

Thermal diffusivity and mechanical properties of polymer matrix composites

Bernd Weidenfeller, Mathias Anhalt, and Stefan Kirchberg

Citation: *Journal of Applied Physics* **112**, 093513 (2012); doi: 10.1063/1.4764098

View online: <http://dx.doi.org/10.1063/1.4764098>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/112/9?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Electromagnetic and microwave absorbing properties of raw and milled FeSiCr particles](#)

J. Appl. Phys. **115**, 17B536 (2014); 10.1063/1.4869064

[A crowding factor model for the thermal conductivity of particulate composites at non-dilute limit](#)

J. Appl. Phys. **114**, 064306 (2013); 10.1063/1.4818409

[High thermal conductivity epoxy-silver composites based on self-constructed nanostructured metallic networks](#)

J. Appl. Phys. **111**, 104310 (2012); 10.1063/1.4716179

[Thermal characterization of composites made up of magnetically aligned carbonyl iron particles in a polyester resin matrix](#)

J. Appl. Phys. **111**, 054906 (2012); 10.1063/1.3691592

[Thermal stability and crystallization kinetics of mechanically alloyed Ti C Ti -based metallic glass matrix composite](#)

J. Appl. Phys. **100**, 033514 (2006); 10.1063/1.2234535



AIP | Journal of
Applied Physics

Journal of Applied Physics is pleased to
announce **André Anders** as its new Editor-in-Chief

Thermal diffusivity and mechanical properties of polymer matrix composites

Bernd Weidenfeller,^{1,a)} Mathias Anhalt,^{1,b)} and Stefan Kirchberg^{2,c)}

¹Department of Materials Science, Institute of Particle Technology, Clausthal University of Technology, Arnold-Sommerfeld-Str. 6, 38678 Clausthal-Zellerfeld, Germany

²Institute of Polymer Materials and Plastics Engineering, Clausthal University of Technology, Agricolastr. 6, 38678 Clausthal-Zellerfeld, Germany

(Received 16 April 2012; accepted 9 October 2012; published online 7 November 2012)

Polypropylene–iron-silicon (FeSi) composites with spherical particles and filler content from 0 vol. % to 70 vol. % are prepared by kneading and injection molding. Modulus, crystallinity, and thermal diffusivity of samples are characterized with dynamic mechanical analyzer, differential scanning calorimeter, and laser flash method. Modulus as well as thermal diffusivity of the composites increase with filler fraction while crystallinity is not significantly affected. Measurement values of thermal diffusivity are close to the lower bound of the theoretical Hashin-Shtrikman model. A model interconnectivity shows a poor conductive network of particles. From measurement values of thermal diffusivity, the mean free path length of phonons in the amorphous and crystalline structure of the polymer and in the FeSi particles is estimated to be 0.155 nm, 0.450 nm, and 0.120 nm, respectively. Additionally, the free mean path length of the temperature conduction connected with the electrons in the FeSi particles together with the mean free path in the particle-polymer interface was estimated. The free mean path is approximately 5.5 nm and decreases to 2.5 nm with increasing filler fraction, which is a result of the increasing area of polymer-particle interfaces. A linear dependence of thermal diffusivity with the square root of the modulus independent on the measurement temperature in the range from 300 K to 415 K was found. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4764098>]

INTRODUCTION

Many electronic devices and integrated circuits require an effective temperature management because undesired heat is produced during operation. For the heat conduction from the device to a heat sink, polymer composites containing inorganic fillers with high thermal conductivity can be used^{1–3} although polymers are the worst heat conducting materials compared to metals and ceramics. The heat conductivity of such composites only depends on the volume content of filler particles in the polymer matrix if the heat conductivity of the particles is approximately fifty times higher than the heat conductivity of the polymeric matrix.⁴ While in a polymer the heat is transported solely by phonons, in a metal also electrons contribute to the heat conduction. A typical value for the free mean path length β of phonons in polymers, which strongly influences heat conduction, is $\beta = 0.3$ nm. By crystallization of polymers, and thus a diminution of scattering centers for phonons, the free mean path length can be significantly increased.⁵ Therefore, the thermal conductivity of a highly crystalline polymer can be increased by a factor of 50.^{6,7} However, in many cases, the crystallinity cannot be raised and so the addition of particles is a practicable method for improving thermal conductivity. Below the electrical percolation threshold, which appears for spherical particles in a non conducting matrix around 33 vol. % in the effective medium approximation,^{8,9} the polymer

matrix composite exhibits mainly the mechanical properties of the polymer and has typical polymer processing properties while the composite becomes more and more brittle and harder to process for filler contents above this threshold. Simultaneously, Young's modulus is increased with increasing filler fraction. All these materials' properties are affecting the phonon's mean free path length, which is illustrated here for polypropylene (PP) filled with iron-silicon particles.

THEORY

The thermal diffusivity of a homogeneous composite with a PP matrix of thermal diffusivity α_{PP} filled with the volume fraction x of spherical particles of iron silicon (FeSi) with thermal diffusivity α_{FeSi} can be derived according to the model of Hashin-Shtrikman (HS)¹⁰ by

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

which is the lower boundary $HS-$ for a matrix diffusivity $\alpha_{PP} < \alpha_{FeSi}$. If the matrix consists of a high thermal diffusivity phase surrounding particles of low thermal diffusivity, i.e., an iron silicon matrix would surround polymer particles, the upper boundary $HS+$ would describe this diffusivity behavior

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

For $HS-$, the particles are insulated from each other while for $HS+$ the particles are interconnected into a three

^{a)}bernd.weidenfeller@tu-clausthal.de.

^{b)}mathias.anhalt@tu-clausthal.de.

