



## Conference Proceeding

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# Effect of Mass and Temperature Rate on the Thermal Properties of High-Density Polyethylene Using Differential Scanning Calorimetry

Salman Khan<sup>1</sup>, Atteeq Uz Zaman<sup>2\*</sup>, Massab Junaid<sup>1</sup>, Tauheed Shehbaz<sup>2</sup>, Muhammad Awais Khan<sup>2</sup>, Fahd Nawaz Khan<sup>2</sup>, Muhammad Ramzan Abdul Karim<sup>2</sup>

<sup>1</sup>Faculty of Mechanical Engineering (FME), Ghulam Ishaq Khan (GIK), Institute of Engineering Sciences and Technology Swabi, Topi 23460, Pakistan

<sup>2</sup>Faculty of Material and Chemical Engineering (FMCE), Ghulam Ishaq Khan (GIK), Institute of Engineering Sciences and Technology, Swabi, Topi 23460, Pakistan  
E-mail: zaman.atteeq@gmail.com

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**Abstract:** Mass and heating rates alter the thermal properties, molecular structure, and phase changes of the materials. This study aimed to investigate the influence of sample mass (10-30 mg) and heating rate (4-15 °C/min) on the thermal characteristics of high-density polyethylene (HDPE) using differential scanning calorimetry (DSC). The experiments were conducted in two cycles. In the first cycle, samples of different masses (10-30 mg) were heated to 180 °C followed by cooling at a constant heating rate of 10 °C/min with a mass flow rate of 20 ml/min of purging gas (nitrogen). In the second cycle, a sample mass of 15 mg was used to investigate the thermal characteristics while varying the temperature rates (4, 6, 8, 10, and 15 °C/min). It was concluded that the variation in sample mass significantly affected the thermal properties of HDPE, leading to a slight increase in the melting temperature and latent heat, which shifted towards higher temperatures. In contrast, the temperature rate caused a reduction in the latent heat and crystallization temperatures. The thermograms obtained from the experiments provided insight into the thermal behavior of HDPE under different conditions, and the findings emphasized the importance of carefully considering the effects of mass and temperature rate when measuring the thermal properties of HDPE.

**Keywords:** HDPE, heating rates, thermogram, thermal properties, crystallization temperature, sample mass, DSC

## 1. Introduction

Polymer materials are composed of many small units called monomers. It can either be available naturally or prepared synthetically. Polymers, based on their mechanical and thermal properties, are classified into three groups. Thermoplastics are amorphous or semi-crystalline materials that soften upon heating and solidify upon cooling. There are no noticeable changes in thermoplastic's thermal and mechanical properties, and they can melt and solidify repeatedly. A thermoset polymer is a polymer that cannot be melted once it has hardened and cured. Thermoset polymers involve permanent chemical and structural changes upon heating that are irreversible. The third type is an elastomer, which has weak intermolecular forces, viscosity, and elasticity. It has a low stiffness modulus and a high yield strength [1].

The proportion of amorphous and crystalline phases, or crystallinity, has a significant impact on the thermal and

mechanical properties of polyethylene (PE), a naturally occurring semi-crystalline solid. PE is created by joining several tiny ethylene monomer units together in a process called polymerization [2]. Based on the polymerization process, PE is classified into four types: linear low, low, medium, and high-density polyethylene (HDPE). Linear low-density polyethylene (LDPE) has similar density and crystallinity to LDPE, but it has stronger intermolecular forces than LDPE. LDPE contains macromolecules with many branches that are randomly distributed and are not aligned with one another. Medium-density polyethylene (MDPE) and HDPE also contain a linear arrangement of macromolecules with low branching units and have a regular and aligned structure [3]. Due to the excellent thermal and mechanical characteristics of HDPE, it does not deteriorate and can withstand high temperatures [4]. It is a thermoplastic polymer and has a high ratio of strength to density. It is employed for the fabrication of plastic pipes and bottles, lumber, and geomembranes. It has a density ranging from 930 to 970 kg/m<sup>3</sup> depending upon the composition. Its density is higher than LDPE, but it has strong intermolecular forces and high tensile strength. HDPE has a high specific strength, is tougher, and can withstand a higher temperature of 120 °C [5].

