Factors affecting the radiation grafting of diethylaminoethyl methacrylate onto cotton, polyester and polyamide fabrics

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Factors affecting the radiation grafting of diethylaminoethyl methacrylate (DEAEMA) onto cotton, polyester and polyamide fabrics have been studied to obtain optimum conditions that improve the dyeability of Drimalan reactive dye. It is observed that gamma doses of up to 4 Mrad (40 kGy) do not show any noticeable graft yield until benzoyl peroxide catalyst is added. All the fabrics show maximum graft yield at 0.01% benzoyl peroxide, 10% monomer(DEAEMA) and 1:15 fabric-to-liquor ratio. A dose of 2 Mrad has been used in all the grafting experiments to avoid fabric degradation. Induction period or dose is observed before the start of the grafting process. The induction period is the shortest for cotton (0.2 Mrad corresponding to 0.56 h irradiation) while that for polyamide fabric it is 0.7 Mrad (7 kGy) which corresponds to about 2 h irradiation. The graft yield is considerably higher for the natural cotton fabric than those for the synthetic polyester and polyamide fabrics. The dyeability of the fabrics with Drimalan dye improves considerably as the graft yield increases up to 7% with no further appreciable changes for higher degrees of grafting. The pH of the dyebath affects the dyeability of the fabrics giving an optimum condition at a pH value of 3 for 2% grafted fabrics.

Keywords: Cotton, Diethylaminoethyl methacrylate, Dyeing, Polyamide, Polyester, Radiation grafting

1 Introduction
Graft copolymerization of both natural and synthetic fibres is a convenient method for adding new and desired properties to textiles without drastically affecting the basic properties of the substrate. Radiation and chemical graftings of various vinyl monomers onto a wide variety of natural and synthetic polymers have already been investigated. The dyeing of radiation-grafted nylon-6 with acrylic acid and styrene has also been studied. The dyeing properties of wool fabrics have been improved by radiation grafting of different vinyl monomers. The effect of gamma irradiation on the fixation of reactive Drimalan dye on wool fibres has also been studied.

In the present work, the radiation grafting of diethylaminoethyl methacrylate (DEAEMA) onto cotton, polyester and polyamide fabrics at various radiation doses, monomer concentrations, benzoyl peroxide concentrations and fabric-to-liquor ratios has been studied. The effect of graft yield and dyebath pH on the colour strength of the reactive Drimalan red dye on different fabrics is also reported.

2 Materials and Methods
2.1 Materials
Mill-scoured and bleached cotton fabrics, obtained from El-Beida Dyers Co., Kafr El-Dawar, Egypt, were treated with sodium carbonate (5g/l) and non-ionic detergent (Sandozin NIT liquid) at boil for 4 h, thoroughly washed with cold water, dried at an ambient temperature and then used for grafting.

Polyester fabrics, supplied by Misr Spinning and Weaving Co., Mehala El-Kobra, Egypt, were used without any finishing treatment.

Bleached polyamide (nylon-6) fabrics, supplied by El-Nasr Spinning, Weaving and Knitting Co., Cairo, Egypt, were used directly without any further treatment.

Diethylaminoethyl methacrylate (DEAEMA) monomer, obtained from Rohm & Maas, was used after distillation in a nitrogen atmosphere.

\[
\text{CH}_2\text{C-C-O-CH}_2\text{N(C}_2\text{H}_5)_2
\]

\[
\text{CH}_3
\]

(NDEAEMA)

Nitric acid, Sandozin NIT liquid, benzoyl peroxide and ammonium chloride were used.

Reactive Drimalan red dye (2,4 difluoro-5-chloropyrimidine), supplied by Sandoz, Switzerland, was used.
2.2 Methods

2.2.1 Radiation Grafting

The grafting was carried out by the direct irradiation method in a 60Co gamma source at a dose rate of 1 Gy/s. Dry weighed cotton, polyester and polyamide fabrics were introduced in a wide mouth tube provided with ground-joint stopper. The solvent, monomer and other additives were added so that the fabrics were completely immersed in the monomer solution. The fabrics were placed in the centre of the gamma cell.

The grafted fabrics were removed from the reaction tube after irradiation to the desired dose. The homopolymer was extracted from the polymerized fabrics with boiling water and the fabric samples were dried to constant weights. The degree of grafting was determined as the percentage increase in weight using the following relationship:

\[
\text{Graft yield} = \left[ \frac{W_g - W_0}{W_0} \right] 
\]

where \( W_0 \) and \( W_g \) are the weights of initial and grafted samples respectively.

