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Thermal conductivity model of filled polymer composites

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Abstract: Theoretical and empirical models for predicting the thermal conductivity of polymer composites were summarized since the 1920s. The effects of particle shape, filler amount, dispersion state of fillers, and interfacial thermal barrier on the thermal conductivity of filled polymer composites were investigated, and the agreement of experimental data with theoretical models in literatures was discussed. Silica with high thermal conductivity was chosen to mix with polyvinyl-acetate (EVA) copolymer to prepare SiO_2/EVA co-films. Experimental data of the co-films' thermal conductivity were compared with some classical theoretical and empirical models. The results show that Agari's model, the mixed model, and the percolation model can predict well the thermal conductivity of SiO_2/EVA co-films.

Keywords: polymer matrix composites; thermal conductivity; mathematical models; polyvinyl acetates; silica; filled polymers.

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1. Introduction

With the development of polymer composites in recent years, polymer composites with high thermal conductivity are now required to dissipate heat rapidly in the field of aeronautics and astronautics, microelectronic packaging, heat exchange engineering, chemical engineering, solar energy utilization, *etc*. Generally, the thermal conductivity of polymers varies from 0.15 to 0.25 W/(m·K), so how to increase the thermal conductivity of polymers attracts extensive attention.

The thermal conductivity of polymers can be improved by two methods. The first is to synthesize a structural polymer with high thermal conductivity [1-3], such as a polymer with high crystallinity (parallely stretched high-density polyethylene) based on the thermal conductive mechanism of phonons or electrons (polyacetylene, polyaniline, polypyrrole, *etc*.). The second is to mix the thermally conductive fillers into the polymer matrix [4-7], such as a high-density polyethylene filled with AlN or SiC, where the fillers touch and interact with each other to form a thermally conductive network chain and improve the thermal conductivity of filled polymer composites with the formation of a structural configuration of net or line in the system [8]. The synthesis of structural polymers with high thermal conductivity is usually complicated and only subjected to some polymers. The filler mixed into polymers can improve the thermal conductivity of many polymers. The thermal conductivity of filled polymer composites depends on the granularity, dispersion state of fillers, and its interfacial thermal barrier [9-12], but the thermal conductivity mechanism is fairly complicated, especially for a highly filled system, and it can be very different according to various empirical or theoretical models [13-16]. Based on a polymer with good mechanical and adhesive properties, researchers have paid much attention to its thermal conductivity mechanism for a long time to reach its maximum thermal conductivity.

All typical thermal conductivity models of filled polymer composites since 1924 were summarized and the adaptability of literature data with these theoretical models was investigated in this paper. Furthermore, a silica/polyvinyl-acetates (SiO_2/EVA) co-film was fabricated, and the effect

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of silica amount on the thermal conductivity of the SiO_2/EVA co-film was investigated. The adaptability of some typical models in literatures with the experimental thermal conductivity of SiO_2/EVA composites was discussed.

2. Theoretical models

2.1. Effect of the filler amount

2.1.1. Russell's model

This model was proposed by Russell in 1935. The model supposed that the fillers were identical cubes without mutual interaction. According to the similarity between the principle of electric conduction and heat conduction, Russell's model [17] is given as

$$\lambda = \lambda_1 \frac{V^{\frac{2}{3}} + \frac{\lambda_1}{\lambda_2}\left(1 - V^{\frac{2}{3}}\right)}{V^{\frac{2}{3}} - V + \frac{\lambda_1}{\lambda_2}\left(1 - V^{\frac{2}{3}}\right)} \tag{1}$$

where λ, λ_1, and λ_2 stand for the thermal conductivity of the composites, matrix, and filler, respectively; V is the volume fraction of the filler. This model indicates that the thermal conductivity of filled composites is related to the volume fraction of the filler and the thermal conductivity of the composites and filler.

A SiO_2/EVA co-film was fabricated by mixing various volume fractions of silica filler into EVA copolymer, and a comparison between the experimental data and Russell's model is shown in Fig. 1. It shows that the thermal conductivity of the SiO_2/EVA co-film increases with the increase in volume fraction (V) of silica. The experimental curve lies below the theoretical curve with the deviated absolute value less than 0.15 $W \cdot m^{-1} \cdot K^{-1}$. When V reaches 35%, the experimental curve lies above the theoretical curve. This is because the fillers in the theoretical curve are supposed to be identical cubes without mutual interaction, and the fillers in the experiment are unequal particles and have the mutual interaction with each other. When V>35%, the mutual interaction among particles becomes stronger, which leads to a higher thermal conductivity.

