Optimization and design of pigments for heat-insulating coatings

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This paper reports that heat insulating property of infrared reflective coatings is obtained through the use of pigments which diffuse near-infrared thermal radiation. Suitable structure and size distribution of pigments would attain maximum diffuse infrared radiation and reduce the pigment volume concentration required. The optimum structure and size range of pigments for reflective infrared coatings are studied by using Kubelka–Munk theory, Mie model and independent scattering approximation. Taking titania particle as the pigment embedded in an inorganic coating, the computational results show that core-shell particles present excellent scattering ability, more so than solid and hollow spherical particles. The optimum radius range of core-shell particles is around $0.3 \sim 1.6$ μm. Furthermore, the influence of shell thickness on optical parameters of the coating is also obvious and the optimal thickness of shell is 100–300 nm.

Keywords: coating, engineering ceramics, scattering, pigments

PACC: 7820D, 4225F

1. Introduction

The effects of pigments of heat-insulating coatings have attracted much attention since the fabrication of heat insulating or cooling coatings[1−3] due to their excellent light scattering property. Heat-insulating coatings have various applications, such as architectural surfaces, battleship hulls, pigmental polymer foils, satellite panels, high temperature protecting materials[4−13] etc.

A good understanding of light scattering and absorption by small particles in media is of importance in selecting kind, structure and size distribution of pigments. Light scattering from pigmental particles dispersed in coatings can be described by radiative transfer theory. The well-known approximate approach of radiation propagation theory in coatings is Kubelka–Munk (KM) theory. The main parameters in KM model are scattering coefficient and absorption coefficient. Vargas and Maheu *et al.*[14−19] provided average pathlength parameters (APP) and forward scattering ratios (FSR) for establishing the relation between those coefficients of the coatings and the parameter of a single particle. Lastly, scattering model and solution of single particle are provided by Bohren *et al.*[20]

Based on the above theories, scholars try to attain maximum heat insulating property of pigmental coatings.[21] Johnson *et al.*[22] studied the grain size distribution of zinc oxide pigment in a thermal control coatings used for spacecraft walls. Baneshi *et al.*[23] optimized pigmental coatings considering both thermal and aesthetic effects. Moreover, Jaenicke *et al.*[24] developed an empirical formula which can be used to estimate suitable particle size of pigments for infrared reflecting coatings.

Unfortunately, those studies mainly deal with the scattering property of solid spherical particles and optimize its size distribution for given coatings. Selecting mechanism of pigments for heat-insulating coatings is not achieved comprehensively and systematically. Systematic theoretical work that can be used to select pigments kind, size and structure is greatly needed. Furthermore, those studies are concerned only with maximizing solar reflectance in the near infrared region (780–2500 nm). Practically, thermal radiation energy emitted from a heat source in the temperature from 300 K to 1000 K has a broad-wavelength range spectrum (mainly in 0.75–10 μm). Infrared radiation of broad-wavelength range should be insulated by inorganic coatings used in high-temperature environment because the thermal radiation energy is

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important at high temperature.[25,26] So, pigments should have excellent scattering property in a broad-wavelength range for a wide range of industrial applications.

This paper aims to optimize the kinds, structure and size of pigments for heat-insulating coatings. Different kinds and structures of pigments scattering properties are studied by using KM theory and Mie theory. To solid and hollow spherical pigments, particles size range in the coatings for effectively insulating radiative heat transfer is optimized by using Mie theory. Similarly, the size range and thickness of shell of core-shell structural pigments are also optimized. Finally, we compared scattering properties of spherical pigments with core-shell structural pigments.

The rest of this paper is organized as follows. In Section 2 we make use of the radiative transfer and Mie scattering theories to establish computational models. The details of results are presented in Section 3. Finally, Section 4 gives the conclusions.

2. Computational models

2.1. Radiative transfer model in a coating layer

Rigorous solutions of radiative heat transfer equations lead to mathematical and computational challenges. The KM theory gives an approximate approach which bases on the concept of radiation exchange between different flux channels in the coating. We consider a coating layer, as shown in Fig. 1. The thickness of the coating is z_0. We assume that the area of the coating is so large that we can ignore the edge effect. According to the conditions of KM theory, we also assume that the light is perfectly diffused and the dependent scattering is dismissed.

