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Special Issue: Bioactive Surface Functionalization

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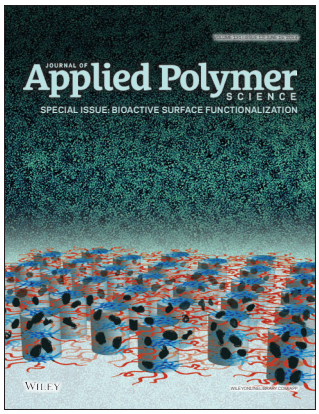

EDITORIAL

Bioactive Surface Functionalization
K. G. Neoh, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40607**

REVIEWS

Orthogonal surface functionalization through bioactive vapor-based polymer coatings
X. Deng and J. Lahann, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40315**

Surface modifying oligomers used to functionalize polymeric surfaces: Consideration of blood contact applications
M. L. Lopez-Donaire and J. P. Santerre, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40328**

Block copolymers for protein ordering
J. Malmström and J. Travas-Sejdic, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40360**

RESEARCH ARTICLES

MS-monitored conjugation of poly(ethylene glycol) monomethacrylate to RGD peptides
O. I. Bol'shakov and E. O. Akala, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40385**

Synthesis and characterization of surface-grafted poly(*N*-isopropylacrylamide) and poly(carboxylic acid)—Iron particles via atom transfer radical polymerization for biomedical applications
J. Sutrisno, A. Fuchs and C. Evrensel, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40176**

Deposition of nonfouling plasma polymers to a thermoplastic silicone elastomer for microfluidic and biomedical applications
P. Gross-Kosche, S. P. Low, R. Guo, D. A. Steele and A. Michelmore, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40500**

Regeneration effect of visible light-curing furfuryl alginate compound by release of epidermal growth factor for wound healing application
Y. Heo, H.-J. Lee, E.-H. Kim, M.-K. Kim, Y. Ito and T.-I. Son, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40113**

Bioactive agarose carbon-nanotube composites are capable of manipulating brain–implant interface
D. Y. Lewitus, K. L. Smith, J. Landers, A. V. Neimark and J. Kohn, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40297**

Preparation and characterization of 2-methacryloyloxyethyl phosphorylcholine (MPC) polymer nanofibers prepared via electrospinning for biomedical materials
T. Maeda, K. Hagiwara, S. Yoshida, T. Hasebe and A. Hotta, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40606**

Nanostructured polystyrene films engineered by plasma processes: Surface characterization and stem cell interaction
S. Mattioli, S. Martino, F. D'Angelo, C. Emiliani, J. M. Kenny and I. Armentano, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40427**

Microtextured polystyrene surfaces for three-dimensional cell culture made by a simple solvent treatment method
M. E. DeRosa, Y. Hong, R. A. Faris and H. Rao, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40181**

Elastic biodegradable starch/ethylene-co-vinyl alcohol fibre-mesh scaffolds for tissue engineering applications
M. A. Susano, I. B. Leonor, R. L. Reis and H. S. Azevedo, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40504**

Fibroblast viability and inhibitory activity against Pseudomonas aeruginosa in lactic acid–grafted chitosan hydrogels
A. Espadín, N. Vázquez, A. Tecante, L. Tamay de Dios, M. Gimeno, C. Velasquillo and K. Shirai, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40252**

Surface activity of pepsin-solubilized collagen acylated by lauroyl chloride along with succinic anhydride
C. Li, W. Liu, L. Duan, Z. Tian and G. Li, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40174**

Collagen immobilized PET-g-PVA fiber prepared by electron beam co-irradiation
G. Dai, H. Xiao, S. Zhu and M. Shi, *J. Appl. Polym. Sci.* 2014, **DOI: 10.1002/app.40597**

Journal of Applied Polymer Science

Collagen-Immobilized Poly(ethylene terephthalate)-*g*-Poly(vinyl alcohol) Fibers Prepared by Electron-Beam Co-Irradiation

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ABSTRACT: Vinyl acetate was grafted onto poly(ethylene terephthalate) (PET) fibers under electron-beam co-irradiation. Then, the grafted products were hydrolyzed under HCl solution to obtain PET-*g*-poly(vinyl alcohol) (PVA) fibers. Afterward, to impart superior hydrophilicity and skin care, collagen was immobilized onto PET-*g*-PVA fibers with glutaraldehyde. The modified fabric was characterized in terms of moisture regain, wettability, and evaporation rate [Ev (%/h)]. The degree of alcoholysis of the grafting product was more than 90% in a 10% HCl solution at 100°C for 4 h, and its moisture regain was 1.4%. The modified PET fabric with collagen showed a shorter drip diffusion time and a higher wicking height than the unmodified PET and PET-*g*-PVA fabric before and after multiple washings. The evaporation ratio and Ev of the collagen-immobilized PET fibers were far below those of the virgin PET fibers. The chemical structure, surface morphology, and element content of the product were characterized by attenuated total reflectance–Fourier transform infrared spectroscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy. This further certified that the collagen-immobilized PET-*g*-PVA fiber was successfully prepared by the previous procedure. Furthermore, the PET–PVA–collagen fabric was capable of withstanding multiple washing cycles. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40597.

KEYWORDS: grafting; hydrophilic polymers; irradiation; polyesters

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INTRODUCTION

It is considered more and more important that textiles should be more comfortable, healthy, functional, and beneficial to our skin in addition to having a good wearable performance. "Green" functional textiles have caught the eyes of researchers. With a consideration of biocompatibility, safety, and biodegradability, natural biological polymers are often used to modify fibers or fabrics as organ and tissue scaffolds; these materials include chitosan, hyaluronic acid, collagen, and heparin.[1–3] Among these, collagen is the most widely used in cosmetics and also gets extensive attention. Collagen contains different kinds of amino acids, including hydroxyproline, glycine, and lysine; these can supply necessary nutrients to the skin layers, increase the activity of collagen in the skin, and firmly lock in moisture, so it can nourish the skin, retard skin aging, and keep the skin moist for a longer time. In daily life, underwear is close to our skin as a last line of defense to the enviroment and is also an important layer for protecting and nourishing our skin. So, the immobilization of collagen onto underwear fabrics should be benefical to our skin and should create a new product for the market.

Cotton and other cellulose fabrics are often used as underwear fabrics because of their good moisture regain and soft handling and especially because they are natural. A simple method for the immobilization is the coating of collagen onto the surface of the cotton and cellulose fabric by finishing methods,[4] but the product lacks the bonding fastness between the collagen and cotton or cellulose fabric. There are three active hydroxyl groups on the cellulose molecular backbone strucutre, so the hydroxyl groups can be oxidized to aldehyde[5,6] by an oxidizing agent such as sodium periodate. Another method is the connection of collagen and cellulose fibers with covalent bonds by dialdehyde.[7,8] Although the aldehyde group can react with both hydroxyl and amine groups, which is rich in collagen, the strength and color of cotton fabrics would decrease because of oxidative degradation.

