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Multifunctional cotton fabrics with graphene/polyurethane coatings with far-infrared emission, electrical conductivity, and ultraviolet-blocking properties

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ABSTRACT

In order to introduce multifunctional properties into flexible cotton fabric, graphene and waterborne anionic aliphatic polyurethane composites were prepared and then deposited on the surface of the fabric substrate through facile pad-dry-cure process. The fabrics thus obtained were characterized by scanning electron microscopy and Fourier transform infrared spectroscopy, and their functional properties such as far-infrared emission, electrical conductivity, and ultraviolet (UV) blocking were studied. The coating process enhanced the far-infrared emissivity up to 0.911 in the wavelength range of 4–18 μm. In addition, the ultraviolet protection factor (UPF) of the fabric with 0.8-wt% graphene could reach 500, up to 60-fold higher than that of pristine cotton fabric (UPF 8.19), and its electrical resistivity was decreased from 1.15×10^7 to 2.94×10^{-1} Ω m, which is almost 8 orders of magnitude. The fabrics have also been found to be stable even after 10 cycles of laundering.

1. Introduction

Flexible fibrous textile functional materials have recently attracted attention for their electrical conductivity [1], antibacterial [2], fire retardant [3], superhydrophobic [4], and ultraviolet-blocking properties [5]. Thus, functional properties are commonly imparted to the fabric via approaches such as pad-dry-cure [6], ultraviolet curing [7], plasma-induced graft polymerization [8,9], sol–gel method [10], magnetron sputter technique [2], and application of molecular layer-by-layer self-assembly techniques [11].

Far-infrared rays with a longer wavelength of 6–15 μm can penetrate 2–3 mm [12] into most biological materials and exert strong rotational and vibrational effects at the molecular level, leading to dilation of blood vessels and therefore, enhancement of blood microcirculation and metabolism [13,14]. Far-infrared-emitting materials would transform the energy absorbed from either sunlight or heat of the human body into far-infrared rays within a specific wavelength range, and then reemit them to the human body [15]. Because the far-infrared radiation enhances blood circulation and metabolism as well as promotes the recovery of fatigued muscles, much attention has been paid to the application of germanium and ceramics to textile materials that have close contact with the skin, such as mattresses, sheet materials, and clothing for therapeutic and health care purposes [13–16].

Graphene is a one-atom-thick planar sheet of sp^2-bonded carbon atoms that are tightly packed into a two-dimensional honeycomb lattice, and is a basic building block for graphite materials of all other dimensionalities [17–19]. Because of its unique electronic, optical, thermal, and mechanical properties, graphene differs from most conventional three-dimensional materials, and has attracted great attention as building block for advanced materials with diverse applications [20,21]. Moreover, functional textiles can also be made using graphene. For instance, some researchers coated textiles with graphene or graphene composites and introduced several significant multifunctional properties such as electrical conductivity [18,22],

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antibacterial activity [17], and thermal conductivity [6]. The potential of graphene to enhance far-infrared emission has not been explored. Therefore, in this study, the graphene nanoplate was notably applied as the functional unit to treat cotton fabric for attaining far-infrared radiation and other special properties.

In this article, graphene and waterborne anionic aliphatic polyurethane composite were reported as a multifunctional finishing agent for the woven cotton fabric by facile pad-dry-cure process. The far-infrared radiation emission, electrical conductivity, and ultraviolet-blocking properties were also investigated. Furthermore, the durability of the aforementioned properties was evaluated.

2. Experimental

2.1. Materials

A 1–3-nm-thick and 20-μm-long graphene nanoplate (GNP) provided by Ningbo Moxi Science and Technology Ltd, China, was stably dispersed in an aqueous solution of 25-mg/mL concentration. Waterborne anionic aliphatic polyurethane (WPU) was supplied by Sinopharm Chemical Reagent Co., Ltd (40 wt%, particle size < 100 nm), and distilled water was used in the preparation of all solutions. Ultrapure (100%) cotton fabric plain weave (190 g/m^2), supplied by Jiangsu Hongdou Industrial Co., Ltd, China, was used as substrate fabric.

2.2. Preparation of multifunctional cotton fabrics

During initial stages of the experiment, GNP and waterborne polyurethane composite (GNP/WPU) was prepared. GNP is exfoliated graphite and was used as-received. First, the GNP aqueous solution was treated continuously with ultrasound (600 W, 40 kHz) for 90 min, and its water bath was kept at a constant temperature of 23 °C by circular flow. The concentration of the final GNP suspension was about 25 mg/mL. Then, the GNP solution was mixed with WPU aqueous emulsion under vigorous stirring for 2 h, until the mixture becomes homogeneous. Fig. 1 depicts the GNP/WPU composite and the corresponding chemical structures of relative compounds [5].

