A Novel Method of Modifying Poly(ethylene terephthalate) Fabric Using Supercritical Carbon Dioxide

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ABSTRACT: For the modification of poly(ethylene terephthalate) (PET) fabric, a type of epoxy compound, glycerol polyglycidyl ether (GPE), was impregnated as a cross-linking agent into PET fabric by means of supercritical carbon dioxide (scCO$_2$), then, a series of immobilization processes were implemented, including the pad-dry-cure process and the solution process to finish the GPE-PET fabric with natural functional agents (sericin, collagen, or chitosan). Chloroform was found to be an effective cosolvent, as evidenced by the mass transfer of GPE to PET during the treatment with scCO$_2$. Chemical analyses by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy showed that GPE can penetrate the surface of the PET fabric in scCO$_2$ pretreatment process, and natural functional agents (sericin, colla-gen, or chitosan) can also be immobilized on the surface of the GPE-PET fabric especially for the method of pad-dry-cure. The nitrogen content in the modified PET fabrics was calculated accurately and confirmed by combustion analysis. The modified PET fabric displayed improvements in surface wettability, moisturization efficiency, and anti-bacterial characteristics against *S. aureus*, which demon-strated that the feasibility of this design for immobilizing natural functional agents (sericin, collagen, or chitosan) onto the surface of the PET fabric. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1897–1907, 2010

Key words: poly(ethylene terephthalate); supercritical carbon dioxide; epoxy compound; impregnation; im-mobilization

INTRODUCTION

In the textile industry, poly(ethylene terephthalate) (PET), has been an important class of fibers ever since it was first created in 1946.[1] Its basic properties satisfy the highest requirements, such as excellent mechanical properties, weather resistance, and so on; moreover, its production cost is low. But then, the PET fabric has also some drawbacks including weak hydrophilicity and poor biocompatibility, because of the lack of active side chain as well as rare active binding on organic backbone. To create cloth in conformity with the health safety require-ments of the living human body, such as somewhat complicated processes are conventionally adopted to add value to PET in textile finishing, involving cospinning,[2] physical coating,[3,4] plasma discharge,[5,6] alkaline treatment,[7,8] graft polymerization,[9,10] etc. Nevertheless, some of these methods have limited practical use, and frequently lead to the hardening of the PET material, elevated production costs, and complicated work procedures. Accordingly, there is a demand for a finishing technology that can be applied to PET fabric more easily and efficiently.

Recently, the use of scCO$_2$ fluid in polymer proc-essing has had a marked effect on dyeing,[11–13] expanding foam,[14] plating,[15] impregnation,[16–18] etc. ScCO$_2$ ($Tc = 31°C$, $Pc = 73.8$ bar) is one of the most commonly used supercritical fluids. It is naturally abundant, chemically inert, nonflammable, essentially nontoxic, easy to handle, and the least expensive sol-vent after water.[19] Moreover, scCO$_2$ is a good solvent for many non-polar (and some polar) low-molecular weight compounds,[20,21] and a few polymers are also known to have good solubility in scCO$_2$;[22] however, it is generally a very poor solvent for high-molecular weight polymers under readily achievable conditions, because of its very low dielectric constant, ε, its low polarizability per volume, α/v, and its reluctance to engage in van der Waals interactions. Although scCO$_2$ is a poor solvent for most polymers, it does have the capability to swell polymers up to several mass percentages;[23,24] thus, a low-molecular weight agent dissolved in scCO$_2$ can diffuse into the polymer phase, achieving the modification of that polymer.[25] The swelling of a polymer occurs only in its

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amorphous phase, and depends on the interaction of the supercritical fluid with the polymer and on the crystallinity of the polymer. The higher the crystallinity, the more difficult it is to swell the polymer.[26] The degree of swelling of the polymeric matrix can be modulated by adjusting the pressure and temperature, and the mass transfer of agents within the polymer can also be controlled in the same way.[27] In addition, a cosolvent participating in scCO$_2$-polymer processing can also increase the solute uptake in polymer, which attributed mainly to the solubility improvement of solute in scCO$_2$.[28]

In the field of polymer fabric modification, sericin,[4,29] collagen,[30] and chitosan[31] are known as top natural functional agents; they have been applied widely to improve the hydrophilicity and biocompatibility of polymer fabric. If these agents can be impregnated into PET fabric, they can impart desirable properties to the PET. However, this is conventionally impossible due to the higher molecular weight of these functional agents. To modify PET fabric with these natural macromolecules, on the basis of use of scCO$_2$ fluid in polymer processing, a type of epoxy compound, glycerol polyglycidyl ether (GPE)[32] is chosen in our present study as a cross-linking agent which will be impregnated into PET fabric with the help of scCO$_2$ to attach functional macromolecules. As far as we know, there are no other conventional techniques which can achieve the same result in impregnation of cross-linking agents into pre-existing polymer without changing their inherent properties but the method of solid-state foaming or swelling with CO$_2$ as a gas blowing agent.[33,14] This project will be a simple, low cost, and environmentally benign process together with a firm penetration of GPE into amorphous region of PET fabric. This epoxy compound is chosen here, because the epoxy group existing at the end of the chain is bared on the surface of the PET fabric and acts as a reactive site for functional nucleophilic reagents, including proteins, polysaccharides, nucleic acids, and various small molecules.[34]

On the basis of the aforementioned considerations, we tried to modify the surface of PET fabric with natural functional agents (sericin, collagen, or chitosan). In this study, the impregnation of GPE into PET fabric was investigated under various supercritical conditions, in pure CO$_2$ as well as in CO$_2$ with a cosolvent, by measuring the mass uptake. The surface immobilization sericin, collagen, or chitosan on GPE-PET fabric was conducted by the solution method and by the pad-dry-cure method.

