THE EFFECT OF CRYSTALLINITY ON THE THERMAL CONDUCTIVITY OF POLYMERS

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Abstract: The aim of this research is investigating the direct effect of crystallinity of thermoplastic polymers on their thermal conductivity values. The study has included many materials, namely: polyoxymethylene (POM), high-density polyethylene (HDPE), low-density polypropylene (LDPE), polypropylene (PP), polyamide (PA) and polyethylene terephthalate (PET). The degrees of crystallinity ranged from high-values (60-70%), mid-values (30-40%) and low-values (10-20%). The work has done theoretically and experimentally. Theoretical work has used mathematical function extracted from reliable empirical relationships. The experimental work has included: manufacturing the specimens; specifying the cooling procedure in order to get the required degree of crystallinity; measuring the coefficient of thermal conductivity for different polymers at various conditions; and finally analyze the data and introduce the experiences obtained from the investigation. In general, theoretical values as well as experimental data were both behave similarly with respect to the variation of thermal conductivity with the degree of crystallinity. The results show that by increasing the degree of crystallinity the thermal conductivity of the polymer has increased by 10-20%.

Keywords: *thermal conductivity, crystallinity, polymer, plastic, heat transfer*

1. Introduction

Polymers have a variety of properties that depend on the field in which they are used, including

physical, mechanical, and chemical properties [1]. The most useful classification of polymers for engineering purposes is based on their thermo-physical reaction. Polymers are known as thermoplastics or thermosets in this scheme. Thermoplastic polymers, as the name implies, melt and flow when subjected to heat and strain. Polyethylene, polystyrene, and nylon are examples of thermoplastic polymers. Crystallinity refers to the degree of structural order in a solid. In a crystalline polymer, the molecules are arranged in a regular, periodic manner. Synthetic polymers are either semi-crystalline or amorphous. The degree of crystallinity has a big influence on physical and mechanical properties [2-4].

Thermal conductivity is one of the most important thermo-physical properties and has an essential impact for many applications, where polymers usually have much lower thermal conductivity than metals or ceramic materials, making them effective as thermal insulators [5]. A few studies have taken into account the linkage between the crystallinity and thermal conductivity of polymers [6-12]. For example, Zarandi M. et al (2012) [7] have studied the effect of crystallinity and irradiation on thermal

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properties of LDPE under different cooling methods. The variation of thermal conductivity (k) of the samples show that when the cooling rate is increased, the percentage of crystallinity is decreased, and the thermal conductivity is decreased as well. Furthermore, Bai L. et al (2018) [10] have studied the effect of crystallinity and molecular chain orientation on the thermal conductivity of polymers. They used poly-L-lactide (PLLA), whose crystallinity and orientation can be adjusted in a wide range. It is found that below T_g , the thermal conductivity of PLLA with different crystallinity increases with temperature and when the temperature is higher than T_g , the thermal conductivity of PLLA with different crystallinity decreases remarkably. It is also demonstrated generally that the thermal conductivity of PLLA increases with the increasing of the crystallinity. These studies involved the crystallinity as an indirect parameter influences on the thermal property of polymer by describing morphological effects or thermal behaviors due to cooling process, chain orientation and crosslinking rather than focusing upon the direct relationship between the degree of crystallinity and the thermal conductivity, as it is proposed in this study. The materials used in the study (POM, HDPE, LDPE, PP, PA and PET) are thermoplastic materials have a range of values of degree of crystallinity.

2. Theoretical Work

Each chosen polymer has an interval of degree of crystallinity (X_c), as shown in Table 1.

