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Evaluation of the effective thermal conductivity of composite polymers by considering the filler size distribution law*

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Abstract: We present an empirical model for the effective thermal conductivity (ETC) of a polymer composite that includes dependency on the filler size distribution—chosen as the Rosin-Rammler distribution. The ETC is determined based on certain hypotheses that connect the behavior of a real composite material A, to that of a model composite material B, filled with mono-dimensional filler. The application of these hypotheses to the Maxwell model for ETC is presented. The validation of the new model and its characteristic equation was carried out using experimental data from the reference. The comparison showed that by using the size distribution law a very good fit between the equation of the new model (the size distribution model for the ETC) and the reference experimental results is obtained, even for high volume fractions, up to about 50%.

Key words: Effective thermal conductivity (ETC), Filler size distribution, Equivalent volume fraction, Composite polymer
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INTRODUCTION

The frequent use of polymer composite materials in various fields of engineering necessitated the development of methods for evaluating their properties as functions of the properties of their components and the way in which they are mixed to form the composite material. In many cases, a certain property of the composite material is determined and used in the frame of the continuum medium model.

A representative volume must be taken into account when the properties of heterogeneous materials are determined. The volume of the heterogeneous material must be sufficiently large to be statistically representative, irrespective of the type of experiment (Ostoja-Starzewski, 2002). A property of crucial importance in many industrial applications that involve heat transfer and the use of polymer composites is the effective thermal conductivity (ETC). In the 19th century, Maxwell studied the thermal conductivity of heterogeneous materials and solved the Laplace equation for randomly distributed spheres in a continuum medium. Since then, a large number of methods for evaluating this property with increasing accuracy have been elaborated. Theoretical methods for determining ETC are either analytic or numerical. A comprehensive review of the analytical methods was presented by Das *et al*.(2008). These methods are based on various models, such as mixing models (Nielsen, 1978; Agari and Uno, 1986), Maxwell type models (Das *et al*., 2008), models including spatial distribution of the filler particles (Cheng and Vachon, 1969; Jeffrey, 1973; Pitchumani, 1999), models including dependence on filler particle shape (Hamilton and Crosser, 1962), models including dependence on interfacial resistance (Hasselman and Johnson, 1987; Filip *et al*., 2007; Jackson *et al*., 2008). However, none of these models considers the filler particle size distribution. The numerical methods use the finite element method and matrix filling algorithms (Cai *et al*., 2005; Ganapathy *et al*., 2005; Tu *et al*., 2005; Annapragada and Dhavaleswarapu, 2006; Kumlutas and Tavman, 2006; Hallouet and Pelster, 2007). These

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models can take into account the size distribution law of filler particles, but have a high degree of complexity.

Experimental studies showed that the filler size distribution law influences the properties of the composite material (Hayes and Seferis, 2002; Karayacoubian *et al*., 2006; Hallouet and Pelster, 2007; Chen *et al*., 2008) and controls the interaction between the filler particles and the packing mode of the composite material (Gupta *et al*., 2002; Tu *et al*., 2005; Hallouet and Pelster, 2007; Zhou *et al*., 2008).

In this study, we present a model that allows for the extension of the analytical models by including in their equations the effect of the filler particle size distribution law using an equivalent volume fraction, denoted in the following as the size distribution model for determining ETC.

DEFINITION OF THE EQUIVALENT VOLUME FRACTION

Let us assume that the thermal behavior of a composite material A, with spherical filler particles of different sizes and of known volume fraction φ, randomly distributed in the polymer matrix, is identical to that of a material B, made of the same components but with filler particles of equal size and having another volume fraction φ_e, that is defined based on the following algorithm.

We choose a representative volume, Ω, in the polymer matrix that contains a number n of particles of different diameters D_i, n being large enough to be statistically representative. The particles are distributed in such a way that each can be included in a volume V_i so that $\sum V_i=\Omega$.

Let us assume that we can choose V_i so that $V_i=V_j=V$, for any i, j, and then it follows that $\Omega=nV$.

We assume that the D_i diameters are distributed according to a distribution function of Rosin-Rammler (Weibull) type, with its probability density function $f(x)$ as:

$$f(x)=\frac{s}{\lambda}\left(\frac{x}{\lambda}\right)^{s-1}\exp\left(-\left(\frac{x}{\lambda}\right)^{s}\right), \tag{1}$$

where $x=D/D_1$, s is the shape parameter and λ is the scale parameter. D is the diameter of a particle and D_1 is the arithmetic mean diameter of filler particles from volume Ω, that is

$$D_1=\frac{\int_0^\infty nDf(x)\mathrm{d}x}{\int_0^\infty nf(x)\mathrm{d}x}=\frac{nD_1\lambda\Gamma(1+1/s)}{n}, \tag{2}$$

where Γ is the Gamma function.

Using this interpretation and considering the above assumptions, the scale parameter has the following form:

$$\lambda=\frac{1}{\Gamma(1+1/s)}. \tag{3}$$

The Rosin-Rammler distribution was chosen because it approximates well the quasi-uniform distributions (a larger s determines more particles with a diameter close to the mean diameter D_1).

