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Simultaneous Cationization and Antimicrobial Treatment of Cotton Khadi Fabric with Poly-Hydroxy Methyl Amino Sillicone (PHAMS) and Poly Ethylene Glycol (PEG).

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Abstract

Cotton Khadi fabric is treated with eco-friendly anti- microbial agents like Polyethylene Glycol (PEG -200), Poly-Hydroxyl Amino Methyl Silicone (PHAMS) and Citric Acid (CA) individually and in their blends as compared to treatment with epoxy-propyl-trimethyl-ammonium chloride (EPTAC) in presence of $MgCl_2$ as mild acidic catalyst by low tensioned padding and drying at 100^0C for 10 min. followed by curing at 120^0C for 4 min. to investigate the effect of such treatment on important textile related properties and microbial resistance and dye-ability with reactive dye. For presence of –OH group, PEG, PHAMS and EPTAC have ability to react with –OH groups of cellulose under acidic catalyst to bound to cellulose macromolecules forming ether linkage and can produce a modified cationized cotton attaching $–NR_3^+$ groups of EPTAC and $–NHR_2^+$or $–NH_3^+$groups of PHAMS. Highest Antimicrobial and salt free dyeing with reactive dye was achieved by combined treatment of PEG and PHAMS (in 3:1 ratio) in presence of $1/5^{th}$ of magnesium chloride. FTIR, XPS and TGA studies have been carried out to understand the nature of reaction and modification occur to support reaction mechanism discussed. The effectiveness of the antimicrobial properties have been assessed by measuring the loss of tensile strength by soil burial test and also by testing as per AATCC-100 and AATCC-147.

Keywords: **Antimicrobial properties; Cotton Khadi Fabric; PHAMS; Citric Acid, PEG; Salt free reactive dyeing;**

1. Introduction

Cotton Khadi Fabrics is an ancient heritage of India. Out of 10.98 lakh persons employed in Khadi (hand spun and hand woven) sector in India, 80% are women. With a low capital investment, Khadi (hand spun and hand woven) cotton fabrics play a pivotal role in socio-economic empowerment of rural artisans [1]. Major advantages of this fabric are its eco-friendliness, hand woven at home. Major disadvantages are lower strength, easy creasing, easy microbial attack, less dimensional stability, sometimes non uniform dyeing and difficult for machine finish except low tensioned padding. Moreover the strength of such woven cotton Khadi fabric is not only on lower side, but further reduced drastically during the chemical processing, storage and also during its use due to washing. Khadi fabric being made of cotton is susceptible to easy microbial attack /rotting, if remained in moist and humid condition for a longer period.

Generally, cellulosic fabrics like cotton and its blends are conventionally treated with some metallic salts (Cupper sulphate, cupper napthanate) or quaternary ammonium compound like (Cetyl trimethyl ammonium bromide-CTAB, Cetrimide or Epoxy-propyl-trimethyl-ammonium chloride (EPTAC)etc) [2]which are some way or other may not be fully eco-friendly in nature and can't become sufficiently wash fast as well as has some objectionable smell preventing its use in apparel sector. Hence, it is imperative to develop treatment of such cellulosic fabrics with suitable eco-friendly antimicrobial as well as rot resistant chemicals which also should not impair its dyeability with reactive dyes, rather in turn facilitate eco-friendly dyeing.

Polymer of Hydroxyl Amino Methyl Silicone (PHAMS) and its potassium salt having methyl array on the outer surface of modified /treated cotton substrate reduces water absorption and thus reduces water imbibation and spalling due to Freeze-thaw and efflorescence, thereby increasing the life of the cellulosic substrate against microbial attack. Hence, PHAMS is used in the present work. Limited and scanty work [3-4] also has been carried out for rot resistance and antimicrobial finishes on cotton fabric, but such work on highly finer variety of cotton muslin fabric or khadi cotton fabric are rare except one recent work [3].

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Moreover, PEG (Polyethylene Glycol) and CA (Citric acid) has been earlier proved to have a reasonable antimicrobial effect on cellulosic and lingo-cellulosic fabrics like jute , as non toxic [4, 5] antimicrobial agents. Hence, PEG and Citric acid have also been used in the present work. Mixture of Citric acid and PEG has been used for imparting rot resistant treatment of jute fabrics, where citric acid acts also as a cross linking agent [4]. Silicones are known to be softener and water repellent chemical [6]. Hence, in the present work Khadi (hand spun and hand-loom woven) cotton fabric has been treated with eco-friendly anti-microbial agents like Polyethylene Glycol (PEG -200), Poly-Hydroxyl Amino Methyl Silicone (PHAMS) and Citric Acid (CA) individually and also in their blends, in presence of $MgCl_2$ as mild acidic catalyst by low tensioned padding followed by drying at 100^0C for 10 minutes and curing at 120^0C for 4 minutes in order to investigate the effect of such eco safe antimicrobial treatment on important textile related properties , microbial resistance and results of salt free dyeing with reactive dyes. The effectiveness of the antimicrobial properties to be developed by the said treatments may be quantified by measuring the loss of tensile strength by soil burial test and also antimicrobial tests for treated and untreated cotton khadi fabric and was compared against a sample treated with commercially available quaternary ammonium compound i.e. epoxy-propyl-trimethyl-ammonium chloride (EPTAC) Possible reaction mechanism have been suggested and supported by FTIR, XPS and TGA studies

