

Thermal Conductivity of Polymers Filled with Particulate Solids

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Synopsis

The thermal conductivities of polystyrene and polyethylene containing several different particulate solids were measured over a range of solid concentrations. Experimental data were compared with results predicted by theoretical models for two-phase media. The equations of Bruggeman and Cheng-Vachon both gave reasonable agreement with measured results. The applicability of these equations does not appear to depend upon the structure of the polymer.

INTRODUCTION

Solid fillers are often added to thermoplastics to obtain composite materials with improved physical properties. For many materials applications, information is needed on their thermal properties, such as thermal conductivity and heat capacity. Published data on thermal conductivity of filled plastics are limited and concerned mainly with crosslinked polymers.¹⁻⁵

In this study, the thermal conductivities of polystyrene and polyethylene containing particulate fillers were measured at several filler concentrations. To cover a range of solid thermal conductivities, the fillers selected were glass, calcium oxide, aluminum oxide, and magnesium oxide. The two thermoplastics differ substantially in structure, since the polystyrene is amorphous whereas the polyethylene is semicrystalline. Measured thermal conductivity data were compared with values predicted by several theoretical models for two-phase systems.

CONDUCTIVITY MODELS

Numerous theoretical and empirical models have been proposed to predict the effective thermal conductivity of two-phase systems. For a given system, the various models may predict mixture conductivities that differ by more than a factor of 2. Reviews of many of these models are given by Gorring and Churchill,⁶ Godbee and Ziegler,⁷ and Cheng and Vachon.⁸ Most models assume that the effective thermal conductivity of the actual two-phase system is the same as that for a system of simple geometry with the same volume fraction of the two phases.

The theoretical expressions are usually classified as "exact" or "simplified" solutions. In exact solutions, no assumptions are made regarding heat flow or temperature patterns. The effective conductivity is obtained by an analytic solution of the conduction equation for a simple idealized geometric configuration. The term "exact" refers to the mathematics of the solution and not to the accuracy of the conductivity predicted by the solution. Simplified solutions usually assume that heat flow lines are straight and parallel or that isotherms are planes perpendicular to the heat flow. The problem is thus reduced to solving an ordinary differential equation instead of a partial differential equation. Since both exact and simplified solutions involve assumptions, it is difficult to generalize on their relative merits in an application.

Although much of the theory has been developed for the field of dielectric permeability, the results can be readily applied to thermal conductivity by analogy. By means of potential theory, Maxwell⁹ obtained an "exact" solution for the conductivity of randomly distributed and noninteracting spheres in a continuous medium:

$$k_e = k_c \frac{k_d + 2k_c + 2\phi(k_d - k_c)}{k_d + 2k_c - \phi(k_d - k_c)}$$

where k_e = conductivity of two-phase mixture; k_c = conductivity of continuous phase; k_d = conductivity of discrete phase; ϕ = volume fraction of discrete phase.

Bruggeman¹⁰ used different assumptions than Maxwell for permeability and field strength in deriving the following equation for dilute suspensions of spheres:

$$1 - \phi = \frac{k_d - k_e}{k_d - k_c} \left[\left(\frac{k_c}{k_e} \right)^{1/3} \right].$$

Based on the simplifying assumption of linear isotherms, Tsao¹¹ developed an equation relating the mixture conductivity to two experimentally determined parameters which describe the spatial distribution of the two phases. Cheng and Vachon¹² obtained an analytical solution to Tsao's model by postulating a parabolic distribution of the discrete phase in the continuous phase:

$$\frac{1}{k_e} = \frac{1 - B}{k_c} + \frac{1}{\{C(k_d - k_c)[k_c + B(k_d - k_c)]\}^{1/2}} \times \ln \frac{[k_c + B(k_d - k_c)]^{1/2} + B/2[C(k_d - k_c)]^{1/2}}{[k_c + B(k_d - k_c)]^{1/2} - B/2[C(k_d - k_c)]^{1/2}}$$

where

$$B = \left(\frac{3\phi}{2} \right)^{1/2} \quad C = \left(\frac{2}{3\phi} \right)^{1/2}$$

