Thermophysical Properties of Composites Formed from Ethylene–Vinyl Acetate Copolymer and Silver-Coated Hollow Glass Microspheres

V. Cecen

Freiburger Materialforschungszentrum and Institut für Makromolekulare Chemie, Stefan-Meier-Strasse 21, D-79104 Freiburg i. Br, Germany

ABSTRACT: The primary purpose of this study was to prepare a new type of silver-coated hollow glass microspheres and to make available this facility for the fabrication of thermally conductive polymeric composites based on ethylene–vinyl acetate (EVA) copolymer. Thermally conducting composites could be produced with a silver coating around the hollow glass microspheres, despite the low silver volume content. The experimental results are discussed and compared to various theoretical models. The thermal diffusivity and the specific heat of the composites were also characterized and are reported. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 685–697, 2011

Key words: composites; heat capacity; thermal properties

INTRODUCTION

Polymers are materials with very low values of thermal conductivity, which roughly vary from 0.15 W m^{-1} K^{-1} for amorphous polymers such as polystyrene or poly(methyl methacrylate) to 0.5 W m^{-1} K^{-1} for highly crystalline polymers such as high-density polyethylene.[1] Plastics, with some exceptions, which include polypyrrole, polyaniline, and polyacetylene, are inherently insulating materials and have electrical conductivities on the order of 10^{-13}–10^{-15} S/cm.[2,3] However, in recent years, conductive composites have attracted considerable interest in both academia and industry because of their potential applications in advanced technologies, for example, in circuit boards, heat exchangers, electronic protection, sensors, and electromagnetic shielding, which require an improvement in the thermal conductivity (λ) of plastics.[4–7]

Thermally conductive materials are designed by the blending of polymeric matrices with conductive fillers. Among typically used fillers belong graphite and metallic powders,[8–11] boron nitride,[12] and synthetic diamond powder.[13] Very recently, some authors have reported the use of carbon nanotubes as prospective fillers for the preparation of thermally conductive polymeric composites.[14] Also, to obtain a low percolation threshold, several conductive fillers can be used, including carbon black,[15] graphite,[16]

metals,[17] metallized organic/inorganic fillers,[18] and carbon nanotubes.[19] The use of exfoliated graphite and carbon nanotubes has led to a substantially higher λ and a much reduced percolation threshold in composites in comparison with the use of conventional fillers.[20–22]

Metallic powders are still very broadly applied as fillers for the preparation of both highly electrically and thermally conductive composites.[23] However, most metallic fillers have a spherical shape, which induces a higher percolation threshold, in contrast to irregularly shaped particles, which induce increases in the filler fraction in the composite, the price of the final material, and its density (ρ). One approach to overcoming this drawback is based on the use of metal as a coating for fillers. To combine the advantages of a low ρ and a lower percolation threshold, metallized organic/inorganic particles and fibers can be used as substitutes for metals.[24–30] The advantages of these materials are the easy metallization of convenient substrates of various shapes, high conductivity, low ρ, and low price compared to pure metals.[31]

Various metal-coated inorganic fillers, such as glass fibers, carbon fibers, and mica, have been frequently studied, especially for Electromagnetic shielding (EMI) shielding applications. Metals commonly used for coatings are silver, copper, and nickel. Silver is a very convenient material for metallization because of its high conductivity and because its oxide is also conductive; therefore, exposure to humidity does not significantly change its conductivity, in contrast to alumina or copper.[32] Successful coatings of polymeric fillers can bring many advantages, including a lower density of the final filler, a

lower price, and variability in the shape of the filler.[33,34]

Surprisingly, many fewer studies have been devoted to the investigation of the thermal conductivity of composites (λ_c) filled with metal coated fillers.[35,36] Very recently, Krupa et al.[29] reported the preparation of a new type of thermally conductive filler based on wollastonite fibers electrochemically coated with silver. They found that λ of pure ethylene–vinyl acetate (EVA) increased 10 times when the polymer was filled with 80 wt % (41 vol %) silver-coated wollastonite. However, the silver volume fraction inside the composite (ϕ_{Ag}) corresponding to this filler loading was much lower (ca. 14 vol %). Similarly, Krupa and coworkers[34,37] reported a significant improvement in the thermal and electrical conductivities of high-ρ polyethylene with silver-coated polyamide particles. Agoudjil et al.[38] investigated the thermal and electrical behavior of EVA composites filled with silver-coated solid glass sphere particles. Their results indicate that thermally conducting composites could be produced with a silver coating around glass particles.

It is known that hollow glass microspheres are a kind of particulate material that has been widely used in paint and coating systems because of their low ρ, excellent chemical and thermal stabilities, and low price.[39] Although hollow, they will stand up to the high pressure of injection molding and the shear force achieved in conventional blending operations with insignificant breakage of spheres. In the light of the information mentioned, one can expect that if hollow glass microspheres are coated with silver, the silver-coated hollow spheres composites could have potential uses in many fields, such as in computer chips, sensors, electronic packaging, electromagnetic radiation shielding, and heat exchangers, as they combine the properties of the hollow glass spheres and the silver together.

The major goal of the research described in this article was to prepare silver-coated hollow glass spheres and to make available the mentioned facilities for the fabrication of the thermally conductive polymeric composites based on EVA copolymer. This study was focused on the experimental investigation and theoretical modeling of λ_c. A periodical method was adapted to perform the measurement of λ of polymeric composite materials. We found that the hollow spheres coated with silver could be effectively used to improve λ_c at low silver volume contents.

EXPERIMENTAL

Raw materials

The raw materials used to fabricate the composites were hollow glass microspheres as fillers and EVA co-

polymer as the matrix system. The hollow glass microspheres ($\rho = 0.45$ g/cm^3) were supplied by Techazil (Zilina, Slovakia), and the particles size varied from 5 to 90 µm. They had λ values in the range 0.1–0.2 W m^{-1} K^{-1}. A commercial EVA copolymer, Levapren400 (Lanxess, Leverkusen, Germany), containing 40 ± 1.5 wt % vinyl acetate and with a melt flow index (190°C/2.16 kg) of 5.0 g/10 min, was chosen as the matrix. The other reagents used in the experiments were analytically pure and were used as received.

Metallization of the hollow glass sphere fillers

The metallization of hollow glass microspheres was carried out with an electroless metallization method.[40] Three solutions were prepared: solution A, which consisted of silver nitride (24 g) and ammonium nitrate (36 g) dissolved in 1500 mL of distilled water; solution B, which was obtained by the dissolution of sodium hydroxide (38 g) in distilled water (1500 mL); and solution C, which consisted of sakaroz (25 g) and tartaric acid (3 g) dissolved in 1500 mL of distilled water. The bath for the electroless deposition of silver was prepared by the mixture of 900 mL of solution A, 900 mL of solution B, and 450 mL of solution C at room temperature. The hollow microspheres were added to the mentioned solution, and the system was then continuously stirred at room temperature for 20 min. The resulting silver-coated hollow spheres were washed repeatedly with distilled water, filtered, and dried at 70°C in an oven for 12 h.

Sample preparation

Neat EVA copolymer was mixed with the silver-coated hollow glass spheres in a 30-mL mixing chamber of a Brabender PLE 331 plasticorder, (Duisburg, Germany) at 120°C for 10 min at a mixing speed of 35 rpm. Taking into account the fact that the loadings of hollow glass microspheres are generally from 5 to 15 vol %, in this study, we filled EVA to a level of 30% loading to increase the possibility of getting good results. After mixing, the compounded material was transferred to a Fontijne 200 laboratory press (Vlaardingen, Netherlands). The specimens, with dimensions of 44 × 44 × 5 mm^3, were compressed and molded at 120°C for 5 min.

Thermophysical properties

A periodic method was used to determine both λ and the thermal diffusivity of the polymer composite materials (a) at room temperature. This method was based on the use of a small temperature modulation in the sample.[41] The samples had a parallel piped shape (44 mm on a side and 5 mm in thickness).

