Preparation and Property of Poly(ethylene terephthalate) Fibers Providing Ultraviolet Radiation Protection

Cuiqing Teng, Muhuo Yu

State Key Laboratory of Modification for Chemical Fibers and Polymer Materials, Donghua University, Shanghai 200051, China

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ABSTRACT: Interest in protection against solar ultraviolet radiation (UVR) among the general public in the world has been increasing steadily. Poly(ethylene terephthalate) (PET) was blended with UVR-protection agents and was spun into modified fibers to provide the property of UVR protection. Investigation of this property using a UV spectrophotometer showed that the modified PET fabrics could be resistant to UVR more than 90% in the UV-B band. The treatment of aqueous alkali on the surface of the fibers to improve the comfortable feel had little influence on the property of UVR protection. Scanning electron microscopy was employed to observe the surface morphology of the fibers. Also, the modified fibers had good heat insulation property and the mechanical properties of the fibers were measured. J Appl Polym Sci 88: 1180–1185, 2003

Key words: ultraviolet radiation; UVR protection; poly(ethylene terephthalate) (PET) fibers; SEM

INTRODUCTION

The known effects of ultraviolet radiation (UVR) on humans may be beneficial or detrimental, depending on a number of circumstances. It is now generally acknowledged that a long period of UVR deficiency may have a harmful effect on the human body. The best known manifestation of "UVR deficiency" is the development of vitamin D deficiency and rickets in children because of a disturbance in phosphorus and calcium metabolism. However, exposure to intensive UVR for a long time, for instance, exposure to the sun in summer, is obviously harmful for skin and other organs of the body.[1–2]

Ultraviolet radiation can be classified into UV-A, UV-B, and UV-C regions. Much less is known about the biological effects of UV-A radiation (320–400 nm), which adjoins the visible light, so the waveband is usually not a topic of discussion. Most observed biological effects of UV-B (280–320 nm) radiation are extremely detrimental to living organisms. Because solar UVR below wavelengths of 290 nm is effectively absorbed by stratospheric ozone, and no such radiation reaches living organisms from natural sources, the wavelength in the UV-C region (200–280 nm) is considered of little detriment for human beings. Continuous depletion of the stratospheric ozone layer has resulted in an increase in ultraviolet-B (UV-B; 280–315 nm) radiation reaching the Earth's surface. UV radiation has been reported to suppress a number of photochemical and photobiological processes in a wide variety of organisms. However, certain photosynthetic organisms that are exposed simultaneously to visible and UV radiation in their natural environment have developed mechanisms to counteract the damaging effects of UV.

The harmful effects of UVR on the eye consist of the development of photokeratitis, pterygium, and squamous cell cancer of the conjunctiva. The effects on the skin consist of solar erythema, which, if severe enough, may result in blistering and destruction of the surface of the skin with secondary infection and systemic effects. Additional harmful effects are produced by the interaction between UVR and a variety of environmental and medicinal chemicals, resulting in acute and chronic skin changes.[1–4]

Everyone has the potential for developing skin cancer, although the risk depends on the intensity and degree of exposure to solar UVR during one's life span. If all current exposure to solar UVR could be significantly reduced, the incidence of skin cancer would eventually decrease significantly. Although protecting the skin with clothing is a convenient and valid method, common clothing, including cotton, silk, wool, and synthetic fabrics, is not effective for UVR protection because of the high UV-ray transmittance of the fabrics. Thus it is essential to prepare UVR-protection fabrics whose function is to absorb or shield against UV-rays. Coating UVR-protection agents onto a fabric is one method of producing UVR-protection fabrics. However, the fastness to washing of UVR-protection fabric produced by the coating

Correspondence to: M. Yu (ymh6161@163.com).

