A Novel Approach to Excellent UV Protecting Cotton Fabric with Functionalized MWNT Containing Water Vapor Permeable PU Coating

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ABSTRACT: This research paper presented a novel approach of developing excellent protection from ultraviolet (UV) radiation of cotton fabrics by means of water vapor permeable (WVP) coatings containing multiwall carbon nanotube (MWNT), a stable and strongly UV absorbing species. The WVP of MWNT containing UV protective coatings of the present development are formed from solution polymer of hydrophilic polyurethane (HPU). MWNTs were dispersed in HPU solution by functionalization of MWNT. The nanotube containing HPU coating shows excellent protection against UV radiation, with only 1 wt % of MWNT (calculated based on solid content of the polymer), a UV Protection Factor (UPF) of 174 and with 2.5 wt % of MWNT a UPF of 421 was obtained, which stated excellent protection (UPF ≥50) according to the Australian/New Zealand standards. Scanning electron micrographs of coated fabrics surface showed a film like polymer coating, confirming the fabric surface was successfully coated by polyurethane. The coated fabrics would maintain very good water vapor permeability, hence confirmed the wearing comfort. Room temperature (20–23°C) range soft segment crystal melting of HPU enhances the permeability of coated fabrics. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3370–3376, 2007

Key words: coating; UV-blocking; water vapor permeability; carbon nanotube

INTRODUCTION

UV radiation, which is harmful to the skin, is well known. A UV-ray, like visible light, is a segment of the electromagnetic spectrum with a wavelength ranging from 100 to 400 nm, and it is subdivided into three bands: UVA (320 or 315 to 400 nm), UVB (290 to 315 or 320 nm), and UVC (100–290 nm). The terrestrial solar UV consists of only UV with wavelength of 290–400 nm, because UVC and some UVB are absorbed by the stratospheric ozone in the earth's atmosphere.[1] Light radiation of wavelengths 280–400 nm permits tanning of the epidermis. Rays of wavelength 290–320 nm (termed UV-B radiation) causes erythemas and skin burns, which can inhibit skin tanning. Radiation of wavelengths 320–400 nm (termed UV-A radiation) is known to induce skin tanning, but can also cause skin damage, especially to sensitive skin, which is exposed to sunlight for a long period. Examples of such damage include loss of skin elasticity, the appearance of wrinkles, promotion of the onset of erythemal reaction, and the inducement of phototoxic or photoallergic reactions. Some of the more distressing embodiments of skin damage caused by excessive unprotected exposure to sunlight are development of melanomas or carcinomas on the skin. Any effective protection of the skin from the damaging effects of undue exposure to sunlight clearly needs to include means for absorbing both UV-A and UV-B components of sunlight before they reach the skin surface.[2–5] Traditionally, protection of exposed human skin against potential damage by the UV components in sunlight has been affected by directly applying to the skin a preparation containing a UV absorber. In Australia and America, which enjoys especially sunny climates, there has been a great increase in the awareness of the potential hazards of undue exposure to sunlight, compounded by fears of the consequences of alleged damage to the ozone layer. One aspect of the desire to increase the level of skin protection against sunlight has been the consideration of additional measures, over and above the direct protection of the skin.[5] Protection against strong solar radiation is usually afforded by applying a composition that contains a UV absorber (sun cream) direct to the skin. However, the requirements not just to protect the skin directly, but also to provide clothing surrounding the skin as well as textile sun protective articles such as marquees or sunshades with additional protection against UV radiation. Most of the natural and synthetic textile fabrics, whether undyed or dyed, are usually at least partially permeable to UV radiation, therefore, the mere wearing of clothing does not afford adequate protection of the skin from damage induced by UV radiation. Remedy will be

possible here by incorporating UV absorbers in textile fabrics[6] may be by means of coating.

Condensation is of particular interest in a discussion of the merits of coated fabrics when they are used as the outermost layer of any kind of clothing for outdoor activities. To provide wearing comfort to the wearer, the garment should have a high capacity for water vapor transmission, so that the forming perspiration can evaporate and be transmitted from the body to the environment. Earlier, fabrics coated/laminated with rubber or synthetic material, such as PVC, or acrylate had very low water vapor transmission.[7,8] The option may be the hydrophilic polymer, e.g., hydrophilic polyurethane (HPU).