The composite sample was sandwiched between two metallic plates. The front side of the first metallic plate was heated periodically. The temperature was measured with thermocouples inserted in the front and rear metallic plates.[41,42] The thermophysical parameters of the sample were identified by comparison of the experimental and theoretical heat-transfer functions.[41] The system under consideration was modeled with the one-dimensional quadrupoles theory. The experimental heat-transfer function was identified at each frequency as the ratio between the Fourier transforms of the temperatures at the front and rear plates.[41] A parameter estimation technique was applied to estimate both λ and a. The identification of λ and a was a nonlinear optimization problem that was solved iteratively: starting with sufficiently accurate initial guesses for the unknown parameters, we successively refined the estimates by using the Levenberg–Marquardt method.[41,43]

The specific heat capacity (C_p) values of the composite samples were determined with λ and a values, with known ρ:

$$C_p = \frac{\lambda}{\rho a} \qquad (1)$$

Scanning electron microscopy (SEM) observation

Scanning electron microscopes (JEOL-6510, (Nakagami, Japan) Tesla BS 300, (Tesla, Czech Republic)) were used to examine the morphology of the samples. We obtained the observed surfaces of the composite by breaking the samples at liquid-nitrogen temperature (cryofracture).

Granulometry and ρ measurements

Size distribution of the microspheres was obtained with a Fritsch Particle Sizer Analysette 22, (Oberstein, Germany) from the measurements of sedimentation of the particles in water at room temperature.

The specific density of the silver-coated hollow spheres (ρ_f) was determined at room temperature with a pycnometer, and their value was found to be 2.31 g/cm^3. The specific densities of the composite samples (ρ_c's) were determined according to ASTM D 153 with decane as the working substance and a Sartorius R160P, (Chicago, USA) balance.

Differential scanning calorimetry (DSC)

The melting behaviors of pure EVA and its composite were studied with a Mettler-Toledo DSC 821E, (Ohio, USA) which scanned from 0 to 150°C at a heating rate of 10°C/min under a nitrogen atmosphere. Polymer and composite samples weighing about 20 mg closed in aluminum pans were used throughout the experiments. The DSC data of neat EVA and selected composite were recorded at the second heating of the samples with a ramp of 10°C/min. DSC was also used to determine the specific heat capacity of the pure hollow glass spheres (C_{pHGS}). The hollow glass microsphere powder (20.1 mg) was put into an aluminum pan and covered with an aluminum cover. The measurement was conducted at a scan rate of 10°C/min under a nitrogen atmosphere over the temperature range 20–90°C.

RESULTS

Filler characterization

Figure 1(a,b) shows the SEM images of the silver-coated hollow spheres before and after silver electroless deposition, respectively. Figure 1(a) shows the as-received hollow spheres to be intact, with only a small fraction of broken spheres. As shown in Figure 1(b), the silver-coated hollow spheres had rougher surface with many cracks in the coating layer. These cracks were likely due to the volume shrinkage accompanying water loss during drying. The hollow spheres coated with silver, on the other hand, were fractured and gave rise to fragments [Fig. 1(b)]. This perhaps was a feature related to a shearing type of phenomena from stirring the hollow microspheres in a bath solution during the electroless silver coating of the fillers. Notably, as is known from a scientific and practical point of view, even when there was a substantial degree of breakage under the coating process, a thin glass flake was produced with good potential for reinforcing the thermoplastics. Although the hollow sphere surface appeared to be fairly evenly coated with a continuous shell [Fig. 1(c)], these metallic deposits did not form a homogeneous coating or shell [Fig. 1(d)]. Despite this fact, this filler effectively improved λ_c, as shown later.

Granulometric measurement, given in Table I, showed the absence of big agglomerates of particles. The differential and integral volume distributions are shown in Figure 2. The results indicate that most particles had a size in the range from 3 to 90 μm; the most frequently occurring fraction had a size of 30–40 μm.

The thickness of the silver shell (Δ) was estimated from SEM measurements, which yielded an average value between 1 and 1.5 μm [see Fig. 1(e)]. From the cracked silver spheres, the wall thickness of the hollow spheres was estimated to be about 0.5 μm. For simplicity, let us assume that the geometry of the filler is illustrated in Figure 3, where R_G is the radius of the neat hollow glass sphere and R_f is the radius of the silver-coated hollow glass sphere. The ratio between Δ and R_f is specified in the formula by Krupa et al.[37]

$$\frac{\Delta}{R_f} = 1 - \left[\frac{\rho_{Ag} - \rho_f}{\rho_{Ag} - \rho_{HGS}}\right]^{1/3} \qquad (2)$$
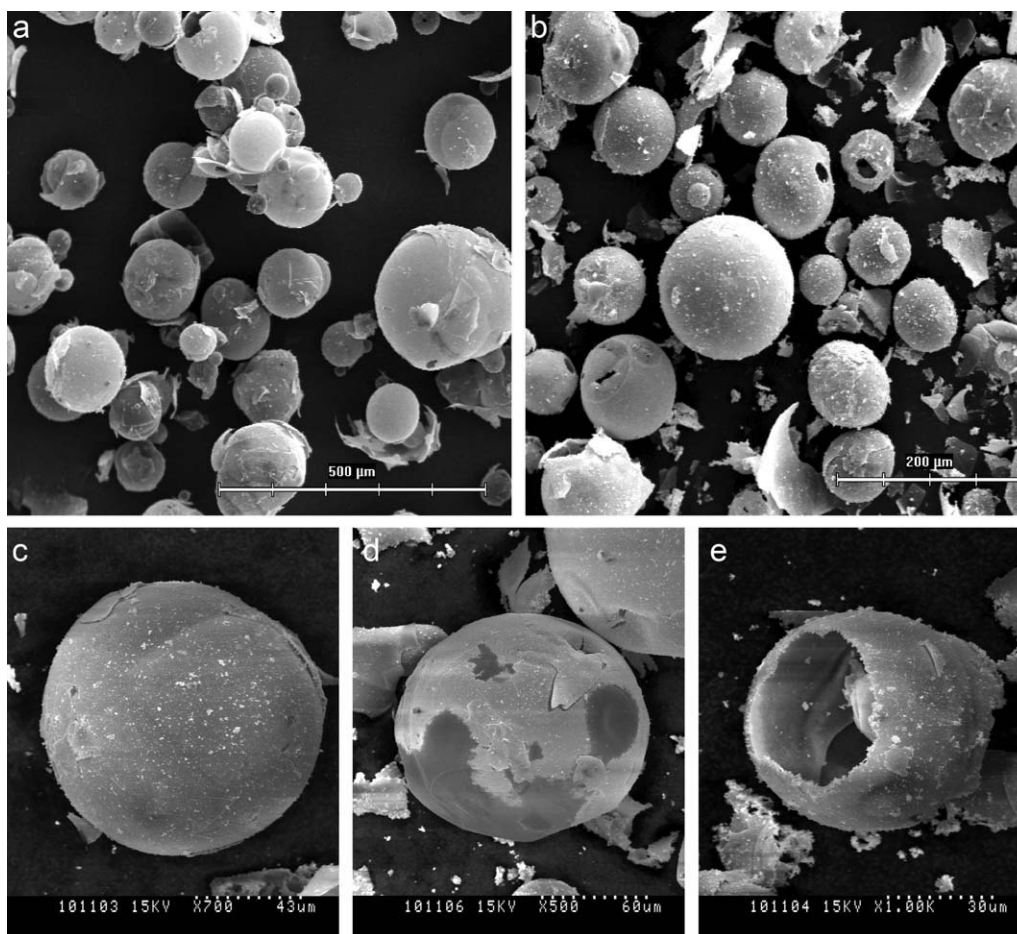
Figure 1 SEM micrographs of the hollow glass microsphere particles: (a) before and (b) after metallization. SEM images of hollow spheres (c) well covered and (d) insufficiently covered by silver. (e) Crushed hollow spheres can be seen in the image.

where $\rho_{Ag} = 10.5$ g/cm^3 is the specific density of silver and $\rho_f = 2.31$ g/cm^3 is the density of the silver-coated hollow glass spheres.

