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Comparative Study between Modal and Cotton after Formic Acid Treatment

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ABSTRACT: Modal fabric is a bio-based rather than natural made from the spun reconstituted cellulose polymer of beech trees. Modal was at first introduced by Lenzing AG Company of Austria who trade named the fabrics identity. Modal fabrics are very soft and smooth with the ability to absorb up to 50% more water than cotton. Fabric made from modal drape well and do not pile like 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 testing's, such as Bending Length, Crease Recovery angle, Effluent Load, FTIR and SEM & EDAX analysis.. These treatments on modal fabrics were correspondingly compared with those of cotton for its effectiveness.

KEYWORDS: Modal Fabric, Formic acid, Bending Length, Crease Recovery angle, SEM & EDAX and FTIR.

I. INTRODUCTION

Lenzing started selling modal fibers in 1964. In 1977, Lenzing started using an environmentally friendly bleaching method for pulp for their cellulosic fibers. Modal's distinguishing characteristics are its high wet strength and its extra softness. It is sometimes referred to as "soft as a feather" and the "softest fiber in the world" (1, 2, 3, 4). The smooth surface characteristics of the modal fiber make it impossible for mineral deposits from water, such as lime scum, to be deposited on the textiles thus preventing fabric hardening after repeated washings (4, 5). It's designed to dye just like cotton and is color-fast when washed in warm water. The softness makes it especially ideal for body contact clothing such as lingerie and under garments (3, 6). They also have very good wear resistant and are strong while maintaining a soft, silky feel. Modal fibers have a wide variety of uses in clothing, outerwear and household furnishings. 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 testing's, such as, physical properties, absorption, K/S values, fastness properties and SEM analysis. These treatments on modal fabrics were correspondingly compared with those of cotton for its effectiveness.

II. LITERATURE SURVEY

The Modal® fibers are extremely smooth and soft, and blending them with cotton or treatment with suitable chemicals helps the yarn to stay soft and vibrantly colored, even after many washes (Kupiainen 2012). Lenzing claims a recovery rate of greater than 95 percent — a tremendous improvement over early rayon and viscose production (Heinze&Liebert 2001; Saalwachter&Burchard 2001). It is cool to the touch and very absorbent. Like cotton, modal dyes easily and becomes colorfast after submersion in warm water (White et al. 2005). The differences in fabric properties such as

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texture, hand, pilling, fibrillation, and dye acceptance generally result from different chemicals and enzymes and their dilution strengths and from processing techniques used during the fiber and finishing (Rous et al. 2006; Joshi et al.2010; Manian et al. 2008) .

III. EXPERIMENTAL

3.1 Materials

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; and the chemicals and dye used in this study were in the commercial grade.

Natural dyes [annatto (bixaorellana), onion (allium cepa), pomegranate (punica granatum), indigo (indigoferatinctoria), myrobalan (terminaliachebula), 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.

3.2 Methods

3.2.1 Pretreatment on modal fabrics

The modal and cotton fabrics (woven and knitted) were pretreated (desizing (for woven) - by 10 gpl H₂SO₄ for 60 minutes at ambient temperature) (scouring – by 3% ovm NaOH for two hours at boil and bleaching – by 1% ovm H₂O₂ for one hour at boil) as per the established technique (9, 10).

3.2.2 Treatment of modal fabrics with formic acid

The pre-treated modal and cotton fabrics were subjected with 98% formic acid with the concentration of 1%, 2%, 3%, 4% & 5% (ovm) for 30 minutes at ambient temperature (27°C).

3.2.3 Physical Properties of Modal and Cotton Fabrics

The modal and cotton fabrics were treated with 98% formic acid. The physical properties such as bending length and crease recovery angle were tested as per the established techniques (11, 12).

3.2.4 Dyeing of Modal and Cotton Fabrics

The dyeing of modal and cotton fabrics (woven and knitted) was carried out by 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 (13, 14).

