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Fabrication pentablock copolymer/silica hybrids as self-assembly coatings

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ABSTRACT

Novel organic/inorganic hybrid for coating material is prepared by the pentablock copolymer PDMS-b-(PMMA-b-PMPS)$_2$ (PMMDMM) and SiO_2 nanoparticles. PMMDMM is obtained via atom transfer radical polymerization (ATRP) by using polydimethylsiloxane (PDMS) as bifunctional macroinitiator. Poly 3-(trimethoxysilyl)propyl methacrylate (PMPS) is designed as the end block for facilitating the chemical bond of triethoxysilane (—Si(OCH$_3$)$_3$) groups with SiO_2 nanoparticles produced by tetraethyl orthosilicate (TEOS), and poly (methyl methacrylate) (PMMA) is designed as the middle block for improving the solubility and the film-forming ability of copolymer. The homogeneous dispersion of SiO_2 nanoparticles in the pentablock copolymer matrix enables PMMDMM/SiO_2 to self-assemble into 210 nm SiO_2 core/PMMDMM shell elliptic or spherical micelles in tetrahydrofuran (THF) solution. This self-assembled aggregate could provide the film surface with uniform distribution of SiO_2 nanoparticles, obvious hydrophobicity (101–102° water contact angles), lower surface free energy (22.3–21.8 nN/m) and lower viscoelasticity. SiO_2 involved into the copolymer matrix could increase the nanostructures roughness. When TEOS is controlled as 20 wt.%, the hybrid performs higher glass transition temperature (T_g = 113 °C) and excellent thermostability (520 °C) than PMMDMM (T_g = 87 °C, 295 °C) due to the introduction of SiO_2 nanoparticles. These excellent properties promise PMMDMM/SiO_2 hybrid as the candidate for coating material.

1. Introduction

The organic/inorganic hybrids composed of organic polymer and inorganic particle have attracted much attention because of their desired properties for coating materials [1–4]. Actually, the final properties of hybrids used as coating applications are controlled not only by the quantity and the dispersion of inorganic particles in the polymer matrix, but also by the covalent bond between them [5–7]. For achieving the durable coatings, the crosslinking between the inorganic particles bearing surface chains and the well-defined polymer could be the key point for the organic/inorganic hybrids. There are many synthetic methods to incorporate inorganic particles into polymer networks, and they are classified into three major approaches according to the chemical bond between polymer and inorganic phases: (1) mix inorganic particles into polymer directly to obtain the mixture without chemical bonding between them; (2) utilize already existing functional groups in the polymer species to react with the hydrolyzed of inorganic precursors, thus introducing chemical bonding between them; (3) use alkoxysilanes R'n Si(OR)$_{4-n}$ as the precursors for the sol–gel process with polymerizable organic groups within the polymer [3]. Therefore, incorporating the nanosilica into the polymer bearing triethoxysilane (—Si(OCH$_3$)$_3$) groups is a encouraging method to obtain organic/inorganic hybrids used as coating materials.

It has been proved that SiO_2 nanoparticles have great advantages in improving the thermostable, high mechanical and anti-chemical properties for final hybrids [8–10]. In general, SiO_2 nanoparticles with a high yield and a uniform size distribution are obtained by the hydrolysis and the condensation of tetraethyl orthosilicate (TEOS) or tetramethoxysilane (TMOS) through sol–gel process [11,12]. When the silica particles produced by TEOS are chemically bonded with —Si(OCH$_3$)$_3$ groups to produce hybrids, it will undergo the hydrolysis of the ethoxy groups to yield silanol and the condensation of different silanol groups to produce siloxane linkages (Si—O—Si) [13], which could form covalent bonds with the alkoxysilanes in organic polymers to prevent the macroscopic phase separation between organic and inorganic constituents [14,15].

On the other hand, the backbone structure of polymer bearing —Si(OCH$_3$)$_3$ groups is also a key point for the hybrids. The suitable design of backbone could render the polymer water repellency due to the low-surface-energy film formed, and could promote

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adhesion of polymer to substrate. Therefore, a typical block polymer with —$Si(OCH_3)_3$ groups is designed [16], based on that the block copolymers could self-assemble into various aggregates in the selective solvents to provide the film with the desirable properties through controlling the chemical composition, the block length and the structure of the blocks. 3-(Trimethoxysilyl)propyl methacrylate (MPS) is one of the most reactive monomer bearing —$Si(OCH_3)_3$ groups [17], in which the double bond in MPS could react with other function groups to form the copolymer backbone, and —$Si(OCH_3)_3$ groups could bond chemically with SiO_2 nanoparticles. If the block copolymer is designed using PMPS as the end block, it not only facilitates this chemical bond for achieving the desirable properties of hybrids [18–21], but also favors the self-assemble of block copolymer to control the film properties for coatings. Furthermore, if the polyacrylate segment, such as poly(-methyl methacrylate) (PMMA), is involved into the block structure, the block copolymer could obtain the desirable film-formation ability and binding strength with the substrate [22,23]. Therefore, the organic/inorganic hybrids composed of the block copolymer containing PMMA/PMPS segments and SiO_2 nanoparticles are promised to serve as the self-assemble coatings.

