Methodology development for through-plane thermal conductivity prediction of composites

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A B S T R A C T

The prediction and tailoring of thermal conductivity of two-phase composites is essential. In this work a new semi-empirical model was developed, which was derived from the rule of mixtures. Furthermore, a new methodology was developed to determine the thermal conductivity of the fillers and the maximum achievable filler content. To validate the new model, polypropylene-based composites were prepared with different fillers, such as talc, boron-nitride and graphite, with 20, 40 and 60 vol% filler content. The results obtained from the proposed model are in good agreement with the experimental data. Various other theoretical models were also introduced and compared to the experiments, but in most cases those underestimate or overestimate the thermal conductivity of composites.

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1. Introduction

It is well-known that polymeric materials have low thermal conductivity ($\lambda = 0.1{-}0.5$ W/mK). Accordingly, foams produced from polymers are widely used by the building industry [1,2]. However, the thermal conductivity of polymers can be improved significantly by compounding them with conductive fillers, such as aluminum nitride, boron nitride, graphite, carbon black, copper powder or some other good thermally conductive material [1,3–8]. Thermally conductive polymer composites have several advantages compared to conventionally used metals, such as low density, good corrosion resistance and low processing costs. These properties generated widespread research and development in this area, and these new materials receive more and more attention in industrial applications [6–10].

To keep the prices of polymer composites as low as possible, it is important that their properties can be tailored to needs. Hence it is important that the composite can be designed using the proper type and ratio of the matrix and fillers [11,12]. However, not only mechanical, but also thermal properties, such as thermal conductivity should be predictable. The thermal conductivity of composite materials is influenced by several factors, such as filler concentration, particle size and shape, filler dispersion and distribution in the matrix, the thermal conductivity of the components, the contact between the particles and the contact surface resistance between the matrix and the filler [1,11]. Although numerous empirical, semi-empirical and theoretical models have been developed for the prediction of thermal conductivity of two- or multiphase polymer composites, its reliable and precise prediction still remains a challenge. The three basic models are the rule of mixtures (parallel model), the inverse rule of mixtures (series model) and the geometric mean model. In the rule of mixtures it is assumed that the components contribute to the thermal conductivity of the composite proportionally. It generally overestimates the experimental values and provides an upper bound for conductivity. This model assumes the existence of a percolation network of the filler in the matrix and perfect contact between the filler particles. On the other hand, the inverse rule of mixtures assumes that there is no contact between the particles, thus it underestimates the experimental values and provides a lower bound for conductivity. The geometric mean model (Equation (1)) is an empirical method for the prediction of the thermal conductivity of composites. It provides better results than the rule of mixtures and inverse rule of mixtures [1,13,14].

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$$\lambda_c = \lambda_f^{\varphi} \cdot \lambda_m^{(1-\varphi)} \tag{1}$$

Besides these basic models, many advanced models have been developed. The most important theoretical equations are the Maxwell [15], Bruggeman [13], Cheng-Vachon [16], Hamilton-Crosser [17] and Meredith-Tobias [18] model. On the other hand, there are numerous second-order empirical and semi-empirical models that contain experimental factors for thermal conductivity and for the volume fraction of the components. Agari and Uno [19] and Lewis and Nielsen [20] developed such models, for example. These models also show good correlation with the experiments up to 30 vol% filler content. Only the Lewis–Nielsen model gives a better fit above 30 vol%, thanks to the introduction of the maximum volume fraction of fillers in the equation [1,13].

One of the theoretical models for the calculation of the thermal conductivity of two-phased systems is the Maxwell model (Equation (2)). Maxwell supposed that spherical filler particles are randomly distributed in the matrix and there is no interaction between them. This model describes the thermal conductivity of composites with a low volume fraction of fillers well, but as filler content is increased, the particles start to develop interactions between each other and form conductive chains [13,15,21,22].

$$\lambda_c = \lambda_m \cdot \frac{\left[2 \cdot \lambda_m + \lambda_f + 2 \cdot \varphi \cdot \left(\lambda_f - \lambda_m\right)\right]}{\left[2 \cdot \lambda_m + \lambda_f - \varphi \cdot \left(\lambda_f - \lambda_m\right)\right]}, \tag{2}$$

where λ_c is the thermal conductivity of the composite, λ_m and λ_f are the thermal conductivity of the matrix and the filler, and φ is the filler fraction. Bruggeman developed another theoretical model. This implicit relation (Equation (3)) also supposes that the spherical, non-interacting particles are homogeneously dispersed in the continuous matrix [11,13,21,22].