The discovery of carbon nanotubes (CNTs) gives new direction for the use of CNTs in polymeric materials to improve several properties, including UV protection. In view of their high axial Young's moduli, high aspect ratio, thermal and electrical conductivity, thermal stability, high specific area, be it single wall nanotubes or multiwall nanotubes, these are excellent nanofillers in polymer matrices.[9–11] Reinforcement of CNT into the polymer matrices would form a new polymeric material with some functional properties. UV-blocking properties of textile treated with polymer containing fillers are extensively studied by researcher. However, too much conventional fillers are required to protect textile from UV rays, which may affect the hand feel and color of the coated fabrics. Moreover, their UV-shielding effect is not enough. In this study, we have coated the cotton fabrics with three different quantity of multiwall carbon nanotube (MWNT) containing (such as 0.25, 1.00, and 2.50 w/w %) HPU and without MWNT containing HPU. The UV protections as well as water vapor permeability of coated and uncoated fabrics were evaluated.

EXPERIMENTAL

Materials

All chemicals and multiwall carbon nanotube (MWNT) (length about 50 μm and diameter 15 nm) were obtained from Aldrich. Polytetra methylene glycol (number–average molecular weight 2900 g mol^{-1}, PTMG 2900) was vacuum oven dried at 80°C for 12 h, and polyethylene glycol (number–average molecular weight 3400 g mol^{-1}, PEG 3400) was vacuum oven dried for 4 h before use. 1,4-butanediol (1,4-BDO) and N,N'-dimethyl formamide (DMF) were dried over 4 Å molecular sieve. 4,4'-methylene(bisphenyl)diisocyanate (MDI) was used as received.

Synthesis of hydrophilic polyurethane

Hydrophilic polyurethane (HPU) was synthesized from bifunctional diisocyanate (MDI), and diol, such as polyol viz. PTMG 2900 and PEG 3400, and chain extender (1,4-BDO) by two steps polymerization process. To get the linear polymer, the mole ratio of NCO to OH was kept at 1.0:1.0. A 500-mL glass reactor equipped with mechanical stirrer, nitrogen inlet, and thermometer was charged with 8.008 g MDI (32.03×10^{-3} mol), 26.0 g PTMG 2900 (8.9×10^{-3} mol), 4.0 g PEG 3400 (1.176×10^{-3} mol), and 50 mL DMF. The reactor was heated in an oil bath up to 85°C and stirred for 2 h to prepare prepolymer. For chain extension, diluted 1.99 g of 1,4-BDO (21.9×10^{-3} mol) with DMF was added drop wise into the reactor and the prepolymer was subsequently chain extended with 1,4-BDO for 4 h at 85°C. DMF was added into the reactor occasionally when the viscosity of the reaction mixture was too high. The final polymer concentration was about 22% (w/w).

Functionalization of MWNT

Being their ultra fine size and hydrophobic nature, the challenges often lie in the achievement of homogeneous dispersion of MWNTs in the polymer matrices. We have dispersed the MWNT homogeneously in the polymer solution by functionalization of MWNT. First of all, MWNT bead was crushed by hand grinding before functionalization. As literature reported, the solubility of nanotube in aniline is up to 8 mg/mL,[12] therefore the MWNT:aniline was kept 8 mg:1 mL in all cases. In a typical functionalization process, 80 mg accurately weighed MWNT were added to 10 mL of aniline and the mixture was heated at reflux with a high-speed shearing stirring by magnetic stirrer for 4 h in the dark. After being cooled down to room temperature, aniline-nanotube solution was diluted with 20 mL of DMF.

Preparation of functionalized MWNT-HPU solution

HPU nanotube solution was prepared with four different content of MWNT such as 0, 0.25, 1.0, and 2.5 wt/wt % (weight percent with respect to polymer solid content). Functionalized and diluted MWNT solution was added into the previously synthesized HPU, and then the MWNT-HPU solution was mixed with high-speed stirring at room temperature for 12 h. The final HPU-MWNT solution concentration was about 15 wt/wt %.

