

An approaching to understand the heat transfer in polymers

Carles M. Rubio¹, Maria Marcinek², Lorena Rodríguez³

^{1,3} Advanced Technology Centre Eurecat, Cerdanyola del Valles, Spain

² University of Technology, Lodz, Poland

*Corresponding author: carles.rubio@eurecat.org

Abstract

The aim of this work is to determine the heat transfer in semicrystalline and amorphous polymers. The method is based on ASTM 5334 using a double needle sensor. The thermal diffusivity will be determined due to its reliability in the used technique. The polymers studied were polycarbonate, polypropylene and polyoxymethylene. The obtained results indicated that the semicrystalline polymers transferred the heat flow better than the amorphous polymers. This was because of the vibrations of the phonons were more efficient in semicrystalline lattice, especially for polymers which had few attached side functional groups. Other important factors contributing to improved heat transfer were the amount of material around the sensor and the orientation of the flow when the polymer is flowing during extrusion process. This fact contributed to the directionality of the heat pulse through the polymer matrix. Eventually, the method was efficient and robust, and increased the knowledge of polymers in this line of research.

Keywords: Polymer, thermal properties, crystallinity, amorphous, thermal diffusivity

1. Introduction

Nowadays there is a major interest in the field of heat transfer devices among scientific researchers, manufacturers and developers. Applications include air-conditioning, refrigeration, general power systems, heat exchangers, power conversion devices, electronics for instance. The use of metal materials, such as steel or aluminum, in constructing heat-exchanging appliances is usually connected with operating limitations. That is why researchers started looking for alternative materials, one of which are polymers. Even though polymers are characterized by low thermal conductivity, they offer substantial number of advantages instead. Primarily, using polymers may decrease cost, volume and weight of the device. Other useful properties include flexibility, resistance to fouling and corrosion and the ease with which they can be tailored to application needs [1].

Enhancing thermal conductivity of polymers has been a huge challenge for a certain time which is why robust understanding of mechanism of heat transfer in polymers is desired.

Heat transfer takes place when thermal energy is exchanged between two physical objects. Thermal energy can be defined as a sum of kinetic energy of atomic motions and potential energy of distortion of interatomic bonds [2]. Heat is transferred from high to low temperature areas of the material and can occur in three different 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 occurs in all phases of matter. Convection takes place when a mass of liquid or gas is transported due to density differences or under the influence of external force. Heat transfer by radiation takes place when the body (solid or fluid) is emitting electromagnetic waves as a consequence of its temperature [3] [4]. The main focus on this research is put on heat transfer in solid state polymers by means of conduction.

Ability of the material to conduct heat can be described by thermal conductivity λ , which is a coefficient in the Fourier's law. The unit of thermal conductivity is $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.

$$q = -\lambda \frac{\partial T}{\partial x} \quad (1)$$

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 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, and $\partial T/\partial x$ the thermal gradient.

Thermal conductivity is temperature dependent. Other factors that may influence thermal conductivity include pressure, chemical phase, thermal anisotropy, density, magnetic field, morphology, orientation, additives, impurities, moisture [5] [6].

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 [7]. 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 $\text{mm}^2 \cdot \text{s}^{-1}$.

$$\alpha = \frac{\lambda}{\rho \cdot C_p} \quad (2)$$

Where α is the thermal diffusivity, ρ is the density of the specimen, and C_p is the specific heat capacity i.e. the amount of energy needed to increase the temperature of 1 one kg of mass by 1 °K.

Heat is transferred by electrons and phonons (waves of lattice displacement). Since polymers are non-metallic substances with no free electrons the heat transfer occurs mainly due to lattice vibrations [2]. Debye described the relationship between thermal conductivity and lattice oscillations by Equation 3 [8].

$$\lambda = K \cdot \rho \cdot C_p \cdot v \cdot l \quad (3)$$

Where K is a dimensionless constant around 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 region.

According to Equation 3, factors that influence thermal conductivity of a polymer are type and strength of the bonds located in the direction of heat transfer.

The goal of this study was to observe the influence of chemical structure and morphology of different polymers on heat transfer, as well as to determine how the dimensions of the sample influence the thermal diffusivity value of the polymer. This would provide better understanding of heat transfer mechanisms inside polymers.

