Modification of cotton fabrics via radiation graft copolymerization with acrylic acid, acrylonitrile and their mixtures

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Radiation-induced grafting of acrylic acid (AAc), acrylonitrile (AN) and their mixtures onto cotton fabrics has been studied at 2.56 Gy/s gamma dose rate and 1:40 fabric-to-liquor ratio. The grafting process was performed in the presence of aqueous AAc containing 0.75% (v/v) Mohr’s salt, and 65:15 methanol-water mixture for AN. The effect of monomer concentration and irradiation time (dose) on the degree of grafting has also been investigated. The dependence of the initial grafting rate on monomer concentration follows a second order kinetics for AN and a negative first order one for AAc. Grafts from monomer mixtures show different kinetic behaviour, depending on AN/AAc ratios in solutions with constant monomers mixture concentration of 20%. The degree of grafting increases with the increase in AN/AAc ratio from 20/80 to 80/20 for all the doses applied. The reaction order changes from a positive order of 0.55 to a negative order of 0.41 as the ratio of AN/AAc decreases. The swelling properties of cotton fabrics improve with the increase in degree of grafting of AAc and deteriorate with the increase in graft yield of AN. Fabrics grafted with monomer mixtures show swelling behaviour between those of AAc and AN. The electrical conductivity of grafts prepared from the monomers or their mixtures shows a fast initial decrease followed by a tendency to level-off as the graft yield increases up to 35%, irrespective of the type of monomer or the mixture ratio. The dyeability of cotton fabrics towards Sandocryl Blue B-3G, a basic dye, improves considerably as the graft yield with AAc increases up to 20% with no further appreciable changes for higher degrees of grafting. Grafts with AN and AAc/AN mixtures show lower dyeing affinity than that for AAc grafts. The pH of the dye bath affects considerably the dyeability of the grafted fabrics, giving an optimum condition at pH 3.9. Proposed schemes for grafting and dyeing of cotton fabrics with Sandocryl Blue B-3G are given.

Keywords: Acrylic acid, Acrylonitrile, Cotton, Dyeing, Radiation-induced grafting

Introduction

Cotton is the most widely used textile fibre due to its abundance, low cost and well-known physical and mechanical properties. It has inherent drawbacks such as poor solubility in common solvents, poor crease resistance, lack of thermal plasticity and poor dimensional stability. These drawbacks directed attention towards improving the properties of cellulose through changing its physical and chemical structure. Radiation grafting is one of the promising methods in this field. The graft copolymer formed modifies the cellulose molecules through creation of branches of synthetic polymers that confer certain desirable properties without destroying its intrinsic properties.

Several researchers have found that graft copolymerization of cotton with different vinyl monomers improves the strength, toughness, flexural resistance and thermoplasticity. The repellency and rot resistance of cotton are improved by grafting the fabrics with acrylate monomers and polyacrylonitrile. It has been shown earlier that the dyeability of cotton fabrics towards Drlimalan Red, a reactive dye, increases with the increase in the degree of grafting with diethylaminoethyl methacrylate. It has also been found that swelling of the fabrics in a proper solvent before irradiation improved the graft copolymerization process. Chapiro and Stannett and Hung and Rapson have reported that pre-swelling of cellulose with dipolar swelling agents, such as water, formamide and formic acid, before radiation grafting in monomer solutions containing methanol, ethanol or acetic acid improves the grafting process considerably. Non-wetting solvents showed poor grafting levels when grafting styrene, methyl methacrylate, vinyl acetate and vinyl pyridine onto cellulose.

This investigation was carried out to modify the physical and dyeing properties of cotton fabrics via direct radiation grafting of acrylonitrile (AN), acrylic acid (AAc) and their mixtures onto cotton fabrics. The
effects of monomer concentration, fabric-to-liquor ratio and irradiation time (dose) on the degree of grafting have been studied to reach the optimum condition that produces uniform and homogeneous grafts all over the fabric.

2 Materials and Methods

2.1 Materials

Mill-scoured and bleached cotton fabrics, obtained from EL-Beida Dye Co., Kafr EL-Dawar, Egypt, were treated with sodium carbonate (5g/L) and non-ionic detergent (Sandozin NIT liquid) at boil for 4h, thoroughly washed with cold water, dried at ambient temperature and then used for grafting. Reagent-grade acryllic acid and acrylonitrile monomers, obtained from Aldrich (Germany) and BDH (England) respectively, were used. Ferrous ammonium sulphate (Mohr’s salt), methanol, acetic acid and Sandozin NIT liquid were used.

