JOURNAL OF MATERIALS SCIENCE 40 (2005) 4163–4167

Anomalous behavior of thermal conductivity and diffusivity in polymeric materials filled with metallic particles

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Thermal properties of two composites prepared by using a polypropylene matrix filled with aluminum (slightly oxidized) and copper fillers were investigated. For each of these fillers two different particle sizes were used. We have shown an anomalous thermal behavior when these metallic fillers are slightly oxidized, i.e. higher thermal transport is obtained for PP/Al composites when using the largest particles. So, the PP/Al composites thermal behavior is not consistent with the PP/Cu ones and with the literature results reported for dielectric or conducting filler particles in a polymeric matrix. Thus, these PP/Al composites exhibit higher thermal transport properties than the homopolymer matrix where as electrical insulating properties of PP are preserved. This kind of composite structure might be of great interest in some technological applications where both good electrical insulation and high thermal conduction are required.

1. Introduction

Polymer materials have been for long time used as insulators because of their low thermal conductivity. The interest for these materials arises from the fact that it is possible to develop new materials and more precisely polymer composites materials with properties adapted to specific applications. This study concerns the thermal behavior of polymeric material filled with metallic particles. In fact, the evolution of thermal properties and more generally of most physical properties depends on several factors: the shape of the particles dispersed in the polymeric matrix, the manufacturing process, the ratio between the properties of the two components, the filler particle size and the filler matrix interactions [1–3]. Unfortunately, the existent theoretical models are not able to predict correctly the thermal behavior of composite material for all filler concentrations [2, 3]. In this paper, we present the study of thermal properties of two composites prepared by using a polypropylene (PP) matrix filled with metallic particles. Our objective is to show an anomalous thermal behavior when these metallic fillers are slightly oxidized. A periodic measurement method was used to obtain the experimental thermal conductivity and diffusivity of both composites [4].

2. Experimental method

2.1. Filler distributions

Two different types of metallic fillers were used, aluminum (slightly oxidized) and copper. For each of them, two filler particles sizes were used. In order to reach high maximum packing fraction in the composite, it is necessary to use particles with a large distribution size. The granulometric parameters of all fillers were obtained using a LS-230 (Beckman Coulter^{TM}) device, based on a light scattering method. The results are presented in Table I. The curves of the particle size distributions are shown in Fig. 1. Subscripts *a* and *b* correspond respectively to the smaller and higher filler sizes. We can show from Fig. 1 that the particle size distribution is contained within narrower limits for $Cu_{(b)}$ than for the other filler particles.

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TABLE I Granulometric parameters of aluminum and copper particles

Type	Mean diameter (μm)	ϕ_{10} (μm)	ϕ_{25} (μm)	ϕ_{50} (μm)	ϕ_{75} (μm)	ϕ_{90} (μm)
			Aluminum powder			
$Al_{(a)}$	8	3.4	5.0	7.8	11.9	17.0
$Al_{(b)}$	44	13.6	25.8	49.9	83.9	119.7
			Copper powder			
$Cu_{(a)}$	23	9.2	15.3	24.6	37.5	53.5
$Cu_{(b)}$	234	149.5	187.6	241.7	313.1	392.5

ϕ_i–i% of volume particles is smaller than ϕ_i dimension.

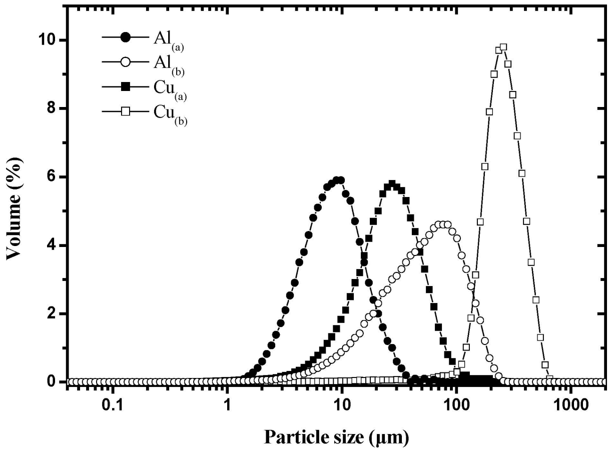

Figure 1 Differential distribution of aluminum and copper particle size.

