LDPE and PP thermal diffusivity in molten state

Difusividad térmica de mezclas de LDPE y PP en estado fundido

G. Yánez[1], M. A. Rodríguez – Pérez[2] and O. A. Almanza[3]

ABSTRACT

Experimental results are reported for measuring the thermal diffusivity of two polymer species: low density polyethylene (LDPE) and polypropylene (PP). Measurements were taken in unsteady state heat flow conditions around the materials' melting temperature, using a device specially constructed for this purpose. The experimental results for the sample's temperature profile (temperature gradient product) were adjusted with the theoretical results obtained by solving the heat conduction equation. Diffusivity values were $\alpha = 6.92 \times 10^{-7} m^2/s$ for LDPE and $\alpha = 5.53 \times 10^{-7} m^2/s$ for PP. This was pioneering work in measuring this property at high temperatures in non-stationary state heat flow conditions and should be useful in the search for improving the conditions for processing these materials.

Keywords: low density polyethylene (LDPE), polypropylene (PP), diffusivity.

RESUMEN

Se reportan los resultados experimentales de la medición de la difusividad térmica de dos especies poliméricas: polietileno de baja densidad (LDPE) y polipropileno (PP). Las medidas fueron realizadas en condiciones de flujo de calor no estacionario, usando un dispositivo especialmente construido para ello y a temperatura alrededor de la de fusión de los materiales. Los resultados experimentales del perfil de temperatura a través de las muestras, producto de la existencia de un gradiente de temperatura en ellas, fueron ajustados con los resultados teóricos obtenidos de la solución de la ecuación de conducción del calor. Los valores de difusividad hallados fueron $\alpha = 6,92 \times 10^{-7} m^2/s$ y $\alpha = 5.53 \times 10^{-7} m^2/s$ para LDPE y PP respectivamente. Este es un trabajo pionero en la medición de esta propiedad a temperaturas elevadas, en condiciones de flujo de calor no estacionario, y ello es útil en la búsqueda de mejoras de las condiciones de procesado en estos materiales.

Palabras clave: PP, LDPE, difusividad.

Introduction

Both thermal diffusivity and conductivity represent the most important physical properties of a material to be measured when the heat transfer through it has to be evaluated. Heat can flow through material in a steady or unsteady way; heat flow through material in the former does not vary as time elapses whereas the latter is characterised by temperature variation (time and position) within material (temperature profile through samples). An understanding of this is essential when designing materials required for specific uses and required thermal specifications. For example, knowledge of a material's thermal properties at temperatures close to melting is of vital importance for improving processing conditions, thereby resulting in materials' improved mechanical and thermal properties since transient cooling affects the degree of crystallisation and increases material resistance and density (J. Papa *et al.*, 2002).

[1] Genhli Yánez. M. Sc. Física, Universidad Nacional de Colombia, Colombia. Affiliation: Universidad Nacional de Colombia, Colombia. E-mail: gyanezd@unal.edu.co
[2] Miguel Ángel Rodríguez Pérez. Dr. Física, Universidad de Valladolid, España. Affiliation: Universidad de Valladolid, España. E-mail: marrod@fmc.uva.es
[3] Ovidio Almanza. M. Sc. Física, Universidad Nacional de Colombia, Colombia. Dr. Física, Universidad de Valladolid, España. Affiliation: Universidad Nacional de Colombia, Colombia. E-mail: oaalmanzam@unal.edu.co

Several researchers have measured thermal properties regarding unsteady heat flow. This has led to designing measurement devices based on resolving a general equation for heat conduction. Gustafsson developed a device named HotDisk for measuring solid and liquid materials' thermal properties (Gustafsson, 1990); the method was based on the transient source plane (TPS) technique using a plane source acting simultaneously as temperature sensor and heat source, like a thin wire being used in the hot wire method (Yi He 2005, 122-134; Bouguerra *et al.*, 2001; Dos Santos, 2005). A TPS element is made of a thin sheet of metal in the form of a double spiral, resembling a thin hot disk, immersed in the material to be measured.

