Thermal Properties of Graphite-Loaded Nitrile Rubber/Poly(vinyl chloride) Blends

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ABSTRACT: The thermal properties (thermal conductivity, thermal diffusivity, and specific heat capacity) of nitrile rubber (NBR)/poly(vinyl chloride) (PVC) blends were measured in the temperature range of 300–425 K. The incorporation of graphite into the NBR/PVC (30/70) matrix improved its thermal properties. Moreover, these properties slightly changed with the temperature. The thermal conductivity values of the prepared samples were compared with values modeled according to the Maxwell–Eucken, Cheng–Vachon, Lewis–Nielsen, geometric mean, and Agari–Uno models. The Agari–Uno model best predicted the effective thermal conductivity for the whole range of blend ratios and for the whole range of graphite contents in NBR/PVC (30/70)/graphite composites. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3171–3177, 2010

Key words: blends; composites; molding; poly(vinyl chloride); (PVC); thermal properties

INTRODUCTION

It has been well established that polymer composites and blends are effective answers to the challenge of developing new polymers with specific sets of properties.[1] One of the goals of materials research is to create new materials with physical properties tailored to a particular application and to understand the physical mechanisms that determine their properties. The thermal conductivity, thermal diffusivity, and specific heat, that is, the thermophysical properties, are the three most important physical properties of a material that are needed for heat-transfer calculations.[2] Information on the thermal conductivity of materials is necessary for determining optimum conditions during the processing of materials and for analyzing heat transport in materials during practical applications. Also, the addition of conductive fillers such as graphite fillers to a polymer matrix is an effective way to increase the thermal conductivity of polymers, as required by several industrial applications. New applications, such as heat sinks in electronic packaging, require new composites with higher thermal conductivity (in electronic packaging, there are applications with decreasing geometric dimensions and increasing power output). Such materials with high thermal and electrical conductivities could be suitable for use in combined electromagnetic interference shielding and heat sinks.[3–5] Higher thermal conductivity can be achieved by the use of suitable fillers such as aluminum,[3] carbon fibers, and graphite.[6] In a more recent study by Gwaily et al.,[7] the thermophysical properties of conductive butyl rubber composites loaded with different concentrations of BaTiO powder and 50 phr lamp black were investigated experimentally in the temperature range of 30–150°C. An empirical formula was suggested to describe the dependence of the effective thermal diffusivity of the composites on the BaTiO content. Overall, the experimental and modeling work reported for the thermophysical properties of polymer composites is very limited. This article provides a complete experimental data set for the temperature-dependent thermophysical properties of graphite-loaded nitrile rubber (NBR)/poly(vinyl chloride) (PVC) blends. The obtained experimental data were fitted to model equations (i.e., Maxwell–Eucken, Cheng–Vachon, Lewis–Nielsen, and Agari–Uno), and these were compared with the experimental data for thermal conductivity.

THERMAL CONDUCTIVITY MODELS

The effective thermal conductivity of a composite material is a complex function of its geometry, the thermal conductivity of the different phases, its distribution within the medium, and contact between the particles. Thus, when such filled polymers are being designed, it is essential to predict the thermal

conductivity of the final products. Therefore, many theoretical and empirical equations have been proposed to describe the thermal conductivity of heterogeneous materials and find suitable applications. Then, through a comparison of the experimental data and calculated values, information can be obtained that facilitates the understanding and analysis of the heat transport in heterogeneous materials.

Many theoretical and empirical models have been proposed to predict the effective thermal conductivity of two-phase mixtures. Comprehensive review articles have discussed the applicability of many of these models.[8,9] In this study, the models proposed by Maxwell and Eucken, Cheng and Vachon, Lewis and Nielsen, and Agari and Uno are compared with the experimental data.

First, several predictive models for the thermal conductivity of composites are listed.

Geometric mean model

In the case of the geometric mean model, the effective thermal conductivity of the composite (k_c) is determined as follows:

$$k_c = k_f^{\phi} k_m^{(1-\phi)} \tag{1}$$

where k_m is the thermal conductivity of the matrix, k_f is the thermal conductivity of the filler, and ϕ is the volume fraction of the dispersed phase.

