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Analysis of thermal diffusivity in aluminum (particle)-filled PMMA compounds

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Abstract

The thermal diffusivity of particulate compounds of polymethylmethacrylate (PMMA) and aluminum powder was evaluated from measurements of temperature in samples during heating in the range of temperature between 100 and 370 K. Samples were prepared with a filler volume fraction of up to 0.15.

Results were analyzed in the framework of the Hashin–Shtrikman relationship, based on variational principles, and within Nielsen's model, modified to describe thermal diffusivity. For this purpose, the dependence of specific heat and density of compounds upon temperature was calculated. It will be shown that Nielsen's model can predict the behavior of the thermal diffusivity within the whole range of temperatures of the tested compounds, while the Hashin–Shtrikman relationship underestimates the experimental values.

Keywords: Aluminum–PMMA compounds; Thermal diffusivity; Thermal conductivity

1. Introduction

Polymers filled with metal powder have better electrical and thermal conduction properties and extend their uses in technological applications. This adds to the mechanical properties achieved with these kinds of material, making them useful for specific requirements. In the literature, there are several reports of the thermal behavior of polymers filled with different types of metal powder [1–5].

The low thermal conductivity of polymers is a decisive factor affecting the use of these materials as thermal insulators. However, composites of a polymer matrix with inorganic fillers increase the coefficient of thermal conductivity. This condition is interesting in several applications and also from the point of view of optimizing heat input into the processing of thermoplastic and thermosetting polymers [6]. On the other hand, molded plastic packages made of composite materials are being used increasingly in electronic systems owing to their ease of manufacturing, light weight and customizable properties [7].

In recent papers we have presented an improved method for the determination of the thermal diffusivity of elastomeric compounds [8–10]. By using this method, the thermal diffusivity can be estimated through the glass transition range [8].

The knowledge of the thermal behavior of a sample is an important requirement for the design of the material. For this purpose, the general differential equation for transient conduction of heat, defined as

$$\rho c \frac{\partial \theta}{\partial t} = \nabla\cdot(k \nabla \theta) + \frac{\mathrm{d}Q}{\mathrm{d}t} \tag{1}$$

must be solved in order to obtain the temperature θ at any time considering the geometry and the boundary conditions of the sample. In Eq. (1), ρ, c and k are the density, specific heat and thermal conductivity of the material, respectively. $\mathrm{d}Q/\mathrm{d}t$ is the heat evolution rate. The knowledge of the thermal parameters, k, c and Q are essential for the correct prediction of the behavior of the material in a given situation.

When materials without heat of reaction are considered

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($dQ/dt = 0$), Eq. (1) can be rewritten in the one-dimensional case as

$$\frac{\partial}{\partial x}\left(k\frac{\partial\theta}{\partial x}\right) = \rho c\frac{\partial\theta}{\partial t} \tag{2}$$

$$\frac{\partial^2\theta}{\partial x^2} + \frac{1}{k}\frac{\partial k}{\partial x}\frac{\partial\theta}{\partial x} = \frac{1}{\alpha}\frac{\partial\theta}{\partial t} \tag{3}$$

where $\alpha = k/c\rho$ is the thermal diffusivity of the material. This parameter relates energy flux to energy gradient.

There are several theoretical and empirical models to predict the thermal conductivity of filled composite systems. These models follow three different approaches that consider: first, solving exactly the transport problem using an effective medium approximation; second, calculating uppermost and lowermost bounds; and finally, using the results of the bond percolation theory [3].

Nielsen [11] has shown that the thermal conductivity depends on the geometry of the filler. Agari and Uno [2] developed an empirical model that considers the filler chain formation at high filler content in order to estimate the thermal conductivity of the composite. Padilla et al [12], based on the ideas of Nielsen [11] and Scarisbrick [13], developed an empirical model for thermal conductivity considering the

