Corona Glow Discharge Plasma Treatment for Hidrophylicity Improvement of Polyester and Cotton Fabrics

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Abstract. The effects of irradiation by a corona glow discharge plasma on hidrophylicity properties of polyester and cotton fabrics were investigated. We used a corona glow discharge plasma reactor with multiple points to plane electrodes, which was generated by a high voltage DC. Factors that affect the hidrophylicity properties were identified and evaluated as functions of irradiation parameters, which include duration of treatment, distance between electrodes, and bias voltage. It was readily observed from SEM examinations that plasma changed the surface morphology of both polyester and cotton fibers, giving result to an increased roughness to both of them. Results also showed that the hidrophylicityof polyester and cotton fabrics improved by the treatment, which is proportional to the time of treatment and voltage, but inversely proportional to the distance between electrodes. Time of treatment that provided the optimum enhancement of hidrophylicity for cotton is 15 minutes which improved the wetting time from 8.16 seconds to 1.26 seconds. For polyester, it took 15 minutes of irradiation time to improve the wetting time from 7340 seconds to 2905 seconds. The optimum distance between electrodes for both fabrics in this study was found to be 2 cm. Further analysis showed that the improved hidrophylicity properties is due to the creation of surface radicals by free radicals in the plasma leading to the formation of new water-attracting functional groups on the fiber surface.

1. Introduction

In textile, plasma treatment is recognized as an alternative technology to replace the chemical refining process and preparation of refinement. This technology offers a number of advantages greater than conventional chemical processes. Surface modification using plasma does not require the use of water and chemical compounds, so it is considered as an inexpensive and eco-friendly technology [1]. Plasma treatment is recognized to be able give a number of changes in the physical and chemical properties on the surface of the textile fabric. Plasma treatment has been reported could improve water absorption on the fiber surface, mainly by oxidation and etching. Plasma treatment has also been used for several applications such as anti shrink, increasing the rub resistance properties and ability to absorb the dye in the wool fibers, and is able to provide improved mechanical properties significantly both through radio frequency and low frequency which includes the shear strength, flexural strength and tensile strength [2-5].The properties changes are caused by the several factors, including: changes in surface morphology and/or the formation of the active chemical functional groups on the substrate fabric due to plasma treatment. Another possibility is the appearance of free radicals on the substrate by plasma treatment, then causing changes in the physical properties of fabric.

The process that takes place in generation of plasma treatment on substrate is that when the power increased, the plasma gas will get more energy for ionization and can be more easily ionized. On the other hand, the speed of electrons under strong electric field will increase, causing an increase in kinetic energy of electrons. These two factors will increase the action of plasma on fiber's surface. The action will cause the surface roughness and the formation of polar oxygen functional groups, which contribute to give hydrophilic properties and improve adhesion on polyester fabrics [6-8].

This study examines the wetting properties changes on polyester and cotton fabrics, respectively selected to represent synthetic and natural fibers, due to the plasma treatment. The type of plasma used in this study is corona glow discharge plasma which generated by multi point to plane electrode configuration. The properties changes observed, as indication of the influence of plasma treatment, were associated with morphology changes and the appearance of free radicals on the surface of treated fabrics.

2. Methods

2.1. Characteristic of electric current – voltage

The research begins by performs characteristic of electric current as a function of voltage on the series of multi-point to plane reactor. The characteristics procedure was performed on some variation of the distance between the two electrodes. While in irradiation process, the treated fabric sample was placed on the surface of plane electrode.

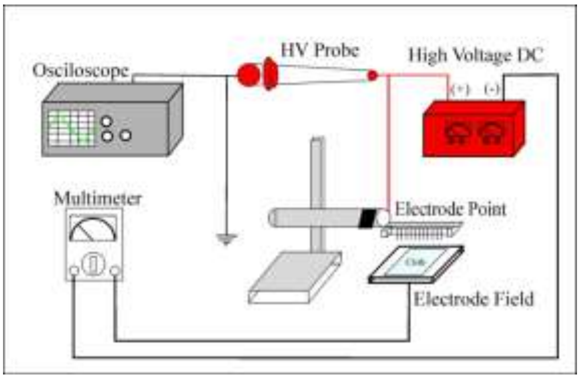


Figure 1. The schematic of the multi-point to plane reactor series.

