

FUNCTIONAL POLYMERS FROM GRAFT COPOLYMERIZATION OF BINARY MONOMER MIXTURES ONTO LIGNOCELLULOSIC BIOMASS: SYNTHESIS, CHARACTERIZATION, AND PROPERTIES EVALUATION

Amar Singh Singha,^{a,*} Raj K. Rana,^a and Ashish Guleria^a

Graft copolymerization of binary mixture of methyl methacrylate (MMA) and acrylonitrile (AN) has been carried out onto *Agave americana* fibers in the presence of Ce (IV) ions at 45.0 ± 0.1 °C. The addition of acrylonitrile as a comonomer has shown a significant increase in graft copolymerization of methyl methacrylate onto the lignocellulosic fibers. A synergistic effect of acrylonitrile on methyl methacrylate has been observed when graft copolymers were prepared using different feed compositions (f_{MMA}) ranging from 0.2 to 0.8 at constant feed molarity of 5.0×10^{-1} mol dm⁻³. The rate of grafting has shown a linear dependence on the concentration of comonomers within the range of feed molarity from 3.5×10^{-1} to 5.0×10^{-1} mol dm⁻³. The variation of grafting parameters such as graft yield and graft efficiency has been studied as a function of feed molarity and feed composition. The graft copolymers were characterized by various techniques such as FT-IR, TGA/DTA, XRD, and SEM. Further graft copolymers were evaluated for the physico-chemical properties such as swelling behavior in different solvents, moisture absorption behavior, and resistance to chemicals as a function of percent grafting. The mechanism for grafting has been proposed based upon experimental observations.

Keywords: Lignocellulosic; synergistic; methyl methacrylate; comonomers; moisture absorption

Contact information: a: Department of Chemistry National Institute of Technology Hamirpur (H.P.) 177005 INDI; Phone: +91-1972-304120 Fax: +91-1972-223834; *Corresponding author: E-mail: singhaasnit@gmail.com

INTRODUCTION

The utilization of lignocellulosic biomass in various industrial applications has gained much attention during the past few decades due to increased environmental concerns. The use of lignocellulosic biomass as fillers and reinforcements in both thermoplastic and thermosetting matrices has gained acceptance in commodity plastics in the past few years (Djidjelli *et al.* 2002; Pan *et al.* 2010). Lignocellulosic fibers exhibit a number of advantages such as low cost, lightweight, less toxicity, nonabrasive nature, relative abundance, renewable nature, and biodegradability (Arib *et al.* 2006; Abu Bakar *et al.* 2004; Idicula *et al.* 2005). However, due to their hydrophilic nature, these fibers have limited scope in the industry. Therefore to enhance the applications of lignocellulosic fibers in different industrial arena including composite materials, it is mandatory to improve the existing properties of the fibers. In addition to moisture absorption, chemical resistance and thermal stability of the cellulosic fibers are also

important properties which greatly influence the potential use of these fibers in various industrial applications.

Therefore to make lignocellulosic fibers as a viable industrial material, their physico-chemical properties such as thermal behavior, chemical resistance, and moisture sensitivity etc., need to be improved. There are various methods such as mercerization, acetylation, benzylation, silane treatment, and plasma treatment which have been employed by various researchers for the surface modification of different natural fibers. Suizu *et al.* carried out mercerization of ramie fibers in high concentration of alkali solutions and used them as reinforcement to prepare unidirectional fully green composites. They observed a two or three times increase in tensile and impact strength of the composites reinforced with mercerized ramie fibers (Suizu *et al.* 2009). Khalil *et al.* (2001) investigated acetylation of oil palm empty fruit bunch fiber and coir fiber using non catalyzed acetic anhydride. Wang *et al.* (2007) subjected flax fibers to mercerization, benzylation, and silane treatments before using them as reinforcements to prepare HDPE composites. Gonzalez *et al.* (1999) modified the surface of short henequen fibers with silane coupling agent in order to study its deposition mechanism and influence of chemical treatment on mechanical properties of composites. Skundric *et al.* (2007) performed plasma modification of hemp fibers through dielectric barrier discharge and studied its influence on physico-chemical properties such as water uptake and wetting of the fibers.

Among the various methods, graft copolymerization is an effective technique for surface modification of natural fibers and has been widely used by many researchers. Ojah and Dolui (2006) carried out graft copolymerization of methyl methacrylate onto *Bombyx mori* initiated by a CdS semiconductor based photo catalyst system. They also studied the effect of additives such as triethylamine and ethylene glycol on percent grafting. Saikia and Ali (1999) carried out graft copolymerization of methyl methacrylate onto cellulose pulp extracted from *Hibiscus sabdariffa* and *Gmelina arborea*.

Graft copolymerization of lignocellulosic fibers with vinyl monomers improves many properties, such as water absorption, thermal stability, hydrophilic nature, and resistance to chemical and micro-bacterial attack (Mcdowall *et al.* 1984). Grafting can be carried out with a single monomer or with a mixture of binary monomers. Grafting of vinyl monomers onto cellulosic fibers introduces the properties of added polymer while retaining the original properties of the backbone fibers. Therefore, it has been a versatile technique to develop tailor made materials for future applications. Many researchers have carried out graft copolymerization of individual vinyl monomers onto lignocellulosic fibers using different initiator systems. Singha and Rana (2010) carried out graft copolymerization of methyl methacrylate onto *Agave americana* fibers using a ceric ions-nitric acid initiator system. Mondal *et al.* (2008) carried out graft copolymerization of vinyl monomers such as acrylic acid, methacrylic acid, acrylamide *etc.* onto cotton fibers pretreated with amines. Zahran (2006) carried out graft copolymerization of methacrylic acid and other vinyl monomers onto cotton fabric using Ce (IV) ion-cellulose thiocarbonate redox system. The extent of graft copolymerization of monomers onto the fiber surface depends not only upon the chemical structure but also on reactivity of the monomer. It has been reported in the literature that in case of grafting of individual

monomers, the extent of homopolymer formed is more compared to graft copolymers (Gupta and Sahoo 2001).

However, grafting of vinyl monomers from their binary mixtures is a useful technique because it introduces dual properties in the backbone polymer and also influences the extent of grafting of a monomer by synergistic effect, which exhibits a 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 (El-Salmawi *et al.* 1997). Therefore, graft copolymerization provides an opportunity to prepare grafted products by using suitable monomers and their feed compositions in the binary mixtures. Graft copolymerization of vinyl monomers from their binary mixtures has been investigated by many workers. Lee *et al.* carried out graft copolymerization of binary mixture of sodium styrenesulfonate and acrylic acid using the electron beam irradiation method (Lee *et al.* 2008). Rattan *et al.* (2008) carried out graft copolymerization of binary mixture of ethyl acrylate and vinyl imidazole onto rayon in aqueous medium initiated by gamma radiations. The grafting must be carried out with an initiator which must be able to generate active sites on the backbone. Ce (IV) ions generate free radicals on the cellulosic backbone in the presence of mineral acids easily, however they undergo hydrolysis in aqueous medium and therefore exhibit lower efficiency (Mino and Kaizerman 1958).

Gupta *et al.* (2001) carried out graft copolymerization of binary mixture of methyl methacrylate and acrylonitrile onto cellulose in the presence of ceric ions with acrylonitrile as the principal monomer. In the present manuscript, efforts have been made to modify the surface of *Agave americana* fibers through graft copolymerization of binary monomer mixture of methyl methacrylate and acrylonitrile using Ce (IV) ion – HNO₃ redox initiator system with methyl methacrylate as the principal monomer. The fibers are obtained from the vessel sheaves of leaves of *Agave americana*. The average length of fibers varies from 0.6 to 1.2 m. The average chemical constituents of the fibers are cellulose (62.3%), hemicellulose (35.6%), and lignin (2.1%) (El Oudiani *et al.* 2009). These fibers are utilized by villagers for domestic purposes such as making ropes, bags, mats *etc.* probably due to their excellent mechanical properties. Msahli *et al.* (2006) studied the physical and mechanical properties of *Agave 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 investigates the industrial utilization of lignocellulosic biomass obtained from wild growing *Agave americana*.

EXPERIMENTAL

Materials

Agave fiber bundles were extracted from *Agave americana* by cutting and immersing the leaves in fresh water at 25 to 30 °C for about 4 to 5 weeks. The leaves were then taken out and fibers were separated from the matrix by calendaring the leaves. Individual fibers were rinsed with distilled water. The fibers were then made free from

impurities of waxes, oils *etc.* by extraction with acetone in a soxhlet extraction apparatus for 72 hours. The monomers, methyl methacrylate (MMA) and acrylonitrile (AN) received from CDH, India were purified by first washing with 5% NaOH and then drying over anhydrous Na₂SO₄. Finally the monomers were subjected to distillation and the middle fraction of distillate was used for further studies. Shimadzu Libror AEG-220 (Kyoto, Japan) balance was used for weighing the samples. All other chemicals were of analytical reagent grade and were used as such without further purification.