TABLE I
Temperature of 7 Sections in the Screw during Melt-Spinning

Section no.	1	2	3	4	5	6	7
Temperature (°C)	285	297	298	298	296	293	290

method is generally too poor to hold up against frequent washing. Another method of producing UVR-protection fabrics is to add UVR-protection agents into the fibers themselves by a process of spinning a polymer into fibers, for instance, poly(ethylene terephthalate) (PET) fibers, polypropylene fibers, and others.[5–9]

In this study, UVR-protection agents were added into PET by a blend method and the modified PET was spun into fibers by melt-spinning technology. The property of UVR protection of the modified fibers was characterized by measuring the ultraviolet transmittance of the fabrics woven from the fibers. The effect of the treatment with NaOH on UVR protection, the heat insulation property, and the mechanical properties of the modified PET fabrics were also studied.

EXPERIMENTAL

Materials

PET was supplied by Shanghai Petrochemical Co. (China) and the intrinsic viscosity was 0.67. The UVR-protection agents included two types: (1) an inorganic compound, titanium dioxide (TiO_2); and (2) 2-(2′-hydroxyl-3′-*tert*-butyl-5′-methylphenyl)-5-azimido-benzene. The weight ratio of the two components was 1 : 1. Azimido-benzene derivatives [including 2-(2′-hydroxyl-3′-*tert*-butyl-5′-methylphenyl)-5-azimidobenzene, 2-(2′-hydroxyl-5′-*tert*-dimethylphenyl)azimido-benzene, and so forth] and diphenyl ketone derivatives [including 2,4-dihydroxyl-diphenyl ketone, 2,2′-dihydroxyl-4-methyoxy-diphenyl ketone, and so forth] can be used as the organic UVR-protection agents. In our experiment, it was found that when TiO_2 and 2-(2′-hydroxyl-3′-*tert*-butyl-5′-methylphenyl)-5-azimido-benzene were added into PET, the blend system had good rheological properties and good spinnability; so we selected these two UVR-protection agents.

Preparation of the modified fibers

PET and UVR-protection agents were mixed using a Haake rheometer (Karlsruhe, Germany) at 275°C for 10 min and the modified PET was cut into particles for convenient melt spinning. The modified PET particles were spun into fibers with 30 monofilaments on an Abe spinning machine (Tokyo, Japan) at the winding rate of 900 m/min; the temperatures in the screw are listed in Table I. Then, a draw ratio of 3.7 of the fibers was conducted on an Edmund Erdmann 4330 drawing machine (Barmag Co., Germany) at a temperature of 175°C.

Characterization of the properties of the modified fibers

The modified PET fibers were woven into plain fabrics on a hydraulic loom for measuring the UVR-protection property. The transmittance of the fabrics was measured on a UV-365 ultraviolet spectrophotometer for characterizing the property of UVR protection of the fibers.

The heat insulation property of the fabrics was conducted on a device shown in Figure 1, which was home-designed in our laboratory. The device with samples tested was exposed to the sun in summer and the heat insulation of the fabric could be characterized by monitoring the change of temperature below the samples.

The modified PET fabrics were boiled in aqueous NaOH (0.25 mol/L). The samples were removed after a given time and dried. The weight loss of the fabrics was calculated by the following equation:

$$\text{Weight loss} = \frac{w_1 - w_2}{w_1} \times 100\%$$

where w_1 and w_2 are the weight of the sample before and after boiling, respectively.

A Camscan-4 SEM was employed to observe the surface morphology of the modified fabrics at an accelerating voltage of 10 kV. The samples were washed in ether for removing the oils and sewage on the surface, and then gold-sputtered before observation.

The mechanical properties of the fibers were measured on an Instron 1122 forcing instrument.

RESULTS AND DISCUSSION

The method used to evaluate the UVR-protection property of fabrics is usually by measuring the transmittance of UV-rays through the fabrics. The less the

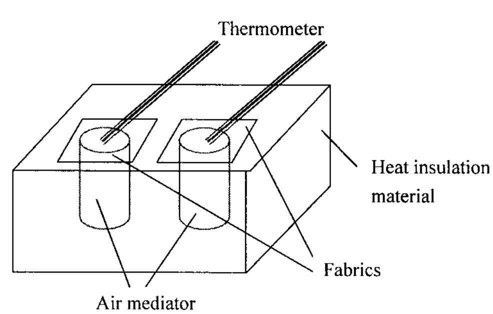

Figure 1 The home-designed device for measuring the heat insulation property of the fabrics.