To generate plasma, the point electrode is given positive polarity. Electric current in the circuit of plasma reactor is measured using a multimeter (Sanwa Japan YX360TRF), while the value of the voltage generated by the high voltage (HV) DC power supply was measured using an oscilloscope connected to probe high voltage (HV Probe DC max Voltage DC 40 kV, AC 28 kV EC code number 1010, EnG1010, Made in Taiwan). There are three parameters were varied in this study, ie: voltage, distance between electrodes, and time of treatment. The distances between electrodes are 1 cm, 2 cm, 3 cm, 4 cm and 5 cm, while the times of treatment are 0, 15, 60, and 90 minutes.

The assessments of physical-chemical properties on treated-fabric are consisting of wetting ability, capillary absorption, surface's morphologycal, and radical density tests. All of these tests results were then compared to the properties of control- and treated-fabrics.

2.2. Ion mobility

When the charge carrier particles of a material were in the electric field would move with the average velocity which called as drifting velocity or drift velocity. The magnitude of the drift velocity is proportional to the magnitude of the electric field and the value of mobility, in accordance to Eq. (1)

$$I_s = \frac{2\mu\varepsilon_0 V^2}{d} \quad (1)$$

where I_s is an unipolar saturated current (ampere), *V* is voltage (volt), μ is unipolar ion mobility (m/Vs), ε_0 permitivy of vaccum (F/m) and *d* is space between electrode (m) (Sigmond,1982).

Variations of irradiation parameters, such as space between electrodes (*d*) and applied voltage (*V*), in addition will effect on the measured current *(I)* they will also affect the value of unipolar ion mobility (μ). The value of unipolar ion mobility can be calculated using Eq.(2).

$$\mu = \frac{I_s.d}{V^2.2\varepsilon_0} \quad (2)$$

But for the case of the multi-point electrode it required to modify the equation above by adding a factor of the number of points of electrode, which is considered as *N*. In addition, the presence of fabric samples in a series of corona plasma reactor can be considered as a dielectric material with a specific dielectric constant value, which can be considered as ε_1, so the equation above becomes:

$$\mu = \frac{I_s.d}{V^2.2\varepsilon_t N} \quad (3)$$

In the characteristic curves, the value of mobility can be calculated based on the value of a linear gradient of the curve so that the above equation becomes:

$$\mu = \frac{(\tan\alpha)^2 d}{2\varepsilon_t N} \quad (4)$$

where: $\tan\alpha = \frac{\sqrt{I_s}}{V^2}$, while the total dielectric constant was calculated for a series configuration by assuming that the air and sample were installed in series.

2.3. *Physical and chemical properties assessment*

Wetting ability is the rate of water spread on the fabric. The principle of this test is to observe a drop of water dropped from a certain height on the surface of a sample. Time for disappearance of water on the sample was measured and recorded as wetting time. This Test conducted under the atmospheric conditions. The fabric sample is placed 1 cm below the tip of the burette droplets.

Capillary absorption is the ability of the fabric to absorb water by capillary absorption. Capillary absorption rate was calculated based on the height of the water absorbed in the fabric h (cm), using the equation:

$$v = \frac{h}{t},$$

where *v* is capillary absorption rate, and *t* is absorption time of 2 minutes.

Morphology of the samples was observed using SEM (Scanning Electron Microscope) to observe changes on fabric's surface. While the density of surface radicals tested using DPPH solution. The wetting properties tests, including wetting ability and capillary absorption rate, have been conducted with immediately and delayed tests to see how the permanence properties obtained from plasma treatment.