2.2.2 Dyeing

Grafted and ungrafted fabrics were dyed with reactive Drimalan red dye. The dye bath contained 2% (owf) reactive dye, 10% common salt and few drops of acetic acid, maintaining the fabric-to-liquor ratio at 1:50. The fabrics were then introduced into the dye solution and the temperature was raised to the boil in 20 min. The solution was kept at the boil for 1 h. The dyed fabrics were rinsed with water, soaped with non-ionic wetting agent (1 g/l Sandozin NIT) at the boil for 30 min and finally dried at room temperature.

2.2.3 Colour Strength Measurement

Colour strength of the dyed samples was measured using a microcolour unit equipped with a data station from Dr. Lang (Germany). The reflectance measurement, expressed as \( K/S \) values, was carried out using the Kubelka-Munk equation:

\[
K/S = \frac{[1 - R]^2}{2R} - \frac{[1 - R_0]^2}{2R_0}
\]

where \( R \) is the decimal fraction of the reflectance of the coloured sample; \( R_0 \) the decimal fraction of the reflectance of uncoloured sample; \( K \), the absorption coefficient; and \( S \), the scattering coefficient.

3 Results and Discussion

3.1 Effect of Benzoyl Peroxide

Mutually irradiated cotton, polyester and polyamide fabrics in aqueous solutions containing 10% monomer (DEAEMA) did not show any significant graft yield up to a dose of 5 Mrad (50 kGy). Hydrogen peroxide was used to assist the initiation of the grafting process but the results remained the same. Thereafter, benzoyl peroxide was used to replace hydrogen peroxide and its catalytic effect showed a reasonable graft yield. The effect of benzoyl peroxide concentration on the graft yield of the different fabrics irradiated at a dose of 2 Mrad and monomer concentration of 10% is shown in Fig. 1. In general, the graft yield increases sharply with the increase in peroxide concentration, reaching the maximum values of 20%, 11.5% and 5.5% respectively for cotton, polyester and polyamide fabrics at 0.01% peroxide concentration. Beyond 0.01%, the initial increase in graft yield by the increase of benzoyl peroxide concentration (slope) is the highest for cotton followed by polyester and polyamide. The values of the slopes are 18000, 3200 and 667 respectively for cotton, polyester and polyamide that these fabrics undergo grafting with other monomers and therefore the responsibility of the fabrics for obtaining any
noticeable graft yield can be excluded. This leads to the conclusion that the irradiated DEAEMA monomer is unable to form enough free radicals to initiate the grafting. Addition of benzoyl peroxide to the monomer solution is a must to obtain a reasonable degree of grafting.

The high initial increase in the graft yield by the increase of benzoyl peroxide concentration (18000) and maximum degree of grafting (20%) for cotton over those for polyester (3200 and 11%) and polyamide (667 and 5.5%) support the above-mentioned discussion and show that the magnitude of free radical formation is higher for cotton followed by polyester and polyamide. Concentrations of benzoyl peroxide higher than 0.01% decrease the grafting by assisting the homopolymerization over that of grafting the monomer onto the fabrics.

In the presence of benzoyl peroxide the fabric macro radicals, created during irradiation, are added to the double bond of DEAEMA, resulting in a covalent bond formation between monomer and fabric with the creation of free radical on DEAEMA. Subsequent addition of DEAEMA to the initiated chain propagates grafting. The initiation and propagation of grafting process are given below:

\[
\begin{align*}
\text{(Fabric free radical)} & \quad R^* + \text{CH}_2\text{CH}_2\text{C}=\text{C}-\text{O}-\text{C}_2\text{H}_4\text{N}([\text{C}_2\text{H}_5]_2) \\
\text{Benzoyl peroxide} & \quad \rightarrow \text{CH}_3 \quad \text{R-CH}_2\text{CH}_2\text{C}=\text{C}-\text{O}-\text{C}_2\text{H}_4\text{N}([\text{C}_2\text{H}_5]_2) \\
\text{Initiated free radical} & \quad +\text{CH}_2\text{CH}_2\text{C}=\text{C}-\text{O}-\text{C}_2\text{H}_4\text{N}([\text{C}_2\text{H}_5]_2) \rightarrow \\
\text{COOC}_2\text{H}_4\text{N}([\text{C}_2\text{H}_5]_2)\text{COOC}_2\text{H}_4\text{N}([\text{C}_2\text{H}_5]_2) \\
\text{R-CH}_2\text{CH}_2\text{C}=\text{C}-\text{CH}_3 \quad \text{CH}_3 \\
\end{align*}
\]

