

Thermo-physical Properties of Thermoplastics: Relationships with Degree of Crystallinity

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ABSTRACT

The purpose of this study is to determine the direct relationship between the crystallinity of thermoplastic polymers and their corresponding thermo-physical properties that influence the performance of plastics in many thermal applications. These properties are glass-transition temperature, melting point and specific heat capacity. The materials used are POM, HDPE, LDPE, PP, PA, and PET which have different values of degree of crystallinity. The study includes theoretical and experimental works. The analytical work has used mathematical functions extracted from reliable empirical relationships. The experimental work included manufacturing the specimens; specifying the cooling procedure to get the required degree of crystallinity; measuring thermo-physical properties and finally analyze the data and introduce the experiences obtained from the investigation. Theoretical values, as well as experimental data, were both behave similarly concerning the physical property. The results show that by increasing the degree of crystallinity the melting point has increased, while glass-transition temperature and specific heat capacity have decreased. It is noticed experimentally that the change in the value of glass-transition temperature between high and low crystalline specimens was in the range of 10-30 °C (5-15%), while the change in the value of melting point for the same specimens was 3-6 °C (5-10%).

KEYWORDS

crystallinity, thermal properties, melting point, glass-transition, thermoplastic

INTRODUCTION

Polymers are classed according to their thermal response as thermosets or thermoplastics. Thermoplastic polymers, as the name implies, such as polyethylene, polyamide, and polypropylene are softened and flow under the action of pressure and heat. Thermoplastics, when compounded with appropriate ingredients, can usually withstand several of heating and cooling cycles without suffering any structural breakdown [1]. In polymers, crystallization refers to phase transition between two solid states (amorphous and crystalline). Crystallization occurs above glass transition temperature (T_g) and below melting point (T_m). Glass transition temperature (T_g) is a crucial physical parameter that affects the thermal behavior of polymer hence the manufacturing process. Molecular motions are frozen and the polymer is glassy and brittle below T_g . Molecular motions are activated and the polymer is viscous and rubbery above T_g [1, 2]. Crystallinity refers to the degree of structural order in a solid. In a crystalline polymer, the molecules are arranged periodically, regularly. Synthetic polymers are either amorphous or semi-crystalline. Semicrystalline polymers, such as thermoplastics, can undergo melting transition, whereas amorphous polymers, such as thermosets, do not. All polymers (semicrystalline and amorphous) go through glass-transition temperature (T_g), as shown in Figure 1.

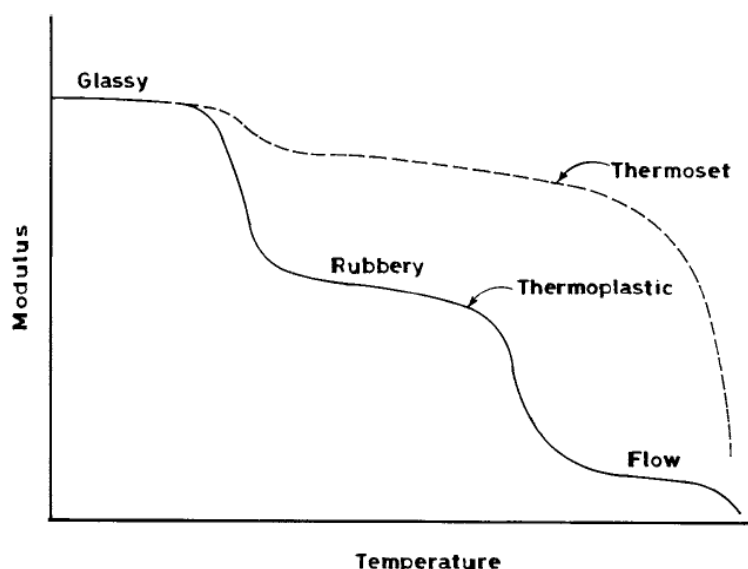


Figure 1. Modulus–temperature curves for thermoplastics and thermosets [1].

