

Printing of Sol-gel Modified Fabrics Using Anionic Dyes

Madiha El kashouti, Tarek Salem, Hanan El Sayad and Shima Salah El-Deen
Mohamed Elhadad

¹Dyeing, Printing and Auxiliaries Department, Textile Industries Research Division,
National Research Centre, 33 El-Buhouth Street, Dokki, Cairo 12622, Egypt.

A different approach is by using sol-gel technique to modify the surface of blend fabrics to render them dyeable with one class of dyes; e.g. anionic, nonionic and functional dyes. The sol-gel technique involves the formation of mineral phases, starting from molecular precursors, following an inorganic polymerization reaction. The reaction is usually at room temperature in water or solvents and different range of pH conditions. The first step in the sol-gel process of silica consists of hydrolysis of silicon alkoxides, then condensation forming the silica nanoparticles and depending on the reaction conditions, these particles can grow and form the sol which can be deposited on the surface of the substrate forming a film. In this section two selected silane precursors were used APTES [(3-Aminopropyl)-triethoxysilane)], GPTMS [(3-glycidoxypropyl)-trimethoxysilane], to modify PET/W, PET/C, cotton and polyester fabrics via film coating with nanosol.

Keywords: Sol-gel; Anionic dyes; APTES; GPTMS; Textile printing.

Introduction

There are several parameters involved in the sol-gel process, influencing the structural properties of the product. The process is affected by the reaction conditions, precursor's type, pH, temperature, solvent type, drying conditions, and by the molar ratio of the reactants. Concerning the precursors, the most common precursors used are salts, oxides, hydroxides, complexes and alkoxides. Among these, alkoxides are the most commonly used [1]. Some examples of the most used alkoxy silane precursors for the sol-gel process are APTES and GPTMS. The type and concentration of the silicon alkoxides affect the rates of hydrolysis and condensation reactions. Hydrolysis and condensation of silicon alkoxides are highly influenced by employing catalysts.

Gel with different properties and microstructures can be produced by different catalysts and consequently different catalytic mechanisms. Film properties such as film thickness, porosity and optical quality depend on the catalyst used in the sol-gel process. Silicon alkoxides reacts slowly with water, the reaction process can be speeded up by the use of catalysts

(acid or base). It was found that, the strength and concentration of the acid or base used affect the extent of reaction. The reactivity of various polymer surfaces toward APTES is studied [2]. A general surface selective modification technique for polar-polymers such as polyesters, cellulosic, etc..., is proposed as follows:

- (a) Initial adsorption of APTES (through hydrogen bonding by the amine) to the polymer substrate.
- (b) lateral bond formation to the nearest neighbors and subsequent multilayer formation, as shown in Fig. (1) [3, 4].

The following section deals with the effect of using four selected different molar ratio of the reactants in the sol-gel process for modification of fabrics on the color strength of their produced prints. These molar ratio were (1:1:0.3 - 1:1:0.6 - 1:1:1 - 1:1:2) for precursors: alcohol: water respectively under acidic hydrolysis conditions. The quantity of water in the sol-gel solution influences the hydrolysis and condensation reaction and the time of gelation. It was stated that, the use of catalysts enhances the reaction process to a greater extent [5].

*Corresponding author: Dr. Shima Elhadad (shimaa.elhadad@yahoo.com)

DOI: 10.21608/jtcps.2020.31016.1038

©2020 National Information and Documentation Centre (NIDOC)

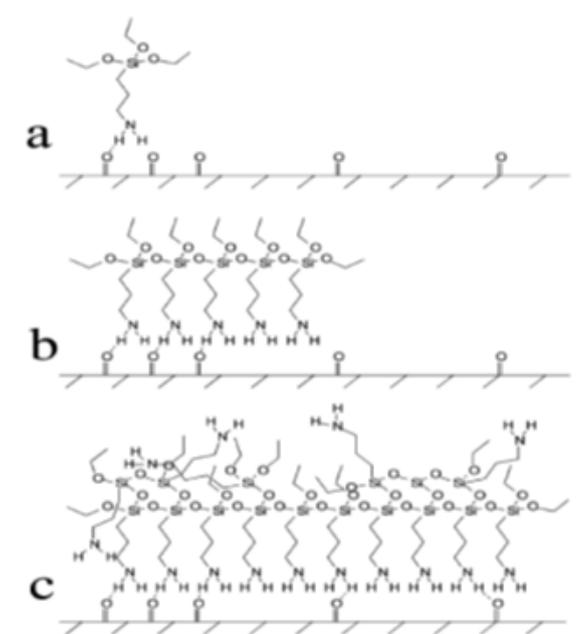


Fig. 1. Proposed mechanism of APTES surface modification: initial adsorption via hydrogen bonding, (b) subsequent lateral bond formation to the nearest neighbors, and (c) multilayer formation.

Materials.

Fabrics.

- Polyester/wool (PET/W).

Polyester/wool [55: 45] knitted fabric of 165 g/m², with plain 1/1 weaving structure, supplied by a private sector company.

- Polyester/cotton (PET/C).

Polyester/cotton [35: 65] knitted fabric of 122 g/m², with plain 1/1 weaving structure, supplied by a private sector company.

- Polyester.

Polyester (PET) knitted fabric of 150 g/m², supplied by a private sector company.

- Cotton.

Cotton knitted fabric of 158 g/m² with plain 1/1 weaving structure.

Silane precursors.

- Three types of silanes were used.

Dyestuffs and auxiliaries.

Dyestuffs.

Auxiliaries.

- Thickeners.

Commercial sodium alginate thickener supplied by pharmaceutical chemicals company.

- Binder.

Commercial binder SME-2 from DACO for chemicals Industry Company.

- Urea.

Commercial urea from El-Nasr pharmaceutical chemicals company.

- Solvents.

Commercial solvents (Acetic Acid, Ethanol and Ammonia) from pharmaceutical chemicals company were used.

Methods.

Preparation of silane solutions (nanosol).

Acid hydrolysis of APTES and GPTMS.

Different silica sols were prepared by using APTES and GPTMS as precursors, acetic acid as catalyst, ethanol and water as solvents. Precursors, ethanol and water were mixed in the molar ratios (1:1:0.3- 1:1:0.6- 1:1:1- 1:1:2) respectively and stirred overnight at room temperature. The pH was adjusted by acetic acid to 3.

Base hydrolysis of APTES and GPTMS.

Silica sols were prepared by using APTES and GPTMS as precursors, ammonia as catalyst, ethanol and water as a solvent. The pH was adjusted by ammonia to 9.

Surface modification of fabrics.

Coating with nanosols.

To modify the surface of (PET/wool, PET/cotton, polyester and cotton) fabrics by sol-gel method, the fabric samples were dipped into the different nanosol solutions, soaked at room temperature for 10 min, then the fabrics were

TABLE 1. Silane precursors.

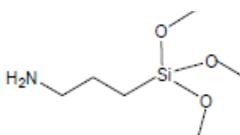
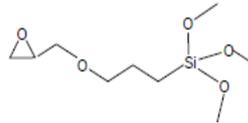
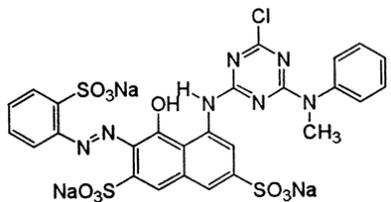
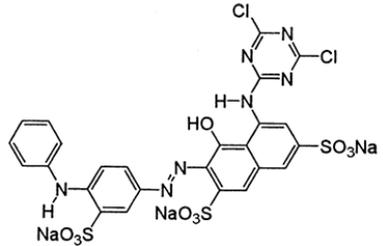
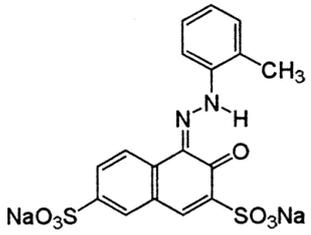
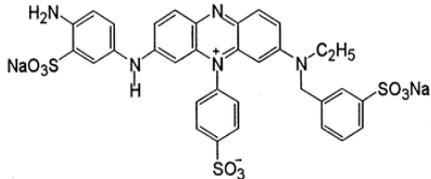
Chemical name	Abbreviation	Chemical structure	Supplier
(3-Aminopropyl) – triethoxysilane)	APTES		Sigma- Aldrich company
(3-glycidoxypropyl) – trimethoxysilane	GPTMS		

TABLE 2. Dyestuffs used.

Dye name	λ_x	Chemical structure	Supplier
Commercial dyes			
C.I. Reactive red 24	525		Young Industrial Company
C.I. Reactive blue 81	590		Young Industrial Company
C.I Acid red 24	525		Sun colors® company
C.I. Acid blue 18	600		Sun colors® company

padding to a wet pick up of 80%. The padded fabric samples were then dried at 60°C for 10 min to evaporate the solvent (ethanol) and then cured at 120°C for 30 min. Then, the samples were rinsed with distilled water and dried. The effects of the type of silane precursor, type of catalyst, and different water/ alcohol/ silane ratios on fabric surface modification were investigated.

Characterization of modified fabrics.

Fourier-Transition Infrared Spectroscopy (FTIR).

Infrared spectroscopy is used to identify chemical compounds, mixtures, extent of reaction, and molecular structure. Different chemical compounds absorb infrared radiation at frequencies corresponding to their own molecular vibrational frequencies [6].

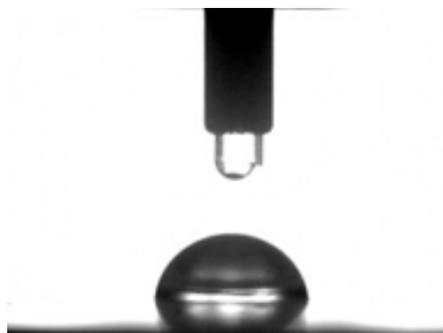
Contact angle measurements.

company, Germany). Environmental Conditions: Temperature 221±°C and RH= 655%±.

Instrument used: Compact video microscope (CVM) that is manufactured by SDL- UK.

Technique used: Horizontal plan camera located perpendicular to liquid droplet plane.

Liquid used: Water grade 3 (DW)



Average Drop volume at 250 mL: The measurements on modified fabrics were performed 20 seconds after the water drop was placed on the textile substrate.

Scanning electron microscope (SEM).

Fabric samples were located on copper coated carbon tap double face, and then coated by the gold layer by evaporation of gold in argon atmosphere using sputter coater. The surfaces of samples were scanned using (Quanta FEG-250). The magnification was set at 200,400 to 1700. All samples were scanned at room temperature.

