Influence of Filler Content, Particle Size and Temperature on Thermal Diffusivity of Polypropylene-Iron Silicon Composites

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ABSTRACT: The filler fraction, particle size and temperature dependence of thermal diffusivity in polypropylene-iron silicon composites were examined by laser flash method. Results show that raising the filler content raises the thermal diffusivity of the composite material only slightly. Nevertheless, the higher the filler content the higher the influence of the filler material expressed by a altered course of the thermal diffusivity versus temperature. Measurement values are compared with selected existing mathematical models whereas a model, originally developed for magnetic permeability, by Hashin and Shtrikman shows the best congruence. Further measurements show that the particle size of the filler does not have an influence on the composite's thermal diffusivity at the examined filler content. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 732–735, 2011

Key words: thermal diffusivity; polypropylene; iron-silicon; particle size; interconnectivity

INTRODUCTION

During the last years the interest in a preparation of electronic components like inductivities, transformers, cores and stators for electronic devices made of polymers filled with iron- or ferrite based particles is growing. By extrusion compounding and injection molding a cheap and reliable preparation method is possible and also unusual geometric shapes of the desired component parts can be realized.

These filler particles also cause changes in processing conditions because of the change of physical properties of the compound like viscosity and thermal properties. With the change in thermal diffusivity the cooling behavior in the mold of the injection molding machine is influenced, where a high thermal diffusivity is responsible for a fast cooling phase and a short molding cycle.

Although many studies dealing with the description of extrusion and injection molding process are present in literature only few experimental data of thermal properties of such composites with high filler fractions are available.[1]

EXPERIMENTAL

Polypropylene (H734-52RNA, DOW, Germany) samples filled with commercially available spherical shaped soft magnetic particles FeSi6.8 (Höganäs S.A., Sweden) with mean particle diameter $d = 58$ μm were prepared with filler content from 0 to 70 vol. % by extrusion compounding (Berstorff ZE 25A, KraussMaffei Berstorff GmbH, Germany) and injection molding (Arburg Allrounder 220C, Arburg GmbH + Co KG, Germany). Additionally PP-FeSi6.8 composites with 50 vol. % filler content and varying particle sieve fractions from 20–40 μm, 40–63 μm, 63–80 μm and 80–100 μm were produced. Afterwards the thermal diffusivity α was investigated in a laser flash apparatus (LFA 427, Netzsch-Gerätebau GmbH, Germany) on samples with the dimension 25.4 mm of diameter and 1 mm of thickness at temperatures from 300 to 420 K under helium atmosphere. Samples were covered by a thin graphite layer to ensure a good absorption of the laser and to prevent damage by the laser pulse. The curves of the detector signals after the laser pulse showed the best fit with the applied Cowan model.[2] The accuracy of this measurement method is 5%.

THEORETICAL

Following models have been chosen for comparison with the experimental data. They are not necessarily developed for calculating the thermal diffusivity but for reasons of mathematical analogy these formulas can be applied for dielectric constant, electric conductivity, heat conductivity, thermal diffusivity, and magnetic permeability of composite materials. Bases

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for the calculation are the filler fraction x, the measurement value from thermal diffusivity of PP α_{PP} and the literature value of thermal diffusivity of the filler FeSi6.8 α_{FeSi}.

Parallel model

$$\alpha_{composite} = \frac{1}{\frac{1-x}{\alpha_{PP}} + \frac{x}{\alpha_{FeSi}}} \quad (1)$$

Agari-Uno[3]

$$\alpha_{composite} = \exp[xC_2 \ln(\alpha_{FeSi}) + (1-x)\ln(C_1\alpha_{PP})], \quad (2)$$

with C_1 the factor of the effect on crystallinity and crystal size of the polymer and C_2 is a factor which describes the ability of the composite to form conductive chains of particles.

