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Investigation of fluorosilicone polyacrylate film forming behavior on steel and PET substrates

Guofang Hao [a], Liqun Zhu [a], Wei Yang [a], Yichi Chen [b,*], Qigu Huang [c]

[a] School of Material Science and Engineering, Beihang University, Beijing, 100191, China
[b] Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, Beijing Key Laboratory of Bio-inspired Energy Materials and Devices, School of Chemistry and Environment, Beihang University, Beijing, 100191, China
[c] Beijing University of Chemical Technology, Beijing, 100029, China

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ABSTRACT

Aggregation behavior of fluorine- and silicon-containing segments in fluorosilicone polyacrylate film formed on steel and PET (polyethylene terephthalate) substrates has been investigated. Surface composition and topography of the films were characterized by ATR-FTIR spectrometry, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Effect of film forming temperatures on surface morphology and water repellency has been evaluated. The results indicated that migration behavior of fluorine- and silicon-containing segments were significantly influenced by polarity of the substrates and film forming temperatures. Fluorine content at the film–steel interface was 0.45% while it reached to 1.69% at the film–PET interface, moreover, fluorinated segments were surface enriched while silicon-containing segments were enriched at film–substrate interface. As the film forming temperature was increased, fluorine content at the film surface decreased and silicon content increased, which was due to that a high film forming temperature favored silicon crosslinking at the film surface.

1. Introduction

Preparation of waterborne polyacrylate emulsions are the major research targets in the field of aqueous coatings. The advantages of waterborne polyacrylate include the low emission of volatile organic compounds (VOC), good adhesion to matrices, excellent UV resistance, good film-forming ability and high transparency. Fluorinated polyacrylate have many desirable features, such as weather durability and chemical stability [1–3]. The surface enrichment property of fluorine chains at the film surface generates low energy surface and preferable hydrophobicity [4–9]. Besides fluorine-containing materials, silicon-containing materials are also incorporated into polymers in order to obtain excellent thermal stability and water repellency of the films [10–12]. Although numerous research articles describing the preparation of fluorine-containing films and their surface properties have appeared in the literature [13–16], only a few efforts have been devoted to the preparation and film formation of fluorosilicone polyacrylate latex particles in the past few decades [17–20]. Kim et al. [21] have synthesized and characterized fluorosilicone polyacrylate, showing that the film exhibited preferable surface and mechanical properties due to the silicon crosslinking in the film. Xiong et al. [22] investigated surface hydrophobicity of fluorosilicone polyacrylate film and revealed that fluorinated segments could be fixed at the film surface by silicon crosslinking. Han et al. [23] prepared fluorosilicone polyacrylate by emulsion polymerization and studied effect of fluorine- and silicon-containing monomers on hydrophobicity and thermal stability of the copolymer. It is suggested that fluorine- and silicon-containing polyacrylate film exhibited satisfied hydrophobicity due to the synergistic effect of fluorine and silicon. Some studies have reported the synthesis and properties of fluorosilicone polyacrylate emulsions, but there has been little research on surface properties of the fluorosilicone polyacrylate film formed in different conditions. Most of previous literatures are focused on water repellency and thermal stability of fluorosilicone polyacrylate, however, there are still many problems needed to be further illustrated, especially in migration behavior of fluorine- and silicon-containing segments during film forming process.

In this study, fluorosilicone polyacrylate latex was prepared by using emulsion polymerization process and surface properties of

* Corresponding author. Tel.: +86 10 82317113; fax: +86 10 82317133.
E-mail addresses: zhulq@buaa.edu.cn (L. Zhu), chenych@buaa.edu.cn (Y. Chen).

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the films formed at 25 °C (RT), 80 °C, 100 °C and 120 °C were examined. Migration behavior of fluorine- and silicon-containing segments in the films on steel and PET substrates was investigated.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), butyl acrylate (BA), methyl acrylic acid (MAA) and hydroxylethyl methacrylate (HEMA) were bought from Dongfang Yakeli Chemical Co., Ltd. (Beijing, China). MMA and BA were distilled under reduced pressure before use. HFBA (CH_2=$CHCOOCH_2CF_2HCFCF_3$) was purchased from XEOGIA Fluorine-Silicon Chemical Co., Ltd. (Harbin, China). Vinyltriethoxysilane (VTES) was purchased from Nanjing Xiangqian Chemical Co., Ltd. Octylphenolpolyoxyethylene ether (OP-10), ammonium *p*-nonylphenoxypolyoxyethylene sulfate (CO-436), ammonium persulfate (APS), sodium bicarbonate ($NaHCO_3$) and ammonia (25 wt%) were all analytical grades and used as received. Stainless steel was bought from Wuxi Yingrui metal materials Co., Ltd. (Jiangsu, China) and PET substrate was purchased from Shenzhen Hongmei film Co., Ltd (Guangdong, China). The substrates were cut into 2×5 cm^2 and cleaned with ethanol before use. Deionized water was used throughout the experiment.