2.1.2. Maxwell-Eucken's model

Maxwell-Eucken supposed that filler particles were homogenous spheres without mutual interaction and dispersed randomly in the polymer matrix. Fewer filler particles would be covered by the polymer and dispersed in the form of isolated islands in the matrix. Maxwell-Eucken's model calculated the energy of the electronic field of Laplace's model based on the similarity between heat and electric conduction [18]:

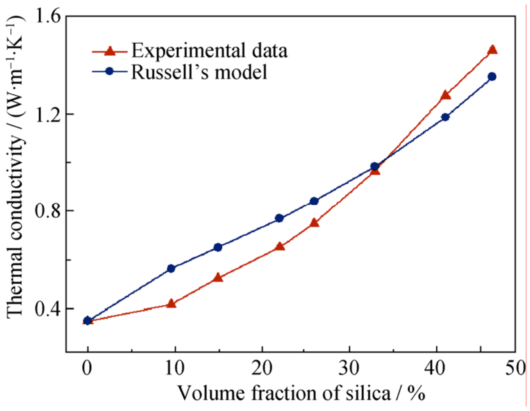

Fig. 1. Thermal conductivity of SiO_2/EVA based on experimental data and Russell's model.

$$\lambda = \lambda_1 \frac{2\lambda_1 + \lambda_2 + 2V\left(\lambda_2 - \lambda_1\right)}{2\lambda_1 + \lambda_2 - V\left(\lambda_2 - \lambda_1\right)} \tag{2}$$

When the volume fraction of graphite is below 10% and that of tin powder below 8%, the experimental data of graphite/polypropylene and tin/polyethylene composites could be predicted well by Maxwell-Eucken's model [19]. The experimental data would be higher when the volume fraction of fillers increased, which deviated from the theoretical curve. The thermal conductivity of composites, such as silica/epoxy resin, alumina/epoxy resin, and aluminum nitride (coated by silica)/epoxy resin were investigated [20]. It was found that when the volume fractions of alumina and aluminum nitride (coated by silica) were lower than 20%, the thermal conductivity of composites would be close to the theoretical value of Maxwell-Eucken.

The comparison of thermal conductivity of SiO_2/EVA co-films between the experimental data and the theoretical value based on Maxwell-Eucken's model is shown in Fig. 2. It shows that the experimental data fit well with Maxwell-Eucken's model when the volume fraction of silica is lower than 15%. With further increasing the filler amount, the experimental data deviate from the model increasingly.

Fig. 2 also shows that Maxwell-Eucken's model can predict well the thermal conductivity of polymer composites under the condition of lower volume fraction of fillers. Because there is no mutual interaction of particles in Maxwell-Eucken's model, and the experimental thermal conductivity deviates from Maxwell-Eucken's model at a high volume fraction.

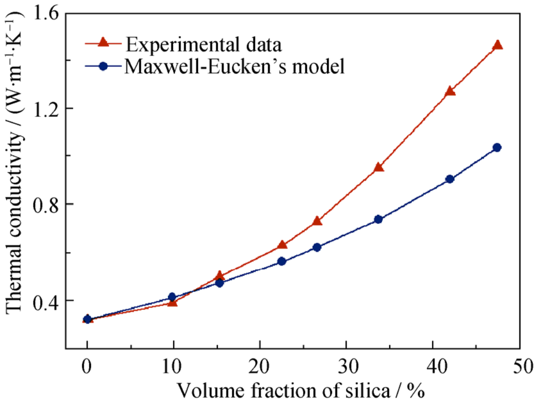

Fig. 2. Thermal conductivity of SiO_2/EVA based on experimental data and Maxwell-Eucken's model.

