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Functionalization of cellulosic fibers by graft copolymerization of acrylonitrile and ethyl acrylate from their binary mixtures

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ABSTRACT

Functionalization of Agave fibers was carried out by graft copolymerization of acrylonitrile (AN) and ethyl acrylate (EA) from their binary solutions in presence of Ce (IV) ions at a temperature of $45 \pm 0.1\,^{\circ}$C. An increase in the graft copolymerization was obtained with the increase in the feed molarity of the comonomers up to certain extent. Contrary to lesser affinity of acrylonitrile to grafting on Agave fibers, a synergistic effect of ethyl acrylate on acrylonitrile was observed when graft copolymers were prepared using different feed compositions (f_{AN}). The graft copolymers were characterized by various techniques such as FT-IR, TGA/DTA, X-RD and SEM analysis. Further swelling behavior of grafted fibers in different solvents, moisture absorption behavior and resistance to chemicals was investigated as a function of percent grafting to define their end uses in different environments.

1. Introduction

The use of cellulosic fibers in various applications especially in polymer composite materials has received increasing attention from environmental and economic point of view. The biodegradability of these fibers in septic tanks as well as main sewage systems enables them to be used for the manufacture of disposable items. These materials offer numerous advantages such as low specific gravity, suitable mechanical properties and recyclability. Further they are obtained from renewable resources, have lower weights and cost less than synthetic fibers such as glass, carbon, aramid, etc. (Li, Wing, & Ye, 2000). However due to the presence of hydrophilic hydroxyl groups on the surface of cellulosic fibers, their use is restricted under moist atmospheres and polar solvents. Further these fibers are more prone to the attack of chemicals such as acids, bases and salts. Therefore these fibers need surface modifications in order to improve their properties before they can be used in various technical applications.

Graft copolymerization of vinyl monomers from their binary mixtures is a significant route to alter the physical and chemical properties of cellulosic fibers for specific end uses, which have been extensibly investigated using different techniques (Lee, Bondar, & Han, 2008; Maiti, Jindal, Kaith, & Jana, 2011; Nurkeeva et al., 2003; Rattan, Maitra, Misra, & Kaur, 2008). Grafting of vinyl monomers from their binary mixtures is a useful technique as it introduces dual properties in the backbone polymer and also influences the extent of grafting of a monomer by synergistic effect which exhibits lesser tendency for grafting individually. The grafting from the binary mixtures is also important since the chains of desired compositions and lengths can be introduced in the backbone polymers by controlling the reaction conditions and proper selection of the individual monomers. Therefore graft copolymerization provides an opportunity to prepare tailor made grafted products by using suitable monomers and their feed compositions in the binary mixtures (El-Salmawi, El-Naggar, & Attia, 1997). (El-Naggar, Zhody, Sahar, & Allam, 2001) graft copolymerized binary mixtures of acrylonitrile (AN)/styrene (S) and acrylamide (AAm)/Styrene (S) onto polyester fabric initiated by the influence of radiations. They investigated the synergism by determining the graft yield fraction for each monomer in the final graft copolymer. The reactivity ratio of individual monomer was also calculated by knowing the mole fraction of each monomer in the grafting solution (Sharma & Chauhan, 2009) graft copolymerized cellulose extracted from pine needles by binary mixtures of 2-hydroxy methacrylate (HEMA) along with comonomers acrylic acid, acrylamide and acrylonitrile initiated by benzoyl peroxide. (Fernandez, Casinos, & Guzman, 1990) grafted a mixture of vinyl acetate and methyl acrylate on cellulose using ceric ions as initiator. In these investigations the extent of homopolymerization is reported to be greater than graft copolymerization. Therefore the grafting must be carried out with a initiator which must be able to generate active sites on the backbone. It has been reported in the literature that ceric ions are capable of generating active site easily (Tsubokaba, Lida, & Takayama, 2000; Mansaur &

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Table 1
Optimization of reaction parameters for grafting of acrylonitrile onto *Agave americana* fibers.

Sr. no.	Time (min.)	Temp. (°C)	[Monomer] × 10^1 Mol dm^{-3}	[CAN] × 10^3 Mol dm^{-3}	[HNO3] × 10^1 Mol dm^{-3}	%GY	%GE
1	30	45	2.92	8.77	2.77	16.7	5.18
2	60	45	2.92	8.77	2.77	23.9	7.42
3	90	45	2.92	8.77	2.77	22.4	6.96
4	120	45	2.92	8.77	2.77	18.3	5.68
5	150	45	2.92	8.77	2.77	16.6	5.14
6	60	25	2.92	8.77	2.77	17.9	5.55
7	60	35	2.92	8.77	2.77	18.9	5.86
8	60	55	2.92	8.77	2.77	21.4	6.63
9	60	65	2.92	8.77	2.77	18.3	5.68
10	60	45	2.92	4.38	2.77	13.5	4.19
11	60	45	2.92	6.58	2.77	21.7	6.73
12	60	45	2.92	10.96	2.77	22	6.86
13	60	45	2.92	13.15	2.77	16.3	5.06
14	60	45	2.92	8.77	1.38	17.7	5.49
15	60	45	2.92	8.77	2.07	18.7	5.81
16	60	45	2.92	8.77	3.46	12.7	3.95
17	60	45	2.92	8.77	4.15	7.6	2.34
18	60	45	0.73	8.77	2.77	1.9	0.61
19	60	45	1.46	8.77	2.77	2.3	0.72
20	60	45	2.19	8.77	2.77	5.6	1.73
21	60	45	3.65	8.77	2.77	24	4.86

Nagaty, 1985). Ce (IV) ions undergo hydrolysis in aqueous medium however they generate free radicals on the cellulosic backbone in presence of acid easily (Mino & Kaiserman, 1958).

In the view of above discussion and since no work on the surface modification of *Agave americana* fibers through graft copolymerization of binary vinyl monomers appears in the literature, in the present manuscript we have reported the graft copolymerization of binary mixture of acrylonitrile and ethyl acrylate in presence of Ce (IV) ions. *A. americana* fibers are attractive in terms of morphology, intrinsic properties and cost. Although these fibers are native to Central America but they are also abundantly available in Himalayan region of India, Nepal and China. These fibers come from vessel sheaves of leaves of *A. americana* plant which is wild growing, monocotyledonous, perennial plant found abundantly in the vicinity of National Institute of Technology Hamirpur (India). The fibers extracted from the plant are utilized by the villagers for domestic purposes such as making ropes, bags, mats, etc. probably due to their excellent mechanical properties. (Chaabouni, 2005; Msahli, Sakli, & Drean, 2006) studied the physical and mechanical properties of *A. americana* fibers and found that these fibers have excellent potential as textile fiber and are a promising candidate as fiber reinforcement for polymer matrix based composites. Therefore the present work ensures the commercial utilization of the fibers extracted from *A. americana* plant and also provides better opportunities for the villagers to earn their living from this waste biomass in the form of small scale industry.

2. Experimental

2.1. Materials

Agave fiber bundles were extracted from *A. americana* plant by cutting and immersing the leaves in fresh water at a temperature of 25–30 °C for about 28 days. The leaves were then taken out and fibers were separated from matrix by calendaring the leaves and individual fibers were rinsed with distilled water. The fibers were then made free from impurities of waxes, oils, etc. by extraction with acetone in soxhlet extraction apparatus for 72 h.

