STRUCTURE AND PROPERTIES OF POLYETHYLENE TEREPHTHALATE TREATED BY SUPERCRITICAL CO_2

by

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Structure and properties of polyethylene terephthalate were characterized by SAM, Fourier transform infrared spectrometry, X-ray diffraction, and thermal analysis to evaluate the effect of supercritical CO_2 on the structural behavior. The dynamic shrinking behavior of polyethylene terephthalate was analyzed using the Kelvin-Voigt model. The results indicated that uneven and significantly different surface of the polyethylene terephthalate fiber was displayed since the spinning oil and other additives added in spinning process were rinsed in supercritical CO_2. The slight shifts for the characteristic bands of polyethylene terephthalate in Fourier transform infrared spectrometry were observed due to some re-arrangements and re-crystallizations of the molecule chains after supercritical CO_2 treatment. Simultaneously, the crystallinities and the fastest thermal decomposition temperatures of polyethylene terephthalate were improved slightly from 80 °C to 120 °C in supercritical CO_2. Furthermore, the shrinkage of the treated polyethylene terephthalate samples was increased gradually from 2.73% to 3.35% with the temperature raising.

Key words: *supercritical CO_2, polyethylene terephthalate, treatment, shrinking dynamics equation, structure and properties*

Introduction

Supercritical CO_2 dyeing, as an anhydrous process, presents low energy consumption, high uptake rate, recycling of dyes and CO_2, as well as zero waste water emission in comparison with conventional water dyeing technique [1-3]. The economic and ecological benefits of supercritical CO_2 are derived from its density, which is intermediate between those of liquids and gases and which is continuously tuned by changes of temperature and/or pressure [4, 5]. Therefore, considerable research activities have been conducted throughout the world since Professor E. Schollmeyer at Deutschen Textilforschungszentrum Nord-West in Germany put forward the patent of textile dyeing in supercritical fluid [3]. To date, dyeing procedures for different fibers, suitable dyes and their solubility, as well as interactions between fibers and dyes have been investigated widely [6, 7].

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Polyethylene terephthalate (PET) is a category of polymers that contain the ester functional group in their main chain, and is extensively used in fibers for clothing, home furnishings, tyre reinforcements, and insulating materials, which makes up about 18% of world polymer production and is the fourth-most-produced polymer. In supercritical CO_2, the equilibrium uptake of disperse azo dyes in commercial PET yarns was superior to conventional water medium [8, 9]. Hence, dyeing of PET in supercritical CO_2 is always a research priority in textile industry. In our previous study, satisfactory and commercialization dyeing with the uniform and bright color were obtained in supercritical CO_2 using disperse blue 79 with dyeing conditions of 120 °C, 24 MPa and 60 min [2]. However, there is little adequate structural behavior information for PET after supercritical CO_2 treatment.

In the present work, the effect of supercritical CO_2 on the structure and properties of PET was evaluated by SEM, Fourier transform infrared spectrometry (FT-IR), X-ray diffraction (XRD), and thermal analysis (TG). Moreover, the dynamic shrinking behavior of PET in supercritical CO_2 was also analyzed.

Experimental

Materials and treatment procedure

The PET fabrics in this study were obtained from Liaoning Chaoyi Industry & Trade Group (Fuxin, China). The CO_2 with a purity of 99.9% was purchased from China Haohua (Dalian) Research & Design Institute of Chemical Industry Co., Ltd. The treatment process of PET was carried out in the same batch system as described elsewhere [10, 11]. The PET fabric was positioned into a treatment vessel. The CO_2 stored in a gas cylinder was firstly liquefied using a refrigerator. The liquefied CO_2 was then heated to above critical temperature (31.10 °C) with a heat exchanger and was pressurized to above critical pressure (7.38 MPa) with a high-pressure pump. The treatment experiments were carried out at 24 MPa and 60 min from 100 °C to 120 °C.

Characterizations

The surface morphological investigations of PET were carried out on an JSM-7800F field emission SEM (JEOL, Japan). The chemical structure changes of PET were recorded by employing an spectrum 10 FT-IR spectrophotometer (PerkinElmer, USA). The crystalline states of PET were conducted with an D/max-3B XRD instrument (Rigaku, Japan). The thermal properties of PET were carried out on an STA PT 1600 TG machine (LINSEIS, Germany).

