Thermal Conductivity of Polymer Filled with Carbon Materials: Effect of Conductive Particle Chains on Thermal Conductivity

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Synopsis

Thermal and electric conductivities of polyethylene and poly(vinyl chloride) filled with carbon materials over a wide range are measured in order to study the effect of formed conductive particle chains on thermal conductivities of the composites. With increase of content of carbon particles, the amount of formed conductive chains exponentially increases and the conductive chains tend largely to increase thermal conductivity of a composite. Some models proposed to predict thermal conductivity of a composite in a two-phase system could not be applied to the system with high volume content of particles. In this study, a new thermal conduction model is proposed to correctly predict thermal conductivity of a composite which contains various amounts of particles ranging from a small content, to the region in which conductive chains largely effect a thermal conductivity of a composite. Thermal conductivity of a polymer filled with high volume content of particles largely decreased with a rise in temperature. This phenomenon can be referred to as a PTC phenomenon in thermal resistance.

INTRODUCTION

Carbon materials are often added to polymers to obtain composite materials with improved mechanical and electric properties, but there are few reports on improving thermal conductivity by adding carbon materials.[1-3] On the contrary, some reports indicate that thermal conductivity of polymer filled with carbon black could not be appreciably elevated.[4,5]

In general, thermal conduction systems in polymers filled with high conductive particles vary with the volume content of particles and can be classified into two systems. One is a system with low content of particles in which dispersed particles hardly touch each other (dispersed system). The Maxwell–Eucken equation can be applied to the thermal conductivity of a composite in this system. The other is a system with higher content, in which conductive chains are exponentially formed by particles and contribute to a large increase in thermal conductivity of a composite (attached system). Electric conduction system of composites quickly changes from dispersed system to attached system when volume content of conductive particles increases, in general, to around 10 vol %, that is, the change from very low electric conductivity $(10^{-14}–10^{-15} \ \Omega^{-1} \ cm^{-1})$ to very high electric conductivity $(10^{-2}–10^{-3} \ \Omega^{-1} \ cm^{-1})$. Since the thermal conduction system has some analogy with the electric conduction system, and electric conductivity of the attached system is much higher than that of the dispersed system, the thermal conduction system of a composite can be clearly distinguished by measuring the electric conductivity of the composite.

In this study, thermal and electric conductivities of polyethylene and poly(vinyl chloride) filled with various contents of carbon materials, that is, graphite or carbon black, are measured to discuss the effect of the change in conductive system on thermal conductivity of the composite. Furthermore, since the thermal conductivity of the obtained composite does not agree with values predicted by any model proposed by Maxwell and Eucken, Bruggeman, Nielsen, or Cheng and Vochen, a new thermal conduction model is proposed. It is obtained by combining, in parallel, a thermal conduction model in general use, that is, Maxwell–Eucken, with the model in which the conductive particle chains contribute to increasing thermal conductivity of the composite.

EXPERIMENTAL

Preparation

Polyethylene Composite

Test specimens were prepared by mixing molten polyethylene with various contents of carbon black or graphite under reduced pressure.

Poly(vinyl Chloride) Composite

Test specimens of 5 mm thickness were prepared by laminating the films which were made by mixing various contents of graphite with polyvinyl chloride using a mixing roll.

The properties of the materials utilized are shown in Table I.

Measurement

Measurements of thermal conductivities were performed by utilizing the Dynatech conductance tester Model TCHM-DV. The Dynatech thermal conductance tester is based on the comparison method to a standard specimen made of Pyrex glass. The size of the specimen was 50 mm in diameter and 5 mm in thickness. The measurements were performed mainly at 50°C, and at various temperatures between 50 and 100°C to determine the variation of conductivity with temperature.