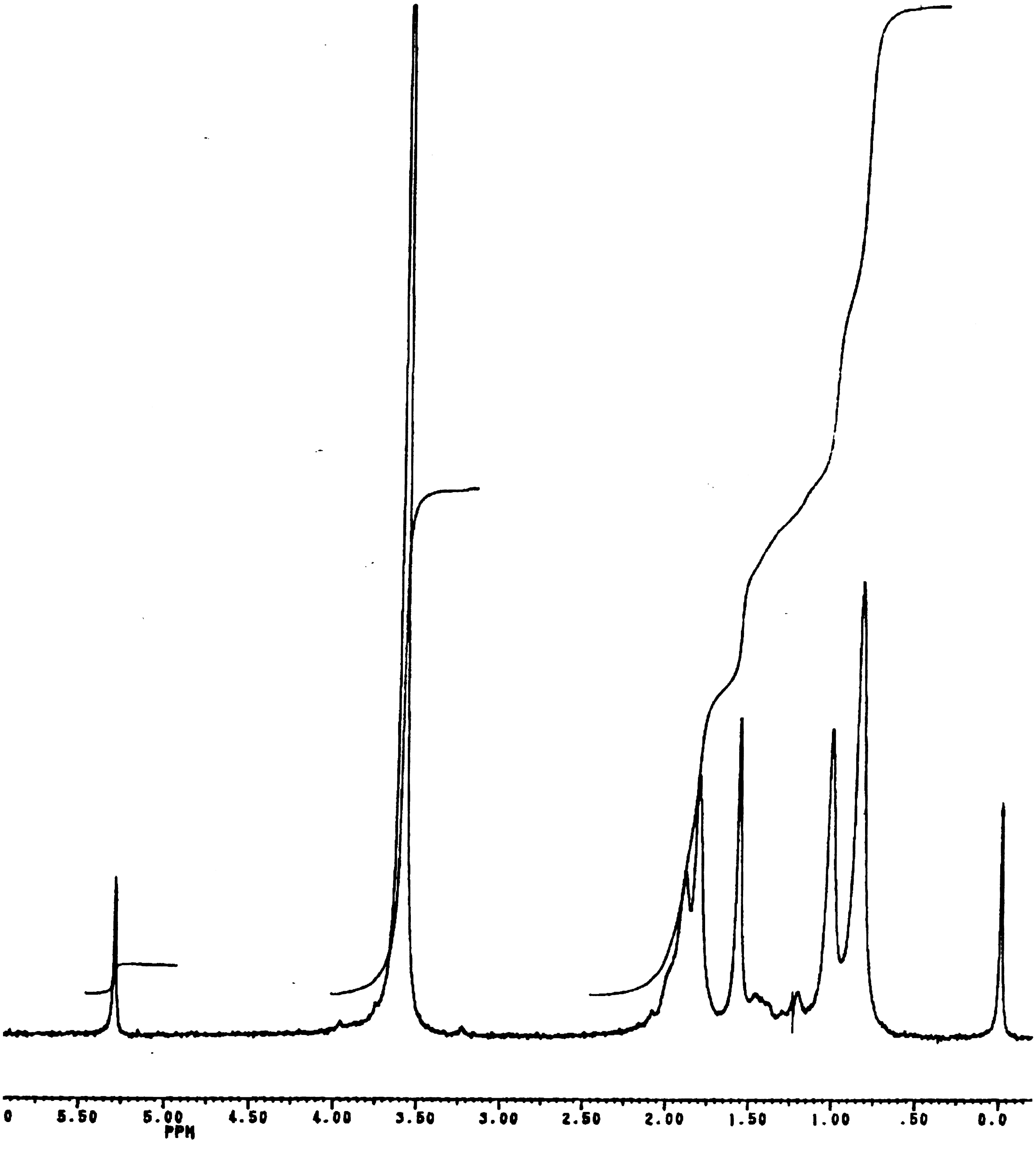

Fig. 1. ^{1}H spectra at 300 K of the prepared PMMA sample.

effect of the filler aspect ratio and the formation of conductive chains at high volume fractions. Ramani and Vaidyanathan [7] used the finite-element method to introduce interfacial thermal resistance and filler dispersion in the calculation of the thermal conductivity of filled composites. Based on variational principles, Hashin and Shtrikman [14,15] (H–S model) obtained upper and lower bonds for thermal conductivity when no information is available about the filler distribution in the matrix.

