MULTIFUNCTIONAL MODIFICATION OF COTTON FABRIC FOR ANTIMICROBIAL, FLAME-RETARDANT AND OLEOPHOBIC PROPERTIES

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In recent times, the investigation and development of multifunctional textiles have become a necessity for the textile and apparel industries. Therefore, this paper explores an innovative approach to enhancing the functional properties of cotton (cellulosic) fabric by integrating advanced technologies to impart oleophobic/hydrophobic, flame-retardant, and antibacterial characteristics. The methodology involves systematically applying chemical treatments utilizing a layer-by-layer finishing technique to achieve the desired multifunctionality in cotton fabric. Silver nanoparticles and a phosphorus-nitrogen-based synergistic flame-retarding agent were employed to finish the fabric. Performance testing encompasses evaluating bacterial reduction, contact angle measurements, water absorption properties, flame-retardant capabilities, and Limiting Oxygen Index (LOI). Characterization techniques such as FTIR, SEM, and EDX analysis, were carried out to assess structural and chemical modifications of the material. The results illustrate a notable transformation of the cellulosic fabric, showcasing enhanced resistance to bacterial attack, improved stain resistance, and heightened flame-retardant performance, without compromising its color indices and air permeability. The fabric retains these multifunctional attributes even after 20 cycles of laundering, which confers durability. The implications of this research extend the application of conventional cotton fabric in diverse sectors, including apparel, home furnishings, and industrial textiles.

Keywords: antibacterial, flame-retardant, cellulosic fabric, multifunctional textiles, silver nanoparticles, water and oil repellence

INTRODUCTION

Cotton, which has long been associated with simplicity and craftsmanship, has become popular because it is breathable and comfortable. Cotton, the most widely used cellulosic fiber, offers breathability, softness, and absorbency, making it suitable for various applications, including apparel and home textiles. The versatility and eco-friendliness of cotton fabric make it a preferred choice in the quest for sustainable and functional textile solutions. In response to the changing demands of the current market regarding fabrics that could offer multifunctional properties in the contemporary society, this research aims to improve the functionality of cotton, so that it can be utilized as a functional fabric for various purposes.[1] Therefore, this research explored the possibility of developing a cotton fabric capable of repelling oils, stains, and water, extending its aesthetic appeal and increasing its applicability in industries requiring oleophobic and hydrophobic properties.[2-6]

The novel approach aims to enhance the functionality and versatility of cotton fabric. By integrating functionalities, such as oleophobic and flame-retardant characteristics, this research aims to augment the fabric's repellence to water and oils, and retardancy to flames, while maintaining its handle values. The multifunctional attributes sought after in this study aspire to meet the evolving demands of modern society, offering sustainable solutions that elevate the performance and applicability of cotton fabric across diverse sectors, including apparel, home furnishings, and industrial textiles.[7-11]

In addition, incorporating antimicrobial properties is also an important measure in bringing cotton fabric into compliance with modern hygiene standards. Since health consciousness is becoming increasingly prominent in many industries, adding antimicrobial properties to fabric guarantees that it will not support the growth of microorganisms.

This makes it a perfect option for applications requiring hygiene and protection.[12-14]

Recently, there has been a growing emphasis on the applications of metal nanoparticles in various industries. The mode of action of these metallic nanoparticles depends on several factors, including the type of metal and the extraction method (chemical, physical, or biological). The most often used nanoparticles are silver (Ag-NP), gold (Au-NP), zinc oxide (ZnO), titanium oxide (TiO_2), silica (SiO_2), and iron oxide (Fe_2O_3). Among these, silver nanoparticles proved the most useful for the field this study deals with. This metal is chemically inert, stable in water, and does not oxidize in air. The optical, thermal, and catalytic properties of silver nanoparticles are influenced by their size, shape, distance, and surroundings. The high surface-to-volume ratio of silver nanoparticles allows them to demonstrate remarkable antibacterial effects, even at low concentrations.[15-21]

This study uses functional additives to confer three novel qualities to cellulosic fabric: oleophobic/hydrophobic, antimicrobial, and flame-retardant properties. These may make the fabric more adaptable and aligned with modern hygiene, durability, and safety needs. This study offers a redefined position for cellulosic fabric in various industries, including fashion, healthcare, and industrial safety.

EXPERIMENTAL

Materials

Cotton fabrics, with the following specifications: GSM – 350, EPI × PPI – 22 × 21, yarn count – 14 Ne, were purchased from Nahar Fabrics Ltd., Lalru. Silver nanoparticles were procured from N9 Pure Silver Company. Commercial finishing chemicals: Pyrovatex CP New (flame-retardant) was procured from Huntsman. Non-ionic detergent (NID) as surfactant, phosphoric acid, and other laboratory-grade chemicals were purchased from SD Fine Chemicals.

Methods

Application of finishing chemicals using layer-by-layer technique

Initial trials were taken with the individual application of silver nanoparticles and FR finishes with varying concentrations. Based on these trials, the combined finish was applied using the layer-by-layer technique (Fig. 1 (a and b)). The first strategy involved applying Ag-NPs to the cotton fabric first, followed by a layer of flame-retardant finish (Fig. 1 (a)). In the second technique, Ag-NPs were applied after the flame-retardant finish was applied, as shown in Figure 1 (b).

A silver nanoparticle suspension was prepared with varying concentrations in the ultrasonic bath. The fabric samples were immersed into these suspensions of silver nanoparticles with MLR 1:40 for 10 minutes. The treated fabric samples were passed through a padding mangle (2 dips – 2 nips) with 70% expression, and then the fabric samples were dried at 90 °C for 2 minutes.

