



An approach for vat color printing on cotton and polyester fabrics with electron beam irradiation curable formulations

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ABSTRACT

Accelerated electrons delivered by electron beam accelerator were used to fix vat colors, incorporated in curable formulations containing diluting monomer and an oligomer, to cellulosic fabric, cotton and polyester fabric. Tetrahydrofurfuryl acrylate, hexane dioldiacrylate, monomers and trifunctional urethane methacrylate, oligomer were used as curable base beside ethylene glycol. The fabrics were printed with these formulations and exposed to various doses of electron beam irradiation generated from the 1.5 MeV (25 kW) electron beam accelerator machine. Critical factors included the irradiation dose, formulation composition, and vat color concentration were studied. The fabrics printed with the vat colors by electron beam irradiation displayed higher color yield than those fabrics printed by the conventional curing at equal vat color ratios. The durable properties of fabrics printed by electron beam irradiation except the roughness properties are extremely better than those printed by conventional fixation method.

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1. Introduction

Cotton and cellulose fibres are still very important textile fibres. They are used worldwide and their consumption is increasing since years and reached a peak in 2010 (Mojca & Vanja, 2008). At present, there is no true alternative to vat dyes (Nahr & Ruppert, 1991), although the total number of vat dyes on the market has drastically diminished (Baumgarte, 1987). The light and wet fastness of reactive dyes as the actual alternative has not yet reached the level of anthraquinone vat dyes invented a century ago (Hihara, Okada, & Morita, 2002). In the coloration of cellulose fibres, vat dyes still represent a relatively large part of the dyestuff market (about 11%); among them about 120 000 tons of vat dyes are being used annually (Roessler, Crettenand, Dossenbach, Marte, & Rys, 2002). It seems that the situation will remain constant also in the near future mainly because vat dyes yield colored cellulosic fibres of excellent all-round fastness, particularly to light, washing and chlorine bleaching.

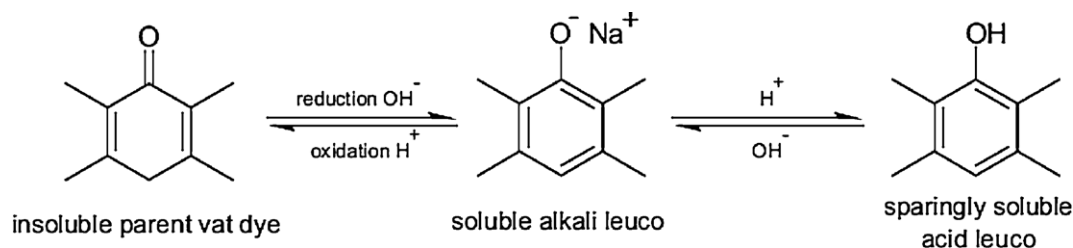
However, vat dye require a complicated application procedure (reduction and oxidation mechanisms) because they are practically

insoluble in water and have no affinity for cellulose fibres in such a state (Bozic & Kokol, 2008).

Vat dyes are used for printing fabrics of cellulose and protein fibres. The dyes contain at least two conjugated carbonyl groups which during their conventional application to cellulosic fibres, are converted by reduction under alkaline conditions to the corresponding, water soluble (Burkinshaw, Brown, & Mod, 1999), 'alkali leuco' form which is applied to the substrate. At the end of dyeing, the alkali leuco form is oxidized, so as to regenerate the insoluble, parent vat dye in situ within the fibre (Burkinshaw & Son, 2010) (Scheme 1).

In conventional vat-dyeing processes, the dye is reduced in a high alkaline medium (pH 11–14) using powerful reducing agents among which sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) is of major importance. To be practically useful, solutions of a vat dye reducing agent must have a level of reducing power (Aspland, 1997) (reduction potential) sufficient to reduce all commercial vat dyes to their water-soluble forms, economically and quickly (Bozic & Kokol, 2008). The quantity of reducing agent is determined by the chemical structure and nature of the particular dye (number of reducible groups, relative molecular mass, and content of the pure dye), the specific surface area of the dye liquor, the temperature of the dye liquor, the agitation of the liquor, and the amount of air present in the dyeing process. Attempts are being made to replace the environmentally unfavourable sodium dithionite by ecologically more

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Scheme 1. Reduction/oxidation of vat dyes.

attractive alternatives (Bozic & Kokol, 2008; Polenov, Pushkina, Budanov, & Khilinskaya, 2001).

The printing of cellulosic fibres with vat dyes however depends on several conditions such as, the drying after printing, the storage prior treatment in the steamer, the duration time in the steamer, the temperature and moisture content in the steamer, washing conditions and oxidizing agents used. These entire difficulties make the process of color formation of vat dyes on the cellulosic fabrics is difficult and complicated.

Radiation curing by electron beam has become a well-accepted technology, which has found a large number of industrial applications mainly in the coating and printing fields (Sherzer & Decker, 2000). It allows the rapid conversion of especially formulated 100% reactive liquids to solids. Initiation by electrons leads to free radical or cationic polymerization and crosslinking (Knolle & Mehnert, 1995). The radiation process is a green technology and offer significant advantages over the thermal process: No solvent release, reduction of the energy consumption and only moderate temperature increase during curing (Mehnert, Naumov, Knolle, & Janovský, 2000). The formulation to be cured or crosslinked by electron beam irradiation which usually contains unsaturated monomers (e.g., vinyl pyrillidone, tetrahydrofurfuryl acrylate, and acrylic acid derivatives), oligomers (e.g., polyurethane acrylates, polyester acrylates, and polyether acrylates as well as epoxy acrylates), and other additives according to the desired properties (Mehnert et al., 2000). Pigment printing with a formulation containing only pigment and reactive chemicals that can be cured rapidly at room temperature by electron beam or ultraviolet radiation is an attractive possibility. Primarily due to the elimination of water and solvents and the roughly 90% reduction in energy needed to evaporate them and cure the conventional binders in addition to the high production rates and smaller space requirements (Abdou, Hakeim, El-Gammal, & El-Naggar, 2009).

