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A Study on Modal Fabric using Formic Acid Treatment for K/S, SEM and Fourier Transform Infrared Spectroscopy

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ABSTRACT

Modal is a second generation regenerated cellulosic fiber obtained from wood pulp, particularly from the beech tree wood. Modal was at first introduced by Lenzing AG Company of Austria. Modal is very soft, shiny in nature and silk feel than mercerized cotton with the ability to absorb up to 50% more water than cotton. In this study, modal fabrics (woven and knitted) are selected and conventionally pretreated and subjected with 98% formic acid in different concentrations. The formic acid treated modal fabrics were then undergone for different testings, such as, physical properties, wicking, K/S values, fastness properties, SEM studies and FTIR analysis. These treatments on modal fabrics were correspondingly compared with those of cotton for its effectiveness.

Keywords: Modal Fabric, Wicking, K/S, SEM, FTIR

INTRODUCTION

Modal is a semi-synthetic cellulose fibre made by spinning reconstituted cellulose, in this case from beech trees

Modal is a second generation regenerated cellulosic fiber and a variation of rayon. Lenzing started selling modal fibers in 1964. In 1977, Lenzing started using an environmentally friendly bleaching method for pulp for their cellulosic fibers. Modal is amazingly comfortable to wear. Measurements of the softness factor show that modal is twice as soft as cotton. The finer the fibre, the finer the textile becomes. The beechwood fibre gives modal a fineness comparable to natural silk and makes modal so silky soft on the skin^{1, 2}. Modal is about 50% more hygroscopic, or water-absorbent, per unit volume than cotton. It's designed to dye just like cotton and is color-fast when washed in warm water. Even after repeated washing, modal remains absorbent, soft and supple. Modal fibers have found a wide variety of uses in clothing, outerwear and household furnishings. The colors in modal typically remain brilliant and strong. Graying, as with 100 %

cotton textiles, does not occur^{3, 4}. They are also wear resistant and strong while maintaining a soft, silky feel. Modal fibers have found a wide variety of uses in clothing, outerwear and household furnishings^{5, 6}. They are often blended with cotton, wool or synthetic fibers and allow easy tone-in-tone dyeing^{7, 8}. In this study, modal fabrics (woven and knitted) are selected and conventionally pretreated to get rid of the basic impurities. The pre-treated fabrics were then subjected with 98% formic acid in different concentrations. The formic acid treated modal fabrics were then undergone for different testings, such as, physical properties, wicking, K/S values, fastness properties, SEM and FTIR analysis. These treatments on modal fabrics were correspondingly compared with those of cotton for its effectiveness.

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MATERIALS AND METHODS

The textile fabrics used in this study were in the following descriptions:

I) Woven Fabrics: a) Modal (100%) : yarn count (both warp and weft) – 27, GSM - 146, ends per inch – 84, picks per inch – 94; b) Cotton (100%) : yarn count (both warp and weft) – 30, GSM - 137.2, ends per inch – 94, picks per inch – 74; and II) Knitted Fabrics: a) Modal (100%) : yarn count – 27.5, GSM 137, loop length–2.6 mm, b) Cotton (100%) : yarn count – 30, GSM - 142, loop length–2.6 mm.

Natural dyes [annatto (*bixa orellana*), onion (*allium cepa*), pomegranate (*punica granatum*), indigo (*indigofera tinctoria*), myrobalan (*terminalia chebula*), bar berry (*berberis vulgaris*)] and synthetic dyes [reactive dye (reactive red HB – C.I. No. Red 24), and sulphur dye (sulphur black – C.I. No. sulphur Black 1)] used were in the commercial grade. The chemicals mentioned elsewhere for this study were in AR grade.

Treatment on modal and cotton fabrics

The modal and cotton fabrics (woven and knitted) were pretreated (desizing (for woven), scouring and bleaching) as per the established technique^{9, 10, 11}. The pre-treated modal and cotton fabrics were subjected with 98% formic acid with the concentration of 1%, 2%, 3%, 4% & 5% (owm) for 30 minutes at ambient temperature (27°C).

Measurement of physical properties of modal and cotton fabrics

The physical properties such as tensile strength⁹, stiffness¹², crease recovery angle^{13, 14} and mean drape coefficient of woven fabric¹⁵; and bursting strength and mean drape coefficient of knitted fabric^{15, 16} of the modal and cotton fabrics was measured by the standard established methods.

