IOSR Journal of Polymer and Textile Engineering (IOSR-JPTE)
e-ISSN: 2348-019X, p-ISSN: 2348-0181, Volume 3, Issue 2 (Mar. - Apr. 2016), PP 19-25
www.iosrjournals.org

One Bath Dyeing and Water Repellent Finishing Of Textile by Sol-Gel Technique

Dr. Ravindra Kale[1], Arunabh Agnihotri[2], Priyanka Jagtap[3], Mrs. Alka Ali[4]
[1,2,3] *(Department of Fibres and Textile Processing Technology, Institute of Chemical Technology, India)*
[4] *(Department of Textile Chemistry, Uttar Pradesh Textile Technology Institute, India)*

Abstract: *Using sol–gel process, functional silica coatings can be deposited on textile materials which lead to new textile properties and applications. In the present study combined dyeing and water repellent finish was applied on cotton and polyester/cotton blend fabrics. Both the fabric samples were dyed with cheap basic dyes by adding glycidoxypropyltrimethoxysilane as cross-linking agent. Hydrophobicity was imparted using long-chained alkyltrialkoxysilanes like octyltriethoxysilane as water repellent agent which has properties quite similar to hydrophobic fluorine-containing sol-gel coatings. The combined effect was obtained at the cost of impairment in fastness properties of the dye and substantial decrease in tearing strength. There was marginal decrease in both tensile strength and percentage of elongation of the fabrics.*

Keywords: *Basic Dyes, Nanotechnology, Silanes, Sol-gel coating, Water repellency*

I. Introduction

Sol-gel process has had a history of more than 100 years as one of the modification and preparation methods of materials since it was invented. Due to the resulting properties of high chemical homogeneity, purity, lower processing temperature, easy shaping, and modification [1] sol-gel process has widely been applied in areas such as ceramics, pharmacy, orthopedics, and it has been applied in functional finishing of textiles in the last decade.

According to its purpose, silica gel can be divided into two categories. First, the functional gels making the treated textiles obtain desired functions, such as anti-abrasion [2], wrinkle resistance [3], water or oil repellence [4,5,6], antistatic [7], UV shielding [8,9], etc. Second the gels used as carriers to immobilize and/or control functional ingredients, such as improving color fastness of dyed Textiles [10,11], preparing bioactive textiles [12], flavor-releasing textiles [13] etc.

Using this process, functional silica coatings can be deposited on textile materials and can lead to new textile properties and application [11, 6]. Also, dyes can be embedded into sol–gel coatings and deposited on several types of materials leading to new possible application, e.g. optical devices or sensors [14, 15].

Mahltig & Böttcher [6] has reported a water repellent textile by coating with different modified silica sols. For this, pure and with 3-glycidoxypropyltriethoxysilane co-condensed silica sols were modified by three types of additives: alkyltrialkoxysilanes, polysiloxane derivatives and a fluorine-containing silane. Different methods were used to evaluate the water repellent properties of such coatings. First investigations were performed by contact angle measurements on coated glass and textiles. For investigations on more customary conditions a spray test and a washing test were performed. Hydrophobic properties of the coatings were gained via addition of hydrophobic agents to commercial available silica sols. In case of the alkylsilane additives, suitable water repellent properties can be only reached via addition of hexadecyltrimethoxysilane while the use of additives containing a shorter alkyl chain length leads to insufficient water repellence [6].

The water repellence of sol-gel coating containing a polysiloxane with a polymerisation degree of 30 is quite similar to the one reached with hexadecyltrimethoxysilane modified coatings. Nevertheless, the water repellence of those polysiloxane containing sol-gel layers show only sufficient washing fastness if an annealing procedure follows the washing. Also suitable water repellent textiles with a sufficient washing fastness could be prepared using fluorine-containing silica sol coatings. Altogether the addition of hexadecyltrimethoxysilane and triethoxytridecafluorooctylsilane to sol-gel coatings offer the most suitable chance for preparation of water repellent textiles by sol-gel coatings. By modification of silica sols with hexadecylsilane sol-gel coatings could be prepared on textiles owning excellent water repellent properties without any addition of fluorine-containing compounds [6].

