

Short Communications

Comparison of biopolymer finishing with functional finishing on wool fibre

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Wool: cotton union fabric has been applied with chitosan biopolymer to impart shrink-proof finish and its performance is compared with two synthetic polymer finishes. Results show that chitosan forms thin film on the surface of wool fibre as in synthetic finishing polymer. The diffusion of chitosan biopolymer inside the wool fibre matrix is found to be better than synthetic polymer, which is confirmed by the cross-sectional view of finished wool fibre. It is concluded that chitosan biopolymer could be preferred over other synthetic polymer to prevent shrinkage of woollen textiles.

Keywords: Biopolymer, Bio finishing, Chitosan, Functional finishing, Polymer finish, Wool/cotton fabric, Wool fibre

Wool, an animal hair fibre has distinct outer scales called cuticle and it protects the wool fibre from environment¹. Woollen textiles can shrink during washing due to development of frictional effect between wool fibres. This type of shrinkage is called felting shrinkage, which is undesirable in frequently laundering garments such as woollen suiting, socks and sports wears². It is caused due to presence of cuticle, hydrophobicity and natural crimp of wool fibre. Shrink-resist processes were developed since 1960's and classified as subtractive, additive and combination of subtractive and additive process.

The subtractive process partially can remove the outer cuticle of the wool fibre; the additive process can mask the surface cuticle by the deposition of polymer, and the third process is the combination of both subtractive and additive process³. Synthetic

polymers like epoxyacrylates, low-temperature-cure acrylic emulsions, amphoteric urethane pre-polymers, amine-terminated polyethers, aziridine-terminated polymers, polyamide-acrylic acid copolymers, urethane semicarbazide emulsions and epoxy functional polyesters have been used to impart shrink resistant finishing⁴.

Chitosan a natural biopolymer, chemically called as beta-(1, 4)-2-(amino)-2-deoxy-D-glycopyranose, exists in a protonated form (NH_3^+) and behaves like a cationic polyelectrolyte. Chitosan can interact with negatively charged functional groups of wool fibre like carboxyl group ($-\text{COO}^-$) through ionic bonding. Chitosan based finishing can improve shrink-resistance, dye ability and antimicrobial properties of woollen textiles⁵. It is found that the literature review on comparison of performance properties of chitosan on wool fibre with other synthetic functional polymer is scanty. Therefore, attempt has been made to evaluate the performance properties of chitosan finish in terms of SEM, DSC, TGA & FTIR studies, moisture regain and felting shrinkage in comparison with fluoroalkyl and DMDHEU based polymer finish.

Experimental

Materials

Wool/cotton union fabric having the specifications 40 ends / inch (2/15's cotton yarn), 15 picks / inch (2.75 Nm woollen yarn), 2/2 twill weave, 340 g/m², 1.50 mm thickness, 67:33 blend ratio⁶ was used for this study.

Chemicals

Finish-VLF (1,3-N,N'-dimethylol,4,5-dihydroxy ethylene urea based cross-linking agent), and Nuva-HPU (cationic perfluoroalkyl acrylic copolymerisate emulsion) were supplied by M/s Clariant Chemicals (India) Ltd., Mumbai⁶, M/s Indian Sea Foods, Cochin, India supplied 81% deacetylated chitosan. All other chemicals used in the study were AR grade

Finishing Treatment

Prior to polymeric finish, experimental fabric was pretreated with 2% Savinase 16.0L-Ex, an alkaline protease enzyme for 30 min at 50°C and 5.5 pH in order to improve the spreading of polymer on the surface of the wool fibre. Experimental fabric was applied with three polymers, namely Finish-VLF

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(60 gpL), Chitosan (10 gpL) and Nuva-HPU (60 gpL) by pad-dry-cure process, followed by drying at ambient temperature. The curing condition for Finish-VLF, Chitosan and Nuva-HPU based finishing were 160°C/ 3 min, 130°C/ 5 min and 150°C/ 3 min respectively.

Evaluation

Performance properties of finished and unfinished experimental fabrics in terms of finish add-on (%), moisture regain (%), wettability (s), and felting shrinkage (%) were evaluated as per standard procedure⁷⁻⁹. Differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), Fourier transformation infra-red (FTIR) spectroscopy, Scanning electron microscopy (surface morphology @ 2500 magnification) and Transmission electron microscopy (cross-sectional view @ 2500 magnification) of finished and unfinished wool fibres from experimental fabric were evaluated as per standard procedure^{10,11}.

