

Radiation Induced Graft Copolymerization of Vinyl Monomers and Their Binary Mixture onto Rayon Fibre

Sunita Rattan,¹ Jaya Maitra,¹ B. N. Misra,² Inderjeet Kaur²

¹Department of Applied Sciences, Amity School of Engineering and Technology, Bijwasan, New Delhi 110 061, India

²Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla 171 005, India

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ABSTRACT: Ethyl acrylate (EA), Vinyl imidazole (VI), and their binary mixture have been copolymerized onto rayon in aqueous medium by mutual method using γ -radiation. The graft yield has been determined as a function of different reaction parameters such as total dose, concentration of vinyl monomers, and amount of water. Effect of surfactant (1-octane sulfonic acid, sodium salt) has been studied on the percentage of grafting of EA, VI, and (EA + VI). A plausible mechanism has been suggested to explain the

observed behavior of the surfactant on grafting. Water retention and moisture regain of the grafted film was determined at appropriate relative humidity. The graft copolymers have been characterized by IR spectroscopy and scanning electron microscopic methods. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3104–3113, 2008

Key words: γ -radiation; graft copolymerization; binary mixture; surfactant; water retention; moisture regain

INTRODUCTION

Modification of properties of cellulosic materials by graft copolymerization is an active area of research that has attracted the attention of chemists all over the world. Grafting of vinyl monomers onto rayon fiber brings about new properties in the backbone polymers depending upon the grafting technique employed. Extensive work has been done on grafting onto rayon fiber by chemical and radiochemical methods.

Misra et al.¹ grafted EA onto cellulose using ($\text{Fe}^{2+} + \text{H}_2\text{O}_2$) as the redox initiator. In another set of experiments,² ferrous ammonium sulfate–potassium persulphate was used as redox initiator towards grafting of Ethyl acrylate (EA) onto cellulose and its reactivity was compared with that of ($\text{Fe}^{2+} + \text{H}_2\text{O}_2$). The graft copolymerization of methacrylic acid, epoxypropyl acrylate, and epoxypropyl methacrylate onto wood fibers initiated by peroxidation has been reported by Daneault et al.³ Grafting of acrylic acid onto cellophane films was studied using ferrous ion-hydrogen peroxide, a redox initiator system.⁴

Stanett and Williams⁵ grafted EA onto rayon by preirradiation method and examined the effect of post decrystallization on the mechanical behavior of the graft copolymer. Chauhan and coworkers⁶ made successful studies on graft copolymerization of methacrylate onto rayon and its impact on thermal prop-

erties. Chauhan and coworkers⁷ carried out the graft copolymerization of styrene onto cellulose and studied the effect of some additives on grafting parameters in limited aqueous medium. Graft copolymerization of methacrylic acid onto cotton fabric using tetravalent ceric ion was investigated under different conditions including pH of the polymerization medium.

The technique of grafting on to rayon has been restricted to grafting of a single monomer, and a meagre amount of work is reported on grafting of binary mixture of monomers, which may be more beneficial because a very large spread in the properties might be incorporated to the cellulose materials that way.

The grafting of binary mixture has been attempted by Williams et al.⁸ and it was observed that elongation of cellulose fiber increases with the extent of grafting of EA but tenacity decreases at the same time. The Ce(IV)-ion induced grafting on cellulose from the binary mixture of acrylonitrile–methacrylate has been investigated in heterogeneous and acidic conditions.⁹ Graft copolymers based on cellulose extracted from pine needles have been synthesized by grafting of poly (glycidyl methacrylate) alone and with comonomers acrylic acid, acrylamide, and acrylonitrile by benzoyl peroxide initiation.¹⁰ Graft copolymerization of acrylamide and EA onto cellulose has been carried out from their binary mixtures using ceric ammonium nitrate as an initiator in the presence of nitric acid.¹¹

Recently, interest in polymer and copolymers containing the imidazole ring has been growing because of their useful properties. The ability of imidazoles to form complexes with metals and bind dyes, the hydrophilicity of its polymers, and their polyelectro-

Correspondence to: S. Rattan (prsunita@rediffmail.com).

lyte behavior have stimulated interest in imidazole containing polymers for potential industrial uses.^{12,13}

Literature survey reveals that no attempts have been made to study the grafting of vinyl imidazole (VI) onto rayon. It was, therefore, considered desirable to study the grafting of VI (donor monomer) onto rayon and use it as one of the monomer in the binary mixture with EA (acceptor monomer), with a view that a suitable combination of donor and acceptor monomer may impart desired properties to the grafted cellulose. Attempts are being made to determine the water content and moisture regain (MR) of rayon-g-poly (EA), rayon-g-poly (VI), and rayon-g-poly (EA + VI) to explore their utility in different areas.

EXPERIMENTAL

Materials

Viscose rayon was obtained from Grassim Industries, Birlagram, Nagda (India) in fiber form. EA was washed with 5% sodium hydroxide followed by water and dried over anhydrous sodium sulfate. The dried monomer was distilled and the middle fraction was used. *N*-Vinylimidazole (VI) monomer (Merck) was distilled as such and the middle fraction was used.

Graft copolymerization

Rayon (100 mg) suspended in a known amount of water was taken in a flask. A definite amount of monomer was added to the reaction flask. The graft copolymerization reaction was performed in a Gamma chamber having 2100 Ci Co⁶⁰ as a source for γ -radiation. The reaction mixture was irradiated with γ -rays in air for different time periods at a constant dose rate (0.12M rad/h). After a definite time period, the reaction flask was removed from the chamber and the graft copolymer was separated from the reaction mixture by solvent extraction method by adding excess of acetone. The mixture was continuously stirred with periodical change of fresh solvent till all of the homopolymer dissolved into the solution. The contents of the beaker were filtered and washed repeatedly with fresh solvent to ensure complete removal of any homopolymer sticking to the fiber. Complete removal of homopolymer was ensured by further extracting the grafted product with acetone for another 48 h and observing no difference in weight in grafted product. The grafted fiber was then dried in a vacuum oven at 50°C till a constant weight was obtained.

The percentage of grafting was calculated from the increase in initial weight of the rayon fiber in the following manner:

$$\% \text{ Grafting} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 are the weights of original rayon and grafted rayon after complete removal of the

homopolymer, respectively. Percentage of grafting has been determined as a function of different reaction parameters such as total dose, concentration of monomer, amount of solvent, and amount of different alcohols. Graft copolymerization of the rayon fiber was also carried out in presence of the surfactant (1-octane sulfonic acid, sodium salt). A known amount of the surfactant was added to the reaction mixture and the graft copolymerization was carried out by the aforementioned method.

