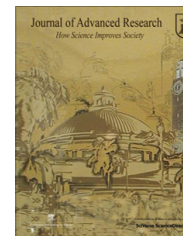




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ORIGINAL ARTICLE

Modification of fiber properties through grafting of acrylonitrile to rayon by chemical and radiation methods



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Abstract Fibrous properties of rayon has been modified through synthesis of graft copolymers of rayon with acrylonitrile (AN) by chemical method using ceric ammonium nitrate (CAN/HNO₃) as a redox initiator and gamma radiation mutual method. Percentage of grafting (Pg) was determined as a function of initiator concentration, monomer concentration, irradiation dose, temperature, time of reaction and the amount of water. Maximum percentage of grafting (160.01%) using CAN/HNO₃ was obtained at [CAN] = 22.80×10^{-3} mol/L, [HNO₃] = 112.68×10^{-2} mol/L and [AN] = 114.49×10^{-2} mol/L in 20 mL of water at 45 °C within 120 min while in case of gamma radiation method, maximum Pg (90.24%) was obtained at an optimum concentration of AN of 76.32×10^{-2} mol/L using 10 mL of water at room temperature with total dose exposure of 3.456 kGy/h. The grafted fiber was characterized by FTIR, SEM, TGA and XRD studies. Swelling behavior of grafted rayon in different solvents such as water, methanol, ethanol, DMF and acetone was studied and compared with the unmodified rayon. Dyeing behavior of the grafted fiber was also investigated.

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Introduction

There are large numbers of useful synthetic and natural organic polymers known today, but still there is a need for new polymer systems to meet various needs, especially for high and low

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temperature use, oil or solvent resistance, flame resistant materials, oxidation resistant polymers, etc. Grafting with suitable monomers imparts desirable properties to the backbone polymer for utilization in selected areas. Modification of the macromolecular properties of cotton and regenerated cellulose fibers by graft copolymerization with selected vinyl monomers impart new textile properties. At low degree of grafting of acrylonitrile (AN), elastic recovery properties of cotton fibers increased. Grafting of vinyl monomers onto cellulosic textiles changes their morphology and increases their abrasion resistance while simultaneously improving their durable press properties. Modification of organo-chemical properties of cellulosic fibers by graft polymerization with specified monomers

impart new chemical properties such as resistance to microbial degradation, improved dye ability and many others.

Grafting of methyl methacrylate (MMA) and butyl acrylate (BA) onto rayon fiber led to poor mechanical properties but with improved thermal behavior. The PMMA grafted fiber improved the interfacial adhesion when PMMA was used as the matrix [1]. Water and equilibrium moisture content of cotton, silk and rayon fibers, graft copolymerized with MMA in the presence of methanol as the swelling solvent were determined [2]. Amorim et al. [3] observed that the results of dyeing of cotton fabrics with bifunctional reactive dyes significantly improved when the fabric after bleaching with hydrogen peroxide was treated with catalase for the elimination of hydrogen peroxide from the fabric. Effect of grafting of MMA onto viscose fiber on thermal properties was studied by Dass et al. [4]. Loleque-Mignard et al. [5] studied the thermal properties of copolymers of α -acetoxy styrene with cyanide monomers (acrylonitrile, methacrylonitrile and vinylidene cyanide). The absorbency of kraft fluff pulp, rayon fiber and short cotton fibers grafted with acrylic acid and AN was found to be higher than the pristine fibers [6]. Grafting of ethyl acrylate and vinyl imidazole and their binary mixture onto rayon fiber by mutual radiation method was carried out and the effect of surfactants on graft percentage was evaluated. Water retention and moisture regain properties of the grafted fibers were compared with those of the unmodified fiber [7]. Recently Bhatt et al. [8] studied different properties and characterized the graft copolymers of cellulose extracted from *Lantana camara* with AN using ceric ions as redox initiator. Badawy et al. [9] studied direct pyrolysis mass spectrometry of AN-cellulose graft copolymer prepared by radiation induced method. Mishra et al. [10] found that the tensile strength and modulus of sisal fibers increased by grafting with 5% AN. The barrier property against oxygen of polyethylene terephthalate (PET) film could be greatly improved by grafting with AN [11]. Graft copolymerization of AN onto cellulosic material derived from bamboo (*Dendrocalamus strictus*) in heterogeneous medium can be initiated effectively with ceric ammonium nitrate [12]. Gupta and Sahoo [13] studied grafting of AN and MMA from their binary mixtures on cellulose using ceric ions.

It is thus observed from literature survey that not much of work on modification of rayon fiber through grafting has been carried out. Recently we reported on successful grafting of acrylic acid onto rayon fiber both by chemical and radiation and it was observed that the radiation method afforded better grafting results and also the fiber with better swelling and thermal behavior [14]. In the present studies we have undertaken modification of fibrous properties of rayon fiber through graft copolymerization of polar vinyl monomer, containing nitrogen as one on the elements, such as AN, to be effective in providing flame retarding properties and also can improve swelling behavior to rayon fiber by chemical and radiation methods. Optimum reaction conditions for affording maximum and homogenous grafting yield were evaluated. The properties like swelling and dyeing behavior of the grafted fiber were evaluated.

Material and methods

The rayon Fiber (Grasim Industries, Birlagram, Nagda, India) was immersed in water at 50 °C for 24 h, filtered and dried in oven to a constant weight, Ceric ammonium nitrate, CAN, (reagent grade) was used as received. Acrylonitrile (AN)

(E. Merck) was freshly distilled before use. Distilled water was used as the reaction solvent. In case of radiation method, the graft copolymerization reactions were carried out in "Gamma-chamber-900" having 2100 curie, Co⁶⁰ as a source of gamma radiation supplied by Bhaba Atomic Research Centre, Trombay, Mumbai, India. All the alcohols such as methanol, ethanol, *n*-butanol, *iso*-butanol and *n*-pentanol were distilled before use.