3.2.5 Effluent load of dye bath after dyeing on formic acid treated woven modal fabrics

After dyeing, the effluent parameters such as pH, TDS, total alkalinity, sulphate ion, BOD, and COD were tested five times each from the effluent load of the dye baths of formic acid treated followed by dyed modal fabrics (15, 16).

3.2.6 FTIR study of Modal and Cotton Fabrics

Fourier Transfer Infra Red (FTIR) spectrophotometer (Shimadzu, Japan) was used to analyze the functional groups of the dyed modal fabrics (17).

3.2.7 SEM-EDX Analysis of Modal and Cotton Fabrics

The formic acid treated and dyed modal fabrics were subjected for Scanning electron microscope studies with 30kV scanning electron microscope JEOL (Japan) Model JSM-6360. The elemental composition of materials present in modal fabrics are determined using Energy Dispersive X-Ray analysis (Oxford Instruments, UK) (18, 19).

IV. RESULTS & DISCUSSION

4.1 Bending Length of Woven Modal and Cotton fabrics

The values of the bending length of formic acid treated modal and cotton woven fabrics are given in Table 4.1. This test was inconvenient on knitted fabrics hence done only on woven fabrics and reported here. There is a reduction in the bending length

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after formic acid treatment on modal fabric compared with those of untreated one. This bending length is reduced with the increase of the concentration of formic acid significantly upto 4% owm, and afterwards it is only insignificant. The warp side gives marginal increase in the bending length over that of the weft side. The similar trend is seen on cotton fabric also correspondingly, but with little edge over that of the modal fabrics. Bending length is also known as the flexibility of the fabric. This is a very important character of the fabric which governs its applications. Fabrics with high bending length are stiffer, they lack good drape, and lack flexibility. They cannot be used as aesthetic fabrics as they are not much comfortable due to their stiffness. Hence bending length can also be defined as the falling length, when a fabric falls under its own weight to a specific length, having specific angle. There are many factors which reveal the bending length of the fabric. But the most important is one of the fiber parameters called flexural rigidity. As different fibers have a different shape factor, some are circular; other can be kidney bean or any other shape. The shape factor of a fiber tells the flexural rigidity of the fibers. The flexural rigidity tells us how much the fiber is stiff to the bending or flexural deformation.

Table 4.1. Bending Length of Woven Modal and Cotton fabrics

S. No.	Formic Acid Treatment(% owm)	Bending Length (mm) of Woven Fabrics			
		Warp (Cw)		Weft (Cf)	
		Modal	Cotton	Modal	Cotton
1	0	10.0	10.6	9.8	10.4
2	1	9.3	9.6	9.2	9.5
3	2	9.2	9.5	9.1	9.4
4	3	9.1	9.4	9.0	9.3
5	4	8.7	9.0	8.6	8.9
6	5	8.6	9.0	8.5	8.9

4.2 Crease Recovery (°) of Woven Modal and Cotton Fabrics

The data of the crease recovery of formic acid treated modal and cotton woven fabrics are given in Table 4.2. The crease recovery is correspondingly increased with the increase of the concentration of formic acid on modal fabrics. The increase in crease recovery is considerable up to the concentration of 4% owm treatment on modal fabric, and afterwards there is no considerable increase. The crease recovery is more in the weft direction than that of the warp direction of the modal fabric. There is more crease recovery of modal fabrics compared with those of the cotton fabrics. Creases are a fold in a fabric introduced unintentionally. They form when fabrics undergo double curvature, which occurs when a flat material is bent in both of its planes. Sufficient force must be applied that the change is permanent to some degree. Some people use the terms 'wrinkle' and 'crease' interchangeably. Crease marks are marks left in a fabric once the crease has been removed and are usually caused by mechanical damage. Crease recovery is a specific measurement of crease resistance that determines the crease recovery angle. It is therefore a quantitative method of analysis.

