Modification of casein for multifunctional finishing of cotton

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Abstract : ***In present research work, a novel green flame retardant material was synthesized by modification of casein. The modification of casein was carried out with melamine, sodium pyrophosphate. Glyoxal was used as cross-linker. The modified casein was then applied on the cotton fabric by exhaust method and sequent percentage add-on was determined. Further flame retardancy performance was investigated by the limiting oxygen index (LOI) value which was found to have improved. The thermo gravimetric analysis (TGA) exhibits improved performance of treated fabrics as compared to untreated cotton fabric. The scanning electron microscopic (SEM) analysis shows very good deposition of modified casein on treated cotton fabric surface. Exceptional rise in ultraviolet protection factor (UPF) of treated cotton fabric was observed. Thus a novel green flame retardant material made through modification of casein provides multifunctional finishing with improved properties.***

Keywords : Casein, Eco-friendly, Flame retardant, Ultra-violet protection factor.

I. Introduction

More than four decades, both industrial and academic researchers have focused their efforts to devise and build up chemicals that will avoid the ignition of polymers or at least immediate spread of fire. Class of chemical entity used for this special function is known as flame retardant (FR) [1]. The most proficient and extensively used chemical moieties in the formulations are halogen-based FRs such as poly brominated biphenyl ethers and polyhalogenated biphenyls. These chemicals have proven to be persistent, bio-accumulative and not only environmentally hazardous but also majorly lethal to all living species on the earth. At the present time, synthesis and application of halogen based FRs are constrained more and more by the European Union and they have been expelled from the USA [2].Therefore, most of the researchers shift their focus from purely synthetic to complete natural or semi synthetic products to make process more and more environmentally sustainable [3].

Nowadays, researchers drill hard to practice eco-friendly methodology to scale it up industrially and make it economical from commercial perspective, few of such has been discussed as follows. Research group lead by Jenny Alongi has been working on sustainable approach for making flame retardant textile. In one study they have used silica, ammonium polyphosphate (APP) and chitosan applied to polyester/cotton blend fabric in varied combination using layer by layer methodology and thermal studies of treated fabrics were evaluated [4]. In another study, they applied and tested aqueous whey protein solution to cotton fabric to impart flame retardant properties [5]. In another work they have studied casein and hydrophobins on to the cotton fabric individually as well as in combination without modifications and its flame retardancy studies have been performed [6].

Alkaline extract of spinach was used to functionalize cotton using different concentrations at boil by exhaust methodology and flame retardant properties in terms of LOI, vertical flammability test were evaluated [7]. In another work, pre-mordant cotton using alum and tannic acid was modified with banana pseudo stem sap solution and further evaluated for thermal studies [8].Nitrogen and phosphorus synergism plays a crucial role for FR activity. Casein, a protein which is a biodegradable material and chiefly extracted from milk with large magnitude. It is a globular protein having amino acids and few of them are phosphorylated intrinsically [9]. Thus, casein with natural source and good inherent potential for flame retardancy to textiles and is used in this work. In the present work inherent synergism of nitrogen and phosphorus of casein has been improvised to achieve flame retardancy, by its chemical modification. The flame retardant properties of the treated cotton are evaluated in terms of limiting oxygen index (LOI) values and vertical flammability testing. Its tensile properties, stiffness along with the crease recovery angle are also studied. The ultra-violet protection factor (UPF) of the cotton after its treatment is eventually measured.

II. Materials and methods

A.Materials

Melamine, sodium pyrophosphate, sodium hydroxide, glacial acetic acid all of AR grade and 40% glyoxal LR grade were procured from SD fine chemicals limited, Mumbai, India. Casein was sourced from Loba Chemie, Mumbai, India.
Substrate: Plain woven (ready to finish) cotton fabric of 140 GSM was supplied by TATA Mills, Mumbai, India.

B. Methods

Modification of casein

The modification of casein was done by reacting it with melamine and sodium pyrophosphate in 5:1:8 ratios for 2 h by continuous stirring at 30°C in a three neck flask. Glyoxal (twice the amount of protein) was used as cross linking agent which is added drop wise to the reaction mixture. The reaction was further continued for 4 h at 80°C and pH 5 was maintained using 20 % acetic acid. Furthermore, for complete dissolution the pH of reaction mixture was adjusted to 8 by using 10% sodium hydroxide. The reaction was further continued for 2 h at 90°C for. Dark brown solution was obtained after the completion of reaction which is dried in an oven at 80°C for 24 h.