$$1 - \varphi = \frac{\left(\lambda_f - \lambda_c\right) \cdot \left(\lambda_m - \lambda_c\right)^{1/3}}{\left(\lambda_f - \lambda_m\right)}. \tag{3}$$

Cheng and Vachon developed another theoretical model (Equation (4) and (5)) for two-phase composite materials. This equation assumes that the discontinuous phase has a normal distribution in the continuous matrix. The parabolic distribution constant was introduced and related to the volume fraction of the filler [13,16,23,24].

$$\frac{1}{\lambda_c} = \frac{1}{\sqrt{C_{cv}\left(\lambda_m - \lambda_f\right) \cdot \left(\lambda_m + B_{cv}\left(\lambda_f - \lambda_m\right)\right)}}$$
$$\cdot \ln \frac{\sqrt{\lambda_m + B_{cv}\left(\lambda_f - \lambda_m\right)} + B_{cv}/2 \cdot \sqrt{C_{cv}\left(\lambda_m - \lambda_f\right)}}{\sqrt{\lambda_m + B_{cv}\left(\lambda_f - \lambda_m\right)} - B_{cv}/2 \cdot \sqrt{C_{cv}\left(\lambda_m - \lambda_f\right)}} + \frac{1 - B_{cv}}{\lambda_m}, \tag{4}$$

$$B_{cv} = \sqrt{\frac{3 \cdot \varphi}{2}}, \; C_{cv} = -4 \cdot \sqrt{\frac{2}{3 \cdot \phi}}, \tag{5}$$

From the literature survey it is obvious that the exact prediction of thermal conductivity for highly filled composites still poses difficulties. The theoretical models often underestimate the results and can be used only up to 30 vol% filler content [2,21,22,25–27]. The semi-empirical models give better correlation with the experiments, but they need more experimental parameters. Our goal

was to establish a mathematical model that can predict the thermal conductivity of composites up to the maximum achievable filler content. In the literature various thermal conductivity values can be found for different fillers. To characterize the thermal conductivity and the maximum packing of these fillers a new methodology was developed.

2. Materials and methods

2.1. Materials

H145 F homo-polypropylene was purchased from Tisza Chemical Group Public Limited Company (Hungary). As fillers to enhance thermal conductivity talc, hexagonal boron-nitride (BN) and graphite were used. The properties of the fillers are summarized in Table 1.

2.2. The preparation of the samples

PP matrix compounds were prepared with 20, 40, and 60 vol% fillers. The components were mixed with a Brabender Plastograph internal mixer at 230 °C for 20 min at a rotational speed of 25 1/min to achieve the desired homogeneity. Then 10 mm thick cylindrical specimens of a diameter of 30 mm were compression molded from the mixture (Collin Teach-Line Platen Press 200E) at 230 °C for 15 min. Five specimens were produced from each series for the thermal conductivity measurements.

2.3. The measurement of thermal conductivity

A thermal conductivity meter was designed and built, based on the comparative longitudinal heat flow method [29,30]. In this method the unknown sample is compressed between the known reference samples and heat flux passes through the measurement unit as a temperature difference is created between the two sides of the unit. The thermal conductivities of the sample and the reference sample are inversely proportional to their thermal gradients. The apparatus developed (Fig. 1) contains two C10 steel (55 W/mK) cylinders with a diameter of 30 mm; and a length of 30 mm. A specimen of a diameter of 30 mm and a thickness of 10 mm is placed between the steel cylinders. On the contact surface thermal grease was applied to decrease heat resistance. 3 thermocouples were inserted in each cylinder (with thermal grease) to detect temperature: one 3 mm below the top, one in the middle and one 3 mm above the bottom ($T_{m1,2,3,4,5,6}$/Fig. 1).

The temperatures were registered with an Ahlborn Almemo 8990-6-V5 data acquisition module, whose resolution is 0.1 °C. NiCr-Ni T190-0 type of thermowires (Ahlborn) were used for the measurements. The diameter of a single wire was 0.5 mm, and the external diameter of the glass fiber coated thermocouple was 1.3 mm. The apparatus was clamped and the temperature difference maintained with a hot press (Collin Teach-Line Platen Press 200E). The assembled unit was insulated with 25 mm tick polyurethane foam hence the radial heat loss can be neglected. When the steady state is reached, the temperature slope is linear along the reference sample and the specimen thickness. Surface temperatures ($T_{1,2,3,4}$/Fig. 1) can be calculated by extrapolation from the measured temperatures. Knowing the thermal conductivity of steel and the temperature difference between the surfaces, the heat flux of the hot and cold sides can be calculated with Fourier's law. From the average of the heat fluxes the thermal conductivity coefficient of the samples (λ_c) can be calculated with Equation (6).