Formation of super-hydrophobic and water-repellency surface with hexamethyldisiloxane (HMDSO) coating on polyethyleneteraphtalate fiber by atmospheric pressure plasma polymerization

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ABSTRACT
It has been reported that plasma treatments are to modify surface properties of polymers such as adhesivity, hydrophilicity and hydrophobicity. The plasma interaction with the surface produces modification of its chemical structure and morphology. In this study, surface modification of polyester fiber with high water-repellency and super-hydrophobic was carried out plasma polymerization coating. Polyester fiber with water-repellency was treated with atmospheric pressure middle frequency (MF) and radio frequency (RF) plasma system using Ar and hexamethyldisiloxane (HMDSO). The Ar gas has been used as carrier gas. The plasma coated PET fiber of HMDSO with water-repellency of 90 rating showed higher water-repellency than untreated PET fiber with water-repellency of 0 rating. The surface morphologies of plasma treated fiber were characterized by scanning electron microscopy (SEM). The Fourier transform infrared (FT-IR) spectrometry analyzed the chemical composition of the polymer surface.

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1. Introduction
The use of plasmas for surface modification and polymerization to deposit thin films are very attractive due to control over surface chemistry. The films deposited by plasma polymerization have a good adhesion to the substrate, are pinhole free, and have mechanical and chemical stabilities. The plasma polymerization technique has also been employed conventionally to fabricate thin functional films that facilitate surface modification of materials [1–3]. When polymeric materials are exposed to plasma, radicals are created in the polymeric chain. These radicals can initiate polymerization reaction when they are in contact with monomers in a liquid or gaseous phase. Electrons in plasma with a polymer surface generate radicals at the surface of the polymer through excitation of the polymer molecules.

As a result, a grafting polymer is formed on the surface of the polymeric material. The produced film has ample range of prospective applications in anticorrosive surfaces, electrical resistors, scratch resistance coating, optical filters, properties, chemical barrier coatings and water-repellency coating [4,5]. Hence, an additional surface modification is required to achieve the desired properties, while maintaining the characteristics of the volume [6,7]. Especially, hydrophobic and water-repellency surface treatments of various substances are of great interest in recent years [8–10]. Among many techniques that can be utilized for super-hydrophobic and water-repellency treatment, plasma based processes have been widely studied and developed [11–13]. To improve the super-hydrophobic and water-repellency, coating material must be added to amplify the hydrophobicity. It is known that chemical modification of artificial materials using fluoropolymeric [14,15] coating induced wastewater and dioxin. However plasma polymerization of silicon compound is an environmentally friendly technology of surface modification for super-hydrophobic material.

In this study, the silicon compounds such as hexamethyldisiloxane (HMDSO) and inactive gas argon (Ar) are used. The Ar gas is used as the carrier gas of the monomer. Hexamethyldisiloxane (HMDSO) is one of the most common materials used for coating. This paper demonstrates a manufacturable method for formation of super-hydrophobic and water-repellency coating on a polyester fiber. The water-repellency coating was produced by an in-line atmospheric middle frequency (MF) and radio frequency (RF) plasmas process using mixture of Ar gas and HMDSO liquid. The system does not
require any vacuum line and is operated in an in-line mode, not in a batch mode. So it can be easily scaled up for application to large substrate surfaces or continuous processing [16,17].

2. Experimental

2.1. Plasma treatment

A schematic presentation of the plasma polymerization system is shown in Fig. 1. The power electrode in Fig. 1 was connected to a 13.56 MHz RF supply through an L-C matching unit (or a 25 kHz MF supply) and was covered with a quartz tube as a dielectric. The 16 cm long and 1 cm wide slit in the ground electrode was machined for plasma evolution downstream. The gap between the quartz tube and the ground electrode was 1 mm. The distance between the plasma device and the sample was 2 mm. The atmospheric MF glow-discharge plasma system was connected to plasma generator (SOFTAL, Germany) 25 kHz with a maximum power of 4 kW and atmospheric RF glow-discharge plasma system was connected to plasma generator 13.56 MHz with a maximum power of 1 kW. All of the samples in this work were treated at the plasma power of 100–300 W, especially 200 W and at a speed of 20 mm/s. The plasma was generated in ambient air with argon gas supplied through a gas hole array. Introduction of argon gas flow was very important for uniform and stable plasma generation within the capability of the RF power supply used for the experiment. The central electrode was powered by a 25 KHz MF source (4000 W maximum power). The MF and RF power source used to check a change of the inherent property such as damage of PET fiber after the plasma treatment.

