Smart Textiles Coated with Eco-Friendly UV-Blocking Nanoparticles Derived from Natural Resources

N. Raman Dhineshbabu and Suryasarathi Bose*

Department of Materials Engineering, Indian Institute of Science, Bangalore 560012, India

Supporting Information

ABSTRACT: Herein, eco-friendly iron titanate nanoparticles, FeTiO₃ (FT), derived from natural resources (like ilmenite sand) were coated onto cotton fabrics (CF) to develop smart textiles with enhanced UV-shielding property. The FT nanoparticles were dispersed in a polyurethane (PU) matrix, and the resulting nanocomposite was coated on CF. In addition, few sandwich architectures were designed by rationally stacking CF coated with PU and FT nanoparticles. The resulting sandwich structures blocked UV−rays mainly by absorption. FT nanoparticles were comprehensively characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, UV−vis, vibrating sample magnetometer, and thermogravimetric analysis. FT was suitably surface-functionalized to enhance the quality of dispersion in PU, thereby facilitating effective coating on CF. The latter was systematically evaluated by microscopic and spectroscopic techniques. In addition, flammability of the coated CF was evaluated and the char was assessed to gain insight into the fire-retardant properties. Interestingly, CF coated with FT exhibited a strong UV-shielding ability in sharp contrast to CF coated with PU. Further, the sandwich architecture consisting of CF with FT and PU resulted in an increase in the ultraviolet−protecting factor value to >50 compared to only PU-coated CF. Our results indicate that the sandwich structure holds excellent promise in the quest of designing smart textiles with enhanced UV shielding.

INTRODUCTION

Cotton fabrics (CF) have been used in various applications for their outstanding properties like softness, biodegradability, and breathability, but they suffer from certain limitations like prone to bacterial attack, poor UV shielding, and flammability.1−3 In recent years, ceramics (TiO₂, SiO₂, ZrO₂, MgO, ZnO) and polymeric materials have been used to coat the fabric to enhance their functional properties.4−6

The physical and optical properties of perovskites have been used in a number of applications like electronics, electro-optics, etc.7−10 Perovskites are one of the most important crystallographic families with general stoichiometry of ABX₃.11 Oxides (ABO₃)12,13 and metal trihalide perovskites (CsPbX₃; here, X = Cl, Br, and I)14 have recently gained wide interest in electronics, photovoltaics, nanotechnology, and biotechnology industries.15−17 Oxides of ABO₃ type, with A being a metal, B being titanium, and O being oxygen, have gained wide attention due to their applications in different technologically relevant fields.11−13 Interestingly, perovskite metal oxides exhibited a variety of interesting physical properties, including ferroelectric, dielectric, pyroelectric, and piezoelectric behaviors.10 During the past decades, composite materials such as transition/rare-earth metal-doped perovskite materials (ABO₃) have been prepared and studied for their unique properties.15

The composition of a naturally occurring sand, ilmenite (with a general formula of MTiO₃), including metals (M) such as nickel (Ni), cobalt (Co), zinc (Zn), iron (Fe), manganese (Mn), and copper (Cu) among others, has been assessed for its unique optical properties.18−22 Among these, iron titanate (FeTiO₃ (FT)) is one of the most common minerals and is well known as a feedstock for industrial production of TiO₂.23,24 Ilmenite is economical, abundant, and can be found in various geographical locations, including America, Australia, India, Europe, Asia, and Africa.25 It is weakly magnetic,26 exhibits a wide band gap (2.58−2.9 eV), and finds application in visible light antiferromagnetic semiconductor materials with a Neel temperature of around 52 K. The wide band gap of FT makes it a potential candidate for spintronic devices, optoelectronics, high-temperature integrated circuit, high-power electronic devices, and photocatalyst activities.27−28 The rhombohedral crystal structure of titanates possess diverse properties.20,26

In recent times, a variety of nanocomposite-based textile products have been studied for flame-retardant, wettability, and sustainable UV-blocking applications.2−3 Recent research focuses on the development of functional textiles using polymeric materials or biomolecules.5,6,29 In this regard, attempts have been made to incorporate nanoparticles in fabrics, which may be readily achieved with a specific polymer using some coating techniques, such as pad-dry cure method,30 dip coating,31 in situ polymerization method,32 knife over roll method,33 etc.
Herein, polyurethane (PU), which exhibits excellent adhesion quality, is used to coat the surface of the fabrics. Attempts have been made to surface-coat the CF with various nanomaterials like Ag/TiO$_2$, graphene, TiO$_2$, and diammonium hydrogen phosphate for electrical conductivity, UV blocking, antibacterial effect, flame-retardant property, etc. In addition, various surface functionalization techniques on the nanoparticle surface have been reported to homogeneously disperse in PU for coating onto the fabrics.