The cotton fabric coating was modified with GNP/WPU composite using pad-dry-cure process as follows: The control fabrics were first impregnated in aqueous solution of GNP/WPU composite for 100 min with a liquor ratio of 1:30 at ambient conditions, and then padded through two dips and two nips with padding nip pressure set to obtain 100% wet pickup. Afterward, the padded fabrics were washed with distilled water to remove the unreacted starting compounds. Then obtained product was dried, followed by curing in a vacuum oven at 70 °C for 10 min and 120 °C for 5 min. The weight of the obtained graphene-coated fabric was 240 mg/m^2, and denoted as GNP/WPU-1. Afterward, the above-described entire process was conducted in the resultant GNP/WPU-1 fabric, which increased the graphene-coated weight of the fabric to 320 mg/m^2, denoted as GNP/WPU-2. Furthermore, the entire process was applied again on GNP/WPU-2, and the resultant graphene-coated weight of the fabric was 480 mg/m^2, denoted as GNP/WPU-3.

2.3. Characterization and measurement

The morphology and structure of GNP material were characterized by the following techniques: the morphology was investigated using scanning electron microscopy (SEM, EVO18, ZEISS, Germany), high-resolution transmission electron microscopy (HR-TEM, HITACHI, H-7650, Japan), Fourier-transform infrared (FTIR, Nicolet 5700, Thermo Nicolet Corp., USA) spectrometer with wavenumber in the range of 500–4000 cm^{-1} (KBr disk), and X-ray photoelectron spectroscopy (XPS Kratos AXIS His spectrometer) with a monochromatized AI KR X-ray source (1486.6 eV photons) at a constant dwell time of 100 m s and a pass energy of 40 eV. The anode voltage and current were set at 15 kV and 10 mA. For peak synthesis, a Shirley-type background was use.

Moreover, the dispersed state of the GNP in the WPU polymer matrix was determined by zeta potential measurements. These measurements were made using a Malvern Zetasizer Nano-ZS90 system with irradiation from a 632.8-nm He–Ne laser. The samples were filled in folded capillary cells. The zeta potential was estimated using Smoluchowski approximation as follows [23]:

$$\xi = \eta\mu/\varepsilon, \tag{1}$$

where η is the solution viscosity and ε is the dielectric constant of the liquid.

The structural characterization of the resultant GNP/WPU composite-coated fabrics was also determined using SEM (JEOL JSM-840, Japan) and FTIR (Thermo Nicolet Corp., USA), and their properties were measured as follows.

IR-2 dual-band infrared emissivity measuring instrument was used to test the infrared emissivity of the coated fabrics with wavelengths in the range of 8–14 μm at 37 °C through the active blackbody radiation source to determine normal reflectivity. (Each sample was tested in six different parts and the average value was obtained.) Emissivity was measured as a relative value, assuming that the emissivity of the blackbody is 1. Infrared effect of graphene-coated fabrics was measured using a thermal infrared photospectrometer.

In this study, the surface electrical resistivity of the composite-coated fabric was measured according to the American Association of Textile Chemists and Colorists (AATCC) Test Method 76-2005 by four-point probe technique (RTS-8, Probes Tech, China). Each specimen was tested in different parts of the fabric five times on each side, and the average values were obtained. The environmental temperature and relative humidity were set at 20 °C and 65%, respectively.

Thermal properties (thermal conductivity and thermal resistance) were measured using heat flow meter thermal conductivity instrumentation (NETZSCH HFM 436 Lambda, Germany). The measurable range of conductivity 0.05–8.0 W m^{-1}K^{-1}, and the measurement method conforms to the American Society for Testing and Materials (ASTM) standards, C518-04 and E1530-06. Furthermore, in order to elucidate the dynamic heat transfer of the graphene-coated cotton fabrics, we used a setup in our laboratory to simulate the dynamic thermal response of fabric specimens under unsteady-state conditions. As shown in Fig. 2, fabric specimens were homogeneously scrolled into a tubular shape and a temperature sensor was placed at the center of the scrolled fabric. Each scrolled fabric specimen was introduced into a 100-°C air bath from an initial temperature of 23 °C, while the fixed temperature sensor measured the temperature curve, which was recorded by a computer system at 1-s interval.

The UV-blocking properties of the composite coated fabrics, as determined by UV protection factor (UPF) and UV transmission spectra, were recorded by a UV spectrophotometer (UV1000F, Labsphere Inc., USA). On the basis of the recorded data in accordance with Australia/New Zealand standard AC/NZS 439:1996, UPF was calculated as follows [24]:

$$\mathrm{UPF} = \frac{\int_{290}^{400} E_\lambda \times S_\lambda \times \mathrm{d}\lambda}{\int_{290}^{400} E_\lambda \times S_\lambda \times T_\lambda \times \mathrm{d}\lambda}, \tag{2}$$

where E_λ is the relative erythemal spectral effectiveness, S_λ is the solar UV spectral irradiance, T_λ is the spectral transmittance of the