2.1.3. Bruggeman's model

Considering the compact stack and mutual interaction among the particles in the composite, Bruggeman's model was obtained by introducing the filler's volume fraction under an integral transformation of Maxwell-Eucken's model as [15]

$$1-V=\frac{\lambda_2-\lambda}{\lambda_2-\lambda_1}\left(\frac{\lambda_1}{\lambda}\right)^{\frac{1}{3}} \tag{3}$$

Some research [1] showed that there was a smaller deviation between the experimental data and the theoretical value of Bruggeman's model. The thermal conductivities of epoxy/silica, epoxy/alumina, and polyimide/aluminum nitride, based on the experimental data and Bruggeman's model, were in good agreement when the volume fraction of fillers attained 40%. An effect factor (k=1.08) is introduced into Eq. (3) to obtain the modified Bruggeman's model, which is to correct the theoretical value of thermal conductivity of a SiO_2/EVA co-film. It can compensate for the effects of particle shape and dispersion, interfacial thermal resistance, and the mutual interaction between particles on the thermal conductivity of the co-film.

$$1-V=\frac{\lambda_2-\lambda}{\lambda_2-\lambda_1}\left(\frac{k\lambda_1}{\lambda}\right)^{\frac{1}{3}} \tag{4}$$

where k is an effect factor of the composite.

Fig. 3 shows the comparison among the experimental thermal conductivity of SiO_2/EVA co-films, Bruggeman's model, and the modified Bruggeman's model. It is found that the thermal conductivity data fit quite well if the volume fraction of silica is below 22.5%, whereas they deviate from each other at a higher volume fraction. In other words, compared with Bruggeman's model, the modified Bruggeman's model can predict the thermal conductivity of the composite at a higher volume fraction of fillers.

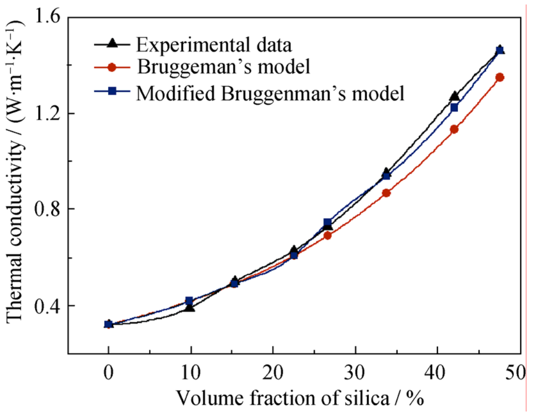

Fig. 3. Thermal conductivity of SiO_2/EVA based on experimental data, Bruggeman's model, and modified Bruggeman's model.

The thermal conductivity of aluminum nitride/polyimide fitted Bruggeman's model well, and the positive effect of the particle shape of aluminum nitride on the thermal conductivity of the composites was almost equal to the negative effect of interfacial thermal resistance, owing to the compensation of both effects in the system [16]. Besides, the disperse state of filler particles and mutual interaction had much effect on the thermal conductivity of the composites [21], whereas the Bruggeman's model did not discuss the effects of particle shape and interfacial thermal resistance on the thermal conductivity.

2.2. Effect of filler shape

2.2.1. Fricke's model

Fricke supposed that filler particles were ellipsoid and dispersed randomly in the polymer matrix, and the thermal conductivity of the polymer conformed to Eq. (5).

$$\lambda=\lambda_1+\left\{\frac{1+V\left[F\left(\lambda_2/\lambda_1-1\right)\right]}{1+V\left(F-1\right)}\right\} \tag{5}$$

where λ, λ_1, and λ_2 stand for the thermal conductivity of the composites, polymer, and filler particles, respectively; V is the volume fraction of the filler; and F is the average temperature gradient ratio of two phases. Because it is too difficult to get the value of F by experiment, there is no experiment verification found for Fricke's model in literatures so far.

2.2.2. Hamilton-Crosser's Model

Hamilton-Crosser considered the filler shape fully, gave an model of average temperature gradient according to

Maxwell's model, and introduced a factor of sphericity ($\psi \leq 1$), which indicated the ratio of specific surface area between a sphere and a filler particle with the same volume, and a factor of the particle shape ($n=3/\psi$). If ψ goes down, n will increase. The thermal conductivity of the polymer composite obtained by taking the particle shape of the filler into consideration is shown as the following equation [15].

$$\lambda = \lambda_1 \left[\frac{\lambda_2 + (n-1)\lambda_1 + (n-1)V(\lambda_2 - \lambda_1)}{\lambda_2 + (n-1)\lambda_1 - V(\lambda_2 - \lambda_1)} \right] \tag{6}$$

When the filler particles are spherical, $\psi=1$, $n=3$, Eq. (6) is consistent with Maxwell's model. The interfacial thermal barrier is negligible for the polymer composites with an identical filler amount. The thermal conductivity of the polymer composite increases with the factor of particle shape n increasing. When $n=3$ (spherical particles), the thermal conductivity of the polymer composites is the least. Fibrous copper can increase polyamide's thermal conductivity significantly, following by sheet copper and spherical copper [22].