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Table 4.2 Crease Recovery (°) of Woven Modal and Cotton Fabrics

S. No.	Formic Acid Treatment(% owm)	Crease Recovery (°) of Woven Fabrics			
		Warp (Cw)		Weft (Cf)	
		Modal	Cotton	Modal	Cotton
1	0	119	115	121	117
2	1	120	116	122	117
3	2	121	117	122	118
4	3	122	117	123	119
5	4	125	120	126	122
6	5	125	120	127	123

4.3 Effluent Load of Dye Bath after Dyeing on Formic Acid Treated Woven Modal Fabrics

The data of effluent loads obtained from different dye baths of natural dyeing and synthetic dyeing on modal fabrics are given in Table 4.3. From the Table 4.3, it is seen that the pH is more [10.4] in the dye baths of without formic acid treatment on modal fabric compared to the formic acid treated modal fabrics dyed with synthetic dyes [reactive and sulphur dyes; av.: 9.05], and natural dyes [annatto, onion, pomogranate, indigo, myrobalan, and bar berry, av.: 8.9] respectively. The reduction in pH may be due to the formic acid treatment which influences in the modal fabrics as well in the dyes.

The TDS is high in the dye baths of without formic acid treatment on modal fabric [4675 mg/l] compared to the formic acid treated modal fabrics dyed with synthetic dyes [reactive and sulphur dyes; av.: 3941 mg/l], and natural dyes [annatto, onion, pomogranate, indigo, myrobalan, and bar berry, av.: 3755 mg/l] respectively. This is due to the effect of formic acid onto the fiber polymers that enhances the considerable increase of dye uptake and leads to the reduced total dissolved salts.

The total alkalinity is more in the dye baths of without formic acid treatment on modal fabric [852 mg/l] compared to the formic acid treated modal fabrics dyed with synthetic dyes [reactive and sulphur dyes; av.: 581 mg/l], and natural dyes [annatto, onion, pomogranate, indigo, myrobalan, and bar berry, av.: 545 mg/l] respectively. The treatment of formic acid in the modal fabrics leads to the decrease in the amount of total alkalinity in the effluent load. The Sulphate ion concentration is excess in the dye baths of without formic acid treatment on modal fabric [756 mg/l] compared to the formic acid treated modal fabrics dyed with synthetic dyes [reactive and sulphur dyes; av.: 671 mg/l], and natural dyes [annatto, onion, pomogranate, indigo, myrobalan, and bar berry, av.: 642 mg/l] respectively.

The BOD and COD are high in the dye baths of without formic acid treatment on modal fabric [354 mg/l, and 728 mg/l] compared to the formic acid treated modal fabrics dyed with synthetic dyes [reactive and sulphur dyes; av.: 247 mg/l, and 423 mg/l], and natural dyes [annatto, onion, pomogranate, indigo, myrobalan, and bar berry, av.: 236 mg/l, and 417 mg/l] respectively. The formic acid treatment is responsible for the low values of sulphate ions, BOD and COD in the effluent load after dyeing on modal fabrics.

Experimental evidences showed that the similar trend is also available for the cotton fabrics treated with formic acid followed by dyeing, and hence the data are not tabulated here. The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes. Wastewater

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from dyeing units is often rich in color, containing residues of dyes and chemicals, and requires proper treatment before being released into the environment. The toxic effects of dyestuffs and other organic compounds, as well as acidic and alkaline contaminants, from industrial establishments on the general public are widely accepted. Increasing public concern about environmental issues has led to closure of several small-scale industries. Interest in ecologically friendly, wet-processing textile techniques has increased in recent years because of increased awareness of environmental issues throughout the world. Consumers in developed countries are demanding biodegradable and ecologically friendly textiles.