EXPERIMENTAL

Materials

The fully oriented yarn PET fabric (warp/weft, 78T/216; 90 g/m^2) used as the substrate for modification
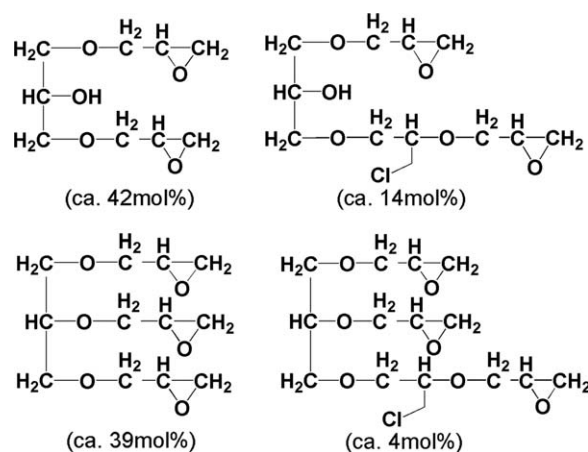
Figure 1 Structural formulas of glycerol polyglycidyl ether (GPE, Denacol EX-313).

in this study was supplied by Toyobo Co., Ltd. First, the PET fabric was washed and stabilized by immersing it in acetone at 30°C for 30 min. The epoxy compound used as a cross-linking agent and impregnated to the PET fabric with the help of scCO$_2$ was glycerol polyglycidyl ether (GPE, Denacol EX-313, Mw: ca. 250), which was supplied by Nagase Chemtex Co. without further purification; its main components have the structural formulas shown in Figure 1. Three natural functional regents, sericin (SERICIN POWDER, Mw: ca. 17,000), collagen (MARINE COLLAGEN CF, Mw: ca. 1,000), and chitosan (low molecular weight) were used as hydrophilic agents together with antimicrobial material for immobilization onto the surface of the PET fabric; the former two were supplied by Seiren Co., Ltd. and Chisso Co., Ltd., respectively, and the third was purchased from Sigma-Aldrich, Inc. Sodium hydroxide (NaOH) and sodium tetraborate decahydrate (Na$_2$B$_4$O$_7$ 10H$_2$O), used for modulating the pH of the functional solutions, were purchased from Nacalai Tesque, Inc. All the functional reagent solutions were prepared with distilled deionized water. The carbon dioxide gas used in all of the experiments was purchased from Uno Sanso Co., Ltd. (99.5% pure). Several organic solvents (acetone, ethyl acetate, chloroform and isopropyl alcohol) were guaranteed-grade reagents obtained from Wako Pure Chemical Industries, Ltd.

Methods

The whole process of PET fabric treatment, including the impregnation of the cross-linking agents and surface immobilization of the functional agents, is shown schematically in Figure 2. The details of each sub-process are described later.
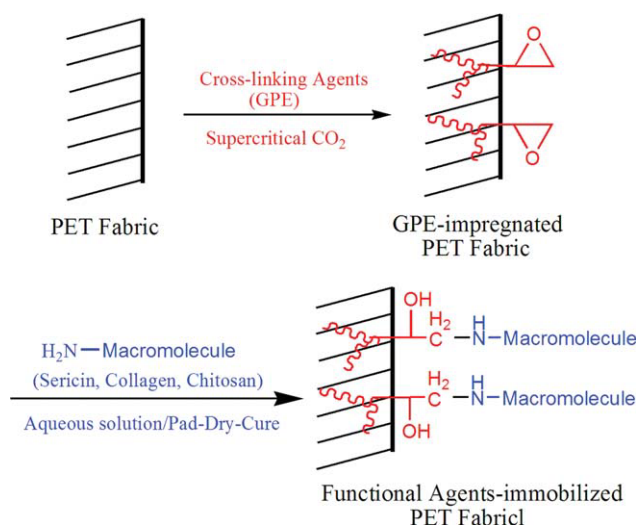
Figure 2 Schematic illustration of the entire process of PET fabric modification. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

Impregnation of the cross-linking agent GPE into PET fabric by means of scCO$_2$

The apparatus for the preparation of the GPE-PET composite consisted of a 50-mL stainless steel vessel ($T_{max} = 200°C$, $P_{max} = 30$ MPa), a magnetic stirrer, a constant-temperature air bath (Model SCF-Sro, JASCO Co., Tokyo), a thermocouple and a pressure gauge. It is a batch system operating in three main steps: charge, impregnation, and discharge. CO$_2$ is stored in a cylinder and pressurized to working pressure by a pump. The PET fabric substrate (10 cm × 12 cm, ca. 1.10 g) was suspended on a stainless steel net inside the vessel, and the cross-linking agent (0.20 g) was placed on the bottom of the vessel. The quantity of cross-linking agent was in large excess of the amount required to saturate the CO$_2$ during the entire course of impregnation into the PET fabric. When the autoclave reached the desired temperature, CO$_2$ was let in slowly (ca. 5 mL/min) and isothermally compressed to working pressure; then, the system was agitated for a certain period of time to impregnate the GPE into the PET fabric. After the impregnation, the system was depressurized at 0.5 MPa min^{-1} and allowed to cool to room temperature in air. The same experiment was performed using a batch program with the addition to CO$_2$ of 4% modifier, (acetone, ethyl acetate, or chloroform). Then, the sample was flushed with air and washed with distilled deionized water at room temperature to remove the cross-linking agent adhered on the surface. Finally, the impregnated sample was dried in an oven at 50°C.

Immobilization of natural functional agents onto GPE-PET and original PET fabrics

The immobilization of natural functional agents onto GPE-PET fabric was performed in two ways: processing in an aqueous solution and processing by the pad-dry-cure method. The mechanism of immobilization relies on the GPE epoxy compound, which can cross-link the functional agents and fabric by the ring-opening reaction of the epoxy groups. In addition, the original PET fabric was also treated with the two methods to anchor functional agents.

Processing in an aqueous solution

For the immobilization of sericin or collagen, 3 wt % finishing solutions were prepared and the pH of the solutions was adjusted to 10–11 with Na$_2$B$_4$O$_7$10H$_2$O so that the amines became unprotonated.[32,34] Then, the sample was immersed in sericin or collagen solution and shaken for 1 week at room temperature. It has been reported that dermal sheep collagen can be cross-linked by epoxy compound at mild condition for a long time.[35] In the case of chitosan, it was first added to a 30 wt % NaOH aqueous solution, stirred for 2 h and placed in a refrigerator; the lyophilized mixture was then thawed and filtered with isopropyl alcohol to prepare the chitosan solution.[36] Then, the sample was immersed in the solution under stirring for 16 h at 50°C. At the end of the immobilization, the samples were taken out, squeezed and air dried. The finished fabric samples were then rinsed with water and finally dried again at 50°C in vacuum and conditioned before testing.

