

Evaluation of the effective properties of cotton knit fabrics radiated by gamma rays emitted from cobalt 60: an advanced step in wet processing of textiles.

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Abstract—Gamma radiation has emerged as state-of-the-art technology in wet processing of textile. 1, 3, 5, 10 and 20 KGy of gamma rays were applied on both grey and dyed states of cotton knit fabrics. After radiation grey fabric was prepared for test by wet processing method. Then essential properties like dyeing, physical, mechanical, and fiber morphology were tested. Grey radiated dyed fabrics showed better dyeing properties like color yield, washing fastness to color, perspiration, rubbing, and dry cleaning than dyed radiated fabrics but lightfastness remain unchanged for both. Although both type of radiated fabrics demonstrated gradually decreasing bursting strength with increasing radiation doses. However it is revealed that both types of fabrics are stiff after irradiated. But 20 KGy radiated grey reactive dyed fabrics gained antibacterial property and 5 KGy radiated same fabric gained anti-odor property. Fiber morphological changes like inter and intra molecular H-bonds were reduced resulting in more free OH in grey irradiated cotton cellulose from ATR-FTIR spectra.

Keywords— Gamma rays, Cellulosic cotton, H-bond, Wet processing preparation.

1 INTRODUCTION

RADIATION is the release of energy from unstable atoms of 'radioisotopes', after releasing energy they become stable; radiation can be of high level, low level, non-ionizing and ionizing and there are three main types α , β and γ radiations [1]. Gamma rays are electromagnetic radiations, and have low ionizing and high penetrating powers than α and β radiations [2]. Cobalt - 60 is the popular gamma ray emitter for medical and industrial applications, and currently about 200 such sources in operation in Member States of the International Atomic Energy (IAEA). Although some typical radiation processing applications are preventing TA-GVHD of blood, pest management, extending shelf life by delaying mold growth and retarding decay of some fruits, delaying spoilage, killing certain pathogenic bacteria in meat, poultry, fish, killing a variety of microorganisms and insects for spices and other seasoning, sterilization for health care products, and cross-linking and grafting for polymers [3]. But in wet processing of textiles, radiation application is an extremely new introduction. In this research work, gamma rays from cobalt-60 were used in wet processing of natural carbohydrate polymer cellulosic cotton knit fabrics. Cobalt-60 gamma radiation changed physical and chemical properties of raw cotton with even small dose of applied

radiation. Although small fiber cracks started almost parallel to the fiber axis from 0.1 Mrad radiation, these increased in number and enlarged in size and depth as well from increasing radiation doses. It is possible due to changes in intra-molecular and inter-fibrillar bonds in cotton [7]. It was observed that there is decreased intermolecular bonding in the irradiated cotton as compared with purified cotton [8].

Nowadays researchers are interested in natural polymer due to their unique characteristics like inherent biocompatibility, biodegradability and easy availability and [6]. Cotton fiber is picked from seed of a wide variety of plant species in *Gossypium* family and naturally it contains about 85-95% cellulose, 1-1.5% proteins, 1% pectin materials, 0.5% wax and small amount of organic acids, sugars and pigments. Fungi and bacteria will grow vigorously on cotton under hot, moist conditions causing unpleasant odor to emanate from it [9]. Chemically cellulose carbohydrate cotton is a polymer of 1-4- β -D-glucose; two such glucose units create one cellobiose unit arranging alternately through the molecular chain: in which the hydroxyl groups attached to carbon atoms C-2, C-3 and C-6 in the glucose are free and the oxygen atom linking the glucose units must be between carbon atoms C-1 and C-4. This linear flat polymer chains are ordered along the fiber axis forming amorphous to fully crystalline regions. In crystalline region intermolecular hydrogen bond are formed between pairs of adjacent hydroxyl groups due to

