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# Study on flame retardant and UV protection properties of cotton fabric functionalized with ppy-ZnO-CNT nanocomposite

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## Abstract

Cotton fabric was modified with 1,2,3,4-butane tetracarboxylic acid (BTCA) as cross-linking agent in presence of sodium hypophosphite (SHP) as catalyst. Polypyrrole-Zinc oxide (ppy-ZnO) and polypyrrole-Zinc oxide-carbon nanotube (ppy-ZnO-CNT) composites were also prepared by in-situ chemical polymerization method. The composite sol was coated on cotton fabric using pad-dry-cure technique. This coated cotton fabric was characterized by FE-SEM with EDAX, XRD, UV-DRS and FT-IR analyses. Flame retardant and UV-protection properties of the coated cotton fabric was tested and compared with uncoated fabric. ppy-ZnO-CNT composite coated cotton was found to possess better properties than with uncoated cotton.

Key words: polypyrrole, ZnO, composite, coating, cotton, UV protection, flame retardant

## 1. Introduction

Cellulose is the most abundant biopolymer found on the earth. It has many excellent properties such as biodegradability, biocompatibility and eco-friendliness<sup>1</sup>. In recent years, textile industries have been focusing on improving its functional properties<sup>2-7</sup>, such as fire retardancy, UV protection, self-cleaning and antibacterial properties. Textile finishers worldwide are

considering a global challenge in materials to make garments comfortable and multifunctional. Attempts have been made to meet the challenges using nanomaterials with a view to introducing new functional properties to textiles. High performance of textile material is greatly appreciated by a more discerning and demanding consumer market. Nanoparticles of metal oxide-ceramics have been used to incorporate functional properties into textiles. Common metal oxides such as titanium oxide (TiO<sub>2</sub>), zinc oxide (ZnO), cupric oxide (CuO) and magnesium oxide (MgO) are in use for providing functional properties<sup>8</sup>. Ultraviolet (UV) resistant cotton fabrics were developed by coating with ZnO and TiO<sub>2</sub> nanoparticles. Nano ZnO coated cotton yarns were found to withstand the knitting operations<sup>9</sup>. Among the transition metal oxides, zinc oxide (ZnO) has received considerable interest in the fabrication of polypyrrole (ppy) hybrid materials because of its variety of applications in optoelectronic devices. Zinc oxide has high refractive index and thermal stability, ultraviolet protection, good transparency, high electron mobility and wide band gap of 3.37 eV<sup>10-11</sup>. ZnO nanorods grown on cotton fabrics possessed an ultrahigh UV protection factor of 379.14. It indicates an excellent protection against UV radiation in comparison with untreated cotton fabrics<sup>12</sup>. Cotton coated with ppy by in-situ oxidative chemical polymerization at room temperature altered the combustion process of cellulose that could be used for potential applications as technical textiles with antistatic (low electrical resistance) heat generation, hygroscopy, antibacterial and high temperature resistance properties<sup>13</sup>. Polyethyleneterephthalate-ppy textile complexes incorporating different anionic dopants have been treated between 60 and 150°C to investigate effects of short term heating on conductivity and stability; 80°C did not significantly change the final resistance of the conducting textile, while 125°C was the most effective. Sulphonic group containing dopants were found to be effective in improving the conductivity and stability<sup>14</sup>. Cotton was functionalized with carbon

nanotube (CNT) using a simple surface coating method. Due to the reinforcement and protection effects of the CNT armor, the cotton exhibited enhanced mechanical properties, extraordinary flame retardancy, improved UV-blocking and super-water repellent properties. Considering the novel physical properties of CNT, the functionalization of textile material with CNT would be of great importance for both fundamental research and practical applications<sup>15</sup>. CNT was coated by an exhaustion method and stabilized on cotton using 1,2,3,4-butane tetracarboxylic acid (BTCA) as cross-linking agent and sodium hypophosphite (SHP) as catalyst. CNT modified surface increased the thermal stability<sup>16</sup>.

From the literature, it is observed that flame retardant finish on cotton fabric is very important for many applications, such as military, buildings and protection clothing. In the present work, it was aimed to develop crosslinked cotton coated with nanocomposites (ppy-ZnO and ppy-ZnO-CNT) for UV-protection and flame retardant finishes.

## 2. Experimental

### 2.1. Material and method

Woven cotton grey fabric of 80 counts was obtained from South Indian Textile Research Association (SITRA), Coimbatore. It was pretreated by one-pot method with a recipe of 0.4 ml HCl, 3.9 g Na<sub>2</sub>CO<sub>3</sub>, 1.9 g NaOH and 1.9 ml H<sub>2</sub>O<sub>2</sub> in 200 ml water. Fabric (8 cm × 4 cm) was immersed in the bath at 80°C for 90 min. ZnO (Sigma Aldrich, 97%) with an average size of 50 nm, BTCA (Alfa Aesar, 98%), ammonium persulfate (APS) (Alfa Aesar, 98%), Single wall carbon nanotube (SWCNT) (Sigma Aldrich, 97%), SHP (S.D fine, 98%), polyethylene glycol (Alfa Aesar, 98%) and pyrrole (Sigma Aldrich, 98%) were purchased and used.

## 2.2. Synthesis of polypyrrole

Pyrrole was purified by double distillation method before use. Pyrrole (0.3 M) was dissolved in 500 ml de-ionized water. After 10 min, APS (0.06 M) in 100 ml de-ionized water was added drop-wise into solution mixture. The content was stirred for 24 h at 20°C. Methanol was used to stop the reaction wherever necessary. Formation of black precipitate was considered as the completion of the reaction. It was filtered and washed with different solvents such as de-ionized water, methanol and acetone. Then the resultant sample was dried at 30°C for 12 h in a vacuum oven<sup>17</sup>.