The pad-dry-cure treatment

Padding is a well-known technique for treating textile materials. The textile is padded into a chemical solution, followed by a squeezing using two pad rolls to remove the excess liquid trapped in the textile. The finishing solutions were prepared as mentioned earlier in Section of "Processing in an Aqueous Solution." The amount of functional agent (sericin, collagen or chitosan) in the solution was in large excess of the cross-linking agent on the surface of the PET fabric. The fabric samples were padded by the two-dip-two-nip process to about 90% wet pickup with freshly prepared aqueous solutions of each of these functional agents. After treatment, the padded fabrics were dried at 85°C for 3 min, cured at 150°C for 3 min, washed thoroughly, and finally dried.

Characterizations

Gravimetric analysis

The absorption of the cross-linking agent into the PET fabric using supercritical CO$_2$ was determined

gravimetrically and is expressed as a percentage of impregnation, according to eq. (1):

$$G_{impregnation}(\%) = (P_1 - P_0)/P_0 \times 100 \qquad (1)$$

where P_0 and P_1 are the weight (g) of untreated PET fabric and impregnated PET fabric, respectively. The immobilization ratio of functional agents onto GPE-PET fabric is defined by eq. (2):

$$G_{immobilization}(\%) = (P_2 - P_1)/P_1 \times 100 \qquad (2)$$

where P_2 represents the weight of the GPE-PET fabric finished with the functional agent.

XPS analysis

Analysis was performed using a photoelectron spectrometer (JPS-9010MCY) with Mg Kα excitation radiation (1,253.6 eV). The X-ray source was run at a potential of 10 kV, a current of 10 mA and an incident angle of 45°. The pressure within the XPS chamber was maintained at 10^{-7} Pa during the measurement. The binding energy of carbon 1s was fixed to 285 eV and used as the internal reference for the binding energy scale. The depth profiling of the samples was performed with argon ion sputtering (1 kV, 8 mA) at an incident angle of 90° for 15 s. Deconvolution analysis of the peaks was carried out using the Gaussian-Lorentzian component profile in the Peakfit software.

Fourier transform infrared (FTIR) analysis

The FTIR spectrum of the cross-linking agents GPE was obtained using a Fourier transform infrared spectroscopy instrument (FTIR-4100, JASCO), by the usual method of making pellets (ca.0.5% w/w) with potassium bromide (KBr), where a total of 32 scans were accumulated at a resolution of 4 cm^{-1}. All spectra of the fabrics were collected at a resolution of 4 cm^{-1} and 200 scans using the same instrument with a 45° ZnSe prism (n = 5) as the internal reflection element wafer set in a single ATR accessory.

Nitrogen content (%N) measurement

Elemental analysis of the functional agents (sericin, collagen or chitosan) and several types of PET fabrics was carried out to precisely determine the amount of nitrogen, the analysis was carried out on an EA 1110-W spectrometer using the classical technique of combustion analysis. In this technique, the sample is burned in an excess of oxygen, and various traps collect the combustion products—carbon dioxide, water, and nitric oxide. The weights of these combustion products can be used to calculate the composition of the sample. Before measurement,

each sample was ground to a crumb and dried at 100°C for 24 h, after which it was analyzed to measure the organic content.

Water contact angle measurement

Dynamic water contact angle used to evaluate surface wettability of the PET fabric was measured in a temperature and humidity controlled room (20°C, 65%) by the sessile droplet method using a contact angle measuring instrument easydrop (RÜSS DSA20). A distilled water droplet of 3 μL was placed on the sample surface and a picture of the droplet was taken within 5 s. A new water droplet of 3 μL was added to the sample surface every 15 s, and the procedure was repeated 5 times (total 18μL) for each advancing step. Then 3-μL water was retracted every 15 s for each receding step. The receding procedure was stopped until the surface water droplet disappeared in camera image.

Moisture measurement

The moisturization of the PET fabric was measured in a humidity chamber (IH400, Yamato) in which a weight meter was installed. For the measurement of hygroscopicity/dehygroscopicity on several PET fabrics, the sample was weighed for a random period of time under two environmental conditions (25°C, 65% RH; 30°C, 95% RH). Moisture regain is defined by eq. (3), in which W_m is the weight (g) of the moisturized sample and W_d is the weight (g) of the sample dried in an oven (100°C, 2 h):

$$Moisture\ regain(\%) = (W_m - W_d)/W_d \times 100 \qquad (3)$$

Antimicrobial measurement

The antimicrobial assessment of the PET fabric was made through the quantitative method of microbe absorption proposed by the Japan Spinners Inspection Foundation. The microbe used here was *Staphylococcus aureus (S. aureus)*, a Gram-positive bacterium, which usually exists in human nose or skin and often causes an infection on the skin as lesions, pimples or boils, even brings pneumonia if the infection got worse. All of the samples were incubated for 18 h at 37°C before the bacterial colonies were counted. The antimicrobial effects of the specimens are evaluated, as a rule, based on the bacteriostatic and bactericidal activities. The bacteriostatic and bactericidal activities were calculated as follows:

$$Bactericidal\ activity = \log A - \log C$$
$$Bacteriostatic\ activity = \log B - \log C$$

where A, B, and C are the number of bacteria in the initial inoculation, the number of colonies on an
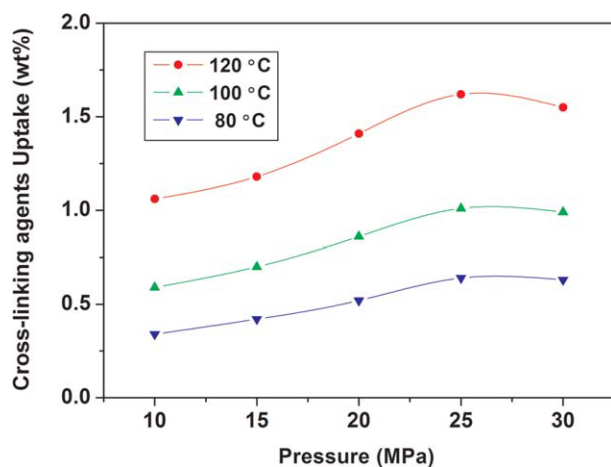
Figure 3 Impregnation of GPE into PET fabric for 2 h in pure $scCO_2$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

incubated piece of control calico, and the number of survivors on the untreated and the modified PET fabrics after incubation, respectively.