Mahltig et al. reported hydrophobic silica sol coatings on textiles with respect to the influence of the solvents and the concentration of the sol. For this purpose, two silica sols, prepared with the hydrophobic additives octyltriethoxysilane and perfluoroctyltriethoxysilane, were diluted by different solvents: water, ethanol and acetone. In case of using pure water for dilution, the hydrophobicity of coated textiles decreases drastically with increasing dilution of the applied sol. For coatings on polyester fabrics or mixed fabrics made from polyester and cotton, the use of the organic solvents ethanol or acetone leads to significant hydrophobicity even in case of strong dilution down to a sol concentration <1%. The hydrophobic effect of coated polyamide textile is less. The use of a combination of water with less inflammable organic solvents such as di (propylene glycol) n-propylether in hydrophobic silica sols yields textile coatings with good hydrophobicity, even in case of low sol concentration [16].

In this research work, attempt has been made to incorporate basic dyes and water repellent compound in the sol-gel coating of cotton and polyester/cotton blend.

II. Experimental

Ready for dyeing plain weave cotton (110 g/m^2, 17 picks/cm, 12 ends/cm) woven fabric was obtained from Tata Mill, Mumbai. Plain weave polyester/cotton (P/C) (160 g/m^2) fabric was obtained from Piyush Syndicate, Mumbai. Tetraethylorthosilicate (TEOS) was obtained Evonik Degussa Pvt. Ltd. Mumbai. Glycidoxypropyltrimethoxysilane (GPTMS) and Octyltri ethoxysilane (OTES) were obtained from Dow Corning India Pvt. Ltd. Mumbai. Sodium Lauryl Sulphate was obtained from S.d Fine Pvt. Ltd. Mumbai. Ethanol (98% pure) and Hydrochloride acid (HCl) used were of laboratory reagent grade. Coracryl Violet C3R was obtained from Colourtex Pvt. Ltd. Surat, Gujarat.

1.1 Preparation of sols

Sols were prepared by taking 50 ml ethanol, 34.20 ml TEOS, 3.8 ml GPTMS and 12 ml 0.01N HCl in a beaker. Modification of the silica sols were performed by substitution of TEOS by OTES in various proportions to make total volume 100ml. The mixture was stirred with magnetic stirrer for 24 hours at room temperature by covering the beaker with polyethylene sheet.

2.2 Application of Sol on fabrics

Coracryl Violet C3R dye (10 gpl) was added to this sol just prior to padding and then the fabrics were padded through this sol using 2 dip 2 nip method for 70% expression for cotton and 60% for P/C. The samples were then dried in air and cured in oven at 120 ^{0}C for 1 hour. It was then soaped at 40 ^{0}C for 2 hours by 10 gpl Sodium Lauryl Sulphate at neutral pH. The sample was then rinsed with water and air dried.

2.3 Color value by reflectance method

The samples were evaluated for colour depth in terms of Kubelka Munk function (K/S) using computer Color Matching System (SpectraScan 5100+) of Premier Colorscan Instruments Pvt. Ltd. Mumbai.

Kubelka Munk (K/S) function is given by:

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \qquad (1)$$

. Where,

"R" is the reflectance at complete opacity,
"K" is the absorption coefficient,
"S" is the scattering coefficient

2.4 Fastness testing of dyed fabric

For washing fastness, light fastness and rubbing fastness, ISO 105 C10, ISO 105-A02 and ISO 105 X-12 test methods were used respectively.

2.5 Tests for Water Repellency

2.5.1 Contact angle measurements

The contact angles were measured using a drop shape analysis apparatus of DSA100, Kruss Company, Germany. The measurements were performed 20 seconds after the water drop was placed on the textile substrate. Contact angle was measured at five different spots on the fabric and reported value is the average of these five readings.

2.5.2 Spray Rating (Rain Test)

The resistance of fabrics to the penetration of water by impact is measured by AATCC 35-2006 test method.

2.5.3 Water uptake test

In this test, fabric sample of 10 ×10 cm was placed in 300 ml distilled water for 1 minute. The water uptake by the textile during placement under water was determined using a balance [6].

2.6 Scanning electron microscopy

Surface morphology of the fabrics was characterized using SEM of JEOL JSM 6380LA, JEOL ltd. Japan.