Grafting Method

The fibers were allowed to swell by immersing them in distilled water for 24 hours prior to the grafting reaction in order to diffuse monomer radicals easily and to expose the reactive sites on backbone. 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, and initiator and monomer concentration were optimized for graft copolymerization of principal monomer (MMA) onto a backbone fiber as per the method reported earlier (Singha and Rana 2010). The results of optimization of different reaction parameters have been given in Table 1. A known amount of ceric ammonium nitrate ($6.58 \times 10^{-3} \text{ mol dm}^{-3}$) dissolved in a definite amount of nitric acid ($2.77 \times 10^{-1} \text{ mol dm}^{-3}$) was added to the reaction mixture containing 0.5 g of fibers. The comonomer mixture was then added drop wise to the reaction kettle in order to maintain overall molarity of 0.50 mol dm^{-3} in the reaction mixture. The mole fraction of methyl methacrylate (f_{MMA}) in the reaction mixture was maintained at 0.5. After the addition of the binary mixture, the reaction was allowed to proceed at constant speed of stirring with the help of an electrically operated magnetic stirrer maintained at a constant temperature of $45 \pm 0.1 \text{ }^{\circ}\text{C}$ for an optimized time interval of 120 minutes. The reaction was stopped after 120 minutes, and the graft copolymer obtained was taken out of the reactor and subjected to the removal of homopolymer formed during the grafting reaction.

Extraction of Homopolymers (Hp)

The homopolymers poly (MMA) and poly(AN) formed during the grafting reaction were removed by soxhlet extraction with acetone and finally with dimethyl formamide (DMF). The extracted homopolymers were precipitated with water-methanol mixture in the ratio of 1:1 (v/v), filtered, and dried to constant weight in a vacuum oven at $60 \text{ }^{\circ}\text{C}$. The percent homopolymers extracted during grafting reactions are given in Tables 2 and 3.

Extraction of Homocopolymers (Hcp)

After the homopolymers extraction, homocopolymers poly (MMA-co-AN) were soxhlet extracted with tetrahydrofuran (THF) for 24 hours. Finally homocopolymers were precipitated with water-methanol mixture in the ratio of 1:1 (v/v), filtered, and dried to constant weight in a vacuum oven at $60 \text{ }^{\circ}\text{C}$.

Grafting Parameters*Percent graft yield (% GY)*

Graft yield was calculated in terms of the ratio of increase in the weight of sample upon grafting to the original weight of the backbone (Singha and Rana 2010).

Percent graft efficiency (% GE)

Graft efficiency was calculated as the ratio of increase in weight of backbone to the weight of monomer (W_m) (Singha and Rana 2010).

Percent homopolymers (% H_P)

Percent homopolymer was calculated as the ratio of weight of homopolymers (W_{Hp}) to weight of monomer (W_m) (Singha and Rana 2010).

Percent homocopolymers (% H_{CP})

Percent homocopolymer was calculated as the ratio of weight of homocopolymers (W_{Hcp}) to weight of monomer (W_m) as in the previous subsection.

Table 1. Optimization of Various Reaction Parameters for Grafting of MMA onto *Agave americana* Fiber in Air

Sr. No.	Monomer (Mol/Lx10 ⁻¹)	CAN (Mol/Lx10 ⁻³)	Nitric acid (Mol/Lx10 ⁻¹)	Time (Min)	Temp (°C)	% GY	P _e	% Hp
1	1.81	8.77	2.77	120	25	13.00	3.45	11.21
2	1.81	8.77	2.77	120	35	21.20	5.62	26.66
3	1.81	8.77	2.77	120	45	26.44	7.01	28.34
4	1.81	8.77	2.77	120	55	15.00	3.98	13.01
5	1.81	8.77	2.77	120	65	14.20	3.93	12.46
6	1.81	8.77	2.77	30	45	8.40	2.23	11.45
7	1.81	8.77	2.77	60	45	15.20	4.03	5.85
8	1.81	8.77	2.77	90	45	24.40	6.48	24.87
9	1.81	8.77	2.77	150	45	18.30	4.86	15.98
10	1.81	2.19	2.77	120	45	3.80	1.01	6.91
11	1.81	4.38	2.77	120	45	17.00	4.51	25.78
12	1.81	6.58	2.77	120	45	43.50	11.54	48.72
13	1.81	10.96	2.77	120	45	25.40	6.74	27.32
14	1.81	13.15	2.77	120	45	23.50	6.24	24.56
15	1.81	6.58	0.69	120	45	15.82	4.19	31.24

16	1.81	6.58	1.38	120	45	19.08	5.06	16.89
17	1.81	6.58	2.07	120	45	27.40	7.27	32.61
18	1.81	6.58	3.46	120	45	23.66	6.28	19.55
19	1.81	6.58	4.15	120	45	19.80	5.25	21.45
20	0.45	6.58	2.77	120	45	6.60	7.00	9.26
21	0.91	6.58	2.77	120	45	8.30	4.41	6.02
22	1.36	6.58	2.77	120	45	16.68	5.90	22.61
23	2.26	6.58	2.77	120	45	9.44	2.00	13.94
24	2.72	6.58	2.77	120	45	10.72	1.89	16.33

Characterizations of Graft Copolymers

Infrared spectroscopy

To confirm graft copolymerization, FT-IR spectra of graft copolymers were recorded on a Perkin Elmer Fourier Transform infrared (FT-IR) spectrophotometer (Massachusetts, USA) using KBr pellets (Sigma Aldrich, USA).

Thermal characterization

Thermo gravimetric analysis (TGA), differential thermal analysis (DTA), and differential thermo gravimetric (DTG) analysis were carried out on a Perkin Elmer thermal analyzer of Pyris Diamond make. Thermal analysis was carried out in the presence of air at a heating rate of 10 °C/ min.

Morphological analysis

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

Crystallinity studies

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

Each sample was finely powdered into a 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 per the method reported earlier (Singha and Rana 2010).

Studies of Physico-Chemical Properties

Swelling studies

A definite weight of sample was immersed in a solvent for 24 hours. After taking out the sample, excess of solvent was removed. The final weight of the sample was noted, and percent swelling was calculated using the method of Singha and Rana 2010. The swelling studies were performed in water, ethanol, DMF, and CCl₄.

Moisture absorption

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 (Swastika India) maintained at a definite humidity level for 2 hours. Each sample was placed in a hot air oven at 60 °C for 12 hours in order to make it moisture free. The sample was then taken out and the final weight was recorded immediately. Percent moisture absorbance was calculated as per the method reported earlier (Singha and Rana 2010).

Chemical Resistance

The chemical resistance of the graft copolymers was studied as a function of percent weight loss. Known amounts (W_1) of graft copolymers were immersed in acids and bases of different strengths for definite time intervals in order to evaluate their chemical resistance. The fiber samples were then taken out and dried to a constant weight at 60 °C. The samples were weighed again to get the final weights (W_2). The percent weight loss was determined using the method reported by Singha and Rana 2010.

RESULTS AND DISCUSSION

Mechanism of Grafting Reaction

Ceric ions generate active sites onto the backbone polymer through a single electron transfer process (Mino and Kaizerman 1958). It has been reported in our earlier work that grafting is low when MMA is alone graft copolymerized onto the cellulosic fibers even at high feed concentrations of monomer (Singha and Rana 2010). However from our investigations and reported studies, it has become evident that grafting of methyl methacrylate can be improved by using comonomers which can promote grafting through their synergistic effect. The extent of grafting of individual monomer depends upon the concentration of the monomer in the reaction mixture. However, in the presence of a comonomer, the grafting not only depends upon molarity of monomers in the reaction mixture but also on 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 (Maslinska and Jedlinski 1973). The complexes facilitate the transfer of monomers onto the reactive sites on the backbone and hence enhance the overall efficiency of grafting (Fanta *et al.* 1979).

