

Influence of Poly Phenolic Organic Compound on the Cationic Dye Ability of Regenerated Cellulose Fibres

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Abstract - Cotton and regenerated cellulosic such as viscose possess very poor affinity towards basic or cationic dyes. However polyphenolic organic compound such as tannic acids in combination with metallic moderants are found to be promising to improve cationic dye ability of cellulosic fibres, by enhancing cation exchange capacity on fibres. Surface treatment of viscose staple fibres with tannic acids have been practiced in the present study in order to develop a commercially viable method to prepare cationic dye able viscose. Fixation of tannic acid on viscose staple fibres was also attempted with metal salt and detailed study was conducted on overall cationic dyeability of treated fibres as compared to acrylic fibres.

Key Words: Viscose¹, Cationic dyes², Tannic acid³, Anioinic⁴

1. INTRODUCTION

Tannins are known to be used commonly for textile applications as well as for preservation of leather [1]. Tannins obtained from gull nuts possess more than 65% tannic acids. Tannic acids are water soluble, slight yellowish colored amorphous powder with characteristic astringent taste and odour. Generally tannic acids are polyphenolic organic compounds having two or three hydroxyl groups per thousand molecular weight and overall molecular weight of tannic acid is approximately three thousand Dalton. Tannic acid which are esters of glucose and gallic acid acyl group, possess carboxylic acid groups in its complex structure apart from the prevalent hydroxyl groups. Thus tannic acids with frequent hydroxyl groups possess strong affinity towards cellulosic substrates due to hydrogen bonding interactions through hydroxyl groups. In addition, the anionicity of cellulosic substrate is increased by tannic acid by added carboxylic acid groups.

Tannic acid are widely known as moderant of cotton due to its strong affinity towards cellulose [2]. Although tannic acid itself possess affinity towards polar cellulosic substrates due to hydrogen bonding interactions between hydroxyl groups, improved fixation of tannic acid on cellulosic substrate might be achieved with selected metallic moderants. These metallic

moderants possess exchangeable ions and they form water insoluble complexes of tannic acid.

Tannic acid treatment on cotton was known from earlier days not only for increasing affinity for cationic dyes but also for uptake of natural dyes [3]–[9]. Even back tanning treatment on dyed nylon is reported to improve wash fastness properties significantly [10], [11]. However the technology lost industrial interest slowly because of long and tedious process of application. Although few researchers has reported the effectiveness of fixation of tannic acid with metallic moderants to realize dyeing of cotton with natural as well as basic dyes, there are very few reports on incorporation of poly phenolic organic compound in to viscose leading to enhanced dye ability towards cationic dyes.

Cationic dyeability of regenerated cellulosic is expected to be advantageous in many respects. Cationic dyeing in acrylic or cationic dyeable polyesters leads to very bright shades at less dye content, salt and soda free dyeing leading to nearly complete dye pick up and hence the process is environment friendly [12]–[14]. In addition to its environment related benefits, cationic dyeable cellulosic can be dyed in single bath process when blended with acrylics or cationic dyeable polyesters. Also melange effect or pattern dyeing can be realized when blended with standard cellulosic, as when subjected to cationic dyeing, anionic cellulose is expected to get dyed not the standard cellulosic fiber.

In the present article, Tannic acid (TA) is surface modified onto viscose with an objective of achieving enhanced cationic dye ability due to increased anionicity of the fiber.

2. Materials and Methods:

2.1 Ingredients:

Cationic dye coracryl red C4G supra, coracryl red CF3B, blue CGNX, blue C5G, yellow C8GL, yellow CGL, supplied by colourtex was used as received. Pharma grade tannic acid was procured from Samana chemicals and potassium antimony tartrate was supplied by Neelkanth chemicals.

2.2 Methods of Functionalization

Viscose fibres were soaked in hot water followed by squeezing. These viscose fibres of known weight were dipped in aqueous solution of tannic acid at 50-60 °C with concentration ranging from 1.5 to 20% for 5 minutes and subjected to squeezing in padding technique leading to wet pick up of 100%. Tannic acid uptake was controlled on the fiber from 1.5 to 20% on the basis of cellulose content. The treated fiber was again dipped in aqueous solution of antimony potassium tartrate commonly known as tartar emetic at 50-60 °C for 5 minutes and squeezed by padding technique. The loading of tartar emetic was controlled to be half of tannic acid. The treated fiber was washed thoroughly in water and dried after application of spin finish to it. Basically tannic acids interact with cellulosic substrates through weak hydrogen bonding. On treatment with antimony potassium tartrate insoluble tannic-tartar emetic complex is formed through exchangeable antimony anions and thus tannic acid gets permanently fixed on to cellulosic fibers as depicted in Fig 1. The detailed composition of tannic acid modified viscose has been tabulated in Table 1.