## 2.3. Synthesis of ppy-ZnO and ppy-ZnO-CNT composites by in-situ polymerization

Pyrrole (0.3 M) was dissolved in 500 ml de-ionized water. After 10 min, BTCA (0.1 M) and SHP (1 g) were added. Molar ration of the material was taken. Stirring was carried out for 30 min at room temperature. Required amount of NaOH was added to bring the pH neutral. APS (0.06 M) was prepared in 100 ml de-ionized water. ZnO (0.25 g) was mixed with the solution. The solution was sonicated for 30 min to get milky white colloidal form. This was added drop-wise into the solution and stirring was carried out for 9 h at 20°C. This mixture was kept overnight for the formation of black coloured composite. It was filtered and washed with different solvents such as de-ionized water, methanol and acetone and dried at 30°C for 6 h in a vacuum oven. This has resulted the synthesis of ppy-ZnO composite at 1:1 ratio. This procedure was extended to prepare ppy-ZnO composites at 1:2 and 1:3 ratios. The similar ratio was further added with CNT ratio at 1:3:1 composite. The ratios were designated as C<sub>1</sub> (1:1), C<sub>2</sub> (1:2), C<sub>3</sub> (1:3) and C<sub>4</sub> (1:3:1).

## 2.4. Coating Sol preparation

ppy-ZnO ratio and ppy-ZnO-CNT composites were prepared by mixing with polyethylene glycol (2 ml). Then, 6 ml deionized water was added into 100 ml absolute ethanol and stirred vigorously at room temperature for 30 min until a homogeneous solution was obtained. Then, 4 ml ammonia was added drop-wise into this solution and kept under ultrasonic irradiation for 30 min to form ppy-ZnO and ppy-ZnO-CNT composite sols. These sols were used for coating of fabric using a pad-dry-cure method<sup>18</sup>. The padded fabrics were air-dried and cured at 180°C for 5 min in a hot-air oven. The ppy-ZnO and ppy-ZnO-CNT nanoparticles were coated on the fabrics due to an exchange reaction between -OH groups of cotton.

## 3. Results and discussion

### 3.1. XRD pattern of ppy and ppy-ZnO (1:1), (1:2), (1:3) and (ppy-ZnO-CNT (1:3:1) composite and composite coated cotton

Fig.1 shows the XRD pattern of the ppy, ZnO and ppy-ZnO composites (C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub>) material. Fig1 a shows the sharp diffraction peak of the ZnO implies that the ZnO is crystalline in nature. It indicated by corresponding peaks to the planes of (100), (101), (102), (110) and (103)<sup>19</sup>. Fig1 b shows the diffraction pattern of ppy, which has broad peak at  $2\theta=24.78^\circ$  indicating the amorphous behaviour of the polymer<sup>20</sup>. Fig1 c and d shows amorous nature. It clearly indicates that no sharp peaks were observed. Crystalline peaks in the XRD were observed by increasing the concentration of ZnO from C<sub>1</sub> to C<sub>4</sub> in the composites. From the Fig 1e and f, it clearly noticed that sharp crystalline peaks responsible for ZnO were observed in C<sub>3</sub> and C<sub>4</sub> composites. The crystallite size of ppy-ZnO calculated by using Scherrer's formula was found to be 15 nm. All the peaks match very well with the standard ZnO of the hexagonal structure (JCPDS card 06-7848). The XRD pattern of polypyrrole functionalized ZnO has a broad peak at

lower diffraction angles  $\sim 22^\circ$ , which indicates their amorphous in nature with no clear indication of crystalline morphology. This broadening of peaks can be confirmed to be the spreading of the polypyrrole chains around  $\text{ZnO}^{21}$ . Additional sharp peak is shown at (002) plane (Fig.1f), which indicates the presents of CNT<sup>22</sup>. The decrease in the intensities of the ZnO peaks in the ppy-ZnO-CNT functionalized average size of about 40-70 nm (Fig.1f).

As a result of composite XRD (Fig.1) ppy, C<sub>3</sub> and C<sub>4</sub> composite were optimized with the crystalline nature. These composite sols were coated on cotton fabric. Fig.2 shows the XRD pattern of the uncoated cotton, ppy coated, C<sub>3</sub> coated cotton and C<sub>4</sub> coated cotton. Fig 2a shows that no sharp diffraction peaks in the uncoated cotton. Fig2 b shows the diffraction pattern of ppy, it indicates the amorphous behaviour of the polymer. The peaks observed at  $31.6^\circ$ ,  $36.1^\circ$  and  $56.4^\circ$  are correlated with the formation of hexagonal ZnO were assigned to (100), (101), (102), (110) and (103) diffraction of hexagonal ppy-ZnO composite fabric. (Fig.2c)<sup>23</sup>. All the peaks were well matched with the values from the standard (JCPDS card 06-7848). The strong with sharp diffraction peaks indicate that the ppy-ZnO is well crystallized. The crystallite size of (002), (100) (002) and (110) planes (Fig.2d). The peaks were well matched with the values from the standard (JCPDS card 89-7213). The equal ratio of ppy-ZnO shows strong peaks. It was observed that the ZnO particle interacts on polypyrrole surface.

### 3.2. FT-IR analysis

Fig.3 represents the FT-IR spectra of uncoated, pristine ppy coated cotton, ppy-ZnO composite coated cotton and ppy-ZnO-CNT coated cotton. The bending vibration of water molecules (H-O-H) is observed at  $1687\text{ cm}^{-1}$  in the spectra of uncoated fabric (Fig. 3a). The cellulose bands observed at  $1024$  and  $1157\text{ cm}^{-1}$  correspond to the bending vibration of C-O, whereas the asymmetric stretching vibration of glucose ring is observed at  $1103\text{ cm}^{-1}$  <sup>24-25</sup>. The spectrum of

ppy is shown in Fig. 3b confirmed the formation of ppy. The Peak at  $1588\text{ cm}^{-1}$  corresponds to the stretching vibration of C-C in the pyrrole ring<sup>26-28</sup>. Peak observed at  $1687\text{ cm}^{-1}$  for the untreated fabric (Fig.3a). This peak is shifted to  $1716\text{ cm}^{-1}$  which may be due to the cross-linking between cotton and BTCA (Fig 3c and 3d)<sup>29</sup>. The peak at  $1387\text{ cm}^{-1}$  corresponds to C-H in-plane deformation modes. ppy shows characteristic C-N and C-H stretching vibration of pyrrole at  $1271\text{ cm}^{-1}$  and  $1017\text{ cm}^{-1}$  respectively. The stretching mode of ZnO appears at around  $868$  and  $870\text{ cm}^{-1}$  due to metal oxide bond. These significant changes in peaks positions and broadening reveal that it is not a simple mixture of ppy and ZnO and can be attributed to some chemical interactions between active sites in ppy, CNT and ZnO to change the polymer conformation (Fig.3c and 3d)<sup>30</sup>.