2. Experimental

2.1 Materials

Conventional bleached plain woven cotton Khadi fabric made out of 13.7texwarp and 14.3 tex weft handspun cotton yarn with 80.3 g/m^2 aerial density and pick density 53 PPI and end density 76 EPI , was used for the present study.
PEG 200 obtained from E Merck (India), PHAMS from Supreme Silicones, Aurangabad and Citric Acid obtained from E Merck India were used as antimicrobial agents. $MgCl_2$obtained from E Merck India was used as catalyst system. CHPTAC (3-chloro-2 hydroxy propyl tri-methyl ammonium chloride, is converted into the reactive epoxide form i.e. epoxy-propyl-tri-methyl-ammonium chloride (EPTAC) and is used for conventional rot resistance finish used conventionally.

2.2 Methods

2.2.1 Anti Microbial treatment

Bleached cotton Khadi fabric was initially treated with 2% aqueous solution 100% exhaustion by pad –dry-cure process (so that application percentage on weight of the fabric is also 2%) for each of PHAMS, PEG and Citric Acid and a binary mixture of these agents in different combinations in absence or in presence of $MgCl_2$ catalyst (1/5th of the antimicrobial agents), to know their effect on antimicrobial property and other important textile related properties..

The same bleached cotton Khadi Fabric was padded in a lab padding mangle with 1.5 kg/cm^2 nip pressure to maintain 100% exhaustion for 2% on weight of fabric application of each of these chemicals individually and also for application of overall 2% on weight mixture of PEG and PHAMS (1:1 initially) , PHAMS and Citric Acid (1:1 initially) and PEG and Citric Acid (1:1 initially) to get 100% wet pick up , followed by drying at 100^0C for 10 minutes and then curing at 120^0C for 4 minutes. The ratio of mixture of PEG and CA, PEG and PHAMS, PHAMS and CA were also varied at later stage to determine the optimum ratio for use of such mixture effectively to obtain the desired effect. In each case, a catalyst ($MgCl_2$) (1/5th amount of the antimicrobial agents) was used to get better wash-fast treatment of the selected chemicals on cotton Khadi fabrics.

In another experiment bleached cotton Khadi fabrics was also padded with (100 % wet pick up) with varying percentage of PEG and PHAMS from 1 to 8% application. All these selected chemically padded fabrics were then dried at 100 ^{0}Cfor 10 minutes and finally cured at 120^0C for 4 minutes followed by rinsing , washing (to remove the unreacted chemicals etc.) and drying in air at ambient conditions.

For comparison of antimicrobial and rot resistance properties the cotton fabric is additionally padded with a solution of 60g/l CHPTAC and 24 g/l NaOH (hydrated) mixture (after keeping the mixture for 10 minutes in room Temperature) to form EPTAC [7] followed by drying and curing in the same manner described above.
Unless otherwise indicated, all such cured fabrics were thoroughly washed and dried in air at ambient conditions.

2.2.2 Testing Methods

Test of Rot resistance: Rot resistant performance i.e. resistance to microbial attack of treated and untreated cotton muslin fabric samples were assessed by determining the % retention of tensile strength after subjecting the fabric to a standard soil burial test for 21 days as per IS 1623:1992 standard [8] test method.
Test of Crease recovery performances: Dry crease recovery angle of both warp way and weft way of selected fabric samples were measured by the Presto crease recovery tester in accordance with IS 4681:1981 standard [9] test method.
Test of Tensile Properties: Tensile strength of selected fabric samples were measured by the ravelled strip method as per ASTM D 5034 standards [10] using Digi strength tester (make Paramount Instruments, India) with a traverse speed of 300 mm/min. The final gauge length (sample size) of the fabric sample was 100 mm x150 mm under the two jaws for test of tensile strength of treated and untreated cotton muslin fabrics.
Test of Fabric stiffness (bending length):Fabric stiffness as expressed in terms of bending length of the selected cotton muslin fabric samples were measured as per IS 6490:1971 standard [11] test method using standard cantilever type stiffness tester.
Whiteness Indices: Whiteness Index (WI) [12] for the selected cotton muslin fabric samples were evaluated as per CIE standard using a computer aided colour-eye Xth reflectance spectrophotometer (with D65 standard illuminant and 10 deg standard observer setting).
Yellowness Indices: The Yellowness Index (YI) was measured in the same colour eye Xth reflectance spectrophotometer as per ASTM- E313-00) standard [13]
Brightness Index: The Brightness Index (BI) (equivalent to TAPI 452) was measured using standard CIE formula using colour eye Xth reflectance spectrophotometer as per (ISO 2469 and 2470-1977) standard [14].

X ray diffraction study

X ray diffraction study of the cotton muslin fabric samples were carried out on X' Pert Pro X ray diffractometer using copper K-α X rays of 1.542^0A radiation with the diffraction angle (2θ) varying from 10 to 35^0 by transmission mode [15].