Coating of fabrics

HPU at different concentrations (0, 0.25, 1.00, and 2.50% w/w) of MWNT was further dissolved homogeneously in N,N'-dimethyl formamide (DMF) in ultra sound bath. Scoured and bleached white cotton fabrics of weight 118 g m^{-2} were coated by knife roller machine (Weamer Mathis AG). The coated fabrics were dried at 90°C for 20 min to remove the N,N-dimethylformamide and then cured at 120°C for

TABLE I
Coding of Coated and Uncoated Fabrics

Sample code	Descriptions
F_0	Uncoated fabrics
F-PU	Coated fabrics with HPU solution containing no MWNT
F-0.25CNT	Coated fabrics with HPU solution containing 0.25 w/w% MWNT
F-1.00CNT	Coated fabrics with HPU solution containing 1.00 w/w% MWNT
F-2.50CNT	Coated fabrics with HPU solution containing 2.50 w/w% MWNT

10 min. The thickness of the uncoated and coated fabric was 0.21–0.22 mm and 0.33–0.50 mm respectively, measured by Mitutoyo thickness gauge (accuracy 0.001 mm). To easily identify the coated and uncoated fabrics throughout the discussions, the samples are coded and tabulated in Table I.

The add-on % on the coated fabric was about 30%, which was calculated by using the formula:

$$\text{Add-on} = [(X - Y)/Y] \times 100\%$$

where Y is the conditioned weight of the control fabric and X is the conditioned weight of the coated fabric.

Characterizations

The surface of coated and uncoated fabrics was observed by scanning electron microscope (SEM) made with a Leica Stereoscan 440 equipped with an Oxford energy dispersive X-ray system, operating at 20 kV.

UV properties of coated and uncoated fabrics were measured according to the Australian/New Zealand standard (AS/NZS 4399 : 1996) with a Varian Cary 300 Conc UV–visible spectrophotometer. The UV spectrophotometer measures the UV properties in terms of UV protection factor (UPF). With a UPF of 50+ defines excellent protection according to Australian/New Zealand standards. The so-called UV-protection factor (UPF) is defined as:[1]

$$\text{UPF} = \frac{\int_{290}^{400} E_\lambda S_\lambda d\lambda}{\int_{290}^{400} E_\lambda S_\lambda \tau_\lambda d\lambda}$$

where λ (nm) represents the wavelength, E_λ is the relative erythemal effectiveness, S_λ (W m^{-2} nm^{-1}) is the solar UV spectral irradiance in (data from Albuquerque, NM are used in this study), τ_λ is the spectral transmittance of the specimen and $d\lambda$ (nm) is the wavelength increment.

A PerkinElmer UV–vis spectrophotometer (Lamda 18) was used to measure the absorbance spectra of the polymer solution (concentration 0.5% w/v) in the wavelength range of 200–700 nm.

PerkinElmer DSC 7 was used to characterize the thermal properties of polyurethane polymers. HPU films were made by removing solvents at 60°C for 12 h in oven and another 12 h at 80°C in vacuum oven. Each samples weighing from 5 to 10 mg was scanned from −50 to 120°C at a scanning rate of 10°C min^{-1} under dry nitrogen purge.

Water vapor permeability (WVP) of coated and uncoated fabrics was measured according to ASTM method (E 96-80B). Round-mouth conical plastic cups with diameter of 60 mm and a height of 90 mm were filled with deionized water. The coated and uncoated fabrics were placed over the top of the cups, and secured the perfect sealing between cup and fabric sample. The gap between the fabric and water surface was about 4 mm. Cups were placed in a constant temperature chamber at the desired temperature (12, 18, 25, 35, or 45°C). During all WVP measurements, air surrounding the fabric had a constant temperature and 70% of relative humidity. An average of three different readings were used for each WVP measurements, which are expressed in units of g m^{-2} d^{-1}, where d is a day (24 h).