Graft copolymerization

Graft copolymerization of AN onto rayon fiber has been carried by the following two methods:

Chemical method

Rayon fiber (0.100 g) was immersed in 20 mL of distilled water and known amount of the monomer (AN), and the initiator i.e. CAN and HNO₃ as then added to the reaction mixture. The contents were refluxed at a constant temperature for a specific period (90–210 min) of time. After the stipulated time period, the reaction mixture was filtered. The grafted fiber was thoroughly washed with dimethyl formamide (DMF) for the complete removal of the homopolymer, by a solvent extraction method.

Radiation method

Grafting of AN onto rayon fiber was carried out by mutual radiation method. Rayon (0.100 g) was suspended in a known amount of water in a flask. A definite amount of monomer (AN) was added to the reaction flask. The reaction mixture was irradiated in air for different time periods at a constant dose rate (3.456 kGy/h). After a definite time period, the flask was removed from the chamber and the contents were filtered and transferred to a beaker containing DMF. The mixture was continuously stirred with periodical change of DMF till the entire homopolymer poly (AN) goes into the solution. The contents of the beaker were filtered and washed thoroughly with DMF to ensure complete removal of any homopolymer sticking to the fiber. The grafted fiber was then dried in oven at 50 °C till constant weight was obtained. Percentage of grafting (Pg) was calculated gravimetrically by the following equation:

$$Pg = \frac{W_1 - W_0}{W_0} \times 100$$

where W_0 and W_1 , respectively, are the weights of pristine rayon and the grafted rayon after complete removal of the homopolymer.

Optimum reaction conditions for maximum percentage of grafting were evaluated as a function of concentration of monomer, CAN, nitric acid, amount of water, reaction time, reaction temperature and total dose.

Evidence of grafting

FTIR

FTIR spectra were obtained on a Perkin-Elmer FTIR spectrometer using KBr pellets.

Thermogravimetric analysis (TGA): Thermogravimetric analysis was carried out on a Shimadzu Simultaneous Thermal Analyzer in air at a heating rate of 20 °C/min.

Scanning electron micrography (SEM): Scanning electron micrography (SEM) was taken on a Jeol JSM-6100 scanning electron microscope at 3000× magnification.

X-ray Diffraction analysis (XRD): The X-ray diffraction (XRD) patterns of the samples were recorded on a Philips PANALYTICAL X'PERT PRO X-ray powder diffractometer.

Swelling studies

Swelling behavior of rayon and rayon grafted with acrylonitrile (AN) prepared by chemical and radiation methods in different polar and nonpolar solvents such as water, ethanol, methanol, acetone and DMF has been studied as a function of percentage of grafting and temperature.

Rayon and grafted rayon fiber, (0.100 g), with different percent graft levels were separately suspended in 50 ml of the solvent and kept at 35, 45 and 55 °C for 120 min undisturbed. After the specified time period, the samples were filtered. The adhered surface water on the swollen polymer was removed by softly pressing the fibers between the folds of the filter paper and weighed immediately. The increase in weight was recorded. Percent swelling was determined from the increase in weight over that of the dry sample.

Dye uptake studies

Rayon and rayon-g-poly (AN) were dyed with a 0.0125% aqueous solution of crystal violet and malachite green, and the dyes uptake were determined from the standard curve of the dyes. The optical density was measured on a Labtronics photoelectric colorimeter model L-112.

The graft copolymers rayon-g-poly (AN) was dye adsorption studies. A known weight of the pristine and grafted rayon samples were separately suspended in an aqueous solution (0.0125%) of crystal violet and malachite green at room temperature and kept undisturbed for different time periods. After the stipulated time period, the fiber samples were removed from the dye solution and the absorbance of the residual solution was measured at 590 and 624 nm respectively using UV-Visible spectrophotometer. The concentration of the dye uptake was determined from the standard curve. Percent dye absorption was calculated from the following equation:

$$(\%) \text{ Dye adsorption} = \frac{C_0 - C_e}{C_0} \times 100$$

where C_0 is the initial concentration, C_e is the final concentration of the residual dye solution.

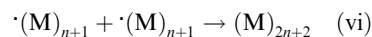
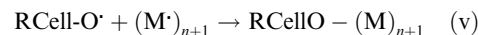
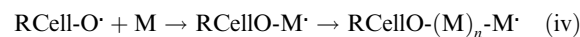
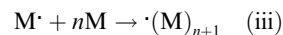
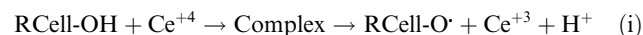
Results and discussion

Mechanism of grafting by chemical method

The reactivity of rayon in a redox initiated graft copolymerization depends on the ability of glycolic —OH groups to form a complex with metal ion like Ce^{4+} and on the consequent exchange or transfer of electrons to form radicals, which initiate polymerization and graft copolymerization reactions.

The C_2 , C_3 , C_6 hydroxyl groups in cellulose are the sites for grafting. Ceric ion is known to form complex with hydroxyl groups and C_2 and C_3 glycolic hydroxyl groups are the preferred sites for the complex formation. The complex disproportionates to generate free radical sites, where appropriate

vinyl monomers can be grafted. Following are the possible reactions of grafting acrylonitrile onto rayon.

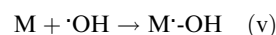
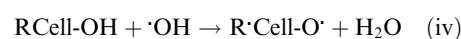
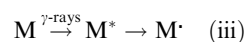
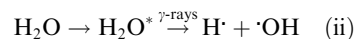
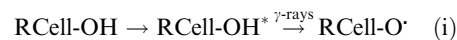


The initiation of monomer via complex formation with ceric ion explains homopolymer formation along with the grafting reaction. The graft yield and the homopolymer formation are the functions of both the monomer and the initiator. Other reaction variables viz. liquor ratio temperature and time of reaction also influence these reactions.

