Ultrathin Cross-Linked Perfluoropolyether Film Coatings from Liquid CO₂ and Subsequent UV Curing

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Low surface energy films have a wide variety of applications such as oil and water repellents, low adhesion and friction coatings, self-cleanable coatings, biocompatible coatings, and antibiofouling coatings.[1,2] One of the most successful approaches for lowering surface energy of a surface is to incorporate fluorine atoms into polymer architectures and to apply coatings of the fluorinated polymers on a surface. Thin film coatings of traditional fluoropolymers such as poly(tetrafluoroethylene) (PTFE), fluorinated ethylene propylene (FEP), and poly(vinyl fluoride) (PVF) are challenging because of poor solubility in conventional organic solvents, low melt flowability, and poor weldability.[3-5] Typically, dispersions or powders of these fluoropolymers must be sprayed on the surface and fused at temperatures as high as 300 °C to form thin films. New fluorinated polymer materials and coating methods have been investigated to overcome the limitations inherent to the traditional fluoropolymers. This include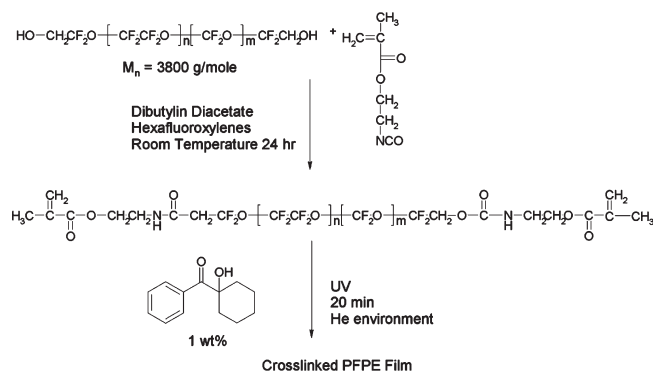s fluorinated polyolefin coatings,[4] organic solvent soluble fluoropolymers,[6,7] water dispersions or even water-soluble fluoropolymers,[8-10] and vacuum-based deposition techniques.[11,12] However, usage of expensive and harmful organic solvents, emission of volatile organic compounds (VOCs), and generation of large quantities of chemical wastes are major concerns in the liquid solvent-based fluoropolymer coating techniques. Utilization of the vacuum-based fluorinated surface preparation techniques is often limited by unpredictable film chemical composition, complexity of operation, and high tool cost.

There is great interest in thin fluorinated polymer coating techniques using liquid carbon dioxide (l-CO₂) or supercritical carbon dioxide (scCO₂) because of the high solubility of fluoropolymers in CO₂, an environmentally benign solvent, and because of the high film qualities resulting from techniques such as a rapid expansion of supercritical solutions (RESS), spin coating, and free meniscus coating.[13-20] The unique physical properties of l-CO₂ and scCO₂, including extremely low surface energy, low viscosity, and tunable density, make them appropriate media for overcoming some of the constraints associated with the traditional fluoropolymer coating techniques. Although highly uniform and ultrathin fluoropolymer films can be deposited using l-CO₂ or scCO₂, a major drawback is only a limited number of polymers are soluble in CO₂. In contrast to the previously reported scCO₂ or l-CO₂ based coating works, this study shows that polymers that have limited solubility in CO₂ can be deposited on a surface using a coating and subsequent reaction technique. It is possible to form ultrathin fluorinated films with chemical resistance characteristics, by first forming photocurable perfluoropolyether (PFPE-DMA) films by high-pressure free meniscus coating (hFMC) using l-CO₂ as the coating solvent with subsequent curing of the coated films. The limited solubility of CO₂ can be overcome using the coating followed by the reaction method. The synthetic procedure used to prepare PFPE-DMA is shown in

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Scheme 1. Preparation of Photocurable Perfluoropolyether and UV Curing

Scheme 1 (materials and preparation method are described in the Supporting Information). PFPEs are a unique class of fluorinated polymers that are liquid over a wide range of temperatures (-100 °C to 400 °C) and exhibit high thermal and chemical stabilities, low toxicity, low surface energy, high insulating properties, and optical clarity.[21]

