Functional Finishing by Using Atmospheric Pressure Plasma: Grafting of PET Nonwoven Fabric

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Received 28 March 2006; accepted 27 August 2006
DOI 10.1002/app.25541
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Poly (ethylene terephtalate) (PET) nonwoven fabric was treated with He/O_2 plasma to produce peroxides and grafted with acrylic acid (AA) for introducing carboxyl groups onto PET surface. The graft yield increased with AA concentration from 1.5*M* to 2.5*M*, and then decreased with further increase in AA concentration. Graft yield increased with sodium pyrosulfite (SPS) concentration from 0.005*M* to 0.02*M*, and then decreased with further increase of SPS concentration. X-ray photoelectron spectroscopy results indicated that both of plasma treatment and AA grafting increased oxygen content and decreased carbon content on the PET nonwoven fabric surface. The grafted PET nonwoven fabric showed increase in moisture regain and dye uptake. And drastic increase in wettability was observed after grafting. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3655–3659, 2007

Key words: polyesters; functionalization of polymers; copolymerization

INTRODUCTION

Poly (ethylene terephthalate) (PET) has excellent mechanical strength and good stability, but it is a relatively inert polymer and so, one of the most difficult to graft without any surface modification to induce functional groups on its surface.[1] In the fast growing nonwoven industry, PET is finding increased acceptance as a substitute for more traditional fibers, such as rayon and viscose. Considerable efforts were made to modify PET surfaces for suitable chemical functionality, bolstering end-use capability with nonwoven technology.

Surface modification of PET film, fibers, and fabrics has been done using plasma, UV, ozone, and radiation-induced graft copolymerization of hydrophilic monomers. Plasma-induced graft copolymerization is a useful method for modifying the surface chemistry and morphology of polymers.[2,3] A selected monomer can be polymerized on the surface of plasma-exposed surface resulting in the formation of active sites for further functionalization. The modification is confined to a depth of a few nanometers without modifying the bulk properties.[2] Since textile fibers and fabrics are much more complicated than films, it is very limited to use those treatment for nonwoven fabrics.

Current interest is to develop a PET nonwoven fabric surface rich in carboxyl groups by plasma-induced graft copolymerization of acrylic acid (AA). PET nonwoven fabric was exposed to atmospheric pressure He/O_2 plasmas and grafted with AA to introduce carboxyl groups onto PET surface. Effects of plasma exposure time, monomer concentration, and reducing agent concentration on graft yield were studied. The surface modifications of PET nonwoven after plasma treatment and grafting were verified by means of attenuated total reflection Fourier transform IR (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), SEM, hydrophilicity, and dye uptake measurements.

EXPERIMENTAL

Materials

PET nonwoven fabric (spunbond, 50 g/m^2) used in this study was manufactured by the Nonwoven Technical Research Center, North Carolina State University, NC. AA was of analytical reagent grade. Sodium pyrosulfite (SPS) and other chemicals used were reagent grade.

Plasma treatment and AA grafting

The He/O_2 plasma treatment of PET nonwoven fabric carried out with He (99%)/O_2 (1%) plasmas. Flow

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Contract grant sponsor: Chonnam National University, Korea.

rates of He and O_2 were 10.09 and 0.13 L/min, respectively. Operating frequency was fixed at 5.0 KHz and exposure time was 1 min. Plasma reactor has been described in detail elsewhere.[4]

The plasma treated PET nonwoven fabrics were immersed in AA aqueous solution with SPS at 70°C for 1 h without degassing. Then grafting samples were washed in 0.1% Triton X-100 aqueous solution for 24 h with an ultrasonic cleaner to remove free homopolymers and rewashed in distilled water using an ultrasonic cleaner and dried. Graft yield was calculated gravimetrically by measuring weight of the PET nonwoven fabric samples before(W_0) and after(W_1) grafting as follows:

$$\text{Graft yield } (\%) = \{(W_1 - W_0)/W_0\} \times 100$$

Characterization

ATR-FTIR (IFS66/S, Brucker Optik GmbH, Ettlingen, Germany) was used to confirm grafting of AA. XPS was carried out using ESCA-2000 spectrometer (VG microtech, East Grinstead, UK) equipped with hemispherical analyzer and a monochromatized Al Kα X-ray source (1286.6 eV). Analysis was carried out under UHV conditions 1.0×10^{-9} mbar at 200 W power of the anode. Spectra were taken at an angle of 90°.The surfaces of plasma treated and AA grafted nonwoven fabric were observed with a scanning electron microscope (JSM-5400, JEOL, Tokyo, Japan).

