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Effects of carbonaceous conductive fillers on electrical and thermal properties of asphalt-matrix conductive composites

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Abstract: The relationship between thermal/electrical conductivity enhancement in asphalt-matrix mixtures and the properties of filling conductive particles is studied. The thermal properties with filling the carbon fiber, graphite conductive particles in asphalt-matrix mixtures are investigated. Based on the generalized effective medium theory (EMT), the effective thermal and electrical conductivity of carbon fiber/asphalt and graphite/asphalt composites are theoretically elucidated. The theoretical results are found to be in reasonably well agreement with the experimental data. Moreover, the theoretical and experimental results show that the large-aspect-ratio shape of particles can help to achieve a large enhancement of effective conductivity, and the use of disk-like high conductivity particles can limit the additive contents for preserving the volumetric properties and mechanical properties of asphalt composites. The generalized effective medium theory model can be used for predicting the thermal and electrical properties of asphalt-matrix composites, which is still available for most of the thermal/electrical modifications in two-phase composites.

Key words: carbonaceous conductive fillers; asphalt-matrix composites; thermal conductivity; electrical conductivity

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Asphalt, a class of complex mixtures, has been a valuable material because it is readily adhesive, waterproof and durable. Asphalt-matrix materials are composites, in which thermal or mechanical functional materials are dispersed in asphalt (or aggregates)[1−6]. Taking account of the advantages from asphalt and functional materials, asphalt-based materials have been widely applied on highway pavements, bridge decks, airport roads and so on[7−8].

Mixing carbonaceous conductive fillers (such as carbon fiber, graphite and carbon black) in asphalt has attracted great interest recently because of their enhanced thermal, electrical and mechanical properties. For thermal properties, graphite powder (9.0% in volume fraction) dispersed in matrix asphalt to enhance the thermal conductivity of asphalt-based materials were reported to increase the softening temperature from 45 to 82 ℃[9]. For electrical properties enhancement, it is theoretically feasible to melt and remove snow or ice on asphalt pavement. Especially, the modification of carbonaceous conductive fillers on asphalt pavement is expected to become the most efficient, convenient, and environmentally protective method to remove snow and ice[10]. Recent experimental studies have also shown that the thermal/electrical conductivity of the asphalt concrete is proportional to the volume fraction of carbonaceous conductive fillers[11−12]. However, the increase in the additive contents without limit will decrease the volumetric properties and mechanical properties of the asphalt pavement. The relationship between the thermal/electrical conductivity enhancement and the properties of filling conductive particles requires quantitative study of heat/electricity transfer processes in asphalt-matrix mixtures.

1 Experiment

In this paper, we study the effects of graphite and carbon fiber powder additives on the thermal conductivity modification in asphalt-matrix mixtures. By taking into account the shape and volume fraction of filling materials, we would like to generalize the Bruggeman effective medium theory[13−14] to investigate the effective thermal conductivity and electrical conductivity in asphalt-matrix conductive composites. Our theoretical predication on the effective thermal and electrical conductivity of asphalt-matrix conductive composites is in good agreement with the experimental results. Furthermore, our model can also elucidate the non-zero percolation threshold for the electrical transport process.

Asphalt (AH-70) was obtained from Wuxi Road Department, Jiangsu, China. In order to investigate the

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effects of particle shape on the electrical and thermal properties of asphalt-matrix conductive composites, we chose graphite (spherical-like) and carbon fiber (large aspect ratio) as conductive fillers. The graphite was obtained from Xingtai Graphite Ore Factory in Hebei province, China. Its particle size is less than 150 μm, and the mass fractions of carbon, ash and icon are 98.9%, 0.2% and 0.03%, respectively. The carbon fiber was supplied by An Shan Eastern Asia Carbon Fiber Co. Ltd., in China. The diameter and average length are 10 and 5 mm, respectively. The electrical resistivity is 10^{-3} Ω · cm.