RESULTS AND DISCUSSIONS

SEM observation of surface

Observation of the uncoated fabrics by SEM revealed that the surfaces are porous [Fig. 1(a)]. In contrast, interfilamental gaps are filled up by polymer after coating. The nonporous HPU layer was formed continuously over the surface of the coated fabric [Figs. 1(b) and 1(c)]. The presence of nonporous HPU layer suggested that the water vapor permeability of coated fabrics originated from the properties of HPU itself, and thus the mobility of HPU at and above its glass transition and melting point temperature is important in permeation of water vapor molecules.

UV properties of fabrics

The UV light fall on fabric was divided into three parts according to the resulting light distribution: reflection, absorption, and transmission. To make the fabric protecting from UV light, the fabric must not allow transmitting any UV ray through the fabrics. This could be possible by reflection and/or absorption. The UV absorption of coated fabric without MWNT containing HPU revealed a UPF rating of 46 (<+50), very good according to the Australian/New Zealand Standard. This UPF results are a very good protection classification because of reflection and bit of absorption, compared to a low UPF rating of 5.6 for uncoated fabrics, which is classified as nonrateable (Table II). From Table II, we can see that UV transmission of coated fabrics contain-
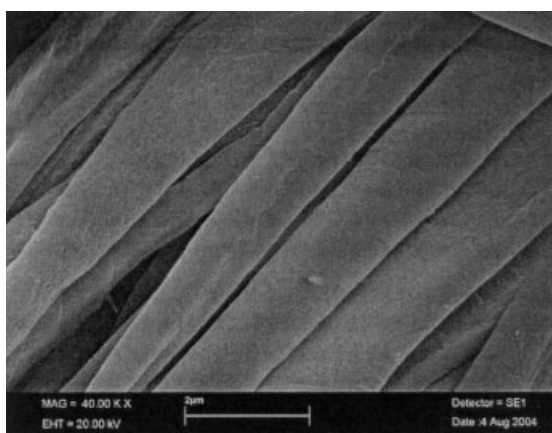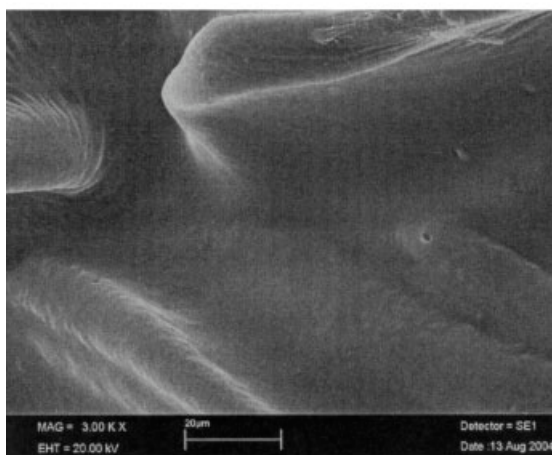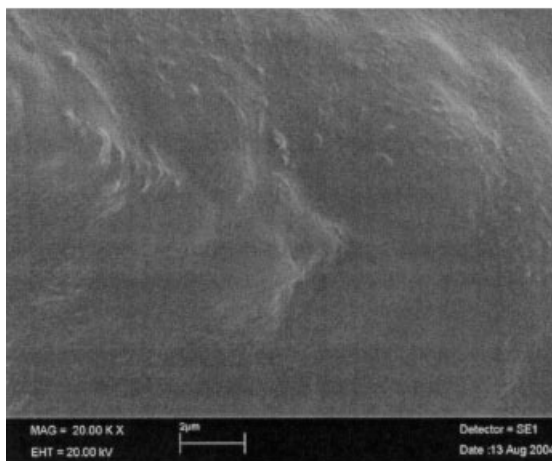
Figure 1 SEM image of (a) uncoated fabric, (b) coated fabric with 0.25% MWNT content PU, (c) coated fabric with 2.5% MWNT content PU.

ing MWNT was almost zero, which is considered the MWNT containing coated fabrics were capable to protect the wearer from UVA as well as from UVB.