2.7 Physical Characteristics of the sol-gel applied fabric

For tensile strength & percentage of elongation ASTM D 5034-95 method was used whereas for tearing strength and stiffness, ASTM D1424-96R04 and ASTM D1388-08(2012) test methods were used respectively.

III. Results And Discussion

3.1 Dyeing Property of the fabrics

Fig 1 shows the plot of Color strength of the fabric samples dyed by Coracryl Violet C3R for Cotton and P/C respectively. It can be seen that addition of OTES results in marginal increase in the color strength. The reason for this behavior is that the dye gets immobilized inside the 3D network created by sol-gel network.

TABLE 1 shows the fastness data of cotton and P/C blend samples. We can observe that the wash and light fastness gets impaired but rubbing gets affected marginally in presence of OTES. The wash fastness of the fabric gets affected because the dye gets hydrolyzed in alkaline medium as isoelectric point of silica coating is between pH_{IEP} 1.5 to 4.5 [17]. The reason of poor light fastness is that the cationic dyes are inherently sensitive to the light energy. Since sol-gel being a coating, the rubbing fastness is not expected to be of excellent quality.

However, one of the most important factors that influence fastness is the electrical net charge of the dye. It is known that silica sol coatings have an isoelectric point around pH 4, so at neutral pH they are negatively charged. For this reason positively charged dyes can interact with the surrounding silica matrix. Therefore their fastness is better than that of uncharged or negatively charged dyestuffs. Hence basic dyes are more suitable for incorporating into silica sols.

3.2 Water Repellent property of fabrics

The values of contact angles and spray ratings for addition of increasing concentrations of OTES on cotton and P/C samples are shown in **TABLE 2 and Fig 2 and 3**.

It was found that only for TEOS/GPTMS coated samples shows water absorbency as when we put a water drop on it, the drop sunk immediately. But with increase in concentration of OTES in the silane mixture the contact angle goes on increasing reaching up to 137^0 for 40% replacement of TEOS with OTES. Also from the spray rating values we can conclude that water absorbent cotton fabric has become water repellent. We can observe similar trend for P/C blend samples as well. However the hydrophobicity is more pronounced for cotton than P/C blend due to more effective bonding of silanes to the easily available hydroxyl groups of cotton fabric.

The results obtained from gain in weight of cotton samples are shown in **TABLE 3**. We can see that for both the samples as the amount of OTES goes on increasing on the fabric sample the water absorbing tendency of the fabric goes on decreasing.

It can be concluded that coatings with silica sols containing long-chained alkylsilane additives show increased hydrophobic properties. The increasing hydrophobicity could be explained by an increased shielding of the hydrophilic silica by the larger hydrophobic alkyl chains of OTES. The presence of coating can be further corroborated by the SEM photographs of the samples as shown in **Fig 4 and 5.**

TABLE 4 and 5 shows the results obtained for tensile strength testing of cotton and P/C fabrics coated with Sol-gel containing OTES compound.

It is observed that for untreated cotton and P/C samples the tensile strength was high which got reduced when treated with TEOS and GPTMS but after addition of OTES it went on increasing with increase in concentrations of OTES for both in warp and weft direction whereas the percentage of elongation for control samples it was low and then got increased when only TEOS and GPTMS was applied but again started decreasing with the addition of OTES. However this change in tensile strength and percentage of elongation was marginal in nature. This is happening because all the silane samples cross-link with the hydroxyl groups of cotton fabrics making it stiffer. This fact is supported by increase in bending length of the samples.

We also studied the tearing strength of sol-gel coated samples and found that the tearing strength got substantially reduced for silane treated samples. These changes in mechanical properties can be attributed to the thick gel film formation on the fiber surface and the adhesion of net-like gel between fibers, which can be obviously observed from SEM in **Fig 4 and 5**.

Thus it is possible to simultaneously dye and give water repellent and stiff finish to the cotton and P/C blend by sol-gel technique.

IV. Conclusion

Cotton and P/C blend can be dyed with cheap basic dyes using sol-gel method by adding GPTMS as cross-linking agent. Long-chained alkyltrialkoxysilanes like OTES could be used to prepare water repellent textiles via sol-gel coatings with properties quite similar to hydrophobic fluorine-containing sol-gel coatings. Simultaneous dyeing and water repellent finishing is possible by this sol-gel technique. The combined effect is obtained at the cost of impairment in fastness properties of the dye. There is a marginal decrease in both tensile strength and percentage of elongation of the fabrics for the lower concentration of the OTES which finally came at par with the control sample.