^{c)}stefan.kirchberg@tu-clausthal.de.

dimensional network. Using the model diffusivities calculated with the approach by Hashin and Shtrikman, the interconnectivity of the conducting phase $X_{interconnected}$ can be revealed according to Schilling and Partzsch^{2,3,11}

$$X_{interconnected} = \frac{\alpha_{measured} - \alpha^{HS-}}{\alpha^{HS+} - \alpha^{HS-}}, \quad (3)$$

with the measured thermal diffusivity $\alpha_{measured}$ of the composite. The as determined interconnectivity is a relative measure of the accordance of the measured values with Hashin-Shtrikman bounds. Interconnectivities with $X_{interconnected} = 0$ represent measurement values coinciding exactly with the Hashin-Shtrikman lower bound, while $X_{interconnected} = 1$ represent measurement values located exactly on the Hashin-Shtrikman upper bound. Typically, $X_{interconnected}$ is between a value of 0 and 1, and also negative values are possible, if measurement values are lying below Hashin-Shtrikman lower bound. Because the interconnectivity $X_{interconnected}$ is calculated for each filler fraction x , the values $X_{interconnected}(x)$ can decrease or increase with increasing filler fraction depending on the location of the measurement values related to the Hashin-Shtrikman bound. Thus, the interconnectivity can be understood as a relative measure of an ideally interconnected network of the phase with high thermal diffusivity. As the diffusivity is dominated by the smallest junctions of the path of high diffusivity, the resultant interconnectivity is dominated by these junctions. If, for example, the phase of high diffusivity is interconnected by point contacts, most of this phase will not directly contribute to the overall diffusivity—not ideally interconnected—and the determined interconnectivity is dominated by point contacts. This especially holds true, if the difference between the diffusivities of the different phases is huge. An interconnectivity equal to 0 would mean that filler particles do not form a network and diffusivity values vs. filler fraction follow the lower boundary of the Hashin and Shtrikman model. In contrary, an interconnectivity equal to 1 means that the filler material forms an ideal 3D network and would follow the upper boundary of the model by Hashin and Shtrikman. Thus, it is imaginable that, in fact, the possible number of particle-particle contacts is increasing with filler fraction but the number of contact points related to the maximum number of possible particle-particle contacts is poor which results in a low interconnectivity.

In each theoretical approach, the resistance of the boundary between matrix and particle is neglected. The presence of this resistance is due to an acoustic mismatch evoked by differing Young's moduli. In a simple model, acoustic phonons can be treated like particles of an ideal gas. Now, the thermal conductivity λ can be defined using Fourier's law

$$\vec{q} = -\lambda \nabla T, \quad (4)$$

with the heat flux \vec{q} and the temperature gradient ∇T . Thermal conductivity is connected with the thermal diffusivity α , specific heat capacity c_p , and specific density ρ by

$$\lambda = \alpha c_p \rho. \quad (5)$$

In this equation, the product $C = c_p \rho$ is the specific heat per volume. Furthermore, the thermal diffusivity can be

described with the Einstein approximation¹² by the product of the phonon's velocity v and its mean free path β

$$\alpha = \frac{1}{3} v \beta. \quad (6)$$

In general, the speed of an acoustic wave in a medium is approximately given by

$$v \approx \sqrt{\frac{K}{\rho}}, \quad (7)$$

and the bulk modulus K can be estimated from Young's modulus E and Poisson's ratio μ from¹³

$$K = \frac{E}{3(1-2\mu)}. \quad (8)$$

Finally, the Poisson's ratio μ_c of the composite consisting of PP and iron-silicon (FeSi) particles can also be estimated using a mixing rule. Hsieh and Tuan¹⁴ discussed several models and advices against Hashin-Shtrikman model. However, due to the big differences in Young's modulus for iron silicon and polypropylene, the differences in calculated Poisson's ratios using Hashin-Shtrikman lower bound or series model are neglecting and thus here the series model

$$\mu_c = \frac{(1-x)\mu_{PP}E_{FeSi} + x\mu_{FeSi}E_{PP}}{(1-x)E_{FeSi} + xE_{PP}}, \quad (9)$$

with the volume fraction x of FeSi particles in the polymer is used. Data for Poisson's ratio can be taken from Refs. 15 and 16. Using Eqs. (7)–(9) in Eq. (6), the phonon's mean free path can be estimated by

$$\beta = \frac{3\alpha}{\sqrt{\frac{E}{3\rho_c(1-2\mu_c)}}}, \quad (10)$$

whereas ρ_c denotes the density of the composite. Furthermore, Eq. (10) shows a proportionality of $\alpha \sim \sqrt{E}$.

In metallic materials, the thermal conductivity λ_m is composed additively of a lattice component due to phonons λ_p , an electronic component λ_e related to thermal transport by electrons, and an interface component λ_{ic}

$$\lambda_m = \lambda_p + \lambda_e + \lambda_{ic}. \quad (11)$$

Thermal energy from metal particles to the polymer can be transported either by coupling of electrons and phonons within the particle and than subsequently to phonons in the polymer or by coupling between electrons of the metal and phonons of the polymer by anharmonic interactions at the metal-polymer interface.¹⁷ Theoretical and experimental works to quantify the metal polymer interactions are rare.¹⁷ In this work, metal-polymer interactions are supposed to be a disturbance, which allow to use a series model. The electronic component can be described by the Wiedemann-Franz law¹²

$$\lambda_e = L\sigma T, \quad (12)$$

where $L = \pi^2/3(k_B/e)^2 = 2.44 \times 10^{-8} \text{ W}\Omega/\text{K}^2$ is the theoretical Lorenz number while experimental values are lying between $2.1 \times 10^{-8} \text{ W}\Omega/\text{K}^2 \leq L \leq 2.9 \times 10^{-8} \text{ W}\Omega/\text{K}^2$,¹⁸ k_B is the Boltzmann constant, σ is the electrical conductivity, and e is the elementary charge. With Eqs. (5) and (12), the thermal diffusivity of the electronic component holds

