Thermal Conductivity of High Density Polyethylene Filled with Graphite

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ABSTRACT: The effect of the grade, the content, and the particle diameter on the thermal conductivity of high-density polyethylene (HDPE) filled with graphite were studied. The results show an increase of thermal conductivity of the HDPE/graphite composite with increase of graphite content. The thermal conductivity of the HDPE filled with the expanded graphite was larger than that of the HDPE filled with the colloid graphite system. At the same volume content (7%), the thermal conductivity of the former was twice that of the latter one. The particle diameter of the graphite also affected the thermal conductivity of HDPE composites. With increase of the particle diameter of the colloid graphite, the thermal conductivity of the HDPE/graphite increased. However, when the particle diameter of colloid graphite was larger than 15 μm, the increase of thermal conductivity of HDPE/graphite changed by inches. Some models proposed to predict thermal conductivity of a composite in a two-phase system could not be applied to HDPE filled graphite powder composites, such as Maxwell-Eucken, Cheng and Vachon, Zieblend, Lewis and Nielsen, Agari and Uno equations. But, according to the increase of thermal conductivity of HDPE composites filled with the colloid graphite, we find that Ziebland equation is suitable except of some constant. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3806–3810, 2006

Key words: graphite; high density polyethylene; thermal conductivity model

INTRODUCTION

Thermal conductive polymeric materials are superior to metals in electronic engineering, cooling systems, and heat transfers at the aspect of chemical resistance. This technology is a substantial improvement since polymers are commonly used due to their thermal isolating properties. The advantages of thermal conductive polymer composites over metals are induced density, increased corrosion, oxidation, and chemical resistance; increased processability. However, polymers have disadvantages, for example, creep, thermal instability, and a limited number of processing techniques.

Many reports[1–3] have been published on the improvement of thermal conductivity of the polymer filled with various types of particles, and several thermal conduction models have been proposed for prediction of two-phase systems. However, most of them discussed relation of thermal conductivity of polymer composites to content of particles such as quartz, Al_2O_3, copper, AlN, and so on. But few[4,5] discussed the case of improving thermal conductivity of high-density polyethylene composites by adding graphite material. Graphite material is often added to polymers to obtain composite materials with improved mechanical and electric properties.

In this study, we discussed the effect of the grade, the content, and the particle diameter on the thermal conductivity of high-density polyethylene (HDPE) filled with graphite. This report discusses application of these thermal conduction models proposed by Maxwell and Eucken, Cheng and Vachon, Zieblend, Lewis and Nielsen, Agari and Uno[6–8] to experimental data up to the region of 0–22 vol %.

EXPERIMENTAL

Materials

[bull] High-density polyethylene (HDPE), RIGIDEX type, TR480FS(Shanghai Golden Philips Petrochemical CO., China), with a melt flow index of 0.11 g/10 min, ASTM D1238 a thermal conductivity of 0.39 W/m K, melting point of 128°C, and density of 0.956 g/cm^3;

[bull] Graphite powder with average particle size (1.5, 2.3, 4.0,10, 15, 30 μm Shanghai Colloid chemical factory, China), with a density of 2.3 g/cm^{3,} a thermal conductivity of 209 W/m K and carbon content of 99.85%;

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Expandable graphite, RIGIDEX type, 19,850(Baoding Lianxing Carbide Co.) with expansion volume of 50 mL/g, with particle size of 150 μm.

Preparation of expanded graphite

Expanded graphite was prepared following a method reported in the literature.[9] A 4:1 by volume mixture of concentrated sulfuric acid and nitric acid was added slowly, under appropriate cooling and stirring, to graphite flakes. After 24 h of reaction, the mixture was filtered, washed with distilled water, and then dried in an oven at 90°C. The treated graphite flakes were then put in an oven at 900°C for rapid expansion and exfoliation. The expansion ratio was as high as 50.

Composites preparation

The composites have been prepared by compounding HDPE with different amounts of graphite powder on a laboratory-rolling machine with roller heated at 165°C. The mixing time was about 10 min after the formation of HDPE sheet on the anterior cylinder of the rolling machine and addition of the graphite powder. The mixtures have been transformed through pressing (preheated for 10 min, pressure for 10 min at 180°C and 20 MPa, cooling through pressure) in $\Phi200 \times 20\ \text{mm}^2$ thick plates, from which specimens have been cut for the determination of the thermal characteristics. Thus, composites with graphite powder content ranging between 0% and 22% by volume have been prepared.

