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Study on thermally conductive ESBR vulcanizates

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Abstract The thermal conductivities of emulsion polymerized styrene-butadiene rubber (ESBR) vulcanizates filled with alumina (Al_2O_3), zinc oxide (ZnO), carbon nanotubes (CNTs), silicon carbide (SiC), are measured by steady-state method. The effects of types and loadings of the fillers and their mixture on thermal conductivities of the ESBR vulcanizates are investigated. The results show that the thermal conductivity of ESBR vulcanizates filled with alumina or zinc oxide, increases nearly linearly with increasing loading when the filler loading exceeded 20 phr; the ESBR vulcanizates filled with CNTs have the highest thermal conductivity at a given filler loading in comparison with other composite vulcanizates. At a given loading of 100 phr, the ESBR vulcanizate filled with two different particle sizes SiC of 1–3 and 5–11 μm at the mass ratio of 1:1 has the highest thermal conductivity and relatively good mechanical properties. The experimental results are analyzed using Geometric mean model and Agari's equation to explain the effect of filler types and particle sizes on the formation of thermal conductive networks. The thermal conductivity of the ESBR vulcanizates filled with Al_2O_3 or ZnO or CNTs could be well predicted by optimized parameters using Agari's equation for a polymer composite filled with mixtures of particles.

Keywords Carbon nanotubes · Emulsion polymerized styrene-butadiene rubber · Mechanical properties · Silicon carbide · Thermal properties

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Introduction

Automobile tires typically experience a significant heat build up as a result of heat produced by repeated deformation and the friction between ground and tires [1]. And a corresponding increase in operating temperature occurs as the tire is being worked. Heat build up in tire treads during the working under load can be rapid to thereby cause such tire treads to operate at relatively high temperature. This temperature increase can be so high that it can cause tyre destruction. For such tires, heat transfer of the tire tread is a factor for the longevity of the tire itself. Incorporation of thermal conductive fillers into such tire treads can increase their thermal conductivity, thus, tire tread region with high thermal conductivity can serve as a thermally conductive path for dissipation of heat from the tire, so enhances the service life of the tyre products [2].

Styrene-butadiene rubber (SBR) is widely used as passenger car tire tread, especially emulsion polymerized styrene-butadiene rubber (ESBR), because of its advantage over solution polymerized styrene-butadiene rubber (SSBR) in lowering cost of products [3]. But in many cases low thermal conductivities (about 0.2 W m^{-1} K^{-1}) restrict the application of ESBR [4]. So, it has important economic meaning to develope thermally conductive ESBR. However, only a few publications have concerned thermally conductive SBR so far. Fujii [5] obtained a rubber composition having a relatively high thermal conductivity by mixing styrene–butadiene–styrene block copolymer elastomer with a specified amount (such as 15 phr) of elastic graphite. Nano-zinc oxide/solution polymerized butadiene styrene rubber (SSBR) composites were prepared [6]. With increasing nano-zinc oxide loading, the thermal conductivity gradually increased, and the measured thermal conductivity was very close to the theoretical value calculated by Nielsen model. CNTs/SBR composites were prepared by spray drying method [7]. Thermal conductivities of the composites were gradually enhanced with the augment of CNTs addition. The measured thermal conductivities of the composites were less than theoretical predictions by Maxwell's and Lichtenecker equation. The influences of three types carbon black N330, N339, and N351 on the heat conductivity of radial tire tread (SBR/BR, 80/20) were investigated [8]. The heat conductivity of tread increased with the particle sizes of the same series black (N300) and quite linearly with the temperature. The heat conductivity of tread increased with the total levels of carbon black. Tang et al. [9] prepared heat conductive SBR composites by incorporation nano-alumina and micro-alumina. The thermal conductivity increased with increasing alumina amount. The SBR composites filled with nano-alumina had higher thermal conductivity than those filled with micro-alumina at the same loading; the SBR composites incorporated with hybrid micro-alumina and nano-alumina at certain ratio exhibited the highest thermal conductivity. The variation of thermal conductivity with temperature for silicone rubber-SBR blends was reported by Bhowmick et al. [10]. Polymers with high chain branching and heavy side groups played a predominant role in their thermal conductivity variation with temperature. The thermal conductivity of the blends increased with temperature and attained a peak value near the T_g of SBR and then decreased rapidly asymptotically to a value near room temperature. Thermal conductivity of SBR filled with lightly cross-linked natural rubber (NR) latex waste was measured in the temperature range of 100–300 K [11]. The thermal conductivity of SBR composites increased linearly with temperature to a peak value at a temperature within the glass transition region of SBR. With further increase of temperature the thermal conductivity decreased asymptotically to a constant value near 300 K. Overall, the experimental and theoretical work reported for the thermal conductivity of SBR is very limited, especially for that of ESBR. The change in thermal conductivity of ESBR after the introduction of thermally conductive filler is not very obvious as reported before in other rubber systems.