RESULTS AND DISCUSSION

Supercritical treatment of PET fabric

$ScCO_2$ can swell PET fiber, and the temperature usually has to reach 80°C in order to exceed the T_g of PET.[23] $ScCO_2$ can also dissolve a wide range of compounds, including epoxy compounds.[37] Here, the solubility of the cross-linking agent GPE in $scCO_2$ was evaluated by using a stainless steel vessel with transparent windows. In the experimental conditions of this study, the fluid had optical uniformity in pure $scCO_2$, but it became clearer in the presence of a cosolvent such as acetone, ethyl acetate, or chloroform. This indicates that these cosolvents can enhance the solubility of GPE in $scCO_2$. The reason why small amounts (typically <5%) of a polar cosolvent as a modifier added to $scCO_2$ increases the solvating power of CO_2 is that the affinity between the solute and CO_2 is improved.[37,38]

To optimize the process of impregnation in the case of pure $scCO_2$, a study on the absorption of the cross-linking agent by the PET fabric at different temperatures (80, 100, and 120°C) and pressures (10–30 MPa) was carried out. It has been reported that the conventional dyeing time for PET fiber in $scCO_2$ is 30–120 min.[11,12] With regard to the swelling of

PET fiber in CO_2, Hirogaki et al.[24] have described that the swelling behavior reached a maximum after 2 h. Therewith, a time period of 2 h was adopted here to impregnate the PET fabric with cross-linking agents in $scCO_2$. Figure 3 shows the influence of pressure on the uptake of the cross-linking agent by the fabric at the three temperatures.

The results show that the uptake of the cross-linking agent by the PET fabric increased initially as the pressure increased up to 25 MPa, but fell at pressures higher than 25 MPa, particularly at higher temperatures. Similar results were obtained when using $scCO_2$ with chloroform as the modifier. The main reason may be for this explanation. First, at higher pressures CO_2 readily swells PET; however, it is also a much better solvent for cross-linking agents, and the partitioning of GPE in the fluid phase is enhanced. This tendency was reinforced at higher temperatures considered as the cause of the decreased fluid density.

In addition, we found that the equilibrium concentration in the fabric is much more sensitive to temperature than to pressure, and that is more profitable to implement the process at a higher temperature. The temperature influences the uptake of the cross-linking agent because it affects the polymer matrix. Above the temperature of the glass transition, the free volume of the polymeric matrix and the chain mobility is increased, and this results in a higher PET saturation concentration. Nevertheless, at higher temperatures, certain accession reactions, including the self-polymerization of the epoxy groups,[39] the formation of styrene carbonate,[40] and the carboxylic-acid end-group modification of PET with the epoxy groups may occur.[26] Thus, the maximum temperature for controlled $scCO_2$ treatment was set at 120°C in this study.

To increase the content of the cross-linking agent absorbed by the PET fabric in $scCO_2$, three cosolvents (4% mol/mol), acetone, ethyl acetate and chloroform, were added to CO_2 for impregnation, respectively, at 120°C and 25 MPa for 2 h. Although alcohols are good modifiers which can enhance the swelling of PET fiber in $scCO_2$,[24] they cannot be used because epoxy compounds react with alcohols. The results for the uptake of the cross-linking agent in supercritical CO_2 with a cosolvent are shown in Table I.

In contrast with the sorption of the cross-linking agent into PET fabric treated with pure $scCO_2$, the

TABLE I
Mass Uptake of the Cross-Linking Agent by the PET Fabric in Supercritical Fluid at 120°C, 25 MPa for 2 h

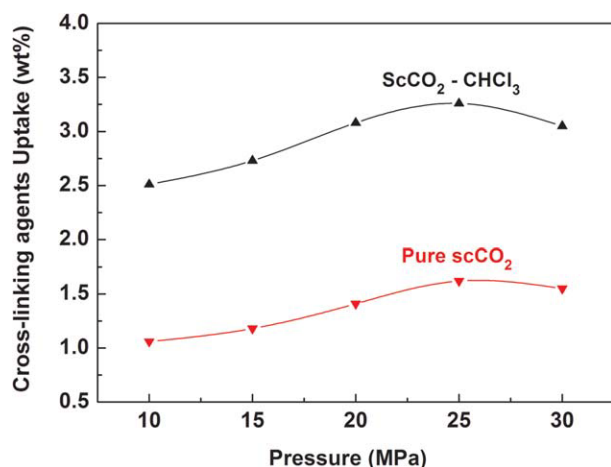| Solvent	Pure CO_2	CO_2-acetone	CO_2-ethyl acetate	CO_2-chloroform
Mass uptake (wt %)	1.62	2.14	2.47	3.26

Figure 4 Comparison of the uptake of the cross-linking agents by the PET fabric in pure scCO$_2$ and scCO$_2$-CHCl$_3$ (4% mol/mol) at 120°C for 2 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sorption increased when the cosolvent entered the supercritical fluid. Chloroform was found to be more effective than the other two cosolvents examined, owing to its lower dielectric constant. The uptake of the cross-linking agent by PET as a function of pressure was also compared in scCO$_2$ with and without CHCl$_3$ at 120°C. The data are shown in Figure 4; the results were similar, but the uptake tended to decline more strongly in the presence of chloroform than in pure CO$_2$ after 25 MPa. This is considered that chloroform enhanced the solubility of GPE in fluid phase more significantly with pressure at the higher pressure. Another reason may be based on H-bonding interactions between the cross-linking agents and the polymer matrix.[41] While more cross-linking agents penetrated into PET with scCO$_2$-CHCl$_3$ at higher pressure, H-bonding may form by the OH-functional group of GPE with the carbonyl group in PET matrix, this bond will introduce more hindrance in polymer matrix, and thus slow down any further diffusion of GPE into PET fabric. Although the uptake of GPE into PET decreased at higher pressure, the incorporation of GPE into the PET fabric was almost twice the value in pure scCO$_2$ for the solubility improvement of GPE or the enhancement on swelling ability of PET in scCO$_2$-CHCl$_3$.