The degree of crystallinity (X_c) of a polymer varies from zero for fully non-crystalline polymers to one for fully crystalline polymers. The degree of crystallinity can be described as a volume fraction (or mass fraction) of the real crystalline portion to the total mass [3, 4]. However, most experimental approaches for assessing the degree of crystallinity presume a mixture of perfect crystalline and disordered regions; transition zones are assumed to account for a significant portion of the total. These approaches include nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). In addition to the foregoing integral approaches, the distribution of amorphous and crystalline areas may be seen using microscopic techniques like scanning electron microscopy (SEM) [5, 6].

The degree of crystallinity has a big influence on physical and mechanical properties, as following [3]:

- Density of semi-crystalline polymer is higher than that of amorphous polymer.
- Semi-crystalline polymers are more impact-resistant than amorphous polymers, and are generally tougher.
- Amorphous polymers with a low degree of crystallinity tend to be transparent, while polymers with high degrees of crystallinity tend to be opaque due to light scattering.

The variation of these characteristics has given a good reason for researchers to focus upon the direct effect of the degree of crystallinity and the thermal properties. For manufacturing purposes, thermoplastics are usually introduced as grains of different sizes and standards. These grains are poured into injection molding machines for melting, mixing, and injecting into the desired molds. The polymer solidifies and assumes the shape of the mold as it cools. The procedure of cooling has a big influence on the obtained value of the degree of crystallinity. Polymers of simple structural chains such as polyethylene and polypropylene which have a slow cooling rate will have a high degree of crystallinity, where sufficient time is available for crystallization to take place. On the other hand, a high cooling rate reduces polymer crystallinity [7]. Many studies have taken the effect of cooling rate under consideration, as in researches by references [8-14]. Anyway, crystallinity is always dependent on the conditions of polymer formation. Usually, in all-polymer networks, the more crosslinked they are the less chance the polymer chains have to fold into the lamellar crystal, i.e. less crystallinity. This behavior is well described by many studies as in references [15-18].

However, these studies involved crystallinity as an indirect parameter influence of thermal properties of polymers, for example by describing morphological and thermal behaviors resulting from the cooling process or the crosslinking rather than focusing upon the direct relationship between the thermal properties and the crystallinity. This study aims to determine relationship that describes the direct effect of crystallinity on the thermo-physical properties of selected thermoplastics: POM, HDPE, LDPE, PP, PA, and PET. The study introduces mathematical relationships as well as experimental works. Mathematical models extracted from

reliable sources under suitable criteria to present the relationships between the crystallinity and effective parameters. Laboratory works are considered to manufacture the samples. Several cooling methods for polymer melts are used to control the degree of crystallinity. Measurements for thermo-physical properties are subjected to appropriate standards which required precise instruments and operation conditions.

THEORETICAL WORK

Thermoplastic polymers are generally semicrystalline with a range of degrees of crystallinity (X_c). Polymers selected for this study are classified into three categories: high-crystallinity polymers (POM and HDPE), mid-crystallinity polymers (LDPE and PP), and low-crystallinity polymers (PA and PET). The range of degree of crystallinity for selected polymers is 0.2-0.8 for high-crystallinity polymers, 0.1-0.5 for med-crystallinity polymers, and 0.1-0.3 for low-crystallinity polymers [1-4]. The crystallinity has high effects on glass transition temperature, melting point, and heat capacity. To find a reliable relationship between the degree of crystallinity (X_c) and glass-transition temperature (T_g), it is important to involve the crosslinking aspect here. The change in (T_g) depends upon the degree of cross-linking (X_{crl}). Cross-linking restricts molecular mobility by connecting the polymer backbones and lowering the peak temperature and degree of crystallinity. As a result, the increase in cross-linking increases the glass transition temperature of the polymer [19, 20]. An empirical equation known by Nielsen gives an interesting relationship between (T_g) and (X_{crl}), as following [3]:

$$T_g = \left[1 + 1.2 \left(\frac{X_{crl}}{1 - X_{crl}} \right) \right] T_{gct} \quad (1)$$