$$\alpha_e = LT \frac{\sigma}{\rho c_p}. \quad (13)$$

EXPERIMENTAL

As polymer, a commercially available PP (H734-52RNA, DOW, Germany) and as filler material spherical micro particles of iron-silicon with 6.8% silicon (FeSi6.8, Höganäs S.A., Sweden) with mean particle diameter $d_{50} = 58 \mu\text{m}$ and particle sizes smaller than $106 \mu\text{m}$ were chosen. The specific electrical resistivity of FeSi6.8 is $\rho_{\text{FeSi6.8}}^{\text{el}} = 85 \cdot 10^{-8} \Omega\text{m}$, specific density is $\rho_{\text{FeSi6.8}} = 7.48 \text{ g/cm}^3$, and the coefficient of thermal expansion is $\beta = 1.2 \times 10^{-5}/\text{K}$.¹⁹ The dynamic storage modulus of iron silicon is in the investigated temperature range constant at $E'_{\text{FeSi6.8}} = 211 \text{ GPa}$.

PP-FeSi6.8 composites with filler content in the range from 0 vol. % to 70 vol. % were prepared by kneading (Rheomix 600p, PolyLab-System, Thermo Haake, Germany). Afterwards, by injection molding (Arburg Allrounder 220C, Arburg GmbH & Co KG, Germany) rectangular specimen ($35 \times 10 \times 4 \text{ mm}^3$) for use in dynamic mechanical analysis (DMA) and disc shaped specimen (diameter $d = 25.4 \text{ mm}$, thickness $t = 1 \text{ mm}$) for thermal diffusivity measurements by laser flash method (LFA) were prepared.

Additionally to the composites, also the thermal diffusivity of a pure iron-silicon alloy (FeSi) sample with 6.5% silicon purchased at Mateck GmbH (Jülich, Germany) was measured.

The thermal diffusivity was investigated in a laser flash apparatus (LFA 427, Netzsch-Gerätebau GmbH, Germany) from 300 K to 415 K under helium atmosphere. Samples were covered by a thin graphite layer to ensure a good absorption of the laser light 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.³ The accuracy of this measurement method is 5%.

For mechanical characterization, a dynamic mechanical thermal analyzer (DMTA) (DMA 2980, TA Instruments, Alzenau, Germany) in forced vibration single cantilever mode was used. The temperature ranged from 200 K to 425 K at a heating rate of 3 K/min and an induced frequency of 8 Hz. An amplitude of $5 \mu\text{m}$ was applied. The maximum strain during the measurement was $\varepsilon_{\text{max}} = 1.4 \times 10^{-4}$. The temperature was calibrated using indium, lead, tin, and zinc standards to achieve a minimum temperature deviation of 0.2 K. The repeating accuracy of storage modulus is 3%.

Crystallinity measurements of samples were carried out from 295 K to 460 K with a heating rate of 5 K/min using a differential scanning calorimeter (DSC 2920 modulated, TA Instruments, Alzenau, Germany). The DSC was calibrated with indium and tin standards. The fraction of crystallization was estimated using a standard melting enthalpy of 207 J/g for 100% crystalline PP.²⁰

Filler fraction in the composites was checked by measurements with thermogravimetric analysis (Q5000 IR, TA Instruments, Alzenau, Germany) in high resolution mode.

RESULTS AND DISCUSSION

In Figure 1, the temperature dependent thermal diffusivity of the investigated polypropylene composites depending on the filler content can be seen. Thermal diffusivity increases at a temperature of $T = 300 \text{ K}$ from $\alpha_{\text{PP}} = 0.14 \text{ mm}^2/\text{s}$ for unfilled polypropylene up to $\alpha_{\text{PP+70\%FeSi}} = 0.8 \text{ mm}^2/\text{s}$ for polypropylene with 70 vol. % FeSi. The thermal diffusivity of unfilled polypropylene is comparable to values ($0.12 \text{ mm}^2/\text{s} \leq \alpha \leq 0.24 \text{ mm}^2/\text{s}$) already published for different types of polypropylene.^{2,3,9,21} The measured thermal diffusivity of the iron silicon alloy with $\alpha_{\text{FeSi}} = 5.5 \text{ mm}^2/\text{s}$ at 375 K is lower than the value of $\alpha = 6.1 \text{ mm}^2/\text{s}$ reported by Geld at about 375 K,²² however, that might be a result of different micro structures of the investigated samples. Using the specific heat capacity of $c_p = 0.54 \text{ J}/(\text{gK})$ measured with differential scanning calorimeter and literature values for density and specific electrical conductivity,¹⁹ a Lorenz number of $L = 1.8 \times 10^{-8} \text{ W}\Omega/\text{K}^2$ at $T = 300 \text{ K}$ with Eq. (13) can be estimated. This value is below the experimental values mentioned in the theoretical part, but it is significant above the value of $L = 1.08 \times 10^{-8} \text{ W}\Omega/\text{K}^2$ found by Beitchman *et al.*²³ Also, Williams *et al.*²⁴ found values around $0.8 \cdot L$ for the Lorenz number, which are significant below the literature values for iron reported in Ref. 18 While Beitchman investigated α -iron, Williams examined different alloys of α -iron.