proximity of cellulose molecules. Water regain of cellulose fibers is 25-30% at 100% relative humidity and 25°C due to its inter fibrillar and amorphous region in cellulose molecule. But water molecules do not penetrate into the crystalline regions of cotton [10]. So conventional wet processed cotton fabrics have limited water absorption and dye up take property, and still contain the food of microbes. We can store our apparel for a few days or more but after that we are not able to wear that garments without wash due to receiving bad smell from it. Odors develop on cotton either because skin microbial decomposition of body sweat or storage in damp condition for more than few days. Odors are perceived from apparel or human body due to body-sweat containing proteins which are broken down to smaller volatile fatty acids by bacteria (skin, hair and garments). This odor is unfortunate side effect of human life [11]. Radiation method is the emerging technique to reduce this unpleasant odor.

Conventionally, hygiene finish using different types of chemicals are applied on textile materials to remove this odor. Unpleasant odors spread from intimate apparel, underwear, socks and athletic wear by the bacterial decomposition of sweat and other body fluids, hygiene finish can reduce or eliminate the problem by controlling bacterial growth, bacteriostatic or by killing them, bactericidal. Both antimicrobial chemicals are applied on textile materials by either controlled release or bound mechanisms. Difficulties in several areas with antimicrobial finished are fabric stiffness, strength loss, color fade, skin irritation, ecological problem, selective effect, tacitly, biodegradability and bioaccumulation [12]. Radiation technologies are well established process in medical field, industrial application, material modification and environmental protection. Radiation sources are compact size gamma irradiators, high-power accelerators with direct e-/X conversion and low-energy electron beam system [13]. Even in textile it was found that radiation process is able to increase dyeing kinetic and shade depth, with no use of chemicals and less energy consumption [14].

In this research work, cobalt -60 gamma rays were applied on both states, grey and dyed fabrics with different doses and dyeing properties like color yield, washing fastness to color, perspiration, rubbing and dry cleaning, light fastness, mechanical property like bursting strength, physical property like bending length, antimicrobial test and morphological changed by ATR FT-IR have been examined before and after application.

2 EXPERIMENTAL

2.1 Sample preparation

Cotton knitted fabrics having 170 GSM, single jersey structure were scoured and bleached in one bath containing 1 g/l Wetting and detergent (Imerol DLJ), 1g/l Sequestering agent (Sirrix 2UD), 1g/l Stabilizer (Stabilizer SOF), 1.5 g/l Sodium hydroxide (adjustable pH 10.5) and

6 ml//l Hydrogen peroxide 35%, material and liquor ratio 1:12. Treatment temperature 95°C, treated time 60 min. After bath drop and hot wash, neutralization was given using acetic acid. Then this fabric was dyed with 1% shade using blue reactive dye-stuffs (Drimaren Blue HF-RL), using 30 g/l Glauber's salt and 15 g/l Soda ash. Maintained dyeing temperature 60°C and dyeing time 40 min. Soaping process was carried out at 80°C for 10 min. containing 1 g/l soaping agent (Ladiquest 1097), then cold wash and normal dry were carried out. This fabric and grey cotton were irradiated with gamma ray dose ranges were 1,3,5,10 and 20 KGY. Grey radiated cotton knit fabrics were scoured, bleached and dyed in the same way. Used dye-stuff and auxiliaries were provided from Archroma (Bangladesh) Ltd.

2.2 Determination of Colorimetric values

Color yield, K/S values of non-radiated and both type of radiated reactive dyed fabrics were measured by the high performance benchtop spectrophotometer (Datacolor, 650TM) incorporating Datacolor Tools software, reflectance mode with D65 illuminant, 10° standard observer, SAV aperture, and operating environment was 25°C and 65% RH [15].