### 3.3. SEM Analysis

The SEM study confirms that ppy-ZnO nanocomposites are grafted on the fabric surface after washing. The uncoated fabric shows a plain surface when compared to ppy, C<sub>3</sub> and C<sub>4</sub> coated fabrics. Fig. 4c shows spherical ppy-ZnO nanocomposites adhering to the fabric surface, whereas needle-like small agglomerated ppy-ZnO-CNT nanocomposites nanocomposite particles are seen in Fig. 4d. EDAX images indicate the presence of zinc, oxygen, and carbon present in the coated fabric. The spherical and needle-shaped morphologies of ppy-ZnO were examined through EDAX. From the above studies, the elemental wt% of C<sub>4</sub> coated fabric (2.20 wt %) is found to be increased when compared to that of the C<sub>3</sub> coated fabric (1.28 wt %). These results confirm the effective coating of the nanoparticles on the surface of the cotton fabric. The weight gain of the original cotton fabric after coated with ppy-ZnO and ppy-ZnO-CNT nanoparticles were tabulated in Table 1.



Table 1.

Sample	Weight gain (%)
ppy coated cotton	17.3
C <sub>1</sub> coated cotton	18.1
C <sub>2</sub> coated cotton	19.3
C <sub>3</sub> coated cotton	20.6
C <sub>4</sub> coated cotton	21.5

### 3.4. TGA-DTA analysis

Flammability is an important issue in the clothing and textile areas as it can lead to bodily injuries and property loss. Flammability of textile products is defined by characterizing their burning behavior, in particular ease of ignition and sustained burning after ignition. The flame retardancy of polymer nanocomposites has been fully investigated based on thermo-gravimetric analysis (TGA). TGA and DTA were shown in the Fig5 a and b. The samples were heated from 0 to 600°C at a heating rate of 10°C/min under a nitrogen flow rate of 20 mL/min. TGA curve summarizes the thermal degradation of the uncoated cotton and that of the coated cotton with C<sub>3</sub> coated cotton and C<sub>4</sub> coated cotton (Fig.5a). As seen from the figure, the TGA curves of cotton consist of three regions of 1, 2, and 3 as initial, main, and char decomposition regions, respectively. In the first stage, the changes of the thermal properties and the weight loss of fibers are due to some physical damages occurring mostly in the amorphous region of the cellulose. In this stage mass loss between 50°C and 205°C is due to the loss of water and unreacted substances. The main thermal stage occurs in the second region, the weight loss between 205°C and 440°C indicated the decomposition of polymer chains. Where the weight loss is significant. It is stated by different researchers that glucose together with all kinds of combustible gases are generated in this region<sup>31</sup>. They found that thermal degradation in this region takes place in the crystalline region of cellulose fibers. The production of char occurs in the third region at the

higher temperature of 540°C. This process is continued further by de-watering and charring reactions, releasing water and carbon dioxide, and increasing the carbon and charred residues<sup>32-33</sup>. The sample cross linked with CNT and BTCA showed higher degradation temperature in the second region. This improvement of thermal properties is attributed to the high heat resistance, the heat insulation effect, and the mass transport barrier toward cellulose molecular chains exerted by the CNT themselves which were measure of flame retardancy. DTG curve shows, the burning step is broadened by the presence of ppy, therefore the associated heat of combustion is spread in a wider range of temperatures. These findings point out that ppy alters the combustion process of cellulose, when coated with ppy-ZnO-CNT. Finally, the residual weight at 390°C for all the coated samples is more than double that of cotton (Fig.5 b).

### 3.5. UV-blocking

According to the wavelength, UV light can be subdivided into three bands: UVA (320 or 315 to 400 nm), UVB (290 to 315 or 320 nm), and UVC (100-290 nm). Terrestrial solar UV consists of only UV with wavelength of 290-400 nm, because UVC and some UVB are absorbed by the stratospheric ozone in the earth's atmosphere. Light radiation of wavelengths 280-400 nm permits tanning of the epidermis. Rays of wavelength 290-320 nm (UVB) causes erythemas and skin burns, which can inhibit skin tanning. Radiation of wavelength 320-400 nm (UVA) is known to induce skin tanning, but can also cause skin damage, especially to sensitive skin which is exposed to sunlight for a long period of time. Examples of such damage include loss of skin elasticity, the appearance of wrinkles, promotion of the onset of erythema reaction, and the inducement of phototoxic or photo allergic reactions. In addition, all types of UV can cause a photochemical effect within the polymer structures, which can lead to the degradation of some

polymers. Obviously, the treatment of textiles with UV-blocking techniques can also improve their service lifetime.

The ultraviolet protection factor (UPF) measurements were made as per Jasco V-670 spectro photometer, with the aim of determining the transmittance of the UV radiation in the conditioned samples, thus evaluating its UV protection properties. This test provides the average UPF value of the sample, after analyzing. UV-blocking properties of uncoated cotton, ppy, C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> coated cotton (a-f) are shown in Fig.6 and the values are tabulated (Table 2). Ultraviolet protection factor (UPF) was computed using the following Eq.1

$$UPF = \frac{\sum_{280\text{ nm}}^{400\text{ nm}} E_{\lambda} S_{\lambda} \Delta_{\lambda}}{\sum_{280\text{ nm}}^{400\text{ nm}} E_{\lambda} S_{\lambda} T_{\lambda} \Delta_{\lambda}} \text{----- (1)}$$

Where S<sub>λ</sub> is spectral irradiation of the skin in UV region (280-400 nm); E<sub>λ</sub> is relative erythemal spectral effectiveness, T<sub>λ</sub> is spectral transmittance of the fabric; Δ<sub>λ</sub> is increment relating to wavelength, and λ is wavelength in nanometer.

