

Hydrophobization of epoxy nanocomposite surface with 1H,1H,2H,2H-perfluorooctyltrichlorosilane for superhydrophobic properties

Research Article

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Abstract:

Nature inspires the design of synthetic materials with superhydrophobic properties, which can be used for applications ranging from self-cleaning surfaces to microfluidic devices. Their water repellent properties are due to hierarchical (micrometer- and nanometre-scale) surface morphological structures, either made of hydrophobic substances or hydrophobized by appropriate surface treatment. In this work, the efficiency of two surface treatment procedures, with a hydrophobic fluoropolymer, synthesized and deposited from 1H,1H,2H,2H-perfluorooctyltrichlorosilane (PFOTS) is investigated. The procedures involved reactions from the gas and liquid phases of the PFOTS/hexane solutions. The hierarchical structure is created in an epoxy nanocomposite surface, by filling the resin with alumina nanoparticles and micron-sized glass beads and subsequent sandblasting with corundum microparticles. The chemical structure of the deposited fluoropolymer was examined using XPS spectroscopy. The topography of the modified surfaces was characterized using scanning electron microscopy (SEM), and atomic force microscopy (AFM). The hydrophobic properties of the modified surfaces were investigated by water contact and sliding angles measurements. The surfaces exhibited water contact angles of above 150° for both modification procedures, however only the gas phase modification provided the non-sticking behaviour of water droplets (sliding angle of 3°). The discrepancy is attributed to extra surface roughness provided by the latter procedure.

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1. Introduction

A well-known phenomenon of surface wetting is dependent on the surface energy of the phases in contact and the interfacial surface tension between them. Surfaces with a high surface free energy (SFE) exhibit high wettability and the water contact angle (WCA) of a droplet is low, or even close to zero degrees in superhydrophilic materials, where a hydration shell forms on the surface. Superhydrophobic materials, at the other extreme, exhibit WCA values exceeding 150° , as a result of low surface free energy, coupled with a low water-surface contact area that is provided by appropriate hierarchical surface roughness. Some of such materials are inspired by plant leaves, notably these of the lotus [1, 2]. Applications of such surfaces include self-cleaning, antifouling or, potentially, icephobic coatings for airplane surfaces. [3, 4]. One of the main routes of obtaining surfaces with high water repellency involves imposition of roughness onto a low SFE material surface. For example, Zhang *et al.* [5] reported a method of obtaining a superhydrophobic film, by stretching a poly(tetrafluoroethylene) (Teflon) film. It contained fibrous crystals with a large fraction of void space in the surface which is believed to be responsible for the superhydrophobicity. The process is mostly one-stage, but is limited by a relatively small number of available materials. Another route consists of the preparation of the required surface texture in a material of choice, regardless of its SFE, and its subsequent hydrophobization with a thin layer of a low SFE compound [1, 6–10]. Various surface modification techniques can be utilized, either physico-chemical processes (such as physical vapour deposition, plasma enhanced PVD), chemical vapour deposition or wet chemical reactions. The compounds suitable for surface hydrophobization include widely used silanes or fluoropolymers. Cho's group [11] recently described the fabrication of lotus leaf-like superhydrophobic surfaces employing perfluorosilanes. Hosono *et al.* [12] used chemical bath deposition (CBD) to prepare nanostructured surfaces. The effectiveness of two types of modification technique of rough surfaces in the process of obtaining superhydrophobic materials is compared in this work – the deposition of 1H,1H,2H,2H-perfluorooctyltrichlorosilane from the gas and from the liquid phases. Because of good mechanical and environmental resistance, low price and potential technical application (superhydrophobic and icephobic coatings), epoxy resin was used as a substrate. The materials don't have to be biocompatible, because of their potential outdoor applications. The hierarchical surface roughness was imposed by incorporation of dual fillers – glass microbeads and alumina nanoparticles – and subsequent sandblasting with corundum microparticles.

2. Experimental

2.1. Materials

To obtaining composite samples, diglycidyl ether of bisphenol-A (DGBA) epoxy resin (Epidian 5, the average molecular mass: 390, Z. Ch. "Organika-Sarzyna", Poland) and IDA amine hardener (Z. Ch. Organika-Sarzyna) were used. Aluminium oxide nanoparticles (ALNP, gamma - Al_2O_3 , 99%, 10 nm, Nanostructured and Amorphous Materials Inc.) and glass microbeads (GMB, average size of 30 μm) were added as a fillers to the synthesis of epoxy resin composites. Corundum particles (250 μm) were used in the sandblasting process. Hydrophobic thin films were obtained using 1H,1H,2H,2H-perfluorooctyltrichlorosilane (PFOTS, $CF_3(CF_2)_5CH_2CH_2-SiCl_3$, 97%, ABCR GmbH and Co. KG) in hexane (95%, Chempur, Poland) solutions.