Measurement

Measurements of thermal conductivities were performed by utilizing thermal conductive apparatus (QTM-D_2, SHOWA DENKO, 0.02–10 W/m K, $<\pm8\%$) according to GB/T10297–1998. The dimensions of the specimen were $150 \times 50 \times 20\ \text{mm}^3$. The measurements were performed mainly at 25°C. The thermal conductivity of polymers is measured by a GB/T 10,297–1998. The used technique is especially optimized for measurements of polyphase aggregates. A temperature signal is transferred to the upper side of the sample and registered by a thermocouple. The transferred temperature signal starts a thermal equilibration process in the specimen, which is recorded by a difference thermocouple on the rear surface and used for the evaluation of thermal conductivity. A least square algorithm is used to determine the thermal conductivity when it is varied systematically in a specially designed finite-difference scheme. The accuracy of the measurement of the polyphase aggregates is 8%

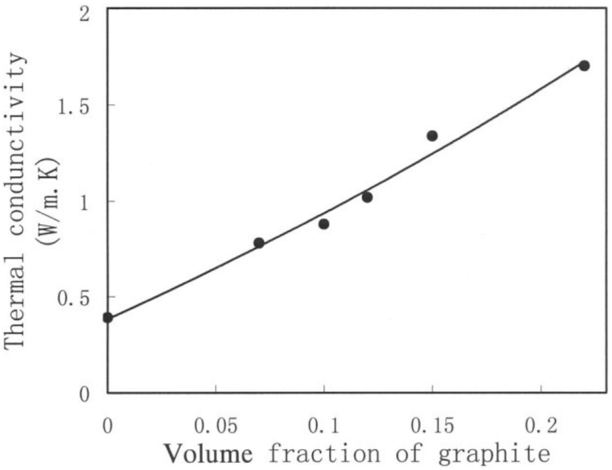

Figure 1 Thermal conductivity of HDPE filled with colloid graphite/4 μm.

RESULTS AND DISCUSSION

Influence of volume content of colloid graphite on thermal conductivity of HDPE/graphite

Thermal conductivity of HDPE filled with various volume contents of colloid graphite are indicated in Figure 1.

With the increase of the graphite content, the thermal conductivity of the HDPE/graphite composites increased. The propagating rate of the thermal flow through a nonmetallic solid depends on the coupling intensity of the vibration movements of the atoms and groups of adjacent atoms. Intense couplings occur in the materials with covalent bonds, the thermal transmission showing a slight deficit in the case of highly ordered crystalline networks.[10] In the case of graphite, the process of thermal energy transmission from one point to another, by means of atomic vibration, contributes to thermal conduction of HDPE filled with graphite. With the increase of volume content of graphite, many graphite particles touch each other to begin to form graphite conductive chains, which may connect one electrode with the other. So the thermal conductivity of the HDPE/graphite composites increased.

Thermal conductivities of HDPE filled with grade of graphite

Like layered silicates, natural flake graphite is also composed of layered nanosheets. Moreover, it is a good thermal conductor with a thermal conductivity of 209 W/m K at room temperature. It can be divided into the colloid and expandable graphite.[11] The thermal conductivities of HDPE filled with the colloid and expanded graphite were indicated in Figure 2. The thermal conductivity of the HDPE filled with the ex-

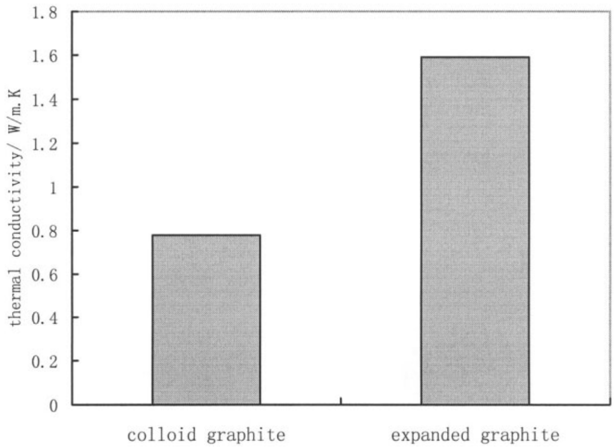

Figure 2 Influence of the graphite species on the thermal conductivity of HDPE composites (Volume content and particle diameter of graphite: 7%,4 μm).