In this study, an eco-friendly and facile approach of coating perovskites on CF is designed to enhance the fire-retardant and UV-blocking properties of the textile. To achieve this, naturally derived FeTiO$_3$ nanoparticles were prepared by acid extraction method from ilmenite sand. The microstructures and morphology of the FT nanoparticles were well characterized. PU solution containing FT nanoparticles was prepared via in situ polymerization method and coated onto CF by dip-coating method. The coating of PU and FT/PU composites onto CF is a facile and industrially viable route for coating at large scales. The resultant fabrics were examined by scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) to assess the surface morphology and thermal stability, respectively. The limited oxygen index (LOI), wettability, and UV-blocking properties were investigated systematically. Taken together, this study opens new avenues in the smart textile domain with enhanced UV protection.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of FT Nanoparticles.

The X-ray diffraction (XRD) pattern of FT nanoparticles is shown in Figure 1a. All of the observed peaks matched with the standard JCPDS file 01-075-1211, and the peak positions at 2$\theta$ = 24.9, 32.69, 35.47, 40.81, 48.61, 54.18, 62.58, and 64.10°, corresponding to (012), (104), (110), (023), (024), (116), (124), and (300) planes are evident. It is confirmed that the prepared FT nanoparticles are rhombohedral and no impurities were found in the XRD pattern. The average crystallite size is calculated using the Debye-Scherrer equation to be ca. 30 nm. The surface morphology of the prepared nanoparticles is analyzed by SEM. The globular-shaped morphology of the nanoparticles with an average size of 100 nm can be seen from Figure 1b. The quantitative energy-dispersive spectrometry (EDS) analysis reveals the elemental composition of the samples, which consists of Fe, Ti, and O, and is shown in Figure 1c. The weight fractions of all elements (Fe, Ti, and O) are determined from EDS and are presented in the table shown in the inset of Figure 1c. The transmission electron microscopy (TEM) image shows that the particles are mostly agglomerated (Figure 1d). The obtained concentric ring in the selected area electron diffraction (SAED) pattern (inset of Figure 1d) shows that the diffraction pattern confirms the crystalline nature of the prepared FT particles.

The hysteresis loop of FT nanoparticles is shown in Figure 2a (from $-20$ to 20 kOe), and the expanded view from $-100$ to 100 Oe at 300 K is shown as inset. The observed results show that $M$–$H$ loops do not saturate even up to 20 kOe, which is due to the paramagnetic or antiferromagnetic nature of the material. Magnetic parameters like saturation magnetization ($M_s$), remanent magnetization ($M_r$), and coercivity ($H_c$) are obtained from hysteresis loops, which are measured at (0, 0) point as 0.11 emu/g, 0.062 emu/g, and 67 Oe, respectively. Squareness ratio and anisotropy constant are also determined from the above-mentioned equation, and the resultant values are 0.56 and 7.52 Oe, respectively.

To confirm the decomposition of FT nanoparticles, TGA was carried out. A three-step (a–c) degradation is observed for FT nanoparticles, which is shown in Figure 2b. In step (a), a
A dominant weight loss of ca. 7.079\% is observed between 496 and 782 °C in step (b), which is attributed to the oxidation of carbon to form volatile species, such as CO and CO$_2$. In step (c), FT nanoparticles completely decomposed. The amount of FT nanoparticles is calculated to be ca. 83\% from TGA.

**Surface Analysis of UC and Coated Fabrics.** For direct comparison, the surface morphologies of coated (PUC, FTPC) and UC fabrics are analyzed by SEM, as shown in Figure 4a–f. The recorded SEM image of UC fabric (Figure 4a) is shown at lower magnifications. From the SEM images, it is observed that PU is covered on the fabric surface. Moreover, extended network-like structure of FT particles appears on the surface of the cotton fibers, as observed in Figure 4e. EDS measurements are carried out to confirm the elemental composition of coated and UC fabrics, and the results are summarized in Figure 4b,d,f. The EDS analysis shows that C and O elements are present in the FTPC fabrics along with Fe (06.69 wt \%) and Ti (07.06 wt \%).