2.2. Synthesis of hierarchical topography substrates

Nanocomposite hierarchical topography substrates were obtained by mixing the epoxy resin with the amine hardener (1:1 by weight). Alumina nanoparticles were then added to the uncured mixture (in the proportion of 1:7.5 to the total Epidian 5 and IDA weight) and the mixture was ultrasonicated. The same steps were applied to the addition of glass microbeads to the mixture (in the proportion of 1.1:1 to the total Epidian 5 and IDA weight). Nanoparticles and microbeads are responsible for obtaining micro and nano- roughness of surfaces after the sandblasting process. Next the composite was degassed and deposited onto microscopic glass slides (the thickness of the coatings was about 2 mm) and allowed to cure at room temperature for 7 days. To enhance the hierarchical topography, a sandblasting process was used. The resulting micro- and nano-sized surface features provide the lotus-like structure to the material. The samples were sandblasted using corundum particles, according to the procedure described by Z. Cui, and others [13]. The size of the corundum grains influences the roughness of sandblasted surfaces. Surface roughness, or the microstructure should match the typical water drop diameter used in the experiments, to provide superhydrophobic behaviour. For this reason the corundum particles were chosen to have a diameter of about 250 μm (which gave the best results). After ultrasonic cleaning with deionized water, the low pressure air plasma system (Diener Electronic Plasma-Surface-Technology, Zepto, 40 Hz, 100 W) was used to remove impurities and generate reactive OH groups on the surfaces (20 minutes). This process is important because the chemical modification by chloro-alkyl silanes

proceeds more effectively for activated surfaces (with OH groups), which is shown by C. Haensch and others [14]. Finally, the surfaces were modified with PFOTS/hexane solutions, according to the following procedures.

2.3. Modification from the liquid phase

After the RF air plasma surface activation the samples were put for 30 minutes in a 1% PFOTS solution in hexane (at room temperature). Then, the samples were cleaned with toluene, dried with nitrogen gas and heated at the temperature of 40°C for 24 h.

2.4. Modification from the gas phase

A 0.3% solution of PFOTS in hexane was placed in a desiccator, along with samples after air plasma surface activation. After evacuating the desiccator, the deposition process was carried out for 2 hours. Then, the samples were removed from the desiccator and heated at 100°C for 2 h.

2.5. Synthesis of reference coatings

Epoxy resin surfaces, obtained by mixing Epidian 5 with IDA (in the proportion of 1:1, by weight), degassing, deposition on microscopic glass slides, and crosslinking at room temperature for 7 days, were used as reference samples. The thickness of the coatings was about 2 mm. Next, the samples were used for further modification, either as flat surfaces, or after sandblasting with corundum particles, to verify the effect of surface topography on their hydrophobic properties after modification.

2.6. Surface characterization methods

The surface topography of the coatings was investigated using scanning electron microscopy (SEM, JEOL JSM-5600). SEM characterization was performed with an accelerating voltage 20 keV and Si(Li) detector. The PFOTS layers on flat epoxy resin coatings were examined using atomic force microscopy (AFM, Solver P47, NT-MDT, in oscillation mode, operating in air under ambient conditions). Epoxy resin coatings with hydrophobic properties (WCA of about 80 degrees or more) were examined using oscillation mode, which minimizes the influence of the affinity of the Si of the SiN cantilever (spring constant about 14 N/m) to distortions of the surface features. The hydrophobic properties of the surfaces were examined using a DSA-100 Drop Shape Analysis System (KRÜSS GmbH). The sessile droplet WCA and sliding angle (SA) values were measured at room temperature, by applying

the Laplace-Young fitting algorithm to images recorded by a CCD camera (the droplet volume was about 5 µL). The average WCA values were obtained from measurements at five different locations on a coating. XPS measurements were performed employing a PHI-5702 multifunctional spectrometer using Al $K\alpha$ radiation, and the binding energies were referenced to the C_{1s} line at 284.8 eV of adventitious carbon. To minimize the surface damage due to radiation, the XPS measurement time was limited to 10 minutes or less.