Unfortunately, most other polymers, such as polyester and polyamide, for fabrics do not have active groups or have less active groups in their molecular structure. The addition of collagen into the spinning solution is a good method for obtaining fibers containing collagen. Meanwhile, many other functional polymers, such as poly(vinyl alcohol) (PVA), polyacrylonitrile,

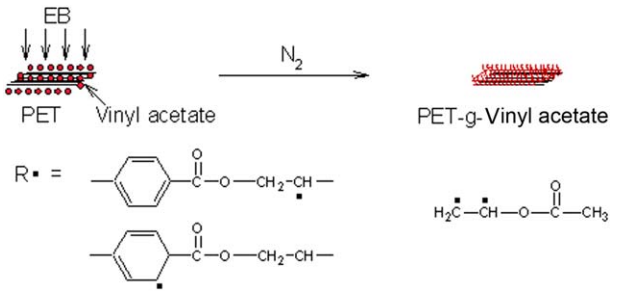

Figure 1. Mechanism for the EB-induced graft polymerization of the vinyl monomer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chitosan, hyaluronic acid, poly(ethylene glycol), and chondroitin sulfate, can be blended with collagen[9,10] in the spinning solution. However, because of the thermal instability, easy degeneration, and loss of activity for animal collagens above 37–40°C, this method is only suitable for wet spinning; for example, PVA can be blend with collagen[11,12] in solution and spun into fibers. It is not suitable for melt spinning with a high melting temperature, and this is the most important spinning method for most fibers, such as poly(ethylene terephthalate) (PET).

Polyester is widely used for underwear in sportswear and outdoor clothing because of its better drying and wicking properties compared to those of cellulose. It is also used for organ and tissue scaffolds,[13–15] such as artificial vascular blood, heart valves, pipes, and implantable sutures. To improve its biomedical adaptability, the surface of the polymer is often modified with bioactive compounds.[16,17] To improve the activity of functional groups with covalent bonding, PET must be modified to generate reactive groups and immobilize biological macromolecules. In many studies, polymer materials without active groups have been introduced to functional groups, such as carboxylic acid, sulfonic acid, amide, amine, acrylate, and pyrrolidone, by electron-beam (EB) or γ irradiation.[18–21] Compared with conventional processes, irradiation processing can be operated at normal or lower temperatures with energy-saving and pollution-free advantages. EB irradiation uses electrical energy to form high-energy EBs, so the switch control is easy, and it is a continuous and rapid process with a high dose rate.

In this study, PET fibers were co-irradiated with EBs to graft vinyl acetate. This was followed by alcoholysis in an HCl solution, and then, the collagen was covalently bonded to PET-*g*-PVA fibers with glutaraldehyde (GA), which has hygroscopic and skin care effects. The moisture regain of the PET-*g*-PVA fibers significantly improved and improved further with immobilized collagen.

EXPERIMENTAL

Materials

PET fibers (FDY, 83dtext/36f) and 100% PET fabric (plain weave, fabric weight = 77 g/m^2) were provided by Zhejiang Rongsheng Chemical Fiber Co., Ltd. (China). Collagen (molecular weight = 300–400 kDa, BioNet, France), vinyl acetate, GA, $CuSO_4{\cdot}5H_2O$, methanol, and other reagents were purchased from China National Pharmaceutical Group C.

Experimental Method

Grafting of Vinyl Acetate onto the PET Fibers by EB Irradiation. The PET fibers were extracted for 24 h in a Soxhlet extractor to remove surface impurities and were then dried in air. The PET fibers were dipped in a polyethylene bag containing different contents of vinyl acetate and a $CuSO_4$ mixture in methanol and were deaerated by bubbling nitrogen for 10 min and then sealed. These polyethylene bags were then irradiated by EB supplied by Beijing Normal University (Beijing, China).

The irradiation equipment was a BF-5 Linac. Its main performance characteristics were as follows: energy range = 3–5 MeV, average beam current = 0–200 mA, beam power = 700 W, irradiation thickness = 1.6–3.0 cm, and scanning width = 60 cm.

The possible EB irriadiation mechanism is shown in Figure 1.

Hydrolysis Reaction. The vinyl acetate grafted PET fibers were treated for different times with hydrochloric acid at 100°C. The concentration of hydrochloric acid in water was 1–10% w/v. In all cases, after hydrolysis the fibers were washed with considerable amounts of deionized water, dried at 105°C for 4 h, and cooled in a desiccator.

Collagen Immobilization on the Modified PET Fibers. The PET-*g*-PVA fibers were soaked in the 6.25% w/w GA aqueous solution at 60°C for 30 min and continuously shocked. Afterward, these fibers were washed three times with Phosphate

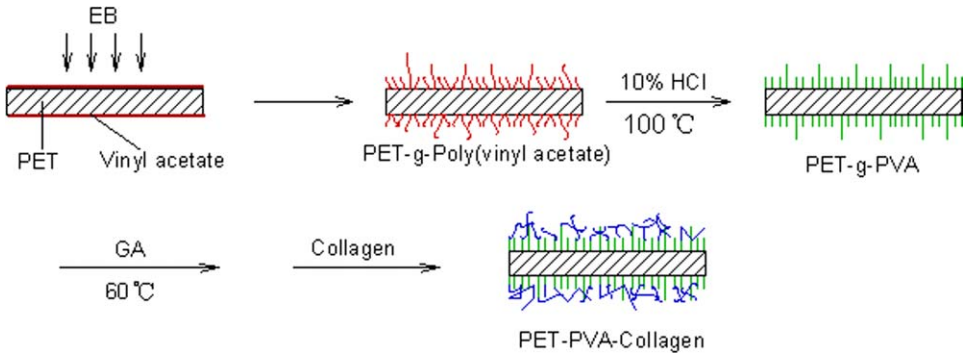

Figure 2. Whole process for collagen immobilization on the PET fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

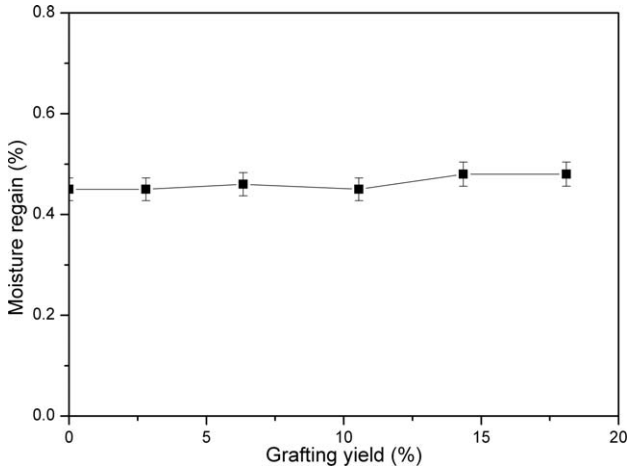

Figure 3. Variation of the moisture regain with the grafting yield.

buffer solution (PBS) and deionized water and then dried in an oven at 65°C. These fibers were then immersed in collagen solutions with concentrations from 1 to 5 g/100 mL for 1 h. Afterward, these fibers were extracted by a Soxhlet extractor with methanol for 24 h to remove the residual GA and collagen and then dried in a vacuum oven at 40°C for 48 h.