2.3 Assessment of washing fastness to color

Non-radiated and both types of radiated reactive dyed samples were tested according to Domestic laundering washing fastness to color ISO-C06-C2S method. The test specimen and multifiber were sewed and immersed into an aqueous solution containing 4 g/l ECE non phosphate detergent, 1 g/l sodium carbonate, 1 g/l sodium perborate, 25 steel balls, with liquor ratio 1:50. Adjustable pH 10.5, at 60°C for 30 min., the samples were then removed and rinsed in hot and cold by distilled water and dried at 60°C. After conditioning, shade change and staining on multifiber were measured by above mentioned spectrophotometer [16].

2.4 Assessment of Perspiration fastness to acid and alkali

Non-radiated and both type of radiated reactive dyed fabrics were tested following ISO 105 E04:1994 (www.iso.org.) and shade change of test sample and staining on multifiber were assessed by spectrophotometer (colorimetric method A04). Perspiration fastness to acid test was carried by wetting out the test specimen and adjacent fabric thoroughly in an alkaline perspiration solution containing: 0.5 g/l l-histidine monohydrochloride monohydrate, 5g/l sodium chloride, 2.5 g/l disodium hydrogen phosphate dehydrate (adjustable pH 8 with 1 n caustic soda), liquor ratio 50:1, were treated for 30 min. at 25°C., was squeezed hydrophobic material with a glass rod, after pouring off excess solution, test specimen was placed between 2 glass or acrylic plastic plates under a pressure of 12.5 KPa and

was placed in a drying oven for 4 hours at 37°C. Later these test samples were hanged to dry in warm air at max. 60°C. Perspiration fastness to alkali tests were done in same way but perspiration solution containing: 0.5 g/l l-histidine monohydrochloride monohydrate, 5 g/l sodium chloride, 2.2 g/l sodium dihydrogen phosphate dehydrate (adjustable PH 5.5 with 1 n sodium hydroxide)[16].

2.5 Assessment of rubbing fastness to color

Non-radiated, grey and dyed radiated reactive dyed fabrics were subjected to the ISO 105X12:1993 test method and stained rubbing fabrics were evaluated by spectrophotometer (colorimetric method A04). In this test method, two tests were carried out: rubbing fastness to dry with a dry rubbing fabric and rubbing fastness to wet with a wet rubbing fabric. The rubbing fabric is used according to ISO 105-F09. To do dry rub, the test sample was rubbed using rubbing fabric with the Crockmeter a down ward force of 9N to and fro on the test sample and for wet rub, the test sample was rubbed using rubbing fabric which was soaked in demineralized water (100% pick-up) with the Crockmeter under a downward force of 9 N to and fro on the test specimen. After drying the stained rubbing fabric at room temperature was assessed[16].

2.6 Determination of dry cleaning fastness

Non-radiated, grey and dyed radiated reactive dyed fabrics were tested following dry cleaning: ISO 105-DO1. The test sample (size: 4cm x 10cm) was sewn with 12 steel plates in a cotton woven bag (size: 10 cm x 10 cm) and was placed in a steel beaker and was treated with perchloroethylene (tetrachloroethylene) for 30 minute at 30°C in the Launder-Ometer. Then the test sample was removed, was squeezed and hanged to dry at room temperature. After filtering off the remaining solvent which were assessed visually (ISO 105-AO3) against a white back ground. Shade change of the test samples were assessed by colorimetric method (ISO 105-A05)[16].

2.7 Determination of light fastness

Non-radiated, grey and dyed radiated reactive dyed samples were tested following ISO 105-B01: Color fastness to light: Daylight. The test samples and ISO light fastness scale (Blue wool reference scale 1-8) were exposed until the contrast (change in color) on the test sample corresponds to grey scale 4 and then until it corresponds to grey scale grade 3 but at maximum until the blue wool reference 7 shows a contrast corresponding to grey scale grade 4. The ratings were assessed corresponding to the number of the blue light fastness reference which showed a similar contrast to the test sample [16].

2.8 Determination of bending length

Objective test to measure handle property of non-radiated and both types of radiated reactive dyed fabrics were tested by Shirley stiffness tester following BS 3356; 1990 method. The higher the bending length in cm, stiffer the cotton fabric in handle [17].