The polymer's chemical and physical properties are strongly influenced by the addition of additives and its processing methods. The prominent thermal properties of the polymers are (1) the onset, peak, and end melting points during the melting; (2) the initial, peak, and end crystallization temperatures during cooling; (3) the enthalpies of melting and crystallization and crystallinity [6]. For the thermal analysis of polymers, copolymers, polymer blends, and composite materials, differential scanning calorimetry (DSC) is used. It determines the difference in temperature between the sample with the reference, which is usually an empty pan of aluminum or silica [7, 8]

Morphological characteristics are heavily influenced by the crystallinity of the polymers. The crystallinity of HDPE pipes was analyzed and tested. Samples of HDPE were investigated at the temperatures (25-300 °C) at a 5 °C/min rate of heating under nitrogen. The results reveal that the degree of the crystallinity of the HDPE was significantly influenced by the temperature [9]. The samples were tested in two ways: (a) First, samples were heated at rates of 10, 15, 20, 25, 30, 35, 40, and 80 °C/min, then a cooling rate of 150 °C/min. The temperature rates are not constant during cooling and heating. Secondly, the heating rates were kept constant during the testing of the samples at 5, 10, 20, 30, 40, and 80 °C/min. Here, both the rates of heating and cooling were kept constant [10]. The thermal characteristics of PE samples with varying densities were evaluated using DSC. A sample of PE of mass 5-7 mg was tested at the heating and cooling rates of 10 °C/min. The HDPE samples were first heated to 200 °C to ensure complete melting and eliminate any thermal history, followed by cooling to 40 °C. Subsequently, the samples were heated again to 200 °C to achieve the melting curve. The X-ray diffraction (XRD) and DSC were used to investigate the breakdown and conductance characteristics of the polymers [11]. The study aimed to investigate the influence of the molecular weight of HDPE and LDPE on the crystallization process. DSC was used to perform the investigation [12].

In this research article, a notable research gap concerning the impact of sample mass and heating rate on the thermal properties of HDPE was explored. Previous literature has extensively explored the effect of heating and sample mass on various polymers, yet limited research exists specifically on HDPE. To bridge this gap, we investigated utilizing DSC to examine the influence of sample mass and heating rate on the thermal properties of HDPE. This study aims to provide valuable insights into the behavior of HDPE under different experimental conditions, contributing to a better understanding of its thermal characteristics.

## 2. Materials and methods

The materials utilized in the study were HDPE, and their physical properties are given in Table 1. The principle of DSC is used to measure the temperature difference between the polymers and the reference sample and plot a heat flow curve. The curve is then analyzed to determine the crystallinity of the polymers. If the polymer is completely amorphous, the crystallinity will be zero, but less than unity for semi-crystalline polymers [13]. A sample of various masses was tested at a constant heating rate, and the effect on the thermal characteristics of HDPE was investigated. Secondly, the mass is kept constant, and different heating rates were studied and analyzed for their effects.

**Table 1.** The physical properties of HDPE [14, 15]

Properties	Magnitude	Unit
Density	0.9451-0.9653	g/cm <sup>3</sup>
Elongation	350	%
Modulus of elasticity	660	MPa
Tensile strength	26.1	MPa
Service temperature	-80 to 100	°C
Thermal conductivity	0.29	kcal/m hr °C

## 2.1 Samples preparation

DSC is mostly employed to evaluate the thermal characteristics of materials. The DSC has a heating unit that consists of two chambers: one for the sample and one for reference, which is mostly empty. The procedure involves weighing the mass of the sample on the high-precision digital balance. The sample is placed in the alumina pan with alumina powder. The reference sample mostly consists of inert materials, which do not undergo any physical, chemical, or thermal transition over a wide range of temperatures. The sample and reference are heated to the same temperature, and the temperature difference between them is recorded. Both are heated in the presence of an inert gas, which is nitrogen, at a 20 ml/min of flow rate [16].

## 2.2 DSC

The thermal properties of HDPE were determined using a PerkinElmer apparatus, and it has a temperature range of 15-1500 °C with a heating and cooling rate of 25 °C per minute. The apparatus consists of a heating chamber where the sample and reference are heated to the same temperature. The heating unit is attached to a water chiller, which reduces the sample temperature to 15 °C, and a purging gas cylinder to remove the air and avoid the chemical reaction of the sample in the chamber. The sample is placed in an alumina pan, which is an inert material. The heating chamber controls the temperature of the sample and records it in the form of a heating curve. The curve was analyzed to find the thermal characteristics of the materials. Under the purging gas environment, the sample of different masses is heated at a constant rate, while the sample of constant mass is heated at a different rate. The samples were first melted from 70 to 180 °C, followed by cooling to 70 °C. Two identical crucibles made of alumina, one of which is empty as a reference and the other of which is filled with HDPE, are heated at the same temperature in the control heating unit. The empty crucible warms up quickly and causes differences in temperature with the sample pan. The temperature difference was recorded by the thermocouple attached to the pans. The temperature difference is plotted on a heating curve as a function of temperature. The analysis of the heating curve to calculate the peak, on-set, and end-set temperatures, phase transition (melting and crystallization) temperatures, and enthalpies [13].