Compared to the thermal diffusivity of FeSi of $\alpha_{\text{FeSi}} = 5.2 \text{ mm}^2/\text{s}$ at room temperature $T = 300 \text{ K}$, the values of the composites are quite low indicating a heat transport mainly influenced by the polymeric matrix. This interpretation additionally is supported by the decrease of thermal diffusivity with increasing temperature according to Eqs. (6) and (7) due to the softening of the polymer. This behavior is well known from baryte and magnetite filled polymer composites.²

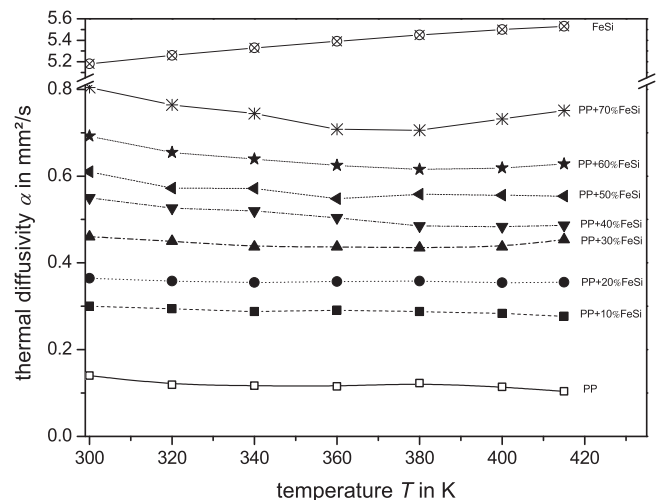


FIG. 1. Thermal diffusivity α of polypropylene filled with 0 vol. % to 70 vol. % content of FeSi particles at different temperatures.

The poor contribution of the FeSi particles to the overall thermal diffusivity can be seen in Fig. 2, in which only data for $T = 300\text{ K}$ and $T = 415\text{ K}$ are shown for reasons of clarity because symbols of all other measured data would overlap the shown symbols. As it can be seen for low filler fractions of 10 vol. % to 20 vol. % FeSi, the measured values are close to the theoretical upper bound. For increasing filler fraction, the measured data are getting closer to the lower bound of the Hashin-Shtrikman model. Using the model interconnectivity $X_{interconnected}$, this finding means that the particles form a good interconnected network for low filler fractions while it becomes worse for higher filler fractions. The as determined interconnectivity can be understood as a relative measure to an ideally interconnected network of the high thermally conducting phase. As the diffusivity is dominated by the smallest junctions of the path of high diffusivity, the resultant interconnectivity is dominated by these junctions. This means that especially at high filler fractions the contribution of the FeSi phase to the thermal diffusivity is poor and the temperature is mainly distributed by the polymer and not by the filler.

As can be seen in Fig. 3, the interconnectivity is around $X_{interconnect} = 40\%$ for polypropylene with 10 vol. % FeSi. The interconnectivity is quite constant for increasing temperature up to $T = 415\text{ K}$. With increasing filler fraction, the interconnectivity decreases and finally it shows negative values for a filler fraction of 70 vol. %. It should be noted here that a decreasing interconnectivity does not mean that there are minor inter-particle contacts but that measurement values are approaching Hashin-Shtrikman lower bound and finally they are below this bound. Contrary to the Hashin-Shtrikman upper bound where the composite properties are dominated by the filler particles, the thermal diffusivity at the lower bound is mainly characterized by thermal properties of the matrix material while the filler does not contribute in a significant manner to the overall thermal diffusivity. Hence, the low values for interconnectivity suggest a temperature distribution in the composite which is mainly controlled by the

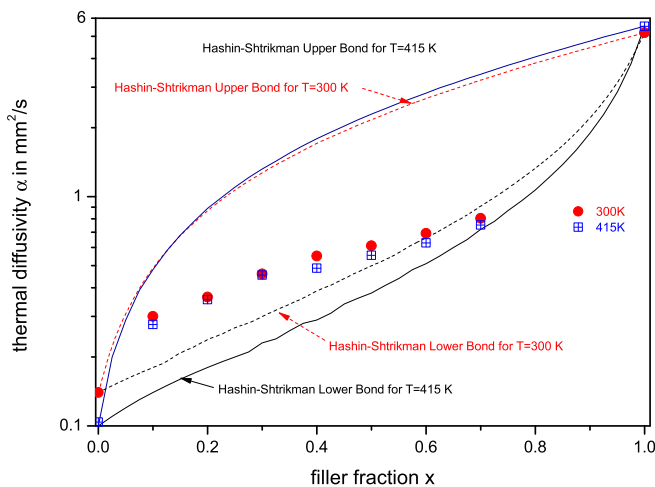


FIG. 2. Measured thermal diffusivity data for $T = 300\text{ K}$ and $T = 415\text{ K}$ of polypropylene filled with 0 vol. % to 70 vol. % content of FeSi particles and for a FeSi alloy compared with theoretical diffusivities calculated with Hashin-Shtrikman model.¹⁰

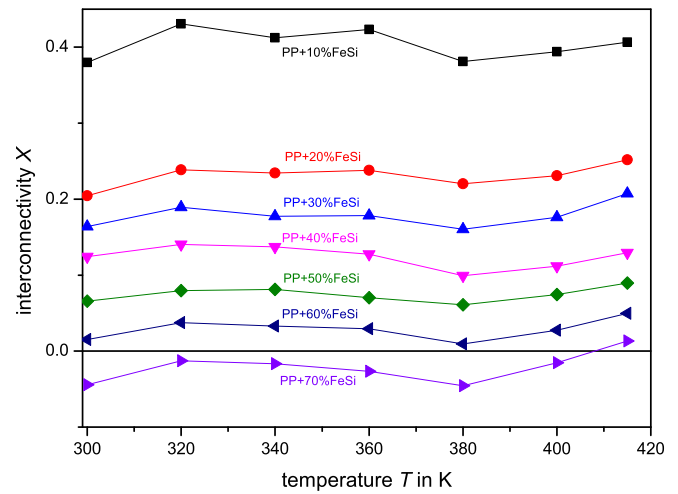


FIG. 3. Interconnectivity X calculated using Eq. (3) for measured thermal diffusivity dependent on filler fraction and temperature.

polymer even at this high filler fractions. The value of the interconnectivity below Hashin-Shtrikman lower bound could lead to the assumption that there might some air, vacuoles, or any additional third phase be trapped in the composite samples. However, this can be avoided in the sample's manufacturing process using a high pressure and after pressure during injection molding process. In fact, vacuoles appeared only in samples of several millimeters thickness in unfilled or low filled polymers while they could not be found in highly filled composites or very thin samples like the specimen used in these investigations. Furthermore, until now measurements of specific gravity as well as high resolution thermogravimetric measurements (not shown here) gave any hints to a third phase but they approved the fact, that all samples were prepared and characterized very carefully.

