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Synthesis and characterization of nanostructured poly(methyl methacrylate) for antireflection coating

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ABSTRACT

Single layer coatings were prepared with poly(methyl methacrylate)/polystyrene nanoparticles blend by spin-coating, demonstrating excellent antireflection performance after selective removal of polystyrene particles. The thickness, refractive indices and surface roughness of the coatings, which significantly affect their optical performance, can be modulated by the coating conditions. The particle size can be well controlled by the operational conditions for the particle synthesis. The surface microscopic roughness of the coating strongly affects its light transmittance and the dimensionless parameter, roughness/wavelength ratio, dominates the deviation of the real transmittance from the theoretically predicted transmittance. By optimizing the reaction and the film preparation conditions, the transmittance of antireflection coatings can be up to 99.17% in the visible light range. Compared with work previously reported in the literature, the transmittance in the visible light range can be significantly improved via surface roughness modification, which was generally a problem, especially at the short wavelength region.

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1. Introduction

Antireflective coatings, which were firstly prepared by Joseph von Fraunhofer via an acid etching method in 1817 [1], are used to reduce or eliminate light reflection on the substrate surface. Antireflective coatings have shown promising properties when integrated into applications such as solar cells [2,3], display panels [4], lenses [5], and windows [6]. Many types of antireflective coatings have been developed, including single-layer coatings, V-coatings and multilayer coatings. The mechanism of antireflection involves the interference between the light reflected on the air-coating interface and coating-substrate interface. For the single-layer film antireflection, two parameters are crucial [1]: (1) the light amplitude reflected at both interfaces should be equal which requires $n_e = \sqrt{n_0 n_s}$, where n_e, n_0, and n_s represent refractive indices of the coating, air and the substrate involved, respectively; and (2) the thickness of the coating should satisfy $n_e d = ((2k+1)\lambda)/4$, where d is the thickness of the coating, k is any positive integer ($k = 1, 2, 3, \ldots$), and λ is the wavelength of the incident light. If both conditions are satisfied, zero reflection can be theoretically achieved. The second condition is not difficult to meet since the coating film thickness can be controlled precisely with quite a few advanced techniques, such as physical/chemical vapor deposition [7,8] and spin-coating [9,10]. For the first condition, the refractive index (RI) of the coating is required to be approximately 1.23 when a glass or plastic material ($n_s \approx 1.5$) is used as the substrate. However, the refractive indices of most inorganic materials are higher than 1.38 (the known inorganic substance with the lowest RI is MgF_2, which is 1.38 [11]) and the RI of organic materials are around 1.30–1.60 (the known substance with the lowest RI is poly(hexafluoropropylene oxide), which is about 1.30 [12]). Therefore these materials cannot be directly used for the single layer antireflection coating. It was reported that the introduction of nanopores into homogeneous films can decrease its apparent RI effectively [13], and various methods have been used to create nanopores in coatings, such as the sol-gel method [5], polymer/solvent/nonsolvent ternary coatings [14,15], sponge-like block copolymer coatings [16,17], layer-by-layer-assembly method for gradient refractive indices [18,19], moth's eye structure coatings [20], inorganic hollow particles coatings [21,22], and other coatings such as those fabricated by photo-curable polymers [23].

There have been a few reports on making antireflective coatings from latex particles [24,25], but how the operating conditions affect the antireflective properties of polymer-based coatings is still not well understood. The antireflection properties of various materials for short-wavelength visible lights were always found poor, and a few studies have been rendered a perspective that microscopic

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surface roughness might affect the coating optical properties prepared by porous polymer [21,26]; however, no study has been done to reveal the effect of the surface roughness of a coating on the transmittance loss.

In this study, emulsion polymerization method was applied to prepare poly(methyl methacrylate) (PMMA) and polystyrene (PS) latex particles, and nanoparticles with various sizes were prepared by adjusting the polymerization conditions. Antireflective coatings were then prepared by spin-coating on poly(methyl methacrylate) substrates with blended nanoparticles, and the porous structures were formed by cyclohexane etching. The anti-reflective properties of the resulted coatings were studied under various operating conditions, and the relationship between surface roughness and transmittance loss with a mathematical model was studied.

2. Experiment

2.1. Materials

Methyl methacrylate (MMA) (CP grade, Sinopharm Chemical Reagent Co. Ltd China), styrene (St) (CP grade, Sinopharm Chemical Reagent Co. Ltd China), ethyleneglycol dimethacrylant (EGDMA) (>98%, Aladdin Chemistry Co. Ltd), potassium persulfate (KPS) (AR grade, Sinopharm Chemical Reagent Co., Ltd. China), sodium dodecyl sulfate (SDS) (≥86% purity, Sinopharm Chemical Reagent Co Ltd. China), cyclohexane (CP grade, Sinopharm Chemical Reagent Co., Ltd. China) and PMMA sheet (Hangzhou Gude Art and Craft Co. Ltd China) were used as received.