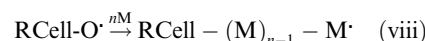
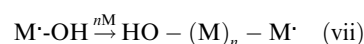
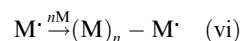
Mechanism of grafting by radiation method

During mutual irradiation, monomer radicals and active sites on the backbone are generated simultaneously hence grafting can be achieved either by the reaction between the growing polymeric radicals and the active sites on the backbone i.e. by the 'grafting onto' method (step ix) or by the 'grafting from' method when monomer initiation takes place directly from the active sites on the cellulose backbone (step viii). Various processes that seem to occur are detailed as:

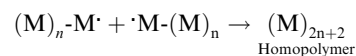
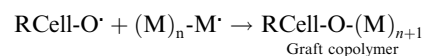
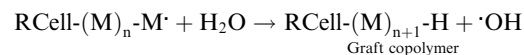
Initiation



Propagation



Termination



The extent of grafting is, therefore likely to be influenced by the number of active sites on the polymer but other reaction parameters such as the extent of exposure to the radiations, i.e. total dose, monomer concentration, liquor ratio also have a vital role in these reactions.

Percentage of grafting of acrylonitrile onto rayon fiber by chemical and radiation methods was, therefore studied as a

function of different reaction parameters and the results are explained in the light of the above mechanisms.

Effect of initiator

$[CAN]/[HNO_3]$

The effect of concentration of CAN and HNO_3 on percentage of grafting of AN onto rayon fiber was studied and the results are presented in Table 1 respectively. It is observed from the Table that after a gradual increase in percentage of grafting with increasing [CAN], maximum grafting (160.01%) was obtained at $[CAN] = 22.80 \times 10^{-3}$ mol/L. Further increase in the concentration of CAN leads to decrease in Pg. The decrease in Pg with increasing [CAN] may be due to the reason that with the increased concentration of CAN, the complex formation between the monomer and CAN is increased leading to initiation of monomer units and hence more of homopolymer formation takes place. Termination of growing grafted chains and polymeric chains by excess Ce^{4+} ions also leads to decreased percentage of grafting.

It is observed from Table 1 that the percentage of grafting increases gradually with increase in the concentration of acid, gives maximum (160.01%) at $[HNO_3] = 112.68 \times 10^{-2}$ mol/L and decrease with further increase in the acid concentration. The lower concentration of acid catalyzes the grafting reactions and hence an increase in Pg is observed. Increase in $[HNO_3]$ also increases the Ce^{4+} concentration, which also leads to decrease in Pg due to termination reaction [15].

Total dose

Percentage of grafting of AN onto rayon fiber was studied as a function time of exposure to gamma radiations, i.e. total dose

given to the reaction mixture and the results are presented in Table 2. It is observed from the table that grafting of AN onto rayon increases sharply with increasing total dose and reaches a maximum value (90.24%) at a total dose of 3.456 kGy, beyond which Pg was found to decrease continuously. The generation of active sites on the polymeric backbone, initiation of monomer directly by gamma radiation or by hydroxyl radicals generated from the radiolysis of water leads to increase in percentage of grafting. However, beyond the optimum total dose, the decrease in grafting percentage is due to preferential homopolymer formation and termination of growing grafted and polymeric chains.

Effect of monomer concentration

Percentage of grafting of acrylonitrile onto rayon by both chemical method and radiation methods was studied as a function of [AN] and the results are presented in Tables 1 and 2 respectively.

It is observed from the tables that percentage of grafting of acrylonitrile by both the methods increases with increasing monomer concentration reaches maximum and decreases thereafter. Maximum grafting (160.01% and 90.24%) using CAN/ HNO_3 and γ -radiations was obtained at $[AN] = 114.49 \times 10^{-2}$ and 76.32×10^{-2} mol/L. A sharp decrease is observed beyond the optimum monomer concentration which is due to the preferred homopolymer formation because of high values of the rate of propagation, k_p , (32,500 L/mol S) and rate of termination, k_t , (4400×10^{-6} L/mol S) [16] of acrylonitrile. Monomer and polymer transfer constant also bring wastage of monomer in the side reaction and hence, decrease in percentage of grafting is observed.

Table 1 Effect of reaction conditions on % grafting and % efficiency of AN onto rayon fiber by chemical method.

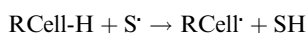
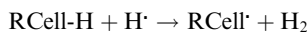
$[CAN] \times 10^{-3}$ moles/L	$[HNO_3] \times 10^{-2}$ moles/L	$[AN] \times 10^{-2}$ moles/L	Amount of water	Temperature (°C)	Time (min)	% Grafting	% Efficiency
13.68	112.68	114.49	20	45	120	19.83	1.63
18.24	112.68	114.49	20	45	120	40.21	3.31
22.80	112.68	114.49	20	45	120	160.01	13.17
27.36	112.68	114.49	20	45	120	69.80	5.74
31.92	112.68	114.49	20	45	120	30.02	2.47
22.80	28.17	114.49	20	45	120	70.32	5.79
22.80	56.34	114.49	20	45	120	90.41	7.44
22.80	169.02	114.49	20	45	120	120.11	9.89
22.80	225.36	114.49	20	45	120	19.56	1.61
22.80	112.68	19.08	20	45	120	100.25	49.51
22.80	112.68	38.16	20	45	120	140.13	34.60
22.80	112.68	76.33	20	45	120	150.20	18.54
22.80	112.68	152.66	20	45	120	69.78	4.31
22.80	112.68	114.49	10	45	120	40.34	3.32
22.80	112.68	114.49	15	45	120	130.00	10.70
22.80	112.68	114.49	25	45	120	110.22	9.07
22.80	112.68	114.49	20	35	120	99.68	8.20
22.80	112.68	114.49	20	40	120	129.88	10.69
22.80	112.68	114.49	20	50	120	50.29	4.14
22.80	112.68	114.49	20	55	120	30.31	2.49
22.80	112.68	114.49	20	45	90	70.06	5.77
22.80	112.68	114.49	20	45	150	140.16	11.54
22.80	112.68	114.49	20	45	180	100.34	8.26
22.80	112.68	114.49	20	45	210	79.92	6.58

Table 2 Effect of reaction conditions on % grafting and % efficiency of AN onto rayon fiber by radiation method.