2. Methodology

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

Polycarbonate

Polycarbonate (PC) is a transparent, thermoplastic polymer. It can be characterized with high stiffness and high impact-resistance. Polycarbonate is amorphous under normal processing conditions. The literature value of thermal conductivity at 23°C falls into range from 0.19 to 0.22 $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and thermal diffusivity at 25°C equals 0.14 $\text{mm}^2 \cdot \text{s}^{-1}$ [9].

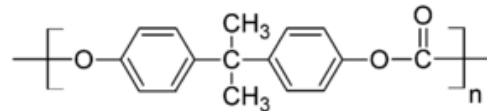


Fig. 1 Chemical structure of polycarbonate

Polypropylene

Polypropylene (PP) is a thermoplastic polymer with a regular and flexible structure which favors crystallization. Most of commercial polypropylene have intermediate degree of crystallinity. The literature value of thermal conductivity at 23°C falls into range from 0.10 to 0.22 $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ [10] and thermal diffusivity at 25°C equals 0.096 $\text{mm}^2 \cdot \text{s}^{-1}$ [11].

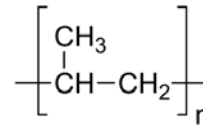


Fig. 2 Chemical structure of polypropylene

Polyoxymethylene

Polyoxymethylene or polyacetal (POM) is a rigid, hard, thermoplastic polymer. The white color of the material comes from high level of crystallinity. The literature value of thermal conductivity at 23°C falls into range from 0.22 to 0.24 $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for homopolymer, and 0.23-0.3 $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for copolymer [12]. Thermal diffusivity equals 0.18 $\text{mm}^2 \cdot \text{s}^{-1}$ [13].

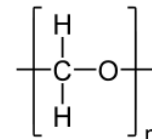


Fig. 3 Chemical structure of polyoxymethylene

The methodology used in this research was based on ASTM D5334. American's standard D5334 is applicable for all type of specimens, yet this test method is suitable only for isotropic materials, usually [14]. In order to obtain a reliable thermal dataset, a simple laboratory methodology needs to be adapted and depicted, according to existing standards and owing to neither the manufacturer nor the standard present whatever methodology to investigate on polymers. Also, since

physicists, chemists, engineers and other current users are demanding these kinds of data for their different applications. The present work describes the first step towards the development of a laboratory procedure to obtain reliable, accurate and rapid thermal properties dataset in polymers, taking into account the current accepted standard [15] is based on.

The measurements were taken using dual-needle sensor, and measurements were collected through 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 measures the three thermal properties by employing the dual needle heat pulse method (DNHP). Although three thermal properties could be measured, only thermal diffusivity will be assessed because of reliability of the method.

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 polymer flow during extrusion (Figure 4).

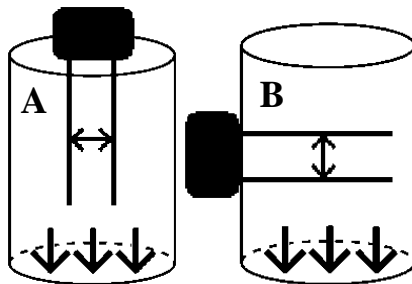


Fig. 4 Samples set up, heat flow measurement and sensor location. Arrows indicate the polymer flow direction. A = perpendicular; B = parallel.

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 interval between successive measurements was 45 minutes. The reader logger was used in high power mode to gather all the data. Two different dual-needle sensors were used to take measurements, thus the sensors reliability and accuracy were verified as well.

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

Sample	perpendicular		parallel	
	Height	Diameter r (mm)	Height	Diameter r
PC	35	25	25	50
		15	15	
		10	10	
PP	40	51	40	51
		25	25	
		15	15	
POM	35	10	10	50
		15	15	
		51	40	

3. Results

Both thermal conductivity and thermal diffusivity showed tendency to decrease 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 smallest diameter or the smallest height exhibit major drop in both values of thermal diffusivity. The reason of this behavior is probably due to the heat escaping from polymer samples. The amount of ambient material around the sensors is too small which allows the heat to escape easily outside polymeric sample. ASTM 5334 and manufacturer guide are not 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 occur.

For the direction of heat flow perpendicular (Figure 5) the values of thermal diffusivity 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 slightly higher values. The difference might be owing to different initial temperatures prior to thermal measurements. POM samples with above-mentioned dimensions exhibited the biggest difference in thermal diffusivity. The initial temperatures of both samples were practically the same so the possible explanation might be the use of different sensors.