Application of modified casein on cotton fabric

The modified casein was applied on pre weighted cotton fabric in an increasing order of concentration for 50g/L, 100g/L, 150g/L and 200g/L

with material to liquor ratio of 1:10. The cotton fabric is immersed in treatment bath at room temperature and treated for 30 minutes further the temperature was raised to 80°C at a time interval of 2°C/min and treatment was carried out for 60 min. Further the treated fabric was dried at 110°C for 3 min and subjected to performance testing.

III. Characterization

A. Fourier Transform Infrared Spectroscopy (FTIR) analysis

The FTIR spectra of the native casein and modified casein were recorded using Attenuated Total Reflection (ATR) module with diamond/ZnSe crystal on FTIR spectrometer (Shimadzu 8400S, Japan), in the range of 4000-600 cm-1.

B. X-ray Diffraction (XRD) Analysis

X-ray diffractometer (Lab X XRD-6100 SHIMADZU, Japan) equipped with Cu Kα radiation was used for XRD analysis of the native casein and modified casein. X ray of wavelength 1.54 A° was used, with 2 θ angle of 5° to 30° was used for scanning. The generator voltage was kept at 40 kV, and generator current was 30 mA. The samples were powdered and placed on sample holder.

C. Thermogravimetric Analysis (TGA)

Native casein, modified casein in powdered form and untreated and modified casein treated cotton fabric were analyzed for thermo gravimetric analysis. For thermo gravimetric analyser, Shimadzu 60H DTG , Japan was used having temperature range 30 to 500°C with rate of heating 10°C/ min under inert nitrogen with 50 mL/min flow rate.

D. Percentage Add-on

The percentage add-on of the treated fabrics was determined gravimetrically using the following formula (Equation 1) [10].

$$\text{Percentage Add On} = \frac{W2-W1}{W1} \times 100 \qquad (1)$$

Where, W_1 and W_2 are the weights of the untreated and treated fabric samples respectively.

E. Computer colour matching analysis

Fabric samples were simultaneously evaluated in terms of CIELAB colour space (L*, a* and b*) values and colour strength in terms of K/S by reflectance method using 100 standard observer. The absorbance of the samples was measured on Rayscan-Spectrascan 5100+ equipped with reflectance accessories.

F. Flammability Assessment

For evaluation of flammability assessment limiting oxygen index (LOI) and vertical flammability tests were performed to evaluate (Equation 2) untreated and treated samples. For LOI, IS 13501:1992 test for textiles was used [11]. LOI testing was done using instrument of make Dynisco, Germany.

$$\text{LOI (\%)} = \frac{[O2]}{[O2]+[N2]} \times 100 \qquad (2)$$

Vertical flammability was evaluated according to ASTM D 6413-09 [12]. Specimen size was 30 cm x 7.6 cm and flame height 38 mm. Sample was given exposure to flame for 12 seconds and, after flame, after glow, and char length were measured. To check reproducibility of results, samples were tested in triplicate and average results were mentioned. Vertical flammability test was done using instrument of make Rossari Labtech. Ltd. Mumbai, India.

G. Ultraviolet Protection Factor (UPF)

UV-2600 (Shimadzu, Japan) spectrophotometer, in the range of 280-400 nm was used for evaluation of UPF values of the untreated cotton fabric and modified casein treated fabric. The test was based on Standard AS/NZS 4399/1996 which analyzes UPF value from the total spectral transmittance [13], [14].

H. Scanning Electron Microscopic (SEM) Analysis

Field emission gun-scanning electron microscope (FEG-SEM, Philips XL-30, D-1217) was used to evaluate the surface morphology of the untreated and modified casein treated cotton fabric. Specimen was cut in to size of 5 mm x 5 mm, and sputter coated with platinum about 300 sec time interval. The beam voltage, magnification and working distances were 10 kV, 1000x magnification, and 6 mm working distance respectively for evaluation of sample.

