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COMPOSITES
THEORY AND
PRACTICE

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EFFECT OF PARTICLE SHAPE AND IMPERFECT FILLER-MATRIX INTERFACE ON EFFECTIVE THERMAL CONDUCTIVITY OF EPOXY-ALUMINUM COMPOSITE

The predictions of major effective medium models and 2-dimensional numerical models implemented in Ansys Fluent were tested against the results of experimental measurements of macroscopic thermal conductivity for a polymer filled with aluminum powder. The examined composite may be regarded as a representative of materials used for heat management purposes, for example for the manufacture of electronic device housings. The study demonstrates the effect of particle shape and imperfect filler-matrix interface on the theoretical value of thermal conductivity of the considered material. It also creates the opportunity to discuss the versatility and accuracy of various methods devised to predict the effective thermal conductivity of heterogeneous materials. It was found that the effective medium approximation proposed by Duan et al., which considers the effect of the particle aspect ratio, outrivaled other predictive schemes in accuracy and cost-effectiveness. Effective medium approximations that assume spherically-shaped reinforcement as well as finite volume models implemented in Ansys Fluent, greatly underestimated the parameter in question.

Keywords: functional materials, heat transfer, interfacial thermal resistance, predictive schemes

EFEKT KSZTAŁTU CZĄSTEK I NIEDOSKONAŁOŚCI GRANICY ZBROJENIE-OSNOWA NA EFEKTYWNĄ PRZEWODNOŚĆ CIEPLNĄ KOMPOZYTU EPOKSYD-ALUMINIUM

Przewidywania popularnych, analitycznych modeli predykcyjnych efektywnej przewodności cieplnej kompozytów cząsteczkowych zostały porównane z danymi eksperymentalnymi uzyskanymi dla kompozytów polimerowych napełnionych proszkiem aluminiowym oraz z wynikami obliczeń numerycznych wykonanych metodą objętości skończonych w programie Ansys Fluent. Testowany materiał reprezentuje grupę materiałów stosowanych w technice cieplnej, np. do wytwarzania obudów urządzeń elektronicznych. Wyniki badania pokazują efekt kształtu wtrąceń oraz niedoskonałego kontaktu termicznego na granicy zbrojenie-osnowa na teoretyczną wartość efektywnej przewodności cieplnej rozważanego materiału. Są też podstawą do dyskusji na temat wad i zalet stosowania analitycznych metod przewidywania przewodności cieplnej materiałów kompozytowych (tzw. effective medium models). Najlepszą zgodność z eksperymentem otrzymano za pomocą jednego z modeli analitycznych (Duan i in.), który uwzględnia wydłużony kształt cząsteczek napełniacza. Przewidywania modeli analitycznych zakładających sferyczny kształt cząsteczek okazały się silnie zaniżone, podobnie jak przewidywania dwuwymiarowych modeli numerycznych zaimplementowanych w środowisku Ansys Fluent.

Słowa kluczowe: materiały funkcjonalne, wymiana ciepła, termiczny opór międzyfazowy, modele predykcyjne

INTRODUCTION

Polymer-based composites are still drawing attention not only due to their relative ease of manufacturing and forming but also owing to the possibility of simple modification of their thermal properties with insulating and conductive fillers. These materials can serve both structural and heat management purposes in electronic, aeronautical, automotive and shipbuilding industries, among others [1, 2]. The thermal conductivity of composites with fibrous or particulate reinforcement can be predicted by means of various methods including analytical, numerical and combined analytical-numerical techniques [3, 4]. The purpose of these predictive schemes is to calculate the value of the thermal conductivity of a composite material based on the knowledge about the thermal conductivity of the matrix as well as the size, shape, orientation, spatial distribution, volume fraction and thermal conductivity of the reinforcement. Predicted thermal conductivities can be used at the stage of material design to estimate the potential of various combinations of matrices and fillers. Effective medium models leading to closed form expressions are especially interesting because of the low computational cost. Such expressions are available for composites filled with particles of basic shapes like spheres, ellipsoids or cylinders [3]. In the 1980s and 1990s, various researchers observed that the thermal conductivity of polymer-based composites strongly depends on their operation temperature. This fact can be related to detachment occurring between the matrix and the reinforcement due to thermal expansion mismatch [5-9]. Subsequent research led to the development of effective medium models for composites that included the effect of the interfacial thermal barrier [5, 7, 10-13]. The downside of effective medium approximations is the limitation of their applicability to filler volume fractions below or near the percolation threshold [3]. This restriction, inherent to the nature of mean-field models, necessitates the use of numerical models for materials with percolating particles [14-17]. Numerous reports suggest the inadequacy of effective medium theories for predictions concerning composites in which the ratio of thermal conductivities of the filler and the matrix is high (> 100) [18, 19], which is the typical case in thermal applications. This kind of composite is examined in the present study. The theoretical effective thermal conductivity of such composites is frequently much lower than the experimental one, which is attributed to the presence of particle chains and clusters promoting heat conduction in the material that are not encompassed by popular effective medium models. Earlier studies have shown that for insulating matrices and highly conductive fillers, thermal conductivity is also strongly influenced by the aspect ratio of the particles [20].

