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UV LED Curing of Hydrogel-Modified Textiles with High Anti-Fouling Resistance

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The hydrogel grafted polyethylene terephthalate (PET) textiles were envisioned to have oil-repelling properties due to the synergistic of combining hydrophilic hydrogel onto PET textiles surfaces. In this work, PAAm hydrogels were grafted i.e. via immersion or dipping methods onto pristine (PPET) and alkaline treated (APET) PET textile surfaces using UV LED light source. The obtained samples were then characterized based on the degree of grafting (*DG*), Fourier transformed infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), surface wettability by contact angle and oil fouling test. APET was found to be more efficient for grafting compared to the PPET due to the surface modification made after the alkaline treatment. APET surface turned to be more hydrophilic than PPET due to the presence of hydroxyl group (-OH) as proven in the FTIR. In addition, the PAAm hydrogel was confirmed to be successfully grafted onto the APET textile via immersion or dipping methods with the optimum *DG* obtained was at 20 minutes of UV time. This finding has also proven the potential of UV LED as a promising technology to replace the conventional UVA for hydrogel curing. Higher *DG* was obtained for immersed grafting sample (PAAm-*g*-APET$_{imm}$; *DG*=160 wt%) when compared to the dipped sample (PAAm-*g*-APET$_{dip}$; *DG*=60 wt%) which indicates that higher mass fraction of PAAm could be attached to the surface of PAAm-*g*-APET$_{imm}$. Apart from that, PAAm-*g*-APET$_{imm}$ shows lower water contact angle (*WCA*) with *WCA*=60.90° as compared to PAAm-*g*-APET$_{dip}$ with *WCA*=83.15° which could be due to higher thickness of hydrophilic layer that resulted in slower rate of oil fouling performance. To summarize, the PAAm hydrogel grafted onto PET textiles were significantly improved and possessed excellent surface towards oil staining performance. By comparing both textile modifications, grafting via dipping was more preferable. Even though the *DG* obtained was slightly lower, its thin layer of hydrogel grafted on the APET textile surface was sufficient to de-stain oil from the textile surface at a faster rate (~0.60-0.70 seconds). To some extent; the hydrogel modified textiles via UV LED curing has bright vision in the near future as promising tools for oil/water separation.

Keywords: PET textiles, Photografting, PAAm hydrogel, UV LED, Anti oil-fouling resistance

1. Introduction

Photografting is progressively proposed for its efficiency in surface modification. It offers unique ability to tune and manipulate surface properties without damaging the bulk materials [1, 2]. Besides that, the utilization of UV LED as a light source for UV curing is a promising technology that can be used to replace the conventional UVA system. There are also limited studies in UV curing by UV LED for preparation of hydrogel grafting [3]. In the meantime, recent studies on hydrogels have focused on oil/water

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separation field due to their oil-repelling characteristics [4-6]. PAAm hydrogel-coated mesh also shows self-cleaning characteristic [7], oil-fouling resistance [8] and special wettability with both underwater super-oleophobic and low oil-adhesion characteristics in oil/water/solid three phase systems [9,10]. Meanwhile, the use of engineering PET as a substrate is highly feasible as PET has outstanding mechanical properties similar to metal at a lower cost. However, due to its limitation with regard to their surface properties as it is less hydrophilic in nature, some modification is necessary. It is reported that alkaline treatment has been proven to enhance the hydrophilicity of PET [11] and offer compatibility for hydrogel grafting. Therefore, the first aim of this work was to investigate the feasibility of UV LED for photografting a thin layer of PAAm hydrogels onto pristine PET (PPET) textile surfaces via immersion and dipping methods. Ultimately, the efficiency of UV LED light source in enhancing the *DG* is correlated to surface wettability and the oil staining performance of the hydrogel-modified PET textiles for oil/water separation application.

2. Experimental

The non-woven PET textiles of 85 g/m^2 were obtained from China. Acrylamide (AAm), was obtained from Acros Organics and *N*,*N*'-methylenebisacrylamide (MBAAm) from Sigma Aldrich. In addition, benzophenone (BP; "type II" photoinitiator), sodium hydroxide (NaOH), acetic acid (CH_3COOH) and ethanol (C_2H_5OH) were obtained from Rahn AG in Germany and Fisher Scientific (M) Sdn Bhd, respectively. AAm was recrystallized from n-hexane while other chemicals were used as received without further purification.