Maxwell–Eucken model

Using potential theory, Maxwell[10] obtained an exact solution for the conductivity of randomly distributed and noninteracting homogeneous spheres in a homogeneous medium:

$$k_c = \frac{2k_m + k_f + 2\phi_f(k_f - k_m)}{2k_m + k_f - 2\phi_f(k_f - k_m)} \times k_m \tag{2}$$

where ϕ_f is the volumetric fraction of the filler (Graphite) in the cured composites.

Cheng–Vachon model

In this model, the equivalent thermal conductivity of a two-phase solid mixture is derived in terms of the distribution function and the thermal conductivity of the constituents for $k_f > k_m$:

$$\frac{1}{k_c} = \frac{1}{\sqrt{C(k_f - k_m)[k_m + B(k_f - k_m)]}}$$
$$\times \ln \frac{\sqrt{(k_m + B(k_f - k_m))} + \frac{B}{2}\sqrt{C(k_f - k_m)}}{\sqrt{(k_m + B(k_f - k_m))} - \frac{B}{2}\sqrt{C(k_f - k_m)}} + \frac{1 - B}{k_m} \tag{3}$$

where $B = \sqrt{\frac{3\phi_f}{2}}$ and $C = -4\sqrt{\frac{2}{(3\phi_f)}}$.

Lewis–Nielsen model

Lewis and Nielsen derived a semitheoretical model by modifying the Halpin–Tsai equation[11] to include the effects of the shape of the particles and the orientation or type of packing for a two-phase system:

$$k_c = k_m \left[\frac{1 + AR\phi_f}{1 - R\phi_f\psi} \right] \tag{4}$$

where $R = \frac{(k_f/k_m)-1}{(k_f/k_m)+A}$, $\psi = 1 + ((1 - \varphi_m)/\varphi_m^2)\varphi_f$, ϕ_m is the maximum packing fraction of the disperse phase (for randomly distributed spherical particles, $\phi_m = 0.637$), and A is a constant depending on the shape and orientation of the disperse particles (for randomly distributed spherical particles, $A = 1.5$, whereas for randomly distributed aggregates of spherical particles, $A = 3$).

Agari–Uno equation

Agari and Uno[12] proposed a new model for filled polymers that takes into account parallel and series conduction mechanisms. According to this model, the expression that governs k_c is

$$\log k_c = \phi_f C_2 \log k_f + \left(1 - \phi_f\right) \log(C_1 k_m) \tag{5}$$

Parameters C_1 and C_2 are experimentally determined constants of order unity. C_1 is a measure of the effect of the particles on the secondary structure of the polymer, such as the crystallinity and crystal size of the polymer, whereas C_2 measures the ease with which the particles form conductive chains. The more easily particles are gathered to form conductive chains, the more the thermal conductivity of the particles contributes to changes in the thermal conductivity of the composite, and C_2 becomes closer to 1.

EXPERIMENTAL

Preparation

NBR [density = 0.98 g/cm^3; acrylonitrile content = 34%; Mooney viscosity ML(1+4) at 100°C = 45+5 (ASTM D 1646); average molecular weight = 163,376; glass temperature = −36°C], suspension-polymerized PVC in a powder form [density = 1.38 g/cm^3; K value (molecular mass) = 66–69; melting point = 80°C; glass temperature = 87°C], and the other compounding ingredients listed in Table I and used for preparing the blends were supplied by Transport and Engineering Co. (Alexandria, Egypt). Graphite powder from Merck Co. (Germany) with a bulk density of 20–30 g/100 mL and a particle size

TABLE I
Formulations of NBR, PVC, and NBR/PVC Blends Containing Different
Concentrations of Graphite (10, 20, 30, 40, 50, 60, and 70 phr)

Material	Pure PVC	Blends (phr)				Pure NBR
		NBR/PVC (30/70)	NBR/PVC (40/60)	NBR/PVC (50/50)	NBR/PVC (60/40)	
NBR	—	30	40	50	60	100
PVC	100	70	60	50	40	—
Graphite	—	0–70	—	—	—	—
Stearic acid[a]	—	0.6	0.8	1	1.2	2
Zinc oxide[a]	—	1.5	2	2.5	3	5
DOP[b]	—	X	X	X	X	15
MBTS[a]	—	0.45	0.6	0.75	0.9	1.5
TMTD[a]	—	0.15	0.2	0.25	0.3	0.5
PβN[a]	—	0.3	0.4	0.5	0.6	1.0
Sulfur[a]	—	0.6	0.8	1	1.2	2