In this test, 1 liter per minute (lpm) argon was introduced for stable discharge. Since the plasma was operated in a glow-discharge mode, it could be directly applied to metallic substrates, in addition to non-conducting substrates without arc or streamer. HMDSO (98%, Aldrich) was maintained at 100 °C and was bubbled by 0.1 lpm argon. And then HMDSO was injected at approximately 0.017 lpm. In the atmospheric HMDSO–Ar plasma treatment for high water-repellency coating, two important parameters were the speed at which the sample was moved under the plasma head and the treatment times. When the plasma treatment speed was increased by more than 20 mm/s, we needed more cycles of plasma treatments to get the water-repellency. But treated surface became like white layer when treatment time increases above 30 times.

2.2. Material

In this work, hexamethyldisiloxane (HMDSO) of Fig. 2 was obtained from Aldrich (98% pure) and used as received. Pointfours Corporation provided the sample of polyester fiber (polyester 92%, spandex 8%). Argon was used as carrier gas (500 sccm) and a HMDSO (10 ml/h) was used as a reactive material.

2.3. Characterization methods

The chemical composition of the PET fiber was characterized by fourier transform infrared (FT-IR) spectroscopy (Nicolet Avatar 370) which is suitable for the collection of spectra in the range between 650 and 4000 cm\(^{-1}\).

Each spectrum with a resolution of 4 cm\(^{-1}\) was recorded by 32 scans. The morphology of the surface was observed with scanning electron microscope (SEM, Philips XL-30 CP). The thermal characterization of the plasma treated PET fiber was carried out by thermogravimetric analysis (TGA) in nitrogen at a heating rate 10 °C/min with a TGA 2050 (TA instruments). The flow rate was maintained at 10 and 90 cc/min for the balance part and the furnace area, respectively. In this case, the sample weighed about 100 mg.

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<th>Table 1 Water-repellency standard chart</th>
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2.4. Water-repellency test

To measure the water-repellency of plasma coating, test was performed according to American Association of Textile Chemists and Colorists (AATCC). Generally, the AATCC spray test uses a set small quantity of water placed about four inches over a fabric. The fabric is set at a 45° angle to the stream of the liquid. The liquid is then allowed to gravity feed through a standardizer spreader nozzle. The duration of exposure is about 30 s at a glancing angle 45° to the fabric. A visual rating of how well the water beads up, based on a scale of 100 points, is given to the fabric. Evaluation is accomplished by comparing the wetted pattern with a standard chart of Table 1 [18].

3. Results and discussion

The water-repellency on PET fabrics was obtained from the MF and RF HMDSO plasma coated fibers treated for 20 passes.

The case of the MF plasma in Fig. 3, before the plasma treatment, water-repellency test on PET fiber was less than 50 rating. The water-repellency did not change noticeably for samples treated with one pass. Sample treated 15 times with the plasma started showing water-repellency test of 70 rating and treated over 20 times with water-repellency test of 90 rating. As shown in Fig. 3(a), the PET fiber without plasma completely absorbed sprayed-water. As the plasma treatment passes increased, on the other hand, the ratings increased from 50 to 90.

The water-repellency test presented in Fig. 3(b) shows differences of plasma treated fiber and untreated fiber. Untreated polyester fiber expressed water-repellency test of 0 rating. In contrast, plasma coated polyester fiber improved water-repellency class from 0 to 90 rating follow to AATCC 22 standard test. The reason of this result is that super-hydrophobic surface was formed by silicon compounds with HMDSO plasma treatment. The silicon compounds coated PET fiber showed the water-repellency property.

The FT-IR spectra of HMDSO-coated PET fiber are shown in Fig. 4. The peak attributed to Si–O–Si bonds appeared at around 1080 cm⁻¹. The peaks around 1030 cm⁻¹ are attributed to Si–O–C. The Si–(CH₃)₂ and Si–C was assigned at 790 cm⁻¹ and 851 cm⁻¹, respectively [19].