Table 4.3 Effluent Load of Dye Bath after Dyeing on Formic Acid Treated Woven Modal Fabrics

S.No.	Dyes	Effluent Parameters (mg / lit) After Formic Acid Treatment and Dyeing					
		pH *	TDS	Total Alkalinity	Sulphate	BOD	COD
1	Annatto	08.92	3764	537	645	247	422
2	Onion	08.64	3828	522	637	224	414
3	Pomegranate	08.96	3795	546	648	231	420
4	Indigo	08.98	3856	567	655	248	424
5	Myrobalan	08.93	3767	562	631	241	413
6	Bar berry	08.94	3522	533	636	226	407
7	Reactive Dye	09.04	3935	578	668	249	424
8	Sulphur Dye	09.06	3947	584	674	244	422
S.No.	Dyes	Effluent Parameters (mg / lit) (No formic Acid Treatment)					
		pH *	TDS	Total Alkalinity	Sulphate	BOD	COD
1	Annatto	10.3	4508	811	732	350	725
2	Onion	10.0	4586	796	723	325	715
3	Pomegranate	10.3	4539	814	735	330	722
4	Indigo	10.4	4613	838	740	352	728
5	Myrobalan	10.3	4514	836	718	343	714
6	Bar berry	10.3	4276	807	722	325	710
7	Reactive Dye	10.4	4675	852	756	354	728
8	Sulphur Dye	10.4	4685	855	762	348	725

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4.4 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 1. In Figure 1a, 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 1b, 1c, and 1d respectively. The FTIR graphs for this indigo dyed modal fabrics are analyzed as per the following data in Table 4.4. 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 1c, the 4% formic acid treated modal fabric gives a considerable change in the FTIR graph when compared with Figures 1a and 1b. When the concentration of formic acid is increased beyond 4% there is no change in the FTIR graph as seen in Figure 1d.

Table 4.4. Standard data for the analysis of FTIR graph

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	Cyanocompounds,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

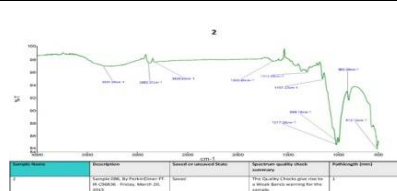
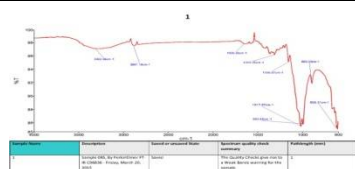
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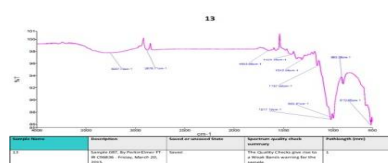
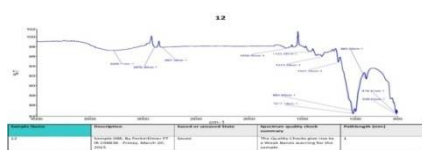
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S.No.	Peak range(cm^{-1})	Functional groups
25	700-800	Skeletal -C-C- vibrations
26	600-700	Aliphatic Bromo compounds
27	500-600	-C-I- stretch



1-a) No formic acid treated & Indigo dyed modal fabrics 1-b) Formic acid treated (1%) & Indigo dyed modal fabrics



1-c) Formic acid treated (4%) & Indigo dyed modal fabrics 1-d) Formic acid treated (5%) & Indigo dyed modal fabrics
Fig. 1: Formic acid treated and indigo dyed modal fabrics.

