A Study on Grafting of Acrylonitrile onto Bleached Sulphonated Jute-cotton Blended Fabric

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Summary: A study of the graft copolymerization of acrylonitrile onto bleached sulphonated jute-cotton blended fabric, using $KMnO_4/H_2SO_4$ redox-initiator system has been made.The polymerization reaction was studied with the respect to graft yield, graft efficiency and homopolymer. Optimization of various parameter of grafting viz. time, temperature, initiator, sulphuric acid and monomer concentration was carried out. Grafting has improved the light fastness of bleached sulphonated jute-cotton blended fabric with basic dyes. More than 13.5% graft yield could be achieved in the present investigation

Introduction

Chemical modification through grafting of vinyl monomers onto jute fibre and cotton fibres has been receiving considerable interest in recent years [1,2]. Although jute fibre possesses high dimensional stability, certain unfavorable textile properties like high sliflhess, very low elasticity, susceptibility towards sunlight, etc. have tremendously limited their use. Therefore, to minimize the undesirableness for intensified textile uses, graft copolymerization of vinyl monomers onto jute fibre has been attempted during the recent years using chemical, photochemical and radiation induced method of initiation where the grafted fibres show improved tenacity, dyeability and tensile properties [3]. Further, among the methods of initiation, chemical methods of initiation of grafting involving oxidising agents like $KMnO_4$, $Na_2S_2O_3$, KaS_2O_8. $KHSO_5$, etc. are promising froni the economic and industrial points of view and are quite selective in nature. Among the chemical initiators permanganate has a separate identity of it own. Permanganate ions is known to act as strong oxidizing agent in an aqueous solution, and either alone or in the presence of an actival-or has been used as an initiator of vinyl polymerization. However, the use of permanganate redox system as initiator of graft copolymerization of vinyl monomers onto cellulosic substrates was recognised in 1963. Since then permanganate ion with suitable catalyst has been used for initiating graft copolymerization onto various cellulosic substrates [4,5]

In the present investigation, an effort has been exerted to modify bleached sulphonated jute-cotton blended fabrics with vinyl monomers, such as acrylonitrile initiated by $KMnO4/H_2SO_4$ systems. In order to make the modification process more economical, attempt has also been made to find out the optimum modification conditions depending on the concentration of monomer, initiator, catalyst, modification time and temperature.

Results and Discussion

Effect of Monomer Concentration

Figure 1 shows that the percent of graft yield and homopolymer increases with the increase of

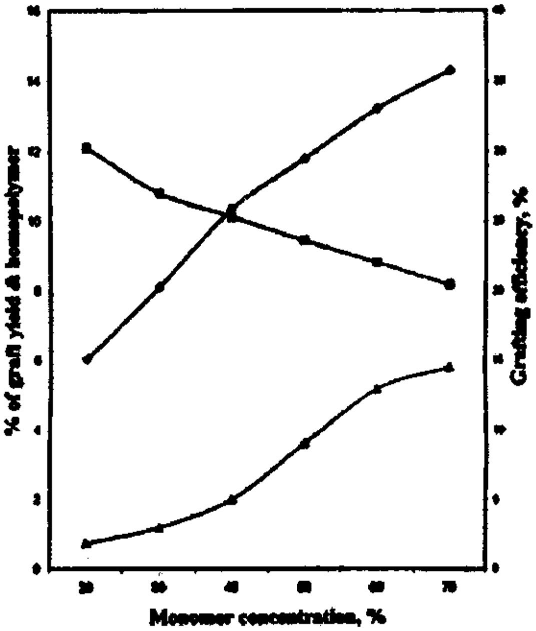


Fig. 1: Draft yield, Graft efficiency and Homopolymer vs Monomer concentration ◆Graft yield, ■ Graft efficiency ▲ Homopolymer

monomer concentration upto 60% (AN) and then it slightly increases further increase of monomer concentration , but the percent of graft efficiency decreases with the increase of monomer concentration. This may be due to higher availability of monomer molecules in the proximity of cellulose macroradicals as well as in the polymerization medium at higher monomer concentration [6,7].