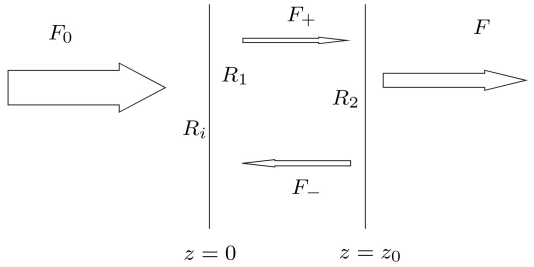


Fig. 1. Heat radiation fluxes transmitting a coating of thickness z_0. Where R_i denotes the external diffuse reflectance at the front interface and R_1 is the internal diffuse reflectance at the same location, namely, $z=0$, R_2 denotes the diffuse reflectance at the back interface, $z=z_0$.

The radiative transfer in the coating layer can be described in terms of the two-flux model of Kubelka and Munk. The radiative transfer equations can be written as two different equations:[20]

$$\begin{cases} \dfrac{\mathrm{d}F_+}{\mathrm{d}z} = -(K+S)F_+ + SF_-, \\ \dfrac{\mathrm{d}F_-}{\mathrm{d}z} = (K+S)F_- - SF_+, \end{cases} \tag{1}$$

where F_+ and F_- are positive and negative diffuse radiation flux, respectively. The K and S are the absorption coefficient and backscattering coefficient within the layer, respectively.

Maheu, Vagas and Niklasson introduced the average pathlength parameter (APP) to describe the light propagation property through single-scattering. The absorption coefficient K and backscattering coefficient S can be expressed as[14–19]

$$K = \xi\rho C_{\mathrm{abs}}, \quad S = \xi\rho(1-\sigma_{\mathrm{c}})C_{\mathrm{sca}}, \tag{2}$$

where ξ is the APP, ρ is the number density of the pigment particles, σ_{c} is the forward scattering ratio, C_{abs} is the absorption cross section of single particle respectively, and C_{sca} is the scattering cross section of single particle.

The light is diffuse and isotropic in coating layer according to KM theory. In this case, APP is equal to 2. The absorption coefficient K and backscattering coefficient S are changed to

$$K = 2\rho C_{\mathrm{abs}}, \quad S = 2\rho(1-\sigma_{\mathrm{c}})C_{\mathrm{sca}}. \tag{3}$$

Or

$$K = 2\rho C_{\mathrm{abs}} = \frac{3f}{2a}Q_{\mathrm{abs}}, \quad S = \frac{3f(1-\sigma_{\mathrm{c}})Q_{\mathrm{sca}}}{2a}, \tag{4}$$

where Q_{abs}, Q_{sca} and σ_{c} will be determined by Mie theory, a is the radius of particle, f denotes the volume fraction of the particles.

2.2. Mie scattering model

According to Mie theory, the extinction efficiency of a sphere is written as[19,27]

$$Q_{\mathrm{ext}} = \frac{C_{\mathrm{ext}}}{\pi a^2} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)\mathrm{Re}(a_n+b_n). \tag{5}$$

And the scattering efficiency is

$$Q_{\mathrm{sca}} = \frac{C_{\mathrm{sca}}}{\pi a^2} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)(|a_n|^2+|b_n|^2). \tag{6}$$

The absorption efficiency is written as

$$Q_{\mathrm{abs}} = Q_{\mathrm{ext}} - Q_{\mathrm{sca}}, \tag{7}$$

where $x = 2\pi a/\lambda$ is the size parameter of the particle (λ is the wavelength in vacuum). The coefficients of the scattering functions a_n and b_n can be expressed as[20]

$$\begin{cases} a_n = \dfrac{m\psi_n(mx)\psi_n'(x) - \psi_n(x)\psi_n'(mx)}{\psi_n(mx)\zeta_n'(x) - \zeta_n(x)\psi_n'(mx)}, \\ b_n = \dfrac{\psi_n(mx)\psi_n'(x) - m\psi_n(x)\psi_n'(mx)}{\psi_n(mx)\zeta_n'(x) - m\zeta_n(x)\psi_n'(mx)}, \end{cases} \tag{8}$$

where ψ_n and ζ_n are the Riccati–Bessel functions and m is the refractive index of the particle relative to the coating substrate, i.e., $m = m_1/m_2$ (where m_1 and m_2 are the refractive indices of the particle and the substrate).