Information concerning the manner in which the cross-linking agent was impregnated into the PET polymer with the scCO$_2$-CHCl$_3$ treatment can be obtained from the XPS signals shown in Figure 5. It can be seen that the XPS spectrum of original PET mainly contains carbon (C) 1s and oxygen (O) 1s peaks. After the scCO$_2$-CHCl$_3$ treatment of PET fabric with GPE, new peaks appeared at 199.8 eV and 269 eV, which were attributed to chlorine (Cl) (2p

and 2s) electrons, regardless of the implementation of argon (Ar) ion etching. These results suggest that the cross-linking agent (at least the chlorine-containing compounds) was impregnated into the PET fabric by scCO$_2$. After Ar ion etching of GPE-impregnated PET, the content of C1s increased markedly and the peak of O1s decreased in height, indicating that the depth profiling of PET removed its surface contaminants (hydrocarbon) and oxides at the same time. It was also noted that the surface N1s peak disappeared completely.

To analyze the surface of original PET and GPE-PET fabric, deconvolution analysis of the C1s peak in the XPS spectra was carried out, as shown in Figure 6. The C1s signal of original PET contained three separate peaks at 284.9 eV, 286.6 eV, and 288.7 eV, which were assigned to the functional groups of C—C, C—O and O—C=O, respectively. In the XPS signal of GPE-PET [Fig. 6(b)], a fourth peak appeared around 286.3 eV, attributable to the epoxy carbon atoms. Moreover, an increase of the C—O band peaking at 286.6 eV was observed relative to the spectra for the original PET fabric. These data further confirm that the cross-linking agent was impregnated into the PET fabric by means of scCO$_2$.

The FTIR spectra of the cross-linking agent GPE, original PET fabric, and PET fabric GPE-impregnated scCO$_2$-CHCl$_3$ are shown in Figure 7. Compared with the original PET spectrum, in the GPE-PET spectrum, a prominent epoxy ring signal occurred at 847 cm^{-1}, and the intensity of 2900 cm^{-1} attributed to the —CH$_2$ stretching increased clearly, which was caused by the GPE moieties bared on the surface of PET; furthermore, a new band at a higher frequency (3400 cm^{-1}) was discernable, which suggests that a weaker hydrogen-bonding interaction occurred in O—H···O—H due to the increase in the

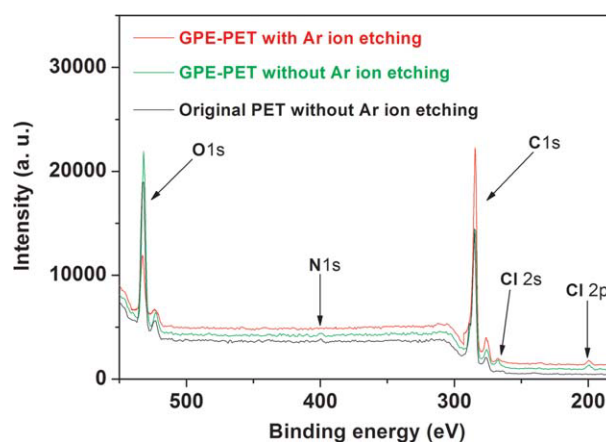**Figure 5** Changes in the surface elements on PET substrate and GPE-PET fabric obtained in scCO$_2$-CHCl$_3$ with/without argon ion sputtering. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
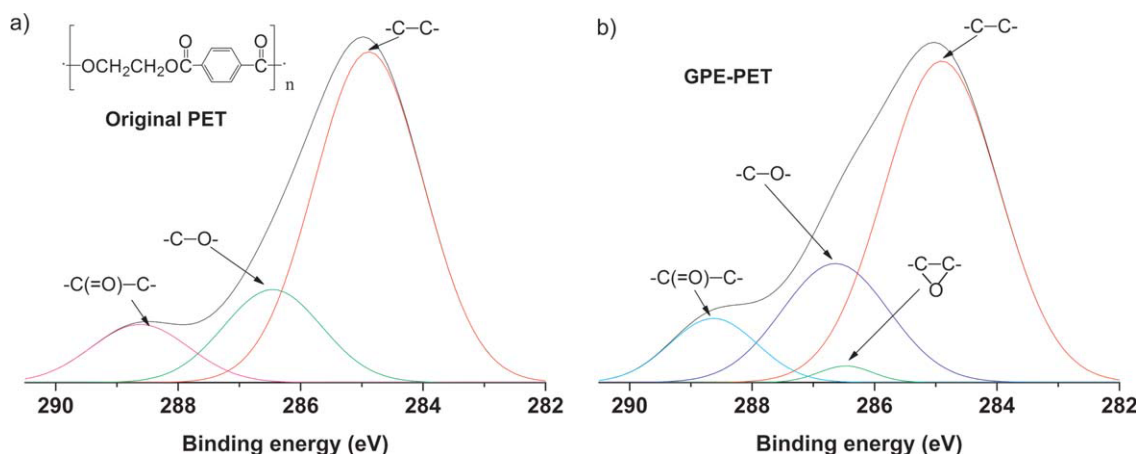
Figure 6 Deconvolution of the C1s peak in the XPS spectra of PET recorded for (a) Original PET fabric and (b) GPE-PET fabric obtained in scCO$_2$-CHCl$_3$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

number of hydroxyl groups in GPE. Also, the area ratio of C=O band to C—C—O band was observed to be different from the spectrum of original PET to GPE-PET owing to the influence of C—O band of GPE.