Cheng-Vachon[4]

$$\frac{1}{\alpha_{composite}} = \frac{1-B}{\alpha_{PP}} + \frac{1}{\sqrt{C(\alpha_{FeSi}-\alpha_{PP})[\alpha_{PP}+B(\alpha_{FeSi}-\alpha_{PP})]}} \times \ln\frac{\sqrt{\alpha_{PP}+B(\alpha_{FeSi}-\alpha_{PP})}+\frac{B}{2}\sqrt{C(\alpha_{FeSi}-\alpha_{PP})}}{\sqrt{\alpha_{PP}+B(\alpha_{FeSi}-\alpha_{PP})}-\frac{B}{2}\sqrt{C(\alpha_{FeSi}-\alpha_{PP})}} \quad (3)$$

$$\text{with } B = \sqrt{\frac{3x}{2}} \text{ and } C = \sqrt{\frac{2}{3x}}$$

sym. Bruggeman[5]

$$\alpha_{composite} = \frac{1}{4}\left[3x(\alpha_{FeSi}-\alpha_{PP}) + 2\alpha_{PP} - \alpha_{FeSi} + \sqrt{(1-3x)^2\alpha_{FeSi}^2 + 2(2+9x-9x^2)\alpha_{FeSi}\alpha_{PP} + (3x-2)^2\alpha_{PP}^2}\right] \quad (4)$$

Hashin-Shtrikman[6]
lower boundary HS−:

$$\alpha_{composite} = \alpha^{HS-} = \alpha_{PP}\frac{2\alpha_{PP}+\alpha_{FeSi}-2x(\alpha_{PP}-\alpha_{FeSi})}{2\alpha_{PP}+\alpha_{FeSi}+x(\alpha_{PP}-\alpha_{FeSi})} \quad (5)$$

upper boundary HS+:

$$\alpha_{composite} = \alpha^{HS+} = \alpha_{FeSi}\frac{2\alpha_{FeSi}+\alpha_{PP}-2(1-x)(\alpha_{FeSi}-\alpha_{PP})}{2\alpha_{FeSi}+\alpha_{PP}+(1-x)(\alpha_{FeSi}-\alpha_{PP})} \quad (6)$$

The deviation of the measured thermal diffusivity from the calculated one gives information about the particle distribution in the composite. The ratio of interconnected particles to isolated particles is deduced from a comparison between measured and modeled (α^{HS+} and α^{HS-}) thermal diffusivities.

Following definition for the interconnectivity[1] is used:

$$X_{interconnected} = \frac{\alpha_{measured}(x) - \alpha^{HS-}}{\alpha^{HS+} - \alpha^{HS-}} \quad (7)$$

while for HS+ the particles are interconnected into a 3D network and in HS− the particles are insulated from each other.

RESULTS AND DISCUSSION

Results of the thermal diffusivity measurements show an increase of thermal diffusivity from 0.14 (pure PP, literature value 0.12 mm^2/s[7]) to 0.8 mm^2/s (PP+70vol.% FeSi6.8) at 300 K (Fig. 1) by increasing the content of the iron-silicon filler material. Since thermal diffusivity of pure FeSi6.8 is about 6.1 mm^2/s[8] the extremely low thermal diffusivity of PP with 70 vol. % FeSi6.8 is somehow unexpected. Thus, heat transport is mainly influenced and dependent on the polymer matrix. Nevertheless, a similar behavior was already reported for the dependence of magnetic permeability for soft magnetic particle filled polymers[9] which is showing a steep incline in permeability only for filler fractions $x > 0.7$.

A comparison of the course of the thermal diffusivity α of the composites versus filler fraction x with various models can also be seen in Figure 1. Most models, despite of the parallel model from eq. (1), show an acceptable congruence with the experimental data for low filler fractions up to $x = 0.4$. The parallel model already deviates from the measurement points at low filler content close to $x = 0$ and its values are below the experimental data for all calculated filler fractions.

The model derived by Agari and Uno [eq. (2)] shows a good congruence for filler fractions $x \leq 0.4$ with $C_1 = 0.84$ and $C_2 = 1$. But for higher filler fractions the modeled values are clearly higher than experimental values. C_1 and C_2 were determined empirically since a computed fit could not be applied satisfactory due to the fixed values of thermal diffusivity at $x = 0$ and $x = 1$. Additionally, adjusting the values C_1 and C_2 mainly shifts the values at $x = 0$ and $x = 1$ but does not change the overall course in a way that it completely concurs with the experimental curve. On first sight it is astonishing that the Agari-Uno model does not show a better agreement to the measured data although this model

