Effect of Supercritical Carbon Dioxide Dyeing Conditions on the Chemical and Morphological Changes of Poly(ethylene terephthalate) Fibers

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ABSTRACT: Commercially available regular denier poly(ethylene terephthalate) (PET) fabrics were used in this investigation. PET fabric samples were wound on a bobbin and then exposed to supercritical CO_2 under conditions representing a typical supercritical CO_2 dyeing cycle. Infrared spectroscopy, X-ray diffraction, differential scanning calorimetry, and scanning electron microscopy were used to characterize the chemical and morphological changes of the PET fibers. The results showed that exposure to supercritical CO_2 did not cause chemical changes in the fibers; the crystal size and the T_{mp} of the PET fabric after treatment in supercritical CO_2 did not significantly change; the crystallinity decreased; and the treatment in supercritical CO_2 at higher temperature caused surface morphology changes (increased oligomer migration). However, there was no pitting, cracking, or crazing on the surface of the treated fibers. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2008–2012, 2004

Key words: polyesters; FTIR; X-ray; differential scanning calorimetry; morphology

INTRODUCTION

Water is increasingly being recognized as a valuable raw material, the availability of which is not unlimited, and which must be protected by appropriate legal measures. Up to the present day, the dyeing of textiles depends on water as solvent or as transport medium for the dyestuffs. Take synthetic fibers as an example. Polyester fabrics, which are dyed with disperse dyes, require chemical auxiliaries such as surfactants, dispersing agents, and so forth, in the aqueous dye liquor, because of the low solubility of dyes in water. After dyeing, however, auxiliaries and unused dyestuffs remain in the liquor and cause pollution. As a rule, to decolorize the effluent, chemicals are added that destroy the dyestuff or precipitate it from the dye liquor. This leads to additional pollution of the wastewater and to problems with sludge disposal. The wastewater problem is thus one of the most urgent issues of the textile finishing industry.[1]

This is where the idea of dyeing in supercritical fluids finds its origin. Supercritical fluids are characterized by a very high solute diffusivity and a lower viscosity. Consequently, in supercritical fluids all transport process becomes much faster. For its peculiar properties, the most commonly employed supercritical fluid is carbon dioxide ($T_c = 31.3°C$, $P_c = 7.4$ MPa). Dyeing with supercritical carbon dioxide (SCD) was developed to completely avoid the use of water during dyeing, thus creating no pollution. No auxiliary agent is used in the process and residual dye can be recovered in a reusable form with this novel technique.[2] As a solvent, SCD shows ideal properties in that it is cheap, recyclable, and extremely safe. The carbon dioxide that is used in such a process is obtained as a by-product from fermentation and ammonia synthesis, and does not therefore add to the greenhouse effect.[3,4]

Schollmeyer's team at the DTNW in Krefeld, Germany is responsible both for the idea of using SCD instead of water for dyeing polyester fibers with disperse dyes and for the first fundamental experiments.[5] Some researches on dyeing of synthetic fibers in supercritical fluid have been done, such as the dyeing of synthetic fibers in SCD[1,6–8] and solubility of disperse dyes in SCD.[9–12]

However, very little has been published about the effects that SCD may have on either morphological or chemical change of polyester. If the fiber properties are adversely affected as a result of morphological and chemical changes, the potential commercial use of CO_2 as a dyeing medium would be limited in the future. Thus, the principal objective of the research reported here was to identify and characterize any chemical and morphological changes in poly(ethylene terephthalate) (PET) fibers that occurred under supercritical CO_2 dyeing conditions.

For this study, commercially available regular denier PET fabrics were used. The PET fabric samples

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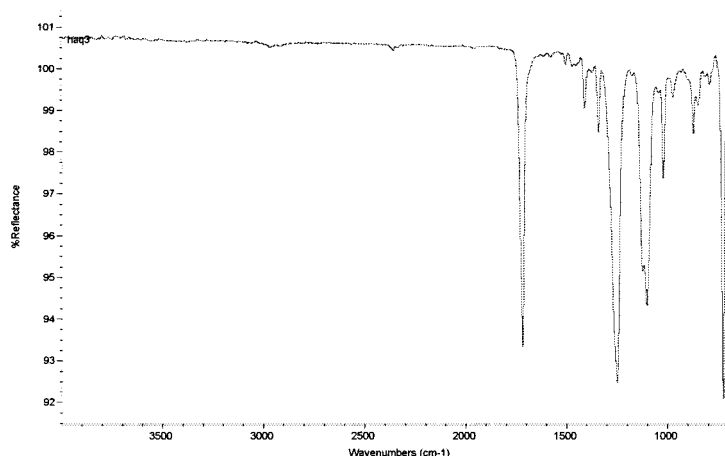*Correspondence to:* A. Hou (houaiqin@mail.dhu.edu.cn).