Antimicrobial study

Antimicrobial properties of these treated and untreated samples are studied as per AATCC 147 -2011 and AATCC 100-2012 standards in the incubation condition of 37^0C for 24 hours.

XPS Study

XPS analysis was carried out on PHI 5000 Versaprobe II and UV (340 Nm wave length) exposure was carried out at standard atmospheric condition with 0.35 w/m^2 irradiance.

FTIR study: FTIR Spectroscopy analysis was done in a double beam FTIR spectrophotometer by ATR (Attenuated Total Reflectance) attachment.

3. Results and Discussion

3.1 Effect of treatment of PHAMS, PEG, Citric Acid and their binary mixtures on properties of bleached cotton khadi fabric with $MgCl_2$ catalyst system

In this part of work, Cotton Khadi bleached fabric was treated with the selective agents i.e. PHAMS, PEG and Citric Acid individually and binary mixture of these and relevant results of textile related properties and antimicrobial/rot resistance properties are shown in Table 1 and Table 2.Only Citric acid or combination of Citric acid with either Polyethylene Glycol (PEG -200), and Poly-Hydroxyl Amino Methyl Silicone (PHAMS) have not shown desirable resistance to microbial attack though invariably it is better than the control untreated cotton fabric.

With the above preliminary results, a series of experiments were further undertaken with varying percentage of both the chemicals to arrive at the optimum concentration and ratio of mixture of PEG and PHAMS and their performance for antimicrobial resistance and other properties. This has been also compared with such effects on the same fabrics for a conventional treatment with a quaternary ammonium compound known as EPTAC (2,3-epoxy-propyl trimethyl ammonium chloride, in presence of alkali or acid (reaction conditions).

3.1.1 Tensile and other Textile Related Properties

Table 1 indicate data ontenacity, rot resistance (% retention of strength after soil burial test) , dry crease recovery angle , bending length and surface appearance properties like whiteness index (WI), Yellowness Index (YI) , brightness index (BI) and colour strength value (K/S value) of untreated bleached cotton Khadi fabric and the same fabric after treated with single as well as 1:1 mixture of, PEG, PHAMS, CA under the specific condition of treatment with catalyst ($MgCl_2$-$1/5^{th}$ of the treatment agents in g/l).

Between 2% PEG, 2% PHAMS and 2% CA treatment separately on cotton Khadi fabrics, CA shows higher strength loss (about 13.2% loss) than PHAMS (5.5% loss) and PEG (7.3% loss) while mixture of 2% PHAMS and 2% CA show almost 13.9% loss in tensile strength, mixture of 2% PEG and 2% CA gives 19.9% loss indicating that PEG in presence of citric acid forms more cross linking brittleness in cotton and loss of strength due to the said treatment is higher than 2% mixture of CA and PHAMS. However, 2% PEG and 2% PHAMS is minimum i.e. around 7.3% which appears to be better, if its rot resistance and antimicrobial properties are satisfactory. Hence rot resistance properties of all these treatments were tested and can be arranged in the following order.

2% PEG+2% PHAMS > 2% CA +2% PHAMS > 2% PEG+2% CA

Considering these results, the surface appearance properties and bending /crease recovery properties have also been compared and found that when CA is present in the mixture of PEG+CA or PHAMS+CA, the CRA is somewhat lower than other treatment with PEG+PHAMS. This unexpected result, despite higher cross linking potential of CA for cellulose may be explained by the fact of some degree of chain scission by CA at 120^{o}C during curing for more free acidity , which also supported by higher strength loss due to treatments wherein CA was present in the mixture. Due to these said treatments, whiteness and brightness index of all samples goes up to a noticeable extent which however, is less reduced in treatments with any combination where CA is present due to its acidic leaching and cleaning of surface by CA itself. Same is the trend for brightness index of the samples. Hence further experiments (Table 2) were carried out for varying proportions of PEG and PHAMS for finding a suitable optimal ratio of the two.

Corresponding results are shown in Table 2. The results in Table 2 indicate that with the increase of PEG content in the mixture of PEG and PHAMS, the retention of tenacity after soil burial test increases and highest tenacity retention can be obtained either by 4% PHAMS and 4% PEG (tenacity retention 77%) or 2% PHAMS and 6% PEG (tenacity retention 79.4%).

Table 1: Effects of treatment with (1:1/1:2) PHAMS, PEG, CA and their binary mixtures on properties and rot resistance of cotton khadi fabric treated in presence of $MgCl_2$ catalyst

Treatment	Tenacity (cN/ tex)	Retention of tensile strength on treatment (%)	% Retention of tensile trength after soil burial of 21 days (rot Resistance)	Crease recovery angle in deg (warp +weft)	Bending length in (cm)	Whiteness Index(WI) (CIE scale)	Brightness Index (BI) (TAPPI-452 scale)	Yellowness Index (YI) ASTM E 313-00	K/S Value
Control Fabric	1.66	---	23.0	100.8	1.40	26.9	62.04	18.26	0.208
2% PEG	1.54	92.7	30.0	107	1.30	9.08	54.13	24.10	0.310
2% PHAMS	1.57	94.5	44.0	106.2	1.25	9.98	54.89	23.74	0.304
1% PHAMS +2% PEG	1.24	84.7	36.0	108	1.29	9.20	54.21	23.90	0.308
2% PHAMS +1% PEG	1.28	87.1	21.7	109.1	1.27	9.80	54.72	23.80	0.302
1% PHAMS+1% PEG	1.28	87.1	38.5	107.1	1.30	9.40	54.14	23.10	0.285
2% Citric Acid	1.44	86.7	13.0	96.2	1.30	15.67	57.94	22.72	0.254
2% PHAMS+2%	1.54	92.7	73.1	102.5	1.33	4.06	49.99	28.25	0.407

