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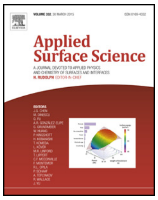

Enhancing the low surface energy properties of polymer films with a dangling shell of fluorinated block-copolymer

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ABSTRACT

Stabilizing long-term, low energy surface properties is a key issue in designing fluorinated polymer network, because the fluorinated surface could reorganize or hydrolyze upon contact with water. Here we report an exploring to enhance the low energy surface performance by bonding a dangling shell of fluorinated block copolymer, poly((1H,1H,2H,2H-perfluorodecyl acrylate)-b-poly(caprolactone) (PFDA-b-PCL)), to the polyurethane network. The PFDA and PCL block are the fluorinated shell and the dangling chain, respectively. The fluorinated shell protects the surface from rearrangements and hydrolysis when in contact with water, while the soft polyester block provides the required flexibility for fluorinated components to segregate to the surface. Surfaces with water contact angle up to 120° and surface energy down to 18 mN/m were obtained. We then evaluated the effects of fluorinated species on the surface properties of the polyurethane network both with and without the fluorinated shell or polyester spacer. The surfaces functionalized with the fluorinated dangling shell are highly hydrophobic and exhibited better hydrophobic stability. The oligoester spacer connecting the fluorinated shell to the polymer network is critical for the segregation and rebuilding of low energy surfaces.

1. Introduction

Materials with a low surface energy and good mechanical properties of the host matrix are of interest for many applications ranging from self-cleaning and self-healing coatings, biomaterials for drug release [1–4]. A common way to manipulate the surface properties of polymer materials is through the introduction of a small amount of fluorinated components, which will segregate from the host matrix and aggregate preferentially at the air–polymer interface driven by their low compatibility with the polymer matrix [5–16]. Many approaches have been developed for water and oil repellent fluorinated surfaces copolymerization of methacrylate monomers with (perfluoroalkyl)ethyl methacrylate [17]; block copolymers of poly (styrene-b-isoprene) with 1-, 2- and 3-armed semi-fluorinated monodendrons attached on the isoprene block in tandem with block copolymers of styrene with perfluoroalkyl acrylates [18–20]; polymeric films with nanoscale phase-separated fluorinated surfaces made with solventless liquid oligoesters and partially fluorinated isocyanates [21]; and perfluoroalkyl dangling chains covalently bound to a crosslinked polymer network prepared through the reaction of fluorinated oligoester precursors with a poly-(isocyanate) cross-linker. The fluorine weight fractions required for the low surface energy materials have been decreased from relatively large fractions down to less than 1 wt%. Surfaces with low surface energy, super low wettability, and even with self-healing properties have been made on the cross-linked polymer film composed of the polar urethane groups [22–25].

It has been realized that the surface composition and morphology of fluorinated species greatly affect the surface activity [26,27]. Sophisticated studies [18–20] by Ober et al. reveled that a thin layer of fluorinated components is insufficient to prevent the reconstruction of the top layer components when in contact with a polar liquid, such as water. Maintaining long-term low surface energy in the film is critical when designing surface fluorinated polymers for practical application, especially when the coating may contact with polluted air or water [13,28,29]. Recently, With et al. reported a particularly successful system consisting of a cross-linked polyurethane network with chemically bonded fluorinated dangling chains. The cross-linked films show a self-replenishing behavior by the reorientation of the dangling chains upon damage of the films. This group further combined this system with dual-size silica nanoparticles to construct a superhydrophobic coating with self-replenishing behavior [21–25].

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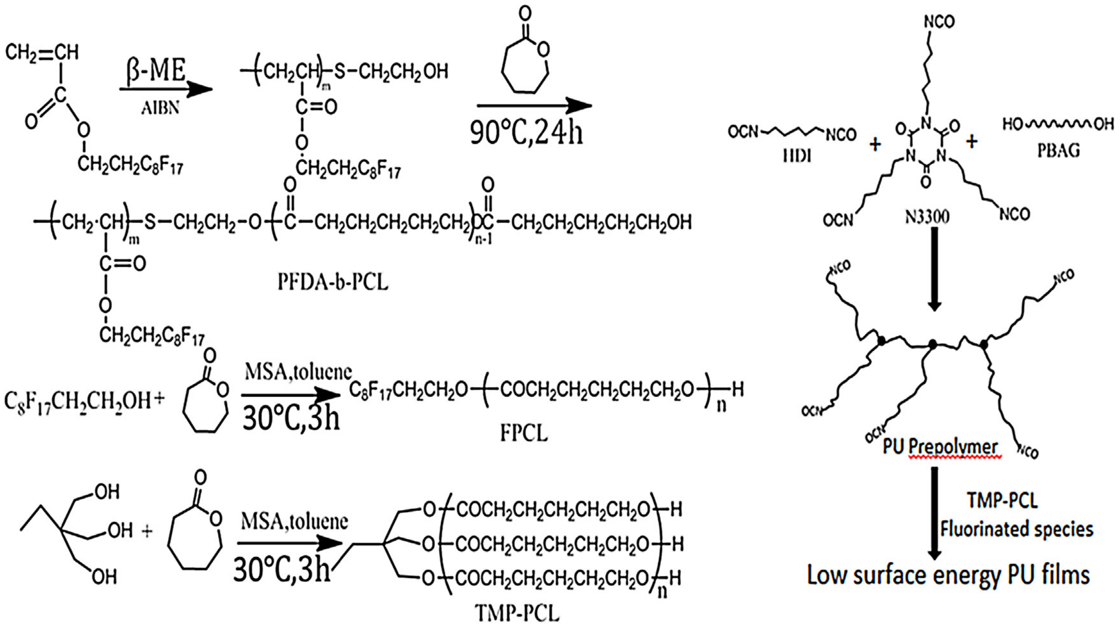

Scheme 1. The preparation of low surface energy FPU films.