2.2. Characterization methods

Morphology of latex particles was characterized by transmission electron microscopy (TEM, JEM-2100, JEOL, Japan). The copolymer latex was dropped on a carbon coated copper grid and negatively stained with an aqueous solution of 2 wt% phosphotungstic acid. Dynamic light scattering (DLS) analysis was performed on a LS 13 320 Laser Diffraction Particle Size Analyzer (BECKMAN COULTER, USA). Fourier transform infrared spectra were recorded on a NEXUS-470 FTIR analyzer (Nicolet, USA). Spectra for transmittance mode was collected from 4000 cm^{-1} to 500 cm^{-1} with a resolution of 8 cm^{-1} and the OMNI-SAMPLER accessory was used for attenuated total reflectance (ATR-FTIR) measurement. ATR-FTIR spectra of the films were collected with the Thermo Nicolet Smart Endurance device equipped with a Ge crystal ATR objective, which allows nondestructive microscopic surface analysis. X-ray photoelectron spectroscopy (XPS) was performed on ESCALAB 250 system (Thermo Fisher Scientific, USA) using a monochromatic Al Kα X-ray source operating at 200 W. The takeoff angle and spot size are 45° and 650×650 μm^2, respectively. Atomic force microscopy (AFM) was carried out on a Veeco DI instrument in tapping mode with a scan size of 5×5 μm^2. Water contact angles were measured by a DSA20 instrument (KRÜSS, Germany) at room temperature (RT, 25 °C). Contact angle of the film was the average value of five measurements (5 μL/drop) on different positions at the film surface.

2.3. Preparation of fluorosilicone polyacrylate latex and the film

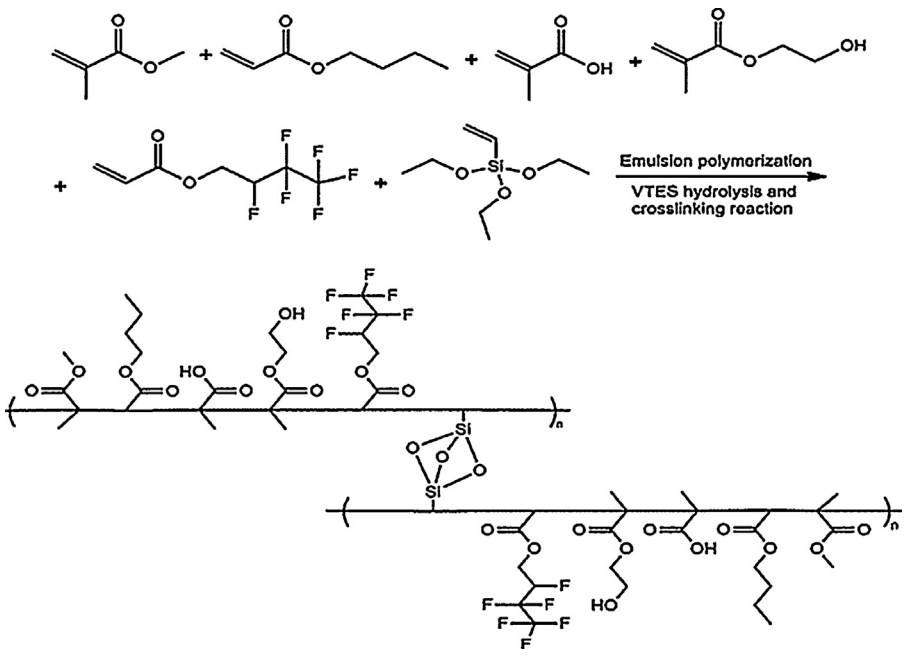
Scheme 1 illustrates the structure of fluorosilicone polyacrylate and Table 1 shows the formulation for emulsion polymerization.

The polymerization was carried out in a 250 ml four-neck flask equipped with a thermometer, a stirring paddle, a dropping funnel and a reflux condenser. Typically, the components of **S1** were charged into the reactor with mechanical stirring and the polymerization was continued at 78 °C for 20 min. After that the pre-emulsion and APS solution of **S2** were fed into the reactor for 3 h and 1 h, respectively, and the reaction was continued for 30 min. Subsequently, APS solution of **S3** was added for 20 min and the polymerization was further continued for 1.5 h. After the reaction completed, the emulsion was cooled down and pH value was regulated to 7–8 by ammonia. Monomer conversion was calculated to be 95% by gravimetric method. The film was prepared by casting the latex onto the glass slide and dried at RT, 80 °C, 100 °C and 120 °C, respectively.

3. Results and discussion

3.1. TEM and DLS analyses of fluorosilicone polyacrylate latex particles

Morphology and particle size of fluorosilicone polyacrylate latex are shown in Fig. 1. It can be seen that the fluorosilicone polyacrylate latex particles have been synthesized by emulsion



Scheme 1. Preparation of fluorosilicone polyacrylate.