Comparing Thermal Resistivity between Semicrystalline and Amorphous Polymers

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ABSTRACT

Determining heat transport in semicrystalline and amorphous polymers is the goal of this investigation. The technique uses a twin-needle sensor and is based on ASTM 5334. Because of the technique's dependability, the thermal resistance will be ascertained. Polycarbonate, polypropylene, and polyoxymethylene were the polymers under investigation. The results showed that compared to amorphous polymers, semicrystalline polymers have a reduced thermal resistance. In essence, the distance between energy atomic levels and phonon vibrations was to blame. In a semi-crystalline lattice, the efficiency was higher, particularly for polymers with fewer side functional groups attached. The amount of material surrounding the sensor and the direction of the flow when the polymer is flowing during the extrusion process were two other significant elements that boosted heat transfer. In the end, the approach proved to be reliable and effective, and it helped deepen our understanding of polymers in this area of study.

Overview

Polypropylene (PP) and polyamide (PA), two common polymers, are electrical insulators with limited heat conductivity. Although measurements of thermal conductivity on metals have been made at least from the late eighteenth century, Lees did not create a quantitative technique for researching weak conductors or thermally insulating materials until 1898. [1] Because of the polymer material's ability to insulate heat, current research is more concerned with thermal resistivity (Rho, R) than the widely utilized thermal conductivity measurement.

Additionally, the textile and construction sectors frequently use thermal resistance measurements based on the material's purpose. Units like the R-value (resistance) and the U-value (transmittance) are used in the building sector. Rand U-values rely on the product's thickness even though they are connected to the material's thermal conductivity when employed in insulation. Similar to the Rvalues used in the building sector, the textile industry uses several units, such as the tog and the clo, to represent a material's thermal resistance.

Therefore, for decades polymer materials have been distinguished by a low heat conductivity, or in other terms a high thermal resistivity. Low heat transfer of the polymers is now known to be caused by the great distance separating the valence layer from the layer of conduction-related energy. As stated otherwise, this data represents the distance the atoms should cross so that the energy be

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transferred between them; i.e. along the molecular structure. To comprehend how the atoms function in heat transmission, it is said that each isolated atom contains electron orbitals named energy levels (e.g. s, p, d, f...). These well-defined energy levels are filled by electrons by their quantum numbers. Generally speaking, these atoms create the substance in which they are arranged in layers or mixings of orbitals. These layers' atoms are arranged from lowest to highest energy level.

Furthermore, recall that the highest energy level containing electrons is known as the valence layer. Conversely, the conduction layer is the lowest energy level that does not contain electrons. Heat transfer thus results from the valence layer's electrons crossing up to the conduction layer so enabling the material to transmit a heat flow.

The material will have insulating characteristics, on the other hand, if the gap between the two layers is sufficient and the electrons cannot cross between levels. Polymers are a particularly good example of these qualities. Although their insulated heat transfer, they give a substantial number of advantages. Primarily, employing polymers may decrease the cost, volume, and weight of the gadget. Other useful features include flexibility, resistance to fouling and corrosion, and the ease with which they can be tailored to application needs [2]. Enhancing the thermal conductivity of polymers has been a big difficulty for a long time which is why a comprehensive understanding of the process of heat transfer in polymers is sought.

Heat transfer takes place when thermal energy is exchanged between two physical things. Thermal energy can be defined as a sum of the kinetic energy of atomic movements and the potential energy of the deformation of interatomic bonds [3]. Heat is transmitted from high to low-temperature parts of the material and can occur in three main modes: conduction, convection, and radiation. Conduction is a result of interactions between electrons, vibrating atoms, and molecules. Transferring heat by conduction requires direct contact and happens in all stages of matter.

Convection occurs when a mass of liquid or gas is transported due to density variations or under the influence of external force. Heat transfer via radiation takes place when the body (solid or fluid) is emitting electromagnetic waves as a consequence of its temperature [4] [5]. The main attention of this research is centered on heat transfer in solid-state polymers using conduction mode. The ability of the material to conduct heat can be represented by thermal conductivity λ , which is a coefficient in Fourier's law. The unit of thermal conductivity is W·m-1·K1.

