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Heat resistance and surface properties of polyester resin modified with fluorosilicone

Bing Wang [a], Tao Qian [a,b], Qinghua Zhang [a,*], Xiaoli Zhan [a], Fengqiu Chen [a]

[a] College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China
[b] Hangzhou Jihua Polymer Material Co., LTD, Hangzhou 311234, China

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ABSTRACT

In this work, fluorosilicone modified polyester resin (FSP) prepared from polyester (PET) and fluorosilicone resin (FS) with excellent heat resistance and surface wettability was reported. FS was synthesized by hydrolysis and condensation reaction of 1H,1H,2H,2H-perfluoroalkyltriethoxysilane (FTEOS), methyltriethoxysilane (MTEOS), phenyltriethoxysilane (PTEOS), dimethyldimethoxysilane (DMDMOS), and diphenyldimethoxysilane (DPDMOS). The surface chemical composition and morphology of the resins were determined by Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The surface wettability and thermal property of the FPS films were studied via contact angle measurements and thermogravimetric analysis (TGA), respectively. The modified resin displayed excellent heat resistance, water and organics repellence due to the native high bond energy and low surface free energy of fluorosilicone. For the FSP resin containing 50 wt% of fluorosilicone resin (F5SP50), the starting decomposition temperature T_{d10} (10% weight loss) reached 360 °C, which was 40 °C higher than that of neat PET. The residual weight at 700 °C was also remarkably increased. Moreover, hydrophobicity, oleophobicity and hardness of FSP films were enhanced by optimizing the addition of fluorosilicone in polyester resin. The prepared fluorosilicone modified polyester resin has a great potential in the application of high-temperature coating.

1. Introduction

Heat resistant coating can be defined as a kind of coating with stable chemical and physical structure which could be used above 200 °C, and it has a broad application prospects in the field of modern industry, military and aerospace [1,2]. Heat resistant coatings are generally based on silicone resin, which is known to be cross-linked semi-inorganic polymer with Si—O—Si as backbones and some organic groups as side chains. As the inorganic Si—O—Si bonds form the backbone of silicon resin, silicone polymers display unusual physical and chemical properties compared with homologous carbon-based polymers. The silicon atom possesses low electronegativity and the Si—O bond is a kind of covalent bond with half ionic bonding property having high bond energy (460 kJ/mol) [3,4]. Therefore, the high (Si—O) bond dissociation energy endows the silicone polymers with excellent thermal stability. Large (Si—O—Si) bond angle causes a reduced energy barrier for the rotation of the organic groups attached to the silicon atom, which provides substantial flexibility to the silicone polymer backbone [5]. The silicon resin shows prefect heat stability, resistance to oxidation, low glass transition temperature, high dielectric constant, hydrophobicity, biocompatibilities and low surface free energy [6–9]. It has been widely used in the fields of electronic technology, aeronautics, nuclear power generation, military weaponry, and architecture [10,11]. However, its mechanical property, solvent resistance, and adhesion to the substrates are poor due to the low interaction between the molecular chains [12]. Besides, the long curing time and high curing temperature limit its further application in more fields.

In order to improve the mechanical properties of silicone materials, some silicone-modified resins, including epoxy resin, acrylic resin, polyurethane (PU), and polyester resin (PET), have been successfully prepared [13–21]. Owing to the significant difference in the solubility parameter values, the compatibility between the silicone resin and other organic resins was poor [22–24]. Phase separation would appear and form instability mixtures while blending the silicone resin with other organic resins. Therefore, chemical modification was considered as an efficient method, forming block, graft or interpenetrating network copolymer through covalent bond between silicone resin and organic resins [25,26].

Polyesters are commercially available in a variety of products including fibers, fillings, coatings and textiles [27]. Polyester resin exhibits many attractive properties, such as excellent impact resistance, adhesion property and chemical corrosion resistance, and polyester film is plump and bright. However, the neat polyester resin is hard to satisfy the increasingly strict requirements in high temperature and high humidity environment, and the heat resistance, surface wettability and

* Corresponding author.
E-mail address: qhzhang@zju.edu.cn (Q. Zhang).

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water repellence of PET materials need to be further improved. Considering the complementary properties of silicone resin and polyester resin, it is of great interest to develop new silicone-modified resins with excellent integrated properties of silicone-based materials and good performance of polyester resins. Several publications are available on the modifications of polyester resins with silicones, and it is found that silicones can improve the corrosion resistance, hydrophobicity, hardness and weathering stability of coatings [13,17]. However the thermostability and surface wettability of these modified resins are very difficult to meet the request of performance and expanding applied field.

It is well known that the fluorine-containing carbon chain can efficiently reduce the surface tension of the materials [28–30]. Fluorinated chains have the tendency to migrate toward interface and preferentially locate at the interface minimizing the interfacial energy due to its low surface free energy [31,32]. Thus, relative lower fluorine content substance can obviously improve surface property of the coatings [33–35]. Fluoropolymer also has a good thermal stability, deriving from the high bonding energy of C—F [36]. Because of the thermal stability, hydro-oleophobicity, insulation and biocompatibility properties of the fluorine polymer, it is a kind of ideal functional polymer material which has been widely investigated [37–40].