**Structural and Wettability Studies of Cotton Fabrics.** The crystallographic nature of UC and coated (PUC and FTPC) cotton fabrics are investigated by XRD, and the results are shown in Figure 5. Typical diffraction peaks of cellulose I fibers (JCPDS file no. 03-0226) were observed at 2θ = 15.4, 16.8, and 23.1°, which can be indexed to (101), (101), and (002) planes, respectively. It is observed that the diffraction peak of cotton fabrics is similar to that of PU-coated fabrics because of the amorphous nature of polyurethane. Nevertheless, the FT nanoparticles are adhered to the surface of fabrics, as is evident from Figure 5. On the other hand, the FTPU-coated fabrics exhibited peaks at 27, 48.5, and 67.3°. This observation indicates that the FT nanoparticles are accumulated on the surface of the cotton fabrics.

**Figure 2.** (a) Vibrating sample magnetometer (VSM) and (b) TGA of FT nanoparticles.

**Figure 3.** Optical properties of FeTiO$_3$ nanoparticles: (a) absorption and transmittance and (b) band gap.
The surface wettability property of coated and UC fabrics is evaluated from the static contact angle of water on its surface, as shown in Figure 6. It can be seen that the water droplet is completely absorbed on UC fabric (Figure 6a) due to the hydrophilic nature of cotton (water contact angle (WCA) angle = 0°), which is ascribed to the −OH group of cellulose and its weave structure.40 After coating with PU, the surface of the coated fabrics becomes rough and the contact angle for PUC fabrics remains unaltered (Figure 6b), as the water droplet flattens. In Figure 6c, the contact angle for FTPC fabric is observed to be 86.2°, due to the presence of hydrophobic silane coupling agent41 on the surface of FT nanoparticles. This hydrophobicity in the organically modified FT nanoparticles might lead to an enhancement in the dispersion of FT nanoparticles.

Evaluation of Thermal Decomposition Behavior of UC and Coated Fabrics. Flammability of textile materials is well understood by describing their burning behavior, in

Figure 4. (a, c, e) SEM images and the corresponding EDS images of UC, PUC, and FTPC.

Figure 5. XRD patterns of all coated and uncoated fabric samples.

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Evaluation of Thermal Decomposition Behavior of UC and Coated Fabrics. Flammability of textile materials is well understood by describing their burning behavior, in
particular, easiness of ignition and sustained burning after ignition. An effectual flame-retardant action is specified by the high thermal stability and char residue for coated and UC fabrics. Thermal decomposition behaviors like weight loss and residual char of the UC and coated cotton fabrics are comprehensively investigated by TGA, and the results are depicted in Figure 7a and Table 1. As seen in Figure 7a, TGA of the cotton fabric shows a three-step decomposition process.

![Figure 6. Contact angles of (a) UC, (b) PUC, and (c) FTPC.](image1)

![Figure 7. (a) TGA measurements, (b) char residue at 650 °C, (c) LOI test, and (d) relation between char residue and LOI of all coated and uncoated fabric samples.](image2)

| s. no. | samples | $T_{max1}$ (°C) | $T_{max2}$ (°C) | $T_{max3}$ (°C) | residue at 650 °C (%) | LOI (vol %) |
|-------|---------|----------------|----------------|----------------|----------------------|------------|
| 1     | UC      | 237            | 335            | 542            | 8.33                 | 19.8       |
| 2     | PUC     | 240            | 336            | 478            | 13.30                | 19.9       |
| 3     | FTPC    | 259            | 339            | 593            | 14.03                | 21.1       |
In the initial stage, the fabric is decomposed due to the evaporation of water and char formation from the amorphous region of cellulosic fiber. In the second stage (230–460 °C), the decomposition of residue from the carbonization process is manifested. The thermal degradation of the char occurs in the last stage (460–800 °C and above 800 °C), where the complete decomposition or oxidation or ignition of the carbonaceous species is expected. Here, the UC fabric is completely degraded. In Figure 7a, the initial weight loss of the degradation of UC cotton fabric is observed to be 5% below 100 °C. This weight loss may be attributed to the removal of moisture. The major weight loss of UC fabrics begins at 300–700 °C, as shown in Figure 7a.

