Hydrophilic Improvement of PET Fabrics Using Plasma-Induced Graft Polymerization

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Poly(ethylene terephthalate) (PET) fiber knit-fabrics were irradiated by glow-discharge plasma (GDP) at one-atmosphere, then subsequently grafted with a hydrophilic acrylic acid (AA). Degradation of GDP-treated surface was determined by weight loss ratio. This degradation is proportional to time of exposure. The wicking-time method was used for roughly estimating hydrophilic durability of grafted surfaces versus the time of exposure and times of washing. On the grafted surface, characterized by X-ray photoelectron spectroscopy (XPS), carbon contents C_{1s} decreased while oxygen contents O_{1s} considerably increased. This results in an amount of oxygen polar functional groups like carboxylic ($O-C^*=O$) and carbonyl ($C^*=O$) groups introduced into the grafted surface. Grafted surface morphology observed by scanning electron microscopy (SEM) displays some large area of corn-structure compared to relative smooth morphology of the control fabric. It also suggested that hydrophilic improvement was closely related to oxygen containing functional groups incorporated onto the grafted fiber surface and the surface roughness.

1. Introduction

Hydrophilicity or hydrophobia is closely related to physico-chemical properties of a fiber surface-layer. Textile fabrics produced by poly(ethylene terephthalate) (PET) fibers cannot usually absorb moisture and be dyed at one-atmosphere owing to the high degree of crystalline, density and lack of functional polar groups on the fiber's surface such as $-COOH$ and $-OH$. This causes the fiber to have low surface free energy and poor wettability. PET fiber fabrics, therefore, require surface modification to improve their hydrophilicity.

Surface modification is usually used to roughen fiber surfaces to enhance mechanical interlocking, and form chemical groups on the surface that improve wetting and/or chemical bonding.¹⁾ The conventional surface modifications have been performed by various chemical treatments. These processes are usually accompanied with damaging bulk fibers, and affect fiber's properties.²⁾

Exposed to glow-discharge plasma (GDP), polymer fibers can enhance their dyeing behavior, moisture absorption, and especially surface adhesion etc. Furthermore, the surface modified by the GDP is, in general, confined to a thin layer less than 100 μm . And desirable properties of bulk materials are usually maintained.

The GDP has been applied to surface modification of polymers since more than two decades.^{3,4)} Most of works have so far dealt with the GDP at low pressure less than 133 Pa and ambient temperature. Chen et al.⁵⁾ studied effects of gas types on wettability of PET films treated at low-pressure plasma. Irradiated by various gases for short time; the film showed its hydrophilicity. Later, Carlotti et al. modified PET fibers with argon and oxygen plasma to enhance the adhesion between the fiber and rubber matrices. Adhesion strength measured by peeling tests of the treated fiber was considerably increased.⁶⁾ Moreover, effects of discharge power, time of exposure and gas-pressure on improvement in wettability, dyeing and bonding capability of various polymer fibers were also investigated.^{7–10)} Nevertheless, the plasma process at low pressure has not

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widely been developed in the textile industry as its reactors were used in high vacuum that is not familiar with conventional textile machine lines.

Recently, high compact plasma reactors, which even operated at one-atmosphere and room temperature, have been developed. Kanazawa et al. tried to establish stable-glow plasma at an atmospheric pressure with various gas-types and He used as the diluted gas. States of discharge plasma and contact angles on the PET film's surface treated by such plasma were compared to those of the surface irradiated at the low-pressure plasma.¹¹⁾ Later, Tsai et al. have reported significant changes in the plasma treated surface of the polypropylene melt-blown non-woven fabric. Treated at one-atmosphere in the GDP reactor developed in their laboratory¹²⁾, the fabric considerably improved in wettability, wickability, and surface free energy.

However, most of the papers mentioned above were concerned in plasma irradiation to improve hydrophilicity of the fiber surface, even some of them also reported that the plasma treated surface gradually restored its hydrophobia¹³⁾ as fragmented low polymer-chains on the surface reoriented into the hydrophobic bulks resulting in decreasing a number of functional groups on the treated surface.^{14, 15)} Nevertheless, none of papers has yet reported how to maintain the functional groups to be stable for a long time on the fiber surface.

In order to develop plasma technique on an industrial scale, the modified surface should be stable in time. In fact, aging effects can be slowed down and fiber's wettability will be improved if the functional groups are grafted with hydrophilic monomers because plasma-induced graft polymerization not only maintains durability of the polar groups but also provides chemical modification by the covalent bonding of new molecular on top of the fiber. This method also imparts additional properties on the fiber surface without effects on the bulk properties by a careful selection of suitable monomers.