TABLE I
Properties of Materials

Material	Density (g/cm^3)	Thermal conductivity (cal/s cm °C)	Electric conductivity (Ω^{-1} cm^{-1})
Polyethylene[a]	0.938[e]	6.96×10^{-4}	2.5×10^{-16}
Polyvinyl chloride[b]	0.971[e]	4.03×10^{-4}	1.1×10^{-12}
Graphite[c]	2.307[e]	$5.0 \ \times 10^{-1}$	1.4–2×10^3
Carbon black[d]	1.839[f]	—	—

[a] Reported by Allied Chemical: MW = 5000.
[b] Reported by Shinetu Kagaku: MW = 800.
[c] Reported by Showa Denko.
[d] Ketjen black EC.
[e] By air-comparison method.
[f] By pycnometer method.

Electric conductivity of the same specimen that was used for the measurement of thermal conductivity was measured. Electric conductivity of high-resistivity material was calculated by measuring the current yielded when a voltage of 500 VDC was applied, while for low-resistivity material, a voltage of 10 VDC was applied. The temperature for measurement was 23 ± 2°C, and the relative humidity was 50 ± 5%.

RESULTS AND DISCUSSION

Thermal Conductivity of Polyethylene Filled with Graphite

Thermal and electric conductivities of polyethylene filled with various volume contents of graphite are indicated in Figure 1. Electric conductivity begins to increase rapidly around the point where graphite accounts for 10% in volume, indicating that many graphite particles touch each other to form graphite conductive chains which may connect one electrode with the other. Thermal conductivity increases gradually, at around 10 vol %. The large gap between the value obtained in this study and the value predicted by Maxwell–Eucken equation becomes evident at this point. Particles begin to form conductive graphite chains at around 10 vol %, and there is a change in the conductive system from the dispersion system to the attached system, resulting in the rapid increase in thermal conductivity.

The thermal conductivity of polyethylene filled with graphite increases less rapidly than the electric conductivity (which is plotted on a log scale); because the electric conductivity of graphite is much greater than that of polyethylene (8 × 10^18 times), most of the electric current flows through the formed conductive graphite chains. On the other hand, because the thermal conductivity of graphite is not as great as that of polyethylene (1.5 × 10^3 times), heat flows not only through the formed conductive graphite
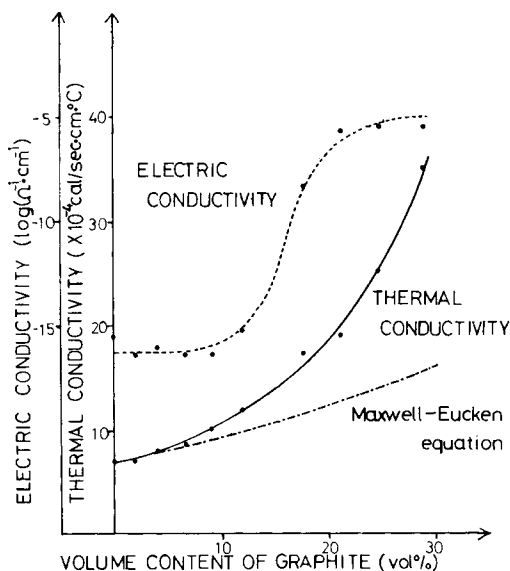

Fig. 1. Thermal and electric conductivities of polyethylene filled with graphite.

chains, but also through the polyethylene itself. Consequently, thermal conductivity is less influenced than electric conductivity by the exponential increase of the number of the conductive chains.

Figure 2 shows the relation between the vol % of the graphite particles and thermal conductivity of polyethylene filled with graphite particles. When the particles occupy a large percentage, the thermal conductivity of polyethylene filled with the coarse particles is higher than that filled with the fine particles. The first reason is that coarse particles, already composed of aggregates of fine particles, are much more capable of forming the conductive chains than fine particles. Secondly, the number of contact points of coarse particles required for forming the same length of conductive chain is smaller than the number of contact points of fine particles, and, therefore, the amount of heat scattered around the contact points in the case of coarse particles is smaller than in the case of fine particles.