Results and discussion

The SEM analysis

The SEM was used to investigate the surface morphology changes of PET fiber before and after supercritical CO_2 treatment. Figure 1 shows a comparison of the SEM images of the untreated PET fiber and the fibers treated in supercritical CO_2 at 80 °C, 100 °C, and 120 °C, respectively. It can be seen from fig. 1(a) that the surfaces of the control fiber sample was relatively clean and smooth. The similar integrated and clean surface was observed for the PET sample treated at 80 °C in supercritical CO_2, as shown in fig. 1(b). However, when the treated temperature was increased to 100 °C, uneven and significantly different surface of the PET fiber was displayed in fig. 1(c), which implied that spinning oil and other additives added in the spinning process could be rinsed in supercritical CO_2. With the further increase of treated temperature to 120 °C, clean fiber morphology was emerged gradually, as shown in fig. 1(d). This is maybe because most of the spinning oil had already been detached after supercritical CO_2 treatment.

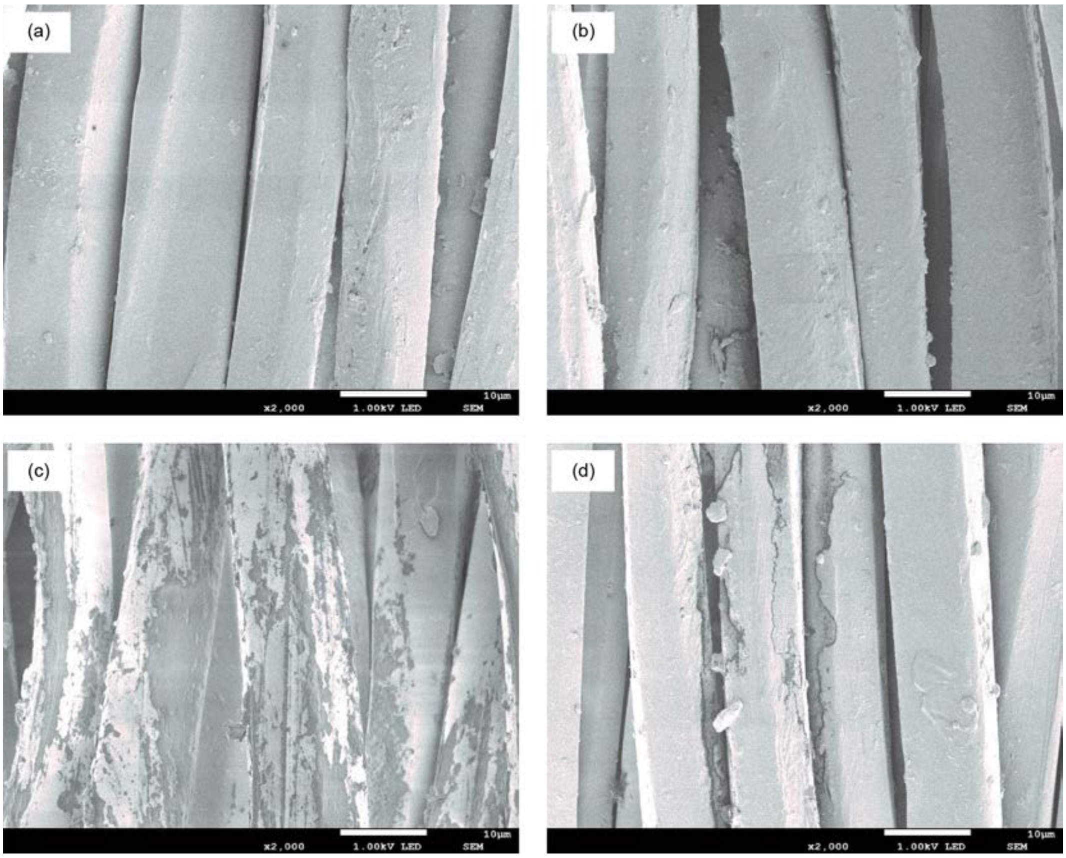

Figure 1. The SEM images of the PET fibers: the control sample (a), and treated at 80 °C (b), 100 °C (c), 120 °C (d) in supercritical CO_2