In this study, PET fiber knit-fabrics were irradiated with a mixture of helium-argon gases at atmospheric pressure, subsequently grafted with hydrophilic monomer like acrylic acid (AA) to enhance their durable hydrophilicity. Effects of various time of the irradiation on fabric's wettability were investigated. Grafting degree and wicking time were measured to roughly estimate hydrophilic capability of the treated fabric. Chemical compositions of the control surface characterized by X-ray photoelectron spectroscopy (XPS) were compared to those of the surface treated by plasma-induced graft polymerization. And, changes in

morphology of the grafted surface compared to the control one were observed by scanning electron microscopy (SEM).

2. Experimental Procedure

2.1 Sample preparation

Rib fabric, supplied by Nissin Fiber Co., Ltd., Japan, was fabricated using 75 denier PET fibers. Their stitch densities, corresponding to weight of 135 g/m², measured in the wale and course directions were 44 loops and 59 loops per inch, respectively.

The PET fiber fabric demonstrates the high resistance to water penetration. Wicking time is over 900 s when placing a distilled water droplet of 10 μ l on the fabric's surface until the droplet completely loses its reflective power. **Figure 1** (a) illustrates the knit-fabric's structure. Curve yarns oriented in three-dimensional direction interlock together and are created into knitted loops with a loosen structure and air space being inside. In PET polymer structure, shown in Fig. 1 (b), the aromatic ring and its associated C - C bonds provide rigidity to the structure. And furthermore, fragmentation of PET polymer chains on the fiber surface might occur at C - H and C - C molecular bonds when the polymer chain absorbs energies from

(a)

(b)

Fig. 1 SEM micrograph of (a) the PET fiber knit-fabric and (b) PET polymer structure.

Fig. 2 Schematic diagram of a reactor generated with glow discharge plasma at one-atmosphere.

activated species during plasma irradiation.

Washed in 60 neutral-detergent water to remove starch, grease and colloids attached to fiber surfaces, a sample of 120 × 120 mm was dried in a vacuum desiccator.

A glow discharge at one-atmosphere was generated in a parallel-plate electrodes covered with dielectric barriers of a conventional plasma reactor operated at 20 kHz (Fig. 2). The sample placed between two electrodes was exposed to a mixture of He-Ar inert gases. The major component, He gas, possessing a great amount of energy is necessary to sustain the GDP. The addition of Ar gas molecules possessing much lower excited energy level but longer the lifetime than those of He gas leads to increase the density of discharge carriers. A mixture of He-Ar gases constantly flowed into a discharge region with a ratio of 850 ml/150 ml min⁻¹ (STP), respectively. Samples were irradiated with time of exposure varied from 10 s to 3 min.

The sample was immediately weighted to estimate degradation of surface-layer polymers after the GDP treatment. The polymer degradation characterized by weight-loss ratio was calculated in the following expression:

$$W_L (\%) = \frac{W_0 - W_1}{W_1} \times 100 \quad (1)$$

Where: $W_L (\%)$ is the weight-loss ratio; W_0 and W_1 are the weight of a sample before and after the GDP treatment. The irradiated sample was then grafted with AA (99.5 % conc.) in a glass tube evacuated to 133 Pa at two levels of constant temperature: 60 as well as 70 ; the grafting process lasted for 8 h and 1 h, respectively.

Taken from the glass tube, the sample was extracted by hot methanol in a Soxhlet extractor for over 2 h to remove unreacted remaining monomer. The wettability

of the grafted sample was characterized by the grafting degree, which was used to estimate the degree of the glow discharge subsequent to graft polymerization:

$$\text{Grafting degree } (\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad (2)$$

Where: W_1 and W_2 are the sample's weight measured before and after the graft polymerization, respectively.

2.2 Washing durability of the treated fabric

The grafted sample was washed several times in the neutral-detergent water at 60 ; the durable wettability was estimated by the wicking technique. A droplet of distilled water was introduced on the grafted surface by a micro syringe and time for the droplet completely losing its reflective power was measured.

2.3 Surface characterization of the grafted fabric

XPS measurement was performed on a Shimadzu 3300 spectrometer employing MgK α (1253. 6 eV) X-ray source was used. The electron take-off angle was 60 ° with respect to the fabric surface. The pressure in the analysis chamber was maintained at 10⁻⁵ Pa during data acquisition. The X-ray source was run at an anode voltage of 8 kV and current of 30 mA.

2.4 Observation of surface morphologies

The treated surface morphologies were observed using a scanning electron microscope (SEM)-model JEOL JSM-5200. For better electric conductivity, the sample's surface was coated with thin gold layer before the examination. The observation was performed to determine the quality of polymer depositions, and especially to check whether micropores were on the fiber surface.