The intention of the presented research was to investigate the degree of influence of the particle aspect ratio, grouping and interfacial thermal resistance on the intensification and reduction of heat conduction in particulate composites with a high contrast of thermal conductivities of the constituents. To achieve that goal, selected effective medium models were used alongside 2-D finite volume models (FVM) prepared in Ansys Fluent software [5, 7, 12, 13, 21].

METHODS

Sample preparation and characterization

Experimental samples were produced in different variants with particle volume fractions from zero (pure matrix) to 38%. The pyrotechnical atomized aluminum powder was subjected to vibrational sieving to obtain fractions of different particle sizes. The 20÷40 μm fraction was selected to prepare the experimental samples. The epoxy mixture was prepared by hand mixing from *Epolam 2031* resin and *Epolam 2031* hardener (produced by the Axson company) using the standard 100:26 mass ratio. The mixture was homogenized ultrasonically for 5 minutes and cast in cylindrical silicone molds. The samples were then left for 12 h in room conditions and cured at 50°C for 6 hours and for another 6 hours at 100°C. The thermally treated samples were hand-shaped using P100 and P240-grit sandpaper. The geometry of the samples was optimized for thermal diffusivity measurements by the flash technique [22].

The results of the thermal characterization of the samples are grouped in Table 1. The filler volume fraction for each sample was determined based on the densities of its constituents. The density of the cured epoxy was retrieved hydrostatically with a RADWAG AS-series analytical balance (est. accuracy ±1.5%). The density of the aluminum powder was obtained with a Micrometrics AccuPyc II 1340 helium pycnometer with an estimated relative error of ±0.3%. The thermal diffusivities of the samples were obtained by flash measurements by means of a Netzsch LFA447 diffusometer with ±3% accuracy, as declared in the instrument specifications. The Cowan model with pulse correction was used for data analysis [23].

TABLE 1. **Thermophysical properties of materials used in the study, where: D - thermal diffusivity, c_p - specific heat, ρ - density, k - thermal conductivity**

TABELA 1. **Właściwości termofizyczne materiałów użytych w badaniach, gdzie: D - dyfuzyjność cieplna, c_p - ciepło właściwe, ρ - gęstość, k - przewodność cieplna**

Property	D	c_p	ρ	k
Unit	$\left[\frac{\mathrm{mm}^2}{\mathrm{s}}\right]$	$\left[\frac{\mathrm{kJ}}{\mathrm{kg}\cdot\mathrm{K}}\right]$	$\left[\frac{\mathrm{g}}{\mathrm{cm}^3}\right]$	$\left[\frac{\mathrm{W}}{\mathrm{m}\cdot\mathrm{K}}\right]$
Epolam 2031/2031	0.129	1.380	1.163	0.207
Aluminum powder	89.25[1]	0.867	2.623	203.12
Ep/Al 15%	0.189	1.24	1.399	0.3280
Ep/Al 24%	0.407	1.12	1.517	0.6920
Ep/Al 31%	0.532	1.04	1.61	0.8900
Ep/Al 38%	0.715	1.07	1.717	1.3140

[1] assumed the same as for aluminum alloy A1050 (założono wartość taką samą jak dla stopu A1050)

The samples were sprayed with a thin layer of GRAPHIT 33 spray produced by Kontakt Chemie on the top and bottom surfaces to optimize radiation absorption and emission. The thermal diffusivity of the aluminum particles was assumed to be equal to the value measured on a high-purity aluminum sample made of A1050 alloy.

Specific heat measurements were performed with a Perkin-Elmer DSC 7 calorimeter which utilizes the null balance principle [24] (est. accuracy ±2%). The measurements of density ρ, thermal diffusivity D and specific heat c_p allowed thermal conductivity k of the samples to be calculated according to the equation:

$$k = \rho D c_p \tag{1}$$

The samples were subjected to SEM examination to obtain information about the distribution, orientation and shapes of the particles. In Figure 1 examples of micrographs showing the microstructures of two manufactured samples are presented. The micrographs reveal the presence of holes which may occur due to entrapped air or may be left by pulled-out particles.

