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Enhanced mechanical properties of low-surface energy thin films by simultaneous plasma polymerization of fluorine and epoxy containing polymers

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ABSTRACT

Thin films of poly(2,2,3,4,4,4 hexafluorobutyl acrylate-glycidyl methacrylate) (P(HFBA-GMA) were deposited on different surfaces using an inductively coupled RF plasma reactor. Fluorinated polymer was used to impart hydrophobicity, whereas epoxy polymer was used for improved durability. The deposition at a low plasma power and temperature was suitable for the functionalization of fragile surfaces such as textile fabrics. The coated rough textile surfaces were found to be superhydrophobic with water contact angles greater than 150° due to the high retention of long fluorinated side chains. The hydrophobicity of the surfaces was observed to be stable after many exposures to ultrasonification tests, which is attributed to the mechanical durability of the films due to their epoxide functionality. FTIR and XPS analyses of the deposited films confirmed that the epoxide functionality of the polymers increased with increasing glycidyl methacrylate fraction in the reactor inlet. The modulus and hardness values of the films also increase with increasing epoxide functionality.

1. Introduction

Surfaces with water contact angle greater than 150° are generally called superhydrophobic. Superhydrophobicity depends on several factors including surface chemistry, homogeneity and roughness.[1,2] Superhydrophobic surfaces have very low contact angle hysteresis. If a water droplet is placed on an inclined superhydrophobic surface, the droplet moves freely without wetting the surface and there is not a significant difference between the contact angles at the front or at the back. In order to change the wetting behavior of a surface, usually a thin coating which has relatively lower surface energy than the original surface is introduced. Low surface energy polymeric thin films are desirable in many applications such as antifouling coatings [3,4], textiles [5,6], biocompatible surfaces [7,8], liquid resistant papers [9], and microelectronics [10]. Poly(tetrafluoroethylene) and poly(dimethylsiloxane) are widely used as polymeric coating materials due to their extremely low surface free energies.[11,12] Although polymeric thin films can be formed on different surfaces using either solution based or vapor based techniques, the desired technique should allow rapid coatings with a high degree of retention of chemical functional groups and the method should be applicable for fragile and geometrically complex substrates. Solvents used in the solution based methods are not compatible for most of the fragile substrates and they cause major environmental problems. Plasma enhanced chemical vapor deposition (PECVD) method, on the other hand, has gained great interest in recent years because of its ability to produce well-defined defect-free polymeric films on many different substrates with low energy inputs. In literature, many monomeric species that contain polymerizable bonds has been deposited by PECVD on many different substrates. [13–16] Also, the conformal nature of the PECVD allows uniform coatings on geometrically complex substrates.[17,18]

The aim of this study is to develop a stable hydrophobic surface with improved mechanical properties. Previously, chemical vapor deposition approach has been successfully used to deposit thin films of low surface energy materials to develop hydrophobic finishes [5,19,20], but these approaches are subject to some limitations, such as severe conditions, and low durability of the coatings due to weak physical interactions. To preserve the structure and the hydrophobicity, PECVD of fluorocarbons has been carried out in mild or pulsed plasma conditions.[13,15,21,22] In this study, thin films of 2,2,3,4,4,4 hexafluoro butyl acrylate (HFBA) and glycidyl

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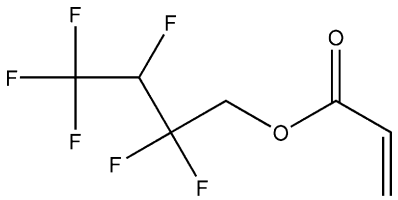
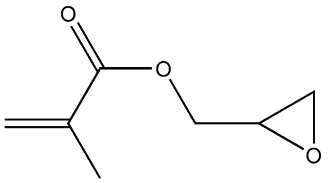


2,2,3,4,4,4-Hexafluorobutyl acrylate



glycidyl methacrylate

Fig. 1. Chemical structures of monomers used in PECVD of thin films.

methacrylate (GMA) are synthesized on silicon wafer and cotton fabric surfaces using PECVD method. The effects of the incorporation of GMA on the mechanical and wetting properties of the final P(HFBA-GMA) coating were discussed.

2. Experimental

2.1. Materials

The monomers 2,2,3,4,4,4 hexafluoro butyl acrylate (95%) (HFBA) and glycidyl methacrylate (97%) (GMA) were purchased from Sigma–Aldrich. The monomers were used as-received without any further purification. The chemical structures of monomers used in this study are given in Fig. 1. Films were deposited on (100, p type) silicon wafers and raw cotton fabric surfaces.