Table.2

Composition	UPF value	UV protection
Uncoated cotton	6	Not considerable
ppy coated cotton	13	Not considerable
C <sub>1</sub> coated cotton	17	Good
C <sub>2</sub> coated cotton	22	Good
C <sub>3</sub> coated cotton	28	Good
C <sub>4</sub> coated cotton	40	Excellent

Fig.6 shows the UV transmission curve of uncoated cotton and coated cotton samples. In the Fig.6a indicating that almost 45% of the UV-A and UV-B can penetrate into the uncoated cotton. In samples C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub> the transmittance values decreases which confirming the presence of UV blocking material (ZnO nanoparticles) in the coated cotton. These particles are able to absorb wavelengths less than 358 nm. In curve **c**, decrease in transmittance (39%) was observed. This may be due to higher possibility of contact between UV wavelength and particles with the presence of BTCA-ZnO molecules<sup>32</sup>. Curves **d**, **e** and **f** show the decrease in the value of transmittance of 36%, 34%, 28% respectively. It shows that at high concentration, CNTs can provide perfect UV blocking to the coated cotton fabric. UV-blocking results reveal that when the ratio of ZnO increases, the UV blocking efficiency is also increases. The UPF values of 28 and 40 were observed for C<sub>3</sub> and C<sub>4</sub> coated samples respectively.

### 3.6. Evaluation for Flame retardant

Fig. 7 shows the combustion process of pristine cotton fabric, ppy coated cotton fabric, C<sub>3</sub>, C<sub>4</sub> composite coated fabric. Due to the surface CNT coatings, the color of the treated cotton looks gray. The untreated cotton fabric and the composite treated cotton samples were hung on a metal supporter, and then the samples were ignited with a lighter simultaneously. As shown in Fig.7, the untreated cotton sample catches fire immediately and with the progress of burning, the untreated cotton sample burns to ashes completely. However, the C<sub>3</sub> and C<sub>4</sub> composite coated cotton did not burn at all and was just charred at the edge, forming a stiff sinter (transfer of CNTs on the cotton substrates was observed during combustion). The results in Fig.7 provide direct evidence of the flame retardant effect of CNT on cotton textiles. The results of the vertical flammability test are summarized in Table 3. The results depict that the performed treatment decreased the flammability of the coated samples. Noticeably, BTCA cross linked with ppy-ZnO

and ppy-ZnO-CNT composite coated cotton were effective in reducing flammability of coated fabrics in the presence of SHP, The cotton with C<sub>3</sub> and C<sub>4</sub> composite coated fabric showed decreased char length and increased char yield. These results confirmed the impregnation of phosphorous on coated fabric. The flammability of uncoated and coated samples is compared in the Fig.7. C<sub>4</sub> shows the low char yield compared to other fabric due to the uniform deposition of the composite.

Table.3

Sample	Flammability (45°C)	
	Char length (cm)	Char yield (%)
Untreated cotton	2.0	85
ppy coated cotton	1.9	65
C <sub>1</sub> coated cotton	1.5	90
C <sub>2</sub> coated cotton	1.0	92
C <sub>3</sub> coated cotton	0.5	93
C <sub>4</sub> coated cotton	0.4	98

The efficient composite sol of C<sub>1</sub> and B<sub>2</sub> were applied to military uniform. It was designated as MC<sub>3</sub> and MC<sub>4</sub> respectively. The char length of uncoated fabric is 7.5 cm and char yield 72%. MC<sub>3</sub> coated shows char length of 5.5 cm and char yield 80%. The char length of MC<sub>4</sub> coated is 3.5 cm and char yield is 68 %. It shows more efficient than other coated fabric (Fig.8).

Results of Table 3 depicts that the performed treatments were decreased the flammability of the treated samples. Evidently, BTCA cross linked with ppy-ZnO and ppy-ZnO-CNT composite coated fabric are effective in reducing flammability of treated fabrics in the presence of SHP. Char length of samples was measured in the vertical flammability test and reported in Table 3. The differences in the burning behaviour and char length in vertical flame test for uncoated sample compared to the composite composite coated fabrics were shown in Fig.7. The results

showed that, they performed treatment was decreased the flammability of the samples. It can be concluded that increasing of ZnO and CNT ratios leads to decrease the fabric flammability (Table 3). It is interesting to note also that the charred surface of the C<sub>3</sub> and C<sub>4</sub> coated samples was very uniform indicating that the nanoparticle uniformly covered in the fabric surface.

### 3.7. Physical properties of the fabrics (Table 4)

Table 4

Specimen	Absorbency (seconds)	Tensile strength (lbf)		Tearing strength (lbf)		CRA (W+F) °
		Warp	Weft	Warp	Weft	
Uncoated	6	63.5	52.5	3.8	3.2	120
ppy	6	64.5	53.4	3.7	3.6	121
C <sub>1</sub>	7	66.5	59.4	3.4	3.1	115
C <sub>2</sub>	7	65.1	58.7	3.5	3.1	125
C <sub>3</sub>	8	66.5	59.2	3.7	3.2	135
C <sub>4</sub>	10	74.5	60.2	3.8	3.3	140

Water Absorbency of coated fabric was compare to uncoated fabric, when the absorbency was superior for fabric coated with C<sub>3</sub> and C<sub>4</sub> composite coated fabric. The Tensile strength of C<sub>4</sub> coated fabric with catalyst has enhanced performance that the other coated samples C<sub>3</sub>. This may be ascribable to the intermolecular and intramolecular crosslinking which reduces the possibility of getting even the stress distribution, causing reduction in the capacity to resist shipment. Tearing strength of sample C<sub>3</sub> has improved performance than uncoated one. This may be due to the crosslinking ability of BTCA, hindered by the presence of hydroxyl groups in the structure. Sample coated with composite showed a moderate increase in CRA (Crease recovery angle) values. CRA angle of composite sample C<sub>4</sub> was reached up to 140°, when compared to uncoated fabric. This shows that the crosslinking affected by the esterification reaction of coated cotton has imparted better crease recovery behaviour. This may be ascribable to the fact that BTCA has

one more carboxylic acid group which bonds to the adjacent carbons in their molecular backbones<sup>35</sup>.

### 3.8. Washing Stability

Table.5

Cleaning agent	No. of washing cycles	Char length (cm)					
		Uncoated	ppy	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>
Tap water	5	2.0	1.5	1.6	1.5	1.4	1.9
	10	char	char	0.3	char	char	0.3
Detergent solution (0.3%)	5	1.5	1.4	1.3	0.5	0.4	1.2

From the Table 5, the uncoated and C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub> coated samples shows the low char length after the flammability test in all applied washing conditions. After 10 cycles of washing with tap water, these samples show significantly low char length compared to untreated cotton fabric. Hence these samples were opted for further thermal decomposition studies.