Wettability (AATCC 39-1980) was assessed by measuring absorption time to absorb 10 μL of distilled water completely. Moisture regain (ASTM Test Method D2654-76) was measured by following standard procedure. A basic dye (Maxilon Blue 5G, Ciba-Geigy, Highpoint, NC) was used for dyeability experiment. Dyeing conditions were 3% (owf) dyestuff, 0.1% (owb) sodium acetate, 0.1% (owb) acetic acid, 100°C, 60 min. Dyeability was determined by measuring K/S value with a Macbeth coloreye 3000 (Datacolor, NY).

RESULTS AND DISCUSSION

The electrical energy applied from plasma reactor dissociates gas into electrons, free radicals, ions, photons, and metastable species. The free radicals and electrons collides with the polymer surface and rupture covalent bonds. The free radicals are created on the polymer surface may then combine with oxygens and moistures in air to form oxygen functionality including hydroperoxide on the polymer surface.[5] This modified surface is relatively unstable undergoing reorganization, leading to a decrease in surface hydrophilicity. Therefore, subsequent modification by grafting of AA was carried out to maintain the surface functionality. Reaction mechanism of graft copolymerization of PET with AA is depicted in Figure 1.

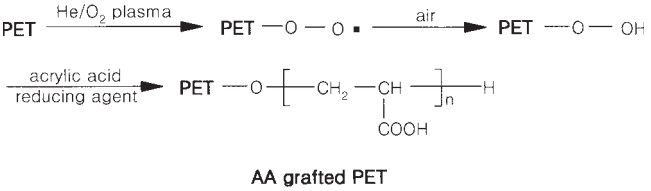

Figure 1 Plasma treatment and graft copolymerization on PET nonwoven fabric.

Graft yield

The influence of the plasma exposure time on the graft yield is shown in Table I. The longer the plasma treatment time was, the higher graft yield was. This is due to the active sites involved in the graft reaction increased with plasma exposure time. This seems to agree with oxygen-containing groups increased with plasma exposure time from 30 to 90 s, indicated by the increase of O_{1s}/C_{1s} ratio. He and Gu have reported that graft ratio increased with increasing irradiation dose within a certain range.[6]

Figure 2 shows the effect of monomer concentration on graft yield using samples exposed for 30 s by He/O_2 plasma. Hydroperoxide groups produced by He/O_2 plasma on the PET surface are main functionality. The hydroperoxide groups on the PET surface are thermally labile and initiate the graft copolymerization of AA.[7,8] The results shown in Figure 2 were obtained using 0.01*M* of reducing agent. The graft yield increases with AA concentration from 1.5*M* to 2.5*M*, and then decreases with further increase in AA concentration. More AA molecules in the reaction medium increase chances for the PET macroradicals to encounter more monomer units for grafting and lead to high grafting yield. There is also a greater chance for competing between graft copolymerization and homopolymerization. Further increase in monomer concentration above 4.0*M* seems to result in prevailing homopolymerization over graft copolymerization. The homopolymer increases the viscosity of reaction medium and this inhibits the AA molecules to diffuse to the active site on the PET macroradicals, resulting in the decrease of graft yield. And the decrease in the

TABLE I
Graft Yield Depending on Exposure Time and O_{1s}/C_{1s} Ratio

Exposure time(s)	O_{1s}/C_{1s}	Graft yield (%)
0	0.38	0.72
60	0.42	0.85
90	0.46	1.03