Acrylonitrile (AN) and Ethyl Acrylate (EA) were received from CDH, India and were purified by first washing with 5% NaOH and then drying over anhydrous Na_2SO_4. Finally the monomers were subjected to distillation and the middle fraction of distillate was used for the further studies. Ceric ammonium nitrate (CAN) and other chemicals such as acetone, dimethyl formamide (DMF), CCl_4, toluene were of analytical reagent grade and used as received without further purification. All the solutions were prepared in double distilled water. Shimadzu Libror AEG-220 make balance was used for weighing the samples.

2.2. Procedure for graft copolymerization

The fibers were immersed in double distilled water for 24 h prior to the grafting reaction. The grafting reaction was carried out in a reactor containing 100 ml of double distilled water. Prior to grafting with binary vinyl monomers, various reaction parameters such as reaction time, temperature, concentration of nitric acid, initiator and monomer concentration were optimized for graft copolymerization of principal monomer onto backbone fiber as per method reported earlier (Singha & Rana, 2010a). The results of optimization of different reaction parameters have been given in Table 1. A known amount of ceric ammonium nitrate dissolved in definite amount of nitric acid was added to the reaction mixture containing 0.5 g of fibers to keep the concentration of CAN and nitric acid 8.77×10^{-3} mol dm^{-3} and 2.77×10^{-1} mol dm^{-3}, respectively, which were kept for about 15 min so that primary radicals are formed on the fiber backbone as a result of interactions of ceric ions and cellulosic backbone. The comonomer mixture was then added drop wise to the reaction kettle to maintain overall molarity of 0.5 mol dm^{-3} in the reaction mixture. The mole fraction of acrylonitrile (f_{AN}) in the reaction mixture was maintained at 0.70. After addition of binary mixture the reaction was allowed to proceed at constant speed of stirring with the help of electrically operated magnetic stirrer cum hot plate maintained at a constant temperature of 45± 0.1 °C for an optimized time interval of 60 min. At specific time interval of grafting (60 min.), reaction was stopped and graft copolymers were taken out of the reactor, washed with double distilled water in order to remove unpolymerized monomers. The samples were finally dried to constant weight at 60 °C in a hot air oven.

2.3. Extraction of homocopolymer (H_{cp})

The graft copolymers were sexhlet extracted with dimethyl formamide and toluene in order to remove poly (acrylonitrile-co-ethyl acrylate) homocopolymers formed during grafting reaction. The extracted homocopolymers were precipitated with

Table 2a
Effect of feed molarity on grafting parameters [Ce (IV)] = 8.77×10^{-3} mol dm^{-3}, [HNO3] = 2.77×10^{-1} mol dm^{-3}, fAN = 0.7, Temp. = 45 °C, Time = 60 min.

[AN + EA]mol dm^{-3}	%GY	%GE	%H_{cp}
0.35	32.74	7.86	9.63
0.4	37.86	7.42	11.52
0.45	42.30	7.00	17.24
0.5	48.50	6.95	21.64
0.55	45.16	5.70	23.63
0.6	38.46	4.34	27.85

Table 2b
Effect of feed composition on grafting parameters [Ce (IV)] = 8.77×10^{-3} mol dm^{-3}, [HNO3] = 2.77×10^{-1} mol dm^{-3}, Temp. = 45 °C, Time = 60 min.

f_{AN}	%GY	%GE	%H_{cp}
0.2	24.88	3.85	7.54
0.4	28.72	4.54	9.81
0.5	38.30	6.20	11.24
0.7	48.50	8.03	17.64
0.8	39.26	6.65	21.46
0.9	30.42	5.26	24.63

water-methanol mixture in the ratio of 1:1 (v/v), filtered and dried to constant weight in vacuum oven at 60 °C. The percent homo copolymers extracted during grafting reactions have been given in Tables 2a and 2b.

2.4. Grafting parameters

2.4.1. Percent graft yield (% GY)

Graft yield was calculated as the ratio of increase in the weight of sample upon grafting to the original weight of the backbone.

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

where W_1 is the Initial weight of backbone; W_2 is the final weight of backbone.

2.4.2. Percent graft efficiency (% GE)

Graft efficiency was calculated as the ratio of increase in weight of backbone to the weight of monomer (W_{m}).

$$\%GY = \frac{W_2 - W_1}{W_{\mathrm{m}}} \times 100$$

where W_{m} is the weight of monomer.

2.5. Percent homocopolymers (% H_{CP})

Percent homocopolymers were calculated as ratio of weight of homocopolymers (W_{Hcp}) to weight of monomer (W_{m}).

$$\%H_{cp} = \frac{W_{H_{cp}}}{W_{\mathrm{m}}} \times 100$$

3. Characterizations of graft copolymers

3.1. FT-IR analysis

To confirm graft copolymerization FT-IR spectra of graft copolymers were recorded on Perkin Elmer Fourier Transform infra red (FT-IR) spectrophotometer using KBr pellets (Sigma Aldrich, USA). The composition of graft copolymers was determined by optical density ratio (ODR) as determined by following relationship and calibration curve prepared between the ODR and copolymers of known compositions.

$$\mathrm{ODR} = \frac{\log(\mathrm{baseline}\%T/\mathrm{EA}\%T)}{\log(\mathrm{baseline}\%T/\mathrm{AN}\%T)}$$

3.2. Thermal analysis

Thermogravimetric analysis, differential thermal analysis and differential thermogravimetric analysis were carried out on Perkin Elemer thermal analyzer of Pyris Diamond make. Thermal analysis was carried out in presence of air at a heating rate of 10 °C/min.

3.3. Scanning electron microscopy (SEM)

Scanning electron micrographs of *A. americana* fibers and its graft copolymers with binary mixture were recorded on Leo Electron Microscopy machine (435-VP). Before focusing electron beam on the samples they were coated with Gold suspension in order to make them conducting. The image resolution was set at 500×.

3.4. X-Ray diffraction studies

X-ray diffraction studies were performed on X-ray diffractometer (Brucker D8 Advance). X-RD studies were carried out using Cu Kα (1.5418 Å) radiation, a Ni- filter and a scintillation counter as a detector at 40 KV and 40 mA on rotation from 5 ° to 50 ° at 2θ scale.

Each sample was finely powdered into small particle size and homogeneously mixed before subjecting to X-ray exposure. The randomly oriented powdered sample with uniform surface was exposed to X-rays from all possible planes. The angle of scattering of diffracted beam was measured with respect to the incident beam of X-rays and relative intensity was obtained.

Percent crystallinity and crystallinity index (C.I.) was calculated as per method reported earlier (Singha & Rana, 2010b).

4. Studies of physico-chemical properties

4.1. Swelling behavior in different solvents

A definite weight of sample was immersed in a solvent for 24 h and after taking out the sample, excess of solvent was removed. The final weight of the sample was noted down and percent swelling was calculated as per method reported (Singha & Rana, 2010a). The swelling studies were performed in water, ethanol, DMF and CCl_4.

4.2. Moisture absorption studies

Moisture absorbance behavior was studied under different humidity levels ranging from 40% to 100%. A sample of known weight was placed in the humidity chamber maintained at a definite humidity level for 2 h. Each sample was placed in hot air oven at 60 °C for 12 h in order to make it moisture free. The sample was then taken out and final weight was noted down immediately. Percent moisture absorbance was calculated as per method reported (Singha & Rana, 2010a).

4.3. Chemical resistance studies

The chemical resistance of the graft copolymers was studied as a function of percent weight loss. Known amounts (W_1) of graft copolymers were subjected to the effect of acids and bases of different strengths for definite time interval in order to evaluate their chemical resistance. The samples were weighed again to get the final weights (W_2). The percent weight loss was determined as per method reported earlier (Singha & Rana, 2010a).