3. Results and Discussion

3.1. *Characteristic of electric current – voltage*

The purpose of this characterization in general is to: get the area corona glow at some variations of distance between electrodes, and to analyze the charge carrier mobility which allegedly influence the changing of wetting properties on the surface of treated fabric. In addition to distance, the characterization of the current-voltage function is also carried out in a state by and without fabric sample between the electrodes. It aims to analyze the influence of the textile material presence to electric current at the same voltage, and to get the area range of glow discharge corona plasma when there is a fabric sample between the electrodes.

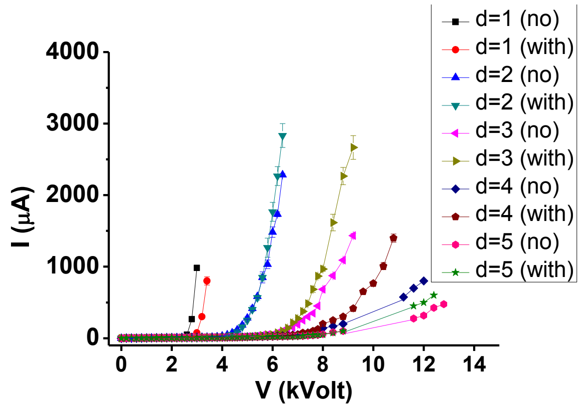


Figure 2. Figure 2. Characteristic of electric current as a function of voltage. The characteristics has been observed with variations of distance between electrodes *d*, with and without samples between electrodes.

In general it can be concluded that the presence of the fabric sample between electrodes has increased the value of electric current. It is occurs because the fabric has a certain thickness and appears to be a negatively charged when electrons flowing from the electrode field causing an effective reduction in distance between the positive electrode and the field electrode, and finally rising the electric current.

3.2. *Ion Mobility*

The calculation of ion mobility has been conducted based on the characteristic graphs of electric current as function of voltage. Figure 3 shows the ion mobility as a function of distance between electrodes in corona discharge region.

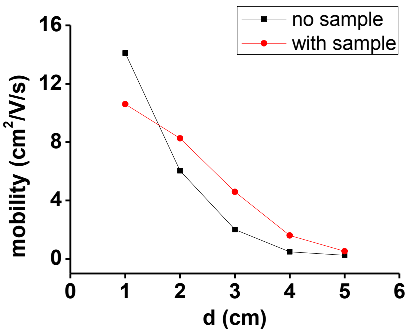
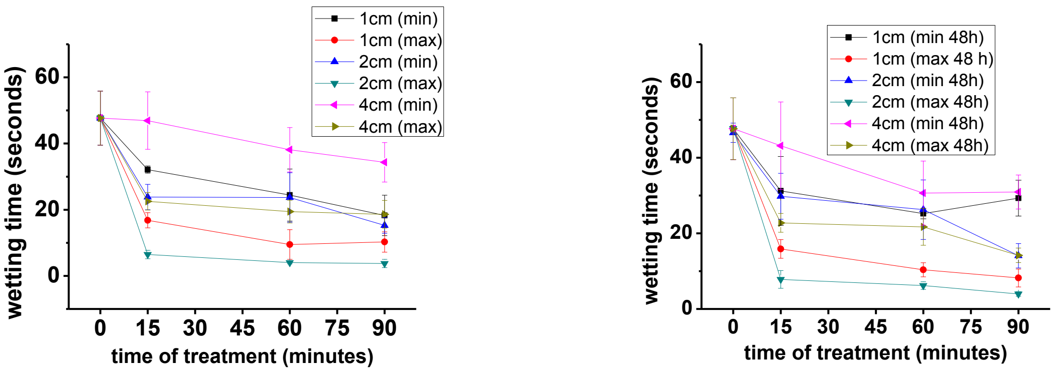


Figure 3. Ion mobility as a function of distance between electrodes *d.*

The results showed that the ion mobility values obtained from some variation of *d*, approaches the ion mobility under atmospheric pressure from the study by Langevin. In this study, ion mobility value is from 0.25 to 14.1 cm2/V.s. while mobility from Langevin's study is approximately ± 2 cm2/V.s for atmospheric pressure [9].