4.5 Scanning electron microscopy and energy dispersive X-ray characterization of modal fabric

The analysis of SEM images and EDAX spectra of no formic acid treated; formic acid treated; and formic acid treated and indigo dyed woven modal and cotton fabrics are given in the representative Figures 2, 3, 4, & 5. Figure 2 reveals about the SEM micrographs of a) no formic acid treated; b) formic acid treated, and c) formic acid treated and indigo dyed woven modal fabrics. Figure 3 reveals about the SEM micrographs of a) no formic acid treated; b) formic acid treated, and c) formic acid treated and indigo dyed woven cotton fabrics. Figure 4 reveals about the EDAX spectra of a) no formic acid treated; b) formic acid treated, and c) formic acid treated and indigo dyed woven modal fabrics. Figure 5 reveals about the EDAX spectra of a) no formic acid treated; b) formic acid treated, and c) formic acid treated and indigo dyed woven cotton fabrics. These figures show clearly about the effect of formic acid in the corresponding materials and the subsequent dyeing. The effect of formic acid is clearly seen from the SEM micrographs as given in the Figures 2 & 3 for modal and cotton fabrics. This effect is confirmed in the EDAX spectra as shown in the Figures 4 & 5 for modal and cotton fabrics. The formic acid treatment makes the fabrics uniform so as to get improvement in their behaviours.

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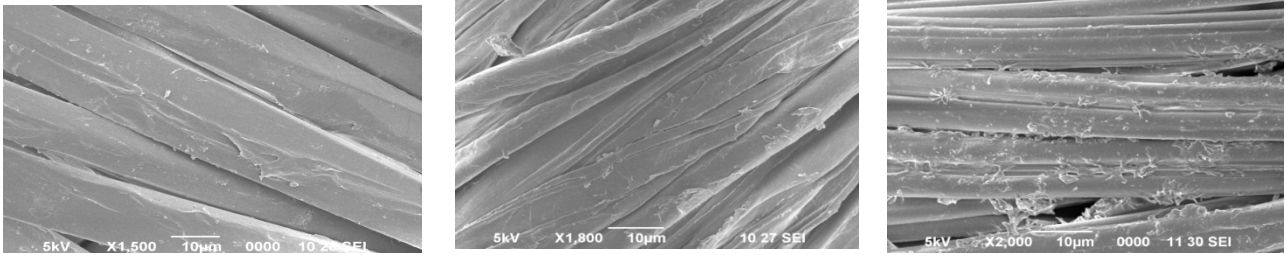


Figure 2. a) No formic acid treated b) Formic acid treated & c) Formic acid treated and Indigo dyed woven modal fabrics

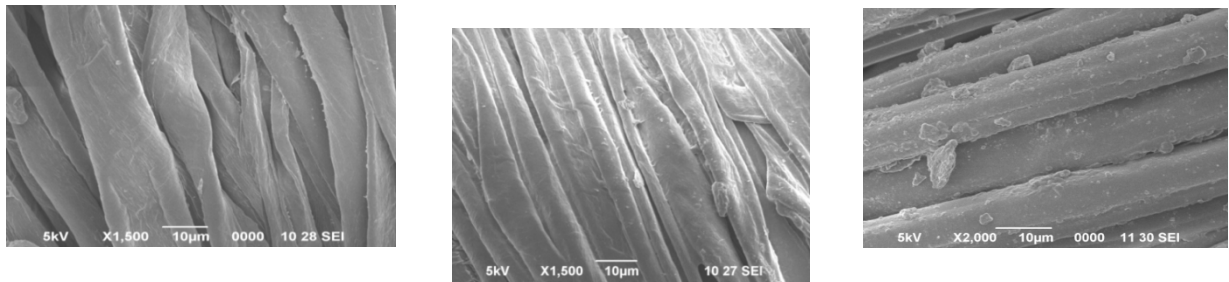
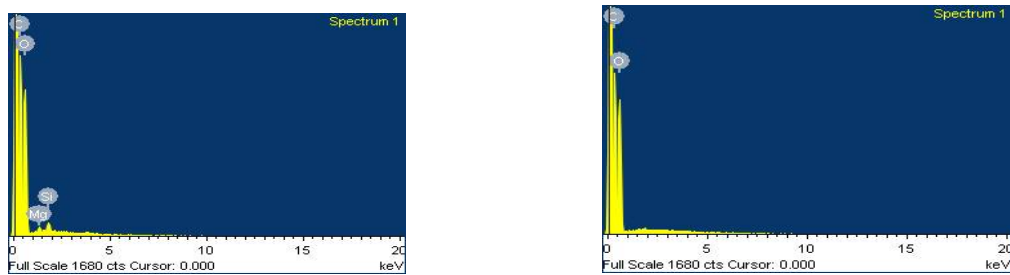
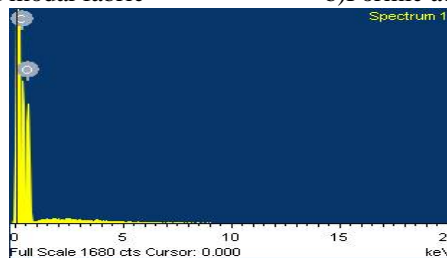