5. Results and discussions

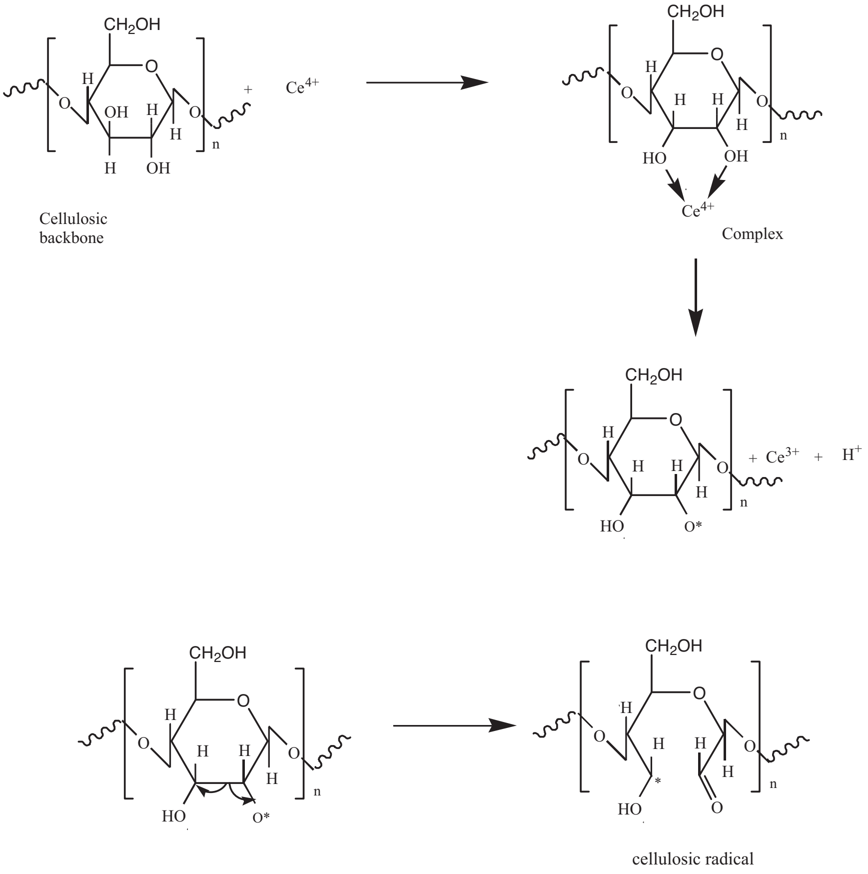
5.1. Grafting mechanism

Ceric ions create active sites on backbone polymer through single electron transfer process (Mino & Kaiserman, 1958). It has been reported in the studies of grafting of pure acrylonitrile on cellulose backbone that grafting occurs to a smaller extent even at high feed concentrations of acrylonitrile. However from our investigations and reported studies it has become evident that grafting of acrylonitrile can be improved by optimizing grafting conditions and using comonomers which can promote grafting through their synergistic effect (Tsuchida & Tomono, 1971). The extent of grafting of individual monomer depends upon the concentration of monomer in the reaction mixture, but in presence of comonomer, the grafting not only depends upon molarity of monomers in the reaction mixture but also affected significantly by possible interactions occurring with comonomers in the reaction mixture. Further the extent of these interactions between comonomers will depend upon feed molarity of comonomers, feed compositions and structures of the monomers. The monomers in the binary mixture form donor–acceptor complexes as confirmed by UV and NMR studies. The complexes facilitate the transfer of monomers onto the reactive sites on the backbone and hence enhance the overall efficiency of grafting. (Kaku, Toshinmaka, Yushimaka, & Niro, 1967).

During the grafting reaction hydroxyl groups present on C-2, C-3 and C-6 act as active sites. Ceric ions form chelate complexes with the cellulose molecules thorough hydroxyl groups at C-2 and C-3 of glucose units. Ce (IV) ions are reduced to Ce (III) by breaking of bond and transfer of electron from cellulose molecule as a result of which free radical sites are generated on the backbone (Dhiman, Kaur, & Mahajan, 2008). The free radicals are also generated in the monomer chains which are then transferred to the free radical reactive sites present on the backbone and form graft copolymer. Ceric ammonium nitrate forms bulkier [Ce–O–Ce]$^{+6}$ ions when dissolved in water. These bulky ions are not able to form chelate complex with cellulosic backbone. Nitric acid plays a vital role in the grafting reaction initiated by ceric ions as it prevents the formation of bulky [Ce–O–Ce]$^{+6}$ ions by shifting the equilibrium towards the formation of Ce^{4+} ions.

Based upon the experimental data collected as a result of various reaction parameters during the grafting reaction, the following steps have been proposed for the grafting of acrylonitrile and ethyl acrylate onto Agave fiber backbone in the presence of ceric ions.