The particle size distribution suggested that the hollow glass microspheres coated by silver possessed a bimodal size distribution data with a maximum at about 38 μm. With this value and eq. (2), the thickness of silver shell was found to be about 1.25 μm. This identified the approximate range of the shell thickness.

With regard to the approximate range of the wall Δ and the hollow spheres noted in this section, the approximate volume ratios of air, the pure hollow glass spheres, and silver for the filler could be easily found from geometric calculations by means of the model geometry of the coated spheres. The calculated values of the volume ratios of air, silver, and the pure hollow spheres were 74.8, 18.5, and 6.7%, respectively.

Morphology of the composites

Figure 4(a) displays the SEM micrographs of the composite with 10 wt % hollow glass microspheres, which demonstrated a fair dispersion of fillers, with no obvious agglomeration. Most of the hollow spheres on the fracture surfaces were broken. This indicated that the hollow spheres were not strong enough to resist cracking. It was confirmed that some surviving hollow microspheres of specimens

TABLE I
Granulometric Parameters of the Particles of the Filler

D_5 (μm)	D_{10} (μm)	D_{20} (μm)	D_{50} (μm)	D_{80} (μm)	D_{90} (μm)	D_{99} (μm)
10.64	13.93	18.62	31.04	47.75	57.18	77.36

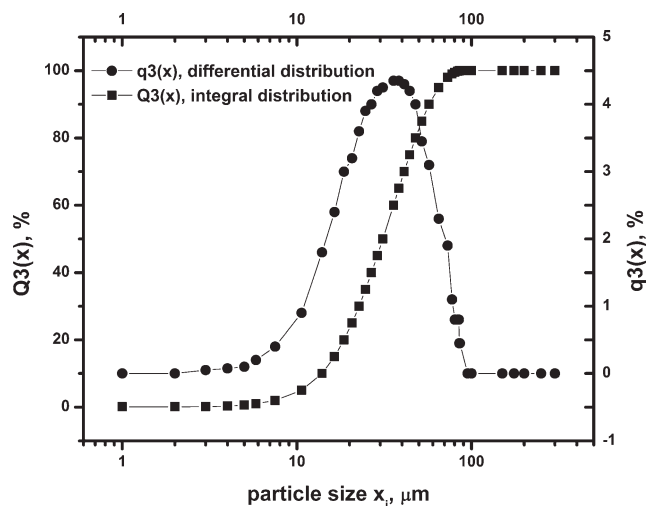$D_i - i$ % of the volume of particles was smaller than dimension D_i.

Figure 2 Particles size distribution of the fillers.

were the ones that had their equators embedded well below the fracture surface but partially exposed to cracking [Fig. 4(b)]. The cavities obviously seen in the higher magnification micrograph also indicated a lack of adhesion between the polymer and the hollow spheres; this was a sign of poor interfacial interaction. In addition, it was virtually impossible to avoid damaging these microspheres, but when there was a substantial degree of breakage in the compounding machine, a thin glass flake was produced with good potential for reinforcing the thermoplastic composite.

Thermal conductivity of the composites

The λ_c values and their associated uncertainties are summarized in Table II and are plotted in Figure 5 versus the filler volume fraction (ϕ_f). λ for the polymers containing 30 vol % silver-coated hollow spheres achieved a maximum increase of 0.36 W m^{-1} K^{-1}; this was 90% above the value for the pure polymer (0.19 W m^{-1} K^{-1}). This increase of λ was

Figure 4 SEM micrographs of the EVA/hollow sphere–Ag composite (90/10 w/w).

foreseeable because the filler had a significantly higher λ than the polymeric matrix, as discussed later.

A somewhat surprising feature was that the increase in λ became less significant with increasing filler content. Clearly, a further increase in hollow spheres caused a considerable divergence of the λ values from the nonlinear tendency of the experimental
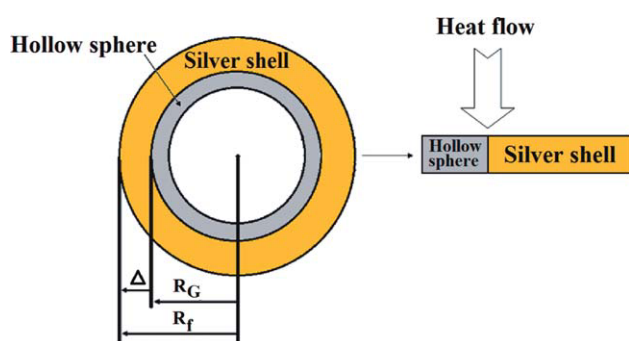

Figure 3 Model geometry of the silver-coated hollow glass microspheres. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
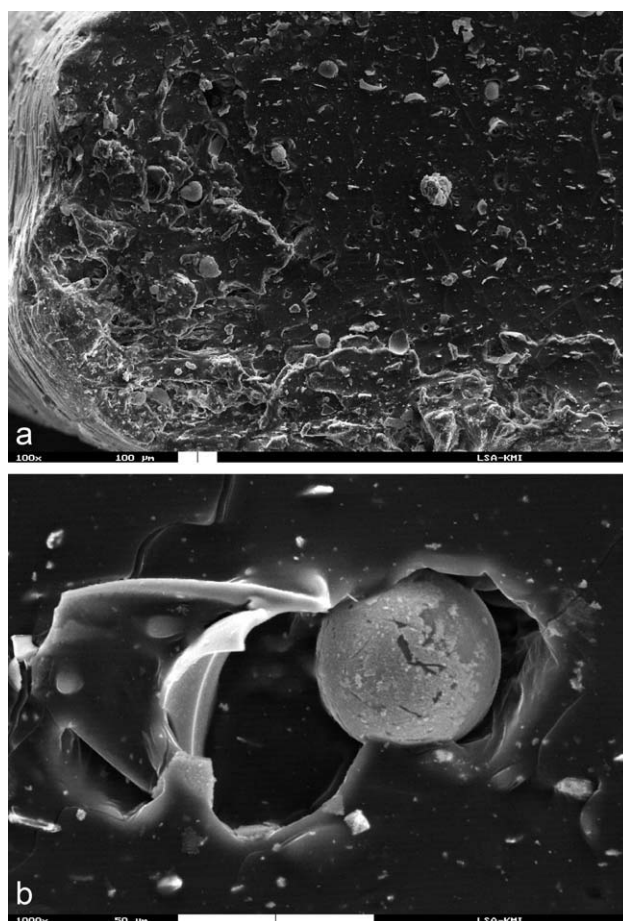
TABLE II
Measured Values of λ_c and ρ_c

w_f	ϕ_f	ρ_c (g/cm^3)	$w_{f,Ag}$	$\phi_{f,Ag}$	λ_c (W m^{-1} K^{-1})
0	0	1.000 (0.008)	0	0	0.188 (0.005)
0.02	0.008	1.012 (0.012)	0.017	0.002	0.190 (0.004)
0.06	0.026	1.035 (0.014)	0.050	0.005	0.205 (0.002)
0.08	0.036	1.048 (0.016)	0.067	0.006	0.197 (0.006)
0.10	0.045	1.060 (0.019)	0.083	0.008	0.213 (0.005)
0.12	0.055	1.073 (0.023)	0.100	0.010	0.211 (0.002)
0.20	0.096	1.128 (0.026)	0.167	0.017	0.237 (0.004)
0.30	0.154	1.205 (0.031)	0.250	0.027	0.262 (0.003)
0.40	0.221	1.294 (0.035)	0.334	0.039	0.328 (0.006)
0.50	0.298	1.396 (0.043)	0.417	0.052	0.357 (0.009)