Thermal Conductivity of Poly(vinyl Chloride) with Graphite

Thermal and electric conductivities of poly(vinyl chloride) filled with various contents of graphite are indicated in Figure 3. The conductive graphite chains increase rapidly at ca. 10 vol % of graphite as in the case of polyethylene filled with graphite, and also the conductive graphite chains contribute to the rapid increases in thermal and electric conductivities.

Thermal Conductivity of Polyethylene Filled with Carbon Black

Figure 4 shows thermal and electric conductivities of polyethylene filled with carbon black, in the form of fine powder. The electric conductivity begins to increase rapidly at around 2 vol % of carbon black, indicating
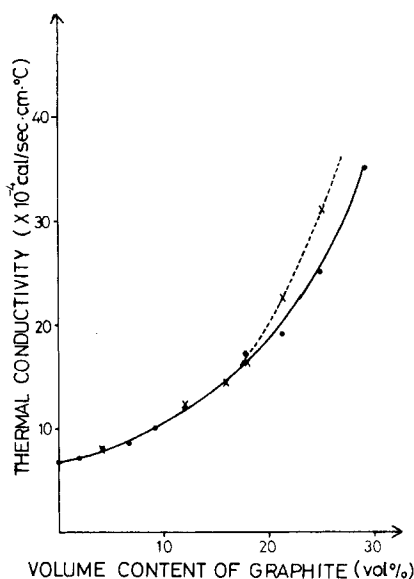

Fig. 2. Thermal conductivity of polyethylene filled with various particle size of graphite (below 44, 74–149 μm); (—) below 44 μm; (- - -) 74–149 μm.
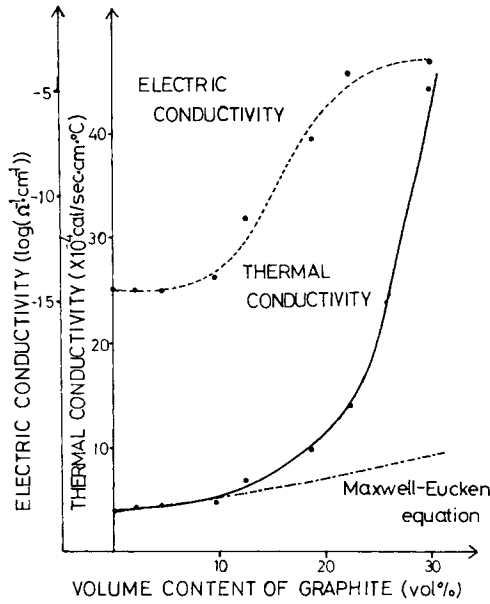
Fig. 3.   Thermal and electric conductivities of polyvinyl chloride filled with graphite.

that conductive carbon black chains begin to form at this point. On the other hand, the thermal conductivity begins to increase largely at around 3 vol % of carbon black. Thermal conductivity of polymers are elevated by carbon black conductive chains. Moreover, only a small amount of carbon black is required to elevate electric and thermal conductivities in comparison with the amount of graphite required to have the same effects. This occurs because carbon black is able to form conductive chains more easily than graphite.
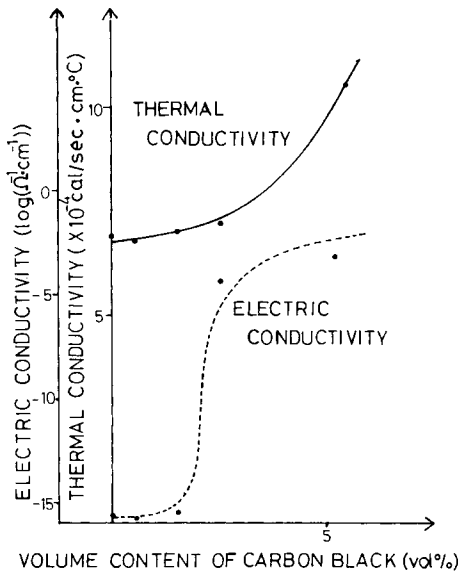