Wicking of modal and cotton fabrics

Absorbency is the time taken for a water drop to penetrate into the textile material. The wettability of modal and cotton fabrics was determined as per AATCC test method 79¹⁷. The wicking height of the modal and cotton fabrics was determined^{18, 19}. Fabric samples measuring 10 cm y! 2.5 cm were taken. Each of the sample pieces was clamped to a scale and held at a position such that the tip of the sample just touched the water taken in a beaker. 1% reactive dye (Reactive Red M8B, CI No.: Reactive Red 11) was added for tracking the movement of water. The height of water reached after five minutes was measured²⁰.

Dyeing and K/S analysis of modal and cotton fabrics

The dyeability of modal and cotton fabrics (woven and knitted) was investigated using natural and synthetic dyes. Dyeing was carried out at boil for two hours with a material to liquor ratio of 1:20 as per the established technique of dyeing for natural and synthetic dyes. The dyed samples were washed, soaped and dried^{10, 21, 22}. Colorimetric data of natural and synthetic dyed modal and cotton fabrics were determined by AATCC Test Method -135²³ using a Datacolor SF 600 plus spectrophotometer interfaced to a PC. Measurements were taken regarding colour presence, brightness, dullness and colour intensity with the specular component of the light excluded and the UV component included using illuminant D65 and 10° standard observer. Each fabric was folded once so as to give two thickness and average of five readings were taken each time.

Color fastness analysis of the modal and cotton fabrics

The natural and synthetic dyed samples were washed under condition IIIA of AATCC Test Method 124-2001 to determine the color change

No. Materials Modal (T) Modal (T)	Materials I. MODALModal (UT)	(N) W	nath	St	Stiffness [Bending	ă	Crease	Mean Drane	Burs	Nutted Fabric Bursting strength	oric ength	Mean drane
I. MODA Modal (1 Modal (1	L.Modal (UT)	мр			th cm]	ang	angle (°)	Coefficient			ŭ	coefficient
I. MODA Modal (1 Modal (1	ALModal (UT)		Wt	м М	Mt	d M	Wt	(%)	Test Area (cm²)	(kPa)	Mean heightat burst (mm)	(%)
Modal (7 Modal (7 Modal (7		431	370	0.99	0.97	117	119	65	7.1	497	10.1	47
Modal (7	Modal (T)1% (owm)	428	366	0.99	0.97	118	120	65	7.1	496	10.1	47
Modal (7	Modal (T)2% (owm)	425	359	0.97	0.98	120	122	67	7.0	494	10.0	49
	Modal (T)3% (owm)	420	354	0.95	0.95	122	123	68	6.9	493	9.9	50
Modal (1	Modal (T)4% (owm)	416	348	0.94	0.94	125	126	70	6.7	489	9.7	53
Modal (1	Modal (T)5% (owm)	405	338	0.89	06.0	127	128	71	6.6	488	9.6	54
	II. COTTONCotton (UT)	360	314	1.05	1.04	110	112	79	6.9	626	11.8	61
8 Cotton (⁷	Cotton (T)1%(owm)	359	312	1.05	1.03	110	113	80	6.9	624	11.7	61
9 Cotton (⁷	Cotton (T)2%(owm)	356	309	1.04	1.02	112	114	81	6.8	622	11.6	62
10 Cotton (⁷	Cotton (T)3%(owm)	353	307	1.02	1.01	114	115	81	6.7	620	11.5	63
1 Cotton (Cotton (T)4%(owm)	348	301	0.99	0.98	118	118	84	6.5	614	11.2	66
2 Cotton (Cotton (T)5%(owm)	340	292	0.97	0.97	119	119	85	6.4	612	11.1	67

Table 1: Physical Properties of Modal and Cotton Fabrics

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effect of dyed fabrics^{24, 25}. Light fastness tests (AATCC, 2003), were carried out according to AATCC Test Method 16 E-1998²⁶. The samples were exposed to 5, 10 AFUs (AATCC Fading Unit) to determine the color change AATCC 16-1998²⁷. AATCC standardized crock meter was used to determine the rubbing fastness of natural dyed fabrics under wet and dry condition to assess the color change and staining property AATCC 61-1996²⁸.

