



## Graft Copolymerization of Acrylonitrile onto Banana Cellulose Fiber

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The graft co-polymerization of acrylonitrile monomer (AN) onto banana cellulose fiber (BCF) was carried out using ceric ammonium nitrate (CAN)/oxalic acid (OA) as redox pair in the aqueous nitric acid medium at 90 °C. The effect of different reaction conditions on the grafting has been studied by determining the grafting parameters, *i.e.* concentration of acrylonitrile, ceric ammonium nitrate, oxalic acid, nitric acid, reaction time and temperature were carefully optimized to achieve the highest rate of grafting polymerization (RG), highest percent grafting yield (%GY) and grafting efficiency (%GE). All the reagents enhanced the RG%, GY% and %GE, with an increase of concentration up to a certain extent and then found to decline, except for the concentration of nitric acid. The grafting parameters were also increased with time/duration and temperature. The water retention value (WRV) of the grafted co-polymer was also measured. Activation parameters such as energy of activation ( $E_a$ ), enthalpy change ( $\Delta H$ ), entropy change ( $\Delta S$ ) and free energy change ( $\Delta G$ ) can also be reported by using the Arrhenius plot. The evidence of grafting can also be predicted by the FTIR spectral analysis, moreover, the organic reaction mechanism has been proposed.

**Keywords:** Copolymerization, Banana cellulose, Grafting efficiency, Water retention value, Activation parameter.

### INTRODUCTION

Cellulose is the most abundant biomass material in nature and possesses some promising properties, such as great mechanical strength, hydrophilicity, biocompatibility, relative thermostabilization, biodegradability, high absorption capacity and alterable optical appearance [1-3]. Thus, cellulose has been widely applied in many fields and it is frequently modified in the preparation of a wide range of new materials that have proved to be very useful in several and diverse applications [4,5]. Cellulose graft co-polymers are very attractive because their products can readily be made to possess any number of the required properties [6,7]. A great number of grafting methods have been developed, but the free radical methods of generating radicals on the cellulose backbone before grafting has received the greatest attention [8-11]. Chemical modification of natural fibers through graft co-polymerization is an effective method to incorporate useful properties into the main polymer backbone and these are useful in many applications in diverse fields.

Natural polymers are vulnerable to degradation by acids, bases, or water. These limitations can be improved by graft co-polymerization of vinyl monomers to the polymeric backbones. This improves their chemical resistance, moisture repellent, solvent resistance and dye uptake.

Graft co-polymerization can be carried out with different initiator reagents, *e.g.* potassium persulfate, benzoyl peroxide, ammonium persulfate, azobisisobutyronitrile and ceric ammonium nitrate are widely used for the synthesis of graft copolymers [10-13]. There are a number of ways to alter the physical and chemical characteristics of the natural polymers, but graft copolymerization stands out as the most promising [14,15]. In recent years, the graft co-polymerization of various monomers was initiated by ceric ammonium nitrate [16-18] ammonium persulfate [19], potassium persulfate [20-22], ferric ion with hydrogen peroxide [23] and  $\gamma$ -rays [24]. Redox-initiated grafting is a favourable approach for chemical initiation due to its ability to be conducted under gentler circumstances and with less side reactions, because of the existence of a redox system. The tetra-

valent ceric ion has garnered significant attention due to its exceptional grafting efficiency and minimal homopolymer production, making it a noteworthy redox system [25,26].

In this work, the graft co-polymerization of acrylonitrile monomer (AN) onto banana cellulose fiber (BCF) was carried out using ceric ammonium nitrate (CAN)/oxalic acid (OA) as redox pair in aqueous nitric acid medium under an optimized set of conditions.

## EXPERIMENTAL

Banana leaves were collected from the local agro-waste farm field. AR grade chemicals, acrylonitrile (S.D. Fine Chem. Ltd., Mumbai India), ceric ammonium nitrate (Sisco Research Lab. Pvt. Ltd., India), oxalic acid and nitric acid were procured. Double distilled water was used throughout the experiment.

**Preparation of banana cellulose fiber:** The collected central long vein of the banana leaves was allowed to dry for more than 4 days. Then the raw material was cut into  $1 \times 1''$  pieces and boiled with 1 N NaOH solution for 2 h to remove non-cellulosic materials. Later, it was washed with distilled water several times to attain pH 7. It is then sun-dried to get moisture content of 11-12%. The material thus obtained was ground to 100-200  $\mu\text{m}$  size powder in a Wiley mill and termed as banana cellulose.

**Purification of acrylonitrile monomer:** Acrylonitrile was washed with 5% NaOH followed by dil.  $\text{H}_3\text{PO}_4$  and finally with distilled water. It was dried over anhydrous  $\text{CaCl}_2$  and distilled under reduced pressure in a nitrogen atmosphere. The middle fraction was collected and stored at 278 K [27].