IR spectroscopy

IR spectra were measured for the grafted rayon using Perkin-Elmer Model 983 spectrophotometer.

Moisture regain

Percent moisture regain (MR) was determined at appropriate relative humidity and temperature. Relative humidity was measured by dry and wet bulb method. The percent MR was calculated as:

$$\text{MR \%} = \frac{\text{Sample wet weight} - \text{Sample dry weight}}{\text{Sample dry weight}} \times 100 \quad (1)$$

Water retention capacity

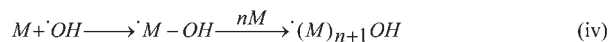
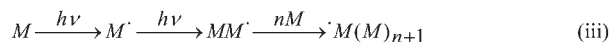
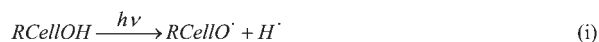
Water retention values (WRV) were determined by a method based on the centrifugal technique.¹⁴ In general, a known quantity of the sample was equilibrated with water for 2 h followed by centrifugation for 30 min. The centrifuge tubes were capped to prevent any evaporation of water and were equipped with a fine-mesh strainer at the bottom to allow excess of water to drain away. The weight of the wet sample was recorded; sample was dried overnight at 80°C and then reweighed. WRV has been calculated for each sample as follows:

$$\text{WRV (g/g)} = \frac{\text{Sample wet weight} - \text{Sample dry weight}}{\text{Sample dry weight}}$$

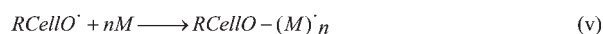
RESULTS AND DISCUSSION

When cellulose is immersed directly in the monomer and irradiated by γ -rays usually only a small amount of graft copolymer is formed.¹⁵ This is due to the fact that cellulose is a highly hydrogen-bonded polymer and vinyl monomers are simply not able to penetrate beyond the surface of the cellulose substrate. A simple way of overcoming this obstacle is to carry out mutual irradiation grafting of cellulose in the presence of a swelling

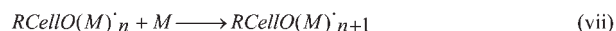
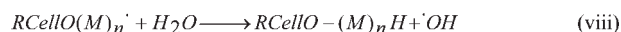
INITIATION



PROPAGATION



TERMINATION

(i) *By Recombination*(ii) *By Transfer*

Scheme 1

agent, which penetrates the cellulose and allows the monomer to enter inside the polymer matrix. The use of solvent-monomer mixtures rather than pure monomer was found by various investigators^{16,17} to give substantially increased grafting. It is believed that the success of this method is due to the combination of two effects. (a) greater accessibility of the monomer to the swollen cellulose and (b) radiolysis of the solvent leading to radicals capable of abstracting hydrogen atoms from the cellulose, and thereby giving rise to additional grafting sites. In the present study modification of rayon fiber has been attempted by mutual irradiation in aqueous medium. The following probable mechanism is suggested to explain the graft copolymerization of EA and vinylimidazole onto rayon initiated by γ -radiation by the mutual of the direct method (Scheme 1).

On the basis of the earlier proposed mechanism it becomes easier to explain the results. It is observed from the proposed mechanism that the reactive sites on the backbone polymer can be generated by step (i). The hydroxyl radical formed by radiolysis of water (step ii) initiates the polymerization reaction to produce growing polymeric chain (step iv), which can attach to the active sites of the backbone polymer to give the graft copolymer (step vi). Alternatively, the growing polymeric chains can lead to the formation of homopolymer [step (iii) and (iv)].

Termination of various active species in the reaction mixture may take place by recombination [step (vi) and (vii)] or by transfer process (step viii).

The extent of grafting may be influenced by the availability of the number of active sites on the polymer backbone. Other variables, which influence grafting, are the various reaction parameters including total dose, concentration of monomer, and amount of solvent. The following discussion deals with the effect of these parameters on percentage of grafting of EA, VI, and binary mixture of (EA + VI) onto rayon and the results are explained in the light of the earlier proposed mechanism.

Effect of total dose

Figure 1(a,b) describe the effect of total dose on grafting of EA and VI, respectively, onto rayon. It is observed from Figure 1(a) that grafting of EA onto rayon increases with increasing total dose and reaches a maximum value of 40% at a total dose of 2.52M rad, beyond which it decreases slowly. Figure 1(b) reveals that percentage of grafting of VI onto rayon increases sharply with increasing total dose giving maximum grafting (15%) at a total dose of 1.56M rad, beyond which it becomes constant. Increase in percentage of grafting in both cases is due to the fact that with increasing total dose various initiation steps leading to the generation of active sites on rayon backbone, initiation, and propagation of the monomer, etc are accelerated.

Decrease in percentage of grafting of ethyl acrylate onto rayon [Fig. 1(a)] at higher dose beyond 2.5M rad may be explained by the fact that at higher doses energy transfer processes occur in the irradiated mixture causing the intramolecular scission of the grafted branches. The growing grafted chains, which still have active sites, may attack the neighboring grafted branches thus bringing in chain scission and chain termination simultaneously. As a consequence of back biting by the growing grafted chains, the length of the grafted branches is considerably reduced thus decreasing the overall weight of the grafted polymer and hence decrease in the grafting is observed.

Figure 1(b) presents the percentage of grafting of VI onto rayon fiber. VI being soluble in water is expected to give higher percentage of grafting than EA. The anomalous behavior can be explained by the fact that since, VI is soluble in water, most of it is hydrogen bonded with water molecules and preferentially would form homopolymer at the expense of grafting. Chapiro et al.¹⁸ also observed that VI produces small amount of graft when grafting was attempted onto Teflon FEP film by mutual method.

