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Learning Materials of Atmospheric Pressure Plasma Process: Turning Hydrophilic Surface to Hydrophobic

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Abstract**—**This paper investigates the use of atmospheric pressure plasma for improving the surface hydrophobicity of polyurethane synthetic leather with tetramethylsilane (TMS). The atmospheric pressure plasma treatment with TMS is a single-step process to enhance the hydrophobicity of polyurethane synthetic leather. The hydrophobicity of the treated surface was examined by contact angle measurement. The physical and chemical surface changes were evaluated by scanning electron microscopy (SEM) and infrared spectroscopy (FTIR). The purpose of this paper is to provide learning materials for understanding how to use atmospheric pressure plasma in the textile finishing process to transform a hydrophilic surface to hydrophobic.

Keywords**—**Learning materials, atmospheric pressure plasma treatment, hydrophobic, hydrophilic, surface.

I. INTRODUCTION

SMOOTH surface artificial leather is composed of a polymer (e.g. PU or PVC) with a flexible backing of woven fabric (usually composed of cotton and polyester) [1]. Plasma treatment of polymer surfaces is a well-established technique because of its unique ability to form a hydrophobic thin film on a surface [2]. Atmospheric pressure plasma overcomes the disadvantages of low pressure plasma - its integration into an in-line production process is cumbersome and expensive [3]. Traditional plasma sources include transferred arcs, corona discharge and dielectric barrier discharge (DBD). Corona and DBD produced plasmas are non-equilibrium, with gas temperature ranges between 50 ºC and 400 ºC, which may limit their usage in material processing [3]. On the other hand, atmospheric pressure plasma offers the advantages of temperature a range from 20 ºC to 200 ºC with high concentration of reactive species from 10 ppm to 100 ppm [3]. Atmospheric pressure plasma jet is an effective way to create a plasma zone with its movable torch [4]. A number of researchers have studied the possibility of application of plasma torch [4], [5]. It could be a single step method for hydrophobisation. Organosilane is one of the monomers for introducing hydrophobic surface because of its stability and low toxicity [6]-[9]. In this paper, the study of the application of atmospheric pressure plasma using organosilane for surface hydrophobisation is presented. Contact angle was used for analyzing the changing in surface hydrophobility. The surface physical and chemical changes were evaluated by SEM and FTIR. This paper is also serving as reference materials for those who are interested in learning the application of atmospheric pressure plasma treatment in changing material surface property.

II. EXPERIMENTAL

A. Materials Used

Polyurethane synthetic leather (face: 100% polyurethane; back: 60% cotton and 40% polyester) was used and the synthetic leather was cut into pieces of width 1 cm x 2.5 cm for atmospheric pressure plasma treatment. The sample was stored in a conditioning room at 65±2% relatively humidity and 21±1 ºC for 24 hours prior to experiment.

B. Atmospheric Pressure Plasma Treatment

An atmospheric pressure plasma generator was used for the atmospheric pressure plasma treatment. The feasible width of the jet slit is 2.5 cm. Gas discharge was ignited by applying a radio frequency of 13.56 MHz. The atmospheric pressure plasma jet was placed vertically over the sample in the experiment. Fig. 1 schematically shows the experimental set-up for the atmospheric pressure plasma treatment. Helium was used as carrier gas and TMS was applied as a precursor. Various combinations of process parameters, discharge power (30W, 40W, 50W and 60W), flow rate of helium (7.5 Litre per minute (LPM), 10 LPM, 12.5 LPM, 15 LPM and 17.5 LPM), amount of TMS (0.1ml, 0.15ml, 0.2ml and 0.25ml), jet distance (10mm) and treatment dwell time (30 sec.) were used for optimizing and fabricating the hydrophobic surface.

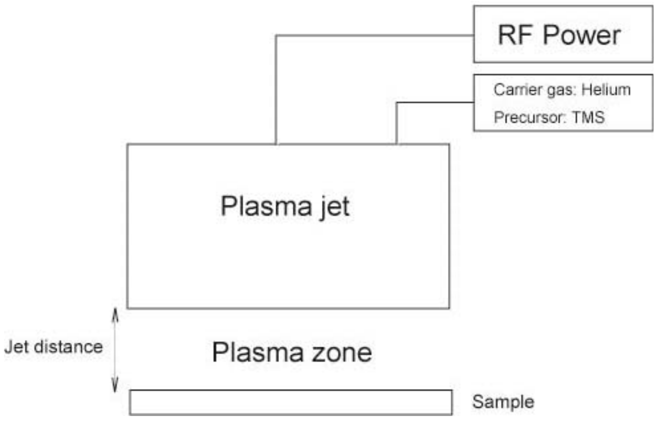

Fig. 1 Schematic diagram of APP treatment

C. Contact Angle Measurement

The surface hydrophobicity was quantified by measurement of a sessile drop static contact angle with contact angle meter [10]. A drop of 5 µl deionized water was probed on the sample surface and its images were recorded by a high-resolution