Printing of modified fabrics.

In this work, Silk screen printing was used.

Print paste recipe.

The printing pastes were prepared according to the recipes shown in Tables (III and IV). The dye was mixed with urea and pasted with some water. The dye paste was diluted with hot water (60°C) while stirring to homogenize the dye solution. The latter was then poured on the thickener suspension, and the whole mixture was thoroughly stirred while adding the wetting agent, sodium chlorate and ammonium sulphate or formic acid. The total mass of the whole paste was then adjusted to 1 Kg by adding the necessary amount of water.

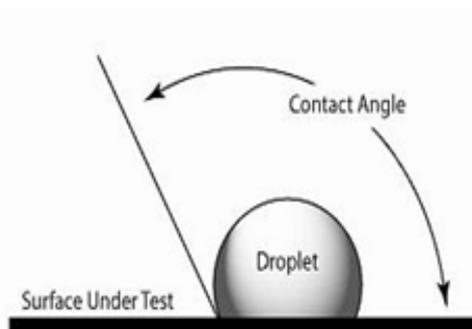


TABLE 3. Acid dye printing paste.

Dye	2 g
Urea	5 g
Sodium alginate	5 g
Sodium chlorate	1.5 g
Ammonium sulphate	6 g
Water	X
100 g	

TABLE 4. Reactive dye printing paste.

Dye	2 g
Urea	5 g
Sodium alginate	5 g
Sodium chlorate	1.5 g
Formic acid (85%)	1 g
Water	X
100 g	

Fixation technique.

Print fixation was performed by steaming for 20 min at 102°C in a high- temperature steamer.

Fastness measurements:

The light fastness, rubbing, perspiration and washing properties were tested to the unmodified and modified printed fabrics.

Result and discussion*FTIR*

The FTIR spectra of the unmodified and sol-gel modified PET/C and PET/W fabrics were done to determine the chemical changes that could have occurred as a result of a sol-gel treatment. Fig. (2) shows the FTIR spectra of the unmodified and modified PET/C fabrics with acid hydrolyzed silanes. All the absorption peaks are labeled with the wave number values, the spectrum of the unmodified PET/C fabric (broken line) was very complex because it included absorption bands characteristic of both cellulose and polyester. In the polyester component spectrum, the following bands were observed: an absorption band at 1720 cm⁻¹ due to the strong C=O symmetric stretching vibrations of carbonyl group

of the ester bond; and bands at 850, 793 and 720 cm⁻¹ caused by the C-H and C-C vibrations of the benzene ring. The absorption bands at 1370, 1338, 1240 and 1095 cm⁻¹, belonging to the $\nu(\text{C-OH})$ and $\nu(\text{C-O-C})$ vibrations of the polyester fibers, were blurred by the absorption bands characteristic of the cellulose component fingerprint region. Interference of the absorption bands of cellulose also occurred in the 2850-2600 cm⁻¹ spectral region due to the stretching vibrations of νCH_2 , νCH_3 and C-H, as well as in the absorption band region of 3500-3250 cm⁻¹ characteristic of O-H stretching and of adsorbed water molecules [7].

Chemical changes that occurred on polyester and the wool components of fibers by sol-gel coating process were measured using FTIR spectral analysis of the unmodified and sol-gel modified PET/W. Fig. (3) represents the FTIR spectra of the unmodified and modified PET/W fabrics with acid hydrolyzed silanes. In the wool spectrum, the strongest peaks occurring at around the following bands were observed an absorption band at 1690 cm⁻¹ and 1511 cm⁻¹ are attributable to primary and secondary amide (-CONH) respectively.

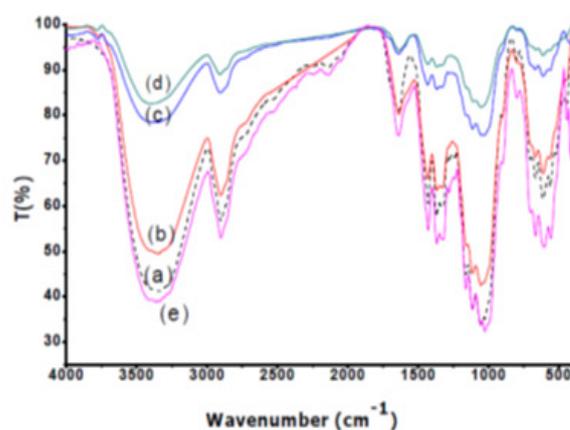


Fig. 2. FTIR spectra of the unmodified and modified PET/cotton fabrics with acid hydrolyzed silanes; (a) Unmodified, (b) APTES, (c) GPTMS.

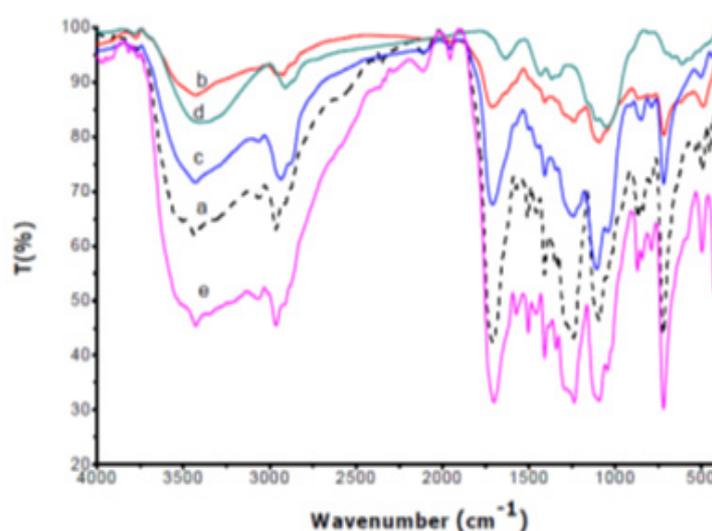


Fig. 3. FTIR spectra of the unmodified and modified PET/wool fabrics with acid hydrolyzed silanes; (a) Unmodified, (b) APTES, (c) GPTMS.

It was also found that, it is difficult to observe the expected Si-O-Si and Si-OH bonds in the IR spectra of the silane modified PET/W and PET/C fabrics. Consequently, further investigations were carried out using another surface sensitive technique (X-ray photoelectron spectroscopy) (XPS) to point out and clarify the surface changes occurred during these modification tests. For this investigation, we selected one precursor (APTES) as an example

X-ray photoelectron spectroscopy (XPS)

XPS is a popular and powerful technique for the investigation of surface composition; it does provide qualitative information on the chemical changes. The XPS examinations, confirmed the introduction of nitrogen functionalities onto PET/W and PET/C fabrics surface by treatment with acid or base-hydrolyzed APTES as shown by the results in Tables V & VI. This proves that the surface chemical changes resulting from sol-gel treatment are confined to a very thin surface layer which is detected by the XPS technique. Hence, the local concentration of the formed nitrogen functionalities on the fabric surface layer is not high enough to be sensed by FTIR spectroscopy. Therefore, XPS can offer the benefits of investigating approximately only the first 10 nm of the coating. The elemental surface compositions of surface region and the corresponding atomic ratios of the unmodified and APTES modified PET/C fabrics are summarized in Table V. Surface chemical composition obtained by acid- or base-catalyzed hydrolysis of APTES coating was

determined by XPS analysis during 30 min after modification.

The results obtained after the deposition of APTES onto PET/C fabric surface regardless of the type of catalysis system used indicate that, the nitrogen and silicon content increases. As a result, the [N]:[C] atomic ratio increases. For instance, after modification of PET/C fabrics with acid-hydrolyzed APTES the [N]:[C] atomic ratio increases from 0.011 to 0.052, while after modification with base-hydrolyzed APTES the [N]:[C] atomic ratio value increases to 0.057 indicating the incorporation of nitrogen-containing functional groups onto the PET/C surface. Likewise, after modification of PET/C with acid-hydrolyzed APTES [Si]:[C] atomic ratio increases from 0.158 to 0.178 indicating the incorporation of silicon-containing functional groups onto the PET/C surface.

The elemental surface compositions of surface region and the corresponding atomic ratios of the unmodified and APTES modified PET/W fabrics are summarized in Table VI. Surface chemical composition of coating obtained by acid- or base-catalyzed hydrolysis of APTES was also determined by XPS analysis during 30 min after modification. The results obtained after the deposition of APTES onto PET/W fabric surface regardless of the type of catalyst system used indicate that, the nitrogen and silicon contents increase, while the carbon contents decrease in the surface region. As a result, the [N]:[C] atomic

ratio increases. For instance, after modification of PET/W fabrics with acid hydrolyzed APTES the [N]:[C] atomic ratio increases from 0.085 to 0.121, while after modification with base hydrolyzed APTES the [N]:[C] atomic ratio value increases to 0.134. These results demonstrate that the incorporation of nitrogen-containing functional groups onto PET/W surface. Likewise, after modification of PET/W with acid hydrolyzed APTES [Si]:[C] atomic ratio increases from 0.006 to 0.097, while after modification with base hydrolyzed APTES the [Si]:[C] atomic ratio value increases to 0.101. These results indicate that the incorporation of silicon-containing functional groups onto the PET/W surface.

The increase in [N]:[C] and [Si]:[C] atomic ratios prove that there are some changes in the surface chemistry. These changes indicate the formation of sol-gel derived layer, which is covalently anchored to the surface of blend fabrics. Silica sols behave in a similar manner to dye molecules during wet chemical processing. In case of PET/C blend, the alkoxy silane groups may condense irreversibly with free -OH groups under mild conditions to form strong fabric-O-Si and Si-O-Si linkages. On the other hand, wool fiber

has been known to have free amino and carboxyl groups in the wool backbone as important reactive sites. Therefore, the facile reaction between -NH₂ or -COOH groups on the PET/W fabric with alkoxy silane groups is expected to occur (Fig (4)).

3.2 Scanning electron microscope SEM.

As mentioned before, scanning electron microscopy (SEM) was used to study the surface characteristics of the unmodified and modified fabrics.

The SEM images of unmodified and modified PET/W fabric surfaces with APTES and GPTMS sols were illustrated in Fig. (5). The SEM images show uniform coatings onto the modified, PET/W fabric and it is expected that, these coating layers would help in rendering the dye molecules attachable to the fabric.

