Photoacoustic measurement of thermal properties of polystyrene metal oxide composites

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ABSTRACT

Thermal properties (diffusivity, effusivity and conductivity) of polystyrene filled with low content of metal oxide (ZnO and MnO) particles are measured using heat transmission configuration of photoacoustic technique. The results show that ZnO changes thermal transport properties of polymer more effectively than MnO. The obtained data of the thermal conductivity are well explained by Lichtenecker's equation for thermal conductivity of two phase system. The experimental values of thermal conductivity of the composites have been used to estimate thermal conductivity of metal oxides. The data presented here show that this method is sensitive enough to detect variations in thermal properties of polymers due to addition of slight amount of particulate solids.

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1. Introduction

Measurement of thermal parameters such as thermal diffusivity, thermal conductivity and thermal expansion coefficient of materials is very essential for their applications, particularly in the fabrication of devices. The thermal diffusivity, α ($m^2 s^{-1}$) is a significant thermophysical parameter which measures how effectively phonons carry heat through the sample. Whereas the measurement of the heat exchange rate or the thermal impedance for heat exchange of a given material is essentially determined by its thermal effusivity, e (W $s^{1/2}$ m^{-2} K^{-1}). e is a relevant thermophysical parameter for surface heating or cooling processes as well as in quenching processes. These quantities are defined by $\alpha = k/\rho c$ and $e = \sqrt{k \rho c}$, where k is the thermal conductivity, c is the specific heat capacity and ρ is the mass density. Knowing α and e, the sample thermal conductivity can be obtained from the relation $k = e\sqrt{\alpha}$. Apart from the pure academic interest, knowledge of the thermal conductivity (k) of polymers generally, aids in the selection of candidate for engineering applications such as parts of computers and automobile engines. The ability to transfer heat away from hot parts and allow them to cool down makes the candidate useful.

Over the last couple of decades, thermal wave physics emerged as a valuable tool for the characterization of materials.

Absorption of intensity modulated optical radiation by a sample (solid/liquid/gas) leads to periodic heat generation thereby causing excitation of thermal waves in the specimen. Among the various methods used to study these thermal waves, the gas-microphone photoacoustic (PA) technique is one of the most commonly employed experimental approaches. Therefore, besides this technique is noncontact nondestructive, PA method has gained more popularity due to its simple, elegant experimental technique as well as the versatility in employing different configurations to measure the required thermophysical parameters with great accuracy [1–7]. PA technique has two different configurations, heat reflection configuration where the illumination and detection of the signal are from the same side of the sample, and heat transmission configuration where the illumination is at the front surface whereas the signal is detected at the rear surface. In particular, heat transmission configuration is becoming increasingly popular for thermal diffusivity evaluation, especially for dielectric materials [4–7].

Generally, determination of unknown e using PA technique needs reference sample of known e which is not needed for the determination of α. In addition, diffusivity can be measured through either transmission or reflection configurations under different conditions while e is measured usually through reflection configuration for optically opaque and thermally thick samples [8–13]. Consequently, the mathematical formulation of the problem is different in the two cases. These may be the causes that determination of k through measurement of both e and α is rarely done. Here, we utilize heat transmission configuration to determine

both thermal diffusivity and thermal effusivity of polymer composites films at the same time using the same mathematical relation [14]. In the present study, thermal properties of polystyrene (PS) filled with little amount of metal oxide (ZnO and MnO) particles are measured.

PS is a thermoplastic substance, normally existing in solid state at room temperature, but melting if heated (for molding or extrusion), and becoming solid again when cooling off. PS is one of the most widely used kinds of plastic. The ordinary (weight-average) molecular weight of commercial PS is >10^5. Pure solid polystyrene is a colorless, hard plastic with limited flexibility. It can be cast into molds with fine detail. PS can be transparent or can be made to take on various colors. Solid PS is used, for example, in disposable cutlery, plastic models, CD and DVD cases, and smoke detector housings. PS is very poor thermally conductive polymer, so it is suitable to examine the sensitivity of PA technique for thermal parameter measurements of very insulating dielectric materials. In addition, PS filled with slight amount of moderately thermally conductor (ZnO) and low thermally conductor (MnO) are also investigated to show the ability of this method to detect small changes in thermal parameters of two phase composite materials.