Many other models were examined in this study, including those of Rayleigh,¹³ Fricke,¹⁴ Russell,¹⁵ Jefferson,¹⁶ and Peterson.¹⁷

EXPERIMENTAL

Thermal conductivity measurements were made with a Colora Thermoconductometer, which is described in detail by Schröder.¹⁸ A cylindrical test sample is placed between two silver plates that are maintained at constant temperature by liquids with different boiling points. Saturated vapor from the liquid with the higher boiling point condenses on the lower silver plate and transfers energy to the sample. The liquid with the lower boiling point evaporates from the upper silver plate, and the generated vapor is condensed and collected in a graduated container.

Several standard samples with known thermal resistance are used to establish a calibration curve of thermal resistance versus time to collect a specified volume of condensate. For the unknown test sample, the time is measured and the corresponding thermal resistance is then obtained directly from the calibration curve. Thus, it is not necessary to measure temperature or rates of energy transfer. The accuracy of the technique is about 3%.

The boiling liquids used in the study were Freon 11 (23.8°C) and methylene chloride (40.1°C). The temperature drop across the test sample was thus 16.3°C and the mean temperature in the sample was about 32°C. The plastic materials were commercial polystyrene and low-density polyethylene. The glass was in the form of spheres with a diameter range of 62–88 microns; the calcium oxide, aluminum oxide, and magnesium oxide were powders with a size range of 62–125 microns. To prepare test samples, the plastic and filler were mixed intimately, melted under pressure in a mold, and then solidified by cooling. At least two samples of each composition were made and tested. The maximum difference in the measured values between replicates was 4%; the average difference was 2.5%.

RESULTS AND DISCUSSION

The thermal conductivities of the materials used in this study are listed in Table I. The measured values for pure polystyrene and polyethylene are in reasonable agreement with values reported in the literature.²⁰ The

TABLE I
Characteristics of Materials

| Material | Sp. gr., g/cc | $k_c \times 10^4$, | $k_d \times 10^4$, ^a | k_d/k_c | |
|--------------------------------|------------------|---------------------|----------------------------------|-------------|--------------|
| | | cal/sec cm °C | cal/sec cm °C | polystyrene | polyethylene |
| Polystyrene | 1.05 | 3.70 | | | |
| Polyethylene | 0.924 | 8.01 | | | |
| Glass | 2.50 | | 24 | 6.5 | 3.0 |
| CaO | 3.31 | | 360 | 97 | 45 |
| Al ₂ O ₃ | 3.96 | | 740 | 200 | 92 |
| MgO | 3.58 | | 1310 | 354 | 164 |

^a From ref. 19.

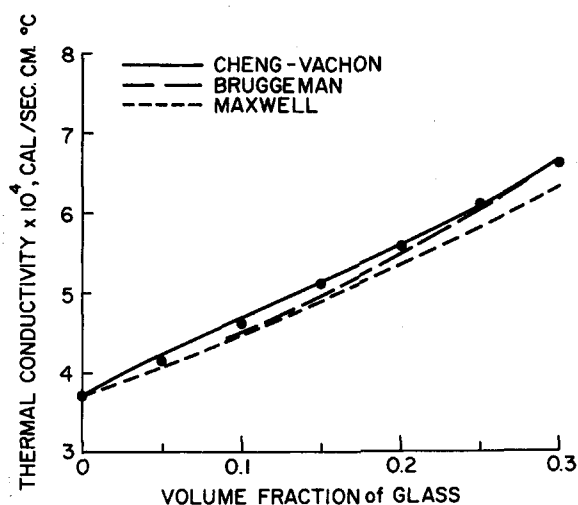


Fig. 1. Comparison of experimental and predicted thermal conductivities for polystyrene filled with glass.