Calculation of scattering coefficient and absorption coefficient of core-shell structure pigments also needs the above equation. However, the coefficients of the scattering functions are different from spherical pigments and can be expressed as[28,29]

$$a_n^{\rm cs} = \frac{\psi_n(y)[\psi_n'(m_2y) - A_n\chi_n'(m_2y)] - m_2\psi_n(m_2y)[\psi_n(m_2y) - A_n\chi_n(m_2y)]}{\xi_n(y)[\psi_n'(m_2y) - A_n\chi_n'(m_2y)] - m_2\xi_n'(y)[\psi_n(m_2y) - A_n\chi_n(m_2y)]}, \tag{9a}$$

$$b_n^{\rm cs} = \frac{m_2\psi_n(y)[\psi_n'(m_2y) - B_n\chi_n'(m_2y)] - \psi_n'(y)[\psi_n(m_2y) - B_n\chi_n(m_2y)]}{m_2\xi_n(y)[\psi_n'(m_2y) - B_n\chi_n'(m_2y)] - \xi_n'(y)[\psi_n(m_2y) - B_n\chi_n(m_2y)]}, \tag{9b}$$

$$A_n = \frac{m_2\psi_n(m_2x)\psi_n'(m_1x) - m_1\psi_n'(m_2x)\psi_n(m_1x)}{m_2\chi_n(m_2x)\psi_n'(m_1x) - m_1\chi_n'(m_1x)_n\psi_n(m_1x)}, \tag{9c}$$

$$B_n = \frac{m_2\psi_n(m_1x)\psi_n'(m_2x) - m_1\psi_n(m_2x)\psi_n'(m_1x)}{m_2\chi_n'(m_2x)\psi_n(m_1x) - m_1\psi_n'(m_1x)\chi_n(m_2x)}, \tag{9d}$$

where $x = ka$, $y = kb$ (a is the radius of core, b is the radius of core-shell sphere), $k = 2\pi m_3/\lambda$ is the wave number in media 3, $\chi_n(z)$ is the Riccati–Bessel function, and $\chi_n(z) = -zy_n(z)$ ($y_n(z)$ is spherical Neuman function).

3. Results and discussion

Thermal infrared reflecting coatings are designed to reflect infrared radiation. In these coatings, inorganic or metal pigments are the principal active ingredients which reflect thermal infrared radiation strongly. Common inorganic pigments were used for those coatings and their refractive indexes are shown in Table 1.

Table 1. Common inorganic pigments refractive indexes.

pigments	refractive index
TiO_2	2.8
SiC	2.6
Ta_2O_5	2.50
Fe_2O_5	2.35
ZrO_2	2.10
CaO	1.84
Al_2O_3	1.70
SiO_2	1.54

Titanium dioxide is the most important commercial pigment used in thermal infrared reflecting coatings. It is widely used because it efficiently scatters infrared light due to high refractive index, thereby imparting whiteness, brightness and opacity when incorporated in a coating. Crystalline titanium dioxide most commonly occurs in one of two crystal structures: anatase and rutile. Rutile titanium dioxide pigments are preferred because they scatter light more efficiently, and are more stable and durable than anatase pigments.

We choose titanium dioxide as the pigment and sample the wavelengths in a 0.75–10 μm window. Silica is chosen as the medium for the coatings due to its low refractive index and high temperature resistance. Within our computation we set $f = 0.05$. Scattering properties of different structural pigments were studied by using above models, including solid spherical titania, SiO_2@TiO_2 core-shell particle and hollow spherical titania.

Scattering coefficients of spherical titanium dioxide particle as a function of infrared wavelength for selected radii are computed and plotted in Fig. 2. From this plot, the general trend in greater scattering efficiency on wavelength for smaller particle diameter is clearly evident. For all diameters, the shape of the S value distribution curve tends to be lognormal with respect to wavelength.

The highest scattering coefficient (0.20 μm^{-1}) of 0.3 μm particle occurs at the wavelength of 1 μm. At larger radius, the highest scattering coefficient is smaller than smaller radius, with the highest scattering coefficient occurring at longer wavelength. It is quite evident from the plot that there is an optimal radius of particle for the highest scattering coefficient of selected wavelengths. Namely, if we want to scatter infrared radiation effectively from 0.75 μm to 10 μm wavelength range, optimal particle size distribution is needed.