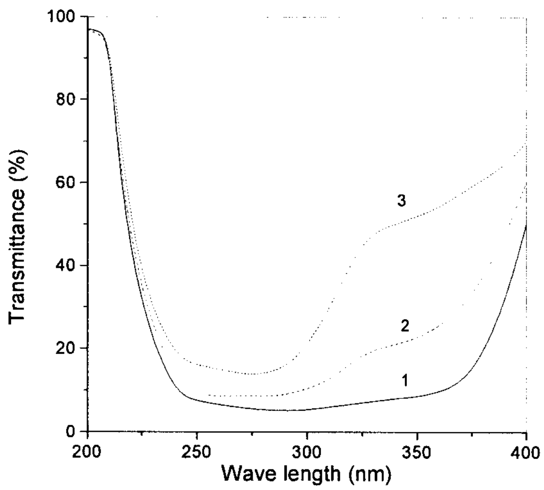

Figure 2 Spectrograms of UV-ray transmitting through the modified PET fabric with both warp and weft (curve 1), PET fabric with only warp (curve 2), and nonmodified PET fabric fabrics (curve 3).

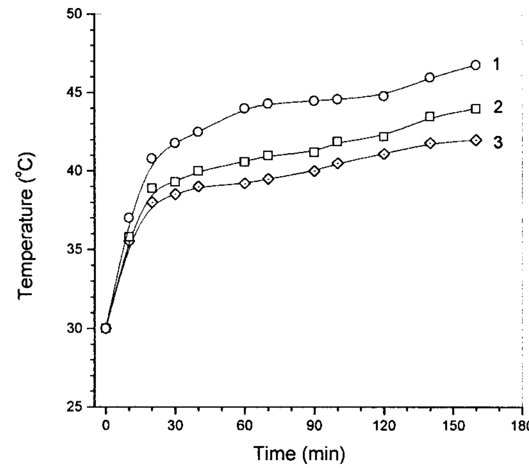

Figure 4 The changes of the temperature under fabrics exposed to the sun with time. Curve 1: the nonmodified PET fabrics; curves 2 and 3: modified PET fabrics whose percentage of UVR-protection agents in the fabrics is 1.1 and 3.0%, respectively.

UV-ray transmittance of a sample, the better the UVR-protection property of that sample. Generally, fabrics will be evaluated as good when the transmittance of UV-rays is less than 10%. The transmittance of UV-rays can be measured on an ultraviolet spectrophotometer. For characterizing the property of UVR protection of modified fabrics in this study, three samples were prepared: (1) the check fabrics (i.e., nonmodified PET fabrics); (2) fabrics with only warp of the modified PET fibers; and (3) modified PET fabrics with both warp and weft. Spectrograms of the samples are shown in Figure 2.

As shown in Figure 2, the transmittance of UV-rays of the three fabrics was slightly different in the wavelength range from 200 to 280 nm, which was the UV-C region. Thus the property of UVR protection of the modified PET fabrics was not improved more than that of the nonmodified fabrics in this waveband. However, when the wavelength range was 280–370 nm (which belonged to the UV-B region and part of the UV-A region), the transmittance of the UV-ray of the modified PET fabrics (curve 1) was less than 10%, whereas that of the nonmodified PET fabrics (curve 3) sharply increased from 18 to 58%. As a result, the property of UVR protection of the modified PET fabrics had improved more than that of nonmodified fabrics for the UV-B region and part of the UV-A region. For the PET fabric with only the warp (curve 2 in Fig. 1), the property of UVR protection was better than that of nonmodified fabrics and worse than that of the fabrics with both warp and weft.

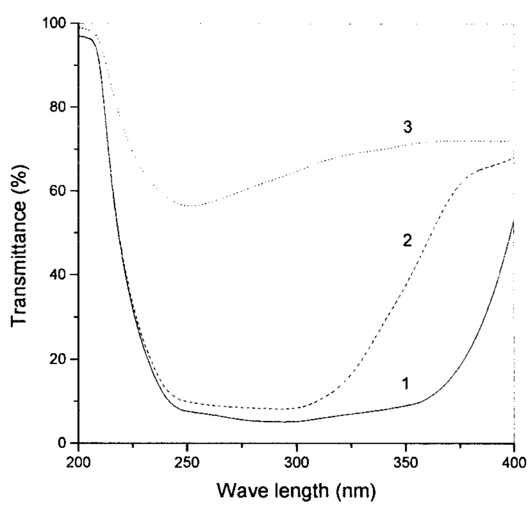

Figure 3 Spectrograms of UV-ray transmitting different fabrics: modified PET fabrics (curve 1), commercial PET fabrics (curve 2), and full cotton fabrics (curve 3).