2.9 Determination of bursting strength

Bursting strength of non-radiated and both types of radiated fabrics were measured using bursting strength tester, manufacturer: Laboratory supply company, brand: mesdan, model: 338B, origin: Germany, method: ASTM D 3787[18].

2.10 Odor determination test

This subjective test was performed with reference to SNV 195651. Each test specimen having 40 g was placed on top of 300 ml sodium carbonate saturated solution and has been kept in a closed container, desiccators. This closed container was put into an oven set to a temperature of 37+/- 2°C for 15 hours. Six people judged the odor intensity and rated it according to the intensity scale: Grade 1-odourless, grade 2- weak odor, grade 3 - tolerable odor, grade 4 - annoying odor, grade 5 - intolerable odor[19].

2.11 Antibacterial Activity Assessment of Textile Materials: Parallel Streak Method (AATCC Test Method 147-2004)

It is a qualitative test method where one 4 mm loopful of the diluted inoculum was transferred to the surface of TSA (Tryptone Soya Agar) plates by making five streaks approximately 60 mm in length, spaced 10 mm apart covering the central area of a standard Petri plates without a refilling of loop. Test specimens sized (25X50) mm were placed to inoculate TSA transversely across the five inoculum streaks. Petri plates were incubated for 24 hours at 37°C. The streaks will stop the growth at the edge of the tested samples and there is no growth under the sample, the result will be reported as a pass. This method provides a nice visual demonstration of contact inhibition. Bacteriostatic properties of non-radiated, 20 KGy radiated of both grey and dyed fabrics were tested according to this method. Used two types of bacteria strains were *Staphylococcus Aureus* (ATCC 6538, Gram positive) and *Klebsiella Pneumoniae* (ATCC 4352, Gram negative)[20].

2.12 ATR FT-IR Spectra

The spectra of grey cotton knit, both grey and dyed cotton knit fabrics were radiated with 20 KGy and spectra were measured by FT-IR ATR (Attenuated Total Reflectance) Spectrophotometer, IR Prestige-21, Shimadzu, serial no A2100450183/LP, Japan. Attenuated total reflection (ATR) is a sampling method used in conjunction with FT-IR which

enables to be examined directly in the solid state without further preparation[22].

3 RESULTS AND DISCUSSION

3.1 Color yield of non-irradiated and both types of radiated reactive dyed fabrics.

Color yield, K/S is a value of measurement the amount of colorant on the surface of the fiber where K and S means absorption and scattering of the colorant; this has been derived from Kubelka-Munk equation. Higher values of K/S means more colorant on the fiber surface [23]. Functional group of reactive dyes covalently bonded with primary, secondary and tertiary hydroxyl groups of cellulosic cotton in alkaline condition. But primary hydroxyl group is more reactive than secondary and tertiary although it depends on the functional group of reactive dyes also. If there are increased free primary hydroxyl groups then possibly more dyes will be covalently bonded with cotton fiber [24]. Even small dose of gamma rays can create cracks almost parallel to the fiber axis which are increased in number and enlarged in size at higher doses, as a result inter and intra molecular H-bonds are broken down and the surface area of cotton fiber was increased. [25]. So more dyes will possibly form covalent bond with functional group of dyes. Although more reactive dyes covalently bonded with cellulose ion (Cell-O-) of cotton increasing the value of K/S, but finer filament shows paler shade (less K/S values) [26].