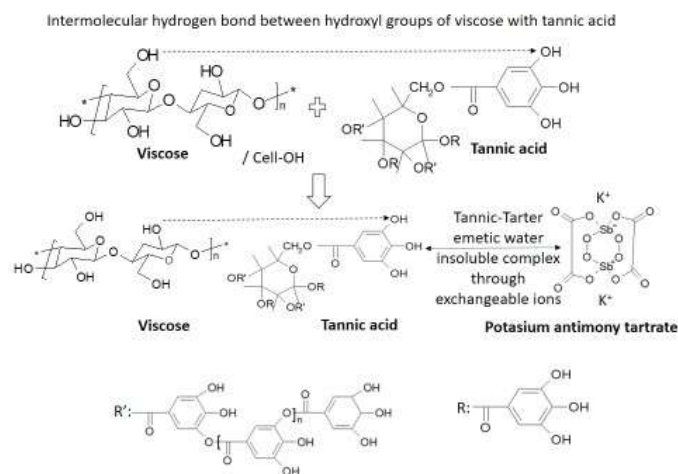


Fig -1: Tannic acid fixation on viscose by surface treatment approach

3. Results and Discussion:

3.1 Method of dyeing:

Fibre samples were subjected to dyeing with each of the mentioned cationic dye (coracryl red C4G supra, coracryl red CF3B, blue CGNX, blue C5G, yellow C8GL, yellow CGL) with 1% dye on fibre at a pH of 4-4.5. Fibre to liquor ratio were maintained at 1:20 and fibers dipped into dye bath were dyed in dye master heated at a rate of 1.2°C up to 60°C and kept on hold for 45 minutes followed by cooling up to 40°C. The dyed fibers were soaped with 2 g/L non-ionic soap at 50°C for 15 minutes followed by cold and hot rinses. The exhausted dye baths were collected for measurement of dye bath exhaustion (DBE).

Table1: Compositions of tannic acid modified viscose fibres

Sample Name	% of tannic acid on cellulose	% of tartar emetic on cellulose
TA-VSF1.5	1.5	0.75
TA-VSF2.5	2.5	1.25
TA-VSF5.0	5.0	2.5
TA-VSF10.0	10.0	5.0
TA-VSF20.0	20.0	10.0

3.2 Measurement of color intensity:

Konica Minolta spectrophotometer C-3600A was used for Colour measurements where K/S values were quantified considering corresponding dyed acrylic fiber as the benchmark with K/S 100. The color measurement data is tabulated below in Table 2-4. K denotes absorption coefficient and S is the scattering coefficient,

$$K/S = (1 - R^2) / 2R, \text{ where } R \text{ is reflectance.}$$

The Matching of color with respect to target dyed acrylic fiber increases as K/S value comes closer to 100. Also L*, a*, b* values help to evaluate the color differences between different shades. The darker is the shade becomes darker with increase in L*. Redness in a dyed fibre increases with positive values of a*, Greenness in a dyed fibre increases with negative values of a*. Similarly yellowness in a dyed fibre increases with positive values of b*, and blueness in a dyed fibre increases with negative values of b* [12].

In Table 2, color measurements of different tannic acid treated viscose fiber samples after dyeing with cationic dye CF3B has been tabulated. As observed, K/S values tannic acid modified viscose fibres made by surface treatment, increases with tannic acid content from 1.5 to 20% progressively. However, K/S values increased more than 40% as tannic acid content was increased from 1.5 to 2.5%. Further increment of K/S with increased tannic acid content from 2.5 to 20% was found to be only 8%. The above interpretation can be clearly observed in Fig 2. Hence 2.5% tannic acid incorporation is considered as an optimum content to satisfy performance enhancement of viscose fibers in terms of cationic dye uptake. All other dyeing experiments with other cationic dyes were performed only with 2.5% tannic acid modified viscose in either of the two approaches. Also from Table 2, it is observed that b* value of acrylic fiber was positive indicating towards yellowishness in red shade while in case of all tannic acid modified viscose fibers exhibit negative b* values indicating towards bluishness in red shade. Thus tannic acid modified viscose exhibit shade change to some extent when compared to acrylic fiber dyed with same cationic dye.

