Egg White Protein-Hypophosphorous Acid Based Fire Retardant Single Bilayer Coating Assembly for Cotton Fabric

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Research Article

Keywords: Hypophosphorous acid, Layer by Layer, Protein, Fire retardant, Cotton

Posted Date: February 12th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-188572/v1

Abstract

Egg white proteins (W) in combination with hypophosphorous acid (HA) were investigated for making flame retardant coating over cotton fabric adopting layer by layer (LbL) assembly technique. A novel phosphorous-nitrogen based non-inflammatory pathway was produced due to strong electrostatic interactions between egg white protein and HA. The coated cotton fabric was characterized using FESEM, ATR-FTIR, TGA and flame tests. Vertical flame test (VFT) and BS EN ISO 15025 tests were performed to understand the combustion pattern of coated fabric. The cotton fabric coated with egg white protein followed by HA (CT_{W+HA}) showed self-extinguish properties with fragile char structure, whereas uncoated fabric was completely burnt with ash residue. Thermogravimetric analysis revealed that initial decomposition temperature of coated fabric got lowered but raised the char residue at 800 ℃. Moreover, surface morphology after VFT of CT_{W+HA} showed swollen char structure that prevented the interaction of combustible products with oxygen and heat. Thus, the developed coating could serve as excellent fire retardant due to the synergistic effect of HA and egg white protein.

1. Introduction

Clothes are made up of mainly cotton, which protects human body from harsh environments and gives comfort. Cotton clothes are used by common people, military, medical staff, and fire-fighters. Further, cotton is commonly used in home furnishings and various industrial items due to its softness, respiration, and moisture absorption characteristics (Rehan et al. 2018). Unfortunately, cotton is flammable with low limiting oxygen index and gets ignited at lower temperature (360–425°C) leading to fire hazards, which might lead to loss of many lives and severe damage to property (Shariatinia et al. 2015). During fire hazards, flammability is enhanced due to combustion of cotton as it is rich source of hydrocarbons (Wang et al. 2018). Thus, imparting resistance from burning or developing fire retardant coatings for cotton fabric is a challenge for textile industries (Liu et al. 2020).

According to the National Fire Protection Association (NFPA, USA) report, a total of 1.31 million fire accidents happened in 2018. In total, around 3,655 people lost their lives, 15,000 civilians got injured and more than $25.6 billion property got lost in fire accidents. More number of accidents/deaths occurred in home, ~ 74% of total fire accidents and cases were 3% higher than previous year (2017) (Evarts 2019). Cotton clothes facilitates propagation of fire in these accidents. Different methods were tried for developing a flame retardant coating over cotton and layer by layer assembly is one such technique. Layer by layer (LbL) assembly creates nanostructured surface for fireproofing (Malucelli et al. 2014) on cotton fabric. At the time of ignition and combustion, the polymer surface nanostructure is an essential part that creates a thermal barrier between the gas and condensed phase, which controls the heat transfer. When a higher amount of heat comes in contact with the polymer surface, volatile products flow out of the surface which minimizes the intensity of heat and in this process nanostructures form making LbL assembly method unique (Decher and Hong 1991). LbL assembly method has gained significant attention and is promising methods to prepare efficient fire retardant coatings (Li et al. 2010). This method is ecologically safe and economic to produce thin, multilayer films over complex substrates such

as textiles through electrostatic attraction between cations and anions or nanoparticles (Qiu et al. 2018). Some other approaches utilize attractive forces like, e.g., hydrogen bonds (Bergbreiter et al. 2001), donor/acceptor (Shimazaki et al. 1997) and covalent bonds (Sun et al. 2000) are also used to form LbL assembly. Grunlan *et al.* used LbL method for the first time to make fire resistant fabric in 2009 using branched polyethylenimine (PEI) and sodium montmorillonite (MMT) (Priolo et al. 2010).

During last decade, most commonly used flame retardants used were mostly halogen containing compounds such as pentabromodiphenyl ether, decabromodephenyl ether and polychlorinated biphenyls (van der Veen and de Boer 2012), which are not ecologically safe as toxic gasses used to get released in case of fire and halogen compounds released used to cause endocrine interference (Rahman et al. 2001; Legler and Brouwer 2003) besides polluting the environment (Carosio et al. 2015). Recently, halogen based flame retardants have been banned in the United States and European countries (Abou-Okeil et al. 2013). Instead, environmentally benign flame retardants are being preferred (Pan et al. 2014, 2019; Liu et al. 2017), which don't release toxic gases during combustion. Till date, commercially available phosphorus based fire retardants, e.g., ammonium polyphosphate based salts (Wu and Wang 2008; Vakhitova et al. 2016) and phosphorus derivative phenyl dichlorophosphate (PDCP) (Yuan et al. 2012), etc. have been used, but some phosphorous compounds such as tetrakis(hydroxymethyl)phosphonium chloride (THPC), containing hydroxymethyl group may emit formaldehyde during coating process, which again is carcinogenic (Nielsen and Wolkoff 2010). Therefore, there is an urgent need of developing novel, non-toxic (i.e., halogen-free and formaldehyde-free) and economically feasible fire retardants.

Some biomolecules, e.g., proteins (Liu et al. 2020), chitosan (Xiong et al. 2019), starch (Carosio et al. 2015), hydrophobins (Alongi et al. 2014), phytic acid (Cheng et al. 2019) and DNA (Carosio et al. 2013) derived from renewable sources appears ideal replacement for halogen/phosphorous based flame retardants. Alongi *et al.* applied casein (a phosphorus based compound found in milk protein) and hydrophobins (sulphur rich proteins obtained from filamentous fungi) to improve flame retardancy and thermal stability of cotton (Alongi et al. 2014). Extraction process of proteins from their sources is tedious involving multiple stages and time-consuming, which makes it cost intensive. These limitations restrict the production of costly proteins in large scale. Recently, egg white protein and phytic acid combination was reported for coating cotton fabrics which improved fire retardancy. Egg white proteins is quite rich in various amino acids along with abundant amount of calcium, ferric and phosphorous compounds and is quite cheap. On the other hand, phytic acid (PA) is a natural compound extracted from plant seeds and its extraction also involve multiple steps making it expensive (Oatway et al. 2001). Furthermore, highly acid nature of phytic acid (containing six phosphate compounds) affected mechanical and chemical properties of cotton fabric and resulted in multiple cracks over the surface of cotton fabric.

Hypophosphite with phosphorous content was demonstrated as an effective flame retardant for cotton textiles. Braun *et al.* used two different metal phosphinates with and without melamine cyanide on glass-fiber reinforced poly (butylene terephthalate) (PBT / GF) and measured their thermal decomposition and combustion behavior (Braun et al. 2008). Results showed that gas-phase mechanism was dominant for both phosphinate containing materials. Furthermore, flame retardancy of PBT containing aluminum

diethylphosphinate (AlPi) and/or nanometric metal oxides was measured. AlPi mainly worked in gas-phase by releasing diethylphosphic acid, which inhibited flame (Gallo et al. 2009). Yang *et al.* used pad-dry-cure method to prepare sodium hypophosphite and malic acid crosslinked coating over cotton fabric. Fire retardancy of coated fabric was increased due to presence of phosphorous containing groups (Yang et al. 2010). Recently, Liu *et al.* investigated fire retardancy effect of hypophosphorous acid modified chitosan along with polyethylenimine (PEI) on polyester-cotton (PTCO) fabric by LbL assembly (Liu et al. 2017). Results revealed that gaseous pyrolysis products of coated samples got reduced compared to those of uncoated ones.