[a] The ingredient concentrations (phr) are presented with respect to NBR.
[b] X means that the weight of DOP equals 50% of the weight of PVC.
DOP, dioctyl phthalate with a molecular weight of 390.75 g/mol was used as a plasticizer; TMTD, tetra methyl thiuram disulfide; Pβ, phenyl-β-naphthylamine were of chemically pure grade; MBTS, mercaptobenzothiazole (Vulkacit Merkapto produced by Bayer).

of less than 50 μm was used too. The formulations of the blends are shown in Table I. The blends were prepared on a conventional laboratory-size rubber mill with a diameter of 150 mm, a working distance of 300 mm, a slow roll speed of 18 rpm, and a gear ratio of 1.4. The mixing occurred for 40 min at 298 K, and it was left for 24 h before vulcanization. Crosslinked samples of the desired thickness were produced by compression molding at 425 K and about 0.4 MPa for 30 min in an electrically heated press (Karl Kolb, Germany).

Weight parts per hundred parts of rubber (phr) is a common unit used in the rubber industry and means that for each 100 g of rubber, a compound contains L grams of the filler. The following equation relates the phr value (L) to the volume fraction (V_f) for a compound:[13]

$$V_f = \frac{L\rho_m}{100\rho_f + L\rho_m}$$

where ρ_m and ρ_f are the matrix density and filler density, respectively.

Experimental measurements

Density measurement

The density balance was used to determine the volume percentage at room temperature of the composite samples studied for the thermal conductivity, specific heat capacity, and diffusivity measurements. Measurements were taken for disk-shaped samples with a 1-cm diameter and a 1-mm thickness with a Mettler–Toledo (Germany) AT61 delta range balance. According to Archimedes' principle, a body immersed in a liquid receives a pressure equal to

the displaced liquid. Therefore, if we know the density of the liquid, it is simple to calculate the volume of the sample and its specific mass. The density of the sample (ρ), which is the inverse of its specific volume, can be calculated as follows:

$$\rho = \frac{\rho_w p_a}{p_a - p_w}$$

where p_a and p_w are the sample weights in air and a liquid, respectively, and ρ_w is the density of distilled water.

Thermal conductivity, specific heat capacity, and diffusivity measurements

The samples for thermal measurements were cut into disk shapes with a 1-cm diameter and a 1-mm thickness. The thermal conductivity was evaluated with the laser flash thermal diffusivity method (LFTD; the technique was described by Gwaily et al.[7]). The LFTD method is based on the application of a high-intensity and short-duration heat pulse to one face of a parallel-sided test piece and the monitoring of the temperature increase on the opposite face as a function of time. The thermal diffusivity of the sample (α) is then calculated according to the following formula:

$$\alpha = 0.139 l^2 / t_{1/2}$$

where l is the thickness of the specimen and $t_{1/2}$ is the time from the initiation of the pulse until the rear face of the test sample reaches one-half of its maximum temperature. The LFTD method measures the thermal diffusivity and specific heat capacity of the sample. The thermal conductivity of the sample (k) is determined as follows:

TABLE II
Measured and Predicted Thermophysical Properties of the NBR/PVC Blends at 303 K

Sample		Thermal diffusivity ($\times 10^{-7}$ m^2/s)	Specific heat ($\times 10^3$ J kg^{-1} K^{-1})	Density (g/cm^3)	Thermal conductivity (W m^{-1} K^{-1})	Model-predicted values		
Blend	Blend ratio					Raylegh–Maxwell	Geometric mean	Agari–Uno
PVC	0/100	—	—	1.38	0.16	0.16	0.16	0.15
NBR/PVC	30/70	0.25	4.06	1.34	0.13	0.15	0.14	0.13
	40/60	0.22	4.23	1.24	0.12	0.14	0.13	0.12
	50/50	0.19	4.64	1.23	0.11	0.14	0.12	0.11
	60/40	0.16	5.28	1.21	0.10	0.13	0.12	0.10
NBR	100/0	—	—	0.98	0.09	0.10	0.09	0.09

$$k = \rho \alpha C_p$$

where C_p is the specific heat capacity and ρ is the density of the sample.