$w_{f,Ag}$, weight fraction of silver in the composite; $\phi_{f,Ag}$ volume fraction of silver in the composites. The corresponding uncertainties are given in parentheses.
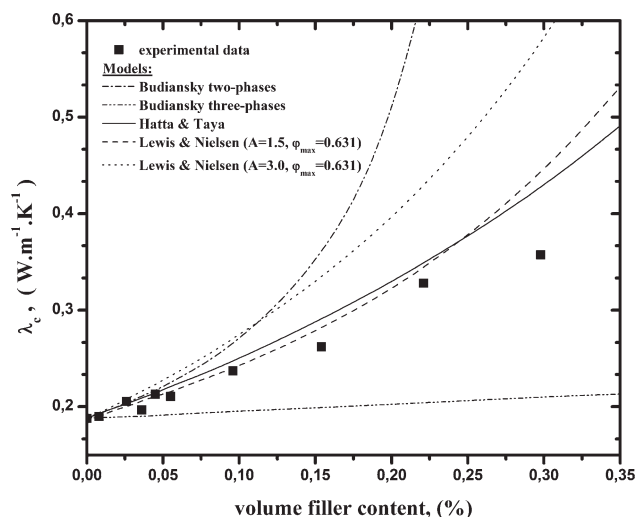
Figure 5 Comparison of the experimental values of the EVA/hollow sphere–Ag composites to some reported models.

data (∼ 30 vol %, see Fig. 5). The reason for this interesting result may have been the nonhomogenous dispersion of filler in the polymer matrix, although the possible formation of an interparticle network may also have been created within the matrix at the mentioned level of concentration. Notably, the homogeneous dispersion of the filler was of prime importance because nonhomogenous dispersion would have produced a defect at the interface, which would have hindered the percolation network of the fillers in the composite and, hence, limited λ_c.

On the other hand, the small rise and fall in λ observed at the low filler concentrations was of concern. As is well known, λ_c critically depends on the mixing quality of the heterophase polymer composition. However, this could not always be fulfilled during the preparation of the composites. Insufficient homogenization usually creates complicated problems, especially those related to λ. With regard to the arguments that are briefly discussed here, we concluded that the mentioned smaller rise and fall in λ was probably due to possible insufficient homogenization due to the lower mixing quality of composite melts at low filler loadings.

DSC

DSC was used to observe the influence of the fillers on the melting point of the EVA matrix and the heat of fusion of the EVA matrix (ΔH_{mEVA}). The results are given in Table III. For testing, pure EVA and its composite with 50 wt % silver-coated hollow spheres were used. The degree of crystallinity (w_x) was calculated from the heat of fusion obtained from the area under the DSC curve. The value

$\Delta H_m^+ = 293$ J/g was used for the heat of fusion of 100% crystalline polyethylene.[29,44]

The filler only very slightly influenced the melting point of the polymer, a fact that was caused by the change in the lamellar thickness of the crystallites.[29,45] Clearly, the presence of up to 50 wt % silver-coated hollow spheres in EVA had little influence on the crystallite sizes. Pure EVA had a melting enthalpy of 3.4 J/g; this value rose to 3.9 J/g when 50 wt % hollow spheres were introduced. Table III shows that the values of w_x were almost the same for pure EVA and its composite containing 50 wt % hollow spheres. The slight increase in w_x with filler loading was believed to be due to the fact that the probable agglomerates of the hollow spheres acted as nucleating agents and slightly facilitated the crystallization process. This was consistent with the studies done by Misra and coworkers[46,47] and Huang et al.[48] They found that the addition of fillers could either facilitate or hinder the crystallization of the polymer matrix, depending on the dispersion of the filler in the polymer. The well-dispersed fillers did not have a nucleating effect and mainly acted as obstacles, but the agglomerates of the fillers acted as nucleating agents and slightly improved the crystallization.

a values

The measurements of the thermal diffusivity transport coefficient (a) of the silver-coated hollow glass spheres filled EVA versus those of the spheres are shown in Figure 6. In general, a increased with increasing hollow sphere content within an acceptable uncertainties; this is a typical characteristic of filled composites.[17,29] As observed previously in the case of λ results, the spread of the data was detected at low filler concentrations, as shown in Figure 6.

ρ and specific heat

As described previously in this article, the computation of C_p values requires the knowledge of sample ρ. A plot of ρ versus ϕ_f is given in Figure 7. We also compared the measured values to a theoretical curve computed according to the rule of mixture [eq. (3)] considering a two-phase system and using ρ values

TABLE III
DSC Results for the Pure EVA Matrix and Its 50/50 Composite

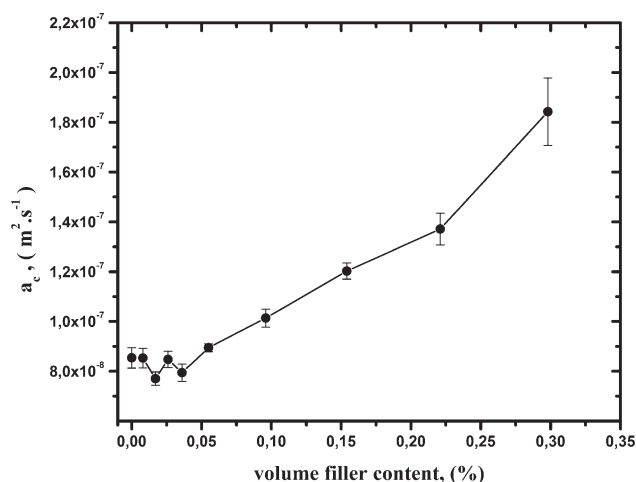| Sample	Melting temperature (°C)	ΔH_{mEVA} (J/g of EVA)	w_x (%)
EVA	44.1	3.4	1.2
50/50	43.6	3.9	1.3

Figure 6 *a* values of the EVA/hollow sphere–Ag composites.

of the EVA matrix (ρ_{EVA}) and the silver-coated hollow spheres (ρ_f) of 0.98 and 2.31 g/cm^3, respectively:

$$\rho = \rho_{EVA}\phi_{EVA} + \rho_f\phi_f \qquad (3)$$

where ϕ_{EVA} is the volume fraction of the EVA matrix. As shown in Figure 7, the experimental data behaved linearly according to the additive rule, with high accuracy in the whole range of ϕ_f tested.

The specific heat values of the composites at different filler contents are normally obtained with eq. (1) when λ and a of the composites are known. The plot of the specific heat versus filler loading is presented in Figure 8. The data shown in Figure 8 exhibited large uncertainty bounds. This might have been due to the propagation of ρ and λ and a uncertainties. A linear dependence of the specific heat upon the weight filler fraction was observed for
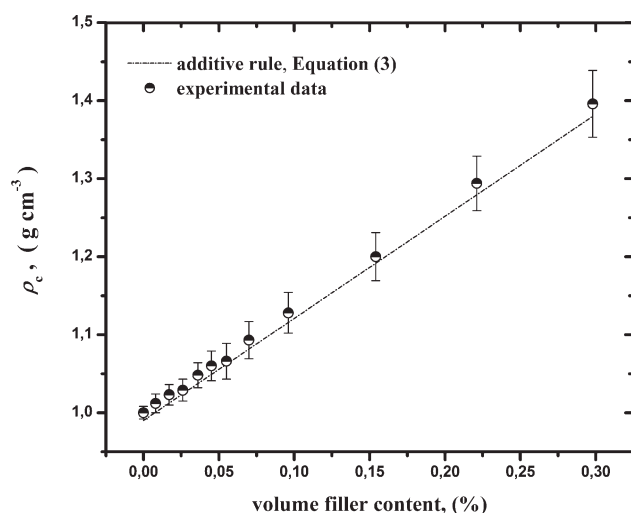

Figure 7 Dependence of ρ of the EVA/hollow sphere–Ag composites on the volume filler content.
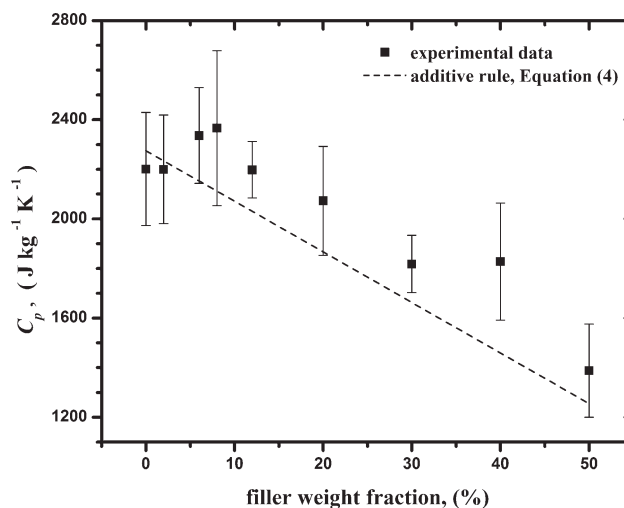

Figure 8 C_p versus w_f for the EVA/hollow sphere–Ag composite samples.

these composites, except for low filler weight fractions (w_f's; weight < 10%).