There are other techniques for measuring unsteady state thermal diffusivity and conductivity (Chudzik, 2012; Dos Santos *et al.*, 2005; Dos Santos, 2005; Pope, 2002) but many of these have done so at temperatures well below the materials' melting temperature. Some have taken measurements at different temperatures to show that material diffusivity is dependent on this variable (Goyanes *et al.*, 1999). The need for diffusivity values in material's molten state is important for optimising processing conditions.

This paper was aimed at solving an unsteady, one-dimensional, heat conduction equation and designing a device for measuring thermal diffusivity in polymer-based samples. The device (experimental section) was a modification of one developed by Pope *et*

al., (Papa *et al.,* 2002). The samples measured were low density polyethylene (LDPE) and polypropylene (PP). The measurements were made in unsteady heat flow conditions, at temperatures close to the materials' melting temperature.

Resolving an unsteady state heat conduction equation

An experiment such as that shown in Figure 1 was supposed, involving material stored in a cylindrical container placed between the plates of a press which could be heated to temperatures T_1 and T_2, with $T_2 > T_1$. If the material were a polymer, a heat conduction equation in a non-stationary regime, assuming temperature gradient was only in z direction, or having a cylindrical axis, and assuming no convective heat transfer, would be given by the following expression (Papa *et al.,* 2002)

$$\frac{\partial T}{\partial t} = \alpha \left(\frac{\partial^2 T}{\partial z^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} \right) + q \frac{d\chi}{dt} \qquad (1)$$

in which

$$q = \frac{\rho \Delta H_c}{\rho_c C_p} \qquad (2)$$

where T was temperature, α thermal diffusivity, r radial position, z axial position, ΔH_c latent heat of crystallisation, ρ density, C_p heat capacity at constant pressure and χ the fraction of crystallised polymer. q gave the latent heat associated with any polymer change of state from molten to solid state and thus decrystallisation rate (Papa *et al.,* 2002), i.e. q was related to exothermic or endothermic processing of the polymer's crystalline region when subjected to heat flow and must be considered when curing polymer materials.

Assuming q contribution to temperature profile as being negligible compared to the heat transferred along the z axis and considering the device's radial dimensions to be large enough and that the radial temperature gradient was very small compared to the temperature gradient along the z axis, equation (1) would be described as follows:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial z^2} \qquad (3)$$
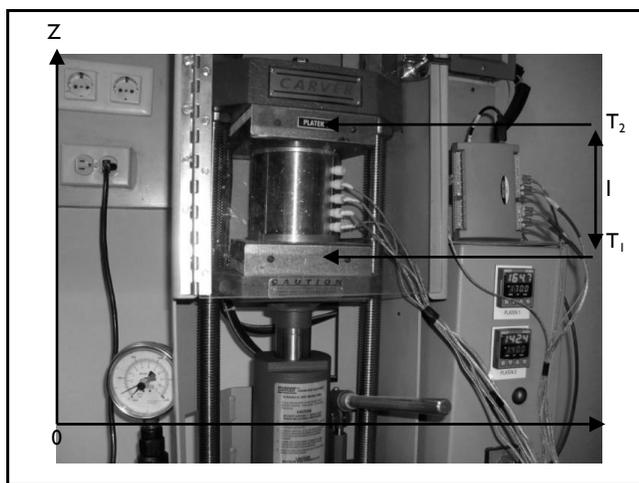

Figure 1. Experimental design for measuring thermal diffusivity. Material with cylindrical geometry, placed between the plates of a press which could be heated to temperatures T1 and T2 with T2 > T1

The experiment's initial and boundary conditions are detailed in 4:

$$\begin{aligned} T(z,0) &= T_2 \\ T(0,t) &= T_1 \\ T(l,t) &= T_2 \end{aligned} \qquad (4)$$