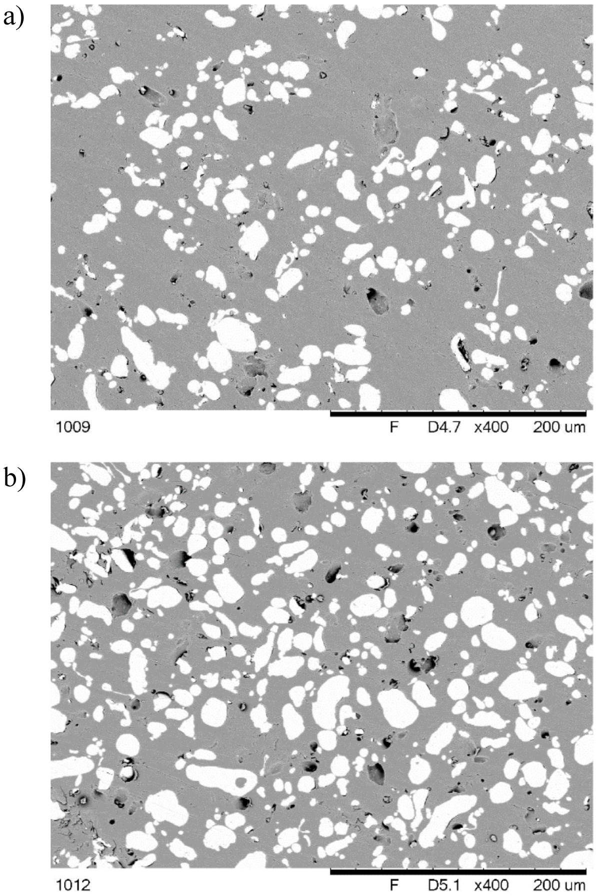

Fig. 1. Micrographs of manufactured composites obtained by SEM: a) composite containing 24% aluminum particles (volumetrically), b) sample with 31% filler content

Rys. 1. Mikrografie wytworzonych kompozytów uzyskane metodą SEM: a) kompozyt zawierający 24% cząsteczek aluminium (objętościowo), b) próbka zawierająca 31% cząsteczek

Analytical methods

Analytical effective medium models were used to examine the effect of particle shape and imperfect filler-matrix interface on the thermal conductivity of the composites. The spatial distributions of the particles and their effect on thermal conduction were not reflected in these calculations. In all the considered models, the particles were assumed to be uniformly and randomly distributed in the matrix.

The Bruggeman assymetric [5] and Hasselman-Johnson [7] models for spherical particles were selected due to historical reasons and for the sake of comparison with a more detailed model. In the Duan et al. model [12, 13], the filler particles can be spheroidal. A spheroid can be unambiguously described by two parameters - aspect ratio r and equivalent radius R. Aspect ratio r is defined as the ratio of polar length (a) to equatorial length (b) of the spheroid. Equivalent radius R is the radius of a sphere whose volume is equal to the volume of the considered spheroid. It is given as:

$$R = \sqrt[3]{ab^2} \tag{2}$$

Based on the SEM micrographs it was decided to treat the filler particles as prolate spheroids. The dimension of the sieve holes was 40 μm for the upper sieve and 20 μm for the lower one. Therefore, the equatorial radius of spheroids in the Duan et al. model was set at 15 μm, which corresponds to a diameter of 30 μm - the mean of the upper and lower sieve hole dimensions. Polar length a was varied to obtain different aspect ratios of particles, even those which resulted in particle lengths greater than 40 μm, as such particles would not be stopped by the upper sieve. The variation of the aspect ratio allowed the model to be adjusted to the experimental data. In models that allow for spherical particles only, their diameter was set as 30 μm. The alignment of the particles was not controlled in any way during the manufacturing process, therefore the particles were considered to be randomly oriented.

Numerical modeling

The usual approach to numerical predictions of the thermal conductivity of composite media is to consider heat conduction within a representative volume element (RVE) of the material [3]. In the presented case, 2-dimensional models of a matrix phase containing elliptical particles were generated in the Ansys Design Modeler application for filler volume fractions of 10, 20, 30, 40, 50 and 60%. The shapes, orientations and spatial distributions of the particles were made to reflect the shapes, orientations and distributions visible in the SEM micrographs of actual samples. The type of applied mesh was conformal, quadrilateral dominant with increased density in the neighborhood of the filler-matrix boundary, as shown in Figure 2.