In this study, the thermal conductivity of ESBR vulcanizates filled with various inorganic fillers was investigated using steady-state method at room temperature. These fillers included silicon carbide (SiC), aluminum oxide (Al_2O_3), zinc oxide (ZnO), and carbon nanotubes (CNTs). Effect of the intrinsic thermal conductivity of the fillers, filler loadings, and filler sizes on the thermal conductivity of ESBR vulcanizates was investigated. Furthermore, to fabricate ESBR vulcanizates with high thermal conductivity, we attempted to maximize the abundance of thermally conducting paths by using mixed fillers consisting of different SiC particle sizes. Mechanical properties of filled ESBR vulcanizates were measured and analyzed. Finally, thermal conductivity of the ESBR vulcanizates was evaluated by Geometric mean model and Agari's equation.

Experimental

Materials

ESBR tire compound (a typical passenger tread compound filled with silica and carbon black N234) obtained from the second step of mixing process in mixer, was kindly provided by Hangzhou Zhongce Rubber Co., Ltd., China. SiC with two different particle sizes (Qingdao BMK international trading Co., Ltd, Shandong, China), Al_2O_3, ZnO (Sinopharm Chemical Reagent Shanghai Co., Ltd, Shanghai, China), Carbon nanotubes (Nanocyl s.a., Sambreville, Belgium) were used as conductive fillers. Other ingredients are analytically pure reagents. The physical properties of the matrix and fillers are listed in Table 1.

Sample preparation

The basic recipe of vulcanizated ESBR compositions: ESBR tire compound 171.5 (containing 100 phr ESBR); ZnO (zinc oxide) 1.20; antioxidant RD 0.24; accelerant D 0.57; accelerant DM 0.24; accelerant NS 1.70; oil-extended sulfur 1.85. The mixing of ESBR tire compound was carried out in an internal mixer using a two-stage mixing procedure and a batch size with a fill factor of 0.62. Polymer, silica, carbon black, and other ingredients (without curatives) were mixed for 4.5 min and dumped at a temperature of 150–160 °C. The silane coupling agent was added together with the filler during the first stage of the mixing in order to promote the interaction between the silane coupling agent and the filler during mixing. Then,

Table 1 Physical properties of the ESBR and conductive fillers

Material	Density ($g\ cm^{-3}$)	Diameter (μm)	Particle shape	Thermal conductivity ($W\ m^{-1}\ K^{-1}$)
Matix				
ESBR	0.93	–	–	0.2
Filler				
SiC 1#	3.15	1–3	Irregular	80
SiC 2#	3.15	5–11	Irregular	80
Al_2O_3	3.95	75–150	Irregular	10
CNTs[a]	1.30	0.004[b]/0.012[c]	Tubulous	2400
ZnO	5.61	45	Irregular	25

[a] Average length of CNT is 1.5 μm

[b] Average inner diameter of CNT

[c] Average outer diameter of CNT

ESBR tire compound, thermally conductive filler, and all of other ingredients including curatives were mixed on a laboratory-scale, 6 inch two-roll mill in the temperature range from 40 to 60 °C. Thermal specimens with size of 10.0 cm in diameter and 1.0 cm in thickness, and vulcanized ESBR sheets used for testing the mechanical properties with dimensions of $120 \times 60 \times 2\ mm^3$ were molded at 160 °C under a pressure of 10 MPa for 15 min.

Characterization

Thermal conductivity measurement

Thermal conductivities of ESBR vulcanizates were tested with a thermally conductive probe instrument YBF-3 (Hangzhou Dahua Instrument Manufacture Co., Ltd, Zhejiang, China) by the steady-state method [12–14]. Measurements were carried out with the thermal pads clamped between the two calorimeters. Then, two thermocouples were used to determine the respective temperature of the two blocks. When thermal equilibrium was achieved between the blocks and the specimen, the thermal conductivity of the specimen was calculated from the Fourier's law, as is shown in Eq. 1, based on the assumption that the heat flow is one-dimensional in the perpendicular direction, and no heat loss occurs in the lateral direction:

$$K = \frac{Qh}{A(T_{\mathrm{hot\_in}} - T_{\mathrm{hot\_out}})} \tag{1}$$

where K is the thermal conductivity of thermal pads ($W\ m^{-1}\ K^{-1}$), Q the heat flux generated by the thermal specimen, $T_{\mathrm{hot\_in}}$ the interface temperature of the heating calorimeter (K), $T_{\mathrm{cold\_out}}$ the interface temperature of the cooling calorimeter (K), A the surface area of tested thermal pads (m^2), and h the thickness of thermal pads (m). The average heat flux (Q) is the amount of heat generated by two cartridge heaters. When equilibrium is achieved, the heat flux of specimen is that of the cold block. If we measure the heat flux of the cold block at this time, Q can be obtained.

