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Citation

As Published
http://dx.doi.org/10.1016/j.phpro.2013.07.045

Publisher
Elsevier

Version
Final published version

Citable link
http://hdl.handle.net/1721.1/90578

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Nineteenth European Conference on Chemical Vapor Deposition, (EUROCVD 19)

Super-Hydrophobic and Oleophobic Crystalline Coatings by Initiated Chemical Vapor Deposition

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Abstract

Preferred crystallographic orientation (texture) in thin films frequently has a strong effect on the properties of the materials and it is important for stable surface properties. Organized molecular films of poly-perfluorodecylacrylate p(PFDA) were deposited by initiated Chemical Vapor Deposition (iCVD). The high tendency of p(PFDA) to crystallize has been fully retained in the polymers prepared by iCVD. The degree of crystallinity and the preferred orientation of the perfluoro side chains, either parallel or perpendicular to the surface, were controlled by tuning the CVD process parameters (i.e. initiator to monomer flow rate ratio, filament temperature, and substrate temperature). Super-hydrophobicity (advancing water contact angle, WCA, of 160°, low hysteresis of 5°), and oleophobicity (advancing CA with mineral oil of 120°) were achieved. Low hysteresis was associated with high crystallinity, particularly when the orientation of the crystallites resulted in the perfluoro side groups being oriented parallel to the surface. The latter texture resulted in smoother film (RMS roughness < 30 nm) than the texture with the chains oriented perpendicularly to the surface. This can be very advantageous for applications that require smooth but still crystalline films.

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Selection and peer-review under responsibility of Organizing Committee of EUROCVD 19.

Keywords: iCVD, perfluoroacrylate coatings, PFDA, super-hydrophobicity.

1. Introduction

Interest continues into seeking a simple method for preparing artificial surfaces that exhibit both hydro- and oleo-phobic properties to resist fingerprints and avoid food stains on textiles. Low-surface-energy surfaces
have a wide range of applicability, as biocompatible surfaces (Ozaydin-Ince, Coclite, & Gleason, 2012), antifouling coatings (Yang, Asatekin, & Gleason, 2012), and low dielectric constant material for microelectronics (Lau, Murthy, Lewis, Caulfield, & Gleason, 2003).

Super-hydrophobicity (WCA > 150° and hysteresis - i.e. difference between advancing and receding WCA - below 10°) is highly sought but often fluorocarbon coatings exhibit undesirably high WCA hysteresis (>30°) (Mao & Gleason, 2006). Many reasons can cause high hysteresis: surface reorientation and chain mobility, morphology that trap the water drops, chemical composition heterogeneities, presence of differing amounts of trapped low molecular weight polymeric species, etc (Cassie & Baxter, 1944; Wenzel, 1936).

Fluorocarbon polymers have been demonstrated to have super-hydrophobic properties when some –CF₃ groups are exposed to the surface and when the polymeric chains have low mobility (A. M. Coclite, Y. J. Shi, & K. K. Gleason, 2012b; Lau, Bico, et al., 2003).

Fluorocarbon coatings are difficult to process into this film form because of the insolubility of these polymers in most of the commonly used solvents.

The possibility of depositing fluoropolymers by CVD is very attractive because there is no need of solvents or surfactant, which are difficult to find, expensive and persistent in the environment. Furthermore CVD allows depositing the fluorocarbon coating directly on microchannels, devices, hydrogels and this widens and simplify the applicability of this type of material. Among the CVD techniques, iCVD allows to obtain pure polymers with high structural retention, using low energy input and at high deposition rate. In iCVD the reactor is fed with an initiator, typically a peroxide, containing a labile bond. The thermal decomposition of the initiator occurs when a filament array, suspended few centimetres above the substrate, is heated. For peroxides, typical decomposition temperatures are below 300°C, which are too low to decompose also the monomer. Once the initiator is decomposed, its radicals react with the vinyl bonds of the monomer adsorbed on the substrate, kept at temperatures below 60°C. The polymerization propagates on the surface by adding more monomer molecules to the growing chains with radical ends. The polymerization terminates when the radical ends of the growing chains are capped by reaction with other radicals.

In particular, perfluoroacrylates offer fast polymerization due to the unsaturated acrylate group and hydrophobicity for the fluorinated pendant chain. As a result of the –CF₃ terminated side groups and comb-like structure, the typical range of surface energies for fluorinated acrylic polymers is very low (5.6 to 7.8 mN/m) (Gupta & Gleason, 2006).

In this contribution we would like to outline the major results concerning the correlation between CVD deposition conditions and crystalline organization, with its effects on wettability. One innovative aspect will be also the investigation of the adhesion of the coating on the substrate.