Where, (T_{gct}) is the typical glass-transition temperature for crystalline polymer, which is: 213 K, 138 K, 148 K, 253 K, 333 K, and 343 K, respectively for POM, HDPE, LDPE, PP, PA, and PET [1-4]. Now, since the degree of crystallinity (X_c) is decreased by increasing the degree of cross-linking (X_{crl}), thus the two parameters can be related by assuming:

$$X_c = X_{cm} - m X_{crl} \quad (2)$$

Or

$$X_{crl} = (X_{cm} - X_c) / m \quad (3)$$

Where, (X_{cm}) is the maximum degree of crystallinity for a certain polymer as a reference point. While, (m) is an average index that represents the intensity of crosslinking of the certain polymer, which is extracted from references [1-4, 15-27], as follows: 2.4, 2.0, 2.2, 2.6, 2.7, and 2.9 respectively for POM, HDPE, LDPE, PP, PA, and PET. It is seeking to state a direct relationship between the melting point and the degree of crystallinity. Usually, the melting point of the polymer tends to decrease when the degree of crystallinity goes lower. For example, LDPE has a lower melting point comparing to HDPE due to a less crystalline structure that offers rigidity and greater chemical resistance [3]. Now, the following linear equation is assumed;

$$T_m = T_{mc} - (1 - X_c) F \quad (4)$$

Where (T_{mc}) is the melting point for the crystalline polymer which is: 443 K, 413 K, 338 K, 438 K, 503 K, and 533 K, respectively for POM, HDPE, LDPE, PP, PA, and PET [1-4]. The constant (F) is extracted from references [1-4, 17, 23, 28-35], as following: 20, 24, 10, 18, 16 and 8 respectively for: POM, HDPE, LDPE, PP, PA and PET. Usually, the specific heat capacity has a reciprocating influence with the density, thus it can be expected that (C_{pc}) is lower than (C_{pa}). In other words, heat capacity tends to decrease by the increase in the crystallinity of the polymer, as can be recognized from references [36-39]. However, the value of specific heat capacity of polymers has different behavior below (T_g) or above it, and it is often estimated with many mathematical models. According to the simple mixing rule [30], the following formula can be used for the semicrystalline polymer;

$$C_p = X_c C_{pc} + (1 - X_c) C_{pa} \quad (5)$$

Where (Cpc) and (Cpa) are the specific heat capacities for crystalline and amorphous structures, respectively. Since (Cpa > Cpc) by a constant ratio (R), which is greater than 1, so the last equation can be re-arranged as

$$C_p = [R - (R-1) X_c] C_{pc} \quad (6)$$

The specific heat capacity for crystalline structure (Cpc) and the constant (R) can be extracted from references [1-4, 40] for certain polymers, as shown in Table 1.

Table 1. Typical values of heat capacity for selected polymers [1-4, 40]

Polymer	Cp of crystalline structure (J/kg.K)	R = Cpa/Cpc
POM	1500	1.6
HDPE	1900	1.4
LDPE	2000	1.3
PP	1800	1.2
PA	1600	1.1
PET	1100	1.1

EXPERIMENTAL WORK

The work has conducted at Chemical Lab in Materials Engineering Department, Mustansiriyah University during the period Nov 2020 – May 2021. Several devices and instruments have been used to manufacture the samples such as: oven, thermometer, weight scale, molds, as well as some tools and auxiliaries. The GPC, DSC and SEM tests have done at the Laboratory of Packing Materials in Ministry of Industry and Minerals (MOIM). The requested thermoplastic materials have been collected from the local market as grains. In the beginning, measurements of molecular weight have done by gel permeation chromatography (GPC), as follows: 80000, 300000, 50000, 140000, 90000, and 75000 g/mol respectively for POM, HDPE, LDPE, PP, PA, and PET. The work has included manufacturing a set of specimens by melting the grains in a suitable oven brand JRAD, with a thermostat that operates up to 260 °C. The period that the plastic grains spent in the oven to get melting was ranged between 20-25 minutes starting from room temperature (20-22 °C), at a constant rate of heat (10 °C/min). The specimen then cooled using different procedures to get different cooling rates, thus different degrees of crystallinity. The procedures include either cooling in the shut-off oven (with 1-2 °C/min cooling rate), in the still air (with 3-5 °C/min cooling rate), or in a fridge (with 6-8 °C/min cooling rate). After solidifying, the polymer grinded into small particles, about 2.36 mm maximum diameter or Mesh 8, to be ready for DSC tests, as shown in Figure 2.