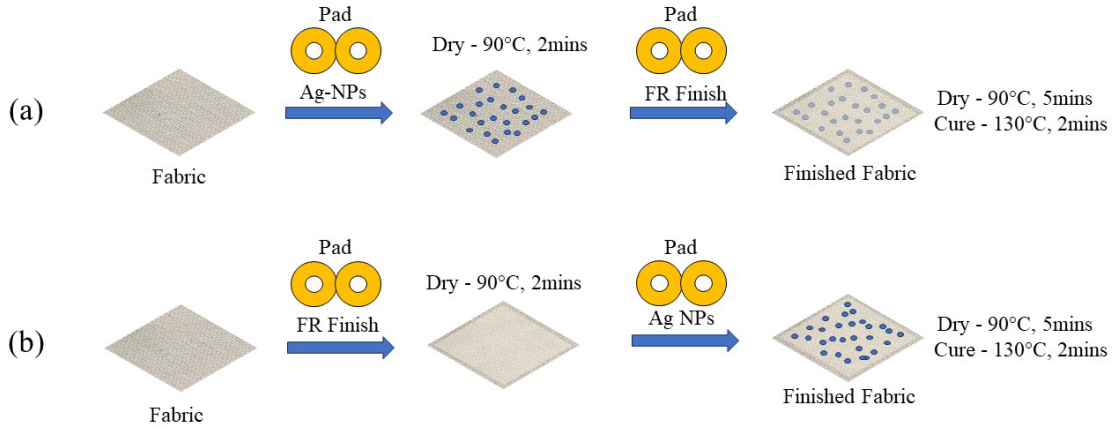

Figure 1: Layer-by-layer application of finishing chemicals

Similarly, the commercial flame-retardant finishing agent Pyrovatex CP was applied with varying concentrations. The cotton samples were immersed in the solution containing Pyrovatex CP with phosphoric acid with MLR 1:40 for 10 minutes. The treated fabric samples were passed through the padding mangle (2 dips – 2 nips) with 70% expression and dried at 90 °C for 2 minutes. Finally, after layer-by-layer application of chemicals, the finished samples were cured at 130 °C for 2 min and washed at 80 °C for 20 minutes with 2 g/L Na_2CO_3 and 1 g/L non-ionic detergent (NID) and dried at room temperature.

Characterization

The chemical characterization of the treated and untreated cotton (cellulosic) fabric samples was carried out by FTIR (Fourier transform infrared) spectroscopy using a Bruker ATR (Alpha) instrument. The surface morphology of the samples was analyzed with a scanning electron microscope (SEM) (EVO 18 Special, AG Carl Zeiss Ltd., Germany) to examine the deposition of nanoparticles on the samples. Elemental studies of treated cellulosic samples were carried out using energy-dispersive X-ray microanalysis (EDX) (QuanTax 200, Bruker Co., Germany).

Testing

Chemical add-on %

The uptake of chemicals (add-on %) on treated fabric was calculated using Equation (1):

$$Add\ on\ \% = \frac{W_F - W_O}{W_O} \times 100 \quad (1)$$

where W_F is the treated sample's standard condition weight, and W_O is the standard condition weight of the untreated sample.

Flame retardancy

The flame retardancy of samples was evaluated by the LOI/COI (limiting/critical oxygen index, the minimum volume percentage of oxygen in a mixture of oxygen and nitrogen) value according to the ASTM D2863-08/ISO 4589 standard method using an oxygen index measuring instrument (Spectrum Automation and Control, India). Fabric samples of size 10 cm × 5 cm were prepared and placed in a cylinder, through which a mixture of nitrogen and oxygen was passed, and the minimum amount of oxygen required to support the combustion was evaluated using a gas analyzer.

The burning behavior of the treated samples was evaluated using the digital flammability tester of Paramount (digiFLAME-I, 45° inclined type) as per the ASTM D 1230 standard. This test method determines the ignition and burning times of the materials subjected to a small flame under controlled laboratory conditions. The sample of size 150 mm x 50 mm (6 inches x 2 inches) was fixed in a stainless-steel frame and placed on an inclined plane inside the chamber. The sample was exposed to a 2.5 cm flame from a burner for a specified time. The digital timer recorded the time for ignition and burning or extinguishing.

Hydrophobicity and oleophobicity

The water-repellence of the samples was evaluated using a spray tester of IKON Industries as per the AATCC 22-2014 test method. In this test method, the face of the fabric specimen was exposed to the water spray using a ring in an inclined position. Then, 250 mL of distilled water at 27 °C was poured into the funnel of the tester and sprayed onto the test specimen for 25–30 seconds. After that, the changes in the specimen and the sticking or wetting of the specimen face were assessed. The rating was made according to AATCC Test Method 22–2014, which is technically equivalent to ISO 4920.

The hydrophilicity and oleophobicity of the cotton fabric samples were evaluated using the AATCC 79-2000 test method, where the contact angle measurements were done with water and oil drops. Distilled water/oil droplets were carefully dispensed onto the fabric surfaces from a syringe. The water contact angle was measured 60 seconds after the droplets were placed on the fabric's surface using a high-resolution digital camera. For statistics, 5 separate measurements were performed in different locations, and the results were averaged to obtain the average contact angle mean and standard deviation.

Antibacterial property

The antibacterial properties of the treated cotton samples were evaluated against *Escherichia coli* (gram-negative bacterium) and *Staphylococcus aureus* (gram-positive bacterium) using the suspension method. The suspension tests were performed using AATCC 100-2004 as a quantitative technique. Antibacterial activity was expressed in terms of bacterial reduction (BR) % and calculated using Equation (2):

$$Bacterial\ Reduction\ Efficiency\ (BR)\% = \frac{(A-B)}{A} \times 100 \quad (2)$$

where A is the number of bacteria recovered from the inoculated treated test specimen incubated for 24 h, and B is the number of bacteria recovered from the inoculated treated test specimen immediately after inoculation (at '0' contact time).

Whiteness and yellowness indices

The change in color of the cotton samples was evaluated in terms of whiteness and yellowness indices. These indices were used to assess the effect of finishing on the appearance of the fabric. The measurements were performed on a Macbeth computer color matching system, with D65 illuminated at 10° observer. The whiteness index was measured as per the Hunter scale, and the yellowness index was measured as per ASTM – E313. Each fabric sample was folded four times, and three scans were done on the fabric surface at distinct portions.

Wash durability

The durability of washes was assessed by AATCC Test Method 61-2000, Test No. 2A, utilizing a Launder meter to simulate washing conditions. The fabric samples underwent 10 and 20 washing cycles to evaluate their performance under repeated laundering.

RESULTS AND DISCUSSION

Preliminary experiments

The preliminary experiments were performed with individual applications of flame-retardant

finish and silver nanoparticles. Silver nanoparticles (Ag-NPs) were applied with varying concentrations (0.5% to 4.5%) on cotton fabric samples, and the bacterial reduction (R, %) was evaluated and represented in Figure 2. The results show that the silver nanoparticles effectively reduce bacteria against gram-negative and gram-positive bacteria. The untreated cotton sample shows only 4% bacterial reduction, while the one treated with a concentration beyond 2% Ag-NPs shows almost 100% bacterial reduction.

The antibacterial activity of Ag-NPs is due to the release of Ag ions. It has been established that silver ions interact with phospholipids connected to the proton pump of bacterial membranes and proteins, explicitly reacting with the negatively charged thiol groups. This results in the collapse of the membrane proton gradient and the breakdown of many mechanisms of cell metabolism, resulting in cell death.[18,22] Silver ions have more than one mode of action. Their interactions with different bacteria lead to various consequences, including growth inhibition, loss of infectivity, and cell death. The mechanism depends upon the concentration of silver ions and the susceptibility of microbiological organisms to silver.[23,24]

Similarly, the flame-retardant finish was applied using Pyrovatex CP with phosphoric acid (PA). The LOI values of the cotton samples treated with varying concentrations of Pyrovatex and phosphoric acid are presented in Figure 3.

