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Surface topography and hydrophobicity of waterborne fluorinated acrylic/silica hybrid coatings

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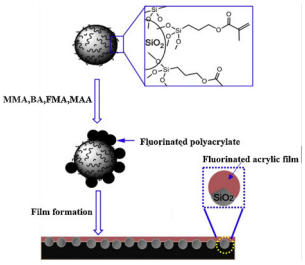
HIGHLIGHTS

- Fluorinated acrylic/silica hybrid particles were prepared and studied.
- Fluorinated acrylic copolymer has been grafted onto silica nanoparticles.
- Functionalized silica in the polymerization favored the film hydrophobicity.
- Fluorine content was increased at the film surface due to the presence of silica.

GRAPHICAL ABSTRACT



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ABSTRACT

Fluorinated acrylic/silica hybrid latexes have been prepared by mini-emulsion polymerization in the presence of silica nanoparticles functionalized by 3-(methacryloxy) propyltrimethoxysilane. The hybrid particle size and morphology were determined by transmission electron microscopy (TEM). Surface topography of the coating was investigated by atomic force microscopy (AFM) and chemical composition of the surface was analyzed by energy dispersive spectroscopy (EDS). Surface hydrophobicity of the coating was evaluated by water contact angle measurement. The results showed that polymeric latex particles were grafted onto silica. The presence of modified silica in fluorinated acrylic coating favored enrichment of fluorine at the film surface, which contributed to the hydrophobicity of the hybrid film.

1. Introduction

Increasing demand for innovative finishes and films has arouse much attention to focus on the preparation of polymer/inorganic nanocomposites, and in particular for one-step processes for the production of multifunctional surfaces. Addition of filler in polymer affects matrix structure and hence affects final material properties. Organic/inorganic nanocomposites, because of their attractive mechanical [1–3], thermal [4], magnetical [5], optical [6], and electrical [7] properties, are used for different purposes in paints, magnetic fluids, paper films, microelectronics and biotechnology, etc. These unique properties are achieved and affected by nanosized filler in polymer matrix. The nanocomposite preparation includes: mixing in solution, mixing in the melt and in situ polymerization of polymer and/or inorganic phases [8–16].

Silica nanoparticles are widely applied as inorganic component in the polymer matrix because of its high chemical stability, high specific surface area and accessibility. Surface of the silica filler is hydrophilic, and preferentially modified with various agents such as silanes before use [17–20], which enable tailoring of the

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matrix filler interface and accordingly properties of materials as a whole. Bourgeat-Lami et al. [21–23] have studied morphology of polymer/silica hybrid particles and mechanical properties of the composite films. The results showed that encapsulation of silica beads by polystyrene can be successfully achieved if the silica have been previously modified by grafting the coupling agent, in addition, silica bead size is an important parameter for controlling the composition and shape of the composite particles. The incorporation of silica particles in polymer latexes leads to a significant increase in Young's modulus of the resulting films due to a mechanical coupling effect of the two phases. Moreover, mechanical properties of the composite materials at large strains are greatly improved when the polymer formed are chemically linked to the inorganic particles through the methacryloyl groups of the grafting agent. Cheng et al. [24] reported PMMA/silica composite particles with different morphologies by using emulsion polymerization and studied the formation mechanisms of composite particles. Wu et al. [25] investigated surface properties of waterborne polyurethane/fluorinated polymethacrylate (WPU/FPMA) and high-hydrophobic silica contained hybrid films, showing that after addition of silica, the nano- and submicron papillae formed on the film and the film surface became hydrophobic. Li et al. [26] prepared fluorinated polyacrylate (FPA)/silica hybrid coatings by mixing of FPA and hydrophobic silica. They reported that by adding different amount of silica particles, the surface morphology and wetting behavior of the FPA/silica hybrid coatings can be controlled. The addition of hydrophobic silica increased surface roughness and superhydrophobic surface was obtained. Although much efforts have been devoted to prepare polymer/silica nanocomposites, few research has been concentrated on in-situ polymerization of acrylic monomers in the presence of hydrophobic silica and there is no investigation on film forming mechanism of such kind of hybrid latexes.