Figure 2. Samples prepared for DSC tests

The most common approach for estimating polymer crystallinity is to calculate the specific enthalpy at melting point using the DSC method and comparing this value to the standard melting heat value of fully crystalline polymer, which is: 326, 202, 290, 207, 226, and 136 (J/g), respectively for POM, HDPE, LDPE, PP, PA, and PET [10, 41-45]. Hence, the degree of crystallinity (Xc), is determined by [10]:

$$X_c = \frac{\Delta H_f}{\Delta H_{fc}} \quad (6)$$

DSC analyzer brand SHIMADZU (DSC-60) is used for this purpose, as shown in Figure 3-a. The technique requires small samples weight between 2-10 mg that is heated and melted in the DSC. The DSC premise is that the amount of energy necessary to heat the sample is measured and compared to the amount of energy necessary to heat a reference sample that does not experience any phase change in the range of interest[8]. DSC technique is used also to measure: glass transition temperature, melting point, and specific heat. SEM scanning, using (VEGA-II) device shown in Figure 3-b, is used to obtain microstructure images which are important to analyze the morphological variation in the plastics due to different procedures of cooling.

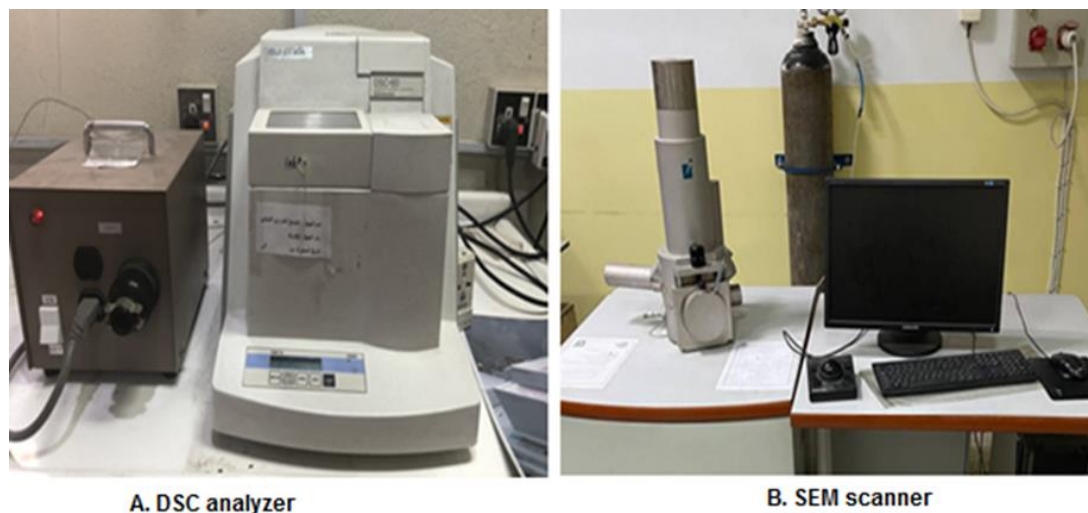


Figure 3. Devices used to analyze and measure thermo-physical properties of plastics

RESULTS AND DISCUSSION

The degree of crystallinity measured by DSC shows different values for each polymer depending on the cooling rate. The degree of crystallinity was the highest when the specimen was cooled in a shut-off oven, then less value when it is cooled in still air and it has the least value when the cooling was in the fridge, as shown in Table 2. This behavior happens because a higher cooling rate leads to lower diffusion and volume fraction thus fewer crystalline portions or lamellae. Note that thermoplastic polymers of simple structural chains such as POM, HDPE, LDPE and PP usually show higher variation in degree of crystallinity comparing to more complex polymers such as PA and PET.

Table 2. Measured values of degree of crystallinity for selected polymers

Polymer	Xc for fridge cooling	Xc for still air cooling	Xc for shut-off oven cooling
POM	0.33	0.42	0.64
HDPE	0.20	0.38	0.70
LDPE	0.13	0.25	0.38
PP	0.14	0.20	0.42
PA	0.08	0.12	0.17
PET	0.09	0.12	0.19

To check this behavior, some SEM images have been taken for certain polymers. For example, the microscopic images of the HDPE specimen shown in Figure 4, for shut-off cooling, clear that the chain structure is regular as linear packed of compact lamellae forms. There are some irregular or random boundary areas whose percentage was around 25% of the total area. Thus it can be estimated that the crystalline ratio is around 75 percent, which is closed to the value obtained from the DSC test. On the other hand, the image of the specimen cooled in the

fridge shows extreme amorphous chains with many interfacial block patterns and vacancies that led to fewer crystalline portions.