Similar trends were also observed, with the SEM images of unmodified and modified PET/C fabric surfaces with APTES and GPTMS sols were illustrated in Fig. (6). The aforementioned SEM images resulting from both modified PET/W and PET/C fabrics imply that different forms of adhered silane layer were noticed on both fabrics which will help in attaching the dye molecules to them.

TABLE 5 .Elemental surface compositions and atomic ratios determined by XPS examination for the unmodified and APTES modified PET/C fabrics using acid and base catalysis.

Fabrics	C (at.%)	O (at.%)	N (at.%)	Si (at.%)	[N]:[C]	[O]:[C]	[Si]:[C]
Unmodified PET/C	60.61	29.32	0.67	9.49	0.011	0.487	0.158
Modified PET/C using acid catalysis	61.46	23.09	3.19	10.95	0.052	0.376	0.178
modified PET/C using base catalysis	60.55	24.86	3.47	10.13	0.057	0.411	0.167

TABLE 6. Elemental surface compositions and atomic ratios determined by XPS for the unmodified and APTES modified PET/W fabrics using acid and base catalysis.

Fabrics	C (at.%)	O (at.%)	N (at.%)	Si (at.%)	[N]:[C]	[O]:[C]	[Si]:[C]
Unmodified PET/w	73.56	16.08	6.22	1.98	0.085	0.219	0.0065
Modified PET/w using acid catalysis	67.65	16.06	8.18	6.58	0.121	0.237	0.097
Modified PET/w using base catalysis	67.25	15.78	8.99	6.79	0.134	0.235	0.101

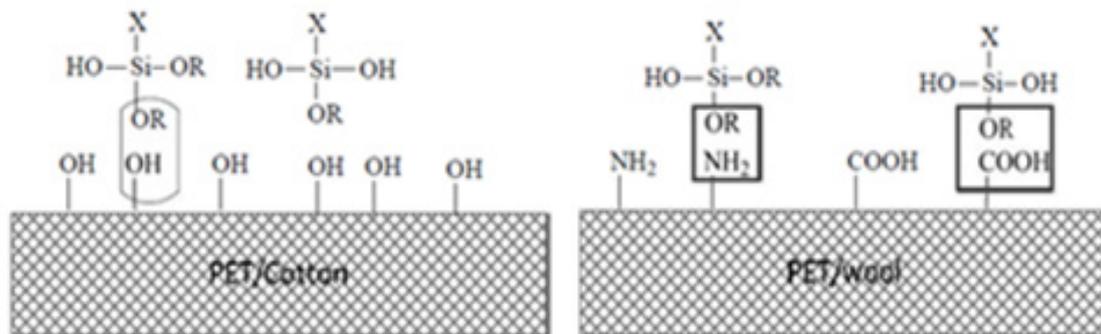


Fig. 4. Schematic representation of the expected reaction between the alkoxy silane groups and the blend fabrics.

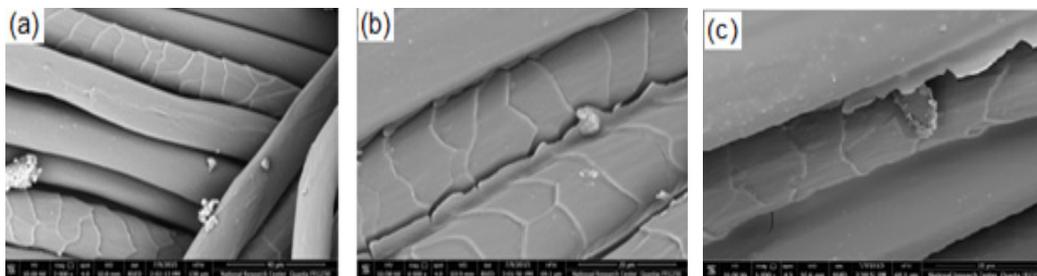


Fig. 5. SEM images of (a) unmodified polyester/wool fabrics, (b) APTES modified fabrics; (c) GPTMS modified fabrics.

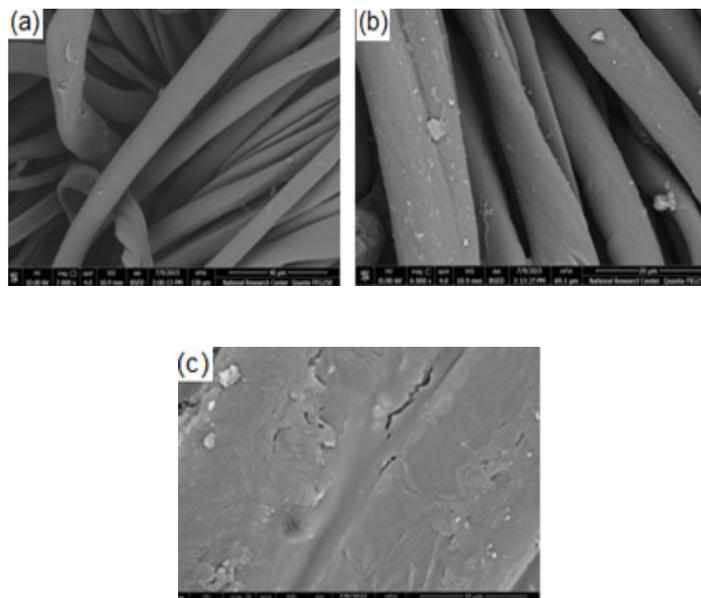


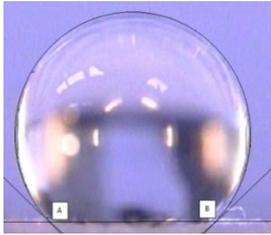
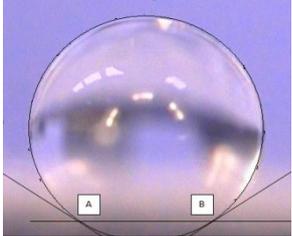
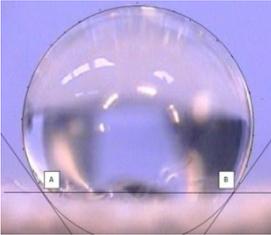
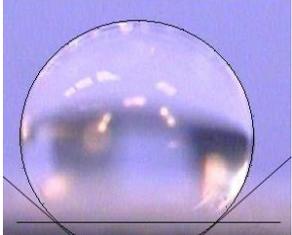
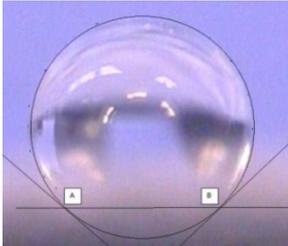
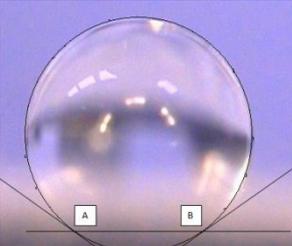
Fig. 6. SEM images of (a) unmodified polyester/cotton fabrics, (b) APTES modified fabrics; (c) GPTMS modified fabrics.

contact angle

Table VII shows the surface wettability and absorbency results of unmodified and modified PET/W, PET/C, polyester and cotton fabrics. These results indicate that, the hydrophobicity of the fabrics increased due to the sol-gel treatment. The average contact angle results for all tested APTES modified fabrics (PETW, PETC, PET and cotton) increased from 139-146°, 129-139°

and 139-145 ° and up to 144° when compared to the corresponding unmodified fabrics. This means that, the hydrophobicity of the modified fabrics has increased to a high extent due to the modification treatment. The change in the wetting properties may be attributed to the presence of siloxane bonds (Si-O-Si) which were introduced by sol-gel treatment. These bonds enhance water repellency.

TABLE 7. surface wettability and absorbency results of unmodified and modified PET/W, PET/C, polyester and cotton fabrics.

Fabric	Before surface modification	After surface modification
PET/wool		
	Average contact angle=139°	Average contact angle=146°
PET/cotton		
	Average contact angle=129°	Average contact angle=139°
PET		
	Average contact angle=139°	Average contact angle=145°
Cotton		
	Wetting time 4 sec	Average contact angle=144°

Printing of modified fabrics.

Different molar ratio parameter:

Acid dyes.

Two acid dyes namely acid red 24 and acid blue 18 were used in this investigation for printing modified PET/wool and PET/cotton as well as cotton and polyester fabrics. The color strength results of silk screen printed modified blend fabrics with acid hydrolyzed APTES using different molar ratio with the two aforementioned acid dyes were represented by Figs (7, 8). It is clear from the results that the effect of the PET/wool and PET/cotton fabric modification on the color strength of their prints is very clear as compared to the results of their unmodified fabrics. This applies for the two acid dyes used, at whatever molar ratio which were used. As regards to the molar ratio of reactants, the only variable here is the water concentration which

seems to play some role in this process. Concerning the selected water ratios in this investigation, which range between 0.3 to 2 moles, the effect is not remarkable, A reactant molar ratio of 1:1:1 represents the most favorable choice. It can also be seen that, the structure of the acid dyes used plays an important role in the color strength results which reflects the role of the dye chemical structure and composition. It can be safely concluded that, the fabric surface modification with acid hydrolyzed APTES rendered the blend fabrics more acceptable to the acid dyes.

The color strength results of screen printed, modified single fabrics (cotton and polyester) with acid hydrolyzed APTES using different molar ratio and the two aforementioned acid dyes are represented by Figs (9, 10). The results conform to the above findings.

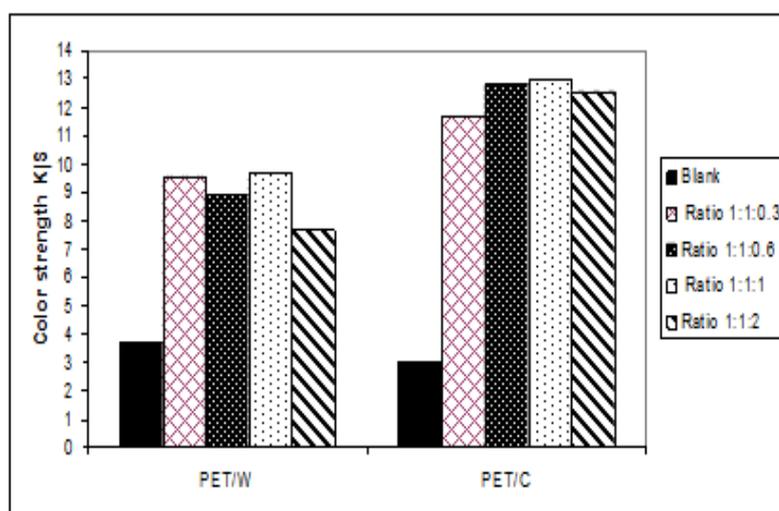


Fig. 7. Color strength of modified, screen printed * blend fabrics with acid hydrolyzed APTES using different molar ratio;
* Using acid red 24.

