FABRICATION OF HYDROPHOBIC COATING ON FILTER PAPER BASED ON PDMS/SiO_2 PARTICLES

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Abstract - In this paper, the organic-inorganic hybrid hydrophobic coating was modified using polydimethylsiloxane (PDMS) as well as nano particles SiO_2, with the objective of significatly enhancing the hydrophobic performance of filter paper through a dipping coating process. The prepared PDMS-SiO_2 coating were characterized by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS), Fourier transform infrared spectroscopy (FTIR). The incorporation of PDMS annd SiO_2 particles was confirmed by EDS. In addition, the presence of organic groups (PDMS) on the surface of SiO_2 particles were confirmed by Fourier Transform Infrared Spectroscopy (FTIR). The PDMS-SiO_2 coating exhibits a hydrophobic layer on the paper surface, with a maximum water contact angle of 83.5°, and hydrophobic properties were tested using methylene blue solution.

Key words – SiO_2 nano particles; hydrophobic; PDMS.

1. Introduction

Hydrophobicity is a prevalent phenomenon found in nature and has become increasingly important for understanding basic interfacial wetting processes [1-2]. Over the last few decades, numerous studies have focused on interfacial phenomena related to superhydrophobicity, showing that this property arises from a combination of surface micro- and nanostructures alongside materials with low surface energy. As a result, a variety of methods have been developed for fabricating SHCs, such as electrospinning, sol-gel processes, chemical etching, and chemical vapor deposition. Hydrophobic coatings (HCs) have gained significant interest because of their potential applications in various sectors, such as self-cleaning [3], anti-icing [4-5], corrosion resistance [6], anti-biofouling [7], drag reduction [8], and oil-water separation [9]. To address environmental challenges effectively, it is essential to implement viable strategies for oil removal from water resources. Researchers have dedicated considerable effort over the past few decades to develope numerous techniques for this purpose, including oil skimmers, containment booms, in-situ burning methods, dispersants, solidifiers, and an array of organic, natural, and synthetic polymers and adsorbents. However, despite these advancements, the efficiency of these methods is frequently constrained by issues such as low separation efficiency, insufficient buoyancy, slow biodegradability, poor selectivity, and overall subpar performance [10].

Cellulosic filter papers attract researchers due to their low cost, biodegradability, porosity, and wide availability [11]. Numerous studies have focused on surface modification of cellulose filter paper for oil-water separation applications [12].

In general, harmful volatile organic solvents such as alcohols, alkanes, arenes, and ketones are commonly utilized as reaction media for producing hydrophobic coatings (HCs), as materials with low surface energy can be effectively dispersed in these organic solvents. However, the complete removal of organic solvents from HCs at the end of the process is undesirable, leading to preparation methods that are environmentally polluting [3, 13].

Polydimethylsiloxane (PDMS) is a non-toxic, optically clear polymer used in soft lithography and medical devices. Its hydrophobic surface, due to methyl groups, makes it ideal for creating superhydrophobic surfaces without additional chemical modifications. SiO_2 nanoparticles can serve as nanofillers, enhancing water resistance and durability. Additionally, these nanoparticles contribute to the formation of mesoporous and macroporous structures that exhibited surface roughness [14]. In this study, we developed an easy and cost-effective porous hydrophobic coating on cellulosic filter paper using a solution-casting technique that incorporated a combination of PDMS and nanoparticle SiO_2.

2. Method and characterization

2.1. Materials

Polydimethylsiloxane (PDMS) was sourced from Tianjin Bodi chemical. Nano-SiO_2 (50-250 nm in diameter) were obtained from Aladdin Technology Co., Ltd, China. Toluene, Ethanol and Acetone were purchased from Xilong Chemical Co., Ltd, China.

2.2. Synthesis of PDMS-SiO_2 Hybrid

In this process, PDMS functioned as a modifier, facilitating the achievement of superhydrophobicity in the particles. The method for grafting PDMS onto SiO_2 nanoparticles is detailed below. Initially, 50 mg of the SiO_2 powders was dispersed in 5 ml of toluene using sonication for 30 minutes. Subsequently, PDMS and SiO_2 were mixed in a Teflon-lined autoclave at a mass ratio of 5:41. The resulting mixture was then sealed and heated at 180 °C for above 10 hours to ensure complete reaction. The synthesized PDMS-SiO_2 nanoparticles were thoroughly cleaned with acetone via vacuum filtration, and the resulting solid was dried in an oven at 70 °C for 10 hours. Finally, the dried powder was ground to yield the PDMS-SiO_2 nanoparticles [15].