2. Theory

The main idea of PA technique is that the sample is placed in a closed chamber filled with a gas such as air and illuminated with monochromatic radiation of any desired wavelength, with intensity modulated at some suitable acoustic frequency; the nonradiative decay of the absorbed radiation results in a periodic heat diffused from the sample to the air adjacent to the sample surface. This temperature variation produces a pressure fluctuation in the air within the cell which is detected as an acoustic signal by a sensitive microphone attached to the chamber. Accordingly, the PA signal contains information about the optical absorption within the sample in addition to the way with which the heat is diffused through the sample.

In the heat transmission configuration, that is used in this study, assuming that the sample is optically opaque where the whole modulated energy is absorbed at the sample surface, consequently the periodic heat that is generated at the same place will penetrate through the sample to its rear surface. The heat thus reaches the sample air interface where the acoustic signal is produced. According to the one-dimensional heat flow model of Rosencwaig and Gersho [15], we can show that the periodic pressure variation in the air chamber is given by

$$Q = \frac{\gamma P_o I_o (\alpha_g \alpha_s)^{1/2}}{2\pi T_o l_g k f} \frac{e^{j(\omega t - \pi/2)}}{\sinh(l\sigma)} \quad (1)$$

where γ is heat capacities ratio of air; P_o is ambient pressure; T_o is temperature ambient; I_o is intensity of the incident light; f is modulation frequency; l is thickness of the sample; k is sample thermal conductivity; l_g is length of the gas column; α_s is thermal diffusivity of the sample; α_g is thermal diffusivity of the gas; σ is complex quantity $= (1 + i)a_s$; a_s is thermal diffusion coefficient (reciprocal of the thermal diffusion length μ) $= (\omega/2\alpha_s)^{1/2}$; ω is the angular frequency $= 2\pi f$.

Now, if the sample is thermally thick ($a_s l \gg 1$) i.e., thermal diffusion length is much smaller than the thickness of the sample, then the PA signal amplitude is given by

$$q_s = C \frac{1}{e_s f} \exp\left(-\frac{\pi^{1/2} f^{1/2} l_s}{\alpha_s^{1/2}}\right) \quad (2)$$

where $C = (\gamma P_o I_o \alpha_g^{1/2}/2\pi T_o l_g)$. This relation is usually used to determine α_s of the sample of known thickness l_s from the slope of $\ln(q_s f)$ as a function of $f^{1/2}$. The determination of the effusivity e_s from Eq.
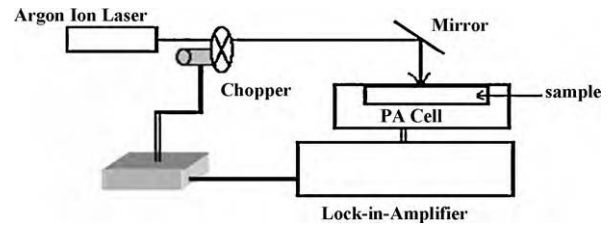

Fig. 1. Experimental set-up for thermal measurements.

(2) requires elimination of the constant factor C by normalizing the signal measured for the sample (of unknown thermal parameters) to the signal measured for a reference sample (at the same experimental conditions). Accordingly the reference signal is given by

$$q_r = C \frac{1}{e_r f} \exp\left(-\frac{\pi^{1/2} f^{1/2} l_r}{\alpha_r^{1/2}}\right) \quad (3)$$

where e_r and α_r are effusivity and diffusivity of the reference sample respectively while l_r is its thickness. Dividing Eq. (2) by Eq. (3), we get the inversely normalized amplitude as

$$q_n^{-1} = \frac{q_r}{q_s} = \frac{e_r}{e_s} \exp\left(\frac{\sqrt{\pi f} l_s}{\sqrt{\alpha_s}} - \frac{\sqrt{\pi f} l_r}{\sqrt{\alpha_r}}\right) \quad (4)$$

Then

$$\ln(q_n^{-1}) = \ln\left(\frac{e_r}{e_s}\right) + \sqrt{\pi}\left(\frac{l_s}{\sqrt{\alpha_s}} - \frac{l_r}{\sqrt{\alpha_r}}\right)\sqrt{f} \quad (5)$$

It is clear that this linear relation ($\ln(q_n^{-1})$ vs. $\sqrt{f}$) can be used to determine both of α_s and e_s at the same time, from the slope and direct extrapolation to the values at $f^{1/2} = 0$ respectively.