Where T_2 is the sample initial temperature (T_2 above its melting point) and is the same temperature as the upper press plate, l is the length of the device and the sample. As shown, this problem presents non-homogeneous boundary conditions which can be solved directly by making appropriate modifications and by the method of variables separation, reducing it in one to homogeneous boundary conditions. Bearing in mind that when $t \to \infty$ reaches a steady state in the material, the solution can be expressed as the sum of a temperature distribution at steady state $v(z)$ and another non-stationary distribution $w(z,t)$ (Richard C Boyce, William E. Diprima, 2005; David E. Penney C. Henry Edwards, 2009); write as follows:

$$T(z,t) = v(z) + w(z,t) \qquad (5)$$

The one-dimensional steady-state solution $v(z)$ with $T_2 > T_1$ is

$$v(z) = (T_2 - T_1)\frac{z}{l} + T_1 \qquad (6)$$

And bearing in mind that we can write

$$w(z,t) = G(z)F(t) \qquad (7)$$

We found that in conjunction with the boundary conditions (4) and the equation (5), we could arrive at the solution of equation (3), given as:

$$T(z,t) = (T_2 - T_1)\frac{z}{l} + T_1$$
$$+ \sum_{n=1}^{\infty} b_n exp\left(\frac{-n^2\pi^2\alpha t}{l^2}\right) sen\frac{n\pi z}{l} \qquad (8)$$

with $b_n = \frac{2(T_2 - T_1)(-1)^{n+1}}{n\pi}$

EXPERIMENTAL

Figure 2 is a side view of the device constructed for the measurement of thermal diffusivity. This is made up of two stainless steel concentric cylinders, with insulation between them and closed by two aluminium caps at the bottom and top. The lower cover is fixed and is fitted to both cylinders, while the upper cover has a plunger which, when pressure is applied, can slide inside the inner cylinder containing the polymer sample, removing trapped air or gas within the cylinder and sample.

The device is equipped with a set of thermocouples (Type 5 J, -Iron-Constantan, 0°C to 760°C), regularly spaced from the bottom cover and located on the vertical axis of the device. The thermocouples can slide through the cylinder wall to make contact with the sample by means of special fittings which prevent the escape of material from the inside. The signal delivered by each of the thermocouples is sent to an acquisition module (USB-TC), which in turn sends the signals to a PC with a data acquisition program developed in LabView, thus storing the information during the characterization process across all of the programmed temperature range.
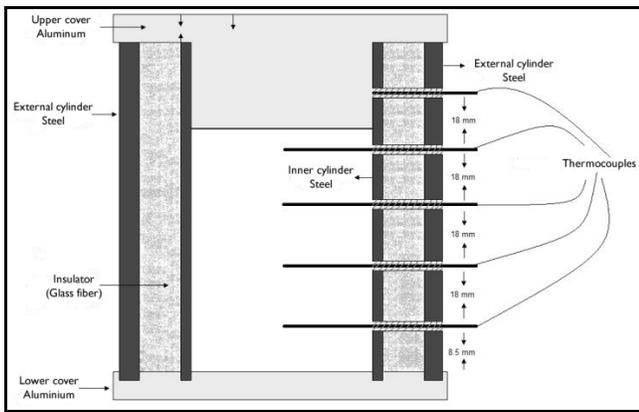
Figure 2. The device built for measuring thermal diffusivity.

The sample was placed within the device's inner cylinder for determining the polymer material's thermal diffusivity and the thermocouples were placed in their respective positions. The device then put in an oven at a temperature above the melting temperature of the sample. The thermocouple-related temperature profile was recorded during sample melting until uniformity with pre-established temperature was ascertained. After confirming the sample's complete melting, the device was removed from the oven and placed between two plates of a Fred Carver press. Each dish was equipped with a heating system controlling its temperature at a set value. The press's upper plate was set at the same temperature as that for the furnace, while the lower plate was 30°C lower than that for the upper plate). This was taken as the moment in which t = 0 in temperature measurement. The total mass of the sample used for each material (LDPE and PP) was 1,200 grams. The polymers used were polypropylene homopolymer ISPLEN N2M 074, 0.905 g/cm^3 density, and LDPE ALCUDIA PE-003, 0.920 g/cm^3 density (Repsol YPF).

