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Synthesis and characterization of fluorinated polyacrylate as water and oil repellent and soil release finishing agent for polyester fabric

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ABSTRACT

A new kind of multifunctional polyacrylate latex containing fluorinated and hydrophilic groups (FHPA) was synthesized by semi-continuous emulsion polymerization. Particle size, particle size distribution and zeta potential were tested to evaluate the emulsion stability and high-resolution transmission electron microscope (TEM) was used to observe the particle morphology. Afterwards, FHPA as finishing agent was coated onto polyester fabric by a pad-dry-cure method. Thermal and surface properties of FHPA coated polyester fabric were characterized by thermal-gravimetric analysis (TGA), atomic force microscope (AFM), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and energy dispersive spectrometer (EDS). It was found that the fluoroalkyl groups preferentially enriched on the film-air interface and could decrease the surface free energy of FHPA film to 18.4 mN/m, generating a hydrophobic and oleophobic surface. The static contact angle tests also confirmed this point. Furthermore, the water and oil repellency and soil release properties of FHPA on polyester fabric were investigated, and the experimental results showed that the introduction of hydrophilic chains in fluorinated acrylate polymer could significantly improve the soil release performance of the fluorine-containing finished polyester fabric by producing a roll-up mechanism for oil removal during washing.

1. Introduction

In the past few decades, with the development of society and the improvement of people's living standard, the demand for functional textiles has increased dramatically [1,2]. Among various natural and synthetic textiles, the most widely used textile is polyester fabric such as curtains, tablecloths, outdoor clothing and vehicle interior, etc., due to its good thermal stability, chemical resistance and excellent mechanical properties [3–5]. Therefore, it is of great necessity for polyester fabric to be finished with special functions, especially water-, oil-repellent and soil release properties [6–10].

Nowadays, fluorocarbons, due to their unique properties including high C—F bond energy and low surface free energy, have been thoroughly studied as functional materials for surface coating applications [11–15]. In particular, perfluoroalkyl polyacrylates have emerged as the most widely used finishing agents [16–19]. It is widely acknowledged that the surface properties of perfluoroalkyl polyacrylates depend on the side perfluoroalkyl (R_f) groups. The textile finishing agents containing long perfluoroalkyl pendant chains (R_{fn}, $n \geq 8$) have excellent hydrophobic and oleophobic effects. However, there is one common defect of fluorochemical finishes for textiles. They all present an essentially fluorinated surface in all environments, i.e., the same nonpolar surface in water during laundering, as well as in air [20]. Once oils are forced onto the finished textiles, it is difficult to remove them during conventional laundering because of the hydrophobic nature of the finished fabric.

To solve this problem, some researchers have introduced the hydrophilic segment into the fluorine-containing polymer to realize the soil-release finish of textile. For instance, Samuel and his co-workers synthesized a series of classic copolymers containing long perfluorocarbon and tetraethylene glycol dimethacrylate groups in a single molecule with the proper ratios, and these copolymers provided good soil release performance to cotton-polyester blended fabric [21,22]. Abo-Shosha et al. prepared four adducts as water/oil repellent and oily stain release finishing agent for cotton fabric by reacting 2, 4-toluene diisocyante, perfluorinated aliphatic alcohols and polyethylene glycol with different molecular weight. These adducts with hydrophilic segments weakened the hydrophobic effect of perfluorinated segments, but repelled oily stains in air and released them during washing [7,23]. Unfortunately, it has been reported that long perfluorocarbon chain

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with strong toxicity, bioaccumulation and difficult biochemical degradation, especially perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), severely threats the ecological environment and human health [24–27]. Therefore, these materials are concerned by the public, and some of them have accordingly been either banned or voluntarily withdrawn from the market under the pressure of the US Environmental Protection Agency (EPA) and EU REACH legislation [28,29].

In this paper, we designed and synthesized a new block acrylate copolymer containing both hydrophobic and hydrophilic segments. Firstly, the acrylic monomer (PEGA) containing polyether hydrophilic segment was synthesized. Subsequently, PEGA reacted with other acrylic monomers by semi-continuous emulsion polymerization to prepare the corresponding polyacrylate latex containing fluoroalkyl and hydrophilic groups (FHPA), which could possess low surface free energy and avoid the environmental problems caused by long-chain perfluoroalkyl. Afterwards, FHPA as finishing agent was coated onto polyester fabric by pad-dry-cure method. The surface and application properties of coated polyester fabric were then characterized and evaluated.

2. Experimental

2.1. Materials

Polyethylene glycol (PEG-600, 99.5%), acrylic acid (AA, 98%), butyl acrylate (BA, 98%), hydroxyethyl methacrylate (HEMA, 97%), fatty alcohol polyoxyethylene ether-9 (AEO-9, 98%), ammonium persulfate (AP, 99%), acetic acid (99.7%), Na_2CO_3 (99.7%) and ethyl acetate (99.7%) were obtained from Qiangsheng Functional Chemicals Co., Ltd. and used without further purification. Hydroquinone (99%), p-toluenesulfonic acid (PTS, 98%) and hexadecyltrimethylammonium chloride (CTAC, 99.5%) were purchased from Aladdin Chemistry Co., Ltd. And 2, 2, 3, 4, 4, 4-hexafluorobutyl methacrylate (TFBMA, 96%) was purchased from Harbin Xuejia fluorin silicon Chemical Co., Ltd. The fabric used in this study was a 100% polyester fabric (plain weave, weight: 106 g/m^2, density: 88 × 134/inch) from Wujiang Sanlian Printing & Dyeing Co., Ltd. The commercial water and oil repellent finishing agent of C6FA (viscosity: 4.55 mPa·s, colour: milky white, also known as six carbon fluorine series of UNIDYNE™) was supplied by Daikin Fluorochemicals (China) Co., Ltd.