The measurements were mainly performed at 25 °C, for each specimen, the thermal conductivity was measured three times, and the average value was used for analysis.

Mechanical property measurement

Dumbbell-like specimens with dimensions of 2 × 4 × 20 mm^3 in the test part were punched out from the molded sheets. The tensile strength, moduli at 100 and 300% elongation and elongation at break of the samples were measured with a ZMGI 250 electric tensile instrument (Shenzhen SANS Material Test Instrument Co., Ltd., Shenzhen, China) at a crosshead speed of 500 mm min^{-1}.

Results and discussion

Thermal conductivity of ESBR vulcanizates

Effects of the intrinsic thermal conductivity and loading of fillers

Adding fillers with high intrinsic thermal conductivity is a common method for obtaining polymer composites with high thermal conductivity. Figure 1 showed a comparison of the thermal conductivity of ESBR vulcanizates with three different fillers: Al_2O_3, ZnO, and CNTs, as a function of the filler loading. The effects of these three kinds of fillers on the improvement of thermal conductivity for rubber matrix were different. At the same loading, ESBR vulcanizates filled with CNTs had the highest thermal conductivity. At low filler loading, the thermal conductivity of ESBR vulcanizates filled with alumina or zinc oxide increased slowly with increasing filler loading, and increased fast and nearly linearly with increasing alumina or zinc oxide loading when the filler loading exceeded 20 phr. These phenomena could be interpreted by the following reasons: in the dispersion system with low volume content of filler, few particles contributed to form conductive chains, and at this time the matrix polymer was almost continuous. Thus, the contribution of fillers to the thermal conductivity of a composite seemed to be less than that of the matrix, so that the ESBR vulcanizates showed low thermal conductivities. With increasing filler loading, many filler particles touched each other to form conductive chains, which greatly contributed to the thermal conductivities of ESBR vulcanizates. The thermal conductivity of ESBR vulcanizates filled with ZnO was lower than that of the ESBR vulcanizates filled with Al_2O_3 when the filler loading exceeded 20 phr. This might be attributed to the higher density of ZnO than that of Al_2O_3, thus the volume fraction of ZnO was smaller than that of Al_2O_3 at a given loading, and that the ease for the formation of thermally conductive chains of the two vulcanizates filled with ZnO and Al_2O_3 was different.

Effects of the intrinsic thermal conductivity and particle sizes of fillers

Thermal conductivities of ESBR vulcanizates filled with different types and different particle sizes of the fillers were indicated in Fig. 2. At the same filler loading (100 phr), the thermal conductivity of ESBR vulcanizates were in the order

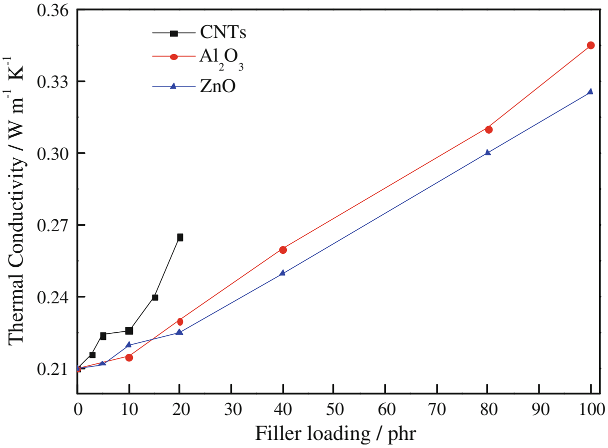

Fig. 1 Comparison of the thermal conductivity of ESBR vulcanizates filled with different fillers as a function of filler loading

of SiC 2# > SiC 1# > Al_2O_3 > ZnO > Control (without filling thermally conductive fillers). Thermal conductivity of SiC is higher than that of Al_2O_3. At the same loading, ESBR vulcanizates filled with the two fillers showed same sequence as SiC > Al_2O_3. This can be explained by the differences in the thermal conductivity of the two fillers. Although, thermal conductivity of ZnO is higher than that of Al_2O_3, at the same loading, thermal conductivity of ESBR vulcanizates filled with the two fillers show sequence as Al_2O_3 > ZnO. This means that intrinsic thermal conductivity is not the only governing factor. As seen in Fig. 2, thermal conductivity of ESBR vulcanizate filled with large-size SiC particles is higher than that of ESBR vulcanizate filled with small-size SiC particles at the same loading. This behavior could be attributed to the larger filler particle sizes, the fewer thermally resistant junctions, which reduced the interfacial phonon scattering between the ESBR matrix and fillers, and the more easy to form thermally conductive chains among filler particles, which led to higher thermal conductivity of the ESBR vulcanizates [15].