In this paper we studied the thermal diffusivity behavior of polymethylmethacrylate (PMMA) filled with different levels of aluminum powder in the temperature range

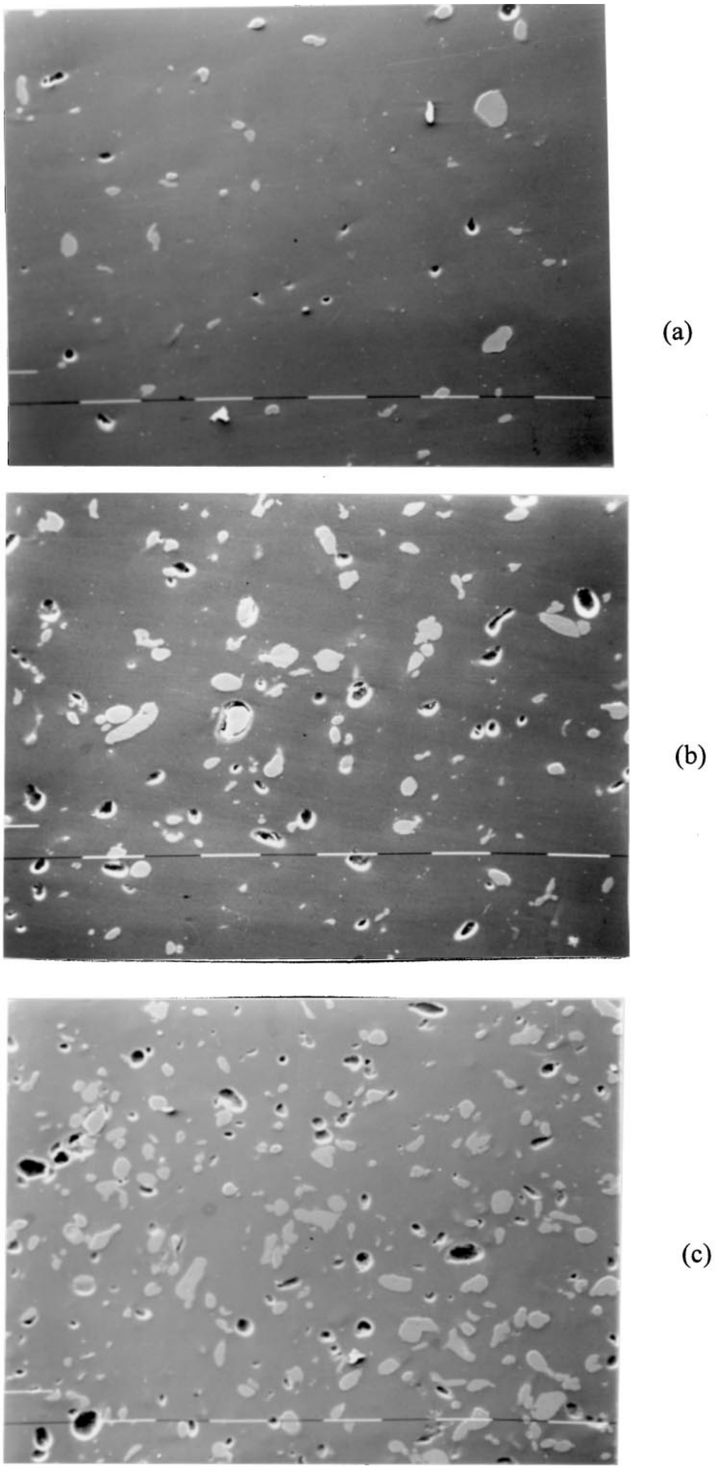

Fig. 2. Scanning electron micrographs of aluminum filler composite for three different volume fractions. (a) $\phi = 0.013$, (b) $\phi = 0.03$, (c) $\phi = 0.10$. Scale = 100 μm.

between 100 and 370 K. Results were analyzed in the framework of the H–S model and with the model proposed by Nielsen, taking into account the values of density and specific heat of the compounds within the whole range of temperatures.

2. Experimental

2.1. Material

The material used in this research was solid atactic PMMA and aluminum powder of a mean diameter between 10 and 40 μm. The molecular weight distribution of the PMMA was measured by GPC using a Shimadzu L-6A liquid chromatogram system with a RID-6A refractive index detector and a Shimpack GPC 802-803-804-805-807 as the column at 303 K. The values obtained for the number and weight average molecular weight were $M_n = 809{,}900$ g mol^{-1} and $M_w = 2{,}213{,}613$ g mol^{-1}, respectively.