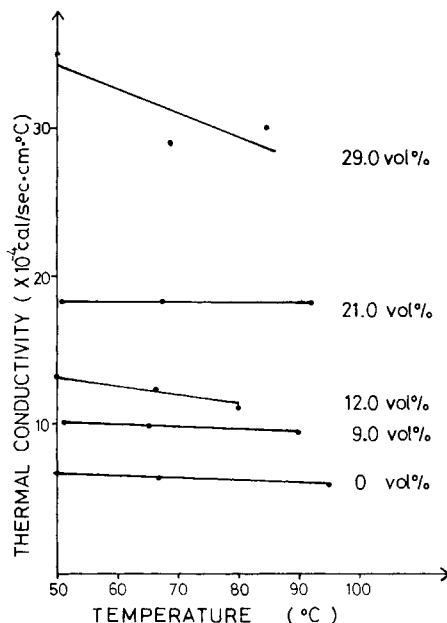Fig. 4.   Thermal and electric conductivities of polyethylene filled with carbon black.

Fig. 5.   Relation of thermal conductivity and temperature in polyethylene filled with graphite.

Variation of Thermal Conductivity of Composite with Temperature

Figures 5–7 show the thermal conductivities of poly(vinyl chloride) filled with graphite or carbon black and polyethylene filled with graphite at various temperatures. At low content of particles (dispersed system), the thermal conductivities of all the composites change little with temperature, ranging from 50 to 100°C. However, a slight decrease can be observed. This is because transmittance of thermal vibration is somewhat disturbed when the distance of macromolecular lattices is widened due to thermal expansion of the polymer. At high content of particles (the attached system), the thermal conductivities of the composite decrease greatly. Specifically, the thermal conductivity of poly(vinyl chloride) filled with 29.6 vol % of graphite changes rapidly; that is, the thermal conductivity at 100°C is less than half of that at 50°C. This is because formed conductive chains are cut or shortened when thermal expansion of the polymer widens the distance between particles while decreasing the thermal conductivity of the polymer itself.

CONDUCTIVE MODEL

Numerous theoretical and empirical models have been proposed to predict the effective thermal conductivity in a two phase system. Recently, there have been some reports that Nielsen and Cheng–Vochen equations agree reasonably well with experimental data for filled polymers, e.g., Al_2O_3.[1,3]

In this study, the models which are proposed by Maxwell and Eucken,[6] Bruggeman,[7] Nielsen,[8] and Cheng and Vochen[9] are compared with the experimental data:
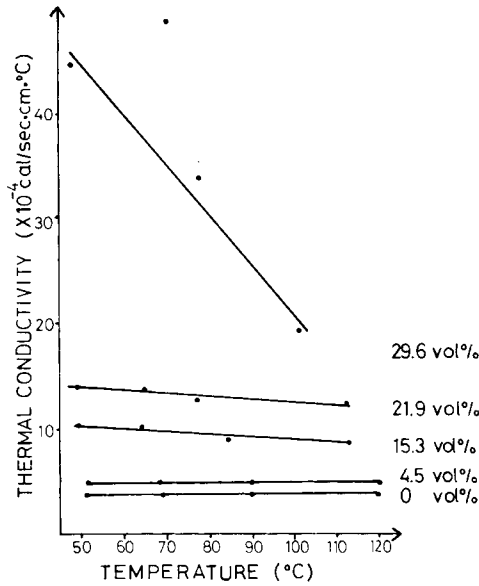
Fig. 6. Relation of thermal conductivity and temperature in polyvinyl chloride filled with graphite.