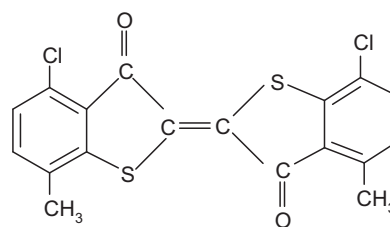
Accelerated electrons delivered by electron beam accelerator were used to fix pigment colors, incorporated in curable formulation containing diluting monomer and an oligomer, to cotton and polyester fabrics. The results showed that cotton and polyester fabrics printed with the pigment colors by electron beam irradiation displayed higher color strength than those fabrics printed by the conventional thermal curing at equal pigment color ratios depending on the kind of pigment color (Abdou et al., 2009).

The major objective of the present work is to avoid the difficulties and complicated processes of the conventional vat color printing by using electron beam irradiation as an alternative fixation tool of vat dyes on cotton and polyester fabrics using radiation curable formulations free from reducing agent and thickener. So far, there have not been any papers published on printing of vat dyes with electron beam irradiation curable formulations. These formulations contain only monomers (tetrahydrofurfuryl acrylate or hexane dioldiacrylate), oligomers (trifunctional urethane methacrylate) and vat dyes. A comparative study will be conducted between the prints by electron beam irradiation and steaming fixation in term of color measurements, and durability properties.

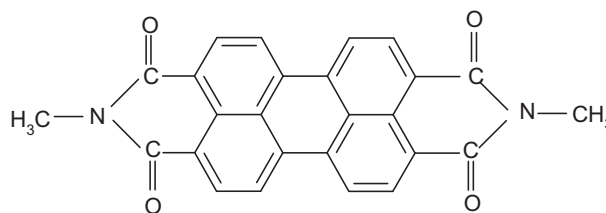
2. Experimental

2.1. Materials

Cotton and polyester fabrics used in this work were received from Misr spinning and weaving, Mehalla El-Kobrra. These fabrics were scoured, bleached, and mercerized, in which cotton fabric was 153 g/m² and polyester fabric was 215 g/m². The size of sample used for electron beam curing was 5 cm × 10 cm. The vat dyes used were kindly supplied by Dystar Co. These dyes are Indanthren Violet RRN (C.I. Vat Violet 3) and Indanthren. Red FGL (C.I. Vat red 23). The chemical structures of these dyes are shown in Scheme 2. The vat colors were fixed on the textile surfaces by incorporating in electron beam curable formulations containing an oligomer and monomer. The oligomer used in this study was trifunctional urethane methacrylate (TFUMA), produced by Bomar Specialist Co., USA, while the diluting monomers were tetrahydrofurfuryl acrylate monomer (THFA) furnished by Sigma Co., Germany and hexane dioldiacrylate (HDDA) produced by UCB Specialist Co., Belgium. Ethylene glycol was purchased from Merck, Germany. The commercial carboxymethyl cellulose (CMC) was supplied by Sichelnesp Scholten, Netherlands and sodium alginate (HV) purchased by Macrocystis pyrifera (Kelp) SIGMA Chemical Co., Germany, were used as a mixture thickening agents in the conventional vat printing by steaming fixation method. Sodium sulfoxylate formaldehyde (Rongalite C) was kindly supplied by BASF.



C.I. Vat Violet 3 (Indanthren Violet RRN)



C.I. Vat red 23 (Indanthren Red FGL)

Scheme 2. Chemical structures of vat dyes.

2.2. Vat printing by electron beam irradiation

The formulations for electron beam curing were prepared by dispersing the vat dyes in the appropriate monomers (tetrahydrofurfuryl acrylate monomer or hexane dioldiacrylate monomer) with high shear polytron homogenizer. This dispersion was then stirred into molten oligomer (trifunctional urethane acrylate oligomer) and mixed, after which ethylene glycol was added with continuous stirring until complete homogeneity. The printing of vat dye with electron beam formulations was carried out according to the following ratio:

Monomer/oligomer formulation	25/75
Ethylene glycol	2.5

Total	100
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Printing was carried out on the surface of the fabrics with a floating coater with a thickness of 25 μm . The printed fabrics were exposed to accelerated electrons using the electron beam accelerator facility of the National Center for Radiation Research and Technology (1.5 MeV and 25 kW), Nasr City, Cairo, Egypt. The required doses were obtained by adjusting the electron parameters and conveyor speed. The printed fabrics were washed by boiling for 5 min in an aqueous solution containing 2 g/L of detergent (Synperonic BD). Finally, the fabrics were rinsed in cold water and air dried.

2.3. Vat printing by conventional method

The printing with vat dyes involves the preparation of stock thickening agent and then incorporating thickening agent in the printing paste according to the following recipes:

Stock thickening:	
Potassium carbonates	160 g
Sodium sulfoxalate formaldehyde (Ronalite C)	125 g
Glycerin	60 g
Thickening agents ^a	X g
Water	Y g
Total	1000

^a The thickening agents were a mixture of sodium alginate (25 g) and CMC (40 g).

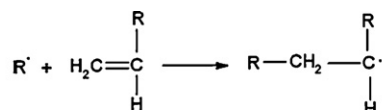
Printing paste:	
Indanthren Violet RRN or Red FGL (vat dyes)	30, 50, 75 g
Stock thickening	800 g
Water	X g
Total	1000

The printing pastes were applied to fabrics through a flat silk screen. After drying, the printed fabrics were subjected to free steam air at 102 °C for 10 min. Then the fabrics were rinsed with cold water to remove the thickening agents and alkali and to oxidize the vat dye. After oxidation, the fabrics were boiled for 5 min in an aqueous solution containing 2 g/L of detergent (Synperonic BD) and sodium carbonate (1 g/L). Finally, the fabrics were rinsed in cold water and air dried.

