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Application of rutile and anatase onto cotton fabric and their effect on the NIR reflection/surface temperature of the fabric

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ABSTRACT

NIR irradiation accounts for 52% of the solar irradiance energy reaching the earth, most of which is transferred to thermal energy. This work was undertaken in order to investigate the possibility of applying NIR reflective coatings on cotton fabric with the purpose of surface temperature reduction when irradiated with solar light. Commercial titania was modified by means of calcination treatments. Phase transition from anatase to rutile and growth in particle size were induced, and both processes resulted in an increase of NIR reflectance of the calcined TiO_2. Irregular-shaped TiO_2 particles with sizes of 293–618 nm were obtained. The highest solar reflectance occurred in the TiO_2 sample with an anatase:rutile ratio of 35:65 and a particle diameter of 563 nm. By applying the NIR reflective coating consisting of calcined TiO_2 on cotton fabric, a lower surface temperature was recorded with a maximum difference of 3.9 °C. It was found that a chitosan-TiO_2 coating could provide a better wash fastness than TiO_2 alone.

1. Introduction

Most cities in the South-East Asia have hot and sunny summers. The temperature can reach 36 °C in cities like Hong Kong and Tokyo. People in those cities desire comfortable clothes which can help them to stay cool. Solar heat energy is mainly generated in 700–1100 nm [1], which is within the NIR radiation portion. The solar thermal energy absorbed by the human body results in a heat gain and causes the body temperature to rise, making people feel hot under the sun. With the advancements in science and technology, a variety of functional garments that can stay cool under the sun have been introduced in the market, providing a cooling effect and hence extra comfort to the wearer. The advancements referred have offered opportunities to add value to both activewear and outerwear garments, and many companies have invested large sums in the research and development of these cooling textiles.

A new approach using the NIR reflective materials in textiles to achieve the cooling effect is therefore proposed in this work. NIR irradiation accounts for 52% of the solar irradiance energy reaching the earth, most of which is transferred to thermal energy. This work was undertaken to investigate the possibility of applying the NIR reflective coatings on cotton fabric with the purpose of temperature reduction, which has not been explored by previous researchers. NIR reflective materials have been used in many different areas and have proven to have a significant cooling effect, with the application in the architectural sector being the most extensively studied. The cool roof coatings for the buildings and construction industry were first introduced in the 1970s, and they were designed to reflect incident solar radiation as well as minimise the transfer of heat to the interior of the structure, thus reducing the energy required for cooling [2–5]. Since then the NIR reflective materials have been studied by many other researchers and their applications expanded to other fields such as military camouflage [6–11], spacecraft thermal control coatings [12–15] and greenhouse screen materials [16,17].

NIR reflective pigments are pigments that have a high reflectance in the NIR region, and hence they are able to reflect most of the solar heat reaching the coated surface and reduce the heat build-up. They reflect the wavelengths in the infrared region in addition to reflecting some visible light selectively, making them appear to be white or other different colours. Conventional pigments tend to absorb near-infrared radiation. The replacement of these NIR absorbing pigments by NIR reflecting pigments that have the ability to reflect more near-infrared radiation can lead to the development of coatings that have similar colours and yet higher solar reflectance [18]. NIR reflective pigments can be classified as inorganic pigments, organic pigments (including chlorophyll [1], black pigments containing copper phthalocyanine [19,20], azo pigments [21] and a few perylene-based pigments [22]) and metallic pigments (aluminium

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flakes [2,23]), metallised mica flakes or finely powdered metals [24,25]). Inorganic pigments have been extensively studied, especially for applications such as cool materials for residential roofing [5]. They exhibit excellent weatherability, heat stability and chemical inertness. They can withstand chemically aggressive environments and still retain their colour [26]. Recently reported inorganic pigments are listed in Table 1.

Among the common inorganic pigments, rutile titanium dioxide has a high NIR solar reflectance of about 87.0% due to its high refractive index. Therefore TiO_2 was selected to be studied in this work due to its well-proven NIR reflective property. Generally, it is used as a white pigment which provides both an effective non-selective light scattering and good hiding power. The main uses of pigmentary TiO_2 are coatings and paints, which accounted for 58.8% of the world's consumption of TiO_2 pigments in 2007 [37]. In addition, it is non-toxic and has been used in sunscreens since 1952. Other advantages include its high availability, biocompatibility, low price, chemical and biological inertness [38,39]. Both the particle size and refractive index would significantly affect the NIR reflectance of TiO_2 particles [1,40]. For the best NIR reflection, dispersed TiO_2 particles are sized at 1/3 to 1/2 of the wavelength of the incident radiation that is to be reflected [26], that is because the Fresnel's rules state that the optimal reflection occurs when the diameter of the particle equals half the wavelength [41,42].$D=\lambda/2$ The scattering efficiency decreases rapidly as the particle size varies from the optimum. This decrease is by about 60% for particles twice the optimum size [39]. Since 700–1100 nm is the most significant heat-producing region in the NIR region, in order to reflect solar heat energy and reduce heat gain, pigments with a particle size of 350–550 nm are required.