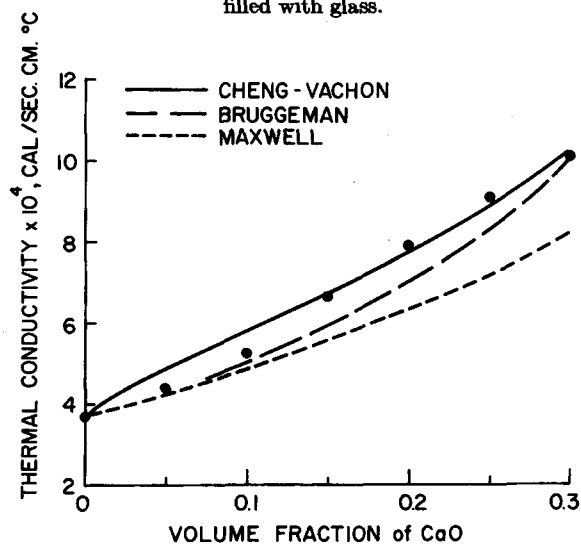


Fig. 2. Comparison of experimental and predicted thermal conductivities for polystyrene filled with calcium oxide.

ratio of k_d to k_c for the composite systems range from 3 for glass in polyethylene to 354 for magnesium oxide in polystyrene. Although the maximum volume fraction of solid in polymer was 0.3, this corresponds to about 60 wt-% for a solid with a specific gravity of 3.5 g/cc. Thus, the study covered a practical range of k_d/k_c and volume fraction for filled plastics. Only one particle size range was used for each type of solid filler. Previous studies^{6,21} have shown that particle size has a minor effect on thermal conductivity of filled polymers.

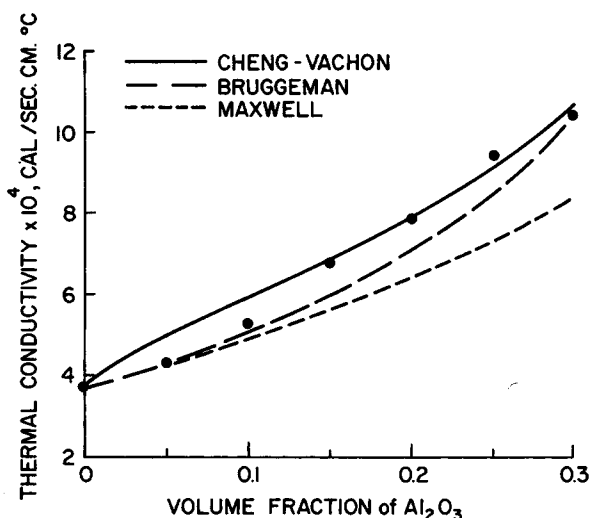


Fig. 3. Comparison of experimental and predicted thermal conductivities for polystyrene filled with aluminum oxide.

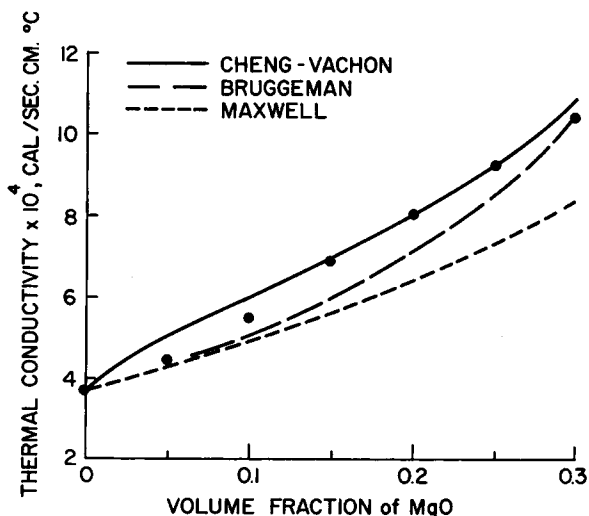


Fig. 4. Comparison of experimental and predicted thermal conductivities for polystyrene filled with magnesium oxide.