Total dose (kGy)	[AN] × 10 ⁻² moles/L	Amount of water (mL)	% Grafting	% Efficiency
0.864	76.32	10	30.04	7.42
1.728	76.32	10	59.82	14.77
3.456	76.32	10	90.24	22.28
6.912	76.32	10	80.14	19.79
10.37	76.32	10	70.31	17.36
13.82	76.32	10	60.09	14.84
17.28	76.32	10	50.19	12.39
20.74	76.32	10	9.95	2.46
3.456	38.16	10	40.07	19.79
3.456	152.66	10	60.28	7.44
3.456	228.99	10	39.87	3.28
3.456	305.32	10	19.83	1.22
3.456	76.32	5	79.73	19.69
3.456	76.32	15	59.68	14.74
3.456	76.32	20	49.76	12.29
3.456	76.32	25	19.68	4.86

Effect of reaction medium/liquor ratio

Graft copolymerization of acrylonitrile onto rayon fiber by chemical and radiation induced methods was studied in aqueous medium and in water-alcohol binary solvent mixture and the results are presented in Tables 1 and 2 and Figs. 1 and 2 respectively. It is observed from the tables that percentage of grafting increases with increasing amount of water giving maximum (160.01% and 90.24%) in 20 ml and 10 ml respectively by chemical and radiation methods. Water as a grafting reaction medium has been found to be very useful since it has a zero chain transfer constant; hence, wastage of monomer inside reaction is minimized. Furthermore, water swells the polymer backbone and increases the accessibility of growing macropolymeric radicals to the active sites giving higher percentage of grafting. In addition to this, when grafting is carried out by the radiolysis of the solvent itself, as a result of radiolysis, H atom and solvent radical S may be formed. These radicals arising from solvent radiolysis [17,18] may help in providing more free radical centers at the trunk polymer sites which may bring forth an increased yield of grafting.



However, with further increase in the amount of water, beyond the optimum value, percentage of grafting experiences a decrease. In addition to the hydrophilic behavior of the backbone polymer towards swelling of trunk polymer and loosening of cellulose hydrogen-bonding, there also exists a possibility of formation of a H₂O-cellulose-monomer complex, which too leads to homopolymer formation and hence decreases Pg. Increased amount of water also constrains the accessibility of the monomer molecule and growing polymeric chains to the active sites on the backbone polymer due to dilution effect leading to decrease in Pg.

The decrease in Pg in radiation method with increasing amount of water may be due to the reason that with increasing amount of water the concentration of hydroxyl radicals increases, which initiate the monomer (step-v) leading to more of homopolymer formation. The formation of molecular hydrogen and hydrogen peroxide in aqueous solution of acrylonitrile was studied by Cottin and Lefort [19] and it was found

that yield of H₂ and H₂O₂ reduced from 0.36 in pure water to 0.33 and 0.15 respectively in acrylonitrile solution suggesting that the monomer is capable of trapping the precursors of molecular products i.e. H, OH, HO₂ formed upon radiolysis of water and hence undergo homo-polymerization reactions preferably.

In another set of experiments, keeping the optimum amount of water fixed at 20 ml and 10 ml for the chemical and radiation method respectively, aliphatic alcohols of varying alkyl chain lengths was added to water as additive and studied their effect on percentage of grafting of AN onto rayon fiber. It is observed from Fig. 1 that in case of chemical grafting, grafting percent of AN increases with increase in the amount of alcohol from 5 ml to 10 ml i.e. (10:10 v/v water-alcohol) giving maximum, which is higher than that obtained in aqueous medium (160.01%). The amount of Pg and the order of alcohol giving maximum percentage of grafting in water-alcohol binary solvent system were observed as shown below:



(230%) (220%) (200%) (180%) (180%)

However, percentage of grafting in pure alcohol (0 ml water) is lower than that obtained in aqueous medium except in pentanol, which gives same amount of grafting (160.01%)

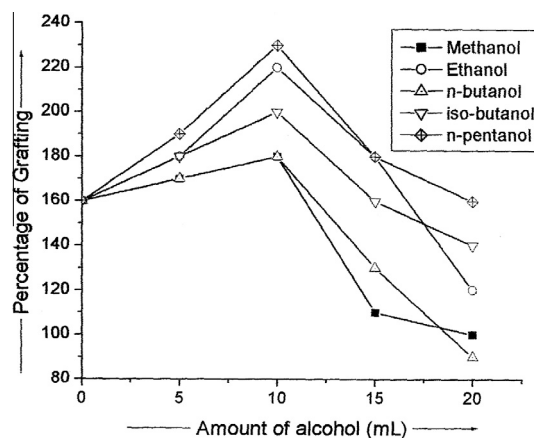


Fig. 1 Effect of different alcohols on percentage of grafting on AN onto rayon by chemical method.

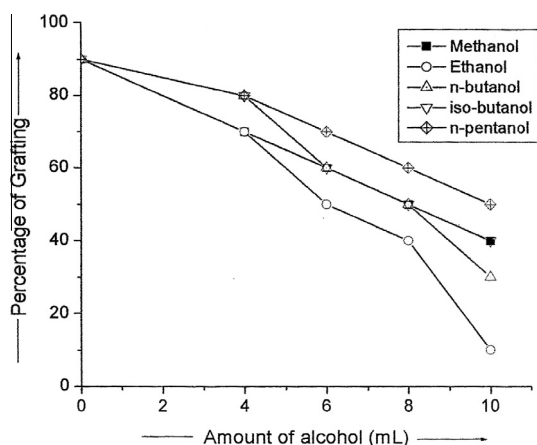
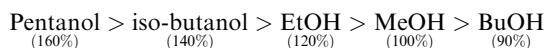


Fig. 2 Effect of different alcohols on percentage of grafting on AN onto rayon by radiation method.