In this report, combined effect of amino acid from chicken egg white protein (W) and hypophosphorous acid (HA) was investigated for development of a cost-effective fire retardant coating. Coating formed through electrostatic interaction between nitrogen-phosphorus compound and cellulose structure. Pre and post burning surface morphology, structure, thermal and flammability behavior of treated cotton were observed to know efficiency of fire retardant coating.

2. Materials And Methods

2.1. Materials

Cotton fabric (150 GSM) purchased from the local cloth market. Eggs and yolk separators were purchased from the supermarket. Hypophosphorous acid (HA, 50 wt% aqueous solution) was purchased from Avra Synthesis Private Limited, India and 2 wt% aqueous HA solution was prepared and used for all experiments.

2.2. Application of fire retardant coating over cotton fabric using egg white protein and hypophosphorous acid

Firstly, cotton fabrics were dipped in distilled water at 80 ℃ temperature for 1 hour and then dried in a vacuum oven overnight at 40 ℃. Egg white protein was removed from the egg with the help of yolk separator, and separated protein (30 wt%) was then dissolved in distilled water using magnetic stirrer speed of 400 rpm for 90 minutes at 30 ℃ (pH = 8.5). The vacuum oven dried fabrics were dipped in egg white protein solution for 5 min and then the excess solution was removed by squeezing and washing with water for 2 min. Protein coated fabric was then dipped for 2 min in 2% HA solution and excess of HA solution was removed by squeezing and washing with water for 2 min, as shown in Scheme 1. The coated fabrics were dried overnight at 90 ℃. This process was used for making four samples besides the control sample (CT), egg white protein coated cotton sample (CT_W), hypophosphorous acid coated cotton sample (CT_{HA}), CT_{HA+W} and CT_{W+HA} were named according to the order of coating, i.e., CT_{HA+W} represents cotton first coated by hypophosphorous acid as primary layer followed by egg white protein as second layer coating whereas CT_{W+HA} represents cotton fabric coated first by egg white protein and then hypophosphorous acid.

2.3. Characterization

Functional groups and nature of bonds present in CT, CT_W, CT_{HA} and CT_{W+HA} were analyzed from IR measurement through fourier transformation infrared spectrophotometer (PerkinElmer, USA) in ATR mode and samples were scanned over the wavenumber range 4000 – 500 cm^{-1}.

The field emission scanning electron microscope (FESEM) was used to capture surface morphology of all samples and residue of char produced after combustion using MIRA3 TESCAN FESEM equipped with Energy Dispersive X-ray spectroscopy AMETEK EDAX. The elemental composition of coated fabric with egg white protein and hypophosphorous acid was determined with the help of Elemental Dispersive X-Ray analysis (EDAX).

The thermal stability of cotton fabric and all coated samples was measured through thermogravimetric analyzer (TGA 55, TA Instruments, USA). The sample was placed in a platinum pan and the pan was placed inside the furnace maintained in nitrogen and oxygen atmosphere, where the temperature increased from 30 ℃ to 800 ℃ with a constant heating rate 10 ℃/min. Weight loss % of sample with temperature was recorded as thermogram.

The vertical flame tests were performed for control fabric and coated fabrics was performed in methane gas flame for 12 s according to ASTM D6413-08 standard test procedure. Total char length was measured using scale after burning. The sample size was taken for the test was 76 × 300 mm^2.

The horizontal flame test was performed for 10 s according to ISO 15025:2016 standard. The methane gas flame of 25 ± 2 mm length was placed horizontally at 20 mm distance above the bottom edge and 17 ± 1 mm distance from the front face. The sample of size 200 × 160 mm^2 was taken for test control and coated fabric

3. Results And Discussion

3.1. Coating growth with layer deposition

As stated elsewhere (Wang et al. 2018), the flame retardancy of coated fabric depends on gain in weight percent (Wg%) compared to the control fabric. Gain in weight percent (Wg%) of coated fabric is expressed as:

$$Wg\% = \frac{W_t - W_c}{W_c} \times 100\% \qquad (1)$$

Where W_t and W_c indicate weights of coated and control sample respectively.

Increased weights of control fabric after treatment with various flame-retardants and their combinations are presented in Fig. 1. Percent weight gain due to application of fire retardants or their combinations were very much dependent on the sequence of application of coatings. Wg% of CT_W was 8.40%, which is higher than that of CT_{HA} (4.3%). Moreover, different coating sequences considerably influenced *Wg%* in

control fabric. If HA was used as a primary layer of coating followed by egg white as secondary, Wg% was found to be higher at 19.8% and was highest among all other samples prepared. When egg white protein was used as primary layer and HA as secondary (CT_{W+HA}), Wg% got lowered 16.3%. Hypophosphorous acid contained one phosphorus and of highly acidic behavior, which reduced the mechanical properties of coated fabric (CT_{HA}) when HA was used as primary layer. After HA treatment the CT_{HA} fabric became so delicate (drop in mechanical strength) that for subsequent egg white protein application it was very carefully handled to obtain CT_{HA+W} fabric. Thus, egg white protein was chosen as primary coating which no doubt increased percentage weight gain over control sample. Egg white protein derived from chicken egg showed alkaline behavior with pH = 8.5, possibly because of amino acids. Electrostatic and hydrogen bonding interactions between the coating and functional groups (-OH groups) of cellulose bonds of fabric facilitated easy adherence.

3.2. ATR-FTIR analysis of control and coated cotton fabric

The IR spectra of control fabric (CT), modified cotton with hypophosphorous acid (CT_{HA}), egg white protein (CT_W) and the combination coatings using egg white protein and hypophosphorous acid (CT_{W+HA}) are presented in Fig. 2. Some characteristic peaks appeared in control cotton (CT) fabric spectra were: H bonded OH stretch at 3320 cm^{-1}, systematic CH_2 stretch at 2910 cm^{-1}, absorbed H_2O at 1645 cm^{-1}, CH wagging at 1432 cm^{-1}, CH bending at 1370 cm^{-1}, CH wagging at 1313 cm^{-1}, CH deformation stretch at 1282 cm^{-1}, C-O stretch at 1024 cm^{-1} and 1000 cm^{-1} and OH stretch at 895 cm^{-1} (Chung et al. 2004). Egg white protein contained amino acids, so that CT_W spectra showed two new peaks at 1630 cm^{-1} and 1525 cm^{-1} indicating amide-I and amide-II (Bosco et al. 2013). In case of CT_{HA}, a new peak appeared at 980 cm^{-1} for P=O due to the presence of phosphorous content in hypophosphorous acid (Yu et al. 2017). According to CT_W and CT_{HA} spectra, in combined spectra of egg protein and HA (CT_{W+HA}) the three peaks found at 1630 cm^{-1}, 1525 cm^{-1} and 980 cm^{-1} would be amide-I, amide-II and P=O. So, these results indicate that hypophosphorous acid binds protein through electrostatic interactions, which makes cotton fire-resistant with single bilayer coating