Maxwell–Eucken equation:

$$\lambda = \frac{2\lambda_1 + \lambda_2 + 2V_f(\lambda_2 - \lambda_1)}{2\lambda_1 + \lambda_2 - V_f(\lambda_2 - \lambda_1)}\lambda_1 \tag{1}$$

Bruggeman equation:

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

Cheng-Vochen equation:

$$\frac{1}{\lambda} = \frac{1 - B}{\lambda_1} + \frac{1}{\{C(\lambda_2 - \lambda_1)[\lambda_1 + B(\lambda_2 - \lambda_1)]\}^{1/2}} \tag{3}$$

$$\times \ln \frac{[\lambda_1 + B(\lambda_2 - \lambda_1)]^{1/2} + B/2[C(\lambda_2 - \lambda_1)]^{1/2}}{(\lambda_1 + B(\lambda_2 - \lambda_1))^{1/2} - B/2[C(\lambda_2 - \lambda_1)]^{1/2}}$$

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

Nielsen equation:

$$\lambda = \frac{1 + AB\,V_f}{1 - B\psi V_f} \qquad B = \frac{\lambda_2/\lambda_1 - 1}{\lambda_2/\lambda_1 + A}, \quad \psi = 1 + \frac{V_f(1 - \phi_m)}{\phi_m} \tag{4}$$

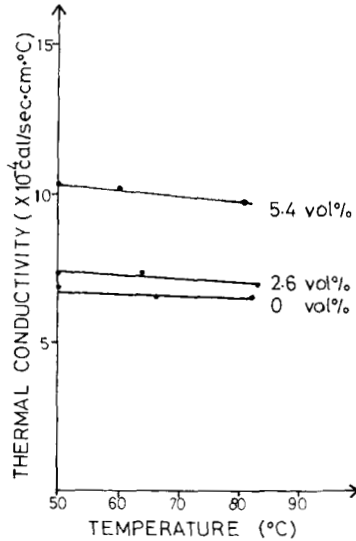A, ϕ_m = coefficients of particle size and shape

Fig. 7. Relation of thermal conductivity and temperature in polyethylene filled with carbon black.

where λ = thermal conductivity of a composite, λ_1 = thermal conductivity of a polymer, λ_2 = thermal conductivity of particles, and V_f = volume content of particles.

Experimental data are compared with values predicted by these equations (Figs. 8 and 9). No predicted value agrees with the experimental data. In particular, in high content of particles, at around the point in which particles appear to gather exponentially to form conductive chains (the at-
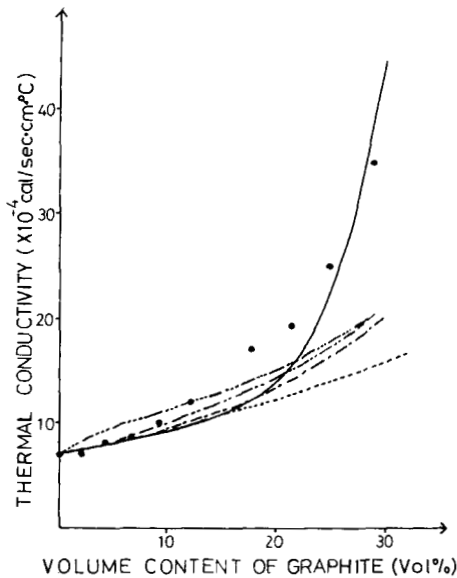