Composites with volume fractions of up to 0.15 were prepared using the following method. First, 70 g of PMMA were dissolved into 350 ml of methylene chloride. The aluminum powder, with a mean diameter between 10 and 40 μm, was pre-dried for 1 h in a vacuum chamber at 393 K before incorporation into the PMMA matrix. Then aluminum powder was added to the solution, stirred and mixed well. The solution was cast in a mold of dimensions larger than the final ones required for the samples. The specimen was put into a drying-chamber in order to make the solvent evaporation slow enough to avoid bubbles appearing in the material. The dimension of the composite sheet was 120 mm × 120 mm × 4 mm.

NMR measurements were made on the PMMA sample without filler. The ^{1}H spectra of the sample were recorded on a Bruker AC-200 spectrometer using ca. 7% (w/v) solution in chloroform. Fig. 1 shows the NMR spectra of the prepared PMMA sample and an anomalous peak appears at 5.3 ppm produced by the presence of remainder solvent in the material.

The same sample was characterized again by means of GPC. The values measured were $M_n = 576{,}700$ g mol^{-1} and $M_w = 1{,}591{,}500$ g mol^{-1}, respectively.

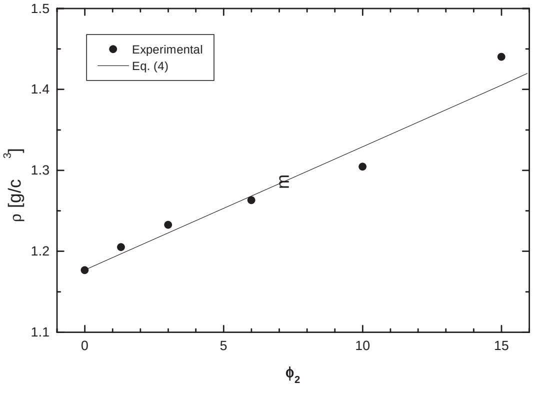

Fig. 3. Density of PMMA/aluminum powder compounds.

Discs of 74.8 mm diameter and 4 mm thickness were cut from the composite sheet. Finally, both faces of the sample were mirror-finished with alumina polishing.

The microscopic photographs of the samples with filler volume fractions of 0.013, 0.03 and 0.10 are shown in Fig. 2. A homogeneous distribution of particles can be observed in the samples with lower filler content and the presence of particle agglomerates increases at higher levels of filler content.

The densities of the compound were measured applying the Archimedean principle considering the weight of the sample in air and water. Fig. 3 shows the values of the density at room temperature as a function of the volume fraction of the aluminum powder in the compound, ϕ_2. Usually, the density of a material of n phases, ρ_c, is expressed by

$$\rho_c = \sum_{i=1}^{n} \phi_i \rho_i \qquad i = 1, 2, \ldots n \tag{4}$$

where ϕ_i and ρ_i are the volume fraction and the density of the i-phase. In this work, subscript 1 corresponds to matrix phase and subscript 2 to filler.

The fitting of Eq. (4) to the experimental data considering two phases in the compound (PMMA and aluminum powder) is shown in Fig. 3. Although some dispersion can be observed in the data, the fit is very good. The scatter can be attributed to the presence of remainder solvent and small air bubbles that could be present in the material. The presence of solvent increases the compound density because of the high value of the density of methylene chloride (1.355 g cm^{-3}). On the other hand, air bubbles will decrease the compound density.

The variation of the density of the compound, ρ_c, with temperature was evaluated from the thermal expansion of each phase. Considering that the thermal expansion of aluminum is much lower than that of PMMA, the change in density with temperature is due mainly to the polymer phase. Then in Eq. (4) the following relationship can be used for calculating the PMMA density at temperature T

$$\rho_1 = \rho_1^0/(1 + \kappa(T - T^0))$$

where ρ_1^0 is the density at room temperature T^0 and κ is the volumetric thermal expansion coefficient. κ was estimated by means of the linear thermal coefficient, λ, as $\kappa \cong 3\lambda$. Values of λ for PMMA in the range of temperature between 298 and 400 K were reported in the literature [16].