$q = -\lambda \ \partial T \ \partial x \ (1)$

Where q is the heat flux i.e. the amount of thermal energy transferred through a unit of area per unit of time, λ is the thermal conductivity in W·m-1 ·K-1, and $\partial T/\partial x$ is the thermal gradient.

In physics, thermal conductivity is the property of a material's capacity to conduct heat. It appears primarily in Fourier's Law for heat conduction. Thermal conductivity or its inverse thermal resistivity forecasts the rate of energy loss or not release (in watts, W) through a piece of material. In the window building industry "thermal conductivity" is expressed as the U-Factor, which evaluates the rate of heat transfer and tells you how well the window insulates.

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Therefore, the lower the U-factor, the better the window insulates.

Thermal conductivity is temperature-dependent. Other factors that may influence thermal conductivity include pressure, chemical phase, thermal anisotropy, density, magnetic field, and morphology, orientation, additives, impurities, and moisture.

A physical property that characterizes unsteady state heat conduction is called thermal diffusivity α . It describes the ability of a material to transmit a thermal disturbance [8]. In other words, it describes how quickly the heat is propagated in the material during temperature change. Thermal diffusivity is simply related to thermal conductivity by Equation 2. The unit of thermal diffusivity is mm2 ·s-1.

$$\alpha = R \rho \cdot C p; R = 1 \lambda (2)$$

Where α is the thermal diffusivity, ρ is the density of the specimen, and Cp is the specific heat capacity i.e. the amount of energy needed to increase the temperature of one kg of mass by 1 °K. Eventually, R (rho) is the thermal resistivity. Heat is transported via electrons and phonons (waves of lattice displacement). Since polymers are non-metallic substances with no free electrons the heat transfer occurs mainly owing to lattice vibrations [3]. Debye characterized the relationship between heat conductivity and lattice oscillations via Equation 3 [9].

$$\lambda = K \cdot \rho \cdot C p \cdot \nu \cdot l \quad (3)$$

Where K is a dimensionless constant of approximately 0.33, v is the transfer speed for elastic oscillations i.e. the sound speed within the mass material, and l is the free length of elastic oscillations i.e. the atomic distance for amorphous thermoplastic area. According to Equation 3, elements that determine the thermal conductivity of a polymer are the type and strength of the bonds positioned in the direction of heat transfer. Besides of these equations, also to compute the thermal resistivity (R) value Equation 4 by IEEE 442 is suggested as follows;

$R = 4\pi \ (T \ 2 \ -T \ 1) \ [2.303q \ \cdot \log \ (\ t \ 2 \ t \ 1 \)] \ (4)$

Where T1 is the temperature measured at some arbitrary elapsed time, T2 is the temperature measured at another arbitrary elapsed time, q is the heat flux dissipated per unit of length, t1 is the elapsed time at which a temperature measurement was recorded and t2 is the elapsed time at which another temperature measurement was recorded. The analytical model (Eq. 4) used to evaluate thermal resistivity was derived assuming that a line heat source of unlimited length dissipates heat in an infinite medium. The purpose of this study was to evaluate the influence of the chemical structure and morphology of different polymers on heat transfer, as well as to examine how the dimensions of the sample influence the thermal resistivity value of the polymer. This will expand the knowledge of heat transfer mechanisms in polymers.

Materials and methods

Samples required to carry out the research work were two semi-crystalline polymers and one amorphous polymer as follows;

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Polycarbonate

Polycarbonate Tecanat (PC) is a transparent, thermoplastic polymer. It can be characterized by high stiffness and high impact resistance. Polycarbonate is amorphous under normal processing conditions. The literature value of thermal resistivity at 23°C falls into the range from 5.26 to 4.54 m·K·W-1 and thermal diffusivity at 25°C equals 0.14 mm²·s-1 [10].