3.3. Thermal stability of control and coated cotton fabrics

Thermogravimetric analysis (TGA) was carried out to understand thermal stability of all samples in presence of both nitrogen and oxygen atmospheres. TGA thermograms obtained with CT, CT_{HA}, CT_W, CT_{W+HA} and CT_{HA+W} are presented in Fig. 3a and 3b, while quantitative data are reported in Table 1 and Table 2. Under nitrogen atmosphere, TGA thermograms indicated occurrence of major weight loss between 200 to 800 °C. TGA analysis of controlled fabric showed two steps of weight loss: (i) cotton got dehydrated and carbonized producing CO_2, H_2O and char, and (ii) cellulose got depolymerized to levoglucosan, which got convert to low molecular weight compounds and secondary char (Lin et al. 2019). In the case of cotton coated with egg white (CT_W), the initial decomposition started at lower temperature, 260 °C compared to the temperature needed for controlled fabric, 294 °C. But, the rate of

weight loss with controlled fabric beyond 350 ℃ was much higher than that of CT_W. At 450 ℃, the residual weight % with control fabric was found to be 12 wt%, whereas it was 39 wt% with CT_W. These results indicate that cotton coated with egg white, CT_W could effectively reduce the rate of cotton decomposition even at higher temperatures. CT_{HA} showed decomposition at lower temperature, 252 ℃ relative to CT and CT_W. At higher temperatures, the rate of weight loss with CT_{HA} got lowered possibly due to presence of phosphoric acid groups of HA, which strongly inhibited depolymerization process of cotton fabric facilitating char formation. With CT_{HA+W} sample, primary degradation temperature was found to be 230 ℃, which is lower than that of CT_{HA} (252 ^{o}C) but carbon residue obtained was higher (7.8 wt%, at 800 ℃) compared to the same noted with CT_{HA} (4.9 wt% at 800^{o}C). As discussed before, strong acidity of HA often damages the fiber length thereby adversely effecting softness and mechanical properties of the fabric. Instead, HA if applied as secondary layer keeping egg white protein as primary layer in CT_{W+HA}, possibly it will improve the fabric performance. TGA analysis of CT_{W+HA} sample showed initiation of decomposition at lower temperature (153 ℃) compared to all other samples, but the rate of weight loss got lowered beyond 350 ℃. The char formation noted at 700 ℃ and 800 ℃ were 18.8 wt% and 11.6 wt% of respectively, which is much higher than the control fabric i.e. 0.64 wt% and 0.28 wt% respectively at 700 ^{o}C and 800 ^{o}C. Therefore, CT_{W+HA} showed appreciable fire retardancy along with considerably higher char formation compared to other samples.

In presence of oxygen, the control fabric produced 0.2 wt% char residue at 800 ℃, while other coated fabrics i.e. CT_W, CT_{HA}, CT_{W+HA} and CT_{HA+W} produced 3.8 wt%, 2.9 wt%, 11.4 wt% and 7.4 wt% of char respectively at 800 ℃. The levoglucosan chains of cotton continued its oxidization in presence of oxygen generating exothermic heat, which facilitated pyrolysis of cellulose. Thus, all fabric samples showed lower char residues compare those obtained with inert nitrogen atmosphere (Lin et al. 2019). Alongi *et al*. separately applied non- toxic/eco-friendly coating materials like caseins and hydrophobins over cotton and the char residues were 18 wt% and 19 wt% respectively at 600 ℃ under nitrogen atmosphere, while in presence of air those got reduced to 2 wt% and 4wt% respectively (Alongi et al. 2014). Annalisa *et al.* tried deposition of DNA derived from herring sperm as coating, which yielded char residue of 23 wt% and 6.9 wt% respectively in nitrogen and oxygen atmospheres (Annalisa et al. 2016). Bosco *et al.* also reported 1.5 wt% and 2.5 wt% of char formation under oxygen atmosphere, while cotton fabric was separately coated with folded and unfolded whey proteins respectively (Bosco et al. 2013). In the present investigation, the coating sequence of egg white protein followed by hypophosphorous acid layer (single bilayer over cotton fabric, CT_{W+HA}) resulted in 37.3 wt% and 11.5 wt% of char residue under nitrogen atmosphere at 600 ℃ and 800 ℃, which got reduced to 27.6 wt% and 11.4 wt% of char under oxygen atmosphere at 600 ℃ and 800 ℃ respectively. Therefore, layer by layer coating of egg white protein and HA i.e. CT_{W+HA} showed relatively better performance compared to earlier reports.

Table 1 TGA data in presence of nitrigen for CT (control fabric), CT_{HA} (hypophosphorous acid coated cotton fabric), CT_W (egg white protein coated cotton fabric), CT_{W+HA} (egg white protein with

hypophosphorous acid coated cotton fabric in sequence) and CT_{HA+W} (hypophosphorous acid with egg white protein coated cotton fabric in sequence).

Sample	T_{10} (°C)	T_{max} (°C)	Char at 600 °C	Char at 800 °C	Ref.
CT	311	346	0.9	0.2	This work
CT_W	278	315	16.7	6.4	This work
CT_{HA}	268	279	14.7	4.9	This work
CT_{W+HA}	168	245	37.3	11.6	This work
CT_{HA+W}	266	285	23.4	7.8	This work
COT_{DNA}			23.0		(Annalisa et al. 2016)
$COT_{\_caseins}$			18.0		(Alongi et al. 2014)
$COT_{\_hydrophobins}$			19.0		(Alongi et al. 2014)

Table 2 : TGA data in presence of oxygen for CT (control fabric), CT_{HA} (hypophosphorous acid coated cotton fabric), CT_W (egg white protein coated cotton fabric), CT_{W+HA} (egg white protein with hypophosphorous acid coated cotton fabric in sequence) and CT_{HA+W} (hypophosphorous acid with egg white protein coated cotton fabric in sequence

Sample	T_{10} (°C)	T_{max} (°C)	Char at 600 °C	Char at 800 °C	Ref.
CT	297	327	0.6	0.2	This work
CT_W	275	308	8.07	3.8	This work
CT_{HA}	251	260	12.9	2.9	This work
CT_{W+HA}	255	267	27.6	11.4	This work
CT_{HA+W}	268	277	18.7	7.4	This work
COT_{DNA}			6.9		(Annalisa et al. 2016)
$COT_{–Folded\ whey\ protein}$			1.5		(Bosco et al. 2013)
$COT_{–Unfolded\ whey\ [protein}$			2.5		(Bosco et al. 2013)
$COT_{\_caseins}$			2.0		(Alongi et al. 2014)
$COT_{\_hydrophobins}$			4.0		(Alongi et al. 2014)

3.4. Surface morphology of control and coated cotton fabrics

The surface morphology analysis of coated and control fabrics using FESEM are presented in Fig. 4. The control fabric (CT) showed a smooth surface without any defect. While the HA coated fabric (CT_{HA}) shows formation of surface cracks on its surface. This is possibly due to destruction of certain cellulose fibers due to corrosive nature of HA. On the other hand, the thickness of egg white layer coated fabric (CT_W) was found higher compared to control fabric. The coating thickness would protect the fiber from corrosive HA during its application as second layer.

Egg white protein and hypophosphorous acid get electrostatically linked through amino acid and phosphorus group of HA. The surface of fabric CT_{W+HA} appeared smooth with no defects. Egg white protein as first layer protected the cotton fabric from damage due to highly acidic HA. HA application resulted in formation of electrostatic linkages between amino acid groups and HA.

3.5. Elemental composition and distribution over surface of coated cotton fabric

The elemental composition and distribution over the surface of fabric was estimated through elemental dispersive X-ray analysis (EDAX) coupled with SEM. Fig. 5 and Table 2 show the elemental composition of CT_{W+HA}. Main elements which impart flame retardancy were nitrogen (N), phosphorus (P), and sulphur (S) and their content on the surface of CT_{W+HA} were found to be 16.03%, 8.09% and 2.33%, respectively.

Results showed that cotton coated with egg white protein and hypophosphorous acid increased fire retardation due to the high amount of N, P and S contents.