3 . Results and Discussion

3.1 Surface degradation

The degradation of the fiber surface irradiated with He-Ar glow-discharge seems to be predominant effects of the discharge interaction on the surface polymer. This process led to a breakdown of C - H or C - C bonds into carbon radicals (shown in Eq. 1) on the fiber surface. Subsequently exposed to air, these radicals were reacted with oxygen in air to form peroxides and hydroperoxides (Eqs. 2, 3).⁷⁾ These peroxides being initiators for the graft polymerization were formed as following reactions:

Where: P - H is the polymer chains in the PET struc-

Fig. 3 Polymer degradation of the PET fiber surface treated with He-Ar plasma for different time of exposure.

ture.

The degradation of molecule chains at the irradiated surface layers versus the time of exposure is indicated in the **Fig. 3**. It is clearly that the weight loss ratio, indicating the level of the degradation, proportionally increased with increasing the time of exposure. The large dispersion of the weight loss may be ascribed to the effect of the density of activated species, which collided with the fiber surface and cross-linking of radicals generated on the surface during the GDP treatment. The similar results have also been found in the report of Yasuda et. al.⁴⁾ who investigated the degradation of PET film under low-pressure plasma with inert helium gas.

3.2 Effects of the exposure time on grafting degree

Figure 4 shows the grafting degree of the grafted fiber surface as a function of the exposure time at different grafting temperatures. The peak of the graft level was achieved at 30 s of the exposure time. With the further exposure, the grafting degree gradually went down then leveled off at over 90 s. This may be ascribed to causing unfavorable etching, cross-linking and degradation of the fiber surface resulting in a no net gain of the surface-activated species for the graft polymerization that are usually accompanied with long time of exposure. When the fiber surface was heated in the presence of the monomer, the hydroperoxides decomposed to give equal number of PO^* and $^*\text{OH}$ radicals.

These PO^* radicals initially served as activated sites

Fig. 4 Grafting degree versus the exposure time of the PET fiber fabric treated with plasma-induced graft at different temperatures.

for the grafting reaction, then reacted with AA vapor to form copolymer (Eq. 5)

while $^*\text{OH}$ radicals were the direct cause of homopolymer (Eq. 6)^{16, 17)}

Although the polymerization time decreased to 1 h, higher grafting degree coincident with a higher amount of homopolymer was gained at grafting temperature of 70 °C as compared to the grafting temperature of 60 °C for 8 h. This may be assigned to increasing in the number of free radicals generated by the thermal decomposition, resulting in more reactive sites along the polymer chains. Another effect of increasing the temperature is that it enhanced the diffusion of the monomer into the fiber. However, the higher grafting temperature than PET glass transition one led to a possibility of decreasing in the number of reactive sites on the polymer backbone of the fiber. Also at higher temperatures, AA has a higher tendency to homo-polymerize resulting in a decrease in the grafting level.¹⁸⁾

3.3 Washing durability of the grafted fabric

Figure 5 demonstrates the wicking time versus the time of exposure with the sample grafted at 70 °C for 1 h. The mean wicking time was taken from at least three different spots. The lowest wicking time attained around 30 s of the exposure time. This means the grafted fabric irradiated for 30 s has the highest affinity to water. More than 30 s as well as less than its

time could not make the grafted fabric more hydrophilic. This result is consistent to the highest grafting degree mentioned in the previous section.

The washing durability illustrated in Fig. 5 was dependent on washing times; the wicking time increased with increasing the times of washing and leveled off when times of washing were beyond 20 times. This can be explained by decreasing amount of the copolymer on the fiber surface caused by friction between water and the fabric's surface; the reaction of the copolymer and the neutral detergent was also one of reasons to reduce the copolymer on the fiber's surface. Another reason is that hydrophilic polar groups bonded to a molecule backbone chain were reoriented themselves to surface layers resulting in the gradual deterioration of the surface hydrophilicity.¹⁴⁾

3.4 XPS measurement

The chemical compositions of the fiber surface were analyzed by XPS. Figure 6 shows wide-scan spectra

Fig. 5 Wicking time as a function of exposure time and washing times for the knit-fabric irradiated with plasma for 30 s and grafted at 70 °C for 1 h.

Fig. 6 Wide-scan spectra of a) the control surface and b) the surface irradiated for 30 s and grafted at 70 °C for 1 h.

of a) the control and b) the surface irradiated for 30 s subsequently grafted at 70 °C for 1 h. Peaks of carbon and oxygen binding energy were at 285 eV and 532 eV, respectively. It is noteworthy that the relative surface oxygen and carbon atomic concentrations have been modified significantly. The O_{1s}/C_{1s} ratio increased from 34.4 % to 42.6 % for the control and grafted surface, respectively. Clearly, the surface has been oxidized by the plasma-induced graft polymerization owing to the oxygen content enhanced from 25.6 % to 29.9 % correspondent to the control and grafted surface, respectively (Table 1).

