Manufacturing and Properties of Various Ceramic Embedded Composite Fabrics for Protective Clothing in Gas and Oil Industries Part I: Anti-Static and UV Protection with Thermal Radiation

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Abstract: Protective clothing in gas and oil industries requires high-performance characteristics, with superior anti-static and ultraviolet (UV) protection and good thermal wear comfort in cold weather regions. This study examined the manufacturing and properties of various ceramic-embedded composite fabrics made from a new scheme (not a coating method) for protective clothing in the gas and oil industries. Therefore, sheath–core yarn specimens embedded with various ceramics, such as aluminum oxide ($\text{Al}_2\text{O}_3$)-graphite, zinc oxide–zirconium (ZnO–ZrC), and zinc oxide–antimony tin oxide (ZnO–ATO) were produced using a bi-component melt spinning machine, which is a novel method that was not tried before. Fabric specimens were also made from these ceramic-embedded sheath–core yarn specimens. UV-protection and anti-static properties of the ceramic-embedded composite specimen were compared with the thermal radiation and far-infrared (FIR) characteristics. The UV-protection factor (UPF) was measured according to the AS/NZ 4399 (1996) standard. ATLAS measuring equipment was used to analyze five duplicate specimens (4 × 8 cm). An anti-static assessment was also conducted using the JIS L 1094 standard method. A light heat emission apparatus was used to assess thermal radiation. A 10 × 10 cm specimen was prepared, and five duplicate assessments were conducted. Statistical analysis (F-test) was performed to verify the statistical significance of the experimental data with a 99% confidence limit. The ZnO–ATO-embedded composite fabric exhibited greater UV protection than the Al$_2$O$_3$-graphite-embedded and regular (control) specimen, indicating the excellent UV-protection property of the ZnO. In addition, the ZnO–ATO-embedded composite specimen exhibited excellent anti-static properties with lower rub-static voltage than the control fabric, which was attributed to the better electrical conductivity of ATO particles. In particular, the ZnO–ZrC-embedded composite specimen showed superior thermal radiation with excellent UPF and relatively good anti-static characteristics. Based on the high-performance characteristics of protective clothing worn in gas and oil industries, ZnO–ATO-embedded composite fabric has practical use for fabricating workwear protective clothing. In addition, considering protective clothing suitable for cold weather, ZnO–ZrC-embedded composite fabric is useful for protective clothing in cold weather regions.

Keywords: UPF; bi-component spinning; thermal radiation; FAST; composite fabric

1. Introduction

Increased attention has been paid to applying ceramics to textiles. Much research has been conducted on infrared (IR) radiation, ultra-violet (UV) shielding, and anti-static properties with the electric conductivity of ceramic particle-incorporated fabrics [1–11]. Sunlight is comprised of IR, visible light, and UV, of which infrared comprises approximately 45% that is transmitted to textiles when exposed to IR radiation [1]. Far-IR (FIR) has wavelengths between 7.5 and 14 μm, particularly in the textile field [2]. Previous studies [2–8] examined the interrelation between the thermal characteristics and the IR radiation, including FIR, using zirconium carbide (ZrC), aluminum oxide (Al$_2$O$_3$), and
silicon dioxide (SiO$_2$)-incorporated fabrics. Kim et al. [3,7] conducted intensive research on heat release and thermal radiation of ZrC/Al$_2$O$_3$-embedded PET fabrics regarding FIR. They reported that ZrC-embedded fabrics showed superior thermal radiation because of FIR, but Al$_2$O$_3$-incorporated fabrics exhibited much brighter and superior colors to ZrC-embedded fabrics after dyeing.

Many studies [9–14] on UV protection agents have used titanium dioxide (TiO$_2$) and zinc oxide (ZnO) nanoparticles (NPs) as UV blockers. Other studies [9,10,13] using a coating method treated with TiO$_2$ NPs reported effective UV protection by treatment with TiO$_2$. ZnO NPs-coated fabric exhibited superior UV protection to the regular one [11,12,14]. In addition, many studies [15–19] have been conducted to increase the UV protection of textiles using a range of methods. Kursun et al. [15] examined the UV property of nylon and PET materials treated with various absorbers. Dimitrovski et al. [16] compared the ultraviolet protection factor (UPF) of structurally different PET monofilament woven fabrics using the theoretical values from a mathematical model. They reported a good correspondence between the experimental and theoretical values. Yu et al. [17] reported that fiber cross-sectional shape was critical in the UV protection of constituent yarn. Katangur et al. [18] reported a new formulation for the ZnO/TiO$_2$ NPs-embedded UV-resistant coating applicable to the Kevlar fabric. Kar et al. [19] examined UPF and antimicrobial characteristics on cotton coated with ZnO NPs. On the other hand, in most studies, a TiO$_2$ and ZnO NPs coating with various concentrations of a UV absorbing agent in the coating process imparted UV protection to the fabrics. Few studies have attempted to increase the UV protection of fabrics using ceramic particle-embedded yarns prepared using a melt-spinning process rather than a coating method.

ZnO and antimony tin oxide (ATO) ceramic powders impart anti-static properties because of their superior electrically conductive properties. Zhou et al. [20] examined the anti-static mechanism of the ZnO whisker, and Wu et al. [21] reported the anti-static characteristics of the nano-ATO-incorporated agent treated to the fabric. In particular, Wong et al. [22] reported that yarns and fabrics treated with ATO particles had heat shielding and electrically conductive properties. In addition, several studies [23–26] have been related to these characteristics of ATO-coated materials. They [23] reported the thermal isolation characteristics of antimony-doped tin oxide materials, and they [24] studied the superior physical property of antimony-doped tin oxide materials. Furthermore, they [25] examined highly conducting nano-sized antimony-doped tin oxide prepared using a new method.