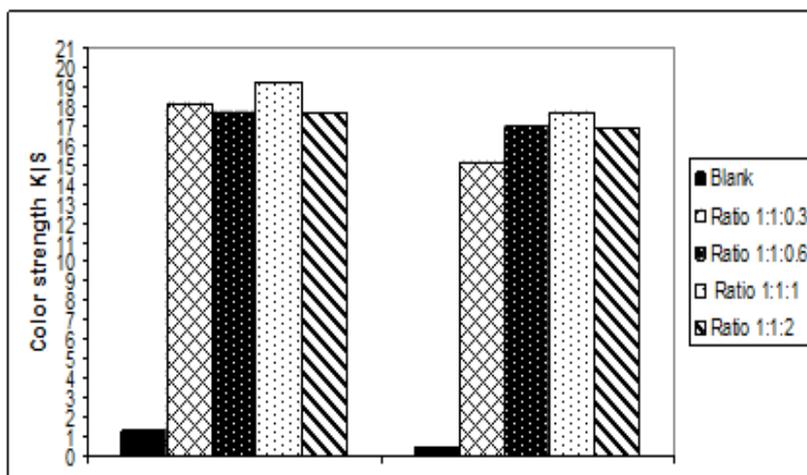


Fig. 8. Color strength of modified, screen printed * blend fabrics with acid hydrolyzed APTES using different molar ratio;
* Using acid blue 18.

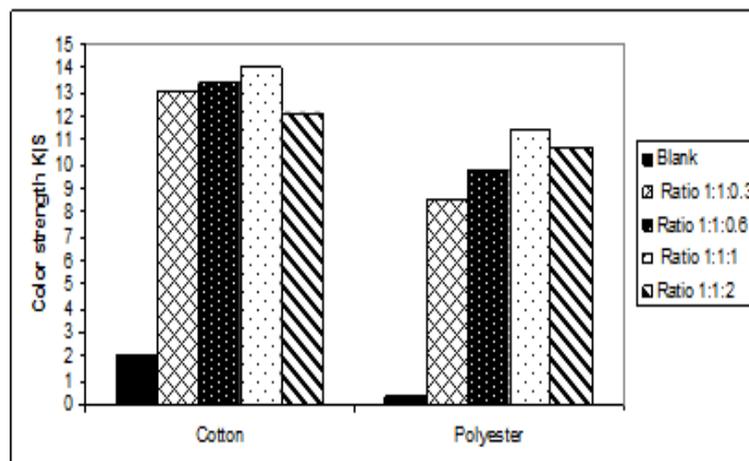


Fig. 9. Color strength of modified, screen printed * single fabrics with acid hydrolyzed APTES using different molar ratio; * Using acid red 24.

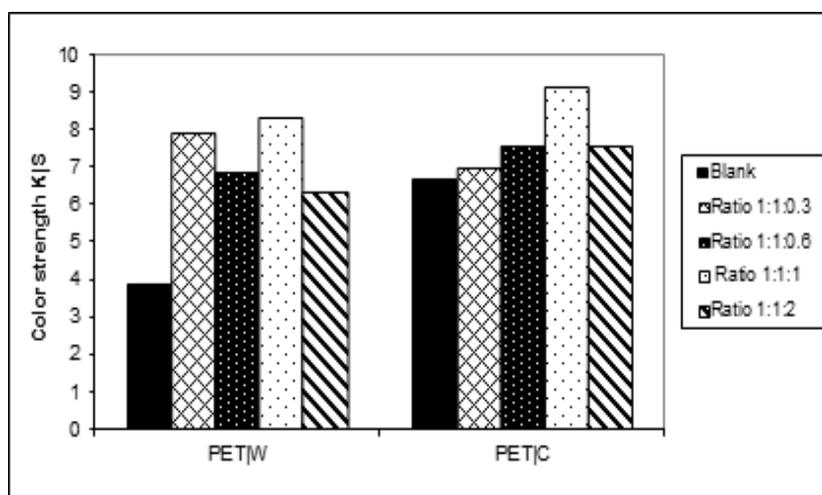


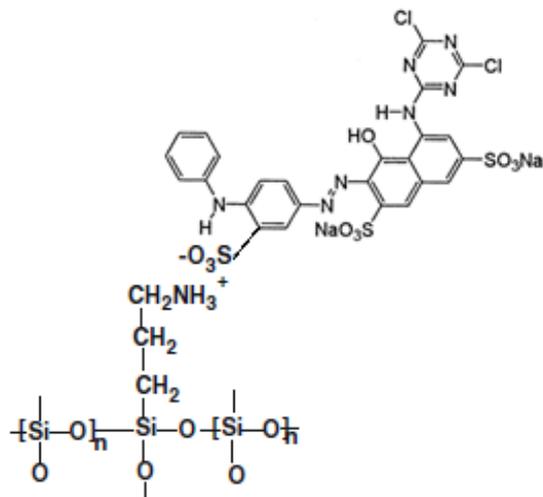
Fig. 10. Color strength of modified, screen printed * single fabrics with acid hydrolyzed APTES using different molar ratio; * Using acid blue 18.

Reactive dyes

Two reactive dyes namely reactive red 24 and reactive blue 81 were selected representing another category of anionic dyes, and used to print modified PET/wool and PET/cotton fabrics as well as polyester and cotton fabrics. The color strength results of screen printed modified blend fabrics with acid hydrolyzed APTES using different molar ratio with the two aforementioned reactive dyes are represented by Figs (11, 12). The results show that, the modification of PET/W and PET/C fabrics has a noticeable effect on the color strength of their prints as compared to the results of their unmodified fabrics. This applies for the two reactive dyes and at any molar ratio used. It can also be shown that, the unmodified blend fabrics possessed noticeable color strength values; this is due to the reactivity of their cotton and wool components to the reactive dyes. It is

also clear in this case that the molar ratio of 1:1:1 seems most favorable. An explanation to the above is that, at fixed silane precursor concentration, an increase in water content leads to a corresponding increase in hydrolysis and condensation rate. On contrary, under low water ratios, a matrix with a more open structure is produced due to incomplete hydrolysis, consequently, less crosslinking in the sol-gel materials. The chemical structure of the reactive dyes used has some role on the color strength of the prints (Scheme 1).

In this case the effect of modifying the surface of PET/W and PET/C on the color strength of their prints is less noticeable compared with the case when using acid dyes; this is of course due to substantively of their wool and cotton components to the reactive dyes.



Scheme 1. Chemical structure of silica sol from (APTES) and reactive dyes.

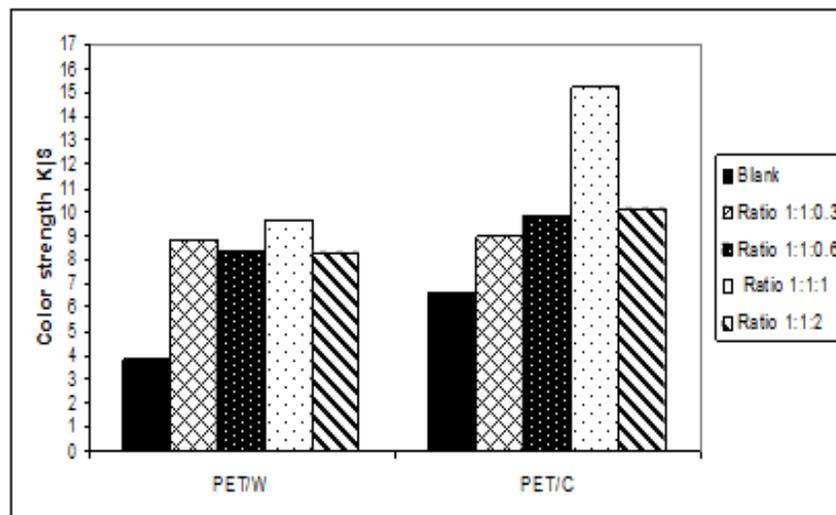


Fig. 11. Color strength of modified, screen printed * blend fabrics with acid hydrolyzed APTES using different molar ratio; * Using reactive red 24.

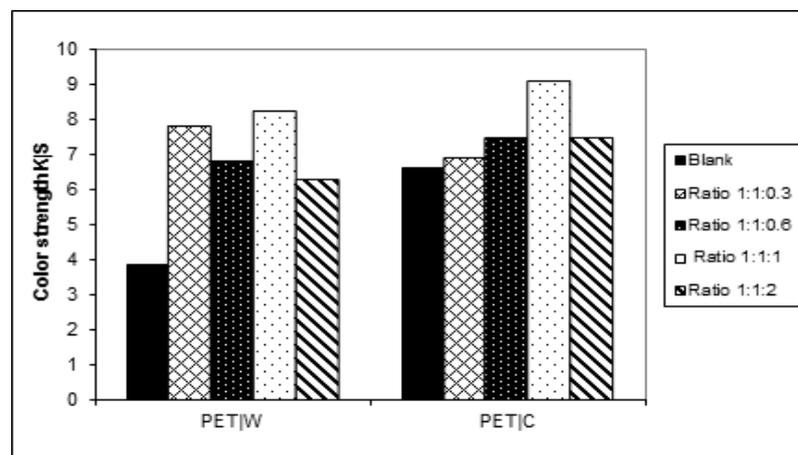


Fig. 12. Color strength of modified, screen printed * blend fabrics with acid hydrolyzed APTES using different molar ratio; * Using reactive blue 81.

The color strength of screen printed, modified cotton and polyester fabrics with acid hydrolyzed APTES using different molar ratio and the two aforementioned reactive dyes are represented by Figs (13,14). Very high color strength values were obtained for cotton modified fabrics due to their original substantivity for reactive dyes in addition to the effect acquired by the surface modification. This is very clear in the case of the modified polyester fabric where the effect of surface modification is the only reason for the increased color strength of the prints.

GPTMS

It was reported that, surface modification with GPTMS has a beneficial effect on the elasticity of

the coating films, and its use in the sol-gel process increase the resistance to shipping of the coating and subsequently the wear resistance of the blend fabrics resulting in a better performance. The reactivity of various polymer surfaces towards GPTMS is studied here, as well as the effect of using different reactant molar ratio (1:1:0.3- 1:1:0.6- 1:1:1 and 1:1:2). GPTMS is a metal organic silane containing a non-hydrolyzed epoxy group and three alkoxy groups under acidic or basic conditions, epoxy rings can open to react with many reactive groups (e.g. amino, carboxyl and hydroxyl groups) through nucleophilic mechanism.