Cotton fabric without any treatment shows an LOI value of 18 and was completely burnt, suggesting that cotton fabric has poor fire retardancy. The LOI value of cotton samples increases with the concentration of Pyrovatex, and a concentration of more than 350 g/L provides LOI values beyond 22. An LOI value below 21 is classified as flammable; 21 < LOI < 28 is considered slow-burning, and beyond an LOI value of 28 the material is self-extinguished.[23,25]

Pyrovatex CP New (N-methylol dimethylphosphonopropionamide, MDPA) is an organophosphorus-based flame retardant (FR), a commonly used agent for cotton fabric. It can react with cellulosic fibers or form crosslinked structures on the fiber. These compounds can increase the formation of char and prevent the formation of levoglucosan and flammable volatiles, thus acting as FRs for cellulose.

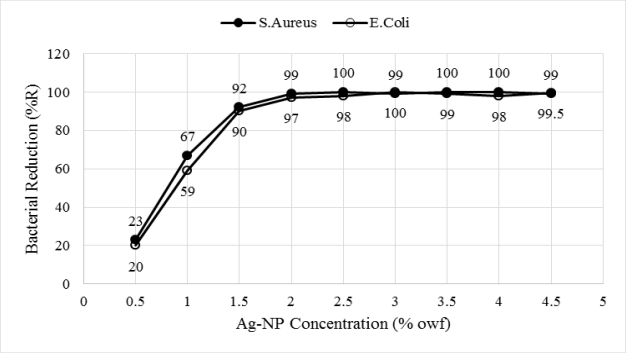

Figure 2: Effect of silver nanoparticle (Ag-NP) concentration on bacterial reduction %

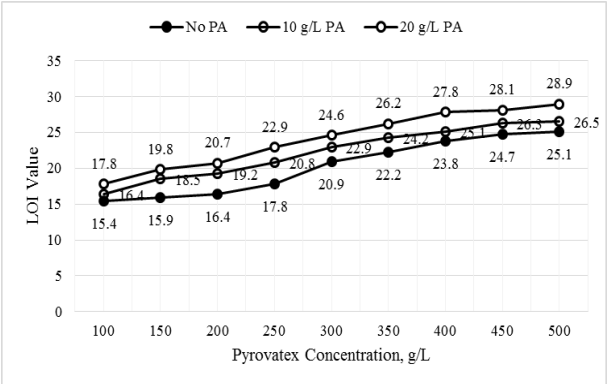

Figure 3: Effect of Pyrovatex and phosphoric acid (PA) concentration on LOI value

Phosphoric acid (PA) can also be used as a flame-retardant finishing for cellulosic fabrics. Therefore, the combination of both works in synergism. Phosphoric acid is used with Pyrovatex to enhance fire retardant performance.[26-28]

The combination of phosphoric acid and Pyrovatex shows an improvement in LOI values. An LOI value beyond 21 is achieved at lower concentrations (300 g/L and 250 g/L) of Pyrovatex with 10 g/L and 20 g/L phosphoric acid, respectively (Fig. 3). Hence, for further experimental study, 400 g/L of Pyrovatex with 20 g/L phosphoric acid was used as flame-retardant finish.

Combined finishing treatment of cotton fabric

Further, the combined finishing was employed using the layer-by-layer technique, where two distinct routes (Fig. 1 (a and b)) were followed. The trials were also conducted with Ag-NPs and Pyrovatex applied simultaneously; however, the agglomeration of Ag-NPs in the presence of Pyrovatex leads to non-uniform application. Thus, it was decided not to apply these simultaneously for further experiments. The characterisation of the samples subjected to the finishing treatments is presented below.

FTIR analysis

FTIR analysis in Figure 4 aids in identifying specific functional groups associated with the applied treatments, elucidating chemical bonds formed or modified during the finishing processes. This information is instrumental in understanding the molecular transformations contributing to the desired functional properties in the treated fabric, such as flame retardancy and antimicrobial activity. The FTIR spectra for three distinct samples – untreated fabric, fabric treated with Ag-NPs + FR finish, and fabric treated with FR + Ag-NPs finish, are depicted in Figure 4, offering a comparative examination of their molecular profiles.

The FTIR spectrum of untreated fabric serves as a baseline, showcasing characteristic peaks associated with cellulose, the primary component of cotton. Peaks at specific wavenumbers correspond to functional groups present in cellulose, such as hydroxyl (OH) groups, carbonyl (C=O) groups, and other characteristic vibrations. C-H stretching vibration peaks around 2936 cm^{-1}, and -C-O-C stretching vibration peaks at 1160, 1104, and 1028 cm^{-1} correspond to typical peaks of the infrared spectrum of cellulosic fiber. From the standard data, the absorption peaks for different bonds are matched. The metallic element shows its characteristic peaks. The presence of Ag can be detected in the fiber polymer matrix with the help of FTIR spectra. The stretching vibration and variable angle vibration of Ag ions create peaks in the 833-861 cm^{-1} region. It confirmed that Ag was present on the fabric's surface. Nanoparticles are bound to the textile substrate with the help of a coupling agent, which, at one end, binds with the fiber polymer and, on the other end, interacts with the nanoparticles.

The stretching vibration peak of O-H on the fabric surface is located at 3332 cm^{-1}, indicating a significant interaction of (-OH) molecules on the Ag ions surface. The peak at 1638 cm^{-1} is due to the absorption of water molecules and is induced by the bending vibration of O-H. Also, Pyrovatex CP forms an amide (CO-NH) bond with the hydroxyl (OH) group of cotton (Fig. 8 (a)). Phosphoric acid has been used in FR finish and has three carboxylic groups. These carboxylic groups form electrostatic interactions with charged nanoparticles. The analysis of FTIR spectra has helped identify the formation of these bonds by providing their characteristic absorption peaks at 2360 cm^{-1}. The FTIR spectrum of the fabric treated with Ag-NPs + FR finish shows notable changes in peak intensities and positions compared to the untreated fabric, indicating the successful incorporation of silver nanoparticles (Ag-NPs) and flame retardant (FR) agents. New peaks or shifts in existing peaks may signify chemical interactions between the treatment components and the fabric.

SEM analysis

In Figure 5 (a) to (c), a comprehensive visual exploration of treated samples is presented through scanning electron microscopy (SEM) images, revealing the discernible presence of silver nanoparticles and of the flame retardant (FR) agent. These microscopic snapshots provide a detailed insight into the surface morphology of the treated materials, showcasing the efficacy of the applied treatments.

The images vividly display the deposition and distribution of silver nanoparticles, emphasizing their uniform dispersion across the treated samples. This visual evidence underscores the successful integration of silver nanoparticles onto the substrate, suggesting potential antimicrobial or catalytic functionalities.