The specific heat of the PMMA was measured by means of a differential scanning calorimeter (DSC) Mettler TA10 with a DSC20 cell. Samples (15–25 mg) were encapsulated in aluminum holders under nitrogen and scanned at 10 K min^{-1} from 120 to 363 K. Data of the specific heat of aluminum were taken from the literature [17]. For particulate compounds, when the weight fraction and specific

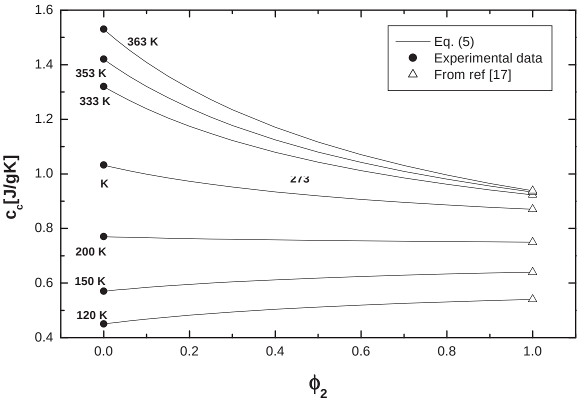

Fig. 4. Specific heat of PMMA/aluminum powder compounds as a function of temperature, according to Eq. (5).

heat of the constituents phases are known, the specific heat of the compound, c_c, may be calculated using a mixture law [18]

$$c_c = \sum_{i=1}^{n} \omega_i c_i \qquad i = 1, 2 \ldots n \tag{5}$$

where ω_i is the weight fraction and c_i is the specific heat of the i-phase of the compound. Using Eq. (5), Fig. 4 shows the variation of c_c with the weight fraction of aluminum powder at several temperatures.

The weight fraction of each phase is related to its volume fraction by $\omega_i = (\rho_i/\rho_c)\phi_i$. Then, in the case of a two-phase system and using Eqs. (4) and (5), it is easy to obtain

$$c_c\rho_c = \xi + \eta\phi_2 \tag{6}$$

where $\xi = c_1\rho_1$ and $\eta = c_2\rho_2 - c_1\rho_1$. The values of the parameters ξ and η for some temperatures are given in Table 1.

2.2. Thermal diffusivity measurement device

A schematic diagram of the device used to perform the thermal diffusivity measurements is given in Fig. 5. Two disks of the material to be analyzed are placed together, and three thermocouples T_1, T_2 and T_3 are used for monitoring the temperatures in the bottom, center and top of the sample. Two specially made brass plates, which are bolted together, maintain the overall thickness at 8 mm. Two thermocouples, T_1 and T_3 are sandwiched between the brass plates and the samples, for monitoring surface temperatures. The three thermocouples are arranged so that their junctions lie as close as possible to the axis of symmetry of the device. The thermocouples were made of iron–constantan wires with 0.2 mm diameter.

For measurements at low temperatures, the device is sandwiched between two heat sink plates, which are air–liquid-cooled by using a controlled flow rate. From room temperature upward, the apparatus is immersed in an oil bath, which is heated continuously by electric immersion heaters while the oil is stirred vigorously. No temperature control is needed at either low or high temperature, but we apply a temperature-heating rate of around $0.15\ \mathrm{K\,s^{-1}}$. Thermocouple data were recorded by a PC with a Keithley DAS8/PGA 12-bit A/D data acquisition board using a customized acquisition program.

With the purpose of improving the procedure, we have used the following method [19]: if n temperature measurements were registered in a time interval Δt, a central value is taken in this interval, and to determine the temperatures corresponding to this value, the following least-squares fit was used

$$E_j^2 = \sum_{i=1}^{n} (f(t_i) - \theta_i)^2 \tag{7}$$

where θ_i is the recorded temperature at time t_i and f is the fit function. A data sampling rate of $100\ \mathrm{s^{-1}}$ and $\Delta t = 10$ s was used, and for simplicity, f was chosen as a second-order polynomial in time.

In order to obtain the thermal diffusivity, the reduction of Eq. (3) to a suitable finite-differences equation results in

$$(\theta_{m+1,n} - 2\theta_{m,n} + \theta_{m-1,n}) + \left(\frac{k_{m+1,n}}{k_{m,n}} - 1\right)(\theta_{m+1,n} - \theta_{m,n})$$

$$= \frac{1}{\alpha_{m,n}} \frac{(\Delta x)^2}{\Delta t}(\theta_{m,n+1} - \theta_{m,n}) \tag{8}$$

where the coordinates of a typical grid point are $x = m\Delta x$

Table 1
Parameters ξ and η of Eq. (6) and k_1 and k_2 of Eqs. (12) and (15) used to fit experimental data of the thermal diffusivity of PMMA–Al composites at different temperatures. k_2 is taken from Ref. [21]