3.3. *Wetting properties*

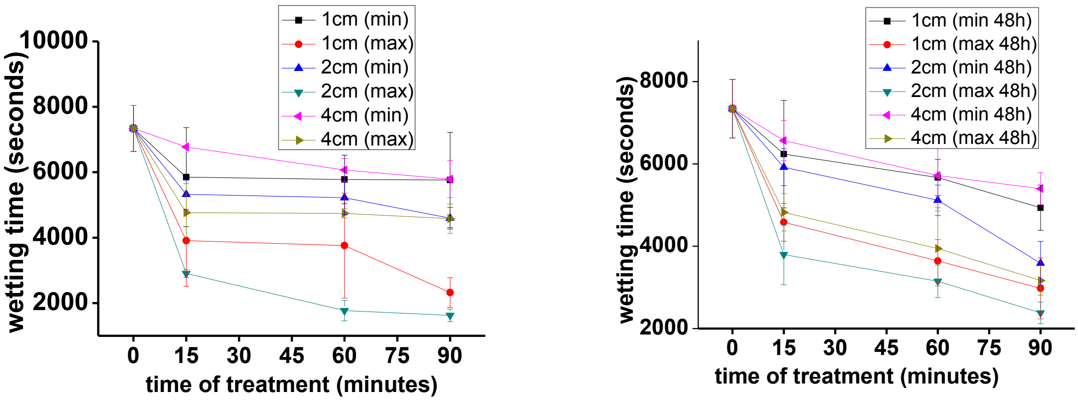
The results show that the treatment with maximum glow provide the greater wetting time reduction than with minimum glow, both on cotton and polyester fabrics. Another result obtained is the distance between electrodes o f 2 cm provides maximum decrease compared to the distance of 1 and 4 cm. If it is associated with wetting time, the result has not the same tendency with ion mobility as a function of distance *d*, which is based on the graph it can be seen that the higher distance between the electrodes provide the smaller value of mobility,



(a) (b)

Figure 4. time of absorption on cotton fabric (a) in immediately test, (b) delayed test, 48 hours after treatment.

Similar results were also obtained on the polyester fabric, the differences are on the order of wetting time. If the cotton fabric takes tens of seconds, the polyester fabric takes tens of minutes to hundreds of minutes (see Figure 5).



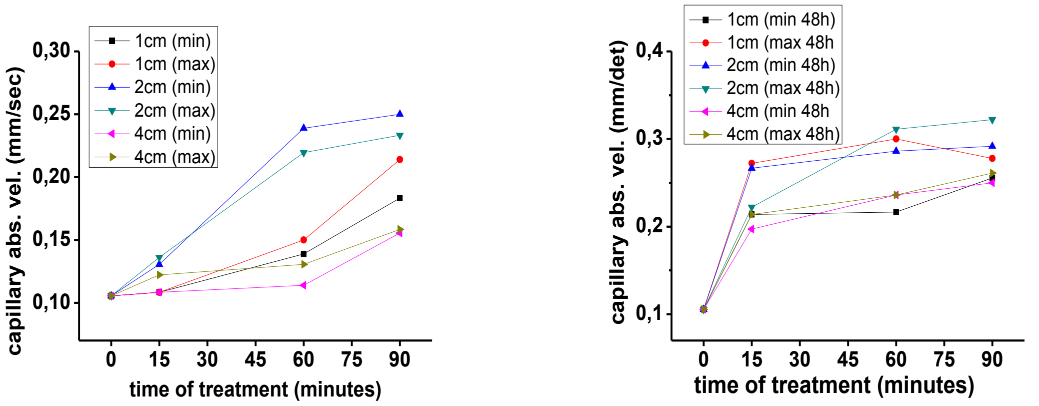
(a) (b)

Figure 5. time of absorption on polyester fabric (a) in immediately test, (b) delayed test, 48 hours after treatment.