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TABLES

Table 1: Fastness properties for dyed and finished Cotton and P/C fabric for different TEOS/GPTMS/OTES ratio

TEOS/GPTMS/OTES Ratio	Cotton					P/C				
	Rubbing Fastness		Wash Fastness		Light Fastness	Rubbing Fastness		Wash Fastness		Light Fastness
	Dry	Wet	Staining	Colour Change		Dry	Wet	Staining	Colour Change	
90/10/0 (Control)	4-5	4	4-5	2	3-4	3-4	4	2	2	3-4
87.5/10/2.5	3	3-4	1-2	2-3	3-4	3	3-4	1-2	2-3	3-4
85/10/5	3	3-4	1-2	2-3	3-4	3	3-4	1-2	2-3	3-4
80/10/10	3	3-4	1-2	2-3	3	3	3-4	1-2	2-3	3
70/10/20	3	3-4	1-2	2-3	3	3	3-4	1-2	2-3	3
60/10/30	3	3-4	1-2	2-3	3	3	3-4	1-2	2-3	3
50/10/40	3	3-4	1-2	2-3	3	3	3-4	1-2	2-3	3

Table 2: Contact angle and Spray test rating for dyed and finished, cotton and P/C fabric for different TEOS/GPTMS/OTES ratio.

TEOS/GPTMS/OTES Ratio	**Cotton**		**P/C**	
	Contact Angle(^{0})	**Spray Rating**	**Contact Angle(^{0})**	**Spray Rating**
90/10/0 (Control)	-	0	-	0
87.5/10/2.5	100	50	90	60
85/10/5	103	55	95	75
80/10/10	110	60	98	80
70/10/20	125	65	100	85
60/10/30	130	70	101	90
50/10/40	137	70	103	90

Table 3: Water Uptake for dyed and finished, cotton and P/C fabric for different TEOS/GPTMS/OTES ratio

TEOS/GPTMS/OTES Ratio	Gain in Weight (%)	
	Cotton	P/C
90/10/0 (Control)	61	42
87.5/10/2.5	19	25
85/10/5	15	18
80/10/10	13	12
70/10/20	11	10
60/10/30	9	9
50/10/40	5	8

Table 4: Mechanical properties of dyed and finished cotton fabric for different TEOS/GPTMS/OTES ratio

TEOS/GPTMS/OTES Ratio	Cotton						
	Tensile Strength (kgf)		Elongation (%)		Tearing Strength(kgf)		Bending Length (cm)
	Warp	Weft	Warp	Weft	Warp	Weft	
Untreated	63.90	33.36	11.46	17.07	1.22	1.41	2.41
90/10/0 (Control)	57.70	30.55	14.21	19.03	0.68	0.74	2.81
87.5/10/2.5	57.93	31.27	14.02	19.00	0.59	0.58	3.39
85/10/5	58.30	31.87	13.87	18.76	0.57	0.52	3.80
80/10/10	58.97	32.26	13.43	18.32	0.55	0.50	3.89
70/10/20	60.32	33.42	12.21	17.49	0.48	0.48	3.95
60/10/30	61.56	34.65	11.87	17.12	0.45	0.47	4.03
50/10/40	63.95	34.85	11.21	17.05	0.43	0.45	4.15

Table 5: Mechanical properties of dyed and finished P/C fabric for different TEOS/GPTMS/OTES ratio

TEOS/GPTMS/OTES Ratio	Polyester/Cotton				
	Tensile Strength (kgf)		Elongation (%)		Bending Length (cm)
	Warp	Weft	Warp	Weft	
Untreated	137.7	63.30	51.7	31.5	1.53
90/10/0 (Control)	117.8	52.80	55.24	36.47	1.03
87.5/10/2.5	120.2	53.40	54.23	35.78	1.29
85/10/5	126.3	54.30	53.04	34.84	1.38
80/10/10	130.6	55.32	52.54	33.19	1.48
70/10/20	134.3	57.45	51.39	32.39	1.53
50/10/40	135.3	59.30	51.49	31.32	1.57