T (K)	ξ (10^6) ($\mathrm{J\,m^{-3}\,K^{-1}}$)	η (10^6) ($\mathrm{J\,m^{-3}\,K^{-1}}$)	k_1 (10^{-1}) ($\mathrm{W\,m^{-1}\,K^{-1}}$)	k_2 (10^2) ($\mathrm{W\,m^{-1}\,K^{-1}}$)
120	0.544	0.913	0.58	2.80
150	0.686	1.041	0.72	2.48
200	0.914	1.105	0.90	2.37
273	1.219	1.129	1.08	2.36
333	1.544	0.974	1.25	2.38
353	1.657	0.861	1.31	2.40
363	1.782	0.749	1.38	2.40

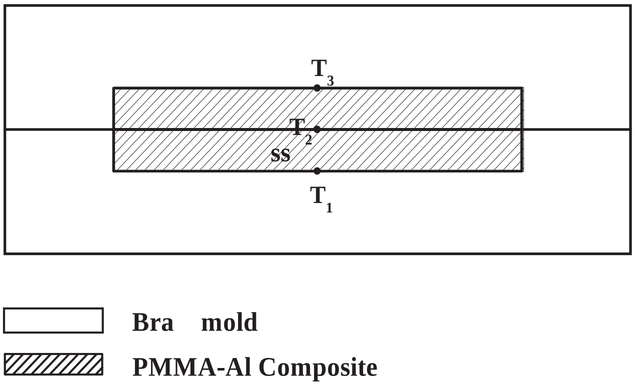

Fig. 5. Schematic diagram of the thermal diffusivity device.

and $t = n\Delta t$, with m and n being integers. If the effect of the conductivity term in Eq. (3) is not taken into account, then the error in the thermal diffusivity is low [20]. The thermal diffusivity results can be obtained by processing the thermocouple data. The results presented in this paper were achieved through off-line processing of the recorded thermocouple data.

From Eq. (8) the thermal diffusivity is estimated as

$$\alpha_{m,n} = \frac{(\Delta x)^2}{\Delta t}\left[\frac{\theta_{m,n+1} - \theta_{m,n}}{\theta_{m+1,n} - 2\theta_{m,n} + \theta_{m-1,n}}\right] \tag{9}$$

3. Results

From the data of temperature as a function of the test time in the top, center and bottom of the sample, and using Eq. (9), the thermal diffusivity was calculated for all the prepared samples. First, we analyzed the diffusivity of PMMA without filler, which is showed in Fig. 6. An interesting point is observed when the material is tested several times in the range of temperatures between 100 and 370 K. A considerable difference is found out among the first run and the successive ones. The variation of α is less at the same temperature in the first run than in the others. This is due to the presence of remainder solvent in the sample that is evaporated during the test. This behavior was detected in the tests of the filled compounds too. For this reason, the first run was not considered in the analysis of the results and we used the second run. The results of thermal diffusivity as a function of temperature for all the compounds studied are shown in Fig. 7.

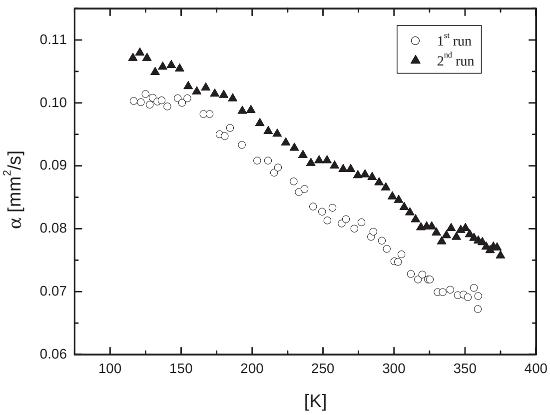

Fig. 6. Dependence of thermal diffusivity (α) upon temperature for PMMA without filler, for successive runs.

In order to analyze our results in the frame of a model, we consider the approach of Hashin and Shtrikman [14,15] based on variational principles. The value of the thermal conductivity would be between the upper and lower bounds of the H–S relationships

$$k_{(-)} = k_1 + \frac{\phi_2}{\dfrac{1}{(k_2 - k_1)} + \dfrac{\phi_1}{3k_1}} \tag{10}$$

$$k_{(+)} = k_2 + \frac{\phi_1}{\dfrac{1}{(k_1 - k_2)} + \dfrac{\phi_2}{3k_2}} \tag{11}$$

where the subscripts 1 and 2 correspond to the matrix and the filler, respectively.