In conclusion, filler particles with a smaller ψ can improve thermal conduction for the filled polymer, but the specific surface area of filler particles is difficult to obtain by the experiment, and the sphericity ψ is also difficult to obtain by calculation, so the application of this model is limited.

2.3. Effect of the interfacial thermal barrier

Generally, the filler with high thermal conductivity can facilitate the thermal conduction of polymer composites. However, some researches do not support this point well, because the small particle filler with high thermal conductivity cannot improve the thermal conductivity obviously as expected, and sometimes the thermal conductivity of filled polymers is even lower than that of the polymer matrix [14-16]. The reason for this phenomenon is the existing of interfacial thermal barrier between the polymer and filler. The interfacial thermal barrier of metal/liquid helium was tested by Kapitza for the first time in 1941, which was called Kapitza interface.

By taking the interfacial thermal barrier into consideration and supposing that orbicular particles dispersed randomly in the polymer, the thermal conduction model of polymer composites was obtained by Hasselman *et al.* [12]:

$$\lambda = \lambda_1 \frac{\lambda_2(1+2\alpha) + 2\lambda_1 + 2V\left[\lambda_2(1-\alpha) - \lambda_1\right]}{\lambda_2(1+2\alpha) + 2\lambda_1 - V\left[\lambda_2(1-\alpha) - \lambda_1\right]} \tag{7}$$

where $\alpha=(a_k/a)$ is the interfacial thermal barrier, and represents the effect of interfacial thermal barrier on the thermal conductivity of polymer composites; a is the radius of spherical particles; $a_k=R_{Bd}\lambda_1$, stands for the Kapitza radius which represents the transitional radius of sphere particles; R_{Bd} is defined as the difference between the polymer and filler per heat flow. R_{Bd} and a_k are both constants for certain polymer composites.

Wang [23] calculated and verified the effect of α on the thermal conductivity of polyimide/aluminum nitride composite. It was found that the thermal conductivity data based on the experiment was greater than that of the theoretical model according to Eq. (7). When $\alpha<1$, namely $a>a_k$, the fillers would improve the thermal conduction of the polymer; When $\alpha>1$, namely $a<a_k$, the fillers would weaken the thermal conduction of the polymer; When $\alpha=1$, namely $a=a_k$, the thermal conduction of the polymer would not be affected by the filler, in this case, Hasselman's model conformed to Maxwell's model.

Hasselman's model considered the interfacial thermal barrier and explained why the high thermal conductive filler could not increase the thermal conductivity of polymer composites qualitatively, and sometimes even lower it. However, the model was only adapted for the lower amount of spherical particle filled polymer composites. Furthermore, the measurement of interfacial thermal barrier of polymer composites was very difficult.

2.4. Effect of the filler amount, shape, and interfacial thermal barrier

By taking the effects of particle shape and interfacial thermal barrier into consideration, the model is created by Wang [24] based on Maxwell's model.

$$\lambda = \lambda_1 \frac{\left\{\lambda_2\left[1+(n-1)\alpha\right]+(n-1)\lambda_1\right\}+(n-1)V\left[\lambda_2(1-\alpha)-\lambda_1\right]}{\left\{\lambda_2\left[1+(n-1)\alpha\right]+(n-1)\lambda_1\right\}-V\left[\lambda_2(1-\alpha)-\lambda_1\right]} \tag{8}$$

Research in Ref. [17] showed that the thermal conductivity of polyimide/aluminum nitride composites based on the experiment was smaller than the calculated value by Eq. (8), while a large number of fillers were in the polymer. Wang built up the following model for polymer composites with a high amount of fillers on the basis of Every's theory [11].

$$(1-V)^n = \left[\frac{\lambda_1}{\lambda}\right]^{(1+n\alpha-\alpha)/(1-\alpha)} \left[\frac{\lambda - \lambda_2(1-\alpha)}{\lambda_1 - \lambda_2(1-\alpha)}\right]^{n/(1-\alpha)} \tag{9}$$

Eq. (9) can be simplified to Every's model, when the particles are spherical, namely n=3; and it is simplified to Bruggeman's model, while the interfacial thermal barrier among spherical particles is negligible, namely n=3 and α=0. By taking the interfacial thermal barrier and particle shape into consideration, the experimental thermal conductivity of polyimide/aluminum nitride with V=60% was in agreement with the calculated value from Eq. (9) [16]. This indicated that Eq. (9) proposed by Wang *et al.* could be used to predict the thermal conductivity of polymer composites with a great amount of fillers.