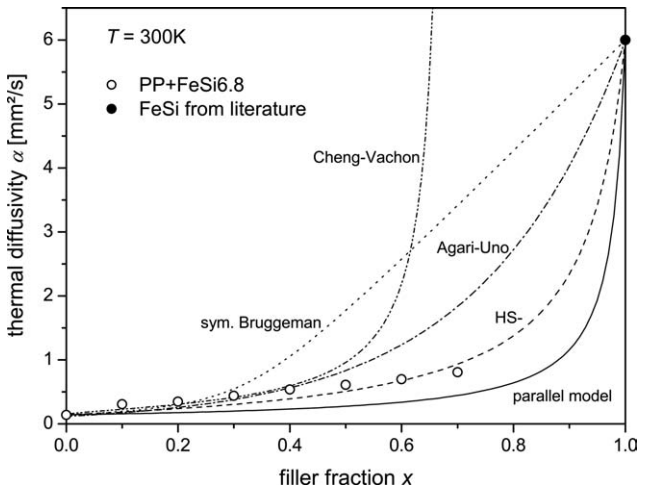

Figure 1 Thermal diffusivity α of polypropylene-FeSi6.8 samples versus filler fraction x at a temperature T = 300 K. Symbols are measurement values and from literature, respectively, the lines are fits.

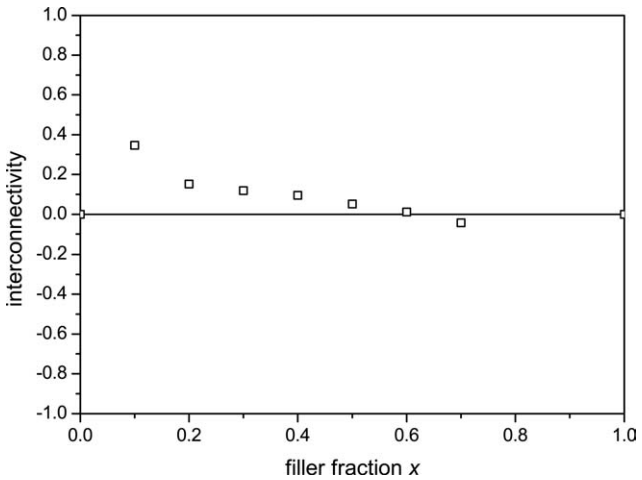

Figure 2 Interconnectivity of polypropylene-FeSi6.8 samples versus filler fraction x at a temperature T = 300 K.

gives often the best fit to experiments (compare[3,10,11]). However, in literature always only measurement values of the composite were fitted to the model while the thermal properties of the filler materials were ignored. Nevertheless, it is unclear what relation the C_1 and C_2 values have to the crystallinity and interactions of particles in the polymer.

For a filler fraction $x \leq 0.4$ a similar course of thermal diffusivity can be seen for the model by Cheng and Vachon [eq. (3)]. At a higher filler fraction the values of the calculation converge to very high values and can not be used. Thus the model is only valid for calculating thermal diffusivity at small filler contents.

The calculation of the effective medium theory applied to the Bruggeman model is in accordance with the measurement points up to a filler fraction of $x = 0.3$. The model was developed for calculating electrical conductivity in composite materials and it is known for its strong percolation threshold at $x = 0.33$, which is present for electrical conductivity. Due to this, the calculated values are too large compared with the measurement data for $x > 0.3$.

In contrary to the other models the lower boundary α^{HS-} of the model by Hashin-Shtrikman [eq. (5)], which was originally developed for calculating the permeability of multiphase materials, shows a good congruence (Fig. 1) with the measured values in the range of measured data.

In Figure 2 it can be seen that all values of interconnectivity (X) are around $X_{\text{interconnected}} \approx 0$. These low values mean that the particles form a poor interconnected network in the polymer. This is the result of the spherical shape of FeSi6.8 particles which leads to small point-like contacts between the particles and also a good wetting of FeSi6.8 particles with PP.

A further interesting observation can be seen in Figure 3. Increasing the temperature T induces a decline of the thermal diffusivity for all materials. The higher the filler fraction the larger is the drop in thermal diffusivity versus temperature. Interestingly enough, at a temperature of about 370 K an increase of thermal diffusivity in materials with a filler fraction $x > 0.5$ can be seen again. The decrease and increase is stronger, the higher the filler fraction of FeSi.