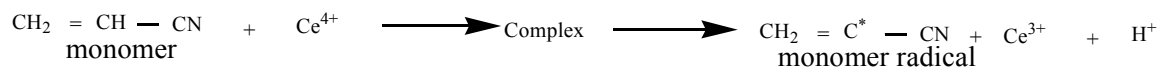
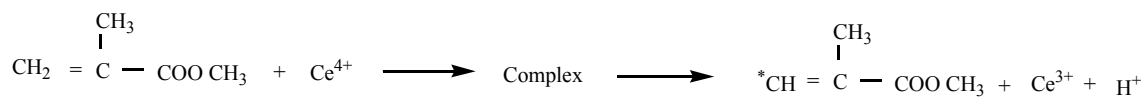
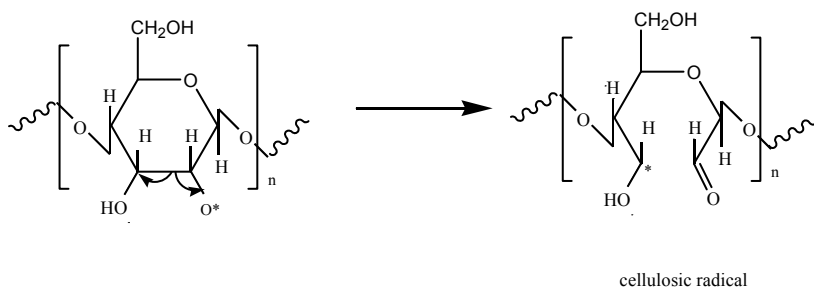
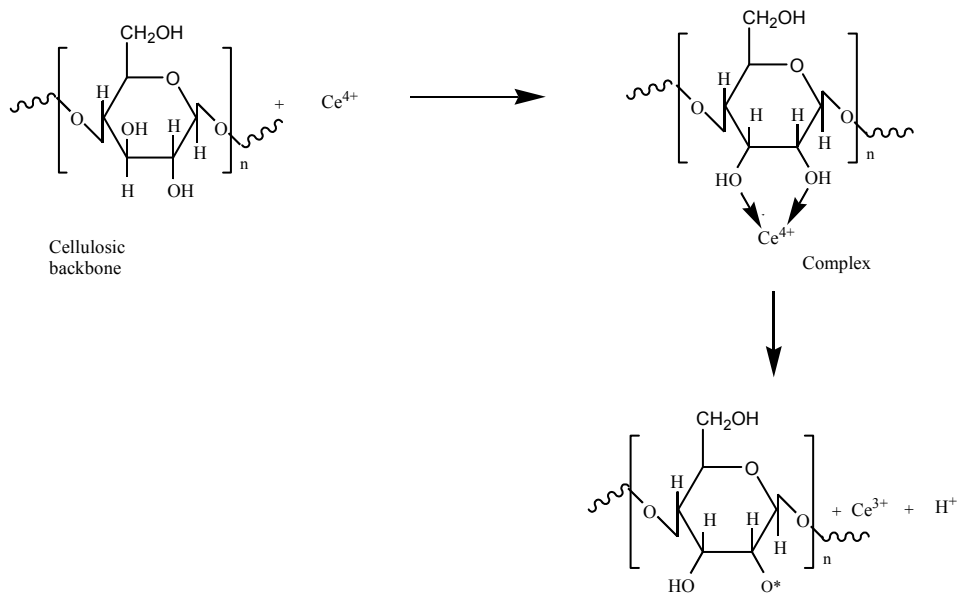
During the grafting reaction, hydroxyl groups present on C-2, C-3, and C-6 act as active sites for the attack of monomer radicals. Ceric ions form chelate complexes with the cellulose molecules through hydroxyl groups at C-2 and C-3 of glucose units. Ce (IV) ions are reduced to Ce (III) by breaking of the bond and transferring of an electron from cellulose molecule as a result of which free radical sites are generated on the backbone. The free radicals are also generated in the monomer chains. They are then transferred to the free radical reactive sites present on the backbone and form graft copolymer. Ceric ammonium nitrate forms bulkier $[\text{Ce-O-Ce}]^{+6}$ 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 $[\text{Ce-O-Ce}]^{+6}$ ions by shifting the equilibrium toward the formation of Ce^{4+} ions.

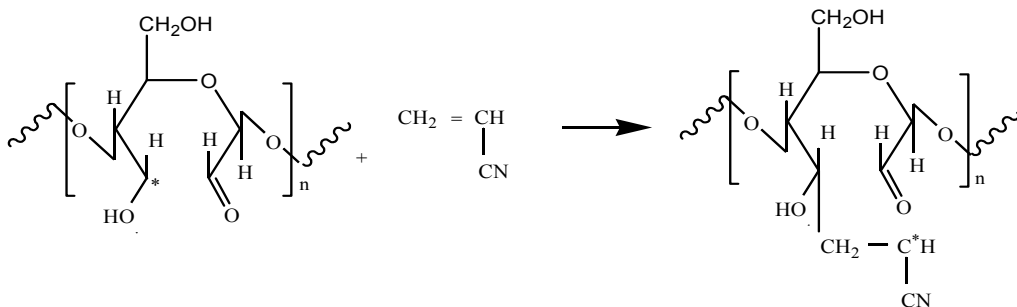
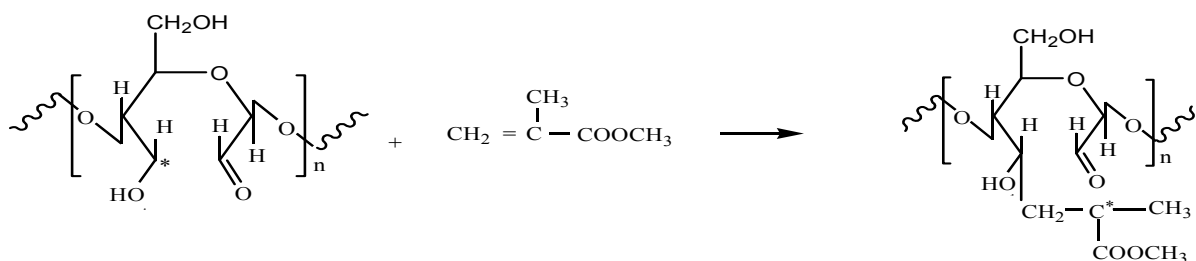
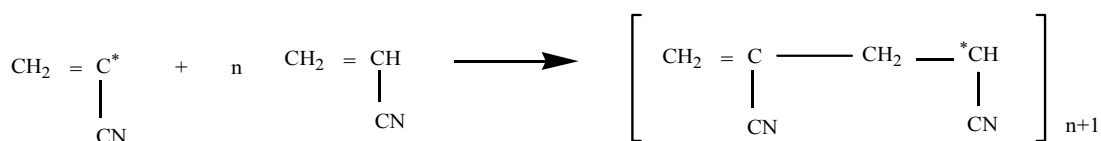
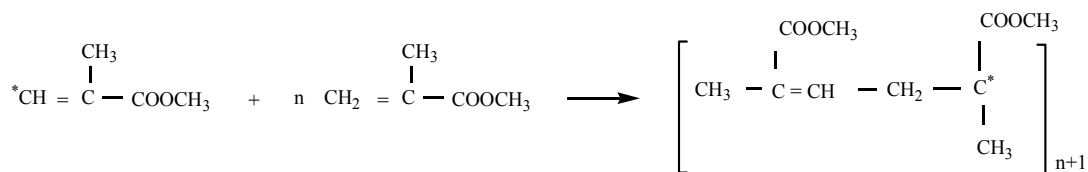
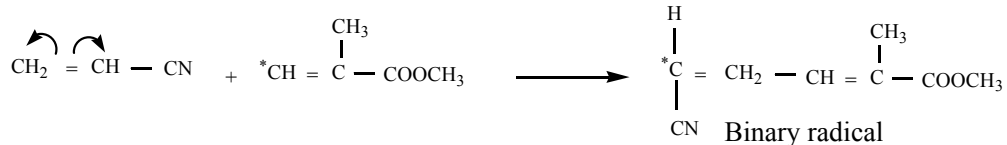
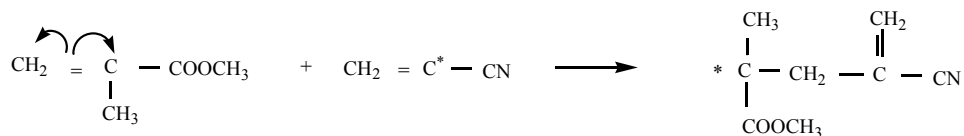
Based upon the experimental data collected as a result of various reaction parameters during the grafting reaction, the following mechanism has been proposed for the grafting of methyl methacrylate and acrylonitrile onto agave fiber backbone in the presence of ceric ions.