Table 3 Surface element composition of CT_{W+HA} (Egg white protein with hypophosphorous acid coated cotton fabric in sequence).

Element	Wt %	At %
C	43.06	51.44
O	30.49	27.35
N	16.03	16.42
P	8.09	3.75
S	2.33	1.04

3.6. Flame retardancy behavior of control and coated cotton fabric

Vertical Fire Test (VFT) for 12 s and BS EN ISO 15025 standard test of 10 s were carried out to establish the flame retardancy performance of CT_{W+HA} sample and compared to control fabric (CT). Fig. 6 and Fig. 7 show images of control fabric and coated fabric before and after burning through VFT and BS EN ISO 15025 tests and related data on flammability are presented in Table 3 and Table 4. The control fabric did not produce any char and afterglow time was 26 ± 5 s in VFT and 130 ± 5 s in BS EN ISO 15025 test, whereas CT_{W+HA} sample resulted in significant fragile char and no afterglow phenomenon could be observed. Coating played a crucial role in promoting dehydration reaction and char formation during burning. After VFT test, morphologies of control fabric (CT) and coated cotton fabric (CT_{W+HA}) were separately tested using FESEM (Fig. 7). The control fabric generated ash with no char, but continuous char layer appeared with CT_{W+HA}. The char formation occurred due to dehydration of cellulose, which get catalyzed due to presence of phosphorous atom of hypophosphorous acid. FESEM images of CT_{W+HA} interestingly showed appearance of numerous bubbles due to escape of volatile masses from the surface and thus a swollen fibrous structure of char appeared. This special swollen structure of char prevented interaction of combustible mass from areal oxygen and heat (Liu et al. 2017; Zhang et al. 2018). These bubbles also conform to the intumescent behavior of coating. Results indicated that synergistic effect between nitrogen (egg white protein) and phosphorus (hypophosphorous acid) resulted in formation of char network.

Table 4 Vertical flame test data of CT and CT_{W+HA}.

ASTM D6413 results	CT	CT_{W+HA}
After-flame time (s)	15 ± 5	1 ± 0
After-glow time (s)	26 ± 5	0
Char length (mm)	300	7.9
Occurrence of meting or dripping	no	no
Hole formation	yes	no
Comments	complete burn off, ash	strong char
Test passed	no	yes

Table 5 Results for CT and CT_{W+HA} in accordance with BS EN ISO 15025.

BS EN ISO 15025 results	CT	CT_{W+HA}
After-flame time (s)	74 ± 5	1 ± 0
After-glow time (s)	130 ± 5	0
After-glow beyond flame area	no	no
Hole formation	yes	no
Comments	complete burn off, ash	extinguishes suddenly and strong char
Test passed	no	yes

4. Conclusions

Layer by layer fire retardant coating was developed over the surface of cotton fabric adopting the water based method and with the combining of egg white protein and hypophosphorous acid (HA)

1. Gain in weight percentage with CT_W, CT_{HA}, CT_{W+HA} and CT_{HA+W} were 8.4%, 4.3%, 16.3% and 19.8%, respectively. A remarkable lowering in Wg% with HA layer is attributed to corrosive nature of HA, hence egg white layer was preferred as primary layer.
2. ATR-FTIR confirmed electrostatic interactions (nitro-phospho) between egg white protein and HA which resulted in P=O, amide-I and amide-II peaks with CT_{W+HA}.
3. TGA analysis under nitrogen and oxygen environment showed most of the mass loss between 200-800 °C. CT_{W+HA} showed minimum weight loss compared to all other samples and char residues were 37.3 wt% and 11.6 wt% at 600 ℃ and 800 ℃ in nitrogen and 27.6 wt% and 11.4 wt% in oxygen environment at 600 ℃ and 800 ℃ respectively.

4. EDAX analysis of the surface of CT_{W+HA} coating showed Nitrogen (N), phosphorus (P) and sulphur (S) to be 16.03%, 8.09% and 2.33%, respectively.
5. CT_{W+HA} fabric exhibited improved flame retardancy and self-extinguishing properties as estimated through VFT and BS EN ISO 15025 tests. The control fabric did not produce any char and afterglow times were 26 ± 5 s and 130 ± 5 s respectively with VFT and BS EN ISO 15025 tests. But, CT_{W+HA} fabric resulted in significant char formation and showed no afterglow phenomenon. Thus, coating promoted dehydration reaction and char formation during burning.
6. Evolution of volatile gases resulted in formation of numerous bubbles and swollen structure (FESEM images) over char while burning of CT_{W+HA}, which prevented interaction of combustible mass from oxygen and heat.

Therefore, coating made with egg white protein (as a primary layer) followed by HA resulted in excellent performance as fire retardant which can be safely used over cotton fabric.

Declarations

Acknowledgments

Financial support to execute the experimental work is gratefully acknowledged to MHRD (Ministry of Human Resources Development) Plan grant (2019-20) and IIT Roorkee (Indian Institute of Technology Roorkee (No. IITR/SRIC/OH-35-71-142), India.

Declaration

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. No animal/human studies were carried out by authors in this work.