On the basis of these considerations, this paper presents for the first time the novel organic/inorganic hybrids PMMDMM/SiO_2, formed by pentablock copolymer PDMS-b-(PMMA-b-PMPS)$_2$ (PMMDMM) and SiO_2 nanoparticles for the self-assemble coatings. PMMDMM is synthesized by atom transfer radical polymerization (ATRP), in which polydimethylsiloxane (PDMS) segment as bifunctional macroinitiator is designed at the central block for restricting the strong phase separation and improving the mutual miscibility between PMMA and poly[3-(trimethoxysilyl)propyl methacrylate] (PMPS), PMMA segment is designed as the middle block for improving the solubility and the film-forming ability of copolymer, and PMPS segment bearing —$Si(OCH_3)_3$ groups are architected as the end block for chemical bonding with SiO_2 produced by TEOS. After PMMDMM is obtained, TEOS is hydrolyzed and condensed for covalent bonding with —$Si(OCH_3)_3$ groups in PMMDMM to obtain hybrids PMMDMM/SiO_2. The dispersion of SiO_2 nanoparticles produced by 10–50% TEOS in the PMMDMM copolymer matrix has great influence on the self-assembled aggregates of hybrids in tetrahydrofuran (THF) solution and on the surface properties of hybrid films investigated by transmission electron microscopy (TEM), dynamic light scattering (DLS), static contact angle (SCA), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscope (AFM) and the quartz crystal microbalance with dissipation (QCM-D). The thermal property of PMMDMM/SiO_2 is improved by introducing SiO_2 nanoparticles through differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) characterization.

2. Experimental

2.1. Materials

α, ω-Dihydroxy terminated polydimethylsiloxane (HO-PDMS-OH, liquid, Mn = 4000 g mol^{-1}) is supplied by Xuejia Fluorine-Silicon Chemical Co. Ltd. (China). 3-(Trimethoxysilyl)propyl methacrylate (MPS, $H_2C{=}C(CH_3)CO_2(CH_2)_3Si(OCH_3)_3$, >96 wt.%) is provided by Silicone New Material Company of Wuhan University. MPS is dried over CaH_2 for 24 h and is distilled under reduced pressure before using [24]. Methyl methacrylate (MMA, 99 wt.%) supplied by Aldrich is rinsed with 5 wt.% NaOH aqueous solution and ion-free water until the rinsed water reaches pH = 7, followed by drying it over anhydrous magnesium sulfate for 24 h to remove inhibitor. Cyclohexanone and tetrahydrofuran (THF) are stirred over CaH_2 for 12 h at room temperature, and are distilled under reduced pressure prior to use. Cuprous chloride (CuCl) is purified according to the method of WhiteSides [25]. 2-Bromoisobutyryl bromide (BiBB), 4-(dimethylamino) pyridine (DMAP), triethylamine (TEA), tetraethoxysilane (TEOS, >98 wt.%, Aldrich) and tetramethylethylenediamine (TMEDA) in analytical purity are purchased commercially and are used as-received without further purification.

2.2. Preparation of pentablock copolymer PMMDMM by ATRP

PMMDMM is prepared by two-step ATRP approaches. The first step is to synthesize triblock copolymer (Br-PMMA-b-PDMS-b-PMMA-Br) (PMDM) using Br-PDMS-Br macroinitiator as Scheme 1I and II [26]: after CuCl is added into a dry Schlenk tube which is sealed with a rubber septum prior to three vacuum/N_2 cycles, the mixture of MMA (4.88 g), Br-PDMS-Br (1.0 g), TMEDA (0.044 g) and cyclohexanone (10 g) is introduced under N_2 atmosphere. After the reaction lasts for 24 h at 80 °C in an oil bath, the left catalyst is removed by passing the copolymer solution through an alumina column using THF as the solvent. When the excess solvent is removed under reduced pressure, the colorless solution is re-precipitated into methanol and dried in a vacuum oven overnight, and the triblock copolymer PMDMA is obtained.

The second step is to prepare pentablock copolymer PMMDMM by PMDM and MPS as Scheme 1III: When 2.61 g (20 mmol) PMDM is dissolved in 10 g cyclohexanone in a Schlenk tube, the mixture of 1.22 g MPS, 0.014 g CuCl and 0.033 g TMEDA is charged under N_2 atmosphere. Then, the reaction is permitted to last for 24 h at 120 °C in an oil bath. The left catalyst and the excess solvent are removed using the same way as above. The resulting PMMDMM is obtained in a yield of 72–79%. The detailed polymerization recipes are listed in Table 1.

The comparison of the film for Samples I, II and III with different amounts of MMA in Table 1 indicates that the higher molecular weight (Samples III) gives the better film. But the comparison of the film for Samples I, IV and V with the different amounts of MPS reveals that the higher content of MPS gives much active points for chemical bonding with SiO_2. However, when MPS content is increased to 2.4390 g (Sample V), the gelation is produced due to the excess of MPS. Therefore, Sample I is selected as the next step for preparation of PMMDMM$_2$/SiO_2 hybrids by sol–gel process.

2.3. Preparation of PMMDMM/SiO_2 hybrids by sol–gel process

When 0.3 g PMMDMM is dissolved in 30 mL THF in the reaction flask, the pre-hydrolyzed TEOS (in THF and 0.2 M HCl by stirring vigorously at 50 °C for 30 min) is added into the flask. A homogeneous solution is formed after stirring 4 h. After the left THF, the produced methanol and water are evaporated at room temperature, and the hybrid PMMDMM/SiO_2 is obtained in Scheme 1. The detailed recipes are listed in Table 2.

2.4. Characterization

Proton nuclear magnetic resonance (^{1}H NMR) measurement for PMMDMM is performed on a Bruker AV-500 spectrometer using $CDCl_3$ as solvent. Tetramethylsilane (TMS) is used as the internal reference. The molecular weights of the block copolymers are measured using a gel permeation chromatography (GPC, Wyatt DAWN EOS MZ 103 + MZ 104) system at 25 °C and are calibrated by the polystyrene standards. THF is used as the eluent at a flow rate of 0.5 mL min^{-1}.

The self-assembled aggregates of PMMDMM/SiO_2 in THF solution are investigated by transmission electron microscopy (TEM) and dynamic light scattering (DLS). 0.01 g mL^{-1} sample solution is prepared by filtering through a 0.45 μm disposable