The material properties of the epoxy matrix and aluminum particles were set according to Table 1. For one set of models, a thermal barrier between the matrix and particles was added in the software boundary conditions menu. In the Fluent application, this barrier is modeled as a thin layer of additional material with thermal resistance equal to the desired thermal interface resistance. The temperatures at the lateral walls were constrained to 270 and 300 K. The top and bottom walls were set as adiabatic. The temperature fields in the domains were calculated assuming steady state conditions. Figure 3 presents the temperature fields obtained for a representative block of material containing 20% particles volumetrically, with and without the ITR. The presence of ITR equal to $3.81 \cdot 10^{-5}$ m^2 K W^{-1} results in a “screening” effect in which the influence of highly conductive aluminium particles on the transfer of heat in the material is completely suppressed by the imperfect interface. This effect is not present in the models with null ITR, where higher macroscopic thermal conductivity was obtained (see the Results section for details). The value of ITR between the polymer matrix and aluminium particles was chosen according to the experimental data obtained by Garnier et al. [25].

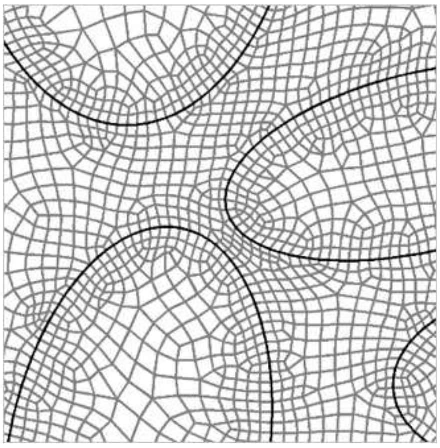

Fig. 2. Fragment of computational mesh showing increased mesh density around filler-matrix interface

Rys. 2. Fragment siatki obliczeniowej ukazujący zwiększoną jej gęstość w pobliżu granicy zbrojenie-osnowa

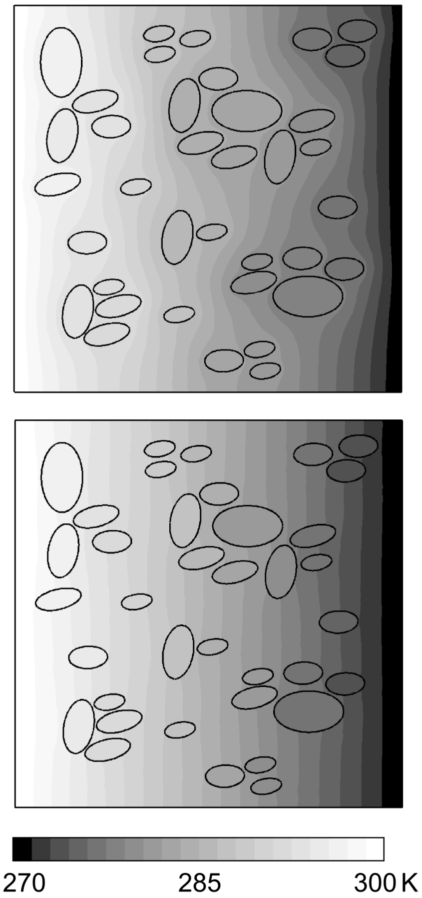

Fig. 3. Temperature fields within modeled block of composite material (aluminum 20% vol.) obtained with Ansys Fluent. Image on top is without ITR. Image at bottom shows screening effect of ITR on heat flow. Magnitude of applied ITR is 3.81 · 10^{-5} m^2 K W^{-1}

Rys. 3. Pola temperatury w modelowanym bloku materiału kompozytowego (aluminium 20% obj.) otrzymane za pomocą oprogramowania Ansys Fluent. Górny obraz przedstawia przypadek bez termicznego oporu międzyfazowego. Na dolnym obrazie widać efekt izolacji spowodowany międzyfazowym oporem termicznym. Wartość użytego termicznego oporu międzyfazowego wynosi 3.81 · 10^{-5} m^2 K W^{-1}

The Ansys Fluent postprocessor enables the calculation of total heat transfer rates at chosen walls of the model [21]. For every block, heat flux q at the left boundary was computed and used to determine the effective thermal conductivity, according to the equation:

$$k = \frac{q\,L}{\Delta T\,H}, \qquad (3)$$

where k is the thermal conductivity, ΔT is the temperature difference between the left and right wall, q is the heat flux, H and L are the height and width of the representative block, respectively.

RESULTS AND DISCUSSION

The experimental thermal conductivity of the manufactured epoxy/aluminum composites with different filler volume fractions is presented in Figure 4 along with predictions of the effective medium theories and Ansys Fluent models. It should be noted that the experimental results are very close to those reported by Lin et al. [18].