To study the effect of donor monomer, VI on percentage of grafting of EA, an acceptor monomer, graft copolymerization was carried out using binary mixture of (VI + EA) as a function of total dose and the results are presented in Figure 1(c). It is observed from the figure that when a binary mixture of (VI + EA) is used as a mixed monomer system, percentage of grafting increases with increasing total dose with the same trend

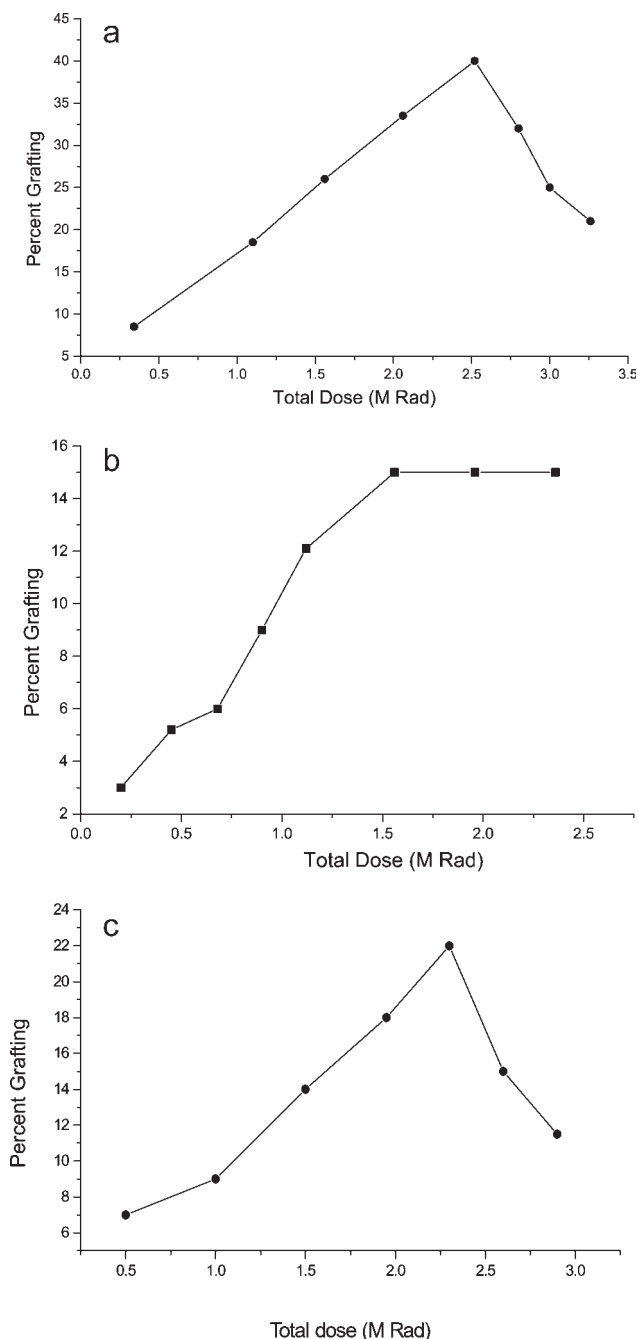


Figure 1 (a) Effect of total dose on percentage of grafting of EA onto rayon fibre. Rayon = 100 mg; Dose Rate = 120M rad; Water = 20 mL; [EA] = 9.2×10^{-3} moles. (b) Effect of total dose on percentage of grafting of VI onto rayon fibre. Rayon = 100 mg; Dose Rate = 112M rad; Water = 20 mL; [VI] = 1.1×10^{-2} moles. (c) Effect of total dose on percentage of grafting of (EA + VI) onto rayon fibre. Rayon = 100 mg; Dose Rate = 112M rad; Water = 20 mL; [EA] = 4.6×10^{-3} moles; [VI] = 5.5×10^{-3} moles.

as shown by EA giving maximum (22%) at an optimum dose of 2.3M rad beyond which it decreases. The addition of donor monomer, VI decreases the percentage of grafting of EA (40% at 2.5M rad) to 22% at a lower total dose i.e., 2.3M rad. The decrease in percentage of graft-

ing of the binary mixture (VI + EA) is explained by the fact that VI itself gives still lesser grafting (15%) at a much lower total dose i.e., 1.53M rad. This indicates that VI is a poor monomer for grafting as compared to the acrylate monomer. Graft copolymerization of VI to PET fibers has produced as low as 2.7% of grafting as reported by Halil Ibrahim.¹⁹ The decrease in grafting on addition of VI in a binary mixture may be attributed to the formation of charge transfer complex between the electron donor (VI) and electron acceptor (EA) monomer. The formation of such a complex decreases the diffusion of the monomer to the active sites leading to the decrease in percentage of grafting. Similar observations have been made by Garnett et al.²⁰ and Kaur et al.²¹

Thus, from the foregoing discussion, it is observed that there exists an optimum total dose for affording maximum percentage of grafting, which varies with the type of the monomer used for grafting. If the number of active sites generated on irradiation was the only reason for affording maximum percentage of grafting then all the monomers regardless of their reactivity would have produced maximum grafting at a single total dose under optimum conditions. Therefore, it appears that the number of active sites formed on irradiations is not the only reason for affording maximum grafting. Structure of the monomer, solubility of the monomer in the solvent system used, diffusion of the monomer to the active sites, and the reactivity of the growing polymeric chains are some of the factors, which may influence the maximum grafting under optimum conditions.

Effect of monomer concentration

The effect of concentration of EA and VI on percentage of grafting onto rayon is presented in Figure 2(a,b), respectively. It is observed from Figure 2(a) that the percentage of grafting increases continuously with the increase in monomer concentration of EA and reaches a maximum value (47%) at [EA] = 12.8×10^{-3} moles. Further increase in the concentration of EA leads to excessive homopolymerization and it becomes difficult to extract homopolymer entangled in the rayon fiber. When VI is grafted onto rayon, slow increase in percentage of grafting is observed with increasing the concentration of VI, giving maximum (30%) at [VI] = 5.5×10^{-2} moles, beyond which it decreases and becomes constant. Increase in grafting percentage with increasing monomer concentration in both the cases is expected. At higher monomer concentrations, more monomer would be available in the polymer medium for reaction with cellulose thereby enhancing the grafting degree. However, decrease in percentage of grafting with further increase in concentrations beyond the optimum monomer concentration of VI may be explained by the fact that at higher concentrations formation of homopolymer in preference to