Based on the observations using FTIR_ATR, Kan et al found that the polymeric hydroxyl groups on the cotton fabrics decreased after plasma treatment. It occurs due to the polymeric hydroxyl groups related with starch-based sizing material is removed by plasma treatment. This suggests that the plasma treatment can physically remove the starch-based sizing material and wax from the surface of the fibers and thus the wetting properties of the plasma-treated fabrics are sharply increased [10]. In this study, the effect of durability/permanency of plasma was observed only until the 2nd day, and not obtained any significant decline in wetting properties on polyester (Figure 5.b) and cotton (Figure 4.b) fabrics. These results are consistent with the results obtained by Cheng et al, that under 5 days after treatment does not occur enhancement of contact angle and even occurs a slightdecrease in the contact angle [11].

3.4. *Capillary absorption*

Figure 6 shows the change of capillary absorption rate on cotton fabrics. The capillary absorption rate increased with increasing time of treatment. In contrast to the results obtained in wetting ability, in immediately test, time of treatment of 15 minutes not sufficient to provides a significant change to capillary absorption (Figure 6.a). Then, it required longer time to provide sizeable change on capillary absorption rate. In accordance by the results obtained from wetting ability test, the capillary absorption test also showed that the highest capillary absorption rate obtained in distance between electrodes of 2 cm. Figure 6.b shows the changes of capillary absorption rate of 48 hours test after treatment. It's found that he highest enhancement in capillary absorption rate obtained on the 15 minutes treated fabric, while the capillary absorption rate on 60 minutes and 90 minutes treatment get very little enhancement and even tends to saturate.

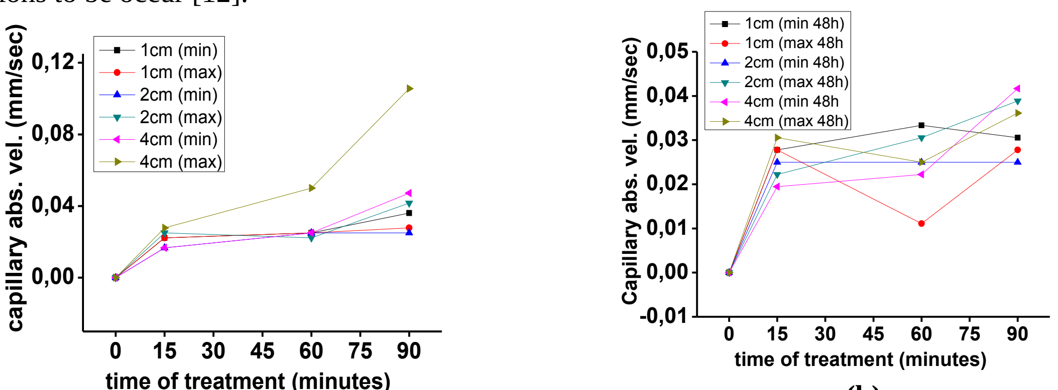


(a) **(b)**

Figure 6. Capillary absorption velocity on cotton fabric(a) in immediately test, (b) delayed test, 48 hours after treatment.

In polyester fabrics, capillary absorption rate is very low at under 0.1 mm/sec (see Figure 7.a.). Capillary absorption rate on the control fabric is 0 mm/sec. Both of immadiately and delayed test have provided the similar changes of capillary absoprtion rate. The maximum rate was about 0.03 and 0.04 mm/sec, but the highest rate was obtained at *d*=4cm in 90 minutes plasma treatment that was 0.11 mm/sec (Figure 7.a). Delayed test after 48 hours has relatively showed the similar rising as immediately test in capillary absorption test of cotton fabric (Figure 7.b).

Wang et al. confirmed that the increase in plasma discharge power will increase the height of the capillary absorbency of fabrics. Theoretically, as a surface modification technology, the forming of energetic and active plasma species was influenced by the discharge power. The Low discharge power typically causes the limited number of active plasma species. The larger discharge power allows for more effective plasma penetration into the fibers, tougher physical etching and plasma chemical reactions to be occur [12].



(a) **(b)**

Figure 7. Capillary absorption velocity on polyester fabric(a) in immediately test, (b) delayed test, 48 hours after treatment.