Employees in oil and gas industries need to wear anti-static protective clothing because of the hazard imparted by static electricity, which is a particular problem in cold weather regions [27,28]. In addition, employees exposed to sunlight are also required to wear UV-protective clothing. In particular, anti-static and UV-protective characteristics of workwear protective clothing with heat release need to be maintained after repeated laundering, i.e., washing durability is needed, which cannot be obtained by coating treatment to the workwear protective fabrics [29,30]. On the other hand, previous studies focused on these properties using ATO and ZnO-coated sheets, not ZnO and ATO particles-embedded yarns and their fabrics. Hence, a new method is needed.

Workwear protective clothing in oil and gas industries requires high-performance properties with superior UV protection and anti-static and good thermal radiation while wearing clothing. Hence, further investigation is needed to determine how the anti-static and UV-protection characteristics of the various ceramic particles embedded fabrics for thermal wear comfort for protective clothing change with the mixing of the various ceramic particles embedded in the yarns. Furthermore, the multifunctional characteristics of ceramic particle-embedded fabrics, such as heat release, UV protection, and anti-static properties, have not been reported despite their importance in workwear clothing.

In this study, we evaluated the anti-static and UV-protection characteristics of various ceramic particle-embedded composite fabrics. Composite fabrics were produced from sheath-core yarns incorporated with different ceramic particles. Anti-static and UV-
2. Materials and Methods

2.1. Spinning of Ceramic Particles-Embedded Bi-Component Yarn Specimens

Three ceramic particle-incorporated sheath–core yarns were produced on a conjugated spinning machine using five master batch (M/B) chips prepared on a compounding machine. Table 1 presents each ceramic-embedded M/B [30]. Each M/B was produced by mixing each ceramic particle with a PET polymer, and the wt.% of each ceramic was 10 for Al$_2$O$_3$, 20 for ZrC, 5 for graphite, 20 for ATO, and 20 for ZnO particle, respectively. The mean size of the filtered ceramic particles in Table 1 was measured using a hydro 2000S (Malvern Panalytical, Malvern, UK). The uniformity of the particle size in Table 1 is quoted in a prior study [7] and defined as follows.

\[
\text{Uniformity} = \frac{\sum Vi |d(V, 0.5) - di|}{d(V, 0.5) \sum Vi}
\]

where \((V, 0.5), Vi,\) and \(di\) are referred to in prior studies [7]. The intrinsic viscosity (IV) in Table 1 was measured using an Ubbelohde viscometer (Canon Instrument Company, State College, PA, USA). IV is quoted in a prior study [7] and defined as the relative ratio converted by the speeds of the solvent and polymer treated with ortho-chlorophenol (solvent) as it fell to a constant height [7].

<table>
<thead>
<tr>
<th>M/B Chip</th>
<th>Al$_2$O$_3$</th>
<th>ZrC</th>
<th>Graphite</th>
<th>ATO</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (wt.%)</td>
<td>10</td>
<td>20</td>
<td>5</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Uniformity (-)</td>
<td>0.564</td>
<td>0.548</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mean size (nm)</td>
<td>869</td>
<td>548</td>
<td>700</td>
<td>200–300</td>
<td>200–300</td>
</tr>
<tr>
<td>IV (dℓ/g)</td>
<td>0.542</td>
<td>0.535</td>
<td>0.637</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1. Specimens of ceramic particle-incorporated chips [30].

___

Al$_2$O$_3$-graphite-incorporated yarn was produced using the polymers (50 wt.%, core) mixed with 0.7 wt.% Al$_2$O$_3$ and 0.1 wt.% graphite master batch chips with 50 wt.% PET polymers in the sheath, ZnO-ZrC-embedded yarn mixed with 0.5 wt.% ZnO and 0.3 wt.% ZrC master batch chips, and ZnO-ATO-embedded yarn mixed with 0.5 wt.% ZnO and 0.3 wt.% ATO master batch chips. Table 2 lists the master batch mixing ratios for the sheath–core PET yarn specimens. The optimal mixing ratio among each M/B was determined by preliminary spinning with different mixing ratios. The first preliminary spinning was prepared using an M/B mixing ratio of 0.8 wt.% Al$_2$O$_3$ and 0.5 wt.% ZrC failed because of the increased pack pressure; the spinning nozzle clogged during spinning. The second attempt using 0.8 wt.% Al$_2$O$_3$ and 0.2 wt.% graphite had end break problems during spinning. The third spinning using M/B mixed with 0.4 wt.% ZrC and 0.4 wt.% ZnO also failed for the same reason. Finally, spinning was achieved with the M/B mixing ratio listed in Table 2. Figure 1 presents the sheath–core yarn spinning. A 75 d/24 f spin draw yarn
A 75 d/24 f spin draw yarn (SDY) with a 0.2 mm capillary diameter and a 0.5 mm length was produced using a 24-hole spinneret. Sheath–core ratio was 50/50 (%).

Table 2. Details of yarn specification with an M/B mixing ratio [30].

<table>
<thead>
<tr>
<th>Yarn Specimen</th>
<th>Ceramic Embedded PET Yarns</th>
<th>PET Base Chip (kg)</th>
<th>M/B Chip (kg)</th>
<th>Total Weight (kg)</th>
<th>Al₂O₃ Graphite ZnO ATO ZrC Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yarn specimen 1</td>
<td>Al₂O₃–Graphite PET (75/24)</td>
<td>45.5</td>
<td>Al₂O₃ 3.5</td>
<td>50</td>
<td>0.7 0.1 0.8 3.5 1.0 0.8</td>
</tr>
<tr>
<td>Yarn specimen 2</td>
<td>ZnO–ZrC PET (75/24)</td>
<td>48.0</td>
<td>ZnO 1.25</td>
<td>50</td>
<td>0.5 0.3 0.8 1.25 0.75 0.8</td>
</tr>
<tr>
<td>Yarn specimen 3</td>
<td>ZnO–ATO PET (75/24)</td>
<td>48.0</td>
<td>ZnO 1.25</td>
<td>50</td>
<td>0.5 0.3 0.8 1.25 0.75 0.8</td>
</tr>
</tbody>
</table>