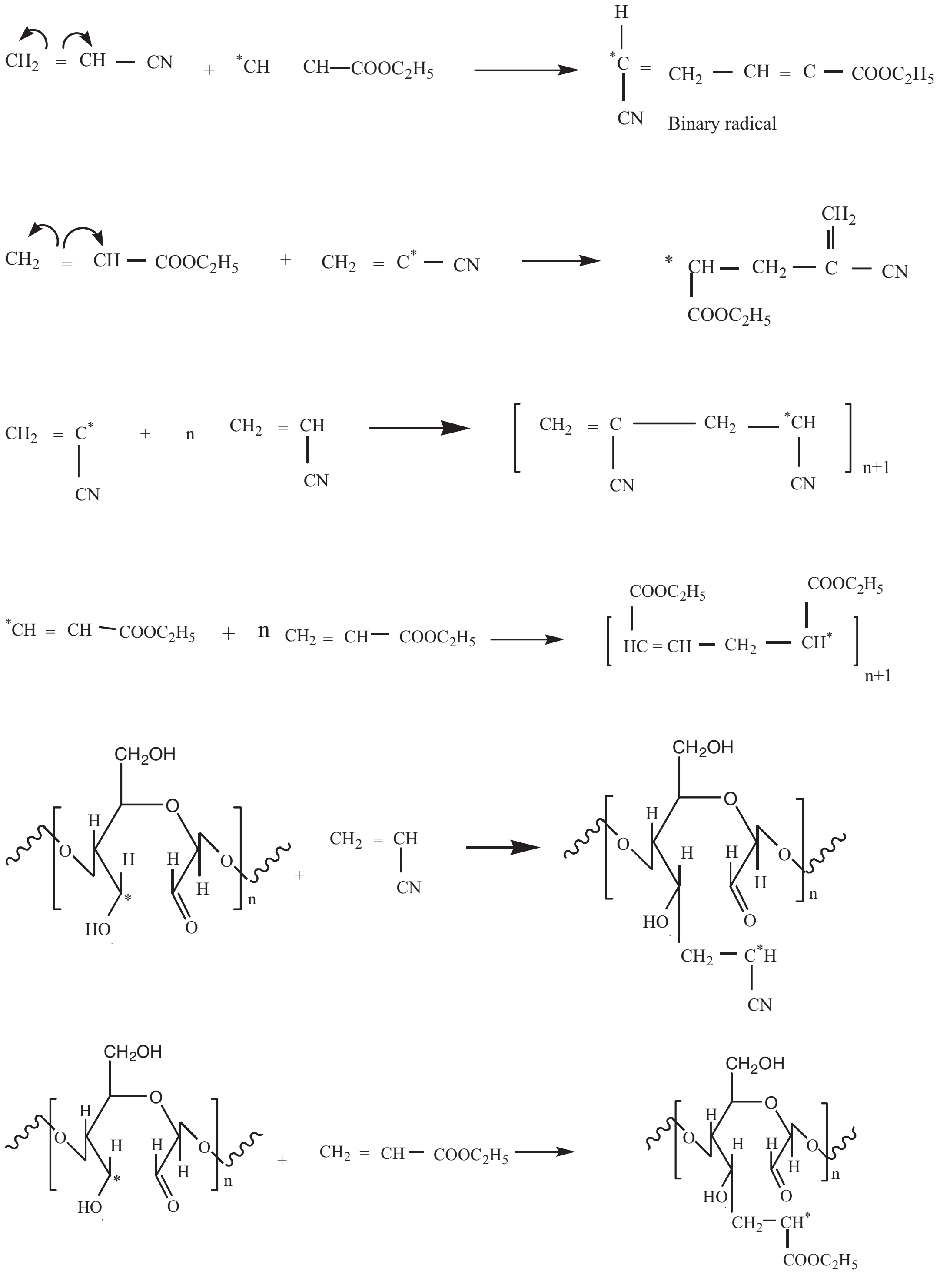
(1) Radical generation



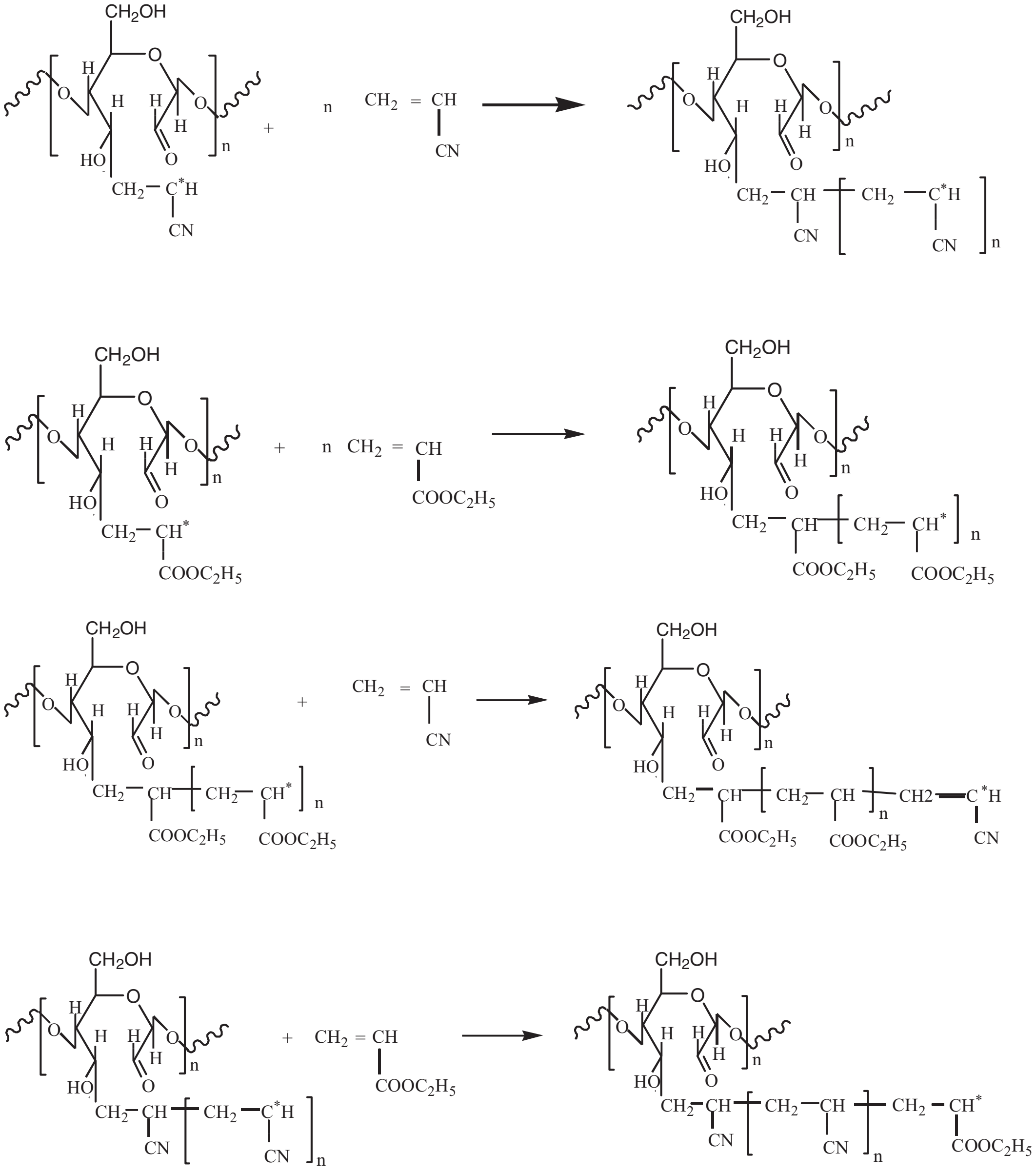
$$\underset{\text{monomer}}{CH_2 = CH — CN} + Ce^{4+} \longrightarrow \text{Complex} \longrightarrow \underset{\text{monomer radical}}{CH_2 = C^* — CN} + Ce^{3+} + H^+$$

$$\underset{\text{monomer}}{CH_2 = CH — COOC_2H_5} + Ce^{4+} \longrightarrow \text{Complex} \longrightarrow \underset{\text{monomer radical}}{\overset{\text{chemistry}}{{}^*CH = CH — COOC_2H_5}} + Ce^{3+} + H^+$$