It is apparent that cellulose macroradicals are immobile, and for grafting the monomer should be in the vicinity of the cellulose. It is also apparent that greater availability of the monomer in the polymerization medium acts in favour of molecular collision thereby enhancing polymerization in general or homopolymer formation in particular [1]. The decreased graft efficiency suggests that homopolyerization prevails over grafting at higher monomer concentration [8|.

Effect of Initiator Concentration

Figure 2 shows that the percentage of graft yield and graft efficiency increase with the increase of permanganate concentration upto 0.6% (based on the sample weight) when bleached sulphonated jute-cotton blended fabric is grafted with acrylonitrile and beyond this. the graft yield and graft efficiency decrease. The same is true for homopolymer. The increasing trend of percent grafting might be due to formation of great number of grafting sites [9|, It may be explained that, the enhancement of percent graft yield and graft efficiency may be attributed to increase in the number of active sites on the backbone of sulphonaled jute-cotton blended fabrics [1,10]. Another explanation is that a significant amount of graft formation occurs in the presence of $KMnO_4$ since a certain amount of MnO_2 deposited on the bleached sulphonated jute - cotton blended fabric.

Conversely, the decrease of percentage of graft yield, graft efficiency and homopolymer observed at high $KMnO_4$ concentrations could be interpreted in terms of retardation of monomer diffusion and faster rate of termination. A large amount of MnO_2 could be deposited on the fabric when higher $KMnO_4$ concentrations are used. Besides impeding monomer diffusion, MnO_2 colloid particles act as a source of excess Mn_2 which may contribute to oxidation of sulphonated jute-cotton blended fibre macroradicals, and termination of growing poly (AN) chain [6]. Abundance of primary free radicals may also lead to termination by coupling, thereby decreasing the overall polymerization yield. It is also probable that higher MnO_2 concentration gives rise to higher amount of inhibiting oxygen [1].

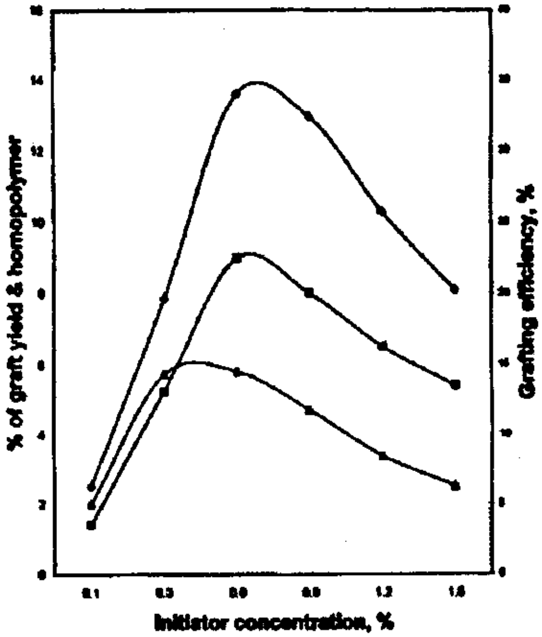


Fig. 2: Graft yield. Graft efficiency and Homopolymer vs Initiator concentration ♦Graft yield, ■ Graft efficiency ▲ Homopolymer

Effect of Time

The effect of time of reaction on grafting is reported in the Figure 3. It is seen that percentage of graft yield and graft efficiency both increase with the increase of reaction time upto 2.5 hours and beyond this time, they decrease. But the percentage of homopolymer increases with the increase of reaction time and maximum percent homopolymer is formed in solution during grafting in 3 hours. This tendency of graft to first increase, attain a maximum value, and then decrease may be accounted for by the increasing extents of initiation and propagation of the reaction initially with time [11]. The decrease in grafting after a particular time may be due to the detrimental effect of the high temperature onto the grafted side chains of AN [8,11].