The data in Table 1 show that the degradation of cellulose species leads to the formation of residue of all fabrics. In contrast, the coated cotton fabric has a higher $T_{\text{max}}$ with respect to the UC cotton fabric (Table 1) due to the presence of FT nanoparticles. Compared to that of the UC fabric, the $T_{\text{max}}$ values of the PUC- and FTPC-coated cotton fabrics obtained are found to be higher, 240 and 259 °C, respectively. The obtained results revealed that the FT nanoparticles can accelerate the dehydration and char formation of the coated fabrics. This is advantageous for reducing volatile species during combustion and preventing underlying materials from further burning. The major weight losses of UC, PUC, and FTPC fabrics were recorded at 335, 336, and 339 °C respectively.

In addition, the formation of the residue at 650 °C, which corresponds to the weight loss of all of the fabric samples, is shown in Figure 7b and Table 1. In particular, FTPC fabric induces a large amount of char residue compared to PUC and UC fabrics. This result indicates that the enhancement of thermal stability of the coated fabrics significantly improved their fire-resistant performance compared to UC fabric.

**Flammability Performance of UC and Coated Fabrics.** LOI evaluates the flame-retardant properties of coated and UC fabrics. In this test, a mixture of N$_2$ and O$_2$ is passed through a cylindrical heat-resistant glass chimney containing fabric samples clamped vertically from the bottom. A Bunsen burner is used to ignite the sample from the top. The minimum amount of oxygen needed to ignite the sample is noted and is reported as LOI. Basically, textile materials are considered to be easily flammable and flame-retardant materials when LOI values fall in the range of 23% and above. All of the coated and UC fabric samples have been tested, and the results are listed in Table 1 and Figure 7c. The LOI values of the UC, PUC, and FTPC fabrics are found to be 19.8, 19.9, and 21.1%, respectively. Therefore, the LOI values of all coated fabrics are found to be higher than the control UC fabric (Table 1). From the results of thermal degradation (TGA) and LOI, it is evident that the % of char residue at 650 °C and the minimum concentration of oxygen (vol %) required to ignite the sample support the flame-retardant property of coated fabrics. This observation is shown in Figure 7d.

**Assessing the Surface Morphology of Fabric Samples after LOI Test.** A detailed investigation of the morphology of the char is carried out by SEM, as shown in Figure 8. For UC fabrics, the combustion of the fabric shows complete degradation and the fiber weave structure is apparent (see Figure 8a). In contrast, the residue obtained from the coated fabric (Figure 8b,c) suggests that the weave structure is preserved. Remarkably, the residue of FTPC also suggests that the interlace structure of fibers is well preserved compared to that of PUC and UC, as inferred from Figure 8c. It is envisaged from the SEM images that the incorporation of FT into cotton fabrics can remarkably increase the stability and compactness of the fiber. It is clearly seen from the SEM images that the coated fabrics retained the interweave structure, which can be attributed to FT nanoparticle and PU matrix on the surface of...
the fabrics. Moreover, the ignition temperature of coated fabrics was higher due to the addition of FT nanoparticles. Hence, the structure and stability of FTPC fabrics suggest that they exhibit excellent fire-retardant properties and can be further explored for commercial applications.

**Assessment of UV-Shielding Properties of UC and Coated Fabrics.** The shielding properties of UC and coated (PUC and FTPC) cotton fabrics against UV radiation are analyzed in the wavelength range of 280–400 nm, as shown in Figure 9. The average transmittance percentage of UC fabrics is ca. 77% for both UV-A and UV-B. As seen in Figure 9, the blocking percentage of the coated fabrics indicates minor transmittance of UV radiation compared to UC fabrics. The blocking % of coated fabrics shows that the percentage of blocking UV-B radiation is higher than that of UV-A (see Table 2). The PUC fabrics show higher UV blocking, ca. 90%, because of reflection and little absorption, compared to UC fabrics. On the other hand, the reduction in transmittance is observed in FTPC fabrics. Here, FeTiO3 nanoparticles aid in strong UV absorption ability. It is interesting to note that the blocking % of FTPC fabric is higher than PUC fabrics.