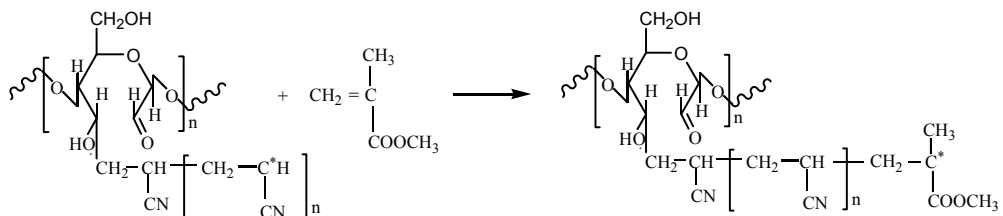
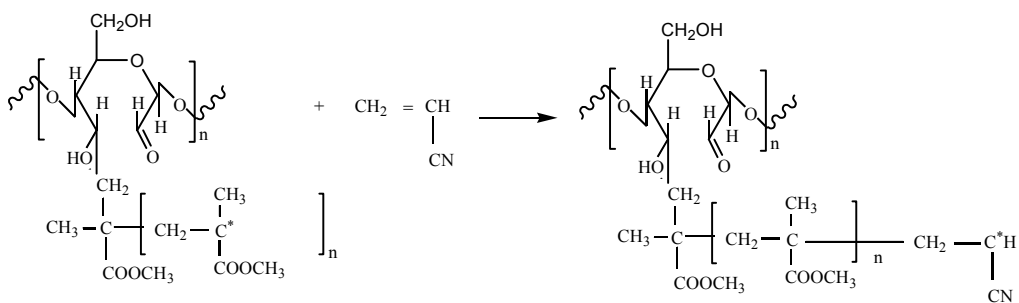
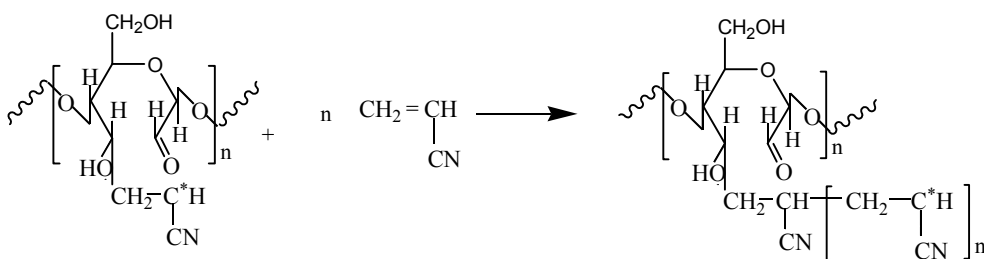
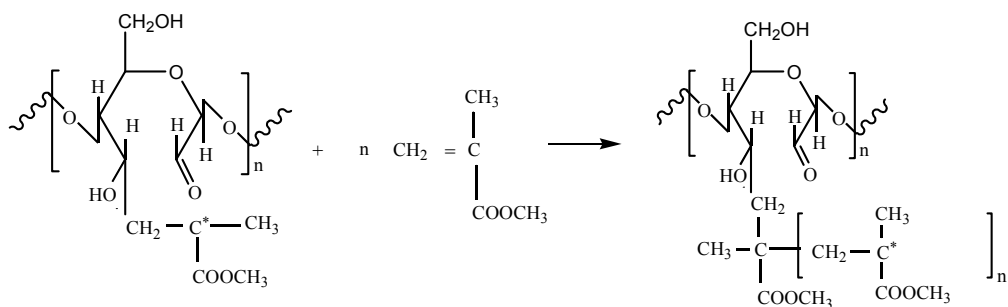
Effect of Feed Molarity

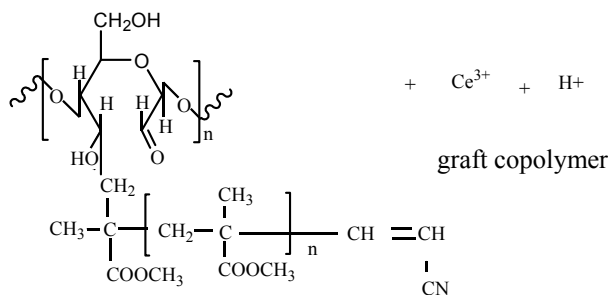
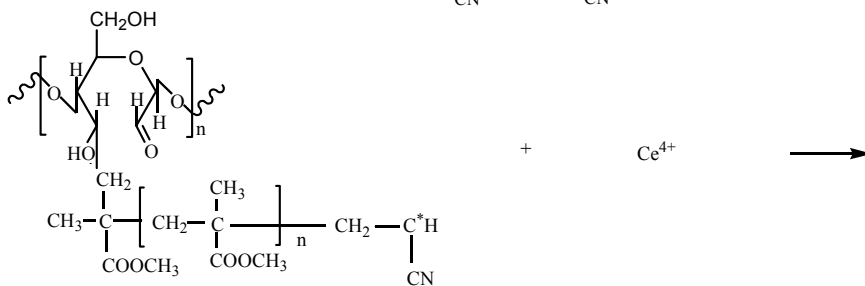
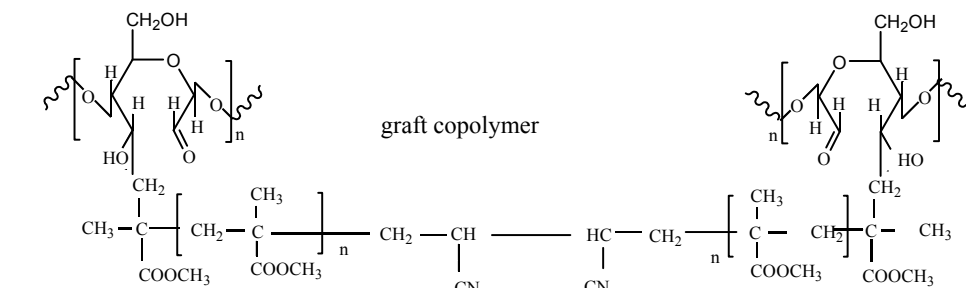
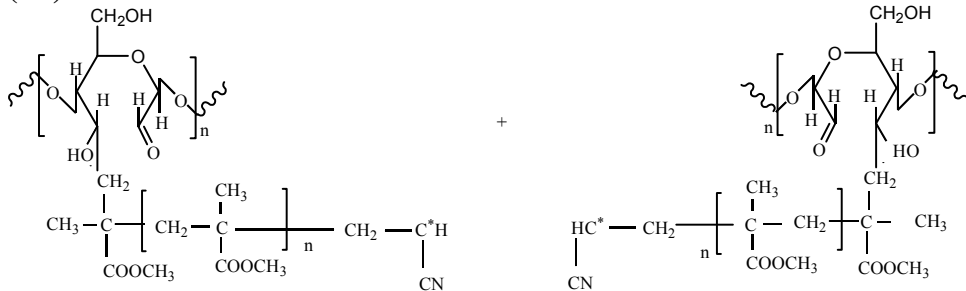
The grafting of mixture of binary vinyl monomers (MMA-co- AN) onto agave fibers has been investigated at different feed molarities ranging from 0.35 to 0.60 mol dm^{-3} at a fixed mole fraction of methyl methacrylate ($f_{\text{MMA}} = 0.5$). From Table 2 it is evident that there is a considerable increase in percent graft yield when feed molarity is increased from 0.35 to 0.50 mol dm^{-3} . However, with further increase in feed molarity of comonomer mixture beyond 0.50 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 0.50 mol dm^{-3} is due to an 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.