2.5. Effect of the dispersion of fillers

Based on an ideal dispersion of fillers in the polymer, the above thermal conduction models took the effects of filler numbers, shape, and interfacial thermal barrier into account. In practice, the uniform dispersion of fillers existed in certain areas of the polymer composite, especially in a system with a high volume fraction of fillers.

Cheng-Vachon *et al*. supposed that the dispersion of filler particles conformed to the Gaussian law [13], and the dispersion factor is a function of V based on Tao's probability model [14]. Cheng-Vachon's model is described as

$$\frac{1}{\lambda}=\frac{1-B}{\lambda_1}+\frac{1}{\left\{C(\lambda_2-\lambda_1)\left[\lambda_1+B(\lambda_2-\lambda_1)\right]\right\}^{1/2}}\ln\frac{\left[\lambda_1+B(\lambda_2-\lambda_1)\right]^{1/2}+B/2\left[C(\lambda_2-\lambda_1)\right]^{1/2}}{\left[\lambda_1+B(\lambda_2-\lambda_1)\right]^{1/2}-B/2\left[C(\lambda_2-\lambda_1)\right]^{1/2}} \qquad (10)$$

where B and C are both related factors of V.

The experimental thermal conductivity of stannum/high-density polyethylene composites [25] did not fit well with the theoretical value from Eq. (10). It did not change much with the increase in filler amount when V was under 10%, but increased rapidly when V was above 10%.

Experimental data of the thermal conductivity of SiO_2/EVA composites were compared to the value from Eq. (10). It is found that thermal conductivity increases with the increase in filler number, and the tendency of change is well consistent with Eq. (10), and there is only an error of 0.1 W·m^{-1}·K^{-1} between them, as shown in Fig. 4.

Cheng-Vachon's model took the effect of filler dispersion into consideration, and suggested a Gaussian distribution of silica particle size and a homogeneous dispersion in the polymer. The effects of particle shape and interfacial thermal barrier offset each other. The experimental thermal conductivity of filled composites is very near to the calculated value from this model.

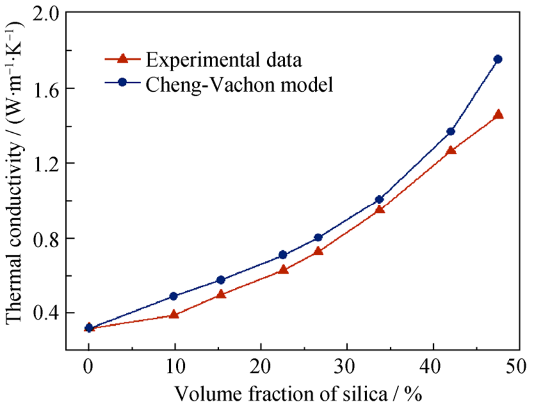

Fig. 4. Thermal conductivity of SiO_2/EVA based on experimental data and Cheng-Vachon's model.

3. Empirical models

3.1. Nielsen's model

By revising the Halpin-Tsai formulation, Nielsen *et al.* obtained the empirical model to predict the thermal conductivity of polymer composites [13]:

$$\lambda=\lambda_1\frac{1+ABV}{1-B\Phi V} \qquad (11)$$

where $A=K_{\mathrm{E}}-1$, $B=\dfrac{\lambda_2/\lambda_1-1}{\lambda_2/\lambda_1+A}$, $\Phi=1+\dfrac{1-V_{\mathrm{m}}}{V_{\mathrm{m}}^2}V$.

Here A and V_{m} are the factors related to particle size and shape, V_{m} is the maximum compacted volume fraction of fillers; K_{E} is an Einstein constant, which is related to the shape and orientation of particles; B is a constant, which is related to the thermal conductivity of each part and particle parameter; and Φ is a function related to the volume fraction of fillers. Some A and V_{m} values [17] can be considered, such as A=1.5, V_{m}=0.637 for spherical particles dispersed randomly; A=3 and V_{m}=0.640 for the particles without fixed shape dispersed randomly in polyimide/aluminum nitride composites [23].