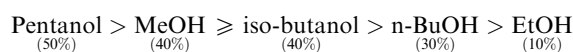
as is obtained in aqueous medium. The order of reactivity of alcohols (when used alone) towards grafting of AN lies in the following order:



The saturated monohydric alcohols cannot form a three dimensional network of hydrogen bonds, but instead are susceptible to chain like association or cyclic association. The degree of association decreases markedly with the increasing mass of the alcohol, transition from straight chain alcohols to branched-chain ones and with increasing temperature. Higher alcohols such as *n*-pentanol and 2-methyl propanol, do not swell the backbone as effectively as water, since the relative sorption and swelling properties fall markedly in proceeding through the alcohol series. They do not form an effective complex with the Ce^{4+} ion, which is also dependent on the size/molecular mass of alcohol. This fact was experimentally verified by observing the optical densities of the Ce^{4+} -alcohol system on a Spectronic-20 spectrophotometer. Thus, the generation of additional active sites via a Ce^{4+} -alcohol complex is inconsequential, yet, these alcohols produce a higher grafting percent than that obtained in water. This observation may be explained by the fact that since higher alcohols do not have any interactions with the backbone polymer and the Ce^{4+} ion, the normal grafting process, i.e. the generation of active sites and graft formation reactions take place undisturbed. In the case of lower alcohols, i.e., methanol and ethanol, they break the H-bonded structures formed between rayon and water molecules and the associated structure of water and instead form hydrogen-bonded structure with water. This leads to decrease in swelling of the fiber and hence the exposure of the active sites. The destruction of structure of water is accompanied by the decreasing factor of auto diffusion that restricts the accessibility of the monomer to the active sites, thus lowering the percentage of grafting.

The effect of added alcohols to water was also studied during radiation induced grafting and it is observed from Fig. 2 that addition of alcohol to water continuously decreased percentage of grafting. In pure alcohols (0 ml water) also, Pg of AN was less than that obtained in aqueous medium

(90.24%) and the following order of reactivity of different alcohols (when used alone), towards grafting was observed.



In addition to the effect of the added alcohols due to their structural behavior as discussed, radiolysis of alcohols takes place during exposure to gamma rays that lead to the generation of nonreactive radicals that suppress the grafting reactions thereby decreasing percentage of grafting.

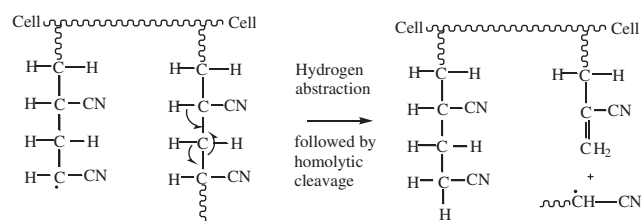
Effect of temperature

Table 1 represents the effect reaction temperature on percentage of grafting of AN onto rayon fiber. It is observed from the Table that percentage of grafting increases gradually with increasing temperature giving maximum (160.01%) at 45 °C beyond which it decreases sharply. Initially increase in Pg with increase in temperature is co related to the enhanced swelling of the trunk polymer which helps in exposing the active sites. An optimum temperature is required for the decomposition of the redox system and as the temperature increases, an accelerated decomposition of the redox system, takes place generating maximum free radicals and hence maximum Pg (160.01%) at optimum temperature (45 °C) is observed. The mobility of the monomer molecule and the growing polymeric chains are also increased with increasing temperature, which helps in enhanced diffusion and hence higher percentage of grafting is observed. The monomer chain transfer constant (C_M) [20–22] increases from 0.17×10^{-4} at 40 °C to 0.27×10^{-4} and/or 8.2×10^{-4} at 50 °C, while the polymer transfer constant [21] at 50 °C is 4.7×10^{-4} . Higher chain transfer constants at higher temperatures lead to various side reactions leading to decrease in percentage of grafting.

Effect of reaction time

Percentage of grafting of AN by chemical method was studied as a function of reaction time and the results are presented in Table 1.

It is observed from the Table that percentage of grafting increases with increase in the reaction time from 90 to 120 min, where maximum grafting (160.01%) was obtained beyond which a continuous decrease in Pg was observed. This trend in Pg with time is explained by the fact that as time progresses, monomer backbone and initiator interaction increases, generating higher amount of radical species leading to increase in percentage of grafting. Beyond the optimum time period, degrafting by chain scission processes i.e. backbiting of the growing grafting chain by the living radical takes place leading to decrease in percentage of grafting.



Evidence of grafting

Scanning electron microscopy

Figs. 3a, 3b and 3c represent the scanning electron micrographs (SEM) of rayon and rayon-g-poly (AN) by chemical and radiation method respectively. The comparison of the SEM of the pristine and the grafted fiber give a clear indication of change in the topology of the grafted samples. Grafting of vinyl monomer on rayon backbone opens up its matrix and shows considerable deposition of poly (AN) on the surface of the backbone polymers.

FTIR spectroscopy

FTIR spectra of pristine rayon and rayon-g-poly (AN) by chemical and radiation methods are presented in Fig. 4. The FTIR spectrum of pristine rayon fiber shows a broad band at 3435.9 ($\nu_{\text{O-H}}$ str), 2893.5 ($\nu_{\text{C-H}}$ str), 1064.9 ($\nu_{\text{C-O-C}}$ str) and 896.1 cm^{-1} ($\nu_{\text{C-C}}$ str) vibrations. The grafted fiber, on the other hand shows an additional peak at 2245.2 cm^{-1} ($\nu_{\text{C=N}}$) due $-\text{CN}$ group of the grafted poly (acrylonitrile) chains indicating that the poly (AN) chains are chemically bonded to the rayon fiber.

Thermogravimetric analysis

Primary thermograms of rayon and rayon-g-poly (AN) fiber prepared both by chemical and γ -radiation methods are presented in Fig. 5.

The initial decomposition temperature (IDT) and decomposition temperature at every 10% weight loss are presented in Table 1. The IDT of the grafted fiber obtained by chemical method (232.4 °C) and radiation method (243.9 °C) is higher than that of the pristine fiber (231.1 °C).