It was found that the XPS and FTIR spectra of the PET fabric GPE-impregnated with pure scCO$_2$ (spectrum not shown) were analogous with the spectrum of PET fabric GPE-impregnated with scCO$_2$-CHCl$_3$, except that the intensity of some bands decreased markedly. This implies that few GPE molecules penetrated the surface of the PET fabric, leading to the small impregnated amount.

Immobilization of functional agents (sericin, collagen, or chitosan) onto GPE-PET and original PET fabrics

Samples of GPE-impregnated PET fabric in pure scCO$_2$ and in scCO$_2$-CHCl$_3$ were treated for the immobilization of functional agents. The results of the immobilization of the three functional agents onto GPE-PET fabric obtained in scCO$_2$-CHCl$_3$ are shown in Table II. From the data, it was concluded that the pad-dry-cure method gives a higher yield than treatment in an aqueous solution. This indicates that high temperatures, like nucleophilic reagents, can induce the ring-opening of the epoxy groups. Moreover, the low amount of immobilization in the aqueous solutions might be due to the unstable contact of the functional agents with the GPE-PET fabric. Collagen was immobilized onto GPE-PET fabric to a higher degree than the cases of sericin and chitosan, which can be explained for the high-molecular weight reactant such as chitosan or sericin, the low-molecular weight collagen had predominance to access the epoxy ring bared on the surface of the PET fabric. Regardless of the immobilization

method, i.e., aqueous solution versus pad-dry-cure, there was a small increase of weight, less than 0.30%, in the GPE-PET fabric obtained in pure scCO$_2$. About the immobilization of functional agents to the original PET fabric, it was unsuccessful in either immobilization method, owing to the changeless weight of fabric once the treated sample was washed by water. Thus, the GPE-PET fabric obtained in scCO$_2$-CHCl$_3$ fluids was elected as the optimal object for immobilizing functional agents, the pad-dry-cure treatment was also considered as a better immobilization method to finish GPE-PET fabric with functional agents.

GPE-PET fabrics modified with the three functional agents by the pad-dry-cure method were further investigated by XPS spectral analysis, and wide scan spectra for the identification of the elements on
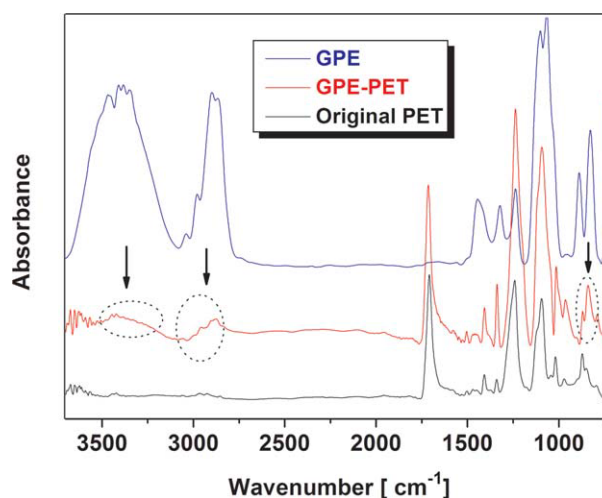

Figure 7 FTIR spectra of the cross-linking agents GPE, original PET fabric, and PET fabric GPE-impregnated in scCO$_2$-CHCl$_3$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Amounts of Functional Agent Immobilized onto GPE-PET Fabric and Nitrogen
Contents of GPE-PET Fabric Finished with Functional Agents

Functional agent	Finishing processes	Immobilization amount (wt%)	Nitrogen content (%)
Sericin N(%):21.1997	Aqueous solution	0.18	0.0365
	Pad-dry-cure	0.83	0.1739
Collagen N(%):22.7477	Aqueous solution	0.22	0.0474
	Pad-dry-cure	1.24	0.2791
Chitosan N(%):10.7254	Aqueous solution	0.15	0
	Pad-dry-cure	0.78	0.0818

the PET surface are presented in Figure 8. In contrast with the spectra of GPE-PET and original PET, there is an obvious N1s peak at 399.5 eV in the spectrum of GPE-PET fabric modified with each functional agent. This is a convincing qualitative argument that the functional agents were immobilized on the surface of the GPE-PET fabric. The order of intensity of the N1s signal was as follows: collagen-GPE-PET > sericin-GPE-PET > chitosan-GPE-PET; however, the element content obtained from the peak ratio did not mean the essential value of nitrogen in the fabric because the measurement belongs to surface analysis. To precisely calculate the effect, the nitrogen contents of all the materials were measured by combustion analysis instead of XPS analysis. The values of N (%) are shown in Table II; the quantitative order of nitrogen in the PET fabrics modified with the three functional agents by the combustion method accorded with the intensity order of N1s in the XPS spectra. The three measured values were almost consistent with the values calculated from the immobilization amounts and nitrogen contents of the functional agents (sericin, collagen and chitosan), except when chitosan solution was used for finishing the GPE-PET fabric. In Figure 8, corresponding to the spectra of GPE-impregnated PET,
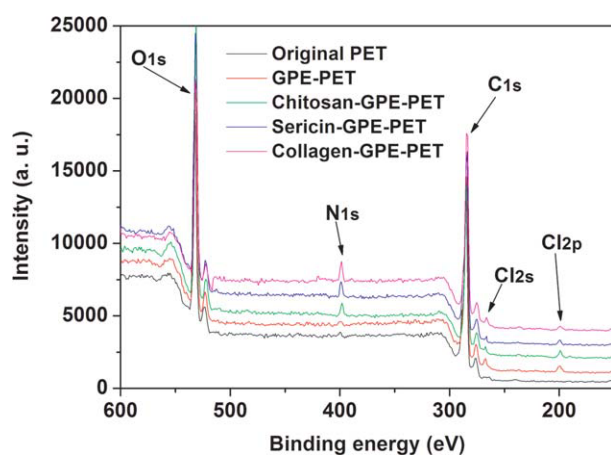
we also found that the peak heights of Cl2p and Cl2s decreased in the spectra of the three functional PET fabrics. This was probably due to the fact that the chloride on the GPE-PET surface participated in the reaction with the functional agents.