For PET alkaline treatment preparation, the pristine PET textiles (disk shape, diameter ~ 4.5 cm) were washed with deionized water and immersed in 10 wt% NaOH solution at 60 ºC for 2 hours. Then, the textiles were rinsed with water, neutralized with dilute acetic acid and re-rinsed with distilled water. Finally, the alkaline treated PET textiles (APET) were dried in the oven at a temperature of 45 ºC for 24 hours.

For the surface activation of APET textile, at first, photoinitiator type II solution was prepared using 0.9 w/v% of BP in 10 mL of ethanol (C_2H_5OH). Then, PET textiles (PPET and APET) were immersed in the photoinitiator solution for an hour to activate the surface and shortly washed with pure solvent. Next, the monomer solution was prepared from 15 wt% of AAm and 5 wt% of MBAAm crosslinker, respectively. Filter paper was used as a spacing to improve the distribution of the pre-gel solution onto the PET textiles surfaces by positioning the filter paper at both top and bottom sides of the PET textiles (Fig. 1). For the immersion grafting method, the photoinitiator activated PET textiles were sandwiched between two Petri dishes containing 5 mL of monomer solution and subsequently exposed to different times of UV curing (5, 10, 15, 20 and 30 minutes) using UV LED light source (Hönle LED Cube 100 IC) at 365 nm. This procedure was repeated similarly for dipping grafting technique; where the textiles were quickly dipped and removed from the monomer solution to avoid polymerization on the outer PET textiles surface (Fig. 1) [12]. Thereafter, the PET textiles were soaked in the distilled water for 24 hours in order to wash out the residual chemicals and unreacted monomers, dried in the oven for about a day at the temperature of 45 ºC. The *DG* of obtained samples were evaluated using Eq. (1),

$$DG = \frac{w_2 - w_1}{w_1} \times 100\% \qquad (1)$$

where w_1 and w_2 are the weight of APET textile before and after grafting, respectively. Next, the surface functional group of the textiles was characterized using Fourier transformed infrared spectroscopy (FTIR) (Shimadzhu IRTracer-100) while surface morphology (field emission scanning electron microscopy, FESEM) (JEOL JSM-6701F), oil fouling and water wettability test (VCA Optima). The flow chart of overall experimental outline is shown in Fig. 1.

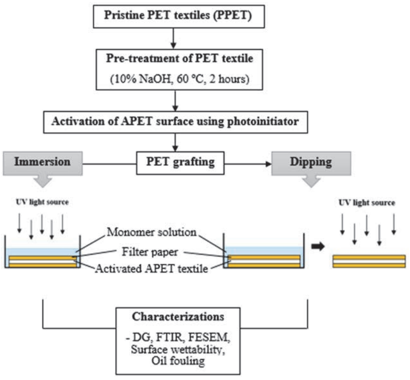

Fig. 1. Flow chart of the experimental design outline which consists of pre-treatment step of PPET, surface activation of APET using photoinitiator, grafting of APET via immersion and dipping methods and the characterization of post-cured APET textiles.

3. Results and discussion

3.1. Degree of grafting

The *DG* was determined as an indicator to the hydrogels capability to be grafted on APET surfaces. Figure 2 shows the comparison between the immersion and dipping methods on the *DG* at different times of UV LED curing. Clearly, the values of *DG* are depending upon the time of curing via UV LED system. Generally, the *DG* increased as the curing time increased. The illustration of PAAm hydrogel attachment onto the APET textile via both immersion and dipping method is illustrated in Fig. 3.