However, using Eq. (10), the mean free path length of phonons β in the investigated composites (cf. Fig. 4) can be calculated using measurements of the storage modulus E' (cf. Fig. 6). In Fig. 4, it can be observed, that the mean free path length of the phonons β is increased from $\beta \approx 0.3\text{ nm}$ at

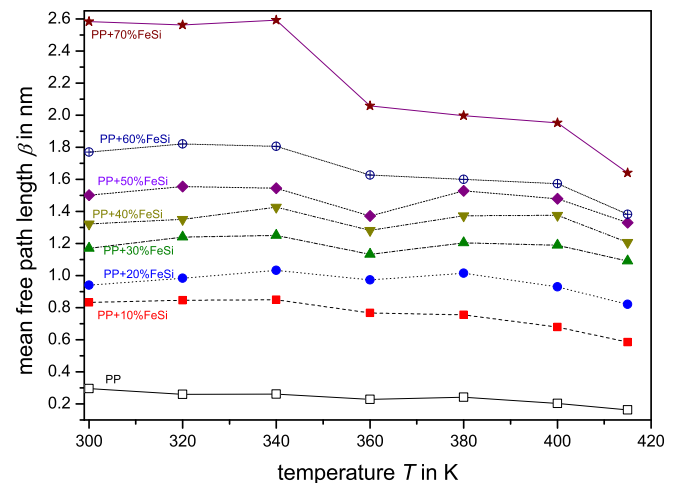


FIG. 4. Calculated mean free path length of phonons in polypropylene-FeSi composites for FeSi content up to 70 vol. % using Eq. (10) and modulus data taken from Fig. 6. Poisson's ratio of the composites was taken from Ref. 15.

a temperature of $T = 300$ K in polypropylene to $\beta \approx 2.6$ nm at $T = 300$ K for polypropylene with 70 vol. % FeSi. The mean free path length shows a slight decrease with increasing temperature. While especially for the composites with 70 vol. %, 60 vol. %, and 10 vol. % of FeSi a decline of the mean free path appears between $T = 340$ K and $T = 360$ K the other composites seem to show a depression at $T = 360$ K. The free path length of phonons in amorphous polymers is in the range of the distance of the carbon atoms. In the case of amorphous PP, the distance is about 0.154 nm, which is two times the radius of carbon atoms with $r = 0.077$ nm. The investigated polymer is a semi-crystalline polymer with a crystallinity of about 50% (cf. Fig. 5). Thus, the transmission of vibration is favored compared to amorphous polymers and the mean free path of phonons enlarges dramatically.⁵ It can be assumed that the modeled mean free path length of $\beta = 0.3$ nm for polypropylene might be the result of the high amount of crystallites.

Fig. 5 shows that the crystallinity of all investigated samples is nearly identical and lies in the range from 52% to 57%.

Nevertheless, it can be seen that a composite filled with 10 vol. % FeSi shows a higher crystallinity than an unfilled one. Raising the filler content leads to a decrease of crystallinity and ends up in a crystallinity grade at 70 vol. % which is smaller than in the unfilled polymer. It might be that FeSi particles act as nucleation agent for the growth of crystallites. In contrary larger amounts of filler seem to hinder crystallites to be formed, which is due to the increasing interface area between particles and polymer. However, the influence on the free path length of the phonons in the polymeric matrix can be neglected since differences in crystallinity are too small.

Therefore, the mean free path length of phonons in the polymeric matrix of the composite should have identical values and the increase in free mean path length of FeSi filled polymer must be the result of the FeSi particles.

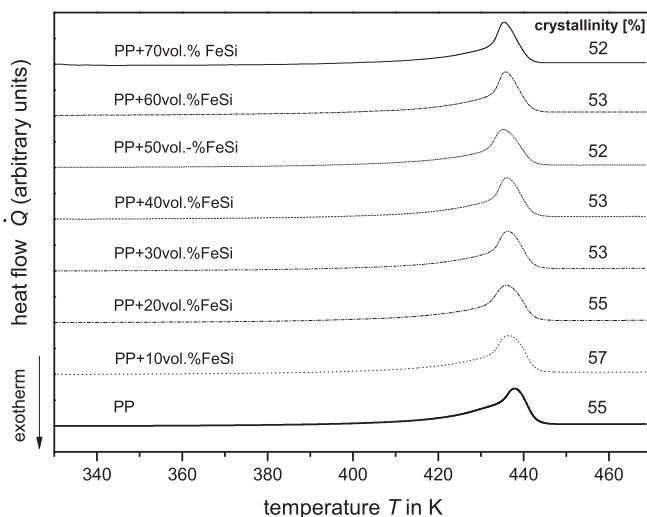


FIG. 5. Temperature dependent heat flow (DSC curves) of polypropylene-FeSi-composites with different FeSi contents at a heating rate of 5 K/min. The fraction of crystalline polypropylene was estimated by comparison of the measured enthalpy with standard enthalpy for 100% crystalline polypropylene. The crystalline melting temperature is around $T_{cryst} = 438$ K.