In the case of ungrafted rayon (Fig. 5a), the initial loss in weight between 100 and 200 °C is principally due to dehydration beyond which starts the degradation. It is generally believed that cellulose undergoes three major primary reactions during thermal destruction i.e. Thermoxidation, dehydration and the formation of glucosans. The first substantial stage occurs between 231.10 °C and 343.1 °C with 60% weight loss beyond which starts the second stage. The decomposition continues up to 420 °C. The rate of decomposition is fast during the first stage up to 60% weight loss. This is reflected in the

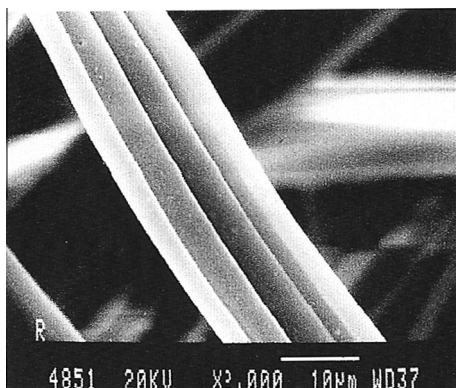


Fig. 3a SEM of rayon fiber at magnification ($x = 3000$).

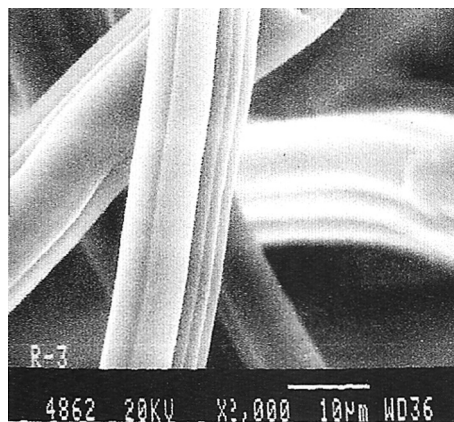


Fig. 3b SEM of rayon-g-poly (AN) at magnification ($x = 3000$) (chemical method).

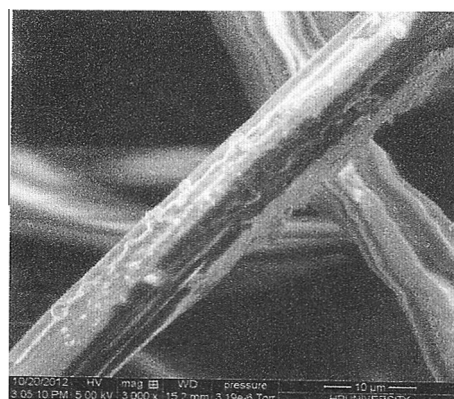


Fig. 3c SEM of rayon-g-poly (AN) at magnification ($x = 3000$) (radiation method).

small temperature difference between every 10% weight loss. The decomposition in the second stage becomes slower with much higher temperature difference between every 10% weight loss. At the end 13% of the residue was left.

The AN-grafted rayon prepared by radiation method (Fig. 5b) shows the first stage of decomposition between 243.9 and 363.5 °C with 60% weight loss. Thereafter begins the second stage which continues up to 485.7 °C. The residue left is 24%. The decomposition temperature of the rayon-g-poly (AN) grafted by chemical method is very high beyond 60% weight loss as compared to the one prepared by the radiation method.

Primary thermogram of rayon-g-poly (AN) prepared by chemical method (Fig. 5c) shows the first stage of decomposition between 232.4 and 355 °C with 35% weight loss. The second stage of decomposition begins thereafter and was found to remain stable without any weight loss till 447 °C beyond which the decomposition continues up to 59 °C with 65% weight loss. The temperature difference between every 10% weight loss in the first stage is small which increases in the second stage.

On comparison with the grafted rayon samples with ungrafted rayon, the graft copolymerization of AN has improved the thermal stability of the fiber.

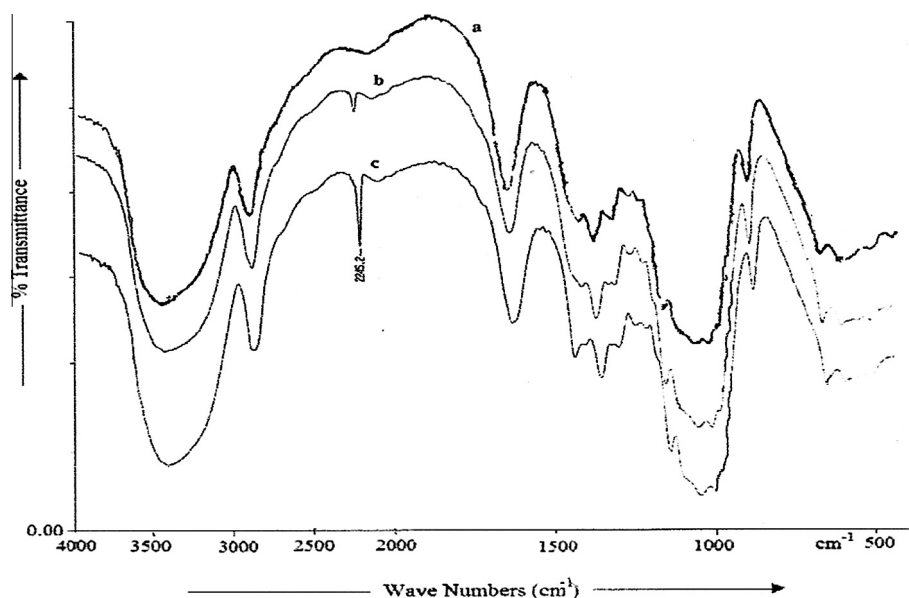


Fig. 4 FTIR spectrum of (a) rayon fiber, (b) rayon-g-poly (AN) by chemical method, and (c) rayon-g-poly (AN) by radiation method.

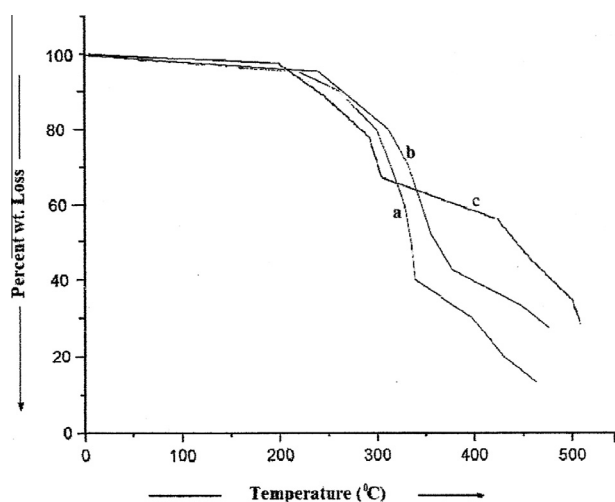


Fig. 5 Primary Thermogram of (a) rayon fiber, (b) rayon-g-poly (AN) (chemical method), and (c) rayon-g-poly (AN) (radiation method).