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>iCVD</td>
<td>initiated Chemical Vapor Deposition</td>
</tr>
<tr>
<td>PFDA</td>
<td>perfluorodecylacrylate</td>
</tr>
<tr>
<td>p(PFDA)</td>
<td>poly- perfluorodecylacrylate</td>
</tr>
<tr>
<td>TBPO</td>
<td>tert-butyl peroxide</td>
</tr>
<tr>
<td>WCA</td>
<td>water contact angle</td>
</tr>
</tbody>
</table>
2. Experimental details

The deposition chamber was described in details in our previous work (A. M. Coclite et al., 2012b). The liquid monomer (1H,1H,2H,2H-perfluorodecyl acrylate, PFDA, 97% Aldrich) and initiator (tert-Butyl Peroxide, TBPO, 98% Aldrich) were used without further purification. p(PFDA) samples were deposited on a tricholorovinylsilane-pretreated and an untreated silicon wafer. The deposition conditions were as follows: monomer flow rate of 0.6 sccm, pressure of 200 mTorr, substrate temperatures of 40°C. The initiator flow rate was changed from 0.3 to 3.6 sccm, following the initiator over monomer flow rate ratio (I/M) reported in Table 1. The filament temperature was varied from 240 to 300°C. Each film was deposited up to a thickness of 200 ± 10 nm, monitored real-time by reflecting a He-Ne laser (JDS Uniphase) off the substrate/thin film and recording the interference laser signal intensity as a function of time.

The film thicknesses were measured by ex-situ variable angle spectroscopy ellipsometry (VASE, JA Woollam M-2000). The crystalline state of the p-PFDA thin films was determined by X-ray diffraction (XRD). Contact angles (CA) were measured using a goniometer equipped with an automated dispenser (Model 500, Rame-Hart). The CA was measured using as liquid distilled water, mineral oil (Sigma Aldrich, CAS Number: 8042-47-5), n-heptane (99% Aldrich), n-octane (99% Aldrich) and n-decane (1000 μg mL⁻¹ Aldrich).

Surface film morphology was investigated by Atomic Force Microscopy (AFM – Digital Instruments, D3100-1) and by Scanning Electron Microscopy (SEM, Hitachi, TM 3000) with an acceleration voltage of 15 kV. The elemental analysis was done using angle-resolved X-ray photoelectron spectroscopy (ARXPS). Adhesion to silicon wafer was tested by following the standard procedure reported in ASTM International tape test D3359-02. For this test, adhesive tape (3 M Scotch tape #600 as recommended in ASTM procedure) was applied on the sample surface and rapidly removed. The percentage of delamination was determined by dividing the tested surface into equally spaced grids and then manually counting the number of grids, which showed delamination.

3. Results and Discussions

The iCVD poly-(1H,1H,2H,2H-perfluorodecylacrylate), p(PFDA) has been widely studied either pure (Gupta & Gleason, 2009; Haller, Frank-Finney, & Gupta, 2011) and copolymerized with other monomers (Baxamusa & Gleason, 2009; Coclite, Lund, Di Mundo, & Palumbo, 2013; Lau & Gleason, 2007). The side chains with eight perfluorinated carbons were completely retained during the polymerization giving interesting properties to the iCVD polymer such as hydrophobicity, oleophobicity, and crystallinity.

The fluorinated chains of the p(PFDA) pending from the polymer backbone have a natural tendency to reorient toward themselves and form a crystalline bilayer structure, called smectic B phase. Semicrystalline polymers give stable surface properties, without hydrophobic recovery and create generally rough surfaces (root mean square roughness higher than 30 nm), which can be useful for enhancing cell growth or enhancing the hydrophobicity of the surface.

The object of this study is showing that by tuning the iCVD parameters (initiator over monomer flow rate ratio and filament temperature), it is possible to tune also the degree of crystallinity in the film and the orientation of the crystallites (perpendicular or parallel to the surface) (A. M. Coclite et al., 2012b). Grafting the polymeric p(PFDA) chains to the surface has been investigated to enhance the crystallinity and wettability of the surfaces (A. M. Coclite, Y. Shi, & K. K. Gleason, 2012a).

X-ray diffraction (XRD) analysis of the iCVD p(PFDA) showed the same crystal structure observed in conventionally synthesized p(PFDA), characterized by three main peaks assignable to successive diffraction
orders of the bilayer structure: 32.4 Å (the length of the double layer), 16.2 Å (the length of a single chain) and 6.4 Å, characteristic of the hexagonal packing of the fluorochains. The crystallinity index (CI), calculated as the ratio of the areas of the crystalline peaks to the total area under the scattering curve, is reported in Table 1. Changing the initiator over monomer flow rate ratio (I/M), resulted in different crystalline organization. At high I/M, the diffraction peaks were broad (low CI), while at low I/M sharp peaks have been observed (high CI). The differences in crystalline aggregation influenced the deposition rate, the wettability and the morphology. When the crystallinity index was its maximum the WCA hysteresis was minimal, while the contrary applied to the samples characterized by a low CI. The films with low CI were smoother than the film with high CI.

