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PREPARATION AND CHARACTERIZATIONS OF PTFE GRADIENT NANOSTRUCTURE ON SILK FABRIC

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Superhydrophobic materials have been extensively studied because of their wonderful array of properties and applications. In this study, normal and superhydrophobic surface of silk fabric have been prepared via deposition of different shapes of PTFE nanostructure using magnetron sputter coating. The effects of PTFE sputter coating on surface morphology and surface chemical properties were characterized using atomic force microscopy (AFM) and ATR-FTIR (attenuated total reflection-Fourier transform infrared spectroscopy). The wettability of the fabric was characterized through measuring the surface contact angle by drop shape analysis apparatus and dynamic contact angle by Wilhelmy technique. As evaluated by water contact angle measurements, all the treatments resulted in a significant enhancement in the hydrophobicity of silk fabric, while larger sputtering pressures brought bigger PTFE nanoparticles, which led to higher contact angles. The results have also revealed that alternant working pressures, could bring gradient nanostructures which generated both high contact angle and less contact angle hysteresis.

Keywords: Superhydrophobic; magnetron sputtering; AFM; nanostructure.

1. Introduction

Silk has been used in textile industries for many centuries due to its superior properties. Like other natural and synthetic fibers, it has some disadvantaged properties, which has become a main force driving the research on fiber modification in material science.

In recent years, wettability modifications, especially superhydrophobic coating, have attracted a great deal of attention due to its wide range of applications and excellent prospects. Wettability of solid surfaces with water is known to be influenced by two main factors, i.e. surface chemistry and topography.[1,2] In the past decades, most modifications, particularly some chemical treatments, were focused on surface chemistry. However, recently, based on the understanding of the superhydrophobicity behavior of some natural plants such as lotus and paddy leaf, the effect of surface roughness has been revealed and emphasized by more and more researchers.

For obtaining water-repellent surface, it is necessary to prepare one type of surface with small surface tension. Previous works have showed that the surfaces could be obtained by uniformly applying fluoromethyl ($-CF_3$) groups on them.[3,4] The fundamental effect of surface structure on super water-repellency has been established since the initial publications of Cassie and Wenzel.[5,6]

In recent years, the use of plasma vapor deposition (PVD)[7] to modify surface properties of materials has experienced rapid growth. PVD is a process by which a thin film of material is deposited on a substrate. One of the most promising techniques in PVD technology is sputtering, which has been widely used to modify various materials in many industries. Therefore, sputter coating was used in this study to deposit polytetrafluoroethylene (PTFE) on one side of silk fabric for improving the hydrophobic property of the material through obtaining both low surface energy and appropriate surface roughness.

2. Experimental

2.1. *Materials and methods*

The sample used in this study was silk twill fabric with a mass of 36 m/m (145 g/m^2).

The deposition was performed in a JZCK-420B magnetron sputtering arrangement including a molecular vacuum pump, RF power source, and a control unit. A pure sputtering target (99.99%) of PTFE mounted on the cathode and argon, 99.99% purity as the bombardment gas, were used in this study. The substrate was located 100 mm from the magnetron. Different pressures were adopted to investigate the shape and structures of PTFE nanoclusters formed on the fiber. The sputter coating was performed for 90 min for each sample.

2.2. *Atomic force microscopy*

Topographic observation was performed employing a CSPM-4400 atomic force microscopy (AFM) which is one of the most effective tools to examine the microstructures of materials. In this study, Scanning was carried out in contact mode AFM using a silicon nitride cantilever CSC11 with a nominal force constant of 0. 35 N m^{-1}. All images were obtained at ambient conditions.

2.3. *Fourier transform infra-red spectroscopy*

The surface chemistry of the fabric was examined by a Fourier Transform Infra-Red (FTIR) spectroscopy produced by Thermo Electron Corporation. Spectra were recorded in air by the use of a FTIR Nexus spectrometer. The analysis software used was Omnic5.2 provided by Thermo Nicolet. Spectra were corrected for H_2O and CO_2 content in the optical path. Approximately 64 scans were co-added to achieve the signal-to-noise ratio shown. The spectral resolution was 4 cm^{-1}.

