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Modification of Polytetrafluoroethylene-fiberglass Composite Film Using Polydopamine Deposition with Improved Hydrophilicity

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Abstract: The surface of polytetrafluoroethylene (PTFE)-fiberglass composite film was modified with polydopamine (PDA) in order to improve hydrophilic properties and hence to expand its perspective usage for biomedical and blood-contacting applications. Scanning electron microscopy, atomic force microscopy, energy dispersive spectrometer and fourier transform infrared spectra were employed to analyse the surface morphology and the chemical structures of the modified PTFE-fiberglass composite films. Hydrophilic property of PTFE-fiberglass composite films was investigated by using water contact angle measurement. The effect of treatment time on the surface morphology and hydrophilicity of PTFE-fiberglass composite films was investigated. The results showed that a dense layer of PDA was formed on PTFE-fiberglass composite films, the water contact angle decreased gradually with the increase in modification time. Moreover, the fastness of PDA layers deposited on the PTFE-fiberglass composite films was studied by using UV/VIS/NIR spectrometer. It was revealed that the PDA layer was stable in distilled water, 0.1 M hydrochloric acid solution and alcohol, but had a poor resistance to 0.1 M sodium hydroxide solution.

Keywords: Polytetrafluoroethylene-fiberglass composite film, Polydopamine, Hydrophilic, Surface modification

Introduction

Polytetrafluoroethylene (PTFE) is a new type of materials with chemical inertness, high temperature resistance, low temperature resistance, excellent heat endurance and strong mechanical strength, which makes it to be a good candidate for the applications in the fields of water treatment, chemical industry, textile, electronics, medical treatment, military, aerospace and so on [1-4]. The PTFE paint coated on the surface of fiberglass woven fabric is a new type of high performance and multipurpose composite material. However, PTFE has strong hydrophobicity, which limits its wide applications [5,6].

In order to improve the hydrophilicity of PTFE-fiberglass composite film, surface modification to PTFE-fiberglass composite film is generally required. Methods for the surface modification of PTFE-fiberglass composite films mainly include chemical etching [7-9], plasma treatment [10-12], radiation grafting [13,14] and surface deposition modification [15,16] and so on. Although chemical etching has the capability of easily destroying the surface structure of the PTFE-fiberglass composite film, the produced chemical waste causes serious pollution problem to the environment. Plasma treatment and radiation grafting have the advantages of time saving, no pollution discharging and easy operation, but they have a high requirement for the equipment and also have the difficulty in maintaining the modified effect for a long time [17]. A novel method based on the self-polymerization of dopamine has proven to be efficient in the surface modification of various organic/inorganic materials [18]. Dopamine, which is a catechol-containing amine compound, is a major component of adhesive proteins in mussels. In an alkaline solution, the catechol functional group in dopamine oxidizes to quinone and forms the polydopamine (PDA) coating on almost any solid materials [19,20], such as PTFE, polyvinylidene fluoride (PVDF), polyethylene (PE), iron, glass and fiber, etc. [15,21,22]. The super adhesion property of dopamine was attributed to the catechol and amino groups in its molecule [23-25]. These functional groups increase the surface activity of the PDA-coated material with the enhancement of hydrophilic properties, thus expanding its applications in membrane distillation [26], pervaporation separations [27], medical devices [28] and so on. Depending on the intrinsic characteristic of the base material, they could be combined with PDA through covalent bonding and other strong intermolecular forces, such as coordinate bond, hydrogen bond and Van der Waals forces [29-31]. In addition, compared with other methods, surface modification based on self-polymerization of dopamine possesses many advantages, such as environmental friendly, simple operation and so on [32,33]. In recent years, dopamine has been widely used in the hydrophilic modification of various materials [21]. For example, Xi *et al.* [34] had successfully improved the hydrophilicity of PE, PVDF, PTFE by using self-polymerization of dopamine. Lee *et al.* [18] had transformed superhydrophobic surfaces of noble metals, oxides, polymers, semiconductors, and ceramics into hydrophilic substrates by immersing substrates into dopamine solution.