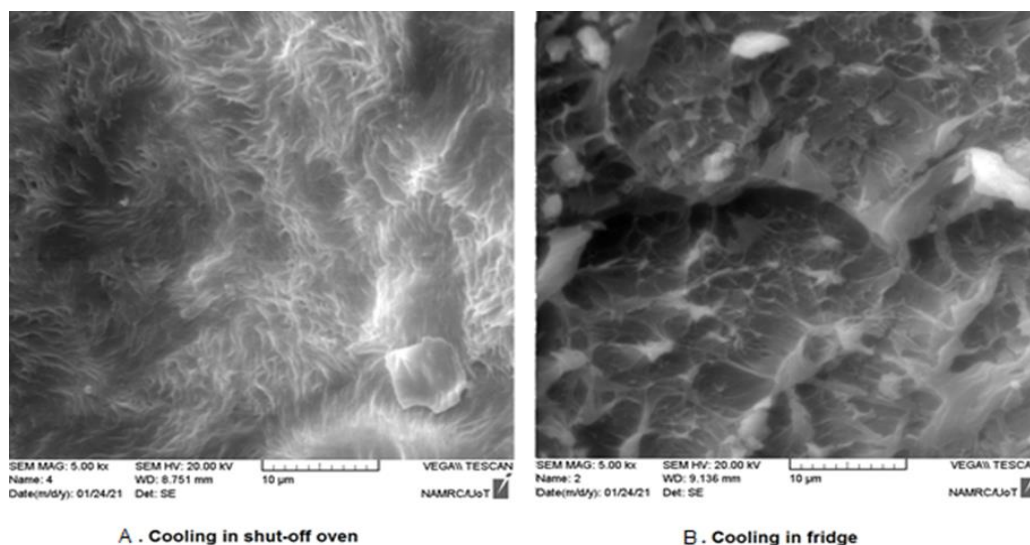


Figure 4. SEM images for HDPE skin showing the morphology of the microstructure

This morphological disparity has a big influence on the thermo-physical properties; such as glass-transition temperature, melting point, and specific heat capacity. The relation of the glass-transition temperature with the degree of crystallinity shows an inverse behavior, as shown in Figure 5. This is because the increase in the crystallinity means a decrease in the crosslinking which enhances molecular mobility thus decreases the glass-transition temperature of the polymer. It is noticed experimentally that the change in the value of T_g between high and low crystalline specimens was in the range of 20-30 °C for high crystalline polymers such as POM and HDPE, while it was between 10-20 °C for medium or low crystalline polymers. In general, the change in the degree of crystallinity from the lower value (due to cooling in the fridge) to the higher value (due to cooling in shut-off oven) leads to a decreasing by 5-15% for T_g . However, theoretical values have higher variation due to the recommended equation used for calculation which is a general empirical formula.

Figure 6 shows the relation of the melting point with the degree of crystallinity. The results show higher melting points for higher crystalline specimens. This behavior is due to the packed lamellae which required extra heat for melting. It is noticed that the change in the value of T_m between high and low crystalline specimens was between 3-6 °C (5-10%). Furthermore, the difference between theoretical and experimental values was less than 4%. Figure 7 shows the relation of the specific heat capacity with the degree of crystallinity. The C_p of higher crystalline specimens is lower than that of less crystalline ones by 100-400 J/kg.K (10-25%). Even though that the theoretical and experimental values have similar behaviors of functionality but they show much higher variation. Anyway, the overall difference between theoretical and experimental values is attributed to the inaccuracy in the mathematical equations used, since they are either extracted from different figures or tables and for limited conditions. On the other hand, a percentage of error could be found in the experimental readings.