3. Experimental

Samples were prepared by dissolving commercial PS resin GIPS-155 (obtained from SABIC Company, KSA) in toluene solvent with concentration of 0.6 g/cm^3 and stirred at 30 °C by a magnetic stirrer for 2 h until highly transparent polymer solution was formed. The fine powders of metal oxide (MO) (ZnO or MnO, Sigma–Aldrich CO., purity of 99%) were added at different ratios. The weight contents of the filler inside the composites varied within 1–5 wt%. The solution of the composites again stirred for 24 h until the solution composition became highly viscous and nearly homogeneous distribution of metal oxide particles in the polymer solution was obtained (certainly complete homogeneity has not been verified where small aggregates were formed). This viscous solution carefully cast in a glass Petri dish (diameter of 10 cm) where the solvent was evaporated at room temperature for 24 h and placed inside oven at 40 °C for 2 h. Samples in the form of films with thickness in the range of 0.190–0.23 mm of pure PS or PS – MO composites were kept inside vacuumed desiccator. A schematic diagram of the PA experimental set-up is presented in Fig. 1. Continuous wave laser at 514.53 nm from an Ar$^+$ laser is used as the excitation beam. Laser power of 20 mW is employed for the measurements. A mechanical chopper is used to modulate the pump beam at the desired frequency. The cell is attached with microphone whose sensitivity 50 mV/Pa. Samples are fastened to a thin layer of aluminum foil of thickness 20 μm. This layer is thermally very thin consequently the heat generated at the laser-irradiated surface will be instantaneously transferred to the polymer sample and the thermal waves propagate through it to reach the microphone chamber. Also, samples and reference are adhered carefully to a transparent backing in order to damp the unwanted mechanical vibrations "drum effect" which is related to transverse thermal expansion and temperature gradient through
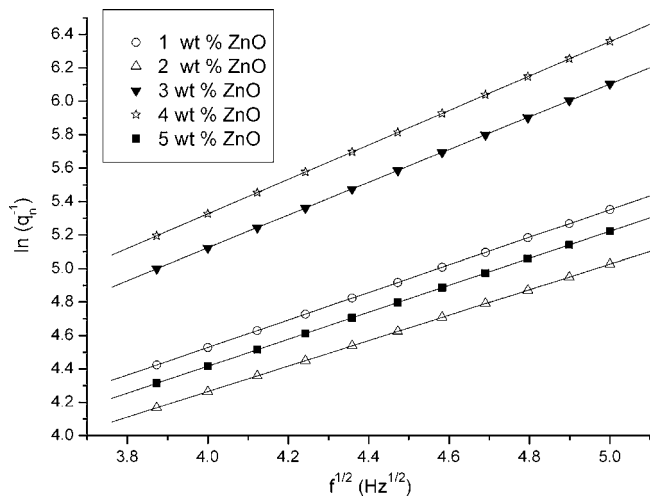
Fig. 2. Inverse normalized amplitude of PA signal for PS/ZnO with different ZnO wt% vs. $f^{1/2}$.

the thickness of the sample. The amplitude of the signal as a function of modulation frequency of the laser beam is recorded using a dual channel digital lock-in amplifier (SR830). The reference signal q_r was obtained using quartz glass sample of thickness 0.2 mm with α_r (8.7×10^{-7} m^2/s) and e_r (1.503×10^3 W s$^{1/2}$ m^{-2} K^{-1}) and heated through the same aluminum foil. The thermally thick condition is verified by working in modulation frequency range such that the thermal diffusion length $\mu (\alpha/\pi f)^{1/2}$ is smaller than the thickness l. Achieving this condition is simple for our reference sample of known α and this confirms that the condition is also verified for the polymer samples in the same frequency range, where α for quartz is larger than that for most polymers. In addition, the experimental data will not obey Eq. (2) or Eq. (5) except under thermally thick condition. To take homogeneity of particle distribution into account, the measurements were repeated 5 times for each sample using 5 different pieces of the sample sheet.

4. Results and discussion

Variation of the inversely normalized amplitude $\ln(q_n^{-1})$ *vs.* $f^{1/2}$ for the polystyrene film obeys the linear dependence on $f^{1/2}$. The data were recorded in the region where the sample is thermally thick (where the thermal diffusion length μ_s as a frequency dependent parameter is much smaller than the thickness of the sample) as required by Eq. (5). The thermal diffusivity (α) is directly obtained from the slope of the line while thermal effusivity (e) is obtained from the linear extrapolation to the values at $f^{1/2} = 0$. The measured values for α (1.020×10^{-7} m^2/s) and e (0.437×10^3 W s$^{1/2}$ m^{-2} K^{-1}) are used to calculate thermal conductivity of PS k ($e\alpha^{1/2} = 0.140$ W m^{-1} K^{-1}) which is close to the reported value of k for PS in the literatures [16]. These results indicate that the method used here is convenient to measure both of thermal diffusivity and thermal effusivity from the data obtained at the same configuration of the PA technique.