2.2. Sample preparation

The composites were prepared by mixing pellets of polypropylene (PP) provided by Finapro (7060)^{TM} with the metallic powders (aluminum or copper) in a 68 cm^3 mixing chamber of a Rheomix mixer (Haake-Polylab^{TM}) at 180°C, for 700 s and using a mixing speed of 25 rpm. The polymer and the powder were mixed until the stabilization of the torque was obtained which indicates a good filler dispersion in the matrix. Then, composite samples (square plates of 10 cm × 10 cm and 3 mm thickness) were obtained by compression molding at 195°C, under a pressure of 200 bars for 5 min. The dispersion of the filler in the polymeric matrix is very important in this study because we measure effective thermal conductivity and diffusivity of composite samples. Consequently, the overall morphology of composites was studied by SEM observations. The observed surfaces were obtained by breaking the samples at liquid nitrogen temperature. Fig. 2 displays the microstructure of a composite sample containing 30% of $Cu_{(b)}$ and 10% of $Al_{(b)}$ volume fraction in the polypropylene matrix. It can be clearly seen that the copper and the aluminum particles are randomly dispersed and surrounded by the polymeric matrix. We can also see that the filler particles have different sizes and are not perfectly spherical. The same observations were done for the other filler concentrations.

2.3. Thermal properties measurements

The thermal conductivity and diffusivity of polymer composite materials were determined with an original method in only one measurement [4, 5]. These thermophysical parameters were obtained at room temperature with their corresponding statistical confidence bounds. Besides, this method has several advantages, such as its simplicity, good sensitivity and short-time for a complete characterization of polymer or polymer composite material thermal parameters with the ability to perform non-destructive probing [4, 5]. The sample under study is fixed between two metallic plates (44 mm × 44 mm) (Fig. 3). A good thermal exchange between the different elements is insured by a high thermally conductive grease. The whole device is placed in a vacuum chamber connected to a pumping system. The front side of the first metallic plate is fixed to a thermoelectric cooling device and is heated periodically using a sum of five sinusoidal signals. The rear side of the second metallic plate is in contact with gas at ambient temperature and pressure lower than 10^{-5} mbar. The temperature is measured with K-type thermocouples that were placed inside both the front and rear metallic plates. The experimental heat transfer function is then calculated at each excitation frequency as the ratio between the Fourier-transformed temperatures of the front and rear plates [4, 5]. Finally, a parameter estimation technique (Levenberg–Marquardt method) is applied to estimate simultaneously both thermal conductivity (k) and diffusivity (a) [6].

3. Results

3.1. PP/Cu composites

The thermal conductivity values of PP/Cu composites and their associated uncertainties are presented in Fig. 4 versus filler volume fraction. As expected, we note an increase of thermal conductivity with increasing filler volume fraction. At a given filler concentration, the composite filled with smaller copper particles ($Cu_{(a)}$) has a higher thermal conductivity than the one filled with the larger particles ($Cu_{(b)}$). This difference is more significant at higher filler concentrations. The same phenomenon is observed in Fig. 5 in the thermal diffusivity case. In Figs 4 and 5, the lines plotted have to be considered only as guidelines for eye and do not correspond to any physical model.

3.2. PP/Al composites

The thermal conductivity and diffusivity results of PP/Al composites are also presented respectively in Figs 4 and 5. We observe a non-linear raise of these two thermal parameters when the filler concentration increase. This increasing was foreseeable, because the fillers have a higher thermal conductivity and diffusivity than the polymeric matrix. However, for a given concentration, the composite filled with large particles has a higher thermal conductivity and diffusivity than the one filled with small particles. We note that the effect of particle size on the thermal behavior is not the same between both PP/Al and PP/Cu composites. Besides, as expected, we show that for a given filler concentration (Al and Cu) the composites filled with copper particles