## 3. Results

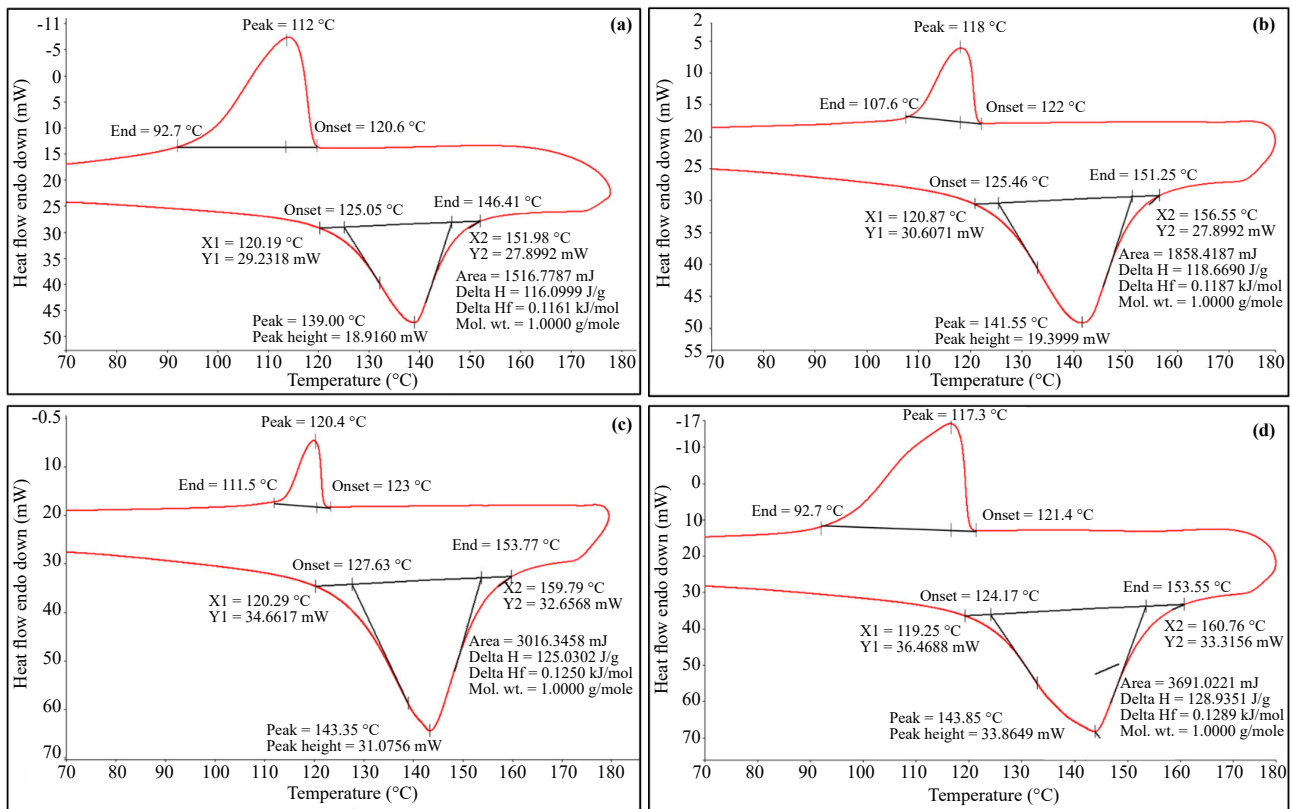
### 3.1 Influence of sample mass

The samples of HDPE were weighed using a digital physical balance. The sample of different masses of 10, 15, 25, and 30 mg were prepared and tested at a rate of heating and cooling of 10 °C per minute within an environment of inert gas. The effect of the weight of the sample on the thermal characteristics of HDPE was investigated. The samples are first heated to 180 °C to melt, and then they are cooled for recrystallization. The melting and crystallization temperatures of the 10 mg of sample were 139 and 112 °C, respectively, as shown in Figure 1(a). The HDPE loses its solid phase and converts into a semisolid phase at 90 °C, which is the glass transition temperature. The melting enthalpy of HDPE is 116.1 J/g. Fully crystalline polymers have no glass transition. HDPE is a semi-crystalline polymer. After melting, the sample was cooled from 180 to 70 °C at a cooling rate of 10 °C per minute. The upward peak is the cooling