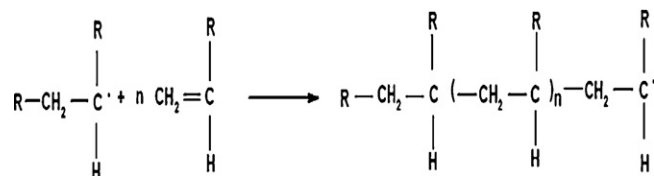
2.4. Measurements and analysis

2.4.1. Color measurements (ΔE)

A microcolor unit manufactured by Dr. Bruno Lang GmbH, Königsweg 10, D-1000, Berlin, Germany, was used for color measurements. The L^* , a^* , b^* system used throughout this work is based on the CIE-color triangle (Commission Internationale de E'claire units X, Y, Z). In this system, the L^* value represents the dark-white axis, a^* represents the green-red axis while the b^* represents the blue-yellow axis (Judd & Wyszecki, 1975). The L^* , a^* , and b^* values of control and printed fabrics with the different methods were measured and the color difference ΔE^* which was used as a reference



Initiation (oligomer or monomer)



Propagation



Termination by coupling

Scheme 3. Mechanism of radical polymerization.

for color yield of the printed fabrics was determined as follows and expressed as color difference:

$$\Delta E^* = \{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\}^{1/2}.$$

2.4.2. Surface roughness

The surface roughness of the printed samples was measured by surface roughness measuring instrument SE 1770X, Kostaka Lab, Company.

2.4.3. Fastness properties

The color fastness to crocking and perspiration was determined according to AATCC 8-1993 (West, 1981). Washing fastness tests were carried out according to BS1006: C02 Test 2 with a soap solution (5 g/L, liquor ratio = 50:1) for 45 min at 48–50 °C (Achwall, 1985).

3. Results and discussion

3.1. Vat dye printing on cotton and polyester fabrics by electron beam irradiation

Acrylates, methacrylates and their prepolymers (oligomers) show typical free radical addition polymerization. In free radical polymerization, a monomer or oligomer joins with a free radical and in effect, it forms a larger free radical that acts upon another monomer or oligomer and forms an even larger molecule, which is followed by coupling termination as it shown in the mechanism of a classical chain reaction in Scheme 3. The reactivity of monomers and oligomers towards electron beam curing, also, the compatibility between them in the formulation and the surface to be printed is very important factor, in this regard a preliminary experiments were conducted using various types of oligomers (e.g., epoxy acrylates, urethane acrylates, and acrylic acrylates) and monomers (e.g., tetrahydrofurfuryl acrylate and hexane dioldiacrylate). The screening experiments showed that TFUMA oligomer and THFA, HDDA, monomers are compatible with each other and to the surface of the cotton and polyester fabrics, they gave the desired properties of printing formulation in term of viscosity and stiffness, thus they became the application of choice. The radiation curable formulations used for printing vat dyes on cotton and polyester fabrics consist of tetrahydrofurfuryl acrylate monomer, trifunctional urethane methacrylate oligomer, ethylene glycol and

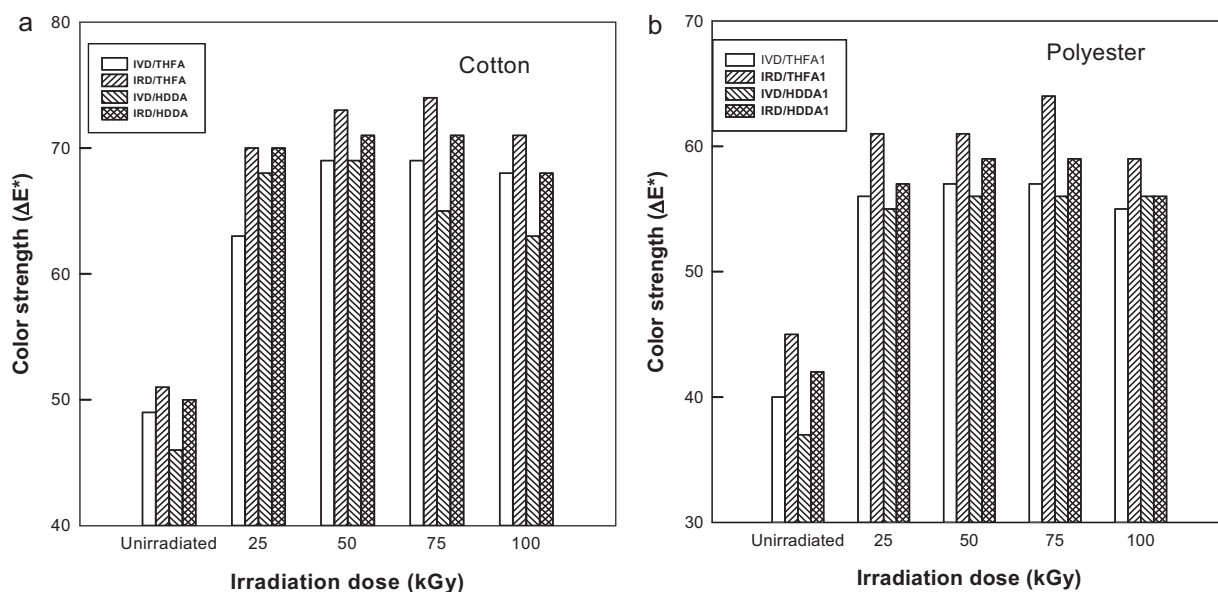


Fig. 1. Effect of irradiation dose on the color yield of (a) cotton fabrics and (b) polyester fabrics.

vat dyes. In addition, hexane dioldiacrylate monomer was used in this study, as a bifunctional monomer to study the reactivity and functionality of the monomer towards the durability properties of the cured prints by electron beam irradiation. These formulations cured (crosslinked) giving a solid film on the surface of the substrate by the action of accelerated electrons delivered from electron beam accelerator machine.