We calculated the theoretical C_p values according to the rule of mixture [eq. (4)] considering a three-phase system and using specific heat capacity values of EVA (C_{pEVA}), the hollow glass spheres (C_{pHGS}), and silver (C_{pAg}) of 2275, 370, and 209 J kg^{-1} K^{-1}, respectively:

$$C_p = C_{pEVA}w_{EVA} + C_{pAg}w_{Ag} + C_{pHGS}w_{HGS} \qquad (4)$$

where w_{EVA}, w_{HGS}, and w_{Ag} are the weight fractions of EVA, the neat hollow glass spheres, and silver, respectively. The specific heat capacity of the neat hollow glass microsphere was determined experimentally with DSC. The experimental data for the specific heat were compared to the theoretical curve in Figure 8. From closer observation of the experimental and theoretical data, we revealed that the silver-coated hollow spheres were able to lower the specific heat of EVA simply through the rule of mixture. The silver-coated hollow spheres had a lower specific heat than the pure EVA; mixing them together created a system that resulted in a compromise between the two constituents.

DISCUSSION

Modeling of the thermal conductivity of the silver-coated glass sphere fillers (λ_{Ag})

As is well known, the evaluation of experimental data according to various models requires knowledge of the thermal conductivity of the filler (λ_f).[29] Because the direct measurement of λ_f is very complicated, λ_{Ag} was estimated with a simple model. In the common case, where λ of the metal is several orders of magnitude greater than λ_f, the parallel

conduction model has general validity. On the other hand, the series conduction model is of use only when the relative λ's of the two phases are similar, and its predictions have little validity. According to Krupa et al.,[37] λ_f can be estimated as follows: the hollow spheres coated with a silver shell can be roughly considered as a parallel set of two thermal resistors, namely, glass and silver resistors. Then, λ_f can be estimated as follows:

$$\lambda_f = \lambda_{\mathrm{HGS}} + \left(\lambda_{\mathrm{Ag}} - \lambda_{\mathrm{HGS}}\right)\varphi_{\mathrm{Ag}} \tag{5}$$

where λ_{HGS} is the thermal conductivity of the neat hollow glass spheres and ϕ_{Ag} is the volume fraction of silver in the fillers.

ϕ_{Ag} can be calculated according to eq. (6):

$$\varphi_{\mathrm{Ag}} = \frac{\rho_f - \rho_{\mathrm{HGS}}}{\rho_{\mathrm{Ag}} - \rho_{\mathrm{HGS}}} \tag{6}$$

where ρ_f, ρ_{HGS}, and ρ_{Ag} refer to the specific densities of the filler and the densities of its pure components, namely, the neat hollow glass spheres and silver, respectively.

ϕ_{Ag} was equal to 0.18. After that, λ_{Ag} could be computed as 77.52 W m^{-1} K^{-1} ($\lambda_{\mathrm{HGS}} = 0.15$ W m^{-1} K^{-1}, $\lambda_{\mathrm{Ag}} = 430$ W m^{-1} K^{-1} [49]). Recall that λ_{HGS} was determined by the extrapolation of λ_c filled with neat hollow glass spheres to a weight content of $w_{\mathrm{HGS}} = 100\%$. In this case, $\lambda_{\mathrm{HGS}} \approx 0.15$ W m^{-1} K^{-1}. This value was in accordance with values described in the literature.[50]

Comparison of the experimental data with the models

Many theoretical or semi-empirical models can be found in the literature to predict λ values of two-phase, particulate filled composites. Fortunately, periodic reviews have been published to provide critical analyses of the most useful models.[4,51–54] This study was focused on the comparison of the experimental data with those of the models described later. In the following equations, λ_m is the thermal conductivity of the polymeric matrix, and ϕ_f is the volume portion of the filler in the composite.

Hatta and Taya[55] developed a model based on the analogy of λ to the modulus that was originally developed by Eshelby.[56] The equation Hatta and Taya arrived at is as follows:[4,55]

$$\lambda_c = \lambda_m \left[1 + \frac{\varphi_f}{S\left(1 - \varphi_f\right) + \frac{\lambda_m}{\lambda_f - \lambda_m}} \right] \tag{7}$$

where $S = 1/3$ for spherical filler particles.

Hashin[57] produced the following equation to describe the effect of spherical filler particles on λ of a randomly dispersed two-phase system:

$$\lambda_c = \lambda_m + \frac{\varphi_f}{\frac{1}{\lambda_f - \lambda_m} + \frac{1 - \varphi_f}{3\lambda_m}} \tag{8}$$

Lewis and Nielsen developed a model for λ based on the Kerner equations describing the modulus of two-phase systems that provides a different response that of the second-order lower bound model.[58,59] The following equations were part of this model, which was found to be quite useful by a number of investigators:[4,51,52]

$$\lambda_c = \lambda_m \frac{1 + AB\varphi_f}{1 - B\psi\varphi_f} \tag{9}$$

where

$$\begin{cases} \psi = 1 + \frac{(1 - \varphi_{\max})\varphi_f}{\varphi_{\max}^2} \\[2ex] B = \frac{\frac{\lambda_f}{\lambda_m} - 1}{\frac{\lambda_f}{\lambda_m} + A} \end{cases} \tag{10}$$

The coefficient A depends on the geometry and orientation of the filler particles. Different values of the maximum packing fraction of the filler ($\phi_{\max}$) are possible with spherical fillers because of the differences in either the packing arrangement or particle size distribution. A value of 0.637 was derived for the maximum packing of monodisperse particles randomly dispersed in a matrix.[4] However, a whole space of matrix must be available for filler distribution in this case. This is true for fully amorphous matrices.[29] In the case of a semicrystalline matrix, the crystalline part is not available for the distribution of the filler, and therefore, the aforementioned value must be recalculated with consideration of only the amorphous part of the polymer. w_x of pure EVA was found to be 1.2 wt %. From the knowledge of the specific density of pure EVA ($\rho_{\mathrm{EVA}} = 0.98$ g cm^3) and from the density of the crystalline phase of polyethylene's component of the EVA copolymer ($\rho_x = 0.997$ g cm^{3} [44,60]), the volume portion of the crystalline phase of EVA (ϕ_x) could be estimated from eq. (9):

$$\varphi_x = \frac{\rho_{\mathrm{EVA}} w_x}{\rho_x} \tag{11}$$

Thus, the volume portion of the crystalline phase in EVA was equal to 0.01. The amorphous volume portion was 0.99, and the maximum volume fraction of the filler (ϕ_m^a) in EVA could be estimated as follows: $\phi_m^a = \phi_x \phi_{\max} = 0.631$. As for parameter A,

TABLE IV
Summary of the Experimentally Determined Values of λ_c and λ Predicted from the Models