2.4. *Contact angle measurements*

Wettability was measured using sessile drop observations and the Wilhelmy technique, which are two major techniques for contact angle measurement. The first method is often a static contact angle measurement, while the Wilhelmy technique can obtain the results of both advancing and receding contact angles and hence contact angle hysteresis.

In this study, DSA100 apparatus produced by KRUSS Company was employed to measure the static contact angle. De-ionized water was dropped onto the sample from a needle on a microsyringe during testing. A picture of the drop was taken a few seconds after the drop was set onto the fabric. Static contact angles can be calculated by the software through analyzing the shape of the drop.

Dynamic contact angles and hysteresis measurements were made using a Camtel CDCA-100F apparatus based on Wilhelmy technique. Advancing and receding contact angles were obtained by calculating the change of force while dipping the fabric into water materials or retrieving it from water.

3. Results and Discussion

3.1. *Surface chemistry*

The FTIR spectrum of the fabric, sputtered with PTFE at 2 Pa in argon is shown in Fig. 1. This spectrum shows the PTFE character on the fabric surface compared to the spectrum for the original fabric in Fig. 2. The main absorption band situated at about 1400–1100 cm^{-1} is composed of the two peaks at 1290 and 1172 cm^{-1} with a shoulder at about 1150 cm^{-1}, while the spectrum of PTFE block has two peaks at 1228 and 1157 cm^{-1}, which can be attributed to the different C–F structures between the sputtered film and block of PTFE. As shown in Fig. 1, the width of the stretching vibration peak of C–F on the sputtered PTFE film is wider than that of PTFE blocks, and also the polarity of C–F is altered because of the contact between CF_4 and

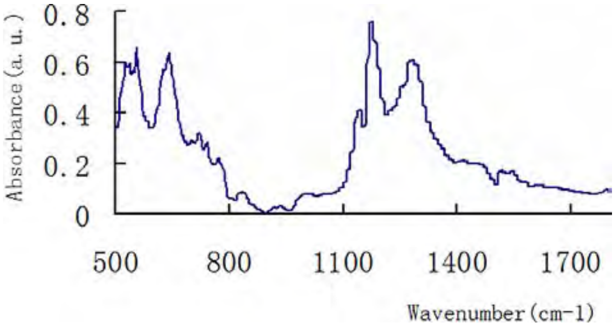

Fig. 1. FTIR spectrum of silk fabric sputtered with PTFE.

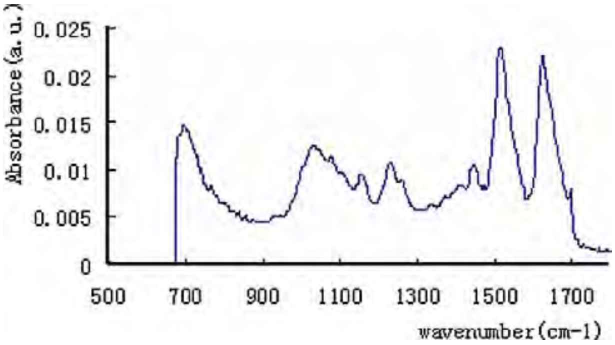

Fig. 2. FTIR spectrum of silk fabric untreated.

silk. The two peaks in the non-crystal zone and crystal zone, with equal intensity at 641 and 528 cm^{-1} reflect the crystallinity of the sputtered PTFE film. From this result, it can be concluded that the sputtered PTFE film has low crystallinity.

Since free radicals caused by Ar+ sputtering could unite into new bonds, some new absorbance peaks occur in the spectrum. An important band of deformation vibrations of CF_3 groups can be observed at 731 cm^{-1}.

3.2. *Surface morphology and gradient nanostructure*

The roughness of a surface is in general not constant during ion irradiation. The surface roughness originating from ion bombardment depends on the incident ion species and the target structure.[8] Furthermore, the roughness changes with the ion consistency until steady-state conditions are reached.