The whole experimental procedure is depicted in Figure 2.

Characterization

Evaluation of Moisture Regains. The fiber sample was prehumidified under standard atmospheric conditions [temperature = 20°C, relative humidity (RH%) = 65%] for 24 h to balance humidity. They were then placed into a weighing box and weighed together by an electronic balance (minimum scale value = 0.001 g). After that, we placed the weighing box containing the fiber sample into a blast oven (precision = ±3°C) and opened the lid; it was held there for 1 h at 105°C. The weighing box was quickly covered with the lid and put into the desiccator; it was then weighed when it was cooled to room temperature. Each sample was measured three times.

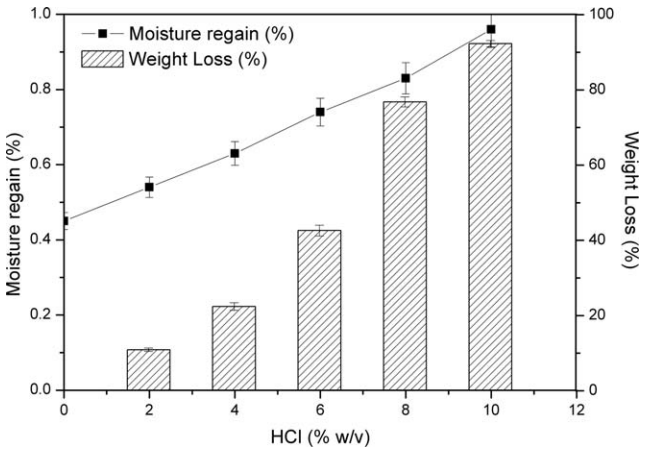

Figure 4. Variation of the moisture regain with the HCl concentration (w/v). Reaction conditions: grafting yield = 19.68%, temperature = 100°C, and time = 4 h.

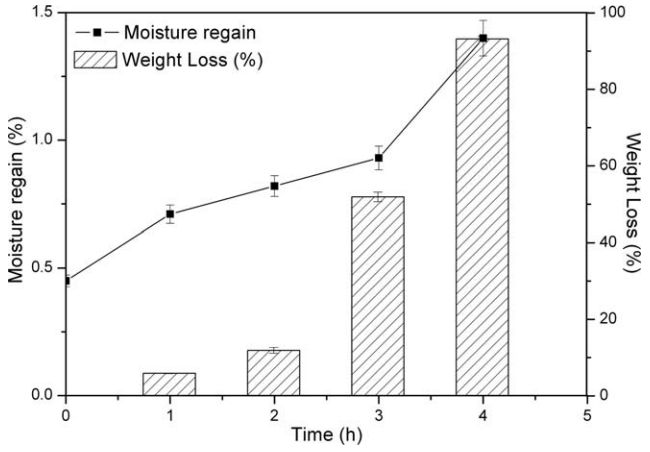

Figure 5. Variation of the moisture regain with the treatment time in the HCl liquid. Reaction conditions: grafting yield = 24.9%, temperature = 100°C, and HCl = 10% w/v.

The moisture regain of manmade fibers was determined gravimetrically with the following expression:

$$\text{Moisture regain}\,(\%) = \frac{W_M - W_H}{W_H} \times 100$$

where W_M and W_H are the weights of the unheated and heated fibers, respectively.

Evaluation of the Wettability. The wettability of PET-*g*-PVA and after the collagen was immobilized on the fabric was evaluated by two different tests: drip diffusion time and wicking height. To measure the drip diffusion time, we cut the fabric samples into 10 × 10 cm^2 pieces. The fabrics were placed under standard atmospheric conditions (temperature = 20°C and RH% = 65%) for 24 h to balance the humidity. The fabric was flat and 0.2 g of distilled water was dripped on the surface with a pipette, in which the distance between the pipette mouth and the surface of the sample was no more than 1 cm. We carefully observed the spread of the water droplet and recorded the time (accurate to 0.1 s) from when the water droplet contacted the fabric surface to complete diffusion (no specular reflection). Three repeated tests were performed for each sample.

To evaluate the wicking height, the fabric sample was cut into 3 × 25-cm^2 samples and held at the top with an iron clamp. The bottom edge of the fabric was immersed into distilled water for 30 min. The height the water had moved up was then measured. Three repeated tests were performed for each sample.

Evaluation of the Evaporation Rate [Ev (%/h)]. The samples were placed under standard atmospheric conditions (temperature = 20°C and RH% = 65%) for 24 h to balance the humidity. Then, the initial samples were weighed to an accuracy of 0.001 g. The samples were placed into a container with three stages of water and naturally sank because they absorbed water. After 5 min, the samples were removed from the water, suspended vertically, and stretched as far as possible. The samples were held for 90 min and were then weighed without drips to an accuracy of 0.001 g. After that, the samples were weighed

Table I. Moisture Regain of the Polyester Fabrics Treated with Various Methods

Treatment method	Moisture regain (%)	Testing method	Reference
Cationic nanocrystalline cellulose (NCC) coating	3.99	—	Zaman et al.[24]
Polyethylene glycolated bisphenol A (PEGBPA) coating	0.2–0.6	AND AD-4715	Ploymalee et al.[25]
Cutinase treatment	4.7 ± 0.5	ASTM D 629-99	So Hee and Wha Soon[26]
Enzymatic treatment	1.2–1.65	ASTM D 629-99	Hye Rim and Wha Soon[27-29]
Gaseous sulfur oxide activated	1.6	NF G 08-001	Kordoghli et al.[30]
He/O_2 plasma treatment	0.65	ASTM D 2654-76	Younsook et al.[31]
Acrylic acid grafting	1.03	ASTM D 2654-76	Younsook et al.[32]
Acrylic acid grafting	2.1	GB9995-88	He and Gu[21]
Acrylamide / Itaconic Acid (AAm/IA) grafting	0.6	—	Coçkun et al.[33]
Methacrylamide grafting	3.01	—	Alakara et al.[34]
Hydrolysis of PVAc grafting	1.1	—	Faterpeker and Potnis[23]

once every 10 min to an accuracy of 0.001 g. Each sample was measured three times.