Similarly in Table 3 and 4, color measurement values of acrylic fibres with anionic viscose are tabulated when dyed with C8GL and CGNX yellow and blue cationic dyes respectively. Considering dyed acrylic fibres as benchmark, k/s values of dyed anionic viscose could reach more than 90% only at 2% dye loading on fibre basis.

Table 2: Color measurement data of red CF3B dyed fibres considering acrylic fiber as bench mark with K/S 100

Sample	Dye content on fiber	Dye used :Red CF3B			
		L*	a*	b*	K/S
Acrylic Fiber	1%	45.96	65.42	11.23	----
TA-VSF1.5		44.18	52.71	-14.53	34.29
TA-VSF2.5		41.64	56.92	-12.5	50.09
TA-VSF5.0		41.06	56.76	-13.93	53.76
TA-VSF10.0		40.92	55.14	-13.14	52.8
TA-VSF20.0		41.31	56.17	-13.89	54.42
TA-VSF2.5	2%	35.74	56.25	-6.28	95.28

Table 3: Color measurement data of yellow C8GL cationic dyed fibres considering acrylic fiber as bench mark with K/S 100

Dye used	Dye content on fiber	Yellow C8GL			
		L*	a*	b*	K/S
Data Name	1%	81.84	1.14	99.13	----
Acrylic Fiber		76.16	4.56	86.27	60.68
TA-VSF2.5		74.25	10.83	93.96	92.28
TA-VSF2.5	2%	74.25	10.83	93.96	92.28

Table 4: Color measurement data of blue CGNX cationic dyed fibres considering acrylic fiber as bench mark with K/S 100

Dye used	Dye content on fiber	blue CGNX			
		L*	a*	b*	K/S
Data Name	1%	25.88	10.84	44.75	----
Acrylic Fiber		34.44	-3.42	39.09	56.34
TA-VSF2.5		24.57	4	37.29	93.6
TA-VSF2.5	2%	24.57	4	37.29	93.6

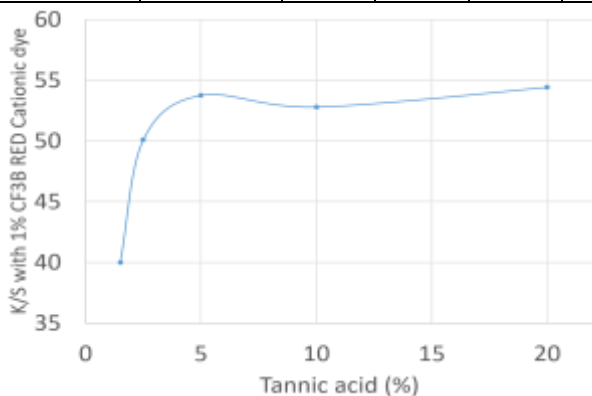


Fig-2: K/S values as a function of tannic acid content

3.3 Measurement of Dye bath exhaustion:

Solution of cationic dye coracryl yellow C8GL were made in water in various concentration and UV-Visible spectroscopy were done as shown in Fig 3. Absorbance of Characteristic peak at 430 nm were noted and plotted against concentration in grams per litre (gpL). A straight line passing through origin is obtained following Lambert Beers law as depicted in Fig 4. Using this calibration curve the concentration of remaining dye in an exhausted dye bath can be measured which can easily give us quantitative information of dye bath exhaustion (DBE).

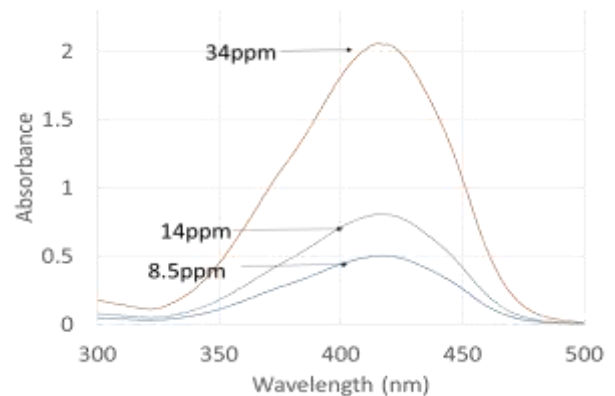


Fig 3: UV-Visible spectrum of red coracryl cationic C8GL dye at varying concentration

As observed in the calibration curve in Fig 4 , the obtained equation following Lambert Beers law is $y=56.34x$, whereas y is absorbance at 430nm and x is concentration of dye in grams per Liter (gpL). Using this equation the remaining concentration of dye in a dye bath after exhaustion was measured from the detected value of absorbance at 430nm which can be easily converted into dye bath exhaustion (DBE %) as the initial concentration is known.