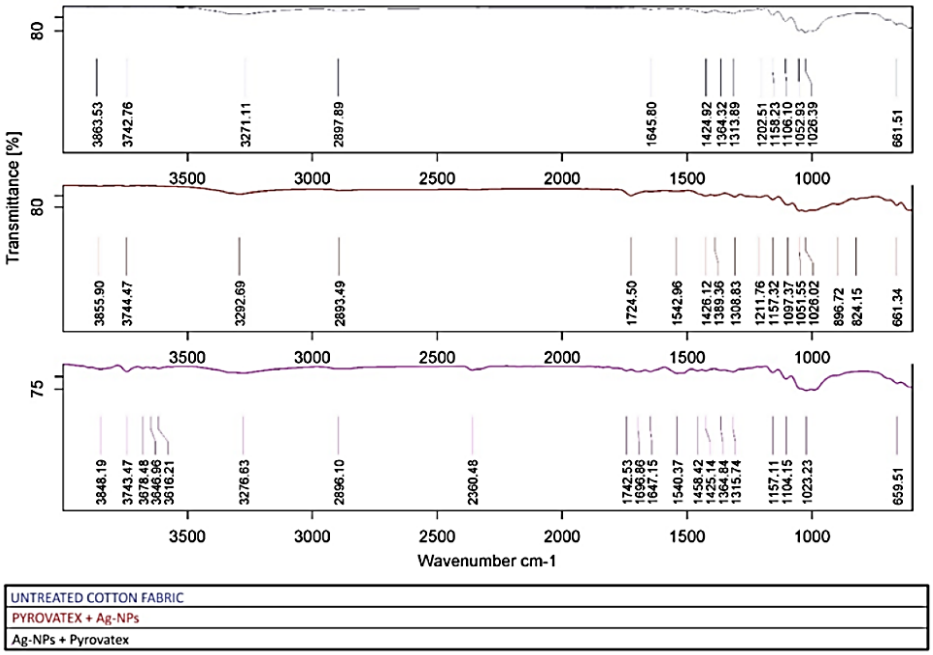

Figure 4: FTIR spectra of (a) untreated, (b) Ag-NPs + FR finished, and (c) FR + Ag-NPs finished fabric samples

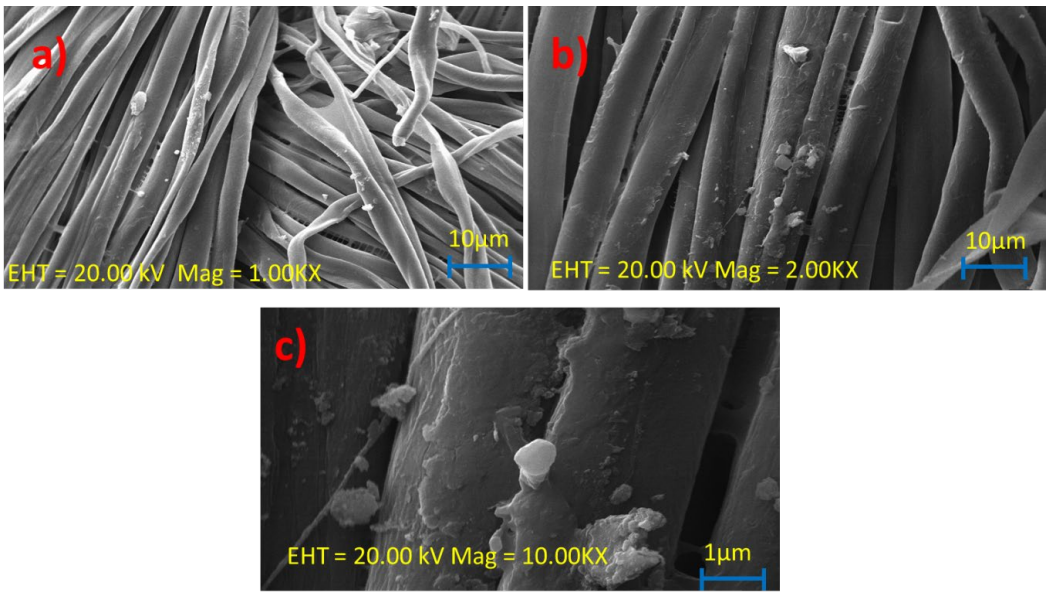

Figure 5: SEM micrographs of (a) untreated, (b) Ag-NPs + FR finished, and (c) FR + Ag-NPs finished fabrics

In addition to showcasing the presence of silver nanoparticles and the FR agent, Figure 5 ((a) to (c)) also provides a comparative analysis of surface roughness between the treated and untreated samples. The SEM micrographs allow for a qualitative surface topography assessment, highlighting any alterations induced by the applied treatments. These observations contribute valuable insights into the impact of silver nanoparticles and the FR agent on the material's texture, offering a holistic understanding of the surface modifications. Overall, Figure 3 visualizes the successful incorporation of silver nanoparticles and the FR agent onto the treated samples, while presenting a comparative surface roughness analysis to untreated counterparts.

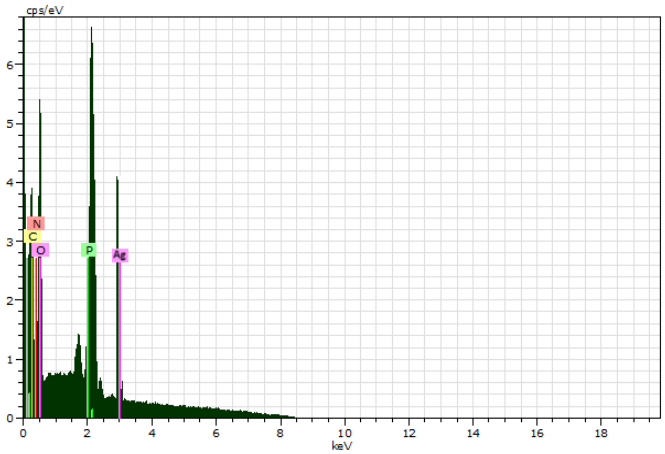

Figure 6: EDX spectrum of FR + Ag-NPs finished fabric

EDX analysis

The energy-dispersive X-ray (EDX) analysis results offer valuable insights into the elemental composition of the treated fabric. The EDX spectrum in Figure 6 provides a quantitative assessment of the presence of specific elements, notably silver (Ag), phosphorus (P), and nitrogen (N), each of which plays a crucial role in imparting the desired functional properties to the fabric. The EDX analysis for the Ag-NPs treated sample reveals a distinct peak corresponding to silver (Ag), appearing at 3 keV, which could be attributed to the silver signal of Ag-NPs, confirming the successful incorporation of silver nanoparticles onto the fabric. The presence of silver is of significant interest due to its well-known antimicrobial properties. Introducing silver nanoparticles is instrumental in conferring antibacterial attributes to the fabric, thereby enhancing its utility in applications where microbial resistance is paramount.