Similar results were also obtained by Ferrero were testing the wetting ability on synthetic fabrics due to treatment by RF plasma that generated at 0.64 mbar using capillary rise [13]. In a particular power, height of capillary absorption increased with increasing treatment time, where at a given time the height of absorption increased with the increasing of electric power but decreases with increasing aging time. These results are in accordance with the increase in the contact angle after the plasma treatment, due to the emergence of polar groups on the polymer surface or the chain breaking process.

It was reported that the effects of the surface tends to be unstable and and decreasing wettability as the increase of storage time [13].

3.5. *Radical Density*

In this study, the changes of surface radical density due to plasma treatment were only observed as function of time of treatment on cotton and polyester fabrics (Figure 8.a.) with d=2 cm, and as function of distance between electrodes in maximum glow and time of treatment of 15 minutes (Figure 8.b). Figure 8.a. showed that the surface radicals density increased with increasing plasma treatment time. While Figure 8.b showed that the surface radicals density ecreases with increasing distance between the electrodes. These results showed have the same tendency of ion mobility on corona glow discharge plasma. The higher distance between electrodes provides the smaller value of ion mobility (see Figure. 3). The radical activity was also affected by charge carrier mobility.

In his study, using atmospheric pressure jet plasma generated with radio frequency (RF), Widodo et.al. reported that surface radical density increased by increasing of electric power on kevlar fabric and PPTA film [14]. The similar results also obtained by Poncin-Epaillard and Wang, using microwave plasma and nitrogen gas, that surface radical density rised exponentially by the electric power. In addition, Poncin-Epaillard dan Wang also found that surface radical density decrease with increasing distance between electrodes and increase as function of time of treatment of 0 to 5 minutes and then decrease after over 5 minutes treatment [15].

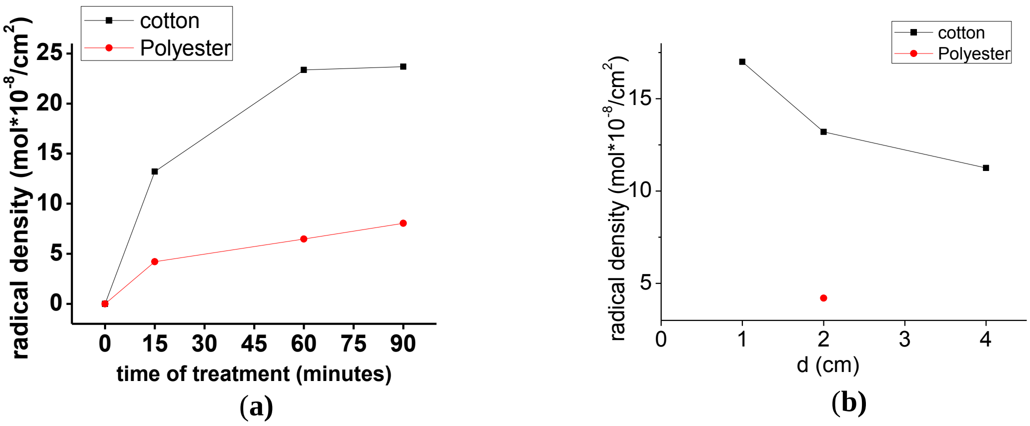


Figure 8. Radical density on fabric samples as function of **(a)** time of treatment with*d*=2 cm in maximum glow, **(b)** distance between electrodes*d* with time of treatment of 15 minutes in maximum glow.

3.6. Morphological changes

Interaction of active species in plasma with substrate may causing the particles addition to the substrate or particles release from the substrate. Morphological changes on fabric's surface was observed by comparing the morphology of control and treated fabrics. Figure 9 and 10 show the SEM image of cotton and polyester fabric, respectively. Based on the SEM image, it can be seen that control fibres, both cotton and polyester, have a smooth surface. While the fibers of treated fabrics have a rougher surface than control fabrics. The second thing can bee seen is that the surface roughness increase with increasing time of treatment. Then the third thing can be observed by SEM Image is that the polyester fabric seems to have rougher surface than cotton fabric (see Figure 9 and 10).