Table 2: Wicking of Modal and Cotton Fabrics

S. No.	Textile Materials	Wick Woven	ing (cm) Knitted
1	I. MODALModal (UT)	13	11
2	Modal (T)1% (owm)	14	12
3	Modal (T)2% (owm)	15	12
4	Modal (T)3% (owm)	16	13
5	Modal (T)4% (owm)	19	16
6	Modal (T)5% (owm)	20	17
7	II. COTTONCotton (UT)	14	13
8	Cotton (T)1%(owm)	15	14
9	Cotton (T)2%(owm)	16	15
10	Cotton (T)3%(owm)	17	15
11	Cotton (T)4%(owm)	19	18
12	Cotton (T)5%(owm)	20	19

SEM study of modal and cotton fabrics

The surface morphology of modal and cotton fabrics was observed in SEM (JOEL JSM-6360 model microscope, Japan)^{29, 30}

FTIR study of modal fabrics

Fourier Transfer Infra Red (FTIR) spectrophotometer (Shimadzu, Japan) was used to analyze the functional groups of the dyed modal fabrics^{31, 32}.

RESULTS AND DISCUSSION

Physical properties of modal and cotton fabrics

The physical properties such as tensile strength, stiffness, crease recovery angle and mean drape coefficient of woven fabric; and bursting strength and mean drape coefficient of knitted fabric for modal and cotton fabrics are shown in Table 1. The modal fabric shows higher values of tensile strength (431 N (warp) and 370 N (weft) – untreated) and crease recovery angle (117 (warp) and 119 (weft) – untreated) respectively both in warp and in weft directions compared to that of the cotton fabric. However, the stiffness (0.99 cm (warp) and 0.97 cm (weft) – untreated) and mean drape co-efficient (65%) are less in modal fabric over that of cotton fabric. In the case of knitted fabric, cotton shows greater values than that shown by modal fabric

Table 3: K/S values of Modal and Cotton Fabrics

S.No.	Dyes	Colours		S values of		
		obtained	M	odal	C	otton
			Woven	Knitted	Woven	Knitted
1	Annatto	Orange	13.98	13.10	13.72	12.77
2	Onion	Orange Red	14.50	13.17	13.70	12.98
3	Pomogranate	Brown	14.47	13.52	13.76	12.84
4	Indigo	Blue	14.60	14.33	14.01	13.45
5	Myrobalan	Green	14.45	13.62	13.66	13.76
6	Bar berry	Yellow	14.54	13.41	13.95	13.32
7	Reactive Dye	Red	15.07	14.95	14.42	14.25
8	Sulphur Dye	Black	14.65	14.32	14.21	13.65
No For	mic acid treatme	nt	12.12	12.84	12.95	12.62
React	ive dye): Red					

					ű	astnes	ses of t	Fastnesses of the dyed fabrics	d fabric	ş						
				Mo	Modal							-	Cotton			
S. Dyes		Ŵ	Woven				Kni	Knitted				5	Woven		Knitted	ted
No.	≥	-	œ		≥	-	œ		≥	-	œ		≥	-	œ	
			Wet	Dry			Wet	Dry			Wet	Dry			Wet	Dry
1 Annatto	3-4	5	2-3	4	3-4	4-5	2-3	3-4	3-4	4-5	2-3	3-4	m	4	2-3	3-4
2 Onion	4	2	2-3	4	3-4	4-5	2-3	3-4	3-4	ß	2-3	3-4	3-4	4	2	ю
3 Pomogranate	3-4	ß	2-3	3-4	ო	4-5	2-3	3-4	ო	ß	2-3	3-4	ო	4-5	2-3	ო
4 Indigo	4-5	5-6	ო	3-4	4	ŋ	2-3	ო	4	5-6	2-3	3-4	4	Ŋ	N	ო
5 Myrobalan	3-4	5-6	2-3	3-4	3-4	ŋ	2-3	3-4	3-4	2	2-3	3-4	3-4	Ŋ	N	3-4
6 Bar berry	3-4	4-5	2-3	4	ო	4-5	2-3	4	ო	4-5	2-3	3-4	3-4	4	2-3	4
7 Reactive Dye	4-5	9	ო	4	4-5	5-6	2-3	4	4-5	9	ო	3-4	4	5-6	2-3	4
8 Sulphur Dye	4-5	9	2-3	3-4	4	5-6	2-3	ო	4	5-6	2-3	ო	4	Ŋ	N	ო
No Formic acid	3-4	4	N	3-4	ო	4-5	N	ო	ო	4-5	2-3	ო	ო	4	N	ო
treatment																
(Reactive dye)																
W – Wash Fastness		L – Lig	L – Light Fastness	less		R – Rul	bbing F	R – Rubbing Fastness								