**Preparation of graft copolymer:** The grafting reaction was carried out under a nitrogen atmosphere in a three-necked flask equipped with a nitrogen inlet and a reflux condenser immersed in a constant temperature water bath (Remi, India  $\pm 1^\circ\text{C}$ ). A  $5.0 \times 10^{-3}\text{M}$ – $12.0 \times 10^{-3}\text{M}$  of CAN solution of varying concentrations were prepared by dissolving the required molar concentration of CAN salt in 1% of nitric acid. In a typical reaction, 0.5 g of banana cellulose in acrylonitrile solution for 5 min and then added dissolved CAN in nitric acid at  $90^\circ\text{C}$  for 2 h. After 2 h, the dried sample was treated with DMSO to remove homopolymer, filtered and finally dried.

The different parameters of the grafted copolymerization of acrylonitrile onto cellulose were studied such as monomer concentration, initiator concentration, accelerator concentration, acid concentration and temperature effect. The percent polymerization, percent grafting yield (%GY) and percent grafting efficiency (%GE) were calculated as follows:

$$\text{Grafting polymerization (RG) (\%)} = \frac{W_1 - W_0}{W_0} \times 100$$

$$\text{Graft yield (GY) (\%)} = \frac{W_2 - W_0}{W_0} \times 100$$

$$\text{Graft efficiency (GE) (\%)} = \frac{W_2 - W_0}{W_1 - W_0} \times 100$$

where  $W_0$  is the weight of banana cellulose taken,  $W_1$  is the weight of grafted sample before treating with DMSO and  $W_2$  is the weight of the grafted sample after treating with DMSO.

**Grafting procedure:** Inhibitor free acrylonitrile (0.30 M), oxalic acid (0.01 M), nitric acid (0.004 M), 0.5 g of banana cellulose fiber and distilled water (for volume constant) were taken in a reaction vessel and thermostated at  $60^\circ\text{C}$ . The system was flushed with oxygen-free nitrogen for about 20-30 min to remove dissolved oxygen. At the end of duration, cerium(IV) solution about (0.01 M) was added to the reaction vessel. The reaction was then sealed with a rubber gasket to ensure an inert atmosphere. Polymerization grafting starts without any induction period and after the desired interval of time of about 120 min, 0.1 M ferrous ammonium sulfate solution was added to terminate the polymerization/grafting reaction. The poly-(acrylonitrile) and poly(acrylonitrile-graft-co-polymer (PAN g-banana cellulose co-polymer) was filtered from the reaction mixture using a glass funnel with Whatmann filter paper no 41, washed several times with distilled water and finally dried at  $60^\circ\text{C}$  to a constant weight. The homopolymer, grafted acrylonitrile banana cellulose co-polymer, percentage of grafting yield (%GY) and percentage of grafting efficiency (%GE) were calculated. The water absorbency of banana cellulose was also measured.

### Grafting yield:

$$\text{GY (\%)} = \frac{\text{Final cellulose weight} - \text{Initial cellulose weight}}{\text{Initial cellulose weight}} \times 100$$

### Grafting efficiency:

$$\text{GE (\%)} = \frac{\text{Final cellulose weight} - \text{Initial cellulose weight}}{\text{Total polymer weight} - \text{Initial cellulose weight}} \times 100$$

### Water absorbency or water retention value:

$$\text{WRV (g/g)} = \left( \frac{\text{WET} - \text{DRY}}{\text{DRY}} \right)$$

where WET = weight of the sample after immersing in water for 24 h, DRY = dry weight of the sample.

$$\text{WRV (g/g)} = \left( \frac{3.181 - 0.984}{0.984} \right)$$

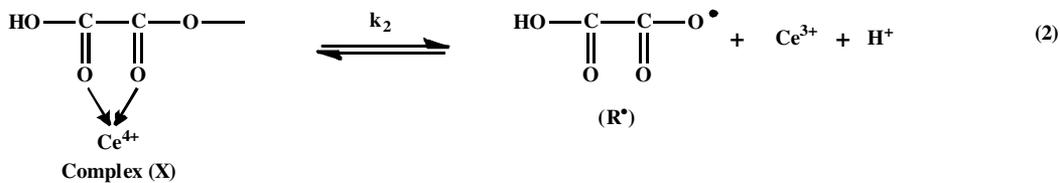
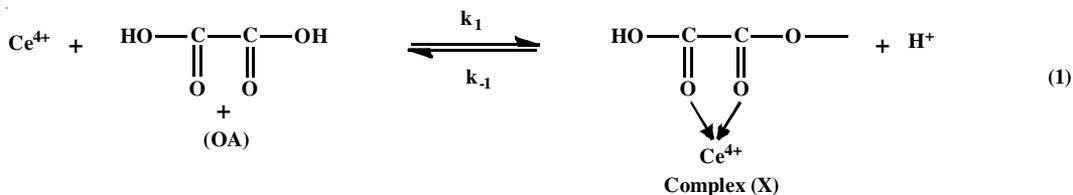
The water absorbency of raw banana cellulose fiber is found to be 3.04 or 300% approximately.