3.1.1. Effect of electron beam irradiation dose

Fig. 1(a) shows the effect of electron beam irradiation dose on the color yield of cotton fabrics printed with Indanthren violet and red vat dyes incorporated in two different formulations. The first contains tetrahydrofurfuryl acrylate monomer (THFA)/trifunctional urethane methacrylate oligomer (TFMUA) of (25/75 wt%) and the other one contains hexane dioldiacrylate monomer (HDDA)/trifunctional urethane methacrylate oligomer (TFMUA) of (25/75 wt%). It should be noted that all formulations

contain constant ratio of 5% of vat dyes and 2.5% of ethylene glycol. It can be seen that the color yield of the exposed fabrics to even a relatively low irradiation dose is much higher than the unirradiated fabrics (printed only with the formulation). Beside that the color yield of cotton fabrics printed with the Indanthren red dye is much higher than those printed with the violet dye at equal irradiation doses. However, there is no significant difference in the color yield of the printed cotton fabrics by the two different formulations that contain (THFA/TFUMA) or (HDDA/TFUMA). On the other hand, the effect of irradiation dose on the color yield of cotton fabrics printed with (HDDA/TFUMA) formulation is not significant, regardless of the kind of vat dyes. This trend may be explained based on the reactivity of HDDA monomer since it contains two acrylic groups, hence the formulation cured rapidly even at a relatively low irradiation doses. However, the color yield of cotton fabrics printed with (THFA/TFUMA) formulation was affected by the variation of electron beam irradiation dose. It increases constantly by increasing the

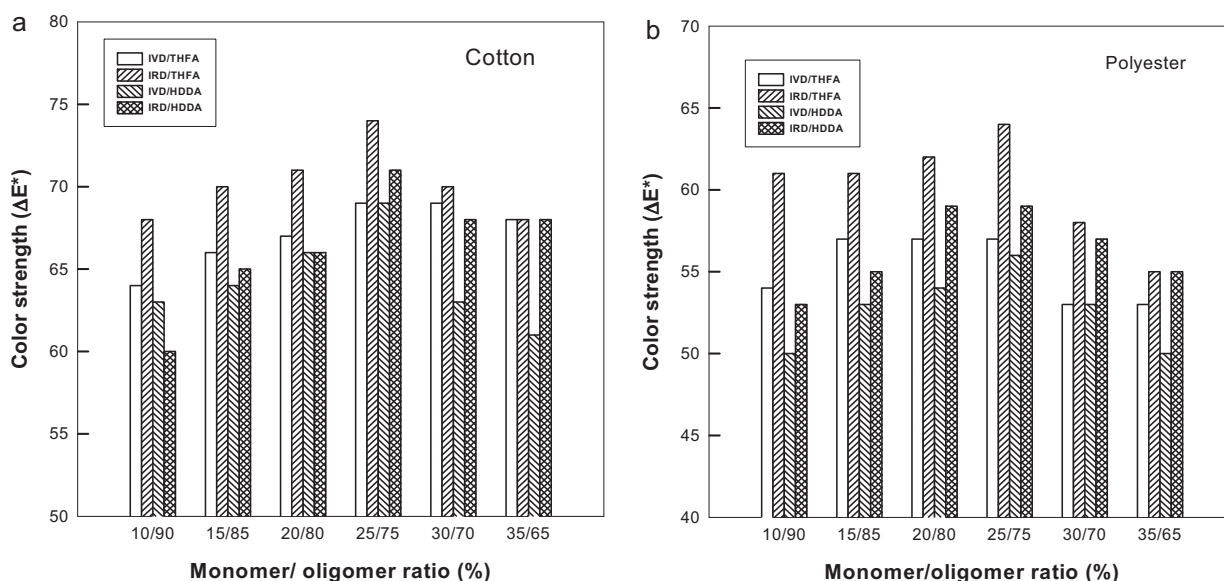


Fig. 2. Effect of monomer/oligomer ratio on the color yield of cotton and polyester fabrics.

irradiation dose, in which the dose of 75 kGy is the most effective dose at which the highest color yield was achieved for the red or violet vat dyes.

Fig. 1(b) shows the effect of electron beam irradiation dose on the color yield of polyester fabrics printed with Indanthren violet and red vat dyes incorporated in the same formulations as in the case of cotton fabrics. It should be noted that all the formulations contain a constant ratio of 5% of vat dyes and 2.5% of ethylene glycol. It can be seen that the color yield of the printed polyester fabrics with (THFA)/(TFMUA) formulation is slightly higher than the same fabrics printed with (HDDA)/(TFMUA) formulation, regardless the type of vat dyes. However, the color yield of the printed polyester fabrics with (HDDA)/(TFMUA) formulation does not depend on the irradiation dose. Generally, the irradiation dose of 75 kGy is still the most effective dose at which the highest color yield was achieved.

3.1.2. Effect of monomer/oligomer composition

Fig. 2(a) shows the effect of monomer/oligomer (THFA)/(TFMUA) and (HDDA)/(TFMUA) ratio on the color yield of cotton fabrics printed with different vat dyes. It should be noted that all the formulations contain a constant ratio of ethylene glycol of 2.5 wt% and the fabrics were exposed to a constant dose of 75 kGy of electron beam irradiation. It can be seen that the color yield of the printed cotton fabrics was found to increase with increasing the monomer ratio from 10 to 25% in the formulation, regardless the type of vat dyes or monomers used. This finding may be attributed to the increase of the rate of polymerization and crosslinking reactions by increasing the monomer ratio in the formulation. Beyond the ratio 25% of both THFA and HDDA monomers, a considerable drop in the color yield was observed. Generally, a composition of 25% of THFA or HDDA and 75% of TFUMA is the best mixture of monomer/oligomer ratio, which displayed the highest color yield in the case of all vat dyes.