Taking into account the filler particle size distribution law, the total volume occupied by the particles is:

$$\begin{aligned}V_\mathrm{p}&=\frac{4\pi}{3}\int_0^\infty nD^3f(x)\mathrm{d}x=\frac{4\pi nD_1^3}{3}\int_0^\infty x^3f(x)\mathrm{d}x\\&=\frac{4\pi nD_1^3}{3}\frac{\Gamma(1+3/s)}{\Gamma^3(1+1/s)},\end{aligned} \tag{4}$$

and the actual volume fraction φ is

$$\varphi=\frac{V_\mathrm{p}}{\Omega}=\frac{4\pi D_1^3}{3V}\frac{\Gamma(1+3/s)}{\Gamma^3(1+1/s)}. \tag{5}$$

According to its definition, the Sauter mean diameter of the particles, D_{32}, is

$$D_{32}=\frac{\int_0^\infty D^3f(x)\mathrm{d}x}{\int_0^\infty D^2f(x)\mathrm{d}x}=D_1\frac{\Gamma(1+3/s)}{\Gamma(1+1/s)\Gamma(1+2/s)}. \tag{6}$$

The D_{32} diameter characterizes the ensemble of n particles from the standpoint of the specific area, i.e., the ensemble of n particles of different diameters D_i has the same specific area as the ensemble formed by n identical particles of diameter D_{32}. We assume that

the representative volume of material B is equal to that chosen for material A, that is Ω=nV. Also, we assume that material B is obtained by replacing the particles of diameter D_i from material A with particles of diameter, D_{32}, and thus the specific area of the ensemble of particles remains the same. This hypothesis allows us to determine the equivalent volume fraction that corresponds to material B, as follows:

$$\varphi_e = \frac{n4\pi D_{32}^3/3}{nV} = \frac{4\pi D_1^3}{3V}\left[\frac{\Gamma(1+3/s)}{\Gamma(1+1/s)\Gamma(1+2/s)}\right]^3. \quad (7)$$

Further, we can obtain the relationship between the equivalent volume fraction, φ_e, of material B and the volume fraction of material A (the actual material), φ:

$$\varphi_e = \varphi\frac{\Gamma^2(1+3/s)}{\Gamma^3(1+2/s)} = \chi\varphi, \quad (8)$$

where

$$\chi = \frac{\Gamma^2(1+3/s)}{\Gamma^3(1+2/s)} \quad (9)$$

is a constant that depends only on s, the shape parameter that defines the filler particle size distribution law. We observe that if s goes to infinity, the equivalent volume fraction φ_e becomes equal to the actual volume fraction φ.

DETERMINATION OF THE EFFECTIVE THERMAL CONDUCTIVITY USING THE SIZE DISTRIBUTION MODEL

According to the initial hypothesis, the thermal behavior of material B is identical to that of material A. As the particles embedded in the polymer matrix B are identical and uniformly distributed, we can apply any of the accepted equations to determine the ETC for this type of material.

We took into consideration the Maxwell equation that is relatively rigorously determined under the assumption of a small volume fraction:

$$\begin{aligned} k_e &= k_m\frac{k_f+2k_m+2\varphi_e(k_f-k_m)}{k_f+2k_m-\varphi_e(k_f-k_m)} \\ &= k_m\frac{k_f+2k_m+2\chi\varphi(k_f-k_m)}{k_f+2k_m-\chi\varphi(k_f-k_m)}, \end{aligned} \quad (10)$$

where k_e is the ETC, k_m is the matrix thermal conductivity and k_f is the filler thermal conductivity.

The model can be further developed by introducing the interface resistance and by applying the shape factor in the case of non-spherical particles.

VALIDATION OF THE SIZE DISTRIBUTION MODEL

Usually, variation in thermal conductivity is presented in the literature as a function of the volume fraction, with information regarding the size distribution being limited mostly to the mean diameter, irrespective of whether theoretical or experimental results are reported (Lee and Yu, 2005; Zhou *et al.*, 2008; Tekce *et al.*, 2007).

The acceptance of an empirical model as valid must be based on the agreement between its results and experimental data. To validate the size distribution model for ETC, we compared its results with experimental results selected from the reference as follows:

(a) For the reference case where only the dependency of the ETC on the volume fraction of a composite material is known, we compared this dependency with the results obtained using the Maxwell model and those obtained using the size distribution model (with the shape parameter s chosen so that the best fit was obtained);

(b) For the reference case where the experimental size distribution is known, we determined a Rosin-Rammler distribution which approximated sufficiently well the reported experimental size distribution. Then, using the obtained size distribution and the size distribution model we calculated the ETC. The results were compared with the experimental data and those given by the Maxwell model.