Figure 1 FTIR spectra of the untreated fabric.

were wound on a bobbin and then exposed to supercritical CO_2 under conditions representing a typical supercritical CO_2 dyeing cycle. Infrared, X-ray diffraction (XRD), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) were used to characterize the chemical and morphological changes of the PET fibers.

EXPERIMENTAL

Materials

The PET fabric (60 g/m^2, plain weave, weft 100 d, warp 100 d) with pretreatment used in this study was a commercial product of Wujiang Textile Factory of China.

Treatment with supercritical CO_2

PET fabric samples were suspended on a stainless-steel core, then placed in a dyeing autoclave. The system was heated to the desired temperature. CO_2 was then introduced into the liquid phase from a cylinder and isothermically compressed to the working pressure. When the system reached the desired temperature (in this study 80, 100, 120, and 130°C) and pressure (20 MPa), the fluid was passed through the dyeing autoclave with the circulation pump (to be the same as the dyeing procedure). After a certain period (40 min) of treatment, the dyeing autoclave was cooled under the glass-transition temperature (T_g) of PET as soon as possible. After the pressure was reduced gradually to atmospheric pressure by a separating vessel, the sample was removed from the dyeing autoclave.

FTIR

FTIR spectra of the untreated and treated PET fabrics were measured by a OMNI Sampler of the Nexus–670 FTIR–Raman spectrometer (Nicolet Analytical Instruments, Madison, WI), using a single ART reflecting method.
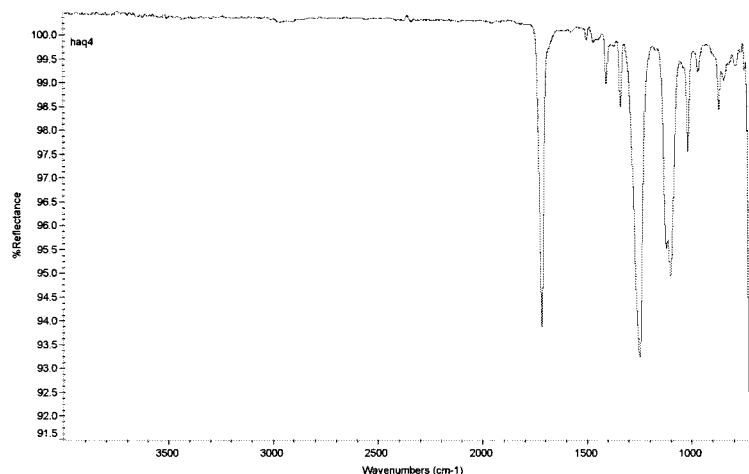

Figure 2 FTIR spectra of the treated fabric under conditions of 120°C, 20 MPa, 40 min.

XRD

Fiber samples were cut into powder. The X-ray diffraction patterns of the fabrics were measured with a D/MAX-B X-ray diffractometer (Rigaku, Japan), which used a Ni-filtered Cu–K_α target at 40 kV and 40 mA, λ = 1.542 Å.

DSC

A DSC822e differential scanning calorimeter (Mettler/Toledo, Greifensee, Switzerland) was used. Samples of about 5 mg, placed in a DSC pan, were heated from 25 to 300°C at a scanning rate of 10°C/min, under a constant flow of dry nitrogen.

SEM

For SEM analysis, the fibrous materials were sputtered with gold and then examined with a JSM 5600LV scanning electron microscope (JEOL, Tokyo, Japan), operated at 15 kV.

RESULTS AND DISCUSSION

The principal objective of this study was to characterize whether exposure to supercritical CO_2 under dyeing conditions resulted in significant changes in regular denier PET fabric. The main experimental objective was to compare the effects of supercritical CO_2 exposure to the control condition. The choice of a CO_2 treating condition was based on our experiments concerning the dyeing of PET with the disperse dyes in supercritical CO_2.

Chemical changes induced in PET by supercritical CO_2

The FTIR spectra of the original and treated PET fabrics in the wavenumber ranges of 4000–500 cm^{-1} are shown in Figure 1 and Figure 2, respectively. There are no differences between Figure 1 and Figure 2. Thus, no molecular structure changes took place after the PET fabric was treated in supercritical CO_2; that is, there was no effect of supercritical CO_2 dyeing conditions on the chemical structure of PET fibers.