Furthermore, the detection of phosphorus (P) and nitrogen (N) in the EDX spectrum indicates the presence of a flame retardant (FR) agent on the fabric. Phosphorus and nitrogen-based flame retardants are known for their efficacy in reducing the flammability of materials. Collectively, the EDX analysis in Figure 6 provides a comprehensive understanding of the elemental composition of the treated fabric. The presence of silver, phosphorus, and nitrogen underscores the multifunctional nature of the treatment, endowing the fabric with antimicrobial, flame-retardant, and enhanced durability of the desired properties.

Antibacterial property

The results of bacterial reduction (R%) for the untreated and differently finished cotton fabric samples are depicted in Table 1. The data in Table 1 and Figure 7 (a) indicate that the untreated cotton fabric has no antibacterial effect, with bacterial reduction % of only 3% (*S. aureus*) and 2% (*E. coli*), which is because the untreated cotton fabric does not have any antibacterial agent on its surface. The fabric treated with Ag-NPs exhibited almost 100% reduction of both types of bacteria. Combining Pyrovatex (FR) over the Ag-NPs had a tangible effect on the antibacterial activity of treated cotton fabrics – *S. aureus* (85%) and *E. coli* (78%) – Figure 7 (b). Meanwhile, the samples coated with Ag-NPs over Pyrovatex (FR) exhibited a 99% reduction in *S. aureus* and 97.5% in *E. coli* (Fig. 7(c)).

Table 1
Antibacterial properties of cotton fabric samples

Cotton fabric sample	Bacterial reduction (R%)	
	S. aureus	*E. coli*
Untreated	3	2
Ag-NPs treated	99.5	98.5
FR finished	5	3.5
Ag-NPs + FR finished	75	68
FR finished + Ag-NPs	99	97.5

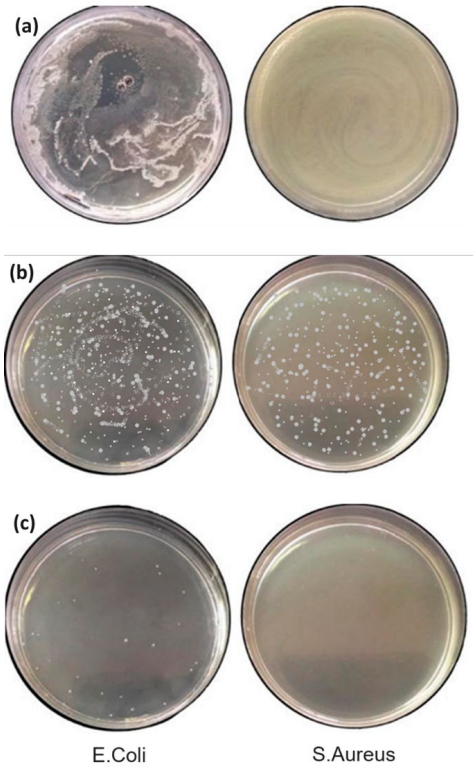

Figure 7: Bacterial reduction efficiency against *E. coli* and *S. aureus* of (a) untreated, (b) Ag-NPs + FR finished, and (c) FR + Ag-NPs finished cotton fabric samples

In comparison with the application of Ag-NPs alone and the Ag-NPs applied over the FR finishing, the cotton fabric sample treated with FR over the Ag-NPs application yields a lower bacterial reduction percentage. The Pyrovatex CP used as FR finish is also crosslinked with the free hydroxyl groups of the cellulose (Fig. 8(a)). Specifically, the surface of Ag-NPs oxidizes in water or moist air to release Ag ions. Ag ions are primarily responsible for the bacteriostatic action of Ag-NPs, which is determined mainly by the amount of Ag ions released. These Ag ions are oxidants because they are positively charged cations that cause cell death in bacteria.[29,30] Therefore, Ag-NPs at the surface release more Ag ions than the sample where a flame-retardant finish was applied over the Ag-NPs (Fig. 8(b)). Hence, the sample with FR over Ag-NPs results in low antibacterial properties.

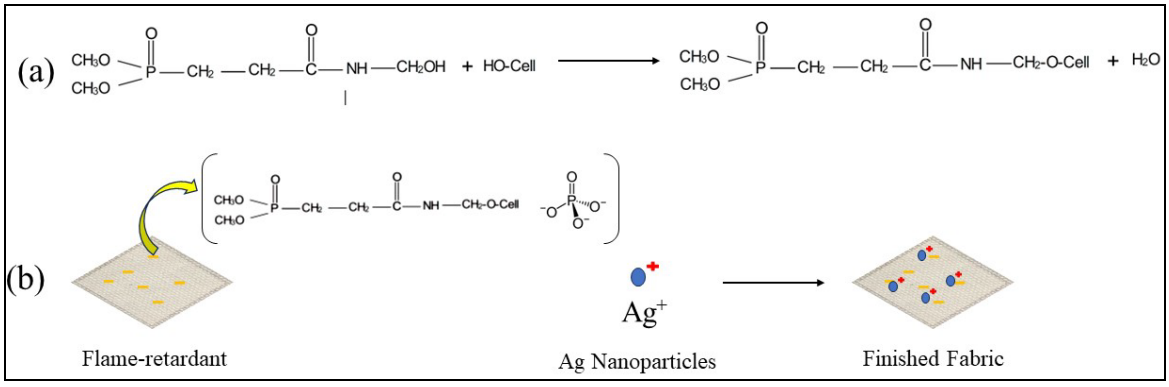

Figure 8: (a) Crosslinking reaction between Pyrovatex CP New and cellulosic fabric, (b) Presence of Ag ions on the surface of finished samples anchoring via electrostatic interaction with FR finish

Table 2
Flame retardancy and burning behavior of cotton fabric samples

Fabric sample	Flame retardancy				
	LOI value	Burning time (seconds)	Char length (mm)	State of fabric	Self-extinguishing
Untreated	18.5	25	Completely burnt	Ash	No
Ag-NPs treated	18.7	32	Completely burnt	Ash	No
FR finished	28.3	3	40	Ash + Char	Yes
Ag-NPs + FR finished	27.2	3	48	Ash + Char	Yes
FR finished + Ag-NPs	25.2	6	52	Ash + Char	Yes