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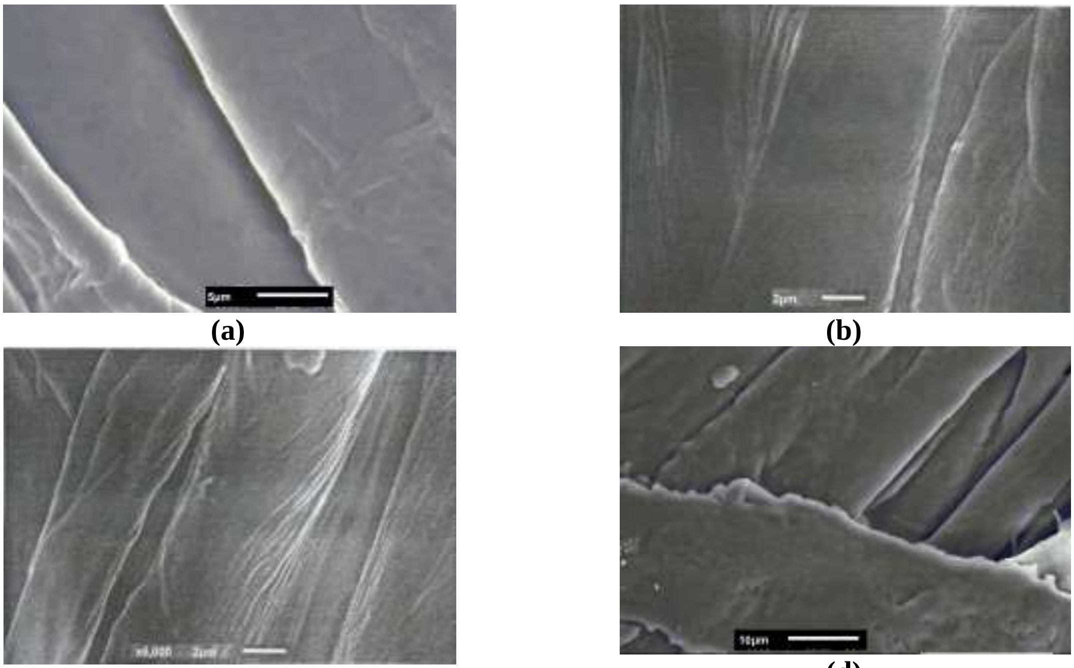
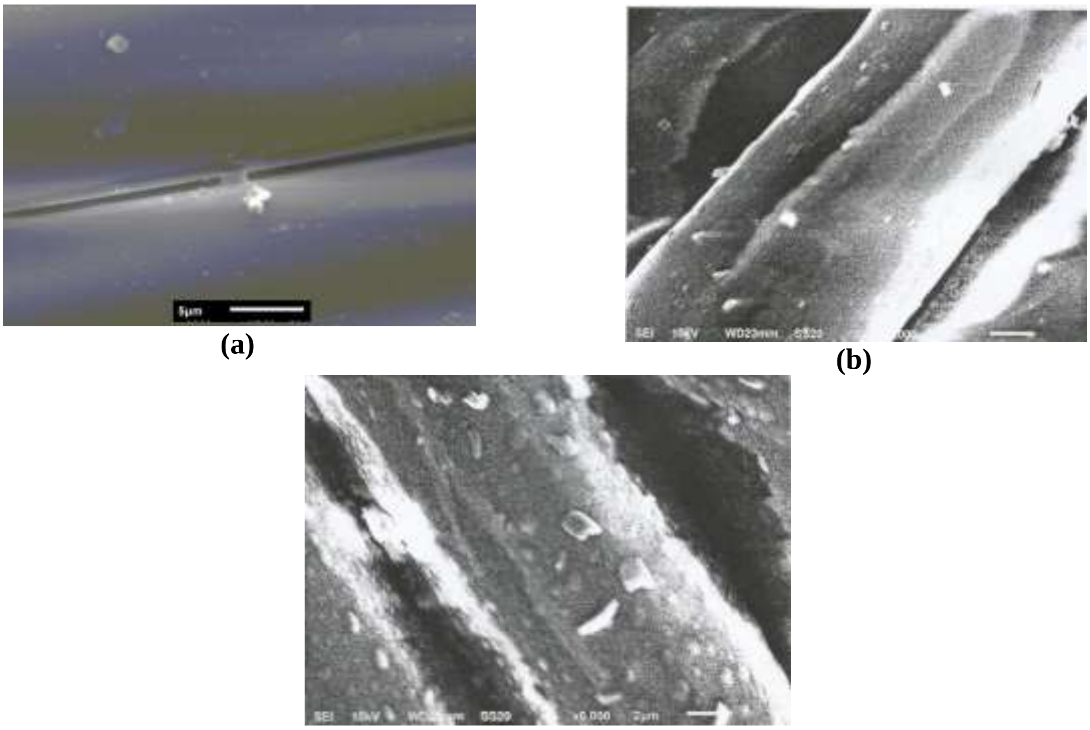