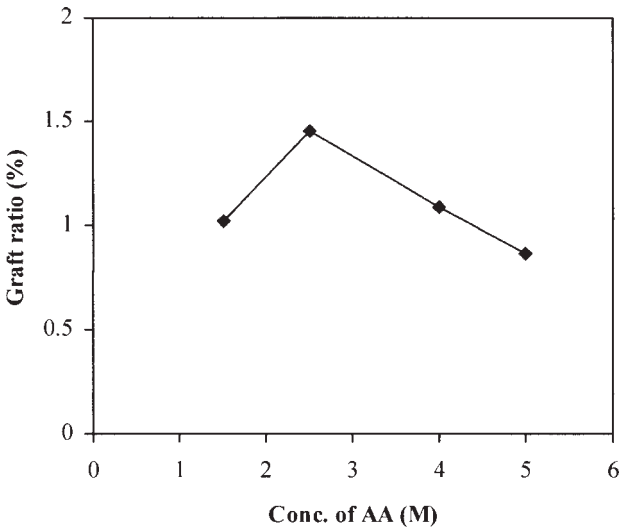

Figure 2 Effect of monomer concentration on graft yield.

graft yield could be also caused by the reduced effective monomer concentration because of the extensive homopolymerization. This resulted in the decrease of the propagation rate, and chain transfer to the homopolymer in solution started to dominate over chain propagation. Once the homopoymerization was extensive, the monomer depletion favored more chain transfers in the system.[8] As a result, the degree of grafting showed a decreasing trend.

Figure 3 shows the effect of reducing agent concentration on AA graft yield at 1.5*M* of AA concentration. Graft yield increases with SPS concentration from 0.005*M* to 0.02*M*, and then decreases with further increase of SPS concentration. At higher SPS concentration, homopolymerization seems to prevail over graft copolymerization. It was observed that reaction medium got more viscous at higher SPS concentration, resulting from the formation of AA homopolymer.

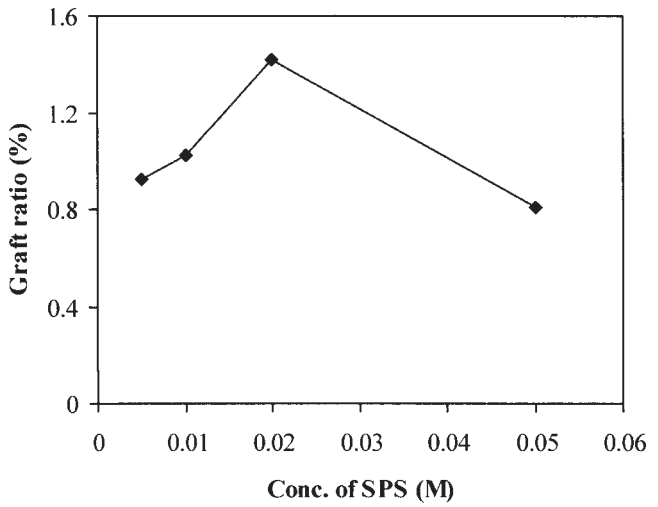

Figure 3 Effect of reducing agent concentration on graft yield.

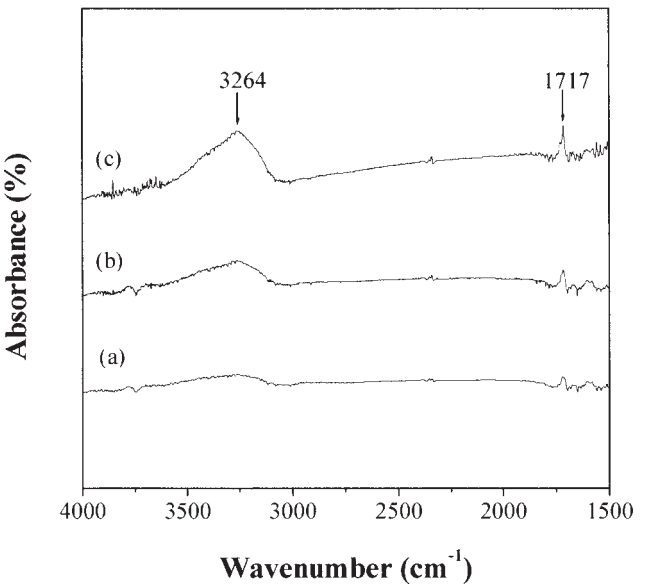

Figure 4 FTIR-ATR spectra of samples; (a) control, (b) plasma treated, and (c) grafted.