The absorbed water of the per unit mass fiber sample was determined gravimetrically with the following expression:

$$\text{Absorbed water}\,(M)=\frac{M_1-M_0}{M_0}\times 100$$

where M_0 and M_1 are the weights of the initial sample and the fibers held for 90 min after sinking in water under standard atmospheric conditions, respectively.

The evaporation ratio of the per unit mass fiber sample was determined gravimetrically with the following expression:

$$\text{Evaporation ratio}\,(\%)=\frac{M-M_i}{M}\times 100$$

where M and M_i are the weights of the absorbed water of the per unit mass fiber sample held for 90 min under standard atmospheric conditions and at time i after that, respectively.

Ev was obtained by the slope of the tangent from the time–evaporation ratio curve.

Attenuated Total Reflectance (ATR) Fourier Transform Infrared (FTIR) Spectroscopy. The functional groups of the ungrafted, grafted, alcoholysis, and collagen-immobilized samples on the modified PET fibers were studied with a Varian 3100 FTIR Excalibur Series instrument. The spectra were recorded from 4000 to 500 cm^{-1}, and all of the spectra were background-corrected with an average of 32 scan signals at a resolution of 2 cm^{-1}.

Scanning Electron Microscopy (SEM). Scanning electron micrographs of the ungrafted, grafted, and alcoholysis PET fibers were obtained with a JEOL model JSM-7500F microscope. Before scanning, these fibers were coated with gold.

X-ray Photoelectron Spectroscopy (XPS). The XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific with 300 W of Mg Kα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

RESULTS AND DISCUSSION

Moisture Regain Properties

Effect of the Grafting Yield on the Moisture Regain. Moisture regain is an important index for the hygroscopic degree of textile materials; this was the percentage of the water content of fiber to the dry weight of fiber. The effect of the grafting yield on the moisture regain is given in Figure 3. The moisture regain of the graft samples increased slightly with

Table II. Drip Diffusion Times of PET, PET-*g*-PVA, and PET–PVA–Collagen Before and After Multiple Washings

Sample	No washes	First wash	Third wash	Fifth wash
PET	22.02	19.98	19.93	19.96
PET-*g*-PVA 1#	16.27	16.45	16.55	16.48
PET-*g*-PVA 2#	13.1	13.44	13.56	13.59
PET-*g*-PVA 3#	10.36	10.79	10.86	10.81
PET–PVA–collagen 4#	4.48	5.67	5.75	5.83
PET–PVA–collagen 5#	3.12	4.67	4.78	4.80
PET–PVA–collagen 6#	2.05	3.40	3.57	3.62

1#, the PET-*g*-PVAc (3.23%) was hydrolyzed with 10% w/w HCl at 100°C for 4 h; 2#, the PET-*g*-PVAc (4.46%) was hydrolyzed with 10% w/w HCl at 100°C for 4 h; 3#, the PET-*g*-PVAc (5.38%) was hydrolyzed with 10% w/w HCl at 100°C for 4 h; 4#, 4% w/w collagen was immobilized on PET-*g*-PVA 1# with GA; 5#, 4% w/w collagen was immobilized on PET-*g*-PVA 2# with GA; 6#, 4% w/w collagen was immobilized on PET-*g*-PVA 3# with GA.

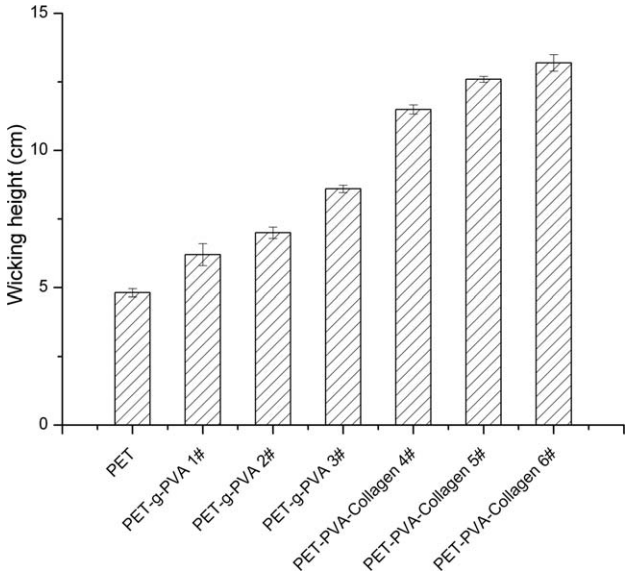

Figure 6. Wicking heights of the PET, PET-*g*-PVA, and PET–PVA–collagen fabric.

further increases in the grafting yield of vinyl acetate; this was not very great in comparison with similar studies in the literature.[22] With increasing graft chain length, the flexibility of the side chain and the grafting also resulted in an increase in the surface roughness of the PET fibers. This caused an increase in the moisture regain.

Effects of the HCl Concentration on the Moisture Regain and the Mass Loss Rates. The alcoholysis reaction of the vinyl acetate grafted PET fibers was carried out with an HCl solution.[23] The moisture regain and mass loss rates of the vinyl acetate grafted PET fibers after alcoholysis under different HCl concentrations are drawn in Figure 4.

The alcoholysis degree of the vinyl acetate grafted PET fibers was estimated by the mass loss rate (the ratio between the mass loss and the theoretical mass loss of the polyvinyl acetate after alcoholysis). As the HCl concentration increased, the mass loss rate of the samples increased. Meanwhile, the alcoholysis degree of the grafted poly(vinyl acetate) increased, and the moisture regain also increased because of the increase in the hydrophilic hydroxyl groups. The PET fibers grafted with 19.68% poly(vinyl acetate) were treated in a 10% w/v HCl solution at 100°C for 4 h. As a result, the alcoholysis degree of the grafted poly(vinyl acetate) was up to 92%, and the moisture regain was close to 1%.

Effect of the Reaction Time on the Moisture Regain. The relationships between the hydrolysis time, alcoholysis degree, and moisture regain of the samples are shown in Figure 5. After hydrolysis for 4 h of the PET fibers grafted with 24.9% poly(vinyl acetate), the alcoholysis degree was up to 93%; this indicated that about 93% of grafted poly(vinyl acetate) had been become PVA, and the moisture regain was up to 1.4%. We observed that the moisture regain of the alcoholysis sample depended on the grafting yield under identical hydrolysis conditions.