3.2 Effect of Monomer Concentration on Grafting

The effect of monomer concentration on the graft yield of the different fabrics irradiated at a dose of 2 Mrad in the presence of 0.01% benzoyl peroxide is shown in Fig. 2. The results show that for all the fabrics, graft yield increases as the monomer concentration increases, reaching a maximum at a monomer concentration of 10% followed by a slow decrease with further increase in monomer concentration up to 20%. The initial rate of increase in graft yield is higher than the rate of decrease for the same interval of monomer concentration. Cotton fabric shows a change in graft yield amounting to 2.75 between 2% and 10% monomer concentration while the rate of decrease between 10% and 20% monomer concentration is 0.4. Also, cotton fabric gives a maximum degree of grafting (24%) while polyester and polyamide fabrics show almost similar behaviour at all the monomer concentrations used. The difference between cotton and other fabrics is in the rate of increase in graft yield (2.75 and 1.5 respectively). All the fabrics show almost the same rate of decrease (0.4) in graft yield.

The increase in graft yield with the increase in monomer concentration for all the fabrics was expected in consistence with the earlier findings. Moreover, the rate of increase in grafting for cotton over that for polyester and polyamide (2.75 and 1.5 respectively) and the maximum values of graft yield (24% and 12.5% respectively) at 10% monomer concentration can be explained by the fact that the rate of free radical production is higher for cotton fabrics compared to that for polyester and polyamide fabrics. Further increase in monomer concentration over 10% shows a slow decrease in graft yield. This may be attributed to the overcoming effect of homopolymerization over grafting with the increase in viscosity of grafting solution. Accordingly, the
diffusion of the monomer into the fabric molecules is hindered.

3.3 Effect of Fabric-to-liquor Ratio on Grafting

The effect of fabric-to-liquor ratio on the graft yield of different fabrics irradiated at 2 Mrad dose is shown in Fig.3. Benzoyl peroxide concentration of 0.01% and the monomer concentration of 10% were used. Generally, the grafting increases slowly up to a maximum at fabric-to-liquor ratio of 1:15 followed by a rather steep decrease to its lowest value at 1:30 fabric-to-liquor ratio. Cotton fabric shows higher graft yield at all the fabric-to-liquor ratios while the other two fabrics show similar behaviour but with lower graft yield than that for cotton. The graft yield increases 9% for cotton and 4% for polyester and polyamide at fabric-to-liquor ratios between 1:5 and 1:15 while it decreases 24% and 11.5% respectively for cotton, and polyester and polyamide as the fabric-to-liquor ratio increases from 1:15 to 1:30. The optimum fabric-to-liquor ratio is found to be 1:15 where the graft yield is maximum.

The increase in graft yield with the increase in fabric-to-liquor ratio up to 1:15 is expected as the amount of monomer in the grafting solution is increased. However, the relatively high decrease in graft yield with the increase in fabric-to-liquor ratio above 1:15 is somewhat confusing as leveling in the graft yield is expected. However, direct observation of the irradiated liquor solution shows an increase in its viscosity as the fabric-to-liquor ratio is increased. This suggests that the diffusion of the monomer into the fabrics decreases with the increase in fabric-to-

liquor ratio, resulting in decrease in graft yield. The increase in liquor viscosity is due to the increase in homopolymerization of the DEAE monomer.

3.4 Effect of Radiation Dose on Grafting

The effect of radiation dose (dose rate, 1 Gy/s or 100 rad/s) on graft yield of different fabrics immersed in aqueous solution having 0.01% benzoyl peroxide, 10% monomer and 1:15 fabric-to-liquor ratio has been studied and the results are shown in Fig. 4. It is observed that the graft yield increases linearly with the increase in radiation dose from 0.8 Mrad to 1.4 Mrad, depending on the fabrics used. This is followed by a second linear but slower graft rate as the dose is further increased up to 4 Mrad. The results also show that cotton fabric gives higher graft yield than polyester and polyamide at all the doses used. The initial rate of increase in graft yield for cotton accounted to 12% per hour while that for polyester and polyamide it amounted to 5% per hour. It is observed from Fig. 4 that before an induction period or dose no significant graft is obtained. The induction dose depends on the type of irradiated fabrics. Cotton fabric shows the shortest induction dose of 0.2 Mrad which corresponds to irradiation time of 0.56 h, whereas polyamide fabric does not show any noticeable graft yield until a dose of 0.7 Mrad (2 h) is reached. Polyester fabric gives an induction period between cotton and polyamide.