The Al₂O₃–graphite sheath–core yarn specimen was produced with the base polymer and Al₂O₃–graphite mixed polymer, as shown in Figure 1a. The ZnO–ZrC yarn specimen was also produced with the base polymer and ZnO–ZrC mixed polymer. Finally, the ZnO–ATO yarn specimen was produced with the ZnO–ATO mixed PET polymer. Each yarn was spun with PET base polymer in the sheath, as shown in Figure 1a. Details of the PET base polymers used in this study are referred to prior studies [30]: Table 3 lists the detailed spinning conditions of these three yarns. The temperature of the spin beam and manifold in the spin beam (Figure 1b) was distributed between 280 and 320 °C (Table 3) according to the ceramics embedded in the yarns. The 1st and 2nd godet roller (G/R) speeds differed as listed in Table 3. The 1st G/R temperature was 80 °C for the Al₂O₃–graphite yarns and 90 °C for the other yarns. The 2nd G/R temperature was 105 °C and 120 °C, respectively. The feed roller (F/R) speed for the Al₂O₃–graphite was 3100 m/min and 4000 m/min for the other yarns. High-resolution scanning electron microscopy (SEM) was conducted to observe the ceramics embedded in cross-sections of a filament. The filament spun down from the spinneret in the conjugated machine was used as a specimen, which was cut before drawing at the drawing zone of the spinning apparatus.
Table 3. Detailed manufacturing conditions of the yarn spinning [30].

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Al₂O₃–Graphite PET</th>
<th>ZnO–ZrC PET</th>
<th>ZnO–ATO PET</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin beam temp (°C)</td>
<td>287</td>
<td>280</td>
<td>280</td>
</tr>
<tr>
<td>Manifold temp (S/C) (°C)</td>
<td>290/290</td>
<td>295/285</td>
<td>295/285</td>
</tr>
<tr>
<td>Extruder heating temp. (S/C) (°C)</td>
<td>280</td>
<td>310–320/305–315</td>
<td>310–320/305–315</td>
</tr>
<tr>
<td>1st godet speed</td>
<td>3160</td>
<td>1360</td>
<td>1300</td>
</tr>
<tr>
<td>2nd godet speed</td>
<td>3100</td>
<td>4010</td>
<td>4050</td>
</tr>
<tr>
<td>1st godet temp (°C)</td>
<td>80</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>2nd godet temp (°C)</td>
<td>105</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Feed roller speed</td>
<td>3100</td>
<td>4000</td>
<td>4000</td>
</tr>
<tr>
<td>Yarn number (d/f)</td>
<td>SDY75/24</td>
<td>SDY75/24</td>
<td>SDY75/24</td>
</tr>
<tr>
<td>Sheath-core ratio</td>
<td>50:50</td>
<td>50:50</td>
<td>50:50</td>
</tr>
</tbody>
</table>

2.2. Manufacturing of the Fabric Specimens

Composite fabrics were produced on the weaving machine (ZW-315X, Tsukakoma, Kanazawa, Japan). The detailed dyeing and finishing processes are referred to prior studies [3]. The four composite woven fabric specimens were processed on the dyeing and finishing processes. The fabric surface and its cross-section were measured to determine the structural characterization of the fabricated yarns and fabrics using SEM. Table 4 lists the detailed specifications of the composite specimens.

Table 4. Specifications of the composite fabric specimens [30].

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Yarn Type</th>
<th>Fabric Sett (Picks, Ends/cm)</th>
<th>Thickness (mm)</th>
<th>Mass (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wp</td>
<td>Wf</td>
<td>Wp</td>
<td>Wf</td>
</tr>
<tr>
<td>1</td>
<td>PA</td>
<td>Al₂O₃–graphite embedded</td>
<td>51.6</td>
<td>35.4</td>
</tr>
<tr>
<td>2</td>
<td>PA</td>
<td>ZnO–ZrC embedded</td>
<td>51.6</td>
<td>35.4</td>
</tr>
<tr>
<td>3</td>
<td>PA</td>
<td>ZnO–ATO embedded</td>
<td>51.6</td>
<td>35.4</td>
</tr>
<tr>
<td>4</td>
<td>PA</td>
<td>Reg</td>
<td>51.6</td>
<td>35.4</td>
</tr>
</tbody>
</table>

Note: PA: polyamide (nylon).

2.3. FIR Emissivity Assessment and Ingredient Analysis of Yarns

The FIR emissivity measurement for the yarn specimens was carried out to assess the thermal radiation emitted from the ceramics incorporated in the yarn using a Fourier transform infrared (FT-IR). The emissivity of the four specimens was measured, and their mean values for five readings were calculated.

Energy dispersive X-ray spectroscopy (EDS) was conducted to determine the elemental distribution of the ceramic particles embedded in the yarns. The yarn cross-sections were observed by SEM and optical microscopy (I-Camscope 305A, Seoul, Republic of Korea).

2.4. Light Heat Emission Assessment

The light heat emission was measured to assess the temperature change by the heat emanating from the ceramics in the fabrics using a thermal radiation system. Figure 2 presents the thermal radiation apparatus [7]. A heat bulb was placed 30 cm away from the fabric specimen, and the surface temperature of the fabric was measured for 30 min. The maximum surface temperature (MST) was recorded 10 min from the start to detect the heat emanating from the ceramic particle-embedded yarns. Five duplicated assessments were conducted.
2.4. Light Heat Emission Assessment

The light heat emission was measured to assess the temperature change by the heat emanating from the ceramic particle-embedded yarns. Five duplicated assessments were conducted.

Figure 2. Thermal radiation apparatus ((a) schematic diagram, (b) apparatus) [7].