Although there are some reports on surface modification of PTFE using dopamine, few reports focus on the influence of treatment time on the property of PTFE-fiberglass

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composite films. Furthermore, PTFE-fiberglass composite films are generally used in harsh conditions, it is inevitably to contact with various solvents, which makes it necessary to investigate the fastness of the deposited PDA layer on PTFE-fiberglass composite films. However, there are very few reports on this. In this paper, dopamine was employed to treat PTFE-fiberglass composite film, and the change of surface morphology, chemical structure and water contact angle related with modification time was also investigated. The stability of deposited PDA layer on PTFE-fiberglass composite films in a range of different solvents including distilled water (H_2O), hydrochloric acid (HCl) and sodium hydroxide (NaOH) was also studied.

Experimental

Materials

PTFE-fiberglass composite film was provided by Nanjing E-Thread Polymer Materials Co., Ltd., China on the method of coating the fiberglass woven fabric with Teflon paint; Dopamine hydrochloride, Tris-HCl buffer solution (pH=8, 10 mM), NaOH and alcohol were purchased from Macklin, China.

Sample Preparation

PTFE-fiberglass composite films with a diameter of 50 mm were polished for 5 s with sanding paper (800 mesh) to remove impurities on the surface. The polished films were then cleaned with alcohol under ultrasonic for 1 h to further clean the specimen. Finally, PTFE-fiberglass composite films were cleaned with distilled water three times and dried in vacuum oven.

A 2.0 g/*l* aqueous solution of dopamine was prepared by dissolving dopamine hydrochloride powder in deionized water. Tris-HCl buffer solution and 10 wt % NaOH solution were then added to adjust the pH of the dopamine solution to 8.5 [35]. Subsequently, PTFE-fiberglass composite films were immersed in dopamine solution for 12 h, 16 h, 20 h, 24 h and 28 h respectively. After treatment, the films were washed with deionized water and dried in vacuum oven. The modified films were named M_1-12, M_1-16, M_1-20, M_1-24 and M_1-28 respectively. Figure 1 shows a schematic description of the reaction process. The unpolished PTFE-fiberglass composite film that washed and sunk in the dopamine solution for 24 h was named M_2.

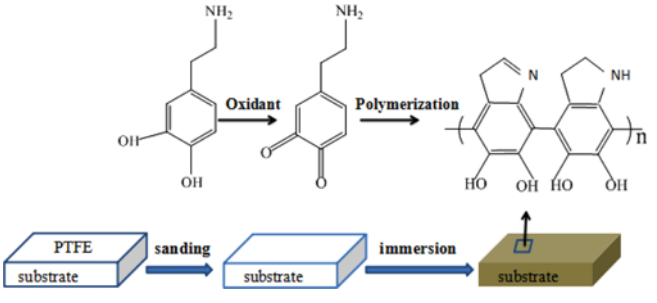

Figure 1. Schematic description of the modification process to PTFE-fiberglass composite films.

Characterization

Surface Morphology

Surface morphology of the modified film was observed by using scanning electron microscopy (SEM, Phenom, Netherlands) and atomic force microscopy (AFM, CSPM 5500, Being Nano, China).

Surface Chemical Structure

The change of fluorine/carbon (F/C) ratio after surface polished was measured using energy dispersive spectrometer (EDS, INCAx-Sight6427, Oxfod Instruments, England). The surface chemical compositions of the samples were determined through fourier transform infrared spectra (FTIR, BY 2000, Being Nano, China).

Water Contact Angle Measurement

Contact angle of PTFE-fiberglass composite films with water were measured by an optical contact angle meter (JY PHb, Chengde Jinhe, China) in order to characterize the hydrophilic properties of PTFE-fiberglass composite films.