Similar trends were observed in the case of the printing of polyester fabrics with the different monomer/oligomer ratio as shown in Fig. 2(b).

3.1.3. Effect of irradiation dose and vat dye ratio

The effect of electron beam irradiation dose and vat dye ratios on the color yield of the printed cotton fabrics with different vat dyes is shown in Fig. 3a and b. It should be noted that the printing was conducted with formulations containing constant ratio of 25% of THFA monomer and 75% of TFUMA oligomer.

It can be seen that the color yield of cotton fabrics printed with Indanthren violet dye is highly affected than that of the fabrics printed with the red vat dye by increasing the vat dye ratio. In this regard the increase in color yield of cotton fabrics printed with the violet vat dye resulted from the increase in the dye ratio from 3 to 5% and from 5 to 7.5% at the irradiation dose of 75 kGy was calculated to be ~17 and 3%, respectively. Also the increase in the color yield of cotton fabrics printed with the red vat dye resulted from the increase in the dye ratio from 3 to 5% and from 5 to 7.5% at the same irradiation dose was ~7 and 5% respectively.

From the above results, it can be concluded that the color yield of cotton fabrics printed with the violet vat dye at any irradiation dose displayed a relatively higher change by increasing the dye ratio from 3 to 5% than the printing with the red vat dye. However, the change of the color yield of the fabrics printed with the red vat dye from 5 to 7.5% is higher than in the case of the printing with the violet vat dye.

Similar trends were observed in the case of the printing of polyester fabrics with various ratios of the different vat dyes and exposed to various irradiation doses as shown in Fig. 3c and d. In this regard, the color yield of polyester fabrics printed with the violet vat dye at the dose of 75 kGy was increased by ~10 and 3.3% when the ratio was increased from 3 to 5% and from 5% to 7.5%,

respectively. The change in color yield of polyester fabrics printed by increasing the ratio from 3 to 5% and 5 to 7.5% of the red vat dye at the same dose of electron beam irradiation was calculated to be ~0 and 5%, respectively.

Based on the results in Figs. 1–3, few points may be concluded; (1) the process of color formation of vat dyes on cotton and polyester fabrics by electron beam irradiation is a pigmentation process, in which the electron beam irradiation is responsible for fixing the vat dyes in the curable formulation and converting the leuco form to the insoluble form through crosslinking and oxidation reactions. (2) The highest color yield was observed in the case of the printing of cotton and polyester fabrics with the red vat dyes. However, the color yield of cotton fabrics is much higher than polyester fabrics, regardless of the vat dyes kind. (3) The most effective dose of electron beam irradiation was 75 kGy, at which the maximum color yield was achieved, regardless of the fabric or vat dye kind. However the exposure of the printed fabrics with the different formulations to relatively higher doses up to 100 kGy resulted in a slight decrease in the color yield, regardless of the kind of fabric or vat dye. While, the color yield of cotton fabrics printed with the violet and red vat dyes was decreased by 1.4 and 0.2%, respectively by increasing the irradiation dose from 75 to 100 kGy, the decrease in color yield of polyester fabrics printed with the same vat dyes was found to be 3.4 and 3.5% within the same irradiation dose respectively. These findings indicate that higher irradiation doses causes oxidative degradation to cotton fabrics, whereas the slight decrease in the color yield of the polyester fabrics occurred by increasing irradiation dose from 75 to 100 kGy is due to the presence of the benzene rings along the structure of polyethylene terephthalate, which dissipates radiation energy.

3.2. Comparison between the printing by electron beam irradiation and conventional methods

Vat printing by conventional method is one of the most complicated printing methods which need a lot of chemistries including reduction and oxidation. The printed fabrics were exposed to electron beam irradiation or steaming in the case of vat colors. Where the vat printing by the radiation method involved the printing in one step, the conventional vat printing was performed in two steps; steaming at elevated temperature followed by oxidation process. In this work, the vat printing on cotton and polyester fabrics by electron beam curing was compared with the vat printing on cotton and polyester fabrics with the same colors by conventional method. In this method the vat dye was incorporated in a paste containing sodium alginate and carboxymethyl cellulose as a base thickener. Sodium sulphoxylate formaldehyde was used as a reducing agent and potassium carbonate was used as the alkaline medium. The printed cotton and polyester fabrics were dried and finally fixation is conducted using saturated steam at 102 °C for 10–15 min.

3.2.1. Color yield

Fig. 4 shows the effect of vat dye ratio on the color yield of cotton and polyester fabrics printed with the different vat dyes. It is clear that there is no optimum ratio of the vat dyes, in which the color yield increases progressively with increasing the ratio up to 7.5%, regardless of the kind of the vat dye or the fabric kind.