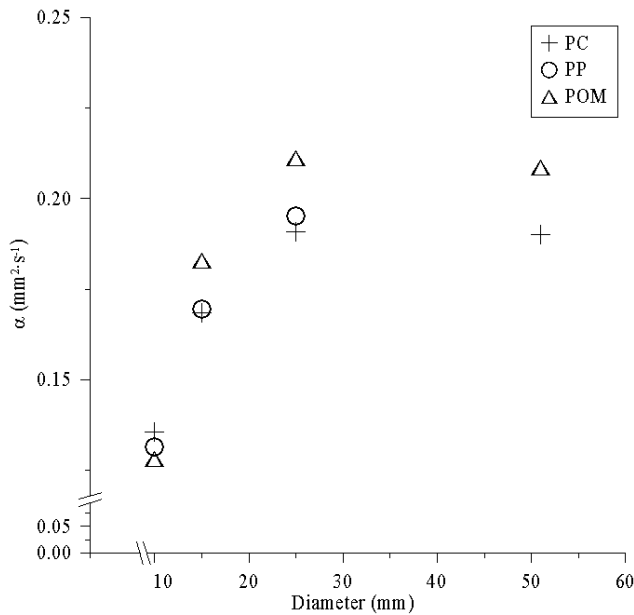


Fig. 5 Relationship between thermal diffusivity and diameter samples on polymer flow perpendicular direction.

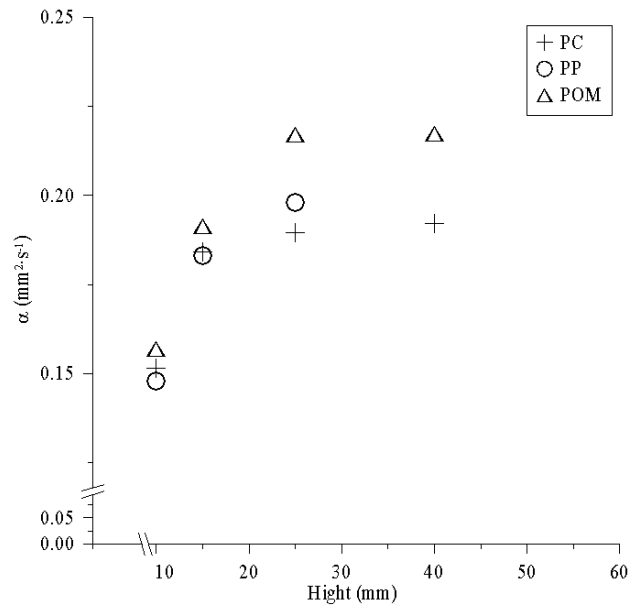


Fig. 6 Relationship between thermal diffusivity and diameter samples on polymer flow parallel direction.

For the direction of heat flow parallel (Figure 6) the values of thermal diffusivity for the samples with dimensions; 25 mm high, 50 mm diameter and 40 mm high, 51 mm diameter were similar as well. Heat transfer behavior on the whole of the samples was exactly equal, i.e. increasing the value when the diameter increased.

Comparing values of thermal diffusivity for the samples with biggest dimensions in different directions of heat flow, observe that generally values are very similar but in the direction parallel to the direction of polymer flow during extrusion, values of thermal diffusivity are few higher. The increased values may be attributed to the fact that during extrusion polymer chains are partially aligned in the direction of polymer flow because of the tensile stress which is created during forcing polymer through a nozzle [16]. The orientation of polymer chains increases heat diffusivity in the direction of polymer flow during extrusion because longer phonon mean free paths are provided parallel to the direction of chain alignment. Strong covalent bonds along polymer chains transport heat more effectively than physical interactions (as van der Waals force for instance) perpendicular to the backbone.