FIGURES

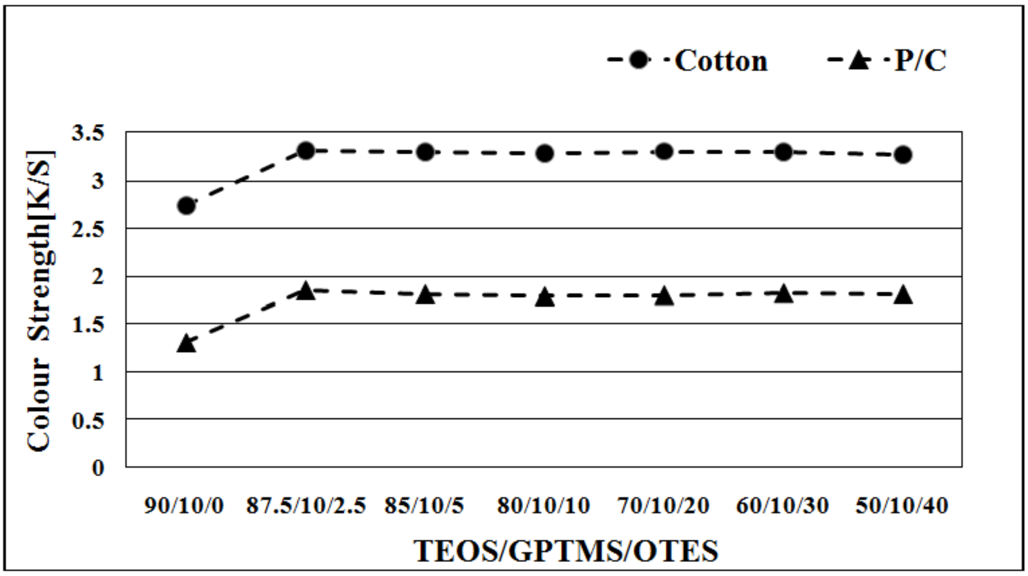

Figure 1: Plot of Color Strength (K/S) for dyed and finished cotton and P/C fabric for different TEOS/GPTMS/OTES ratio

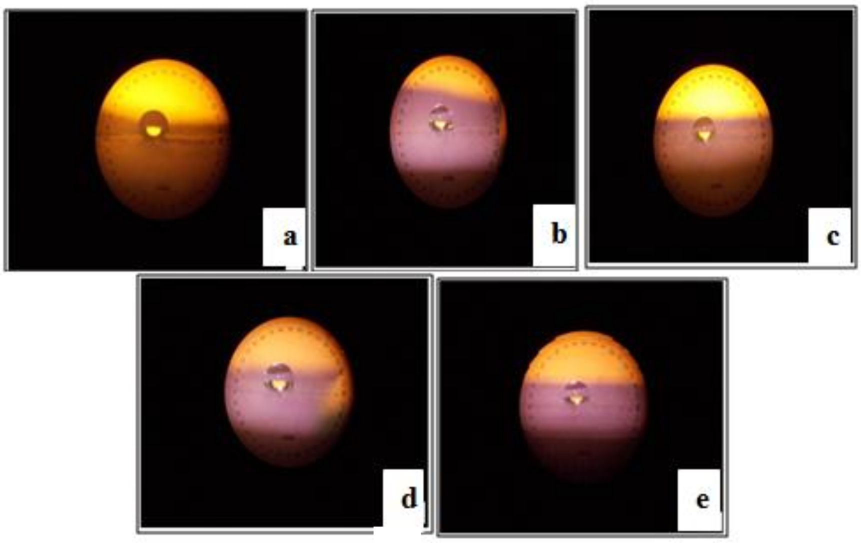

Figure 2: Contact angles for dyed and finished cott **d** bric for different TEOS/GPTMS/OTES ratio
a: 87.5/10/2.5 b: 85/10/5 c: 80/10/10 d: 70/10/20 e: 50/10/40