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Figures

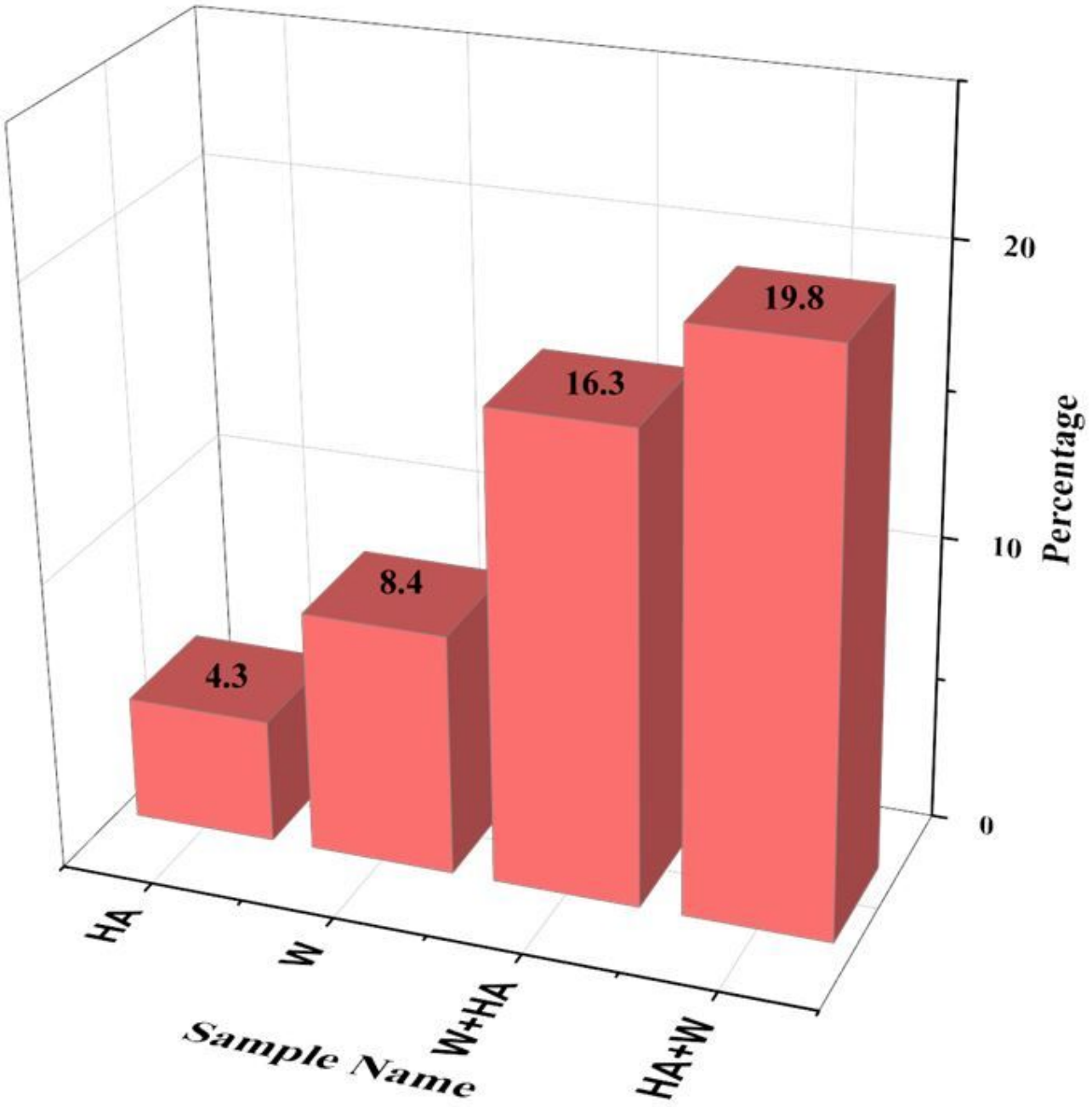

Figure 1

Gain in weight percent (Wg%) of cotton fabric by hypophosphorous acid (CTHA), egg white protein (CTW), combination of egg white protein with hypophosphorous acid (CTW+HA) and combination of hypophosphorous acid with egg white protein (CTHA+W).

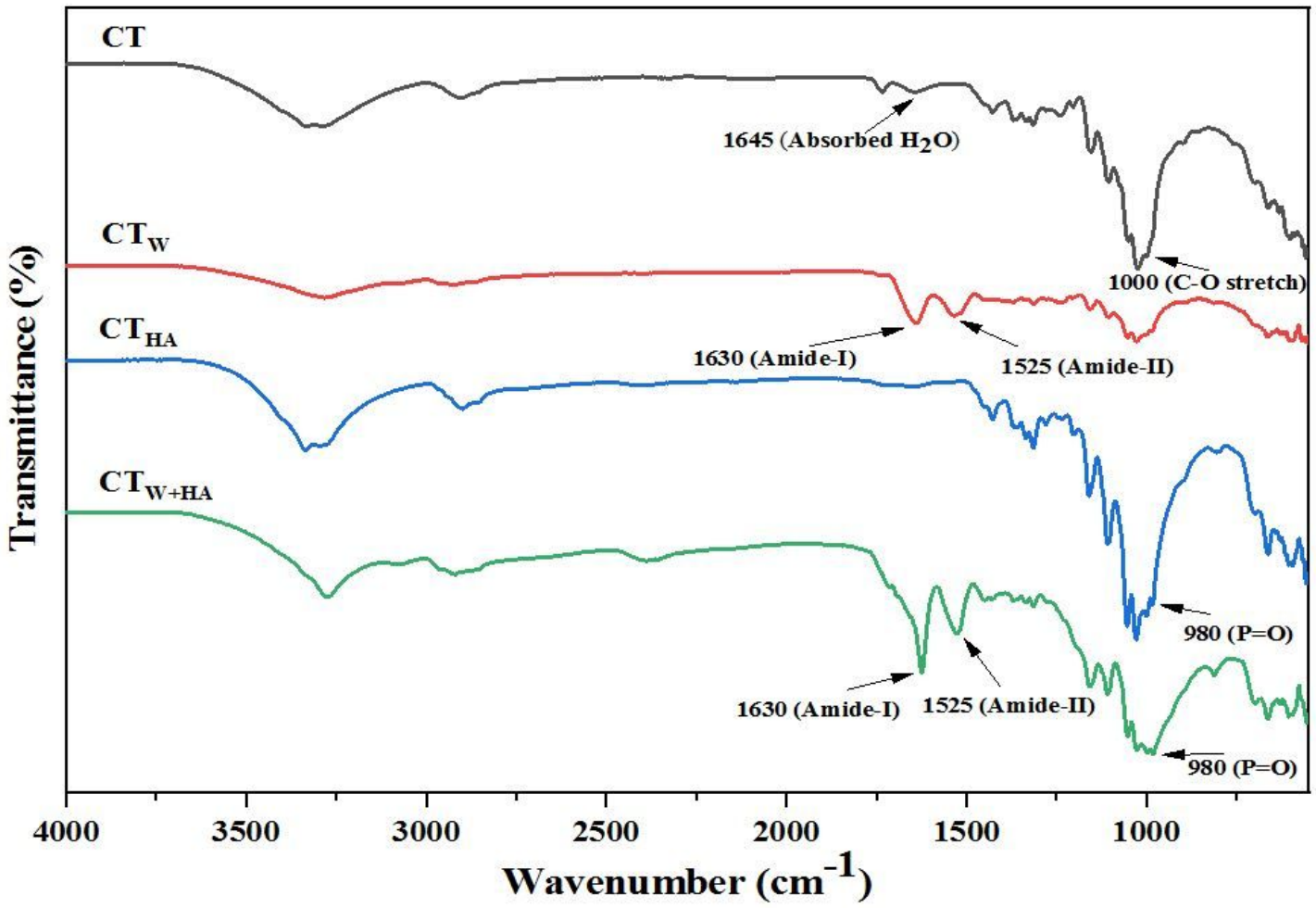

Figure 2

FTIR spectra of CT (control fabric), CTW (Egg white protein coated cotton fabric), CTHA (Hypophosphorous acid coated cotton fabric) and CTW+HA (egg white protein with hypophosphorous acid coated cotton fabric in sequence).