Results and Discussion

Performance Properties

The performance properties evaluated from unfinished and finished experimental fabric in terms of finish add-on(%), moisture regain (%), wettability (s), felting shrinkage (%) are given in Table 1.

It is observed that the percentage add-on of chitosan remains in-between the add-on of Finish-VLF and Nuva-HPU finish. Finish-VLF polymer has more hydroxyl groups and those groups are cross-linked with functional groups of wool and cotton fibre easily, and so the add-on of this finish is higher than other finishing. Chitosan has protonated amino ($-\text{NH}_3^{\oplus}$) group which forms ionic bonding with carboxylate ($-\text{COO}^{\ominus}$) ionic group of wool fibre. In addition to ionic bonding, hydrogen bonding is formed between $-\text{OH}$ group of chitosan and $-\text{NH}_2$ group of

wool fibre. These two bondings are responsible for fixation of chitosan film on the wool fibre. Nuva-HPU forms fluorocarbon film by polymerization of fluoroalkyl monomer on the surface of the wool and cotton fibre. Being slightly cationic in nature, cationic groups of pre-polymer forms ionic bonding with carboxylate ($-\text{COO}^{\ominus}$) group of wool fibre¹².

Moisture regain and wettability of textile materials decrease, if the availability of H-bonding groups and porosity of constituted fibres are decreased¹³. It is clearly seen that after polymer finishing, the wettability and moisture regain of finished fabrics are reduced in comparison with unfinished fabric. Chitosan forms a continuous polymer film on the surface of the fibre and hence reduces 10% moisture regain in comparison with unfinished fabric. Nuva-HPU forms uniform hydrophobic film, which decreases the surface free energy of the fibres. Hence, it shows more (21%) reduction in moisture regain than other polymer finishing in comparison with unfinished fabric.

Shrinkage of woolen fabric mainly depends on presence of cuticle scales. After polymer based finishing, cuticle scale of wool fibre is masked by polymeric film and hence all finished fabrics show lesser shrinkage than unfinished fabric. Chitosan finish shows 72% reduction in shrinkage in comparison with unfinished fabric and the reduction is better than that of Nuva-HPU (64%) and Finish-VLF (29%) finished fabrics. SEM photographs of unfinished and finished wool [(Figs 1(a)-(d)] indicate that unfinished wool fibre shows distinct cuticle scales on the surface, while finished wool fibre polymer masked the scales.

Thermal properties

DSC study

Wool fibre is a keratinous protein polymer and has α -helix, β -sheet, amorphous and crystalline region³. During thermal treatment, these structures are modified and denatured at a particular temperature. The denaturation depends on the proportion and modifications/ cross-linking of each components of wool fibre. DSC curve of unfinished and finished wool fibre (Fig. 2) depicts glass transition temperature (T_g), moisture vaporization temperature, denaturation temperature and decomposition temperature of wool fibre. Generally, glass transition temperature (T_g) of wool fibre occurs between 40°C and 60°C, which depends on the amount of moisture present in the fibre¹⁴.

Table 1—Performance properties of finished and unfinished wool /cotton union fabric

Wool fabric	Finish add-on %	Wetting time, s	Shrinkage %	Moisture regain, %
Unfinished	-	12	8.62	13.4
Chitosan	4.12	93	3.12	12.1
Finish-VLF	5.20	19	6.09	12.8
Nuva-HPU	3.35	>360	2.45	10.6