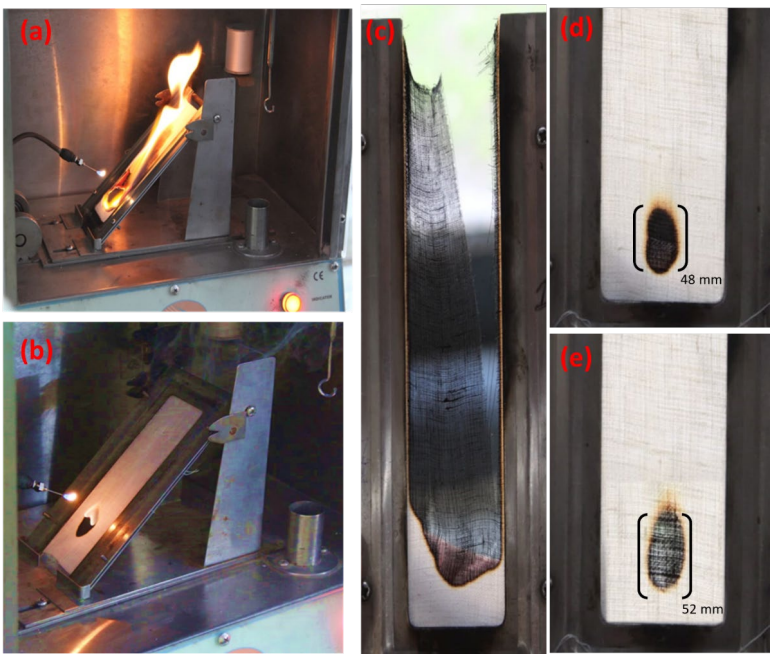

Figure 9: Burning behavior of (a) untreated, (b) finished fabric; Char length of (c) untreated, (d) Ag-NPs + FR finished, and (e) FR + Ag-NPs finished cotton fabric samples

Flame retardancy

The LOI values and burning behavior of the untreated and treated cotton fabric samples are shown in Table 2. Cellulosic textiles are highly flammable, with an LOI of 18, and completely burnt to ash within 25 seconds (Fig. 9 (a and c)). Fabric treated with Ag-NPs also burnt completely during the flammability test (Table 2). Therefore, it is quite clear that Ag-NPs on their own cannot impart any fire retardancy characteristics to the cotton fabric.

Nevertheless, the cotton fabric treated with Pyrovatex (FR) showed good flame retardancy with LOI 28.3, and it demonstrated self-extinguishing behavior with a 40 mm char length. The fabric exhibits exceptional flame-retardant properties when applying FR treatment after using Ag-NPs with an LOI value of 27.2. There is a slight decrease in LOI in the cotton fabric sample with Ag-NPs over the FR (Pyrovatex + phosphoric acid) – Table 2 (LOI value 25.2).

The complexation of PA and Ag ions created coordination bonds between O atoms in -OH and metal ions. This led to less -OH in PA and higher concentrations of derivatives, such as phosphoric acid, produced by burning Ag NP-loaded flame-retardant fabrics. This reduced the flame-retardant performance of the fabrics. Overall, both the combined finished samples exhibit excellent flame-retardancy with self-extinguishing behavior with char lengths of 48 and 52 mm, respectively (Fig. 9 (d) and (e)).

Hydrophobicity and oleophobicity

The untreated cotton sample shows a wetting time of less than 3 seconds, resulting in 0 rating in the spray test (Fig. 10(a)), indicating the hydrophilicity of cotton (Table 3). The Ag-NPs

and FR treated samples show an AATCC value of 70, indicating that some water drops stick to the surface or less wetting of the fabric surface occurs (Fig. 10(b)). In the combined Ag-NPs and FR-treated samples, the value 90 indicates that the water drops are slightly randomly stuck on the fabric face, *i.e.*, maximum water drops are repelled (Fig. 10(c)). Thus, both samples result in standard water repellency ratings.

The analysis of the contact angles at the interface between the water and the treated cotton-fabric surface confirmed hydrophobicity. The contact angle of water drops on the surface of textiles is measured by putting a droplet of water on its surface. Hydroxyl groups in the structure of untreated fabric fabrics have led to a contact angle of 0°, meaning they are highly water absorbent. A contact angle greater than 90° is considered hydrophobic. All the treated fabric samples offered hydrophobic characteristics at time zero (contact angle >90°), as shown in Table 3.

Table 3
Hydrophobicity and oleophobicity of fabric samples

Fabric sample	Water repellence		Drop test (contact angle)	
	Spray test (rating)	Wetting time (s)	Hydrophobicity	Oleophobicity
Untreated	0	3 ± 2	0°	0°
Ag-NPs treated	70	95 ± 1	120°	108°
FR finished	70	84 ± 4	95°	95°
Ag-NPs + FR finished	90	169 ± 1	125°	115°
FR finished + Ag-NPs	90	165 ± 3	140°	128°

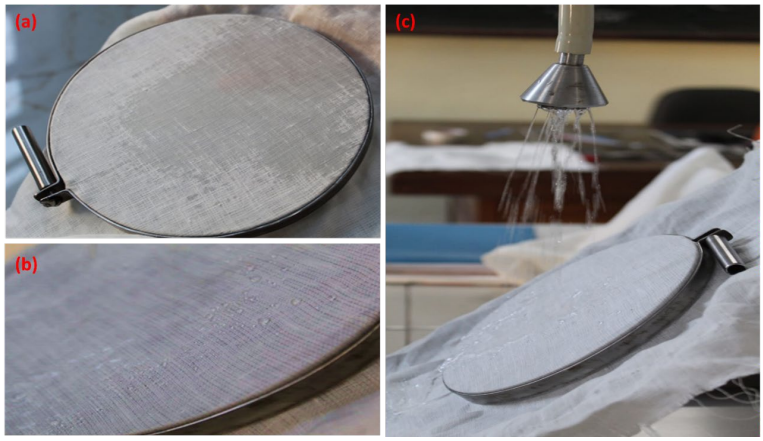

Figure 10: Spray test results for (a) untreated, (b) Ag-NPs + FR finished, and (c) FR + Ag-NPs finished samples

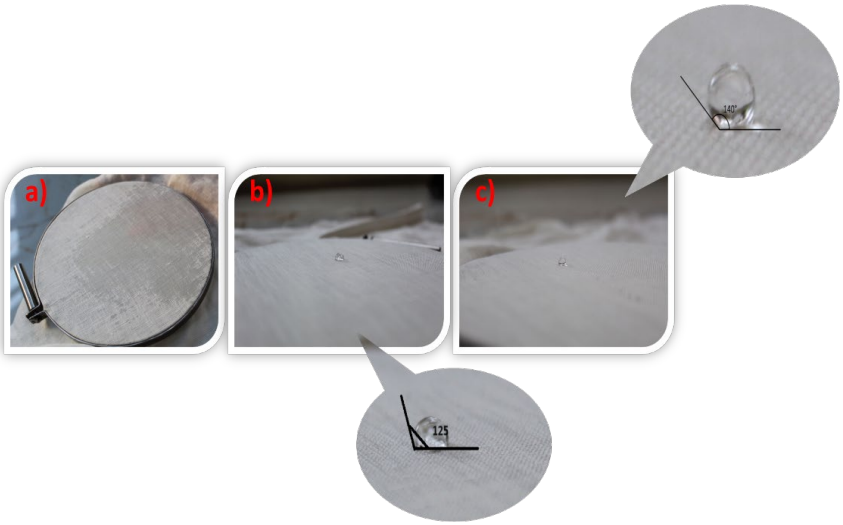

Figure 11: Contact angle with water droplets for (a) untreated, (b) Ag-NPs + FR finished, and (c) FR + Ag-NPs finished fabrics