Comparing different polymer samples, the highest values of diffusivity were obtained for POM samples and the lowest for PC samples. Probably the most important factor which influences heat transport is degree of crystallinity. Both values of thermal conductivity and diffusivity increase with increasing degree of crystallinity. Disorder and lack of regularity increases the effectiveness of phonon scattering in heat transfer mechanism and thus decreases heat conductivity. PC is amorphous and has a high-disorder structure which leads to lower thermal conductivity and diffusivity than obtained for highly-crystalline POM. PP usually has intermediate degree of crystallinity which is why its values of thermal diffusivity are in between of those measured for PC and POM. Another factor that may influence heat transport mechanism in examined samples is the size of side groups attached to polymer backbone. The bigger the size of bulky groups, the bigger the disorder and thus decreased thermal diffusivity. For instance, methyl (CH_3) groups attached to polypropylene main chain increase the disorder and decrease thermal diffusivity compared to POM backbone with no side groups.

However, obtained values of thermal diffusivity for all polymers by ASTM D5334 differ from the values found in literature and these are much higher. The reason might be the use of different method to evaluate thermal properties on polymers. Furthermore, the morphology of the samples used in literature was not defined, and this could be a crucial point on these values.

Moreover, crystallinity have a great impact on heat conduction. Thermal properties, specially thermal diffusivity depends on the degree of crystallinity. Amorphous polymers with high-disorder have lower thermal diffusivity than crystalline ones because disorder and lack of regularity increases the effectiveness of phonon scattering [13].

Strong covalent bonds that build polymer chains transport heat more effectively than physical interactions between chains, such as the van der Waals force. Thus, thermal conductivity is higher along the polymer backbone than perpendicular to it [17].

Consequently, orientation of polymer chains caused for example by stretching of the material increases heat conductivity in the direction of chain alignment. Thermal conductivity is higher parallel to stretching (orientation) direction than perpendicular to it [17]. More extended chain morphology results in higher thermal conductivity because it provides longer phonon mean free paths [18]. Defects in polymer structure such as chain ends, entanglements, random orientation, voids and impurities act as stress concentration points and phonon scattering centers [19]. Rod-like polymers that are characterized with great stiffness of polymer chains exhibit increase in thermal conductivity due to tendency for crystallization and therefore chain orientation [20] [21].

Other factors that can influence the order of polymer structure and thus heat conductivity are amount and size of side groups. The bigger the size of bulky groups attached to polymeric chain, the bigger the disorder and thus decreased the thermal diffusivity. The same rule applies to the amount of the side groups. Increasing number of different groups placed along polymer chain as well as branching reduces regularity of the structure and decreases the quantity of heat transferred [22].

4. Conclusions

In summary, both chemical structure and morphology of the sample have had a great impact on thermal properties. Probably, the most decisive factor has been a degree of crystallinity of the sample. High degrees of crystallinity lead to high values of thermal diffusivity.

Moreover, dimensions of the sample have had significantly influence on thermal properties. The amount of ambient material around the sensor can not be too

small, otherwise the error can occur and the measured values might be distorted. The value of thermal diffusivity α have a tendency to decrease with decreasing diameter or height of the sample. Samples with the smallest diameter or height have exhibited major drop in values of thermal diffusivity due to heat escaping outside the sample.

Process of extrusion orientated polymer chains in the direction of polymer flow and therefore heat diffusivity was increased in the direction of chain alignment, i.e. parallel to direction of polymer flow during extrusion.

Dual thermal needle probe test used in this study has been a fast and efficient method to obtain values of thermal diffusivity of polymeric materials. Although, the study of thermal properties of different polymeric samples with different dimensions enabled greater understanding of heat transfer mechanism in polymers, yet still a further deal of research should be done to fully understand this aspect of polymer science.

Acknowledgments

The authors thank to European Erasmus Program and the ACCIO Program from Government of Generalitat of Catalonia to grant this research project. Also, authors appreciate the Advanced Technology Centre Eurecat for its support in this research.

References

- [1] C. T'Joel, Y. Park and Q. Wang, "A review on polymer heat exchangers for HVAC&R applications", *Int. J. of Refrigeration*, 32, 5, 2009, pp. 763–779.
- [2] D. R. Askeland, P. P. Fulay and W. J. Wright *The science and engineering of materials*, Sixth Edition, Cengage Learning Inc., 2010.
- [3] J. Vlachopoulos and D. Strutt, "Basic heat transfer and some applications in polymer processing", *Plastics Technician's Toolbox*, 2, 2002, pp. 21-33.
- [4] J. R. Howell, R. Siegel and M. Pinar Mengüç, *Thermal radiation heat transfer*, CRC Press Taylor & Francis Group 5th Edition, Boca Raton, Florida USA, 2010.
- [5] D. Poulikakos, *Conduction heat transfer*, Prentice Hall, 1994.
- [6] J. Bicerano, *Prediction of polymer properties*, revised and expanded Third Edition, New York, 2002.