According to AS/NZS 4399:1996 standard, a ultraviolet-protecting factor (UPF) value of >50 indicates excellent protection against UV radiation. The resultant UPF values of all fabric samples are listed in Table 2. The UPF value of coated fabric is much higher than 50, which reveals higher blocking of UV radiation.

Additionally, the sandwich layer of the coated fabrics for UV-shielding applications is shown in Figure 9a. The schematic representation of the layered coated fabrics is shown in Figure 9b. The UV-blocking percentage and UPF of sandwich fabrics (PFTPC) are 99.9% and 2000, respectively, where the former is similar to the UV-blocking percentage of FTPC fabrics. Therefore, PFTPC fabric can be used as a UV-shieldable material. To check the UV shielding of recent synthetic materials like functionalized carbon nanotube

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**Figure 9.** UV-blocking property: (a) transmittance spectra of all coated and uncoated fabric samples and (b) scheme of sandwich structure of coated fabrics.

**Table 2. UV Blocking % of All Coated and UC Fabrics**

| s. no. | fabric | T (UV-A) (%) | T (UV-B) (%) | % blocking UV-A | % blocking UV-B | UPF value |
|-------|--------|--------------|--------------|----------------|----------------|-----------|
| 1     | UC     | 22.8         | 24.11        | 77.2           | 75.82          | 12        |
| 2     | PUC    | 14.54        | 5.84         | 85.46          | 94.16          | 467       |
| 3     | FTPC   | 0.23         | 0.06         | 99.77          | 99.94          | 1218      |
| 4     | PFTPC  | 0.05         | 0.05         | 99.95          | 99.95          | 2000      |
(CNT),\textsuperscript{44} we coated CNT with PU onto cotton fabrics. The composite-coated fabrics were then evaluated for UV-shielding ability (see Figure S1). In Figure S1a, the UV transmittance properties of CNPC and the sandwich layer of FTPC and PUC along with CNPC fabrics are measured in the wavelength range of 280–400 nm. Table S1 lists UPF values and blocking percentage of UV transmittance in the wavelength ranges of 280–315 and 315–400 nm for UV-B and UV-A, respectively. The results indicate that excellent UV-shielding property is exhibited by PU/acid-functionalizedCNT-coated fabrics (inset of Figure S1a) and the blocking percentage is 92%, which is higher than that of the PUC fabric but lower than that of FTPC fabrics. Therefore, although CNT has strong UV absorption ability and is used as a blocking agent against UV radiation, our results indicate that eco-friendly material derived from natural resources can block UV more efficiently. In general, CNT has a large band gap (10–50 eV) and the electrons that absorb the photon energy go to the excited state and produce a pair of electrons and holes. This results in effective absorption of UV.\textsuperscript{45–47}

Additionally, the sandwich layer of the coated fabrics is shown in Figure S1, which is used for UV-shielding applications. The shielding mechanism of the layered coated fabrics shows excellent UV-blocking properties, as shown in Figure S1b. Furthermore, the intermediate layer of CNPC fabrics placed between two layers of PUC fabrics also exhibited better UV-shielding property than CNPC fabrics. Additionally, FTPC fabrics inserted in the PCNPC fabrics were also evaluated for UV-shielding performance. The observed results indicate that PCNPC fabrics also showed excellent UV-blocking ability compared to PCNPC and FTPTC. The sandwich fabrics (FTPC, PCNPC, and PFPCPC) showed higher UPF than polymer-coated fabrics (FTPC > CNPC > PUC) and UC fabrics.

Taken together, our study reveals that eco-friendly and naturally derived FT nanoparticles can block UV effectively compared to other synthetic blocking agents. Further, when these coated fabrics are rationally stacked, the UPF values are significantly higher compared to single layer. Thus, the results presented here suggest that FT-coated fabrics can be a potential candidate for UV shielding in textile, optoelectronics, and packaging applications.

\section*{CONCLUSIONS}

In summary, FeTiO\textsubscript{3} nanoparticles were successfully synthesized by acid extraction method and systematically characterized. The band gap of FT nanoparticle was determined to be 2.9 eV, and the VSM results indicated that FT nanoparticles show antiferromagnetic properties at room temperature. A composite mixture of FT nanoparticles and PU solution was prepared by in situ polymerization method and coated onto cotton fabrics. The FTPC fabrics showed higher LOI values compared to other coated and UC fabric samples. FTPC formed a layer wrapping around the cotton fabrics to protect them from being damaged by heat and glow. Moreover, the intrinsic UV-blocking property of FT nanoparticles resulted in excellent UV protection in the coated fabrics. Few sandwich structures consisting of PU coating and FT resulted in excellent UV-blocking performance and showed higher UV-blocking ability compared to single layers. Thus, our results indicate that naturally derived FT nanoparticles-coated CF can block UV effectively and can further be explored for myriad applications.