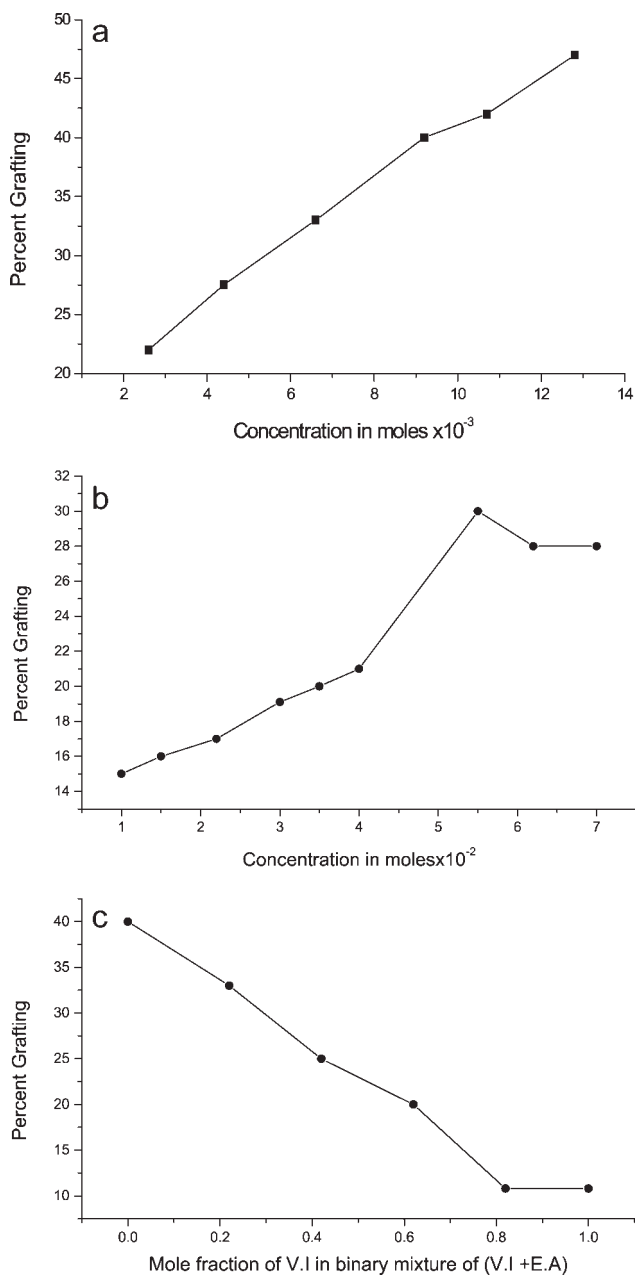


Figure 2 (a) Effect of [EA] on percentage of grafting onto rayon fibre. Rayon = 100 mg; Total Dose = 2.5M rad; Water = 20 mL. (b) Effect of [VI] on percentage of grafting onto rayon fibre. Rayon = 100 mg; Total Dose = 1.56M rad; Water = 20 mL. (c) Effect of [VI] on percentage of grafting of (VI + EA) onto rayon fibre. Rayon = 100 mg; Total Dose = 2.5M rad; Water = 20 mL.

grafting takes place leading to decrease in percentage of grafting. Further, poly VI being soluble in water leads to an increase in viscosity of the reaction medium thereby restricting the mobility of the growing polymeric chains to the active sites, and hence a decrease in grafting percentage is observed. Similarly, the formation of excessive homopolymer in case of grafting by EA suggests that the availability of the monomer for grafting decreases considerably, and

hence percentage of grafting would be low with further increase in concentration of EA.

To study the effect of concentration of VI on percentage of grafting of EA in a binary mixture, the amount of VI was varied keeping the amount of EA constant.

Figure 2(c) presents the effect of the mole fraction of VI in the binary mixture (VI + EA) on percentage of grafting. It is observed from the figure that percentage of grafting decreases regularly with increase in mole fraction of VI. This is due to the fact that VI prefers to undergo homopolymerization and hence as the amount of VI increases in the binary mixture, and percentage of grafting decreases.

Effect of amount of water

The presence of water as a reaction medium in the grafting reactions has been found to have a very important effect on percentage of grafting of vinyl monomers on rayon. To study the effect of amount of water during grafting of EA and VI graft copolymerization of these monomers has been carried out as a function of amount of water and the results are presented in Figure 3(a,b), respectively. It is observed from Figure 3(a) that percentage of grafting of EA shows an initial jump in percentage of grafting with increasing amount of water, from 20 to 30 mL giving maximum (47%) in 20 mL and then decreases sharply on further increase in the amount of water and becomes almost constant. Rayon molecules are capable of forming strong hydrogen bonds between hydroxyl groups of its neighboring chains. The polar solvent would primarily cause loosening of the hydrogen bonds and obviously a solvent having high dielectric constant like water would be more effective in this regard and would thus lead to swelling of the fiber. This enhances the accessibility of monomer to the active sites on the rayon resulting in the increase in grafting percentage. Decrease in percentage of grafting beyond 20 mL of water may be explained by the fact that as the amount of water is increased, number of hydroxyl radicals ($\cdot\text{OH}$) also increases simultaneously by radiolysis of water (step ii). The excess of hydroxyl radicals would initiate more of monomer leading to homopolymer formation and various side reactions, which can lead to decrease in percentage of grafting. Also with increasing amount of water, termination of growing grafting chains (step viii) and dilution of the monomer takes place, leading to decrease in grafting.

From Figure 3(b), it is observed that percentage of grafting of VI decreases beyond 10 mL of water. This behavior is quite expected since VI being soluble in water prefers to undergo homopolymerization at the expenses of the graft. Moreover, the formation of homopolymer increases the viscosity of the reaction