Additionally, the value of the mean free path length in the polymeric matrix must be a combination of the mean free path length of phonons in the amorphous and of the crystalline part of the polypropylene. This means that the mean free path length of phonons must be reduced for the polypropylene sample as well as for the composites when temperature first exceeds glass transition temperature at $T_g = 300$ K of polypropylene (cf. Fig. 6) and secondly crystalline melting temperature $T_{cryst} \approx 438$ K (cf. Fig. 5) of the polypropylene. Unfortunately, these temperatures are not lying within the measured temperature range of thermal diffusivity. Nevertheless, for higher temperatures between glass transition temperature and crystalline melting temperature, the phonon mean free path is reduced, which especially can be seen for temperatures above $T \geq 340$ K (cf. Fig. 4). This behavior corresponds with a softening of the polymer which is obvious in Fig. 6 showing the decline of the temperature dependent storage modulus E' in this temperature range.

The measurement results in Fig. 6 are illustrating a significant drop of the storage modulus E' especially around the glass transition temperature $T_g = 300$ K. Furthermore, the significant influences of the FeSi particles can be clearly observed in the glassy region at temperatures below glass transition temperature of polypropylene. In the high temperature region above the crystalline melting temperature of $T_{cryst} = 348$ K, the mechanical properties of the PP-FeSi composites are mainly affected by the polypropylene matrix which leads to a very low storage modulus. In the examined temperature range an increase in the filler content results in a rising storage modulus. The influence of particles on storage modulus is eliminated by raising the temperature. The reinforcement of the particles can be attributed to its stiffness, particle-matrix interactions, and connections, respectively, and increasing particle-particle interactions at higher filler contents. The percolation threshold is around 30 vol. % filler content. Below this amount, the homogeneously distributed particles are completely separated from each other and surrounded by the PP matrix.^{2,9,25} As can be seen in Fig. 6, the modulus of the composite with 70 vol. % FeSi is lower than the modulus of the composites with 40, 50, and 60 vol. % of

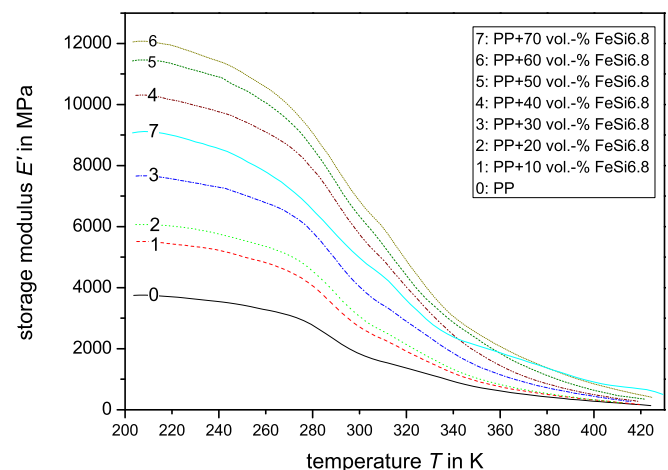


FIG. 6. Temperature dependent storage modulus E' of polypropylene-FeSi composites with different FeSi contents measured with a DMA at a heating rate of 3 K/min.

FeSi filler. Around this filler fraction, a random close packing for polydisperse particles can be found.²⁶ Therefore, particles can come into close contact. It can be assumed that due to the low amount of polymer in this composite many particle-particle contacts exist without or only with a low amount of polymeric matrix between particles bonding them together. This leads to the decrease of the storage modulus. For a temperature higher than the glass transition temperature, where the polymer chains become more and more mobile, and approaching the crystalline melting temperature the storage modulus of PP with 70 vol. % FeSi is higher than the modulus of composites with lower filler fraction. At these temperatures, the polymer is sticking the particles together and thus the modulus is higher than the modulus of the composite with 60-vol. % particles. Also here, the assumption of a third phase (e.g., air inclusions) can be excluded. A low amount of air in the composite would mean, that the resulting storage modulus would follow the Hashin-Shtrikman upper bound. Then, a very high volume fraction of air would be necessary to decrease the storage modulus in the observed dramatic manner. Furthermore, such a high volume fraction of air would lead to a dramatic lower specific density of the samples, which was not observed.

Using the data from Fig. 6, the relation $\alpha \sim \sqrt{E}$ of Eq. (10) is shown in Fig. 7. It is remarkable that the temperature dependent diffusivity values for the polypropylene and the polypropylene-FeSi composites can be fitted by a straight line within the investigated temperature range. With increasing filler fraction, the scatter of diffusivity values from fit lines is increasing. In spite of this, the deviation of measurement values from fit line is only $0.03 \text{ mm}^2/\text{s}$ for the composite with 70 vol. % FeSi. Also this scatter is within the measurement accuracy. However, this might be explainable with the poor connection of the particles also leading to an unrealistic low storage modulus. Nevertheless, without this unrealistic low storage modulus, it can be expected that the values for this composite are lying on the same fit function. This can be expected because the \sqrt{E} values for measurement temperatures higher than 380 K, which are lying on this

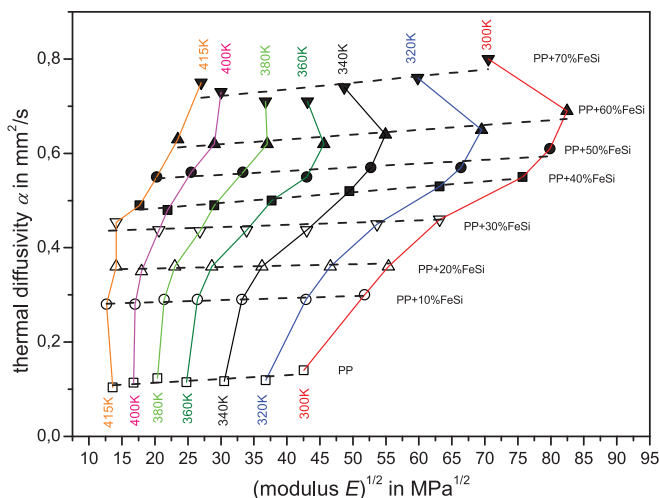


FIG. 7. Relation between square root of the modulus and thermal diffusivity for different polypropylene-FeSi composites using Eq. (10).

function obviously seems to be correct and only measurement values for lower temperatures are moved to lower values of the storage modulus.