ϕ_f	b	c	ϕ_{Ag}	ϕ_{HGS}	λ_c (W m^{-1} K^{-1})	λ_c^3 (W m^{-1} K^{-1}, three-components model)	λ_c^{H-S} (W m^{-1} K^{-1})
0	859.5	−97.3	0	0	0.188	0.188	0.188
0.008	854.4	−97.3	0.002	0.007	0.190	0.189	0.189
0.026	846.7	−97.1	0.005	0.022	0.205	0.190	0.191
0.036	844.1	−96.9	0.006	0.030	0.197	0.190	0.191
0.045	838.9	−96.9	0.008	0.038	0.213	0.191	0.193
0.055	833.8	−96.9	0.010	0.046	0.211	0.192	0.194
0.096	815.7	−96.6	0.017	0.081	0.237	0.195	0.198
0.154	789.9	−96.1	0.027	0.129	0.262	0.199	0.203
0.221	759.0	−95.7	0.039	0.185	0.328	0.204	0.211
0.298	725.5	−95.0	0.052	0.250	0.357	0.210	0.218

λ_c, thermal conductivity of the composites according to the experimental data; λ_c^3, thermal conductivity of the composites according to eqs. (14a)–(14e); λ_c^{H-S}, thermal conductivity according to the Hashin–Shtrikman model [eq. (8)]; b, c, parameters of eq. (14); ϕ_{Ag}, volume fraction of silver in the filler; ϕ_{HGS}, volume fraction of the hollow glass spheres in the filler.

according to results found in the literature, values of 1.5 and 3.0 were chosen for spherical filler particles.[4]

A self-consistent calculation of λ_c presented by Budiansky[61] was based on an analogy with an electrostatic problem.[62] This model makes it possible to define λ of N-component systems from only knowledge of the thermal conductivities (λ_i) and volume fractions (ϕ_i) of the pure components according to eq. (12):

$$\sum_{i=1}^{N} \phi_i \left[\frac{2}{3} + \frac{1}{3} \left(\frac{\lambda_i}{\lambda_c} \right) \right]^{-1} = 1 \qquad (12)$$

For a two-phase system (matrix and filler), after algebraic manipulation, eq. (12) can be written in the form given by eqs. (13a)–(13d):

$$\lambda_c = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \qquad (13a)$$

$$a = 2 \qquad (13b)$$

$$b = \lambda_f - 2\lambda_m - 3(\lambda_f - \lambda_m)\phi_f \qquad (13c)$$

$$c = -\lambda_f \lambda_m \qquad (13d)$$

The composites investigated in this study were composed of three components, namely EVA, the hollow glass microspheres, and silver. However, the system could be represented by only two components, the EVA matrix and the filler, which was composed of the hollow glass microsphere core and the silver shell. A few models have also been developed for the prediction of λ of polymers filled with coated particles. These models assume that each inclusion has a coating of the same shape that occupies the same volume fraction of each inclusion. The coating has a λ dissimilar to both the continuous

phase and the coated dispersed phase. The self-consistent scheme described by Krupa et al.[37] was used to formulate solutions for a composite with randomly dispersed coated spherical fillers. In that case, λ of a three-component system, derived from eq. (12), is given by eqs. (14a)–(14e):

$$a\lambda_c^3 + b\lambda_c^2 + c\lambda_c + d = 0 \qquad (14a)$$

$$a = 4 \qquad (14b)$$

$$b = 2\lambda_2 + 2\lambda_3 - 4\lambda_1 + 6(\lambda_1 - \lambda_3)\phi_3 + 6(\lambda_1 - \lambda_2)\phi_2 \qquad (14c)$$

$$\begin{aligned} c = \lambda_2\lambda_3 - 2\lambda_1\lambda_3 - 2\lambda_1\lambda_2 \\ + 3(\lambda_1\lambda_3 - \lambda_2\lambda_3)\phi_2 + 3(\lambda_1\lambda_2 - \lambda_2\lambda_3)\phi_3 \end{aligned} \qquad (14d)$$

$$d = -\lambda_1\lambda_2\lambda_3 \qquad (14e)$$

where volume concentrations of components 2 and 3 are as follows:

$$\phi_2 = \frac{\rho_c(\rho_3 - \rho_{23})w_{23}}{\rho_{23}(\rho_3 - \rho_2)} \qquad (15)$$

$$\phi_3 = \frac{\rho_c(\rho_2 - \rho_{23})w_{23}}{\rho_{23}(\rho_2 - \rho_3)} \qquad (16)$$

where the subscripts 1, 2, 3, c, and 23 symbolize the matrix (EVA), core (hollow glass microspheres), shell (silver), composite, and filler (hollow glass spheres coated by silver), respectively; w is the weight fraction; and ρ is the specific density. The results found from eqs. (14a)–(14e) are given in Table IV.

Figure 5 shows a comparison of the predictions of the models of Budiansky, Hatta and Taya, and Lewis and Nielsen with the experimental data for the composites filled with silver-coated hollow glass spheres, in which the relative λ of the dispersed phase was approximately 410 times greater than that of the matrix. The Lewis and Nielsen model used

values of 1.5 and 3.0 for coefficient A and retained a value of 0.631 for ϕ_{max}. Clearly, the data were not described by either model but did provide Lewis and Nielsen ($A = 1.5$, $\phi_{max} = 0.631$) and Hatta and Taya models that encompassed the data.

From an observation of the curves calculated according to the model of Lewis and Nielsen, good agreement between the experimental values and theoretical data was reached when parameter $A = 1.5$ and $\phi_m = 0.631$. It is well known from the literature that the main problem of the Lewis and Nielsen model is the *a priori* definition of the correct set of parameters A and ϕ_m to match the real situation without any experimental data.[37] Thus, the use of this model to estimate λ_c is sometimes venturesome.

From the analysis of the results, we concluded that both the Lewis and Nielsen ($A = 1.5$, $\phi_{max} = 0.631$) and Hatta and Taya models provided a good fit of λ_c and demonstrated their ability to account for the effect of λ_f. Both models were in good agreement with experimental results up to a volume fraction of 0.22; the variation between the models and the experimental data was less than 10% up to this point. Comparing the two theoretical curves, we concluded that the Hatta and Taya model appeared to provide a better fit to the data than the Lewis and Nielsen model, although both theoretical models provided satisfactory predictions below a volume fraction of 0.22. This value likely corresponded to the filler volume concentration at which the possible formation of an interparticle network was created within the matrix, as reported by some authors.[4,38] This concentration was not only far less than ϕ_{max} for randomly dispersed spheres but also below the percolation threshold of Bruggeman.[4] Bruggeman showed that a network of randomly dispersed spheres developed in a polymer matrix at a volume concentration of 0.33, a phenomena that has not been observed experimentally except in a system in which the matrix phase is not a continuum.[4] Of interest is that both theoretical models appeared to overestimate the increase in λ above a volume concentration of 0.22. Further, we also observed that the Lewis and Nielsen model predicted a higher λ than the experimental values and the prediction of the Hatta and Taya model as the concentration of filler particles approached ϕ_{max}. Bigg[4] reported that the inclusion of ϕ_{max} in the Lewis and Nielsen model had the effect of amplifying concentration effects at high filler loadings. This was consistent with observation that predictions become difficult to make as the filler concentration approaches ϕ_{max}.

At first sight, the Budiansky three-component model underestimates λ_c, except at the lowest filler concentrations ($\phi_f < 4\%$), although the value of λ obtained for the coated hollow glass spheres with this model was equal to 77.52 W m^{-1} K^{-1}.