Diffuse reflectance is sensitive to the value of refractive index, it is determined by the formula Np/Nm, where Np is the refractive index of the material in question, and Nm is the refractive index of the adjacent medium (air in this study). The larger the difference between the refractive index of the pigment and that of the medium in which it resides, the greater the refractive light scattering. The refractive index of air is impossible to be altered, but by choosing pigments with high refractive index, which are usually good reflectors, it is possible to increase reflection [21,41]. The average refractive index of rutile is 2.73, compared to 2.55 for anatase [43,44]. By annealing anatase TiO_2 powder, it is possible to increase the scattering efficiency through the phase transformation to rutile.

Recently, the effect of calcination on the phase transition and morphological evolution of TiO_2 was studied. Zhao et al. and Choudhury et al. proposed that the anatase-to-rutile phase conversion and grain growth were temperature-dependent [45,46]. Thermal treatment first removed the grain boundary of the closely associated smaller nanocrystallites in the agglomerates, they then migrated from the interface to larger crystallites, and the grains grew in size. Finally, phase transformation and grain growth to larger rutile nanocrystallites were resulted with more severe annealing. In the present study, the phase transition and morphological evolution of the TiO_2 particles upon several different calcination conditions have been studied. Besides, NIR reflectance of the TiO_2 particles has also been measured to investigate the effect of calcination, crystal structure and morphology on the NIR reflection.

2. Material and methods

2.1. Sample preparation

Cotton fabric was cleaned using BASF Kieralon F-OLB conc (detergent concentration = 2 g/L, liquor-to-goods ratio = 50:1) at 80 °C for 30 min and dyed at 1/1 standard depth with Levafix Amber CA (amber), Levafix Fast Red CA (red), Levafix Blue CA (blue) and Remazol Deep Black RGB (black) according to ISO 105-A06. Anatase titanium dioxide powder was obtained from Aldrich. It was calcined at different temperatures and duration to obtain eight mixtures of anatase and rutile with different ratios, as shown in Table 2. X-ray diffraction (XRD) patterns of the TiO_2 powders were collected using a Rigaku Smartlab X-Ray diffractometer, operating with Cu Kα radiation. Anatase to rutile percentages were calculated from the resulting diffractograms using the Spurr equation [47]:

$$\%_{\mathrm{Rutile}} = \frac{1}{1+0.8[I_A(101)/I_R(110)]}$$

where I_A is the intensity of (1 0 1) peak of anatase and I_R is the intensity of (1 1 0) peak of rutile. The average diameter of titanium dioxide powder was measured by dynamic light scattering (DLS) using a Brookhaven ZetaPlus zeta potential analyzer. Stable samples were prepared by dispersing the powder in deionised water, with a trace amount of sodium pyrophosphate as a stabilising agent, followed by sonication to break the agglomerates. The average diameter was derived from the results of 10 runs using the same dispersed sample.

The titanium dioxide powder was applied onto cotton fabric by a pad-dry-cure method, with chitosan as a mediator. The dyed cotton fabric was first padded with chitosan (1% in aqueous acetic acid (1%)) at 80% pickup using a 2-roll horizontal padder (Type HF, Werner Mathis AG) and then oven dried at 80 °C for 5 min, followed by soaking in a sodium carbonate solution (1%) overnight and then washed repeatedly until the pH was 7. A TiO_2 (4% (w/v)) dispersion was prepared by sonicating the TiO_2 powder in deionised water in a sonication bath for 3 h, followed by the addition of triethylene glycol (0.5%(w/v)) and magnetic stirring for 30 min. The chitosan-padded fabric was padded twice with the TiO_2

Table 1
Recently reported NIR-reflective pigments.

Researcher	Pigment(s) reported	Colour of the pigment(s)	Performance
George et al. (2011) [27]	Si-doped yttrium molybdate	Dark yellow	NIR reflectance = 98% (at 1100 nm region)
	Pr-doped yttrium molybdate	Dark brown	NIR reflectance = 92%
Gonome et al. (2013) [28]	Submicron-copper oxide	Black	No figures reported
Han et al. (2013) [29]	Fe-doped $YMnO_3$	Blue-green	NIR reflectance = 53% Solar reflectance = 33%
Jose et al. (2013) [30]	Lanthanum–strontium copper silicates	Blue	NIR solar reflectance = 67%
Jose et al. (2014) [31]	Y_2BaCuO_5	Bright green	NIR solar reflectance = 38%
Li et al. (2013) [32]	Cr_2O_3-$3TiO_2$	Orange	NIR reflectance = 53%
Sreeram at al. (2008) [33]	$Ce_{25}Pr_{0.8}FeO_y$ and $Ce_{25}Pr_{0.8}MoO_y$	Reddish brown and reddish orange	NIR reflectance = 70–80% (in 1000–2200 nm)
Sangeetha et al. (2012) [34]	La- and Pr- doped chromium(III) oxide	Green	NIR reflectance = 85%
Wang et al. (2012) [35]	Cu-doped sodium zincophosphate	Black	NIR reflectance = 51%
Wang et al. (2013) [36]	Nickel titanate	Yellow	NIR reflectance = 62%