\section*{EXPERIMENTAL DETAILS}

\subsection*{Materials.} The ilmenite ore used in this study was obtained from Tamil Nadu, India. Bleached and mercerized cotton fabrics (116 ends/84 picks) with a weight (15 × 15 cm\textsuperscript{2}) of 138.84 g/m\textsuperscript{2} were commercially obtained and used as substrate. 4,4-Methylene bis(p-phenyl isocyanate) (MDI, M\textsubscript{w} = 250 g/mol), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}, 29–34 wt %), and (3-aminopropyl)triethoxysilane (99%, APTES) were procured from Sigma-Aldrich. Poly(ethylene glycol) (PEG, M\textsubscript{w} = 4000 g/mol) was obtained from SLR Chemicals, India. Analytical-grade sulfuric acid (H\textsubscript{2}SO\textsubscript{4}), sodium hydroxide (NaOH), ammonium hydroxide (NH\textsubscript{3}OH), and N,N-dimethylformamide (DMF) solution were procured from SD Fine Chemicals Limited.

\subsection*{Synthesis of Precursors from Raw Ilmenite.} Raw ilmenite was used as the starting material for this synthesis process. The obtained ore was subjected to digestion with concentrated H\textsubscript{2}SO\textsubscript{4} (about 98% GR) at 300 °C for 3 h in a muffle furnace. The resulting dry cake of the mixture was allowed to cool to room temperature. After digestion, it was leached using deionized (DI) water to yield a water-soluble iron titanium sulfate solution, which is shown in Scheme 1.

\subsection*{Synthesis of FT Nanoparticles.} The precursor solution prepared above was used as a base material to synthesize FeTiO\textsubscript{3} nanoparticles (see Scheme 2). The obtained iron titanium sulfate precursor solution (500 mL) was taken in a 1000 mL beaker and stirred vigorously at 700 rpm. Then, the reducing agent (25 mL of ammonia) was added dropwise into the precursor solution and maintained at pH 7. Later, the obtained solution was centrifuged at 10 000 rpm and the particles were collected. The collected particles were kept in a hot air oven at 80 °C for 12 h, followed by annealing at 450 °C for 3 h. Finally, reddish brown FT nanoparticles were obtained and were used for further investigations.

\subsection*{Characterization of FT Nanoparticles.} The crystalline phase of FT nanoparticles was characterized by X-ray powder diffraction. The measurement was obtained using a X'Pert PRO X-ray diffractometer with Cu K\textsubscript{α} (λ = 1.54 Å) radiation. The morphology and purity of the FT nanoparticles were characterized using a scanning electron microscope equipped with an energy-dispersive spectrometer (SEM-EDS, Ultra SS). The FT nanoparticles were dispersed in ethanol using an ultrasonic bath drop-cast directly on a carbon-coated copper grid for transmission electron microscopy (TEM, Titan.
Themis 300 kV) analysis. Thermal analysis was carried out using a thermogravimetric analyzer from TA Instruments. Magnetic responses of the FT nanoparticles were measured at room temperature using a Lakeshore vibrating sample magnetometer (JDM-13) with an applied force of −8000 to 8000 Oe. To get further information about the magnetic properties of the FT nanoparticles, the squareness ratio and anisotropy constant ($K$) were calculated using the following equation:

$$\text{squareness ratio} = \frac{M_r}{M_s}$$

$$K = \frac{H_c M_s}{0.98}$$

where $M_r$ is the remanent magnetization; $M_s$ is the saturation magnetization; and $H_c$ is the coercivity.

The optical properties (absorption spectra) were recorded using a UV–vis–NIR spectrometer (Shimadzu MPC3600). The optical band gap energy ($E_g$) was obtained from the transmittance spectra of FT nanoparticles. The optical band gap energy ($E_g$) is given by

$$(a h \nu)^2 = A (h \nu - E_g)$$

where $A$ is a constant, $h \nu$ is the photon energy, and $a$ is the absorption coefficient.