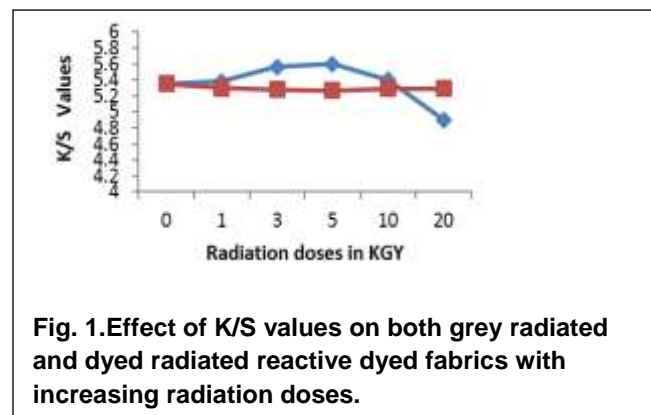


Fig. 1. Effect of K/S values on both grey radiated and dyed radiated reactive dyed fabrics with increasing radiation doses.

So it is apparent from above figure that grey irradiated with 5KGy reactive dyed cotton showed more colorant on fiber surface than dyed irradiated fabrics and later decreased due to surface area of the fiber is increased and fiber would be finer.

3.2 Bursting strength of both reactive dyed fabrics which were irradiated with different doses in grey and reactive dyed states.

Although decreasing bursting strength with increasing radiation doses for both types of irradiated fabrics, but decreasing rate are more of grey irradiated fabrics than dyed irradiated fabrics.

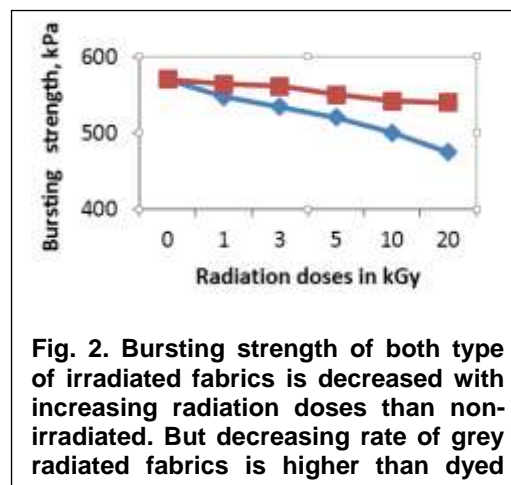


Fig. 2. Bursting strength of both type of irradiated fabrics is decreased with increasing radiation doses than non-irradiated. But decreasing rate of grey radiated fabrics is higher than dyed.

So it is deduced from above figure that grey radiated fabrics have more amorphous region than dyed radiated fabrics in their cellulosic molecular chains.

3.2 Bending length of non-irradiated, grey irradiated and dyed irradiated reactive dyed fabrics.

Higher bending length means stiffer of fabrics. So from figure 3 it is concluded that grey irradiated dyed fabrics are stiffer than dyed irradiated fabrics with increasing radiation doses.

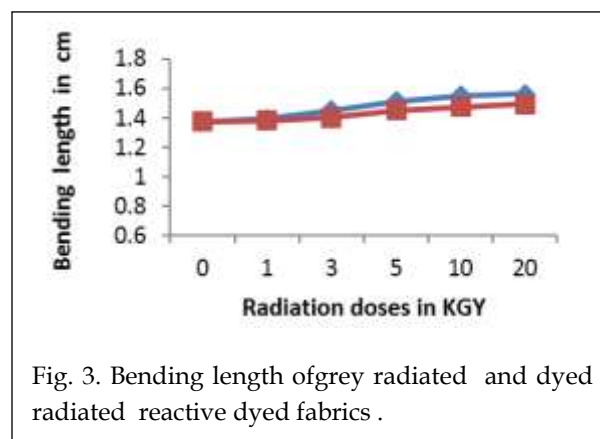


Fig. 3. Bending length of grey radiated and dyed radiated reactive dyed fabrics.

Grey irradiated fabrics are much stiffer than dyed irradiated fabrics with increasing dose of gamma radiations

3.3 Color fastness to wash, perspiration, wet rubbing, dry cleaning and light fastness of grey irradiated(a) and dyed irradiated(b) fabrics.