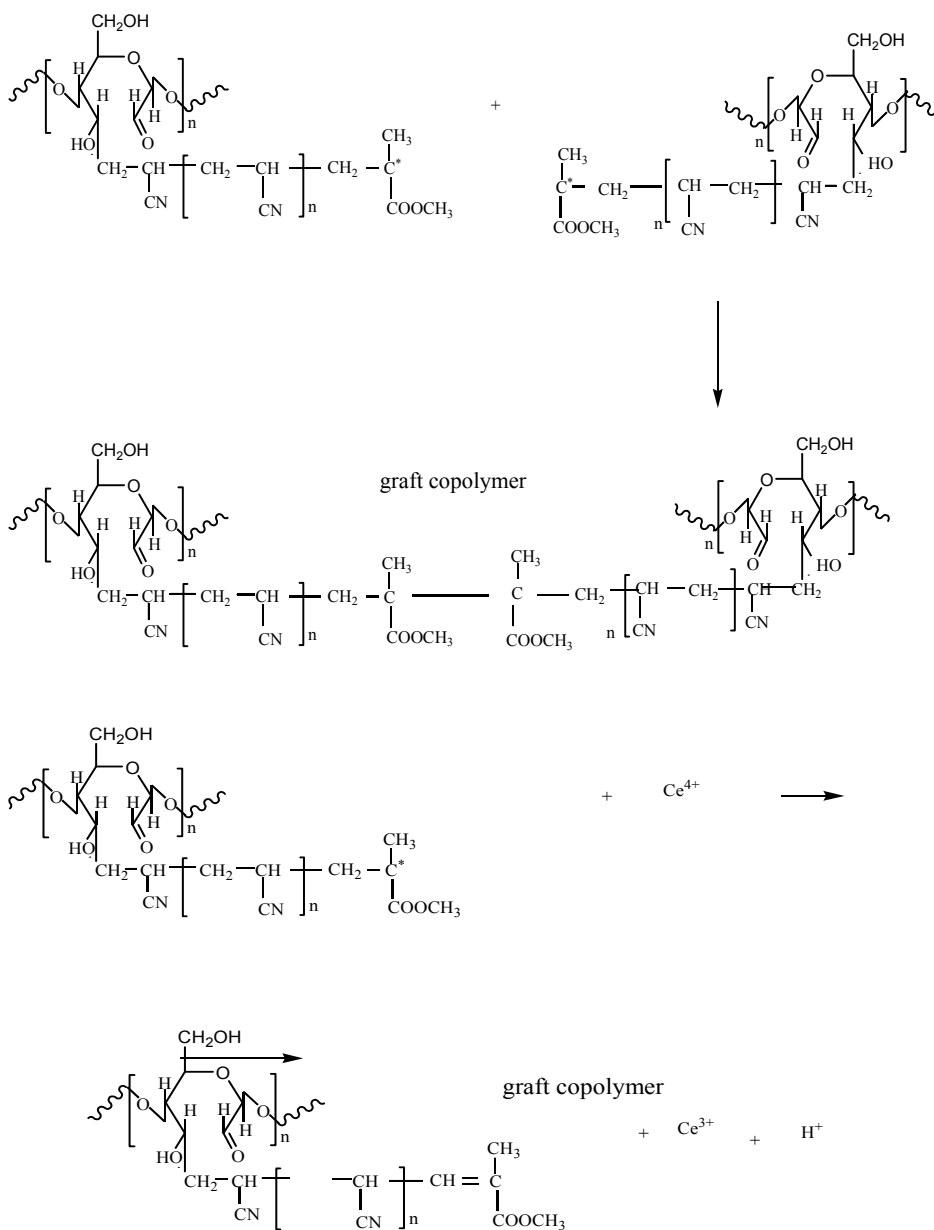
With an increase in the feed molarity, propagating polymer chains get more and more comonomers to grow to their maximum degree of polymerization. Also, sufficient free reactive sites are available on the backbone which is occupied by comonomers radicals. This results in the initial increase in the percent graft up to feed molarity of 0.50 mol dm^{-3} . However, beyond certain a concentration (0.50 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 an increase in the viscosity of reaction medium (Gupta and Sahoo 2001). Therefore percent graft yield decreases with further increase in the feed molarity up to 0.60 mol dm^{-3} . From Table 2, it is clear that the extent of homo copolymer formation has increased with an increase in the molarity of comonomer feed. This result may be attributed to the increased interactions of donor-acceptor monomer complex with an increase in feed molarity.

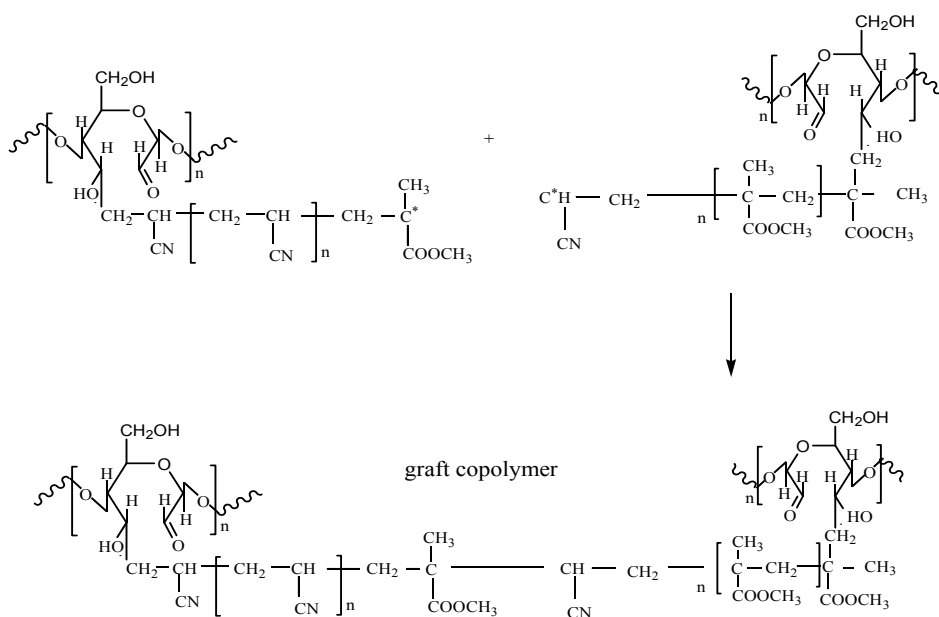
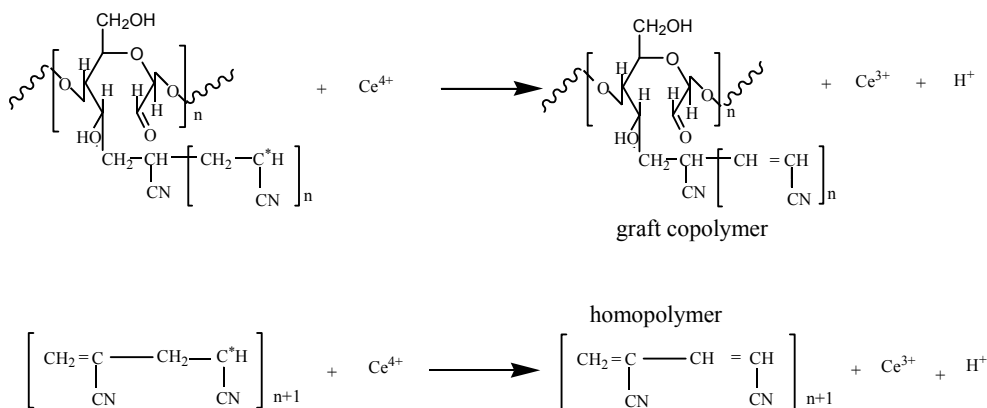
(I) Radical Generation

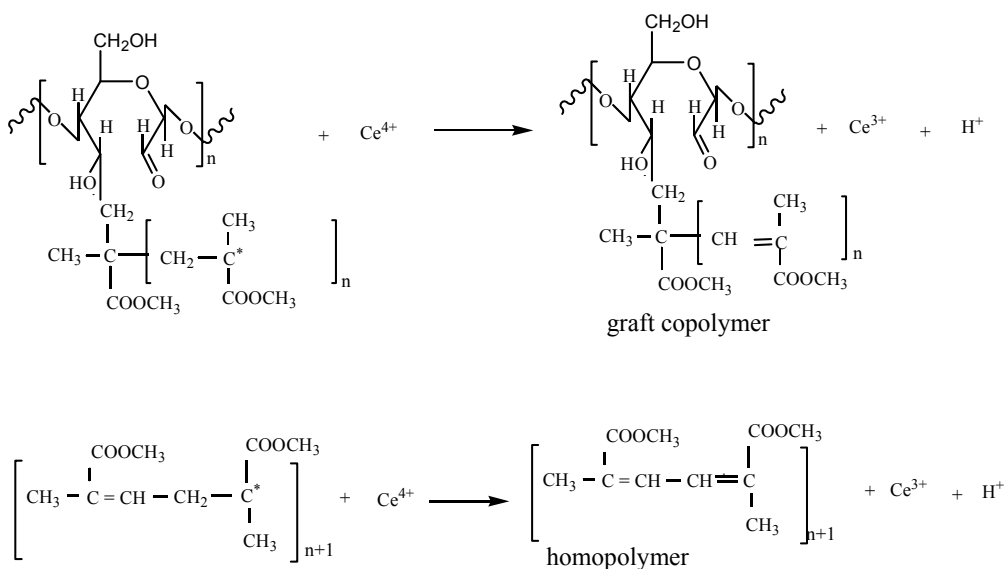
(II) Chain Initiation

(III) Chain Propagation

(IV) Chain Termination



**(V) Oxidative Termination**



The rate of grafting has been found to be dependent linearly on monomer feed up to 0.50 mol dm^{-3} as is clear from the slope value (Fig. 1a). Further the rate of grafting decreases with increase in the feed concentration beyond 0.50 mol dm^{-3} , 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.

Table 2. Effect of Feed Molarity on Grafting Parameters

$[Ce(IV)] = 6.58 \times 10^{-3} \text{ mol dm}^{-3}$, $[HNO_3] = 2.77 \times 10^{-1} \text{ mol dm}^{-3}$

$f_{MMA} = 0.5$, Temp. = 45°C , Time = 120 min.