It can be noticed that, increasing the time of exposure in plasma, there is an increase of Si–O–Si, Si–(CH₃)₂ and Si–C bonds relatively to untreated PET fiber. The contents of silicon compounds were increased by plasma treatment time of long term. But fiber surface was covered with white powder when plasma treatment was done more than 30 times. Also, inherent peak of PET fiber was decreased by HMDSO plasma. The peak of aromatic C–H (730 cm⁻¹), O–C=O (1250 cm⁻¹) and ester C=O (1750 cm⁻¹) little decrease and the peak at 1350 cm⁻¹ and 1410 cm⁻¹ sign to the aliphatic C–H substantially decreased relatively to untreated PET. We postulated on the basis of FT-IR results that fragmentation mechanism of HMDSO and reaction mechanism between PET and HMDSO by plasma. From generated

![Fig. 3. Water-repellency test of (1) raw polyester, (a) HMDSO MF plasma coated polyester for (2) 10 times, (3) 15 times, (4) 20 times and (b) HMDSO RF plasma coated polyester for (2) 10 times, (3) 15 times, (4) 20 times.](image)

![Fig. 4. FT-IR spectra of HMDSO-coated polyester fiber (a) raw material, plasma coated fiber of HMDSO for (b) 15 times and (c) 20 times.](image)

![Fig. 5. Fragmentation mechanism of the HMDSO.](image)
electron by plasma process, fragmentation of the monomer was suggested by M. Goujon [20]. The Si–O bond (8.3 eV) is broken by high-energy electron collisions. Also, Si–C (4.5 eV) and C–H (3.5 eV) bonds are broken by lower energy electrons (Fig. 5).

The C–H radical groups were generated by plasma at fiber surface, because chain scission of PET took place [21] through in order from low dissociation energy to high dissociation energy (C–H (3.5 eV), C–O (3.7 eV), C=O (7.6 eV)). Consequently, the radical groups bonded to the activated specious of HMDSO (Fig. 6).

The change of the PET surface morphology is mainly caused by the bonding of activated species and depends on the plasma condition in coated processes using HMDSO. Plasma coated fiber showed white layer such as silicon compound in Fig. 7. And these white layers were analyzed by EDX to confirm whether these are silicon compounds or other compounds. The EDS results of Fig. 8, the Si content of plasma coated PET fiber were 20% higher than that of untreated PET fiber (Table 2). In the SEM image of Fig. 7, we confirmed white layer such as silicon compounds. The inherent property of PET fiber investigated temperature for 10% mass loss through TGA analysis of Fig. 9. These data were compared with those for raw PET. Raw PET fiber and RF plasma treated PET fiber showed temperature for 10% mass loss in the
TGA curve at about 378 °C, but MF plasma treated PET fiber caused to temperature for 10% mass loss in the TGA curve at about 363 °C, which the RF plasma do not change the inherent property of the fiber as compared with the MF plasma. A much-increased amount of non-volatile residue was observed at 700 °C for the MF and RF HMDSO plasma coated fiber, compared with the untreated PET fiber. We postulated that the increase in the non-volatile residue of HMDSO-coated PET fiber from the interaction of HMDSO with PET. That is, Si compounds were coated by HMDSO plasma treatment on PET fiber.

4. Conclusions

The improved water-repellency of PET fiber was obtained from atmospheric MF and RF plasma of HMDSO. Such improvement was attributed to the introduced silicon atoms on the fiber surface or a formed of new silicon compounds layer. Activation of HMDSO in plasma process may lead to HMDSO molecules grafting or HMDSO coating as observed by FT-IR. SEM confirmed the new silicon compounds layer of PET fiber. Also, amount of non-volatile residue showed evidence of silicon compounds through TGA. A much-enhanced amount of non-volatile residue of the maximum 10.1 wt.% was observed at 700 °C for the HMDSO-coated fiber, whereas amount of non-volatile residue of 3.5 wt.% was observed for raw PET fiber. Raw PET fiber and RF plasma treated PET fiber showed temperature for 10% mass loss in the TGA curve at about 378 °C, but MF plasma treated PET fiber caused to temperature for 10% mass loss in the TGA curve at about 363 °C, which the RF plasma do not change the inherent property of the fiber as compared with the MF plasma. According to FT-IR result, increasing the time of exposure in plasma, there is an increase of Si–O–Si, Si–(CH₃)₂ and Si–C bonds relatively to untreated PET fiber. These silicon compounds on PET fiber improved water-repellency property. Therefore the plasma coated PET fiber of HMDSO with water-repellency of 90 rating showed higher water-repellency than untreated PET fiber with water-repellency of 0 rating.

References