Table 1

It is seen that staining on multifiber and shade changes of grey irradiated fabrics are better than dyed irradiated fabrics. But all values are excellent due to all decimal values would be reported as 5 for both type of irradiated fabrics and in color fastness scale 5 is the highest value [27].

(a) Radiation doses in KGY	Shade change of wash fastness to color	Staining on only polyester	Shade change of perspiration fastness
0	4	4.7	3
1	4	4.8	3
3	4	4.8	3
5	5	5	4
10	5	5	4
20	5	5	4

(b) Radiation doses in KGY	Staining on all fibers	Wet rubbing	Dry cleaning	Light fastness
0	5	4.7	4	5
1	5	4.8	4	5
3	5	4.9	4	5
5	5	5	4	5
10	5	5	5	5
20	5	5	5	5

(c) Radiation doses in KGY	Shade change of wash fastness to color	Staining on only polyester	Shade change of perspiration fastness
0	4	4.7	3
1	4	4.8	3
3	4	4.8	3
5	5	5	4
10	5	5	4
20	5	5	4

(d) Radiation doses in KGY	Staining on all fibers	Wet rubbing	Dry cleaning	Light fastness
0	5	4.7	4	5
1	5	4.8	4	5
3	5	4.9	4	5
5	5	5	4	5
10	5	5	5	5
20	5	5	5	5

Color fastness to wash, perspiration, wet rubbing, dry cleaning and light fastness of non-irradiated dyed cotton (0 radiation) and dyed irradiated with different doses of cotton fabrics(c) & (d).

All wet rubbing fastness is improved and good. Because decimal value like 4.8 is a reporting value 5. So it is proved that radiation doses not have any influence on wet rubbing fastness. 3 and 5 KGY grey irradiated fabrics showed worse wet rub than dyed irradiated fabrics with same radiation doses but lower and higher radiation doses both are same. Gamma radiation improved rubbing fastness property of cotton knit fabrics.

3.3 Odor test of both reactive dyed fabrics which were irradiated with different doses in grey and reactive dyed states.

It is deduced from figure 5, 5 KGY gamma rays irradiated grey cotton knit fabric after one step scouring-bleaching and dyeing show odor free material whose odor intensity rating is 1. But dyed irradiated fabrics exhibit odorous materials with all radiation doses whose odor intensity ratings are 4 to 5. That means grey irradiated fabrics after scouring-bleaching have less pectin material than dyed irradiated which is the food of microbes.

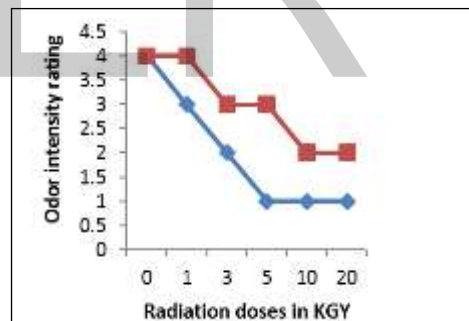


Fig. 5. Odor test rating of both types of irradiated fabrics: grey irradiated and dyed irradiated dyed

Color fastness to wash, perspiration, wet rubbing, dry cleaning and light fastness of non-irradiated dyed cotton (0 radiation) and grey irradiated with different doses of dyed cotton fabrics(a), (b), (c) & (d).