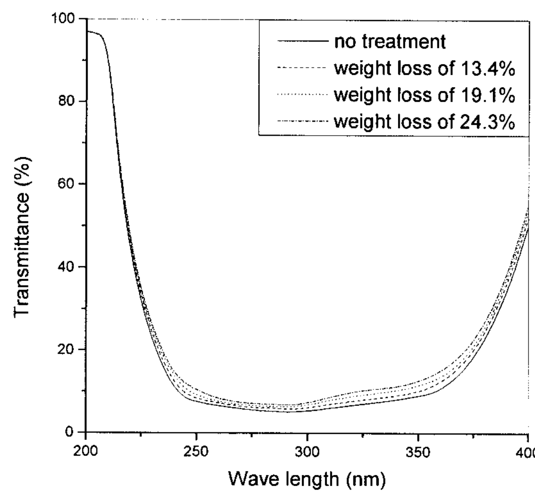

Figure 5 Spectrograms of UV-ray transmitting through fabrics treated with aqueous NaOH.

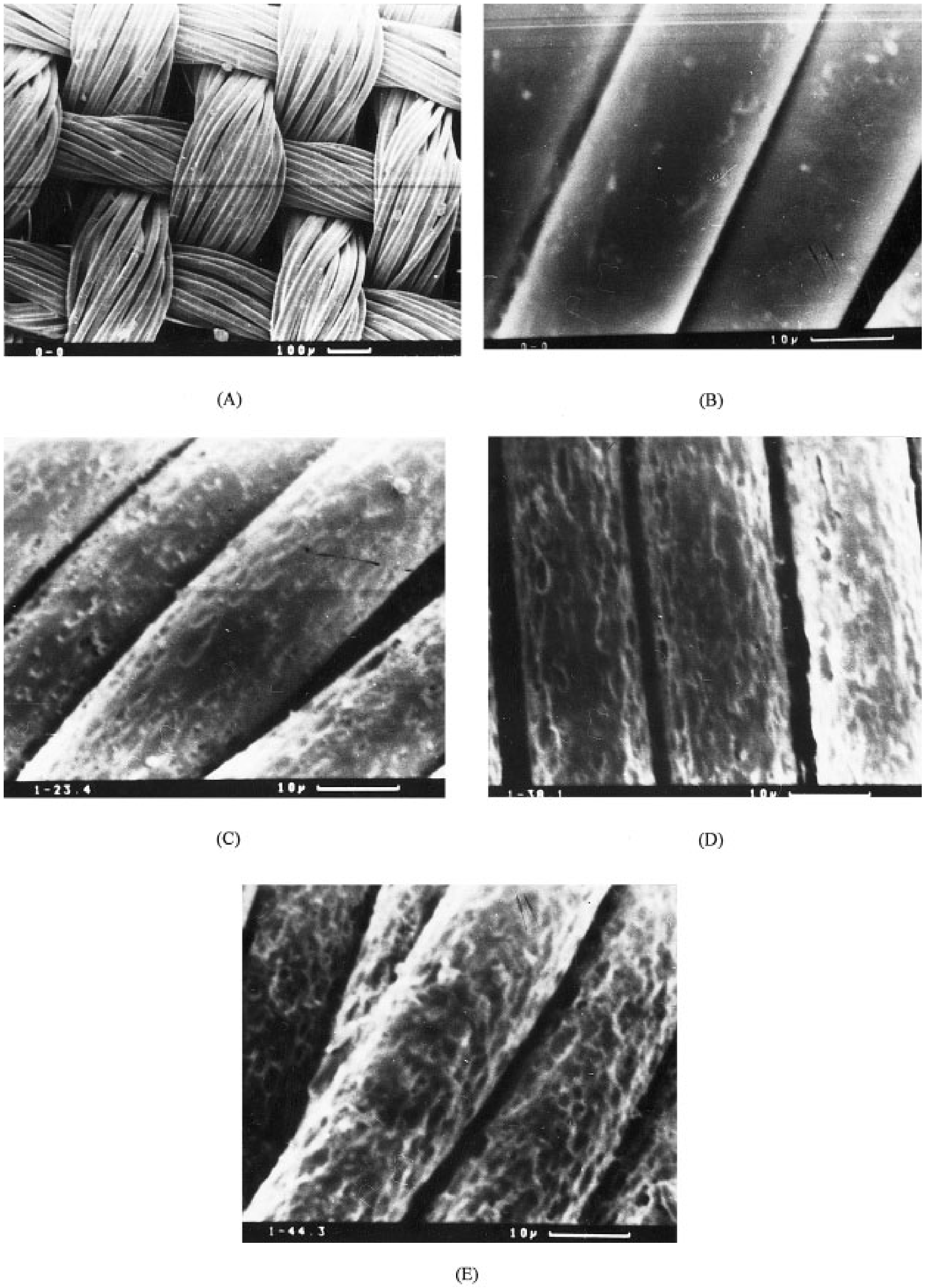

Figure 6 SEM micrographs of the nontreated fabrics (A and B) and the treated fabrics using aqueous NaOH for 1 h (C), 3 h (D), and 5 h (E).

In summer, people usually wear thin clothes with cuff or long apron to avoid direct exposure of skin to the sun, for instance, cotton, silk, and man-made clothing. What is the effect of UVR protection of these fabrics? Full cotton fabrics and the commercial PET fabric without dye and finish were compared with the modified PET fabrics prepared in this study. The spectrograms of UV-rasy transmitting through the samples are shown in Figure 3.

Because the transmittance of a given sample was affected by the thickness of the fabrics, samples with the same or similar thickness should be required. In Figure 3, the thickness of the full cotton fabrics, the commercial PET fabrics, and the modified PET fabrics was 220, 240, and 220 μm, respectively. Figure 3 shows that the transmittance of the cotton sample (curve 3) exceeded 58%, irrespective of the wavelength, and the effect of the resistance to UVR was thus very poor. For

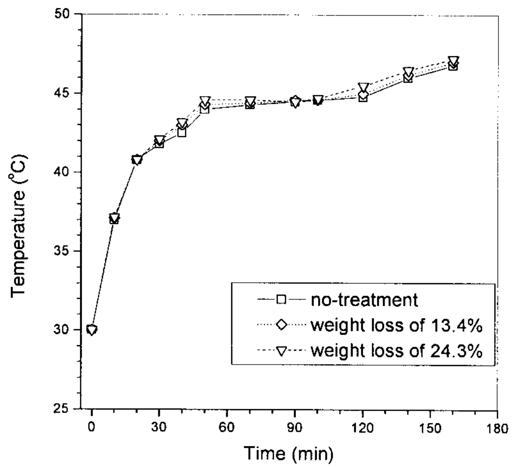

Figure 7 Effect of treatment for the fabrics using aqueous NaOH on the heat insulation.

the commercial PET fabrics (curve 1), the resistance to UVR exceeded 90% in the wavelength range of 240–300 nm, whereas it decreased from 85 to 40% when the wavelength increased from 320 to 370 nm. It was also shown that the commercial PET fabrics (curve 2) affected the resistance to UVR in the UV-B band range because the commercial PET fabrics contained small amounts of TiO_2 as the flattening agent, whose function conferred UVR protection.

The heat insulation property of the fabrics is shown in Figure 4. With greater time exposure to the sun, temperatures under the three samples all increased. At a given time, the modified PET fabrics had a better heat insulating property than that of the check fabrics. When sunshine lasted 0.5 h or more, the difference of temperature (ΔT) between that under the check fabrics (curve 1) and that under the fabrics with UVR-protection agents of 1.1 wt % (curve 2) was 2.5–3.2°C. The temperature under the fabrics with UVR-protection agents of 3.0 wt % (curve 3) was lower by about 4°C than that under the check fabrics. Therefore, the modified PET fabrics had both UVR protection and heat insulation properties.