Figure 1 shows AFM images of PFPE-DMA films and the average film thickness at solution concentrations of 5−30 wt % and at a withdrawal velocity of the sample through the l-CO$_2$ interface of 0.1 cm/s. The evaporation driving force, the pressure difference between the coating vessel pressure and the vapor pressure of the solution (ΔP),[20] was set to zero in all the coating runs. As the solution concentration increased from 5 wt % to 30 wt %, the film thickness increased from 2.8 to 12.5 nm. The increase of the dry film thickness with an increase in the solution concentration is due to the increased solution viscosity at higher concentrations. At a concentration of 5 wt %, a very uniform PFPE film with no evidence of dewetting was obtained (Figure 1a). When the solution concentration increased to 10 wt %, a 3.8 nm thick film was coated. As shown in Figure 1b, dewetting of this film was initiated via the formation of droplets. The diameter of droplets was in the range of ∼100 nm, and the height was ∼3.5 nm. It can be also seen that neighboring droplets tend to coalesce, forming larger size droplets with irregular shape. Thin films of hydroxyl group terminated PFPEs (Zdol) on substrates such as native oxide of silicon (SiO$_x$) and amorphous nitrogenated carbon (CN$_x$) exhibit autophobic dewetting behavior, an inability of the liquid film to wet its own monolayer, when the film thickness exceeds monolayer thickness.[22−24] The polar hydroxyl end groups are anchored to the polar or other active sites of the substrates via strong attractive inter-
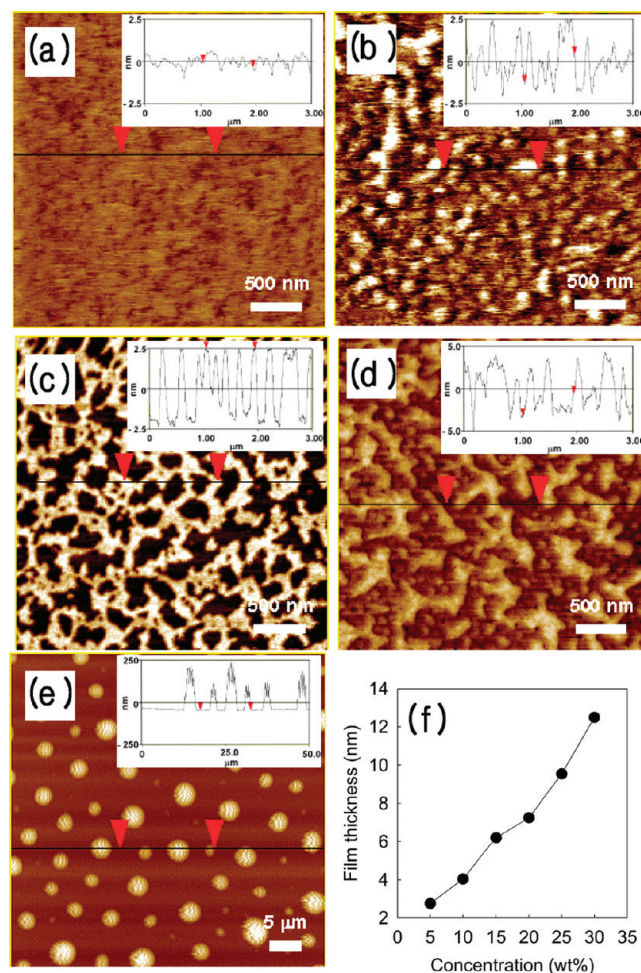
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Figure 1. AFM images of PFPE-DMA coated on SiO$_x$ by l-CO$_2$ hFMC at various concentrations of (a) 5 wt %, (b) 10 wt %, (c) 15 wt %, (d) 20 wt %, (e) 30 wt %, and (f) dependence of the average film thickness on the solution concentration for PFPE-DMA films coated on SiO$_x$ by l-CO$_2$ hFMC before curing. (a, b, c) height scale 5 nm, (d) height scale 10 nm, (e) height scale 500 nm.

actions.[22,25,26] This leads to exposure of nonpolar PFPE backbones to the air/polymer interface and formation of an ordered monolayer with thickness comparable to two times the radius of gyration (R_g) of the polymer. The ellipsometric thickness of the 2.8 nm film coated at 5 wt % is approximately equivalent to two times the radius of gyration of PFPE-DMA (1.5 nm). This indicates that a monolayer of PFPE-DMA was coated on the surface. This is in good agreement with previous works by other groups showing that dewetting did not occur when the film thickness of the high polar group terminated PFPEs was less than $2R_g$.[22,24] Meli et al. observed that dewetting of polystyrene thin films on SiO$_x$ substrates in CO$_2$ depended on film thickness, temperature, and CO$_2$ volume fraction, and they developed a theory to explain the results.[27] When a larger quantity of the PFPEs than the quantity required for a monolayer thickness was coated on the substrates, dewetted film morphologies such as

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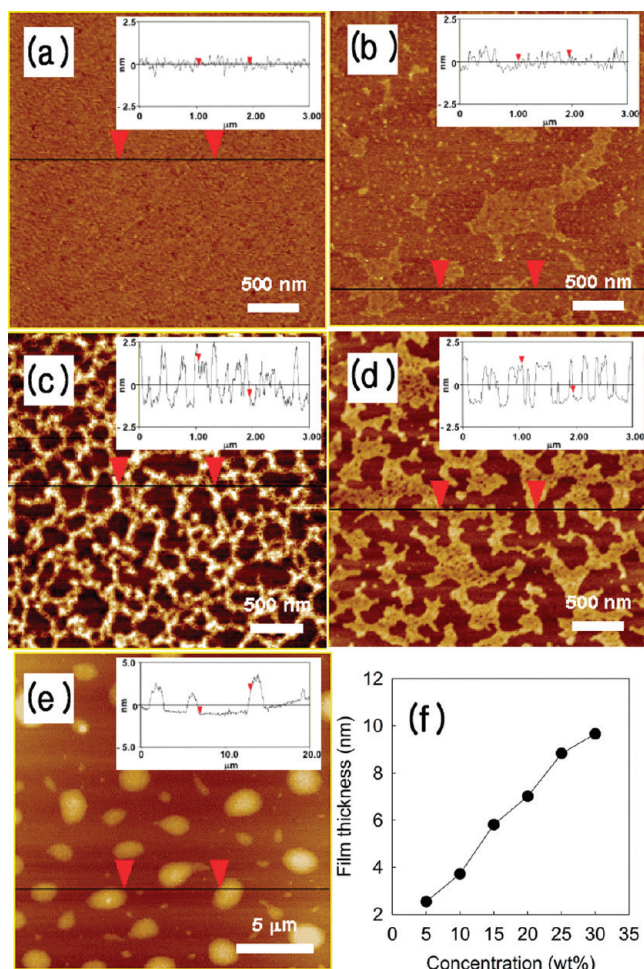(27) Meli, L.; Pham, J. Q.; Johnston, K. P.; Green, P. F. *Phys. Rev. E* **2004**, *69*, 051601.