TABLE I
Half-Peak Breadth of Diffraction Peaks, Spacing d of Diffraction Planes, and Crystal Size of Untreated PET Fabric

2θ (°)	Half-peak breadth (Å)	Spacing d (Å)	Crystal size (Å)
17.850	3.500	4.965	22.736
23.100	3.500	3.874	22.925
25.900	3.281	3.437	24.576

TABLE II
Half-Peak Breadth of Diffraction Peaks, Spacing d of Diffraction Planes, and Crystal Size of Treated PET Fabric

2θ (°)	Half-peak breadth (Å)	Spacing d	Crystal size (Å)
17.750	3.062	4.993	26.011
22.600	3.938	3.931	20.371
25.650	3.062	3.470	26.358

Morphological changes induced in PET by supercritical CO_2

For comparison of treatment on the fiber fine structure, experiments with PET fabrics in supercritical CO_2 at 120°C, 20 MPa were carried out. The fibers were characterized by XRD. The X-ray diffraction analyses of untreated and treated PET fibers are listed in Table I and Table II, respectively.

The crystal sizes of untreated and treated PET fabric can be calculated from the Scherrer equation and are also listed in Table I and Table II, respectively. Table I and Table II show that the crystal size of treated PET fabric changes only slightly, although the interplanar distance practically has no change, compared with that of untreated PET fabric.

DSC was performed on the samples to obtain a measure of percentage crystallinity, to qualitatively characterize the melting behavior and also to compare the structure state of the PET samples before and after treatment. From the DSC curves for untreated and treated PET fabrics, the T_g endotherms were very weak, the crystallization exotherm did not appear, and only melting endotherms appeared at about 258°C. For all of the PET samples, the only transition observed was the melting endotherm. In addition, multiple melting peaks were not observed to be characteristic of any of the PET fabrics. The means of the peak temperature of melting (T_{mp}) and enthalpy of melting (ΔH_{mp}) data for untreated and treated PET fabrics and CO_2 treatment conditions are summarized in Table III.

The crystallinity index X_c can be calculated from the following equation[13]:

TABLE III
Summary of DSC

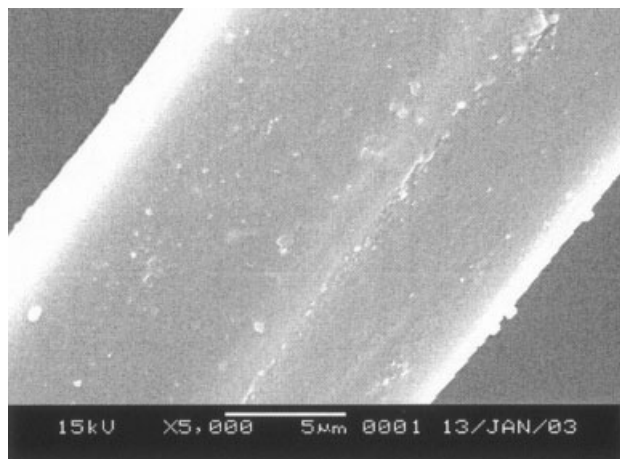| Treating temperature (°C)	T_{mp} (°C)	ΔH_{mp} (J/g)	X_e (%)
Untreated PET Sample	258.64	69.78	70.19
80	258.69	56.67	57.00
100	258.36	55.95	56.28
120	256.82	54.36	54.68
130	254.65	53.36	53.68

Figure 3 SEM micrograph of an untreated fiber sample.

$$X_c = \frac{\Delta H_{mp}}{\Delta H_{mp}^{\circ}}$$

where ΔH_{mp} is the measured melting enthalpy of the polymer, obtained directly from the DSC traces and ΔH_{mp}° is the melting enthalpy of the completely crystallized polymer. $\Delta H_{mp}^{\circ} = 99.4118$ J/g was assumed for PET.[14] The results of the calculation of crystallinity index X_c of untreated and treated PET fabrics are listed in Table III, too.