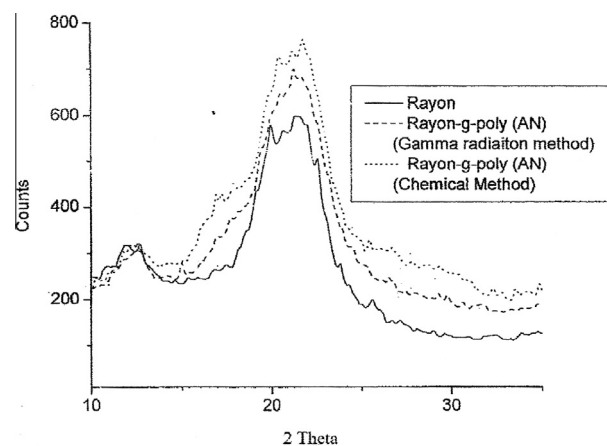


Fig. 6 X-ray diffraction pattern of rayon (—), rayon-g-poly (AN) (gamma radiation method, - - -), rayon-g-poly (AN) (chemical method, ·····).

X-ray diffraction studies

X-ray diffraction pattern and data of rayon and rayon-g-poly (AN) fiber prepared both by chemical and γ -radiation methods are presented in Fig. 6 and Table 3 respectively.

It is observed that the X-ray diffraction pattern of ungrafted rayon shows small peaks between 11.94 – 12.70° (2θ) and an intense peak in the region 19.99 – 22.59° (2θ) with 8.78% peak intensity (599 counts) structure presented in the rayon fiber. The main characteristics peaks at 12.70° , 20.68° and 22.59° 2θ value with FWHM, intensity and crystalline size are presented in Table 2.

Similar peaks in the X-ray diffraction pattern of cellulose has been reported by Canché-Escamilla et al. [1]. Fibers from regenerated cellulose have a semi-crystalline structure and

therefore, are composed of crystallites together with more or less disordered (amorphous) regions [23].

On grafting with acrylonitrile by chemical and gamma radiation methods leads to changes in the X-ray diffraction pattern of rayon. A change in the amorphous zone is observed. Intense peaks in the region of 20.43 – 21.79° (2θ) in case of grafting by chemical method and 20.48 – 21.67° (2θ) in case of grafting by gamma radiation method were observed. The counts and intensities of the peaks in the grafted sample have been found to increase. Maximum intensity 89.80% was observed for grafted sample prepared by gamma radiation. These changes (peak value, peak intensities, particle size, etc.) indicate an increase of the crystalline structure of grafted rayon due to the presence of poly (AN) at the inner structure of the fiber. The d-spacing in the polymer matrix increases upon grafting indicating increase in crystalline behavior. The particle size

Table 3 X-ray Diffraction data of rayon, rayon-g-poly (AN) prepared by chemical and gamma radiation method.

Samples	2θ value	Counts	FWHM	Relative intensity (%)	d-spacing (Å)	Particle size (Å)
Rayon	21.5850	599.3753	0.06460	8.78	3.93726	21.83
Rayon-g-poly (AN) (chemical method)	21.7750	764.3424	0.06774	53.40	4.08540	20.83
Rayon-g-poly (AN) (gamma radiation method)	21.2750	700.3821	0.06757	89.80	4.18414	20.87

Table 4 Percentage of swelling of rayon and rayon-g-poly (AN) in different solvents at different temperature.

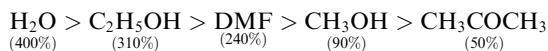
S. No.	Percent grafting	Temp. (°C)	Percent swelling				
			Water	Methanol	Ethanol	DMF	Acetone
1	0.00	35	400.00	90.00	310.00	240.00	50.00
2	50.00		85.00	30.00	50.00	100.00	20.00
3	70.00		104.50	36.00	65.00	140.00	15.00
4	110.00		126.00	38.00	87.20	161.50	10.00
5	0.00	45	262.00	70.00	235.00	128.00	35.00
6	50.00		75.00	24.00	27.00	85.00	19.00
7	70.00		87.00	26.00	46.00	108.00	14.50
8	110.00		105.00	27.50	65.00	135.00	3.00
9	0.00	55	227.00	65.00	200.00	95.00	25.00
10	50.00		65.00	14.00	23.00	83.40	7.00
11	70.00		75.00	17.50	43.00	125.00	4.00
12	110.00		100.00	21.00	64.00	148.00	3.00

calculated applying Scherer equation shows that particles size decreased upon grafting.

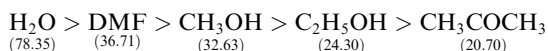
The variation in X-ray diffraction pattern upon grafting evinces the changes rayon fiber undergone upon grafting.

Swelling studies

Percent swelling of rayon and acrylonitrile grafted rayon fiber in different solvents such as water, methanol, ethanol, DMF and acetone at 35 °C, 45 °C and 55 °C was studied as a function of percentage of grafting and temperature, and the results are presented in Table 4. It is observed from the table that the percent swelling of rayon in different solvents decreases with an increase in temperature. Maximum swelling (407%) was observed in water followed by ethanol (322%) at 35 °C. The following order of different solvents towards swelling of rayon in decreasing order was observed:



Higher percent swelling in water is expected, as water enters into H-bonding with the hydroxyl groups of rayon fiber consisting of anhydro-glucose units. These bonding take place in the amorphous region of the polymer where the hydroxyl groups are exposed for such interactions. Strong intra hydrogen bonding of the glucose units with in the fiber inhibits any other interaction. Swelling behavior of different solvents is based on the dielectric properties and the structures of the alcohols. As regards the dielectric constants, the order of the solvents studied is as follows:



Structurally water, methanol and ethanol have intermolecular H-bonded associated structures, while DMF and acetone are polar aprotic solvents. The swelling of rayon fiber in these solvents depends upon the extent on interaction of these solvents with the hydroxyl groups of rayon. Water as explained, having higher dielectric constant form H-bond with the hydroxyl groups and gives maximum percent swelling. However, between methanol and ethanol, although methanol has higher dielectric constant than ethanol, yet gives lower percent swelling. This may be explained by the fact that the H-bonded polymerized structure of methanol does not easily break to form H-bonded structure with the hydroxyl groups of the rayon fiber. It is known that methanol dissolves in water with relatively little volume loss, i.e. it retains its H-bonded structure occupying the cluster framework sites.