Sandoaryl Blue B-3G, a basic dye, supplied by Sandoz, Switzerland, was used.

2.2 Methods

2.2.1 Radiation Grafting

Grafting of the fabrics was carried out by the direct irradiation method in a 60Co gamma source at a dose rate of 2.56 Gy/s. Samples were immersed in the respective monomer-solvent solution, de-aerated with bubbling nitrogen for 5 min and left overnight before being placed in the gamma cell.

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

\[
\text{Degree of grafting} = 100 \left( \frac{W_f - W_i}{W_i} \right)
\]

where \(W_i\) and \(W_f\) are the weights of initial and final grafted samples respectively.

2.2.2 Determination of Water Uptake

Grafted and ungrafted fabrics with known weights were immersed in distilled water at ambient temperature until equilibrium was reached. The samples were then removed and the excess water deposited on the surface was quickly removed with blotting paper and then weighed. The percentage water uptake was calculated as follows:

\[
\text{Water uptake} \ (\%) = 100 \left( \frac{W_w - W_d}{W_w} \right)
\]

where \(W_w\) and \(W_d\) are the weights of wet and dry samples respectively.

2.2.3 Electrical Conductivity Measurement

Conductivity measurements were carried out using a Mega ohm meter from WTW Instruments, Germany. The average value of the electrical resistance of the sample was measured by applying different voltages and recording the corresponding currents. The electrical conductivity \(\sigma\) was calculated as follows:

\[
\sigma = \frac{R}{A \cdot \ell} \ \Omega^{-1} \ \text{cm}^{-1}
\]

where \(R\), \(A\) and \(\ell\) are the ohmic resistance, area and thickness of the sample respectively.

2.2.4 Dyeing

Aqueous dye bath containing 2% (ovf) dye was prepared from Sandoaryl Blue B-3G at a fabric-to-liquor ratio of 1:50. The required weight of dye was pasted in acetic acid before the addition of the distilled water. The dyeing process was carried out in the presence of 10% sodium sulphate and 0.1g/L Sandozin NIT liquid as a wetting agent. The pH of the dye bath was adjusted to 3.9 and the temperature was then raised to the boil in 20 min. The solution was kept at the boil for 1h. The dyed fabrics were rinsed with water, soaped with Sandozin NIT (0.1%) at the boil for 30 min and finally dried at room temperature.

2.2.5 Colour Strength Measurement

The colour strength of the dyed samples was measured using ICS–Texicom UV/Vis Spectrophotometer at a maximum wavelength of 600 nm. The colour strength, expressed as \(K/S\), was calculated from the Kubelka-Munk equation:

\[
K/S = \left| \frac{(1-R)^2/2R} - (1-R_c)^2/2R_c \right|
\]

where \(R\) and \(R_c\) are the decimal fraction of the reflectance of the coloured and uncoloured samples; \(K\), the absorption coefficient; and \(S\), the scattering coefficient.

3 Results and Discussion

It is of prime importance in radiation-induced graft copolymerization to choose the proper solvent that gives the highest degree of grafting together with a homogenous distribution of the grafts over the surface of the fabric. Experiments were carried out on AAe and AN monomers using different solvents and monomer-to-liquor ratios. Best results were
obtained when the distilled water was used in grafting AAc onto cotton fabrics, while methanol-to-water (65:15) gave high and homogeneous graft yield of AN onto the fabrics. Fabric-to-liquor ratio of 1:40 was used for both the systems during this work.

3.1 Grafting with Acrylic Acid

Preliminary experiments to graft cotton fabrics in aqueous AAc solutions gave low graft yields. To enhance the grafting process, Mohr’s salt was added to inhibit the homopolymerization process. Fig. 1 shows the dependence of the graft yield on the concentration of Mohr’s salt for fabrics irradiated at a dose of 10 kGy and 10% aqueous AAc solution. The results indicate that a maximum graft yield is obtained at inhibitor concentration of 0.75% (own). This concentration was used in all AAc experiments.

The effect of fabric-to-liquor ratio on the graft yield of fabrics irradiated at a dose of 10 kGy and 10% AAc solution containing 0.75% Mohr’s salt is shown in Fig. 2. The results indicate a linear increase in the graft yield from 13% to 17% as the fabric-to-liquor ratio is increased from 1:10 to 1:40. No further increase in graft yield is noticed at higher ratios. This ratio was kept constant throughout this study.