Fig. 1: Chemical structure of polycarbonate

Polypropylene

Polypropylene Moplen HP556E (PP) is a thermoplastic polymer with a regular and flexible structure that favors crystallization. Most commercial polypropylene has an intermediate degree of crystallinity. The literature estimate of thermal conductivity at 23°C falls within a range from 10 to 4.54 m·K·W-1 [11] and thermal diffusivity at 25°C equals 0.096 mm²·s-1 [12].



Fig. 2: Chemical structure of polypropylene

Polyoxymethylene

Polyoxymethylene or polyacetal Resal Yuncon M25 (POM) is a rigid, hard, thermoplastic polymer. The white hue of the material stems from a high level of crystallinity. The published value of thermal conductivity at 23 °C falls into the range from 4.54 to 4.16 m·K·W-1 for homopolymer, and from 4.35 to 3.33 m·K·W-1 for copolymer [13]. Thermal diffusivity equals 0.18 mm²·s-1 [14].

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Fig. 3: Chemical structure of polyoxymethylene

The methodology employed in this research was based on the transient method of the hot wire. The framework of the method is based on the notion that the temperature of a thin hot wire rises exponentially when a constant power (heat flow) is applied as it is dragged in the center of a sample of infinite length. This allows for determining the thermal conductivity of the material based on the heat flow (power and intensity), the properties of the heating wire (length, radius and resistance), and the growth of temperature in the wire in a particular time [15].

ASTM D5334 and IEEE 442 gather and refine this technique. Both American's standard D5334 and IEEE 442 are applicable for all sorts of specimens, although this test method is acceptable only for isotropic materials, usually [16] [17]. This test method is suited to dry materials throughout a wide temperature range from below 0 to more than 100 °C, depending on the compatibility of the thermal needle probe construction to temperature extremes. This approach may also be utilized for specimens containing moisture. However, care must be taken to prevent significant inaccuracy from the redistribution of water due to thermal gradients arising from the heating of the needle probe, and the phase change (melting) in specimens with temperatures higher than their melting point. Both of these mistakes can be decreased by adding less total heat to the specimen either through minimizing the power applied to the needle probe and/or minimizing the heating period of the measurement [16] [17].

To produce a trustworthy thermal dataset, a simple laboratory technique needs to be adapted and depicted, according to existing standards and owing to neither the manufacturer nor the standard present whatever approach to research on polymers. The present work describes the first step towards the establishment of a laboratory process to produce a reliable, accurate, and rapid thermal properties dataset in polymers, taking into account the current accepted standard [18] is based on the measurements were performed using dual-needle sensor, and measurements were acquired by reader-logger.

The dimensions of the sensor are; 1.3 mm diameter, 3 cm long and 6 mm spacing between the two needles. SH-1 thermal sensor evaluates the three thermal characteristics by employing the dual needle heat pulse method (DNHP). For each type of polymer 8 samples with different dimensions were measured (Table 1). Data was collected with two different heat flow directions; these depended on sensor orientation, which was in regard to the direction of polymer flow during extrusion, i.e. perpendicular to the direction of polymer flow during extrusion and parallel to the direction of

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polymer flow during extrusion (Figure 4).



Fig. 4: Samples set up, heat flow measurement, and sensor location. Arrows indicate the polymer flow direction. A = perpendicular; B = parallel.

All measurements were carried out at room temperature, around 25°C. Five measurements were taken for each sample. The read time was set for 2 minutes and the delay between successive measurements was 45 minutes. The reader logger was utilized in high-power mode to gather all the data. Two distinct dual-needle sensors were utilized to take measurements, so the sensor's dependability and accuracy were validated as well.