In this work, fluorinated acrylic/silica hybrid latexes have been prepared by mini-emulsion polymerization. Surface topography and hydrophobicity of the fluoropolymer/silica hybrid films have been studied, and the probable mechanism that silica particles enhanced hydrophobicity of the hybrid film has been proposed.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), *n*-butyle acrylate (BA), and α-methacrylic acid (MAA) were obtained from Xilong Chemical Co., Ltd. (Guangdong, China). MMA and BA were distilled under reduced pressure prior to use. 1*H*,1*H*,2*H*,2*H*-perfluorodecanol ($CF_3(CF_2)_7C_2H_4OH$, FOH) was purchased from Guangzhou Li'er Technology and Trade Corporation. 3-(Methacryloxy) propyltrimethoxysilane (MPS) was obtained from Nanjing Xiangqian Chemical Co., Ltd. Ammonium persulfate (APS) was bought from Tianjin Bodi Chemical Co., Ltd. and recrystallized before use. Toluene, *p*-toluene sulfonic acid (PTSA), hydroquinone, sodium dodecyl sulfate (SDS), hexdecane (HD), sodium bicarbonate ($NaHCO_3$), triethylamine (TEA), ammonia (25 wt%), tetraethoxysilane (TEOS) and silica gel (200–300 mesh) were all used as received. Deionized water was used throughout the experiment.

2.2. Methods

Scanning electron microscopy (SEM) analysis was performed on JSM-6010 equipment (JEOL, Japan). Silica nanoparticles were dispersed in ethanol and dropped on a silicon wafer, then the sample was dried in vacuum and sprayed with platinum (Pt) before observation.

FT-IR spectra were recorded on a Fourier transform infrared spectrum analyzer (Thermo Nicolet AVATAR, USA) in a range from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 8 cm^{-1} using KBr pellet method.

^1H NMR and ^{19}F NMR spectra were obtained from AVANCE III 400 NMR spectrometer (Bruker, Switzerland) and deuterated chloroform ($CDCl_3$) as the solvent.

Morphology of latex particles was characterized by transmission electron microscopy (TEM, JEM-2100, JEOL, Japan). One drop of diluted latex was placed on a 200 mesh carbon-coated copper grid and then stained by 2 wt% aqueous solution of phosphotungstic acid.

The particle size distribution was determined by dynamic light scattering (DLS) using a LS 13 320 Laser Diffraction Particle Size Analyzer (BECKMAN COULTER, USA).

Specific surface area of silica was determined by nitrogen absorption method (BET) on Quantachrome Instruments Quantachrome Autosorb Automated Gas Sorption System (USA).

Carbon and hydrogen contents at surface of silica was determined by a Vario EL III elemental analyzer (Elementar, Germany) and the accuracy of C and H is 0.3%.

The grafting efficiency of MPS was defined as the weight percentage of the grafted MPS to the total MPS added for the modification.

Contact angle measurements were performed on DSA20 (KRÜSS, Germany). Static contact angles were measured depositing a liquid droplet of 5 uL on the surface.

The topography of the film was determined by atomic force microscopy (AFM, Veeco DI, USA) in tapping mode in air with a scan size of 2 μm × 2 μm. Roughness reflects the film surface topography. Root mean square roughness (R_q) is calculated from the following Eq. (1), and R_q was obtained by AFM.

$$Rq = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(Z_i - Z_i'\right)^2} \quad (1)$$

where Z_i is the observed height at a certain point i, Z_i' is the best-fit base place at the point i, and n is the total number of data points in one image.

The film was prepared by spinning emulsion on a glass slide at a speed of 800 rpm for 30 s on a desktop spin coater (KW-4A, Institute of Microelectronics, Beijing, China) and dried at 100 °C for 1 h.

The morphology and composition of the film surface were analyzed by using FESEM JSM-7500F instrument (JEOL, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS). The films formed on glass slides were sprayed with platinum (Pt) before observation.

2.3. Fabrication and surface modification of silica nanoparticles

Silica nanoparticles with a mean size of 200 nm was prepared according to Stöber method [27]. That is, 2 ml of ammonia, 50 mL of ethanol and 10 mL of H_2O were added into the flask and stirring for 30 min at 25 °C, after which 3.5 g of TEOS was added continuously into the flask within 30 min and the reaction was proceeded for 24 h.

The functionalized silica ($MSiO_2$) was prepared as follows: 30 g of silica sol mixed with 0.12 g of MPS (MPS/silica = 0.3 g/g) was stirred in the flask at room temperature for 12 h, then the temperature was increased to 76 °C and stirred for 1 h. The dispersion was centrifuged and washed with ethanol for three times, then the $MSiO_2$ powder was dried overnight in vacuum.