Effects of the particle sizes and loading of filler

Thermal conductivities of ESBR vulcanizates filled with SiC of two different particle sizes at two different loadings are indicated in Fig. 3. When SiC of a single particle size was used, thermal conductivity of ESBR vulcanizate filled with large particle sizes was higher than that of ESBR vulcanizates filled with small particle sizes at the same loading. It could be attributed to the larger size of SiC particles increased the chance of forming thermally conductive chains among filler particles, which may help to improve the heat transferring and decrease the thermal resistance, leading to higher thermal conductivity of the ESBR vulcanizates [15–17].

For a polymer filled with particles, many bulk properties, such as the modulus and dielectric constant, change according to the particle size distribution. In highly filled polymers, the effect of the particle sizes on the bulk property of polymers can

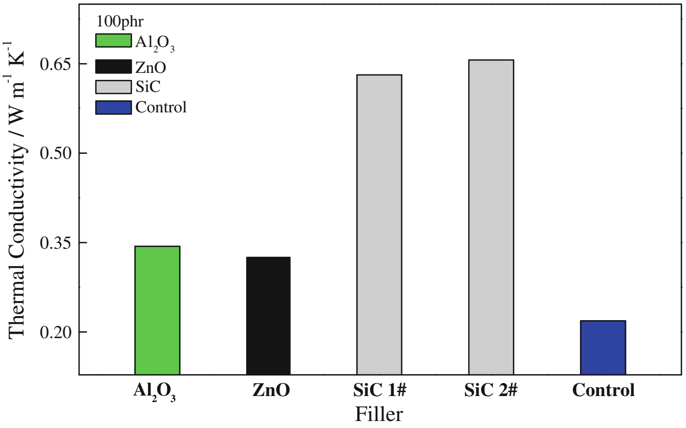

Fig. 2 The thermal conductivity of ESBR vulcanizates filled with different fillers and different particle sizes of the fillers

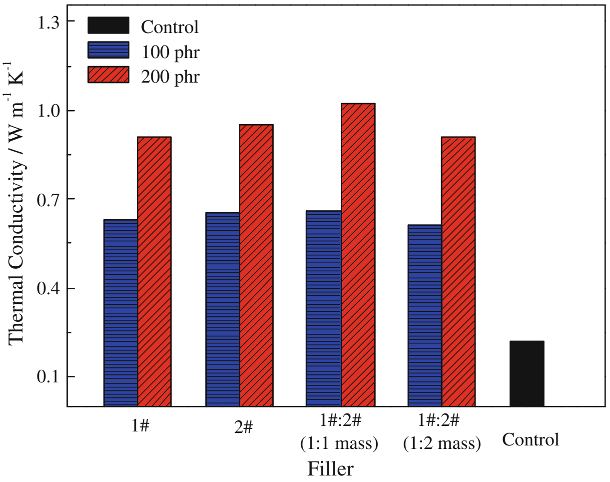

Fig. 3 The thermal conductivity of ESBR vulcanizates filled with different particle sizes of SiC at different loading. (1# the diameter of SiC particle is 1–3 μm; 2# the diameter of SiC particle is 5–11 μm.)

be explained by the maximum packing fraction (Φ_m; real volume of the filler/apparent volume of the filler), and Φ_m will change as the particle sizes of filler vary. A general approach for obtaining a high packing fraction is to use small size particles to fill in the pores in the packed structure obtained from large-size particles. When two kinds (even more kinds) of fillers with different sizes are packed closely enough, Φ_m can reach a maximum, and some of the bulk properties of the polymer will also reach some extreme value [15, 18]. The ESBR vulcanizates incorporated with a mixture SiC of the two different particle sizes (1–3 μm; 5–11 μm) exhibited different results compared with the case in which a filler with a single particle size was used. At the given loadings of 100 and 200 phr, the ESBR vulcanizates incorporated with a mixture SiC of two different particle sizes at the mass ratio of 1:1 (SiC 1#:SiC 2#), had the highest thermal conductivity among all the ESBR vulcanizates, however, the ESBR vulcanizates with a mixture SiC at the mass ratio of 1:2 (SiC 1#:SiC 2#) had the lowest thermal conductivity. At loading of 100 phr, the thermal conductivity of ESBR vulcanizate filled with the mixed fillers at the mass ratio of 1:1 reached 0.661 W m^{-1} K^{-1}, which increased by 200.5% over that of ESBR without filling thermally conductive filler; at loading of 200 phr, reached 1.02 W m^{-1} K^{-1}, which is the highest among that of all the ESBR vulcanizates and increased by 363.6%. From Fig. 3, the thermal conductivity, as one of the ESBR's bulk properties, changed as the particle sizes varied. It can be concluded that it is the optimum particle sizes ratio and quantities that made the filler packing closer, which thus led to formation of more thermally conductive chains. So, we can get equal thermal conductivity with lower loading of mixed fillers at a preferable mass ratio, or with higher loading of a single size of fillers.

