Thermo-Mechanical evaluation of differential calorimetric scanned factors for AD60 VHDPE polymer using OriginPro LabTM Analysis tool version 8.5.1: A review comprising novel experimental optimization approach

1a, 1b*Shubham Sharma, 1a*P. Sudhakara, 1aSK Misra, 2J Singh
1a* CSIR-Central Leather Research Institute, RCED, Leather complex, Jalandhar, 144021, India
1b* PhD Research Scholar, Department of Mechanical Engg., IKG Punjab Technical University, Jalandhar-Kapurthala Road, Kapurthala, 144603, Punjab, India
2Department of Mechanical Engg., IKG Punjab Technical University, Jalandhar-Kapurthala Road, Kapurthala, 144603, Punjab, India

shubham543sharma@gmail.com
shubhamsharmacsirclri@gmail.com
sudhakar678@gmail.com

Abstract. The objective of the present work is to provide a comprehensive overview on the thermal analysis of the virgin high-density polyethylene (VHDPE) graded AD60 material by means of a differential scanning calorimetry (DSC) equipments. In order to verify possible transformations in its molecular structure and change of phases present with the variation of temperature over time. Past literature results reported the testing-analysis of the samples which was 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°C at a temperature of 43°C, 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. As revealed from in-depth studies, results obtained from the thermograms for the seven samples of the high-density polyethylene for the three required cycles, showed approximate values, with variations in centesimal scales that can be disregarded if the slight variations have been analyzed 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. Virgin High-density polyethylene (VHDPE), Differential Scanning Calorimetry Analysis, Molecular structure, Phase change

1. Introduction
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 [1].
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 [2]. 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.

The polymer has two categories, thermosets, and thermoplastics in which they differ through their elasticity chains [3]. 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 Virgin High-Density Polyethylene (VHDPE) graded AD60 polymer. The present study has a main objective is to analyze parameters of the crystallization temperature (Tc), % of crystallinity, melting temperature (Tm) and variation of the enthalpy of fusion (ΔHfm), through an experiment performed by a DSC machine, and thermograms developed with the OriginPro LabTM Analysis software version 8.5.1.

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 (ΔHfm): Calculated by means of the equation (2), referring to the thermogram of heating the material.

2. Literature Review

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 [4]. 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.

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 [5].

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 [6]. 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 CO2, all of which are rich in the basic raw material of the monomers.

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 [7].

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 [3].

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 [8].

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 present research task [9].

The Virgin high-density polyethylene (VHDPE), is understood to be a thermoplastic with high resistance to chemicals and solvents, yet it has a low permeability to gases and vapors [9]. The study 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 [10]. 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. Virgin 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/cm³ [11], Table 1.

Table 1. Thermal, Physical, Electrical and Mechanical Properties of VHDPE graded AD60 polymer [1-2, 4]

| Properties                        | Highly Linear | Low degree of crystallinity |
|-----------------------------------|---------------|-----------------------------|
| Density (g/cm³)                   | 0.962-0.968   | 0.950-0.960                 |
| Refractive index                  | 1.54          | 1.53                        |
| Melting Temperature (°C)          | 128-135       | 125-132                     |
| Fragility temperature (°C)        | -140 to -70   | -140 to -70                 |
| Thermal Conductivity (W/mK)       | 0.46-0.52     | 0.42-0.44                   |
| Combustion Heat (KJ/g)            | 46            | 46                          |
| Dielectric Constant at 1 MHz      | 2.3-2.4       | 2.2-2.4                     |
| Surface Resistivity (Ω)           | 10^15         | 10^15                       |
| Volumetric Resistivity (Ω m)      | 1017-1018     | 1017-1018                   |
| Dielectric Resistance (KV/mm)     | 45-55         | 45-55                       |
| Run-off point (MPa)               | 28-40         | 25-35                       |
| Traction module (MPa)             | 900-1200      | 800-900                     |
| Traction resistance (MPa)         | 25-45         | 20-40                       |
| Elongation (%)                    |               |                             |
| At the Yield point                | 5-8           | 10-12                       |
| At the breaking point             | 50-900        | 50-1200                     |
| Hardness                          |               |                             |
| Brinell Hardness (MPa)            | 60-70         | 50-60                       |
| Rockwell Hardness (MPa)           | R55, D60-D70  | ----                        |
| Shear Strength (MPa)              | 20-38         | 20-36                       |

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 polyethylene’s.

VHDPE graded AD60 polymer 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) [12].

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

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 (VHDPE) samples, in addition to non-efficient chain alignment orientations.
Mechanical and electrical characteristics of virgin high-density polyethylene (VHDPE) graded AD60 polymer are illustrated 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].

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].

- **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].
- **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 temperature gradient which eventually results in change in the enthalpy of specimen [14].

### 3. Methodology

The present scientific article, giving focus to the Differential-DSC Exploration Calorimetry of Virgin High-Density Polyethylene (VHDPE) graded AD60 polymer. The present experimental study 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 Virgin High-Density Polyethylene (VHDPE) graded AD60 polymer. The present scientific article will obtain quantitative results generating data in relation to the points to be analyzed.