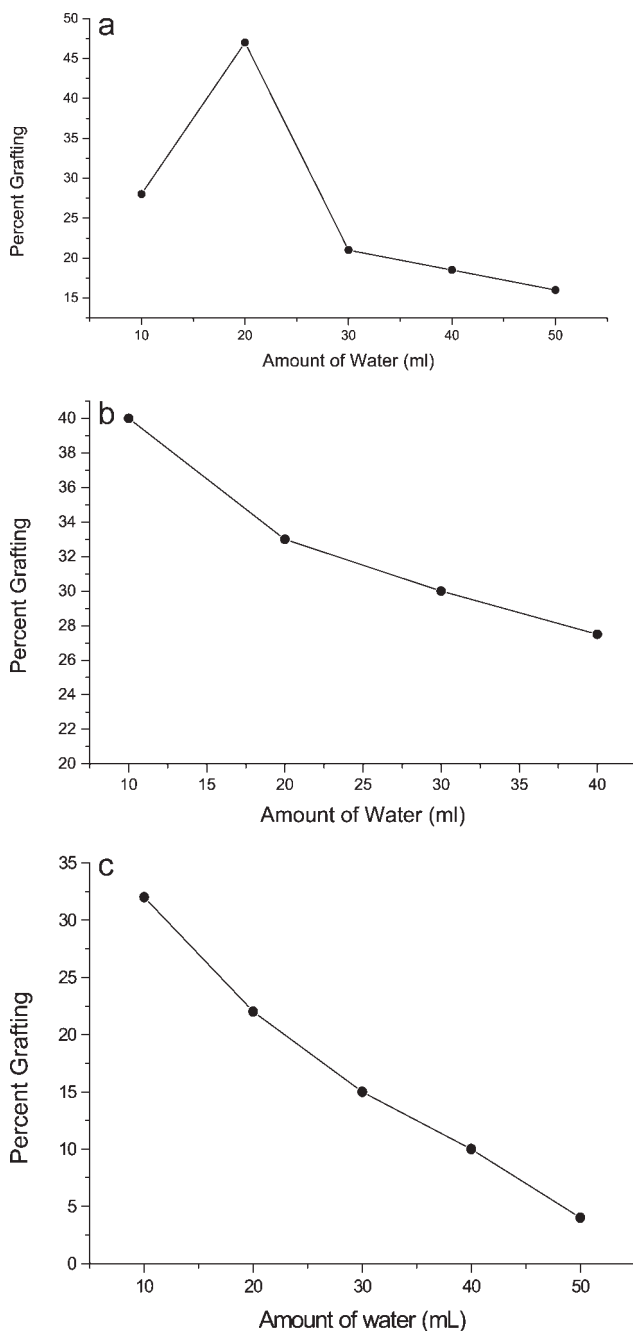


Figure 3 (a) Effect of amount of water on percentage of grafting of EA onto rayon fibre. Rayon = 100 mg; Total Dose = 2.5M rad; [EA] = 12.8×10^{-3} moles. (b) Effect of amount of water on percentage of grafting of [VI] onto rayon fibre. Rayon = 100 mg; Total Dose = 1.56M rad; [VI] = 5.5×10^{-2} moles. (c) Effect of amount of water on percentage of grafting of (EA + VI) onto rayon. Rayon = 100 mg; Total Dose = 2.4M rad; [EA] = 4.6×10^{-3} moles [VI] = 5.5×10^{-3} moles.

medium, thereby decreasing the percentage of grafting.

Percentage of grafting of (VI + EA) as a function of amount of water is presented in Figure 3(c). Thus from the foregoing results, it can be concluded that though water promotes the formation of active sites

by swelling the backbone polymer, other factors, such as solubility of the monomer in water, preferred homopolymerization, viscosity, formation of hydrogen bonds with the polar monomer, and dilution of the monomer with increasing amount of water are also responsible for the decrease in percentage of grafting.

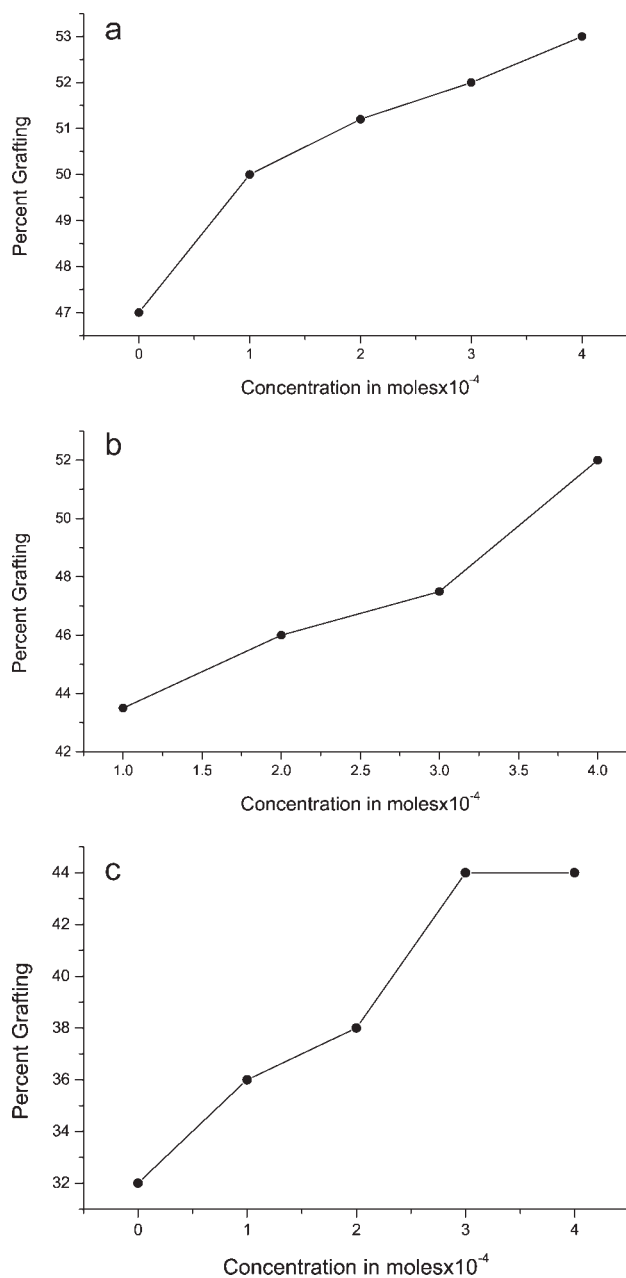


Figure 4 (a) Effect of [surfactant] on percentage of grafting of EA onto rayon fibre. Rayon = 100 mg; Total Dose = 2.5M rad; [EA] = 12.8×10^{-3} moles; Water = 20 mL. (b) Effect of [surfactant] on percentage of grafting of VI onto rayon. Rayon = 100 mg; Total Dose = 1.56M rad; [VI] = 5.5×10^{-2} moles; Water = 10 mL. (c) Effect of [surfactant] on percentage of grafting of (EA + VI) onto rayon. Rayon = 100 mg; Total Dose = 2.4M rad; [EA] = 4.6×10^{-3} moles [VI] = 5.5×10^{-3} moles; Water = 10 mL.

Effect of surfactant

Effect of surfactant (1-Octane sulfonic acid, sodium salt) has been studied on the percentage of grafting of EA, VI, and (EA + VI) onto rayon under optimum conditions and the results are presented in Figure 4(a–c), respectively. It is observed from the figures that percentage of grafting increases continuously with increase in the concentration of the surfactant.

In a heterogeneous polymer–monomer system, diffusion controls the chain growth and chain termination in the internal structures of the polymer. One way of facilitating diffusion is to open up the physical structure of the polymer to allow the monomer to enter in sufficient quantities. Vaskova et al.²² suggested that anionic surfactant usually promotes grafting. In the present study, it is observed that anionic surfactant influenced graft copolymerization. In the presence of surfactant, droplets of monomer are formed, which facilitate the diffusion of the monomer particles to the active sites, resulting in an increase in grafting. Moreover, in the presence of surfactant intracrystalline swelling of rayon due to continued penetration in the crystalline region by the surfactant takes place, which helps in the exposure of active sites thus leading to an increase in grafting yield. Jiang and Yang²³ has also reported the formation of micro domains that are strongly affected by the charged moieties of the surfactants. The sulfonic acid group of the surfactant and the hydroxyl group of the rayon fiber has the strong tendency to interact, making it possible for the surfactant to penetrate through polymer network. Polymer surfactant interactions were also investigated by Maggio et al.²⁴ It was reported that the associated network of the polymer is broken up by the surfactant (dedecyl trimethyl ammonium bromide) as the surfactant molecules adsorb to the polymer backbone, indicating polymer surfactant interactions.