2.3. Synthesis of PDMS-SiO_2/PDMS Coating

PDMS-SiO_2 nanoparticles were mixed with ethanol at a mass ratio of 1:20 in a clean beaker under intense ultrasonication. PDMS was then introduced into the solution, and the mixture was ultrasonicated for 15 minutes. Finally, the PDMS-SiO_2/PDMS coating was applied to filter paper by dipping, followed by heating in an oven at 60 °C for 2 hours to evaporate the solvent and form the firm [16].

The structural and compositional characteristics of synthesized materials were comprehensively analyzed using scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS, JSM-IT200, JEOL, Japan), and Fourier transform infrared spectroscopy (ATR-FTIR, Bruker Alpha-E FTIR, Germany).

Methylene blue (0.02 M aqueous solution) self-cleaning tests were performed on the prepared papers. Besides, the water contact angle (WCA) was measured using a contact angle analyzer (KRUSS DSA10Mk2, Hamburg, Germany) with a 5 µL drop of distilled water. Digital photographs were captured using a digital single lens reflex camera (Sony, Tokyo, Japan).

3. Results and discussion

3.1. FTIR spectroscopy of PDMS-SiO_2 particles

The FTIR spectra of PDMS modified nano SiO_2 was analyzed and results are shown in Figure 1. The characteristic peaks of the spectrum and their assignment to the specific bonds are presented in Table 1. Asymmetric telescopy absorption peaks belongs to Si-O-C were observed at wavelengths of 1030 cm^{-1} and 529 cm^{-1}, respectively. The peak at 2928 cm^{-1}, there is a significant absorption peak which is characterized as the absorption peak of C-H bond in CH_3 (PDMS); while at a wave number of 1493 cm^{-1}, there is an absorption peak belonging to the -OH stretching vibration. In addition, asymmetric telescopic absorption peaks belonging to -OH were observed at wave numbers 1605 cm^{-1}, as well as the presence of a significant absorption peak characterized as Si-O-Si at 1180 cm^{-1} and 840 cm^{-1}. The spectral bands at 915 cm^{-1} and 1605 cm^{-1} denote -OH stretching vibration peaks. The peak at 789 cm^{-1} is related to the antisymmetric stretching of the Si-O-Si bonds of nanoparticles. More specifically, the peak at 690 cm^{-1} comfirmed the copolymerization reactions between Si-OH groups with PDMS molecules. Therefore, we can conclude that the nano-SiO_2 was successfully grafted with PDMS [15-18].

Table 1. *Summary of FTIR spectra on investigating the functional groups of PDMS-SiO_2 coating*

Wavelength (cm^{-1})	Assignment
2928	Antisymmetric stretching C-H bond in CH_3 (PDMS)
2847	Symmetric stretching C-H bond in CH_3 (PDMS)
1605	Antisymmetric stretching Si-O of Si-OH
1493	Antisymmetric stretching O-H
1268	Symmetric bending C-H bond in CH_3 (PDMS)
1180	Copolymerization of PDMS with SiO_2 (Si-O-Si)
1169	Rocking C-H bond in CH_3 (PDMS)
1070	Symmetric stretching Si-O-C (PDMS),
1030	stretching Si-O-C (PDMS)
915	Antisymmetric stretching Si-O of Si-OH
840	Copolymerization of PDMS with SiO_2 (Si-O-Si)
789	Antisymmetric stretching of the Si-O-Si bonds of nanoparticles
690	Copolymerization of PDMS with SiO_2 (Si-O-Si)
529	Asymmetric stretching Si-O-C (PDMS)

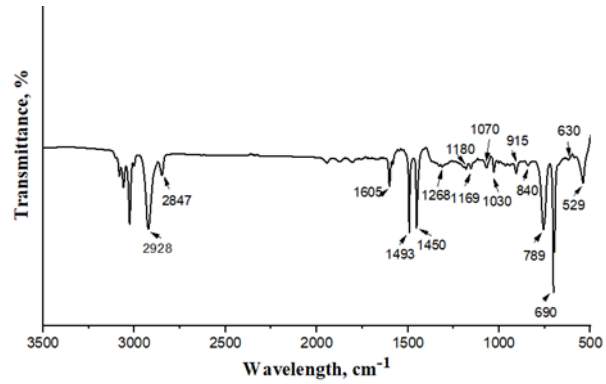

Figure 1. *FTIR spectra of PDMS-SiO_2 NPs*

3.2. Surface Morphology and Compositions

Scanning electron microscopy - energy dispersive spectrometer (SEM-EDS) used in this experimental section was JEOL from Japan. The SEM-EDS was used for observation of microstructural and analysis of chemical composition of the paper surfaces. Figure 2 shows the microstructural of PDMS-SiO_2 observed by SEM and the analysis results of the chemical composition of PDMS-SiO_2 were obtained using EDS, shown in Figure 3.