The slope of the fit curves is dependent on the mean free path of the phonons according to Eq. (10). The fit functions and the mean free path of the phonons calculated from the slope are listed in Table I. The mean free path of phonons in unfilled polypropylene with $\beta = 0.283 \text{ nm}$ is comparable to the value shown in Fig. 4. This is not astonishing, because the values are estimated using the same model and same data. Contrary to the first method of estimation of data from single values now, the data were found by a nearly temperature independent method leading to a mean value of the mean free path of phonons in the material. Second, using the slopes of the regression lines leads to values of the mean free path of phonons which is independent on the changes of the modulus due to the FeSi powder, while the intersection with the ordinate (cf. Fig. 7) shows the influences of iron silicon on thermal diffusivity of the composites or the crystallites of the polypropylene, respectively. Thus, the mean values of all listed values in Table I lead to a mean phonon's free path of $\beta = 0.153 \text{ nm}$ which is just the theoretical value ($\beta_{theory} = 0.154 \text{ nm}$) for amorphous polypropylene.

Regarding the results of the mean free path of phonons as can be seen in Fig. 4, it can be assumed that the estimated phonon's free path is the sum of the free path in amorphous and in crystalline part of the polymer. If the mean free path in the amorphous fraction ($x_a = 50\%$) of the polymer equals $\beta_{amorph} = 0.154 \text{ nm}$ than the mean free path of phonons in the crystalline fraction $x_c = 50\%$ of the polymer must equal $\beta_{cryst} = 0.450 \text{ nm}$ to find a mean free path in the semicrystalline polypropylene of around $\beta_{sc} = 0.300 \text{ nm}$, if an arithmetic mean value $\beta_{sc} = x_a \cdot \beta_{amorph} + x_c \cdot \beta_{cryst}$ is taken. As a maximum change of thermal conductivity in polymers, a factor of 7.5 was found for ideal crystallinity while experimental results have lead to an increase of a factor 2.2 compared with amorphous polymers,⁵⁻⁷ which is according to the here presented result. As can be seen in Fig. 5, the crystallinity of the polymer does not change significantly with the content of particles and therefore also the mean free path of the phonons in the polymeric matrix of the composites does not change for temperatures below glass transition temperature $T_g = 300 \text{ K}$. In fact, a significant change of phonon's mean

TABLE I. Coefficients of linear regression of the type $y = a + b \cdot x$ for straight lines visible in Fig. 7. The mean free paths of phonons β from the slope of the regression lines were calculated using Eq. (10) and $\mu = 0.33$ and calculated material's density.

Material	$a \text{ (mm}^2/\text{s)}$	$b \text{ (}\frac{\text{mm}^2}{\text{svMPa}}\text{)}$	$\beta \text{ (nm)}$
PP + 0 vol. %FeSi	0.09735	8.12213×10^{-4}	0.283
PP + 10 vol. %FeSi	0.27605	4.27150×10^{-4}	0.113
PP + 20 vol. %FeSi	0.35011	3.01002×10^{-5}	0.067
PP + 30 vol. %FeSi	0.43002	4.65010×10^{-4}	0.090
PP + 40 vol. %FeSi	0.46029	1.15000×10^{-3}	0.201
PP + 50 vol. %FeSi	0.53093	7.89578×10^{-4}	0.127
PP + 60 vol. %FeSi	0.58873	1.02000×10^{-3}	0.152
PP + 70 vol. %FeSi	0.67990	1.39000×10^{-3}	0.194

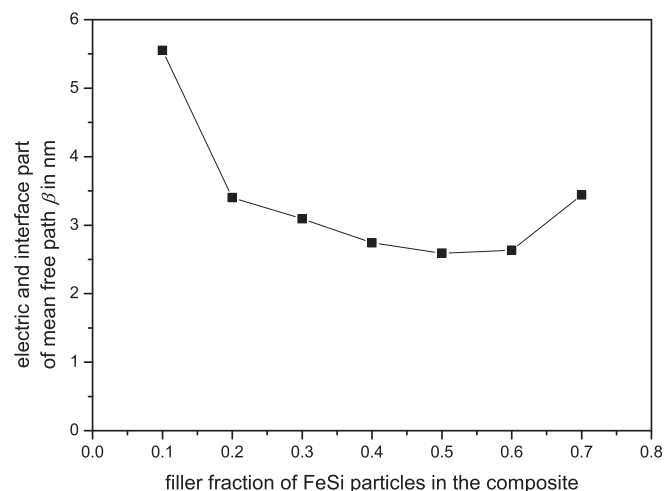


FIG. 8. Electronic and interface part of the temperature conduction in iron silicon particles at a temperature $T=300$ K according to Eq. (11) and calculated using a simple series model.

free path cannot be seen for temperatures below $T=340$ K (cf. Fig. 4). Thus, the changes in the mean free path of the composites β_{comp} with increasing filler fraction which can be seen in Fig. 4 can be attributed to the number of iron-silicon particles and according to Eq. (11) to the electronic part of the mean free path and the interface component in the thermal conductivity.