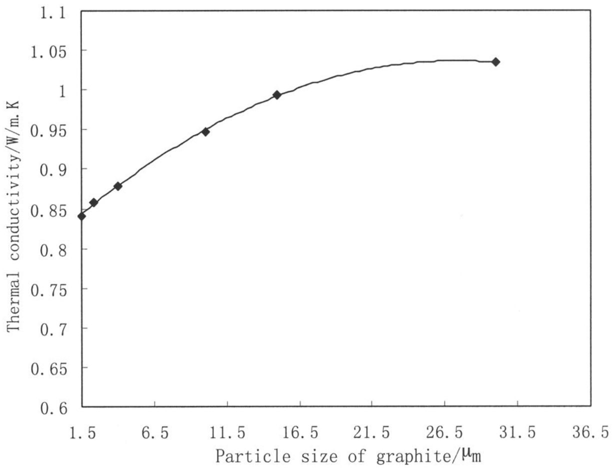

Figure 3 Thermal conductivity of HDPE filled with different particle size of colloid graphite/10 vol %.

panded graphite was 1.590 W/m K; however, the thermal conductivity of HDPE filled with the colloid graphite was 0.779 W/m K, and at the same volume content (7%), the thermal conductivity of the former was twice that of the latter one.

According to Agri and Uno equation[6] $\log k_c = V_f C_2 \log k_f + (1 - V_f) \log(C_1 k_p)$, parameter k_c is the thermal conductivity of the composite, k_p, the thermal conductivity of polymer, k_f, the thermal conductivity of filler, V_f, the volume content of filler, C_1, the factor relating to the effect on crystalling and crystal size of polymer, and C_2 is the factor relating to the ease in forming conductive chains of filler. Values of C_1 and C_2, calculated from the experimental date, are indicated in Table I.

Values of coefficients C_1 and C_2 (no unit, only coefficient) in eq. (5), indicated in Table I, were calculated by the experimental data and two values of C_1 are approximately equal. Hence, the effects of graphite species on crystalling and crystal size of HDPE are same. Each system showed a different value of C_2. The value of C_2 may be affected not only by the ease in forming conductive chains of particles, but also by thermal contact resistance between polymer and particles. Expanded graphite is a loose and porous vermicular product. Its structure is basically parallel boards, which collapse and deform desultorily. The collapse and deformation of the parallel boards form many pores of different sizes ranging from 10 nm to10 μm. Because of the high expansion ratio (generally200–300) of expanded graphite in *c*-axis, the interplanar spacing is larger than that of the nontreated graphite.[6,9] Thus, galleries of expanded graphite can be easily intercalated by suitable high-density polyethylene. Thermal conduction systems containing expanded graphite are "attached" systems in which expanded graphite particles interact with each other and affect the position of expanded graphite particles. Hence, thermal conductivities of HDPE filled with expanded graphite are prior to that of HDPE filled with colloid graphite.

TABLE I
Values of C_1 and C_2 in Agri and Uno equation

Materials	C_1	C_2
HDPE filled with colloid graphite	1.45	1.47
HDPE filled with expanded graphite	1.18	2.35

Influence of particle size of colloid graphite on thermal conductivity of HDPE composites

It is considered that the particle properties (shape, size, surface property, etc.) greatly affect the thermal conductivity of the composite. Thermal conductivity of HDPE filled with different size of colloid graphite is indicated in Figure 3.

The particle diameter of the graphite also affected the thermal conductivity of HDPE composites. The experimental results show that with increase of the particle diameter of the colloid graphite, the thermal conductivity of HDPE/graphite composite increased. However, when the particle diameter of colloid graphite was larger than 15 μm, the increase of thermal conductivity of HDPE/graphite changed by inches. 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. Second, 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.[7]

Models of thermal conductivity

There have been many reports that thermal conductivity of polymers was improved by filling with various types of particles and a thermal conduction model was proposed for two-phase systems.[6–8] In previous report, thermal conduction model proposed by Maxell and Euchen, Cheng and Vachon, Ziebland, Lewis and Nielsen were discussed, focusing on of 0–10 vol % (low) or 10–30 vol % (medium) content of filler particles. Thermal conduction model proposed by Agari and Uno was discussed about the region of 30−60 vol % (high) or larger than 60 vol % (superhigh) content of filler particles.