Results and Discussions

DSC results

Table 1 lists the thermal characteristics of the two samples used in this work. This identified the materials being examined and helped adjust oven and press-plate temperature values.

Table 1. Thermal characteristics of the LDPE and PP used

Sample's name	Melting Point Tm (°C) (First heating)	Fraction of crystallized polymer
LDPE	114,2	41,3
PP	154,5	44,7

Figures 3a and 3b show the experimental values and temperature profile adjustments of the LDPE and PP samples respectively, for the thermocouple located 26.5 mm from the base of the device.

Adjustments were made with equation (8), with thermal diffusivity as the only adjustable parameter. The theoretical adjustment and experimental values differ by no more than 5%. The diffusivity values obtained were $\alpha = 6.92 \times 10^{-7}\ m^2/s$ y $\alpha = 5.53 \times 10^{-7}\ m^2/s$ for the LDPE and PP respectively. These values have the same order of magnitude as those reported by other authors using different measurement techniques (Wilson Nunes dos Santos, 2005, pp 932–941; Wilson Nunes dos Santos et all, 2007, pp 216-221; Wilson Nunes dos Santos, 2007, pp 556-566; W. N.

dos Santos, C. Y. Iguchi, R Gregorio Jr, 2008, PP 204-208; Abderrahim Boudenne, Laurent Ibos et all, 2004, pp 132-139) although it is important to note that the differences may be due to the dependence the diffusivity of these materials have with the temperature.
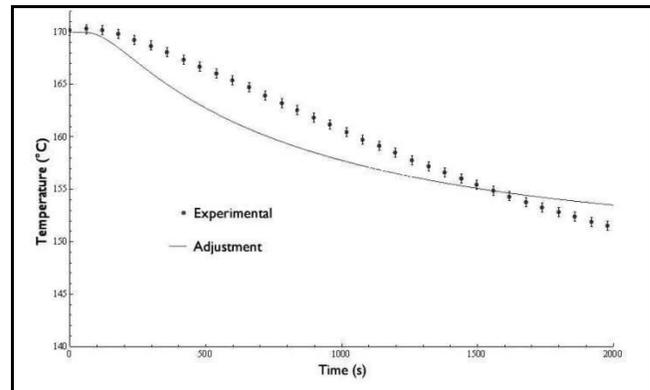

Figure 3a. Temperature profile of molten LDPE as a function of time for thermocouple No. 1, located at x = 26.5 mm and its respective adjustment. With $T_2 = 170$ °C (upper plate) and $T_1 = 140$ °C (lower plate). The points correspond to the experimental profile, whereas the solid line corresponds to the adjustment. The diffusivity value calculated was α = 6.92 x 10^{-7} m^2/s.
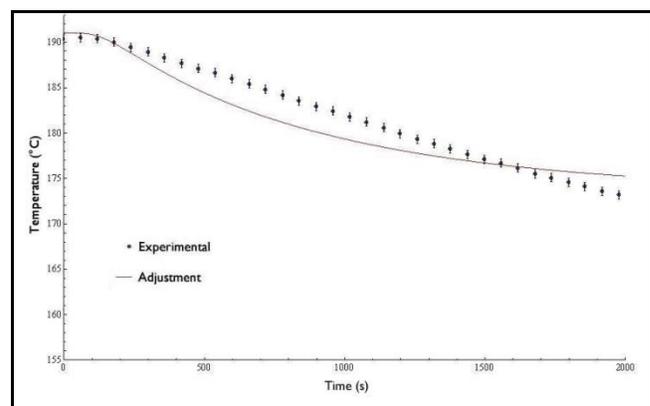

Figure 3b. Temperature profile of molten as a function of time for thermocouple N° 1 located at x = 26.5 mm and its respective adjustment. With $T_2 = 190$ °C (upper plate) and $T_1 = 160$ °C (lower plate). The points correspond to the experimental profile, whereas the solid line corresponds to the adjustment. The diffusivity value calculated was $\alpha = 5.53 \times 10^{-7}\ m^2/s$.