Effective thermal conductivities of the two-phase systems were calculated from several of the equations reported in the literature. Of the expressions tested, the equations of Bruggeman¹⁰ and Cheng-Vachon¹² appeared to be the most suitable. In Figures 1 to 8, experimental data are compared with values predicted by these equations and by the classical solution of Maxwell.⁹ The average deviation between measured and calculated conductivities for each system is given in Table II.

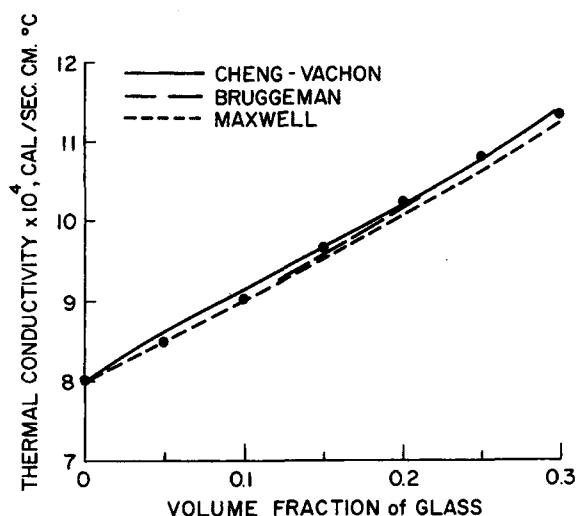


Fig. 5. Comparison of experimental and predicted thermal conductivities for polyethylene filled with glass.

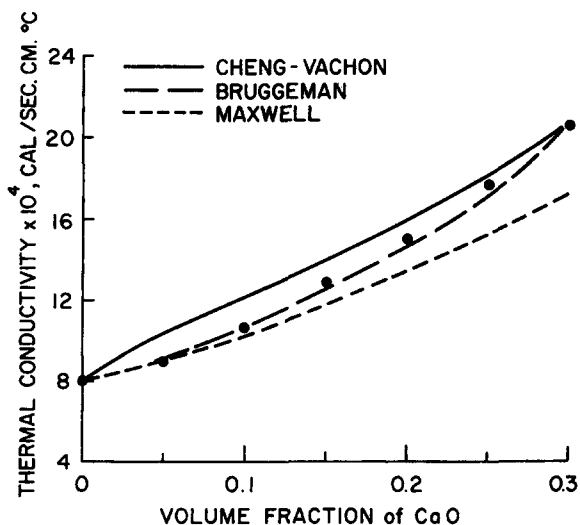


Fig. 6. Comparison of experimental and predicted thermal conductivities for polyethylene filled with calcium oxide.

Both the Bruggeman and Cheng-Vachon equations agree reasonably well with experimental data for all systems. On an overall basis, the average deviation between calculated and measured conductivities is 4.5% for the Bruggeman equation, 4.5% for the Cheng-Vachon equation, and 10.6% for the Maxwell equation. Among other models examined in this study, the average deviation is 10.3% for the Rayleigh equation,¹³ 13.2% for the Russell equation,¹⁵ 11.6% for the Jefferson equation,¹⁶ and 10.8% for the Peterson equation.¹⁷

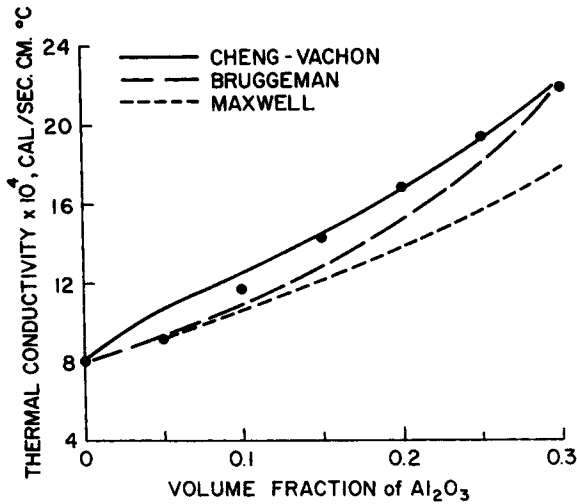


Fig. 7. Comparison of experimental and predicted thermal conductivities for polyethylene filled with aluminum oxide.