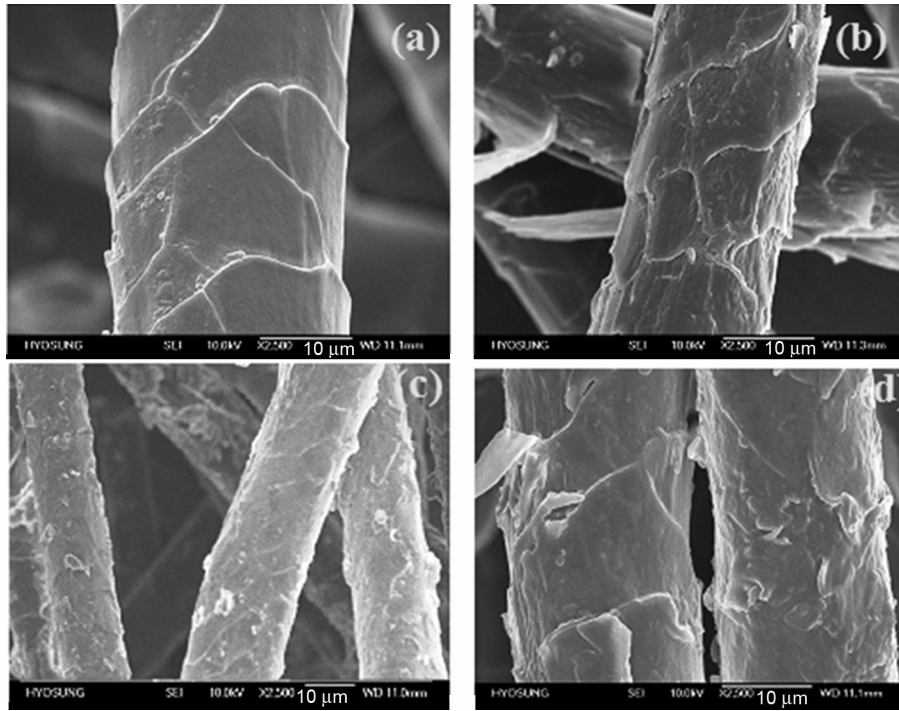


Fig. 1—SEM photographs of (a) unfinished and finished [(b) Finish-VLF, (c) Chitosan and (d) Nuva-HPU] wool fibre ($\times 2500$ magnification)

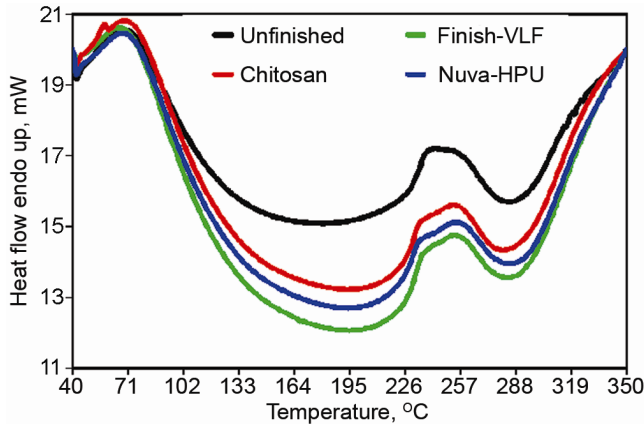


Fig. 2—DSC thermogram of unfinished and finished wool fibres

The T_g value of all wool fibre samples is observed at around 42°C and the first endo-peak is observed at around $67\text{--}69^\circ\text{C}$. It is inferred that there is no difference between unfinished and finished wool fibre during removal of moisture, however the energy required to remove moisture from unfinished wool fibre is higher than that required for finished wool fibre due to more H-bonding between functional groups and moisture.

The first exo-peak is appeared at 181°C for unfinished wool and at 194°C for finished wool fibre. It is inferred that polymer based finishing resists the decomposition of α -helix of wool fibre. DSC curve

also indicates that the amount of energy released from the chitosan finished wool fibre is lesser than that from other finished wool. The second endothermic peak appears at 243°C for unfinished wool and $253\text{--}255^\circ\text{C}$ for finished wool. This peak indicates as thermal denaturation temperature, which is related to the amount of helical protein and crystallinity of fibre¹⁵. At 283°C , the other components of wool fibres are decomposed i.e. melting/ degradation of keratin associated proteins that comprise the highly cross-linked keratins of the inter macro-fibrillar matrix occurred. The results infer that chitosan shows similar thermal behaviour to synthetic polymer.

TGA Study

TGA curve of finished and unfinished wool is shown in Fig. 3 and the percentage weight losses of wool fibre at each particular temperature are given in Table 2.

It is found that there are three stages in the wool fibre pyrolysis. The initial plateau region after the small slope region is ended between 120°C and 160°C . This region is mainly responsible for desorption of moisture that is physico-chemically bound to wool fibre and shows dehydration. The second region is ranged from 200°C to 500°C that is responsible for pyrolysis of wool fibre and hence causes weight loss than in other regions. In this region, initially weak hydrogen-bond peptide helical

Table 2—Weight loss of unfinished and finished and wool fibres in thermal gravimetric analysis

Wool fibre	Weight loss, %						
	50 °C	150 °C	240 °C	300 °C	400 °C	700 °C	850 °C
Unfinished	0.6	5.5	6.6	22.8	53.1	74.6	86.7
Chitosan	0.7	2.9	7.0	23.3	65.4	79.7	83.4
Finish-VLF	2.2	4.8	6.4	23.7	65.4	79.4	83.2
Nuva-HPU	3.4	7.5	9.5	25.4	65.8	80.3	83.9