**TABLE II**
UV Properties of Treated and Untreated Fabrics

Samples	Mean transmission (%)		Calculated UPF	UPF rating
	UVA	UVB		
F$_0$	18.523	13.112	5.600	Nonrateable
F-PU	2.590	0.940	46.128	Very good (<50+)
F-0.25CNT	1.709	0.709	61.919	Excellent (50+)
F-1.00CNT	0.550	0.196	173.987	Excellent (50+)
F-2.50CNT	0.291	0.105	421.198	Excellent (50+)

UPF rating of coated fabric containing 1.00 wt % of MWNT is 174 and for coated fabric containing 2.5 wt % of MWNT is 421. Very high UPF rating for carbon nanotube containing HPU coating is obviously due to the UV-shielding characteristics of MWNT. Absorption of UV-ray increases with increasing MWNT contained in the HPU. The UV-absorption property is a natural attribute of MWNT, which can be explained by the solid band theory. Owing to the extraordinary strength of the carbon–carbon bond, the small atomic diameter of the carbon atom, and the availability of free π-electrons in the graphite configuration, carbon nanotubes exhibits a number of remarkable electronic characteristics, which are summarized in Table III.[13] For application in microelectronics, the most interesting features are the ballistic (scattering free) and spin conserving transport of the electrons along the tubes, the ability to have metallic as well as semiconducting behavior and the access to the energy gap, which depends on the diameter of the tubes. Carbon nanotube is a kind of semiconductor with a large band gap (10–50 eV) having diameter of 10–50 nm and optically active nanostructures.[13–15] When MWNT is illuminated by light with energy higher than its band gaps (i.e., with wavelength shorter than the absorption edges), the electrons will absorb the energy of the photons and be excited to cross the band gaps, so as to produce the pairs of electrons and holes. Electrons and holes are injected from opposite contacts into a single nanotube molecule.[14] The ambipolar domain, where electron and hole current overlap, forms a microscopic light emitter within the carbon nanotube.

TABLE III
Some Important Electrical Characteristics of Carbon Nanotubes[13]

Electrical conductivity	Metallic or semiconducting
Electrical transport	Ballistic, no scattering
Energy gap (semicond.)	E_g [eV] = 1/d [nm]
Maximum current density	$\sim 10^{10}$ A/cm^2
Thermal conductivity	6000 W/km

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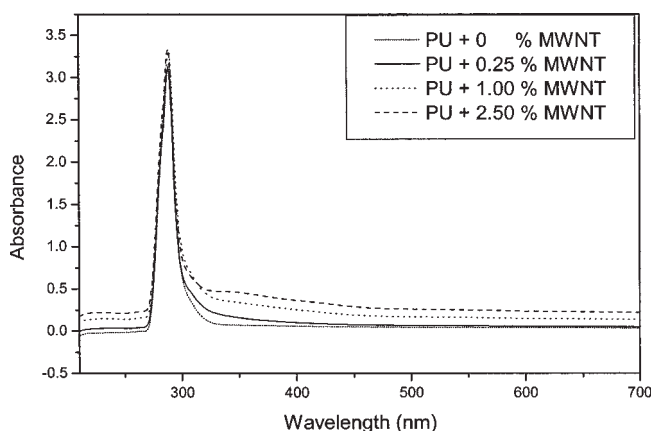
Figure 2 UV–vis spectra of HPU and MWNT content HPU solution in DMF.

Figure 3 Heating and cooling curve of HPU without MWNT.

The photocurrent shows resonances whose energies are in agreement with the energies of excitation states of semiconducting nanotubes of the appropriate diameter. The photocurrent is maximized for photons polarized along the direction of the carbon nanotube.[16] These excited electrons and holes will then result in two competitive consequences: either coming with other holes or electrons, or being captured by the absorbents surrounding MWNT and initiating reduction and oxidation reactions. The former explains how the UV-protector MWNT functions, whereas the latter reveals the mechanism of MWNT as a light catalyzer.[1]