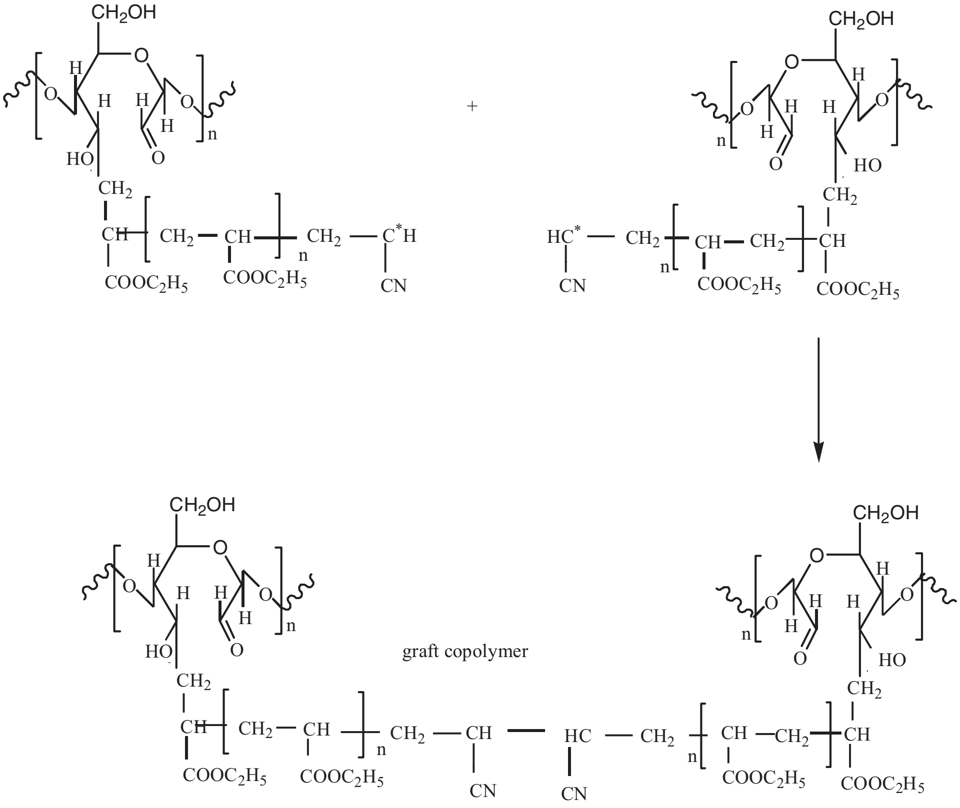
(2) Chain initiation

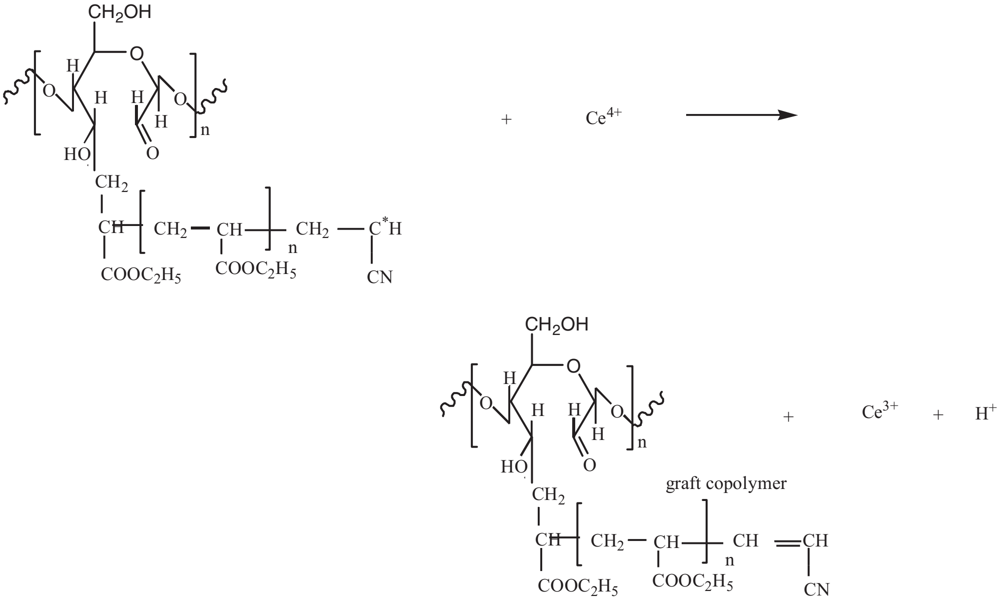


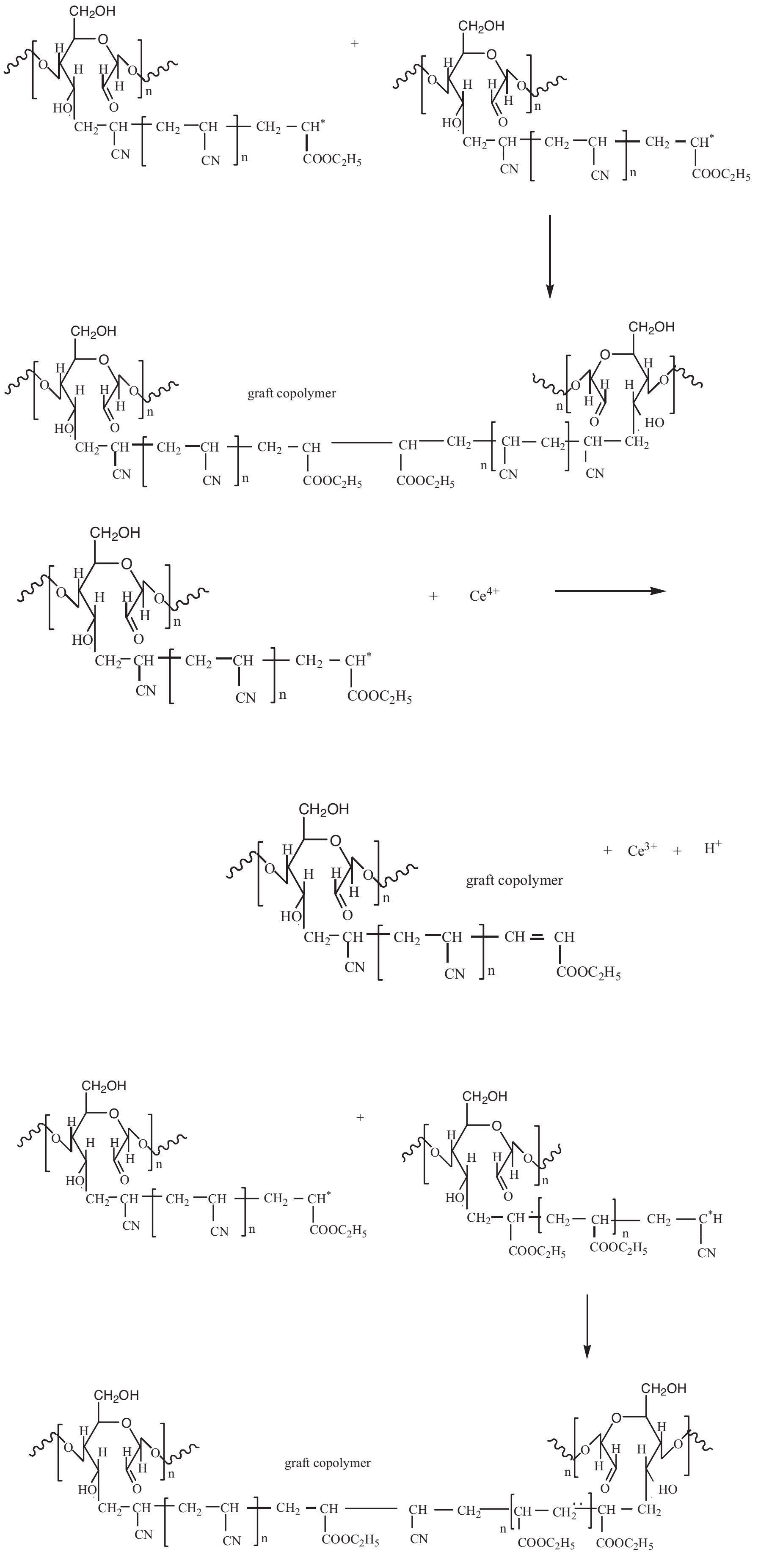
(3) Chain propagation



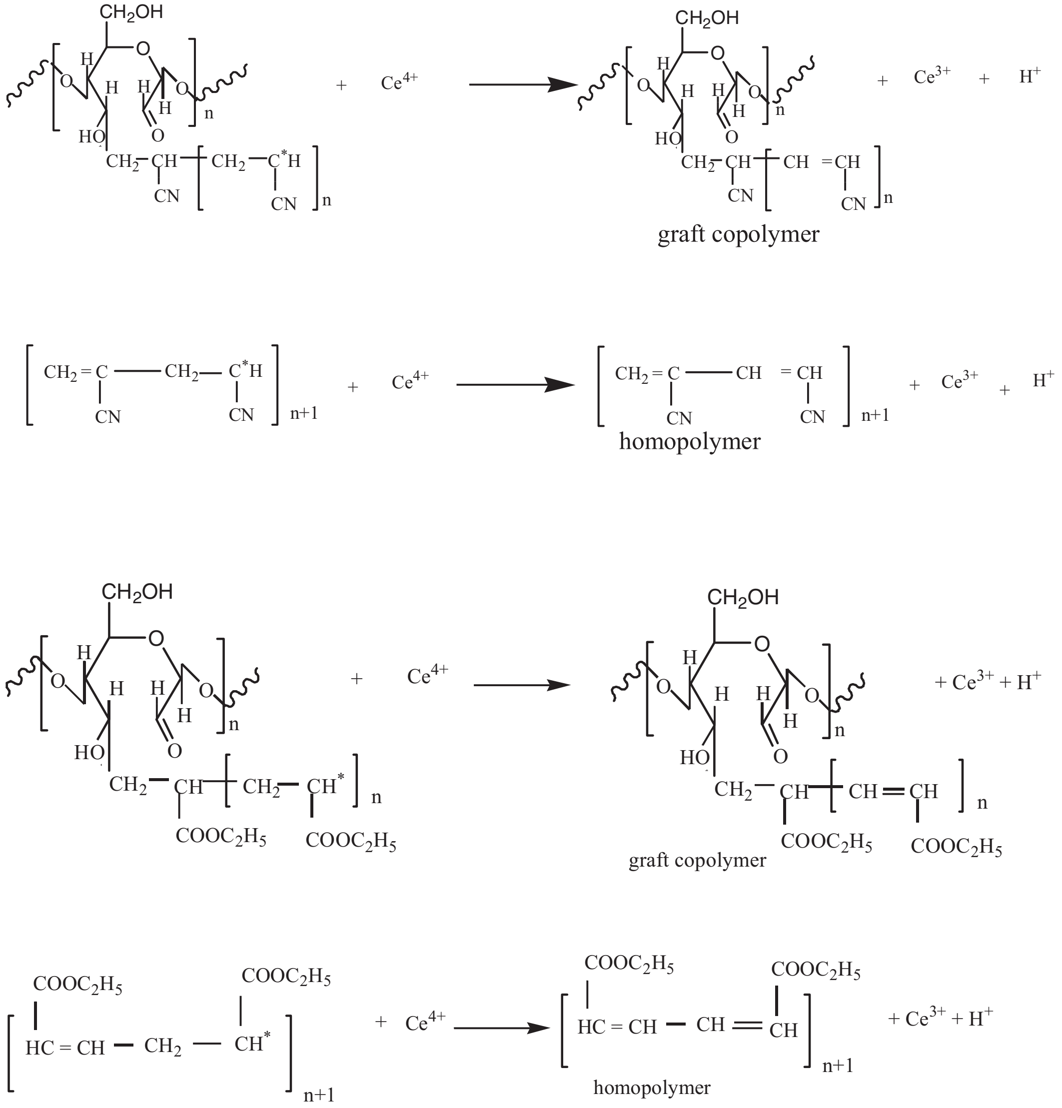
(4) Chain termination






graft copolymer
graft copolymer
+ Ce4+
+ Ce3+ + H+
graft copolymer

(5) Oxidative termination



5.2. Effect of feed molarity

The grafting of mixture of binary vinyl monomers (AN + EA) onto Agave fibers has been investigated at different feed molarities ranging from 0.35 to 0.6 mol dm^{-3} at a fixed mole fraction of acrylonitrile (f_{AN}) = 0.7)). From Table 2(a) it is evident that there is a considerable increase in percent graft yield when feed molarity is increased from 0.35 to 0.5 mol dm^{-3}. However with further increase in feed molarity of comonomer mixture beyond 0.5 mol dm^{-3}, a decrease in percent graft has been observed. The initial increase in percent graft yield on increasing feed molarity from 0.35 to 0.5 mol dm^{-3} is due to increase in the rate of propagation of polymer chains and grafting on the reactive sites of fiber backbone which are free to the attack of monomer radicals. With increase in the feed molarity propagating polymer chains get more and more comonomers to grow to their maximum degree of polymerization. Also more and more reactive sites are occupied by comonomer radicals which results in the initial increase in the percent graft up to feed molarity of 0.5 mol dm^{-3}. However beyond certain concentration (0.5 mol dm^{-3}) of comonomers, rate of diffusion of comonomers i.e. the donor-acceptor monomer complex decreases as a result of hindrance caused by grafted chains and increase in the viscosity of reaction medium. Therefore percent graft yield decreases with further increase in the feed molarity up to 0.6 mol dm^{-3}. From Table 2(a) it is clear that the extent of homo copolymer formation has increases with increase in the molarity of comonomer feed which may be attributed to the increased interactions of donor–acceptor monomer complex