Cotton graft copolymers with AAc having different yields were prepared by performing the experiments under different monomer concentrations and irradiation times. Table 1 shows the effect of irradiation time and monomer concentration (10-40% owf) on the graft yield at 32°C. It is seen that the graft yield increases linearly with the increase of irradiation time in the initial period and then tends to level-off at higher times. For the same irradiation time, the initial graft yield decreases with the increase in monomer concentration. As the irradiation time exceeds the initial stages, the graft yield-time relationship changes and indicates an opposite effect. The end graft yield at 130 min irradiation time (10 kGy) is highest for 40% AAc concentration and lowest for 10% AAc concentration.

The order of the reaction kinetics for grafting AAc onto cotton fabrics is obtained by plotting the logarithm of the initial rate of grafting versus the logarithm of AAc concentration (Fig. 3). The relationship is linear with a slope of -1, indicating a negative first order kinetics. At higher irradiation times, the above dependence changes to a positive one.

The abnormal behaviour of grafting AAc onto cotton fabrics can be explained as follows. For the initial irradiation period, grafting initially occurs at the swollen surfaces by aqueous AAc solution, followed by continuous monomer diffusion through grafted layers to reach the active fabric sites to give homogeneous distribution of the grafted chains in the fabric. The homopolymerization of AAc plays an important role at longer irradiation times or higher doses. Poly(acrylic acid) is insoluble in its monomer and has poor solubility in the aqueous solution at test
conditions and forms a gelatinous layer over the fabric surfaces. The homopolymer, depending on the initial AAc concentration, retards the monomer diffusion to free radicals and hence slows the grafting process. Moreover, the considerably high rate of homopolymerization of AAc (its $G_R$ value of 11 is close to that of cotton) decreases the effective monomer concentration to continue the grafting process specially at high doses where the degree of grafting tends to level off. The increase in the degree of grafting with the increase in monomer concentration at longer irradiation times and at the end degree of grafting (130 min) supports the idea that the degree in grafting is dependent not only on the amount of free radicals but also on the diffusivity of the monomer through the grafted layers which leads to the increase in the final degree of grafting as well as the rate of grafting. Similar results were reported by Hegazi et al.\textsuperscript{15}.

3.2 Grafting with Acrylonitrile

The dependence of the degree of grafting on irradiation time for 10-40\% AN concentration is shown in Fig. 4. The figure shows an induction period after which there is an initial linear increase in irradiation time followed by a tendency to level-off at longer times. The observation of induction periods during the initial irradiation grafting processes is frequently noticed and depends on the different factors such as dose rate, monomer concentration, presence of oxygen in the grafting solutions and the presence of inhibitors in the as-received monomers\textsuperscript{16,17}.

The dependence of the initial grafting rate on monomer concentration is shown in Fig.5. The figure shows the logarithmic plot of grafting rate versus monomer concentration. It is observed that the relationship increases linearly with a slope of 2, indicating a second order kinetics. This high order dependence of AN grafting on cotton is attributed to the larger free radical yield of the polymer (cotton) over that of the monomer (AN). This enhances grafting over homopolymerization as supported by the respective radiation chemical yield ($G_R$ value) of AN(5) and cotton(11) (ref. 16).

3.3 Grafting with Acrylic Acid-Acrylonitrile Mixture

The effect of relative concentrations of AAc and AN monomers on the grafting yield and rate of grafting of cotton fabrics is shown in Figs 6 and 7 respectively. The fabrics were irradiated in mixture solutions having different AAc/AN ratios such that the total monomer concentration in all tests was constant at 20\% wt. The dose rate and fabric-to-liquor ratio were as given before. Fig. 6 shows the dependence of
The slope of the relationship is 0.55 for AN and -0.41 for AAc. The dependence of the grafting rate on monomer concentration in the mixtures of the constant concentration (20%) is as follows:

\[ R_1 = K_1[AN]^{0.55} \]
\[ R_2 = K_2[AAC]^{-0.41} \]

where \( R_1 \) and \( R_2 \) are the grafting rates; and \( K_1 \) and \( K_2 \) the rate constants for AN and AAc in the mixture.