I. Tensile strength

The tensile strength of the specimen was then determined by using H5KS Single Column Universal Tester (Tinius Olsen). Standard test method for breaking force and elongation of fabrics, ASTM D 5035-1995 strip method was used having specimen dimension 25 mm x 150 mm with gauge length 100 mm. The average of 5 samples was reported as final test result.

J. Bending length

ISO-6490-1971 test method was used to evaluate the bending length of the untreated and treated cotton fabrics and evaluated according to the Shirley Stiffness Tester of make Rossari Labtech. Ltd. Mumbai, India. Sample dimensions of 25 mm x 150 mm were used.

K. Crease recovery angle

Test method IS 4681-1981 was used to evaluate the crease recovery properties of the untreated and treated cotton fabrics. Sample of dimension 15 mm×40 mm was used and evaluated using crease recovery tester of make Rossari Labtech. Ltd. Mumbai, India.

IV. Result and discussion

A. Proposed Reaction

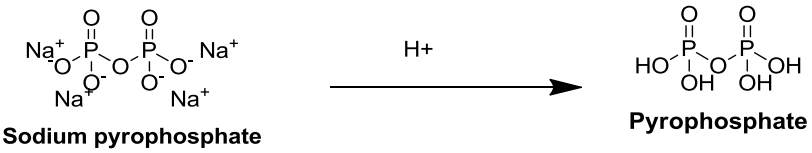

Fig. 1. Proposed reaction Scheme 1[15]

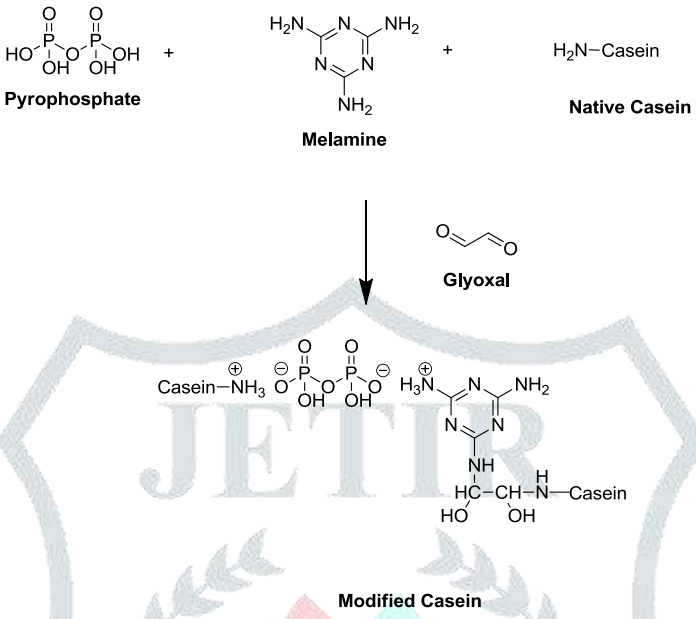

Fig. 2. Proposed reaction Scheme 2 [15]

As mentioned in the proposed reaction schemes 1 & 2, acidic condition around pH 5 helps in the dissociation of sodium pyrophosphate into sodium cation and pyrophosphate anion with the further formation of pyrophosphate moiety. Casein-NH2 represents native casein containing numerous hydroxyl and amino groups. Aldehydic groups of glyoxal react with hydroxyl and amino groups of casein, pyrophosphate and amino groups of melamine; which results in the formation of complex moiety. Thus, glyoxal acts as a cross linking agent that can crosslink with the melamine, pyrophosphate and the native casein. Such modification enriches casein with higher nitrogen and phosphorus contents which is beneficial to improve the flame retardancy of the cotton. [15].