2.2. Synthesis

2.2.1. Synthesis of the polyethylene glycol acrylate (PEGA)

The synthesis equation of PEGA was shown in Scheme 1.

PEG-600 (30 g), AA (4 g), PTS (0.5 g) as catalyst and hydroquinone (0.1 g) as inhibitor were charged into a 250 mL round-bottom flask equipped with a nitrogen inlet and outlet, temperature controller, water separator, and a stirrer. Then the flask was fastened into an oil bath at 130 ℃ for about 6 h with the condensing water removed. After the reaction was completed, the product was dissolved in saturated NaCl solution and neutralized with saturated Na_2CO_3. Then, the product was extracted with ethyl acetate at 50 ℃. Finally, polyethylene glycol acrylate (PEGA) was obtained after the removal of ethyl acetate by reduced pressure distillation. FT-IR (KBr): 3398, 2913, 1750, 1654, 1484, 1377, 1270, 1127, 960, 853 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (*ppm*) = 6.06 (2H, C**H**$_2$=CH), 5.78 (1H, CH$_2$=C**H**), 3.63 (2H, −C**H**$_2$CH$_2$O−).

2.2.2. Synthesis of the fluorinated and hydrophilic polyacrylate latex (FHPA)

The synthesis equation of FHPA was shown in Scheme 2.

Firstly, CTAC (1.08 g) and AEO-9 (1.62 g) were melted in 80 g deionized water as emulsifiers and mixed with TFBMA (35 g), BA (20 g), HEMA (2.5 g) and PEGA (10 g) for 15 min under a vigorous stirring rate of 8000 rpm to get the preliminary latex. Then, the polyacrylate latex with fluorinated and hydrophilic groups was synthesized in a semi-continuous process which has two stages: (i) 1/4 of the pre-emulsion and 1/3 of AP solution (0.08 g AP dissolved in deionized water 3.4 g) were introduced into a four-neck flask equipped with a reflux condenser, a mechanical stirrer, a dropping funnel and an inlet for nitrogen, and the reaction was heated to 75 ℃ for 0.5 h in a water bath; (ii) The remaining of pre-emulsion and AP solution (0.16 g AP dissolved in deionized water 6.6 g) were instilled into the flask, and the dropping time was controlled within 2 h. Then, the reaction was raised to 80 ℃ and kept for 1 h. After the reaction was cooled down to the room temperature, the ammonia was added to adjust the pH value of reaction product in the range of 5 ~ 6. Finally, the fluorinated and hydrophilic polyacrylate latex was obtained and noted as FHPA (viscosity: 2.37 mPa·s, colour: milky white). ATR-IR: 3485, 2923, 2857, 1732, 1457, 1239, 1137, 841, 743 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (*ppm*) = 0.92 (3H, −C**H**$_3$), 1.26 (2H, −C**H**$_2$−), 3.64 (2H, −OC**H**$_2$−), 3.43 (1H, −O**H**), 3.65 (2H, −C**H**$_2$CH$_2$O-), 4.00 (2H, −OC**H**$_2$CF$_2$−), 4.35 (1H, −C**H**F−).

2.3. Application of FHPA on polyester fabrics

Polyester fabric samples (20 × 20 cm) were immersed in the solutions which contained 150 g/L FHPA and 150 g/L C6FA for 15 min and padded through two dips and two nips with a wet pick-up of 90%. Then, the polyester fabrics were pre-dried at 110 ℃ for 5 min and cured at 170 ℃ for 3 min. Finally, the polyester fabrics coated with FHPA (FHPA-fabric) and C6FA (C6FA-fabric) were kept in a desiccator to balance at room temperature for 24 h before tests were conducted.

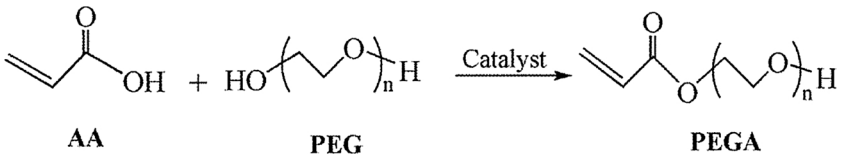
2.4. Characterization

The chemical structures of PEGA and FHPA were studied by Fourier transform infrared (FT-IR) and attenuated total reflection infrared (ATR-IR) spectroscopy, respectively, which were collected by a Nicolet 5700 spectrometer at a resolution of 4 cm^{-1} with 32 scans. ^{1}H Nuclear magnetic resonance (^{1}H NMR) was recorded on Unity INOVA-400 MHz in $CDCl_3$ with Me_4Si as the internal standard, and all chemical shifts were expressed in *ppm*.

Particle size, particle size distribution (PSD) and zeta potential of FHPA were measured by Malvern Zetasizer Nano ZS90. Particle morphology was obtained by high-resolution transmission electron microscope (TEM) with FEI Tecnai G-20 electron microscope at 200 kV.

Atomic force microscope (AFM) analysis was carried out by a Multimode Nanoscope IIIA in tapping mode at room temperature. The sample was prepared by spin-coating on silicon wafer and heated in oven at 105 ℃ for 2 h.

X-ray photoelectron spectroscopy (XPS) measurement was recorded with a Kratos Axis Ultra HAS photoelectron spectrometer, equipped with a monochromatic Al Kα X-ray source (hν = 1486.6 eV). The X-ray



Scheme 1. Synthetic route to the polyethylene glycol acrylate (PEGA).