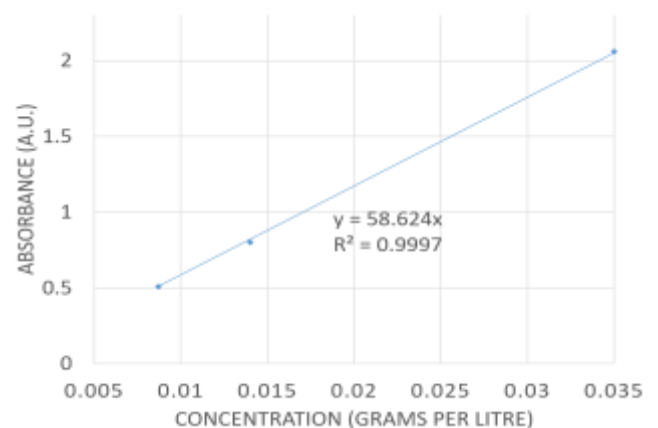


Fig 4: Calibration curve of yellow coracryl cationic C8GL dye at absorbance at 430nm as a function of concentration in gpL

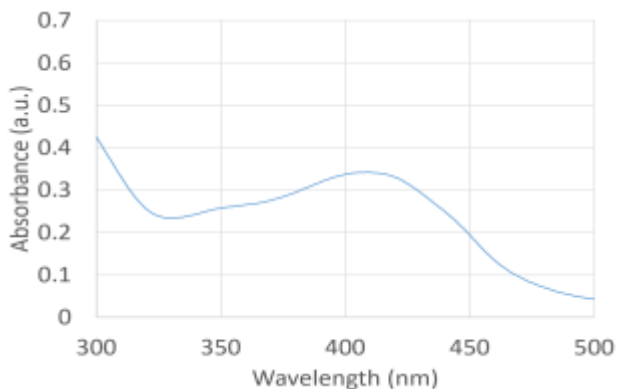


Fig 5: UV-Visible spectrum of exhausted dye bath (coracryl cationic C8GL dye) of different viscose fibers as mentioned

As observed in Fig 5, the dye bath exhaustion is close to 98% for 2.5% tannic acid modified viscose.

3.4 Optimization of dyeing cycle

The dyeing of anionic VSF was carried out by slowly heating the dye bath from room temperature to 60°C followed by holding for 30-40 minutes at the same temperature before cooling. In order to optimize the dyeing cycle, the dye bath exhaustion was measured at different time intervals. As shown in Fig 6, by the time, the temperature approached 60°C, the dye bath exhaustion already reached 99%. On holding the dye bath at the same temperature, the dye bath exhaustion further increased up to 99.8% up to 30 minutes after which no further increase in dye bath exhaustion could be observed. Hence minimum hold time for 60°C dyeing of anionic VSF should be 30 minutes to reach maximum dye pick up.

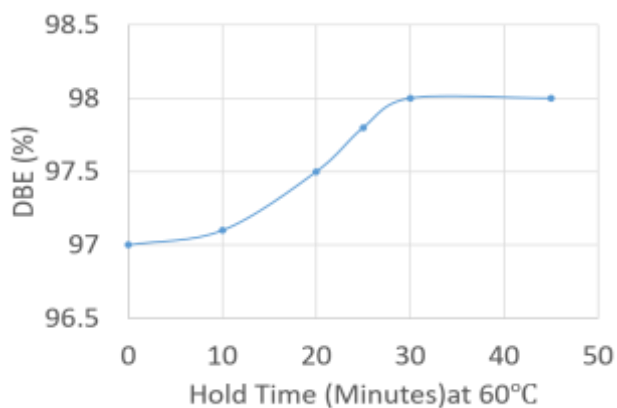


Fig 6: Dye bath exhaustion as a function of hold time of dye bath at 60°C

3.5 Measurement of anionic content in modified Viscose

Didecyl dimethyl ammonium chloride (DDAC) is a quaternary ammonium compound which shows light blue color in presence of bromo phenol blue indicator. Bromo phenol blue shows blue color in cationic reagents, whereas in neutral or anionic reagent the color appears purple [15]. 1gpL each of solutions of tannic acids and Didecyl dimethyl