<table>
<thead>
<tr>
<th>I/M</th>
<th>Tfil (°C)</th>
<th>Grafting</th>
<th>CI</th>
<th>WCA hysteresis</th>
<th>RMS roughness (nm)</th>
<th>Mineral oil contact angle (°)</th>
<th>Delamination (%)</th>
</tr>
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<tr>
<td>0.5</td>
<td>250</td>
<td>no</td>
<td>0.64</td>
<td>15</td>
<td>28</td>
<td>/</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>0.65</td>
<td>18</td>
<td>34</td>
<td>/</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>0.75</td>
<td>9</td>
<td>21</td>
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<tr>
<td>6</td>
<td></td>
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<td>0.15</td>
<td>30</td>
<td>10</td>
<td>/</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>240</td>
<td></td>
<td>0.75 (90°)</td>
<td>5</td>
<td>24</td>
<td>/</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>270</td>
<td></td>
<td>0.2</td>
<td>30</td>
<td>28</td>
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<tr>
<td>2</td>
<td>300</td>
<td></td>
<td>0.5</td>
<td>40</td>
<td>57</td>
<td>/</td>
<td>20</td>
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<tr>
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<td>0.65</td>
<td>5</td>
<td>60</td>
<td>108</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 1. The table shows as the CVD conditions (initiator over monomer flow rate ratio, I/M and filament temperature, Tfil) influenced the film properties (crystallinity index, CI, water contact angle, WCA hysteresis, RMS roughness, mineral oil contact angle and % of delaminated film after tape testing). The CI was calculated considering the diffraction pattern measured when the x-ray beam was oriented at 0° with respect to the normal of the sample surface. Only in the case of the coating deposited at Tfil = 240°C for the CI was calculated for the diffraction pattern measured at 90°.

At high filament temperature, 300 °C, sharp diffraction peaks were observable when the x-ray beam was oriented perpendicularly to the substrate while they were absent when x-ray beam was parallel to the substrate. This indicates a preferential vertical alignment of the perfluoro side-chains, which is called fiber-like structure. At low filament temperature, 240 °C, instead, the diffraction peaks were sharp at 90° and broad at 0° indicating a change to a horizontal alignment. The different orientations have been schematized in Fig.1.
Fig. 1. Schematics of the different chains orientation with respect to the substrate surface. Changing the iCVD conditions it is possible to obtain one texture or the other. The blue balls represent the carbon atoms, the oxygen atoms are in red and the fluorine atoms in gray.

The difference in orientation was attributed to the different TBPO fragments created at temperature below and above 270°C, as it can be seen in Fig. 2. At low filament temperature the bulky tert-butoxy radical cannot penetrate a vertically oriented structure, therefore the chains orient parallel to the substrate. At high filament temperature, instead, the initiation is dominated by small methyl radicals, which allow a vertical orientation of the polymer chains.

Fig 2: TBPO Thermal decomposition paths.

The polymers with the horizontally aligned chains showed lower RMS roughness and lower WCA hysteresis than the cases in which the chains were vertically aligned.

As can be seen from Table 1 all the films deposited on bare Si substrate (i.e. without any grafting) showed delaminations after the tape test to different extent, independently from the crystalline organization. Therefore further investigations were conducted on grafted polymer chains. The use of trichlorovinyl silane as coupling agent resulted in covalent bonding between the substrate and the polymer. The grafted film showed enhanced crystalline fiber-like structures with high roughness. The grafted samples were superhydrophobic with advancing water contact angle of 160°, and hysteresis of only 5°. The grafted samples were also oleophobic as demonstrated by wetting the surface with different hydrocarbon oils drops. The grafted polymer exhibits oleophobicity contrarily to the ungrafted one, which shows much lower CAs. The grafted sample didn’t show any delamination after tape test, showing improved adhesion force to the substrate.
Conclusions

iCVD allows to deposit polymers that are identical to the counterpart deposited by conventional solution-based methods. The possibility of retaining completely the functional groups has important consequences on the polymer properties. The long fluorinated chain of p(PFDA) is totally retained, resulting in crystalline aggregation. The orientation of the crystallites can be controlled by tuning the iCVD deposition conditions. The fine tuning and control of the deposition conditions, allowed also to obtain superhydrophobic and oleophobic surfaces which are very important for technological applications.

Acknowledgements

The authors acknowledge financial support of the MIT Institute for Soldier Nanotechnologies (ISN) under Contract DAAD-19-02D-0002 with the U.S. Army Research Office.

References