Comparison of thermal conductivity measured with theoretical predictions

The measurement of thermal conductivity of ESBR vulcanizates in the laboratory is often time consuming and necessitates very precise instrumentation. Prediction models of the thermal conductivity are thus particularly useful. At this point, it is of value to evaluate the ability to predict the thermal conductivity of ESBR vulcanizates of two of the most used models: Geometric mean model and Agari's equation [16, 17, 19, 20].

Geometric mean model

The geometric mean model for multiphase systems can be given as following [16]:

$$k_\mathrm{c} = k^{\phi_m} k_1^{\phi_1} k_2^{\phi_2} \ldots k_n^{\phi_n} = k^{\phi_m} \prod_{i=1}^{n} k_i^{\phi_i} \tag{2}$$

where m indicates the continuous phase or matrix, n is the total number of dispersed phase or additives, k_i and Φ_i represent the thermal conductivity and volume fraction of the i component, respectively, so that $\Phi_m + \Phi_1 + \Phi_2 + \ldots + \Phi_n = 1$. Based on Eq. 2, one can calculate the thermal conductivity of the composite if volume fraction and thermal conductivity of each component are known.

Agari's model

Agari et al. proposed a new thermal conduction model for a polymer system filled with a mixture of several types of particles [19, 20]. The following equation is derived from the new model:

$$\log k_\mathrm{c} = V(X_2 C_2 \log k_2 + X_3 C_3 \log k_3 + \ldots) + (1 - V)\log(C_1 k_1) \tag{3}$$

where k_1, k_2, k_3, … are the thermal conductivities of polymer and particles; X_2, X_3, … are mixing ratios of particles, and V is the volume content of particles. 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 [17, 20]. The more easily the 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.

For ESBR vulcanizates filled with three types filler (CNTs, Al_2O_3, and ZnO), the comparison of experimentally determined thermal conductivities with those predicted from geometric mean model and Agari's equation was shown in Fig. 4. Geometric mean model tended to overestimate thermal conductivity of the ESBR vulcanizates as the cases in Fig. 4(a–c). Especially, for ESBR vulcanizates filled with CNTs, the thermal conductivity predicted from geometric mean model was much higher than that measured from experiment. It should be attributed to the curvature, twist, and aggregation of CNTs which can result in decreasing the thermal conductivity of CNTs, and the decrease of the amount of thermally conducting paths because of the existence of solitary CNT coated by ESBR matrix [21, 22]. The reason for the deviations is probably that geometric mean model did not take into account the state of filler dispersion in the ESBR vulcanizates.

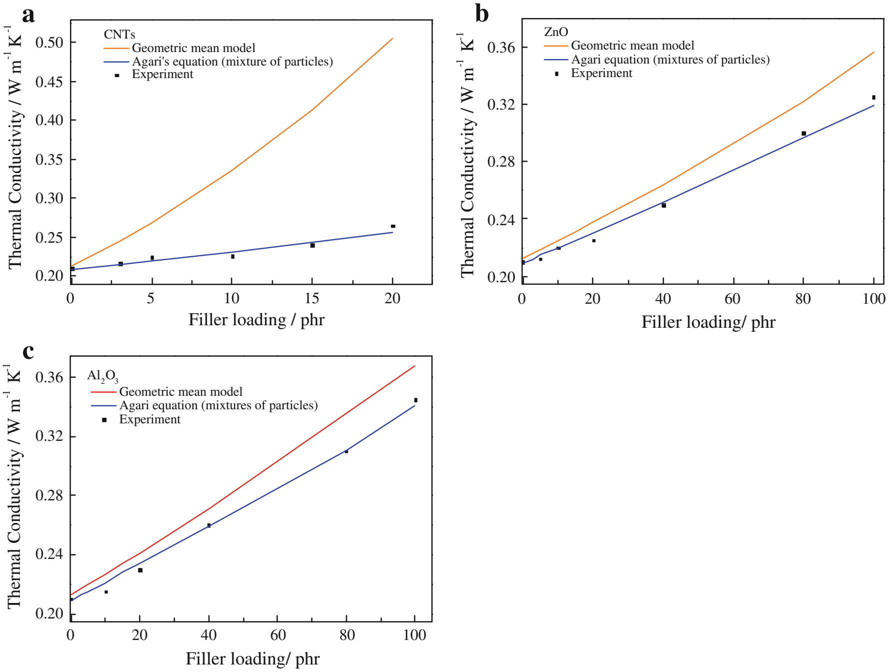

Fig. 4 **a** Comparison of thermal conductivity of CNTs filled ESBR vulcanizates with theoretical predictions. **b** Comparison of thermal conductivity of ZnO filled ESBR with theoretical predictions. **c** Comparison of thermal conductivity of Al_2O_3 filled ESBR with theoretical predictions