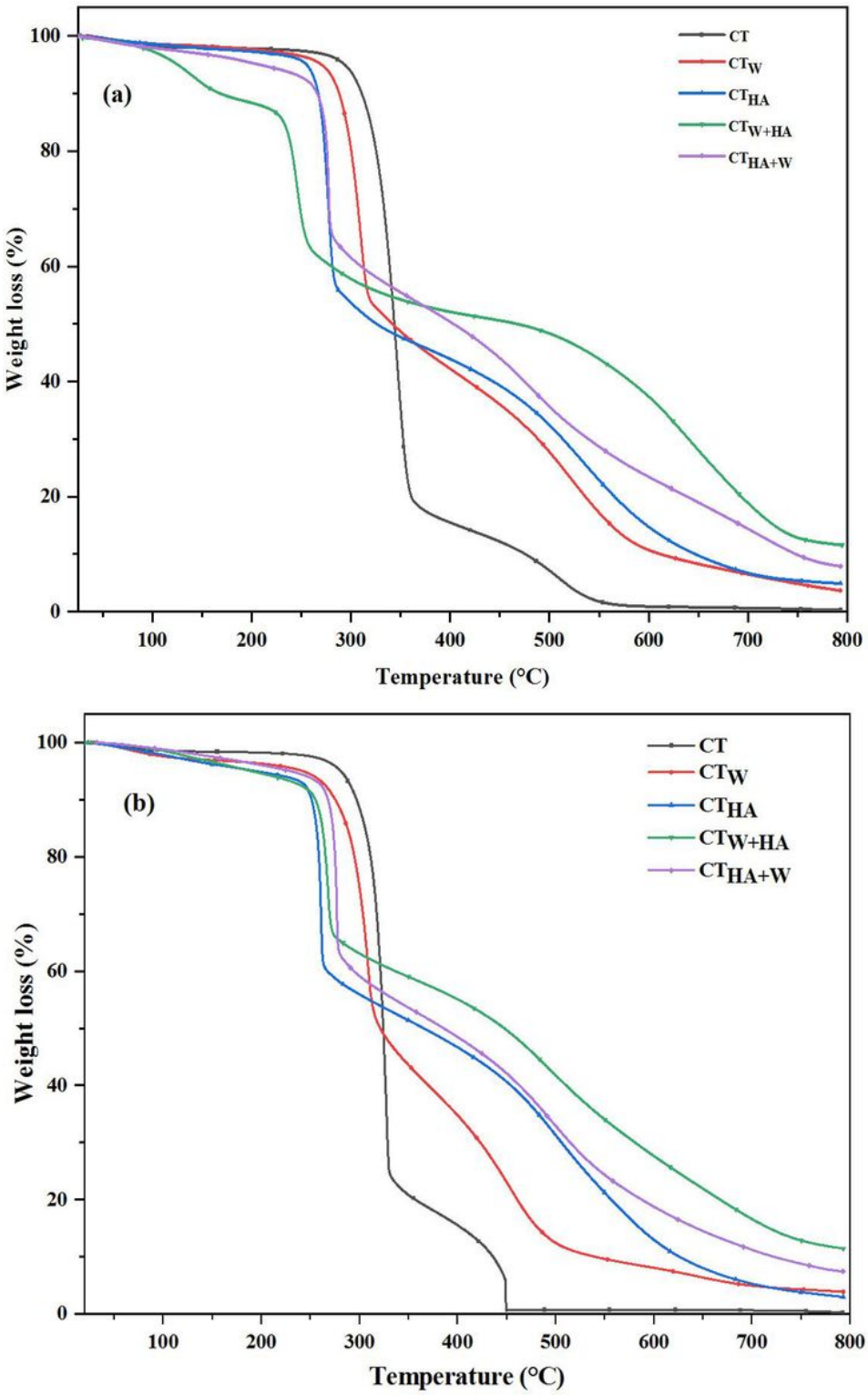

Figure 3

TGA graphs in (a) nitrogen and (b) oxygen atmosphere for CT (Control fabric), CTW (Egg white protein coated cotton fabric), CTHA (Hypophosphorous acid coated cotton fabric), CTW+HA (Egg white protein with hypophosphorous acid coated cotton fabric in sequence) and CTHA+W (Hypophosphorous acid with egg white protein coated cotton fabric in sequence).

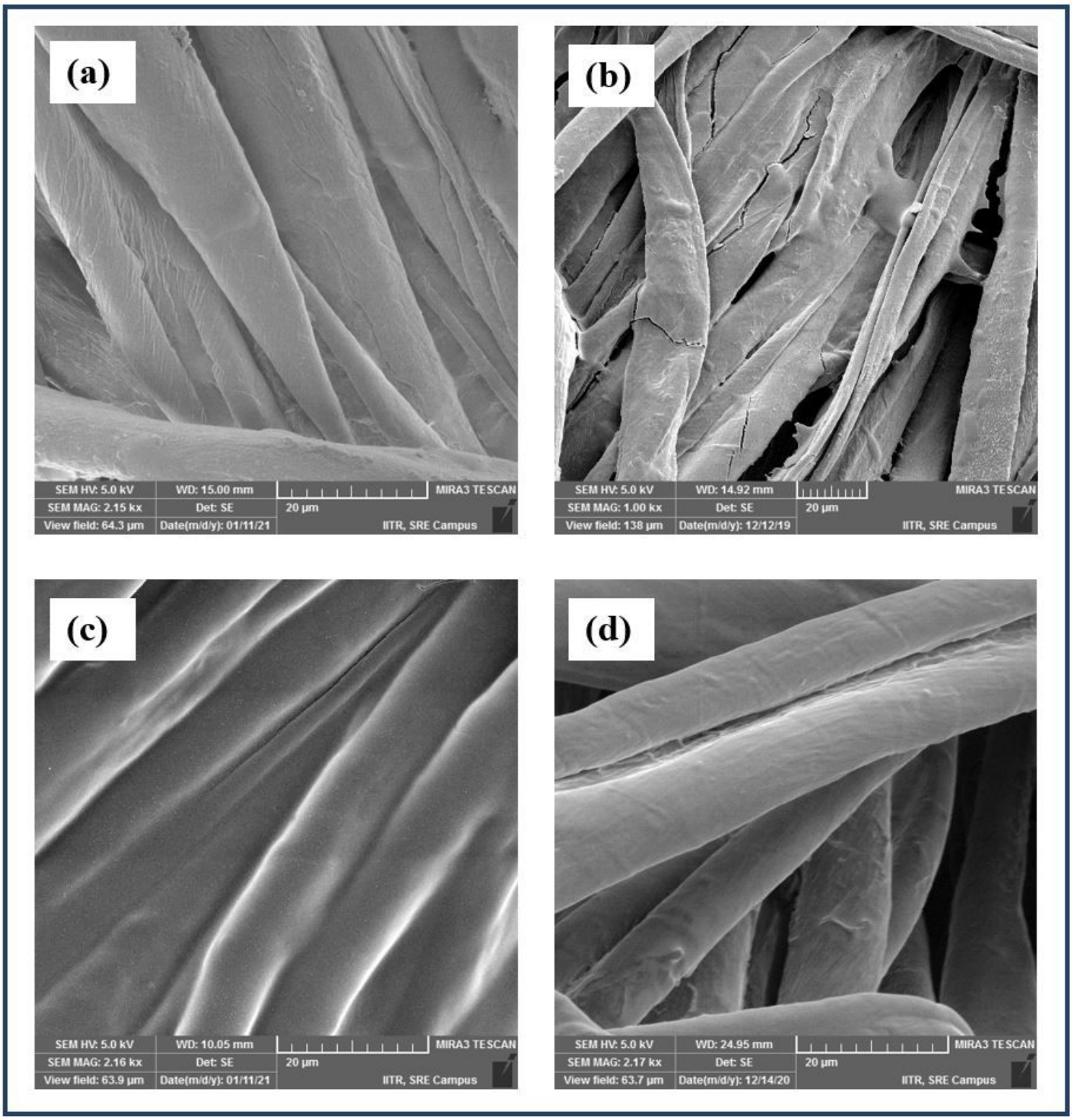

Figure 4

SEM picture of (a) CT (control fabric), (b) CTHA (hypophosphorous acid coated cotton fabric), (c) CTW (egg white protein coated cotton fabric) and (d) CTW+HA (egg white protein with hypophosphorous acid coated cotton fabric in sequence).