Asphalt was heated to (150 ± 5) °C in an oil-bath heating container until it flowed fully. In order to investigate the effective thermal properties of the asphalt-based mixture, the carbon fiber particles and graphite powders of 1%, 3%, 5%, 7%, 9%, 11%, 13%, 15%, 17%, 20% in volume fraction were chosen. Then the carbon fiber particles and graphite powders were filled into the heated asphalt and operated under a high rotation speed for about 20 min to ensure the well dispersion of the additive filling particles in the asphalt-matrix. The thermal conductivity of the asphalt-based mixture was measured by the use of a thermal testing device (ZKY-BRDR).

2 Results and Discussion

In the course of understanding the electrical (thermal) transport behavior of the asphalt-matrix mixture, we would like to generalize the Bruggeman effective medium theory[13-14] to investigate the effective thermal conductivity and electrical conductivity in asphalt-matrix conductive composites. We consider that the carbonaceous conductive fillers composites in which the carbon fiber or the graphite particles with the volume fraction f and the asphalt-matrix with conductivity K_m are randomly mixed. For simplicity, we assume that the asphalt-matrix particles and the graphite particles are spherical, while the carbon fiber conductive particles are spheroidal in shape with radii a, b, c, and $b = c$. For the good dispersion of additive filling particles in the asphalt-matrix, we operate the composites under a high rotation speed for about 20 min. So, the effective conductivity of the asphalt-matrix containing carbonaceous conductive fillers is isotropic[15-16]. For such an asphalt-matrix composite, the effective medium theory (EMT) gives[14]

$$9(1-f)\frac{K_e - K_m}{2K_e + K_m} + f\sum_{j=x,y,z}\frac{K_e - K_{c,j}}{K_e + L_j(K_{c,j} - K_e)} = 0 \quad (1)$$

where $K_{c,j}$ is the equivalent thermal (or electric) conductivity along the j-axis, and the depolarization factor L_j depends on the carbonaceous conductive fillers aspect ratio $p = a/c$, which is expressed as

$$L_z = \begin{cases} \frac{1}{2p^3}\left(-2p + e\ln\frac{e-p}{e+p}\right) & \text{if } e > 1 \\ \frac{1}{2q^3}\left(2q - e\pi + 2e\arctan\frac{e}{q}\right) & \text{if } e > 1 \end{cases} \quad (2)$$

where $L_z[L_x \equiv (1 - L_z)/2]$ is the depolarization factor of spheroidal particles (z denotes the rotational axis); e is the eccentricity; $p = \sqrt{e^2 - 1}$, and $q = \sqrt{1 - e^2}$.

For the thermal transport of asphalt-matrix composites, due to the thermal resistance, the carbonaceous conductive fillers are physically anisotropic[15,17]. Considering the interfacial effects, in the thermal transportation we always assume that the carbonaceous conductive fillers are coated with a layer. The thickness and conductivity of the layer are δ and K_s, respectively. Without loss of generality, the interfacial thermal resistance is assumed to be concentrated on a surface of zero thickness defined as $R_{Bd} = \lim_{\delta\to 0, K_s\to 0}(\delta/K_s)$.

Hence, one has $K_{c,j} = K_p/(1 + QR_{Bd}L_jK_p)$ with $Q = (2a + c)/(ac)$. As a result, Eq. (1) is simplified as

$$9(1-f)\frac{K_e - K_m}{2K_e + K_m} + f\left[\frac{K_e - K_p}{K_e + L_z(K_p - K_e)} + 4\frac{K_e - K_p}{2K_e + (1 - L_z)(K_p - K_e)}\right] = 0 \quad (3)$$

For the electrical transport of asphalt-matrix composites, the interfacial resistance is so small that it can be ignored[17], i. e. $R_{Bd} = 0$. Therefore, we shall substitute $K_{c,j} = K_p$ into Eq. (3) in the electrical transportation of asphalt-matrix composites. Note that Eq. (3) can predict the very low percolation thresholds in self-monitoring asphalt-matrix composites.