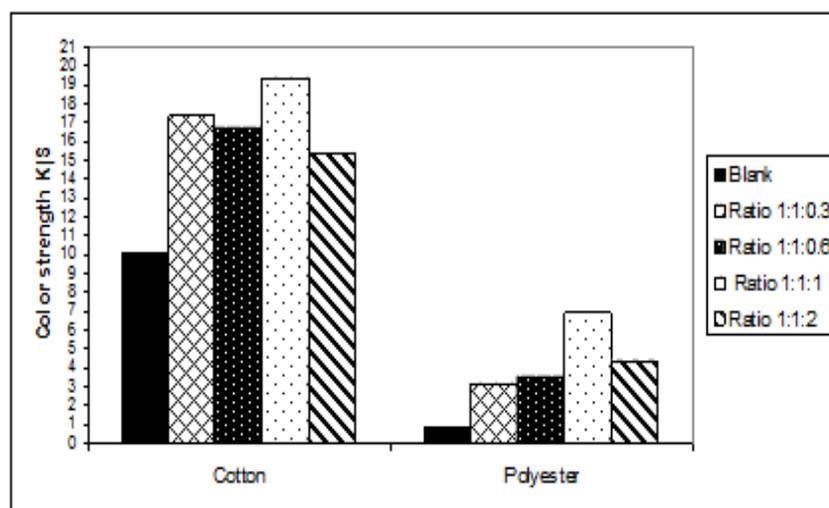


Fig. 13. Color strength of modified, screen printed * single fabrics with acid hydrolyzed APTES using different molar ratio; * Using reactive red 24.

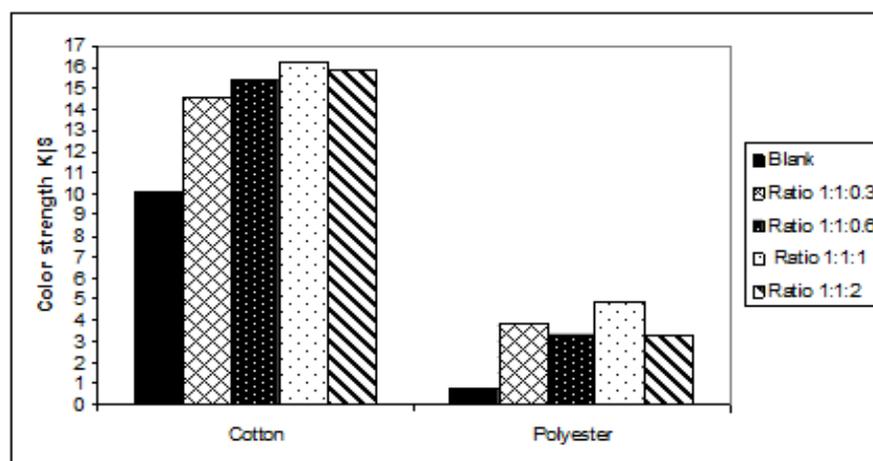


Fig. 14. Color strength of modified, screen printed * single fabrics with acid hydrolyzed APTES using different molar ratio; * Using reactive blue 81.

Acid dyes:

Acid red 24 and acid blue 18 were used in this investigation for printing modified PET/W, PET/C as well as cotton and PET fabrics. The color strength results of screen printed, modified blend fabrics with acid hydrolyzed GPTMS using different reactant molar ratio with the two aforementioned acid dyes are represented by Figs (15, 16). The results show clearly that, the modification of the two blends has noticeably high effect on the color strength of their prints as compared to the unmodified fabrics. This is true for both acid dyes used and at any reactant molar ratio. The only variable in the four selected reactants molar ratio is the water and the variation in results due to that, seems to be not remarkable in that range. A reactant of 1:1:1 molar ratio is considered favorable. Adhesion of the GPTMS to the blend fabrics plays a vital role in the increase of color strength of fabrics. The improved adhesion of the GPTMS is caused by chemical bonding that results from the opening of the some of epoxy ring with different functional groups present on

fabric surfaces. For example, the epoxy ring of GPTMS is opened to react with hydroxyl and/or carboxyl groups in PET fiber at thermal condition. On the other side, amino and/or carboxyl groups in wool fiber may also open up the epoxy ring. The unreacted epoxy rings of GPTMS may react with the applied dyes. The structure of the acid dyes used is also playing an important role on the color strength results.

The color strength results of screen printed, modified cotton and polyester fabrics with acid hydrolyzed GPTMS using the above different molar ratio and the previous acid dyes are represented by Figs (17, 18). The trend of the results conforms to the previous findings. The reactivity of the modified cellulose fabric surface towards the dyestuffs used is clearly much higher than that of the modified polyester fabric surface. Similarly, the reactivity of the modified PET/C blend towards the same dyes is also higher than that of the modified PET/W blend.

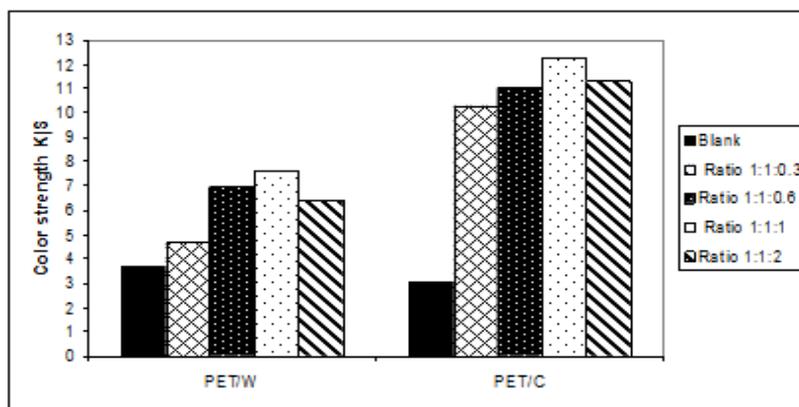


Fig. 15. Color strength of modified, screen printed * blend fabrics with acid hydrolyzed GPTMS using different molar ratio; * Using acid red 24.

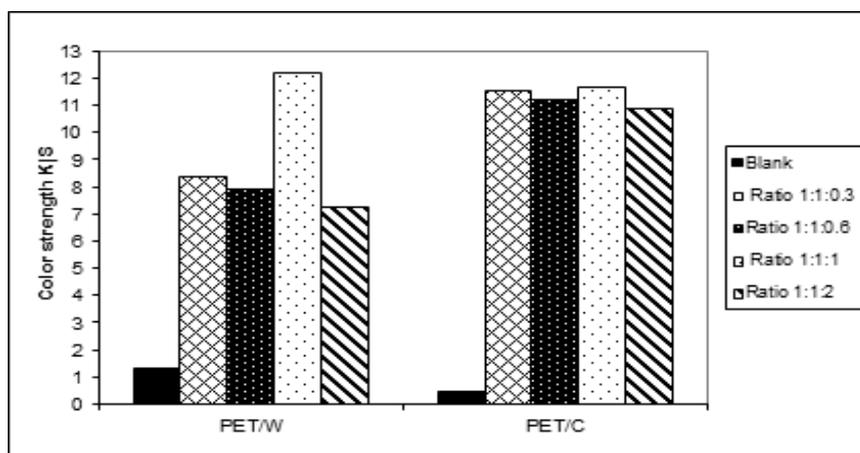


Fig. 16. Color strength of modified, screen printed * blend fabrics with acid hydrolyzed GPTMS using different molar ratio; * Using acid blue 18.

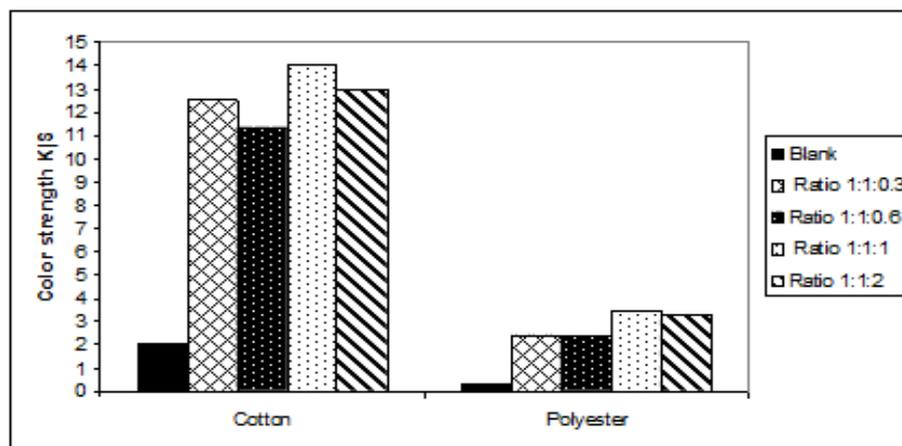


Fig. 17. Color strength of modified, screen printed * single fabrics with acid hydrolyzed GPTMS using different molar ratio; * Using acid red 24.

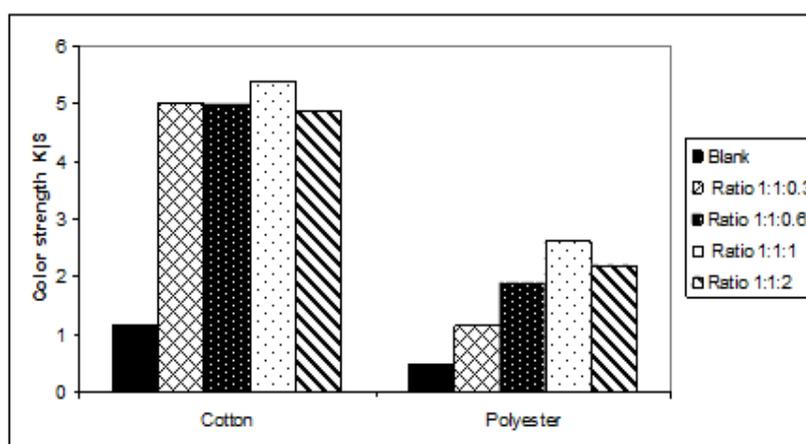


Fig. 18. Color strength of modified, screen printed * single fabrics with acid hydrolyzed GPTMS using different molar ratio; * Using acid blue 18.