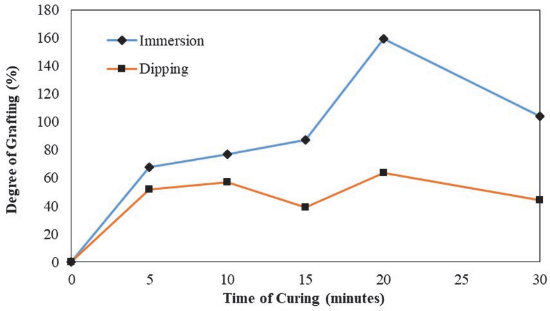

Fig. 2. Degree of grafting at different times of UV LED curing using immersion and dipping methods.

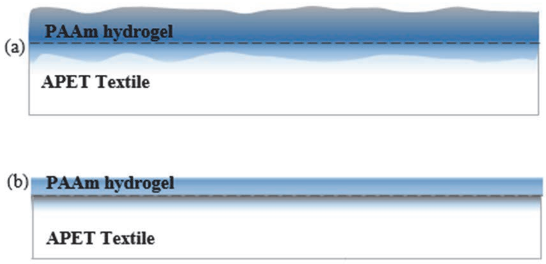

Fig. 3. Illustration of PAAm hydrogel attachment onto APET textile, (a) immersed sample; PAAm-*g*-APET$_{imm}$ and (b) dipped sample; PAAm-*g*-APET$_{dip}$.

From Fig. 2, immersed sample could achieve up to 160 wt% *DG* compared to the dipped sample with only 60 wt% *DG*. This could be explained by the penetration of monomer solution into the pore depth of the textile due to longer contact time between the textile and excess monomer solution during immersion. Thus, this resulted in higher mass fraction of PAAm hydrogel grafted on the alkaline treated PET textile surface (Fig. 3). Additionally, this high *DG* may also represent a thicker hydrogel layer was grafted onto the APET surface (Fig. 3a). Comparing with the dipping method, the contact time between textile and monomer solution was shorter, resulted in slightly lower percentage of *DG* and only a thin layer of hydrogel was grafted on APET surface (Fig. 3b). Essentially, this finding also has proved the potential of UV LED as a light source in photografting to replace the conventional UVA light source including for grafting via dipping method. Nonetheless, it could be observed that the *DG* decreased after 20 minutes of UV exposure for PAAm-*g*-APET prepared via both immersion and dipping grafting. This could be due to the over curing of the PAAm hydrogel. As 20 minutes of curing time displayed the highest *DG*, it was deliberated as an optimum time for UV exposure in this study.

3.2. Fourier transform infrared spectroscopy

The FTIR analysis was further conducted to study the effect of alkali treatment onto the PET surface and to see the difference of spectra before and after grafting. On one hand, Figs. 4(a) and 4(b) show the FTIR spectra of PPET and APET prepared at 10 wt% of NaOH concentration and temperature of 60 ºC for 2 hours, respectively. Obviously, there is a new peak appeared in the spectrum of APET in the region within 3200-3500 cm^{-1} which corresponding to the hydroxyl (–OH) functional group. On the other hand, Figs. 4(c) and 4(d) show the spectra of PAAm-*g*-APET$_{imm}$ and PAAm-*g*-APET$_{dip}$, respectively. Broader peaks at around 3300 cm^{-1} for both PAAm-*g*-APET$_{imm}$ and PAAm-*g*-APET$_{dip}$ spectra indicate the presence of hydroxyl and amide groups of the PAAm hydrogel layer [13].

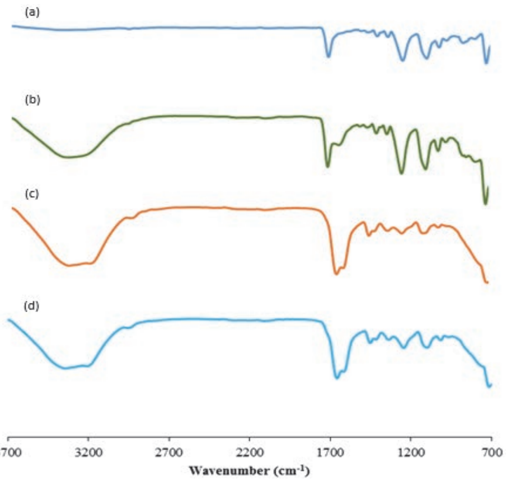

Fig. 4. FTIR spectra of (a) pristine PET, (b) APET, (c) PAAm-*g*-APET$_{imm}$ at 20 minutes of UV LED curing, and (d) PAAm-*g*-APET$_{dip}$ at 20 minutes of UV LED curing.