Table 1. Degree of crystallinity for selected polymers [1-3, 13, 14]

Polymer	Degree of crystallinity (X_c)
POM	0.2-0.8
HDPE	0.2-0.8
LDPE	0.1-0.5
PP	0.1-0.5
PA	0.1-0.3
PET	0.1-0.3

2.1. Thermal Conductivity

A material's thermal conductivity is an indicator of its ability of the material to conduct heat. The coefficient of thermal conductivity (k) is the express that defines the temperature gradient within this substance, making it an interesting parameter in heat transfer problems. Density, temperature, moisture, porosity, chain composition, degree of crystallinity, impurities molecule size and grain orientation are all variables that can influence a material's thermal conductivity [5]. The coefficient of thermal conductivity of polymers, in particular, behaves differently depending on whether the polymer is thermoplastic or thermosetting, and whether it is below glass transition temperature or above it [9]. The density has a strong effect on thermal conductivity, with higher density materials having higher thermal conductivity. Since increasing the crystallinity leads to an increase in polymer density. As a result, thermal conductivity is heavily influenced by the degree of crystallinity (X_c), where the thermal conductivity of crystalline part (k_c) is greater than that of amorphous one (k_a) [6-10]. Simple mixing rule can be used to combine both crystalline and amorphous regions, as following [8, 11]:

$$k = X_c + (1 - X_c)K_a \quad (1)$$

Since ($k_a < k_c$) by a ratio of (Z) which is less than 1, hence the last equation is rewritten as;

$$K = [(1 - Z)X_c + Z]K_c \quad (2)$$

For selected polymers, the value of (Z) can be derived from references [1-12], as shown in Table 2.

Table 2. Typical values of thermal conductivity for selected polymers [1, 12]

Polymer	k of crystalline structure (W/m. K)	$Z = ka/kc$
POM	0.37	0.8
HDPE	0.52	0.7
LDPE	0.32	0.5
PP	0.22	0.8
PA	0.30	0.9
PET	0.19	0.9

3. Experimental Work

The experimental works have done in the Department of Materials, College of Engineering, Mustansiriyah University. The DSC tests have done in the Laboratory of Packing Materials in Ministry of Industry and Minerals (MOIM). While, the thermal conductivity tests have done in the Laboratory of Materials Research in Ministry of Science and Technology (MOST).

3.1. Materials

The demanded thermoplastic materials were gathered as grains from the local market in this regard. Six thermoplastic materials have been collected: Polyoxymethylene (POM), High Density Polyethylene (HDPE), Low Density Polyethylene (LDPE), Polypropylene (PP), Polyamide (PA), and Polyethylene Terephthalate (PET).

3.2. Manufacturing of the Specimens

The work involved melting the grains in a specific oven brand JRAD, with a thermostat operating up to 260 °C, to create a series of circular specimens with 40 mm diameter and 5 mm thickness (according to ASTM C518 – 04), as shown in Fig. (1) and (2). The time it took for the plastic grains to melt in the oven was between 20 and 25 minutes, starting from room temperature (20-22 °C) and at a steady rate of heat (10 °C/min). The specimen was then cooled

using various techniques to achieve varying cooling speeds and, as a result, different degrees of crystallinity. Cooling can be done in a shut-off oven (with a cooling rate of 1-2 °C/min), in still air (with a cooling rate of 3-5 °C/min), or in a fridge (with a cooling rate of 6-8 °C/min).

Figure 1. Shapes of POM, HDPE, LDPE specimens (4cm diameter and 0.5cm thickness) for k-test

Figure 2. Shapes of PP, PA, PET specimens (4cm diameter and 0.5cm thickness) for k-test.

3.3. Measurements

3.3.1 Degree of crystallinity

Differential scanning calorimetry (DSC) is used in order to obtain the resultant degree of crystallinity for the selected polymers. A SHIMADZU analyzer (DSC-60) is used for this test, as shown in Fig. 3.

Figure 3. DSC analyzer type (SHIMADZU)

The procedure necessitates the use of small samples weighing between 2 and 10 mg that are heated and melted in the DSC analyzer. The DSC approach is assumed that the amount of energy needed to heat the sample is measured and compared to the amount of energy required to heat a reference sample that does not undergo any phase transition in the range of interest [15, 16]. For this purpose, some polymers were grounded into small samples with an average diameter of 2.36 mm or Mesh 8 (shown in Fig. 4 and 5) as required for standard DSC tests.

The common way of calculating polymer crystallinity is by measuring the enthalpy of fusion (ΔH_f) by DSC and comparing it to the reference value of melting heat for fully crystalline polymer (ΔH_c), which is shown in Table 3.