The reason for this result may have been the fact that the three-component model does not account for the morphology of composites that tend to maximize the effect of the dispersed phase, particularly at higher filler concentrations. This model estimates λ_c on the basis of volume concentration of the pure component and their λ's. It was clear that λ_c was strongly affected by and perhaps dominated by the conductivity of the silver because $\lambda_{HGS} < \lambda_{EVA}$. However, λ_c exhibited by such composites depends strongly on the distribution of fillers in the matrix. For comparison, computations of the Hashin and Shtrikman model were performed with λ_{Ag} and its volume fraction in the composite. The results are shown in Table III. The results, which indicate that the prediction of the Hashin and Shtrikman model gave almost the same values as the three-component model, were interpreted in the light of the contribution of the morphology of the fillers to λ_c. According to Krupa et al.,[37] this result indicates (1) a strong influence of the morphology of the fillers on the final λ_c and (2) the fact that even a very high λ_f could not significantly increase λ_c when the filler loading was low. Recall that the aforementioned models and conclusions were only discussed for spherically shaped particles.

A close look at the values of λ provided interesting information about the contributions of the filler morphology at play in determining λ_c. As shown in Table III, the composite sample containing 5.2 vol % silver deposited onto the hollow glass spheres exhibited a λ value of 0.357 W m^{-1} K^{-1}; this was about 90% higher than that of EVA, whereas improvements in λ_{EVA} due to the same volume fraction of pure silver were estimated to be 16% with the Hashin and Shtrikman model. The higher contributions to λ_{Ag} were believed to be due to the fact that the morphology of the fillers probably played a crucial role in governing the characteristic changes of λ. Although the measurements of λ_c filled with pure metallic powder were not performed in this study, some studies have confirmed that a low filler content of metals has a slight influence on λ_c.[9]

A comparison of the experimental data with the Nielsen model is shown in Figure 9. Different plots of this model are presented for four pairs of values of parameters A and ϕ_{max}. The Lewis and Nielsen model typically uses fixed data for the parameters A and ϕ_{max}; these are dependent on the filler shape, aspect ratio, and packing. The first two curves were computed with fixed values of A (1.5 and 3.0) and ϕ_{max} (63.1%), as discussed before in this section. The Lewis and Nielsen model allowed us to obtain a good prediction of the experimental values of λ below a volume fraction of 0.22 when parameter $A = 1.5$ and $\phi_m = 0.631$. However, the theoretical λ_c values were calculated with eqs. (9) and (10) by
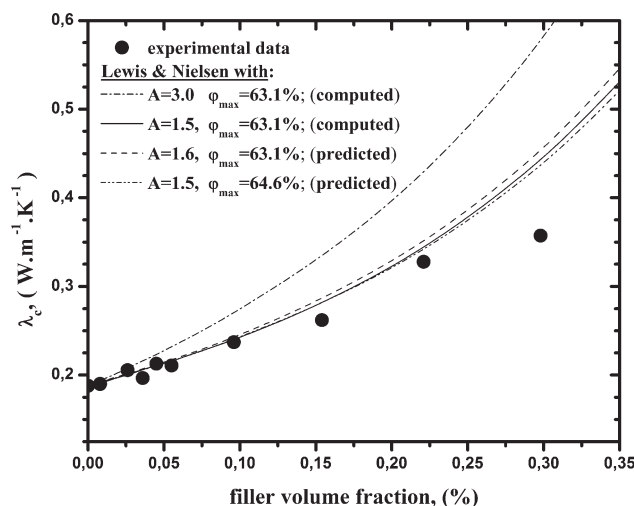
Figure 9 Comparison of the experimental values of the EVA/hollow sphere–Ag composites with the different Lewis and Nielsen model values of A and ϕ_{max}.

Figure 10 Predicted effect of λ_f/λ_m for the silver-coated hollow spheres particles on λ_c/λ_m according to Lewis and Nielsen and Hatta and Taya at ϕ_f values equal to 0.25 and 0.50.

adjustment of the values of the shape factor A and ϕ_{max}. First, we estimated A by fixing the value of parameter ϕ_{max} at 63.1%. Then, we simultaneously estimated both parameters by fitting the experimental data with the Lewis and Nielsen model. Notably, the last experimental data point was not considered during these estimations. The validity of this hypothesis was justified by the results discussed in the Thermal Conductivity of the Composites section of this article.

The values of the parameters estimated for these two fittings are presented in Table V. To quantitatively show how the model compared to the experimental data, the coefficient of linear regression values are given in Table V. A value of $R^2 = 1$ would indicate a perfect fit of the experimental data with the model. The linear regression values indicated that the best estimations were obtained by simultaneous estimation of both parameters. Also, when both parameters were estimated simultaneously, the estimated A values were basically the same, whereas the estimated ϕ_{max} values demonstrated a relative increase compared to the theoretical one (64.6 vs 63.1%). With regard to this argument, the values of parameter A (1.5) and ϕ_{max} (64.6%) seemed to be consistent with those listed in the tables given in ref. [4]. According to these tables,[4] these values ($A = 1.5$ and $\phi_{max} = 0.646$) seemed to correspond to the spherical filler particles that were randomly

dispersed in the polymeric matrix. The ϕ_{max} values reported in ref. [4] for fillers were related to the fully amorphous matrices.

Figure 10 shows the effect of λ_f relative to λ_m over the range of ratios between 1 and 1000, as predicted by the Hatta and Taya and Lewis and Nielsen models. The predictions were essentially the same for ϕ_f values below 0.25. From a closer observation on the curves, above that filler content, the predictions of the Lewis and Nielsen model began to diverge from those of the Hatta and Taya model. This is shown in Figure 10, where predictions for a volume fraction of 0.50 are also shown. The significant difference between the predictions of the models could be explained by the fact that ϕ_{max} in the Lewis and Nielsen model had the effect of amplifying the concentration effects at high filler loadings. Also, the effect of λ_f on λ_c was significant only for $\lambda_f < 20$ W m^{-1} K^{-1}. Both models showed only a minimal effect of increasing λ_f above a ratio of λ_f/λ_m greater than 100. This means that thermally conductive composites can be produced by the use of silver-coated hollow glass microspheres. The same trend was reported in the literature,[29] where metal-coated wollastonite fibers were used as the filler. In that case, a model for the description of λ_c filled with fibers was used. According to Bigg,[4] this result means that inorganic fillers, such as CaO, MgO, and Al$_2$O$_3$, are as effective in increasing the λ values of polymers as metals.

CONCLUSIONS

The preparation and characterization of a new type of thermally conductive filler based on hollow glass

TABLE V
Lewis and Nielsen Fitting Parameters

Parameter	A free and ϕ_{max} fixed	A and ϕ_{max} free
A	1.6	1.5
ϕ_{max}	0.631	0.646
R^2	0.9578	0.9621

microspheres electrochemically coated with silver was reported in this article. This filler was used for the preparation of thermally conductive composites based on EVA copolymer. λ_c was about 90% higher than that of pure EVA when the polymer was filled with 30 vol % silver-coated hollow glass spheres. However, ϕ_{Ag} corresponding to this filler loading was much lower (ca. 5.2 vol %).

We concluded from this study that the Hatta and Taya model correctly described the experimental data up to 22 vol % filler when we used a computed λ value of the coated fillers based on a simple modeling. Also, the Lewis and Nielsen model allowed us to obtain good prediction of the experimental values of λ below a volume fraction of 0.22, especially when parameters $A = 1.5$ and $\phi_{max} = 0.631$ were used. This value likely corresponded to the filler loading at which the possible formation of an interparticle network may have occurred within the matrix. On the basis of the observations of theoretical modeling, the Lewis and Nielsen model predicted a higher λ than the experimental values and the prediction of the Hatta and Taya model as the concentration of filler particles approached ϕ_{max}. The reason for this result might have been ϕ_{max} in the Lewis and Nielsen model, which had the effect of amplifying concentration effects at high filler loadings.

A comparison of the experimental data with the values of λ estimated for composites filled with pure metallic powder would provide interesting information about the morphology of the filler, which plays a crucial role in governing the characteristic changes of λ_c. Closer observation of the estimated data suggested that a low filler content of metals had a slight influence on λ_c.