2.2. Plasma Polymerization of P(HFBA-GMA)

The experiments were carried out in a PECVD system (Fig. 2) designed by Vaksis, Turkey. In this system, a cylindrical quartz tube (7 cm outer diameter, 50 cm length) was used as the vacuum reactor, which was inductively coupled by a copper coil connected to a 13.56 MHz radio frequency (RF) plasma generator. The copper coil (12 turns) was externally wound around the reaction chamber. An LC matching circuit was placed between the coil and the generator for impedance matching. A custom-built water circulated cooling plate was used as substrate holder, which was placed in the middle of the reactor to adjust the temperature of the substrate. Reactor pressure was measured by a capacitance manometer and controlled by a butterfly valve. The series of depositions in this study were performed at a plasma power of 5 W, substrate temperature of 60 °C, and under a pressure of 200 mTorr. The reactor was purged with ultra-pure nitrogen gas flow before and after each deposition. The monomers were vaporized in temperature-controlled stainless steel jars and vapors were delivered to the reactor through metering valves. Flowrate of HFBA was kept constant at 0.25 sccm, and flowrate of GMA was varied between 3.5 and 5.7 sccm. After delivery of the monomers, the plasma was activated for 10 min to deposit films on silicon wafer and cotton fabric surfaces. Effects of the monomer flow rates on the chemical, morphological and mechanical properties of the as-deposited films were investigated in detail.

2.3. Characterization studies

Chemical composition of the films was studied using Fourier transform infrared spectroscopy (FTIR) (Bruker Vertex 70) and X-ray photoelectron spectroscopy (XPS) (Specs spectrophotometer with a monocromatized Al source). FTIR spectra were obtained by using a reflectance accessory (Bruker optics) over a spectral range of 800–4000 cm^{-1} at 4 cm^{-1} resolution. All FTIR spectra were baseline corrected and thickness normalized. Thicknesses of the films deposited on flat silicon substrates (100, p-type) were measured ex-situ by a mechanical profilometer (AES Nano 500). Surface morphologies of the cotton fabrics before and after the depositions were observed by SEM (Jeol). The hardness and the elastic modulus of the films deposited on silicon wafers were measured by a nano-indenter (CSM instruments). For the indentation experiments, at least 500 nm thick films were used in order to minimize the substrate effects. Water contact angle measurements were obtained by using a Kruss Easy Drop contact angle goniometer system at ambient temperature through sessile drop method. Pure water with pH close to 7.0 was used in static contact angle measurements. A magnified image of droplet was recorded by a digital camera. The

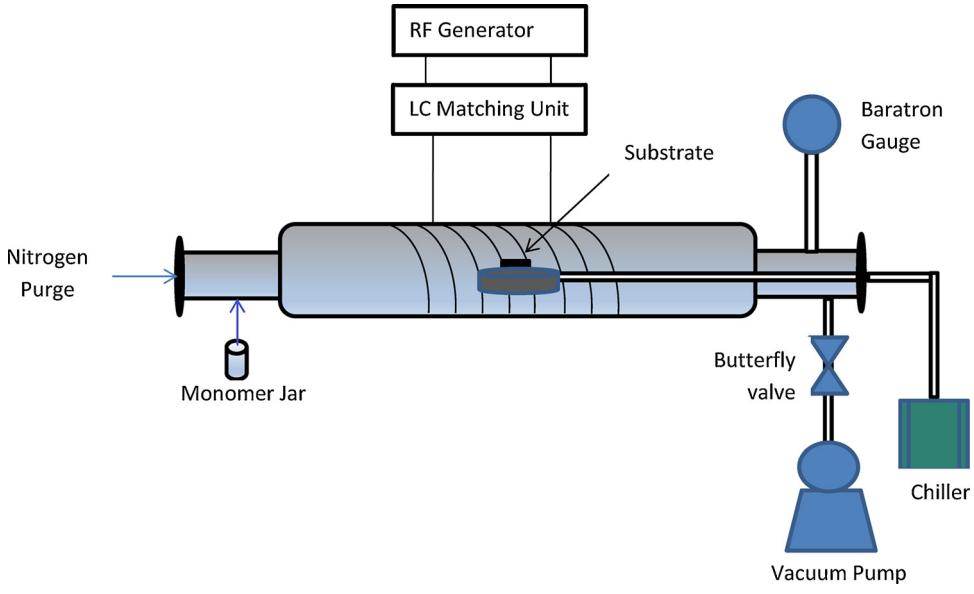


Fig. 2. Schematic diagram of PECVD reactor.