Conclusions

The Thermal diffusivity values of LDPE and PP were measured at a temperature close to the melting point of each. The values found were $\alpha = 6.92 \times 10^{-7}\ m^2/s$ and $\alpha = 5.53 \times 10^{-7}\ m^2/s$ for the LDPE and PP respectively, which differ by more than 20%. These are pioneering measurements for these materials and were made using a device which was easy to construct. The most probable cause for the differences in α, of the materials within this report, may be associated with different molecular weights of the materials and the differing mobility of the molecular chains at the measurement temperature, which can affect the flow of heat between the material's zones. This gives thermal diffusivity the characteristic of being sensitive to temperature.

Acknowledgment

References

Bouguerra, A., Ait-Mokhtar, A., et al., Measurement of thermal conductivity, thermal diffusivity and heat capacity of highly porous building materials using trasient plane source tecnique., Heat Mass Transfer, Vol. 28, No. 8, 2001, pp. 1065-1078.

Boudenne, A., Ibos, L., et al., A simultaneous characterization of thermal conductivity and diffusivity of polymer materials by a periodic method., J. Phys. D: Appl. Phys., No. 37, 2004, pp. 132-139.

Boyce, R. C., Diprima, W. E., Ecuaciones diferenciales y problemas con valores en la frontera., 4ta ed., Limusa Wiley, 2005.

Chudzik, S., Measurement of thermal diffusivity of insulating material using an artificial neural network. Meas. Sci. Technol. 23, 2012, pp. 1 – 11.

David, E., Penney, C., Edwards, H., Ecuaciones diferenciales y problemas con valores en la frontera, cómputo y modelado., 4ta ed., PEARSON, Prentice Hall, 2009.

dos Santos, W. N., Thermal properties of melt polymers by the hot wire technique., Polymer Testing, No. 24, 2005, pp. 932–941.

dos Santos, W. N., Thermal properties of polymers by non-steady-state techniques., Polymer Testing, No. 26, 2007, pp. 556-566.

dos Santos, W. N., et al., Effect of recycling on the thermal properties of polymers. Polymer Testing, No. 26, 2007, pp. 216-221.

dos Santos, W. N., Iguchi, C. Y., Gregorio, R. Jr., Thermal properties of poly (vinilidene fluoride) in the temperature range from 25 to 210 °C., Polymer Testing, No. 27, 2008, pp. 204-208.

Gustafsson, S. E., Trasient plane source tecniques for thermal conductivity and thermal diffusivity measurements of solid materials., Gothenburg, Sweden, Department of physics, Chalmers Institute of technology, University of Gothenburg, 1990.

Goyanes, S. N., Beccar Varela, M. P., Mariani, M. C., Marzocca, A.J., Influence of carbon black dispersion on the thermal diffusivity of an SBR vulcanizate., J. Apl. Polym. Sci., Vol. 72, 1999, pp. 1379 – 1385.

He, Y., Rapid thermal conductivity measurement with a hot disk sensor Part 1 Theoretical considerations., Thermochimica acta, No. 436, 2005, pp. 122-129.

He, Y., Rapid thermal conductivity measurement with a hot disk sensor Part 2 Characterization of thermal greases. Thermochimica acta, No. 436, 2005, pp. 130-134.

Papa, J., Albano, C., Baré, W., Navarro, O., Galárraga, D., Zannin, F., An unsteady state method for the measurement of polymer thermal diffusivity I. Development of a cell., European Polymer Journal, No. 38, Feb., 2002, pp. 2109-2117.