Table I shows the hydrophilicity improvement of the PET materials treated with various methods. As shown in Table I, the cutinase treatment and cationic nanocrystalline cellulose (NCC) coating of the PET materials resulted in higher moisture regains than the other treatments. By comparing the moisture regains of the PET material treated with various methods, we found that the hydrolysis of poly(vinyl acetate) (PVAc)-grafted PET was an effective method for improving the hydrophilicity of the PET material. Grafting as a method is commonly used in PET modification, and it can be maintained for a longer time than plasma treatment and coating finishes because of the covalent bonding with the PET substrate.

Wetting Behavior

Table II shows the drip diffusion time evaluation results for the unmodified and modified PET fabrics. The untreated PET fibers needed 22.02 s for complete diffusion of the 0.2-g water droplet; this was due to the hydrophobic nature of the PET fibers. As shown in Table II, both the PET-*g*-PVA and PET–PVA–collagen fabrics showed a significant decrease in the drip diffusion time. The vinyl acetate grafted PET fabrics were hydrolyzed into PET-*g*-PVA fabrics, which showed a diffusion time of 13.1 s for PET-*g*-PVA 2#, and the diffusion time decreased with increasing grafting yield. The PET–PVA–collagen fabric showed a diffusion time of 3.12 s for PET–PVA–collagen 5# and the diffusion time also decreased with increasing grafting yield; its could be attributed to the presence of carboxyl groups, amine groups, and the three-dimensional helical structure of the collagen macromolecule locking in moisture.

Table II also shows the drip diffusion time of the unmodified and modified PET fabrics after multiple washings. The unmodified PET and PET-*g*-PVA fabrics showed little change in the drip diffusion time, whereas the PET–PVA–collagen fabrics showed a significant increase, which may have been due to the degradation of collagen. Despite the increase in the drip diffusion time after multiple washings, the diffusion time of 3.62 s for PET–PVA–collagen 6# was still far below that of the unmodified PET and PET-*g*-PVA fabrics.

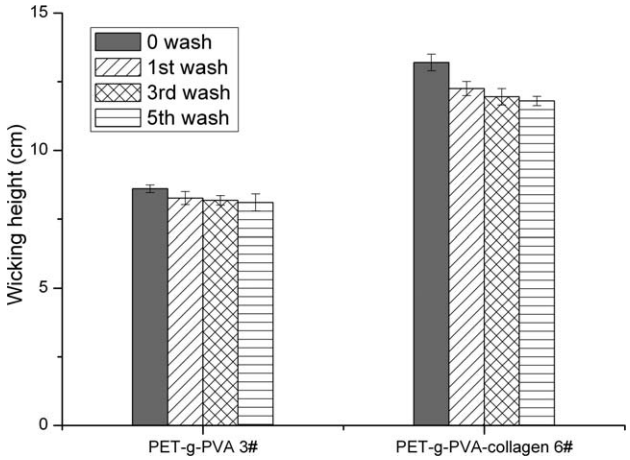

Figure 7. Wicking heights of the PET-*g*-PVA and PET–PVA–collagen fabrics after multiple washings.

Table III. Wicking Heights and Drop Absorption Times of the PET Materials Treated with Various Methods

Treatment method	Wicking height	Drop absorption time	Testing method	Reference
Plasma treatment	4.3 cm/2 min	86 s	—	Karthik et al.[35]
Plasma treatment	17.5 cm	—	—	Kale and Desai[36]
He/O_2 plasma treatment	—	6 min	AATCC 39-1980	Younsook et al.[31]
Plasma and enzyme treatment	11 cm/3 min	—	DIN 53924	Karaca et al.[37]
Enzymatic treatment	—	55 s	—	Hye Rim and Wha Soon[28]
Cutinase treatment	—	58.2 ± 6.7 s	ASTM D 79-1992	So Hee and Wha Soon[26]
poly(urethane) (PU) prepolymer finishing	5.2 cm	9 s	CNS12915	Meng-Shung and Ching-Nan[38]
Polyethylene glycolated bisphenol A (PEGBPA) coating	7-8 cm	—	—	Ploymalee et al.[25]
Acrylic acid grafting	—	<2 s	AATCC 39-1980	Younsook et al.[32]

Figure 6 shows the wicking height of the unmodified PET, PET-*g*-PVA, and PET–PVA–collagen fabrics. The unmodified PET fabric showed a wicking height of 4.82 cm, whereas the PET-*g*-PVA 3# and PET–PVA–collagen 6# showed much higher wicking heights of 8.6 and 13.2 cm, respectively. The results from the wicking height test of the unmodified and modified PET fabrics were in agreement with the drip diffusion time experiments.

Figure 7 shows the wicking heights of the PET-*g*-PVA 3# and PET–PVA–collagen 6# fabrics before and after multiple washings. The PET-*g*-PVA fabric showed a wicking height of 8.1 cm after five washing cycles, whereas the PET–PVA–collagen fabric showed a wicking height of 11.8 cm. Despite the decrease for the PET–PVA–collagen fabric in wicking height after five washing cycles, it was still remarkably higher than that of the PET-*g*-PVA fabric.

Table III shows the wicking heights and drop absorption times of the PET materials treated with various methods. In a comparison of these methods, the PET–PVA–collagen fabrics had excellent drop absorption times and wicking heights before and after multiple washings. This was because molecular collagen immobilized onto the PET substrate with covalent bonds by GA.

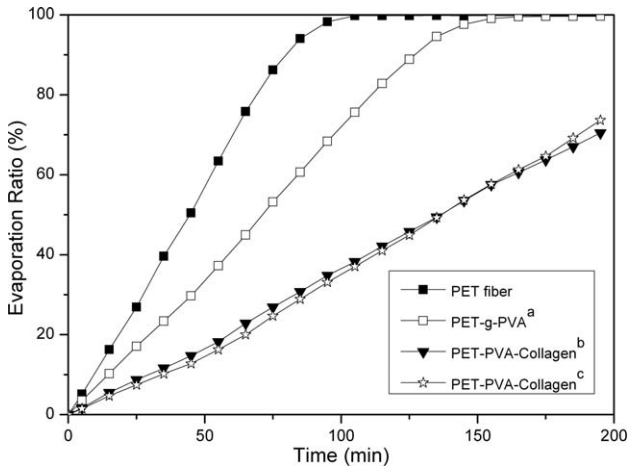

Figure 8. Evaporation ratio per unit mass fiber sample for PET, PET-*g*-PVA [(a) PET-*g*-PVAc (18.91%): 10% HCl, 100°C, and 4 h], and PET–PVA–collagen [(b) PET-*g*-PVAc (19.68%): 10% HCl, 100°C, 4 h, and 4% w/w collagen with GA and (c) PET-*g*-PVAc (17.43%): 10% HCl, 100°C, 4 h, and 1% w/w with collagen with GA].