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camera. Contact angle was precisely measured. Five readings were taken from each sample. The mean of the readings was calculated. The measurement was done immediately after atmospheric pressure plasma treatment. Fig. 2 shows the picture of contact angle meter.

Fig. 2 Contact angle meter

D. SEM

JEOL Model JSM-6490 SEM was used and the samples were coated with gold before SEM analysis. The magnification of the image was 1,000x.

E. FTIR-ATR

A Perkin Elmer spectrophotometer (Spectrum 100, Perkin Elmer Ltd.) equipped with an attenuated total internal reflectance (ATR) accessory was used to analyze the chemical functionalities of the samples. Each FTIR spectrum was obtained after an average of 64 scans with a resolution of 4 cm^{-1}.

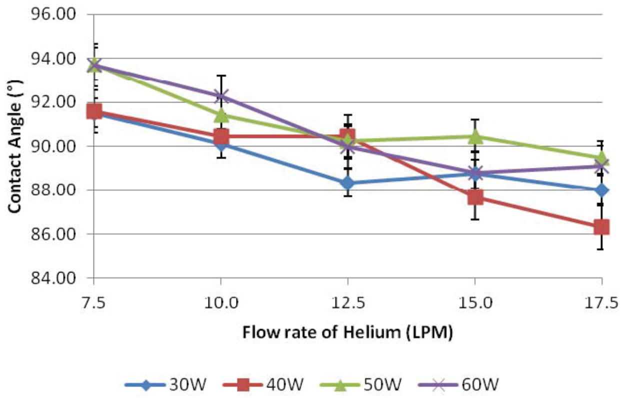

Fig. 3 Contact angle of polyurethane synthetic leather after TMS plasma treatment (Process parameters: Amount of TMS = 0.2ml; Jet distance = 10mm and Treatment dwell time = 30 seconds) (Contact angle of untreated sample ≈ 80°) [11]

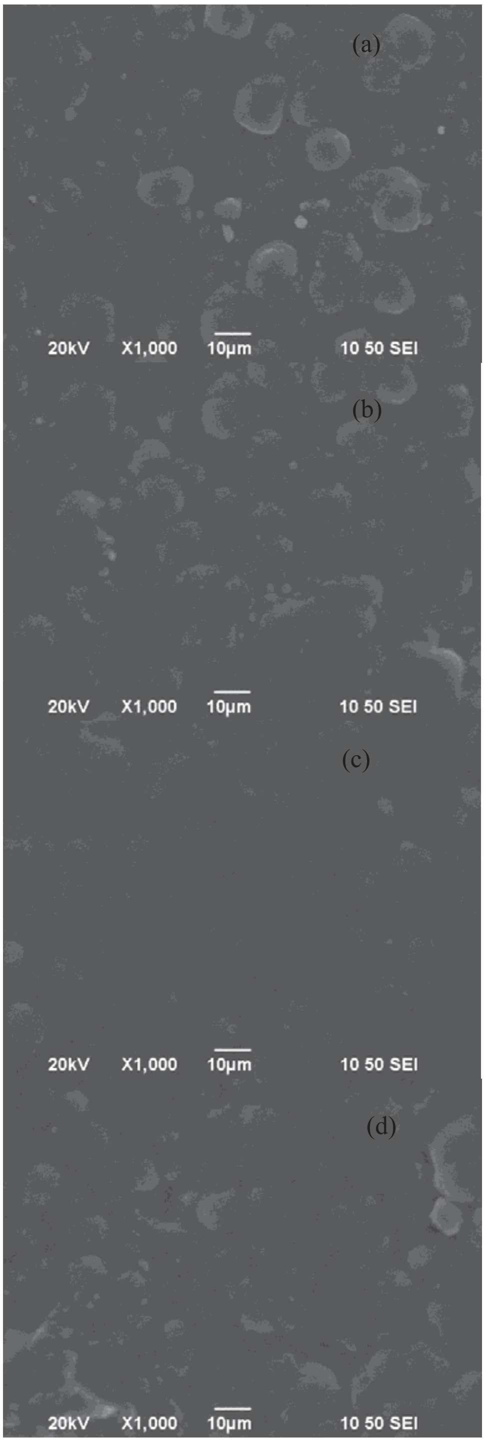

Fig. 4 SEM pictures of polyurethane synthetic leather, after plasma treatment with different amounts of TMS: (a) 0.1ml, (b) 0.15ml, (c) 0.20ml and (d) 0.25ml. (Process parameter: Treatment dwell time = 30 seconds, Flow rate of helium = 7.5 LPM, Jet distance = 10 mm and Discharge power = 50W)