Table 2 Values of C_1 and C_2 obtained form Agari's equation through data fitting

Parameters	Filler		
	A_2lO_3	ZnO	CNTs
C_1	0.895	0.895	0.895
C_2	0.801	0.552	0.440

So, geometric mean model was not suitable for simulating the conductivities of ESBR vulcanizates. From Fig. 4(a–c), experimental values were well fitted into the Agari's equation (for mixture of particles of multi-component systems) at the loading level from 0 to 100 phr. A possible explanation is that the ease for the formation of conductive chains and the crystallinity and crystal size of the ESBR matrix were taken into account in the Agari's equation. Therefore, Agari's equation (for mixture of particles of multi-component systems) was suitable for the ESBR vulcanizates. By fitting our experimental data into the Agari's equation, a possible explanation of the state of filler dispersion in the ESBR could be obtained. Coefficients C_1 and C_2 in Agari's equation were obtained by the fitting of Eq. 3 to the experimental data, and they are shown in Table 2. It can be observed that the addition of ZnO, Al_2O_3, CNTs, SiC into the ESBR vulcanizates will affect the C_2 value (Al_2O_3 0.801; ZnO 0.522; CNTs 0.440) more strongly than the C_1 value ($\approx$0.895, for three different fillers, which agreed with ESBR's noncrystal structure). It has been reported that in the preparation of a composite, particles can affect crystallinity and crystal size of the polymer and change the thermal conductivity of the polymer [20]. According to our results, C_1 value is nearly constant, indicating that three fillers have little effect on the secondary structure of the ESBR vulcanizates. The reason is probably that ESBR is an amorphous polymer. C_2 is a factor of ease in forming thermally conductive chains of particles, and the more easily the particles are gathered to form conductive chains, the more the thermal conductivity of particles contributes to increase that of composite. The obtained C_2 value indicated that the factor of ease in forming thermally conductive chains in the ESBR vulcanizates was in the order of $Al_2O_3 > ZnO > CNTs$, which agreed with the results discussed earlier.

Effects of filler type and loading on mechanical properties of ESBR vulcanizates

The mechanical properties of the ESBR vulcanizates filled with SiC of different particle sizes were shown in Table 3. The tensile strength and elongation at break of ESBR vulcanizates decreased with increasing SiC loading, while the moduli at 100 and 300% elongation increased. The moduli at 100 and 300% of ESBR vulcanizate filled with small SiC particle sizes were higher than that of ESBR vulcanizate filled with large SiC particle sizes at the same loading. The reason is that the thermally conductive filler SiC used as a kind of reinforcing filler is not ideal, which can only increase moduli at 100 and 300%, because of the decrease of the interparticle distance and plastic deformation of ESBR matrix entrapped within SiC clusters with increasing SiC loading. The smaller SiC particles resulted in the more obvious

Table 3 Mechnical properties of ESBR vulcanizates filled with different particle sizes of SiC at different loading

Sample	Modulus at 100% (MPa)	Modulus at 300% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Thermal conductivity (W m^{-1} $K)^{-1}$)
SiC 1# 100 phr	5.04	12.3	13.6	366	0.632
SiC 2# 100 phr	3.52	8.37	13.0	427	0.655
1#:2# (1:1)100 phr	4.58	11.7	13.2	376	0.661
1#:2# (1:2) 100 phr	4.35	10.6	13.8	399	0.613
SiC 1# 200 phr	9.48	–	11.5	204	0.911
SiC 2# 200 phr	5.57	8.08	8.5	312	0.952
1#:2# (1:1) 200 phr	7.19	–	9.39	269	1.02
1#:2# (1:2) 200 phr	6.43	–	9.24	281	0.907
Control	2.49	11.6	20.6	466	0.22

decrease of the interparticle distance and plastic deformation of ESBR matrix entrapped within SiC clusters, thus the moduli at 100 and 300% increased. The tensile strength and elongation at break decreased for the poor interfacial interaction between SiC and ESBR matrix and the poor dispersion of SiC particles at high loadings. Breakage was prone to occur in the portions where SiC particles aggregation occurred, due to weak interfacial adhesion between them. Especially, at the given loading of 200 phr, the elongation at break decreased greatly, which is very important for ESBR vulcanizates and will lead to the lose of their useful value. Overall, at a given loading of 100 phr, ESBR vulcanizate filled with mixed fillers of SiC 1# and SiC 2# at the mass ratio of 1:1 had the highest thermal conductivity and relatively good mechanical properties.