The UV absorption capability of MWNTs could also be proved by UV–vis spetrophotometric analysis. Figure 2 shows the UV–vis spectra of polyurethane solutions as function of MWNT content. For the sake of the comparison, the UV–vis spectrum of pure HPU solution is also shown. The results indicated that there is increase of absorption in the UV range of 200–700 nm with the increase of MWNT content.
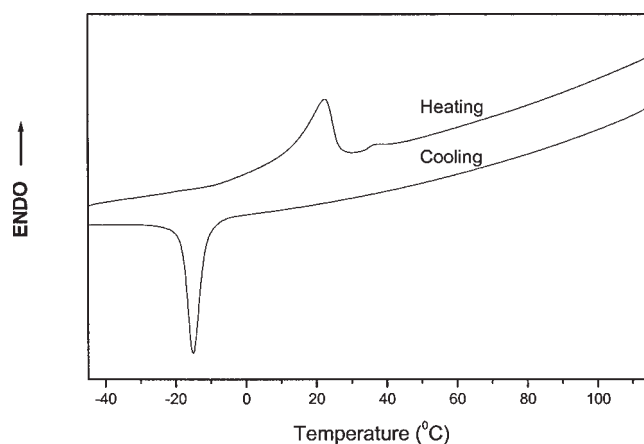
DSC measurements of HPUs

Polymer solution formed thin layer of films on coated fabrics [Fig. 1(b,c)] and the thermal property of film have significant influences on water vapor permeability of coated fabrics at different temperatures. To understand the thermal properties of HPU and MWNT-HPU, we have tested the DSC measurements

TABLE IV
DSC Data of HPU and MWNT-HPU

Samples	ΔH (J g^{-1})	T_{ms} (°C)	ΔH_c (J g^{-1})	T_c (°C)
PU	23.670	22.200	29.196	−15.140
PU-0.25CNT	25.515	22.366	29.025	−16.137
PU-1.00CNT	22.175	21.533	24.890	−14.875
PU-2.50CNT	21.857	20.700	24.257	−15.150

ΔH, heat of fusion; T_{ms}, soft segment crystal melting; ΔH_c, heat of crystallization; T_c, crystallization temperature.

of polymers and results are shown in Table IV and Figures 3 and 4. From the Figures 3 and 4(a), we can see that all samples show sharp endothermic peak, which signifies the presence of crystalline structure in the HPU.

The heat of fusion of the HPU with low content of MWNT (0.25%) is slightly higher than that of sample without MWNT, suggesting that slightly more ordered polymer packing was obtained at 0.25 wt % of MWNT content. This may be due to the presence of small amount of MWNT, which enhances the crystallization process. In fact, crystallization in polymer involved three steps of primary nucleation and relatively rapid spherulitic growth, followed by a slow kinetically difficult improvement in crystal perfection.[17] Little amount of nanoparticles acts as nucleus for crystal, and enhanced the crystallization process. The slightly decrease of crystallization temperature (the temperature corresponding to the maximum of the crystallization exotherm) with 0.25 wt % of MWNT indicates that nanotubes makes the crystallization process easier. There is much lower impact of additional nanotubes, suggesting that almost enough nanotubes are present at 0.25 wt % of MWNT to provide sufficient surface area, so that crystal growth, rather than crystallite nucleation, becomes rate limiting.[18] With the further increase of MWNT decreases the heat of fusion, which is related with the degree of crystallinity. The increasing MWNT content act as filler and suppressed the mobility of soft segment and finally decreased the crystallinity of soft segment in the resulted MWNT-HPU.