2.5. UV-Protection Measurement

The UV-protection factor (UPF) was assessed at 290–400 nm using UPF measuring equipment. After conditioning at 20 °C and 65% RH, the measurement was taken, and the spectral data were recorded as the mean of four scans obtained by rotating the specimens 90°. The UPF was calculated using Equation (1) [29]. Five duplicated measurements were carried out for each specimen [29].

\[
\text{UPF} = \frac{\sum_{\lambda=290}^{400} \text{E}(\lambda) \varepsilon(\lambda) \Delta(\lambda)}{\sum_{\lambda=290}^{400} \text{E}(\lambda) T(\lambda) \varepsilon(\lambda) \Delta(\lambda)}
\]  

(1)

where \( E(\lambda), \varepsilon(\lambda), \Delta(\lambda) \) and \( T(\lambda) \) are referred to prior study [29].

2.6. Anti-Static and Surface Electrical Resistivity (SER) Assessments

Two types of experiments were conducted to investigate the electric conductivity of the ceramic particles-embedded fabrics: anti-static and SER measurements. The anti-static properties were assessed by measuring the static electricity [31]. Five duplicate specimens (4 × 8 cm) were used for each specimen with rubbing fabrics. The static voltage (V) was obtained after a drum revolution for 60 s.

The SER (\( \rho, \Omega/\text{sq} \)) of the fabric specimens was assessed to obtain the electric resistance using an SER measuring system [29]. The SER was calculated from Equation (2) using the KSK 0170 standard method [32].

\[
\rho = 2.73 \times R / \log \left( \frac{r_o}{r_i} \right) \text{ (ohm/sq)}
\]  

(2)

where \( R, r_i, \) and \( r_o \) are referred to in prior studies [29].

2.7. Tactile Hand Feel by FAST System

Another focus of this study was to estimate the tactile hand properties of ceramic-embedded fabrics. The mechanical properties of the fabrics were assessed using a Fabric Assurance Simple Testing (FAST) system [33]. The bending rigidity (B, \( \mu \text{N·m} \)) was calculated using \( C \), as shown in Equation (3) [33].

\[
B = W \times C^3 \times 9.52 \times 10^{-6}
\]  

(3)

where \( C, W, E20, \) and \( E100 \) are referred to FAST Manual [33]. The shear modulus (G, N/m) was calculated using EB5, as expressed in Equation (4) [33].

\[
G = (123/\text{EB5}) \times 1 \text{ N/m}
\]  

(4)

where EB5 is referred to as Manual [33].
3. Results and Discussion

3.1. Elemental Analysis of Ceramic-Embedded PET Yarns

Elemental analysis was performed to verify the ingredients of the ceramic embedded in the sheath–core yarns. The ceramic particles in the four types of yarn specimens were analyzed by EDS. Figure 3a–d present the charts of the ingredients of the four PET yarn specimens, respectively. Figure 3a shows the Al and Ti peaks and Figure 3b presents the Zn, Zr, and Ti peaks. Figure 3c shows the Zn, Sb, Sn, and Ti peaks (ATO: Sb$_2$SnO$_5$). The Ti peak of TiO$_2$-embedded regular PET yarns showed a peak for Ti, which is generally used as delustre in PET yarns (Figure 3d). Figure 3e–h shows microscopy images of cross-sections of the four yarn specimens. The black spots in Figure 3e were attributed to Al$_2$O$_3$ and TiO$_2$ particles and ZnO, ZrC, and TiO$_2$ particles in Figure 3f. The smaller black spots in Figure 3g were attributed to ZnO, ATO (ingredients Sb, Sn), and TiO$_2$ particles and to TiO$_2$ particles in Figure 3h, which were included in regular PET as a delustre (0.36 wt.%).

![Figure 3](image-url)
3.2. Characteristics of Ceramic-Incorporated Sheath–Core PET Yarns

The EDS elemental peaks of the yarn specimens were compared with the microscopy images in the previous section. On the other hand, the characteristics of the sheath–core yarns spun in the bi-component spinning machine need to be characterized by the ceramic embedded in the core of the bi-component yarns. Therefore, two types of SEM images were measured using the S-4800 and S-4300 apparatus. The cross-section of one sheath–core fiber in the yarns were measured using high-resolution SEM (S-4800). The filament spun out from the spinneret in the bi-component spinning apparatus was prepared as a specimen, which was cut for assessing the SEM image before drawing at the drawing zone of the spinning machine. Figure 4a–c presents the cross-section SEM images (×2500) of one filament measured using S-4800; d–f show SEM images (×1500) of the sheath–core yarn specimens after drawing measured using the S-4300 microscope.

Figure 4. SEM images (×2500, ×1500) of the sheath–core yarn specimens. (a,d): Al₂O₃–graphite, (b,e): ZnO–ZrC, (c,f): ZnO–ATO incorporated yarns.

Figure 4a presents cross-section images of the Al₂O₃–graphite incorporated filament; Al₂O₃ and graphite particles are shown as white spots. These particles were larger than the ZrC, ZnO, and ATO particles in Figure 4b,c. The white spots in Figure 4b were attributed to ZrC and ZnO particles and to ATO and ZnO particles in Figure 4c. These could be compared with the particle size of the ceramic particles embedded in the yarn listed in Table 1. As shown in Figure 4d–f, the white spots distributed around the core seen in Figure 4a–c were dispersed over the yarn cross-section, and several white spots were shown at the sheath in SEM images, despite the ceramic being inserted in the core of the sheath–core fiber during
bi-component spinning. This phenomenon was caused by the swelling that developed after spinning out from the spinneret in the bi-component spinning machine.

3.3. UV Protection of the Ceramic-Embedded Composite Fabrics

The UPF was used as a measure of UV protection and measured using an ATLAS M 284D SDL apparatus.