Water Absorption and Ev

The absorption of the water and moisture Ev values in the regulation air conditions of per mass fiber was used to characterize the hygroscopicity. The higher the water absorption was and the smaller Ev was, the higher the hygroscopicity of the fiber was.

Because of the thermal instability, easy degeneration, and loss of activity for the animal collagen above 37–40°C, to characterize its hygroscopicity, the evaporation ratio, absorbed water, and Ev of the per unit mass fiber sample were investigated, and the results are given in Figure 8 and in Table IV.

As shown in Figure 8, the evaporation ratio of the PET fibers reached 98.3% after 95 min, and that of PET-*g*-PVA[a] reached 97.6% after 145 min, whereas those of PET–PVA–collagen[b] and PET–PVA–collagen[c] reached only to 70.47 and 73.67%, respectively, after 195 min. It was demonstrated that the hygroscopicity of PET-*g*-PVA was higher than that of the virgin PET because of the water absorbency of the fiber surface hydroxyl groups, and the hygroscopicity of PET–PVA–collagen was further improved.

Table IV shows the absorbed water and Ev values of the per unit mass fiber sample. The absorbed water of the PET–PVA–

Table IV. Absorbed Water and Ev Values of the Per Unit Mass Fiber Sample

	PET	PET-*g*-PVA[a]	PET–PVA–collagen[b]	PET–PVA–collagen[c]
Absorbed water (g)	0.89	2.08	6.21	4.78
Ev (%/h)	1.16	0.717	0.369	0.384

[a] The PET-*g*-PVAc (18.91%) was hydrolyzed into PET-*g*-PVA with 10% HCl w/w at 100°C for 4 h.
[b] PET-*g*-PVAc (19.68%) was hydrolyzed into PET-*g*-PVA with 10% HCl w/w at 100°C for 4 h. Then, 4% collagen w/w was immobilized with GA.
[c] PET-*g*-PVAc (17.43%) was hydrolyzed into PET-*g*-PVA with 10% HCl w/w at 100°C for 4 h. Then, 1% collagen w/w was immobilized with GA.

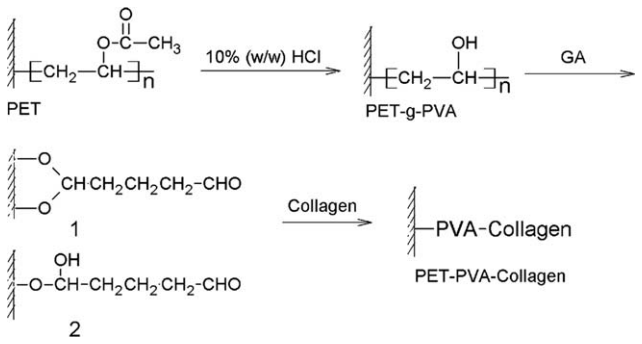

Figure 9. Reaction schemes for the grafting of collagen onto the fiber surface.

collagen was much higher than that of PET and PET-*g*-PVA, whereas Ev was much lower. This demonstrated that the hygroscopicity improved greatly after the collagen was immobilized with GA.

In this study, we used collagen immobilization on the PET surface. It is mainly applied in biomaterials but, because of the hygroscopicity and biocompatibility of collagen and the excellent clothing performance of PET materials, it has enormous potential for underwear in sportswear and outdoor clothing through the previous description.

Chemical Structure, Surface Morphology, and Composition at Different Stages

Vinyl acetate grafted PET fibers were hydrolyzed into PET-*g*-PVA in a 10% HCl solution at 100°C and then soaked in a GA aqueous solution at 60°C for a time. After that, these modified PET fibers were immersed in a collagen solution and subsequently processed. The chemical mechanism in different stages is shown in Figure 9.

Molecular Structure of the Unmodified and Modified PET Fibers. The ATR–FTIR spectra of the ungrafted, grafted, hydrolyzed, and immobilized collagen PET fibers are given in Figure 10, and the chemical structure is demonstrated in Figure 9 at different stages. For PET macromolecules, the absorption peak at 1713 cm^{-1} was related to the ester carbonyl (C═O) stretching vibration [see Figure 10(a)]. Peaks appeared at 2926 and 2853 cm^{-1} corresponding to CH_2 antisymmetric and symmetric stretching vibrations, and peaks at 1245 and 1096 cm^{-1} were due to C—O—C asymmetric stretching vibration and symmetric stretching vibration, respectively. After grafted vinyl acetate, the absorption peak appeared at 1371.71 cm^{-1} [see Figure 10(b)] and corresponded to CH_3 in-plane bending vibration; this was the characteristic peak of CH_3. In the spectra of PET fibers grafted with poly(vinyl acetate) hydrolyzed into PVA, there appeared a characteristic broad band at 3000–3600 cm^{-1} corresponding to OH with the association of the hydrogen bond. The absorption peak corresponded to *v*C—O of PVA appeared at about 1100 cm^{-1}. This overlapped with the absorption peak corresponding to the C—O—C symmetric stretching vibrations of the PET macromolecules, so it was not obvious in Figure 10(c). The spectra of the PET-*g*-PVA fibers with collagen immobilized by GA are given in Figure 10(d). Collagen contains a number of COOH and NH_2 groups, and PVA contains lots of OH groups with formed hydrogen bonds, so the broad and strong absorption peaks appeared at 3200–3600 cm^{-1} and shifted to higher wave numbers. The absorption peaks of *v*C═O and NH_2 plane-bending vibrations for collagen overlapped with the ester groups of the PET macromolecules, so it was not obvious in the spectra. The hydroxyl, carboxyl, and amino groups were hydrophilic groups, so the modified PET fibers had hydrophilic properties. The more hydrophilic groups there were, the greater the hydrophilic properties of the modified PET fibers were.