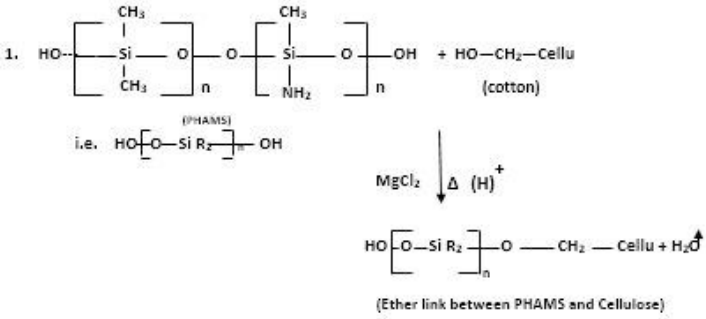
PEG									
2% PEG+ 2% CA	1.33	80.1	64.1	96	1.31	12.80	56.15	23.21	2.780
2% PHAMS +2% CA	1.43	86.1	67.4	95	1.23	13.10	56.31	23.41	0.275

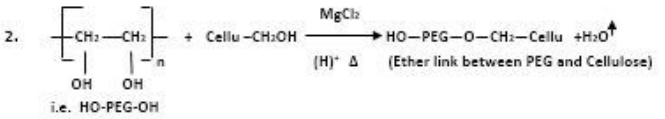
Table 2: Effect of varying proportion of mixture of PHAMS, PEG, CA and their binary mixtures on properties of cotton Khadi fabric treated in presence of $MgCl_2$ catalyst

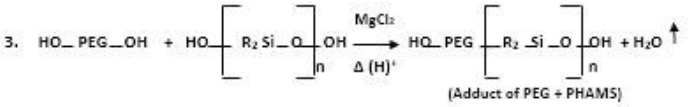
Treatment	Tenacity (cN/tex)	Retention of strength after specific treatment (%)	Strength Loss %	% Retention of strength after soil burial of 21 days	Strength Loss% in soil burial	Crease recovery angle in deg (warp +weft)	Bending length in (cm)	Whiteness Index(WI) (CIE scale)	Brightness Index (BI) (TAPPI-452 scale)	Yellow-ness Index (YI) ASTM E 313	K/S Value
Untreated Fabric	1.66	--	-	23.0	77.0	46.8	1.40	26.9	62.04	18.26	0.208
2% PMS+4% PEG-200	1.46	87.9	12.1	71.5	28.5	53.2	1.30	1.63	52.63	26.88	0.355
2% PMS-+ 6% PEG	1.61	96.9	3.1	79.4	21.6	54.2	1.34	0.93	51.29	26.60	0.375
2% PMS +8% PEG	1.44	86.7	13.3	71.5	28.5	58.7	1.35	3.65	52.61	26.05	0.344
2% PEG+4% PMS	1.54	92.7	7.3	75.7	24.3	52.3	1.32	-0.51	50.15	29.10	0.407
2% PEG+6% PMS	1.37	82.5	7.5	61.5	38.5	53.9	1.29	-15.14	47.11	32.51	0.489
2%& PEG+8% PMS	1.45	87.3	12.7	71.5	28.5	55.4	1.28	6.46	54.67	25.79	0.310
4%PEG+4%PHAMS	1.57	94.5	5.5	77.0	23.0	54.0	1.34	0.33	48.90	28.90	0.480

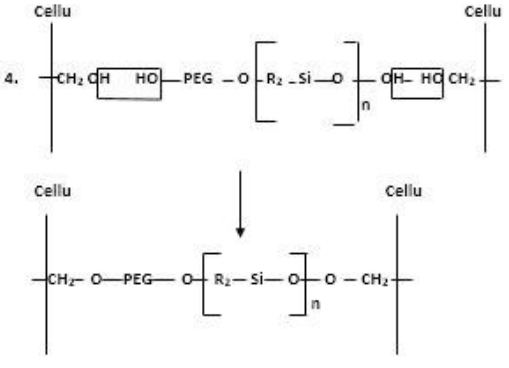
3.1.2 Reaction Mechanism

This action/observation on property data will be more clear and better understood, if one can look into the following mechanism or reaction schemes from 1 to 4 given below.