	Perpendicular		Parallel		
Sample	Height	Diameter	Height	Diameter	
	(mm)				
PC		25	25		
	35	15	15	50	
		10	10		
	40	51	40	51	
PP		25	25		
	35	15	15	50	
		10	10		
	40	51	40	51	
РОМ		25	25		
	35	15	15	50	
		10	10		
	40	51	40	51	

Table 1: Sampling design for the three polymers used. PC=polycarbonate; PP= polypropylene,and POM=polyoxymethylene

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Results & Discussion

Thermal resistance demonstrated a propensity to increase with decreasing height (heat flow parallel to the direction of polymer flow during extrusion) or diameter (heat flow perpendicular to the direction of polymer flow during extrusion) of the sample. Samples with the lowest diameter or the smallest height indicate considerable growth in their thermal resistance value. The reason for this phenomenon is probably due to the heat escaping from polymer samples.

The amount of ambient material around the sensors was too small which allowed the heat to escape easily outside the polymeric sample. It provided an abnormal behaviour of the heat transport inside the sample. Neither the standards nor manufacturer instructions are clear about the quantity of material in terms of polymer materials which must be allowed parallel to the sensor in all directions because the sensor emits heat pulses, otherwise, the error will arise.

When the direction of heat flow was perpendicular (Figure 5) the values of thermal resistance for the samples with dimensions; 35 mm high, 25 mm diameter, and 40 mm high, 51 mm diameter were similar but the smaller (35 mm high, 25 mm diameter) showed somewhat lower values. The difference can be attributed to different initial temperatures before thermal measurements. Polycarbonate samples with the above-mentioned size revealed the biggest difference in thermal resistivity. The initial temperatures of both samples were almost the same; consequently, a possible reason would be the use of various sensors, with a non-accurate calibration.



Fig. 5: Relationship between thermal resistivity and diameter samples on polymer flow perpendicular direction. Height = 35 mm.

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When the direction of heat flow was parallel (Figure 6) the values of thermal resistivity for the samples with dimensions; 25 mm high, 50 mm diameter 40 mm high, and 51 mm diameter were similar, as well. Heat transfer behaviour for the whole of the samples was exactly equal, i.e. reducing the R-value when the height grew.

Comparing values of thermal resistivity for the samples with the biggest dimensions in different directions of heat flow, observed that generally values were very similar but, in the direction, perpendicular to the direction of polymer flow during extrusion, values of thermal resistivity were few higher. Minor resistivity results might be related to the fact that during extrusion polymer chains were partially aligned in the direction of polymer flow because of the tensile stress that was induced while forcing polymer through a nozzle [19]. The orientation of polymer chains provided an increase of thermal diffusivity, i.e. an increase of heat transfer through the sample in the direction of polymer flow during extrusion because longer phonon meant free routes were supplied parallel to the direction of chain alignment. Strong covalent connections along polymer chains carry heat more efficiently than physical interactions (like van der Waals force for instance) perpendicular to the backbone.

Comparing different polymer samples, the highest levels of resistivity were reported for polycarbonate samples and the lowest for polyoxymethylene samples. Probably the most important component which affects heat transmission is degree of crystallinity. The value of thermal diffusivity increased with increasing degree of crystallinity; hence thermal resistivity value dropped. Disorder and lack of regularity improves the effectiveness of phonon scattering in the heat transfer mechanism and hence increase heat resistance; i.e. the material becomes more insulating.



Fig. 6: Relationship between thermal resistivity and diameter samples on polymer flow parallel direction. Diameter = 50 mm

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Polycarbonate is amorphous and has a high-disorder structure which results in higher thermal resistance and lower thermal diffusivity than found for highly crystalline polyoxymethylene. Polypropylene generally has an intermediate degree of crystallinity which is why its values of thermal resistivity were in between of those measured for polycarbonate and polyoxymethylene (Figures 5 and 6).

Another aspect that can influence the heat transport mechanism in investigated samples is the size of side groups grafted to the polymer backbone. The higher the size of functional groups, the bigger the disorder consequently thermal resistivity becomes. For instance, methyl (CH3) groups attached to the polypropylene main chain increase the disorder and increase thermal resistivity compared to polyoxymethylene backbone with no side groups.