3.4 Antibacterial Tests

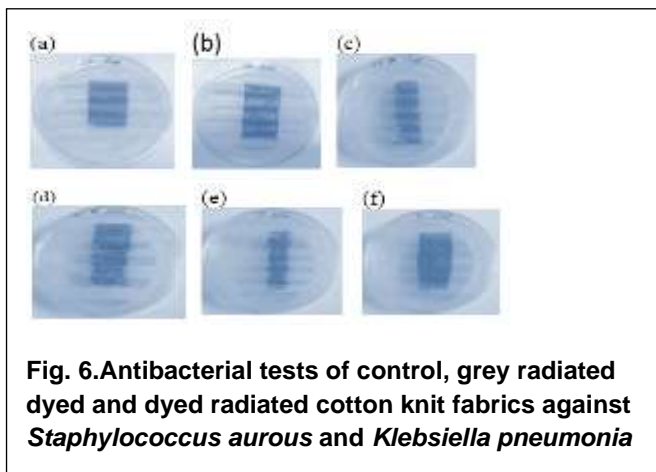


Fig. 6. Antibacterial tests of control, grey radiated dyed and dyed radiated cotton knit fabrics against *Staphylococcus aureus* and *Klebsiella pneumoniae*

From above images it is clearly seen that (a) no antibacterial property of cotton reactive dyed fabrics against *StaphylococcusAureus*; (b) no antibacterial property of cotton reactive dyed cotton knit against *Klebsiella pneumoniae*; (c) little antibacterial property of cotton knit fabric reactive dyed irradiated with 20 KGy against *Klebsiella pneumoniae* (d) no antibacterial property of same cotton against *Staphylococcus aureus*; (e) more antibacterial property of cotton knit grey irradiated reactive dyed with 20 KGy against *Klebsiella pneumoniae*; (f) most antibacterial property of same fabric against *Staphylococcus aureus*.

3.5 Study of fiber morphology of non-irradiated grey, grey irradiated dyed and dyed irradiated cotton cellulose through FT-IR spectra.

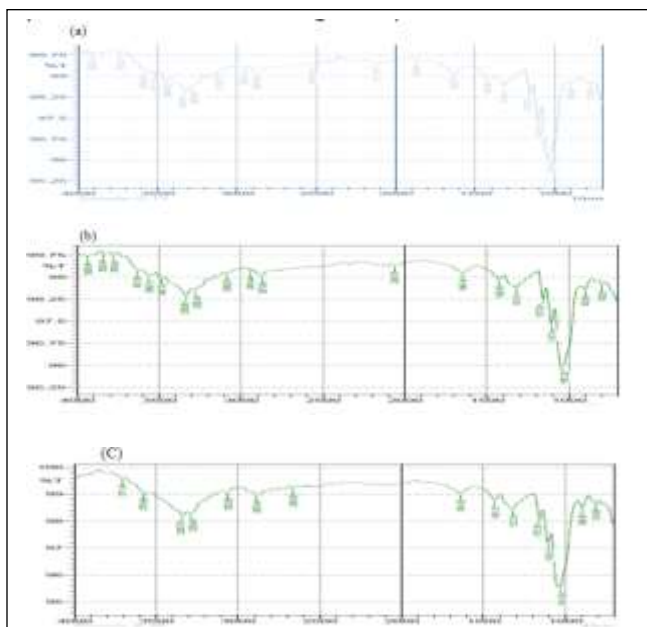


Fig.7. ATR-FTIR spectra of non-irradiated grey cotton (a), grey irradiated dyed cotton (b) and dyed irradiated cotton (c) knitted -fabrics.

FT-IR is the one of the most useful method to provide the characterization of the hydrogen bonds in cellulose. Cellulose is the main constitute in natural fiber which acts as the reinforcing material in the cell wall. A strong crystalline region is produced through extensive hydrogen bonding between cellulose chains which are laid down in micro fibrils. A hydrogen bond is the desirable interaction of a hydrogen atom with an electronegative atom, such as nitrogen, oxygen or fluorine that comes from another molecule or chemical group [28].

Table 2

The recorded ATR-FTIR spectra were summarized in the table.