The FT-IR analysis

The FT-IR was used to investigate the change of segment structure, functional groups, and linking bonds of PET before and after supercritical CO_2 treatment. As depicted in fig. 2, the characteristic bands of the PET fiber (C=O stretching, C–H stretching, and O–H stretching) were observed in IR spectra of all samples. The IR spectra of the untreated PET sample indicated that band at 3428.3 1 per cm was attributed to O–H stretching vibrations ($\nu_{\mathrm{O-H}}$). The peak at 2968.59 1 per cm was because of the stretching vibration of $-CH_2-$ ($\nu_{-\mathrm{CH_2}-}$). The strong peak with absorption band at 1713.69 1 per cm corresponded to the stretching vibration of C=O ($\nu_{\mathrm{C=O}}$). After supercritical CO_2 treatment, slight shifts for the characteristic bands of C=O stretching, C–H stretching, and O–H were also observed at 1713.42-1713.69 1 per cm, 2968.59-2970.35 1 per cm, and 3425.00-3428.3 1 per cm, respectively. This is maybe because the interactions of the macromolecules in the polymer were increased in supercritical CO_2, which led to some re-arrangements and re-crystallizations of the molecule chains of PET [3].

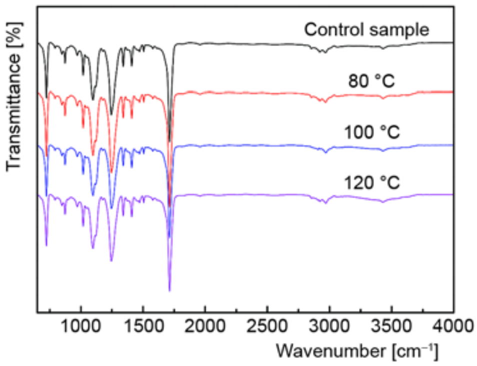

Figure 2. The FT-IR spectra of PET fibers in supercritical CO_2

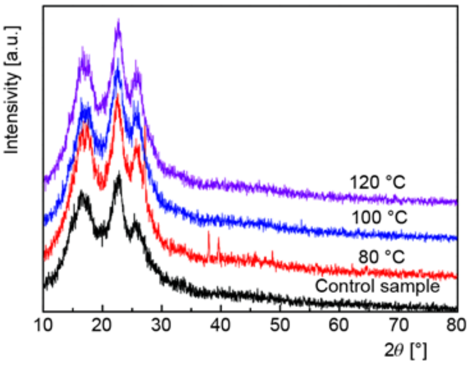

Figure 3. The XRD diffractograms of PET fibers in supercritical CO_2

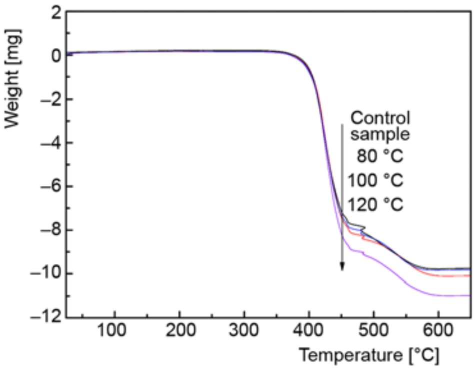

Figure 4. The TG curves of PET fibers in supercritical CO_2

The XRD analysis

In supercritical CO_2 treatment process, the conformation of fiber macromolecule chain segments will be changed due to the interaction between CO_2 fluid and fiber macromolecule chain segments, causing the change of arrangement and orientation of macromolecule chain segments. The recrystallization of polymer will also occur under the role of heat, thereby affecting the crystal structure of fiber. The XRD diffractograms in fig. 3 give the typical X-ray diffraction patterns of PET before and after supercritical CO_2 treatment. The observed diffraction peak of the untreated and treated PET samples was characterized by 2θ about 16.5°, 22.7°, and 25.5°, respectively. However, the intensities of the characteristic diffraction peaks for the treated PET samples were increased from 80 °C to 120 °C in supercritical CO_2. The crystallinities of the treated samples were also increased slightly because of the rearrangement of macromolecular chains of PET under high temperature conditions during supercritical CO_2 treatment process.

The TG analysis

The TG curves of the PET samples before and after supercritical CO_2 treatment are illustrated in fig. 4. It can be seen from fig. 4 that the prominent weight loss of PET was obtained from 350 °C to 600 °C because of the decomposition of the polymer chains. Moreover, the fastest thermal decomposition temperatures of PET were increased from 403.34-406.10 °C with the rising of treatment temperature due to the re-arrangements and re-crystallizations of the polymer chains in supercritical CO_2 fluid. Thus, the results demonstrated that the thermal property of PET samples could be improved moderately with treatment temperatures raising in supercritical CO_2.