The linear relations of $\ln(q_n^{-1})$ *vs.* $f^{1/2}$ for PS films with different ZnO contents as indicated are shown in Fig. 2. Similar relations were obtained for PS mixed with various contents of MnO where α_s and e_s are obtained for each sample with the same manner. The obtained values of e_s and α_s for each set of samples as a function of the weight content of MO are shown in Fig. 3a and b respectively where the solid lines are just for the eye guide. Slight increase can be observed in the thermal effusivity with increasing the concentration of the additives for both sets of samples. The results show that the ZnO is more effective in changing e than
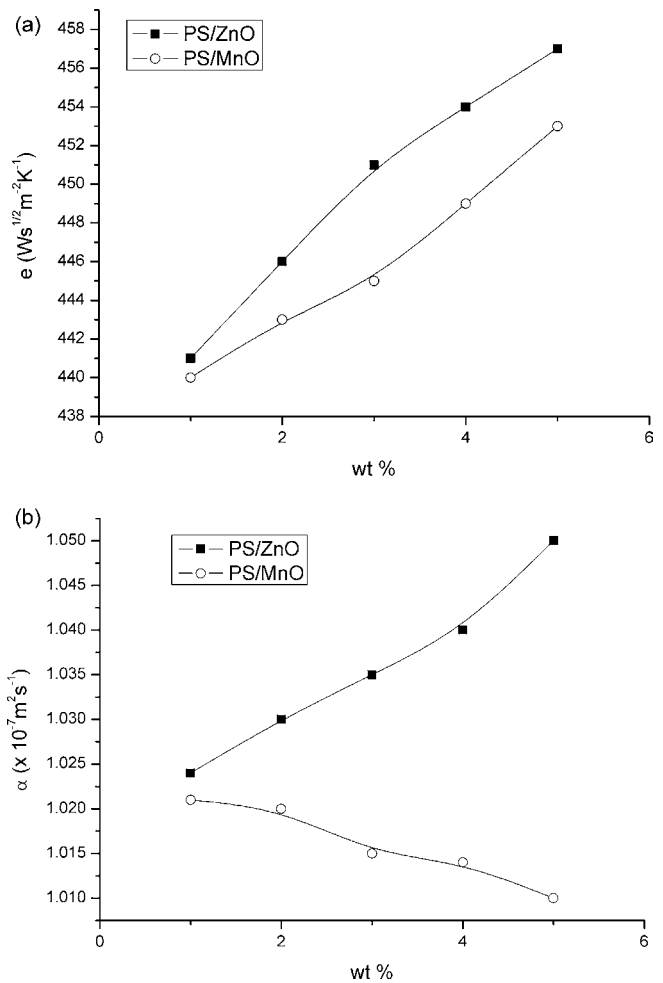

Fig. 3. (a) Effusivity of PS/ZnO and PS/MnO composites as a function of wt% of metal oxides. (b) Diffusivity of PS/ZnO and PS/MnO composites as a function of wt% of metal oxides.

MnO, where the increase in e_s reaches about 4.6% at the highest concentration of ZnO against 3.6% for the same concentration of MnO. On the other hand the behavior of α_s is different. While α_s increases slowly with increasing ZnO concentration, we observe a little drop in it with increasing MnO concentration. These results can be understood as follows, thermal diffusivity is a derived quantity as mentioned before ($\alpha = k/\rho c$) consequently its value may be unchanged or even decreases depending on the changes in k and ρc values. When the increase in k with increasing concentration (shown later) cannot overcome the increase in the denominator specially ρ (considering c is constant for such low concentration used), α will decrease. These results show that addition of ZnO enhances thermal conductivity of PS more effectively than MnO.