[MMA+AN] mol dm^{-3}	%GY	%GE	%Hcp
0.35	40.64	8.87	18.96
0.40	45.82	8.51	22.78
0.50	59.24	9.62	23.03
0.55	42.85	6.14	25.87
0.60	36.79	4.71	29.21

Effect of Feed Composition

During the study of the effect of variation of feed composition on percent graft yield, the feed molarity of binary monomer mixture was kept constant (0.50 mol dm^{-3}). At constant feed molarity, the viscosity of the reaction mixture remained the same; therefore the variation in the graft yield at different feed compositions mainly depends upon the monomer-monomer interactions in binary mixture. During these investigations, the mole fraction of methyl methacrylate was varied from 0.2 to 0.8 at a fixed feed molarity of 0.50 mol dm^{-3} . Table 3 shows that with an initial increase in the mole fraction of methyl methacrylate in the feed from 0.2 to 0.5, percent graft yield increased linearly. However with a further increase in the mole fraction of methyl methacrylate beyond 0.5, graft yield decreased.

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 is assumed to be due to the formation of donor-acceptor monomer complex, which facilitates the transfer of methyl methacrylate molecules to the growing chain on the agave fiber cellulosic backbone. This in turn facilitates the grafting of acrylonitrile molecules and is responsible for the synergistic effect of comonomers in the binary monomer mixture.

Table 3. Effect of Feed Composition on Grafting Parameters

[Ce (IV)] = 6.58×10^{-3} mol dm⁻³, [HNO₃] = 2.77×10^{-1} mol dm⁻³, Temp. = 45°C, Time = 120 min.

f_{MMA}	%GY	%GE	%Hcp
0.3	31.20	6.29	19.61
0.5	43.36	8.61	21.35
0.7	59.24	11.53	23.03
0.8	44.11	8.42	24.63
0.9	32.79	6.14	24.95

With the further increase in the mole fraction of methyl methacrylate in the feed beyond 0.5, graft yield decreased. This result may be due to the variation in the monomer-monomer interactions at higher mole fraction of methyl methacrylate as a result of which synergistic effect of comonomers also decreased. 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_{MMA}) has been shown in Fig. 1 (b).

IR Spectroscopy

The FT-IR spectrum of raw *Agave 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), and showed milder peaks at 1381.2- 1432.0 cm⁻¹ (due to -CH, -CH₂ and -CH₃ 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).

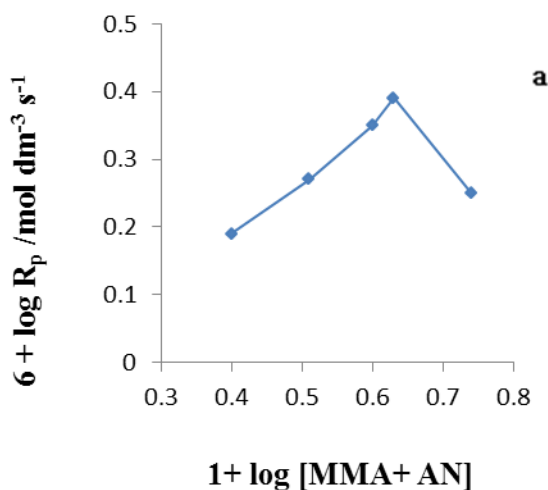


Fig. 1(a). A log-log plot between rates of grafting vs. comonomer concentration
 $[\text{Ce (IV)}] = 6.58 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HNO}_3] = 2.77 \times 10^{-1} \text{ mol dm}^{-3}$
 $f_{\text{MMA}} = 0.5$, Temp. = 45°C , Time = 120 min

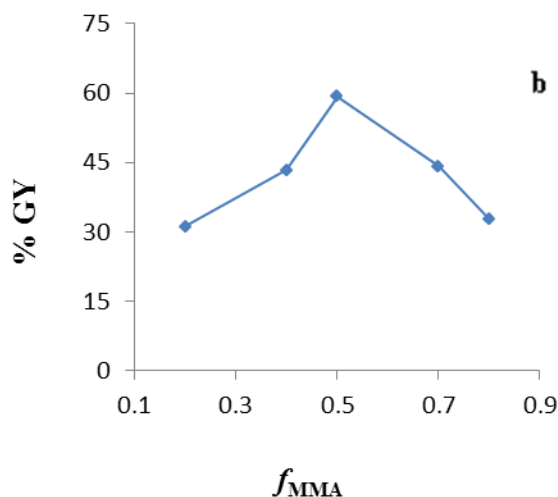


Fig. 1(b). A plot between % GY vs. feed composition
 $[\text{Ce (IV)}] = 6.58 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HNO}_3] = 2.77 \times 10^{-1} \text{ mol dm}^{-3}$
 $[\text{MMA-co-AN}] = 0.50 \text{ mol dm}^{-3}$, Temp. = 45°C , Time = 120 min

However, in the case of Agv-g-poly (MMA-co-AN), additional peaks at 1733.7 cm^{-1} , 1450.7 cm^{-1} , and 1242.6 cm^{-1} , are due to -C=O stretching of carbonyl group, C-H deformations, and -C-O stretching of ester group of methyl methacrylate, respectively. Peaks at 2242.6 cm^{-1} and 2925.9 cm^{-1} are due to -CN stretching in $\alpha \beta$ unsaturated nitrile and C-H stretching of acrylonitrile, respectively, were observed, which gave evidence of grafting poly (MMA-co-AN) chains onto agave fibers.

Thermal Characterization

Figs. 2 (a) and (b) represent 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 to 346 °C (50.6 %) and 346 °C to 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.

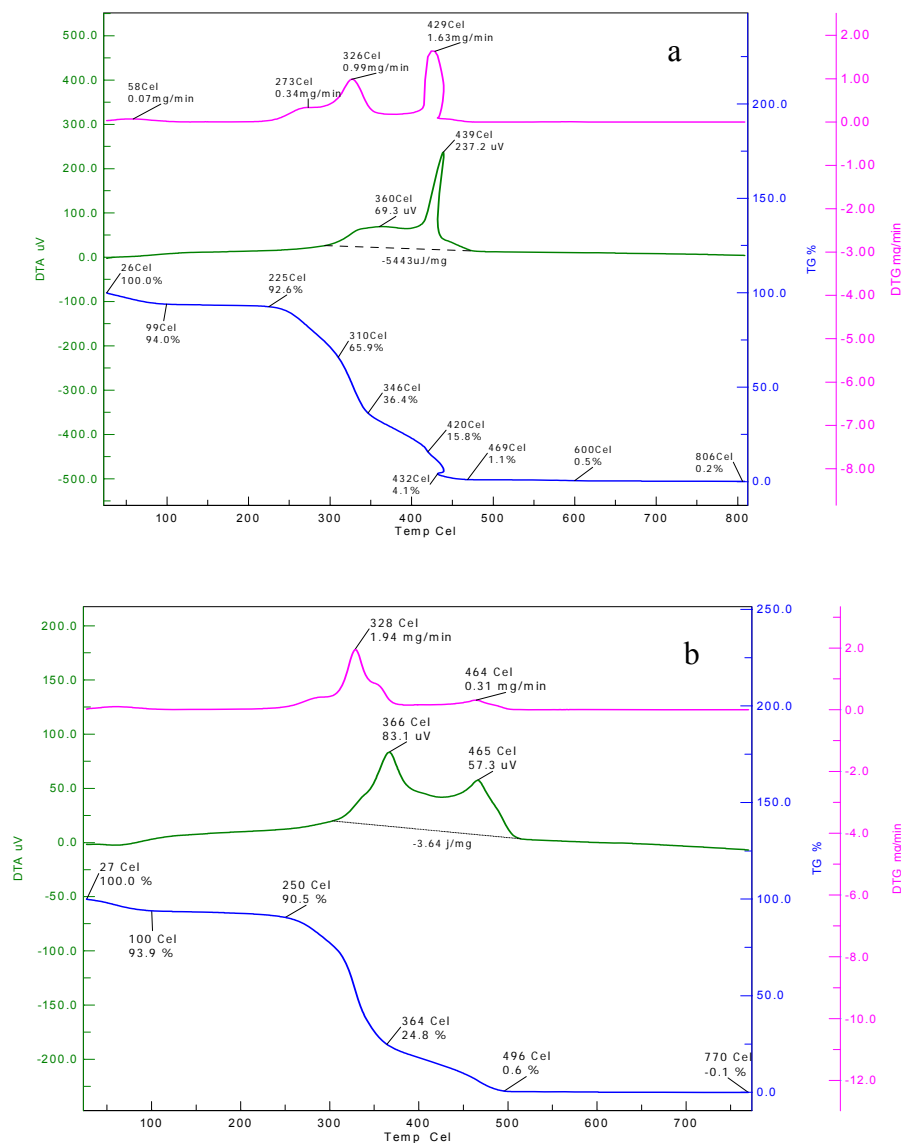


Fig. 2 (a) Thermogram of Raw Fiber (b) Grafted Fiber

The initial and final decomposition temperatures of grafted fiber were 281.00 °C and 496.00 °C, respectively. It is evident from the figures that there was an increase in the initial decomposition temperature of agave fibers upon graft copolymerization with

different binary monomer mixtures. This increase in IDT of graft copolymers of agave fibers with binary monomer mixture may be attributed to the incorporation of (MMA-co-AN) polymer chains of comonomers on the surface of fibers.