RESULTS AND DISCUSSION

Composition dependence of the thermophysical properties

According to the literature, the effective thermal conductivity of a composite or a blend depends on the conductivity of the individual components.[14] The thermal diffusivity, specific heat, and density measurements of NBR/PVC blends covering the whole range of possible compositions are presented in Table II. The experimental and theoretically predicted data (thermal conductivity) are also given in the same table. The results show that the addition of NBR to the PVC matrix induces a reduction of the effective thermal conductivity of the blend: from 0.16 W m^{-1} K^{-1} for the PVC matrix to 0.10 W m^{-1} K^{-1} for NBR/PVC (60/40). This can be explained by reference to the Debye equation:

$$k = (1/3)C \upsilon l$$

where C is the specific heat capacity per unit of volume, υ is the average phonon velocity, and l is the phonon mean free path. It is known that the phonon

free path of amorphous polymers is quite small. Thus, an increase in the distance of polymer chains via blending decreases the average phonon velocity of the polymer.[15] This reduction in the average phonon velocity gives the minimum thermal diffusivity and an increase in the specific heat capacity, resulting in a decrease in the thermal conductivity of the polymer.

Experimental data for the NBR/PVC blend system can be fitted to eqs. (1), (2), and (5). It has clearly been demonstrated that the predicted values of Eq. (5) basically agree well with the experimental data; the average deviation between the calculated and measured conductivities is 0.16% (Table II). The fitted parameters of Eq. (5) (C_1 and C_2) are of the order of unity [Table IV (shown later)]. According to our results, C_1 is close to 1, and this indicates that PVC particles have a strong effect on the secondary structure of NBR. C_2 measures the ease with which the particles form conductive chains; hence, the obtained C_2 value proves that it is very easy to form thermally conductive chains in NBR systems.

To explain the behavior of the effective thermal conductivity of a composite, we need the thermal conductivity values of its constituents, that is, the filler and the matrix. The results of our investigations of the thermophysical properties and the calculated thermal conductivity values for composites based on PVC/NBR (30/70) blends with graphite are presented in Table III. We note increasing thermal

TABLE III
Measured and Predicted Thermophysical Properties of Graphite-Filled NBR/PVC (30/70) Composites at 303 K

Graphite loading (phr)	Thermal diffusivity ($\times 10^{-7}$ m^2/s)	Specific heat ($\times 10^3$ J kg^{-1} K^{-1})	Density (g/cm^3)	Thermal conductivity (W m^{-1} K^{-1})	Model-predicted values			
					Maxwell–Eucken	Lewis–Nielsen	Agari–Uno	Cheng–Vachon
0	0.25	4.06	1.34	0.13	0.13	0.13	0.12	0.13
10	0.35	3.85	1.45	0.19	0.15	0.16	0.15	0.18
20	0.42	3.28	1.47	0.20	0.17	0.19	0.18	0.21
30	0.50	3.02	1.48	0.23	0.19	0.22	0.22	0.24
40	0.65	2.66	1.49	0.26	0.22	0.26	0.26	0.27
50	0.82	2.32	1.50	0.29	0.24	0.29	0.30	0.30
60	1.05	2.15	1.51	0.34	0.26	0.33	0.35	0.34
70	1.51	1.55	1.52	0.36	0.28	0.37	0.40	0.37

