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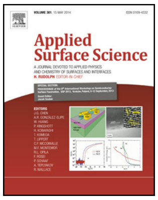

Stable superhydrophobic coatings using PVDF–MWCNT nanocomposite

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ABSTRACT

Thermally stable superhydrophobic coatings have been prepared using polyvinylidene fluoride (PVDF)–multiwalled carbon nanotubes (MWCNTs) by spray coating method. The effects of MWCNT (0–66 wt.%) and temperature (300–623 K) on wettability have been studied. A transformation from hydrophobic to superhydrophoic state has been achieved with increase of CNT content. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) studies reveal that with increase in CNT content, α-phase of PVDF decreases suggesting that MWCNT has strong effect on the phase separation of PVDF. Field emission scanning electron microscopy (FESEM) studies show that the coatings have rough surface with porous structure. With increase in MWCNT content the protrusion like structures decrease that leads to micro/nano scales. The coatings are thermally stable up to 573 K exhibiting superhydrophobicity and thereafter transformed to superhydrophilic state at 623 K. Energy dispersive X-ray spectroscopy (EDXS) analysis shows the absence of fluorine after annealing at 623 K suggesting decomposition of PVDF. X-ray photoelectron spectroscopy (XPS) of C1s and F1s core levels in as-deposited PVDF–MWCNT coating show the presence of CF_2 related species. Concentration of fluorine drastically decreases after heat treatment of the coating at 623 K. The main advantage of the present method is feasibility for application over large area and the coatings are stable up to 573 K.

Introduction

In recent times superhdrophobic surfaces with water contact angle greater than 150° and hysteresis less than 10° have attracted considerable attention due to its potential applications in self-cleaning, anti-sticking, anti-icing and anti-corrosion properties [1–7]. Further, the superhydrophobic surface can be applicable in many fields, such as oil–water separation, structural color, fluidic drag reduction, biosurface, battery and fuel cell application, prevention of water corrosion and so on [5]. The approaches used in making a surface superhydrophobic emphasize the importance of a combination of micro-nanoroughness of the surface and low surface energy. In general, the techniques employed involve a two-step procedure in which a surface is first roughened and then modified to lower the surface energy [8–10]. Two models have been proposed to govern this effect. The Wenzel model states that the surface roughness increases the surface area of the solid and thereby enhances the hydrophobicity [11], whereas the Cassie–Baxter model suggests that the air trapped within the grooves beneath the liquid leads to superhydrophobicity as the drop sits partially on the air [12]. In the last decade, several techniques have been developed to fabricate artificial superhydrophobic surfaces, including plasma etching [13], laser etching [14], chemical vapor deposition [15], electrospinning [16], anodic oxidation [17], electrochemical reaction and deposition [18], sol–gel method [19], layer-by-layer deposition [20] and so on. However, many artificial methods have certain limitations, like severe conditions, complex process control, special equipment and poor durability. Therefore, inventing some simple and effective methods to fabricate superhydrophobic surfaces with durable performance is an inevitable tendency.

Carbon nanotubes (CNTs) are attractive nanofillers for reinforcing polymers due to their large aspect ratio and surface area, good process ability and extradinory mechanical strength resulting in nanocomposites. The research related to superhydrophobic materials based on CNTs has been attractive in the last decade [21–24]. Up to now, superhydrophobic CNTs have been fabricated using functionalized CNTs, such as covalent attachment [25] and noncovalent adsorption or wrapping of various long-chain hydrophobic molecules [26] on the surface of CNTs, which can reduce the surface energy

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of the CNT surface. A solution method is commonly used to fabricate superhydrophobic materials based on randomly laid CNTs, which is advantageous to subsequent coating. MWCNTs treated with cetyltrimethylammonium bromide and hydroxylic MWCNTs treated with perfluorooctanoic acid in water were found to exhibit a remarkable superhydrophobicity after drying [27,28]. However, limitations exist when polymeric materials are exposed to atmospheric conditions where degradation in superhydrophobic properties occurs due to UV-irradiation and exposure to impurities, O_2 and moisture present in the environment.

The present work is mainly concerned on the development of thermally stable superhydrophobic coatings using polyvinylidene fluoride (PVDF)–multiwalled carbon nanotubes (MWCNTs) by spray coating method. The main advantage of the present method is feasibility for application over large area. The thermal stability of superhydrophobicity of coatings is explored after thermal treatment. Thermally stable superhydrophobic coatings are useful in different applications in automobiles and industrial treatment plants. The prepared coatings are well characterized by using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy, 3D surface profiler and X-ray photoelectron spectroscopy (XPS).

Experimental methods

Polyvinylidene fluoride (PVDF) was procured from M/s Pragathi Chemicals, India and multiwalled carbon nanotubes, MWCNT (diameter ranging from 4 to 15 nm and length ranging from 30 to 15 μm) was procured from Intelligent Materials Pvt. Ltd., India. The solvents, acetone and N,N dimethyl formamide (DMF),were obtained from Merck, India. Water was purified by a Millipore water purifying system. 100 mg of as-received PVDF was mixed in 10 ml DMF and magnetically stirred for 10 min to get transparent solution. The solution was then transferred into a spray gun and coated on glass and Al substrates and dried at room temperature overnight. The thickness of the coatings was ∼10 μm.