III. RESULTS AND DISCUSSION

A. Optimum Process Parameters

Fig. 3 shows the contact angle of polyurethane synthetic leather after TMS plasma treatment [11]. The contact angle was enhanced after treatment under all the discharge powers. Discharge power of 30 W caused a smaller enhancement, attributed to insufficiency of discharge power. The ionisation of TMS was unstable with insufficient energy from low discharge power. Thus adequate power is required for plasma deposition. Discharge power of 50W results in significant improvement in contact angle (at flow rate of helium 7.5 LPM). Further increase in power does not increase enhancement in terms of contact angle. The ionisation of the TMS might be situated at the discharge power of 50W. Lower discharge powers and lower flow rates of helium are proven to be applicable to enhance surface hydrophobicity [11].

Irrespective of discharge power, contact angle decreases as the flow rate of helium increases. At high flow rate of helium, silicon compounds do not get sufficient time to deposit on specimen surface and the result is less silicon compound is deposited and hydrophobicity of the surface is lower. It is suggested that TMS plasma treatment with low flow rate of helium could promote a more hydrophobic surface. As the lowest operating flow rate of helium is 7.5 LPM, the most effective power is 50W with flow rate of 7.5 LPM. A short jet distance (10mm) is adequate for the short life time active species to reach the sample surface [11], [12]. The SEM pictures in Fig. 4 illustrate the differences between untreated samples and samples treated with different amounts of TMS. The surface of the sample with 0.10ml TMS clearly shows a scale-like surface structure (Fig. 4 (a)). After TMS plasma treatment, the clearness of scale-like surface decreases. The clearness drops as the amount of TMS increases. This may be due to deposition of TMS monomers on the polyurethane synthetic leather surface. The deposited compounds mask the surface of the treated sample with maximum effect when the amount of TMS is 0.2 ml (Fig. 4 (b)). The clearness does not drop when more TMS is applied, as shown in Fig. 4 (d) (i.e. 0.25 ml). This indicates that excessive TMS does not facilitate further monomer deposition.

Therefore, the optimum process parameters of plasma treatment with TMS to modify the surface hydrophobicity of polyurethane synthetic leather would be: (i) Amount of TMS = 0.2 ml; (ii) Discharge power = 50 W; Flow rate of helium = 7.5 LPM; Jet distance = 10 mm and Treatment dwell time = 30 seconds [11]. These process parameters were used for treating polyurethane synthetic leather and the contact angle of the TMS plasma treated polyurethane synthetic leather is ≈94º (compared with untreated sample ≈ 80°) [11]. By definition, a surface that attains a contact angle greater than 90° is a hydrophobic surface [13]. Thus, the TMS plasma treatment can help to increase hydrophobicity of polyurethane synthetic leather.