3. Results and discussion

The purpose of this work was to compare the effectiveness of two methods of hydrophobization of epoxy resin composites. The aim is to obtain superhydrophobic surface, starting from a hierarchical surface topography, obtained according to a procedure developed in our earlier research (*to be submitted*). SEM images of smooth and sandblasted neat epoxy resin surfaces and the sandblasted composite surface are compiled in Figure 1, along with their respective WCA and SA values. The sandblasted composite surfaces exhibit superhydrophobic WCA values of above 150° after both hydrophobization procedures, however only the modification from the gas phase showed the non-sticking water droplet behaviour with an SA value of 3° as shown in Figure 1. In the samples modified from the liquid phase, the adhesion of the water droplet to the surface is higher than those after the gas phase modification, which is reflected by the SA value of *ca.* 20°. The discrepancy is later attributed to the additional structure formation on the surface of samples modified from the gas phase. The epoxy resin modification reactions were confirmed by XPS spectra (Figure 2). Peaks at the binding energies of 696 eV and 688 eV are seen in the samples modified by both methods and originate from the fluorine atoms in the fluoropolymer deposited in the process. Such peaks are absent in unmodified epoxy resin samples. A closer look at the XPS spectra of the modified surfaces reveals that the fluorine peaks are slightly shifted relative to each other and have different intensities. The differences could be caused by different fluorine atom environments for each case, resulting from different process conditions.

The process of gas phase modification is carried out in modifier and solvent vapours under reduced pressure, at low effective PFOTS concentration. It is hypothesized here that before the modifier layer forms on the surface, PFOTS/hexane vapour diffuses into the epoxy substrate top layer, leading to swelling of the topmost surface layer and developing surface corrugation on drying. During the wet chemical modification of the liquid phase on the other

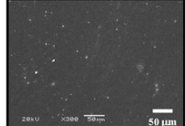
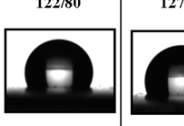
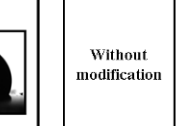
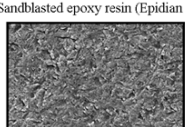
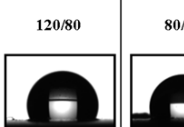

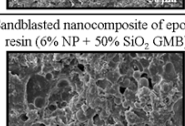
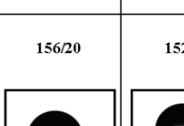
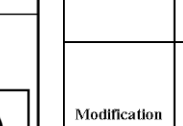
Sample type / SEM image 300x magnification	WCA/SA [°]		
	Without modification	Modification of the liquid phase	Modification of the liquid phase
Smooth epoxy resin (Epidian 5)	78/80 	122/80 	127/80 
Sandblasted epoxy resin (Epidian 5)	-/- 	120/80 	80/80 
Sandblasted nanocomposite of epoxy resin (6% NP + 50% SiO ₂ GMB)	-/- 	156/20 	152/3 

Figure 1. SEM surface topography images and WCA and SA values for the obtained surfaces.

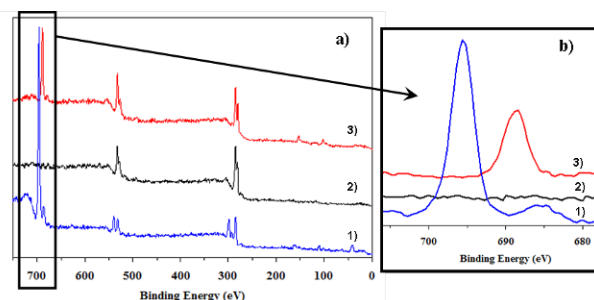


Figure 2. a) XPS spectra, and b) magnified XPS spectra of fluorine peaks of flat epoxy resin samples: 1) after liquid phase modification, 2) without modification, 3) after gas phase modification.

hand, the PFOTS concentration in the solution is much higher, hence the modifier layer growth proceeds much faster, the layer is thicker and prevents the penetration of the substrate with the solution.

The examination of the modified flat epoxy surface topography reveals that the deposition of the fluorine compound on the surface itself alters the substrate roughness. Figure 3 compiles AFM topography images (areas of 5x5 μm), cross-sections and Ra roughnesses for the flat epoxy resin surfaces without modification, after exposure to solvent and after liquid phase modifications. The roughness increases from 1 nm for the unmodified surface to 35 nm for the liquid phase modification. Such a build-up of nanosized deposit protrusions is similar to that reported for 1H,1H,2H,2H-perfluorodecyltrichlorosilane by

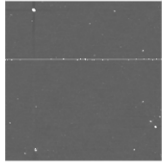
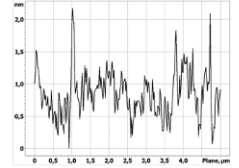
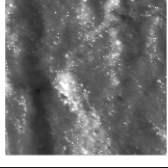
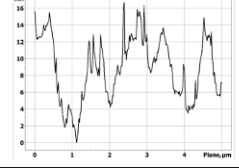
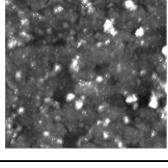
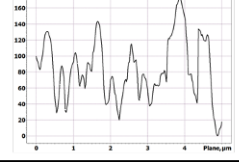
Epoxy resin			
Sample type	Surface topography	Cross	Ra [nm]
Without modification			1
After solvent influence			4
Modification of the liquid phase			35

Figure 3. Surface topography images (5x5 μm) and profiles (AFM) of smooth epoxy resin, without modification, after exposure to solvent, and after liquid phase (PFOTS/hexane) modification.