3.1.3 FTIR Spectroscopic Study

Figure -1 show FTIR spectra of control cotton fabric showing broader peak at 3334 cm^{-1} for both (a) and (b) spectra for absorption of moisture. While FTIR Peak at 855 cm^{-1} for treated cotton fabric indicates Si-O-Si vibration (for anchored PHAMS) which is absent at spectra (a) for control cotton. Another broader peak at 1000 to 1100 cm^{-1}found only in treated cotton is attributed to –C-O-C- deformation and stretching confirming given reaction scheme 1 & 2, which is a absent in Spectra (a) for control fabric. A small and sharp peak of phenolic –OH of cellulose is observed in Spectra (a) at 3698 cm^{-1} which is vanished after treatment with PEG & PHAMS mixture on cotton (treated cotton) , probably due to participation of fewer secondary-hydroxyl (Phenolic –OH) in the reaction of celluloses with PEG and PHAMS, beside Primary alcohol –(CH_2OH) group of celluloses (cotton).

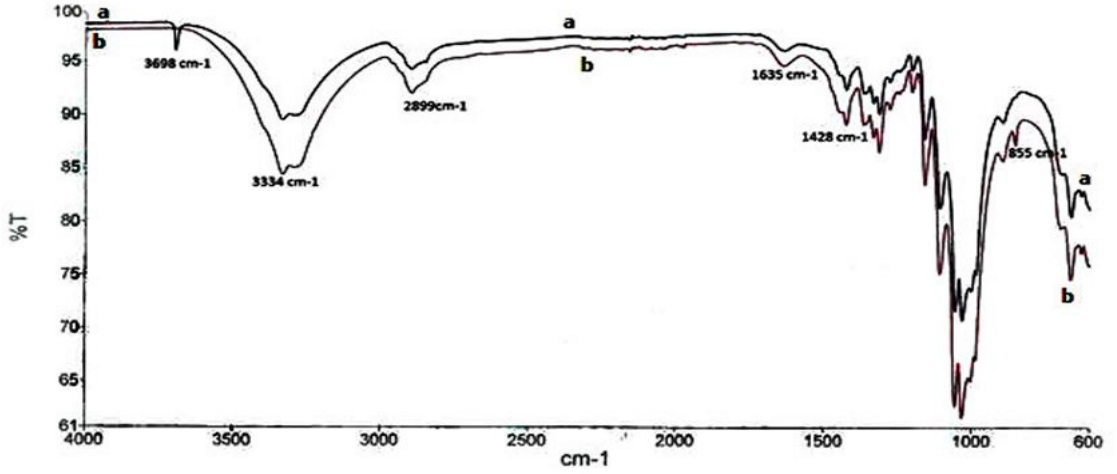


Figure 1 : FTIR spectrogram of (a) control fabric and (b) Fabric treated with 6% PEG and 2% PHAMS

3.1.4 XRD Study

X ray diffraction pattern shown at Figure 2 and corresponding % crystalline data in untreated and treated (with 6% PEG and 2% PHAMS) in Table 3 indicate that there is marginal increase in crystallinity % due to addition of crystallite part of small amount of PHAMS film developed and anchored by cellulose, however there is no change in the size of the crystallite blocks. The X ray diffraction results indicates that fibre crystallinity and orientation has marginal effect on the strength of the treated cotton fabric. On the other hand, the PEG film may be spreading uniformly on the fabric surface thereby making a plastic coating covering up the non uniform surface structure of hand spun yarn woven in handlooms as khadi cotton fabric and ultimately results in better sharing of load among the yarns of the fabric. The mixture of PHAMS and PEG with 3:1 ratio (i.e. 6% PEG and 2% PHAMS) yields the comparable strength of the fabric as addition of such a low molecular weight PEG causes less phase separation with compared to higher molecular weight PEG and with higher number of terminal hydroxyl groups per unit mass expected to interact more intensely due to higher extent of hydrogen bonding with PHAMS by adduct formation as suggested in the reaction Scheme 4.

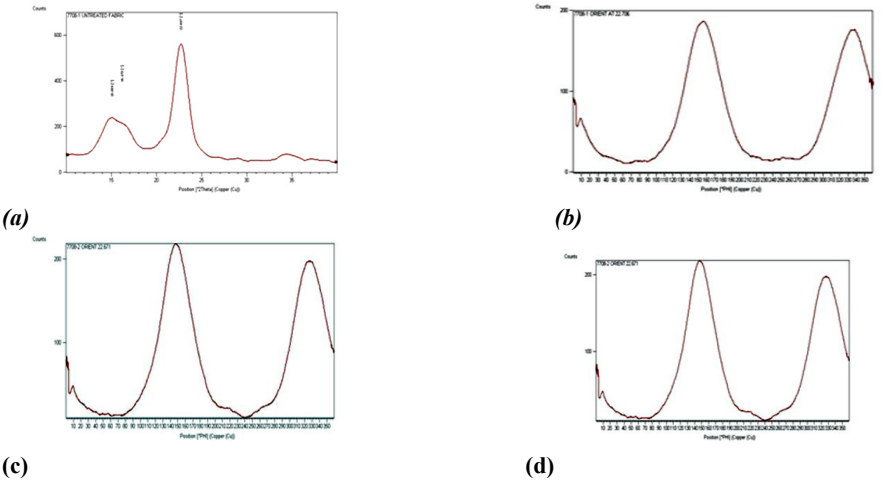


Figure 2 : PXRD Crystallinity curves of (a) Untreated fabric, (b) Orientation curve of Untreated fabric (c) Crystallinity curve of treated fabric with 6% PEG and 2% PHAMS (d) Orientation curve of treated fabric with 6% PEG and 2% PHAMS