Stability of the PDA Layer

In order to obtain modified PTFE-fiberglass composite film with good chemical stability, it is necessary to ensure that the coating layer on PTFE-fiberglass composite film is firm and can not be easily damaged. The resistance of PDA coating layer to water, HCl, NaOH and alcohol was studied. Specifically, samples of M_1-24 and M_2 were immersed in distilled water, 0.1 M HCl, 0.1 M NaOH and alcohol respectively under ultrasonic for 10 min, 20 min, 30 min, 40 min, then the samples were taken out of the solution and the colour change of each solution was observed. UV/VIS/NIR spectra of each solution were obtained by using UV/VIS/NIR spectrometer (Lambda 750, PerkinElmer, America) to quantitively describe the colour change.

Results and Discussion

Surface Morphology

Surface colour of PTFE-fiberglass composite films treated under different conditions is shown in Figure 2. It can be noted from Figure 2 that with the increase of treatment time, surface colour of the film gradually turned brown, indicating an increased amount of polydopamine on PTFE surface. When the processing time exceeded 24 h, the colour basically no longer changed. This is in accordance with other studies which found that the polymerization of dopamine reached a maximum at 24 h and increased no more with further increasing time [18]. It can also be noted from Figure 2 that under the same treatment time, polishing before dopamine modification did not have any significant influence on the surface color of PTFE-fiberglass composite film.

Figure 2. Surface colour of PTFE-fiberglass composite film under different treatment methods and processing time.

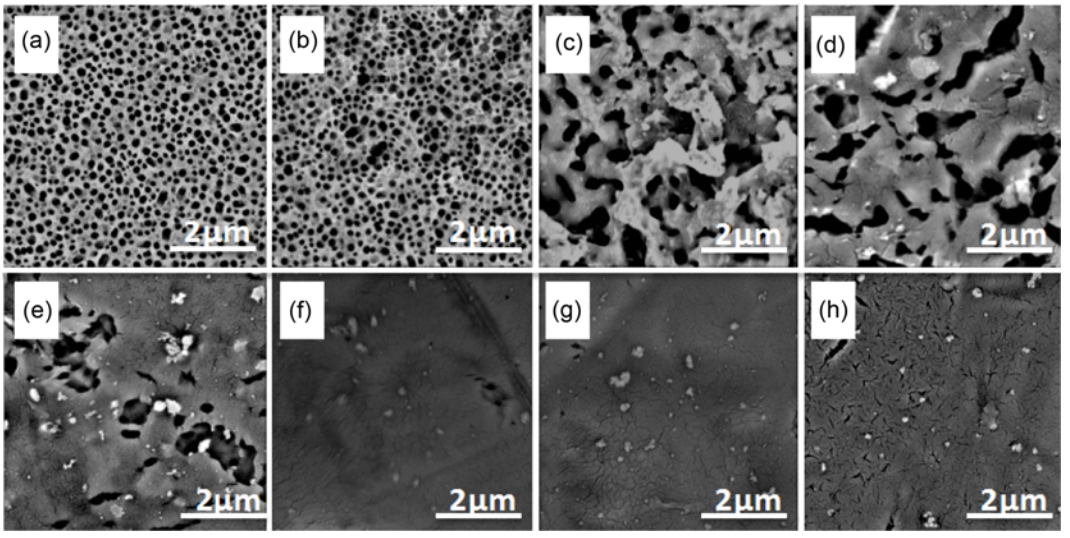

Figure 3. SEM images of (a) uncoated film, (b) polished film, (c) M_1-12, (d) M_1-16, (e) M_1-20, (f) M_1-24, (g) M_1-28, and (h) M_2.