Table 5 lists various physical properties of the ceramic particle-embedded composite fabric specimens. The ANOVA (analysis of variance) was conducted to test the statistical significance of the data in Table 5. Table 6 lists the F-test result for the average value of the physical properties of the four fabric specimens with a 1% significance level. The average values between the four specimens for each physical property were significant, as $F_0 (V/V_e) > F (3, 16, 0.99)$ and $p < 0.01$. Figure 5 shows the UPF of the four composite fabric specimens.

Table 5. UPF and related properties of the composite fabric specimen.

<table>
<thead>
<tr>
<th>No</th>
<th>Specimens</th>
<th>UPF</th>
<th>Rub Voltage (V)</th>
<th>Surface Electrical Resistivity (10^{10} \Omega)</th>
<th>Avg</th>
<th>D</th>
<th>Avg</th>
<th>D</th>
<th>Avg</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al₂O₃-graphite PET</td>
<td>258.8</td>
<td>22.1</td>
<td></td>
<td>4520</td>
<td>178.6</td>
<td>3320</td>
<td>126.3</td>
<td>3.90</td>
<td>0.47</td>
</tr>
<tr>
<td>2</td>
<td>ZnO–ZrC PET</td>
<td>455.7</td>
<td>28.3</td>
<td></td>
<td>5550</td>
<td>163.2</td>
<td>5280</td>
<td>140.2</td>
<td>5.31</td>
<td>0.72</td>
</tr>
<tr>
<td>3</td>
<td>ZnO–ATO PET</td>
<td>479.7</td>
<td>25.2</td>
<td></td>
<td>4740</td>
<td>140.4</td>
<td>3550</td>
<td>98.6</td>
<td>4.07</td>
<td>0.63</td>
</tr>
<tr>
<td>4</td>
<td>Regular PET</td>
<td>349.8</td>
<td>20.2</td>
<td></td>
<td>5950</td>
<td>11.8</td>
<td>114.5</td>
<td>149.5</td>
<td>11.8</td>
<td>1.83</td>
</tr>
</tbody>
</table>

Note: D = max.–min. Avg = average.

Table 6. F-test result of the physical properties.

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>F₀</th>
<th>F (3,16,0.99)</th>
<th>$p$-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>UPF</td>
<td>581.16</td>
<td>5.29</td>
<td>$1.55 \times 10^{-16}$ ($p &lt; 0.01$)</td>
</tr>
<tr>
<td>Rub voltage (V)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cotton</td>
<td>542.21</td>
<td>5.29</td>
<td>$2.69 \times 10^{-16}$ ($p &lt; 0.01$)</td>
</tr>
<tr>
<td>wool</td>
<td>2537.05</td>
<td>5.29</td>
<td>$1.25 \times 10^{-21}$ ($p &lt; 0.01$)</td>
</tr>
<tr>
<td>SER (Ω/sq)</td>
<td>339.79</td>
<td>5.29</td>
<td>$1.08 \times 10^{-14}$ ($p &lt; 0.01$)</td>
</tr>
</tbody>
</table>

Figure 5. UPF of the fabric specimens.

The UPF of the ZnO–ATO fabric specimen showed the highest value, followed by the ZnO–ZrC fabric specimen, regular TiO₂ PET specimen, and the Al₂O₃–graphite fabric speci-
men (Figure 5), indicating that the UV-protection characteristics of the ZnO ceramic particles are superior to those of Al₂O₃ embedded in the fabric specimen, and TiO₂-embedded regular PET fabric has good UV-protection properties. These results are comparable to previous findings [9–12], despite their results being for ZnO-coated fabrics, not ZnO-embedded composite fabrics in this study. Nevertheless, they obtained more efficient UV-protection materials using a nano-sized ZnO coating method.

Wu et al. [10] reported that Zn–ZnO nanoparticles absorb all UV and IR light over the 800–2500 nm wavelength range. Li et al. [11] reported that cotton fabric coated with nano Zn–ZnO ceramics absorbed 95% UV over the 280–400 nm wavelength range, suggesting that ZnO particles are more efficient UV-protection materials. One critical point of this study was how the mixing of different ceramic particles affects the UV protection of multifunctional fabrics. In Figure 5, the composite fabric specimens (ZnO–ATO mixed) and (ZnO–ZrC mixed) mixed with ZnO particles exhibited superior UPF, indicating the superior UV-protection characteristics of ZnO particles mixed with other ceramic particles. The photocatalysis effect of ZnO particles could explain this finding.

In general, ZnO nanoparticles have a very narrow size distribution and minimal aggregation, resulting in higher levels of UV blocking [12]. The photocatalysis effect of ZnO particles under light irradiation is caused by an electron transition in the ZnO particles, resulting in electron–hole pairs where the electrons are reductive and the holes (h+) are oxidative. The h+ reacts with OH⁻ on the ZnO particle surface, leading to protection from UV, i.e., ZnO particles offer superior UV protection [19]. Gupta et al. [13] reported that a mixture (67/33) of TiO₂ and ZnO coated on cotton and nylon fabrics showed significantly higher UV absorption than that of the individual components. Attia et al. [14] reported that the UPF of cotton/polyester blend fabric coated with TiO₂–ZnO nanoparticles was much higher than that of the untreated fabric.

The UPF of the regular (TiO₂-incorporated) fabric was greater than that of the Al₂O₃–graphite-embedded composite fabric because of the excellent UV absorption of the TiO₂ particles in the yarns (Figure 5). These results can be explained partly by the characteristics of TiO₂ particles. In prior studies [34,35], TiO₂ absorbs and scatters both UVA and B, and TiO₂ lowers the transmitted UV by reflecting and scattering UV radiation, which explains the superior UV-blocking property of the TiO₂ particles, as reported elsewhere [29]. Kim [29] examined the UV protection of Al₂O₃–ATO–TiO₂-embedded PET fabrics and reported that TiO₂ particles exhibited a superior UPF to Al₂O₃–ATO mixed particles. The higher UV protection of the TiO₂ particles might be explained by the band theory proposed by Ralaskar et al. [36], which is quoted as follows, “TiO₂ is a semiconductor with a wide bandgap (3.2 eV). Accordingly, when the TiO₂ is activated with light of an energy greater than its bandgap, the electrons will absorb UV light because of its wide bandgap, which is why TiO₂ can protect against UV radiation”.