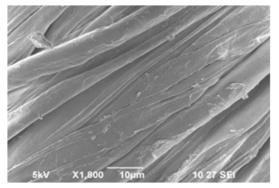
Table 4: Fastness properties of Modal and Cotton Fabrics

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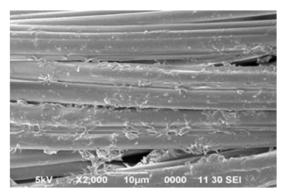
for bursting strength and mean drape coefficient respectively. The modal fabric after treatment with formic acid (98%) at different concentrations for 30 minutes at room temperature show changes in the physical properties. The tensile strength and stiffness of formic acid treated modal fabric are reduced marginally upto the formic acid treatment of 4% (owm), and at 5% (owm) the loss is significant similar to that of cotton fabric. However, the crease recovery and mean drape co-efficient of formic acid treated modal fabric is increased considerably up to the concentration of 4% (owm), and at 5% (owm) it is only marginal. In the case of knitted modal fabric the bursting strength is decreased correspondingly with respect to the concentration of formic acid, while the mean drape co-efficient is increased considerably upto 4% (owm).

Wicking of modal and cotton fabrics

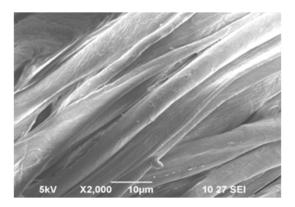
The data of wicking behaviour of modal and cotton (woven and knitted) fabrics are given in Table 2. From table 2, it is clear that the wicking behaviour of all the samples is good, however woven fabrics show some increase over the knitted fabrics. The wicking behaviour shown by cotton is higher than that of modal fabrics both in the case of woven and knitted fabrics. The modal fabric after treatment with formic acid (98%) at different concentrations for 30 minutes at room temperature shows improved wicking compared with the untreated one. The increase in wicking is significant upto 4% (owm) formic acid treatment, and afterwards the increase is only marginal. The similar trend is also observed for cotton fabrics.



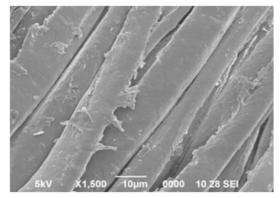
1-a) No formic acid treated & Indigo dyed woven modal fabrics



1-b) Formic acid treated & Indigo dyed



1-c) No formic acid treated & Indigo dyed Knitted modal fabrics



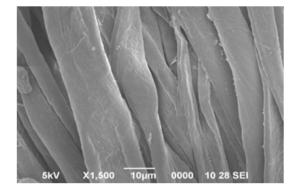
1-d) Formic acid treated & Indigo dyed

Fig. 1: Formic acid treated and indigo dyed modal fabrics

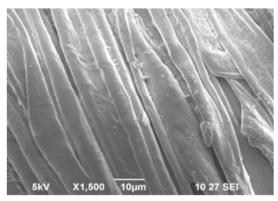
K/S values of Modal and Cotton Fabrics

The K/S values of the dyes such as annatto, onion, pomogranate, indigo, myrobalan, barberry, reactive dye, and sulphur dye applied on formic acid treated modal and cotton (woven and knitted) fabrics are given in Table 3. The formic acid treatment was identified effective at the concentration of 4% (owm), hence that condition was considered as optimum parameter. For dyeing, the modal and cotton fabrics were given formic acid treatment only with 4% (owm) concentration for 30 minutes at ambient temperature. From this table it is observed that woven fabrics show overall high K/S values than the knitted fabrics. The K/S value of formic acid treated modal fabric is high when compared those of the cotton fabrics (woven and knitted). The higher K/S value on the formic acid treated modal fabric is influenced by the higher swelling action of formic acid treatment.