or crystallization curve, and the sample gets solidified. A sample of mass 15 mg has a melting point of 141.6 °C, and its latent heat of fusion is 118.7 J/g as shown in Figure 1(b). Figure 1(c) illustrates a sample of mass 25 mg, and its melting temperature and latent heat are 143.4 °C and 120.4 J/g. Similarly, for the sample of mass 30 mg the latent heat and melting temperatures were 129 J/g and 144 °C, respectively as shown in Figure 1(d). All the results are summarized in Table 2. It can be seen from Table 2 that, with the increase of sample mass, the melting point gets higher and broader. It was also observed that the latent heat also increased with the sample mass due to an increase in storage capacity.

**Table 2.** The thermal characteristics of HDPE of varying mass

Sample mass (mg)	Melting curve (°C)			Crystallization curve (°C)			The heat of fusion (J/g)
	Onset	Peak	End	Onset	Peak	End	
10	125.0	139	146.4	120.6	112	92.6	116.1
15	125.5	141.6	151.3	122	118	107.6	118.7
25	127.6	143.4	154	123	120.4	111.5	125
30	124.2	144	153.6	121.4	117.3	92.7	129



**Figure 1.** The DSC results at different masses (mg) of samples (a) 10, (b) 15, (c) 25, and (d) 30

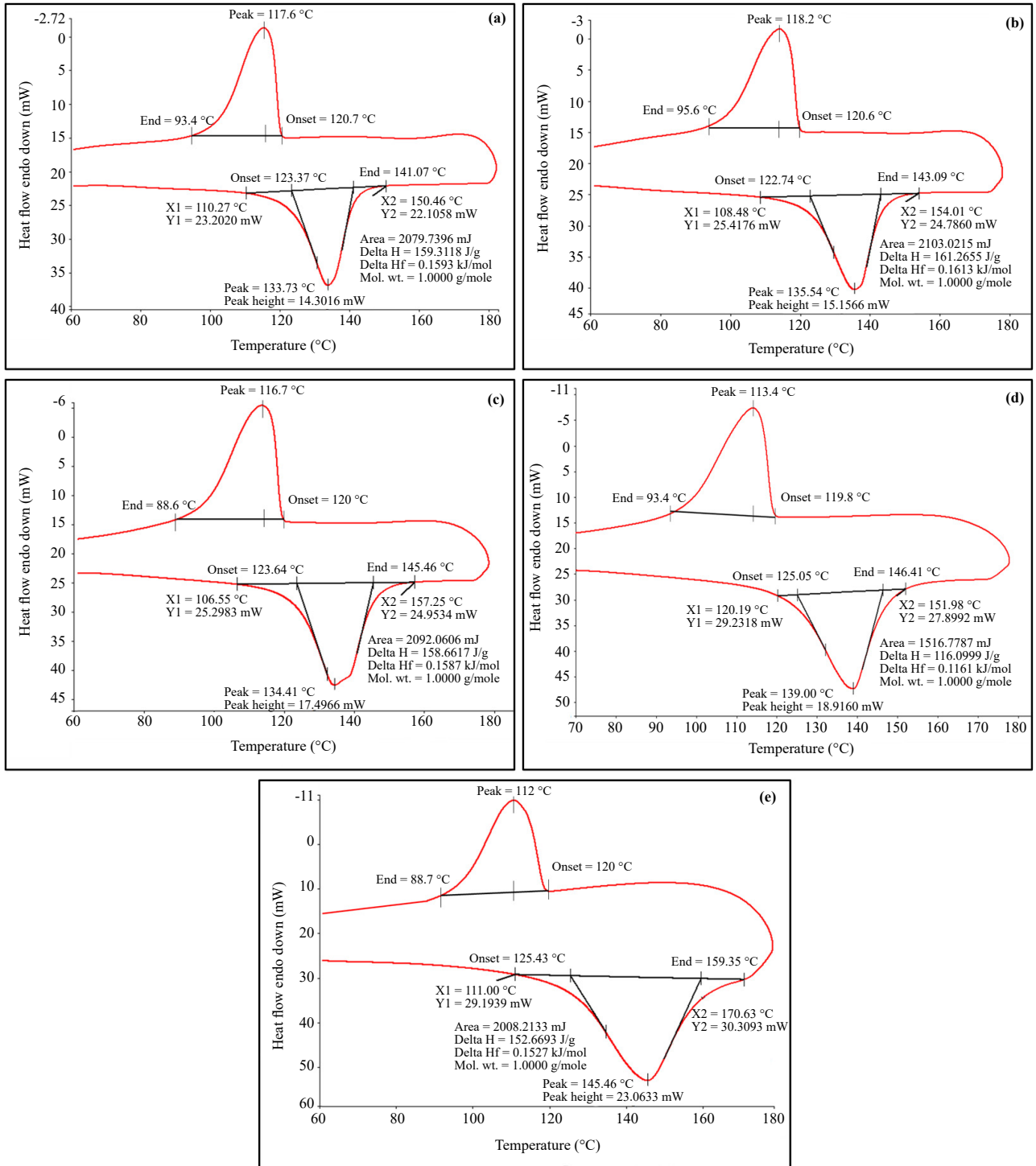
### 3.2 Influence of heating rate

The heating rate alters the thermal properties of the polymers. At a mass of 15 mg, the effect of heating rates of 4, 6, 8, 10, and 15 was investigated. The sample was heated from 70 to 