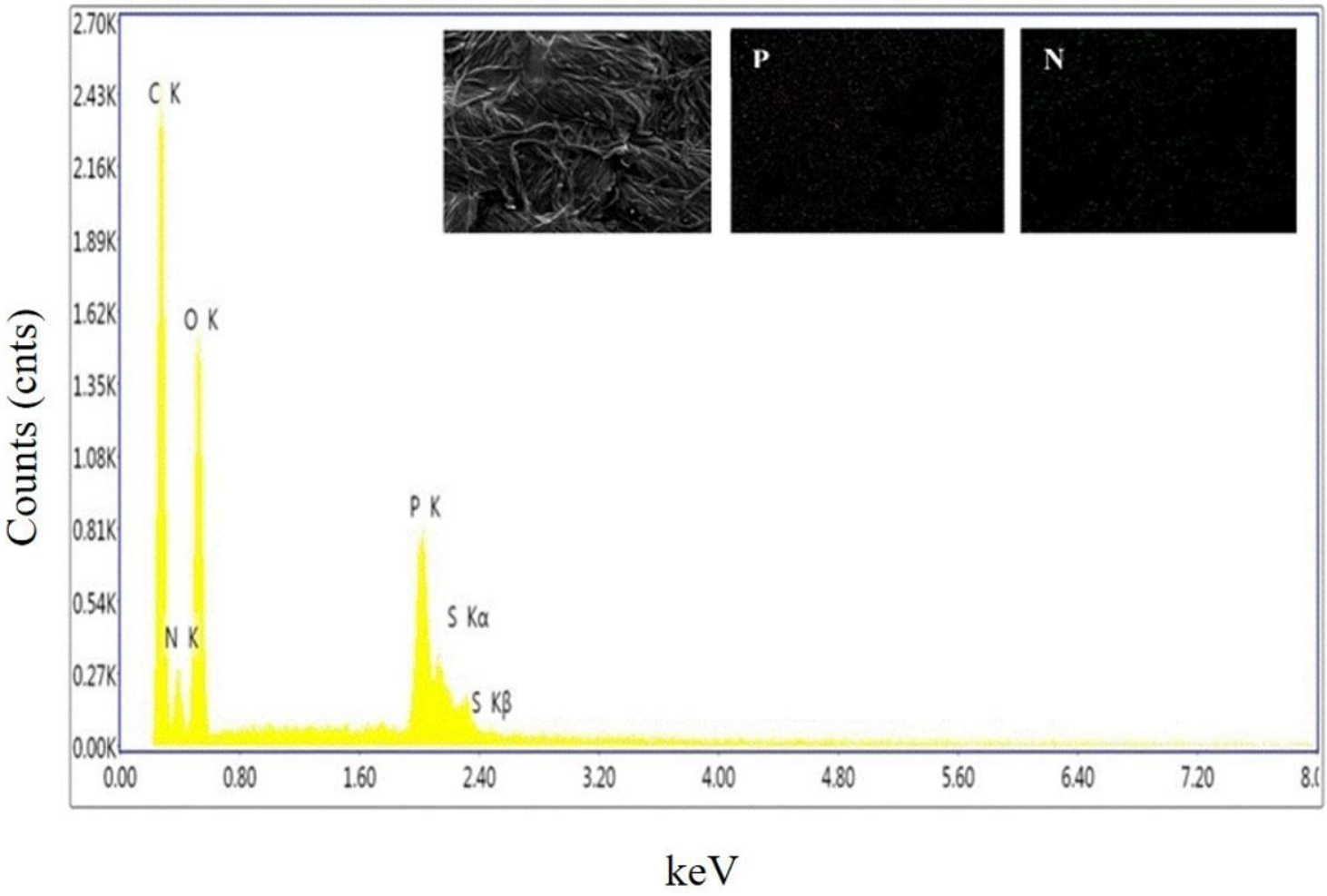

Figure 5

EDAX picture of CTW+HA (Egg white protein with hypophosphorous acid coated cotton fabric in sequence).

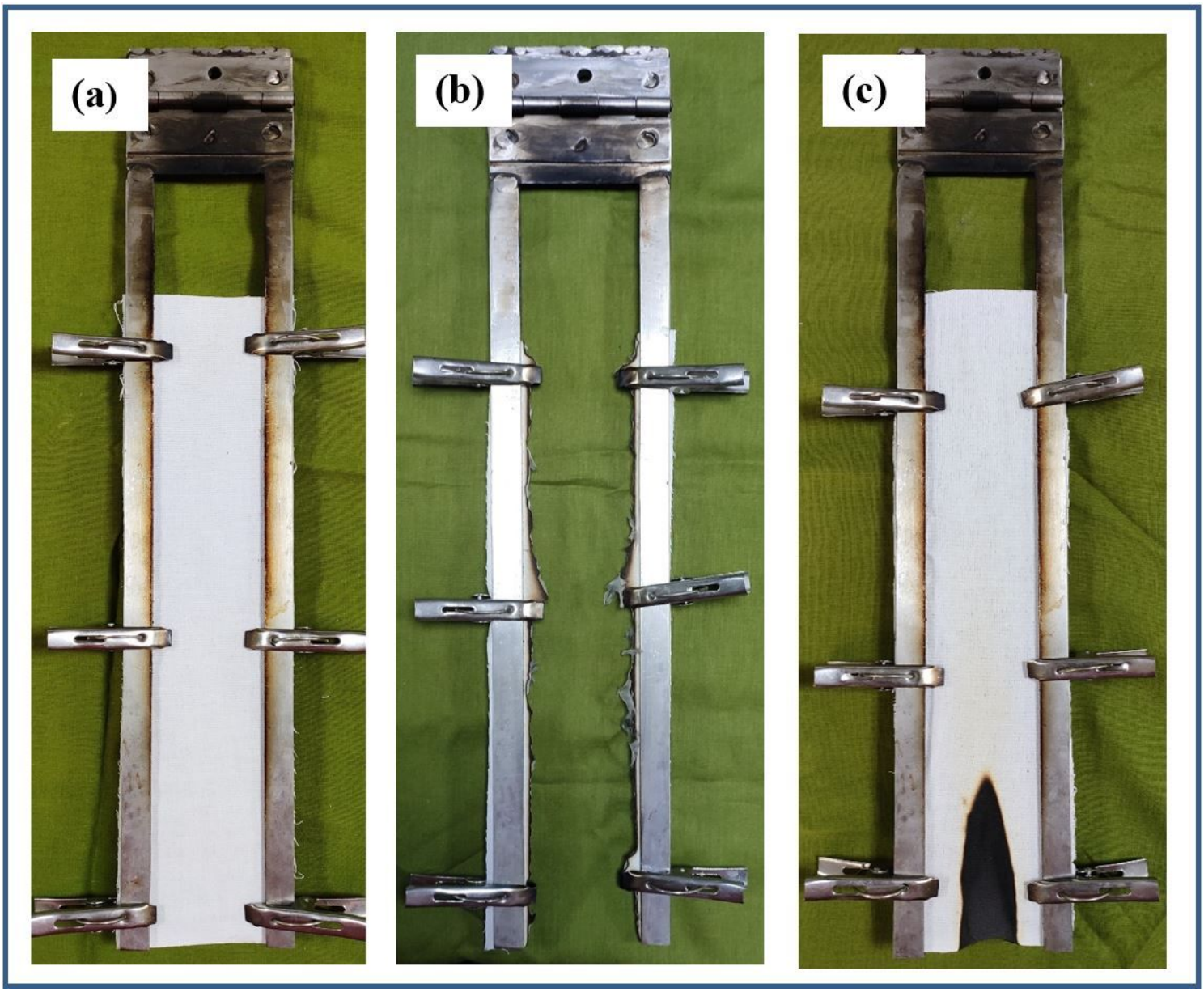

Figure 6

Picture of (a) CT before burn, (b) CT after burn and (c) CTW+HA after burn.