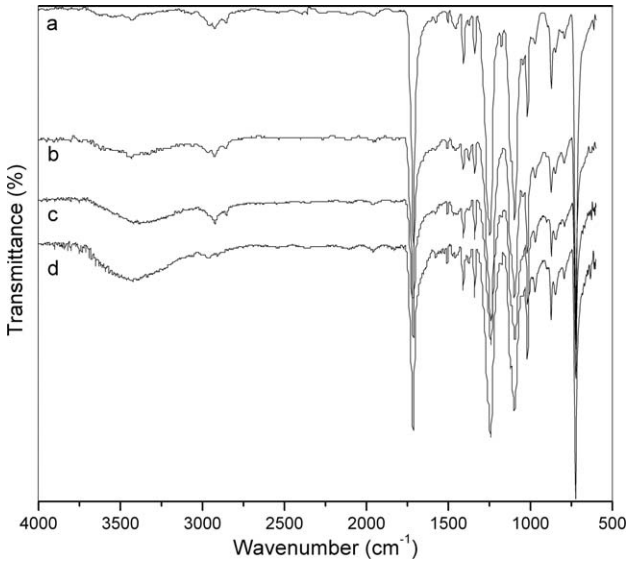

Figure 10. ATR–FTIR spectra of (a) PET, (b) PET-*g*-PVAc (19.68%), (c) PET-*g*-PVA (4 h of hydrolysis), and (d) PET-*g*-collagen.

In addition, the FTIR spectra of the PET fibers grafted vinyl acetate after hydrolysis in a 10% HCl w/v solution are shown in Figure 11. With increasing hydrolysis time, the alcoholysis

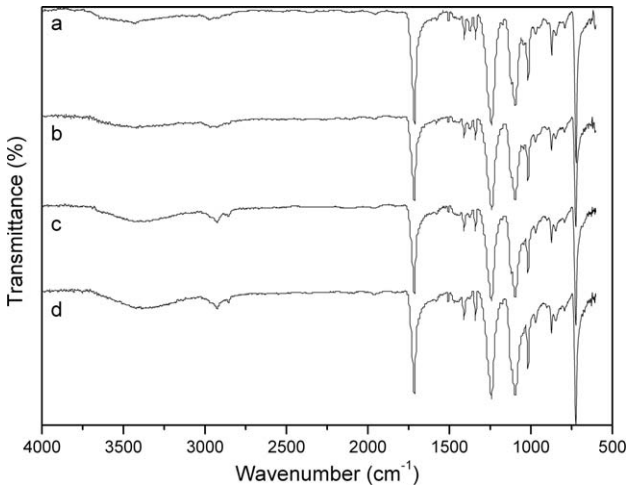

Figure 11. ATR–FTIR spectra of the PET fibers grafted vinyl acetate with different hydrolysis times in 10% HCl w/v solution: (a) 1, (b) 2, (c) 3, and (d) 4 h.

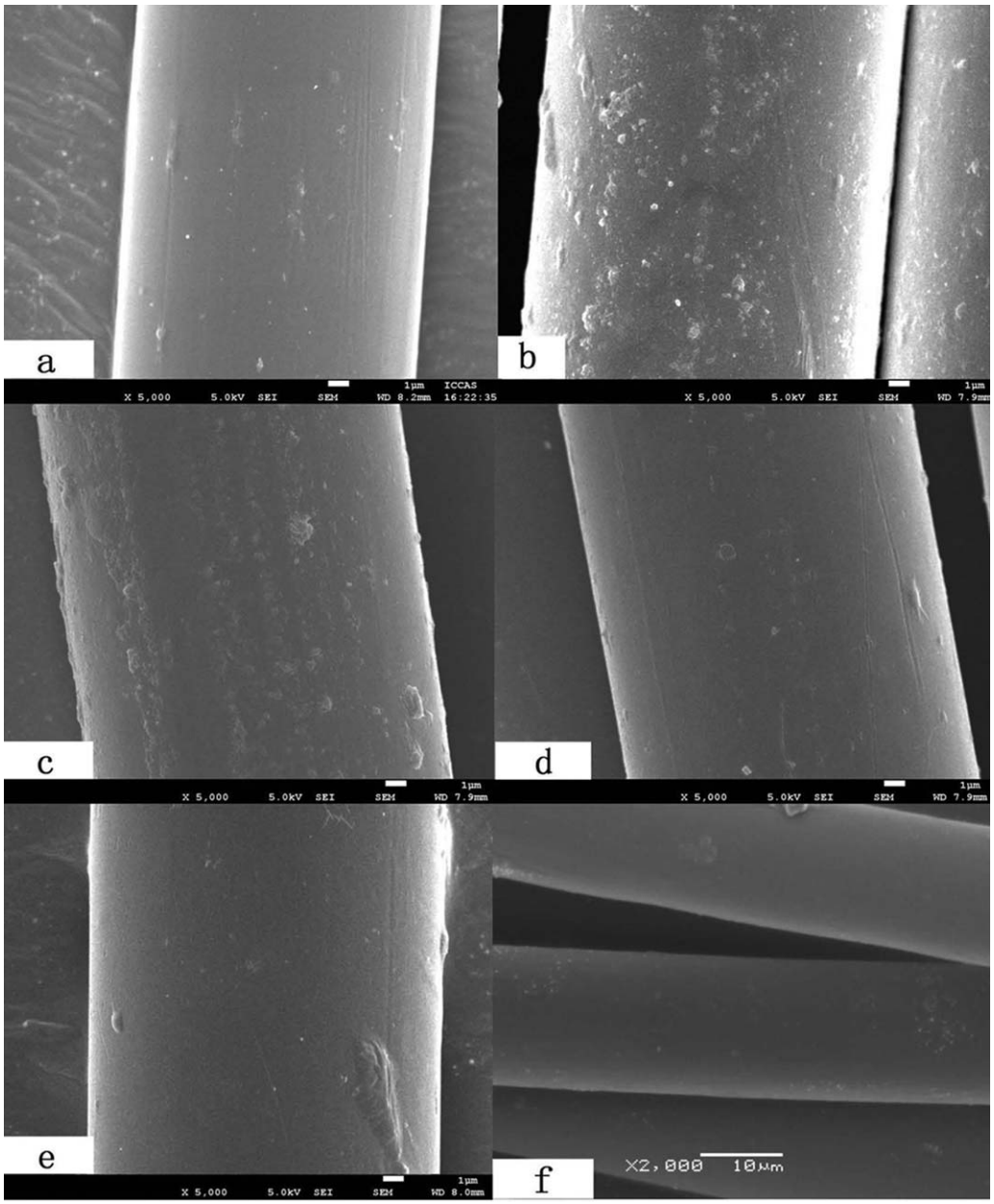

Figure 12. SEM micrographs of the PET fibers: (a) virgin, (b) 12.35% PET-*g*-PVAc, (c) 24.9% PET-*g*-PVAc, (d) 24.9% PET-*g*-PVAc and 2 h of hydrolysis, (e) 24.9% PET-*g*-PVAc and 4 h of hydrolysis, and (f) 24.9% PET-*g*-PVAc and 4 h of hydrolysis with 3% w/w collagen.

degree of the grafted poly(vinyl acetate) increased, and the number of hydroxyl groups increased, so the broad and strong absorption peak appeared at 3200–3600 cm^{-1} because of the association of the hydrogen bond, and the absorption peak intensity increased with a longer hydrolysis time. The moisture regain of the vinyl acetate grafted PET fiber after hydrolysis increased with increasing number of hydroxyl groups. This was consistent with the effect of the hydrolysis time on the moisture regain, as previously mentioned.