DMF, although it is an aprotic solvent, is polar with a high ϵ and dipole moment (3.82D), interacts with the hydroxyl groups of the fiber leading to a substantial percentage of swelling. In the case of acetone, which is also an aprotic polar solvent but with a lower value of ϵ and a smaller dipole moment (2.88D), gives lower percentage of swelling.

Swelling behavior of rayon-g-poly (AN) in different solvents at different temperatures such as 35 °C, 45 °C and 55 °C was studied as a function of percentage of grafting. It is observed from the table that percent swelling of AN grafted rayon fiber in all the solvents and at all temperatures is less than that observed with ungrafted rayon fiber. The reason for this is that the pendant nitrile group of the grafted polymer i.e. poly (AN) is not polar enough to form H-bonded structure with the added solvents and gives higher swelling percentage. It is further observed that in the present case percentage of swelling in all solvents except acetone increases with increasing

Table 5 Dye-uptake (crystal violet) studies of rayon and rayon-g-poly (AN).

Rayon/grafted rayon	% Age grafting	O.D. Residual solution	% Conc. residual solution	% Conc. dye adsorbed	O.D. residual solution after washing with H ₂ O	% Conc. dye residual solution after washing	% Conc. of dye adsorbed after washing	% Dye adsorbed
Rayon	0	1.34	0.00412	0.00838	0.58	0.00120	0.00718	57.4
Rayon-g-poly(AN)	20	1.75	0.01202	0.00230	0.13	0.00025	0.00205	16.4
Rayon-g-poly(AN)	40	1.68	0.0072	0.00535	0.13	0.00025	0.00510	40.8
Rayon-g-poly(AN)	60	1.64	0.0074	0.00510	0.15	0.00030	0.00480	38.4
Rayon-g-poly(AN)	80	1.74	0.0100	0.00250	0.11	0.00022	0.00280	28.4

Table 6 Dye-uptake (malachite green) studies of rayon and rayon-g-poly (AN).

Rayon/grafted rayon	% Age grafting	O.D. residual solution	% Conc. residual solution	% Conc. dye adsorbed	O.D. residual solution after washing with H ₂ O	% Conc. dye residual solution after washing	% Conc. of dye adsorbed after washing	% Dye adsorbed
30 min.								
Rayon	0.0	2.772	0.00931	0.00319	0.202	0.00041	0.00278	25.52
Rayon-g-poly(AN)	100	2.757	0.00862	0.00388	0.012	0.000023	0.00386	31.04
	120	2.765	0.00904	0.00346	0.171	0.00035	0.00311	27.68
60 min								
Rayon	0.0	2.757	0.00862	0.00388	0.210	0.00043	0.00345	31.04
Rayon-g-poly(AN)	100	2.749	0.00825	0.00425	0.012	0.000023	0.00423	34.00
	120	2.750	0.00833	0.00417	0.175	0.00035	0.00382	33.36
120 min								
Rayon	0.0	2.735	0.0076	0.0049	0.378	0.00078	0.00412	39.20
Rayon-g-poly(AN)	100	2.721	0.006897	0.0056	0.028	0.00005	0.00555	44.82
	120	2.728	0.00729	0.00521	0.228	0.00046	0.00475	41.68

percentage of grafting. This is attributed to the reason that with increasing percentage of grafting number of pendant nitrile group increases, which do not have any inter and intra molecular interaction but instead interacts with the added solvent gives higher percentage grafting. Decrease in percent swelling with increasing temperature is due to the breakage of the H-bonded or any other interaction between the nitrile groups and the added solvents.

Dyeing behavior

The percent dye up take (crystal violet and Malachite green) by the pristine and grafted rayon fiber was studied as a function of percentage of grafting and the results are presented in Tables 5 and 6 respectively.

It is observed from Table 5 that for the pristine fiber the dye up (crystal violet) take is 57.4% where as the fiber grafted with AN show lower percent dye uptake. The percent dye uptake increases with increase in percentage of grafting from 20% to 30% beyond which percent dye uptake decreases. The pendant nitrile group ($-C\equiv N$) of the grafted poly (AN) do not seem to have any interaction with the dye molecule and decrease the percent dye uptake of the grafted fiber in comparison to the ungrafted rayon fiber in comparison to the ungrafted rayon fiber.

When malachite green was used as the dye different observations were made (Table 6). The dye uptake was studied as a function of time. It is observed from the table that percent dye uptake increases with increase in time for both the pristine and

the grafted fiber. The pristine fiber uptakes only 39.20% of the dye in 120 min where as the grafted fiber shows higher uptake, maximum percent uptake of Malachite green (44.82%) was observed for the AN grafted rayon fiber with 100% graft level in 120 min. However, the percent uptake decreases with increase in the percent graft level.

Conclusion

Rayon fiber has been successfully grafted with acrylonitrile (AN) by chemical and radiation induced methods. Maximum percentage of grafting of AN onto rayon fiber by chemical method (160.01%) is higher than that obtained by the radiation method (90.24%) obtained under optimum reaction conditions. The grafted fiber has improved swelling and thermal properties in comparison to the pristine fiber. The grafted fiber showed good affinity for both the dyes. At 40% graft level, the percent dye uptake for crystal violet is 40% whereas for the 100% graft level the percent dye uptake for Malachite green is 44.8%. Better swelling properties, thermal properties and affinity for dyes evinces that the grafted rayon fiber can be useful in waste water treatment applications.

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