Reactive dyes

The same aforementioned reactive dyes, reactive red 24 and reactive blue 81 were used to print modified PET/W and PET/C fabrics as well as polyester and cotton fabrics with GPTMS. The color strength results of screen printed modified blend fabrics with acid hydrolyzed GPTMS using different reactant molar ratio are represented by Figs (19, 20). The results show that, the modification of PET/W and PET/C fabrics increased their prints color strength as compared to their unmodified fabrics, although, the effect is relative and not as high as in the case using acid dyes for printing since the unmodified cotton and wool components of the fabrics already possess affinity for the reactive dyes for e.g. reactive dyes react with cellulose through covalent bonds. Consequently the prints of the unmodified blend fabrics possess notable color strength values. The above behavior applies for both reactive dyes used and at any reactant molar ratio used. As found before, a reactant molar ratio of 1:1:1 is the selected ratio for further work. Definitely, the dye chemical structure and the presence of reactive groups in the structure

would greatly affect their behavior towards the modified PET/W and PET/C blends.

The color strength of screen printed modified cotton and polyester fabrics with acid hydrolyzed GPTMS using different reactants molar ratio and the two aforementioned reactive dyes are represented by Figs (21,22). Substantially high color strength values are obtained for the unmodified cotton fabrics in addition to further improvement in the color yield due to the modification especially with a reactant molar ratio of 1:1:1 for prints of the two reactive dyes. The unmodified polyester fabrics acquired much lower color strength values. This means that, the improvement in the color strength of the modified polyester prints is solely due to the modification by the sol-gel technique for both dyes and at any reactant molar ratio. In the following section, experimental work on the sol-gel process under base catalyzed conditions using the selected reactant molar ratio of 1:1:1 for the two precursors APTES and GPTMS will be conducted, since not enough systematic studies on the effects of the type of catalysts in the sol-gel process are available.

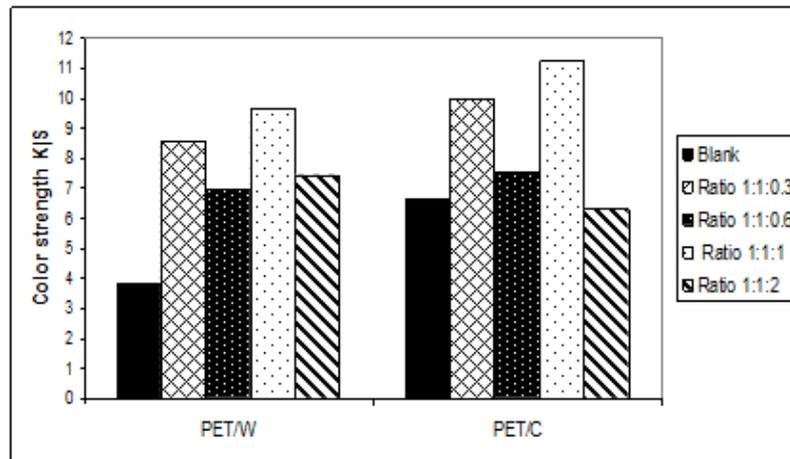


Fig. 19. Color strength of modified, screen printed * blend fabrics with acid hydrolyzed GPTMS using different molar ratio; * Using reactive red 24.

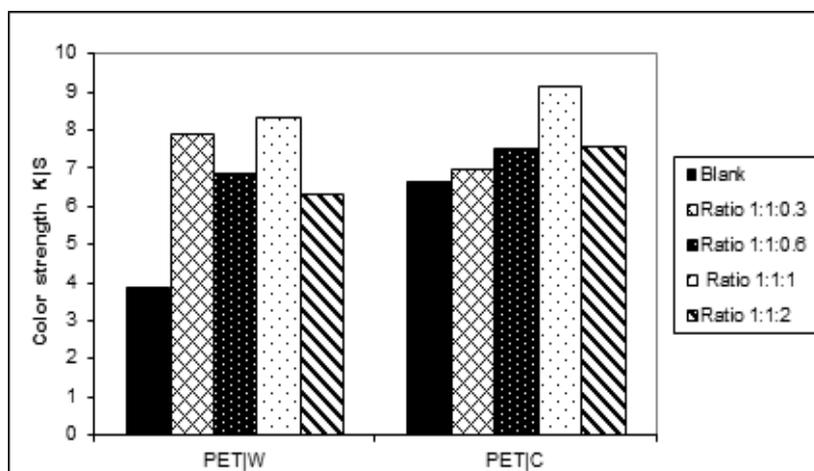


Fig. 20. Color strength of modified, screen printed * blend fabrics with acid hydrolyzed GPTMS using different molar ratio; * Using reactive blue 81.

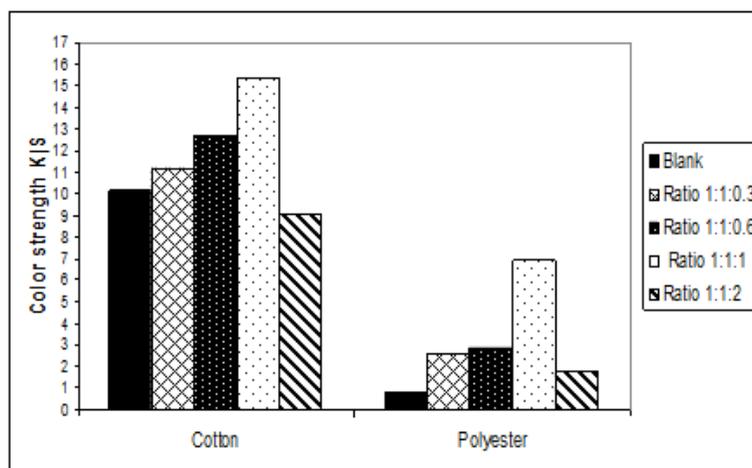


Fig. 21. Color strength of modified, screen printed * single fabrics with acid hydrolyzed GPTMS using different molar ratio; * Using reactive red 24.

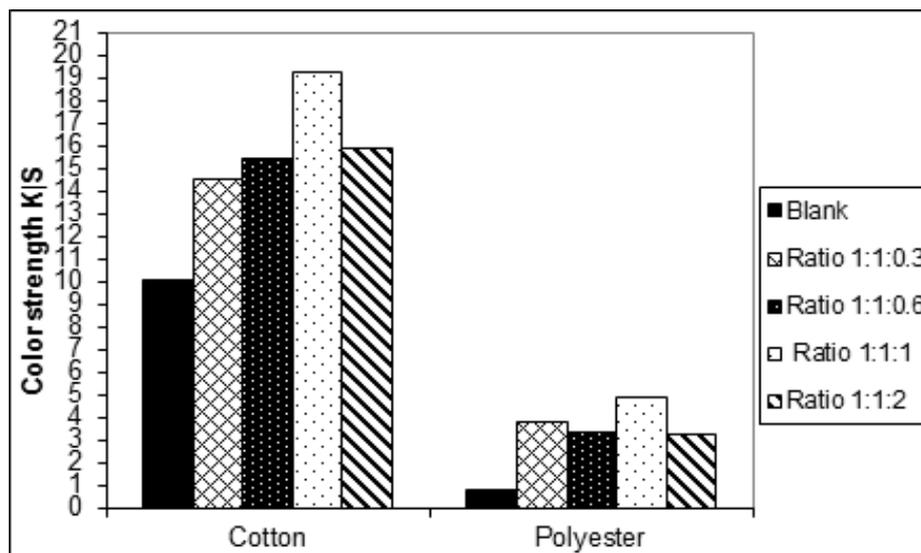


Fig. 22. Color strength of modified, screen printed * single fabrics with acid hydrolyzed GPTMS using different molar ratio; * Using reactive blue 81.

PH condition parameters

It is worthwhile to study the behavior of the two previously used precursors APTES and GPTMS when used to modify PET/W and PET/C as well as cotton and polyester fabrics under basic catalysis conditions using the selected molar ratio of 1:1:1 (precursor: Alcohol: water) using (acid blue 18 and reactive blue 81) dyes as examples. For the sake of comparison, the color strength results of screen printed, modified blend fabrics with both acid and base hydrolyzed APTES and GPTMS using a molar ratio 1:1:1 with acid blue 18 and reactive blue 81 dyes are represented by Figs (23, 24) and (25, 26) respectively. It can be concluded that a general trend is noticed in this case, whether using acid blue 18 or reactive blue 81 dyes that the prints of PET/W, PET/C, cotton and polyester modified fabrics with base hydrolyzed APTES and GPTMS possess always higher color strength values as compared with the corresponding ones modified with acid hydrolyzed APTES and GPTMS. Also modification with APTES produced prints with higher color strength values than the prints of modified fabrics with GPTMS to a certain extent. The prints of modified PET/C and cotton possess higher K/S values when compared to those of the corresponding modified PET/W and polyester fabrics. This is due to the high affinity of cotton component to reactive dyes Figs (25, 26)

The overall results show that, in the sol-gel process the reaction of metal alkoxides and water under acid or base catalysis conditions, forms one

phase solution which subsequently goes through a solution-to gel transition forming a liquid two-phase system comprising of solvent filled pores and solid metal alkoxide. It can be seen that, acid hydrolysis results in weakly cross-linked linear polymers. Formation of additional branches due to entangling of these polymers leads to gelation. Under base conditions, rapid hydrolysis and condensation of the silane precursor's results in forming highly branched clusters. An explanation for this behavior is due to that, silicon oxide is more soluble in alkaline medium than acid medium favoring the inter-linking of silica cluster Fig. (27) [8]. The physical and chemical properties of the produced coating depend largely on the type of catalyst used.