(a) **(b)**

(c) **(d)**

Figure 9. SEM image of cotton fabric with time of treatment of:**(a)** 0 minutes; **(b)** 15 minutes; **(c)** 60 minutes; **(d)** 90 minutes.



(a) **(b)**

(c)

Figure 10. SEM image of polyester fabric with time of treatment of:**(a)** 0 minutes; **(b)** 15 minutes; **(c)** 60 minutes.

In a study on cotton fabric by using a non-thermal plasma and atmospheric air sources, Pandiyaraj and Selvarajan found that micro roughness on the surface of the treated fabric is higher than untreated fabric. In fact they also reported that there were fractures and holes in cotton fibers due to plasma treatment. These surface changes may provide a new pathway for water to enter the fibers and thus will increase hydrophilicity of the materials [16]. Microcracks found on the treated fiber surface indicates that the etching process occurs due to direct bombardment of the active species to the fiber surface [10, 17].

Plasma treatment has generated reactive groups and radicals on the treated-fabric's surface. In polyester fabrics, plasma treatment can oxidize the polyester surface by break the ester bonds and generate radicals. These radicals can react with gas produced and creates polar groups such as hydroxyl, carbonyl, and carboxyl group (or C-O, C=O, C=N, C≡N and N-C-O). Based on the carbon and oxygen compositions determined by XPS, Zhang et al. has reported the decrease in C composition level (from 81.77 to 71,45%) and the increase in O level (from 15.23 to 25.36) on the polyester surface after being treated by plasma, compared to before treated [18]. It expected that C-C bond on the polyester fiber surface has been broken by plasma treatment, then the C=O, C-OH and COOH generated by plasma to form the oxygen-containing polar groups [19]. The enhancement of hydrophylicity is caused by the increased polar groups formed on the fabric surface due to plasma treatment [20]. In addition to generates functional groups, an increase in surface roughness occurred due to the removal of material [21].

4. Conclusions

Corona glow discharge plasma treatment has caused the changes in wetting properties of polyester and cotton fabric. Some conclusions obtained from this study are:

Wetting properties increase with increasing time of treatment, both through wetting time and capillary absorption tests. Time of treatment of 15 minutes provides the optimum changes in wetting properties in this study.

The changes of wetting properties affected by the distance between electrodes, and the distance between electrodes of 2 cm provides the optimum enhancement of wetting properties, both for cotton and polyester fabrics.

One of the factors that caused changes in wetting properties is the morphological changes on fabric's surface. It's found that the enhancement of surface roughness provides enhancement of wetting properties, while the surface roughness increase with increasing time of treatment.

In addition, the presence of surface radical has also caused the changes of wetting properties due to plasma treatment. It was found that the surface radicals density increase with increasing time of treatment and then causing the enhancement of wetting properties. Beside it, it also found that the surface radical density decrease with increasing distance between electrodes.

The changes of wetting properties were caused by free radical reaction on the fabric's surface, the longer time of treatment give the greater radical density and causing the decrease of wetting time on fabrics.

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