CHARACTERIZATION OF THE GRAFTED FIBRES

Water retention capacity

Figure 5(a–c) represent the WRV for rayon-g-poly (EA), rayon-g-poly (VI), and rayon-g-poly (VI + EA), respectively, at different grafting levels. It is observed from the figures that rayon-g-poly (VI) and rayon-g-poly (VI + EA) exhibit an increase in the WRV with increasing percentage of grafting, whereas in rayon-g-poly (EA) the water retention capacity does not change much with increasing grafting levels.

The water retention capacity of rayon is generally thought to result from the interaction through hydrogen bonding of the hydroxyl groups on rayon with water molecules. The effect on water retention by the introduction of vinyl grafts on the rayon backbone

would depend on the frequency of the interposition of the grafted polymer, the fiber–fiber cohesion of the substrate and the nature of the grafted polymer. Grafting also results in opening up of fiber structure thus facilitating the penetration of water molecules. The increase in water retention with increasing grafting levels in rayon-g-poly (VI) and rayon-g-poly (EA + VI) can be ascribed to the opening up of the fiber structure of rayon, which makes penetration of water molecules easier. Moreover, the grafted polymer poly (VI) forms hydrogen bonds with water, increasing the WRV of rayon-g-poly (VI). In the case of rayon-g-poly (EA), however, lower and almost same WRV for all

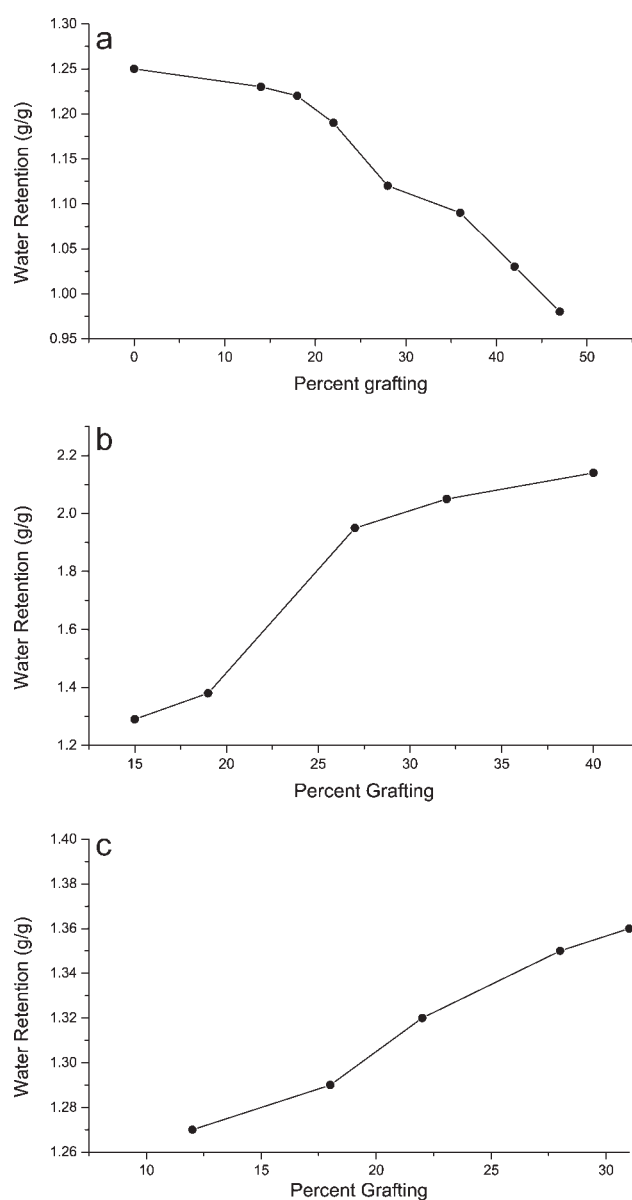


Figure 5 (a) Variation of water retention with percentage grafting of EA onto rayon. (b) Variation of water retention with percentage grafting of VI onto rayon. (c) Variation of water retention with percentage grafting of EA + VI onto rayon.

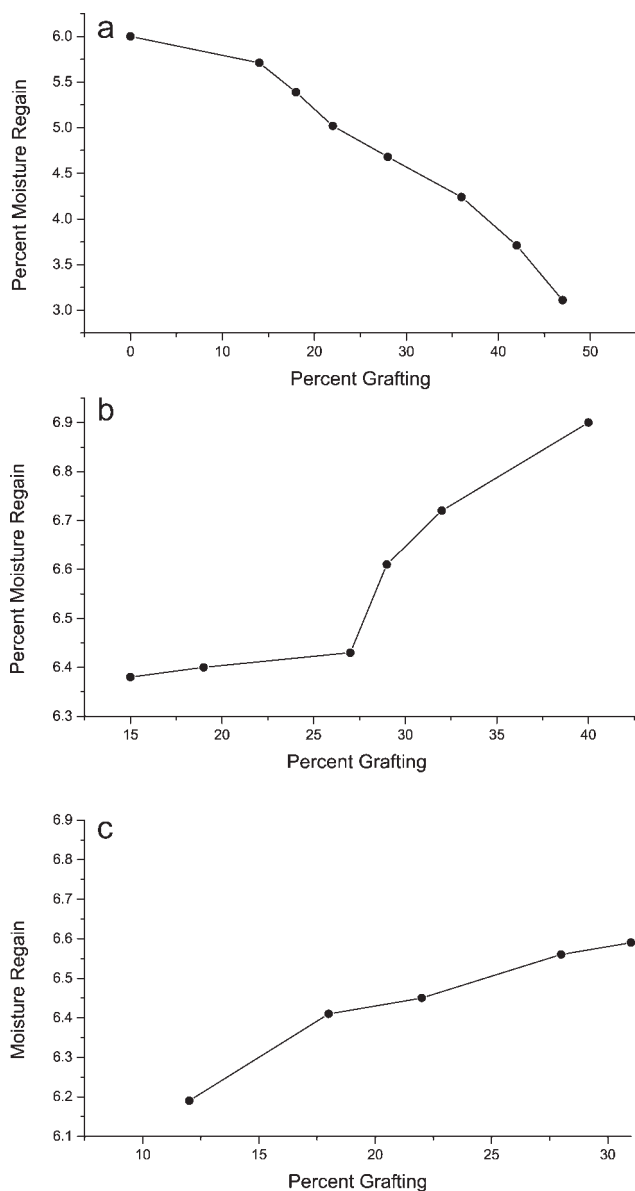


Figure 6 (a) Variation of moisture regain with percentage grafting of EA onto rayon. Relative Humidity = 50%, Temperature = 25°C. (b) Variation of moisture regain with percentage grafting of VI onto rayon. Relative Humidity = 50%, Temperature = 25°C. (c) Variation of moisture regain with percentage grafting of EA + VI onto rayon. Relative Humidity = 50, Temperature = 25°C.