Another strong band can also be seen appeared at around 1650-1580 cm^{-1} from both spectra, which could be explained by the –NH bending vibration in plane deformation of primary amines [14]. Meanwhile, the characteristic PET peaks in between 1300-1000 cm^{-1} in these spectra represent the C-O group. Before being grafted, the intensity of C-O group seems strong but it decreased after an additional hydrogel layer was attached to the surfaces. This phenomenon has confirmed that the PAAm hydrogel had successfully grafted onto PET textile [15]. After all, these data convincingly support the evidence of grafted reaction of PAAm with PET textiles surfaces.

3.3. Surface morphology and wettability by contact angle

Figure 5 shows the FESEM images and water contact angles (*WCA*) for PPET, APET, PAAm-*g*-APET$_{imm}$ and PAAm-*g*-APET$_{imm}$. This analysis clearly discovered the changes of the surface morphology particularly surface pores and roughness on the individual textile as well as the surface wettability. Generally, pristine PET textiles (Fig. 5a) are smooth and round. In contrast to the APET textiles (Fig. 5b), some etch marks are seen on the fiber surfaces which indicates the surface roughness. According to the literature [16], as the treatment time increased, the surface chemistry of PET fibers was altered and the surface roughness increased. This finding is in agreement with the previous studies that investigated the effect of NaOH treatment on the fiber surface micro-morphology [16,17]. As for the contact angle measurement, the droplet of water onto the pristine PET surfaces shows high *WCA* of 105.70º. This could be attributed to intrinsic hydrophobic property of the pristine PET textiles. Generally, the hydrophilicity of the sample is influenced by the changes in its functional group. After undergone the alkaline treatment, the functional group of pristine PET textile surface had converted from –COOH to –OH and turned to be more hydrophilic. Comparing with the APET textile, the surface became more hydrophilic after undergone the 2 hours of alkaline treatment using 10 wt% NaOH at 60 ºC. The APET textile can be completely wetted with water (*WCA*=0º). This indicates that the alkali treatment strongly influenced the hydrophilicity of the PET textiles. This finding is strongly supported by FTIR result as in Fig. 2, where the alkaline treated PET textile becomes superhydrophilic.

Figures 5(c) and 5(d), represent the images of grafted textiles; PAAm-*g*-APET$_{imm}$ and PAAm-*g*-APET$_{dip}$, respectively. From these micrographs, the layer of hydrogel with different thickness was distributed over the APET textile. Furthermore, not only the surface of the PET was intensely covered with PAAm hydrogel but also its pores as well when prepared via grafting immersion method. This observation is in line with the *DG* data as shown in Fig. 2. Therefore, it could be confirmed that the high *DG* was due to the presence of excessive grafted hydrogel layer. On the other hand, for PAAm-*g*-HPET$_{dip}$, the micrograph clearly shows that the hydrogel was lightly covered the PET surfaces. This is because the PET textile was quickly dipped into the monomer solution; which means that the time for the PET textile to be in contact with monomer solution was very short. Therefore, the PAAm hydrogel was not able to penetrate into the textile pores and attached on the surface. Comparing with the immersion method, the PET textile was equilibrated with monomer solution during curing. Since the monomer solution has low viscosity, it may diffuse and penetrate into the depth of PET surface. Hence, the hydrogel was significantly grafted onto the surface as well as its pores.