Table 3: X ray analysis data of control and treated fabric

Sample	Crystallinity Index (%)	Crystallite Size (°A)	Orientation at 2θ (^{0})
Untreated Fabric	71.81	44.50	24.81
2% PHAMS + 6% PEG Treated fabric	73.58	44.49	24.93

3.1.5 Anti Microbial activity

Table 4 shows the antimicrobial properties of three types of fabrics against two common microbes presents in the air and moisture wherein the PHAMS and PEG mixtures shows comparable protection of the fabric against the microbes when compared with EPTAC. After 24 hours of incubation the reduction in microbes is depicted in Figure 3.

The data in Table 4 shows increase in PEG content is increasing the bacteria reduction percentage whereas PHAMS content above 2% has no significant influence on the same. Increasing the content of PEG although retains the at par antimicrobial property, but does not contribute much for tenacity retention% after soil burial in the said cotton fabric as shown in Table 2.

Figure 3: (a) Untreated fabric

Figure 3 (b): Fabric treated with 6%PEG and 2%PHAMS

Figure 3 (c): Fabric treated with EPTAC

Figure 3 : Presence of two microbes *Staphylococcus aureus and Klebsiella pneumonia* after 24 hours of incubation for (a) Untreated fabric (b) Fabric treated with PEG and PHAMS (c) Fabric treated with EPTAC

Table 4: Bacteria reduction percentage of treated Muslin fabric after 24 hours of test culture in the incubation condition of 37^{0}C for 24 hrs

Muslin Fabric treated with	Bacteria Reduction% after 24 hours of Test culture	
	Klebsiella pneumoniae ATCC4352	Staphylococcus aureus ATCC 6538
1 % PEG + 1 % PHAMS	75.0	80.0
2 % PEG + 1 % PHAMS	83.0	80.0
2 % PHAMS + 1 % PEG	70.0	75.0
2% PEG + 2% PHAMS	83.0	80.0
2 % PEG + 4 % PHAMS	98.0	97.0
2 % PEG + 6 % PHAMS	98.0	85.0
2 % PEG + 8 % PHAMS	87.0	95.0
4 % PEG + 2 % PHAMS	95.0	92.0
6 % PEG + 2 % PHAMS	97.0	99.0
8 % PEG + 2 % PHAMS	99.0	99.0
4 % PEG + 4 % PHAMS	99.0	97.0
2% EPTAC	99.58	99.7

3.1.6 Study of SEM

Out of four SEM Photographs shown above in Figure 4 , the SEM photograph (a) for untreated cotton, indicate that the surface of untreated cotton is smooth, but cotton treated individually with PEG or PHAMS uneven surface deposit of powdery residue or discontinuous film respectively as shown in SEM photographs (b) and (c), Figure -4. While, SEM photograph (d) for cotton fabric treated with optimal mixture of PEG and PHAMS (3:1) shows some powdery surface deposit with evenly covered smooth film indicating better anchoring of PHAMS and PEG on surface of cellulose (cotton).

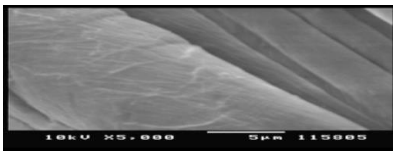


Figure 4 (a) Control fabric

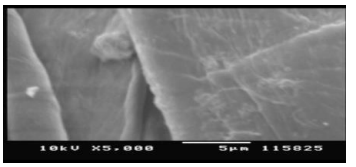


Figure 4 (b) Fabric treated with 6% PEG

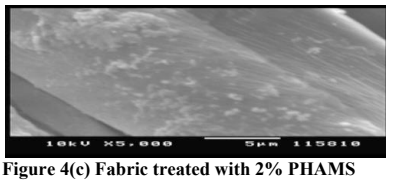


Figure 4(c) Fabric treated with 2% PHAMS

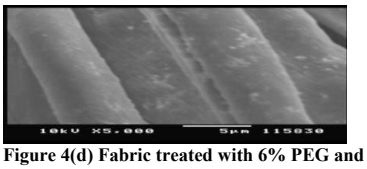


Figure 4(d) Fabric treated with 6% PEG and 2% PHAMS

3.1.7 Xray Photoelectron Spectroscopy (XPS)

Figure5 (a) and (b) show the XPS spectra of C1s[16], wherein the peak of 284.00 eV (C-C) of control fabric has been shifted to 282.5 eV in treated fabric with lesser intensity indicates the presence of Si-C. A strong peak at 293.7 eV attributes to Potassium element in spectra Figure 5 (b) which is absent in untreated fabric (b). An intense peak of Si at 293.5 eV for treated fabric in spectra (b) as against 293.5 eV for spectra untreated fabric (a) indicates more atomic concentration of Si in the former. These figures thus show the quantification data for both derivatized and un-derivatized sample. A peak at 529.5 eV in treated fabric in O1s (Figure5 (b)) is due to metal oxides formed with Si and K whereas the corresponding peak at 531.3 in Spectra (a) of untreated fabric is attributed to organic C-O or metal carbonate and Si content in treated cotton is also proved from XPS results, Figures 5 (c) and (d).