Figure 3 shows surface morphology of the PTFE-fiberglass composite film with and without polydopamie modification. Although polishing was applied for the PTFE-fiberglass composite film, the surface structure was slightly changed, and all of them exhibited a dense microporous structure (see Figure 3(a)-(b)). The formation of the PDA layer on PTFE-fiberglass composite films after different treatment time is shown in Figure 3(c)-(g). As can be seen from the figure, PDA was deposited on the PTFE-fiberglass composite film with different surface morphology. With the increase in treating time, the formed PDA layer on the surface of PTFE became denser and more uniform. Although PDA layer was formed on M_1-12, there were still many holes on the surface indicating a thinner modification layer. The number of holes on the PTFE-fiberglass composite film decreased with increasing treatment time. When the processing time reached 24 h, there were very few holes on the surface of the sample displaying a very uniform PDA layer. There was no significant change in the morphology of the surface treated for 28 h compared with the sample treated for 24 h. The coating layer for sample M_2, was almost the same as that of sample M_1-24, although M_2 was pretreated with polishing.

AFM images for pristine, polished and the modified PTFE-fiberglass composite films are shown in Figure 4. As can be seen from the figure, the average roughness (Ra) increased from 20.2 nm to 36.5 nm after polishing PTFE-fiberglass composite films, revealing that the surface structure was changed. However, Ra dropped when PDA was deposited for 24 h. Ra of M_1-24 decreased from 36.5 nm to 15 nm while Ra of M_2 reduced from 20.2 nm to 16.3 nm. It proves that a smooth layer of PDA was formed on PTFE-fiberglass composite film with or without polishing after PDA deposition for 24 h.

Film Surface Structure

Changes in compositional elements of the surface of

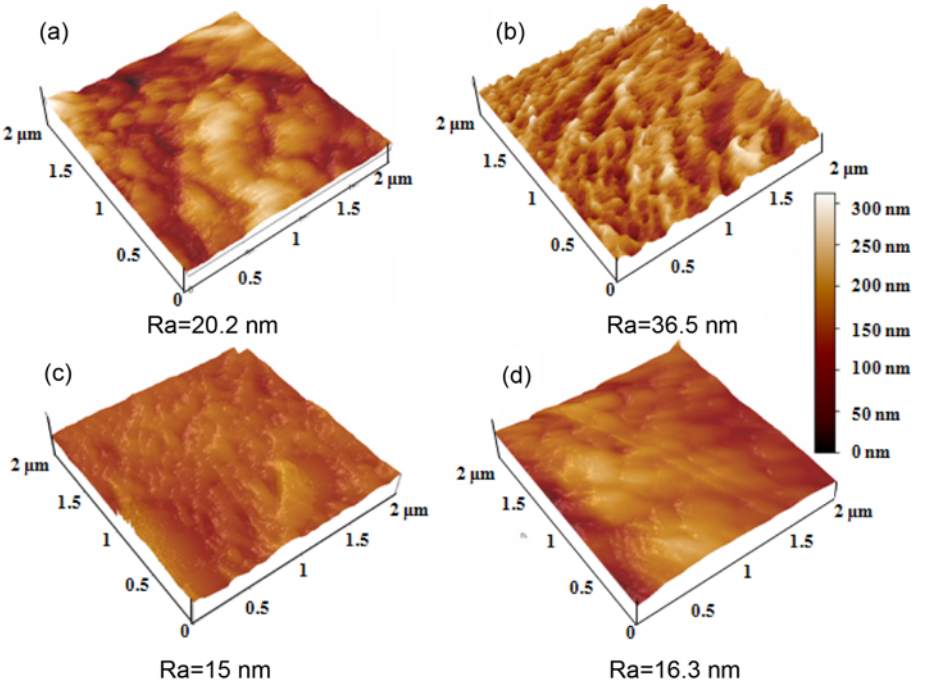

Figure 4. AFM images of (a) pristine film, (b) polished film, (c) M_1-24, and (d) M_2.