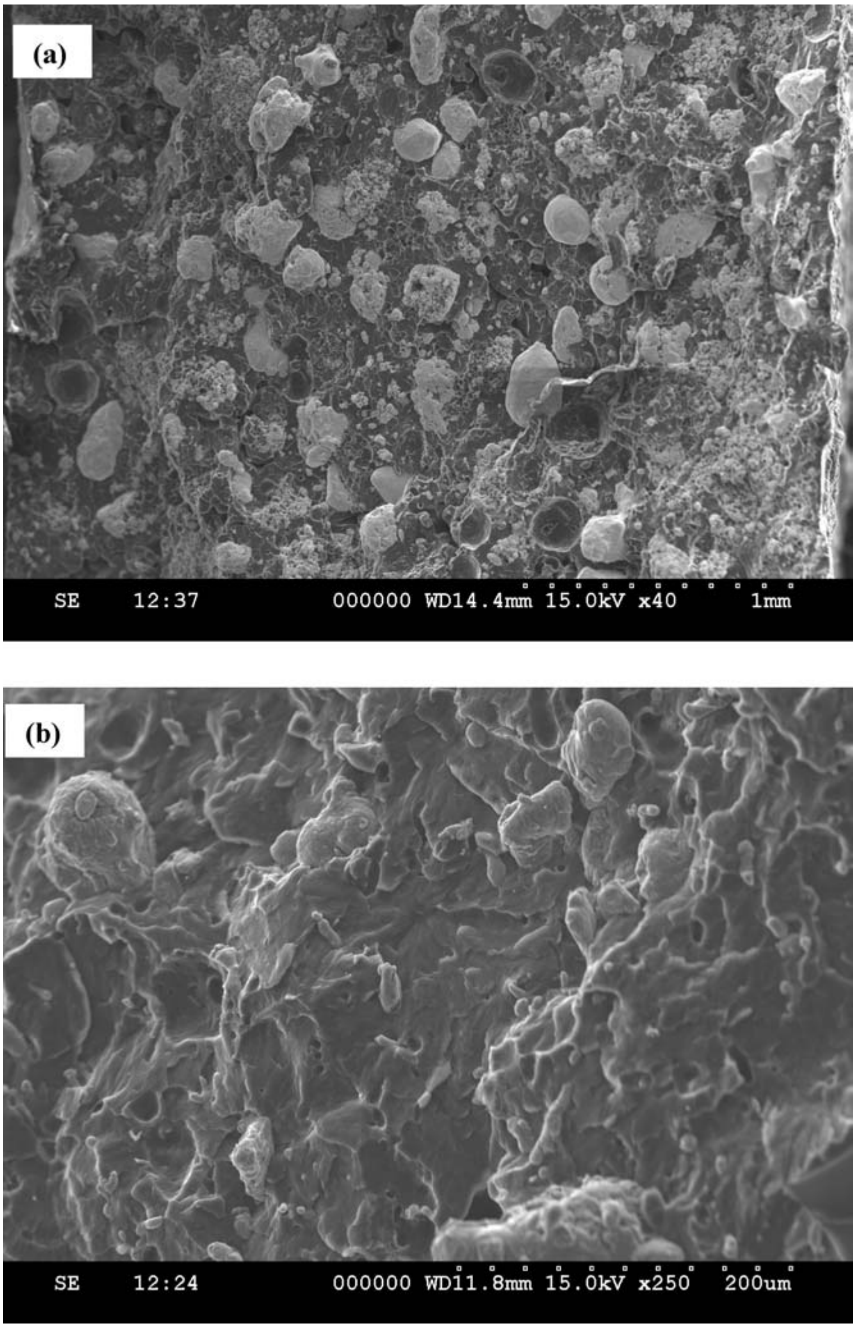

Figure 2 SEM micrograph for (a) 30% of $Cu_{(b)}$ and (b) 10% of $Al_{(b)}$ volume fraction in the Polypropylene matrix.

have a higher thermal conductivity than the ones filled with aluminum, due to the higher thermal conductivity of copper ($k = 387\ Wm^{-1}K^{-1}$) versus aluminum ($k = 237\ Wm^{-1}K^{-1}$).

4. Discussion

The thermal behavior of PP/Cu composites is in agreement with literature works, which showed that the use of small particles increases the thermal conductivity for a given volume fraction [2, 7–9]. This phenomenon is the same for both electrical conducting and insulating fillers [2, 7–9]. This result is generally interpreted by the higher probability of forming conductive chains of fillers when small particles are used [2, 8]. However, in PP/Al composite case, we note an opposite thermal behavior than the literature and PP/Cu ones.

Electrical conductivity measurements (not shown here) were done for Al fillers and the results confirmed that these particles are oxidized and are electrical insulators contrarily to the copper ones. Nevertheless, the thermal behavior observed is not consistent with the ones reported for dielectric fillers [2, 10]. This shows that there is no electron mode transport following conductive chains and that the heat transport mode in the PP/Al composites is not mainly due to electron transport along Al chains contrarily to PP/Cu composites. This was confirmed by performing electrical measurements. These measurements (not presented here) showed that PP/Al composites were always electrical insulators even for the higher filler volume fractions. The principal heat transport mode in the PP/Al case is due to the phonons mean free path. On the other hand, the anomalous thermal behavior of $PP/Al_{(b)}$