However, obtained values of thermal resistivity for all polymers by both standards slightly differ from the values found in the literature and they are greater. Nonetheless, authors such as Radhakrishnan et al. and Karger-Kocsis found the same thermal resistance values in polypropylene filled with silica [20]. The reason can be the use of different methods to compute the thermal characteristics of polymers. Furthermore, the morphology of the samples used in the literature was not defined, and this could be a crucial aspect of these values.

Moreover, crystallinity has a tremendous impact on heat conduction. Thermal characteristics, especially thermal diffusivity rely on the degree of crystallinity.

Amorphous polymers with high disorder have higher thermal resistance than crystalline ones because disorder and lack of regularity improve the efficacy of phonon scattering [14]. Hence, increasing crystallinity increases the heat transfer as occurs in the study samples, where a controlled cooling process of the polymer gives better crystal formation and orientation [20] [21].

Most relevant are the morphological and basic molecular features of the polymers. Strong covalent bond stresses between chain atoms that create polymer chains carry heat more effectively than physical interactions between chains, such as the van der Waals force. Thus, thermal resistance is lower along the polymer backbone than perpendicular to it [22] [23].

Consequently, the orientation of polymer chains generated for example by stretching of the material improves heat conductivity in the direction of chain alignment. Thermal resistivity is lower parallel to the stretching direction than perpendicular to it [22]. More extended chain morphology results in reduced thermal resistivity since it provides longer phonons, hence it indicates free pathways [24]. Defects in polymer structures such as chain ends, entanglements, random orientation, voids, and impurities operate as stress concentration spots and phonon scattering centers [25].

Rod-like polymers that are characterized by great stiffness of polymer chains display a decrease in thermal resistivity due to the tendency for crystallization and therefore chain orientation [26] [27].

Hence, the merely geometrical effect is self-evident. Although, it precisely applies in the case of a fully uniform distribution of identical tie molecules [22] [23].

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As noted earlier, other elements that might influence the order of polymer structure and thus heat flux transfer are the amount and size of the groups grafted to the main chain of the polymer. The effect generated by the inhomogeneity of the micromorphology of the semicrystalline layers sample must be appreciated as folded-chain blocks are not perfectly equal in non-length, width, and orientation The same applies to the amorphous layer sandwiched between the blocks and to the number, length, and lateral displacement of the fixed ends of tie molecules. Moreover, the nonuniform distribution of tie molecules among the amorphous layers and within every single layer produces a wide variation in the cross-section area per molecule and consequently in heat flux transfer, even if the tie molecules are of the same length [22] [28]. Therefore, the rule to drive the heat transmission would be applied to the amount and size of the functional groups. Hence, an increasing number of distinct groups are put along the polymer chain as well.

Conclusions

In summary, both the chemical structure and shape of the sample have had a substantial impact on thermal properties.

Probably, the most crucial aspect has been the degree of crystallinity of the sample. Hence, higher degrees of crystallinity have determined lower values of thermal resistivity.

In addition, one of the variables that has demonstrated greater relevance to the thermal properties of the material has been the dimension of the sample. The amount of material as ambient boundary conditions around the sensor has shown that it must be tiny; otherwise, an error may occur and the measured results may be skewed. This suggests that the value of the thermal resistivity (R) has demonstrated a definite tendency to decrease when the diameter or height of the sample rises. Therefore, the samples with larger diameters or heights have had lower thermal resistance values, especially when the heat does not escape beyond the sample.

Finally, the Dual thermal needle probe test utilized in this study is a rapid and efficient approach to obtain thermal resistivity values in particular and thermal properties of polymer materials in general. Although the study of the thermal properties of different polymer samples with different dimensions has allowed us to complement the investigations on the mechanism of transfer of heat in polymers, however, additional investigations still have to be done that allow us to understand in a more extensive.

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