180 °C at different rates with a flow of inert gas of 20 ml/min. The samples were heated to melt, as represented by the down curve, and then cooled, as represented by the upper curve. The sample heat flow rate of 4 °C/min has a melting and heat of fusion of 133.73 °C and 159.3 J/g, respectively, as shown in Figure 2(a). The onset and end temperatures were 110.3 and 141.7 °C. The polymers absorb heat, the curve moves downward, which is considered latent heat, and the sample gets melted. After melting, the sample was cooled to 60 °C, where it crystallized. During crystallization, the sample gets solidified by evolving the heat at the crystallization temperature of 117.6 °C as shown in Figure 1(a). The melting and crystallization temperatures and latent heat at 6 °C/min were 135.5 °C, 118.2 °C, and 161.3 J/g, respectively as shown in Figure 2(b). The melting and crystallization temperatures and latent heat at 8 °C/min were 123.6 °C, 116.7 °C, and 158.7 J/g, respectively as shown in Figure 2(c). The melting and crystallization temperatures and latent heat at 10 °C/min were 139 °C, 113.4 °C, and 116 J/g respectively as shown in Figure 2(d). Lastly, the melting and crystallization temperatures and latent heat at 15 °C/min were 145.5 °C, 112 °C, and 152.7 J/g respectively as shown in Figure 2(e). All the DSC results are summarized in Table 3. It was also observed that the melting point gets higher with the heating rate.