B. FTIR of casein and modified casein

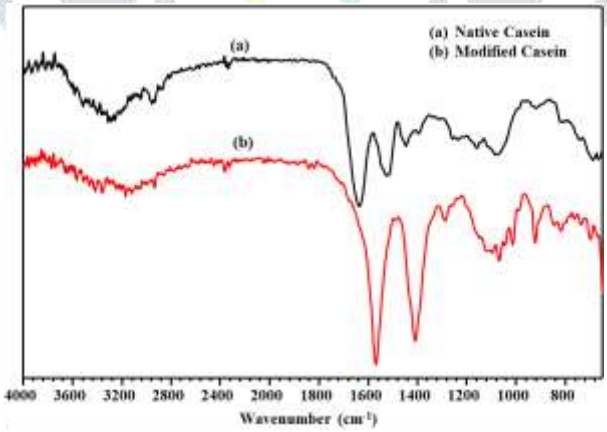

Fig. 3. FTIR of native casein and modified casein

Fig. 3 (a) depicts the FTIR spectroscopy of native casein where –NH stretching has been observed at 3306 cm^{-1}. 1633 cm^{-1} and 1536 cm^{-1} are the characteristic peaks of –CONH- and –NH- functional groups respectively. Fig. 3 (b) illustrates the FTIR spectra of modified casein where broadening of –NH stretching has been observed. Sharp bands at 1568 cm^{-1} and 1409 cm^{-1}have been observed corresponding to –CONH- and –NH- stretchings respectively with a slight shifting compared to that of native casein. Some new bands at 1068 cm^{-1}, 1014 cm^{-1} of P=O, 921 cm^{-1} of P-O-P and 817 cm^{-1} of P-O have also been formed which indicates that the modified casein is having Phosphorus–Nitrogen (P-N) group required for a good flame retardant [15].

C. XRD study of casein and modified casein

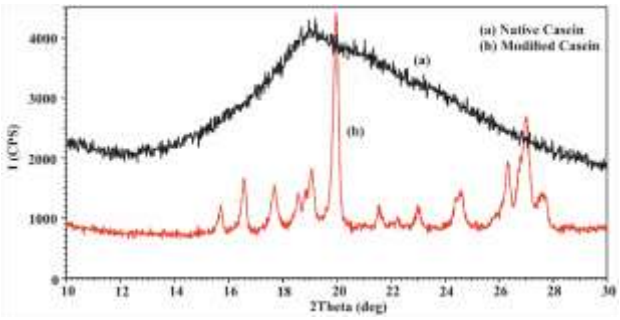

Fig. 4. XRD of native casein and modified casein

Fig. 4 (a) illustrates the X-ray diffractogram of native casein that shows single strongest peak at 18.9° indicating its purity [16]. From corresponding XRD curve of modified casein as in Fig. 4 (b), new peaks at 16.5°, 17.6°, 22.2°, 22.9°, 25.7° have been observed indicating the presence of melamine [17]-[19]. Sharps peaks at 19.9° and 27° corresponds to that of sodium pyrophosphate [20]. Crystallinity of native casein is 14.02% whereas there happens to be an increase in the crystallinity after modification of casein upto 32.49%. Such change in the crystalline structure might be the result of the compactness of the protein backbone due to the introduction of new groups onto the native casein.

D. TGA of casein and modified casein for thermal analysis

Fig. 5 illustrates the TGA curves of native casein and modified casein. From the thermogravimetric curve of modified casein, it is observed that casein after modification becomes much more thermally stable than its pure form as it slightly degrades around 260 °C while the native casein degrades before 200 °C to a greater extent of almost 80% weight loss [21]. Casein based P-N flame retardant consists of polar groups like amino, hydroxyl and carbonyl groups resulting into better thermally stability and of having outstanding char forming property. Thus it could act as an acid source and carbonization agent resisting its decomposition at higher temperature. Char forming tendency is beneficial for good flame retardancy [15].