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Chem. Mater., Vol. 22, No. 8, 2010 **2413**

Figure 2. AFM images of PFPE-DMA coated on SiO_x after 20 min of photocuring in a He environment. (a) 5 wt %, (b) 10 wt %, (c) 15 wt %, (d) 20 wt %, and (e) 30 wt %, and (f) dependence of the average film thickness on the solution concentration for PFPE-DMA films coated on SiO_x by l-CO_2 hFMC after curing. (a, b, c, d) height scale 5 nm, (e) height scale 10 nm.

droplets or holes were found.[22,24] In our case, when the film thickness increased to 4.5 nm by increasing the solution concentration to 15 wt %, dewetting occurred via formation of holes (Figure 1c). The height between the bottom of the holes and the top of the ridges at different locations was very uniform, and the height was ~4.5 nm. A further increase in solution concentration to 20 wt % leads to 6 nm thick film deposition. As shown in the AFM image of the 20 wt % sample (Figure 1d), well-connected ridges ~7 nm in height and isolated droplets 8 nm in diameter formed. When the solution concentration increased to 30 wt %, large size dewetted droplets in the range of 2−4 μm in diameter and 150−250 nm in height resulted (Figure 1e). Therefore, as in the case of hydroxyl terminated PFPE on SiO_x, α-,ω-methacryloxy terminated PFPEs coated on SiO_x exhibit autophobic dewetting behavior when quantities of the polymer larger than the quantity required for a monolayer thickness were coated on SiO_x.

Figure 2 shows morphologies of PFPE-DMA after the UV irradiation in a He environment for 20 min and dry film thickness after the UV curing. After the coated films were cured using UV, the thickness decreased to 5−20% of the film thickness before curing. The thickness decrease after curing is due to density increases during the curing reaction. As shown in Figure 2a, a very uniform film with low root-mean-square (rms) roughness value of 0.24 nm was produced after curing the film coated at 5 wt %. The advancing contact angle for water of this sample, measured after washing with Freon113, was 105°. This suggests that a monolayer PFPE network was produced on the substrate. In the cured film coated at 10 wt %, very small islands of 30 nm in diameter and roughly circular shape and large islands with irregular shape were observed (Figure 2b). The height of each island was in the range of 5−10 nm. The dewetted film morphology of the film coated at 10 wt % (small hemispherical droplets and large coalesced droplets) is responsible for the island structure of the cured film. As shown in Figure 2c, a film with a "mesh" structure was produced when the film coated at 15 wt % was cured. The connected ridge morphology of the film coated at 15 wt % (see Figure 1c) apparently resulted in the mesh-like structure after the UV irradiation. The width of the ridges in the cured sample decreased from ~100 nm to ~60 nm, and the heights decreased from ~4.5 nm to 2.5−3.5 nm, compared with the film before the UV irradiation. When the film coated at 20 wt % was cured, well-connected ridges with height of 2.5 nm formed (Figure 2d). This height value is roughly three times lower than the height of the ridges of the film before curing. Dramatic changes in droplet dimensions were observed when the film coated at 30 wt % was cured (Figure 2e). The diameter the droplets decreased by a factor of 2 (1−2.5 μm) and the height of the droplet decreased by a factor of 50 (4−5 nm) after the UV irradiation.

Water advancing contact angles of each PFPE-DMA film coated on SiO_x were in the range of ~110°, indicating the polymer molecules were successfully coated on the substrate. After the coated film was washed with Freon113, water advancing contact angles decreased to ~35°. This value is approximately 10° higher than the contact angle of SiO_x. This suggests that most of the PFPE-DMA molecules coated on SiO_x were removed after washing with Freon113. After UV curing, each sample was washed with Freon113, and then the water advancing contact angles were measured. The contact angles of the cured films were in the range of 105−115°, suggesting the polymer film formed a network structure during the UV irradiation. Therefore, highly solvent-resistant, optically clear, and low surface energy films with thickness in the range of 2.8−12.5 nm were created using the photocurable PFPE films coated from l-CO_2 hFMC and subsequent curing.