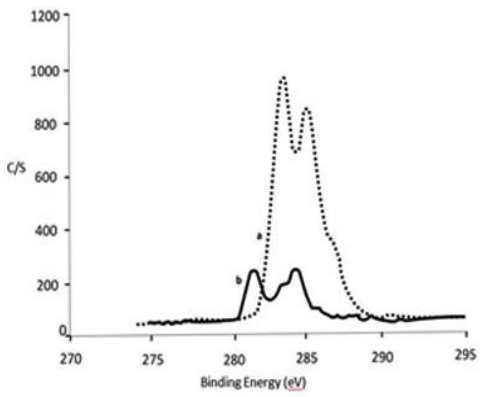


Figure 5(a): C1s spectra of control (a) and treated Fabric (b)

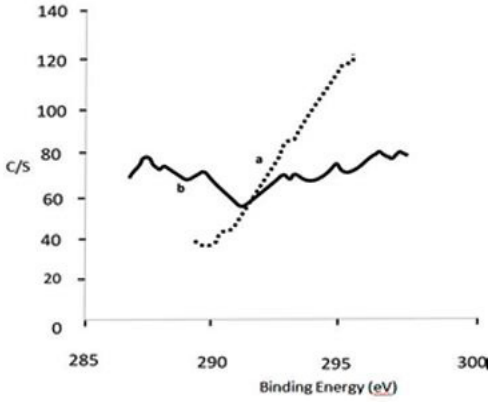


Figure 5(b): K 2p spectra of control (a) and treated Fabric (b).

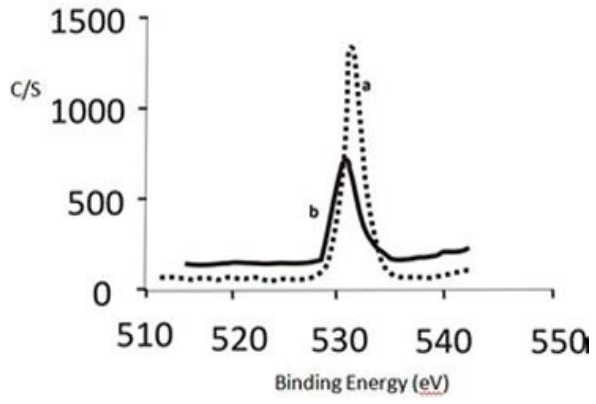


Figure 5 (c): O1s Spectra of control (a) and treated fabric (b).

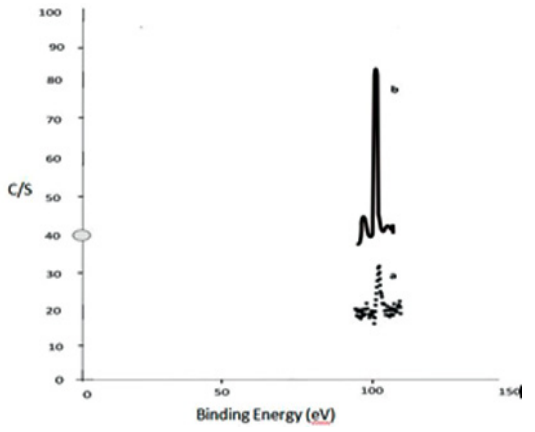


Figure 5(d): Si 2p spectra of (a) control and treated fabrics (b).

3.1.8 Study of Salt Free Dyeing with Reactive dyeing

Poly- Hydroxyl Amino Methyl Siliconate (PHAMS) and EPTAC has ability to react with alcoholic –OH groups of cellulose under acidic catalytic conditions to attach these chemicals covalently bound to the polymer chains of cellulose macromolecules forming ether linkage utilizing hydroxyl groups of EPTAC and /or PHAMS and thus produce a modified cationized cotton substrate creating newer cationic dye sites (by the presence of Pendant Quaternary $–NR_3^+$ groups of EPTAC and $–NHR_2^+$or $–NH_3^+$groups of PHAMS bound to cotton cellulose). Thus these dye sites may strongly attract any anionic dye including anionic reactive dyes, enabling subsequent dyeing of such modified cotton with anionic reactive dyes in acid media /bath without use of the large amount of salt or electrolyte for eco-friendly dyeing[17-18].The K/S values for both control and treated fabric have been shown in Table 5 for both conventional alkali bath reactive dyeing and non-conventional acid bath reactive dyeing dyed with 2% Reactive Red 141.In normal alkaline bath dyeing, K/S values are found higher than the same dyeing in acid bath for PEG and PHAMS treated fabric. This is probably due to higher % use of PEG (a film forming compound) forming a plastic film over the surface of cotton reducing the dye uptake by skin formation by PEG on the surface in the presence of acid-poly PEG film, whereas in alkaline bath due to more swelling action, the accessibility of dye uptake is higher. Hence, the said treated fabrics should be preferably dyed in alkaline bath.

Table 5 : K/S value of control and treated cotton fabric both in acid and alkali bath reactive dyeing.