PTFE-fiberglass composite film with and without polishing were measured by EDS and the results were shown in Figure 5. The F/C ratio was slightly changed from 66.47/33.53 to 65.38/34.62 after the PTFE-fiberglass composite film was polished. This is probably due to the elimination of organic impurities. Surface chemistry structure of original and modified PTFE-fiberglass composite films was evaluated by ATR-FTIR as shown in Figure 6. A distinct difference in the spectra of original and modified PTFE-fiberglass composite films was also described in Figure 6. New peaks at about 1601 cm^{-1} and 3349 cm^{-1} were displayed in the spectra of all PDA modified specimens by comparison with that of the original PTFE-fiberglass composite film. The peak at 1601 cm^{-1} represent the superposition of C=C stretching vibrations in the aromatic ring and the N-H bending vibrations and the peak at 3349 cm^{-1} indicating of N-H stretching vibrations. All of these proved the existence of PDA on the surface of PTFE-fiberglass composite film [24,29].

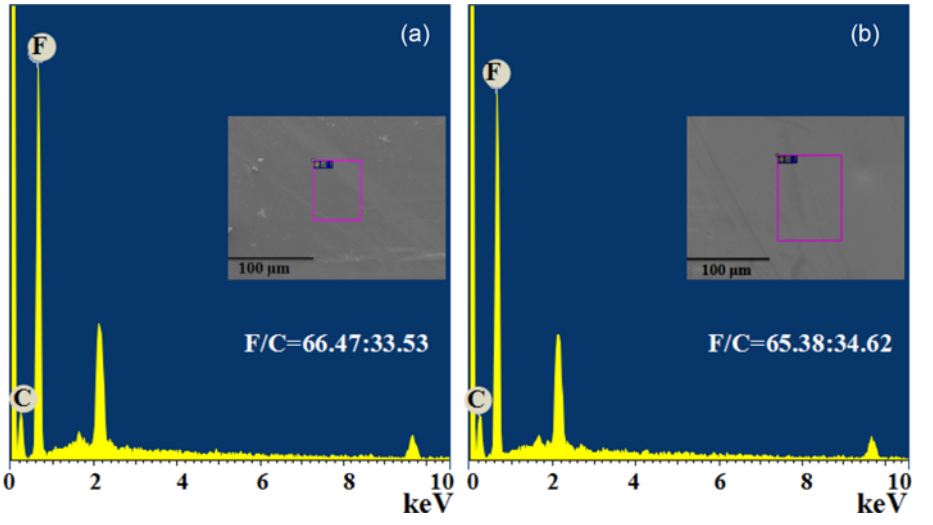

Figure 5. EDS images of (a) pristine film and (b) polished film.

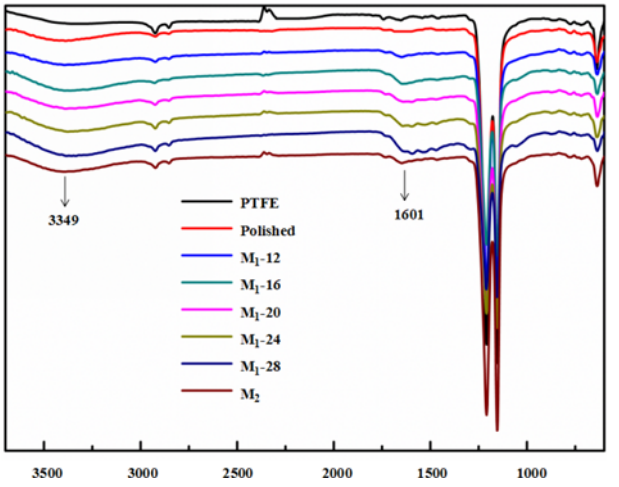

Figure 6. ATR-FTIR spectra of pristine film substrate, polished film, M_1-12, M_1-16, M_1-20, M_1-24, M_1-28, and M_2.

Water Contact Angle (WCA)

The wettability of PTFE-fiberglass composite film under different treatment time was characterized by WCA measurement. The curve of water contact angle for PTFE-fiberglass composite films with different treating time is shown in Figure 7. As can be seen from this figure, the WCA of the polished PTFE-fiberglass composite film was nearly 120 °, and gradually fell as the treating time increased. When treated for 24 h, the WCA of the PTFE-fiberglass composite film was approximately 62 °, which was close to the theoretical WCA of pure PDA film. When the processing time was further increased, the WCA hardly changed. These suggest that the surface of the PTFE-fiberglass composite film have been covered fully by the PDA layer after treatment for 24 h.