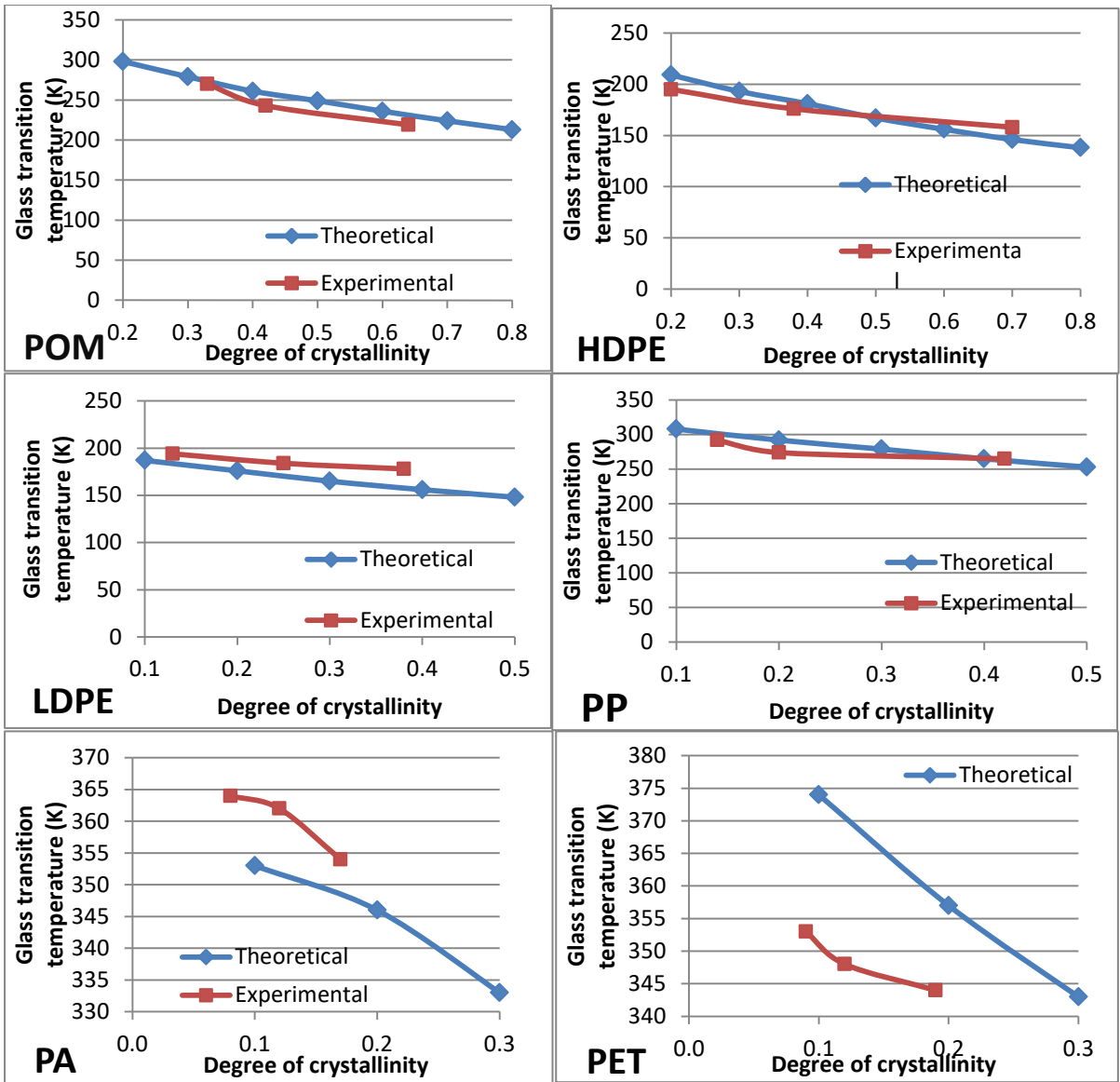


Figure 5. Relation of glass-transition temperature with the degree of crystallinity