Mechanical properties of ESBR vulcanizates filled with three types fillers: CNTs, ZnO, and Al_2O_3 having different particles sizes (CNTs 12 nm; ZnO 45 μm; and Al_2O_3 75–150 μm) at different loading were investigated as shown in Fig. 5. Incorporation of CNTs in ESBR vulcanizates led to a pronounced increase in tensile strength and moduli at 100 and 300% when the filler loading was not more than 5 phr (Fig. 5a–c). It might be attributed to the characteristics of the small nano particles, such as, higher rigidity than ESBR matrix, high specific surface area, and thus sufficient particle–matrix interaction. It is generally known that the presence of strong Van der Waals forces between the smaller size particles would limit its dispersion capability and would result in production of agglomerates of particles in the matrix. Fillers with smaller particles size will agglomerate at lower particles loading than that with bigger particles [23]. So, the decrease of elongation at break of the ESBR filled with CNTs with increasing filler loading above 5 phr implied that the dispersion of CNTs in the ESBR matrix was not very homogenous. When the CNTs particles exceeded the optimal loading, the main interaction became between particles while not between particle and ESBR matrix, causing a change of the mechanical properties. Above the optimal filler loading, the particles started to form clusters bigger in size than the voids. These clusters acted as surface defects

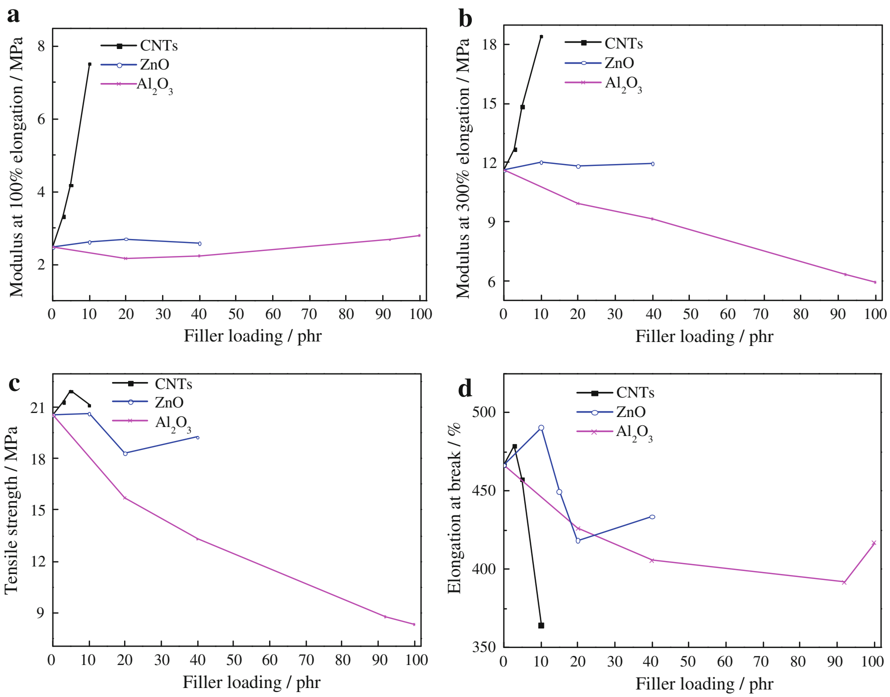

Fig. 5 **a** Modulus at 100% of ESBR vulcanizates filled with three different fillers as a function of filler loading. **b** Modulus at 300% of ESBR vulcanizates filled with three different fillers as a function of filler loading. **c** Tensile strength of ESBR vulcanizates filled with three different fillers as a function of filler loading. **d** Elongation at break of ESBR vulcanizates filled with three different fillers as a function of the filler loading

responsible for losing the high mechanical properties. Mechanical properties of ESBR vulcanizates filled with ZnO had slight change, which might be attributed to the bigger particle sizes of ZnO compared to CNTs. It was worth noting that the tensile strength of ESBR filled with Al_2O_3 decreased with increasing filler loading, implying that Al_2O_3 has hardly reinforcement to ESBR. It was possibly due to the following reasons: the Al_2O_3 particles were so large that the molecular chain of ESBR matrix could not wind on their surface, resulting in the lack of sufficient particle–matrix interaction. Breakage was prone to occur in the portions where Al_2O_3 particles aggregation occurred, due to weak interfacial adhesion between them, thus the mechanical properties became worse.

