros: uma revisão. Semina: Ciências Exatas e Tecnológicas, v. 36, n. 1, p. 67-80, 2015.

[24] Hamester, Letícia. Avaliação do comportamento térmico da blenda PP/PEAD utilizada na fabricação de monofilamentos. 30f. trabalho de conclusão de curso. Departamento de engenharia de materiais, Universidade Federal do Rio Grande do Sul, 2010