diffusivity values with the graphite content. This increase in the thermal diffusivity is foreseeable because the fillers have much higher thermal diffusivity than the polymer matrix. Moreover, the thermal diffusivity uncertainty is more significant at higher concentrations. The specific heat capacity of the composites decreases with increasing graphite content, With an increase in the graphite content, graphite particles touch one another and thus begin to form graphite conductive chains, which may connect one electrode to another. Thus, the thermal conductivity of PVC/NBR (30/70)/graphite composites increases with increasing graphite content. The thermal conductivity values obtained from the experimental study of graphite-filled PVC/NBR (30/70) blends have been compared with several thermal conductivity models. As shown in Table III, the experimental values and all the model values are close to one another at low particle contents ($\phi < 20$ phr), as the particles are dispersed in the polymer matrix and they are not interacting with one another. With particle contents greater than 20 phr, conductive chains are formed by graphite particles, and this causes a large increase in the effective thermal conductivity of the composite. The Cheng–Vachon [Eq. (3)] and Agari–Uno [eq. 5] model predictions of the thermal conductivity are more accurate in this region. In particular, the Agari–Uno model predicts quite well the thermal conductivity values of the composites for the whole range of particle contents. In the Agari–Uno model, the values of coefficients C_1 and C_2 are calculated with the linear regression equation of a plot of the logarithm of the thermal conductivity values from the experimental data versus the volume contents of the particles.

Overall, the average deviation between the calculated and measured conductivities is 1.75% (Table III). By fitting our experimental data to the Agari–Uno model, we have obtained a possible explanation for the state of the filler dispersion in our samples. It can be observed that the addition of graphite fillers to the PVC/NBR blend matrix will affect the C_2 value (0.49) more strongly than the C_1 value (0.92; Table IV). It has been reported that in the preparation of a composite, particles can affect the crystallinity and crystal size of the polymer and change the thermal conductivity of the polymer;[12] this is also the reason that C_1 was introduced. According to our results, C_1 is very close to 1, and this indicates that graphite fillers have little effect on the secondary structure of the PVC/NBR blends. C_2 is a factor of ease in forming conductive chains of particles, and the more easily particles are gathered to form conductive chains; the more the thermal conductivity of the particles contributes to changing the thermal conductivity of the composite. The obtained C_2 value proves that it is not very easy to form thermally con-

TABLE IV
Values of C_1 and C_2 in the Agari–Uno Equation

Material	C_1	C_2
PVC/NBR	0.92	1.11
PVC/NBR filled with graphite	0.92	0.49

ductive chains in graphite-filled PVC/NBR blend systems.

Temperature dependence of the thermophysical properties

The behavior of the thermal conductivity, thermal diffusivity, and specific heat capacity as a function of the temperature was studied for different blend ratios without a filler. Figure 1(a–c) shows the thermal diffusivity, thermal conductivity, and specific heat capacity of the NBR/PVC blends measured from 303 to 425 K. From these figures, we have found that, although the values of the thermal conductivity and thermal diffusivity decrease with increasing temperature, the value of the specific heat capacity increases. This can be explained by reference to the Debye equation.[11]

The thermal conductivity of a polymer above the glass-transition temperature is strongly affected by the average phonon velocity rather than the specific heat capacity.[16] It is thought that the thermal diffusivity decreases because the thermal diffusivity of an amorphous polymer is affected strongly by the decrease in the average phonon velocity and phonon mean free path. On the other hand, with the temperature increasing beyond the glass-transition temperature, according to the Debye equation [Eq. (1)], the distance of polymer chains increases, and the average phonon velocity decreases;[15] as a result, both the thermal conductivity and diffusivity decrease. The main difficulty here lies in the calculation of the mean free path. There exist two types of phenomena that determine the magnitude of the mean free path, namely, the interaction between phonons and the interaction of phonons with defects. As the temperature increases, the free volume increases. This leads to an increase in the mean distance between neighboring chains and, hence, to a increase in the elastic constants caused by the intermolecular interaction.[17] As a result, the thermal resistance is increased, so that both the thermal conductivity and thermal diffusivity decrease for all blends.