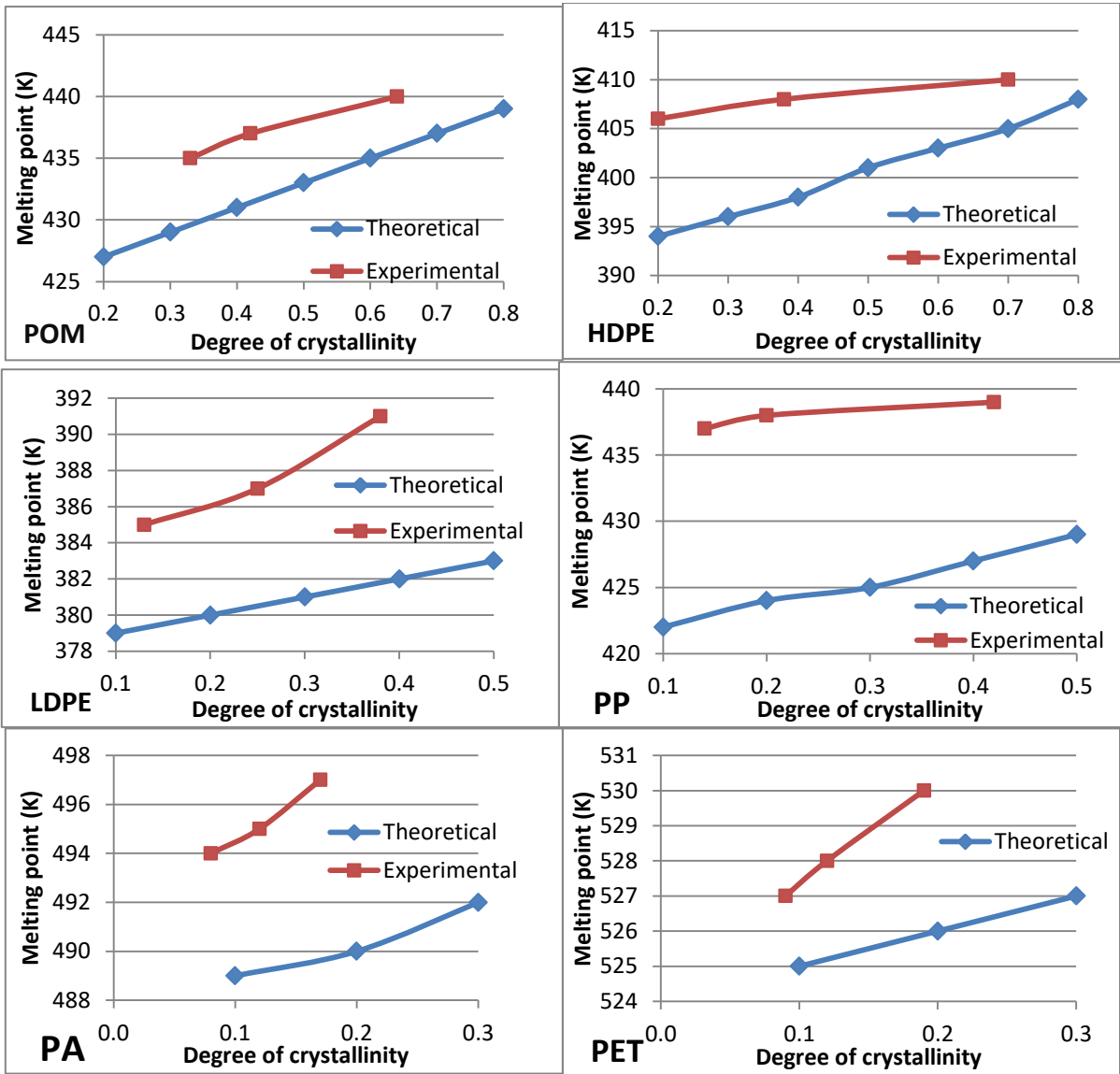


Figure 6. Relation of melting point with the degree of crystallinity

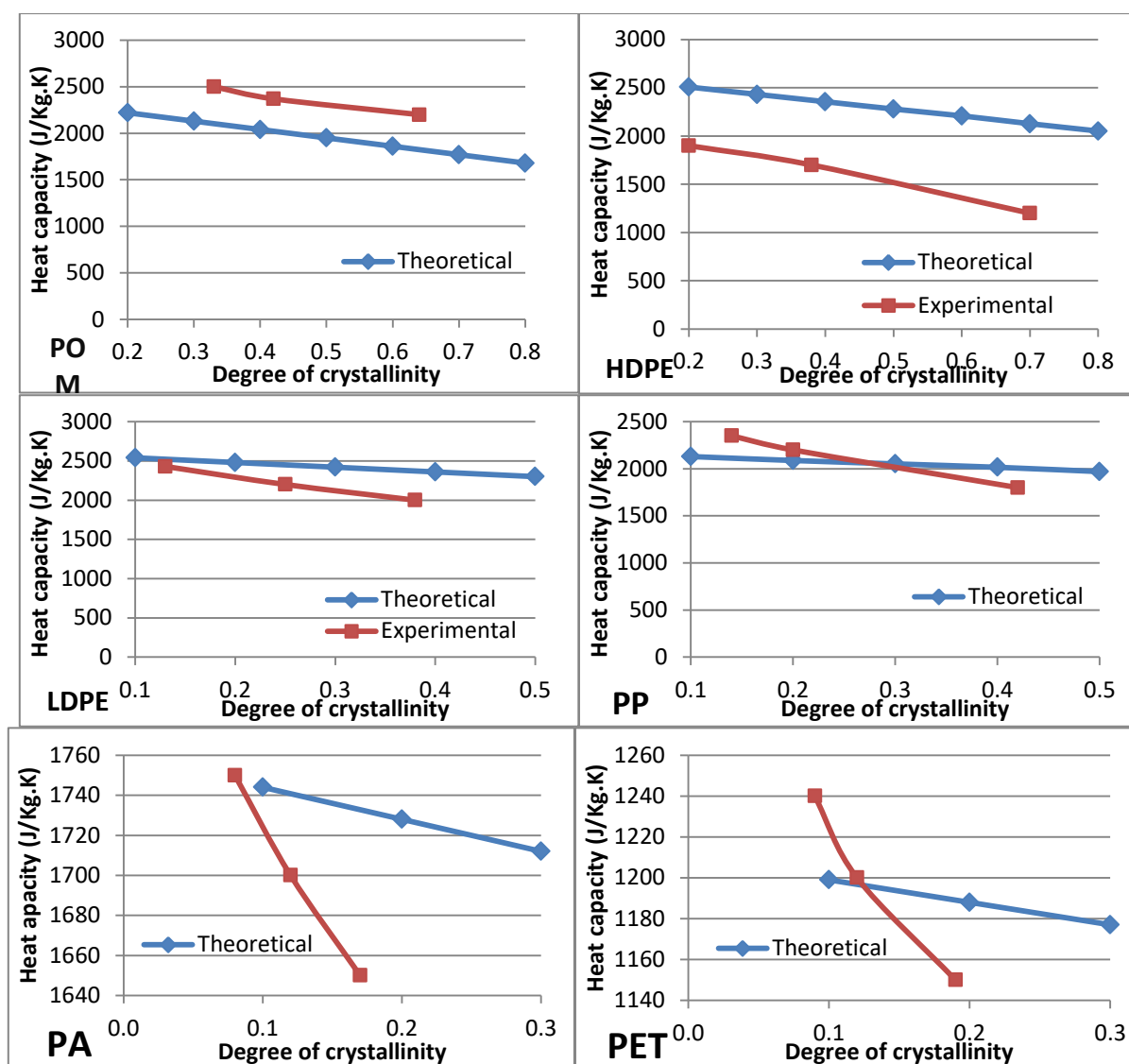


Figure 7. Relation of specific heat capacity with the degree of crystallinity

CONCLUSION

This study shows the relationship between the degree of crystallinity of selected polymers with the thermo-physical properties. Theoretical values, as well as experimental data, were both behave similarly, where the results show that by increasing the degree of crystallinity the melting point have increased, while glass-transition temperature and specific heat capacity have decreased. The following details have been concluded;

- Thermoplastic polymers of simple structural chains such as POM, HDPE, LDPE and PP usually show higher variation in degree of crystallinity comparing to more complex polymers such as PA and PET.
- The cooling rate has a big impact on the degree of crystallinity for produced samples, where slow cooling rate leads to a high degree of crystallinity due to sufficient time for crystallization to take place. On the other hand, high cooling rate reduces polymer crystallinity.
- The degree of crystallinity shows direct effects on the thermo-physical properties of thermoplastics. Where, both theoretical values as well as experimental data behave similarly with respect to the physical property.
- In general, the change in the degree of crystallinity from the lower value (due to cooling in the fridge) to the higher value (due to cooling in shut-off oven) leads to a range of variation for each of the following properties: decreasing by 5-15% for T_g; increasing by 5-10% for T_m and decreasing by 10-25% for C_p.

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