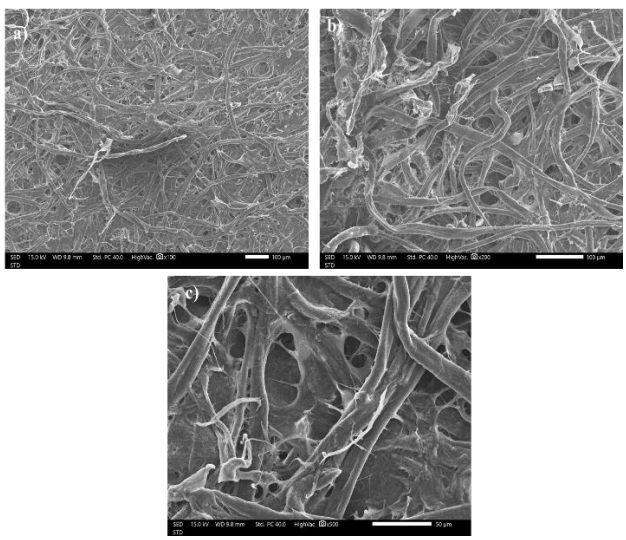

Figure 2. *SEM images of (a) the untreated paper and (b, c) the treated paper at different magnification*

Figure 2a shows the surface of the unmodified paper, while Figure 2 (b, c) display the surface of the modified PDMS-SiO_2 paper at different magnifications. It can be seen that the fibers are crisscrossed, with smooth fiber surfaces and gaps between the fibers (Figure 2a). Figure 2 (b,c) show the fiber surface of the modified paper, and the spaces between the fibers are still present. There are not PDMS-SiO_2 particles visible on the surface of the fibers.

SEM did not confirm the presence of PDMS-SiO_2 particles, the EDS was used to verify it. According to the EDS result for the un-modified paper (Figure 3a) only C, O were present. Figure 3b shows the EDS results for The PDMS-SiO_2 modified paper, again C, O are observed, amd Si is also present. This result confirm that the PDMS-SiO_2 particles has been coated on their surface and the PDMS-SiO_2 may have penetrated deep into the paper, so their presence on the surface of the paper could not be visually observed.

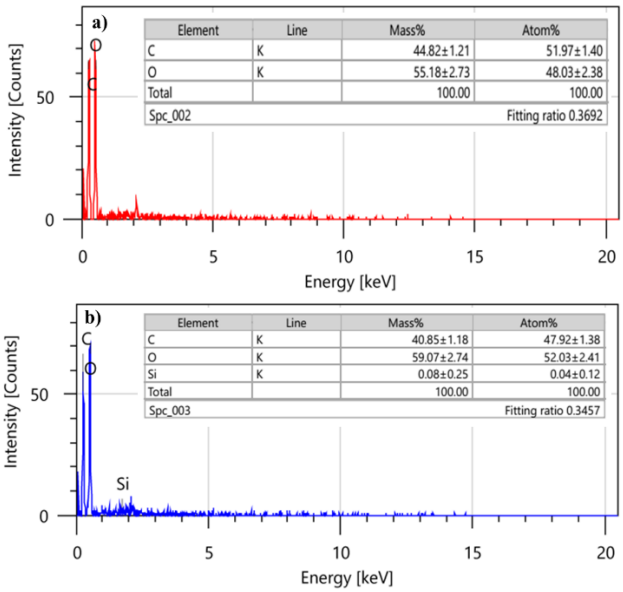

Figure 3. *EDS analysis for a) the untreated paper and b) the treated paper*

3.3. Hydrophobic test

Figure 4 shows a comparison of the hydrophobic properties between the treated paper and untreated paper, based on the methylene blue stain. In the case of the untreated paper, the methylene blue drop spreads out. The treated paper (PDMS-SiO_2 coating) instead is not wetted by the methylene blue solution, the drops rolling off the surface without leaving any trace.