However, it is interesting to compare the color yield of the printed fabrics by electron beam irradiation and conventional method at similar conditions of printing. In this context, the monomer/oligomer composition is equivalent to the reducing agent/thickener paste and the electron beam irradiation of 75 kGy is equivalent to the steaming at 102 °C for 10–15 min. Table 1 shows the color yield of the printed cotton and polyester fabrics with different vat colors and by electron beam and conventional methods. It should be noted that the values of color yield was taken for the

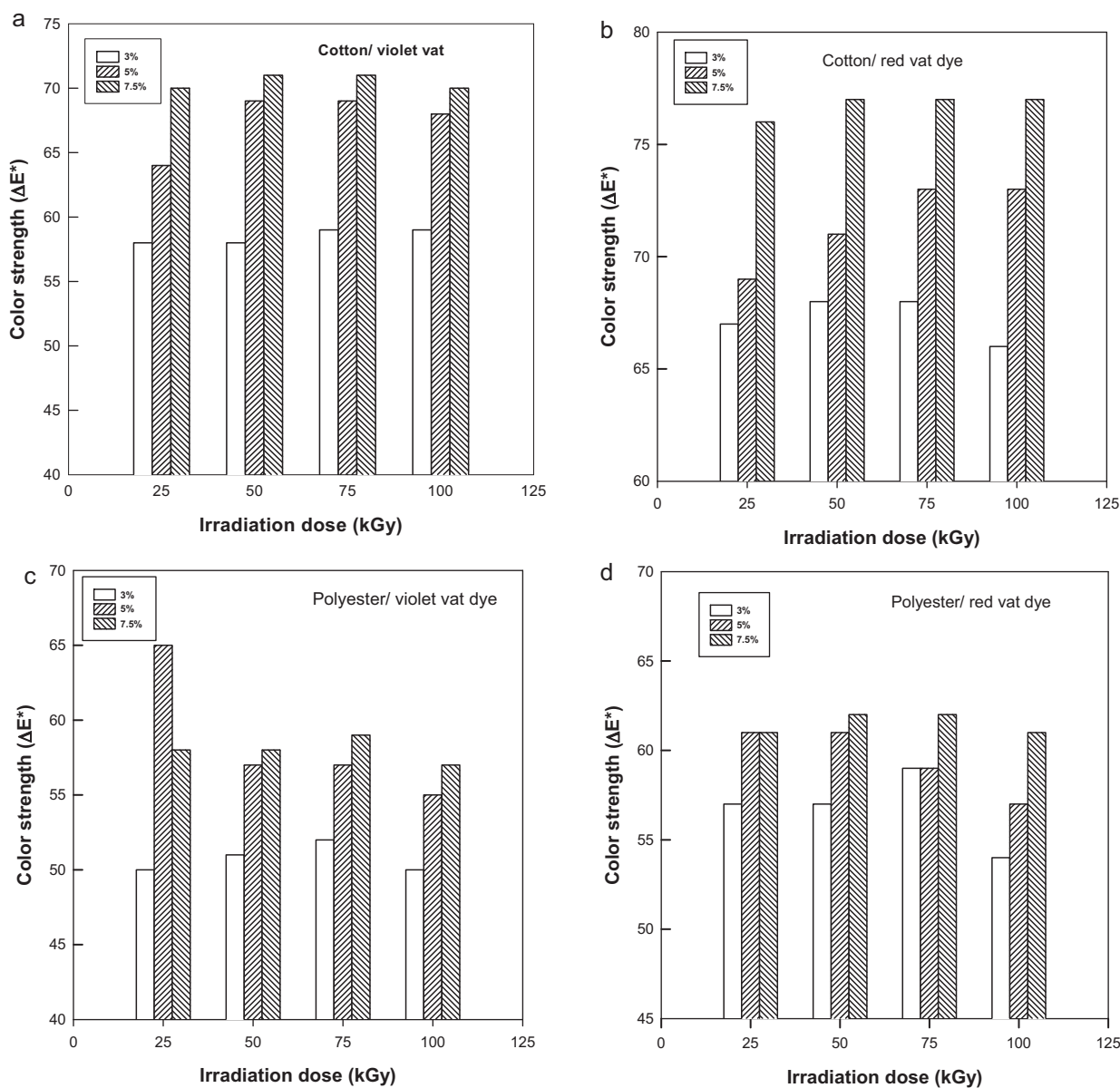


Fig. 3. Effect of irradiation dose and vat dye ratio on the color yield of cotton and polyester fabrics printed by various ratios of the Indanthren dyes.

printed fabrics with constant ratio of 5% in all cases. It can be seen that the vat printing on cotton and polyester fabrics by electron beam displayed higher color yield than the fabrics printed by the steaming/oxidation method. Meanwhile, the vat printing by the steaming method involves multiple steps and that the printing by electron beam irradiation is carried out in one step, which saves in time, energy and materials.

3.2.2. Roughness properties of cotton and polyester prints by electron beam irradiation and thermal curing

The most drawbacks of vat dye printing by electron beam irradiation or conventional method are the roughness and stiffness properties of the prints, i.e., the uncomfortable felling of the wearing of the prints. This was expected in case of electron beam irradiation since the printing with the radiation curable

Table 1
Color yield (ΔE) of cotton and polyester fabrics printed with constant ratio of different vat dyes of 5% by electron beam irradiation and conventional steaming/oxidation fixation method.

Method of printing	Color yield (ΔE)			
	Cotton (ΔE)		Polyester (ΔE)	
	Indant. Violet	Indant. Red	Indant. Violet	Indant. Red
Electron beam curing (75 kGy) ^a	69	74	57	64
Conventional method ^b	64	71	52	55

^a Electron beam conditions: monomer (THFA)/oligomer (TFUMA), 25/75%; ethylene glycol, 2.5%.

^b Conventional vat printing conditions: thickener, sodium alginate 25 g, CMC 40 g and Rongalite C 125 g (based on 1 kg), steaming, 102 °C for 10 min.