Here we enhance the stability of fluorinated surface by covalently binding a fluorinated dangling shell rather than fluorinated groups, to the polymer network. Scheme 1 illustrates the preparations of the polymer network functionalized with a fluorinated shell, oligomer (perfluoroalkyl) ethyl acrylate, through a dangling spacer, oligoester, and PCL. Controls include polymers without the shell or the PCL spacer. The oligo-(perfluoroalkyl) ethyl acrylate linked through the oligoester spacer will form a dangling, yet dense layer on the surface. This offers better protection from, surface component rearrangements and chemical decomposition of the polar ester and urethane groups by hydrolysis than with perfluoroalkyl alone. The oligoester spacer between the fluorinated block and the polymer network provides the mobility necessary for the fluorinated components to segregate on the surface. The present work examines the effects of the fluorinated dangling shell, the length of fluorinated block and the PCL block on the surface properties of surface fluorinated polyurethane films.

2. Experimental

2.1. Materials

1H,1H,2H,2H-perfluoro-1-decanol (PFD, fluorochem, 95%), 1H,1H,2H,2H-perfluorodecyl acrylate (FDA, 98%, Micxy Chemical Co. Ltd., Chengdu), 2-mercaptoethanol (β-ME, Tianhua reagent Co. Ltd., Nanjing, China), fumaric acid, methane sulfuric acid (MSA, Yida Chemical Co. Ltd., Nanyang, China), and cyclohexane were used as received. The ε-caprolactone (ε-CL, 99%, Aladdin reagents, Shanghai, China) was reflux through calcium hydride and then distilled under reduced pressure. The 2,2-azobisisobutyronitrile (AIBN) was purified by recrystallization in methanol and dried under vacuum. The hexamethylene diisocyanate (HDI) and HDI trimer (N3300) were donated by Bayer Material Science, and poly1,4-butylene adipate glycol (PBAG, M_n = 1000 g/mol, XuChuan Chemical Co. Ltd., Suzhou, China) were used as received. Tetrahydrofuran was refluxed and distilled from the deep purple colored solution containing sodium and benzophenone. Trifluorotoluene (TFT, Aladdin reagents, 99%) and toluene were dried over activated molecular sieve.

2.2. Synthesis of the FDA oligomer (PFDA)

FDA (15.54 g, 0.03 mol), β-ME (0.26 g, 3.27 mmol) and 30 ml TFT were added into a 100 ml three necked flask equipped with a condenser, septum and thermometer. Then the solution was degassed with nitrogen for 30 min at room temperature and then heated to 70 °C. The AIBN (0.0246 g, 0.15 mmol) in 7.5 ml toluene were added by syringe with magnetic stirring. After 24 h of reaction, the solution was pour into a beaker and moved into the refrigerator overnight. The precipitate was recrystallized twice with TFT. PFDA as a white power was obtained after drying in vacuum at 40 °C with an 85% yield.

2.3. Synthesis of PFDA-b-PCL

The PFDA (3.2114 g) and fumaric acid (0.18 g, 1.55 mmol) were added into a three-necked flask. The mixture was dried at 60 °C under vacuum for 2 h to remove the trace water. Then ε-caprolactone (1.77 g, 15.54 mmol) and 10 ml anhydrous TFT were added to the flask by syringe. After that, the mixture was heated to 90 °C under dry nitrogen and vigorous stirring. After 24 h of reaction, the mixture was diluted with THF and precipitated with an excess cyclohexane. The copolymer was collected by filtration and subsequently reprecipitated with methanol. The precipitated was filtered and dried under vacuum at 40 °C.

2.4. Synthesis of FPCL and TMP-PCL

These two oligoester were synthesis by ring-opening polymerization with methane sulfonic acid as the catalyst [30]. A typical procedure for the synthesis of the PFD end-capped PCL (FPCL) is as follows: dried PFD (4.64 g, 0.01 mol) and anhydrous toluene (100 ml) was added to the flask, and then heated to 60 °C. When the solid was dissolved completely, stoichiometric CL (21 ml, 0.2 mol) and MSK (0.68 ml, 0.01 mol) were added into the flask. The reaction proceeded at 30 °C under dry nitrogen. After 3 h, the reaction mixture was concentrated with a rotary evaporator. After precipitation in excess of cyclohexane, the raw product was filtered off and dried under vacuum at 40 °C. The product was purified by triplicate precipitation with THF in excess methanol. The final yield was about

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