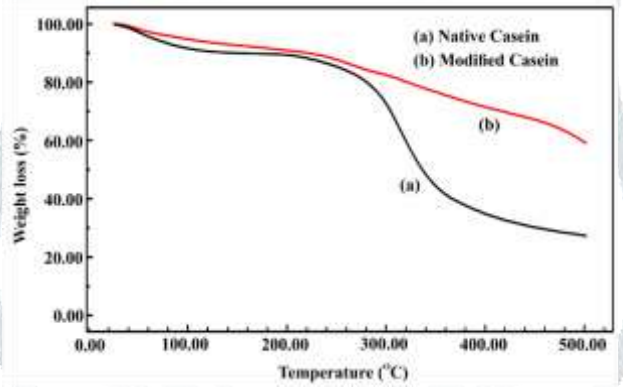

Fig. 5. TGA of casein and modified casein

E. FTIR of untreated and modified casein treated cotton fabric

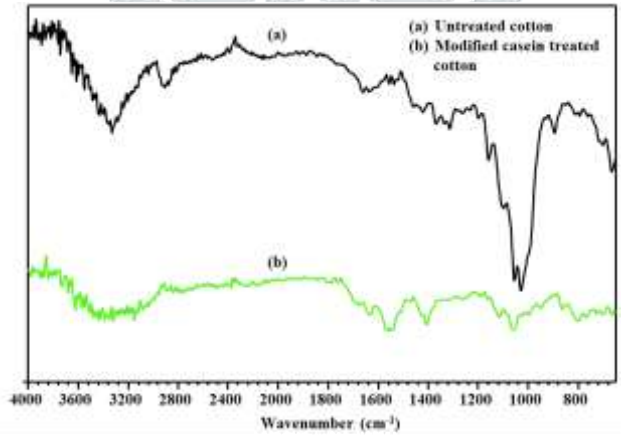

Fig. 6. FTIR of untreated and modified casein treated cotton

Fig. 6 (a) depicts the FTIR spectra of untreated cotton. Bands at 3335 cm^{-1} and 2932 cm^{-1} corresponding to –OH and C-H stretchings respectively have been found. Bands attributed for 1645 cm^{-1}, 1433 cm^{-1}, 1367 cm^{-1} and 1313 cm^{-1} corresponds to absorbed water, C-H wagging (in plane bending), C-H bending and C-H wagging respectively. C-H deformation stretching is observed at 1267 cm^{-1}. Corresponding band at 1198 cm^{-1} attributes for -OH in plane bending, 1053 cm^{-1} signifies asymmetric in plane ring stretching, 1028 cm^{-1} for C-O stretching and 897 cm^{-1} corresponding to glucosidic linkage [22]. According to Fig. 6 (b), cotton fabric treated with modified casein shows new bands at 1566 cm^{-1} and 1541 cm^{-1} due to N-O asymmetric stretching, 1407 cm^{-1} characterized by C-C stretch (aromatic), stretch at 1115 cm^{-1} corresponds to C-N stretching aromatic amine, 800 cm^{-1}signifies P-O stretching, 770 cm^{-1} ascribes N-H wagging of primary

and secondary amines,700 cm^{-1} recognized for C-H stretching (aromatic). Additional peaks in the treated cotton fabric could signify presence of nitrogenous and phosphorus based functional groups onto it after treatment with modified casein [15].

F. Effect of concentration on percentage add-on of treated cotton fabric with modified casein

Table I Effect of concentration of modified casein on percentage add-on of treated cotton fabric

Concentration (g/L)	Percentage add on (%)
Untreated	-
50	11.54
100	21.26
150	26.43
200	32.13

Table I represents that, as concentration of modified casein in treatment bath increases percentage add-on of the solution onto cotton substrate also increases. It can be seen on application of highest concentration i.e. at 200 g/L around 32 % add on onto treated fabric has been achieved and becomes saturated above it. Thus 200 g/L concentration has been followed in the entire study for the treatment of cotton with the modified casein.

Table II Computer Colour Matching (CCM) Study

Sr.no.	Concentration (g/L)	L*	a*	b*	K/S
1	Untreated cotton	93.24	-0.63	3.62	0.04
2	50	93.10	0.89	4.30	5.81
3	100	92.82	0.83	3.87	9.25
4	150	92.54	0.88	3.48	14.72
5	200	92.49	0.92	3.53	15.96

From Table II, application of modified casein results in yellow brown shade to that of untreated cotton fabric. With increase in the concentration of modified casein darker shade formation takes place evident from the increase in the K/S.

G. Wash durability test

Washing was carried out using laundrometer with ECE detergent 5 g/L at 40 °C for 40 min followed by rinsing and drying at 100 °C. After washing flame retardancy was reduced thereby signifying no durability in it.