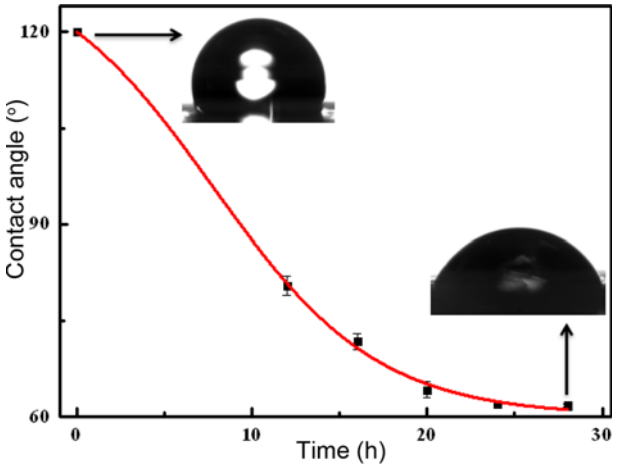

Figure 7. Typical curve of water contact angle of PTFE-fiberglass composite film with different treatment time.

The influence of polishing on the WCA of the PTFE-fiberglass composite film can be seen from Figure 8. Compared with original PTFE-fiberglass composite film, WCA of the polished PTFE-fiberglass composite film increased slightly, which might be due to the increase in the roughness of the PTFE-fiberglass composite film after grinding. However, when the original and polished PTFE-fiberglass composite films were treated with dopamine for 24 hours, M_1-24 showed a smaller contact angle than M_2. Combined with the surface morphology obtained by SEM, it can be known that polish pretreatment is favor of depositing PDA on PTFE-fiberglass composite films.

Stability of the PDA Layer

To verify the stability of the coated PDA layer, M_1-24 and M_2 are soaked in distilled water, 0.1M HCl, 0.1 M NaOH and alcohol respectively under ultrasonic. The photos of color change as well as the UV/VIS/NIR spectra of the solution after different immersing time are shown in Figure 9. It can be seen that the VIS/NIR absorbance of M_1-24 was lower than M_2 at 400 nm to 800 nm, which indicates the modified film with polishing pretreatment has better resistance to erosion. The colour of distilled water, 0.1 M HCl and alcohol did not change significantly indicating that PDA layers on both M_1-24 and M_2 had good resistance to them. However, the discolouration of M_1-24 and M_2 were more obvious in 0.1 M NaOH indicating their weak stability in NaOH solution. These results elucidate the stability of PDA coating and bond fastness between the PDA and the PTFE-fiberglass composite film can be slightly improved by polishing its surface, and the resistance to erosion can be enhanced by polishing first and then modification. Though the detailed binding mechanisms between dopamine and substrate have never been fully explained, some studies [18, 23] have proved that its superior adhesion ability derives from the strong covalent or non-covalent interactions between dopamine and the substrate.

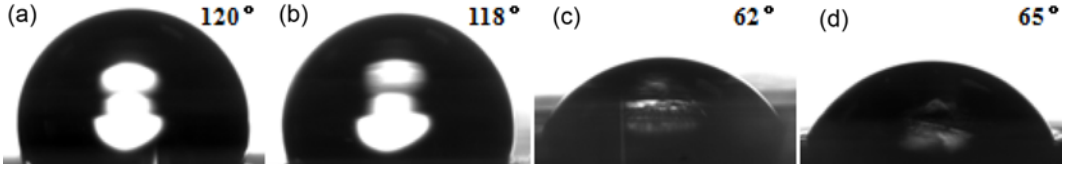

Figure 8. Water contact angle of (a) polished PTFE-fiberglass composite film, (b) original PTFE-fiberglass composite film, (c) M_1-24, and (d) M_2.