Fig. 8. Predicted thermal conductivity of polyethylene filled with graphite; (●) Experimental data; (—) Predicted curve in this study; (- - -) Maxwell-Eucken curve; (— · —) Bruggeman curve; (— · · —) Neilson curve; (— · · · —) Cheng-Vochen curve.
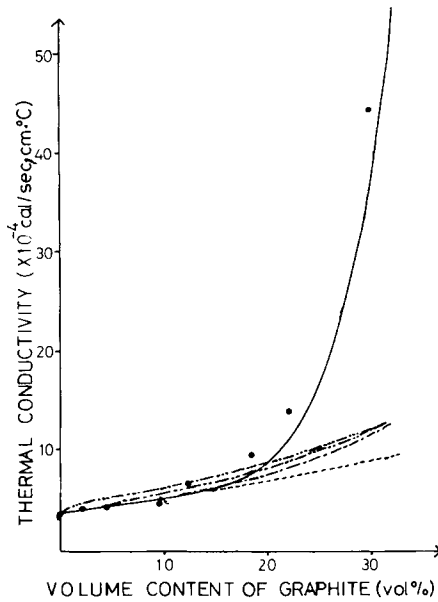
Fig. 9. Predicted thermal conductivities of polyvinylchloride filled with graphite; (●) Experimental data; (—) Predicted curve in this study; (- - -) Maxwell-Eucken curve; (—·—·—) Bruggeman curve; (—··——··—) Nielsen curve; (-····—····-) Cheng-Vochen curve.

tached system), there are large differences between the predicted values and the experimental data. This is due to the fact that although conductive particle chains greatly effect the thermal conductivity, they are not taken into account.

In this study, a new thermal conduction model is proposed. It is obtained by combining, in parallel, a thermal conduction model in general use, that is, the Maxwell–Eucken model, with a thermal conduction model in which only the effect of formed conductive chains on the thermal conduction of a composite is taken into account. Consequently, thermal conductivity predicted by the new model can be estimated by the following equation:

$$\lambda = \lambda_a + \lambda_b \tag{5}$$

λ_a is thermal conductivity predicted by the Maxwell–Eucken model and can be estimated by the equation. λ_b is thermal conductivity predicted by the thermal conduction model in which only the effect of formed conductive chains is taken into account and can be estimated by the following equation:

$$\lambda_b = V_f \times V_f^{V_f \cdot 2/3} \times C^2 \times \lambda_2 \tag{6}$$

where C^2 is a geometrical factor which connects the observable conductivity with the random assembly of conductive chains; $V_f = 3C^2 - 2C^3$. The thermal conduction in which the effect of formed conductive chains is taken into account is based on the Scarisbrick model,[10] which explains electric conductivity by calculating the probability of forming conductive particle chains in a two phase system. Consequently, the system can be estimated by the following equation:

$$\lambda = \frac{2\lambda_1 + \lambda_2 + 2V_{af}(\lambda_2 - \lambda_1)}{2\lambda_1 + \lambda_2 - V_{af}(\lambda_2 - \lambda_1)}\lambda_1 + V_f V_f^{V_f^{-2/3}} C^2 \lambda_2 \tag{7}$$

where V_f = percentage of particles contributing to forming conductive chains and V_{af} = volume content of particles not contributing to forming conductive chains, $V_{af} = (1 - V_f^{V_f^{-2/3}})\, V_f$. Since the value of V_f discussed in this study is up to 0.3, the value of $V_f^{V_f^{-2/3}}$ is less than 0.02. Consequently, V_f is approximately substituted for V_{af}.

In Figures 8 and 9, experimental data are compared with values predicted by the new model. The new model explains the experimental data well. However, thermal conductivities of polyethylene filled with graphite are somewhat higher than values predicted by the new equation (7), in the area ranging from 10 to 20 vol % of graphite. When polyethylene crystallizes, graphite particles, after being pushed out of crystal polyethylene, facilitate the formation of conductive graphite chains.

Thermal conductivity of carbon black could not be measured, because carbon black exists only in granular form. Calculated by the new equation (7), from the thermal conductivities of polyethylene filled with carbon black, the apparent value of carbon black is estimated at 10^8–10^9 cal/s cm °C. The apparent value is unexpectedly very high in comparison with the thermal conductivity of graphite, and we would not expect that carbon black has such a high conductivity. Nevertheless, carbon black particles form conductive chains in polyethylene much more easily than graphite.