with increase in feed molarity. The rate of grafting varies as first power of the concentration of monomer feed (Fig. 1(a)) up to 0.5 mol dm^{-3} and decreases with further increase in the feed concentration which may be due to increase in the viscosity of reaction medium resulting in the slow diffusion of the monomer radicals on to the cellulosic backbone.

5.3. Effect of feed composition

During the study of effect of variation of feed composition on percent graft yield, the feed molarity of binary monomer mixture was kept constant (0.5 mol dm^{-3}). At constant feed molarity, the viscosity of the reaction mixture remains same therefore the variation in the graft yield at different feed compositions mainly depends

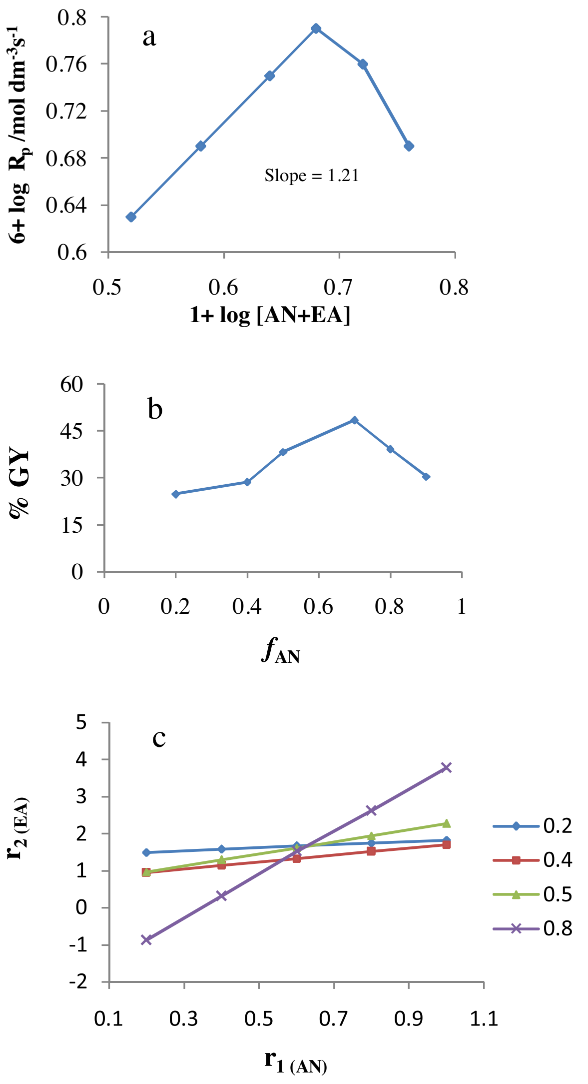


Fig. 1. (a) A log–log plot between rates of grafting vs. comonomer concentration. (b) A plot between % GY vs. feed composition. (c) Mayo and Lewis plot for reactivity ratio.

upon the monomer-monomer interactions in binary mixture. During these investigations, the mole fraction of acrylonitrile has been varied from 0.2 to 0.9 at a fixed feed molarity of 0.5 mol dm^{-3}. From Table 2(b) it is clear that with initial increase in the mole fraction of acrylonitrile in the feed from 0.2 to 0.7, percent graft yield increases linearly. However with further increase in the mole fraction of acrylonitrile beyond 0.7, a decrease in the graft yield has been observed. This behavior of graft yield with different feed compositions suggests a significant variation in the monomer–monomer and cellulose–monomer interactions in different mole fractions of comonomers present in the feed. The initial increase in the graft yield can be assumed to be due to the formation of donor-acceptor monomer complex which facilitates the transfer of acrylonitrile molecules to the growing chain on the Agave fiber cellulosic backbone which in turn facilitates the grafting of ethyl acrylate molecules and is responsible for the synergistic effect of comonomers in the binary monomer mixture.