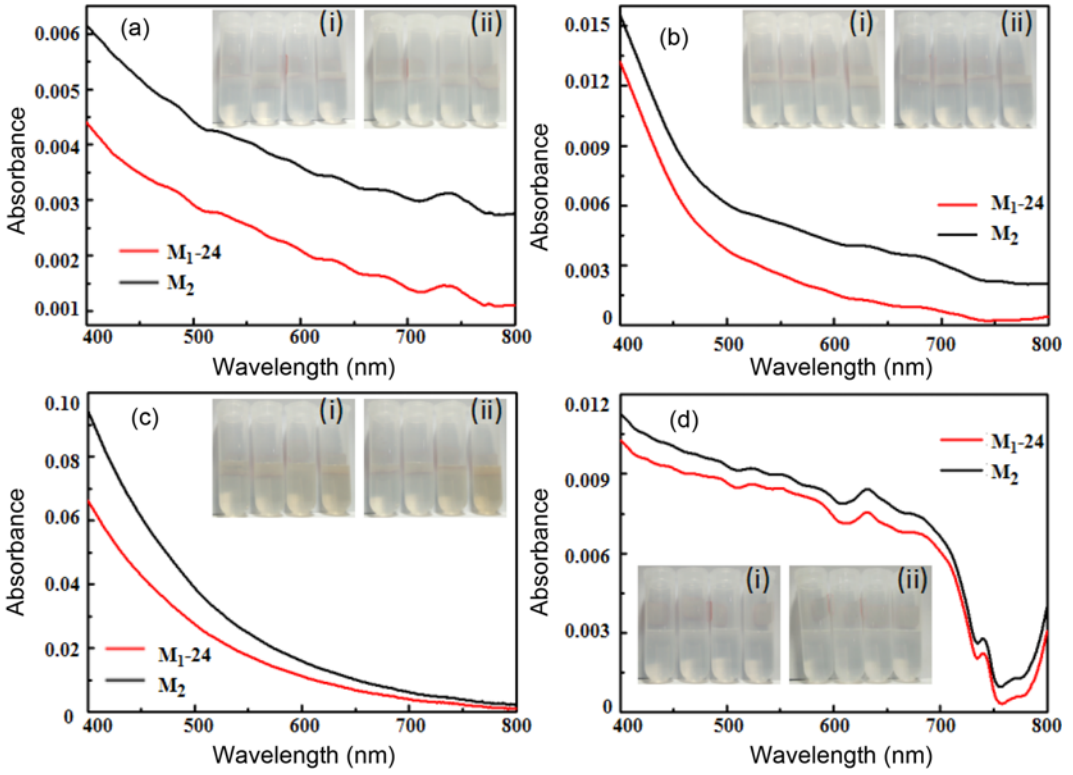

Figure 9. UV/VIS/NIR spectra of PDA-coated PTFE-fiberglass composite film immersed in different liquids; (a) distilled water, (b) 0.1 M HCl, (c) 0.1 M NaOH, and (d) alcohol. The immersion time is 40 min. The illustration corresponds to digital photos of the (i) M_1-24, (ii) M_2 immersed in 10 min, 20 min, 30 min, 40 min, from left to right.

Conclusion

Hydrophobic PTFE-fiberglass composite film was successfully modified based on self-polymerization of dopamine. The effect of treatment time on the surface morphology and hydrophilicity of modified PTFE-fiberglass composite films was explored. PDA layer became denser and the WCA decreased with the increase in modification time up to 24 h and no longer changed with even prolonged time. It is suggested that the most reasonable modification time was approximately 24 h at which a smooth PDA layer was generated and the WCA reached a platform of about 62 °. The PTFE-fiberglass composite film deposited with PDA had better resistance to distilled water, 0.1 M HCl and alcohol, but had weak stability in 0.1 M NaOH. It is expected that the modified hydrophilic PTFE-fiberglass composite film can be used in the fields of water treatment, medical treatment and textile etc.

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