Calculating the mean free path in the filler particles based on the same assumption of an arithmetic mean value the mean free path of phonons in the filler particles and the interface component $\beta_{FeSi+IC}$ can be calculated using the equation $\beta_{comp} = x_{PP} \cdot \beta_{sc} + (1 - x_{PP}) \cdot \beta_{FeSi+IC}$ with the fraction x_{PP} of polypropylene in the composite. However, heat conduction in filler particles has an contribution by phonons and by electrons (cf. Eq. (11)). The contribution by phonons can be calculated to be $\beta_{phonons} = 0.118$ nm using Eq. (10) with the thermal diffusivity $\alpha_{FeSi} = 5.2$ mm²/s, the modulus of $E'_{FeSi} = 211$ GPa, and the Poisson's ratio $\mu = 0.3$ of FeSi. Fig. 8 shows the electronic and interface part of the mean free path plotted against the filler fraction. It can be seen that the mean free path calculated from the electronic and interface part of the heat conduction decreases with increasing filler fraction from $\beta_{FeSi} \approx 5.5$ nm at 10 vol. % FeSi particles in the composite down to $\beta_{FeSi} \approx 2.5$ nm at 60 vol. % FeSi in the composite. Regarding that the filler particles are much larger than the electron-phonon coupling length, it can be assumed that the mean free path within the FeSi particles is constant.¹⁷ Thus, this decrease can be explained by an increase of boundaries between the particles and by an increasing interface area between particles and

polymer which act as scatter centers for the heat conducting electrons and phonons. Only the value at 70 vol. % FeSi particles in the composite shows an increased mean free path. However, most likely this is due the missing polymer matrix between particles leading to an unexpected low value of the storage modulus (cf. Fig. 6) at this filler fraction which finally leads to an incorrect value of the mean free path at this filler fraction.

ACKNOWLEDGMENTS

Thanks go to the German Research Foundation (DFG) for financial support of these investigations

- ¹R. Agrawal, N. S. Saxena, K. B. Sharma, S. Thomas, and M. S. Sreekala, *J. Appl. Polym. Sci.* **89**, 1708 (2003).
- ²B. Weidenfeller, M. Hofer, and F. R. Schilling, *Composites, Part A* **35**, 423 (2004).
- ³M. Anhalt and B. Weidenfeller, *J. Appl. Polym. Sci.* **119**, 732–735 (2011).
- ⁴F. de Araujo and H. Rosenberg, *J. Phys. D* **9**, 665 (1976).
- ⁵M. Pietralla, *J. Comput.-Aided Mater. Des.* **3**, 273 (1996).
- ⁶M. Pietralla, *Large-Scale Molecular System*, NATO-ASI, Ser. B Vol. 258, edited by W. Gans, A. Blumen, and A. Amann (Plenum, London, UK, 1991).
- ⁷D. B. Mergenthaler, M. Pietralla, S. Roy, and H.-G. Kilian, *Macromolecules* **25**, 3500 (1992).
- ⁸G. Milton, *The Theory of Composites*, edited by P. Ciarle, A. Iserless, R. Kohn, and M. Wright (Cambridge University Press, 2002).
- ⁹B. Weidenfeller, F. Schilling, and M. Höfer, *Composites, Part A* **33**, 1041 (2002).
- ¹⁰Z. Hashin and A. Shtrikman, *J. Appl. Phys.* **33**, 3125 (1962).
- ¹¹F. R. Schilling and G. M. Partzsch, *Phys. Chem. Earth, Part A Solid Earth Geod.* **26**, 239 (2001).
- ¹²P. Klemens, *Solid State Phys.* **7**, 1 (1958).
- ¹³J. Anderson, K. Leaver, J. Alexander, and R. Rawlings, *Materials Science*, 4th ed. (Chapman and Hall, 1990).
- ¹⁴C. Hsieh and W. Tuan, *J. Mater. Sci. Eng. A* **396**, 202 (2005).
- ¹⁵S. Kirchberg, M. Anhalt, and B. Weidenfeller, in *Proceedings of the ASME/AJTEC Heat Transfer and Thermal Engineering Conference, Hawaii, USA* (ASME, 2011), pp. T10072–T10072–5, Paper No. AJTEC2011-44054.
- ¹⁶H. Waterman, *Kolloid Z. Z. Polym.* **192**(1–2), 1 (1963/II).
- ¹⁷J. Ordonez-Miranda, R. Yang, and J. Alvarado-Gil, *J. Appl. Phys.* **111**, 044319 (2012).
- ¹⁸G. S. Kumar and G. Prasad, *J. Mater. Sci.* **28**, 4261 (1993).
- ¹⁹R. Bozorth, *Ferromagnetism* (IEEE, New York, 1978).
- ²⁰G. Ehrenstein, G. Riedel, and P. Trawiel, *Praxis der Thermischen Analyse von Kunststoffen* (Carl Hanser Verlag München Wien, 1998).
- ²¹W. Dietz, *Colloid Polym. Sci.* **255**, 755 (1977).
- ²²P. Geld, *Teplotnergetika* **6**, 45 (1956) (in russian).
- ²³J. G. Beitchman, C. W. Trussel, and R. V. Coleman, *Phys. Rev. Lett.* **25**, 1291 (1970).
- ²⁴R. K. Williams, D. W. Yarbrough, J. W. Masey, T. K. Holder, and R. S. Graves, *J. Appl. Phys.* **52**, 5167 (1981).
- ²⁵M. Razzaq, M. Anhalt, L. Frormann, and B. Weidenfeller, *Mater. Sci. Eng., A* **444**, 227 (2007).
- ²⁶R. M. German, *Particle Packing Characteristics* (Metal Powder Industry, 1989).