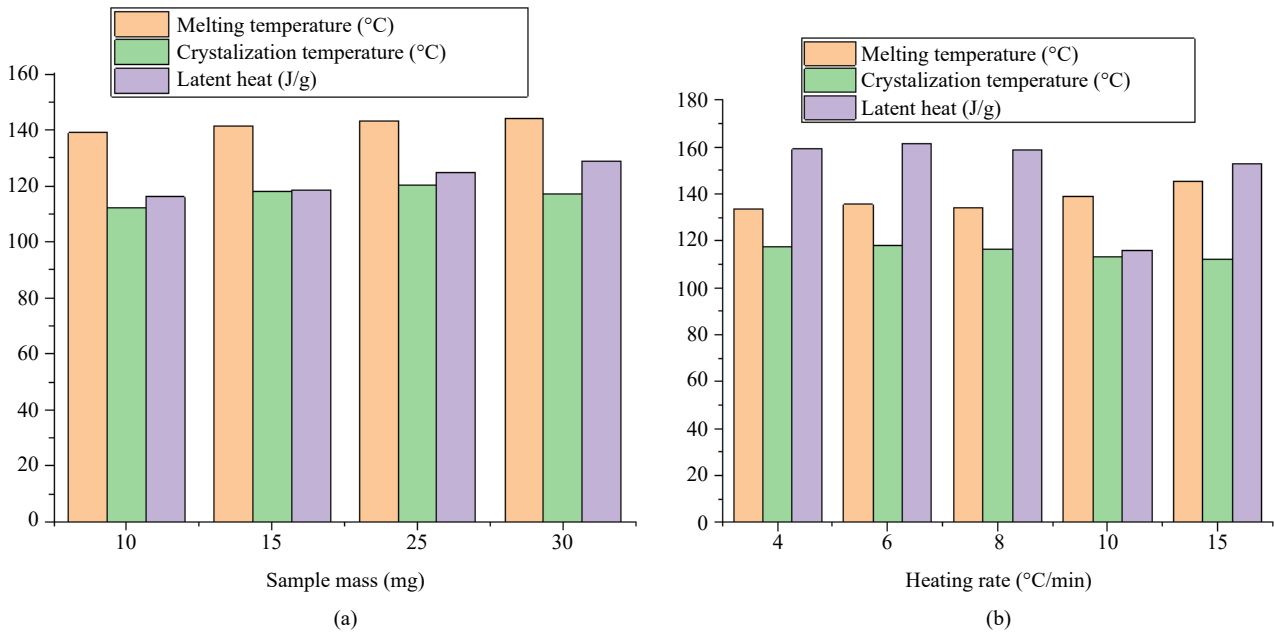
Figure 3(a) demonstrated the impact of the sample mass on the characteristic properties of HDPE. It was indicated that the melting and crystallization points shifted towards higher temperatures with an increase in the sample mass. Additionally, a slight increase in latent heat was observed with the sample mass. It is due to the increase in sample mass, so it will take more time and heat to melt the sample and hence shifting of curves occurred. Similarly, Figure 3(b) showed the effect of the heating rate on the thermal characteristics of HDPE. The melting points shifted towards higher temperatures, while the crystallization temperature and latent heat slightly decreased with an increase in the heating rate.

**Table 3.** The thermal characteristics of HDPE using varying temperature rates

Heating rate (°C/min)	Melting curve (°C)			Crystallization curve (°C)			The heat of fusion (J/g)
	Onset	Peak	End	Onset	Peak	End	
4	123.4	133.7	141.1	120.7	117.6	93.4	159.3
6	122.7	135.5	143.1	120.6	118.2	95.6	161.3
8	123.6	134.4	145.5	120	116.7	88.6	158.7
10	125	139	146.4	119.8	113.4	93.4	116
15	125.4	145.5	159.4	120	112	88.7	152.7



**Figure 2.** The DSC results of samples at a heating rate (°C/ min) of (a) 4, (b) 6, (c) 8, (d) 10, and (e) 15



**Figure 3.** The effect of mass and heating rate on the thermal characteristics of HDPE: (a) sample mass and (b) heating rate

## 4. Conclusions

The thermal characteristic of HDPE can be affected by several factors, including mass and heating rate. The deduced conclusions from the research were summarized as:

The mass of the sample can influence the heat transfer within the sample and affect the thermal behavior of the material. In general, a larger sample mass can result in a slower heating or cooling rate, which can lead to a shift in the melting or crystallization temperature. In general, a varying mass of the mass effect the HDPE's melting and crystallization temperatures, and they shifted toward higher temperatures. However, a small increase occurred in the latent heat with the increasing mass of the sample.

Similarly, the heating rate can also affect the thermal behavior of HDPE. When HDPE is subjected to a faster heating rate, the crystallization peak shifts to higher temperatures due to the reduced time available for the polymer to rearrange its molecular structure. In contrast, a slower heating rate allows more time for the polymer chains to rearrange, resulting in a lower melting temperature. By changing the heating rate, the melting temperatures of the HDPE samples are affected. With the increase in heating rate, the temperature at which the samples transition from solid to liquid increases as well. This leads to broader curves in the peak of the phase transition and a shift towards higher temperatures. However, this also results in a reduction of the crystallization temperature and the amount of latent heat in the samples.

When the furnace is heated slowly, the signals produced are weak and noisy. On the other hand, higher heating rates lead to stronger signals but can cause smearing in materials undergoing a phase transition. This shift causes the recorded peak signal to move towards higher temperatures. To obtain accurate results such as the onset/end set temperatures and the phase transition enthalpy, it is necessary to use multiple heating rates that balance the trade-off between noise and smearing.

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## Conflict of interest

There is no conflict of interest for this study.

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