The grafting of cotton fabrics with AN and AAc can be explained by the addition of fabric macroradical to the monomer double bond to form a covalent bond between monomer and fabric with the creation of free radical on the monomer. Subsequent addition of monomer to the initiated chain propagates grafting. Termination of the grafting process occurs by the formation of a covalent bond between two free radicals. The proposed schemes for the grafting process are given below:

**Grafting with AN**

\[
\begin{align*}
\text{Initiation:} & \quad F' + CH_2 = CH \rightarrow CH_2 = CH' + CH_2 = C' \\
\text{Addition of monomer:} & \quad CH_2 = CH \rightleftharpoons CH_2 = C' \\
\text{Propagation:} & \quad (\alpha - 2) \rightarrow CH_2 = CH \\
\text{Combination:} & \quad FM'_n + FM'_m \rightarrow P_{w,w} \\
\text{Disproportionation:} & \quad FM'_n + FM'_m \rightarrow P_n + P_m
\end{align*}
\]

where \( F' \), M and P are the fabric (free) radical, the monomer and the copolymer respectively.

**Grafting with AAc**

Grafting with AAc is exactly similar to that of AN except that the CN groups are replaced by the COOH groups.

3.4 Properties of Grafted Cotton Fabrics

3.4.1 Water Uptake

The water uptake values for cotton fabrics grafted with AAc, AN and their mixtures are shown in Fig. 8.
It is observed that the water uptake of graft copolymers of AAc increases linearly from 106% for ungrafted cotton to 180% with the increase in the degree of grafting up to 10% followed by a tendency to level-off with further increase in graft yield. Acrylonitrile graft copolymers show an opposite behaviour. The water uptake decreases from 106% to 80% as the degree of grafting is increased to 40%. AAc/AN graft copolymers (40/60 and 80/20) show water uptake values between the two extremes of those for AAc and AN graft copolymers, depending on the relative percentage of the monomers in the grafting solution. The results indicate that the water uptake decreases as the percentage of AN in the mixture increases. The water uptake of the grafted cotton fabrics increases in the following order:

AAc > AAc/AN (80/20) > AAc/AN (40/60) > AN

The increase in the water uptake with the increase in the degree of grafting of AAc-g-copolymers can be attributed to the increase of the carboxylic groups in the grafted fabrics due to their hydrophilic properties. AN-g-copolymers, however, give an opposite effect of the water uptake due to the hydrophobic properties of -CN groups of AN. Consequently, the increase in the degree of grafting with AN results in a decrease in water uptake. Fabrics grafted with different mixtures of the homopolymers are expected to show water uptake depending on the competing effects of AAc and AN in the grafts. This means that the water uptake decreases as the percentage of AN in the grafted fabrics increases. The contribution of AN in a 50/50 mixture towards water uptake is expected to be higher than that of AAc since the degree of grafting with AN is about 6 times higher than that of AAc (Table 1 and Fig. 4) and consequently its participation in the property change is significant.

3.4.2 Electrical Properties

The dependence of the electrical conductivity on the degree of grafting of fabrics grafted with AAc, AN and their 50/50 mixture is shown in Fig. 9. The figure shows a general trend of the decrease of the electrical conductivity with the increase in graft yield, irrespective of the type of the graft copolymer. The rate of change of the electrical conductivity with the change in the degree of grafting is fast at lower graft yields followed by a gradual decrease up to a minimum value at 35% graft yield. The electrical conductivity decreases from $6.5 \times 10^{-14}$ to $2 \times 10^{-14}$ ohm$^{-1}$ m$^{-1}$ as the graft yield increases to 35%. The decrease in the electrical conductivity of cotton fabrics with the increase in graft yield is different from the results obtained for nylon-6 fabrics grafted with NVP$^b$ and fluorinated polymers grafted with AAc$^b$, although in both cases the carboxylic groups are introduced in the fabrics. This apparent difference is due to the fact that the structure of ungrafted nylon-6 fabric does not contain functional groups that can easily conduct electric current. Cotton fabric, however, contains several OH groups that can conduct electricity. The introduction of COOH and/or CN groups via grafting with AAc, AN or their mixtures seems to decrease the overall conducting efficiency of cotton fabric as the degree of grafting increases. Consequently, the electrical conductivity of cotton fabrics is expected to decrease with the increase in graft yield till saturation at 35%.