In the investigation of water repellence properties, fabric samples treated with silver nanoparticles (Ag-NPs) exhibited a noteworthy increase in wetting time, indicating enhanced water repellence upon coating with Ag-NPs. The findings are vividly depicted in Figure 11, illustrating the contact angles of water droplets on untreated fabric and fabric treated with Ag-NPs + FR and FR + Ag-NPs. In Figure 11(b), the contact angle for Ag-NPs + FR treated samples is reported at 125 ± 2°, and in Figure 11(c), the contact angle for FR + Ag-NPs treated samples is recorded at 140 ± 1°. These contact angles, particularly the higher value for the FR + Ag-NPs treated samples, signify a substantial increase in hydrophobicity. The hydrophobic nature of the treated samples is indicative of their water-repelling capabilities, making them suitable for applications where resistance to water and moisture is desired.

The observed enhancement in hydrophobicity is attributed to the increased surface roughness of the fabric, resulting from the coating with Ag-NPs. The presence of silver nanoparticles contributes to altering the fabric's surface texture, creating a rougher topography that promotes water repellence. This modification is crucial for imparting durable and effective water-resistant properties to the fabric.[31-32] In summary, Figures 10 and 11 visually represent the increased water repellence achieved through fabric coating with Ag-NPs. The quantified contact angles underscore the hydrophobicity of the treated samples, with the stability of this property over time further emphasizing the practical applicability and durability of the water-repelling characteristics imparted by the Ag-NPs and flame-retardant treatments.

The comprehensive analysis of the oleophobic characteristics of fabric samples was also examined through the contact angles formed by oil droplets on untreated fabric and fabric treated with Ag-NPs + FR and FR + Ag-NPs. The drop test results with oil reveal noteworthy contact angles consistent with the oleophobic nature of the treated samples. Ag-NPs + FR treated samples reported a contact angle of 115 ± 1°, and the contact angle for FR + Ag-NPs treated samples was recorded at 128 ± 2°. These contact angles surpass 90°, affirming the oleophobic properties of the treated fabric samples. An angle greater than 90° indicates that the fabric repels oil, demonstrating its resistance to wetting and staining by oil-based substances.

Air permeability

The results of the air permeability tests of untreated and treated fabric are shown in Table 4. As per the data in the table, the air permeability of the unfinished fabric sample was 322.4, which means the fabric was highly breathable. The air permeability was reduced slightly after applying the finish to the fabric sample.

Table 4
Air permeability of samples

Fabric sample	Air permeability ($m^3/m^2/min$)		
	Before washing	10 washes	20 washes
Untreated	322.4	325.6	332.8
Ag-NPs treated	275.6	297.2	316.9
FR finished	298.8	308.3	318.5
Ag-NPs + FR finished	265.2	275.7	295.2
FR finished + Ag-NPs	276.4	286.8	302.3

Table 5
Color indices of fabric samples

Fabric sample	Whiteness index (Hunter)	Yellowness index (ASTM E313)
Untreated	97.67	-14.39
Ag-NPs treated	75.65	11.05
FR finished	78.32	14.34
Ag-NPs + FR finished	76.92	12.65
FR finished + Ag-NPs	78.51	13.27

However, it was still close to the value of the unfinished sample, and after 10 washes, the fabric sample still showed a very small change in its breathability. Thus, the breathability of the fabric samples does not change significantly after the finishing treatment.

Whiteness and yellowness indices

The finishing treatment brings a slight change in the whiteness of the fabric. Table 5 shows that the decrease in the whiteness index confirms the change in the appearance of the fabric.

Wash durability

The wash durability of the finished fabric samples was evaluated for 10 and 20 washes (Table 6). Even after 20 washing cycles, the LOI value of the combined finished fabric is around 24, and self-extinguishing was also observed. In addition to that, the bacterial reduction % of FR + Ag-NPs finished sample was still excellent at 96-97% even after 20 washes (Table 6). Thus, the combined finished fabrics were endowed with durable flame-retardant and antimicrobial qualities. Similarly, the finished fabric sample exhibits excellent hydrophobicity and oleophobicity, with a small change in contact angle measurement up to 20 washing cycles, confirming the durability of the Ag-NPs and FR-based finish on the cotton, as shown in Table 7.

Table 6
Wash durability of fabric samples for flame retardancy and antibacterial property

Fabric sample	Flame retardancy			Bacterial reduction (R%)					
	LOI value			*S. aureus*			*E. coli*		
	Before wash	10 washes	20 washes	Before wash	10 washes	20 washes	Before wash	10 washes	20 washes
Untreated	18.5	16	15.5	3	2.5	3	2	3	2.5
Ag-NPs treated	18.7	17	16	99.5	95.8	85.5	98.5	93.6	82.4
FR finished	28.3	28.1	27.8	5	4	2.5	3.5	3	3.5
Ag-NPs + FR finished	27.2	26.8	25.5	85	82.7	80.6	78	77.2	76.4
FR finished + Ag-NPs	25.2	24.8	24.2	99	97.8	96.3	97.5	96.8	95.6

Table 7
Wash durability of fabric samples for hydrophobicity and oleophobicity

Fabric sample	Drop test (contact angle)					
	Hydrophobicity			Oleopbhobicity		
	Before wash	10 washes	20 washes	Before wash	10 washes	20 washes
Untreated	0°	0°	0°	0°	0°	0°
Ag-NPs treated	120°	110°	112°	108°	100°	95°
FR finished	95°	88°	85°	95°	90°	88°
Ag-NPs + FR finished	125°	118°	105°	115°	108°	102°
FR finished + Ag-NPs	140°	135°	132°	128°	117°	110°

CONCLUSION

In conclusion, integrating layer-by-layer the silver nanoparticles and phosphorus-nitrogen-based flame-retardant onto cotton fabric significantly enhances both antibacterial and flame-retardant properties. The application of silver nanoparticles with FR results in a bacterial reduction of 96-97% in *E. coli* and *S. aureus*, even after 20 repeated laundering cycles. The combined finished cotton samples also exhibit excellent flame retardancy with self-extinguishing behaviour, with char lengths of 52 mm and LOI of 24. Additionally, the finished cotton fabric notably exhibits durable hydrophobic and oleophobic characteristics, indicating its suitability for various applications where resistance to liquids is essential. The moderate changes in color indices and air permeability after this treatment imply a marginal impact on the physical characteristics of the fabric. Thus, this

approach of multi-finishing using the layer-by-layer technique validates the suitability of the cotton fabric for everyday use, but also as protective apparel, offering reliable flame resistance and antibacterial performance.