For PVDF–MWCNT coatings, a mixture of commercial PVDF and different percentages of MWCNT (10, 20, 25, 33, 50 and 66 wt.%) were dispersed in 10 ml of DMF using a magnetic stirrer for 10 min and then ultrasonicated for 50 min. The mixture was poured into a beaker containing 80 ml of Milli Q water under stirring that resulted a black precipitate. The precipitate was collected using Whatman filter paper and washed several times with Milli Q water and dried at room temperature and kept in a vacuum oven at 70 °C for 6 h. The superhydrophobic coatings were prepared by using the precipitated PVDF–MWCNT composite dissolved in acetone and subjected to ultrasonication for about 30 min. The sonicated mixture was transferred in to a spray gun and then sprayed on glass and aluminum substrates and cured at room temperature for overnight.

The phase purity of the coatings was examined by XRD (Bruker D8 Advace) by using CuKα radiation with a nickel filter. The surface morphology of the coatings was examined using FESEM (model Carl Zeiss Supra 40 VP). The 3D roughness profile was measured using 3D profilometer (model Nano Map 500LS from AEP Technology, USA). FTIR studies were performed on a Shimadzu IRAffinity-1 spectrometer with KBr pellets. The water contact angle (WCA) of the coatings was measured using a contact angle analyzer (model Phoenix 300 Plus, M/s Surface Electro Optics, Korea). Measurements were made using tangent line-fitting mode. Water sliding angle (SA) was measured using a home-made instrument. The drop volume for WCA and SA measurements was 8 μl. Deionized Milli Q water was used for measurements. An average of five measurements was taken for reporting WCA and the error in measurements is within ±2°. The thickness of the coatings was measured by Mitutoyo digital micrometer and was found to be in the range of 10–12 μm. XPS of as-prepared and heat treated PVDF–MWCNT samples were recorded with a SPECS spectrometer using 150 W non-monochromatic AlKα radiation (1486.6 eV) as an X-ray source. The binding energies reported here were referenced with C1s peak at 284.6 eV with a precision of ±0.1 eV. All the spectra were obtained with pass energy of 25 eV and step increment of 0.05 eV.

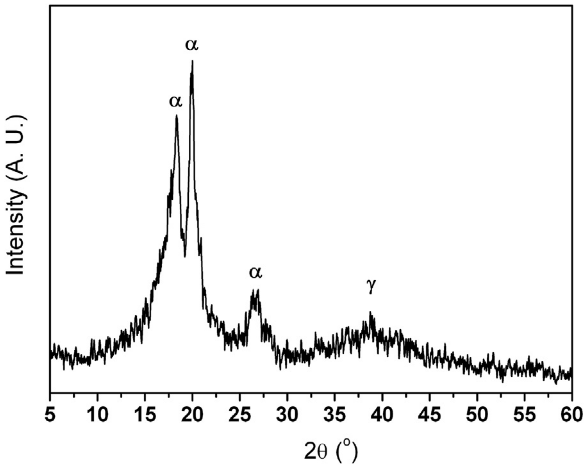

Fig. 1. XRD pattern of as-received PVDF.

Results and discussions

XRD studies

Fig. 1 shows the XRD pattern of as-received PVDF. The diffraction peaks at 2θ values of 18.3°, 20°,and 26° are due to the (1 0 0), (1 1 0), and (0 2 1) reflections of α-phase of PVDF, respectively and the peak at 39° corresponds to γ-phase of PVDF and is assigned to (2 1 1) reflection [29]. In general, PVDF exhibits at least four crystalline forms, i.e. α-, β-, γ-, and δ-phases. Among the four polymorphs, the α-phase is the most common and stable polymorph, while the β-phase is the most important one for several applications. It exhibits outstanding piezoelectric and pyroelectric properties when it is used in practical devices. The β-phase may be obtained by drawing films containing α-phase [30], by applying an extremely high electric field to the α-phase of PVDF [31], by crystallization from solution under special conditions [32], or by crystallization from the melt [33].

Fig. 2 shows the XRD patterns of as-prepared PVDF–66 wt.% MWCNT superhydrophobic coatings: (a) room temperature (300 K), (b) calcined at 623 K for 1 h and (c) pure MWCNT, respectively. From Fig. 2(a) it can be observed that with incorporation of MWCNT to PVDF, a diffraction peak at 2θ value of 26.2° appears in addition to β-phase of PVDF. Levi et al. [34] observed that the addition of MWCNTs led to β-phase formation in PVDF by sonication. In the present work, it has been observed that with addition of MWCNT, the diffraction peak intensities of α-phase of PVDF at 2θ values of 18.3° and 20.02° diminish which might be due to phase separation. The new peak at 2θ of 26.2° can be assigned to the MWCNT [35,36]. Upon calcination at 623 K the β-phase of PVDF disappears leaving the MWCNT peak intact at 2θ of 26.2°. The disappearance of β-phase might be due to the decomposition of PVDF after 623 K supported by TGA results which will be discussed in following section.