This made difficult reducing agent molecules to diffuse effectively to form active site on the PET surface.

Surface modification

Figure 4 shows ATR-FTIR spectra of control (a), plasma treated (b), and AA grafted samples. Broad absorption peak in the range of 3100–3600 cm^{-1} appeared in the plasma treated sample and it becomes stronger in the AA grafted sample because of higher extent of H-bonding of carboxylic acid groups. The peak height at 1717 cm^{-1} due to C=O absorption shows a slight increase on plasma treatment and subsequent grafting. Since ATR-FTIR penetrates deep into the matrix, the top nanoscale change on the surface is diluted to some extent.[2]

Table II shows chemical composition of the untreated, plasma treated, and AA grafted samples. Plasma treatment and AA grafting increase oxygen content and decrease carbon content on the PET surface. In the information depth of XPS, 10 nm, almost pure grafted polymer is present, whereas FT-IR spectra show both the bulk polymer and graft polymer.[9] The oxygen content would increase with increasing graft yield. The C—O component decreases and O=C—O component increases after plasma treat-

TABLE II
Chemical Composition and O_{1s}/C_{1s} Ratio of Samples

Sample	C (%)	O (%)	O/C	C—C (%)	C—O (%)	O=C—O (%)
Control	72.9	27.1	0.372	69.5	14.8	15.7
Plasma treated	70.4	29.6	0.421	68.6	14.5	16.8
AA grafted[a]	69.6	30.4	0.437	66.9	14.7	18.3

[a] 60 μg/cm^2.