Figure 7 demonstrates high-resolution scan of the C_{1s} core-level spectra for a) the control surface and b) the surface irradiated for 30 s subsequently grafted at 70 °C for 1 h. Lineshape analysis by break deconvolution indicates that C_{1s} spectra of the control surface are composed of three distinct peaks at the binding energy (BE) of 285.0, 286.6 and 288.9 eV (Fig. 7 a). These peaks can be assigned to the $C^* - H$, $C^* - O$ (e.g., ether, ester) and $O - C^* = O$ (e.g., carboxylic acid, ester) groups, related to an aromatic ring $-C_6H_4-$, $CH_2 - CH_2 - O$ and $CO - O$ groups, respectively.¹⁹⁾ And these assignments are also in good agreement with the structure of the PET-repeating unit described in Fig. 1 b.

C_{1s} spectra of the grafted surface consist of four peaks: one of them is a peak of carbonyl groups: $C^* =$

Table 1 Atomic percent compositions on the surface irradiated for 30 s and grafted at 70 °C for 1 h.

Treatment	Surface chemical compositions, %		
	C_{1s}	O_{1s}	O_{1s}/C_{1s}
Untreated	74.4	25.6	34.4
Grafted	70.1	29.9	42.6

Fig. 7 Line-shape analysis of the high-resolution of the C peak spectra for a) the control surface and b) the surface irradiated for 30 s and grafted at 70 °C for 1 h.

Table 2 Relative chemical compositions of C_{1s} spectra on the surface irradiated for 30 s and grafted at 70 °C for 1 h.

Treatment	Decomposition of the C_{1s} peak			
	C_{1s} component, %			
	$C^* - H$	$C^* - O$	$O - C^* = O$	$C^* = O$
Untreated	71.4	17.1	11.4	
Grafted	65.9	18.6	12.5	3.0

O at 287.4 eV, and the rest are the same peaks on the control surface (Fig. 7 b). The relative chemical compositions of the C_{1s} spectra on the PET fabric are shown in **Table 2**. There was a relative increase in the content of the $O - C^* = O$ carboxyl group from 11.4 % to 12.5 %, the $C^* - O$ group from 17.1 % to 18.6 %, and also $C^* = O$ carbonyl of 3.0 %, the new group incorporated into the surface while the $C^* - H$ linkage of the aromatic ring decreased from 71.4 % to 65.9 %. These data suggest that plasma-induced graft polymerization mainly involves in the modification of $-C_6H_4-$, $-CO-$ and $O - C^* = O$ groups while post-plasma reaction in air of free radicals generated by broken chains and dehydrogenation mechanisms led to the formation of the carbonyl group, a new linkage from the CO group created by oxidation processes.

3.5 Morphologies of fiber surfaces

Figure 8 shows surface morphologies of the fiber surface non-treated and treated by plasma-induced graft polymerization with distinct magnifications. The control surface (Fig. 8 a) looks like smooth while the modified one (Fig. 8 b) seems to be rough with regular corn-structure that can be seen clearly in a SEM micrograph with higher magnification (Fig. 8 c). The distinction is attributed to the fragmentation of polymer chains caused by the surface etching, and to grafting the monomer onto the radicals decomposed from the

hydroperoxide. It is assumed that the rough surface is one of factors that can reduce a contact angle of a droplet and therefore, decrease time for the droplet's penetration into fiber surfaces.

4. Conclusions

Helium-argon plasma-induced graft polymerization with acrylic acid significantly improved durable wettability of the PET fiber knit-fabric. The highest grafting degree coincident to the lowest wicking time was found when the fiber surface irradiated for 30 s and then grafted at 70 °C. And also, the hydrophilic durability is dependent on the times of washing: the hydrophilicity decreased with increasing the washing times, however, it leveled off beyond 20 times of washing.

The XPS characterization of the treated surface clearly demonstrates a considerable amount of the oxygen-containing functional polar groups were incorporated onto the grafted surface in the form of $O - C^* = O$ and $C^* = O$. It is the polar groups that improve hydrophilicity and increase surface free energy of the PET fiber surface.

The changes in morphologies of the grafted surface demonstrated copolymers like the corn-structure were incorporated on the grafted surface fiber. The grafted surface seems rougher than the control one. It is the rough surface that may reduce the wicking time of the droplet into the fiber surface.

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a)

b)

c)

Fig. 8 SEM micrographs of a) the control surface and the surface irradiated with for 30 s and grafted at 70 °C for 1 h: b) low and c) high magnification.

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