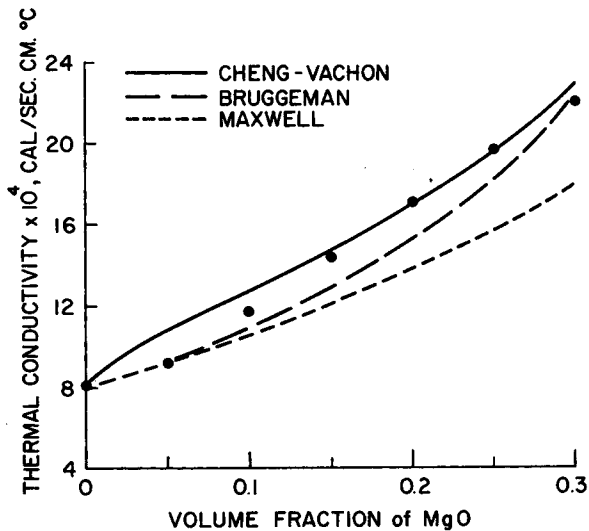


Fig. 8. Comparison of experimental and predicted thermal conductivities for polyethylene filled with magnesium oxide.

In Table III, the errors between predicted and experimental conductivities are shown as a function of volume fraction of filler. Each number in this table represents an average for the eight composite systems. The Bruggeman equation gives better agreement with the data up to 10 vol-% whereas the Cheng-Vachon equation is more accurate in the range of 15 to 25 vol-%. For the systems studied, the Bruggeman and Cheng-Vachon equations cross near 30 vol-% so that the errors are comparable at this filler content.

TABLE II
Average Deviation Between Calculated and Experimental Thermal
Conductivities for Each Composite System

| System | Average deviation, % | | |
|--|----------------------|-----------|--------------|
| | Maxwell | Bruggeman | Cheng-Vachon |
| Glass in polystyrene | 4.1 | 1.9 | 0.8 |
| CaO in polystyrene | 13.8 | 6.0 | 5.3 |
| Al ₂ O ₃ in polystyrene | 14.5 | 6.0 | 5.7 |
| MgO in polystyrene | 15.8 | 7.3 | 4.8 |
| Glass in polyethylene | 0.8 | 0.5 | 0.6 |
| CaO in polyethylene | 8.5 | 1.8 | 7.9 |
| Al ₂ O ₃ in polyethylene | 13.6 | 6.0 | 4.8 |
| MgO in polyethylene | 13.7 | 6.2 | 5.8 |

TABLE III
Average Deviation Between Calculated and Experimental Thermal
Conductivities for Each Volume Fraction

| Volume fraction | Average deviation, % | | |
|-----------------|----------------------|-----------|--------------|
| | Maxwell | Bruggeman | Cheng-Vachon |
| 0.05 | 1.5 | 1.4 | 7.9 |
| 0.10 | 6.0 | 4.2 | 7.9 |
| 0.15 | 9.0 | 8.1 | 1.8 |
| 0.20 | 14.1 | 7.3 | 1.6 |
| 0.25 | 15.2 | 4.8 | 1.2 |
| 0.30 | 14.6 | 0.9 | 2.0 |

The structure of the polymers differ substantially, since polystyrene is amorphous and polyethylene is semicrystalline. The results indicate that the structure of the polymer does not have any appreciable effect on the applicability of the theoretical equations.

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