Figure 2(a–c) shows the thermal diffusivity, thermal conductivity, and specific heat capacity of NBR/PVC (30/70) blends loaded with different graphite contents from 303 to 425 K. These figures show that, although the values of the thermal conductivity and thermal diffusivity slightly linearly decrease with increasing temperature, the value of
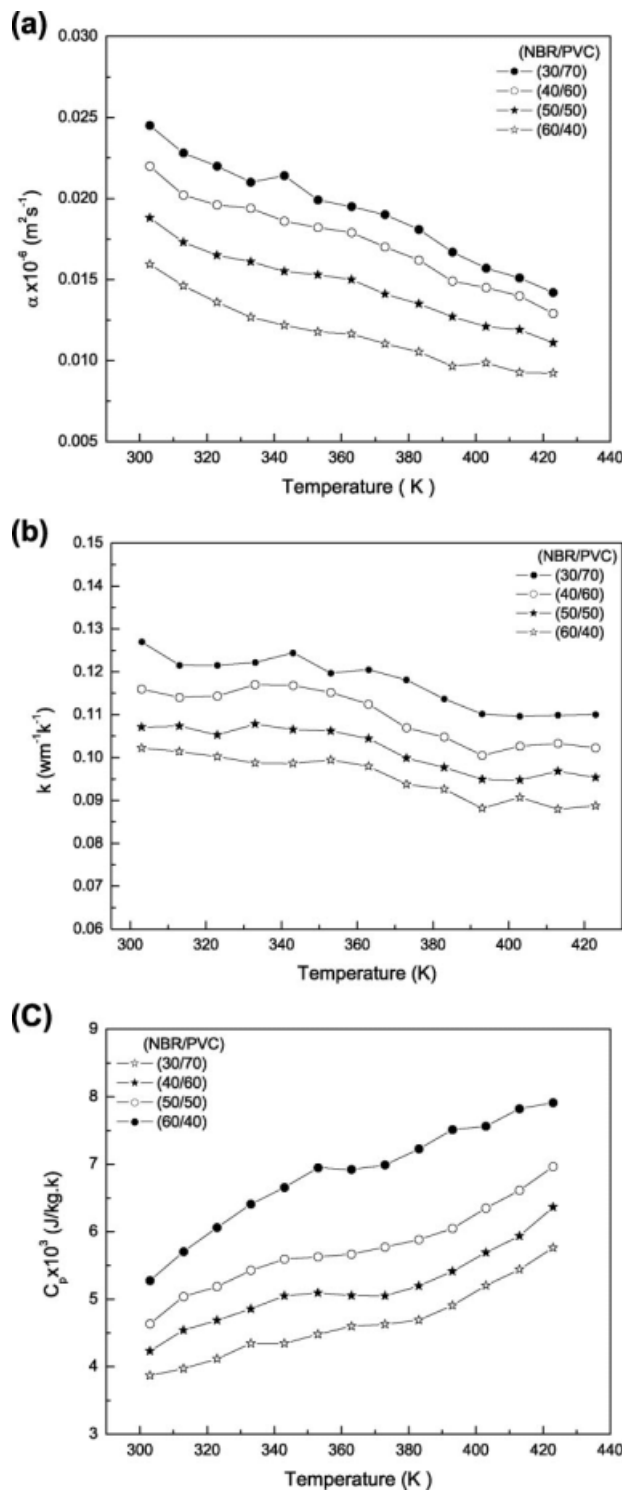
Figure 1 Temperature dependence of (a) the thermal diffusivity (α), (b) the thermal conductivity (k), and (c) the specific heat capacity (C_p) for NBR/PVC blends.

the specific heat capacity increases. Besides, the rate of the decrease of either the thermal conductivity or thermal diffusivity depends on the graphite concentration. With a low content of graphite (the dispersed system), the thermal conductivity values of composites change little with temperature. However,