Effect of Temperature

Figure 4 shows that the percentage of graft yield, graft efficiency and homopolymer during grafting of bleached sulphonated jute-cotton blended

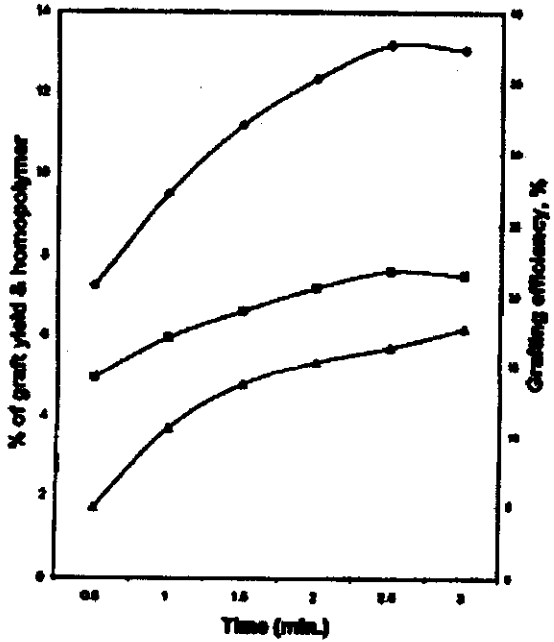


Fig. 3: Graft yield. Graft efficiency and Homopolymer vs Grafting time ♦Graft yield, ■Graft efficiency ▲Homopolymer.

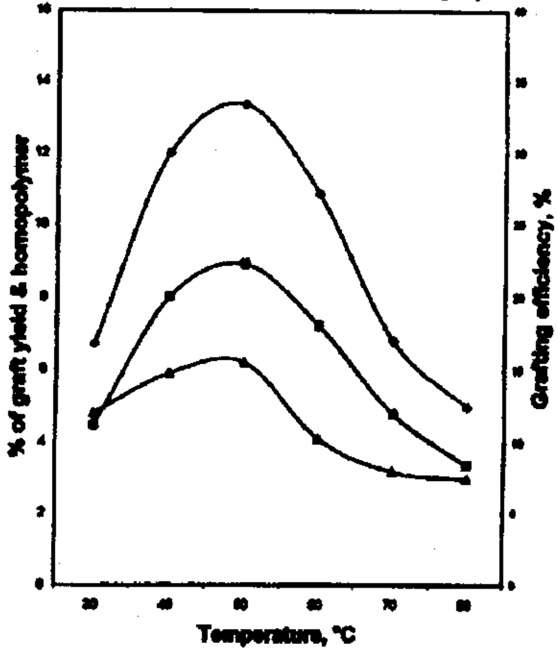


Fig. 4: Graft yield. ♦Graft efficiency and Homopolymer vs Grafting temperature Graft yield, ■Graft efficiency ▲ Homopolymer

fabric increases with the increase of temperature upto 50°C and beyond that they decrease sharply. The increase in percentage of graft yield, graft efficiency and homopolymer upto 50°C may be ascribed to (i) increase in the rate of production of active free-radicals which increase the number of graft sites at a higher rate. The rate of graft initiation by bleached sulphonated jute-cotton blended fibre radicals is thereby increased; (ii) increase in temperature increases the rate of diffusion of acrylonitrile into bleached sulphonated jute-cotton blended fibre matrix where grafting is also initiated by complex monomers [10,12]

The decrease in percentage of grafting beyond 50°C may be attributed to (i) the increase in activation energy i.e. increase in the rate of homopolymerization and (ii) premature termination of growing grafted chains by excess Mn (IV) ions produced on oxidation of Mn (II) ions. Premature termination by higher valency transition metal ions has been observed by Bamford *et al* [13] and Samal *et al* [14].