In this study, the models proposed by Maxwell and Eucken, Cheng and Vachon, Ziebland, Lewis and Nielsen, Agari and Uno are compared with the experimental data Maxwell-Eucken equation :

$$k_c = \frac{2k_p + k_f + 2V_f(k_f - k_p)}{2k_p + k_f - 2V_f(k_f - k_p)} \times k_p \qquad (1)$$

Cheng and Vackon equation:

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

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

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

Ziebland equation:

$$k_c = {k_f}^{V_f} \times {k_p}^{1-V_f} \qquad (3)$$

Lewis and Nielsen equation:

$$k_c/k_p = \frac{1 + ABV_f}{1 - BV_f\psi} \qquad B = \frac{k_m/k_p - 1}{k_m/k_p + A}$$

$$\psi = 1 + \frac{1 - V_m}{{V_m}^2}V_f \qquad (4)$$

Agari and Uno equation

$$\log k_c = V_f C_2 \log k_f + (1 - V_f) \log (C_1 k_p) \qquad (5)$$

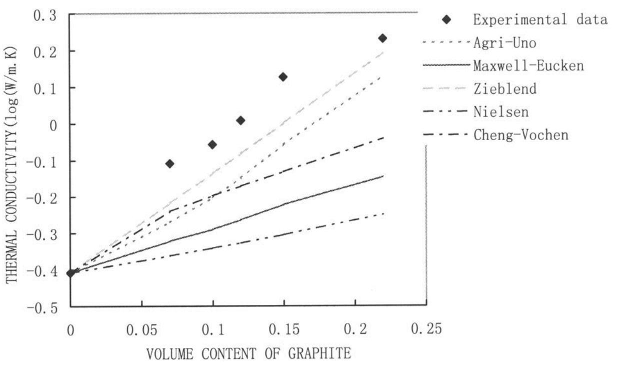

Figure 4 Thermal conductivity of high density polyethylene filled with colloid graphite.

where k_c, k_p, and k_f represent the thermal conductivity values of the composites, polymer, and filler, respectively; V_m, the maximum packing fraction of disperse phase (for randomly distributed spherical particles, $V_m = 0.637$); V_f, the volumetric fraction of the filler; C_1, the factor of the effect on crystallinity and crystal size of polymer; C_2, the factor of ease in forming conductive chains of particles; A, the constant depending on the shape and orientation of disperse particles (for randomly distributed spherical particles, $A = 1.5$ while for randomly distributed aggregates of spherical particles, $A = 3$).

In Figure 4, logarithms of experimental data of thermal conductivities and those of the values predicted by these models are plotted against a wide range of filler content. Comparisons of the experimental data with the predicted values by these models were investigated from 0% to 22% volume content of graphite. Equation (1), (2), (4), and (5) cannot fit the experimental data in the system of HDPE filled with colloid graphite. It is clearly demonstrated that the predicted values of eq. (3) basically agrees with the experimental data for a wide range from 0% to 22% volume content of graphite.

CONCLUSIONS

Graphite is a kind of ideal thermal conductive agent. With the increase of the graphite volume content, the thermal conductivity of the HDPE/graphite composite increased. The thermal conductivity of the HDPE filled with the expanded graphite was larger than that of the colloid graphite system, and at the same volume content (7%), the thermal conductivity of the former was twice that of the latter one. With increase of the particle diameter of the colloid graphite, the thermal conductivity of HDPE/graphite composite increased. However, when the particle diameter of colloid graphite was larger than 15 μm, the increase of thermal conductivity of HDPE/graphite changed by inches. Some models proposed to predict thermal conductivity of a composite in a two-phase system could not be applied to HDPE filled graphite powder composites, such as Maxwell-Eucken, Cheng and Vochan, Ziebland, Lewis and Nielsen, Agari and Uno equations. But, according to increasing trend of thermal conductivity of HDPE composites filled with colloid graphite, we find that Ziebland equation basically agrees with the experimental data for a wide range from 0% to 22% volume content of graphite.

References

1. Weienfeller, B.; Hofer, M.; Schilling, F. Compos Part A: Appl Sci Manuf 2002, 33, 1041.
2. Sofian, N. M.; Rusa, M.; Neagu, R. J Thermoplastic Compos Mater 2000, 14, 20.
3. Pezzotti, G.; Kamada, I. J Eur Ceram Soc 2000, 20, 1197.
4. Wang, Q.; Wang, R.; Hua, Z. Polym Compos 2001, 22, 97.
5. Krupa, I.; Chodak, I. Eur Polym J 2001, 37, 2159.
6. Agari, Y.; Uno, T. J Appl Polym Sci 1986, 32, 5705.
7. Agari, Y.; Uno, T. J Appl Polym Sci 1985, 30, 2225.
8. Agari, Y.; Ueda, A.; Nagai, S. J Appl Polym Sci 1990, 40, 927
9. Pan, Y.-X.; Yu, Z.-Z.; Ou, Y.-C. J Polym Sci Part B: Polym Phys 2000, 38, 1626.
10. Rusu, M.; Sofian, N.; Rusu, D. Polym Eng 2001, 21, 469.
11. Xie, R. C.; Qu, B. J. J Appl Polym Sci 2001, 80, 1190.