The decrease can be explained by the relation of the thermal diffusivity α to the velocity v of phonons and its free path length l according to $\alpha = 1/3vl$. Furthermore v is connected to the bulk modulus K (and specific density ρ) via $v = (K/\rho)^{0.5}$ (Einstein approximation).[12] Looking at the course of the bulk modulus of FeSi filled PP one can observe that the

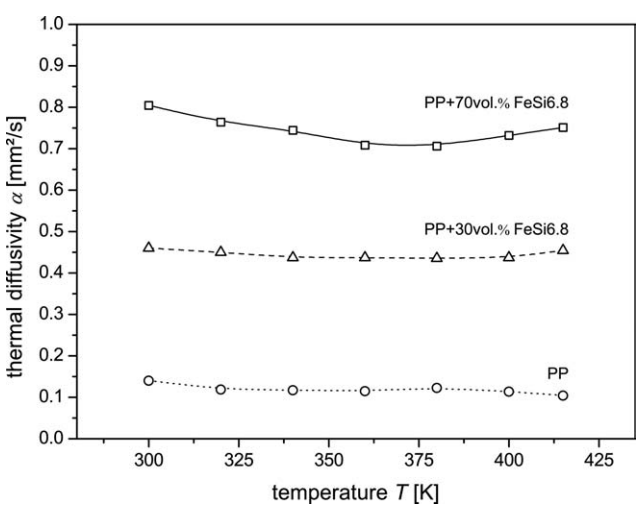

Figure 3 Thermal diffusivity α of polypropylene-FeSi6.8 samples versus temperature T.

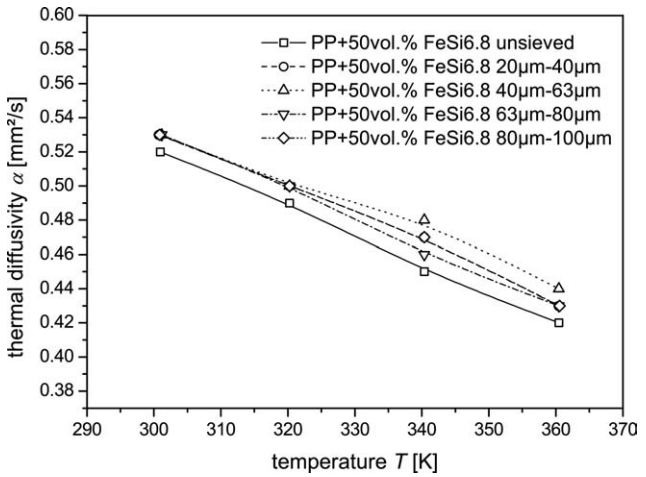

Figure 4 Influence of particle size on thermal diffusivity α versus temperature *T*.

larger the filler fraction of particles in the polymer the stronger is the decrease of bulk modulus versus temperature with an inflection point at about 360 K,[13,14] which corresponds very well with starting increase of thermal conductivity in own measurements. By increasing the temperature above the inflection point the decrease of bulk moduli gets lower and its slopes are approximating to each other. Thus, the thermal diffusivity seems to be reduced stronger for high filler fractions by the higher decrease of bulk modulus versus temperature.

Additionally, the increase of thermal diffusivity for $T > 370$ K can be explained by raised interactions between the particles at high filler content in the composite. The thermal diffusivity of pure iron silicon alloys with high silicon content (>2.5 wt. %) increases between 370 and 600 K.[8] At higher temperatures and higher filler fractions the influence of the properties of the FeSi6.8 filler material gets higher and changes the course of thermal diffusivity of the composite material in that way, that it starts to rise again.

Further measurements dealing with the dependence of thermal diffusivity on filler particle's size for a filler fraction $x = 0.5$ are shown in Figure 4. As can be seen no significant difference in thermal diffusivity related to a changed particle size can be observed. This shows that the thermal diffusivity is not dependent on the number of gaps between the particles, which is higher for smaller particles, but only on the ratio of the mixture of the materials itself. Variances in thermal diffusivity in Figure 4 are due to the measurement accuracy of the LFA or small inaccuracies while mixing the materials, but can be neglected.

CONCLUSIONS

Results show that adding iron based particles to polypropylene is raising the thermal diffusivity α of the composite. Nevertheless, the increase of α is not as strong as expected but it is obvious that the influence of the filler material is getting stronger. Comparing the measurement data with existing mathematical models shows an unsatisfactory result. Only one model by Hashin and Shtrikman, originally developed for calculating the permeability of two-phase materials, agrees with experimental values within the measurement range. An observation of the influence of the particle size of the filler on thermal diffusivity shows that the particle size does not need to be considered at a filler content of 50 vol. %.

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