Then, since our tests were performed in samples with low filler content, we use Eq. (10) to express the thermal diffusivity of the composite, α_c, as

$$\alpha_c = \frac{1}{\rho_c c_c}\left\{k_1 + \frac{\phi_2}{\dfrac{1}{(k_2 - k_1)} + \dfrac{(1 - \phi_2)}{3k_1}}\right\} \tag{12}$$

In order to analyze the experimental data of thermal diffusivity in the framework of Eq. (12) for the different prepared compounds, the product $\rho_c c_c$ was estimated using Eq. (6) with the values given in Table 1. The values of the thermal conductivity of aluminum (k_2) were taken from the literature [21] and are given in Table 1. As can be appreciated in Fig. 8, it is difficult to describe the thermal diffusivity of the Al–PMMA composite with the H–S equation (Eq. (12)). The values of the parameter k_1, obtained from the fitting using Eq. (12) are also given in Table 1.

The poor adjustment of Eq. (12) to experimental data can be attributed to several factors. First, the geometry of the filler is not considered in this model. Besides, if the dispersion of the filler in the compound is not so good, the estimation of the thermal conductivity by means of Eqs. (10) and (11) will be inadequate. As we know, most of the models of thermal conductivities of compounds consider that the fillers are randomly dispersed throughout the matrix. Strictly speaking, it is reasonable to consider a distribution of a cluster of particles instead of a filler distribution. The probability that a particle belongs to one cluster depends on the geometry, kind of filler and dispersion of the

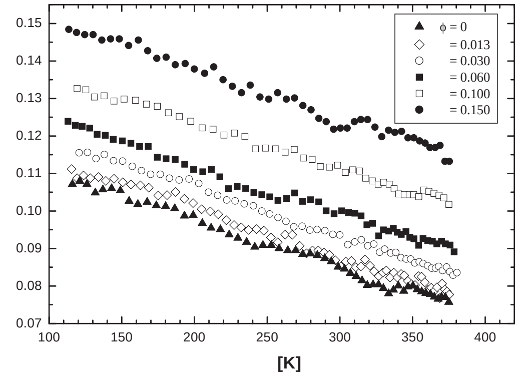

Fig. 7. Dependence of thermal diffusivity (α) upon temperature for different samples.

filler in the matrix [3]. An interesting modification to the H–S relationship was proposed by Bujhard et al. [3]. In order to use Eqs. (10) and (11), they consider the second phase of the compound as a cluster formed by interpenetrating chains of particles in close contact with each other instead of the thermal conductivity of the filler. This fact modifies the value of k_2.The calculation of the thermal conductivity of such a cluster depends on the mean gap separation of the fillers in the cluster, and the lower bound of the H–S relationship is used [3]. To elucidate this point, much work will be necessary.

Then, we decided to analyze the experimental data in the frame of the semi-empirical approach due to Nielsen [11]. This model of thermal conductivity for filled compounds was used over a wide range of fillers [22]. In this framework, k_c is expressed by

$$k_c = k_1\left\{\frac{1+AB\phi_2}{1-B\psi\phi_2}\right\} \tag{13}$$

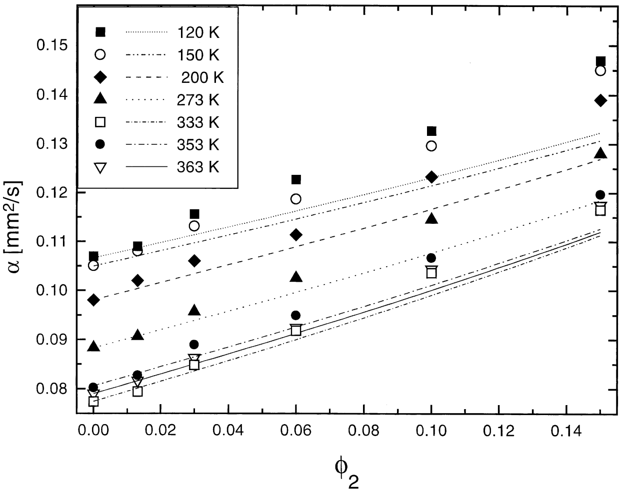

Fig. 8. Thermal diffusivity of PMMA filled with aluminum powder as a function of the volume fraction of the filler and temperature (●, experimental data; —, H–S model).