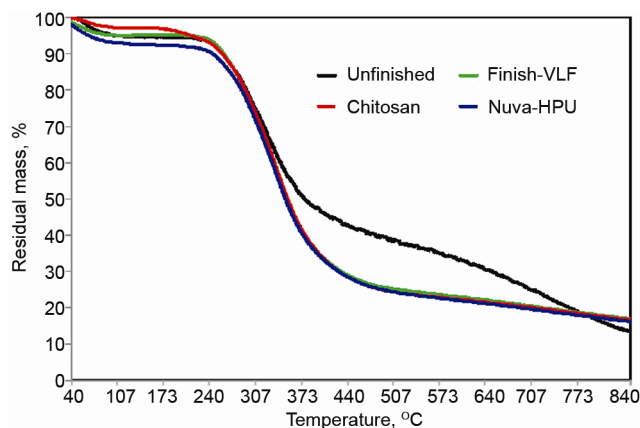


Fig. 3—TGA thermogram of unfinished and finished wool fibres

structure is ruptured followed by the change in solid to liquid phase of ordered crystalline regions of wool fibre and finally cleavage of the disulphide bonds between molecular chains¹⁶. It can also lead to formation of number of volatiles products like hydrogen sulphide and sulphur dioxide. The third plateau region is ranged from 500°C to 850°C, which is responsible for oxidation of charred products.

From Table 2, it is observed that chitosan finished wool has lost lesser mass than unfinished and other finished wool at region 1. In the second region, all finished wool has shown more weight loss than unfinished wool, which may be due to thermal degradation of polymer¹⁷. Generally, some portion of polymer diffuses inside the fibre matrix, which might reduce the crystallinity of wool fibre, so it reduces the thermal stability of wool fibre. This is also another reason for the high weight loss at this region. After 800°C, the charred mass of finished wool fibre has shown more resistance to oxidation than unfinished wool fibre i.e. the residual mass after pyrolysis is higher in finished wool fibre (16.1-16.8%) than in unfinished wool fibre (13.3%)

Surface Morphology

SEM Study

Wool fibre consists of two major morphological parts i.e. cuticle and cortex. The cuticle cells are

laminar and rectangular in structure, which form a sheath of overlapping scales enveloping the cortex. Wool cuticle forms a diffusion barrier to chemicals and other treatment agents¹⁸, so chemical pre-treatment improves the hydrophilicity of wool fibre. Unfinished wool (enzyme pretreated) fibre has shown polished cuticle scales on the surface [(Fig. 1(a))].

Protease enzyme can partially hydrolyze the polymer chains of the wool fibre and forms additional functional groups on the surface, which enhance the spreading, diffusion and adhesion of finishing chemicals on wool fibre¹⁹. All finished wool fibre shows polymeric film coating on the surface of wool fibre and infer that the extend of coating depends on the chemical nature of polymer. Chitosan, being cationic and with lower molecular weight in nature, is easily diffused, spread, adhered and formed more film layer on the surface as well as interior of the wool fibre than other Nuva HPU and Finish VLF.

Cross-sectional View

Cortical cells are spindle-shaped and separated from each other by a cell-membrane complex. Each cortex cell is inter-digitized with the neighboring cells along the fibre axis²⁰. The cell membrane complex consists of non-keratinous proteins and lipids and hence is responsible for the transport of water, dye and chemical inside the wool fibre.

From Fig. 4(a), the cuticle and cortex are distinctly visualized in the cross-sectional view of unfinished wool fibre. On the other hand in finished wool fibre [Figs 4(b), (c) and (d)] some grooves in between the cortex cells are seen, which confirm that the formation of polymeric film in between cortical cells. It is also indicated that the diffusion of chitosan polymer inside the cortical cells of wool fibre is better than in others synthetic polymers.

FTIR Study

The FTIR spectra of unfinished and finished wool fibres in the region 640-1800 cm^{-1} are shown in Fig. 5. The main functional groups in wool fibre are carboxyl (-COOH), amino (-NH₂), and hydroxyl