REFERENCES

[1] V. Sharma, S. Basak and S.W. Ali, *Cellulose*, **29**, 7973 (2022), https://doi.org/10.1007/S10570-022-04709-0/METRICS

[2] H. E. Emam, *Cellulose*, **26**, 1431 (2018), https://doi.org/10.1007/S10570-018-2185-5

[3] H. Zhou, Q. Li, Z. Zhang, X. Wang and H. Niu, *Adv. Fiber Mater.*, **5**, 1555 (2023), https://doi.org/10.1007/S42765-023-00297-1

[4] A. P. Periyasamy and J. Militky, in "Sustainability in the Textile and Apparel Industries. Sustainable Textiles: Production, Processing, Manufacturing and Chemistry", edited by S. S. Muthu and M. A. Gardetti, Springer, Cham, 2020, p. 63, https://doi.org/10.1007/978-3-030-38013-7_4

[5] J. Wang, L. Wang and D. J. Gardner, *Cellulose*, **28**, 4511 (2021), https://doi.org/10.1007/S10570-021-03771-4

[6] P. Senthil Kumar and S. Suganya, in "Sustainable Fibres and Textiles", edited by S. S. Muthu, The Textile Institute Book Series, Woodhead Publishing, 2017, pp. 1-18, https://doi.org/10.1016/B978-0-08-102041-8.00001-9

[7] R. M. Kozłowski, M. Mackiewicz-Talarczyk and J. Barriga-Bedoya, "Handbook of Natural Fibres", Woodhead Publishing, 2nd ed., 2020, p. 747, https://doi.org/10.1016/B978-0-12-818398-4.00022-0

[8] S. Ahmad, S. Miskon, R. Alabdan and I. Tlili, *Sustainability*, **12**, 2632 (2020), https://doi.org/10.3390/SU12072632

[9] M. A. Shah, B. M. Pirzada and G. Price, *J. Adv. Res.*, **38**, 55 (2022), https://doi.org/10.1016/J.JARE.2022.01.008

[10] B. Harsanto, I. Primiana, V. Sarasi and Y. Satyakti, *Sustainability*, **15**, 1549 (2023), https://doi.org/10.3390/SU15021549

[11] H. E. Emam, *3 Biotech*, **9** (2019), https://doi.org/10.1007/S13205-018-1562-Y

[12] D. Dridi, A. Bouaziz and S. Gargoubi, *Coatings*, **11**, 980 (2021), https://doi.org/10.3390/COATINGS11080980

[13] O. N. Aguda and A. Lateef, *Heliyon*, **8**, e09761 (2022), https://doi.org/10.1016/J.HELIYON.2022.E09761

[14] M. Mohsin, S. W. Ahmad, A. Khatri and B. Zahid, *J. Clean Prod.*, **51**, 191 (2013), https://doi.org/10.1016/J.JCLEPRO.2013.01.031

[15] B. Tang, J. Kaur, L. Sun and X. Wang, *Cellulose*, **20**, 3053 (2013), https://doi.org/10.1007/S10570-013-0027-Z/METRICS

[16] K. S. Huang, C. H. Yang and S. L. Huang, *Int. J. Mol. Sci.*, **17**, 1578 (2016), https://doi.org/10.3390/IJMS17091578

[17] M. Shateri-Khalilabad, M. E. Yazdanshenas and A. Etemadifar, *Arab. J. Chem.*, **10**, S2355 (2017), https://doi.org/10.1016/J.ARABJC.2013.08.013

[18] A. Mishra, R. Goswami and N. Bhatt, in: "Advances in Polymeric Nanomaterials for Biomedical Applications", edited by A. K. Bajpai and R. K. Saini, 2021, Elsevier, p. 225, https://doi.org/10.1016/B978-0-12-814657-6.00008-2

[19] J. Shen, J. Liang and X. Lin, *Polymers*, **14**, 82 (2021), https://doi.org/10.3390/POLYM14010082

[20] A. Pal, A. K. Samanta and T. R. Kar, *Cellulose*, **30**, 11813 (2023), https://doi.org/10.1007/S10570-023-05543-8/METRICS

[21] Y. Liu, X. Wang, K. Qi and J. H. Xin, *J. Mater. Chem.*, **18**, 3454 (2008), https://doi.org/10.1039/B801849A

[22] Q. Zhou, J. Chen and Z. Lu, *Materials*, **15**, 2537 (2022), https://doi.org/10.3390/MA15072537

[23] A. Singh, M. Singh and A. Pandey, *Mater. Today Proc.*, **80**, 1530 (2023), https://doi.org/10.1016/J.MATPR.2023.01.353

[24] W. An, J. Ma, Q. Xu and Q. Fan, *Cellulose*, **27**, 8457 (2020), https://doi.org/10.1007/S10570-020-03356-7/METRICS

[25] M. Mohsin, S. W. Ahmad, A. Khatri and B. Zahid, *J. Clean Prod.*, **51**, 191 (2013), https://doi.org/10.1016/J.JCLEPRO.2013.01.031

[26] A. Javed, J. Wiener, J. Saskova and J. Müllerová, *Polymers*, **14**, 3414 (2022), https://doi.org/10.3390/POLYM14163414

[27] M. S. Begum, A. Kader and R. Milašius, *Polymers* (*Basel*), **15**, 2563 (2023), https://doi.org/10.3390/POLYM15112563

[28] S. Anees Ahmad, S. Sachi Das and A. Khatoon, *Mater. Sci. Energ. Technol.*, **3**, 756 (2020), https://doi.org/10.1016/J.MSET.2020.09.002

[29] M. Azizi-Lalabadi, F. Garavand and S. M. Jafari, *Adv. Colloid Interface Sci.*, **293**, 102440 (2021), https://doi.org/10.1016/J.CIS.2021.102440

[30] C. H. Chen, S. Saleemi and X. H. Liu, *J. Nat. Fibers*, **17**, 146 (2020), https://doi.org/10.1080/15440478.2018.1476946

[31] P. K. Saha, R. Mia, Y. Zhou and T. Ahmed, *SN Appl. Sci.*, **3**, 1 (2021), https://doi.org/10.1007/S42452-021-04582-9