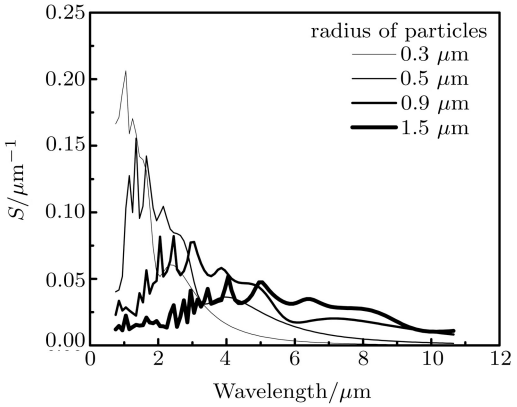


Fig. 2. Scattering coefficients of solid spherical TiO_2 particles as a function of wavelength for selected radii.

For convenience, the relationships between the highest scattering coefficient, corresponding radius of particle and wavelength are plotted in Fig. 3. As indicated in this figure, infrared radiation from 0.75 μm to 10 μm wavelength range is most effectively scattered by solid spherical TiO_2 particle for radii ranging from 0.2 μm to 3 μm. In addition, the highest scattering coefficients become smaller at longer wavelength from 0.34 μm^{-1} to 0.02 μm^{-1}.

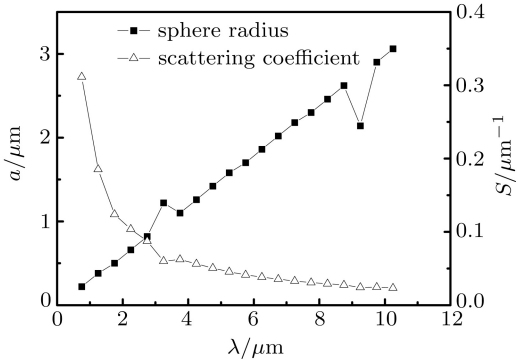


Fig. 3. The maximum scattering coefficient and corresponding radius of solid spherical TiO_2 particle at corresponding wavelength.

Similar results can be obtained from empirical formula for solid spherical particle such that effectively scattering longer wavelength of infrared radiation needs a larger particle. However, the optimum size distribution is 0.4–4.5 μm from empirical formula, which is larger than our predicted value. Most importantly, the empirical formula is not competent for predicting size range of complex structural particles, such as core-shell and hollow particles, etc.

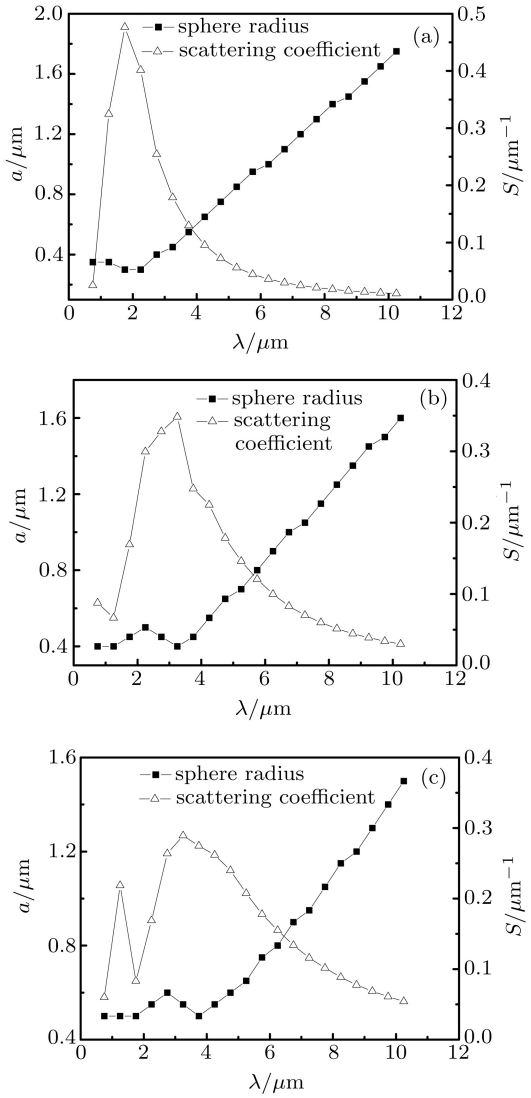


Fig. 4. The maximum scattering coefficient and corresponding radius of SiO_2@TiO_2 core-shell particles for selected wavelength. The shell thicknesses of titania particle were (a) 100 nm, (b) 200 nm and (c) 300 nm.