The fabrics were treated with aqueous NaOH to improve the comfortable feel of the fabrics. The property of UVR protection of the treated fabrics is shown in Figure 5. The transmittance of UV-rays increased slightly with the increase of weight loss that could be controlled by treatment time. Even the weight loss of the modified PET fabrics was up to 24.3%; the transmittance increased by 0.5–2.5%, so the treatment of NaOH had little influence on the property of UVR protection of the modified PET fabrics.

SEM micrographs in Figure 6 describe the surface morphology of the modified fibers with 3% content of UVR-protection agents. The surface of the nontreated fibers with aqueous NaOH was smooth, as shown in Figure 6(A) and (B). However, there were a lot of irregular micropores on the surface of the fibers when the fibers were etched in aqueous NaOH and the micropores were lengthened along the fibers' axis direction, as shown in Figure 6(C–E). The micrographs also show that the micropores became longer and deeper and were characterized by more sags and crests with the prolongation of etching time from 1 to 5 h. As expected, TiO_2 particles along with the PET fell from the surface of the fibers. As a result, there were numerous micropores in the surface and the comfortable feel was improved.

The property of heat insulation of the fabrics treated with aqueous NaOH was measured, in which samples consisted of the fabrics with 3% content of UVR-protection agents; results are shown in Figure 7. Even though the weight loss of the fabrics was up to 24.3%, the property of heat insulation of the fabrics did not decrease. Therefore, the treatment had little influence not only on the property of UVR protection (discussed in Fig. 5) but also on the property of heat insulation.

Addition of UVR-protection agents, including both inorganic and organic particles, in the PET fibers had an influence on both the drawing and the mechanical properties, as shown in Figure 8. As a result, by increasing the amount of UVR-protection agents from 0 to 3.0% in the PET fibers, the break strength of the fibers decreased from 3.6 to 2.7 g/day and the extension at break increased from 27 to 34%. Theoretically, the addition of inorganic and organic particles affected the macromolecular orientation of PET in the drawing process and increased the internal imperfections in the fibers. Therefore, excessive amounts of UVR-protection agents in PET negatively affect the mechanical properties of the fibers.

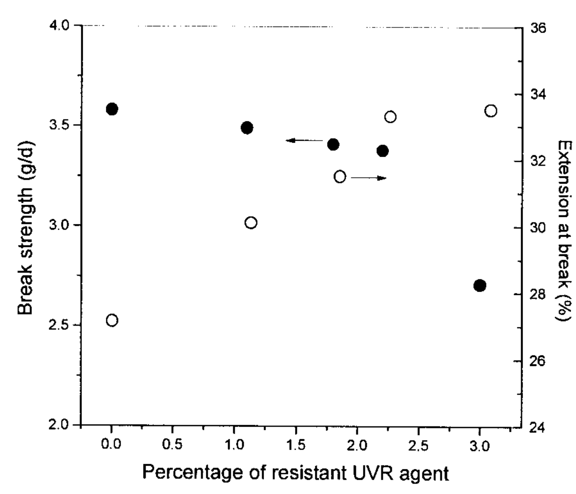

Figure 8 Changes of break strength and the extension of the modified PET fibers at break with the content of UVR-protection agents in the fibers.

CONCLUSIONS

Modified PET fibers and fabrics providing UVR protection were prepared in this study. The transmittance of the modified fabrics was below 10% in the UV-B band, so the fabrics could effectively protect against solar ultraviolet radiation. The property of good heat insulation of the fabrics was measured. The treatment using aqueous NaOH, which resulted in the occurrence of micropores in the surface of the fibers, had little influence on UVR protection and heat insulation of the fabrics. As a comparison, the UVR-protection property of full cotton fabrics and commercial PET fabrics was significantly worse than that of the modified PET fabrics. Measurement of the mechanical properties of the modified fibers showed that the addition of UVR-protection agents resulted in a decrease of the break strength and an increase of the extension at break.

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