**Synthesis of OH-Functionalized FeTiO$_3$ Nanoparticles.** To hydroxylate the FT, 1 g of FT nanoparticles was dispersed in a 400 mL aqueous solution of H$_2$O$_2$ by bath sonication for 15 min. After bath sonication, the suspended solution was refluxed at 106 °C for 4 h, followed by washing with deionized water in sequence for several times. The H$_2$O$_2$-treated FT was then dried in an oven at 80 °C for 24 h and stored in desiccators.

**Synthesis of NH$_2$-Functionalized FeTiO$_3$ Nanoparticles.** The as-prepared hydroxylated FT nanoparticles were refluxed again in the presence of APTS at 80 °C for 24 h. Centrifugation of the obtained mixture followed by washing with toluene for several times to remove the excess APTS.
yielded FT-NH₂, which is denoted as f-FT. Finally, the solvent was evaporated under vacuum.

**Synthesis of f-FT/PU Nanocomposite.** The composite mixture of f-FT/PU was synthesized by a two-step process, as shown in Schemes 3 and 4, using MDI, PEG 4000, and f-FT. In the first step (polymerization), MDI was reacted with PEG 4000 at a molar ratio of 2:1 under N₂ atmosphere with DMF at 80 °C for 3 h. The reaction was constantly stirred with a mechanical stirrer in an oil bath. In the second step, a certain amount of f-FT nanoparticles was predispersed in 20 mL of DMF by ultrasonication, followed by bath sonication for 15 min, and then the obtained solutions were added into the prepolymer of PU in an oil bath under N₂ atmosphere with vigorous stirring at 80 °C for 3 h.

**Coating of Cotton Fabrics.** The cotton fabrics (15 × 15 cm²) were treated by 10% of NaOH under a rotational speed of 200 rpm for 1 h at 60 °C. This treatment was carried out to hydrolyze the surface of the cotton fabrics. The fabrics were then cooled to ambient temperature, thoroughly rinsed in ethanol, washed with deionized water to remove all of the residual NaOH, and subsequently dried at 60 °C for 30 min.

The PU and f-FT/PU nanocomposites were coated on the cotton fabrics by dip-coating (Scheme 5). Separately, the fabrics were submerged in the PU and N-FT/PU emulsion for 10 min under ultrasonication. The coated fabrics were placed between two filter papers and gently pressed, which may remove the excess solution from the coated fabrics. Further, the coated fabrics were kept in a drier at 120 °C for 15 min to cure the coating on the fabrics. Finally, the polymer nanocomposite was coated on the coated fabrics.

The uncoated, f-FT/PU-coated, and PU-coated fabrics are referred to as UC, FTPC, and PUC, respectively, in this study. The average thicknesses (according to the ASTM D1777-96 standard) of the obtained coated fabrics were about 0.29 and 0.28 mm for FTPC and PUC, respectively, which were higher than the average thickness of the UC fabrics (0.21 mm). The variation of the thickness increased due to the adhesion of nanoparticles in polymeric materials on the surface of the fabrics.

**Characterization of Fabric Samples.** The morphological analysis was investigated by scanning electron microscopy (SEM, ULTRA 55) with an acceleration voltage of 10 kV. Before analysis, the fabric samples were sputtered with gold using a sputter coater. The physical structure of the fabric samples was examined by XRD (X’Pert PRO, PANalytical) with Cu Kα radiation generated at 40 kV (λ = 0.1542 nm) and 30 mA.

The coated and UC fabrics were evaluated indirectly by measuring the static water contact angle by the sessile drop method with an OCA 15EC instrument (DataPhysics) at room temperature and 65% relative humidity. The instrument consists of a CCD video camera with 768 × 576 pixel resolution to capture images at a rate of up to 50 per second. The wettability was achieved when 3.0 μL of DI water was drop tended to be static on the surface of the fabric samples for nearly 1 min. Each sample was analyzed several times and the values were recorded.

The thermal degradation properties of the fabric samples were assessed using a thermo analyzer (TA Instruments) from...
Transmittance versus wavelength of various polymeric nanocomposite-coated fabrics and a table listing the UV blocking in percent (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**
E-mail: sbose@iisc.ac.in.

**ORCID**
Suryasarthi Bose: 0000-0001-8043-9192

**Notes**
The authors declare no competing financial interest.

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