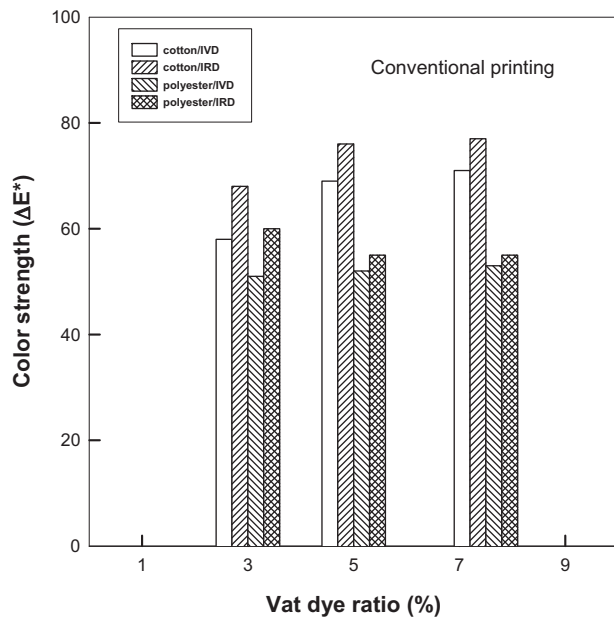


Fig. 4. Effect of dye ratio on the color yield of cotton and polyester fabrics printed with different vat dyes by conventional method.

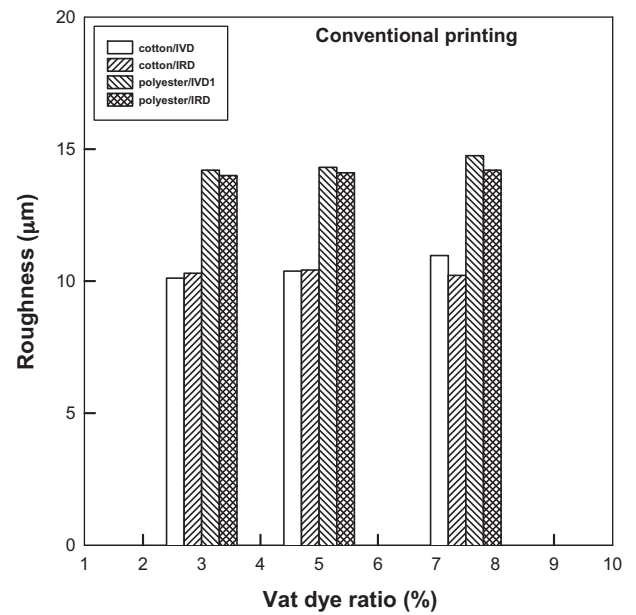


Fig. 6. Effect of vat ratio on the roughness properties of cotton and polyester fabrics printed with different vat dyes by conventional method.

formulations are a surface application and the cured films on the surface of the fabrics are formed through the crosslinking reactions. The durability of printed fabrics in term of roughness is of major importance. Fig. 5a and b shows the effect of electron beam irradiation dose on the roughness of cotton and polyester fabrics printed with two different formulations THFA/TFMUA and HDDA/TFMUA. It should be noted that all the formulations contain a constant monomer/oligomer ratio of 25/75 wt%, 5% of vat dyes and 2.5% of ethylene glycol. It can be seen that the roughness of the unirradiated printed cotton and polyester fabrics is lower than the irradiated printed fabrics, regardless the kind of fabrics or vat dyes. Beside that the roughness was found to increase by increasing the irradiation dose. This was expected since the electron beam irradiation dose is responsible for the formation of the cured films on the surface of the fabrics through crosslinking reactions. Meanwhile, the printed fabrics with the formulation HDDA/TFMUA was found to be rougher

than the prints with THFA/TFMUA at any irradiation dose on the range of study, regardless of the kind of fabrics or vat dyes. This may be due to the reactivity of the monomers used, in which hexane dioldiacrylate is a bifunctional monomer, and hence it can form rapid and rough cured films on the surface of the fabrics rather than the monofunctional tetrahydrofurfuryl acrylate monomer. It can be also seen that the printed polyester fabrics is rougher than cotton fabrics at the same conditions. This can be explained on the basis of higher hydrophilicity of cotton fabrics than the synthetic polyester fabrics. In this regard, the formulation is highly adhered and penetrated to the hydrophilic surface of cotton fabrics rather than the hydrophobic surface of polyester fabrics, which necessitates that the surface of polyester is rougher than cotton.

Fig. 6 shows the effect of vat dye ratio on the roughness properties of cotton and polyester fabrics printed with the different vat dyes by conventional method. It can be seen that the effect of vat