Numerous theoretical and empirical models have been proposed to predict the effective thermal conductivity in a two phase system [17]. All of them lie within the interval between the largest thermal conductivity $k_{//}$ when the system is represented by a parallel set of plates extended in direction of the heat flow

$$k_{//} = k_f v + k_p (1 - v) \qquad (6)$$

to the smallest thermal conductivity $k_\perp$ (when the plates are stacked in series in a plane perpendicular to direction of the heat flow)

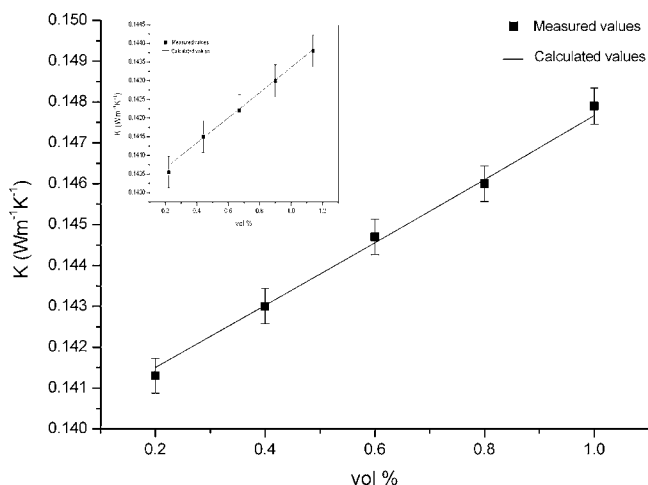$$\frac{1}{k_\perp} = \frac{v}{k_f} + \frac{(1 - v)}{k_p} \qquad (7)$$

Fig. 4. Thermal conductivity of PS/ZnO as a function of vol.% (the inset is the same relation for PS/MnO).

where v is the volume fraction of the filler, k_p and k_f are the thermal conductivity of polymer matrix and filler respectively.

The thermal conductivity of real two phase systems falls within the interval between these two functions and cannot be higher than $k_{//}$ or lower than $k_{\perp}$.

We utilize Eq. (6) to calculate the concentration dependence of k, where the volume fraction v of metal oxides in the composites was calculated using weight contents and densities of the PS and metal oxides. The calculated values for PS/ZnO composites gives good agreement with experimental data when $k_f = 0.95\,\mathrm{W\,m^{-1}\,K^{-1}}$; however this value is unacceptable for thermal conductivity of ZnO. The values of k calculated using Eq. (7) lie lower than experimental points whatever the value of k_f. Hence these boundary relations are not suitable for description of our results.

Some literatures [18,19] have shown that Lichtenecker's equation is appropriate for description of thermal conductivity of the filled systems

$$\log\ k = (1-v)\log k_p + v\log k_f \tag{8}$$

The average values of thermal conductivity measured for PS/ZnO composites are compared with the predicted values of this equation in Fig. 4. The error bars represent standard deviations of the measured values of thermal conductivity using 5 different portions of each sample. This may reflect the homogeneity degree of particle distribution within the samples. Thermal conductivity calculated using Eq. (8) is in good agreement with the experimental results when $k_f = 29\,\mathrm{W\,m^{-1}\,K^{-1}}$ as shown in Fig. 4, which is very acceptable value for thermal conductivity of ZnO [20]. Also Eq. (8) gives reasonable agreement with the experimental results for PS/MnO (inset of Fig. 4) at an acceptable thermal conductivity value for MnO ($k_f = 1.5\,\mathrm{W\,m^{-1}\,K^{-1}}$).

It is clear that the experimental data are well explained by this model for both composites. The noteworthy observation in the results presented here is the ability of this method to detect variations in the thermal parameters due to low load of moderate or low thermally conducting additives.

5. Conclusion

Thermal properties including diffusivity, effusivity of polystyrene filled with low content of moderate (ZnO) and low (MnO) thermally conducting particles are obtained using PA technique in the heat transmission configuration. The results show the capability of this method to detect variations of thermal parameters of polymer composites with low metal oxides loading (1–5 wt%). The effective thermal conductivity has been calculated for composites from the measured values of effusivity and diffusivity where the results show that ZnO enhances thermal conductivity of PS more effectively than MnO. Also Lichtenecker's equation for the effective thermal conductivity in a two phase system allowed predicting acceptable values of the thermal conductivities of ZnO ($29\,\mathrm{W\,m^{-1}\,K^{-1}}$) and MnO ($1.5\,\mathrm{W\,m^{-1}\,K^{-1}}$) Accordingly, this work provides a simple noncontact and nondestructive accurate technique that can be further developed to study thermal properties of polymer composites.

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