H. Flame retardancy analysis of cotton

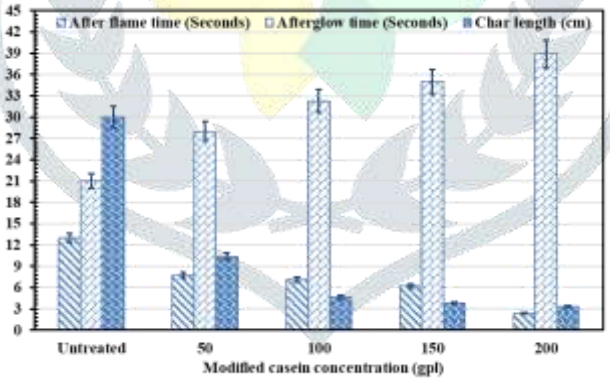

Fig. 7. Limiting Oxygen Index test of untreated and modified casein treated cotton fabric

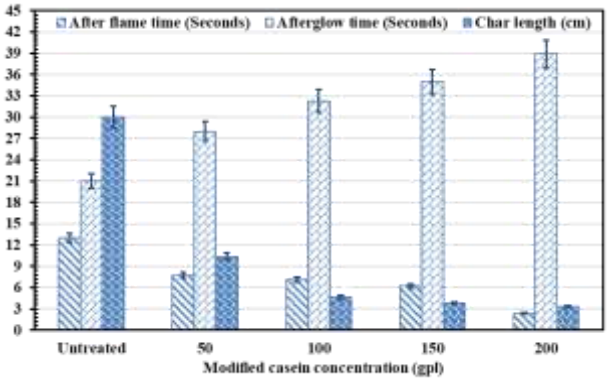

Fig. 8. Vertical Flammability Test of untreated and modified casein treated cotton fabric

Textile substrate showing LOI value of more than 26 can be claimed to be a good flame retardant. LOI of untreated cotton is generally 18,

which signifies that it is fire sensitive [1]. LOI of untreated cotton is found to be minimum i.e., 18 experimentally. Increase in the LOI of treated fabric has been observed with successive increase in concentration of modified casein. LOI of 30 has been obtained on application of 150 g/L solution, which signifies the introduction of flame retardancy onto the cotton and with further increase in concentration to 200 g/L, LOI of 32 has been achieved claiming modified textile substrate to be a good flame retardant.

Minimum values of after flame, char length and afterglow signify that treated sample has been successfully passed the vertical flammability test. In vertical flammability test as shown in Fig. 8, on successive application of increasing concentrations of modified casein decrease in after-flame time, char length and increase in afterglow of treated samples have been observed. Untreated cotton fabric showed after flame time and char length of 13sec and 30 cm respectively that reduces to 2.35 sec and 3.3 cm respectively after treatment, thereby showing significant enhancement in the flame retardancy. Formation of secondary hydroxyl groups in the modified casein might lead to increase in afterglow time of treated fabric than that of control fabric.

I. UPF for UV protection by modified casein treated fabric

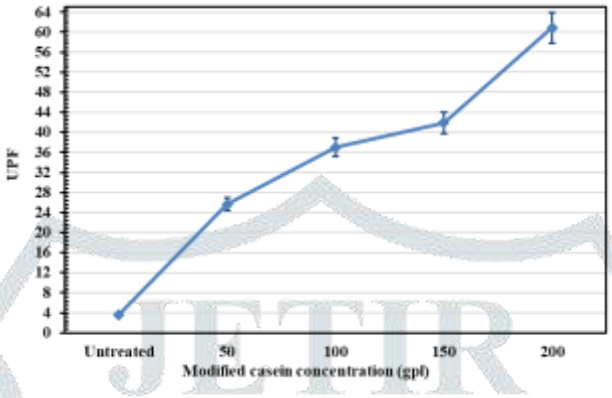

Fig. 9. UPF of synthesized FR treated cotton fabric

From Fig. 9 it can be seen that untreated cotton exhibits UPF of 3.59 indicating poor UV resistance. With increase in the dosage of modified casein exceptional rise in UPF value of treated fabric has been observed. As concentration of modified casein increases there is gradual increase in the absorption of UV radiation. The value for 50 g/L, 100 g/L, 150 g/L and 200 g/L modified casein treated cotton fabric shows UPF factor 25.62, 37.04, 41.91 and 60.90 respectively. Such improvement in the UV protection is due to the introduction of melamine structure onto the cotton substrate having conjugation in assistance of hetero 'N' atom considerably absorbing more UV radiation on exposure [23]. With increase in concentration of modified casein better results were obtained. From observed results, it can be claimed that modified casein quenches UV radiation thereby enhancing the ultra-violet protective property of cotton.