2.2. Synthesis of PMMA and PS latex

PMMA and PS latex were synthesized via emulsion polymerization with potassium persulfate (KPS) as the initiator, and sodium dodecyl sulfate (SDS) as the surfactant. KPS/monomer ratio by weight was 0.2%. In PMMA preparations, ethyleneglycol dimethacrylate (EGDMA) was used as the crosslinking agent with a weight concentration of 6% relative to MMA. The temperature range investigated was 78–82 °C, and the reactions were carried out in a four-necked flask (250 ml) equipped with a condenser, a thermometer, a mechanical stirrer and a constant pressure dropping funnel. Several monomer addition methods were investigated in this study, which included batch, semi-batch and seeded semi-batch methods. In the batch operation, after deionized water and SDS were added into the reactor, the solution was stirred and heated to 80 °C, then all the monomer, EGDMA and KPS were added at the same time, and the reaction was run for 5 h. In the seeded semi-batch operation, a mixture of deionized water, SDS, monomers, and 50% of the KPS was prepared beforehand and stirred for 30 min. Half of the mixture was loaded into the reactor and heated to 80 °C. The remaining 50% of the KPS was then added and stirred for another 20 min. After that, the remaining mixture was fed into the reactor continuously for 40 min, and the reaction was conducted for 4 h. In the semi-batch operation, the monomers and KPS solution were added dropwise after deionized water, SDS, were added and heated to 80 °C. The reaction was run for another 3 hours after the completion of the monomer addition. The pH range of polymerization for PMMA was 6–7 and for PS was 4–6.

2.3. Preparation of porous coating layer

A PMMA sheet (30 mm × 30 mm × 1 mm) was ultrasonically cleaned in an ice cooled ethanol solution for 2 min, and then dried under nitrogen. To prepare the coatings, PS and PMMA latices were mixed in a certain ratio to obtain stable heterogeneous emulsion. SDS with a concentration of 0.1 wt% relative to the latex was added to the emulsion which was then applied to dried substrate with a disposable syringe. Coatings were prepared by spin-coating under a fixed speed for 60 s. All the samples prepared for transmittance test had double-sided coating. Afterwards, the coated substrate was washed with deionized water and soaked in cyclohexane to remove the PS, and then the porous PMMA coating was prepared.

2.4. Characterizations

Nanoparticle diameters were measured by dynamic light scattering (DLS) (Malvern; Zetasizer Nano-ZS). Transmittances were measured by UV–vis spectrophotometry (Shimadzu; UV-3150). Refractive index and thickness were measured with an ellipsometer (J. A. Woollam Co.; Alpha-SE). A scanning electron microscope (SEM) (Hitachi; S-4700) and an atomic force microscope (AFM) (Veeco/Bruker; MultiMode V) were used to observe the coating surface morphology and measure the surface roughness.

2.5. Data Treatment

Eq. (1) below was used to calculate the porosity of a porous material fabricated by PS and PMMA:

$$n_e^2 = n_p^2(1-P) + P \tag{1}$$

where n_e, n_p, and P stand for the apparent refractive index of the porous coating, the refractive index of the bulk particle material, and porosity, respectively.

For a single layer coating, reflectance can be calculated according to Eq. (2) [1]:

$$R = \frac{n_e^2(n_0 - n_s)^2 \cos^2\frac{2\pi n_e \cos\theta}{\lambda}d + (n_s - n_e)^2 \sin^2\frac{2\pi n_e \cos\theta}{\lambda}d}{n_e^2(n_0 + n_s)^2 \cos^2\frac{2\pi n_e \cos\theta}{\lambda}d + (n_s + n_e)^2 \sin^2\frac{2\pi n_e \cos\theta}{\lambda}d} \tag{2}$$

where R, n_s, d, and θ, represent reflectance, refractive index of the substrate, thickness, and the incidence angle.

Transmittances were measured by UV–vis spectrophotometry under the vertical incidence condition. For $\theta = 0^\circ$ applied to transparent substrate (absorption can be ignored), the relationship between transmittance and reflectivity can be calculated by Eq. (3) [11]:

$$T = (1-R)^2 \tag{3}$$

Rayleigh scattering can be described by Eq. (4) when the particle size is far smaller than the wavelength of the incident light and causes scattering, where $I(\lambda)_s$ and $I(\lambda)_i$ stand for the light intensity distribution function of scattered and incident light respectively:

$$I(\lambda)_s \propto \frac{I(\lambda)_I}{\lambda^4} \tag{4}$$

Solid content (ω) of latices in our study were calculated using Eq. (5):

$$\omega = 100\% \left[\frac{(m_1 - m_3)}{(m_2 - m_3)}\right] \tag{5}$$

where m_1, m_2, and m_3 stand for the weight of the synthesized latex after being dried at 60 °C for 24 h, the weight of the latex before drying, and the total weight of KPS and SDS.

3. Results and discussion

Factors that affect the optical properties of single layer coatings in this study include the particle size, PS removal conditions, coating thickness (d), and surface roughness. Eq. (2) was used for predicting reflectance by many studies [16,24]. The coating thickness (d) can be adjusted by the coating conditions, such as the latex solid content [28], the particle size, the spin coating speed,

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