In this study, AFM investigation reveals that the roughness of PTFE films generally increases with the working gas pressure, which is illustrated in Fig. 3. Figure 4 shows the rough surface of a PTFE-sputtered fiber at a working pressure of 50 Pa. In this figure, the diameter of the PTFE cluster is increased to 400 nm from 30 nm at a working pressure of 2 Pa. The higher argon pressure increases the collisions, resulting in higher ionization efficiency and higher plasma density. This may be the main reason for the roughness increase with pressure.

Based on the relationship between working pressure and roughness, a surface with certain gradient roughness which leads to certain surface energy gradient was achieved by controlling the working pressure. Gradient structure was obtained by forming larger clusters on the understratum using higher working pressure firstly and smaller PTFE particles on the superstratum with lower argon pressure consecutively. The result for the working pressures of 10 Pa and 2 Pa continuously is shown in Fig. 5. Figure 6 displays the surface morphology of materials deposited at 50 Pa and consecutively at 10 Pa working pressure. In Fig. 6, the diameter of the bottom PTFE cluster reaches to 1100 nm and that of

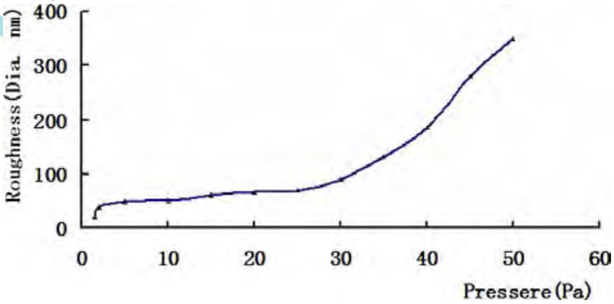

Fig. 3. Surface roughness as a function of sputtering pressure.

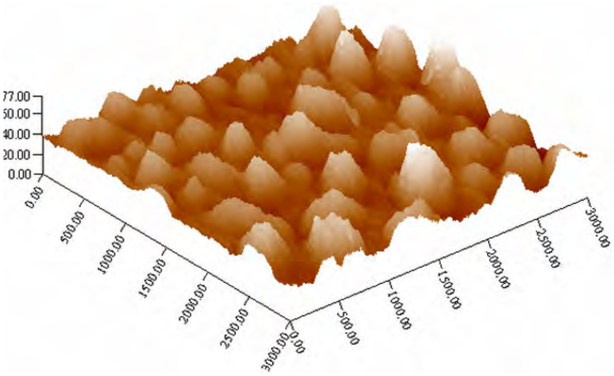

Fig. 4. AFM image of PTFE at 50 Pa argon pressure.

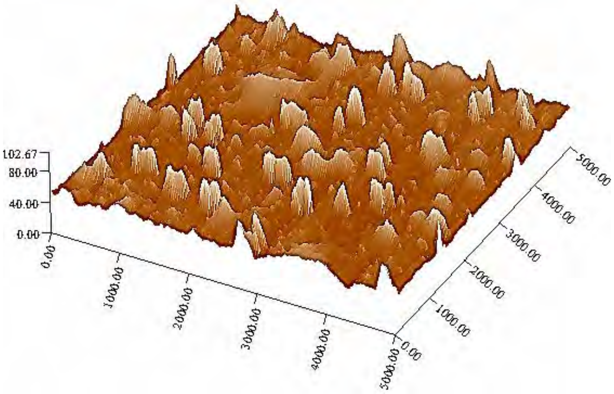

Fig. 5. AFM image of gradient structures at 10 Pa and 2 Pa argon pressures.

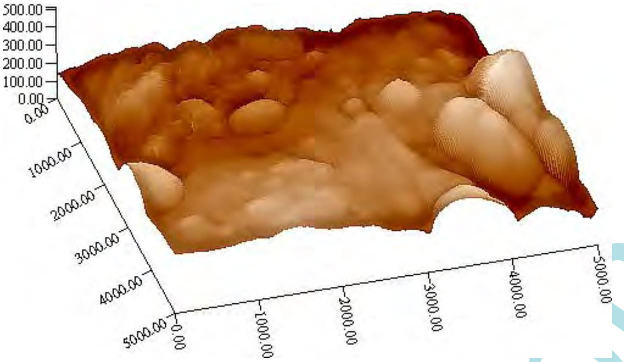

Fig. 6. AFM image of micro-nanostructure at 50 Pa and 10 Pa working pressures.

the upper aggregation is only 80 nm. However, particles of mean 400 nm can be obtained only at 50 Pa argon pressure solely. Table 1 lists some experimental gradient structures at pairs of working pressures. From this table, it can be concluded that continuous and alternate working pressures could generate both gradient structures and larger PTFE clusters, which could demonstrate a strong contact angle enhancement to nearly 160° as discussed whereafter.