The same kinds of samples were also evaluated by FTIR/ATR spectral analysis to investigate the reaction circumstances of the epoxy groups; unfortunately, the three spectra for sericin-GPE-PET, collagen-GPE-PET, and chitosan-GPE-PET were indiscernible in this respect, despite the different structures and spectra of these functional agents (sericin, collagen, and chitosan). It was considered that the typical band of each functional agent overlapped with the band of the PET substrate because of the small immobilization amounts. Figure 9 shows, for comparison, the FTIR/ATR spectra of GPE-PET and sericin-immobilized GPE-PET treated by the pad-dry-cure method. A shoulder band occurred at 3300 cm^{-1} in the sericin-GPE-PET spectrum, which is characteristic of the amide unit, despite the fact that the deformation of amide did not appear clearly at 1654 and 1544 $cm^{-1.}$ At the same time, a remarkable decrease of the bands at 845 cm^{-1} was observed, indicating that the epoxy

Figure 8 Comparison of the surface chemical elements based on the XPS spectra of the PET fabrics. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
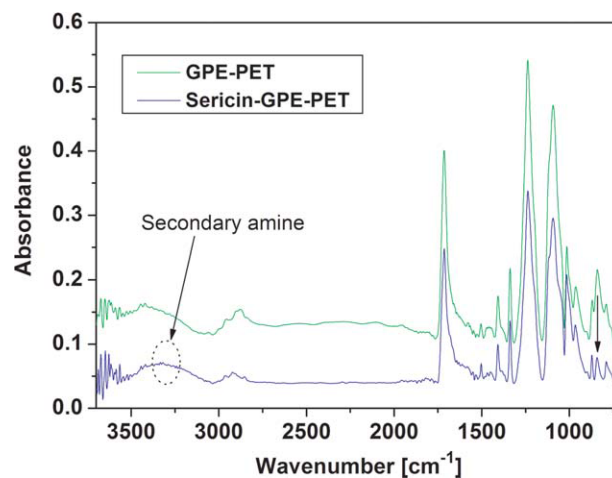

Figure 9 Comparison of the FTIR/ATR spectra of GPE-PET and sericin-immobilized GPE-PET fabric. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Water Dynamic Contact Angle and Retracted Volume of Water Obtained for Original and Several Modified PET Fabrics

Samples	Advancing angle (°) θ_A	Receding angle (°) θ_R	Retracted volume (µL)
Original PET	92.9 ± 1	62.8 ± 0.5	16.2
GPE-PET	73.7 ± 2	31.7 ± 1	13.2
Chitosan-GPE-PET	76.9 ± 3	37.0 ± 1	13.8
Sericin-GPE-PET	80.5 ± 3	41.5 ± 1	14.2
Collagen-GPE-PET	84.3 ± 4	47.2 ± 2	15.0

groups bared on the surface of the PET fabric were ring-opened mostly by sericin.

Surface wettability and moisture regain of the original and the modified PET fabrics

The surface wettability of dissimilar PET fabrics was evaluated by the contact angle of water on the fabric surface. For a sample of nonideal surface such as a tissue or fabric, static water contact angle always change with the contact time, which is accounted for surface roughness, surface heterogeneity, penetration of liquid into the surface region etc. Dynamic contact angle describe the processes at the liquid/solid boundary during the increase in volume (advancing angle) or decrease in volume (receding angle) of the drop, i.e., during the wetting and dewetting processes. Thus, dynamic water contact angle was tested as a replace of static measurement for the advancing contact angle can average negative effect of static contact angle on the surface heterogeneity and the receding angle can make statements about the penetration of water or the roughness of solid sample.

The mean values of water contact angles and the retracted volume of water obtained for several modified PET fabrics and original PET fabric are presented in Table III. The samples of functional agent immobilized GPE-PET fabrics for measurement here were the GPE-PET fabrics processed with the pad-dry-cure method. It can be seen that, compared with the original PET fabric, both of the θ_A and θ_R of the modified PET fabrics were decreased, and the decrease of θ_R was more great than that of θ_A. Therefore, modification degree impacted θ_A slightly and impacted θ_R greatly. The decrease in both of θ_A and θ_R of the modified PET fabrics disclosed the improvement in hydrophilicity of these fabrics, which is mainly deduced that polar functional groups (O─C─O and OH) of cross-linking agents and functional agents interact with water and the interaction contributes to the decrease of the interfacial free energy of the fabric surface. The value of receding contact angle basically reflected surface characterization of polymer reconstruction in water. While the droplet was retracted in the receding step,

surface restructuring minimize the interfacial free energy in water,[42] polar groups of modifiers can be isolated on the surface and θ_R is decreased greatly resulting in great surface wettability improvement. Moreover, the decrease of θ_R here is also affected by the water imbibition mostly. The water imbibition effect is educed by the retracted volume of water as the value (18 µL retracted volume). It can be noted that the GPE-PET fabric held the strongest water imbibition abilities owing to the least volume of retractile water. The desirable effects were not achieved because GPE-PET fabric on which functional agents were immobilized showed some hydrophobicity, unlike simple GPE-PET fabric. This might be due to hardening caused by the reaction between the epoxy groups of GPE and the amine groups of the functional agents. The wettability of the PET fabrics increased in the following order: Original PET < collagen-GPE-PET < sericin-GPE-PET < chitosan-GPE-PET < GPE-PET.

Chitosan-GPE-PET showed better wettability than sericin-GPE-PET and collagen-GPE-PET may be the reason fewer amine groups participated in the reaction with the epoxide in chitosan, as compared with sericin or collagen. The fact that sericin-GPE-PET gave better wettability than collagen-GPE-PET was attributed to the higher molecular weight of sericin than that of collagen, which lessened the reaction opportunity of the amine with epoxide. Another possible explanation of these results may be functional agents immobilized into the PET mesh restrained the penetration of water. The more immobilization quantity, the more difficult is the water penetration.