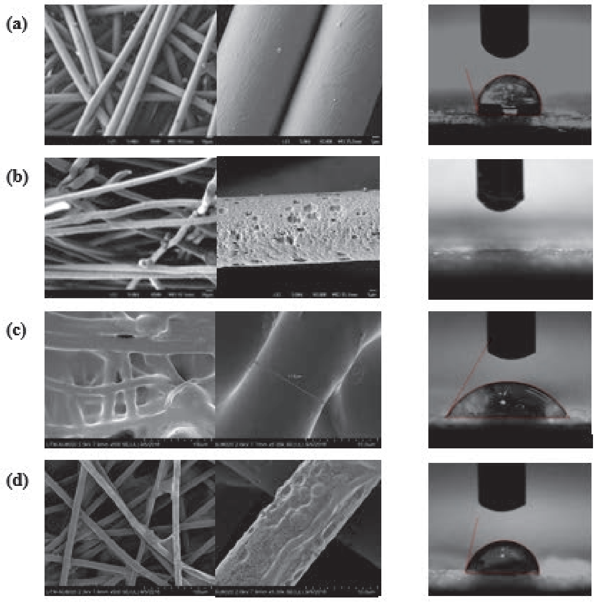

Fig. 5. FESEM images and water contact angles of (a) pristine PET (*WCA* = 105.70º), (b) alkaline treated PET (*WCA*=0º), (c) PAAm-*g*-APET$_{imm}$ at 20 minutes of UV LED curing (*WCA*=60.90º), and (d) PAAm-*g*-APET$_{dip}$ at 20 minutes of UV LED curing (*WCA* = 83.15º) method.

Next, the surface wettability data show that, the *WCA* of immersed sample (PAAm-*g*-APET$_{imm}$) was 60.90º which is lower than the dipped sample (PAAm-*g*-APET$_{dip}$; *WCA*=83.15º). This indicates that PAAm-*g*-APET$_{imm}$ sample is slightly hydrophilic than PAAm-*g*-APET$_{dip}$. Correlating this with finding on *DG*, PAAm-*g*-APET$_{imm}$ has higher *DG* which may correspond to a hydrogel layer with higher water content. Thus, the lower *WCA* could be due to higher thickness of swollen hydrogel layer. From these wettability finding, despite of possessing the *WCA*=0°, the non-grafted APET textiles surface is still susceptible to oil deposition which make it not suitable for oil/water separation. In contrast, for hydrogel-grafted APET textiles, there was additional hydrophilic polymer layer added onto the textile surfaces. Those additional polymer layers prevent the direct contact of oil onto the PET surfaces. This will be further discussed in Section 3.4.

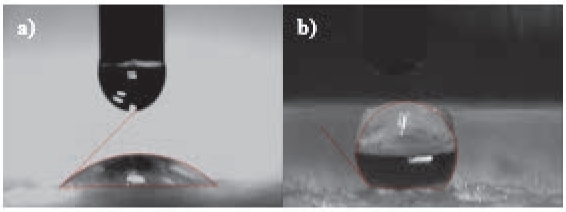

Fig. 6. Oil contact angle of PAAm-*g*-APET$_{dip}$ in two different conditions, (a) dry surface; *OCA*=43.20º and (b) underwater; *OCA*=132.20º using diiodomethane as oil droplet.

Furthermore, in order to evaluate the oil wettability of the hydrogel grafted APET textile, di-iodomethane (oil) was dropped onto the PAAm-*g*-APET$_{dip}$ textile surface. This test was carried out under two different conditions; i.e., i) dried textile in air, and ii) underwater. It was found that the oil droplet had spread on the textiles upon contacting with the substrate in a dried condition as shown in Fig. 6(a). This indicates that in the absence of water, PAAm-*g*-APET$_{dip}$ has oleophilic surface with the oil contact angle of *OCA*=43.20º. Meanwhile from Fig. 6(b), it is clearly shown that the oil droplet in underwater condition was in the shape of a sphere. When the sample was immersed into water, it strongly repelled oil. This reveals that the grafted PET textiles have underwater olephobic properties and it was affected by the swollen hydrogel. As a result, the sample in underwater condition was becoming more hydrophilic and oleophobic. Therefore, with both hydrophilic and oleophobic properties of the hydrogel modified textile, this sample can effectively applied be to the separation of oil and water.