It is also noticed that, during the surface modification of the different fabrics (blends or single fabrics) by the sol-gel method, a nanocomposite dense polymer film is formed on their surfaces. This film thickness is about 10 nm. Another occurring reaction is that of the silanol-SiOH groups of precursors which can possibly react with fiber surfaces forming hydrogen, as well as covalent bonds. Covalent bonds formed between the precursors Si-OH group and the substrate hydroxyl group in the condensation reaction is responsible for increasing the adhesion of the polymer film to the fabric and also improves polymer film orientation [9]. Silicon alkoxides precursors ($\text{Si}(\text{OR})_4$) include reactive alkoxide groups (-OR). They are a class of hybrid organic-

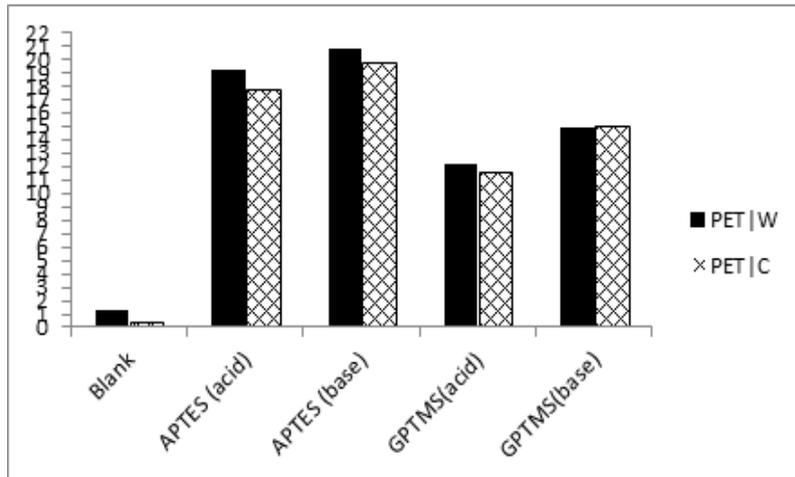


Fig. 23. Comparison of color strength of modified, screen printed * blend fabrics with acid or base hydrolyzed APTES and GPTMS respectively using (1:1:1) molar ratio; * Using acid blue 18.

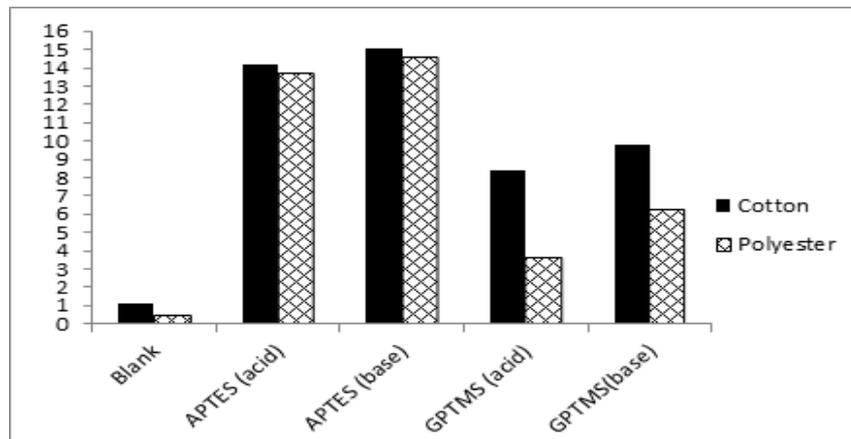


Fig. 24. Comparison of color strength of modified, screen printed * single fabrics with acid or base hydrolyzed APTES and GPTMS respectively using (1:1:1) molar ratio; * Using acid blue 18.

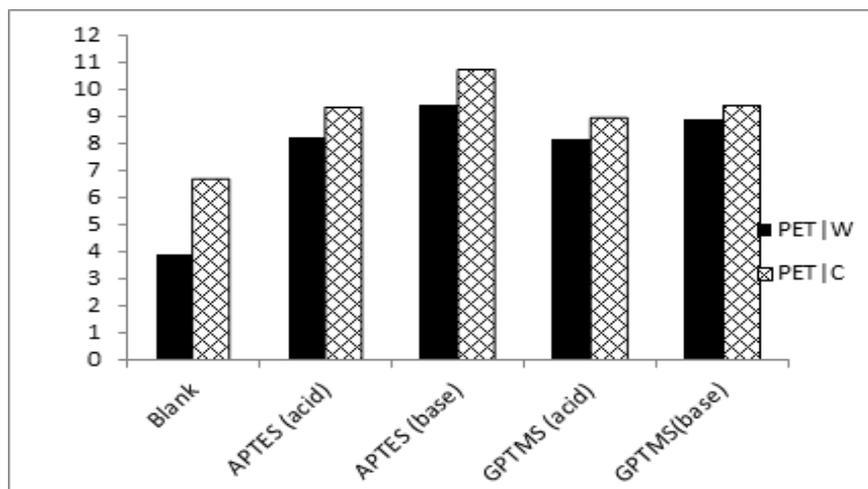


Fig. 25. Comparison of color strength of modified, screen printed * blend fabrics with acid or base hydrolyzed APTES and GPTMS respectively using (1:1:1) molar ratio; * Using reactive blue 81.

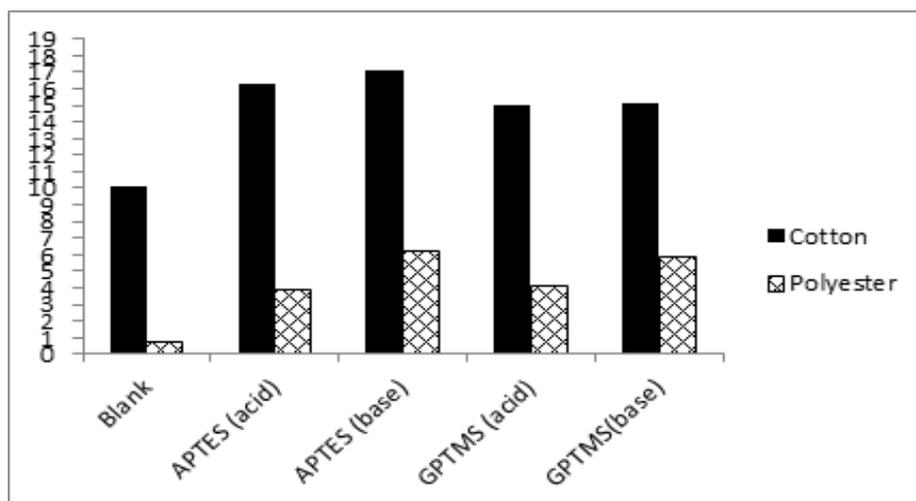


Fig. 26. Comparison of color strength of modified, screen printed * single fabrics with acid or base hydrolyzed APTES and GPTMS respectively using (1:1:1) molar ratio; * Using reactive blue 81.



Fig. 27. AB cartoon showing linear weakly cross-linked and highly branched clusters;

A: acid catalyzed; B: base catalyzed hydrolysis.

inorganic materials able of forming a network of the polymer films with high level of chemical functionality. The produced films possess elasticity of polymer and hardness of ceramic. The very thin polymer film produced, does not harm the physical properties of the fabrics e.g. softness, elasticity and tensile strength. The polymer film does not penetrate between the fibers pores, i.e. keeping the textile breathability, which is very important. Numerous applications for the hybrid organic-inorganic precursors in the textile field (in addition to coloration improvement) are in the field of finishing (hydrophobicity, UV protection, antibacterial activity and electrical conductivity). Combination of different precursors leads to textile with multifunctional properties. Further work could be directed towards more research in the above fields.

4. Fastness properties

The fastness properties of unmodified and modified, screen printed PET/W and PET/C fabrics with acid and base hydrolyzed APTES and GPTMS using acid dyes as well as reactive dyes are represented by Tables VIII, IX, and Tables X and XI respectively. The fastness properties of unmodified and modified screen printed cotton fabrics with acid and base hydrolyzed APTES and GPTMS using acid dyes as well as reactive dyes are represented by Tables XII, XIII respectively.

In general, the fastness properties of all the modified and printed blends PET/W, PET/C, cotton fabrics range from good to excellent ratings with all classes of dyes used as compared to the corresponding values for unmodified and printed fabrics which range from moderate to very good in some cases.

TABLE 8. Fastness properties of unmodified *and modified (silk screen printed **PET|W) with acid and base hydrolyzed APTES and GPTMS respectively.

Dye	Catalyst	Silane type	Rubbing fastness		Washing fastness		Perspiration fastness				Light fastness
			Dry	Wet	Alt	St	Alkali		Acid		
							Alt	St	Alt	St	
Reactive Red 24	Acid hydrolysis	APTES	5	5	5	5	5	5	5	5	4
		GPTMS	5	4-5	5	5	5	5	5	5	3
	Base hydrolysis	APTES	5	4-5	5	5	5	5	5	5	4-5
		GPTMS	4	4	5	5	5	5	5	5	4
Unmodified			3-4	4	4-5	4-5	4	4	4	4	3-4
Reactive Blue 18	Acid hydrolysis	APTES	4-5	4	5	5	5	5	5	5	4-5
		GPTMS	4	4	5	5	5	5	5	5	4
	Base hydrolysis	APTES	4	4	5	5	5	5	5	5	5
		GPTMS	4	3-4	5	5	5	5	5	5	3-4
Unmodified			3-4	3-4	4	4	3-4	4	3-4	4	3-4

* Unmodified printed fabrics.

** Using reactive red 24 and reactive blue 81

Steam fixation temperature 102 °C, Fixation time 20 min.

TABLE 9. Fastness properties of unmodified *and modified (silk screen printed **PET|W) with acid and base hydrolyzed APTES and GPTMS, respectively.

Dye	Catalyst	Silane type	Rubbing fastness		Washing fastness		Perspiration fastness				Light fastness
			Dry	Wet	Alt	St	Alkali		Acid		
							Alt	St	Alt	St	
Reactive red 24	Acid hydrolysis	APTES	3-4	3-4	5	5	5	5	5	5	5-6
		GPTMS	4	3	5	5	5	5	5	5	5
	Base hydrolysis	APTES	4	4	5	5	5	5	5	5	5
		GPTMS	3-4	3	5	5	5	5	5	5	5
Unmodified			2-3	2	4	3	2-3	4	3-4	4	4
Reactive Blue 81	Acid hydrolysis	APTES	4	4	5	5	5	5	5	5	5
		GPTMS	4-5	4	5	5	5	5	5	5	5
	Base hydrolysis	APTES	3-4	3	5	5	5	5	5	5	4
		GPTMS	4	2-3	5	5	5	5	5	5	5
Unmodified			2-3	2-3	3-4	3	3-4	4	4	3-4	3-4

* Unmodified printed fabrics.

** Using reactive red 24 and reactive blue 81.

Steam fixation temperature 102 °C, Fixation time 20 min.

TABLE 10. fastness properties of unmodified *and modified (silk screen printed **PET|C) with acid and base hydrolyzed APTES and GPTMS, respectively.