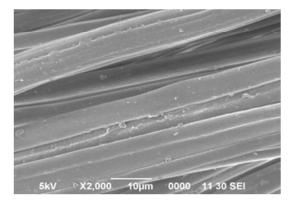
Among the dyes applied on the formic acid treated modal fabrics, there is only a marginal differences in the K/S values; however reactive dye shows the maximum K/S values. Even though the woven and knitted modal and cotton fabrics posses only a small differences in the K/S values for the dyes (annatto, onion, pomogranate, indigo, myrobalan, bar berry, reactive dye, and sulphur dye) applied on these fabrics; there is a uniform trend maintained in these values and the values of woven fabric give an edge over the knitted fabric. The untreated (no formic acid) modal and cotton fabrics were dyed only with the representative dye (reactive). From the table 3, it is evident that the overall K/S values of formic acid (4% owm) treated modal and cotton fabrics are significant compared with that of the untreated dyed fabrics.



2-a) No formic acid treated & Indigo dyed woven cotton fabrics



2-b) Formic acid treated & Indigo dyed

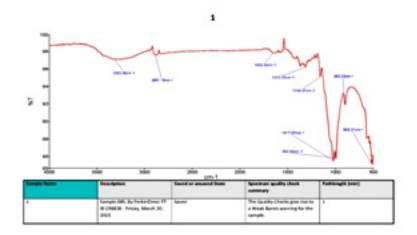


2-c) No formic acid treated & Indigo dyed Knitted cotton fabrics

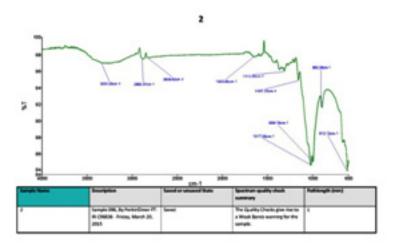
БКV X2,000 10µm 10 27 SEI

2-d) Formic acid treated & Indigo dyed

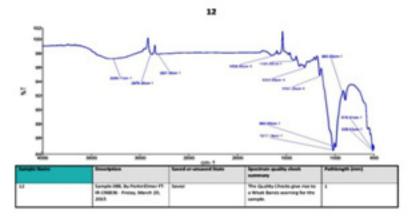
Fig. 2: Formic acid treated and indigo dyed cotton fabrics



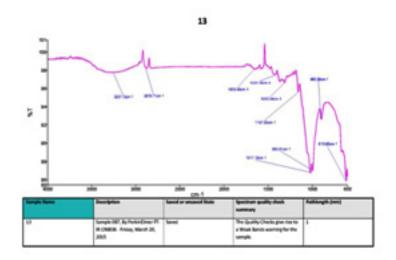
3-a) No formic acid treated & Indigo dyed



3-b) Formic acid treated (1%) & Indigo dyed modal fabrics



3-c) Formic acid treated (4%) & Indigo dyed



3-d) Formic acid treated (5%) & Indigo dyed modal fabrics

Fig. 3: Formic acid treated and indigo dyed modal fabrics

Fastness properties of Modal and Cotton Fabrics

The fastness properties (wash, light and rubbing) of natural and synthetic (indigo, kum kum, bar berry, reactive dye (M), reactive dye (H) and sulphur) dyes applied on formic acid treated (4% owm) modal and cotton fabrics (woven and knitted) are given in Table 4. The wash fastness of the formic acid treated modal fabrics is good as compared with other fatnesses like light and rubbing fastness properties. The good wash fastness property is due to the strong polymeric reaction of the fabric materials and the also of the dye. It is obvious that the light fastness and rubbing fastness properties are moderate to poor only due to their behaviour towards these applications. From this table 4, it is also evident that the overall fastness properties of the formic acid treated and dyed modal fabrics are higher than that of the no formic acid treatment fabrics. The similar trend is also seen for cotton fabrics.

SEM Analysis of Modal and Cotton Fabrics

The analysis of SEM images of formic acid treated and dyed modal and cotton fabrics are given in the representative Figures 1 & 2. Figure 1 reveals about the micrographs of formic acid treated and dyed modal fabrics. Figure 2 reveals about the micrographs of formic acid treated and dyed cotton fabrics. These figures show clearly about the effect of formic acid in the corresponding materials and the subsequent dyeing. There is a clear difference between the no formic treated & dyed; and formic acid treated & dyed (indigo) modal fabrics (woven and knitted). Similar trend is also seen for the cotton fabrics. These micrographs reveal about the enhancement of dyeing after formic acid treatment on modal and cotton fabrics respectively.