## Conclusions

The fabric coated with composites prepared from carboxylic acids and catalysts without metal oxide were evaluated for flame retardancy. BTCA with SHP as catalyst effectively increased the char formation. ppy-ZnO and ppy-ZnO-CNT sols are obtained using the sol-gel method and then coated on to cotton fabric using pad-dry-cure method. The nanoparticles deposited on the fabric surface show stability both before and after washing, which is confirmed through SEM-EDAX analysis. The flammability of C<sub>4</sub> coated fabric is found to be 0.4 cm, which was better than that of uncoated fabric. The UPF value of C<sub>3</sub> and C<sub>4</sub> coated cotton was found to be 28 and 48 respectively. Thus it described suggests that ppy-ZnO-CNT coated cotton fabrics will be promising multifunctional textile materials for military and UPF protection applications.

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### Figure captions

Fig.1. XRD pattern of (a) pristine ZnO (b) ppy (c) C<sub>1</sub> (d) C<sub>2</sub> (e) C<sub>3</sub> (f) C<sub>4</sub> composites.

Fig.2. XRD patterns of (a) uncoated cotton fabric (b) ppy coated cotton (c) C<sub>3</sub> coated cotton and (d) C<sub>4</sub> coated cotton

Fig.3. FT-IR spectra of (a) uncoated cotton (b) ppy coated cotton (c) C<sub>3</sub> coated cotton (d) C<sub>4</sub> coated cotton

Fig.4. Images of FE-SEM with EDAX micrographs of the (a) uncoated, (b) ppy coated (c) C<sub>3</sub> and (d) C<sub>4</sub> composite coated cotton fabrics.

Fig.5. TGA (a) and DTA (b) curves of uncoated, ppy-ZnO composite coated fabric and ppy-ZnO-CNT composite coated fabric

Fig.6. Transmittance versus wavelength for different treated samples in UV analysis

(a) Uncoated cotton (b) pyrrole coated cotton (c) C<sub>1</sub> coated cotton (d) C<sub>2</sub> coated cotton (e) C<sub>3</sub> coated cotton (f) C<sub>4</sub> coated cotton.

Fig.7. Images of vertical flame testing of the uncoated and composite coated cotton fabrics (ppy, C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub>).

Fig.8. Images of vertical flame testing of the uncoated and composite coated cotton fabrics (ppy, MC<sub>3</sub> and MC<sub>4</sub>).

### Table captions

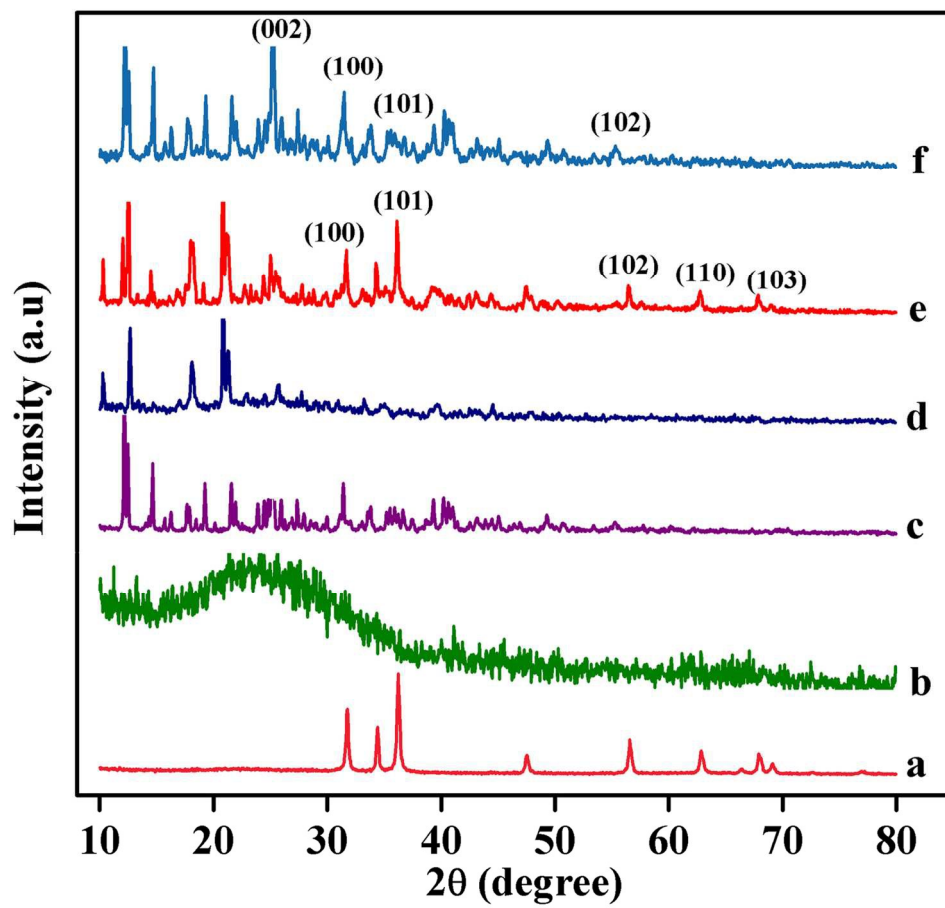
Table 1. The weight gain of the original cotton fabric and composite coated cotton fabric.

Table 2. Effect of ratios of ppy-ZnO and ppy-ZnO-CNT composite coated on cotton for UV protection of uncoated and composite coated cotton fabrics.