Dye	Catalyst	Silane type	Rubbing fastness		Washing fastness		Perspiration fastness				Light fastness
			Dry	Wet	Alt	St	Alkali		Acid		
							Alt	St	Alt	St	
Acid Red 24	Acid hydrolysis	APTES	4	3-4	5	5	5	5	5	5	4
		GPTMS	5	4-5	5	5	5	5	5	5	3-4
	Base hydrolysis	APTES	4	4	5	5	5	5	5	5	3-4
		GPTMS	4	3-4	5	5	5	5	5	5	4
Unmodified			3	2-3	4	3-4	4	4	3-4	4	3
Acid Blue 18	Acid hydrolysis	APTES	4-5	4	5	5	5	5	5	5	4
		GPTMS	5	4	5	5	5	5	5	5	4-5
	Base hydrolysis	APTES	4	4	5	5	5	5	5	5	3
		GPTMS	4	3-4	5	5	5	5	5	5	4
Unmodified			2	2	3	3	3	3	3	3	2

* Unmodified printed fabrics.

** Using acid red 24 and acid blue 18.

Steam fixation temperature 102 °C. fixation time 20 min.

TABLE 11. Fastness properties of unmodified *and modified (silk screen printed **PET|C) with acid and base hydrolyzed APTES and GPTMS, respectively.

Dye	Catalyst	Silane type	Rubbing fastness		Washing fastness		Perspiration fastness				Light fastness
			Dry	Wet	Alt	St	Alkali		Acid		
							Alt	St	Alt	St	
Reactive Red 24	Acid hydrolysis	APTES	4-5	4	5	5	5	5	5	5	4-5
		GPTMS	5	4	5	5	5	5	5	5	5
	Base hydrolysis	APTES	5	4-5	5	5	5	5	5	5	5
		GPTMS	4	3-4	5	5	5	5	5	5	5
Unmodified			3-4	3	4	4	3-4	4	2-3	4	4
Reactive Blue 81	Acid hydrolysis	APTES	4	4	5	5	5	5	5	5	3-4
		GPTMS	5	4	5	5	5	5	5	5	6
	Base hydrolysis	APTES	3	2-3	5	5	5	5	5	5	5
		GPTMS	4-5	3-4	5	5	5	5	5	5	5
Unmodified			4	4	4	4	4	4	3-4	3	3-4

* Unmodified printed fabrics.

** Using reactive red 24 and reactive blue 81.

Steam fixation temperature 102 °C, Fixation time 20 min.

TABLE 12. Fastness properties of unmodified *and modified (silk screen printed **Cotton) with acid and base hydrolyzed APTES and GPTMS, respectively.

Dye	Catalyst	Silane type	Rubbing		Washing fastness		Perspiration fastness				Light fastness
			Dry	Wet	Alt	St	Alkali		Acid		
							Alt	St	Alt	St	
Acid Red 24	Acid hydrolysis	APTES	5	4-5	5	5	5	5	5	5	5
		GPTMS	5	4	5	5	5	5	5	5	4-5
	Base Hydrolysis	APTES	4	4	5	5	5	5	5	5	4
		GPTMS	4-5	4	5	5	5	5	5	5	5
Unmodified			3	2-3	3-4	3-4	3	2-3	4	3-4	3
Acid Blue 18	Acid hydrolysis	APTES	4	4	5	5	5	5	5	5	4
		GPTMS	5	5	5	5	5	5	5	5	3
	Base Hydrolysis	APTES	4	4	5	5	5	5	5	5	4
		GPTMS	3-4	3	5	5	5	5	5	5	3-4
Unmodified			2-3	2-3	2-3	3	3	3	3-4	3	2-3

* Unmodified printed fabrics.

** Using acid red 24 and acid blue 18.

Steam fixation temperature 102 °C, fixation time 20 min.

TABLE 13. Fastness properties of unmodified *and modified (silk screen printed **Cotton) with acid and base hydrolyzed APTES and GPTMS, respectively.

Dye	Catalyst	Silane type	Rubbing fastness		Washing fastness		Perspiration fastness				Light fastness
			Dry	Wet	Alt	St	Alkali		Acid		
							Alt	St	Alt	St	
Reactive Red 24	Acid hydrolysis	APTES	5	5	5	5	5	5	5	5	4
		GPTMS	5	4-5	5	5	5	5	5	5	3
	Base hydrolysis	APTES	5	4-5	5	5	5	5	5	5	4-5
		GPTMS	4	4	5	5	5	5	5	5	4
Unmodified			3-4	4	4-5	4-5	4	4	4	4	3-4
Reactive Blue 18	Acid hydrolysis	APTES	4-5	4	5	5	5	5	5	5	4-5
		GPTMS	4	4	5	5	5	5	5	5	4
	Base hydrolysis	APTES	4	4	5	5	5	5	5	5	5
		GPTMS	4	3-4	5	5	5	5	5	5	3-4
Unmodified			3-4	3-4	4	4	3-4	4	3-4	4	3-4

* Unmodified printed fabrics.

** Using reactive red 24 and reactive blue 81

Steam fixation temperature 102 °C, Fixation time 20 min.

Conclusion

In this work, concept was used for fabric modification; film coating with silica nanosol. The surface morphology of the modified fabrics was characterized by FTIR spectra, X-ray photoelectron spectroscopy, and contact angle and scanning electron microscopy. The FTIR spectra were not able to detect the changes occurred on the modified fabrics clearly this is due to the very thin film produced on the fabrics. Further investigation, using another surface sensitive technique XPS clarified surface changes occurring due to modification using base hydrolyzed APTES which proved that, the surface chemical changes resulting from the sol-gel treatment are confined to a very thin surface layer. The results of contact angle measurements indicated that, the hydrophobicity of the modified fabrics increased due to the treatment. The SEM images of the unmodified and modified PET/W and PET/C fabrics showed uniform coatings on the modified fabrics surfaces. These coating layers are expected to help in rendering the dye molecules attachable to the modified fabrics whether the surface modification is conducted either by silica sol. Acid hydrolyzed APTES and GPTMS were used to modify PET/W, PET/C, cotton and polyester fabric surfaces using different molar reactants ratio of (precursor: Alcohol: water) (1:1:0.3 - 1:1:0.6 - 1:1:1 and 1:1:2) and further printing of the modified fabrics with acid & reactive dyes. The modification treatment with acid hydrolyzed APTES and GPTMS rendered the blend fabrics acceptable to the anionic dyes. The only variable in selecting different molar reactants ratio is the water content, and the variations in results seem to be not remarkable in the range selected. A reactant molar ratio of 1:1:1 (precursor: Alcohol: water) is considered favorable. Base hydrolyzed APTES and GPTMS were used to modify PET/W, PET/C, cotton and polyester fabric surfaces with reactant molar ratio of 1:1:1. The modified fabrics were subsequently printed with acid and reactive dyes. The modification produced prints with much higher color strength values compared to the unmodified fabrics in some cases. For the sake of comparison, the color strength results of screen printed modified blend fabrics with both acid and base hydrolyzed APTES and GPTMS using a molar ratio of 1:1:1 with acid blue 18 and reactive blue 81 dyes were studied. The results trend showed that, modifications with base hydrolyzed precursors APTES and GPTMS produced prints with higher color strength values as compared

with the corresponding modified fabrics with acid hydrolyzed APTES and GPTMS. Modification with APTES produced prints with higher color strength values than prints of modified fabrics with GPTMS to a certain extent. Since under base conditions, rapid hydrolysis and condensation of the silane precursors occurs resulting in formation of highly branched clusters.

References

1. Milea. C.A, Bogartu. C., Duta. A., "The influence of parameters in silica sol-gel process", Vol. 4 (53), No. 1, (2011).
2. John. A., Howarter and Jeffrey. P., Youngblood," Surface Modification of Polymers with 3-Aminopropyltriethoxysilane as a General Pretreatment for Controlled Wettability", *J Macromolecules*, Vol. 40, p.1128-1132 (2007).
3. POPE. E. j. A., and J.D, MACKENIE, *J Non-Cryst solids*, Vol. 87 (185), (1986).
4. Sharma. G, Singh. G, "Sol-Gel processing of silica nanoparticles and their applications", *Advances in Colloid and Interface Science*, p. 50, (2014).
5. Gündüz. B., Cavas. M., Yakuphanoglu. F., "Quality controlling of SiO₂ Thin films by Sol Gel Method", 6 th International Advanced Technology Symposium, p. 16-18, (2011).
6. Elhadad. Sh, master thesis "Synthesis of some heterocyclic azo dyes and their application in printing of synthetic fabrics", university of Applied Arts, p. 62-63, (2011).
7. Colth. N.B., Daly. L.H., Wiberley S.E., "Introduction to Infrared Spectroscopy", 3rd ed., Academic, (1990).
8. Nogami. M., and Nagasaka K., *J Non-Cryst solids*, Vol. 122, p. 101, (1990).
9. Barbara. S, Brigita. T, Boris. O& Ivan. J, "Sol-gel Technology for Chemical Modification of Textiles "Department of Textiles, Faculty of Natural Sciences and Engineering, University of Ljubljana, National Institute of Chemistry, Ljubljana, Slovenia,p.4.

(Received 26 / 5 / 2020 ;
accepted 9 / 6 / 2020)

طباعة الأقمشة المعدلة باستخدام صبغات أيونية

مديحة القشوتي وطارق سالم وحنان الصياد وشيما صلاح الدين محمد الحداد

قسم الصباغة والطباعة والمواد الوسيطة ، شعبة بحوث الصناعات النسيجية ، المركز القومي للبحوث ، الدقي ، القاهرة 12622 ، مصر.

نهج مختلف هو باستخدام تقنية هلام هلام لتعديل سطح الأقمشة الممزوجة لجعلها قابلة للصبغة مع فئة واحدة من الأصباغ على سبيل المثال الأصباغ الأيونية ، الأيونية والوظيفية. تتضمن تقنية sol-gel تكوين أطوار معدنية ، بدءاً من السلائف الجزيئية ، بعد تفاعل البلمرة غير العضوي. عادة ما يكون التفاعل في درجة حرارة الغرفة في الماء أو المذيبات ومجموعة مختلفة من ظروف الأس الهيدروجيني. تتكون الخطوة الأولى في عملية هلام هلام السيليكا من التحلل المائي لألكوكسيدات السليكون ، ثم التكتيف الذي يشكل الجسيمات النانوية للسيليكا واعتماداً على ظروف التفاعل ، يمكن أن تنمو هذه الجسيمات وتشكل محلول Sol الذي يمكن ترسيبه على سطح الركيزة فيلم. في هذا القسم ، تم استخدام سلائف السيلان لتعديل PET / W ، PET / C ، الأقمشة القطنية والبوليستر عبر طلاء الفيلم مع نانوسول.