In the case of grafted fibers, the first stage of decomposition took place at 281.00 °C to 364.00 °C with weight loss of 59.44 %. It can be attributed to the breakdown of hemicellulose and glycosidic linkages of cellulose, whereas the second stage of decomposition occurred between 364.00 °C to 496.00 °C with weight loss of 19.2 %. This may be related to the degradation of grafted poly (MMA-co-AN) chains onto the fiber surface.

DTA and DTG curves of raw, as well as fibers grafted with binary monomer mixtures have also been shown in the thermograms. It has been observed from these curves that in the case of raw agave fibers, exothermic peaks at 360 °C (69.3 μV) and 439 °C (237.2 μV) appear, which correspond to the first and second decomposition stages of TGA curves, respectively. Furthermore, in the DTG curve of raw fiber, there are exothermic peaks at 326 °C with maximum decomposition of 0.99 mg/min and exothermic peaks at 429 °C with maximum decomposition of 1.63 mg/min. Exothermic peaks at 366.00 °C (83.1 μV) and 465.00 °C (57.3 μV) in the case of Agv-g-poly (MMA-co-AN) have been observed in the thermograms. In the DTG curve of Agv-g-poly (MMA-co-AN), exothermic peaks at 328 °C and 464 °C with decomposition of 1.94 and 0.31 mg/min, respectively have been observed. TGA results are supported well by DTA/DTG results for raw fibers and agave fibers grafted with binary monomer mixtures.

Morphological Analysis

The comparison of electron micrographs of raw and binary monomer grafted agave fibers (Fig. 3 a,b) shows that surface topology of agave fibers changes upon grafting. It may be due to incorporation of poly (MMA-co-AN) chains on the cellulosic backbone as a result of which the surface of fiber becomes rough.

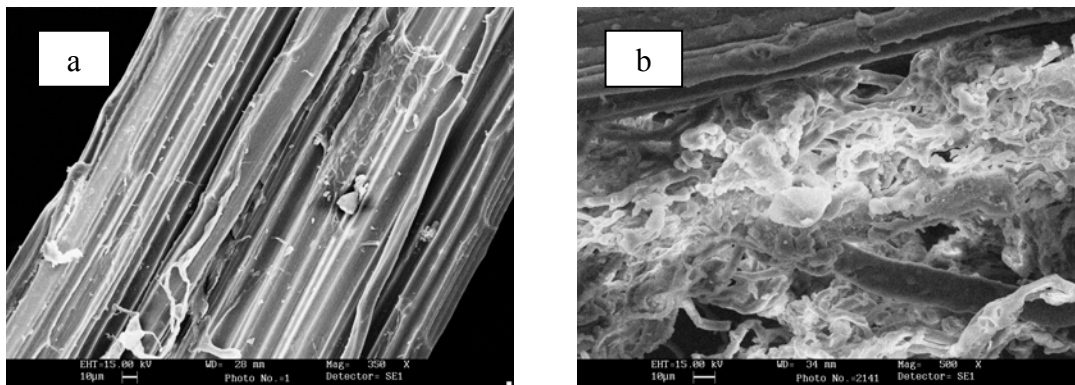


Fig. 3. (a) SEM of Raw Fiber

(b) SEM of Grafted Fiber

Crystallinity

The raw fiber at 2θ scale gave peaks at 22.03° and 14.22° with relative intensities of 97.60 and 46.10, respectively. Similarly Agave-g-poly (MMA-co-AN) shows peaks at 22.20° and 14.79° with relative intensities of 96.40 and 54.00, respectively. The percent

crystallinity of raw and grafted fibers comes out to be 67.92 and 64.10, respectively whereas crystallinity index is 0.53 and 0.44, 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 (MMA-co-AN) chains are incorporated in the fiber.

Swelling Behavior

The swelling behavior of raw and grafted agave fibers in different solvents has been shown in Fig. 4. Different trends in the swelling behavior of raw and grafted fibers were observed in different solvents. Raw fibers exhibited maximum percent swelling in water which decreased with an increase in percent graft yield. It may be due to greater affinity of polar -OH groups present in raw fiber toward water. Furthermore, as percent graft increases, -OH groups are gradually replaced by Poly (MMA-co-AN) chains resulting in lesser 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 (MMA-co-AN) chains toward carbon tetrachloride. Due to the presence of alkyl groups in poly (MMA-co-AN) chains, they are hydrophobic in nature, therefore these hydrophobic chains have strong affinity toward non polar solvents like CCl₄.

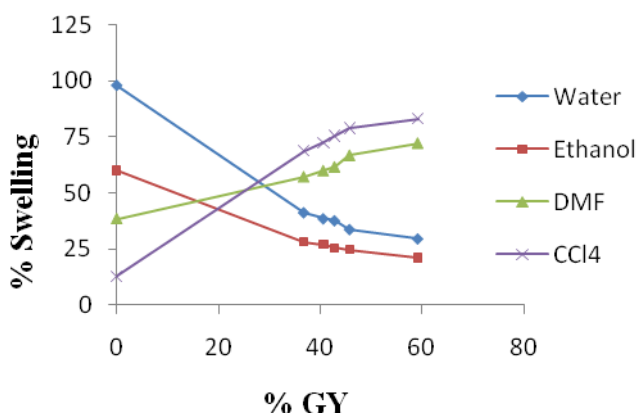


Fig. 4. Swelling behavior in Different Solvents

Moisture Absorption

The results of moisture absorption studies are shown in Fig. 5. The samples of both raw fibers and fibers grafted with (MMA-co-AN) monomer mixtures were exposed to different humidity levels for a definite time interval. It was observed that graft copolymerization of binary monomers onto agave fibers had great impact on moisture absorption behavior. At a particular humidity level, moisture absorbance decreased with an 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 (MMA-co-AN) chains.

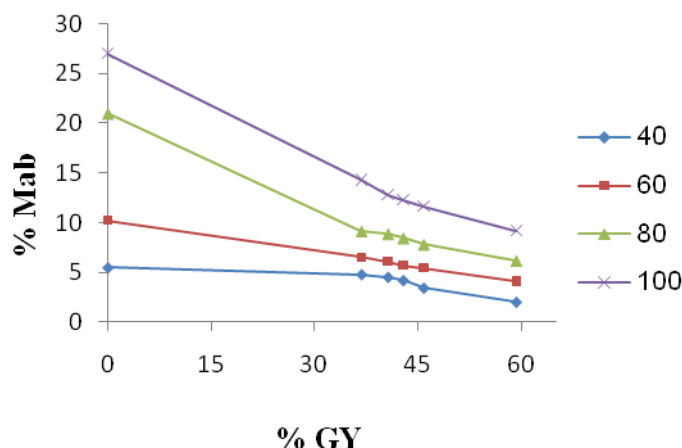


Fig. 5. Moisture absorption behavior in different solvents

Chemical Resistance

The acid and base resistance behavior of raw and grafted fibers was studied in acids and bases of different strengths (Figs. 6 and 7). It has been observed that upon grafting, agave fibers become more resistant to the attack of acids and bases. Moreover, chemical resistance increases with an increase in the percent graft yield. This may be due to the fact that poly (MMA-co-AN) chains grafted on agave fibers are resistant to attack by acids and bases and block the reactive sites on the cellulosic fibers which are prone to the attack of chemicals.