#### 3.1. Thermal Analysis

The residues of Virgin High-Density Polyethylene (VHDPE) graded AD60 polymer in its pure form. The selection was done by 7 units of 28 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 Simultaneous Thermal Analyzer-8000 (STA) model [7-9, 14-17].

The choice of seven HDPE units was based upon the in-depth literature survey, and through experimental results, which showed a little variation in the established criteria and therefore little amplitude of results.

The following analysis was performed on 3 distinct cycles, which [7-9, 14-17]:

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 (T$_c$) obtained in the sample cooling, the melting temperature (T$_m$) observed in the third stage, by means of the second heating, enthalpy of crystallization ($\Delta$H$_c$) calculated by means of the area under the peak exotherm generated by the thermogram and the melting enthalpy ($\Delta$H$_m$) 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 OriginPro Lab™ Analysis version 8.5.1.

The percent crystallization or crystallinity of each sample was computing using equation (1) as mentioned below:

\[
\% \text{ Crystallinity} = \left( \frac{\Delta H_f}{\Delta H_{f_{100\% \text{ crystalline}}}} \times 100 \right) \quad \text{Equation (1)}
\]

\((\Delta H_f)\) is the melting enthalpy change of the sample whose crystallinity percentage is unknown and \((\Delta H_{f_{100\% \text{ crystalline}}})\) is the change in the melting enthalpy of the 100% crystalline sample, whose values are found in the literature [17].

The melting enthalpy change \((\Delta H_f)\) or enthalpy of each sample was calculated by means of equation 2 as follows:

\[
m \Delta H_f = KA \quad \text{Equation (2)}
\]

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 \((\Delta H_f)\) 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.

4. Results and Discussions

The results of the parameters obtained from the thermograms for the seven samples (septuplets) of the Virgin High-Density Polyethylene (VHDPE) graded AD60 polymer 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, STA-8000 model, differential scanning calorimetry (DSC), simultaneous Thermal Analyzer. Consequently, as it appears in the literature only the decimal values with equality for seven samples were used to make the thermograms [7-9, 14-17, 20-24].

The polymer matrices generally have a low strength and low melting point [19]. The thermogram was performed using the analysis of the samples of 28 mg of Virgin High-Density Polyethylene (VHDPE) graded AD60 polymer, through the analysis of Differential Exploration Calorimetry (DSC), for the second cycle, in which a cooling takes place, is represented by figure 1.

An exothermic peak with the onset at 120.16°C can be seen in figure 1 [20-24], having a peak of variation at 113.59°C with a temperature of 75.75°C. Such an exothermic curve of virgin High-Density Polyethylene (VHDPE) graded AD60 polymer 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 [20-24].

According to a study on virgin High-Density Polyethylene (VHDPE) graded AD60 polymer residues in colorless form, 20 mg to 30 mg 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 110.7°C [7-9, 14-17, 20-24].
Differential scanning calorimetry (DSC) was also used for the characterization of an VHDPE, for the experiment was selected from 20 to 30 mg 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 virgin High-Density Polyethylene (VHDPE) graded AD60 polymer through the use of equation (1) was 55.51%, which is in accordance with the percentage of crystallinity for virgin VHDPE found in the literature. Costa et. al., (2014), 20 to 30 mg of HDPE was used for the calculation, resulting in 56.8% of percentage crystallinity [21].

For 20 to 30 mg of commercial HDPE, a crystallinity rate of 57.1% was established at a rate of 10°C/min [21]. 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. For 20 to 30 mg obtained was 166.4 J/g enthalpy of crystallization [21].

Figure 2 shows a heating thermogram for the Virgin High-Density Polyethylene (VHDPE) graded AD60 polymer, whose graph shows an endothermic curve that starts at a temperature of 100.36°C [7-9, 14-17, 20-24]. When compared with the studies related in the literature, the present endothermic curve tends to be the enthalpy of melting of the material.

A virgin High-Density Polyethylene (VHDPE) graded AD60 polymer 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 [23]. 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.

The enthalpy change, as calculated by equation 2, found for pure Virgin High-Density Polyethylene (VHDPE) graded AD60 polymer in the present study was 162.49 J/g, and this value is approximated to the values found in the literature.

Moreira da Costa (2016) studied for a commercial HDPE, under a heating rate of 10°C/min, obtained a melting enthalpy variation of 167.4 J/g [22]. 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 [21].
Figure 2. DSC thermograms during heating of virgin High-Density Polyethylene (VHDPE) graded AD60 polymer [20-24]

5. Conclusions
It was possible to conclude the values of the parameters of the crystallization temperature ($T_c$), the percentage of crystallinity (% C), temperature of crystallinity ($T_c$) melting ($T_m$) and melting enthalpy variation ($\Delta H_{fm}$). The analysis of the thermogram curve in the cooling allowed to find a crystallization range of 120.21°C to 75.81°C, with a maximum peak of 113.65°C. By means of equations 1 and 2, it was possible to find a percentage crystallinity of 55.51% and a melting enthalpy variation of 160 J/g. The thermogram curve on material heating determined a melting temperature range of 136.49°C to 163.85°C, with a peak at 136.49°C. The values found for the four parameters resemble those of pure, commercial and transparent virgin High-Density Polyethylene (VHDPE) graded AD60 polymer under the same assay conditions present in the present 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 survey.