Fig. 1 shows the effective thermal conductivity of asphalt matrix composites with filling carbon fiber particles and graphite powders of 1%, 3%, 5%, 7%, 9%, 11%, 13%, 15%, 17%, 20% in volume fraction, respectively. We find that the effective thermal conductivity enhancement of carbon fiber/asphalt composites is greater than that of the graphite/asphalt composites at the same additive volume fraction. This may be due to the difference of particle shape and the thermal properties of the filling particles. To further verify the validity of our theory, we make a comparison between Eq. (3) and our measured experimental data in Fig. 1. For numerical calculations, the thermal conductivity of carbon fiber, grap-

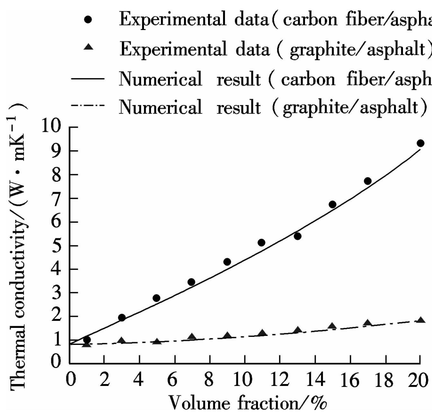

Fig. 1 Effective thermal conductivity of asphalt-matrix composites compared with our numerical results

hite particles, asphalt matrix are taken as 120, 50 and 0.8 W/mK, respectively. The aspect ratio of carbon fiber, graphite particles, asphalt matrix are taken as 500, 3 and 1, respectively[18-19]. The contact thermal resistance is taken as $R_{Bd} = 1.5 \times 10^{-9}$ m^2 · K/W. This estimated R_{Bd} used in our calculation is of the same magnitude as that in the asphalt-matrix composites[19-20]. Our theoretical results are found to be in reasonably good agreement with the experimental data.

The addition of carbonaceous conductive fillers to the conventional asphalt mixture can produce asphalt concrete with excellent electrical performance, which is expected to be used due to its electro-thermal behavior as an efficient method to melt and remove snow or ice on pavements, bridge decks and airport runways. A sudden change of electrical conductivity occurs in asphalt-matrix composites at a very low critical additive volume fraction. The low critical additive volume fraction is called the percolation threshold[10]. Fig. 2 shows the calculation for carbon fiber/asphalt, graphite/asphalt composites[10]. In the calculation, the electric conductivities of asphalt, graphite and carbon fiber are taken as 1×10^{-12}, 1×10^4 and 1×10^3 S/m, respectively[10]. The aspect ratios of graphite and carbon fiber are taken as 3 and 500. We can see that the theoretical results are in good agreement with the experimental data[10]. For carbon fiber/asphalt and graphite/asphalt composites, the percolation threshold f_c is estimated as 5% and 12%, respectively. Such percolation threshold values are of the same order as those reported in experimental study[10].

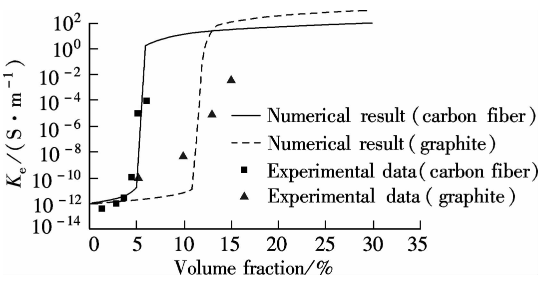

Fig. 2 Enhancement of effective electrical conductivity compared with numerical results