(a) Non-radiated grey Cotton, Wave numbers (cm-1), a	Grey radiated dyed cotton, wave numbers (cm-1), b	Dyed radiated cotton, wave numbers (cm-1), c	Assignments of bonds
3914, w	3939, w	Disappear	Free OH stretching
	3638, w, new	No appear	Free OH stretching
3736, w	3784, w	3711, w	Free OH stretching
	3632, w, new	No appear	Free OH stretching
3576, w	3568, w	3580, w	Free OH stretching
3522, w	Disappear	Disappear	H-bonded OH
3451, m	3487, m	Disappear	H-bonded OH
3329, m	3337, m	3339, m	H-bonded OH stretching
3291, m	3281, m	3293, m	H-bonded OH
3117, w	Disappear	Disappear	H-bond OH
	3088, w, new	3063, w	OH stretching

(b) Non-radiated grey Cotton, Wave numbers (cm-1), a	Grey radiated dyed cotton, wave numbers (cm-1), b	Dyed radiated cotton, wave numbers (cm-1), c	Assignments of bonds
2947, w	2941, w	Disappear	C-H stretching asymmetric
2887, w	2874, w	2887, w	C-H symmetrical bending stretching
		2664, w, new	
2529.65, w	Disappear	Disappear	
2122, w	Disappear	Disappear	
	2066, w, new	No appear	
1871, w	Disappear	Disappear	
1634, w	1649, w	1641, w	OH bending of absorbed water

(c)

Non-radiated grey Cotton, Wave numbers (cm ⁻¹), a	Grey radiated dyed cotton, wave numbers (cm ⁻¹), b	Dyed radiated cotton, wave numbers (cm ⁻¹), c	Assignments of bonds
1425, m	1425, m	1431, m	HCH and OCH in plane bending vibration
1319, m	1319, m	1321, m	In-the-plane CH bending
1157, m	1157, m	1157, m	C-O-C asymmetrical stretching
1105, m	1107, m	1105, m	C-O-C asymmetrical stretching
1032, s	1051, s	1032, s	C-C, C-OH, C-H ring and side group vibrations
899, m	903, m	897, m	Same
775, m	799, m	814, m, new	CH ₂ rocking

Summarized assigned bonds of functional groups of non-radiated grey cotton, grey radiated dyed cotton and dyed radiated cotton cellulose.

ATR-FTIR spectra in the 700-4000 cm⁻¹ region were employed to characterize the structures of non-radiated grey, grey radiated dyed and dyed radiated cellulosic cotton. The major peak positions and their assigned groups were summarized in table 2 (a), (b) & (c).

3914(w), 3736(w), 3576(w), 3522(w) peaks represent the free OH stretching vibration of non-radiated grey cellulosic cotton but grey radiated dyed and dyed radiated cellulosic cotton present 3939(w), 3838(w) new, 3784(w), 3632(w) new, 3568(w) and 3711(w), 3580(w), peaks respectively. It is apparent that after radiation grey radiated dyed cellulosic cotton represents more and increased wave numbers peaks which are shifted to left in the infrared spectrum but dyed radiated cellulosic cotton less weaker peaks [31].

3451(m), 3329(m), 3291(m), 3117(m) peaks of non-radiated grey demonstrate H-bonded OH stretching bands but 3487(w), 3337(m), 3283(m), 3088(w) peaks and 3339(m), 3293(m), 3063(w) H-bonded OH peaks were represented by the grey radiated and dyed radiated cellulosic cotton which are weaker and less.

Grey cotton shows 2530(w), 2122(w) and 1871(w) which are responsible for pectin material. These peaks are absent in grey radiated and dyed radiated cotton except 2066(w, new) in grey radiated cotton. So it is apparent that protein material which is the food of microbes, absent in grey and dyed radiated dyed cotton.

1650 - 799 peaks demonstrate that these three types of cotton are cellulosic materials.

CONCLUSION

It has been seen in this investigation that effective property of knit cotton irradiated by gamma radiation improved in dyeing, physical property like bending length, odor intensity, antibacterial property, and deteriorated in mechanical property like bursting strength. However it has

been shown that there is an overall improvement of the quality of textile through use of this method. It is excellently demonstrated that radiation process is an advanced step in wet processing in textile.

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