In mutual irradiation processes, grafting is probably initiated in part by radiation-activated sites on the surface of the fabrics. The rate of formation of such sites as well as their accessibility to the

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Fig. 3—Effect of fabric-to-liquor ratio on the graft yield [Grafting condition: 2 Mrad dose, 10% monomer and 0.01% benzoyl peroxide]

Fig. 4—Effect of radiation dose on the graft yield [Grafting condition: 10% monomer, 0.01% benzoyl peroxide and 1:15 fabric-to-liquor-ratio]
initiation of graft polymerization is shown by the magnitudes of the induction period and the grafting rates. Therefore, it may be concluded from the above-mentioned results that cotton fabrics produce higher density of radiation-activated sites for the same radiation dose if compared with the other two fabrics. Moreover, the accessibility of the activated sites for cotton is much higher than those for polyester and polyamide fabrics since the degree of swelling of cotton in aqueous solutions as well as its $G_R$ value is higher than those for the other fabrics, resulting in the enhancement of the grafting.

3.5 Effect of Graft Yield on Dyeability of Fabrics

Grafted and ungrafted fabrics were dyed with Drimalan red reactive dye and the effect of DEAEMA grafting on their dyeability is shown in Fig. 5. The general features of the colour strength-graft yield curves are the same. It is observed that the increase in graft yield is associated with the enhancement in colour strength up to maximum values. Further increase in graft yield to higher levels shows a decrease in the dyeing affinity of all the fabrics. The increase in $K/S$ values indicated the increase in the colour strength.

The increase in colour strength ($K/S$) with the increase in graft yield (slope of the straight line) is the highest for polyester fabric (1.7) while polyamide and cotton give values of the slopes amounting to 1.3 and 0.8 respectively. This can be explained by the fact that ungrafted cotton and polyester fabrics have very low colour strength values (around 0.2) while the corresponding $K/S$ value for ungrafted polyamide fabric is 2.2. Moreover, all the fabrics show a decrease in the $K/S$ values after reaching the maximum between 6% and 7% graft yield. Polyamide and polyester fabrics give maximum colour strength at graft yields of 3% and 6% respectively while the corresponding value for cotton is 9%. The results for ungrafted polyamide indicate its high ability for dyeing if compared with ungrafted polyester or cotton fabrics since its colour strength is the highest.

It is worth mentioning that the graft yields as low as 3% and 9% are enough to give the maximum colour strength for cotton and polyamide/polyester. This improvement in dyeing affinity could be interpreted in terms of molecular opening and disruption by the graft, thus facilitating the diffusion and absorption of the dye. There is no reason to believe that these copolymers possess an affinity for dyeing through salt formation or physical bonds. Once this disruption occurs, more resting sites for dye molecules and/or aggregates could be created in the interior of the fibre.

3.6 Effect of pH Values on Dyeability of Fabrics

The effect of pH on the colour strength of grafted and ungrafted fabrics is shown in Fig. 6. All the samples were prepared to give graft yield of about 2% and dyed in aqueous media with pH 3-10. It is observed from Fig. 6 that, in general, grafted and dyed fabrics show higher $K/S$ values if compared with ungrafted ones at all the pH values. However, the colour strength decreases with the increase in pH except for cotton fabric which shows no response when pH of the dyebath is changed. The colour strength of grafted polyester decreases from 2.88 to 0.88 while that of polyamide decreases from 6.5 to 3.26 as the pH value is increased from 3 to 10.
Ungrafted cotton and polyester fabrics show opposite behaviour. The K/S value slightly increases as the pH is increased from 3 to 10. The K/S values increase from 0.16 to 0.6 for cotton and from 0.08 to 0.30 for polyester fabrics. Ungrafted polyamide fabrics, however, show a decrease in K/S from 3.52 to 0.31 as the pH is changed from acidic to alkaline.

The results show a slight improvement in the dyeability of cotton and polyester fabrics while for polyamide fabrics, tremendous drop in the colour strength is observed as the dyeing medium is changed from acidic to alkaline. This may be attributed to the different nature and structure of the fabrics and their affinity to the dye. However, grafted fabrics show improvement in colour strength with the decrease in pH, indicating that the best dyeing condition occurs at pH 3. A proposed scheme for the possible reaction between grafted fabrics and Drimalan red dye is given as follows:

**Hydrolysis of grafted fabrics**

\[
\text{Fabric} \rightarrow [\begin{array}{c} \text{CH}_2 - \text{C} \end{array}]_n \rightarrow \text{Fabric} + \text{OH}^{-} + \text{H}^+ + \text{HOH}^{-}
\]

**Reaction with Drimalan dye**

\[
\text{Fabric} \rightarrow [\begin{array}{c} \text{CH}_2 - \text{C} \end{array}]_n + n \text{Dye}^{-} \rightarrow \text{Fabric} \text{-Dye} + n \text{Dye}^2
\]

The hydrogen ion of the carboxylic group reacts with either of the fluoride ions with the libaration of HF and formation of a bond between the hydrolyzed grafted fabric and the dye.

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