Core-shell or hollow particles were expected to hold enhanced light scattering properties for a difference in the refractive index between the shell and the internal core. For core-shell titanium dioxide particles with different shell thicknesses, the maximum value of scattering coefficient and corresponding radius as a function of wavelength are plotted in Fig. 4. As seen from the figure, the optimal size distribution is

presented in a nearly linearly increasing manner and the maximum value of scattering coefficient does not monotonously increase and there is a peak on the curve. As illustrated in Figs. 4(a), 4(b) and 4(c), it is clear that the maximum value of scattering coefficient is large when wavelength is short (less than 6 μm), and the value is small at long wave band (greater than 6 μm).

The computational results show that scattering coefficients of core-shell TiO_2 pigments are larger than solid spherical pigments when wavelength is shorter than 6 μm. In addition, optimal size range of core-shell particles is from 0.2–1.8 μm which is smaller than solid spherical particles.

The influence of shell thickness on scattering ability of the coatings is provided in Fig. 4. As the thickness increases, the value becomes larger at the long wave band. At the same time, the size range becomes narrow and the largest size is 1.55 μm when the thickness of shell is 300 nm. Thus, core-shell pigmental coatings just need smaller size particles for the most effectively scattering ability.

Like core-shell pigments, hollow spherical pigments present similar scattering properties, including the maximum value of scattering coefficients and size range which are plotted in Fig. 5. From Fig. 5, it is shown that the maximum scattering coefficient decreases with thickness of hollow particle's shell at short wavelength (less than 6 μm) and increases at longer wavelength (greater than 6 μm).

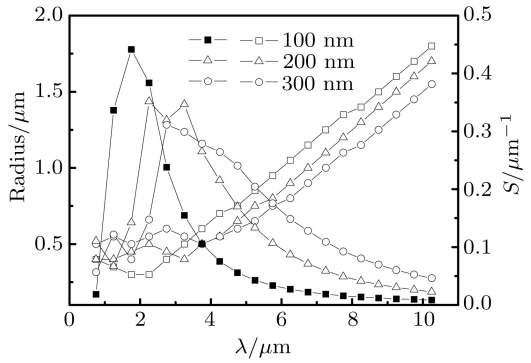


Fig. 5. Optimal radius and the maximum scattering coefficient of hollow spherical TiO_2 particle for different shell thicknesses at selected wavelength. The thicknesses of shell are 100 nm, 200 nm and 300 nm, respectively.

The general trends in optimal size distribution and scattering coefficients for hollow particles are similar to core-shell particles. Also, the influence of shell thickness of hollow spherical particles on scattering ability is similar to core-shell particles. Additionally, after a careful observation, scattering coefficients are slightly smaller than core-shell particles. Therefore, core-shell structure is the optimal structure of pigment for heat-insulating coatings.

4. Conclusions

The scattering of light by pigment particles embedded in a coating matrix should be studied to optimize particle size and structure of pigments in order to obtain the most efficient scattering mechanism. The KM theory and Mie model were used to investigate optical properties of pigmental coatings and predict optimal size distribution and structure of pigments conveniently.

Within the independent scattering approximation, different structural titanium dioxide particles are chosen as pigments to constitute a reflective infrared coating, and the optimized structure and size range are computed by using Mie theory. Scattering ability of core-shell titanium dioxide pigment whose size range is from 0.3 μm–1.6 μm is more excellent than solid spherical and hollow spherical titanium dioxide pigments. Moreover, shell thickness of core-shell titania particle also influences optical properties of the coating and the optimal thickness of shell is 100–300 nm.

The scattering coefficients of other inorganic materials as pigment particles with high refractive index can be predicted similarly by using the above theories, for example ZrO_2, SiC, etc. So, the model can be used in the coating industry conveniently to characterize pigment performance and as a tool in predictive size distribution and structure of particles.

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