Water vapor permeability of fabrics

Water vapor permeability data are tabulated in Table V. The MWNT-HPU is a multiphase system in which the coexistence of phases with different permeabilities
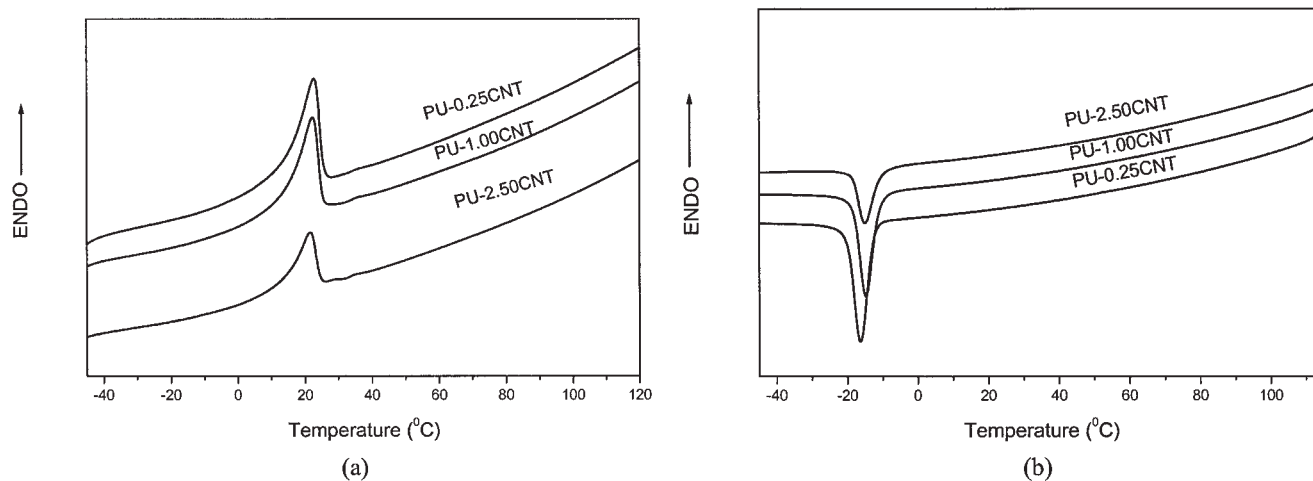
Figure 4 DSC graph of MWNT content HPU. (a) Heating results and (b) cooling results.

can cause complex transport phenomena.[19] In fact, PU polymer phase itself can be considered as a two-phase structure, viz. soft segment and hard segment rich phase structure, the permeability through hard segment is poor. The permeation of small molecules through polymer would enhance when their solubility and diffusivity in polymer increased. The presence of MWNT content may be expected to cause a decrease of permeability due to a more tortuous path for the diffusing molecules that must bypass impermeable nanoparticles. Interestingly, the permeability of coated fabrics with 0.25 wt % of MWNT was increased slightly above the T_{ms}, due the presence of more crystalline structure (DSC results) and their melting enhanced the permeability. Crystal melting would be able to completely plasticize the polymer chains due to presence of water molecules, which leads to a high mobility of polymer chains. At 2.5 wt % of MWNT content, coated fabrics give rise to a lower permeability due to increased stiffness of the polymer chains, which prevents the passage of water vapor molecules. The increase of water vapor permeability is sharp from 18 to 25°C, due to the soft segment crystal melting (20–23°C), which enhances the permeability. Experimental results revealed that there were about 20% reductions of water vapor permeability of coated fabrics as compared with uncoated fabrics at all temperature, except in 18°C, where the reduction of WVP is about 35%. Low permeability at low temperature (12–18°C) is significant, as it keeps the wearer warm by preventing the escape of body heat and/or water vapor losses. Water vapor permeability of coated fabrics increases with increasing temperature, which makes the wearer comfortable in the warm environment.

CONCLUSIONS

We described a novel UV-blocking treatment (coating) for cotton fabrics by functionalized MWNT dispersed HPU solution. Scanning electron micrograph revealed a uniform coating of HPU on cotton fabrics, and gaps between the yarns was filled up by the polymer. The coating protects the cotton fabrics from ultraviolet radiation by providing a strong, broad absorption band in the 280–400 nm range. The UPF of coated fabric is excellent as ranked according to the Australian/New Zealand standard. Instead of that, coated fabric has very good water vapor permeability thus confirmed the thermal and physiological comfort to the wearer.

TABLE V
Water Vapor Permeability Results of Coated and Uncoated Fabrics

Samples	12°C	18°C	25°C	35°C	45°C
F_0	880	1,587	2,125	2,751	3,701
F-PU	715	990	1,735	2,117	3,086
F-0.25CNT	700	1,015	1,760	2,150	3,105
F-1.00CNT	690	970	1,700	2,090	3,000
F-2.50CNT	660	930	1,650	2,011	2,980

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