3.4. Anti-Static Property of the Ceramic-Embedded Composite Fabrics

This study also examined the anti-static properties of the different ceramic particle-embedded composite fabrics for workwear protective clothing. Figure 6 presents the rub-static voltage of the four composite fabric specimens.

For the cotton rubbing fabric attached, the rub-static voltage of the Al₂O₃–graphite fabric specimen was the lowest, followed by the ZnO–ATO fabric specimen (Figure 6). For the wool rubbing fabric, the Al₂O₃–graphite and ZnO–ATO fabrics exhibited a lower rub-static voltage than the ZnO–ZrC and regular PET fabric specimens; hence, they showed superior anti-static properties. These findings suggest that the graphite in the Al₂O₃–graphite PET yarns and ATO in the ZnO–ATO PET yarns improve the anti-static properties, i.e., graphite and ATO have higher electric conductivity than ZnO and TiO₂ embedded in the ZnO–ZrC and regular fabric specimens, resulting in lower anti-static voltages of the Al₂O₃ and ZnO–ATO fabric specimens than the ZnO–ZrC and regular fabric specimens. This result is comparable to Kim [29], who examined the anti-static property of the ATO-embedded PET fabrics with an increase in the wt.% of ATO particles embedded in the
fabric. They reported that the anti-static properties of highly ATO-embedded fabric were superior to those of the low ATO-embedded fabric. This result suggests that the anti-static properties of the ATO particles are superior to Al₂O₃ and TiO₂ particles, which is consistent with the present result.

Muller et al. [25] reported that the excellent electrically conductive characteristics of the ATO particles dissipate the static charge accumulated on the ATO-embedded fabric surface, resulting in excellent anti-static properties of the ATO particles. These properties could be explained by the physical and chemical structures of ATO particles. The structural characteristics of the ATO particles for superior electric conductivity showed appropriate physical and chemical structures with the antimony and its oxidation in the tin oxide lattice. Hence, ATO has superior electric conductivity because of its structural characteristics.

The rub-static voltage (Figure 6) of the fabric specimens was compared with the surface electrical resistivity (SER, Ω/sq). Figure 6 shows the SER of the composite fabric specimens.

The SER of the graphite and ATO-embedded fabric specimens was lower than that of the ZnO–ZrC and regular fabric specimens (Figure 7). These results were consistent with the
lower rub voltages of the Al₂O₃/graphite and ZnO/ATO fabric specimens than that of the ZnO–ZrC and regular fabric specimens, as shown in Figure 6. These findings concur with prior studies [22,24,25], which reported that ATO-incorporated fabrics exhibited superior electric conductivity and conducting properties compared to regular fabric.

In addition, the SER of the ZnO/ZrC-embedded fabric specimen was much lower than that of the TiO₂-embedded regular fabric specimen. Hence, the ZnO particles in the ZnO–ZrC fabric specimen, in part more effective anti-static properties owing to their better electrically conductive characteristics than TiO₂ in the regular fabric specimen. This result is consistent with Zhou et al. [20], who examined the anti-static property of the ZnO whisker. They reported that anti-static composites made from polyurethane, polyvinyl, and natural rubber using tetrapod-shaped ZnO whiskers showed conductive behavior. Moreover, ZnO whiskers were an effective anti-static additive for composite material.

Summarizing the UV-protection and anti-static properties according to various ceramic particles embedded in the yarns, the ZnO and TiO₂ particles impart UV protection, which is suitable for the UV absorbing and scattering agents. In addition, ATO shows excellent anti-static properties, and ZnO particles exhibit relatively good anti-static properties. In particular, the superior anti-static properties of the ZnO–ATO-embedded fabrics eliminate the flame caused by electric discharge while wearing the clothing, which is critical for workwear clothing. Hence, the ZnO–ATO-embedded fabrics are suitable for anti-static protective workwear clothing. Overall, of the various mixed ceramic particles, the ZnO–ATO-embedded fabric showed superior anti-static and UV-protection characteristics, but the multifunctional fabrics for workwear clothing worn in cold weather require excellent thermal wear comfort. Therefore, the light heat emission (thermal radiation) properties of the ceramic particle-embedded composite fabrics were examined.

3.5. Light Heat Emission Characteristics of the Ceramic-Embedded Composite Fabrics

One concern is which ceramic particles exhibit excellent light heat emission with superior UV-protection and anti-static characteristics while wearing workwear protective clothing in cold weather regions. Accordingly, the maximum surface temperature (MST) of the composite fabrics was examined with the emissivity properties. Table 7 lists the MST of the ceramic particle-incorporated specimens measured using the thermal radiation apparatus. The F-test results showed that the mean MST in each specimen was significant (Table 7), as F₀ (V/Vₑ) > F (3, 16, 0.95) and p < 0.05. The MST of the ceramic particle-embedded fabrics was higher than that of the regular PET fabric specimen (Table 7) because of the greater heat released by the FIR emitted from ceramic particles embedded in the yarns. Of the three ceramic particles-embedded fabrics, the Al₂O₃-graphite and ZnO–ZrC-incorporated specimens exhibited a higher MST than the ZnO–ATO-incorporated specimen because of the more effective FIR absorbing power of the Al₂O₃–graphite- and ZnO–ZrC-incorporated specimens than that of the ZnO–ATO-incorporated specimen. The less effective FIR absorbing power of the ZnO–ATO fabric was attributed to the heat-shielding effect of the ATO particles [23,29,30]. Kim [29,30] examined the thermal radiation of Al₂O₃/ATO-incorporated fabrics according to the wt.% of ATO particles in the yarns. They reported that highly ATO-embedded fabrics exhibited lower maximum surface temperature than low ATO-embedded fabrics, which was caused by the heat-shielding effect of ATO particles in the yarns.