Declaration of conflict of Interest
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References
[1] Lin, J., Pan, Y., Liu, C., Huang, C., Hsieh, C., Chen, C., Lin, Z., & Lou, C. (2015). Preparation and Compatibility Evaluation of Polypropylene/High Density Polyethylene Polyblends. Materials.
[2] Liao, C.Z., & Tjong, S.C. (2013). Mechanical and Thermal Performance of High-Density Polyethylene/Alumina Nanocomposites. Materials Science.
[3] Pires, Prestes, and Pamela Galera. Addition of thermosetting residue in a recycled polypropylene
matrix: analysis of thermal and mechanical properties. (2017).

[4] Savu, Adrian & Cosmin, Rosu & Bokor, Ábel & Issa, Ahmad. (2016). Study on the use of Recycled High-Density Polyethylene as a Construction Material. 16th International Multidisciplinary Scientific GeoConference SGEM 2016. 2. 223-230. 10.5593/SGEM2016/B62/S26.031.

[5] From Paoli, Marco Aurelio. Degradation and stabilization of polymers. (2009).

[6] Titanium, Dioxide particles. Thermo mechanical analysis of Nano. 2015.

[7] Pauleski, Dalva Teresinha et al. Characteristics of laminated composites manufactured with high density polyethylene (HDPE) and different proportions of rice husks and wood particles, Ciencia Florestal 17(2):157-170 (2007).

[8] Coelho, Marilia Botelho. Ultra-high molecular weight polyethylene (PEUAPM) composites with rice husks. (2016).

[9] Pauleski, Dalva Teresinha, et al. Characteristics of laminated composites manufactured with high density polyethylene (HDPE) and different proportions of rice husks and wood particles. Forest Science 17.2 (2007).

[10] Munaro, Marilda. Development of polyethylene blends with improved performance for use in the electrical sector. (2007).

[11] Soares, Alexandre R. et al. Nanocomposite of thermoplastic polymer matrix of high-density polyethylene with addition of nanocharge with low thermal expansion of Al2 Mo3 O12. UniFOA notebooks, v. 8, n. 1 (Esp.), P. 67-85, 2017.

[12] Araújo, Joyce. High density polyethylene composite reinforced with curauá fiber obtained by extrusion and injection. 1531. Thesis (Master's degree). Department of Inorganic Chemistry, State University of Campinas - UNICAMP, 2009.

[13] Doak, K.W. – “Ethylene Polymers”. Em: Mark, H.M., Bikales, N.M., Overberg, C.G., Menges, G. – “Encyclopedia of Polymer Science and Engineering”, John-Wiley & Sons, New York, Volume 6 (1986).

[14] Denari, Gabriela Bueno; Cavalheiro, ETG. Principles and applications of thermal analysis. São Carlos: IQSC, 2012.

[15] Craig, DQM, Reading, M. Thermal Analysis of Pharmaceuticals, CRC Press: New York, 2007.

[16] Bernal, Cláudia, et al. Influence of some experimental parameters on the results of differential calorimetric analyzes-DSC. Química Nova 25.5 (2002): 849-855.

[17] Lebanon, EVDG., Leila LY Visconte, and EBAV Pacheco. Thermal properties of polypropylene and organophilic bentonite composites. Polymers 22.5 (2012): 430-435.

[18] Marković, Gordana & Marinović-Cincović, Milena & Jovanović, Vojislav & Samaržija-Jovanović, Suzana & Budinski-Simendic, Jaroslava. (2016). Polymer characterization (II), in book: Polymer science: research advances, practical applications and educational aspects, Publisher: Formatex Research Center, Spain, Editors: A. Mendez-Vilas, A. Solano-Martin, pp.397-403.

[19] Padilha, Angelo Fernando. Microstructure and Properties. São Paulo: Hemus, 1997.

[20] Moreira DA Costa, Helson et al. Thermal analysis and mechanical properties of high-density polyethylene (HDPE) waste. Polymers: Science and Technology, v. 26, 2016.

[21] Costa, HM, Lessa, MCAMD and Ramos, VD. Non-isothermal crystallization kinetics of high-density polyethylene (HDPE) residues. Polymers magazine, Nova Friburgo, v. 24, n. 4, 2014

[22] DA Costa, Helson Moreira et al. Thermal analysis and mechanical properties of high-density polyethylene (HDPE) waste Thermal analysis and mechanical properties of high-density polyethylene (HDPE) scraps. Polymers: Science and Technology, v. 26, p. 75-81, 2016.

[23] Luna, Carlos Bruno Barreto et al. Development of polymeric blends aiming at polymer toughening: a review. Semina: Exact and Technological Sciences, v. 36, n. 1, p. 67-80, 2015.

[24] Gregor-Svetec, Diana & Leskovšek, M. & Tišler-Korljan, B. & Sluga, F.. (2009). Monofilaments produced by blending virgin with recycled polypropylene. Tekstil ve Konfeksiyon. 19. 181-188.