In recent years many of silicone modified polyester resin have been done, but the surface properties of these modified resins are not satisfactory. To further enhance the wettability and non-sticking performance, fluorine-containing silicone monomer was introduced into the modified resin system. In this work, the main aim was to prepare a novel fluorosilicone modified polyester resin and investigate the thermal stability and surface properties of the prepared film. Firstly, the fluorosilicone resin was synthesized by hydrolysis and condensation reaction between alkoxysilanes and fluoroalkylsilane. Then the polyester with different contents was reacted with fluorosilicone. The chemical structure, surface morphology and wettability, thermal property, non-sticking performance, water repellence, hardness, and adhesion property of the fluorosilicone modified polyester resin films were studied in detail.

2. Experimental section

2.1. Materials

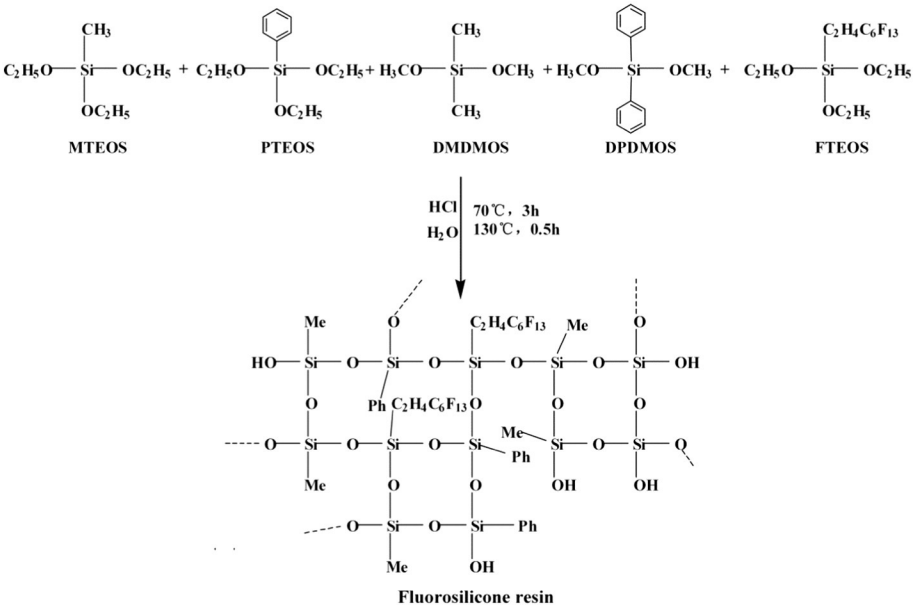
Methyltriethoxysilane (MTEOS), phenyltriethoxysilane (PTEOS), dimethyldimethoxysilane (DMDMOS) and diphenyldimethoxysilane (DPDMOS) were provided by Nanjing Kun Into Chemical Co., LTD. 1H,1H,2H,2H-perfluoroalkyltriethoxysilanes (FTEOS) was provided by Harbin Snow Better Fluorine Silicon Chemistry Co., LTD. Polyester resin (PET), propylene glycol methyl ether acetate (PMA) were kindly provided by Hangzhou JiHua Macromolecule Material Co., LTD. Ethanol, tetrabutyl titanate (TBOT), triphenyl phosphite (TPPI) were purchased from Its Group Chemical Reagent Co., LTD. All reagents and solvents were used as received.

2.2. Synthesis of fluorosilicone resin (FS)

Fluorosilicone resin (F5S) contenting 5 wt% of fluoroalkylsilane was prepared by hydrolysis and condensation method as shown in Scheme 1. Polymerizations were carried out in a 250 mL glass flask fitted with a reflux condenser, a mechanical stirrer, and an inlet for nitrogen gas. 20 g ethanol as a solvent was firstly added into the flask, and then the following alkoxysilanes: 10.04 g MTEOS, 14 g PTEOS, 3 g DMDMOS, 6.1 g DPDMOS and 1.76 g FTEOS were added into the flask. The quality of fluorosilicone resins was determined by R/Si (the average number of organic groups linked to Si atom), and Ph/R (the content of phenyl in substituent organic groups) values, where R = CH_3–, C_6H_5–, $C_2H_4C_6F_{13}$–. Alkoxysilanes were used in the ratio of R/Si = 1.3, and Ph/R = 0.5. Two drops of hydrochloric acid as catalyst were added. After the solution was heated to 70 °C, water calculated from the ratio of H_2O/Si-OR = 1.1 was slowly dripped into the flask with stirring for 30 min, and then maintained at 70 °C for 3 h. After the hydrolysis, the condensation was carried out by heating the solution to 130 °C for 30 min, ethanol and water were removed by evaporation. Finally the fluorosilicone resin was obtained. Silicone resin (F0S) without FTEOS was also prepared by the same method as a control group.

2.3. Synthesis of fluorosilicone modified polyester resin (FSP)

The fluorosilicone modified polyester resin (FPS) was prepared as follows: appropriate amount of fluorosilicone resin and polyester resin were calculated and added into a 250 mL four-necked round-bottom flask, then propylene glycol methyl ether acetate (PMA) as solvent, triphenyl phosphite (TPPI) as heat stabilizer, and tetrabutyl titanate (TBOT) as catalyst were charged into it. The mixture resin was stirred and heated to 160 °C for 4 h until complete removal of water. Then a uniform and transparent resin solution was obtained. And the reaction



Scheme 1. Synthesis process of fluorosilicone resin.