With the further increase in the mole fraction of acrylonitrile in the feed beyond 0.7, graft yield decreases. It may be due to the variation in the monomer–monomer interactions at higher mole fraction of acrylonitrile as a result of which synergistic effect of comonomers also decreases. These observations have clearly indicated that synergistic effect operates within a certain range of feed composition beyond which graft yield changes according to affinity of individual monomer. The variation of percent GY with feed composition (f_{AN}) has been shown in Fig. 1(b).

In order to determine the relative reactivities of monomers, the reactivity ratio of acrylonitrile and ethyl acrylate has been evaluated using Mayo and Lewis method (Mayo & Lewis, 1944) (Fig. 1(c)). The values of reactivity ratios for acrylonitrile and ethyl acrylate have been found to be 0.63 and 1.54. The higher value of reactivity ratio of ethyl acrylate suggested that it has more affinity to transfer copolymer chain onto cellulosic backbone as compared to acrylonitrile. Further the product of r_1 and r_2 is less that unity (0.97) which suggested us to consider alternate arrangement of the monomers in grafted copolymers.

5.4. *FT-IR analysis*

The FT-IR spectrum of raw *A. americana* fiber showed a broad peak at 603 cm^{-1} (due to out of plane –OH bending), 898 cm^{-1} (due to β-glycosidic linkage), 1257.9 cm^{-1} (due to –C–O–C and –C═O stretching in xylan side substituent and lignin aromatic C═O stretching), milder peaks at 1381.2–1432.0 cm^{-1} (due to –CH, –CH$_2$ and–CH$_3$ bending), 1505.8 cm^{-1} (lignin aromatic ring vibration and stretching), 1652.7 cm^{-1} (due to H–O–H bending of absorbed water and for lignin C–H deformation), 2138.7 cm^{-1} (due to O–H stretching of absorbed moisture), 2368.5 cm^{-1} (due to C–H stretching in polysaccharide chains),2918.1 cm^{-1} (for C–H stretching vibration of aliphatic methylene groups) and 3397.1 cm^{-1} (due to bonded –OH group). However additional peaks at 2241.7 cm^{-1} and 1736.1 cm^{-1} were observed in grafted fibers due to the presence of –C≡N group of acrylonitrile and carbonyl group (>C═O) of ester stretching vibrations.

5.5. *Thermal analysis*

Fig. 2(a) and (b) represents TGA curves for raw and grafted fibers, respectively. The results reveal an increase in thermal stability of the fiber upon grafting. The initial and final decomposition temperatures of raw fiber were 240 °C and 432 °C, respectively. Raw fiber exhibited two stage decomposition, with the maximum weight loss between 240 °C and 346 °C (50.6%) and 346–432 °C (32.3%). The first stage of decomposition may be due to cellulosic decomposition and the second stage may be due to the degradation of lignin and oxidation of char.

The initial and final decomposition temperatures of grafted fiber are 275 °C and 567 °C, respectively. In case of grafted fibers the first stage decomposition takes place at 275 °C to 353 °C with weight loss of 61.8%. It can be attributed to the breakdown of hemicellulose and glycosidic linkages of cellulose whereas the second stage of decomposition occurred between 353 °C and 567 °C with weight loss of 37.6%. This may be related to the degradation of grafted poly (AN + EA) chains onto the fiber surface.

5.6. *Scanning electron microscopy (SEM)*

The comparison of Electron micrographs of raw and binary monomer grafted agave fibers [Fig. 2(c) and (d)] shows that surface topology of agave fibers changes upon grafting. It may be due to incorporation of poly (AN + EA) chain on the cellulosic backbone as a result of which the surface of fiber becomes rough.

5.7. *X-Ray diffraction studies*

The raw fiber at 2θ scale gave peaks at 22.03° and 14.22° with relative intensities of 97.6 and 46.1, respectively. Similarly Agave-g-poly (AN + EA) shows peaks at 22.26° and 16.53° with

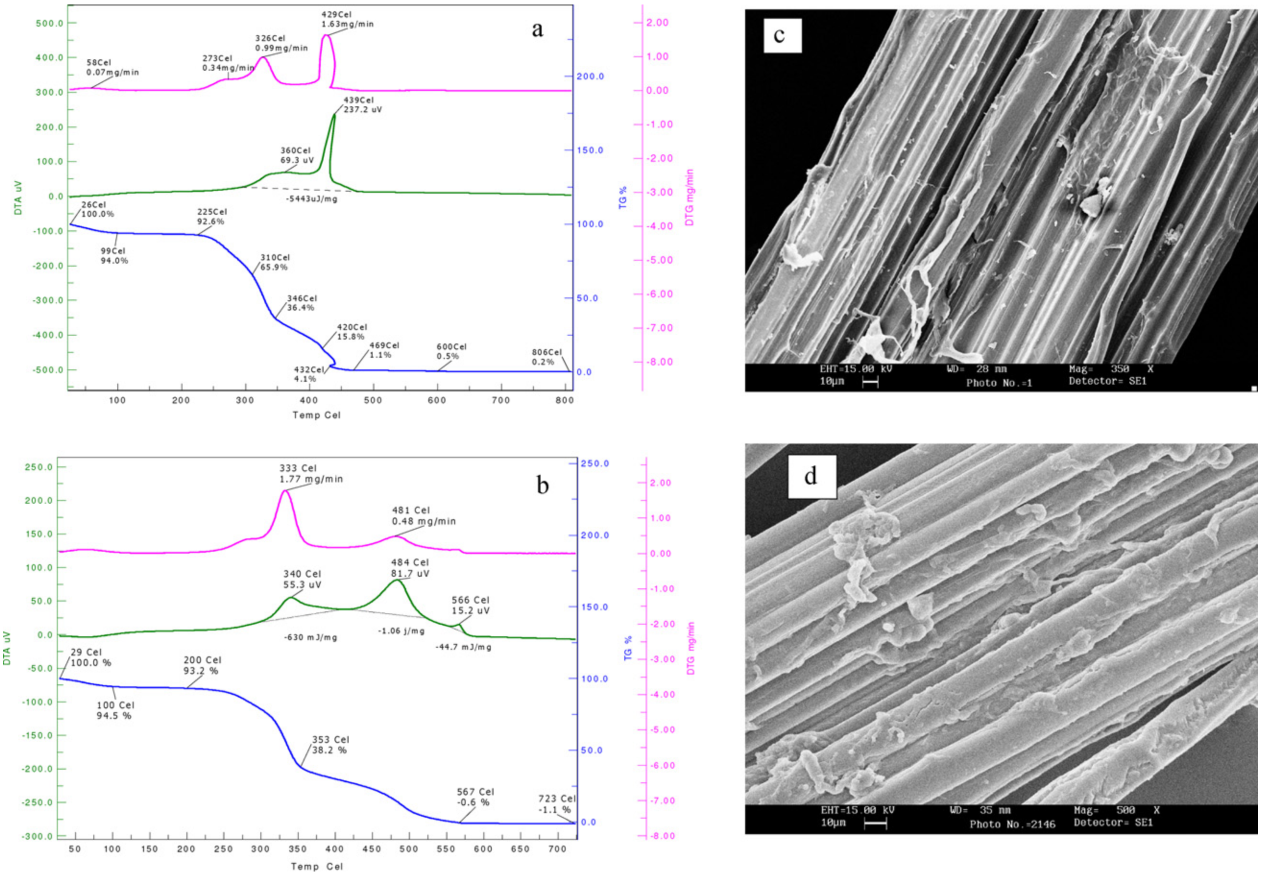


Fig. 2. (a) Thermogram of raw fiber. (b) Thermogram of grafted fiber. (c) SEM of raw fiber. (d) SEM of grafted fiber.