3.4.3 Dyeing Properties

3.4.3.1 Effect of pH on Dyeability of Fabric

The effect of pH on the colour strength ($K/S$) of grafted and ungrafted fabrics is shown in Fig. 10. It is observed that the ungrafted fabrics have no affinity towards Sandocryl Blue in acidic or alkaline aqueous
The colour strength of the grafted fabrics prepared from AAc/AN (40:60) mixture with 13.1% graft yield decreases from 18 to 0.5 as the pH increases from 3.9 to 11.5. The results are similar to those obtained for AAc-graft copolymers with graft yield of 4.5% except that the K/S values are higher than those of the latter at the intermediate pH values. This similarity in the initial and final colour strength values is due to the fact that the effective concentration of AAc in 13.1% graft yield is about 5.2%. This emphasizes that the dyeing affinity of fabrics grafted in the comonomer mixture is only due to the addition of the carboxylic groups to the fabric structure via AAc. The role of AN in the grafted fabric is giving a yellowish orange colour of intensity that depends on the degree of grafting. Upon dyeing, the expected blue colour of dye turns to greenish.

3.4.3.2 Effect of Graft Yield on Dyeability of Fabrics

The effect of the degree of grafting on the colour strength of grafted and ungrafted cotton fabrics dyed in 2% owf aqueous solutions, adjusted to pH 3.9, is shown in Fig. 11. It is observed that the colour strength of dyed fabrics increases as the degree of grafting increases to reach its maximum value and thereafter it levels off or shows a tendency to decrease. Acrylonitrile graft copolymers do not show significant affinity towards basic dye studied since the colour strength increases from 2 (the value of ungrafted fabrics) to 7.5 as the graft yield increases to 28%. Fabrics grafted with AAc or AAc/AN mixture show considerably high increase (from 2 to 25) in colour strength as the degree of grafting increases to 20%. The fabrics grafted with AAc/AN mixture contain almost the same effective graft yield as that obtained in AAc alone. It is clear from the results that AAc rather than AN is responsible for the increase in colour strength of grafted fabrics.

The increase in the colour strength of cotton fabrics with the increase in graft yield can thus be attributed to the increase in the COOH functional groups in the fibre structure. This enhances the dye uptake up to a graft yield of 20%. The leveling off in the colour strength at higher degrees of grafting may be explained by the depletion of the aqueous solution from the dye through the increasing number of active functional groups associated with the grafted fabrics while the dye concentration is kept constant, thus decreasing the driving force for the diffusion of the dye into grafted regions. The reaction between the
basic dye and AAc-grafted fabrics can be presented as follows:

\[
\text{H} \quad \text{F}-[\text{CH}_2-\text{C}(=\text{O})\text{COOH}]_{\text{H}} \xrightarrow{\text{ir}} \quad \text{H} \quad \text{F}-[\text{CH}_2-\text{C}(=\text{O})\text{COO}^-]_{\text{H}} + n \text{H}^+
\]

\[
n \text{HCl} + \text{F}-[\text{CH}_2-\text{C}(=\text{O})\text{COO}^-]_{\text{H}} \xleftarrow{\text{Dye}^+} \{n \text{Dye}^+\} \text{Cl}^{-}
\]

4 Conclusions

4.1 Modification of the properties of cotton fabrics is achieved via direct radiation grafting with AAc, AN and their mixtures. The optimum grafting of the fabrics occurs at 2.56 Gy/s dose rate and 1:40 fabric-to-liquor ratio when the grafting is performed in the presence of aqueous AAc containing 0.75% own Mohr’s salt as inhibitor and in 65:15 methanol-water mixture for AN.

4.2 The grafting process follows a second order kinetics for AN and a negative first order one for AAc. The reaction order for monomer mixtures shows different kinetic behaviour depending on AN:AAc ratio in solution and the total monomers content.

4.3 The swelling properties of cotton fabrics improve with the increase in degree of grafting of AAc and deteriorate with the increase in graft yield of AN. Fabrics grafted with monomers mixture show swelling behaviour between those of AAc and AN.

4.4 The electrical conductivity of grafts prepared from the monomers or their mixture shows a fast initial decrease followed by a tendency to level off as the graft yield increases up to 35%, irrespective of the type of monomer or the mixture ratio.

4.5 The dyeability of cotton fabrics towards Sandocryl Blue B-3G, a basic dye, improves considerably as the graft yield of AAc increases. Slight but steady increase in colour strength of AN-grafted fabrics is obtained as the graft yield increases. The increase in colour strength of fabrics grafted with monomers mixture is due to the effective AAc-grafted content of the fabric.

4.6 The pH of the dye bath affects considerably the colour strength of grafted fabrics. Generally, the maximum colour strength values are obtained in acidic medium at pH 3.9 while no difference in the K/S value of grafted and ungrafted fabrics is observed when dyed in alkaline medium at pH 11.

References