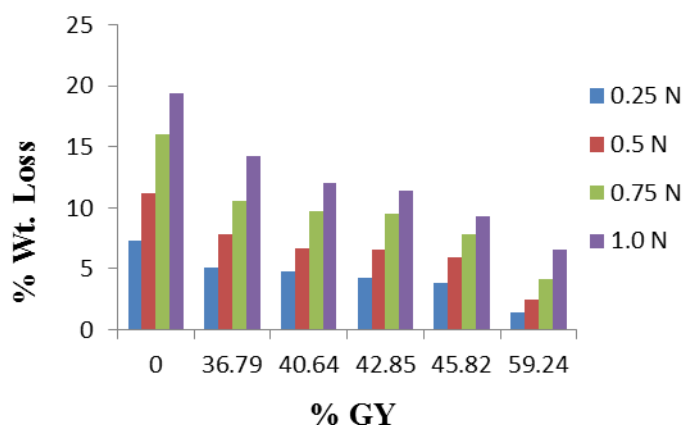


Fig. 6. Acid resistance behavior of raw and grafted Fibers

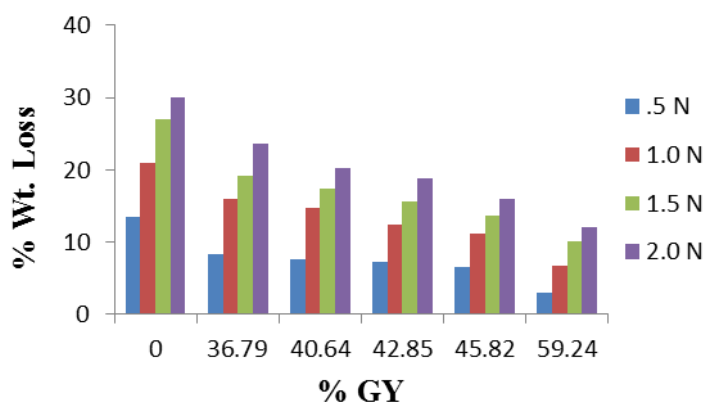


Fig. 7. Base resistance behavior of raw and grafted fibers

CONCLUSIONS

Graft copolymerization of methyl methacrylate and acrylonitrile from their binary mixture has been carried out in the presence of a ceric ion-nitric acid redox initiator system. The results of the study suggest that the presence of acrylonitrile increases the grafting of methyl methacrylate on agave fibers due to synergistic effect.

The graft copolymerization of MMA-co-AN binary mixture has a considerable influence on physico-chemical, morphological, as well as thermal properties. Upon grafting with MMA-co-AN monomer mixture, agave fibers absorb less moisture, become more resistant to the attack of acids and bases, and can withstand higher temperature before decomposition. Therefore the cellulosic fibers graft copolymerized with vinyl monomers from their binary mixtures have improved properties which can ensure the utilization of these fibers in various industrial applications.

ACKNOWLEDGMENTS

Authors are highly thankful to the Director of the National Institute of Technology Hamirpur (H.P.) for providing necessary laboratory facilities to complete this work and to MHRD New Delhi for providing the financial assistance during the course of this present work.

REFERENCES CITED

Abu Bakar, A., Hassan, A., and Mohd Yusof, A. F. (2004). "Thermal degradation of oil palm empty fruit bunch (EFB) – filled PVC-U composites: The effect of filler content and acrylic impact modifier on thermal properties," *J Insti Mater Malaysia* 5(2), 3-19.

- Arib, R. M. N., Sapuan, S. M., Ahmad, M. M. H. M., Paridah, M. T., and Khairul Zaman, H. M. D. (2006). "Mechanical properties of pineapple leaf fiber reinforced polypropylene composites," *Materials & Design* 27(5), 391-396.
- Djidjelli, H., Martinez-Vega, J., Farenc, J., and Benachour, D. (2002) "Effect of wood flour content on the thermal, mechanical and dielectric properties of poly(vinyl chloride)," *Macromol Mater Eng* 287(9): 611.
- El Oudiani, A., Chaabouni, Y., Msahli, S., and Sakli, F. (2009) "Physico-chemical characterisation and tensile mechanical properties of *Agave americana* L. fibres," *J. Text I* 100(5), 430 -439.
- El-Salmawi, K., El-Naggar, A. M., and Attia, S. E. (1997). "Investigation of synergism during radiation graft copolymerization of binary mixtures of vinyl monomers onto different textile fabrics by a dyeing method," *Polym Int* 44(2), 181-190.
- Fanta, G. F., Burr, R. C., Doane, W. M., and Russell, C. R. (1979) "Graft polymerization of vinyl acetate onto starch. Saponification to starch-g-poly (vinyl alcohol)," *J. Appl Poly Sci* 23(1), 229-240.
- Gonzalez, A. V., Cervantes, U. J. M., Olayo, R., Herrera-Franco, P. J. (1999). "Chemical modification of henequen fibers with an organosilane coupling agent," *Compos: Part B*. 30(3), 321-331.
- Gupta, K. C., and Sahoo, S. (2001) "Graft copolymerization of 4-vinylpyridine onto cellulose using Co(III) acetylacetonate complex in aqueous medium," *Cellul* 8(3), 233-242.
- Gupta, K. C., and Sahoo, S. (2001). "Grafting of acrylonitrile and methylmethacrylate from their binary mixtures on cellulose using ceric ions," *J Appl Polym Sci* 79(5), 767-778.
- Gupta, K. C., and Sahoo, S. (2001). "Graft copolymerization of acrylonitrile and ethyl methacrylate comonomers on cellulose using ceric ions," *Biomacromol* 2(1), 239-247.
- Iidicula, M., Malhotra, L. K., Kuruvilla, J., and Thomas, S. (2005). "Dynamic mechanical analysis of randomly oriented intimately mixed short banana/sisal hybrid fiber reinforced polyester composites," *Compos Sci Technol* 65(7-8), 1077-87.
- Khalil, H. P. S. A., Ismail, H., Rozman, H. D., and Ahmad, M. N. (2001). "The effect of acetylation on interfacial shear strength between plant fibres and various matrices," *Europ Polym J*. 37(5), 1037-1045.
- Lee, S. W., Bondar, Y., and Han, D. H. (2008). "Synthesis of cation-exchange fabric with sulfonate groups by radiation-induced graft copolymerization from binary monomer mixtures," *React Funct Polym* 68(2), 474-482.
- Maslinska-Solich, J., and Jedlinski, Z. (1973) "Copolymerization of unsaturated 1,3-dioxane derivatives with maleic anhydride," *J Polym Sci Polym Symp* 42(1), 411-418.
- Mcdowall, D. J., Gupta, B. S., and Stannett, V. T. (1984). "Grafting of vinyl monomers onto cellulose by ceric ion initiation," *Prog Polym Sci* 10, 1-50.
- Mino, G., and Kaizerman, S. (1958). "A new method for the preparation of graft copolymers. Polymerization initiated by ceric ion redox systems," *J Polym Sci* 31(122), 242-243.

- Mondal, M. I. H., Uraki, Y., Ubukata, M., and Itoyama, K. (2008) "Graft polymerization of vinyl monomers onto cotton fibers pretreated with amines: Mechanical property and moisture sorption," *Cellul* 15(4), 581-592.
- Msahli, S., Sakli, F., and Drean, J. Y. (2006). "Study of textile potential of fibers extracted from Tunisian *Agave americana* L.," *AUTEX Research Journal* 6(1), 9-13.
- Ojah, R., and Dolui, S. K. (2006). "Graft copolymerization of methyl methacrylate onto *Bombyx mori* initiated by semiconductor-based photocatalyst," *Bioresource Technol* 97(13), 1529-1535.
- Pan, M., Zhou, D., Ding, T., and Zhou, X. (2010). "Water resistance and some mechanical properties of rice straw fiberboards affected by thermal modification," *BioResources* 5(2): 758-769.
- Rattan, S., Maitra, J., Misra, B. N., and Kaur, I. J. (2008). "Radiation induced graft copolymerization of vinyl monomers and their binary mixtures onto rayon fibre," *J Appl Polym Sci* 108 (5), 3104-3113.
- Saikia, C. N., and Ali, F. (1999). "Graft copolymerization of methyl methacrylate onto high α - cellulose pulp extracted from *Hibiscus sabdariffa* and *Gmelina arborea*," *Bioresource Technol* 68(2), 165-171.
- Singha, A. S., and Rana, R. K. (2010). "Graft copolymerization of methyl methacrylate (MMA) onto *Agave americana* fibers and evaluation of their physicochemical properties," *Int J Polym Anal Ch* 15 (1), 27-42.
- Skundric, P., Kostic, M., Medovic, A., Pejic, B., Kuraica, M., Vuckovic, A., Ovradovic, B., Mitrakovic, D., and Puric, J. (2007). "Wetting properties of hemp fibers modified by plasma treatment," *Journal of Natural Fibers* 4(1): 25-33.
- Suizu, N., Uno, T., Goda, K., and Ohgi, J. (2009). "Tensile and impact properties of fully green composites reinforced with mercerized ramie fibers," *J. Mater. Sci.* 44(10), 2477-2482.
- Wang, B., Panigrahi, S., Tabil, L., and Crerar, W. (2007). "Pretreatment of flax fibers for use in rotationally molded biocomposites," *J Reinf Plast Comp* 26(5): 447-463.
- Zahran, M. K. (2006). "Grafting of methacrylic acid and other vinyl monomers onto cotton fabric using Ce (IV) ion-cellulose thiocarbonate redox system," *J Polym Res* 13(1), 65-71.

Article submitted: Feb 14, 2012; Peer review completed: May 8, 2012; Revised version received and accepted: June 20, 2012; Published: July 10, 2012.