relative intensities of 100 and 58.3, respectively. The percent crystallinity of raw and grafted fibers comes out to be 67.92 and 63.17, respectively whereas crystallinity index is 0.53 and 0.42, respectively.

Crystallinity index gives the quantitative measure of the orientation of the cellulose crystals in the fibers with respect to the fiber axis. The grafted fibers show lower percent crystallinity (%Cr) as well as crystallinity index (C.I.). Lower crystallinity index of the grafted fiber indicates that there may be the disorientation of the cellulose crystals when poly (AN + EA) chains are incorporated in the fiber.

5.8. *Swelling behavior*

Fig. 3(a) shows swelling behavior of raw and grafted Agave fibers in different solvents. Different trends in the swelling behavior of raw and grafted fibers were observed in different solvents. Raw fibers show maximum swelling in water and percent swelling decreases with increase in percent graft yield. It may be due to greater affinity of polar –OH groups present in raw fiber towards water. Further as percent graft increases –OH groups are gradually replaced by Poly (AN + EA) chains resulting in percent swelling. Similarly grafted fibers show maximum swelling in carbon tetrachloride which increases as percent graft yield increases. It may be due to greater affinity of poly (AN + EA) chains towards carbon tetrachloride. Further due to presence of alkyl groups in poly (AN + EA) chains, these are hydrophobic in nature and have strong affinity towards non polar solvents like CCl_4. The trend of swelling behavior in different solvents may be given as below.

Raw fiber

$H_2O > C_2H_5OH > DMF > CCl_4$

Grafted fiber

$CCl_4 > DMF > C_2H_5OH > H_2O$

5.9. *Moisture absorption studies*

The samples of both raw and grafted fiber were exposed to different humidity levels for definite time interval. It was observed that graft copolymerization of binary monomers on to Agave fibers had great impact on moisture absorption behavior. At a particular humidity level moisture absorbance was found to decrease with increase in percent graft yield. This may be attributed to the blocking of reactive sites on the cellulosic backbone which are vulnerable to moisture by poly (AN + EA) chains. Moisture absorption studies have been shown in Fig. 3(b).

5.10. *Chemical resistance studies*

The acid and base resistance behavior of raw and grafted fibers was studied in acids and bases of different strengths (Fig. 3(c) and (d)). It has been observed that upon grafting Agave fibers become more resistant to the attack of acids and bases. Further chemical resistance increases with increase in the percent graft yield. It is due to the fact that poly (AN + EA) chains grafted on Agave fibers have less affinity for acids and bases.

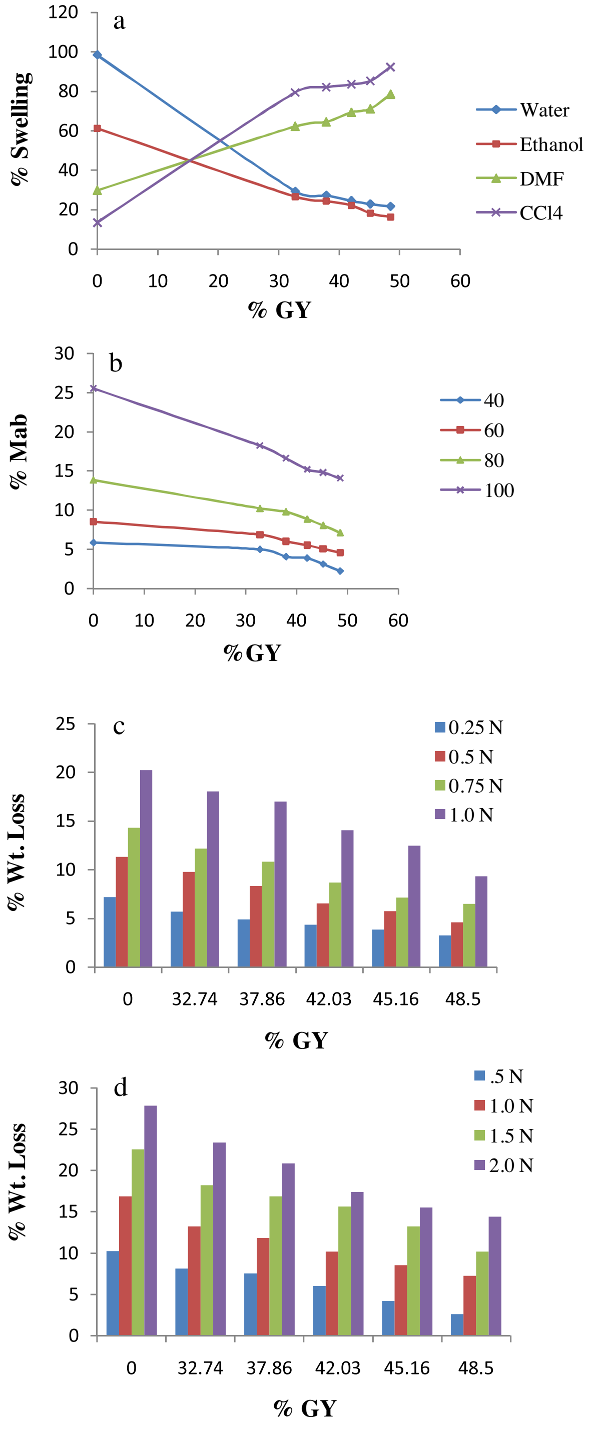


Fig. 3. (a) Swelling behavior in different solvents. (b) Moisture absorption behavior in different solvents. (c) Acid resistance behavior of raw and grafted fibers. (d) Base resistance behavior of raw and grafted fibers.

6. Conclusions

Graft copolymerization of acrylonitrile and ethyl acrylate from their binary mixture has been carried out in presence of ceric ion-nitric acid redox initiator system. The product of reactivity ratios of acrylonitrile and ethyl acrylate has been found to be less than unity, which suggested the alternate arrangement of the monomer blocks in grafted chains. These investigations have suggested that the presence of ethyl acrylate has increased the grafting of acrylonitrile on Agave fibers due to synergistic effect.

Graft copolymerization of binary monomer mixture is an effective method for the modification of various physico- chemical properties of lignocellulosic fibers. The graft copolymerization of AN + EA binary mixture has a considerable influence on physico chemical, morphological as well as thermal properties. Upon grafting with AN + EA monomer mixture Agave fibers absorb less moisture, become more resistant to the attack of acids and bases and can withstand higher temperature before decomposition. However the percent crystallinity and crystallinity index of grafted fibers decreases due to disorientation of cellulosic crystals as a result of incorporation of poly (AN + EA) chains.

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