In Figure 10, electric conductivities of polyethylene filled with graphite are compared with values predicted by the Scarisbrick model. Although experimental data remains almost constant till around 10 vol % and then increases, the predicted values begin to increase rapidly at ca. 3–4 % in
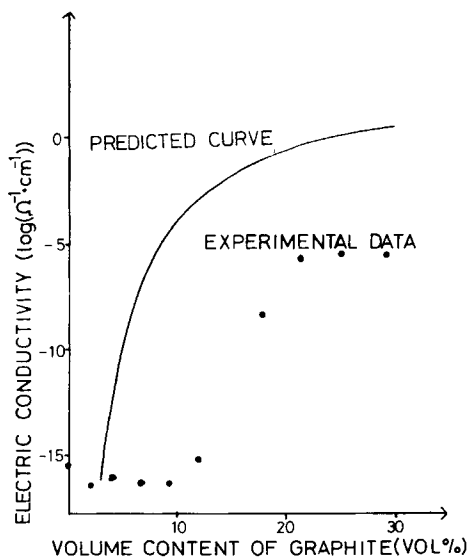

Fig. 10. Predicted electric conductivity of polyethylene filled with graphite.

volume. However, the predicted values increase in a similar pattern with experimental data. Except for the probability of conductive chain formation and electric conductivity of particles, there are other factors (mainly, hindrance of contact between particles due to polymer adsorption on particles) which affect electric conductivity of filled polymer, but not thermal conductivity. Therefore, the Scarisbrick model cannot be applied for electric conductivity in this system without modification.

CONCLUSION

Thermal conductivities of polymers filled with graphite, which have very high thermal conductivity, tend to increase largely in high volume content of graphite (the attached system). This result can not be explained by thermal conduction models such as that of Maxwell and Eucken, Bruggeman, Cheng and Vochen, or Nielsen. In this study, the probability of forming conductive particle chains is estimated, and a new thermal conduction model is obtained by combining thermal conductivity calculated from the probability of forming conductive chains, with thermal conductivity estimated by the Maxwell–Eucken equation. The new model explains the experimental data and can be applied in this two-phase system (dispersion at random). Further investigation is in progress for the new model regarding its application to other systems.

Some reports state that thermal conductivities of polymer filled with carbon black are not high.[4,5] However, in this study, thermal conductivities of polyethylene filled with carbon black tend to increase more than that of polyethylene filled with graphite.

Thermal conductivities of the polymer filled with low content of particles hardly change with the change in temperature ranging from 50 to 100°C. However, thermal conductivities of the polymer with high content of particles decreased with a rise in temperature. In particular, when the temperature rose by 50°C from 50 to 100°C, thermal conductivity decreased by a factor of 2. An analogy with this phenomenon, named PTC (positive temperature coefficient) phenomenon, occurs in electric conductivity of composites. Consequently, this phenomenon can be considered a PTC phenomenon in thermal resistance.

References

1. D. W. Sundstrom and Y. D. Lee, *J. Appl. Polym. Sci.*, **16**, 3159 (1972).
2. R. P. Kusy and R. D. Corneliussen, *Polym. Eng. Sci.*, **15**, 107 (1975).
3. D. M. Bigg, *Polym. Eng. Sci.*, **19**, 1188 (1979).
4. J. H. Atkins and J. E. Sullivan, Jr., *Rubber Chem. Technol.*, **42**, 1314 (1969).
5. J. B. Donnet and A. Voet, *Carbon Black*, Marcel Dekker, New York, 1976.
6. A. Eucken, *Fortchg. Gebiete Ingenieurw., B3, Forschungsheft*, **353**, 16 (1932).
7. D. A. Bruggeman, *Ann. Phys.*, **24**, 636 (1935).
8. L. E. Nielsen, *J. Appl. Polym. Sci.*, **17**, 3819 (1973).
9. S. C. Cheng and R. I. Vachon, *Int. J. Heat Mass Transfer*, **12**, 249 (1969).
10. R. M. Scarisbrick, *J. Phys.*, **D6**, 2098 (1973).