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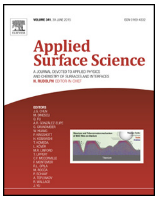

# Surface modification of polyester synthetic leather with tetramethylsilane by atmospheric pressure plasma

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ABSTRACT

Much works have been done on synthetic materials but scarcely on synthetic leather owing to its surface structures in terms of porosity and roughness. This paper examines the use of atmospheric pressure plasma (APP) treatment for improving the surface performance of polyester synthetic leather by use of a precursor, tetramethylsilane (TMS). Plasma deposition is regarded as an effective, simple and single-step method with low pollution. Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) confirm the deposition of organosilanes on the sample's surface. The results showed that under a particular combination of treatment parameters, a hydrophobic surface was achieved on the APP treated sample with sessile drop static contact angle of 138°. The hydrophobic surface is stable without hydrophilic recovery 30 days after plasma treatment.

## 1. Introduction

Polyester synthetic leather is a soft-napped material that resembles natural leather and its demand has grown substantially due to limited supplies and high cost of real animal leather. Owing to hydrophilic nature, it is easily stained. This problem can be alleviated by surface modification. Plasma treatment of polymer surface is a well-established technique because of its unique ability to fabricate a thin hydrophobic film on surfaces [1]. Atmospheric pressure plasma overcomes the disadvantages of low pressure plasma which is cumbersome and expensive for integration into in-line production process [2]. Atmospheric pressure plasma jet is an effective way to create a plasma zone with the movable jet [3]. Because of its stability and low toxicity, organosilane is one of the monomers used for fabricating hydrophobic surface on textile substrates. Nowling et al. [4] demonstrated the deposition of different organosilanes on plastic by means of plasma treatment. Organosilanes serve as a precursor, for example, tetramethylsilane (TMS) [5,6], hexamethyldisilane [7,8], tetramethylcyclotetrasiloxane (TMCTS) [4] and tetraethxysilane (TEOS) [4], forming a thin film on a surface, with a stable performance.

Much works have been done on synthetic materials but scarcely on synthetic leather owing to its surface structures in terms of porosity and roughness. For instant, the capillary action involves in liquid absorbing on textile materials [9]. This paper presents results of a study of surface modification of synthetic leather with TMS by means of atmospheric pressure plasma treatment. Contact angle, FTIR and XPS analysis were applied to study surface chemical composition where SEM analysis was carried out in order to study the morphological changes. Multiple linear regression analysis was applied to study the correlation between the treatment parameters.

## 2. Experimental

### 2.1. Material

100% polyester synthetic leather was supplied by Fifield (Asia) Ltd. The synthetic leather has a hairy-like or suede-like surface structure and it was cut into size of width 1 cm × 2.5 cm for APP treatment. The sample was stored in a conditioning room at 65 ± 2% relatively humidity and 21 ± 1 °C temperature for 24 h prior to experiment. The basic information of the synthetic leather is listed in Table 1.

### 2.2. Atmospheric pressure plasma (APP) treatment

An atmospheric pressure plasma generator (Atomflo$^{TM}$ – 250, Surfx Technology, USA) was used for the APP treatment. Gas discharge was ignited by applying a radio frequency of 13.56 MHz. The

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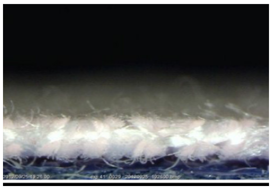
**Table 1**
Basic information of polyester synthetic leather.

| Composition | Picture |
|---|---|
| 100% microfiber polyester |  |

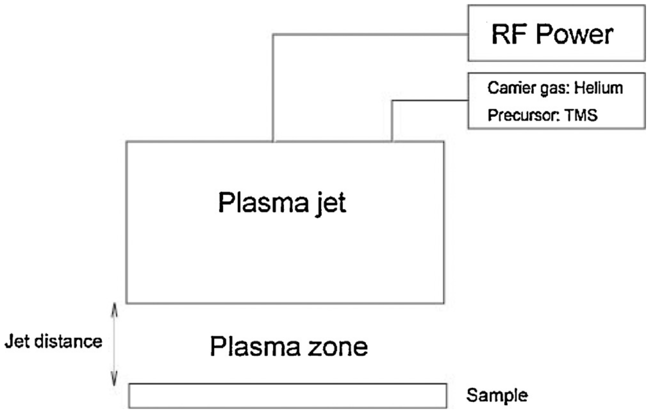
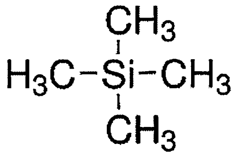