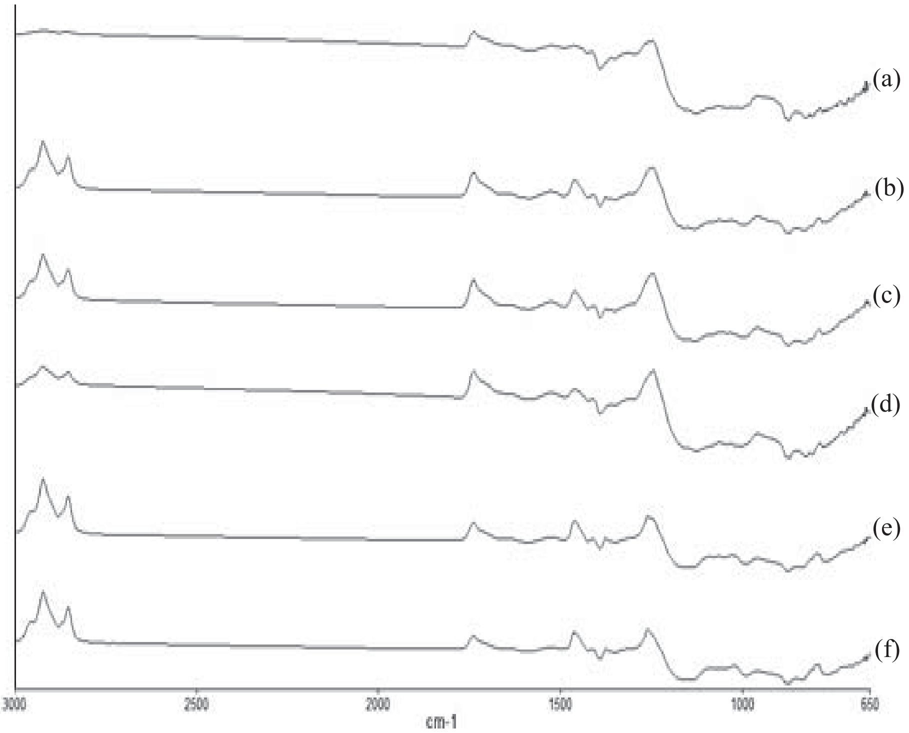

Fig. 5 FTIR spectra of polyurethane synthetic leather after TMS plasma treatment with different flow rate of helium (a) untreated, (b) 17.5 LPM, (c) 15 LPM, (d) 12.5 LPM, (e) 10 LPM, (f) 7.5 LPM. (Process parameter: Amount of TMS = 0.2ml, Jet distance = 10mm, Treatment dwell time = 30sec, Discharge power = 50W) [11]

B. FTIR

FTIR reveals the chemical compositions of the samples. Fig. 5 shows the FTIR spectra of TMS plasma modified polyurethane synthetic leather after treatment at different flow rates of helium [11]. Table I shows the strong absorbances for freshly deposited TMS plasma polymer [6], [9], [14]-[19]. The FTIR spectra in Fig. 5 show the differences between untreated and treated samples. The plasma modified samples exhibit the following features: increase in the peak of 2955 cm^{-1} (C-H asymmetrical stretching in CH_3), 2916 cm^{-1} (C-H asymmetrical stretching in CH_2), 1460 cm^{-1}, 1375 cm^{-1} (Methyl asymmetric bending in CH_3-C), 1408 cm^{-1} (CH_2 symmetrical scissoring in Si-CH_2) and 1250 cm^{-1} (CH_3 symmetric bending in Si[CH_3]$_n$). As the flow rate of helium decreases, all the silicon-related absorbances increase. The greatest intensity of the silicon related peaks occurs at low flow rates of helium, for example, 7.5 LPM. The FTIR result confirms the noticeable surface changes from SEM micrographs [11].

TABLE I
INFRARED ABSORPTION BANDS FOR FRESHLY DEPOSITED TMS PLASMA POLYMER [11]

Absorbance/cm^{-1}	Assignment
2955	C-H asymmetrical stretching in CH_3
2926	C-H asymmetrical stretching in CH_2
2906	C-H asymmetrical stretching in CH_3
2870	C-H asymmetrical stretching in CH_2
1460	Methyl asymmetric bending in CH_3-C
1375	Methyl symmetrical bending in CH_3-C
2110	Si-H stretching
1408	CH_2 symmetrical scissoring in Si-CH_2
1250	CH_3 symmetric bending in Si[CH_3]$_n$
1026	Si-O-Si and/or Si-O-C asymmetric stretching and/or CH_2 wagging in Si-[CH_2]$_n$ -Si
833	CH_3 rocking in Si[CH_3]$_n$, n=2,3
791	CH_3 rocking in Si[CH_3]$_n$, n=2,3
685	Si-C stretching

IV. CONCLUSION

Hydrophobicity of the surface of polyurethane synthetic leather is achieved by means of atmospheric plasma treatment under controlled conditions. The parameters were the key factors for achieving the result. TMS was used as the precursor for plasma hydrophobization. The results show that plasma treatment with TMS enhances surface hydrophobicity. Adequate discharge power (50W) is required to maintain stable ionisation. The flow rate of helium did not contribute much to the resulting hydrophobic alteration. Jet distance of 10mm is suggested as it allows the short life span ions to reach the substrate without degrading the sample surface (due to the heating effect of plasma jet). With the optimum process parameters, a hydrophobic surface of polyurethane synthetic leather was achieved with deionised water contact angle ≈94°. SEM and FTIR results confirm that silicon compounds were successfully deposited on the sample surface.

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