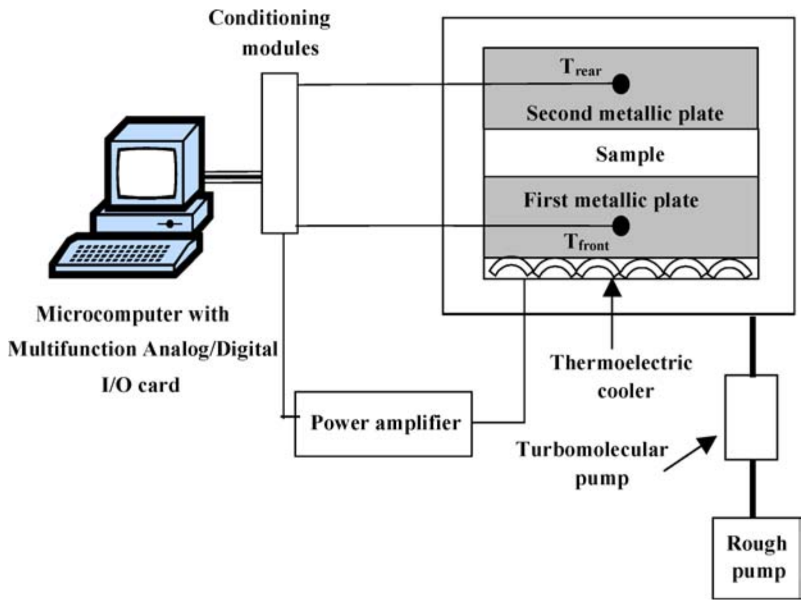

Figure 3 Schematic view of the experimental set-up.

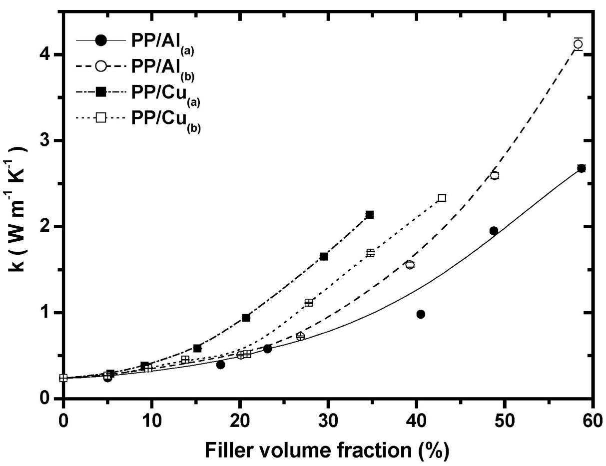

Figure 4 Thermal conductivity of PP/Al and PP/Cu composites.

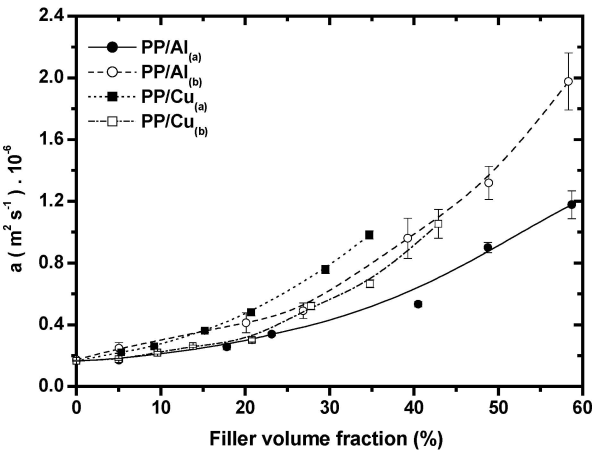

Figure 5 Thermal diffusivity of PP/Al and PP/Cu composites.

composites might also be explained by the higher size dispersion of this filler. Besides, the large filler particles have a higher proportion of aluminum than the smaller ones due to the oxide layer which covers the particles. This gives a higher heat transport ability to the PP/$Al_{(b)}$ composite. Besides, in this case the heat transfer may combine the contribution of phonon and electron transport mode. It is likely that the contribution of electron transport plays a minor role: localized inside the particle and stopped at the oxide layer surrounding the particle. This layer prevents the continuity of the electronic transport mode: the heat propagation between Al particles and between Al particle and PP matrix is restricted to the phonons mean free path [5].

Finally, we can also mention that this phonon mean free path is lower in $Al_{(a)}$ particles than in the $Al_{(b)}$ particles. This also may contribute to lower thermal properties in the case of PP/$Al_{(a)}$ composites contrarily to the PP/$Al_{(b)}$ ones.

5. Conclusion

The thermal conductivity and diffusivity measurements of polypropylene filled with aluminum and copper powders were presented and analyzed. Two sizes of each filler type were used in the sample composite processing. The thermal conductivity and diffusivity of each composite were studied upon filler volume concentrations. We have highlighted the higher heat transport ability of the smaller particles in the PP/Cu composite case. This result is foreseeable and in agreement with the literature results. However, an anomalous behavior of thermal conductivity and diffusivity in PP/Al composites was observed. This weird phenomenon was explained by the partial oxidation of aluminum fillers [5].

The PP/Al composites manufactured exhibit higher thermal transport properties than the homopolymer matrix whereas electrical insulating properties of PP are preserved. This kind of composite structure might be of great interest in some technological applications where both good electrical insulation and high thermal conduction are required.

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Received 8 June
and accepted 17 December 2004