We concluded from the analysis of the results that when the ratio of λ_f to λ_m exceeded 100 : 1, there was little further improvement in λ_c when λ_f increased beyond this ratio. The mentioned observation means that silver-coated hollow spheres were as effective in increasing λ of polymers as metals.

References

1. Bantrup, J.; Immergut, E.; Grulke, E. Polymer Handbook; Wiley: New York, 1999.
2. Lux, F. J. Mater Sci 1993, 28, 285.
3. Gul', V. E. Structure and Properties of Conducting Polymer Composites; VSB: Utrecht, The Netherlands, 1996.
4. Bigg, D. M. Adv Polym Sci 1995, 119, 1.
5. Zhang, Z.; Fang, X. Energy Conserv Manage 2006, 47, 303.
6. Stappers, L.; Yuan, Y.; Fransaer, J. J Electrochem Soc 2005, 152, 457.
7. Klason, C.; McQueen, D. M.; Kubat, J. Macromol Symp 1996, 108, 247.
8. Sundstrom, D. W.; Lee, Y. D. J Appl Polym Sci 1972, 16, 3159.
9. Bujard, P.; Munk, K.; Kuehnlein, G. In Thermal Conductivity; Tong, T. W., Ed.; Technomic: Lancaster, PA, 1994; Vol. 22.
10. Krupa, I.; Chodák, I. Eur Polym J 2001, 37, 2159.
11. Mamunya, Y. P.; Davydenko, V. V.; Pissis, P.; Lebedev, E. V. Eur Polym J 2002, 38, 1887.
12. Hg, H. Y.; Lau, S. K.; Lu, X. Mater Sci Forum 2003, 437, 239.
13. Twitchen, D. J.; Pickles, C. S.; Coe, S. E.; Sussmann, R. S.; Hall, C. E. Diam Relat Mater 2001, 10, 731.
14. Ghose, S.; Watson, K. A.; Working, D. C.; Connell, J. W.; Smith, J. G.; Sun, Y. P. Compos Sci Technol 2008, 68, 1843.
15. Gubbels, F.; Blacher, S.; Vanlathem, E.; Jerome, R.; Deltour, R.; Brouers, F.; Teyssie, Ph. Macromolecules 1995, 28, 1559.
16. Thongruang, W.; Spontak, R. J.; Balik, M. Polymer 2002, 43, 3717.
17. Boudenne, A.; Ibos, L.; Fois, M.; Majesté, J. C.; Géhin, E. Compos Part A 2005, 36, 1545.
18. Wang, F.; Arai, S.; Morinobu Endo, M. Electrochem Commun 2004, 6, 1042.
19. Liang, G. D.; Tjong, S. C. Mater Chem Phys 2006, 100, 132.
20. Fukushima, H.; Drzal, L. T.; Rook, B. P.; Rich, M. J. J Therm Anal Calorim 2006, 85, 235.
21. Kalaitzidou, K.; Fukushima, H.; Drzal, L. T. Carbon 2007, 45, 1446.
22. Xie, S. H.; Liu, Y. Y.; Li, J. Y. Appl Phys Letters 2008, 92, 243121.
23. Boudenne, A.; Ibos, L.; Géhin, E.; Fois, M.; Majesté, J. C. J Mater Sci 2005, 40, 4163.
24. Dai, H.; Li, H.; Wang, F. Surf Coat Technol 2008, 201, 2859.
25. Strzelec, K.; Pospiech, P. Prog Org Coat 2003, 63, 133.
26. Krupa, I.; Mikova, G.; Novák, I.; Janigova, I.; Nógellová, Z.; Lednicky, F.; Prokeš, J. Eur Polym J 2007, 43, 2401.
27. Zeng, W.; Tan, S. T. Polym Compos 2006, 27, 24.
28. Baia, L.; Baia, M.; Kiefer, W.; Popp, J.; Simon, S. Chem Phys 2006, 327, 63.
29. Krupa, I.; Cecen, V.; Tlili, R.; Boudenne, A.; Ibos, L. Eur Polym J 2008, 44, 3817.
30. Cecen, V.; Boudenne, A.; Ibos, L.; Novák, I.; Nógellová, Z.; Prokeš, J.; Krupa, I. Eur Polym J 2008, 44, 3827.
31. Krupa, I.; Novák, I. In Progress in Materials Science Research; Nova Science: New York, 2005.
32. Lin, T. Y.; Davison, K. L.; Leong, W. S.; Chua, S.; Yao, Y. F.; Pan, J. S.; Chai, J. W.; Toh, K. C.; Tjiu, W. C. Microelectron Reliab 2003, 43, 803.
33. Kim, H. C.; Alford, T. L. J Appl Phys 2003, 94, 5393.
34. Novák, I.; Krupa, I.; Chodák, I. Synth Met 2004, 144, 13.
35. Bigg, D. M.; Bradbury, E. J. Conductive Polymeric Composites from Short Conductive Fibers; American Chemical Society: Washington, DC, 1980; Vol. 43, p 746.
36. Gordaninejad, P.; Faramarz, A. Am Soc Mech Eng 1991, 10, 151.
37. Krupa, I.; Boudenne, A.; Ibos, L. Eur Polym J 2007, 43, 2443.
38. Agoudjil, B.; Ibos, L.; Majesté, J. C.; Candau, Y.; Mamunya, Y. P. Compos A 2008, 39, 342.
39. Zhang, Q.; Wu, M.; Zhao, W. Surf Coat Technol 2005, 192, 213.
40. Novák, I.; Krupa, I.; Chodák, I. Eur Polym J 2003, 39, 585.
41. Boudenne, A.; Ibos, L.; Gehin, E.; Candau, Y. J Phys D: Appl Phys 2004, 37, 132.
42. Boudenne, A.; Ibos, L.; Candau, Y. Meas Sci Technol 2006, 17, 1870.
43. Moré, J. J. In The Levenberg-Marquardt Algorithm: Implementation and Theory Numerical Analysis; Watson, G. A., Ed.; Lecture Notes in Mathematics 630; Springer-Verlag: Berlin, 1977.

44. Wunderlich, B. Macromolecular Physics II; Academic: New York, 1973.
45. Chodák, I. Prog Polym Sci 1998, 23, 1409.
46. Tanniru, M.; Yuan, Q.; Misra, R. D. K. Polymer 2006, 47, 2133.
47. Yuan, Q.; Misra, R. D. K. Polymer 2006, 47, 4421.
48. Huang, X.; Ke, Q.; Kim, C.; Zhong, H.; Wei, P.; Wang, G.; Liu, F.; Jiang, P. Polym Eng Sci 2007, 47, 1052.
49. Lide, D. R. Handbook of Chemistry and Physics; CRC: Boca Raton, FL, 2002.
50. Keding, M.; Schmid, G.; Tajmar, M. In Proceedings of the Hydrogen & Fuel Cells Conference: Vancouver, Kanada, 2009.
51. Progelhof, R. C.; Throne, J. L.; Reutsch, R. R. Polym Eng Sci 1976, 16, 615.
52. Bigg, D. M. Polym Compos 1986, 7, 125.
53. Torquado, S. Rev Chem Eng 1987, 4, 151.
54. Mottram, J. T.; Taylor, R. In International Encyclopedia of Composites; Lee, M., Ed.; VCH: New York, 1991; vol. 5.
55. Hatta, H.; Taya, M. J Appl Phys 1985, 58, 2478.
56. Eshelby, J. D. Proc R Soc London A 1957, 241, 376.
57. Hashin, Z. J Appl Mech 1983, 50, 481.
58. Nielsen, L. E. Ind Eng Chem Fund 1974, 13, 17.
59. Lewis, T. B.; Nielsen, L. E. J Appl Polym Sci 1970, 14, 1449.
60. Eiermann, K. Kolloid Z 1965, 201, 3.
61. Budiansky, B. J. Compos Mater 1970, 4, 286.
62. Beran, M. J. Statistical Continuum Theories; Interscience: New York, 1968.