Type of Fabric	Control Fabric		2% PEG and 2% PMS treated Fabric Alkaline bath (pH 10-11)		2% PEG and 2% PMS treated Fabric Acid bath (pH 5.5-6.5)	
	W/O DFA*	With DFA	W/O DFA	With DFA	W/O DFA	With DFA
K/S Value	6.8	10.7	8.4	11.7	4.0	5.4

*****DFA Dye fixing Agent, W/O Without

Conclusions

Amongst all individual and combined applications of above said two chemicals (PHAMS and PEG) , it is observed this combined treatment of PEG and PHAMS (in 3:1 ratio) in presence of $1/5^{th}$ of magnesium chloride on cotton is showing an acceptable and appreciable good result in terms of improvement in antimicrobial /rot resistance performance with minimum loss of tenacity with scope of an optimum balance in other textile related properties showing lowest degradation against microbial attack. The said optimally treated cotton sample subsequently remained also equally dyeable in eco-friendly alkali bath reactive (anionic) dyeing with HE brand of reactive dyeing. This optimally balanced results are thus obtained in the said modified cotton due to incorporation of cationized groups in the amino groups content of PHAMS along with antimicrobial resistance rendered mainly by anchored PEG due to its unique preferential thermal adaptivity, moisture adaptivity and surfactant type action, thereby not allowing any microbes to grow.

References

[1] KVIC, *Annual Report*. Khadi and Village Industries Commission *India (2014)*

[2]Andrew, J. McbainRuth G. Ledder1, Louise E. Moore, Carl Catrenich and Peter Gilbert,. Effects of Quaternary-Ammonium-Based Formulations on Bacterial Community Dynamics and Antimicrobial Susceptibility, *Applied and environmental microbiology* 70(6),(2004)3449-3456.

[3] Samanta A K , Mukhopadyay A , Bhagwat M.M and Kar T R, Application of PEG , Cetrimide , Chitosan and their mixture on cotton muslin fabric to improve rot resistance /antimicrobial property and its salt free reactive dyeing , J Text Inst, 107 (11) (2016), 1386-1405

[4] Samanta, A.K and Bagchi, A., Effect of rot and crease resistance finishing of jute fabric using citric acid and poly ethylene glycol. *J .polym. mater.* 29(3), (2012) 349-359

[5] Ghosh P, Das D. & Samanta A.K. Modification of Jute with cirtric acid,.*J. Polym Mat*, 12: (1995) 297

[6] Fisher C.H. New Cotton properties through chemical research, *Text Res Journal* 25 (1): (1955) 1-11

[7] Montaze M ,Malek R.M.A and Rahimi A.,. Salt free reactive dyeing of cationized cotton, *Fibre and polymers,* 8 (6): (2007) 608-612

[8] IS 1623-1992, Method of testing of jute fabrics for resistance to attack by micro organism, *ISI Handbook of Textile Testing*, Bureau of Indian Standards, (BIS) , New Delhi.

[9] IS 4681-1981,*Method for determination of recovery from creasing of textile fabrics by measuring the angle of recovery*, Indian standard Institute, (BIS), New Delhi.

[10] ASTM D5034 2103, Standard test methods of breaking strength and elongation of textile fabrics (Grab test). *Annual book of ASTM standards,* 07.02, American Society for Testing and Materials Philadelpia, Pennsylvania, USA,8.

[11] ISI (BIS) Handbook of Textile Testing , 1st Ed SP-15 1981 , Beauro of Indian Standards , New Delhi India , (1982), 221-587

[12] Aleksandra, R. Zarubica, Milena, N. Miljkovic, Milovan M. Purenovic, VesnaB.Tomic, Colour parameters, whiteness indices and physical features of marking paints for horizontal signalization.Factauniversitatisseries*: physics, chemistry and technology*, 3(2) (2005) 205 – 216

[13] ASTM E313-00, *Standard Practice for Calculating Yellowness and Whiteness Indices from Instrumentally Measured Color Coordinates*, American Society for Testing and Materials.Philadelpia, Pennsylvania , USA,5. (2006)

[14] ISO 2469 and 2470,1977, International Organisation for standardization, Switzerland,1.

[15] Parikh, D V. Thibodeaux, D.P. and Condon, B. . X-Ray Crystallinity of Bleached and Cross- linked Cottons. *Textile Research Journal*, 77(8) (2007)

[16] M.SC. Eda Jagst., *Surface Functional Group Characterization using chemical derivatization X ray photo electron spectroscopy (CD XPS).* BAM- Disertationsreihe. Band 69.Berlin. 2011

[17] Samanta, A.K, Kar, T.R., Mukhopadhyay A, Shome, D , Konar,A.Cationization of periodate oxidized cotton muslin fabric using natural amino acid extract from soyabean seed waste and its eco-friendly dyeing*, Journal of Materials Sciences and Applications* 1(4), (2015)142-154.

[18] Samanta, A.K, Kar, T.R., Mukhopadhyay A, Shome, D, Konar, A. Studies on dyeing process variables for salt-free reactive dyeing of glycine modified cationized cotton muslin fabric, *J.Inst.Eng.India Ser E.* 15(62) (2015) 4