**Characterization:** FTIR spectra of the banana cellulose and grafted banana cellulose were recorded in Perkin Elmer spectrum version 10.02.00 in the wavelength range 4000-500  $\text{cm}^{-1}$ .

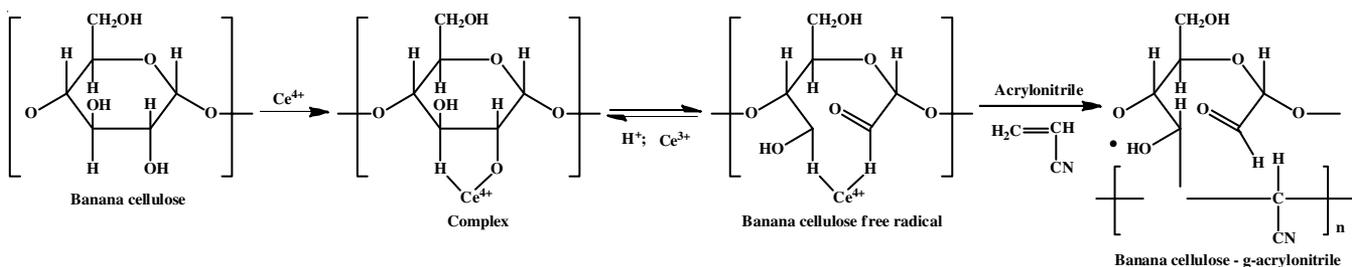
## RESULTS AND DISCUSSION

The mechanism of the polymerization of acrylonitrile monomer as shown in **Scheme-I**, whereas the mechanism of the graft copolymerization of acrylonitrile onto banana cellulose is shown in **Scheme-II**.

**FTIR studies:** The FTIR spectra confirmed that several functional groups were present in the banana cellulose. The spectra revealed band shifting and the potential presence of hydroxyl groups in the vicinity of the broad peak at 3422 and



Scheme-I: Polymerization mechanism of acrylonitrile monomer to polyacrylonitrile homopolymer



Scheme-II: Reaction mechanism of graft copolymerization of acrylonitrile onto banana cellulose

3423 cm<sup>-1</sup>. The appearance of the peaks at 2925 and 2922 cm<sup>-1</sup> are due to the CH stretching vibrations of CH, CH<sub>2</sub> and CH<sub>3</sub> groups. Apart from this, the major visible change is the increase in the C-O carboxyl band 1382 and 1235 cm<sup>-1</sup> (Fig. 1a).

In the FTIR spectra of the optimized sample of grafted banana cellulose, besides the typical signals of cellulose backbone represents the characteristic -OH stretching vibration with strong intensity broadband around 3314 cm<sup>-1</sup> is observed (Fig. 1b). The -OH in-plane deformation from 1452.19-1324.92 cm<sup>-1</sup>

and C-O-C stretching vibration bands from 1124-1046.80 cm<sup>-1</sup> are also observed. The CH vibration at 1452 cm<sup>-1</sup> and the key characteristic medium absorption band at 2235 cm<sup>-1</sup> for nitrile -(C≡N) group introduced and 2933 cm<sup>-1</sup> characteristic for -CH<sub>2</sub> group with decrease intensity were observed, confirmed thereby the evidence that grafting of acrylonitrile has occurred.

A graft co-polymer is a system comprised of a backbone material (cellulose) to which a second polymer is attached (polyacrylonitrile) at reactive sites along the macromolecular chains.