It was found in polyimide/aluminum nitride composites (A=3 and V_{m}=0.64) that the experimental value of thermal conductivity would increase slowly and be close to the predicted value according to Eq. (11), while V was less than 30%. The experimental value of thermal conductivity of the composite started going lower than the theoretical value, when V became larger than 40% and was approaching to V_{m}

(V_m =0.64) [16]. In this case, the error between the experimental and theoretical value would be enlarged with the increase of V [26].

The thermal conductivity of SiO_2/EVA co-films based on the experimental and theoretical data is compared and shown in Fig. 5. It is found that the two curves approach each other until V reaches 40%.

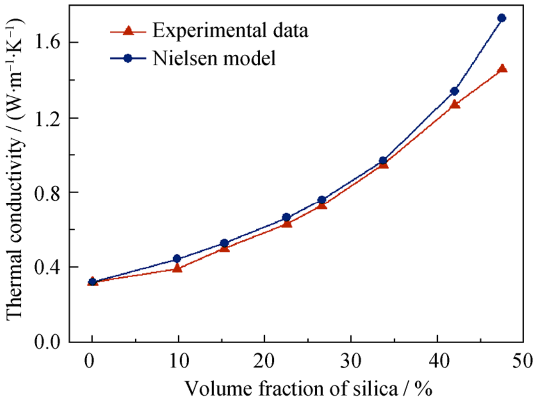

Fig. 5. Thermal conductivity of SiO_2/EVA based on experimental data and Nielsen's model.

Nielsen's model took the mutual interaction among particles into consideration by introducing the V_m value. The thermal conductivity principle of polymer composites can be supposed to form the heat conductive net-chain based on this model.

3.2. Agari's model

Two heat conduction models (parallel and vertical modes) were brought forward to judge the heat flow direction in the polymer composite by Agari [21], based on the formation of thermal conductive net-chain and mutual interaction of particles.

When the heat flow is parallel to the surface of a laminated material, the temperature gradient in each layer will be identical, and the thermal conductive mode is called the parallel model. The heat flows will enjoy priority in passing a highly thermal conductive layer. The thermal conductivity (λ) of laminated materials can be calculated as

$$\lambda = V\lambda_2 + (1-V)\lambda_1 \tag{12}$$

When the heat flows along the thickness direction of a laminated material, the heat flow will be identical in each layer, and there will be a certain temperature gradient in the vertical direction. This thermal conductive mode is called the vertical model. The thermal conductivity of laminated materials can be calculated by

$$\lambda = \left[V/\lambda_2 + (1-V)/\lambda_1\right]^{-1} \tag{13}$$

Whether the parallel model or vertical model, the experimental and calculated values of thermal conductivity for polymer composites are very different. Generally speaking, the experimental thermal conductivity value for most polymer composites is less than the top calculated value of the parallel model, and larger than the bottom theoretical value of the vertical model.

Considering the crystallinity of both the filler and polymer, Agari's model was created based on a hypothesis of homogeneous dispersion of particles in the polymer:

$$\lg\lambda = VC_2\lg\lambda_2 + (1-V)\lg(C_1\lambda_1) \tag{14}$$

where C_1 is a constant, which is related to the crystallinity and crystalline dimension of a polymer; C_2 is a free factor, which indicates the ability of forming a heat conductive net-chain for fillers. The closer the value of C_2 approaches to 1, the easier the thermal conductive net-chain forms, and the higher the thermal conductivity of polymer composites gets. The values of C_1 and C_2 can be both obtained by experiment as shown in Ref. [2]. The value of C_2 changes a little while the particles (such as copper, graphite, alumina, *etc.*) have different thermal conductivities in the same polymer.

The experimental thermal conductivity of a SiO_2/EVA co-film is obtained and its adaptability with the parallel model, vertical model, and Agari's model is shown in Fig. 6. It is found that the experimental value differs from the parallel and vertical models, in which C_1 (0.94) and C_2 (0.96) are valued by the experiment and iterative methods, and coincide with the theoretical curve according to Eq. (14). In other words, the thermal conductivity of a SiO_2/EVA co-film can be predicted well by Agari's model.

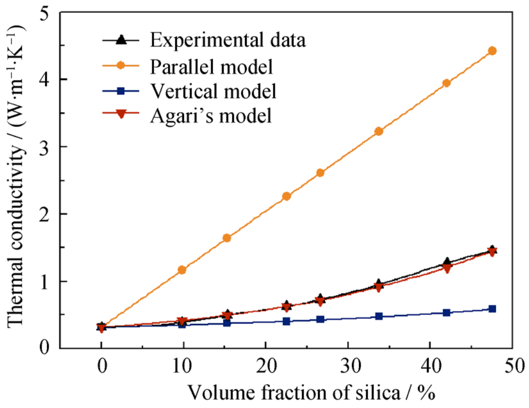

Fig. 6. Thermal conductivity of SiO_2/EVA based on experimental data, parallel model, vertical model, and Agari's model.