Conclusion

Thermally conductive ESBR vulcanizates filled fillers with different types, loading, and particle sizes were prepared. The thermal conductivity of ESBR vulcanizates filled with alumina or zinc oxide, increased nearly linearly with increasing filler loading when the filler loading exceeded 20 phr. The ESBR vulcanizates filled with

CNTs had highest thermal conductivity at a given loading. The thermal conductivity of ESBR vulcanizates filled with large SiC particle sizes was higher than that of ESBR vulcanizates filled with small SiC particle sizes due to the fewer thermally resistant junctions, which reduced the interfacial phonon scattering. At a given loading (100 phr), ESBR filled with mixed fillers of 1–3 μm SiC and 5–11 μm SiC at the mass ratio of 1:1 had the highest thermal conductivity (0.661 W m^{-1} K^{-1}) and relatively good mechanical properties. Compared with geometric mean model, Agari's equation is more suitable for fitting the experimental data. The thermal conductivity of ESBR filled with Al_2O_3 or ZnO or CNTs could be well predicted by optimized parameters using Agari's equation for a polymer composite filled with mixtures of particles.

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References

1. Zhang S (1988) Mechanics and energetics of tyres (in Chinese). Chemical Industry Press, Beijing
2. Spadone LR, Sandstrom PH (2005) Tire with tread of rubber composition containing diverse carbon blacks. EP 1,557,294, US
3. Marwede GW (1993) Current status of tire elastomers in Europe. Kautsch Gummi Kunstst 46:380–388
4. Medalia A (1991) Heat generation in elastomer compounds: causes and effects. Rubb Chem Technol 64:481–491
5. Fujii M (1990) Rubber compositions containing elastic graphite. JP 02 292344, Japan
6. Fan L, Liu L, Zhang L (2009) Study on thermal conductivity of nano-zinc oxide/SSBR composite (in Chinese). China Rubber Ind 56:207–211
7. Zhou X, Zhu Y, Song P, Liu C, Xiong G, Ji L, Dong J, Yu S (2009) Thermal properties of carbon nanotubes/styrene-butadiene rubber composites (in Chinese). Polym Mater Sci Eng 25:62–65
8. Ma L, Cui Q, Zhang F, He Y, Gao F (2007) Influence of carbon black on heat conductivity of radial tire tread (in Chinese). China Rubber Ind 54:76–79
9. Tang M, Rong M, Ma C, Zhang M, Ye J (2003) Effect of surface treatment and particle size of alumina filler on thermal conductivity of SBR (in Chinese). China Synth Rubber Ind 26:104–107
10. Bhowmick T, Gupta BR, Pattanayak S (1992) Thermal conductivity and thermal diffusivity of silicone–poly(styrene butadiene) rubber blends from 60 to 300 K. Cryogenics 32:623–627
11. Saxena NS, Pradeep P, Mathew G, Thomas S, Gustafsson M, Gustafsson SE (1999) Thermal conductivity of styrene butadiene rubber compounds with natural rubber prophylactics waste as filler. Eur Polym J 35:1687–1693
12. Tan JC, Tsipas SA, Golosnoy IO, Curran JA, Paul S, Clyne TWA (2006) A steady-state bi-substrate technique for measurement of the thermal conductivity of ceramic coatings. Surf Coat Technol 201:1414–1420
13. Curran JA, Clyne TW (2005) The thermal conductivity of plasma electrolytic oxide coatings on aluminium and magnesium. Surf Coat Technol 199:177–183
14. Schroder J (1963) Apparatus for determining the thermal conductivity of solids in the temperature range from 20 to 200 °C. Rev Sci Instru 34:615–621
15. Lee GW, Park M, Kim J, Lee J, Yoon H (2006) Enhanced thermal conductivity of polymer composites filled with hybrid filler. Compos Part A 37:727–734
16. Shojaei A (2007) Thermally conductive rubber-based composite friction materials for railroad brakes—thermal conduction characteristics. Compos Sci Technol 67:2665–2674
17. Mansour SA, Al-Ghoury ME, Shalaan E, El Eraki MHI, Abdel-Bary EM (2010) Thermal properties of graphite-loaded nitrile rubber/poly(vinyl chloride) blends. J Appl Polym Sci 116:3171–3177
18. Nielson LE (1970) Generalized equation for the elastic moduli of composite materials. J Appl Phys 41:4626–4627

19. Agari Y, Tanaka M, Nagai S, Uno T (1987) Thermal conductivity of a polymer composite filled with mixtures of particles. J Appl Polym Sci 34:1429–1437
20. Agari Y, Uno T (1986) A simple model for thermal conductivity of carbon nanotube-based composites. J Appl Polym Sci 32:5705–5712
21. Nan CW, Shi Z, Lin Y (2003) A simple model for thermal conductivity of carbon nanotube-based composites. Chem Phys Lett 375:666–669
22. Yang DJ, Zhang Q, Chen G, Yoon SF, Ahn J, Wang SG, Zhou Q, Wang Q, Li JQ (2002) Thermal conductivity of multiwalled carbon nanotubes. Phys Rev B 66:165440–165445
23. Al-Turaif HA (2010) Effect of nano TiO_2 particle size on mechanical properties of cured epoxy resin. Prog Org Coat 69:241–246