FTIR study of indigo dyed modal fabrics

The modal fabrics are dyed with different dyes. However as representation only indigo dyed woven modal fabric is selected for FTIR study. The indigo dyed modal fabrics are studied and their FTIR results are shown in Figure 3. In Figure 3a, the FTIR graph of the modal fabric without any formic acid treatment is seen. Subsequently the FTIR graphs of the indigo dye after application on the formic acid treated (1%, 4%, & 5%) woven modal fabrics are given in the Figures 3b, 3c, and 3d respectively. The FTIR graphs for this indigo dyed modal fabrics are analyzed as per the following data in Table 5. The FTIR graph of 1% formic acid treated modal fabric when compared with that of no formic acid treatment modal fabric there is no difference between them. However, Figure 3c, the 4% formic acid treated modal fabric gives a considerable change in the FTIR graph [33] when compared with Figures 3a and 3b. When the concentration of formic acid is increased beyond 4% there is no change in the FTIR graph as seen in Figure 3d.

S.No.	Peak range(cm ⁻¹)	Functional groups
1	3600-3700	Non bonded hydroxyl group-OH-
2	3300-3400	Alkyne –C-H- stretch
3	3200-3300	Hydroxyl group (H-bonded –OH- stretch)
4	3000-3200	Aromatic ring (-C-H- stretch)
5	2900-3000	Methylene –CH- stretch
6	2700-2800	Terminal aldehyde –CH- stretch
7	2600-2700	Hydrogen bonded –OH- group
8	2500-2600	Thiols (-S-H- stretch)
9	2400-2500	-CH- stretch of aromatic compounds
10	2300-2400	-OH-stretching of Carboxylic acid
11	2200-2300	Cyano compounds, disubstituted alkynes
12	2100-2200	C-triple bond-C- stretch
13	2000-2100	Cyanide ion and related ion
14	1800-2000	Transition metal carbonyl group
15	1700-1800	Carbonyl group
16	1600-1700	-C-double bond-C stretch
17	1500-1600	Aromatic ring stretch-NH-bend
18	1400-1500	Organic Sulphates
19	1300-1400	-OH- bend
20	1200-1300	Aromatic primary amine –CN- stretch
21	1100-1200	Secondary amine –CN- stretch
22	1000-1100	-C-C- stretch
23	900-1000	Cyclo hexane ring vibrations
24	800-900	Peroxides -C-O-O-stretch
25	700-800	Skeletal –C-C- vibrations
26	600-700	Aliphatic Bromo compounds
27	500-600	-C-I- stretch

Table 5: Standard data for the analysis of FTIR graph

CONCLUSIONS

The tensile strength of modal fabric both in warp and weft direction and crease recovery angle are very good in comparison with cotton fabric. Whereas the stiffness [warp & weft] and mean drape co-efficient are less in modal fabric over that of cotton fabric. In the case of knitted fabric, cotton shows greater values than that shown by modal fabric for bursting strength and mean drape coefficient respectively. The modal fabric after treatment with formic acid (98%) at the concentration of 4% (owm) for 30 minutes at room temperature gives considerable changes in the physical properties under the favorable limit suitable for the application. The wicking is improved in the modal fabric (woven and knitted) after treatment with formic acid (98%) at the concentration of 4% (owm) for 30 minutes at room temperature similar to that of cotton fabric. The K/S values of the dyes such as annatto, onion, pomogranate, indigo, myrobalan, barberry, reactive dye, and sulphur dye applied on formic acid treated modal (woven and knitted) fabrics are good compared with that of no formic acid treated one, similar to the trend of cotton fabrics. The fastness properties (wash, light, & rubbing) of the formic acid treated and dyed (annatto, onion, pomogranate, indigo, myrobalan, bar berry, reactive dye and sulphur dye) woven and knitted modal fabrics are comparatively good over that of no formic acid treated one, as that of cotton fabrics. In general, the overall fastness properties are more in formic acid treated fabrics. SEM micrographs reveal that the formic acid treated & dyed modal and cotton fabrics

give good dyeing effect compared with that of no formic acid treated one. FTIR graphs reveal that the formic acid treatment of 1% gives no effect whereas 4% formic acid gives considerable changes on the modal fabric; after 4% of formic acid treatment the effect is negligible only.

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