J. SEM of untreated and modified casein treated cotton fabric

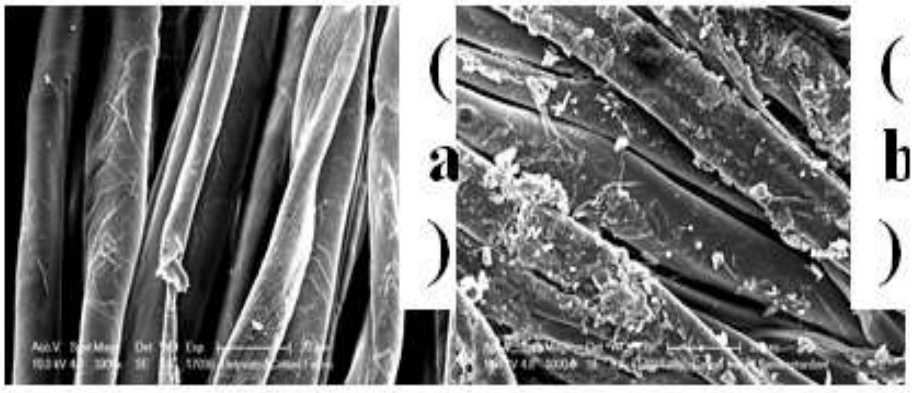

Fig. 10. SEM of untreated and modified casein treated cotton fabric

Scanning electron micrographs are used to analyse the surface of untreated and treated fabrics with modified casein. Fig. 10 (b) illustrates good deposition of modified casein onto treated cotton surface, which is not present in case of untreated cotton as observed in Fig. 10 (a).

K. TGA of untreated and modified casein treated cotton fabric

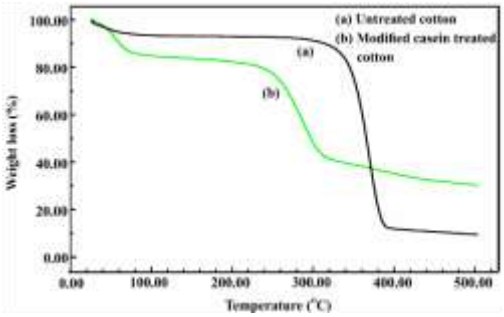

Fig. 11. TGA of untreated and modified casein treated cotton

Fig. 11 demonstrates the thermal degradation behaviors of the untreated and treated cotton fabric. It can be seen that initial weight loss in both untreated and treated fabrics happens to be in the range of 80-100°C due to the evaporation of water molecules bound to respective fabrics [24]. In case of untreated fabric, drastic weight loss (70 %) is found around 320°C whereas for treated fabric lower weight loss is observed though earlier at 260°C. This may be attributed to the formation of lower oxides of nitrogen and phosphorus of modified casein and early evaporation of the traces of volatile matters present in it. Formation of oxides of nitrogen and phosphorus at higher temperature endures higher thermal stability to the treated cotton fabric.

L. XRD analysis of untreated and modified casein treated cotton fabric

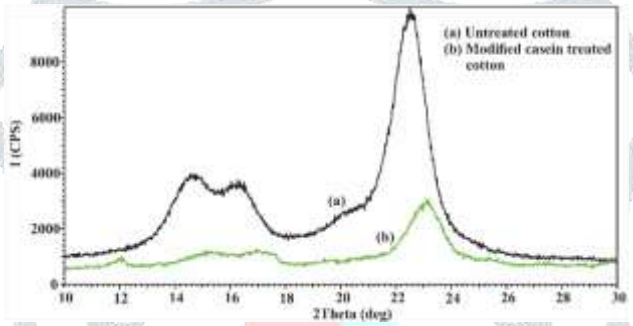

Fig. 12. XRD untreated and modified casein treated cotton

In Fig. 12 (a), doublet at 14.86°, 16.48° and 22.76° of intensities 1010, 861 and 3282 were seen. XRD examination of treated sample shows relatively less intense peak at 15.32°, 16.90° and 23.02° with intensities 189,193 and 876 respectively can be seen in fig. 12 (b). Shift of all characteristic peak was also been observed. Crystallinity of untreated cotton is found to be 42.18% whereas that of treated cotton fabric gets reduced to 30.17%. Disruption of hydrogen bonds between cellulosic molecules owing to intercalation of modified casein might cause decrease in tensile strength of treated fabric than that of untreated one [25].