- [7] J. Blumm, S. S. Lemarchand and J.B. Henderson, "A new method for the temperature calibration of laser flash systems, in Proceed. 26th Int. Thermal Conductivity Conf. And 14th Int. Thermal Expansion Symp., R. B. Dinwiddie and R. Mannello (Eds.) Cambridge Massachusetts USA, 2001.
- [8] R. Klein, Laser welding of plastics, First Ed., Wiley-VCH Verlag GmbH & Co. KGaA, 2011.
- [9] X. Zhang, W. Hendro, M. Fujii, T. Tomimura and N. Imaishi, "Measurements of the Thermal Conductivity and Thermal Diffusivity of Polymer Melts with the Short-Hot-Wire Method", *J. Thermophysics*, 23, 4, 2002, pp. 1077-1090.
- [10] B. Weidenfeller, M. Höfer and F. R. Schilling, "Thermal conductivity, thermal diffusivity, and specific heat capacity of particle filled polypropylene", *Composites Part A: Applied Science and Manufacturing*, 35, 4, 2004, pp. 423-429.
- [11] G. W. Lee, M. Park, J. Kim, J. I. Lee and H. G. Yoon, "Enhanced thermal conductivity of polymer composites filled with hybrid filler", *Composites Part A: Applied Science and Manufacturing*, 37, 5, 2006, pp. 727-734.
- [12] S. Lüftl, P. M. Visakh and S. Chandran *Polyoxymethylene Handbook: Structure, Properties, Applications and their Nanocomposites*, Wiley Scrivener Publishing LLC, 2014.
- [13] C. L. Choy, F. C. Chen and W. H. Luk, "Thermal conductivity of oriented crystalline polymers", *J. Polymer Science Part B: Polymer physics*, 18, 6, 1980, pp. 1187-1207.
- [14] American Standard for Testing Materials, Standard Test Method for determination of thermal conductivity of soil and soft rock by thermal needle probe procedure D-5334-08, 2008.
- [15] C. M. Rubio, "A Laboratory Procedure to Determine the Thermal Properties of Silt Loam Soils Based on ASTM D 5334", *Applied Ecology and Environmental Sciences*, 1, 4, 2013, pp. 45-48.
- [16] E. A. Algaer, M. Alaghemandi, M. C. Böhm and F. Müllert-Plathe, "Anisotropy of the thermal conductivity of stretched amorphous polystyrene in supercritical carbon dioxide studied by reverse nonequilibrium molecular dynamics simulations", *J. Physical Chemistry B*, 113, 44, 2009, pp. 14596-14603.
- [17] A. Peterlin, "Bond rupture in highly oriented crystalline polymers", *J. Polymer Science Part B: Polymer physics*, 7, 7, 1969, pp. 1151-1163.
- [18] C. L. Choy, F. C. Chen and E. L. Ong, "Anisotropic thermal expansion of oriented crystalline polymers", *Polymer*, 20, 10, 1979, pp. 1191-1198.
- [19] M. He, J. Ge, Z. Li, X. Feng, X. Wang, H. Lu, Y. Yang and F. Qiu, "thermopower enhancement in conducting polymer nanocomposites via carrier energy scattering at the organic-inorganic semiconductor interface", *Energy & Environm. Sci.*, 5, 8, 2012, pp. 8351-8358.
- [20] A. Mahendrasingam, D.J. Blundell, C. Martin, W. Fuller, D.H. MacKerron, J.L. Harvie, R.J. Oldman, and C. Riekel, "Influence of temperature and chain orientation on the crystallization of poly(ethylene terephthalate) during fast drawing", *Polymer*, 41, 21, 2000, pp. 7803-7814.
- [21] A. Keller and M. J. Machin, "Oriented crystallization in polymers", *J. Macromolecular Sci., Part B: Physics*, 1, 1, 1967, pp. 41-91.
- [22] A. Peterlin, "Crystalline character in polymers", *J. Polymer Sci.: Polymer Symposia*, 9, 1, 1965, pp. 61-89.