**Fig. 1.** Schematic diagram of APP treatment.

APP jet was placed vertically over the sample in the experiment. Fig. 1 schematically shows the experimental set-up for APP treatment. Helium was used as carrier gas and tetramethylsilane (TMS) (ACROS, 99%) was applied as the precursor. Fig. 2 shows the chemical formula of TMS. TMS was applied directly on the sample surface. Various combinations of treatment parameters, discharge power (80 W, 90 W, 100 W and 110 W), flow rate of helium (7.5 litres per minute (LPM), 10.0 LPM, 12.5 LPM, 15.0 LPM and 17.5 LPM), amount of TMS (0.1 ml, 0.15 ml, 0.2 ml and 0.25 ml), jet distance (10 mm, 15 mm, 20 mm and 25 mm) and treatment time (30 s) were used for making the hydrophobic film.

### 2.3. *Contact angle and surface energy*

The surface hydrophobicity was quantified by measurement of sessile drop static contact angle with contact angle goniometer [10]. A drop of 5 μl deionised water was probed on the sample surface. Droplets' images were recorded by a high-resolution camera. Contact angle in the picture was precisely measured. Five readings were taken from each sample. Mean values of the readings were calculated. The measurement was done immediately after APP treatment. Greater the contact angle is, the more hydrophobic the surface will be.



$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-CH_3$$

**Fig. 2.** Chemical formula of TMS.

### 2.4. *Scanning electron microscopy (SEM)*

JEOL Model JSM-6490 SEM was used and the samples were coated with gold before SEM analysis. Magnification of the image was 5000×. Accelerate voltage was 20 kV.

### 2.5. *Fourier transform infrared spectroscopy (FTIR-ATR)*

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

### 2.6. *X-ray photoelectron spectroscopy (XPS)*

XPS analysis was carried out by a SKL-12 spectrometer (Sengyeong, China) modified with VG CLAM 4 multi-channel hemispherical analysis equipped with Al/Mg twin anode. The spectrometer was operated with non-monochromatic Mg Kα (1253.6 eV) radiation for the characterization of the plasma-modified substrate under vacuum condition of $8 \times 10^{-8}$ Pa. XPS measurement was conducted with the sample perpendicular to the detector axis (normal takeoff angle is 90°). To compensate for surface charging effects, all binding energies were referenced to C 1s peak at 285.0 eV. Spectra were analyzed with the aid of software XPSpeak.

### 2.7. *Stain resistance*

Stain resistance of polyester synthetic leather was evaluated by staining it with coffee and milk tea. Instant coffee (Nescafe, Premium white coffee, prepared by dissolving 35 g instant coffee powder in 180 ml distilled water (25 °C) at room temperature) and instant milk tea (Lipton, Gold Milk Tea, prepared by dissolving 16.5 g instant milk tea powder in 150 ml distilled water (25 °C) at room temperature) were used for simulating the actual use condition. A drop of coffee and milk tea was placed on the sample surface and the contact angle was measured. The larger the contact angle is, the better is the stain resistance.

### 2.8. *Multiple linear regression model*

SPSS 14.0 was used for regression model development, to find the correlation between dependent and independent parameters.

## 3. Results and discussion

### 3.1. *Effects of discharge power and flow rate of helium*

Fig. 3 shows results of measurements of the contact angles (CA) of polyester synthetic leather after TMS plasma treatment. Plasma treatment with 80 W resulted in a relatively smaller enhancement in CA. Thus, 80 W cannot provide sufficient power to maintain a stable discharge of TMS. On the contrary, 90 W provides sufficient power for discharging of TMS. Considerable amount of silicon compounds were deposited on the sample surface. 90 W power resulted in the greatest improvement in CA. Discharge power beyond 90 W (100 W and 110 W) did not show further improvement in CA. Low power is preferable on the grounds of energy savings aspect also. It is assumed that the higher the discharge power in APP treatment, larger is the quantity of plasma species generated and their reactivity on the material surface is increased. Discharge power beyond a threshold results in high temperature and the plasma jet becomes too hot, leading to degradation of synthetic leather surface [11,12]. As a result, the contact angle values are affected. Moreover, if more