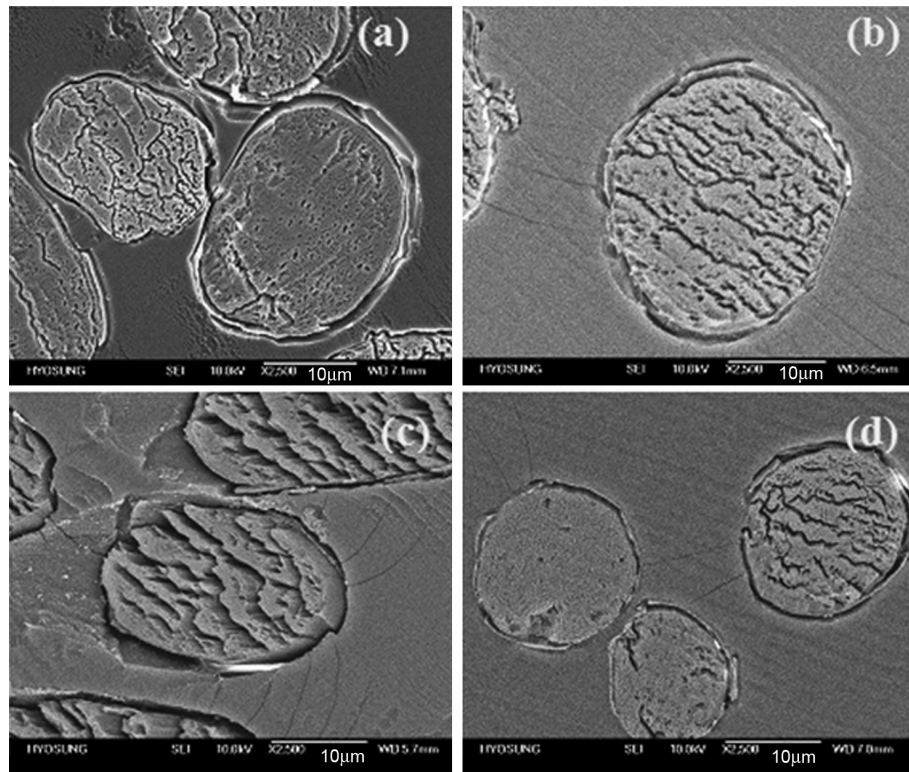


Fig. 4—TEM photographs of cross sectional view of (a) unfinished and finished [(b) Finish-VLF, (c) Chitosan and (d) Nuva-HPU] wool fibre ($\times 2500$ magnification)

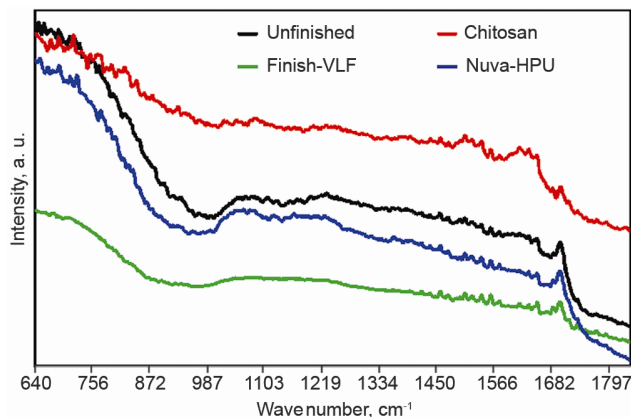


Fig. 5—FTIR spectra of unfinished and finished wool fibres in wave number region $640 - 1800 \text{ cm}^{-1}$

(-OH), amide (-CONH-), and disulphide (-S-S-) groups. In IR spectroscopy, the main characteristic peaks appear between 1000 cm^{-1} and 1700 cm^{-1} , including amide I (1670 cm^{-1}), amide II (1540 cm^{-1}), amide III (1270 cm^{-1}), and -SO- contraction (1100 cm^{-1}). When wool fibre is finished with chitosan, FTIR spectra shows a vibration at $1616\text{-}1624 \text{ cm}^{-1}$ corresponding to -CONH- group, which confirms that amino (-NH₂) group of chitosan and carboxyl (-COOH) group of the wool fibres reacts

and forms secondary amide groups. Similarly, there is change in intensity of FTIR spectra in the range $1200\text{-}820 \text{ cm}^{-1}$, which is due to the formation of chemical bonding between -OH/-COOH group of wool fibre and -NH₃[⊕] group of chitosan and -OH group of Finish VLF²¹.

Enzyme treated woollen fabric is finished with three different finishing polymers and the performance properties of chitosan finished woollen fabric are found to be better than in other finished fabrics. Thermal properties of chitosan finished wool are similar to synthetic polymer finish. Chitosan finish resists the denaturation of wool fibre better than that of other synthetic finishes. Surface morphology of wool fibre shows that masking of cuticle scales by chitosan finish is better than that of other synthetic finishes. Cross-sectional view study infers that chitosan can also be diffused well inside the wool fibre. It is concluded that chitosan based shrink resistant finishing could be preferred over synthetic polymer finish for woollen materials.

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