ammonium chloride were prepared in presence of bromophenol blue indicator as shown in Fig 7. Known volume of 1gpL DDAC solution was added into known volume of 1gpL tannic acid solution containing said indicator until desired color change was observed from purple to blue. From here millimoles of DDAC required to titrate per gram of tannic acid was measured and the value found to be 5.5.

Similarly 2grams of modified Viscose was subjected to extraction in 100ML of water at boiling temperature under 6hours exposure. The bromophenol indicator was added into the extract. Known volume of DDAC was added into it until desired color change observed. Thus it was found that 0.14 Millimoles of DDAC required to neutralize per gram modified fibre. Hence Tannic acid fixation on viscose is 2.5%. Similarly anionic content in all tannic acid modified viscose fibres could be evaluated.

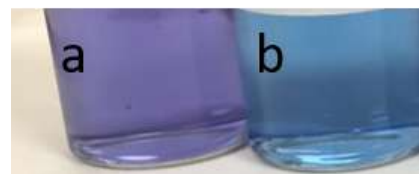


Fig 7: Color of Bromophenol blue in (a) Tannic acid (b) DDAC solutions

3.6 Scanning electron Microscopy:

As observed from scanning electron microscopy, Fig 8 (a) and (c) the serrated cross section of viscose remains unaffected on tannic acid modification by surface treatment. Similarly in case of control viscose as seen in Fig 8(b), the surface appeared to be smooth and uniformly serrated and free from any visible particle. However visible particles and localized agglomerates could be detected in longitudinal sections of tannic acid modified viscose made by surface treatment approach as observed in Fig 8 (d), which indicates towards possible irregularity in the structure and non-uniformity of surface treatment.

4. CONCLUSIONS

Tannic acid treatment of viscose fibers leads to improved cationic dye uptake capacity on viscose fiber. The water insoluble complex of tannic-tartar emetic on the surface of cellulosic substrate enhances the anionic content significantly. Completely salt and soda free dyeing of cellulose with cationic dyes in addition to better environmental sustainability, provides additional advantages of reduced cost of dyeing as well. Bright shades are achievable at low dye consumption resulting in 98 to 100 percent dye bath exhaustion which lowers the effluent load in exhausted dye bath significantly.

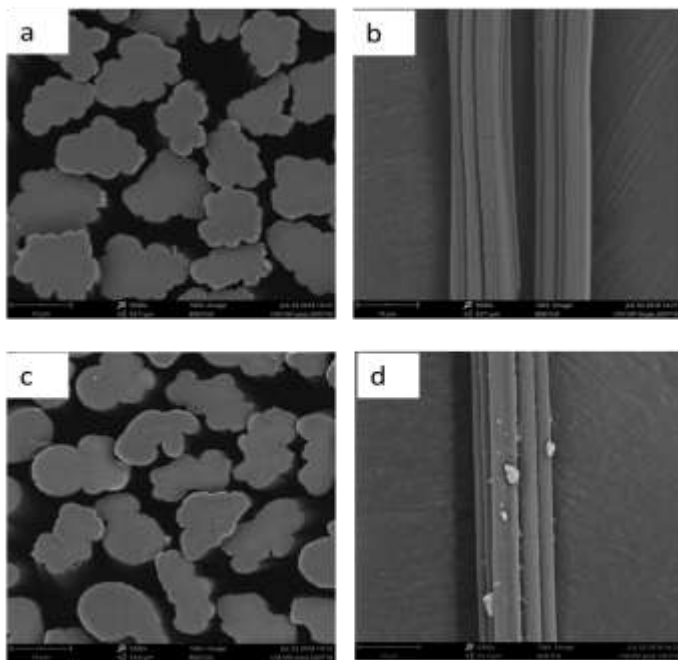


Fig 8: Scanning electron microscopic images in transverse sections of (a) control viscose and (c) tannic acid treated viscose made in surface treatment approach and longitudinal sections of (b) control and (d) tannic acid treated viscose made in surface treatment approach

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