The error between the experimental and theoretical values of Agari's model was mainly from C_1 and C_2, which were related to the variety and property of the filler and polymer. Agari's model emphasized the dispersion state and mutual interaction of particles in the polymer, but neglected the border combination strength. Therefore, a revised Agari's model was built by adding an interfacial factor (A, usually A=0.8-1.2) [27]:

$$\lg\lambda = \lg A + VC_2\lg\lambda_2 + (1-V)\lg(C_1\lambda_1) \tag{15}$$

Furthermore, Agari [18] suggested another model to predict the thermal conductivity of a multiphase system:

$$\lg\lambda = V\left(X_2C_2\lg\lambda_2 + X_3C_3\lg\lambda_3 + \cdots + X_nC_n\lg\lambda_n\right) + (1-V)\lg(C_1\lambda_1) \tag{16}$$

where λ, λ_1, λ_2, λ_3, ···, λ_n represent the thermal conductivity of the polymer, filler 1, filler 2, ···, filler (n−1), and composite, respectively; V is the total volume fraction of all fillers; X_2, X_3, ···, X_n are the volume fraction for each filler, respectively.

3.3. Mixed empirical model

The mixed empirical model of polymer composites was built on the basis of the parallel and vertical models:

$$\lambda^{\xi} = (1-V)\lambda_1^{\xi} + V\lambda_2^{\xi} \tag{17}$$

where ζ is a constant with the values between −1 and +1 based on the experiment. Also, −1 is the lower limit of the theoretical value according to the vertical model, and +1 is the upper limit of the theoretical value according to the parallel model. The same polymer composite has the similar thermal conductivity.

For a polyimide/aluminum nitride composite, ζ=0.222, its thermal conductivity calculated value still accorded well with the experimental value, even when the V value of filler was up to 60% [17]. For the SiO_2/EVA co-film in Fig. 7, ζ=−0.03, the experimental value is consistent with the calculated value according to Eq. (17), even when the V value of fillers is up to 50%.

In the same way, a mixed empirical model for a multiphase system was built up:

$$\lambda^{\xi} = \sum_i V_i\lambda_i^{\xi}\left(\frac{1-V}{1-V_c}\right)^n \tag{18}$$

where λ_i and V_i represent the thermal conductivity and volume fraction of component i, respectively. Few verified experiments for this model were made, owing to the difficulty in the determination of ζ value by experiment.

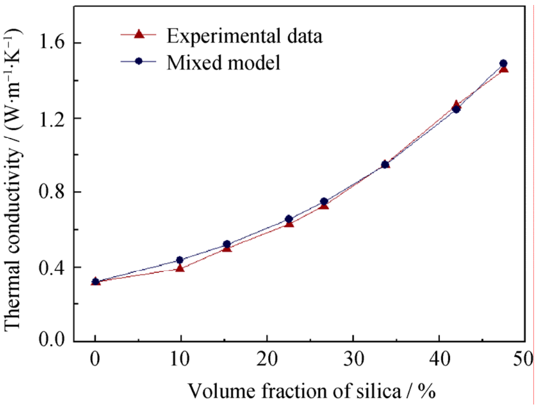

Fig. 7. Thermal conductivity of SiO_2/EVA based on experimental data and the mixed empirical model.

3.4. Percolation model

The percolation model deals with unordered systems with a random geometrical structure in filled polymer composites [28]. An explicit, clear, and visual model was introduced to explain the effect caused by the variation of connection with each other in an unordered system. Some behaviors in macroscopic state happened or disappeared suddenly, while some factors (such as density and intension) increased to a certain degree in an unordered system (the threshold of percolation) [29]. The percolation model was built up based on the following hypothesis for filled polymers. (1) The dispersion state of fillers in polymer composites would cause the change of polymer geometric structure. (2) A nonlinear change in the thermal conduction of polymer composites would be produced by a linear increase in the volume fraction of fillers, and there was still a critical threshold. (3) The critical threshold of filler volume fraction and the thermal conduction of composites were related to the size and shape of particles. (4) The geometric structure of fillers dispersed uniformly in macroscopic state. (5) A totally continuous phase existed in the composite without any void, impurity, and interfacial defects in filled polymers.