The FIR emissivity of the Al₂O₃–graphite- and ZnO–ZrC-embedded yarns was higher than that of the ZnO–ATO and regular PET yarns, as shown in Table 8 [30], which might explain the higher MST (Table 7) of the Al₂O₃–graphite and ZnO–ZrC-embedded composite fabrics than the ZnO–ATO and regular PET fabrics. The higher FIR emissivity of the Al₂O₃–graphite and ZnO–ZrC yarn specimens allow greater heat released from the Al₂O₃–graphite- and ZnO–ZrC incorporated yarns than from the ZnO–ATO and regular PET yarns, resulting in a higher MST of the Al₂O₃–graphite and ZnO–ZrC composite fabric specimens. Hence, the ATO particles incorporated in the ZnO–ATO-embedded yarns shield the FIR emitted from the light, resulting in the lower emissivity of the ZnO–ATO-embedded
yarns and lower heat release. Although the ZnO embedded in the ZnO–ATO-and ZnO–ZrC-incorporated yarns show lower heat release, the ZrC in the ZnO–ZrC embedded yarns are much more effective in heat release, resulting in a higher MST (Table 7) because of greater FIR emissivity (Table 8) of the ZnO–ZrC incorporated yarns. Hence, ZnO and ATO particles must be mixed with ZrC particles to achieve good thermal radiation properties with anti-static and UV-protection characteristics.

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Al₂O₃–Graphite Fabric</th>
<th>ZnO–ZrC Fabric</th>
<th>ZnO–ATO Fabric</th>
<th>Regular Fabric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg D</td>
<td>Avg D</td>
<td>Avg D</td>
<td>Avg D</td>
<td>Avg D</td>
</tr>
<tr>
<td>Maximum surface temperature (°C)</td>
<td>42.1</td>
<td>42.0</td>
<td>40.9</td>
<td>38.7</td>
</tr>
<tr>
<td>F-test result</td>
<td>F-value (F₀)</td>
<td>F(3, 16, 0.95)</td>
<td>1.4 × 10⁻²⁰</td>
<td></td>
</tr>
<tr>
<td>p-value</td>
<td>1874.13</td>
<td>3.329</td>
<td>1.4 × 10⁻²⁰</td>
<td></td>
</tr>
</tbody>
</table>

Note: D = max.–min. avg = mean.

Table 8. Emissivity and F-test results of the fabric specimen [30].

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Al₂O₃–Graphite Yarn</th>
<th>ZnO–ZrC Yarn</th>
<th>ZnO–ATO Yarn</th>
<th>Regular Yarn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg D</td>
<td>Avg D</td>
<td>Avg D</td>
<td>Avg D</td>
<td>Avg D</td>
</tr>
<tr>
<td>Emissivity</td>
<td>0.881</td>
<td>0.880</td>
<td>0.875</td>
<td>0.865</td>
</tr>
<tr>
<td>F-value (F₀)</td>
<td>F(3, 16, 0.95)</td>
<td>p-value</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-value</td>
<td>50,651.81</td>
<td>3.329</td>
<td>5.04 × 10⁻³²</td>
<td></td>
</tr>
</tbody>
</table>

Note: D = max.–min. avg = mean.

Summarizing thermal radiation characteristics with UV-protection and anti-static properties, ZnO–ZrC-embedded fabric mixed with ZnO to improve UV-protection and anti-static properties showed superior thermal radiation. Therefore, ZnO–ZrC-embedded composite fabric is suitable for workwear protective clothing in cold weather regions because of the excellent thermal radiation with superior UV protection and relatively good anti-static properties. In addition, the ZnO–ATO-embedded composite fabric exhibited better thermal radiation than the regular fabrics with higher maximum surface temperatures and FIR emissivity. Based on multifunctional characteristics for high-performance protective clothing, the ZnO–ATO-embedded composite fabric is suitable for workwear protective clothing because of relatively good thermal radiation with excellent UV protection and anti-static properties.

3.6. Tactile Hand Feel of Ceramic-Embedded Composite Fabrics

Understanding how the ceramic particles incorporated in yarns affect the tactile feeling of a fabric is essential for the tactile wear comfort of a fabric. The tactile hand feeling of ceramic particle-embedded composite fabrics was examined from the mechanical properties according to the ceramic particles embedded in the fabrics. Table 9 lists the mechanical properties of the four fabric specimens. Figure 8 compares the relative mechanical properties of the ceramic particle-incorporated composite fabrics with a regular PET fabric. The various mechanical properties (E20, E100, ST, B, and G) of the ceramic particle-incorporated composite fabrics were plotted as a function of the ratio alongside those of the regular PET fabric specimen.
Table 9. Mechanical properties of the ceramic embedded fabrics.

<table>
<thead>
<tr>
<th>Fabric Specimen No.</th>
<th>Extensibility Wp(Wf)</th>
<th>E 20(%)</th>
<th>E 100(%)</th>
<th>Shear Modulus G (N/m)</th>
<th>Bending Rigidity B(µN·m)</th>
<th>Compression ST (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Al₂O₃–graphite PET</td>
<td>0.310 0.296 0.300</td>
<td>0.567 0.600 0.580</td>
<td>121.9</td>
<td>48.2 44.8 46.5</td>
<td>0.062</td>
<td></td>
</tr>
<tr>
<td>2 ZnO–ZrC PET</td>
<td>0.367 0.433 0.400</td>
<td>0.633 0.967 0.800</td>
<td>106.9</td>
<td>47.2 41.2 44.2</td>
<td>0.074</td>
<td></td>
</tr>
<tr>
<td>3 ZnO–ATO PET</td>
<td>0.333 0.367 0.350</td>
<td>0.617 0.767 0.690</td>
<td>114.2</td>
<td>43.3 41.0 42.2</td>
<td>0.082</td>
<td></td>
</tr>
<tr>
<td>4 Regular PET</td>
<td>0.412 0.512 0.460</td>
<td>0.652 1.025 0.840</td>
<td>91.8 42.0 40.8 41.4</td>
<td>0.091</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 8. Relative mechanical properties of the ceramic particle-embedded fabrics to the regular PET fabric.