Effect of Catalyst Concentration

Figure 5 shows that percentage of graft yield, graft efficiency and homopolymer increases with the increase of sulphuric acid concentration upto 1.25% and then it is decreased gradually as the acid concentration is increased. The plausible explanation of such behaviour is that sulphuric acid in the cellulose grafting baths assists in the enhancement in grafting, both by causing inter-and intra-crystalline swelling of the substrate and also by acting as a catalyst in the hydrolysis of cellulose, leading to uncoiling of the chains and improving the monomer accessibility [15]. Further, they show that homopolymerization is also enhanced in the presence of acid. A higher concentration of acid, however, may cause degradation of the backbone cellulose as well as of the graft chains [16,17].

Mechanism

The mechanism of graft copolymerization of acrylonitrile onto bleached sulphonated jute-cotton blended fabrics initiated by $KMnO_4$ in the presence of H_2SO_4. Substantial amounts of MnO_2 were deposited on the bleached sulphonated jute-cotton blended fabric when the latter was soaked in $KMnO_4$ solution. Furthermore, the Mn(IV) ion in the presence of H_2SO_4 was found to induce polymerization of AN with bleached sulphonated jute-cotton blended fabric, indicating that $KMnO_4/H_2SO_4$ forms an effective initiation for polymerization. Characterization of the polymerization products revealed that significant

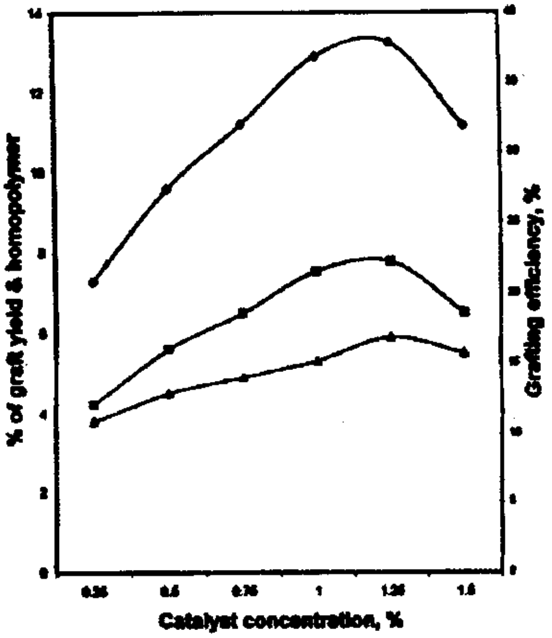


Fig. 5: Graft yield, ◆Graft efficiency and Homopolymer vs Catalyst concentration Graft yield, ■ Graft efficiency ▲ Homopolymer

amounts of the polymer are probably grafted. Radical formation is likely to occur through reduction of Mn(IV) to either Mn(III) or Mn(II), the radical attacks cellulose forming a cellulose macroradical which in the presence of vinyl monomers (AN) induces grafting. Essential reactions involved in grafting may represented as suggested by the scheme shown in equations 1-5.

$$\mathrm{Mn(IV)} + H_2O \rightarrow \mathrm{Mn(III)} + H^+ + {}^{\bullet}OH \qquad (1)$$

$$\mathrm{Mn(III)} + H_2O \rightarrow \mathrm{Mn(II)} + H^+ + {}^{\bullet}OH \qquad (2)$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \qquad (3)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2 + H_2O \qquad (4)$$

$$HSO_4^- + -{}^{\bullet}OH \rightarrow SO_4^{\bullet} + H_2O \qquad (5)$$

Once these free radical species (R') are created, they produce cellulose macroradicals via direct abstraction of hydrogen atom from the hydroxyl groups of the cellulose as suggested by equation 6.

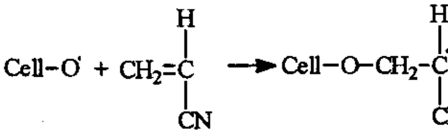
$$\mathrm{Cell\text{-}OH} + R \rightarrow \mathrm{Cell\text{-}O} + R\text{-}H \qquad (6)$$

Furthermore. formation of cellulose macroradicals may also occur via abstraction of hydrogen atoms as results of direct attack of MnIV or MnIII ions on the cellulose molecule, as suggested by equation 7 and 8.