Now we are looking at the dependence of K_e on the shape of filling conductive particles. Fig. 3 shows the results ($f = 0.05$, $K_p/K_m = 1\ 000$). We can conclude that for both oblate ($P < 1$) and prolate ($P > 1$) particles, K_e/K_m increases significantly with an increase in the geometric anisotropy. It can be well understood that when filling conductive inclusions with a large aspect ratio (prolate) or a small aspect ratio (oblate), it is helpful to form a path for heat flow through the composites. For instance, carbon fiber (prolate) produces a long uninterrupted conductive path and tends to easily contact with each other to form a conductive network. As a result, the conductivity enhancement of filling particles with a disk-like shape ($P \to 0$) may be greater than those with a needle-like shape ($P \to \infty$). It indicates that the use of disk-shaped conductive inclusion may be helpful to realize the effective conductivity enhancement. Previous researches have shown that additive contents that increase without limit will decrease the volumetric properties and mechanical properties of the asphalt pavement [10-12, 19]. We suggest that choosing suitable shapes of filling conductive particles such as disk-like high conductivity particles can limit the additive contents.

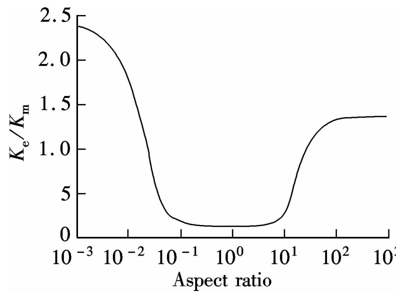

Fig. 3 K_e/K_m as a function of aspect ratio

We further study the dependence of effective thermal conductivity on the conductivity ratio K_p/K_m in Fig. 4. Obviously, filling oblate-shaped conductive particles can achieve higher thermal conductivity enhancement than filling prolate or spherical inclusions. The enhancement of effective thermal conductivity K_e/K_m increases with the increase in the ratio of K_p/K_m. As a result, the thermal conductivity and the shape of the constituents play key roles in the enhancement of the effective thermal conductivity.

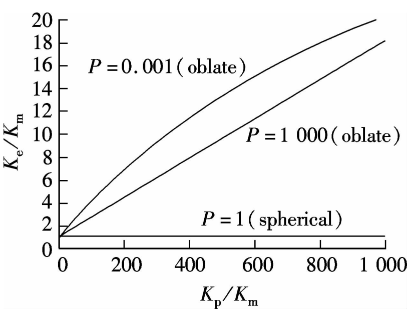

Fig. 4 K_e/K_m vs. K_p/K_m

3 Conclusion

In this paper, we investigate the thermal conductivity modification of the carbon fiber/asphalt and graphite/asphalt composites. We find that the effective thermal conductivity enhancement of the carbon fiber/asphalt composites is greater than the graphite/asphalt composites with the same additive volume fraction. Based on the generalized EMT, we theoretically elucidate the effective thermal and electrical conductivity of carbon fiber/asphalt and graphite/asphalt composites. Our theoretical results are found to be in reasonably good agreement with the experimental data. A particular point is that our model can describe the value of the percolation threshold for the electrical transport process in conductive asphalt composites. Moreover, we predict that the disc-shaped conductive particles can give a great thermal conductivity enhancement.

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碳质传导颗粒对沥青基传导复合物的电、热性质影响

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摘要:研究了传导沥青基混合物的电、热传输性质的增强与添加的传导颗粒热导率、电导率的关系. 分析了碳纤维、石墨传导颗粒对沥青基质的热导率改性效果. 根据改进的有效媒质理论,研究了碳纤维/沥青、石墨/沥青混合物的有效热导率和电导率. 理论计算与实验数据吻合. 此外,理论及实验计算结果显示:使用颗粒纵横比大的传导颗粒可以获得更大的传导增强;使用盘状的高传导颗粒可以限制添加量,进而保证沥青基质的体性质和机械性质. 改进的有效媒质理论模型不仅可以使用于预测沥青基复合介质的电、热性质,而且适用于所有两相复合体系.

关键词:碳质传导颗粒;沥青基复合物;热导率;电导率

中图分类号:O472.2