Surface Morphology Changes in the PET Fibers at Different Stages. The scanning electron micrographs of various unmodified and modified PET fibers are shown in Figure 12. The virgin PET fiber surface [Figure 12(a)] exhibited a smooth and relatively homogeneous surface. With increasing grafting yield up to 12.35%, the fiber surface got rougher and rougher [Figure 12(b)]. It looked like more and more dots on the surface. When the grafting yield arrived at 24.9%, the grafted side chain seemed to cover the whole PET fiber surface [Figure 12(c)]. The fiber surface of the hydrolyzed PET-*g*-PVA fiber was smooth again and got smoother with longer hydrolysis times. Pictures of the 24.9% grafted PET-*g*-PVA fiber after hydrolysis in a 10% HCl w/v solution at 100°C for 2 and 4 h of hydrolysis are shown in Figure 12(d,e), respectively. This could have been due to the macromolecular

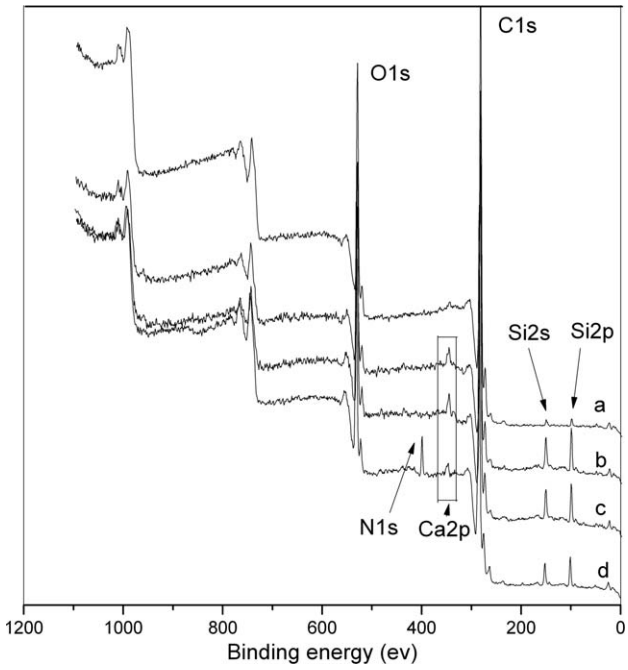

Figure 13. Overview XPS spectra of the (a) virgin PET, (b) 24.9% PET-*g*-PVAc, (c) after the hydrolysis reaction conversion to PET-*g*-PVA with 10% HCl at 100°C for 4 h, and (d) after immobilization with collagen with GA.

rearrangement for PVA. With the hydrogen bonds of the hydroxyl groups, the side chain intermolecular force was large and closely arranged to each other, so the fiber surface was smooth. Compared with the virgin PET fibers, the modified fiber diameters all increased.

The surface of the PET-*g*-PVA immobilized collagen is shown in Figure 12(f). We found that the fiber surface became rough again because the collagen was immobilized on the PET-*g*-PVA fiber with GA.

Surface Composition of the Unmodified and Modified PET Fibers. XPS overview spectra for the virgin PET, PET-*g*-PVAc (24.9%), PET-*g*-PVA, and PET–PVA–collagen are shown in Figure 13. The virgin PET fibers gave C1s, O1s, and Si2p peaks at binding energies of 284.83, 532.29, and 101.77 eV, respectively [Figure 13(a)]. The Si element was introduced with SiO_2 as a matting agent during the spinning process. After grafting with vinyl acetate, a new peak appeared at 347 eV corresponding to Ca2p [Figure 13(b)]; this could be introduced as an impurity during the course of processing the sample. The following hydrolysis conversion to PET-*g*-PVA gave a spectrum similar to that of PET-*g*-PVAc [Figure 13(c)]. After the immobilization of collagen with GA for PET-*g*-PVA, a new peak appeared at 399.9 eV that was assigned to N1s, which shown clearly in Figure 13(d).

The surface elemental composition of the virgin and modified PET fibers, as investigated by XPS, is presented in Table V. For PET-*g*-PVAc, the C/O ratio was lower than that of the virgin PET because of the introduction of vinyl acetate. After hydrolysis conversion to PET-*g*-PVA, the C, O, and Si elemental contents changed a little, but for PET–PVA–collagen, the nitrogen elemental content amounted to 4.28 atom%, and the C/O ratio decreased with the immobilization of collagen on the surface of the PET-*g*-PVA fibers with GA. Because each coupling collagen macromolecule contained a large number of amide bonds, the oxygen and nitrogen elemental contents increased on the modified PET fiber surface layer.

CONCLUSIONS

The collagen was successfully immobilized on the modified PET fibers. First, poly(vinyl acetate) was grafted onto PET by EB irradiation, and then, the grafted products were hydrolyzed into PVA by an HCl solution, and finally, collagen was immobilized onto PET-*g*-PVA. The improvement in the hydrophilicity was determined in terms of moisture regain, wettability, and evaporation ratio measurements. The moisture regain of the virgin PET fibers and the PET-*g*-vinyl acetate was similar and very low, whereas after hydrolysis, the moisture regain increased to more than 1%, depending on the hydrolysis time. The PET–PVA–collagen fabric showed excellent hygroscopic performance in drip diffusion and wicking height before and after multiple washings and had a lower evaporation ratio and Ev than the unmodified PET fibers.

This procedure was simply and new and easily realized. What is more, the collagen on the fibers provided good skin care functions and kept the skin moist. It could be a new valuable material for underwear or medical usage.

Table V. Surface Content of the Elements (Atom %) Obtained by XPS for the Virgin PET, PET-*g*-PVAc (24.9%), PET-*g*-PVA, and PET–PVA–Collagen

Sample	C (atom %)	O (atom %)	Si (atom %)	Ca (atom %)	N (atom %)
Virgin PET	78.39	20.41	1.2		
PET-*g*-PVAc(24.9%)	71.75	19.53	7.61	1.1	
PET-*g*-PVA[a]	71.69	19.14	7.94	1.24	
PET–PVA–collagen[b]	67.22	23.05	4.97	0.48	4.28

[a] The PET-*g*-PVAc (24.9%) was hydrolyzed into PET-*g*-PVA with 10% HCl at 100°C for 4 h.
[b] The PET-*g*-PVA from part a immobilized with 3% w/w collagen (molecular weight = 200–300 kDa) with GA.

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