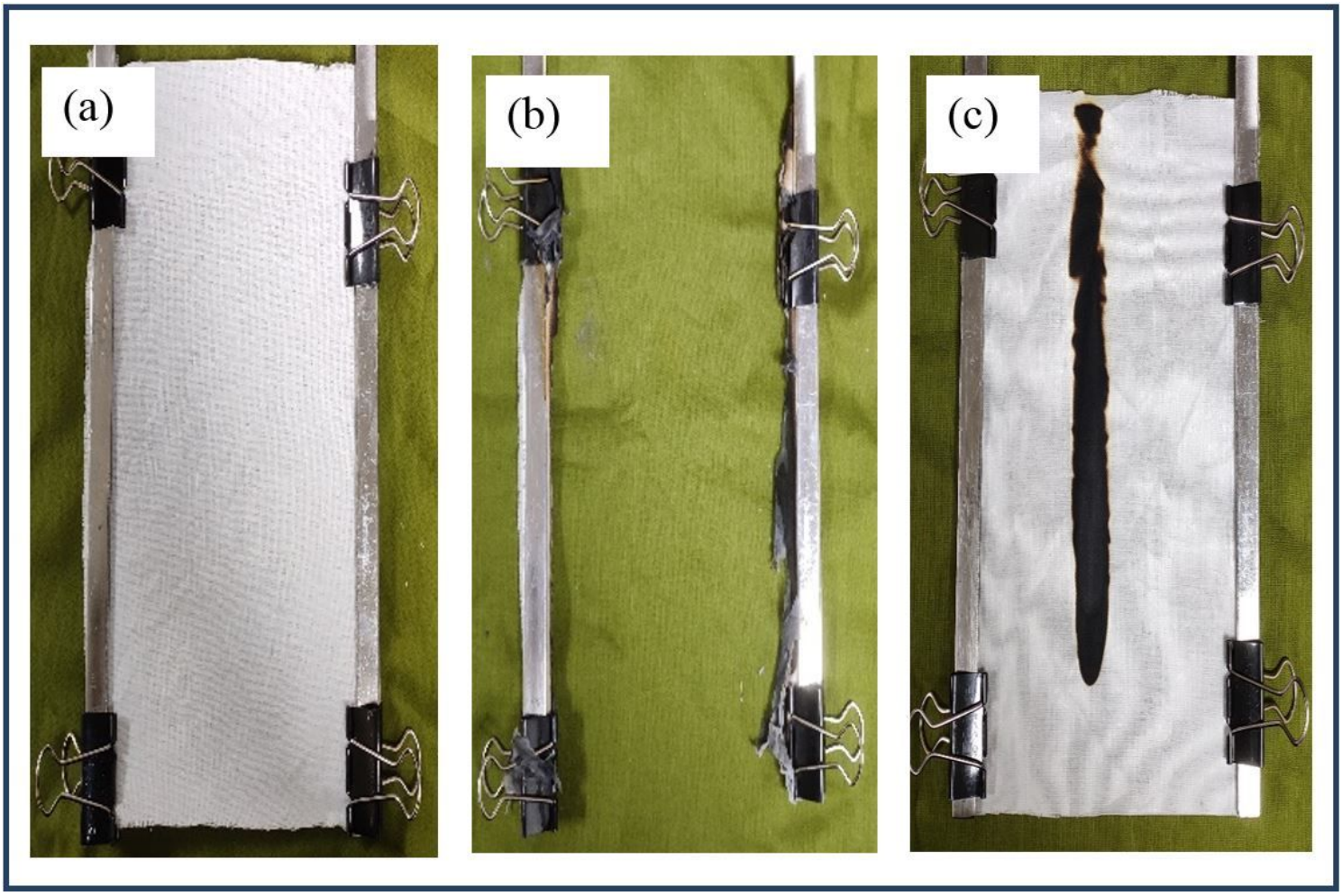

Figure 7

Images of (a) CT before burn, (b) CT after burn and (c) CTW+HA after burn.

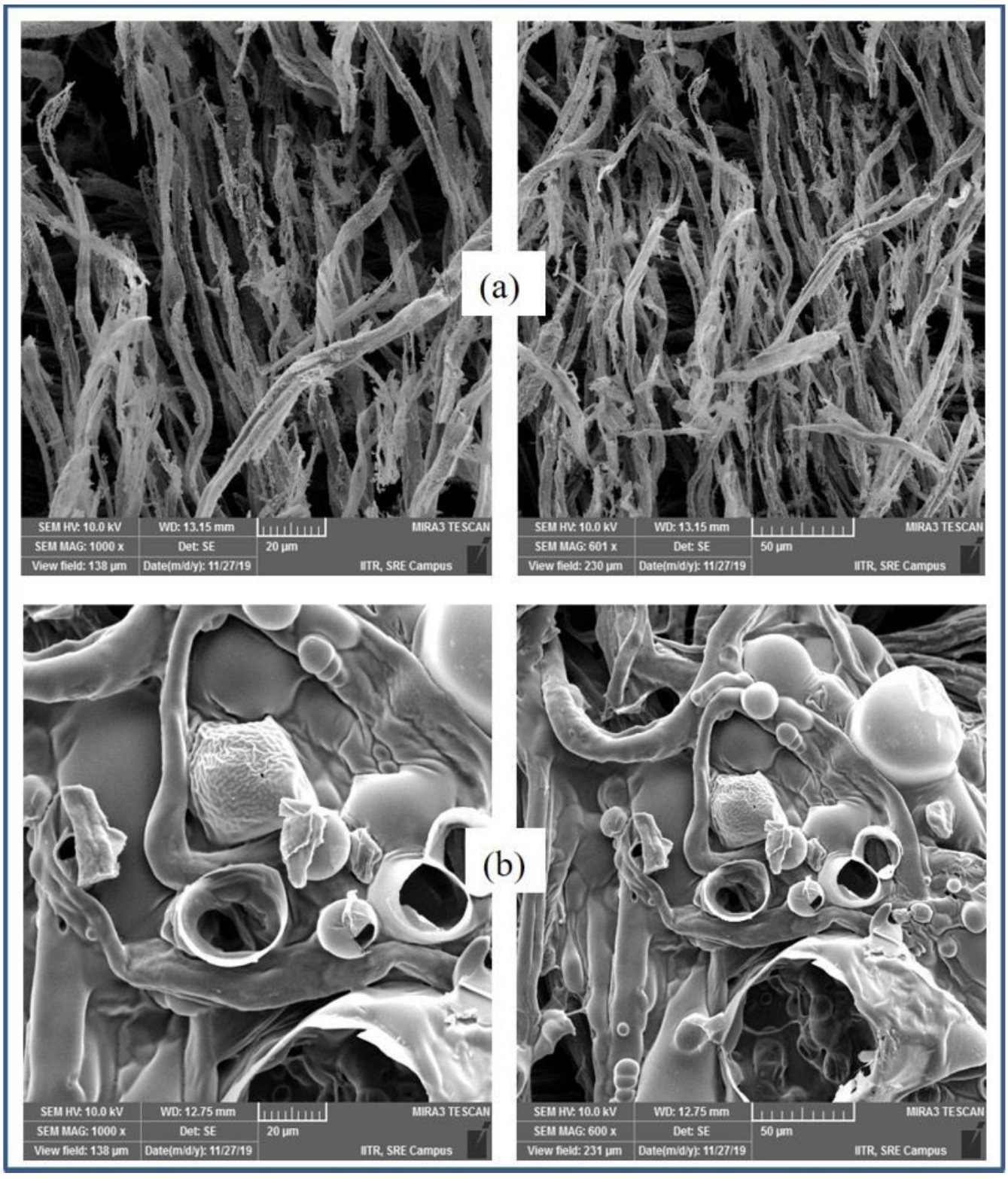

Figure 8

SEM image of (a) CT after burn, (b) CTW+HA after burning. The scale bar and magnification of right side image are 50 µm and 600. The scale bar and magnification for left side are 20 µm and 1000.

Supplementary Files

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- scheme1.jpg