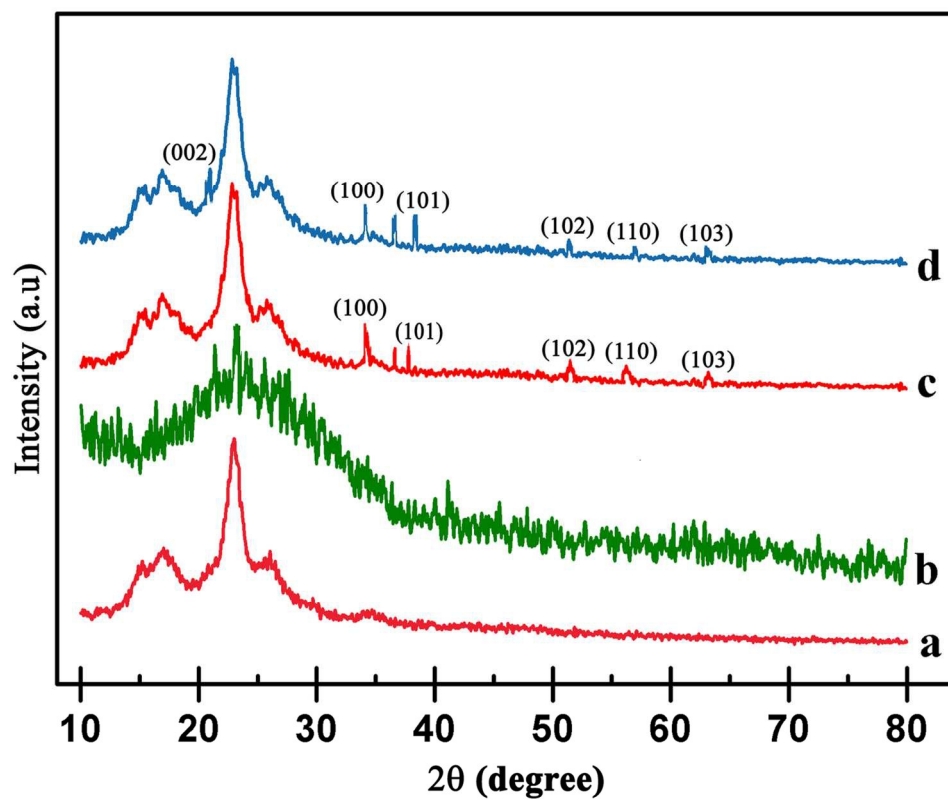
Table 3. Effect of different ratios of ppy-ZnO, ppy-ZnO-CNT composite on flammability of untreated and treated cotton fabrics.

Table 4. Physical properties of uncoated, ppy, C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub> composite coated fabric

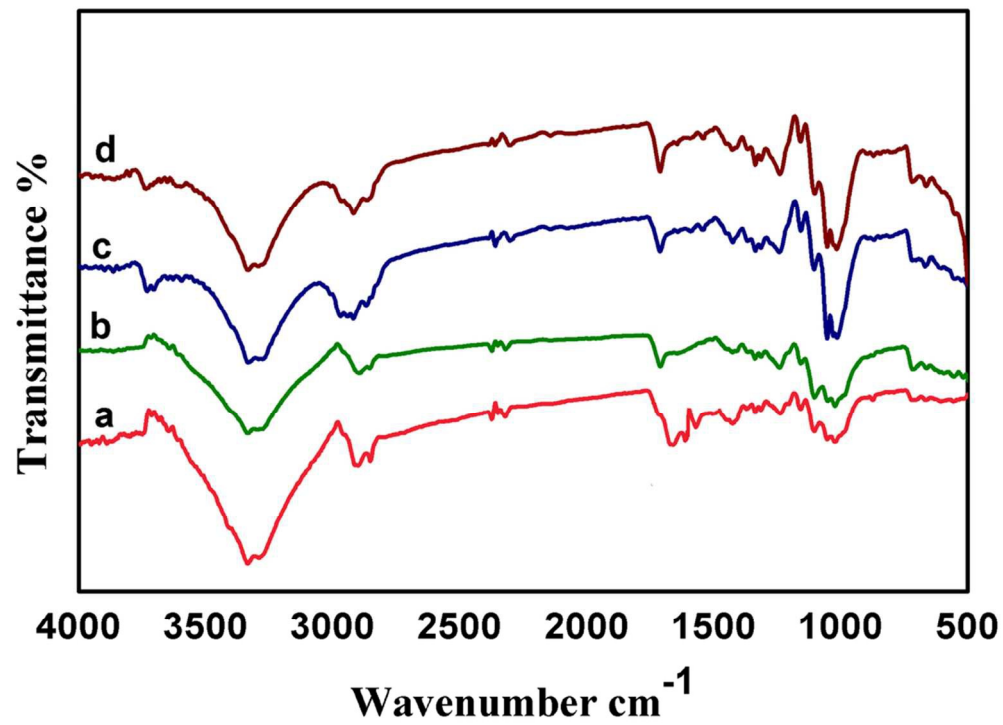
Table 5. Washing stability of uncoated and composite coated cotton fabric