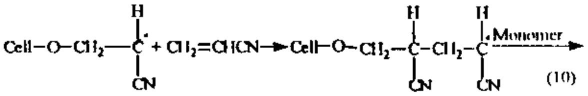
$$\mathrm{Cell\text{-}OH} + \mathrm{Mn(IV)} \rightarrow .\mathrm{Mn(III)} + H^+\ \mathrm{Cell\text{-}O}^{\bullet} \qquad (7)$$

$$\mathrm{Cell\text{-}OH} + \mathrm{Mn(III)} \rightarrow \mathrm{Mn(II)} + H^+ + \mathrm{Cell\text{-}O}^{\bullet} \qquad (8)$$

In the presence of a vinyl monomer, such as acrylonitrile ($CH_2{=}$ CHCN), the cellulose macroradical is added to the double bond of this monomer, leading ultimately to graft copolymer as suggested by the reaction scheme shown in equation 9 and 10



$$\mathrm{Cell{-}O}^{\bullet} + CH_2{=}\overset{\displaystyle H}{\underset{\displaystyle CN}{C}} \longrightarrow \mathrm{Cell{-}O{-}}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle CN}{\dot{C}}} \qquad (9)$$



$$\mathrm{Cell{-}O{-}}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle CN}{\dot{C}}} + CH_2{=}CHCN \longrightarrow \mathrm{Cell{-}O{-}}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle CN}{C}}{-}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle CN}{C}}{}^{\bullet} \xrightarrow{\text{Monomer}} \qquad (10)$$

Characterization of the Grafted blended fabrics

Infrared Spectra

The infrared spectra of the control (bleached) sulphonated jute-cotton blended fabric and grafted (bleached) sulphonated jute-cotton blended fabrics are shown in the figure 6.The Figure 6A shows that the absorption bonds of hydroxyls and carboxyls around 3315-3455 cm^{-1} and 1639-1725 cm^{-1}. The absorption bonds at 1659, 1540, 1437, 1404 and 1369 cm^{-1} further confirmed the presence of further confirmed the presence of guaiacyl and syringyl groups. The presence of 1310-1334 cm^{-1} bond show the presence of syringyl nucleus. Absorption bond at 1233-1278 cm^{-1} is characteristics of syringyl nucleus. The absorption bond at 1157-1178 cm^{-1} show the presence of syringyl type of aromatic C-H in plane deformation and peak at 1003, 907 and 810 cm^{-1} for the presence of epoxy oxirane link [18]. It is seen from the figure 6(B) that the grafted (AN) fabric sample additional peak are obtained at 2235 cm^{-1} is visible which characteristic for the nitrile group corresponding to AN grafted onto bleached sulphonated jute-cotton blended fabric. In the case of grafted fabric, the removal of the carboxyl peak indicated the possible site for grafting. This eventually proves that the bleached sulphonated jute-cotton blended fabric is being grafted with acrylonitrile [1].

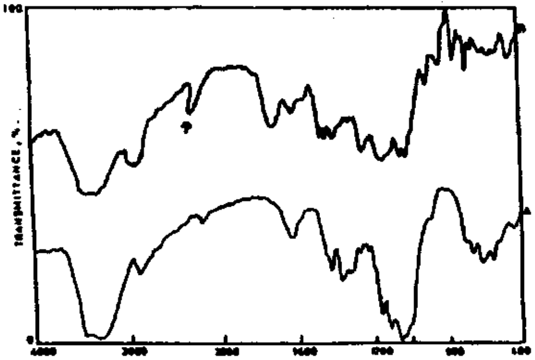


Fig. 6: Infrared Spectra of (A) Bleached blended fabric and (B) AN-grafted bleached blended fabric.