the samples can be attributed to the hydrophobic nature of the grafted monomer. As the grafting of poly (EA) onto rayon progresses, opening up of fiber structure occurs in this case also, but it appears hydrophobic poly (EA) chains do not contribute in water retention capacity. The results lead to the suggestion that the relatively hydrophobic nature of poly (EA) grafts has compensated for the effect of reduced interfibre cohesion because of grafting on the water retention capacity of rayon-g-poly (EA).

Zahren²⁵ suggested that grafting of vinyl monomers does not substantially increase the water absorption

without decrystallization of the grafted samples. They obtained samples having WRV as large as $38.8 \text{ cm}^3 \text{ g}^{-1}$ with the increasing grafting level of rayon-g-poly (AAc) followed by decrystallization with 3% NaOH. No such attempts of decrystallization have been made, however, in the present case.

Moisture regain

Figure 6(a–c) represent the percent MR of rayon-g-poly (EA), rayon-g-poly (VI), and rayon-g-poly (VI + EA), respectively, (at 50% RH and 25°C). It is observed from the Figure 6(a) that percent MR decreases with increase in percentage of grafting of EA onto rayon. Rayon-g-poly (VI) and rayon-g-poly (VI + EA) exhibit a small increase in MR values with increasing percentage of grafting.

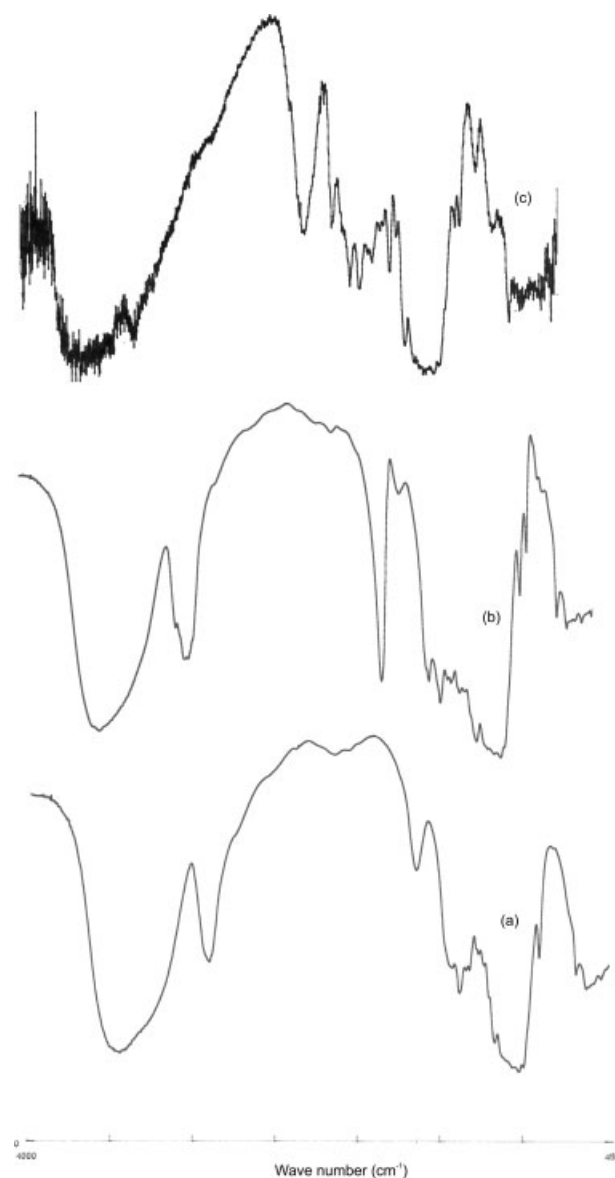


Figure 7 IR Spectra (a) Rayon ungrafted (b) Rayon-g- EA (c) Rayon-g-VI.

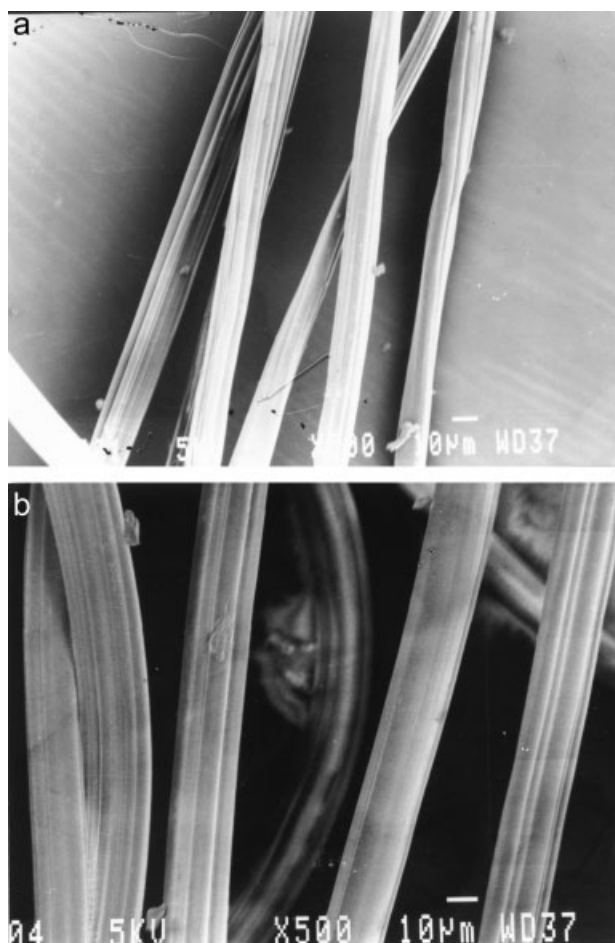


Figure 8 (a) Scanning electron micrograph of rayon fibre ($\times 500$). (b): Scanning electron micrograph of rayon-g-VI ($\times 500$).