For case (a) we selected as references the results from Tavman (2004) and Zhou *et al*.(2008). Tavman (2004) showed the experimental results for the ETC of a mixture between high density polyethylene and

Al_2O_3 particles, for different volume fractions (at 15 °C). A comparison with other empirical models was also presented, but no information was given regarding the Al_2O_3 particle size distribution law. Fig.1 shows the results obtained with the size distribution model, the reported experimental data of Tavman (2004) and the results given by the Maxwell model. The Rosin-Rammler distribution that we used to fit the reference results was defined by s=2.3.

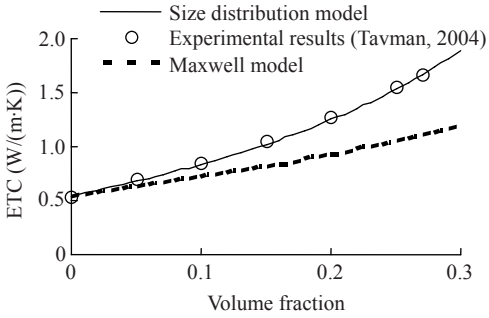

Fig.1 Comparison of the size distribution model and the Maxwell model, with experimental data for polyethylene matrix with Al_2O_3 filler particles

Zhou *et al*.(2008) reported experimental results for polymethylsiloxane reinforced with silicone nitride (Si_3N_4), for the filler mean diameter of 2 μm. For this value of the filler mean diameter, the theoretical results using the size distribution model and the experimental data fitted well for s=5. Fig.2 shows the comparison between the results obtained using the size distribution model, the reference experimental data and the results given by the Maxwell model.

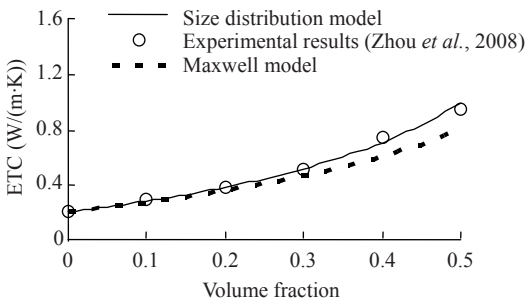

Fig.2 Comparison of the size distribution model and the Maxwell model, with experimental data for polymethylsiloxane matrix with Si_3N_4 filler particles

Cai *et al*.(2005) presented both experimental data and a finite element model to determine the ETC of a composite material—polytetrafluoroethylene matrix with graphite filler particles—taking into account the filler particle size distribution law of a known form. Fig.3 shows the experimental cumulative distribution function of Cai *et al*.(2005) and its approximation using the Rosin-Rammler distribution with the shape parameter s=4.3.

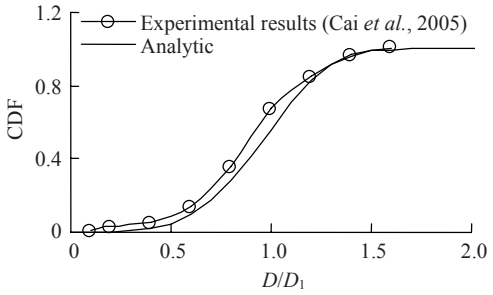

Fig.3 Comparison between the experimental cumulative size distribution function (CDF) law for graphite particles and its analytic Rosin-Rammler approximation

The obtained Rosin-Rammler distribution was introduced in the size distribution model to calculate the ETC. Fig.4 shows a comparison between the theoretical results given by the size distribution model and the Maxwell model, and the reported experimental data of Cai *et al*.(2005).

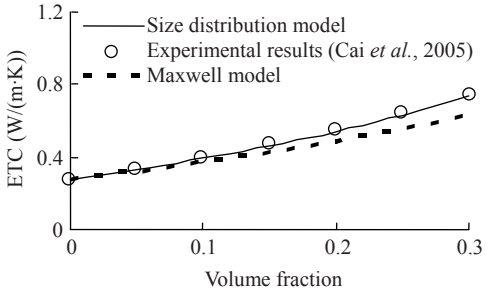

Fig.4 Comparison of the size distribution model and the Maxwell model, with experimental data for PTFE matrix with graphite filler particles

The above comparisons demonstrate that by applying the size distribution model to estimate the ETC of a composite material, an excellent agreement with experimental data can be obtained. A knowledge of the size distribution law allows for the possibility of obtaining theoretical results in accordance with experimental data.

CONCLUSION

The size distribution model can be used to

determine the ETC of a material with two components. Although empirical, it allows for an excellent agreement with experimental results, even for relatively high volume fractions (for the hypotheses of validity of the Maxwell model).

A knowledge of the matrix thermal conductivity, the filler thermal conductivity and the volume fraction is not enough to calculate the ETC. It was proven that the size distribution law of the filler particles influences the value of the ETC and that this model offers the possibility to quantify this dependence. This is a very important issue in the context of modern manufacturing technologies for various types of filler particles where the size distribution law of the produced particles can be controlled. As with any empirical model, this model will need further experimental validation to be accepted.

PROSPECT

The authors consider that this study is an important work that will improve the present theoretical models for evaluation of the ETC of a composite, by introducing the effect of the filler size distribution law. Further validation of the size distribution model will be carried out.

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