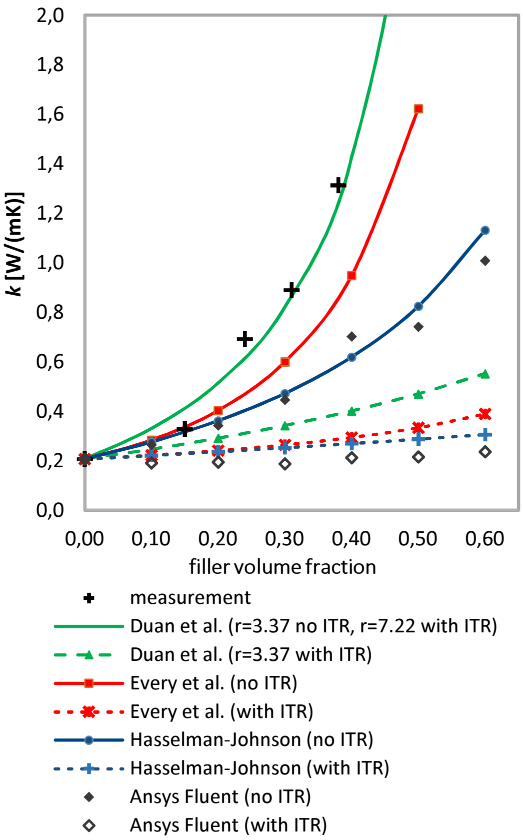

Fig. 4. Comparison of experimental and predicted effective thermal conductivities for epoxy/aluminum composite. Best approximation is provided by Duan et al. model with assumption of perfect interface and aspect ratio of particles r = 3.37. Identical curve is obtained for imperfect interface and r = 7.22

Rys. 4. Porównanie eksperymentalnych i przewidywanych efektywnych przewodności cieplnych dla kompozytu epoksyd/aluminium. Najlepsze dopasowanie uzyskano dla modelu Duan i in. przy założeniu idealnego kontaktu i wydłużenia cząstek r = 3,37. Identyczną krzywą uzyskano dla niedoskonałego kontaktu i r = 7,22

Predictions of two types are shown in Figure 4, the first of which is the case of a perfect interface, and the second - the case in which an ITR equal to $3.81 \cdot 10^{-5}$ m^2 K W^{-1} was assumed (the value measured by Garnier et al. [25]).

Among the methods devised for composites with spherical particles, the predictions using the Bruggeman assymetric model [5] proved to be better than those by means of the Hasselman-Johnson model [7]. Nevertheless, the predictions of both models were extremely far from the experimental values if ITR was included in the calculations. When the interfacial thermal resistance was neglected (ITR = 0), the best approximation was given by the Duan et al. model with the aspect ratio of spheroids equal to 3.37. That aspect ratio roughly corresponds to the aspect ratios observed in the SEM micrographs. The predicted effective thermal conductivity fell profoundly below the experimental values for the same aspect ratio ($r = 3.37$) when the presence of ITR was included (see Fig. 4). To obtain a reasonable match of the data and the Duan et al. model with the presence of ITR, the aspect ratio of particles should be around 7.22, which is above the aspect ratios observed for the experimental samples. The numerically-predicted thermal conductivities which included the effect of particle shape were similar to those given by the Hasselman--Johnson model for spherical particles [7]. As proved by the calculations based on Duan et al. expressions, the shape of the particles strongly affects the thermal conductivity of the material. The discrepancy between the numerical and experimental results may be related to percolation [3]. Some studies suggest that effective medium approximations tend to underestimate the thermal conductivity for composites with a high contrast between the conductivities of the filler and matrix. This flaw is attributed to their incapability to model particle chains and clusters [18, 19]. Nevertheless, the study discussed in this paper demonstrated that an effective medium model can give relatively good predictions if it considers the non-sphericity of particles (the Duan et al. model [12, 13]).

CONCLUSIONS

1. The best match to the experimental values of effective thermal conductivity was obtained by the effective medium model by Duan et al. [12, 13] with the assumption that aluminum particles can be treated as prolate spheroids.
2. The particle groupings reflected in the Ansys Fluent models had no effect on the predicted values of conductivity. Models that allow for direct heat transfer between the neighbouring particles should be tested in future.
3. Effective medium approximations that neglect the non-spherical shape of particles greatly underestimated the value of effective thermal conductivity of the composite. Among these models, the best estimate was obtained using the Bruggeman assymetric model [5] under the assumption of a perfect filler-matrix interface.

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