and using Eq. (6), the thermal diffusivity of the compound is

$$\alpha_c = \frac{k_1}{\rho_c c_c}\left\{\frac{1+AB\phi_2}{1-B\psi\phi_2}\right\} \tag{14}$$

$$\alpha_c = \frac{k_1}{(\xi+\eta\phi_2)}\left\{\frac{1+AB\phi_2}{1-B\psi\phi_2}\right\} \tag{15}$$

with

$$B = \frac{(k_2/k_1)-1}{(k_2/k_1)+A} \tag{16}$$

$$\psi = 1 + \left(\frac{1-\phi_m}{\phi_m^2}\right)\phi_2 \tag{17}$$

where A is a function related to the generalized Einstein coefficient k_E, $A = k_E - 1$. The parameter A depends on the shape and orientation of the dispersed particles [1,5]. ϕ_m is the maximum filler content possible while still maintaining a continuous matrix phase.

Fig. 9(a) and (b) shows the fitting of the thermal diffusivity data to Nielsen's relationship, Eqs. (15)–(17), considering $B \approx 1$ ($k_1 \ll k_2$). From the fitted curves, k_1 was obtained for each analyzed temperature and is given in Table 1. As can be seen, these are equal to those obtained in the fitting with the H–S model. The average values of $A = 2.50 \pm 0.19$ and $\phi_m = 0.635 \pm 0.014$ were obtained.

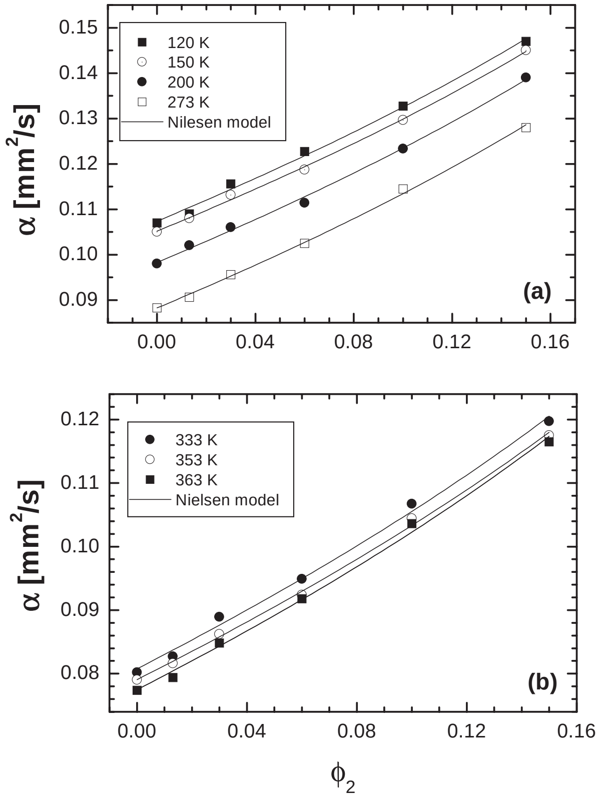

Fig. 9. Thermal diffusivity of PMMA filled with aluminum powder as a function of the volume fraction of the filler and temperature (●, experimental data; —, Nielsen model).

According to the literature [1], $\phi_m = 0.637$ corresponds to a random close packing, which is very close to that found in this work.

In other papers mentioned in the literature, the shape factor was fixed previously according to the geometry of the particles. As can be seen in Fig. 2, our particles do not have a defined shape. When the composite is made using irregularly shaped particles, normally a value of *A* between 2 and 3 is used [1,5,11]. In our work, *A* lies between both values but it must be considered that this parameter was estimated directly from the experimental data.

4. Conclusions

The model of thermal conductivity for particle-filled systems proposed by Nielsen, adapted to thermal diffusivity, was used successfully to describe the experimental results of aluminum-filled PMMA with a filler fraction volume of up to 0.15. Usually, in the literature, results of thermal conductivity using Nielsen's relationship are only presented at room temperature. In this work, it is shown that this formalism can be applied in an extended temperature range between 120 and 463 K.

The shape factor *A* and the parameter ϕ_m were evaluated directly from the experimental data and the values obtained are close to those proposed in the literature. Finally, it must be mentioned that the formalism of Hashin and Shtrikman underestimates the thermal diffusivity behavior of this composite.

Acknowledgements

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