It was concluded that all of the samples in Table III had approximately the same T_{mp}, and the crystallinity of PET fabrics treated in supercritical CO_2 decreased, compared with that of the untreated sample, but decreased slowly with increasing temperature of the treatments. With respect to the influence of SCD on the crystallinity of PET in CO_2, very different data have been published.
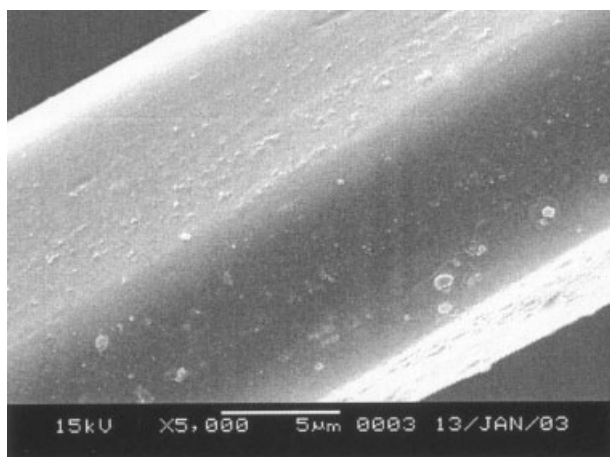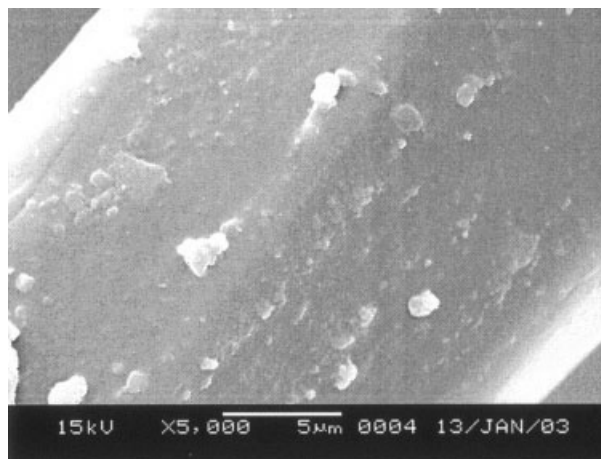

Figure 5 SEM micrograph of a treated fiber sample under conditions of 100°C, 20 MPa, 40 min.

SEM analysis was used to characterize any changes in the surface morphology of the fibers as a result of the treatments applied, such as the appearance of pitting, cracking, crazing, or oligomer migration and crystal formation. Representative SEM micrographs, taken at a magnification of ×5000, of all kinds of PET fibers are shown in Figures 3 through 6. Figure 3 is the SEM micrograph of untreated PET fiber. Figure 4 is the SEM micrograph of the PET fiber treated under conditions of 80°C, 20 MPa, and 40 min in supercritical CO_2. In Figures 3 and 4, there appears to be no appreciable difference in the appearance of the surfaces of the untreated and treated fibers in CO_2 at 80°C, 20 MPa, and 40 min. Oligomer crystals cannot be detected on either of these two samples. Figures 5 and 6 are the SEM micrographs of the PET fiber treated in CO_2 at 100 and 120°C, respectively. Oligomer crystals shown in Figures 5 and 6 are clearly present on the fiber surface. This observation seems to suggest that at
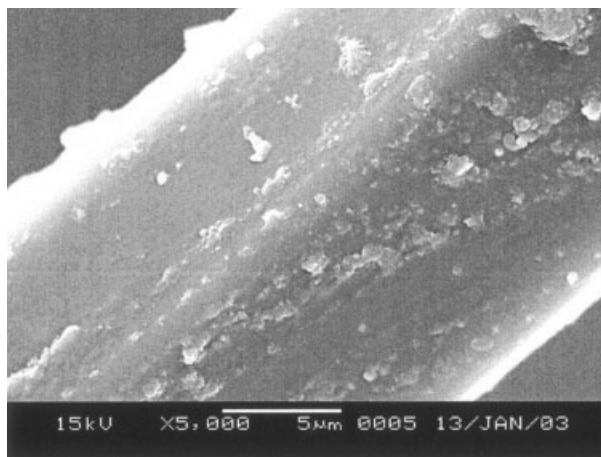

Figure 4 SEM micrograph of a treated fiber sample under conditions of 80°C, 20 MPa, 40 min.

Figure 6 SEM micrograph of a treated fiber sample under conditions of 120°C, 20 MPa, 40 min.

higher temperature supercritical CO_2 does penetrate into the fiber and promotes the migration of oligomer from the polymer to the surface.[2] However, for the untreated and all the treated fibers, there was no pitting, cracking, or crazing on the surface of the fibers.

CONCLUSIONS

The primary objective of the research was to compare the chemical and morphological changes of the PET fabrics untreated and treated in supercritical carbon dioxide under dyeing conditions.

- FTIR analysis of the PET fabrics untreated and treated in CO_2 showed that exposure to supercritical CO_2 did not cause chemical changes in the fibers.
- X-ray diffraction and DSC analysis confirmed that the crystal size and T_{mp} of the PET fabric after treatment in supercritical CO_2 did not significantly change, but the crystal index decreased.
- SEM analysis of the fiber surfaces showed that the treatment in supercritical CO_2 at higher tempera-

ture caused changes in surface morphology (increased oligomer migration). However, there was no pitting, cracking, or crazing on the surface of the treated fibers.

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