The moisture-retaining property is another important issue in the study of hydrophilicity of a fabric. A hygroscopicity/dehygroscopicity experiment was performed to evaluate the moisture-retaining property of the same kinds of PET samples measured on wettability. Figure 10 shows the changes in moisture regain of the PET fabrics from the hygroscopicity to dehygroscopicity phase. During the entire course of the experiment, hygroscopic equilibrium was reached after 40 min without reference to any phase at (25°C, 65% RH) or (30°C, 95% RH), but, the dehygroscopic behavior went on for close to 2 h. By contrast with the original PET fabric, the modified PET fabric became hygroscopic quickly and dehygroscopic slowly. Furthermore, the moisture regains of these PET samples maintained the same order as the water contact angles in wettability measurement with sessile droplet method.

The samples of functional agents immobilized onto GPE-PET fabrics in aqueous solution were also measured on water contact angle and moisture-retaining properties. Although the samples exhibited goodish hydrophilicities in two aspects, the effect is
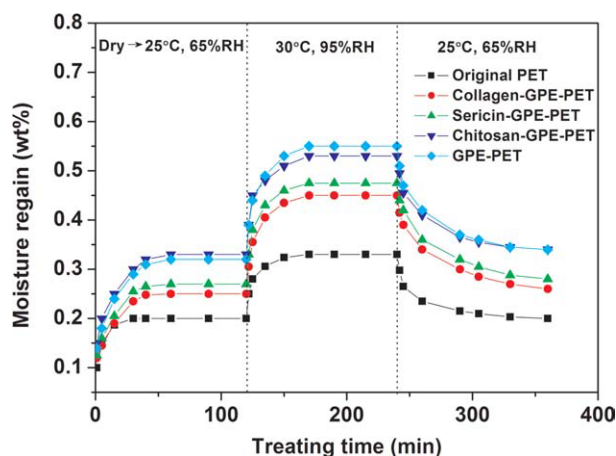
Figure 10 Changes in hygroscopicity and dehygroscopicity with the change in the environmental conditions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

not appreciated because these data were almost similar with that of GPE-PET. As viewed from lesser immobilization quantities by this method, this came down to the cause that GPE bared on the surface of PET fabric only a little participated in reaction with functional agents in solution.

Antibacterial efficiency of the untreated and the modified PET fabrics

In the experiment for microbial absorption, a log (B/A) value of ≥ 1.5 was considered necessary to claim antibacterial activity due to the intrinsic variability of the antibacterial test results. In order for a sample to be considered to have antibacterial activity, the value of the bacteriostatic activity should be over 2.0, and the value of the bactericidal activity should over 0.0. Here, the number of *Staphylococcus aureus* bacteria at the initial inoculation was $A = 2.1 \times 10^4$, and the number of colonies of *S. aureus* on an inoculated piece of control calico was $B = 8.3 \times 10^6$. Table IV lists the data for the antibacterial effect of the PET fabrics against *S. aureus*. The results show that the original PET fabric had no effect against *S. aureus*, which is in agreement with the current literature. The GPE-impregnated PET fabric showed some

inhibition of the growth of *S. aureus*, although it could not kill the bacterial cells. The number of viable cells decreased after they were inoculated on GPE-PET fabrics on which sericin, collagen or chitosan had been immobilized, which indicates that these functional modified PET fabrics killed bacterial cells at a high rate and had a high antibacterial activity.

According to the immobilization amounts of sericin, collagen or chitosan on GPE-PET fabric listed in Table II, collagen-GPE-PET containing higher immobilization amounts of collagen did not show higher antibacterial values than the other two fabrics. This implies that the antibacterial efficiency of collagen is naturally lower than that of sericin or chitosan.

The antibacterial test was also performed with GPE-PET fabrics on which functional agents were immobilized in an aqueous solution, but no antibacterial effects against *S. aureus* were found. It was considered that the immobilization amounts of functional agents onto GPE-PET fabric were too few to kill the bacterial cell. This demonstrates that the pad-dry-cure method is more effective than the solution method for the immobilization of the functional agent (sericin, collagen or chitosan) onto the surface of GPE-impregnated PET fabric again.

CONCLUSIONS

The results obtained show that the method of impregnating a cross-linking agent by means of scCO$_2$ can be used to prepare intermediate PET fabric on which various functional agents can be immobilized. The scCO$_2$ technique is a powerful method of modifying fibers. The scCO$_2$ process can not only swell the polymer but also impregnate finishing agents or cross-linking agents into the polymer under controlled temperature and pressure conditions and in the presence of cosolvents. In the process of impregnation of an epoxy cross-linking agent into PET fabric, a good cosolvent proved to be chloroform, which greatly boosted the uptake of GPE into the PET fabric in scCO$_2$.

Two methods of immobilizing functional agents onto GPE-impregnated PET fabrics were compared,

TABLE IV
Antibacterial Activities of the Original and the Modified PET Fabrics Against *S. aureus*

Samples	Cell number [C]	log C	Bactericidal activity	Bacteriostatic activity
Original PET	7.9×10^6	6.9	−2.6	0
GPE-PET	4.8×10^4	4.7	−0.4	2.2
Sericin-GPE-PET	1.0×10^3	3	1.3	3.9
Collagen-GPE-PET	1.6×10^3	3.2	1.1	3.7
Chitosan-GPE-PET	2.5×10^3	3.4	0.9	3.5

the pad-dry-cure method and the solution method; the former was found to be more effective in terms of the immobilized amounts of functional agent and the antibacterial efficacy. The surface hydrophilicity of the PET fabric can be improved to a certain extent by immobilizing of a functional agent such as sericin, collagen or chitosan.

Conventional methods of modification of polymer fiber using $scCO_2$ rely on changes in the fiber structure which lead to the improvement of the physical and mechanical properties of the fiber. However, cross-linked intermediate fibers can also participate in the reaction with functional agents for further, surface modification. Generally, this $scCO_2$ pretreatment is expected to represent a new approach as simplifying the process, lowering the cost of surface modification of polymer fabrics; also, the subsequent chemical immobilization of functional agents onto the fiber surface is stronger and more stable when $scCO_2$ pretreatment is carried out.

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