Figure 3. a) No formic acid treated b) Formic acid treated & c) Formic acid treated and Indigo dyed woven cotton fabrics



a) No formic acid treated modal fabric b) Formic acid treated modal fabric



b) Formic acid treated and Indigo dyed modal fabric
Figure 4. EDAX spectra of a) No formic acid treated b) Formic acid treated & c) Formic acid treated and Indigo dyed woven modal fabrics

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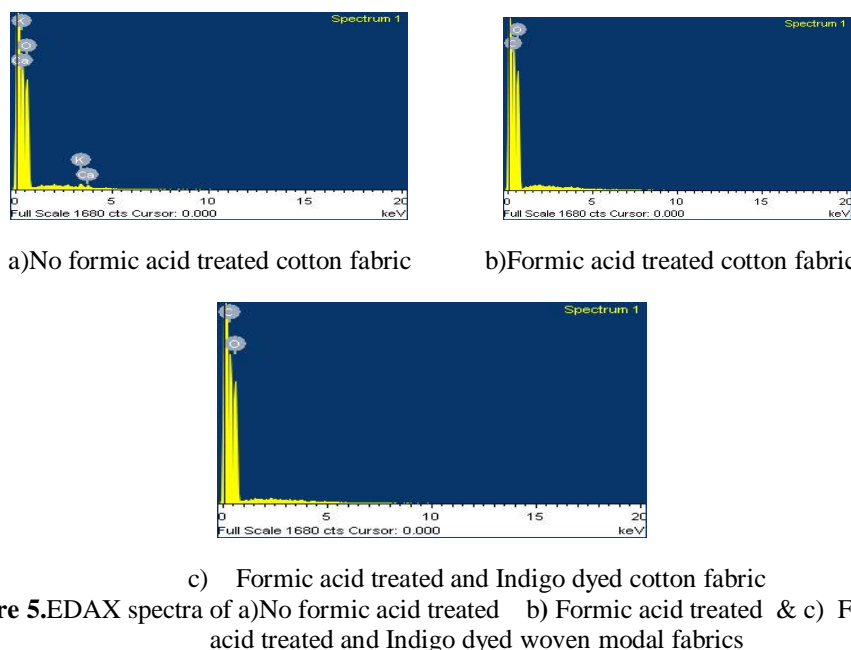


Figure 5. EDAX spectra of a) No formic acid treated b) Formic acid treated & c) Formic acid treated and Indigo dyed woven modal fabrics

V. CONCLUSIONS

1. The bending length in both warp and weft directions of formic acid treated modal fabrics is improved considerably. The trend is common in both warp and weft directions, however the warp materials have an edge over the weft materials for the bending length.
2. The crease recovery in both warp and weft directions of formic acid treated modal fabrics is minimum compared to untreated one. The trend is common in both warp and weft directions, however the weft materials have a little edge over the warp materials for the crease recovery.
3. The effluent load in the residual dye bath after dyeing on modal fabrics treated with formic acid followed by dyeing with natural and synthetic dyeing is considerably reduced.
4. 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.
5. SEM –EDX 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.

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