The thermal conductivity of filled polymers has a characteristic of the percolation network structure, which is similar to the electrical conduction of composites. Therefore, the critical volume fraction of fillers (V_c) was introduced to create a thermal conductive percolation model based on Vysotsky's electrical conductive model [30]:

$$\lambda = \lambda_2(\lambda_c/\lambda_2)^{\left(\frac{1-V}{1-V_c}\right)^n} \tag{19}$$

where λ and λ_2 represent the thermal conductivity of the composite and filler, respectively; λ_c means the thermal conductivity of the composite in the condition of V_c; the percolation network exponent (n) is dependent on many factors, such as the particle size, particle shape, and the distribution of fillers in the composite. The thermal conductivity of filled polymers would be defined, while V_c, λ_c, and n were determined. There were two methods to determine the V_c value. One was an experimental method; the V value (0.10-0.25) that made the thermal conductivity nonlinearly and rapidly increase was the critical percolation volume fraction of fillers (V_c), and the corresponding thermal conductivity of composites was λ_c. The other was a calculated method; first, selecting a volume fraction between 0.10-0.25 as a V_c value to calculate the thermal conductivity of filled polymer composites (λ_c) by Maxwell-Eucken, Bruggeman, or Agari's model; then, a little higher volume fraction (V_c+ΔV) and λ_c were used in Eq. (19) to get a value of λ. When $(\lambda-\lambda_c)/\lambda \leq 5\%$, the set volume fraction was the exact value of V_c, otherwise, another volume fraction would be given again for further calculation until the relative error between λ and λ_c met the demand. The most accurate percolation network exponent (n) can be determined by experiment, but it is time-consuming, so it is often estimated by calculation. First, V_c and λ_c were determined by calculation, then substituted it into Eq. (19) to check the calculated value. If the volume fraction of fillers is equal to 0, the calculated thermal conductivity by Eq. (19) is equal to or close to the thermal conductivity of the polymer matrix, and the value of n is exactly the percolation network exponent, which is usually valued between 0-1. For the graphite/polytetrafluoroethylene and graphite/polypropylene composites [3], V_c was valued as 0.15 and 0.16, λ_c 0.44 and 0.40 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$, and n 0.5 and 0.68, respectively. The results show that the experimental thermal conductivity of composites accords well with the theoretical value based on the percolation model, even when V is up to 60%. There is some deviation between the experimental and theoretical values, but the deflection is limited, while V is over 60% or even up to 80%.

For the SiO_2/EVA co-film, the critical volume fraction of silica (V_c) was valued as 0.15, the corresponding thermal conductivity of composites (λ_c) was 0.5 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$, and the percolation network exponent (n) was 0.99. No obvious deviation between the experimental and theoretical values of the thermal conductivity of SiO_2/EVA co-films is found as shown in Fig. 8.

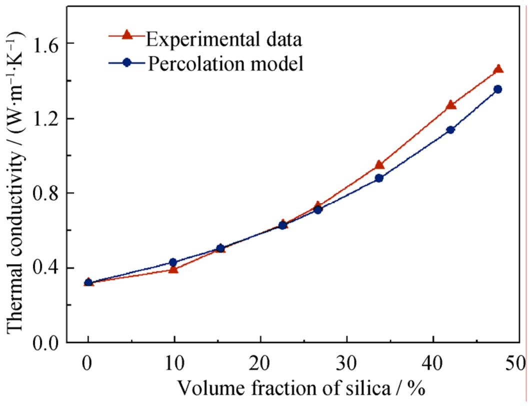

Fig. 8. Thermal conductivity of SiO_2/EVA based on experimental data and percolation model.

4. Conclusion

The thermal conductivity of polymer composites can be predicted by corresponding theoretical or empirical models. Each model has its own limits and cannot reach every aspect of the matter. Thermal conductivity is not only related to the size, shape, amount, surface property, and dispersion of fillers, but also related to the mutual interaction and interfacial distances among the particles, aggregate structures of polymers, *etc.*

To predict the thermal conductivity of filled polymers more accurately and reasonably, many factors of polymers and fillers are needed to be considered synthetically. A proper selection of theoretical models is essential, and sometimes further adjustment of the model is also needed.

The thermal conductivity of SiO_2/EVA co-films can be predicted well by Agari's model, the mixed empirical model, or the percolation model.

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