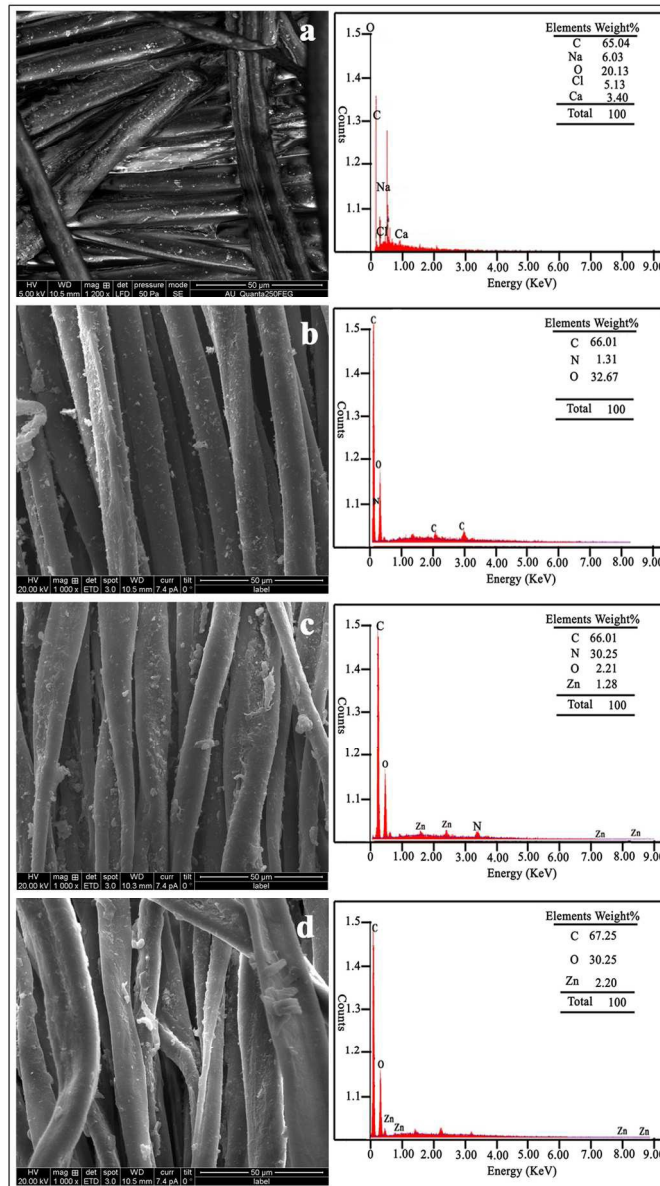
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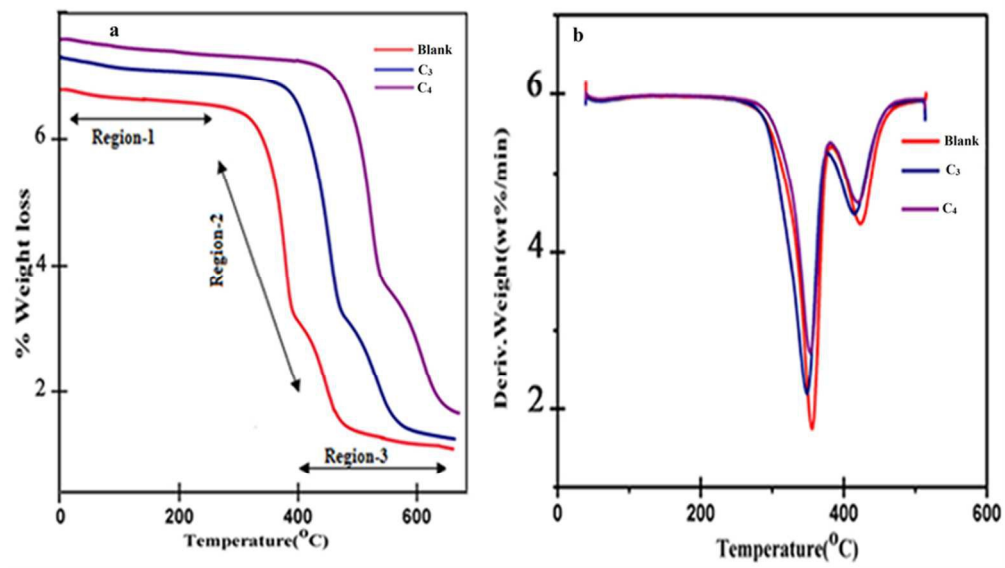


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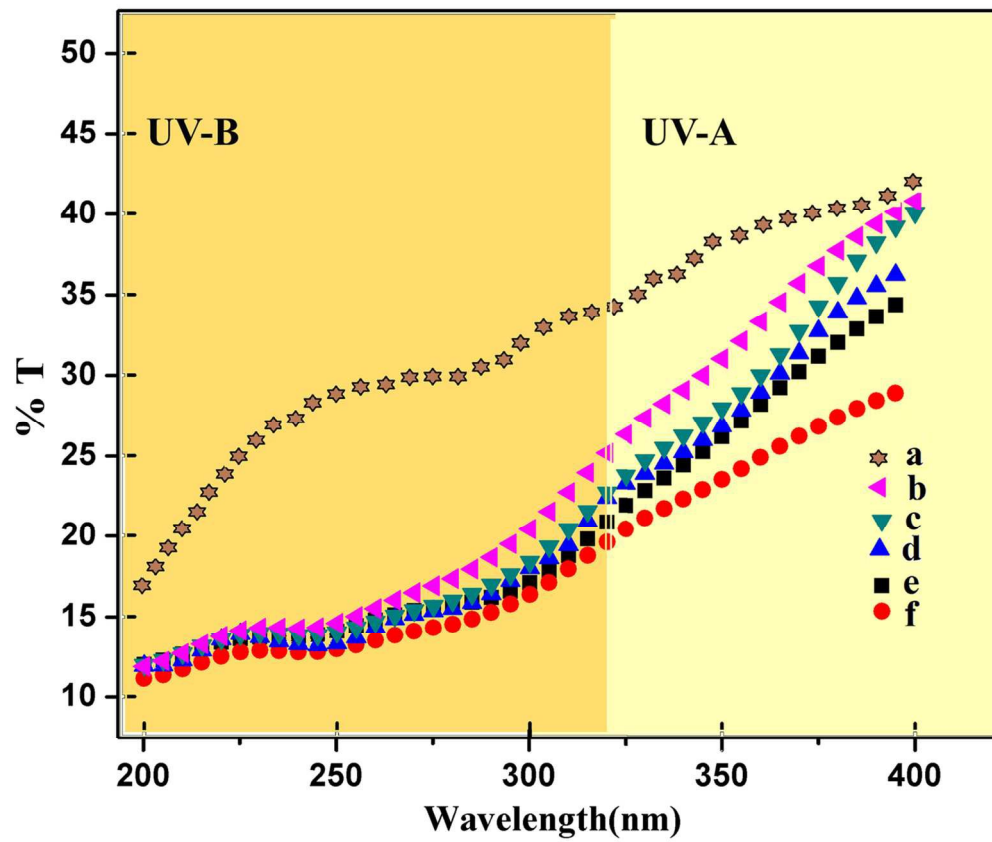