M.A. Raza *et al.* [15], who considered the siloxane nanostructures to contribute to the surface superhydrophobicity. The roughness of the surface modified from the liquid phase however is still smaller than that of the surfaces after the gas phase modification. Because the surface features height variations, exceed the AFM scanners vertical range of 4 μm , the Ra values of these surfaces could not be established using AFM imaging. Roughness was calculated from all measured areas, using Image Analysis 2.2.0 software. Ra is the arithmetic average of the roughness profile (arithmetic average of the absolute values deviations from the profile average line). The extent of the surface topography alteration by the gas phase modification is illustrated in Figure 4, where optical microscopy images of flat epoxy resin surfaces without modification, after immersion in the hexane solvent, gas phase modification (hexane vapours only) to verify the influence of the solvent on surface topography, and after liquid and gas phase modifications are shown.

The surface roughness is at the micrometer scale after the gas phase modification (in PFOTS/hexane vapours) and can be seen under the optical microscope. Such a surface corrugation adds to the hierarchical topography structure and decreases the water-substrate contact area, thus contributing to superhydrophobic properties of the composite. It should be noted here however, that the WCA on such a surface is 77° and water droplets are attached to the

surface, thus the nanosized PFOTS protrusions and microscopic surface corrugation do not themselves create all the topographical hierarchy needed for the superhydrophobic behaviour to occur and the nanocomposite surface roughness is necessary.

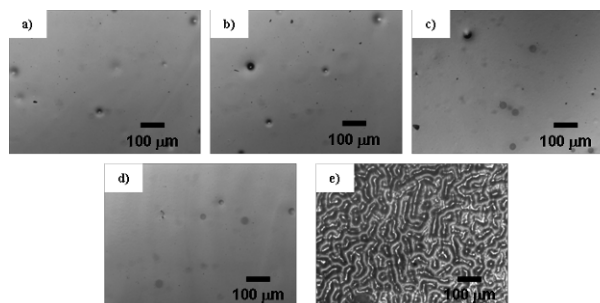


Figure 4. Optical microscope images of smooth epoxy resin samples: a) without modification, b) after immersion in hexane for 30 minutes at room temperature, c) after gas phase modification (hexane vapours only), d) after liquid phase modification (PFOTS/hexane solution), e) after gas phase modification (PFOTS/hexane vapours).

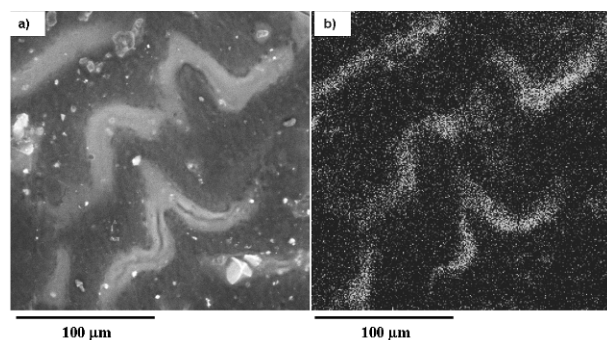


Figure 5. SEM images of: a) epoxy resin surface after gas phase modification (PFOTS/hexane vapours), b) X-ray mapping of the element F (white areas) on the surface of the same sample.

Separation of fluorine rich PFOTS on flat epoxy substrates after gas phase modification is clearly seen in EDX microanalysis images (Figure 5). The phenomenon increases the WCA of modified samples by about 5°, slightly enhancing their hydrophobic properties.

4. Conclusions

The influence of the deposition method of 1H,1H,2H,2H-perfluorooctyltrichlorosilane on a hierarchical surface structure in epoxy nanocomposite has been investigated. Chemical hydrophobization from the gas phase provided better superhydrophobic properties, with a water contact

angle of 152° and a sliding angle of about 3°. The liquid phase modification led to a similarly high WCA, but the water droplet attachment to the surface is higher, as manifested by the SA value of about 20°. Better hydrophobic properties of surfaces modified from the gas phase can be attributed to the development of additional surface roughness, caused by the build-up of nanosized PFOTS deposits and by microscopic swelling of the surface by the PFOTS/hexane vapours.

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