a slight decrease can be observed. The reason is that the transmittance of thermal vibrations is somewhat disturbed when the distance of macromolecular lattices is widened because of thermal expansion of the polymer. With a high content of graphite (the attached system), the thermal conductivity of the
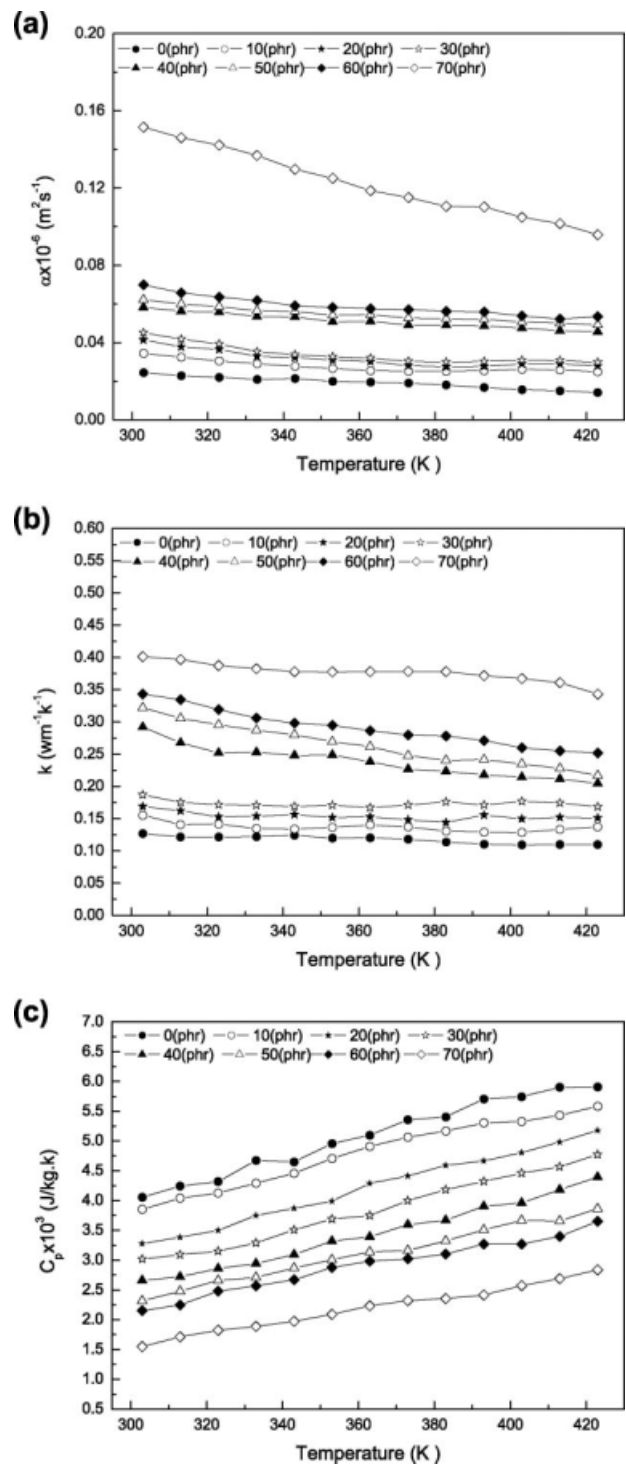

Figure 2 Temperature dependence of (a) the thermal diffusivity (α), (b) the thermal conductivity (k), and (c) the specific heat capacity (C_p) for NBR/PVC (30/70) blends loaded with different graphite contents.

composites decreases greatly. This is because the formed conductive chains are cut or shortened when thermal expansion of the polymer widens the distance between particles, whereas it reduces the thermal conductivity of the polymer itself. This phenomenon is analogous to the positive temperature coefficient phenomenon,[18] which occurs for the electrical conductivity of composites. Consequently, this phenomenon can be considered a positive temperature coefficient phenomenon in thermal resistance.

CONCLUSIONS

The basic characteristics of the thermophysical properties of NBR/PVC blends (thermal conductivity, thermal diffusivity, and heat capacity) vary monotonically with respect to the ratio of the blend components. The known two-phase Maxwell, geometric mean, and Agari–Uno models satisfactorily describe the experimental thermal conductivity of the blends. We have found that the Agari–Uno model predicts well the effective thermal conductivity values for the whole range of blend ratios. The incorporation of graphite into the NBR/PVC matrix improves its thermal properties. Some models proposed to predict the thermal conductivity of a composite in a two-phase system, such as the Maxwell–Eucken, Cheng–Vachon, Lewis–Nielsen, and Agari–Uno equations, have been applied to NBR/PVC (30/70) composites filled with graphite powder. However, according to the increasing trend of the thermal conductivity of those composites, we have found that the Agari–Uno model predicts quite well the thermal conductivity values of the composites for the whole

range of particle contents and basically agrees with the experimental data for the whole range of graphite contents. The effect of temperature (303–425 K) on the thermal properties (thermal conductivity, specific heat capacity, and thermal diffusivity) of these samples has been investigated, and it has been shown that these properties are slightly changed with the temperature.

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