Vinyl graft copolymerization onto rayon usually reduces the MR because of the generally hydrophobic nature of the grafted branches. In case of rayon-g-poly (EA), though the accessibility of the graft increases with grafting, presumably owing to the opening of the fiber structure by EA branches, the production of a hydrophobic environment around the backbone polymer causes a decrease in the MR. Demint et al.¹⁶ observed similar behavior on grafting of styrene onto cotton cellulose, the MR ranges from 7.5% for the untreated sample, to 2.7% for a sample with add on of 165%. The small increase in MR in the case of rayon-g-poly (VI) and rayon-g-poly (VI + EA) can be attributed to the formation of hydrogen bonds between water and electronegative nitrogen in the pendant grafted chains along with the opening up of the fiber structure, which facilitates the MR.

IR spectrum

IR spectra of rayon fiber, rayon-g-poly (EA) and rayon-g-poly (VI), were examined (Fig. 7). IR spec-

trum of rayon-g-poly (EA) showed a sharp peak at 1725 cm^{-1} because of the carbonyl group of poly (EA) [Fig. 7(b)], whereas a peak at 1585 cm^{-1} is observed in the IR spectrum of rayon-g-poly (VI), which is assigned to C=N group of poly (VI) [Fig. 7(c)]. In addition to the above, a peak at 1229 cm^{-1} is present, which is due to C—N stretching in the imidazole ring. No such peaks were present in the IR spectrum of rayon fiber indicating that the grafted polymer is attached to the backbone polymer by covalent bond.

Scanning electron microscopy

Figure 8(a,b) show scanning electron micrograph of rayon and rayon-g-poly (VI), respectively, with 500 times magnification. Figure 9(a,b) present the scanning electron micrograph and rayon-g-poly (VI) with a magnification of 1000 times. The comparison of scanning electron micrograph of the grafted samples with that of ungrafted samples gives clear evidence of grafting as the size of the grafted samples is larger than that of ungrafted ones. The grafted samples show

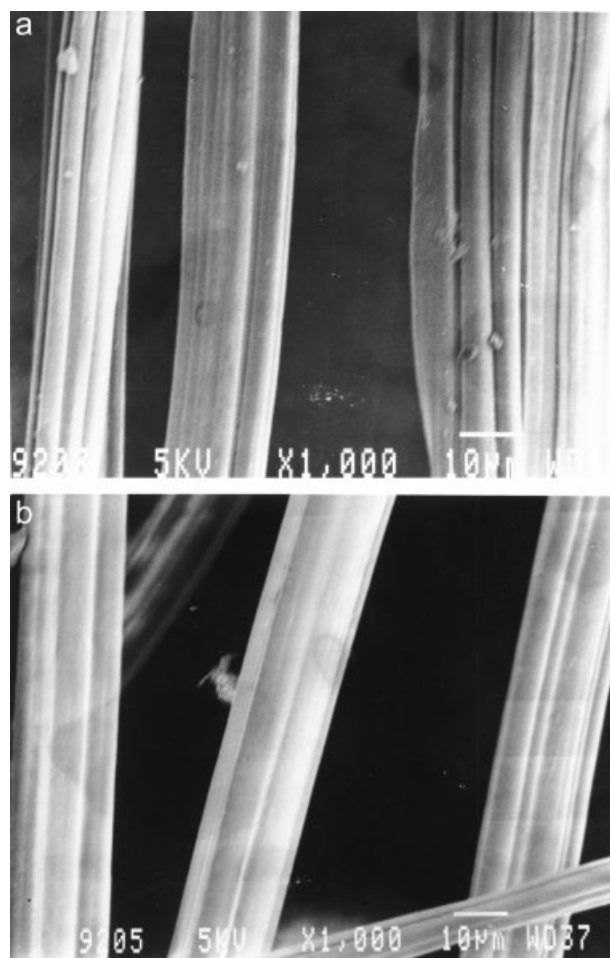


Figure 9 (a) Scanning electron micrograph of rayon fibre ($\times 1000$). (b) Scanning electron micrograph of rayon-g-VI ($\times 1000$).

TABLE I
Optimum Conditions for Maximum Grafting of Rayon with Different Monomers and Their Binary Mixture

Grafted rayon	Total dose (M Rad)	Concentration of the monomer used (moles)	Amount of water (mL)	Percentage of grafting
Rayon-g-poly (EA)	2.52	12.8×10^{-3}	20	47
Rayon-g-poly (VI)	1.56	5.5×10^{-2}	10	40
Rayon-g-poly (EA + VI)	2.4	[EA] = 4.6×10^{-3} , [VI] = 5.5×10^{-3}	10	32

considerable deposition of poly (VI) on the surface of the backbone polymer.

COMPARISON OF REACTIVITY OF EA AND VI AND EFFECT OF AN ELECTRON DONOR MONOMER ON % GRAFTING OF EA, AN ELECTRON ACCEPTER MONOMER

From the foregoing discussions, it is observed that EA produces higher percentage of grafting (47%) as compared to VI. Optimum conditions pertaining to maximum percentage of grafting are tabulated in Table I. It is observed from the table that EA produced higher percentage of grafting (47%) at lower monomer concentration (12.8×10^{-3} moles) and higher optimum total dose (2.52M rad) as compared to VI in which case the maximum percentage of grafting (40%) is observed at higher monomer concentration (5.5×10^{-2} moles) and lower optimum total dose (1.53M rad). These results suggest that EA is a better monomer for grafting than VI.

VI being water soluble should be easily accessible to the reactive sites giving higher percentage of grafting. Lower grafting of VI is attributed to the fact that VI does not propagate at a rate similar to other vinyl monomers leading to a slow growth of the polymeric chains, which mutually annihilate to give homopolymer as compared to grafting. Poly (VI) being soluble in water increases the viscosity of the system, which restricts the mobility of the growing polymer chains to the active sites leading to the decrease in percentage of grafting. Therefore, lower percentage of grafting is obtained at higher monomer concentrations but at a lower total dose.

The addition of VI to EA in a binary mixture also affects the grafting of the later. In addition to this both these monomers are held in charge transfer complex, which hinders their reactivity towards grafting.²⁰ Maximum grafting (32%) of the binary mixture (EA + VI) is also less than that obtained with EA (40%) and is obtained at a little lower total dose (2.4M rad).

Thus it may be concluded that rayon fibers can be modified by grafting of VA and its binary mixture

with EA for better MR and water retention properties while grafting with EA introduces some hydrophobic character to the fiber.

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