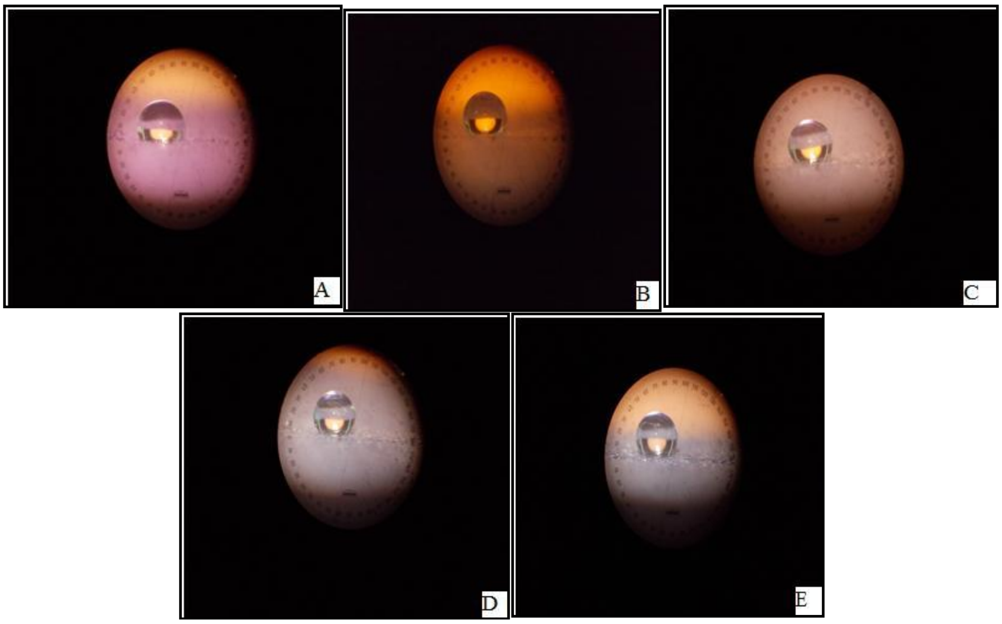

Figure 3: Contact angles for dyed and finished P/C fabric for different TEOS/GPTMS/OTES ratio a: 87.5/10/2.5 b: 85/10/5 c: 80/10/10 d: 70/10/20 e: 5/100/40

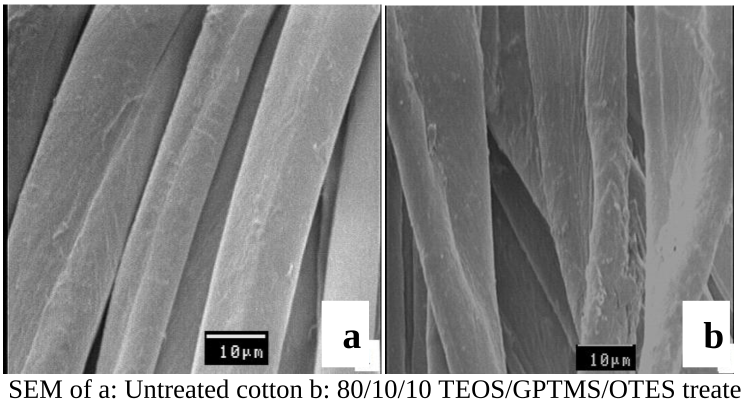

Figure 4: SEM of a: Untreated cotton b: 80/10/10 TEOS/GPTMS/OTES treated cotton

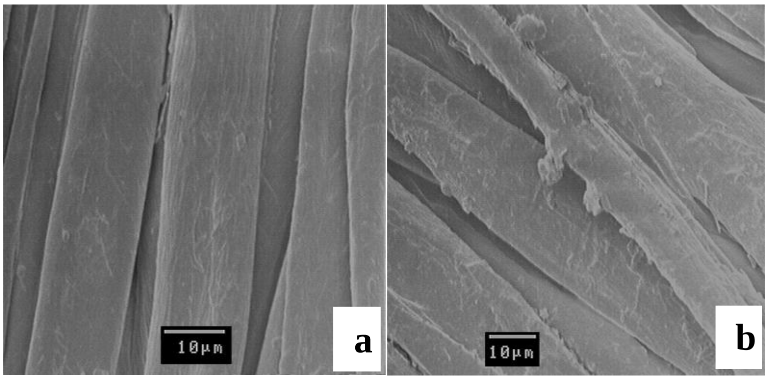

Figure 5: SEM of a: Untreated P/C b: 80/10/10 TEOS/GPTMS/OTES treated P/C