M. Physical properties
Tensile strength study

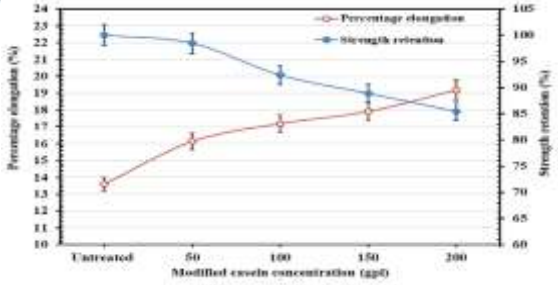

Fig. 13. Tensile strength of modified casein treated cotton fabric

From the fig. 13 it is observed that as the concentration of modified casein increases, tensile strength of the treated fabric decreases to around 15 % whereas there has been an increase in the elongation to almost 22 %. These results were observed at highest concentration on application of modified casein onto cotton fabric, but observed reduction in tensile strength found to be under permissible limit. Reduction in the tensile strength after treatment is because of the decrease in its crystallinity after modification of cotton. Since, treatment with modified casein intercalates between cellulosic moieties, it disrupts its hydrogen bonds due to which there happens to be a loss in crystalline structure and finally reduction in the tensile strength and increase in the elongation at break [25].

N. Bending length and crease recovery of untreated and modified casein treated cotton fabric

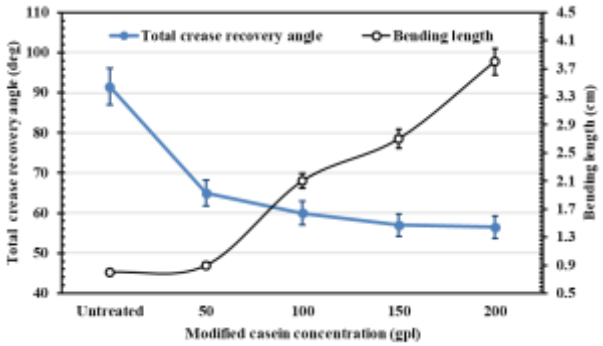

Fig. 14. Bending length and crease recovery of modified casein treated cotton fabric

The effects of treatment of modified casein on bending length and crease recovery angle of cotton fabric are graphically represented in fig.14. As the concentration of modified casein increases, bending length increases with a decrease in the total crease recovery angle. Such effect can be attributed to the deposition of modified casein on the cotton fabric that leads to stiffening of the treated fabrics as compared to untreated fabric. At concentration 200 g/L of modified casein, the treated cotton is found to be stiffest due to maximum deposition of modified casein onto it indicative from the % add-on in Table 1.

V. Conclusion

The present study indicates the modification of casein to achieve bio based eco-friendly material which can impart flame retardancy and ultraviolet protection properties to the cellulosic textile substrate. After application of casein based synthesized FR, the flame retardancy measured in terms of LOI, improved extensively. The thermal stability of the cotton fabric was also increased and in the vertical flammability test, treated samples showed self extinguishment property with minimum char length and lower after flame time. Better flame retardancy in the case of the casein based flame retardant might be attributed to the presence of intrinsic phosphate groups, and phosphate from pyrophosphate moieties, intrinsic nitrogen content, and additional nitrogen from melamine moieties. Such nitrogen and phosphorus (N-P) synergism seems to have played important role to improve overall thermal stability. Though the flame retardancy is having no durability, it could have good application in the segments like hometech and protech where durability is not considered to be of prime importance. Moreover modified cotton fabrics showed excellent ultraviolet protection due to the presence of hetero aromatic triazine and ring phenolic amino acids suitable for quenching of the UV radiations. It is not only biodegradable, nontoxic but also an eco-friendly. One of the major limitation found is coloration of fabric on finishing which can be used creatively however to get over this limitation further research is needed. Therefore, it can be said that the results clearly indicate the promising potential for casein based FR multifunctional finishing of cotton provided durability and coloration issues are mitigated.

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