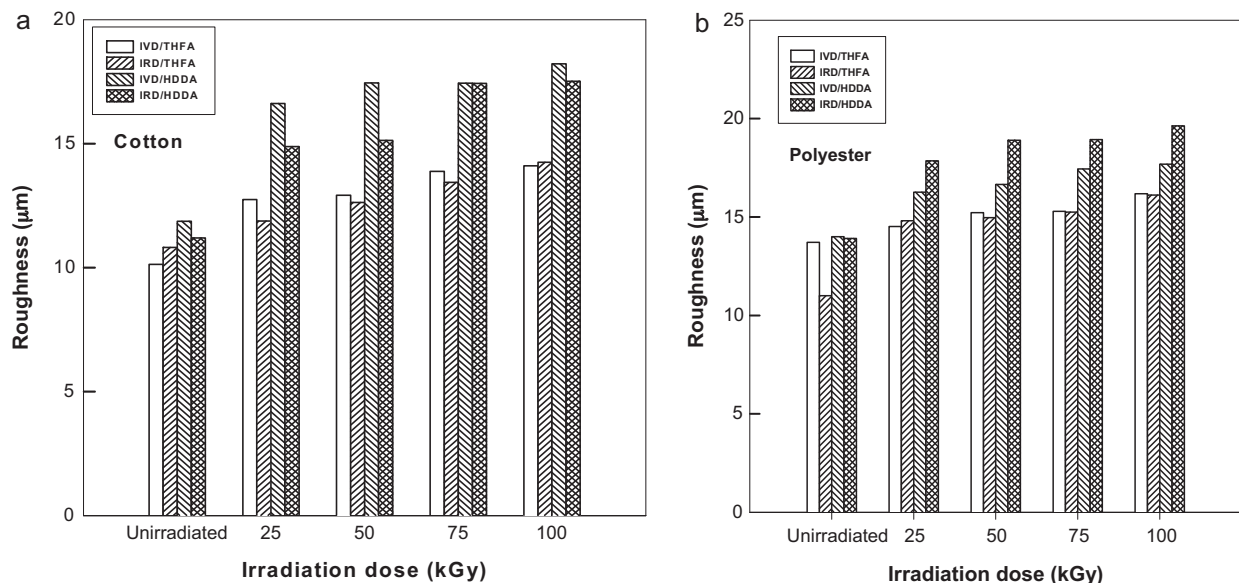


Fig. 5. Effect of irradiation dose on the roughness properties of cotton and polyester fabrics printed by constant ratio of different vat dyes.

Table 2
Fastness properties of cotton and polyester fabrics printed with Indanthren violet and red vat dyes by electron beam irradiation and conventional steaming/oxidation fixation method.

Method of printing	Indanthren violet										Indanthren red											
	Rubbing		Washing			Perspiration					Rubbing		Washing			Perspiration						
	Dry	Wet	SC	SW	Alt.	Acidic			Alkaline		Dry	Wet	SC	SW	Alt.	Acidic			Alkaline			
						SC	SW	Alt.	SC	SW						Alt.	SC	SW	Alt.	SC	SW	Alt.
Electron beam curing																						
Cotton	4	3	4-5	4-5	4-5	4-5	4-5	4-5	4	4	4	3-4	2-3	4-5	4-5	4-5	4-5	4-5	4	4	4	4
Polyester	4	3	4-5	4-5	4-5	4-5	4-5	4-5	4	4	4	4	3	4-5	4-5	4-5	4-5	4-5	4	4	4	4
Conventional method																						
Cotton	3-4	2-3	4	3-4	4	4-5	4-5	4-5	4-5	4-5	4-5	4	3	3-4	4	4	4	4	4-5	4-5	4-5	4-5
Polyester	3	2	3-4	3-4	3	4-5	4-5	4-5	4-5	4-5	4-5	3	2	3-4	3-4	3	3-4	3-4	3-4	4	4	4

SC = staining on cotton, SW = staining on wool and Alt. = change of color.

dye ratio has no significant effect on the roughness properties; the roughness of the 3% dye ratio is nearly the same at 5% dye ratio.

Beside that, an increase in vat color ratio from 5 to 7.5% was accompanied by a slight increase in the roughness, regardless of the kind of fabrics or vat color.

On the basis of the roughness properties of the printed fabrics with either electron beam irradiation or thermal curing, few points may be indicated; (1) generally, there is no any distinctive trend for the increase or decrease in the roughness properties of printed fabrics, regardless of the kind of fabric or vat color. (2) On the other hand at roughly similar conditions of printing by electron beam irradiation (5% vat ratio and dose of 75 kGy) and thermal curing (5% vat ratio and 102 °C for 10–15 min), the printed cotton and polyester fabrics with the different vat dyes by electron beam irradiation is rougher than those fabrics printed by the conventional steaming/oxidation fixation method. This can be explained based on the formation of a crosslinked film on the surface of the fabrics by the action of the electron beam irradiation which gives the relatively harsh feeling of the fabrics.

3.2.3. Color fastness properties of the printed fabrics by electron beam irradiation and thermal curing

The durability of vat printing on cotton and polyester fabrics by electron beam irradiation and conventional steaming/oxidation fixation method was evaluated in term of fastness towards rubbing, washing, and perspiration using the gray scale according to I.S.O. recommendations as shown in Table 2. The I.S.O. recommendations was issued in such way that color difference in the National Bureau Standards (N.B.S.) units 0, 4, 8, 16, and 32 have the fastness rating 5, 4, 3, 2, and 1 on the gray scale, respectively.

On the basis of the assessments shown in Table 1, several points may be addressed:

- (1) As shown in Table 1 for the rubbing properties, cotton fabrics printed with the violet vat color by electron beam irradiation are more resistant against rubbing than those cotton fabrics printed with the same vat color by thermal curing, in the dry and wet state of assessment. However, polyester fabrics printed by electron beam irradiation displayed higher color fastness towards rubbing than those printed with the same vat color by thermal curing.
- (2) While the washing fastness of the printed cotton and polyester fabrics by electron beam irradiation is better than those fabrics printed by the conventional method, regardless the kind of vat dyes. On the other hand, comparable results were obtained in the case of the perspiration fastness of the printed cotton and

polyester fabrics by electron beam irradiation and conventional steaming/oxidation fixation method.

4. Conclusions

Cotton and polyester surfaces were coated with different formulation containing different vat dyes, tetrahydrofurfuryl acrylate or hexane dioldiacrylate monomers and the trifunctional urethane acrylate oligomer and exposed to various doses of electron beam irradiation. The process of color formation of vat dyes on cotton and polyester fabrics by electron beam irradiation reduces all the processes of conventional method in one step, in which irradiation fixed the vat dyes in the curable formulation and converting the leuco form to the insoluble form through crosslinking and oxidation. The most effective conditions for vat printing by electron beam irradiation were: monomer/oligomer ratio of (25/75 wt%) and irradiation dose of 75 kGy at which the maximum color yield was achieved for cotton and polyester fabrics as well as the durability properties in term of rubbing, washing and perspiration. The results showed that the vat printing on cotton and polyester fabrics by electron beam irradiation affords color yield higher than the vat printing by conventional steaming/oxidation fixation method. On the other hand they gave rougher samples than those printed by the conventional method.

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