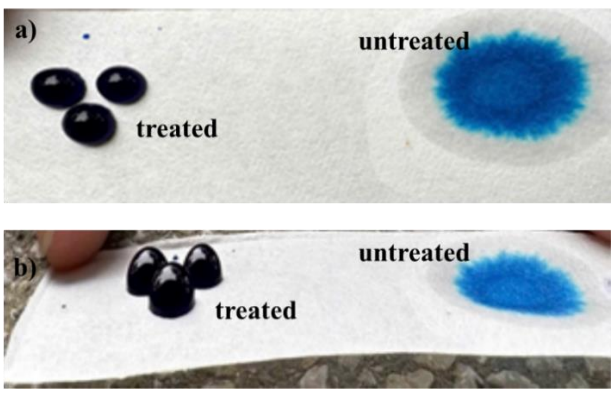

Figure 4. *Methylene blue test on the untreated and treated paper at a) top view, b) side view*

Figure 5 depicts the water static contact angles in successive times for untreated and treated samples. The remarkable increase of the contact angle (83.5°) in the treated surfaces indicate that sufficient surface hydrophobicity was achieved.

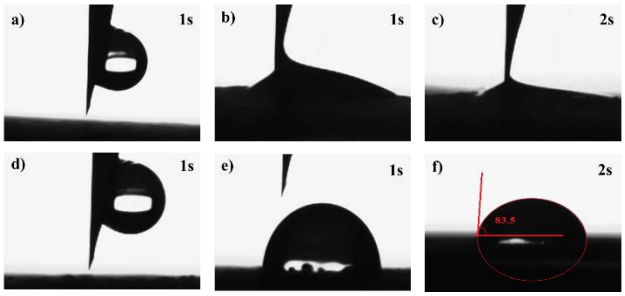

Figure 5. *Water static contact angles of papers before (a,b,c) and after (d,e,f) treatment by PDMS-SiO_2 coating, at different times*

The surface modification of particles by chemical treatment between nano particles SiO_2 with PDMS is illustrated in Figure 6. The water cannot penetrate the porous surface of PDMS-SiO_2 on the filter paper and the hydrophobicity is consequently enhanced. The hydrophobic behavior of the treated paper is due to the increased surface roughness, which is explained based on the Cassie-Baxter equation [1-2,19]. Cassie and Baxter derived an equation for the equilibrium contact angle, θ_r^{CB} on a two-component composite smooth solid surface with varying degrees of heterogeneity, as:

$$cos\theta_r^{CB} = f_1 cos\theta_1 + (1 - f_1)cos\theta_2$$

Where f_1 and f_2 are the liquid/ solid contact area fractions of solid components 1 and 2 on the surface, respectively, and θ_1 and θ_2 are the equilibrium contact angles of the same liquid on each of the flat surfaces of the components. In the Cassie–Baxter model, a water droplet will sit on top of the rough surface and air pockets are trapped underneath the droplet.

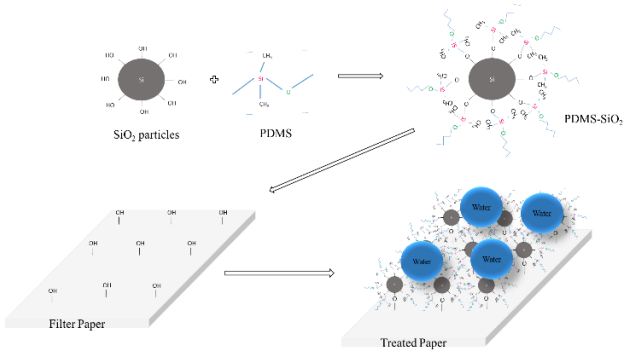

Figure 6. *Schematic illustration of the SiO_2 NPs/PDMS reaction and the hydrophobic behavior of the treated paper*

4. Conclusion

The PDMS modification of silicon dioxides nano particles was successfully synthesized. SEM/EDS, FTIR and WCAs results revealed the surface morphology, compositions and hydrophobic properties of the treated paper. The incorporation of organic solvent into the coatings not only added hydrophobic groups to safeguard the convex−concave structure of the nanoparticles, thereby potentially enhancing hydrophobic properties, but also enhanced the manufacturing the hydrophobic layer. The PDMS-SiO_2 coating is a key parameter that determines the surface hydrophobicity of the filter paper, with the highest recorded water contact angle being 83.5°.

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