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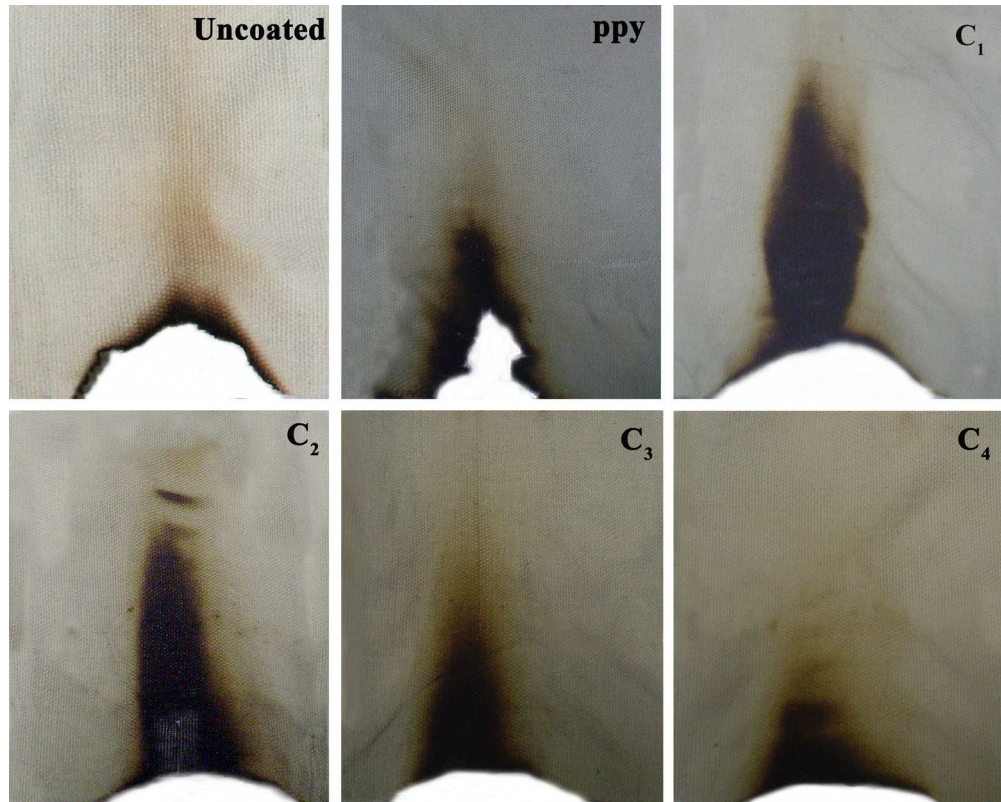




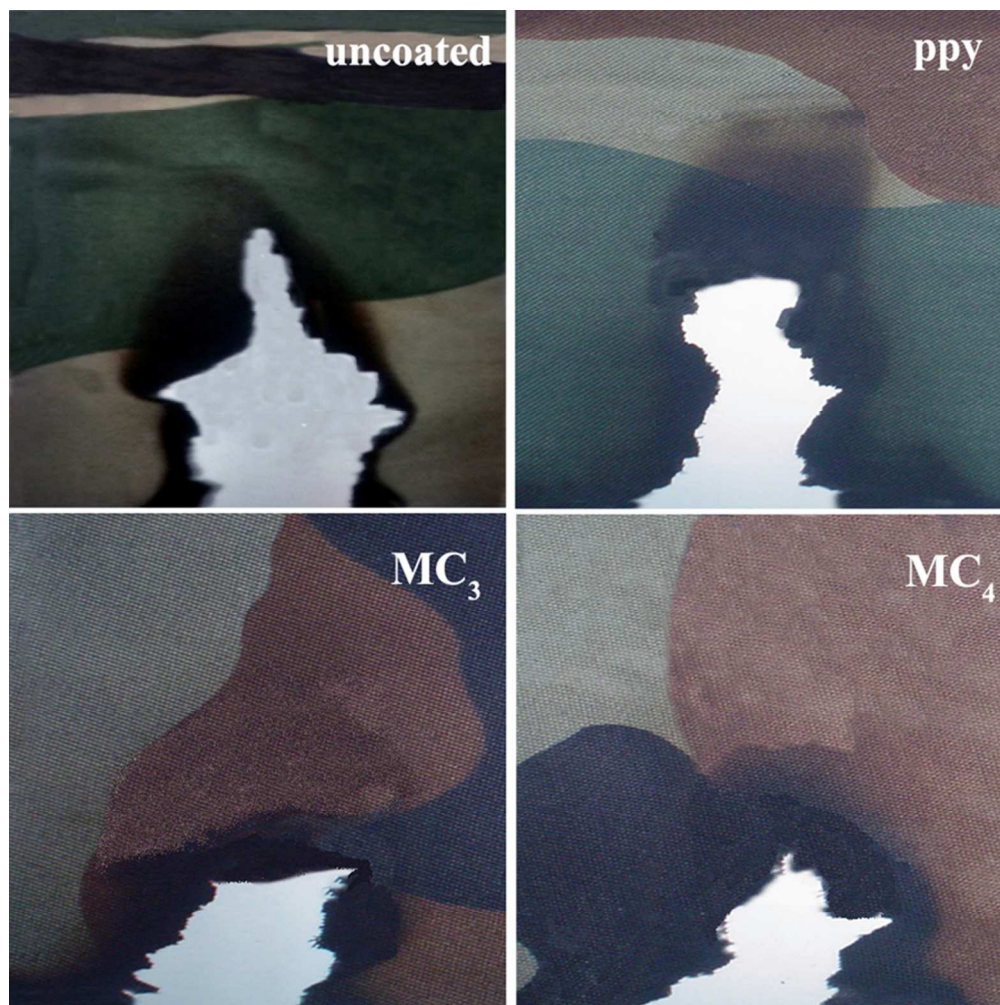
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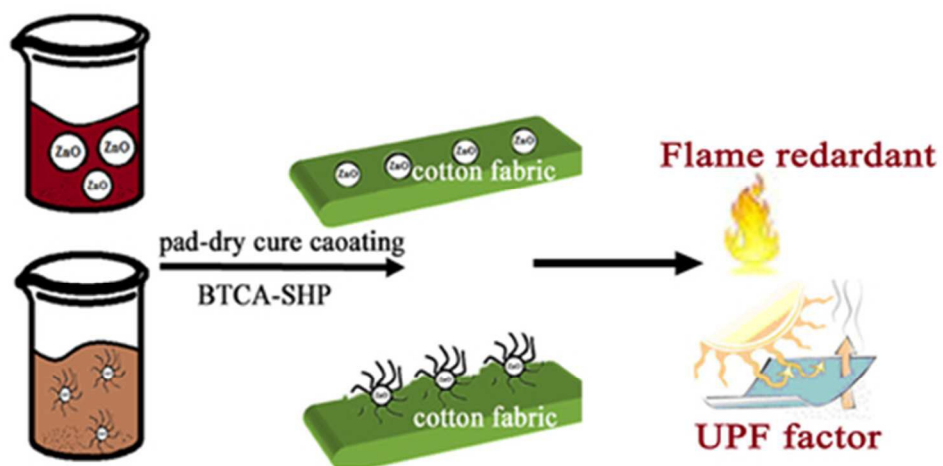
129x108mm (300 x 300 DPI)



170x135mm (300 x 300 DPI)



76x76mm (300 x 300 DPI)



39x19mm (300 x 300 DPI)