Table 1. Design of gradient PTFE structures with different associated working pressures.

Consecutive working pressures (Pa)	10/2	20/2	20/5	30/5	50/10
Diameter of gradient cluster (nm)	109/35	187/35	200/75	400/80	1100/80

3.3. *Contact angle and hysteresis*

At a constant working pressure, roughness increases with working pressure as discussed in Sec. 3.2. And the results of static contact angle measurements are listed in Fig. 7. It clearly shows that PTFE sputter coating significantly increases the surface contact angle of the silk fabric. The image in Fig. 8(a) shows a water droplet formed on the PTFE sputter coated silk fabric. The high contact angle in the image clearly reveals the hydrophobic behavior of the PTFE sputter coated fabric. The static contact angle is increased to 134(±3)° for the fabric sputtered at 50 Pa from 63° for the original fabric. Figure 5 also indicates that working pressure has little effect on the static contact angle of the fabric, but remarkable effect on dynamic contact angles. The diagram in Fig. 5 shows an obvious decrease in contact hysteresis as the working pressure is increased. At 50 Pa working pressure, the hysteresis between advancing contact angle and receding contact angle reaches 11(±3)°.

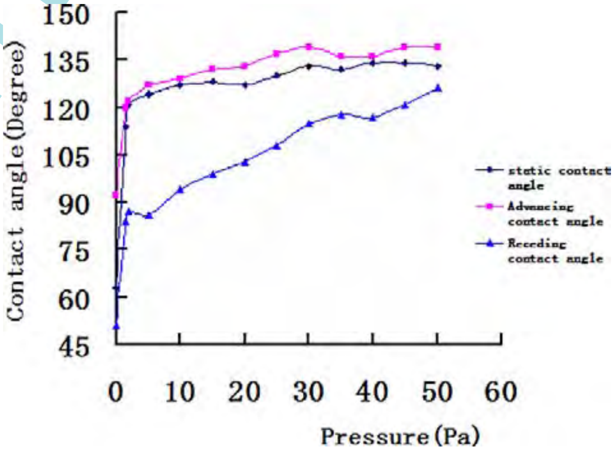

Fig. 7. Static and dynamic contact angles alter with single working pressure.

(a) (b)

Fig. 8. Shape of droplet on (a) PTFE surface at single pressure (b) dual rough surface.

It was well known that superhydrophobicity, large contact angle and low hysteresis, is linked to the use of an appropriated roughness combined with a low surface energy material. And earlier studies have disclosed the mystery of the surface of some well water-repellent plants, such as lotus, which have hierarchical, micron and nanometer, roughness.[9] In this study, we attempted to create a lotus-like surface with gradient structure to enhance hydrophobicity and reduce hysteresis. As illustrated in Fig. 8(b), static contact angle of water on gradient roughness surface at 50 Pa-associate-10 Pa working pressure reaches 152(±3)°, indicating enhanced hydrophobicity, but the hysteresis of contact angle drops to approximately 5°. This phenomenon can be explained by Cassie and Wenzel mechanisms which have predicted that the wetting behavior of a surface will be enhanced by roughness or surface texture.[5,6]

4. Conclusions

The different layers obtained exhibited contact angles from 119° up to 153°, depending on the preparation conditions. FTIR spectra indicated the chemical compositions on the fabric surface before and after PTFE sputter coating. To obtain superhydrophobic surface, we designed a gradient rough PTFE film through controlling working pressure. The observations of the topography by AFM revealed the increase of surface roughness with working pressure. It was found that the presence of dual size PTFE clusters on the surface of the substrate enhanced superhydrophobicity.

Acknowledgment

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