Table 3. Melting heat (heat of fusion) for fully crystalline polymers [17-23]

Polymer	ΔH_c (J/g)
POM	326
HDPE	202
LDPE	290
PP	207
PA	226
PET	136

Hence, the degree of crystallinity (X_c), is given by [1-3]:

$$X_c = \frac{\Delta H_f}{\Delta H_c} \quad (3)$$

Figure 4. Samples prepared for DSC test of (POM, HDPE and LDPE)

Figure 5. Samples prepared for DSC tests of (PP, PA and PET)

3.3.2 Coefficient of thermal conductivity

Lee discs apparatus is used to calculate the coefficient of thermal conductivity. The unit is made up of a chamber and a reader. As shown in Fig. 6, the chamber contains an electric heater and a collection of disks, with the specimen placed between the hot and cold discs. The electric circuit should be turned on before equilibrium is achieved. The reader used sensors attached to a thermometer to record the temperatures on the both sides of the specimen. The reported values have been compensated using a special equation designed specifically for this unit. The general equation that regulates heat transfer in solid materials, on the other hand, is based on a one-dimensional steady-state heat equation (Fourier equation), as [24]:

$$Q = KA \frac{(T_1 - T_2)}{t} \quad (4)$$

Where;

Q = Heat Transfer (W).

k= thermal conductivity (W/m.K).

A= the specimen's cross-sectional area (m²).

t = thickness of the specimen (m).

T1 = surface point reading at the hot side of the specimen (K).

T2 = surface point reading at the cold side of the specimen (K).

Figure 6. Lee discs apparatus

4. Results and Discussions

Since the rate of cooling was different from a sample to another for the same polymeric material, thus it gives a range of degrees of crystallinity. This leads to different thermal conductivity values based on the degree of crystallinity for each sample. The thermal conductivity has the highest value when the specimen was cooled in shut-off oven, then less value when it is cooled in still air and it has the least value when the cooling was in fridge, as shown in Fig. (7-12). This behavior occurs because the increasing of crystallinity means more packed structure, which acts as a shield, restricting the movement of conduction heat transfer from the material's surface to its core. The theoretical values differed than experimental values by less than 10%, and they both behaved similarly. It is worth noting that the rise was linear for theoretical values but curvilinear for experimental values. In both cases, POM and

HDPE show highest influence in the k-value due to wide range of degree of crystallinity. On the other hand, PA and PET show the least influence. In the overall, samples with the highest degree of crystallinity exhibit higher thermal conductivity by 10-20% as compared to samples with the lowest degree of crystallinity. This behavior can be recognized in the previous studies even though they have not referred to the percentage of variation between the degree of crystallinity and the coefficient of thermal conductivity. However, some errors are expected due to the variation in the reference values that extracted from different resources used in this study for both thermal conductivity and melting heat values. On the other hand, a percentage of error could be found in the experimental readings.

Figure 7. Variation of k-value with the degree of crystallinity for POM

Figure 8. Variation of k-value with the degree of crystallinity for HDPE

Figure 9. Variation of k-value with the degree of crystallinity for LDPE

Figure 10. Variation of k-value with the degree of crystallinity for PP

Figure 11. Variation of k-value with the degree of crystallinity for PA

2021

Figure 12. variation of k-value with the degree of crystallinity for PET

5. Conclusions

This study demonstrates for the direct influence of crystallinity on thermoplastic thermal conductivity, where the investigation concluded the following points:

- Theoretical values and experimental data behaved similarly, where the increasing in the degree of crystallinity leads to increase the k-value.
- The increasing in the value of thermal conductivity was 10-20% for samples that show the highest degree of crystallinity comparing to that show the lowest degree of crystallinity.
- However, these findings are limited to pure structure polymers (POM, HDPE, LDPE, PP, PA, and PET).

Acknowledgements

Authors are grateful to all support given by College of Engineering, University of Mustansiriyah for academically supporting.

Conflict of Interest

The authors confirm that the publication of this article causes no conflicts interest.

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2021

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