Shrinkage dynamics equation of PET

Theoretically, the thermal shrinkage behavior of PET can be depicted by using linear viscoelastic model [10]. As shown in fig. 5(a), the Kelvin-Voigt model, also known as the

Voigt model, consists of a Newtonian damper and Hookean elastic spring connected in parallel. Its simplified model was displayed in fig. 5(b).

In supercritical CO_2, the deformation equation of PET can be calculated according to the Kelvin-Voigt model:

$$\varepsilon(t) = \varepsilon_{30} + \frac{\sigma t}{\eta_3^*} + \frac{\sigma}{E_2}(1 - \mathrm{e}^{-t/\tau_2}) + \varepsilon_{20}\mathrm{e}^{-t/\tau_2} \quad (1)$$

where ε is the strain that occurs under the given stress, σ – the stress, t – the time, E – the elastic modulus of the material, η – the viscosity of the material, and τ – the characteristic relaxation time.

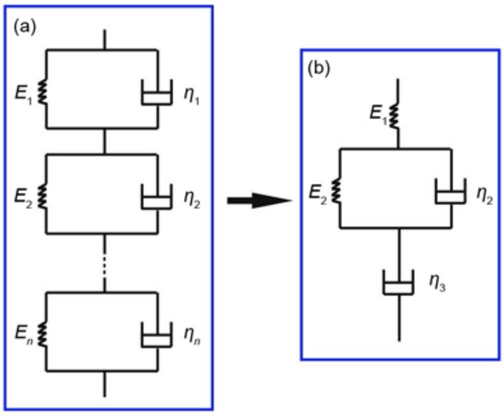

Figure 5. Schematic diagram of linear viscoelastic model for PET

The shrinkage of PET, $\Delta\varepsilon$ (t), is the negative difference between the deformation at time, t, and the initial deformation ε (t = 0):

$$\Delta\varepsilon(t) = -[\varepsilon(t) - \varepsilon(0)] = -\frac{\sigma t}{\eta_3^*} + \left[\varepsilon_{20} - \frac{\sigma}{E_2}(1 - \mathrm{e}^{-t/\tau_2})\right] \quad (2)$$

For the shrinkage at certain condition, eq. (2) can be simplified as eq. (3) since $(\varepsilon_{20} - \sigma/E_2)$ is the constant term:

$$\Delta\varepsilon(t) = -\frac{\sigma t}{\eta_3^*} + A\mathrm{e}^{-t/\tau} + B \quad (3)$$

where B is the constant.

In the actual fiber shrinkage process, there are numerous viscoelastic relaxation processes of different shrinkage units, and the shrinkage dynamics equation can be depicted by:

$$\Delta\varepsilon(t) = -\frac{\sigma}{\eta_3^*}t + A_1\mathrm{e}^{-t/\tau_1} + A_2\mathrm{e}^{-t/\tau_2} + \cdots + A_n\mathrm{e}^{-t/\tau_n} + B \quad (4)$$

where A_1, A_2, … A_n are the contribution of each component unit to the total shrinkage, τ_1, τ_2, … τ_n are the characteristic relaxation time of each component unit.

As listed in tab. 1, with the increase of treatment temperature, the area of the PET samples were reduced from 77.81-77.32 cm^2 in comparison with the control sample. In addition, after supercritical CO_2 treatment, the shrinkage of the treated PET samples was increased gradually from 2.73-3.35%.

Table 1. The shrinkage of PET before and after supercritical CO_2 treatment

Samples [°C]	Area [cm^2]	Shrinkage [%]
Control sample	80	–
80	77.81	2.73
100	77.42	3.22
120	77.32	3.35

Conclusion

The PET was treated in supercritical CO_2 at 24 MPa and 60 min. The effects of different system temperatures on the surface morphology, chemical and crystal structures, thermal, as well as shrinkage property of PET were investigated. The SEM analysis showed that the uneven surface was displayed on the PET fiber with the raising of treatment temperature because of the rinse effect of supercritical CO_2. The FT-IR analysis presented slight shifts for the characteristic bands of C=O stretching, C–H stretching, and O–H stretching after supercritical CO_2 treatment. The XRD analysis revealed that the crystallinities of the treated PET were increased slightly due to the rearrangement of macromolecular chains of PET under high temperature conditions during supercritical CO_2 treatment process. The TG analysis indicated that the thermal property of PET was also improved moderately with the increase of treatment temperatures. Furthermore, shrinkage dynamics equation of PET was proposed in supercritical CO_2 according to the Kelvin-Voigt model as the shrinkage occurred after supercritical CO_2 treatment.

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