3.4. Oil fouling test

The ability of oil droplet to detach from the surface (oil disappearance) is a crucial element in this study to compare the oil fouling performance of grafted PET textile. Figure 7 shows the comparison of oil fouling behavior for PAAm-*g*-APET$_{imm}$ and PAAm-*g*-APET$_{dip}$ at various curing time. It can clearly be observed that the time taken for the oil droplet to detach from PET textile shorten as the curing time increases. However, by comparing both immersed and dipped samples, PAAm-*g*-APET$_{imm}$ needed a longer time to de-stain oil due to the excessive layer of PAAm hydrogel attached on the APET surface. The intense coverage for immersed sample was not only on the surface but on the pores as well. It differs from the PAAm-*g*-APET$_{dip}$ as the hydrogel was lightly covered on the textile surface. This could be supported by the finding from FESEM in Fig. 5. In addition, even though both samples showed the shortest time to de-stain oil at 30 minutes, the difference for oil disappearance time is very insignificant for samples cured between 20 and 30 minutes; <0.80 seconds. Thus, curing at 20 minutes is more appropriate to be chosen as the optimum UV time (PAAm-*g*-APET$_{imm}$ = 0.59 seconds, PAAm-*g*-APET$_{dip}$ = 0.49 seconds). Hence, it is not worth to extend the UV time as the longer curing will increase the energy consumption of the UV system and would directed to the over curing process.

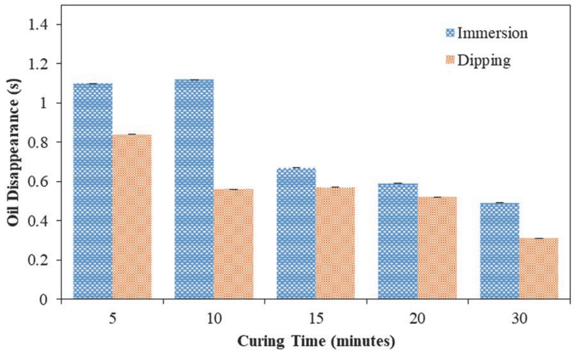

Fig. 7. Oil fouling test of grafted PET at different times of UV LED curing for PAAm-*g*-HPET$_{imm}$ and PAAm-*g*-HPET$_{dip}$.

Figure 8 demonstrates the APET and PAAm-*g*-APET$_{dip}$ after oil fouling test. The samples were then subsequently rinsed with water. As can be seen, the oil is still attached onto the APET surface even after being washed with abundant of water. Even though APET sample turned out to be more hydrophilic after undergone the alkaline treatment, its surface was directly exposed to foulant and there was no layer protecting the surface from direct contact with the oil. Thus, oil fouling occurred. Hence, the grafted PET textile was confirmed to be the preeminent material towards the oil fouling resistance.

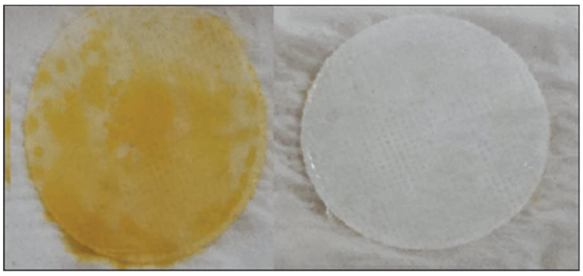

Fig. 8. Photograph of samples after oil fouling test and subsequently rinsed with water for APET (left) and PAAm-*g*-APET$_{dip}$ at 20 minutes of UV LED curing.

4. Conclusion

The alkaline treatment process had successfully improved the hydrophilicity of the PET textiles. Through the *DG* analysis and FTIR spectra evaluation, the PAAm hydrogel had confirmed to be successfully grafted onto PET textiles regardless methods of grafting used; either immersion or dipping techniques. This has proved the potential of UV LED as a light source to replace the conventional UVA lamp in photografting as it is flexible to graft the hydrogel onto PET surface either via immersion or dipping methods. Comparing both immersion and dipping grafting method, it could be summarized that the dipping method was the most preferable in the oil/water separation application. Even though the obtained *DG* of dipped sample was slightly lower than immersed sample, the thin layer of PAAm hydrogel layer on the PET textile surface via dipping is sufficient to de-stain the oil from PET textile surface at a faster rate (~0.60-0.70 seconds) as proven in oil fouling test. To some extent; this innovation has bright vision in the near future as promising tools for oil/water separation.

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