The extensibilities (E20 and E100) of the Al₂O₃–graphite, ZnO–ZrC, and ZnO–ATO fabrics were lower than those of regular specimens. In particular, the shear moduli (G) of these fabrics were much greater than those of the regular fabric specimen, meaning that ceramic particle-incorporated composite fabrics are less extensible and more rigid than the regular fabric. This was attributed to the ceramic particles incorporated in the yarns, which may have prevented the in-plane deformation of tensile and the shear of the fabrics, resulting in low extensibility and high shear modulus.

In particular, of the ceramic particle-incorporated composite fabrics, the Al₂O₃–graphite-embedded fabric specimen exhibited the lowest extensibility and the highest shear modulus compared to the ZnO–ZrC and ZnO–ATO incorporated fabrics. This was attributed to the larger particle sizes (869 and 700 nm diameter, respectively) of the Al₂O₃ and graphite than the ZnO, ATO, and ZrC (200–300 and 548 nm diameter, respectively) (Table 1).

On the other hand, the compressibility (ST) of the Al₂O₃–graphite, ZnO–ZrC, and ZnO–ATO fabric specimens was lower than that of regular specimens. In particular, the Al₂O₃–graphite-embedded composite fabric showed lower compressibility than the ZnO–ZrC- and ZnO–ATO-incorporated composite specimens. Hence, the ceramic particle-incorporated composite fabrics are less compressible than the regular fabric, and the Al₂O₃–graphite specimen is also less compressible than the ZnO–ZrC and ZnO–ATO incorporated specimens. This was attributed to the larger particle sizes of the Al₂O₃ and graphite than those of ZnO, ZrC, and ATO.

The bending rigidity (B) of the ceramic particle-incorporated composite specimens was greater than that of the regular specimen because of the longer deflection caused by the larger particle size of the ceramic particles incorporated in the yarns. This resulted in
greater B, as explained in Equation (3). Of three ceramic particle-embedded composite fabrics, the Al₂O₃–graphite incorporated fabric exhibited greater bending rigidity than that of the ZnO–ZrC- and ZnO–ATO-incorporated fabrics. This was also attributed to the larger particle sizes of the Al₂O₃ and graphite incorporated in the yarns than those of the ZnO, ZrC, and ATO, as mentioned previously, which was verified by SEM images of the fabric specimens. Figure 9 shows SEM images of the fabric surfaces and cross-sections. In Figure 9a–d, white spots on the fabric surface appeared, which appear to be ceramic particles embedded in the sheath of the yarns in the ceramic-embedded composite fabric.

![SEM images of fabric specimens](image)

**Figure 9.** SEM images of the surface (×300) and cross-section (×600) of fabric specimens: (a,e): Al₂O₃–graphite fabric, (b,f): ZnO–ZrC fabric, (c,g): ZnO–ATO fabric, (d,h): regular fabric.
In addition, SEM images of the cross-sections of fabrics revealed many white spots in the yarns and between the filaments in the yarns (Figure 9e–h). Figure 9e–g shows ceramic particles (white spots) in the Al$_2$O$_3$–graphite-, ZnO–ZrC- and ZnO–ATO incorporated yarns, in which the particle sizes of the Al$_2$O$_3$, ZrC, ZnO, and ATO are larger than that of the regular fabric shown in Figure 9h, resulting in the low extensibility and high shear modulus to the ceramic-embedded composite fabrics with low compressibility and great bending rigidity. Considering these mechanical properties, ceramic particles embedded in the yarns are assumed to impart an uncomfortable tactile feel to the ceramic particle-incorporated composite fabrics compared to the regular PET one. On the other hand, the durability and washability of the ceramic-embedded fabrics in protective clothing are essential for determining the resistance to abrasion and the washing of ceramic-embedded fabrics. A prior study [37] reported that the SEM images of ceramic-embedded fabrics before and after abrasion and washing were similar. Nevertheless, the resistance to abrasion and mechanical stress before and after repeated washing cycles requires further study.

4. Conclusions

This study examined the multifunctional characteristics of the various ceramic particle-incorporated composite fabrics for workwear protective clothing worn in gas and oil industries with thermal radiation, UV protection, and anti-static properties.

Combining the UV-protection and anti-static characteristics with the thermal radiation of various ceramic particle-incorporated composite fabrics, superior UV protection, and excellent anti-static properties with relatively good thermal wear comfort appeared in the ZnO–ATO-embedded composite fabric, and the ZnO–ZrC embedded composite fabric showed superior thermal radiation properties with excellent UV-protection and relatively good anti-static properties. Nevertheless, the ceramic particles incorporated in the yarns imparted an uncomfortable tactile feel to the fabric.

While based on high-performance characteristics for workwear protective clothing worn in the gas and oil industries, the ZnO–ATO embedded composite fabric is useful for fabricating this type of clothing because of an excellent UV-protection factor, superior anti-static properties, and relatively proper thermal radiation. Furthermore, considering workwear protective clothing worn in cold weather regions, ZnO–ZrC-embedded composite fabric is suitable for this type of clothing because of its superior thermal radiation, UV-cut, and relatively proper anti-static properties. Nevertheless, an in-depth study on the resistance to abrasion and mechanical stress before and after repeated washing treatment is needed.

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**References**


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