Light Fastness of Dyed Fabric

Basic dyed bleached sulphonated jute-cotton blended fabric and AN-grafted bleached sulphonated jute-cotton blended fabric were tested for light fastness. Results given in the Table-1 indicate that light fastness of grafted fabric is comparatively higher than that of non grafted fabric. This may be explain that maximum co-valent bonds forms with grafted fabric due to higher amorphous spacing capability [19].

Table 1 Light fastness of basic dyed bleached sulphonated jute-cotton blended fabric and grafted bleached sulphonated jute-cotton blended fabric.

Exposure Period, Hr	Light fastness grade Dyes used			
	Magenta		Crystal Violet	
	Bleached Blended fabrics	AN-grafted bleached blended fabrics	Bleached blended fabrics	AN-grafted bleached blended fabrics
0	5	5	5	5
60	3	4-5	3-4	4-5

Experimental

Materials

As a material for investigation, bleached sulphonated jute-cotton blended fabric was used. The monomer, such as acrylonitrile (Ridel-dehaen), was used with purification. A non-ionic wetting agent, namely, sandipen DTC was supplied by Sandoz chemicals Ltd.. Switzerland. Potassium permanganate (MERCK), potassium persulphate (BDH), sulphuric acid (AnalaR), ferrous sulphate (Poland) and potassium bromide (BDH) were reagent grade.

Method

Product of Fabric

Jute fibre was sulphonaled with sodium sulphite [20]. Sulphonatedjutc was blended with 40% cotton for production of (60x60) plain woven fabric

Bleaching

Sulphonated jute-cotton blended fabric was bleached with hydrogen peroxide [21].

Purification of Monomer

The acrylonitrile (AN) monomer was purified by the method ofGupta and Nandy [22].

Grafting

One gram bleached sulphonated jute-cotton blended fabric is taken for each experiment. Initially, blended fabric is treated with .09% $KMnO_4$ (w. o. f.) at 50°C for 10 min. Using material-liquor ratio 1:30 & the sample Is washed with water thoroughly and squeezed between two filter papers before immersing in the polymerization solution . The permanganate treated sample was introduced in an 100 ml conical flask containing an aqueous -solution of vinyl monomer and sulphuric acid. Material-to-liquor ratio 1:40 was used- The contents are then placed into a thermostatic water bath, the temperature of which is kept at 50°C for 2 hr without any disturbance.The sample is then washed with water thoroughly and dried.

Measurement of Grafting Parameter

Percent of graft yield (%G.Y), graft efficiency (%G.E.) and homopolymer were calculated as follows

$$\%\,G.Y \quad \frac{A-B}{B}$$

$$\%G.E= \frac{A-B}{C}$$

Where

A= Weight of the grafted bleached sulphonated jute-cotton blended fabric.

B= Weight of the original bleached sulphonated jute-cotton blended fabric.

C= Weight of total monomers used.

Measurement of Homopolymer

The homopolymer formed during grafting was estimated by filtering out the polymer in a sintered crucible and drying at 105°C until a constant weight was obtained. The percent conversion to homopolymer was calculated as follows [23]

$$\%\ \text{Homopolymer} = \frac{\textit{Weight of homopolymer}}{\textit{Weight of monomer}} \times 100$$

Dyeing

Grafted bleached sulphonated jute-cotton blended fabric was dyed with magenta and crystal violet at 90°C for 1,0 hr [24]

Determination of Lightness

The light fastness of the basic dyed grafted blended fabric was determinated by Xenotester under the following condition. [19]

1. Relative Humidity 78%
2. Black panel temperature 45°C
3. Radiation Generated : Xenon Burner surrounded by optical filter system
4. Exposure period 60 hr

Spectroscopic Analysis

Infrared (IR)

The infrared spectra of the samples were recorded on Simazdu IR-470 infrared spectrophotometer [9]. Two milligrams of the cut sample were mixed with 198 mg of potassium bromide and the pellet was prepared. Scanning was carried out from 4000 to 400 cm^{-1} at a slow speed.

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