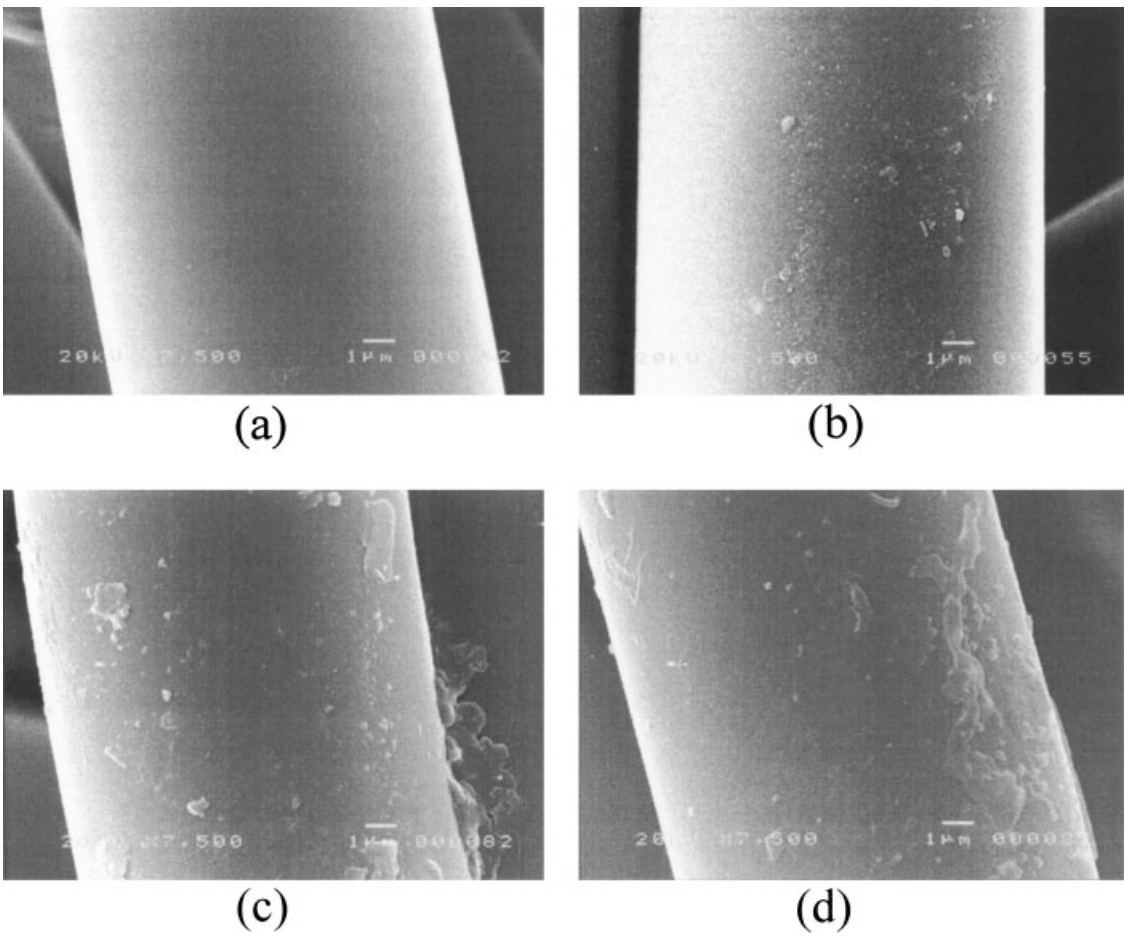

Figure 5 SEM pictures; (a) control, (b) plasma treated, (c) and (d) grafted samples.

ment. As graft yield increases, C—O component increases relatively within the grafted samples. The result indicates that carboxyl groups are introduced on the surface of PET.

Figure 5 shows SEM pictures of the control (a), plasma (90 s) treated (b), and AA grafted samples (c and d). The control sample appears as a smooth surface and the plasma treated sample shows some redeposited particles etched away during plasma treatment. Some lumps are observed on the surface of AA polymers grafted samples. They seem to be the excess of AA polymers. The plasma attacks preferentially the amorphous region of PET and peroxides are formed. The lumps are formed because of an inhomogeneity of the amorphous region of PET fiber.[10]

Wettability, moisture regain, and dye uptake

Table III shows the effect of plasma treatment and graft yield on wettability, moisture regain, and dye uptake(K/S). The untreated sample takes more than 60 min to absorb 10 mL of distilled water. The improved wettability of plasma treated sample has been attributed to increasing the amount of polar groups, surface oxidation, and increased surface roughness.[11] Wettability increases drastically after grafting with AA. Since contact angle is reduced on the surface grafted with hydrophilic monomer, the surface absorbs water almost instantly regardless of graft yield. Moisture regain of the AA grafted samples increases steadily with graft yield. This is attributed to more hydrophilic groups on the surface of samples as graft yield increases. Dye uptake of Basic Blue 3 increases marginally with the increase of graft yield. This result is consistent with moisture regain measurement. The basic dye molecules react with carboxyl groups on the grafted chains and chain ends of the PET. Therefore, the dye uptake indicates the amount of carboxyl group on the grafted PET nonwoven.

TABLE III
Wetting Time, Moisture Regain, and Dye Uptake of Samples

Samples	Graft yield (%)	Wetting time	Moisture regain (%)	Dye uptake (K/S)
Control	–	>30 min	0.22	0.259
Plasma treated	–	15 min	0.45	0.253
Grafted				
1	0.85	<3 sec	0.47	0.430
2	1.52	<2 sec	0.82	0.534
3	2.15	<2 sec	1.03	0.620

Since, dye molecules are much larger than moisture, their accessibility to carboxyl groups could be limited and so less effective for improving dye uptake. Introducing functional groups like carboxyl groups, the modified PET nonwoven surface is suitable for attaching functional, bioactive compounds.

CONCLUSIONS

The results obtained indicate that it is possible to graft AA onto PET nonwoven fabric by He/O_2 plasma treatment. The graft yield increases with AA concentration from 1.5*M* to 2.5*M*, and then decreases with further increase in AA concentration. Graft yield decreases with increase in SPS concentration. AA grafting increases wettability drastically. The grafted PET nonwoven fabric shows the improvement of moisture regain and dyeability with a basic dye.

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