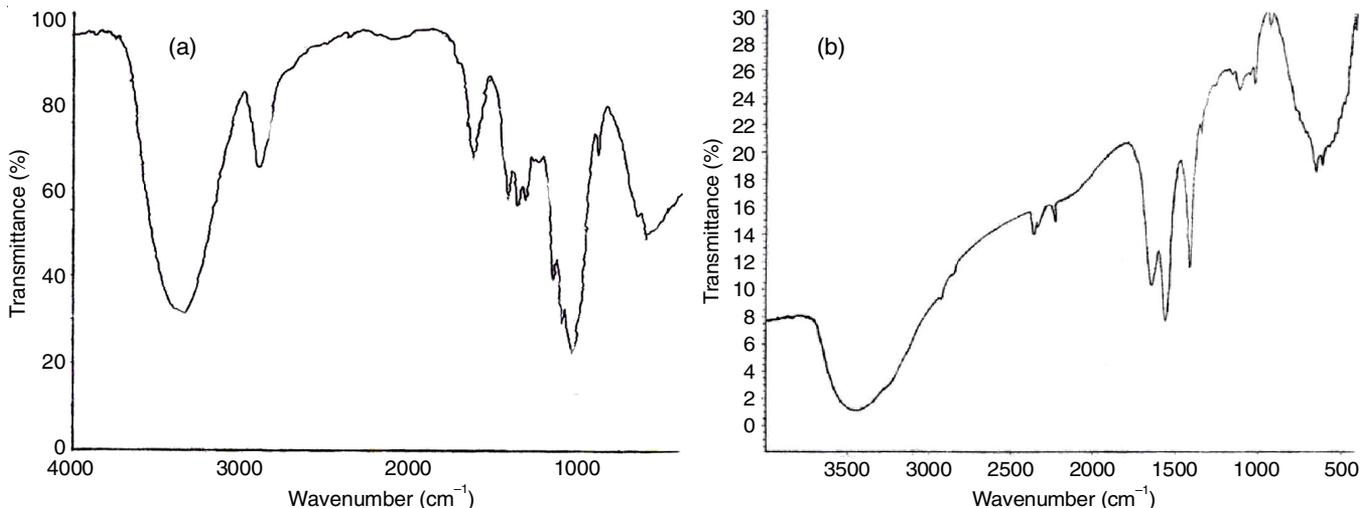
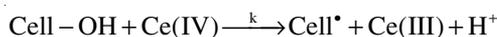


Fig. 1. FTIR spectra of pure banana cellulose (a) and grafted banana cellulose

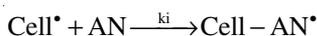
The grafting of vinyl monomer to banana cellulose is a typical free radical polymerization reaction, which involves three distinct aspects, such as initiation, propagation and termination. The formation of free radicals on the cellulose can occur. The locations of the free radical sites on the cellulose are dependent on the method of initiation of such sites and on the physical and chemical properties of banana cellulose. The ceric ion initiation of grafting has gained considerable importance because this method can be applied for initiating the grafting of synthetic monomers to several macromolecules.

### Mechanism

#### Radical formation:



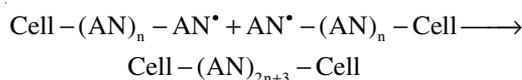
#### Initiation:



#### Propagation:



#### Termination:



**Effect of monomer concentration:** The graft co-polymerization of acrylonitrile onto banana fiber (cellulose) was carried out by varying monomer concentrations from 0.606 mol/dm<sup>3</sup> to 3.034 mol/dm<sup>3</sup>, keeping constant all the variables, the amount of monomer used was varied. The results show that as the monomer concentration increases from 0.606 mol/dm<sup>3</sup> to 1.820 mol/dm<sup>3</sup>, there is an increase in (rate of grafting) %RG, grafting yield (%GY) and % grafting efficiency (GE), reaching a maximum value of (238)%RG, (156)%GY and (194) %GE (Table-1). Further, an increase in monomer concentration results in a decrease of RG% (130), % GY (92) and % GE (69.07). This may be due to the formation of more homopolymer as compared to graft co-polymer at higher monomer concentration [28-30]. Moreover, due to homopolymerization, the viscosity of the reaction medium increases, which creates a hindrance in the movement of the free radicals towards active sites or macro radicals thereby resulting in less graft yield [31].

The enhancement of %RG, %GY and %GE by the increasing monomer concentration of optimum value could be ascribed to the greater availability of monomer to grafting sites. However, the decreasing trend of % RG, %GY and %GE beyond optimum monomer concentration may be due to the competition between homopolymerization and graft copolymerization, where the former prevails over the latter at higher acrylonitrile

concentration [1,3,5,14]. The increase in chain transfer to monomer molecules may be another possible reason for decreasing the graft copolymerization. These findings are in agreement with those reported in literature [10,11,32,33]. With a further increase in acrylonitrile concentration, the gel effect was also more pronounced. Due to this gel effect, the chain transfer from banana cellulose macro radicals onto monomer increased, leading to the lowering of graft yield and leading to the preferential formation of homopolymer at higher concentrations. The degree of homopolymerization increases and the grafting percentage decreases [34]. The growing polymeric radical at higher concentration may terminate the grafting process [35,36] leading to a decrease in grafting parameters. The result (Fig. 2) shows that increasing the acrylonitrile concentration up to 1.820 M increases the %RG and %GY due to the increasing number of monomer molecules. Further increasing monomer concentration above 1.820M, increase the viscosity of the reaction mixture and retards the penetration of monomer molecules to the active sites of the banana cellulosic backbone due to the formation of bulk polymer and grafting yield decreases [37,38]. The order of the grafting yield %RG and % GY was found to be a fractional order (0.7).

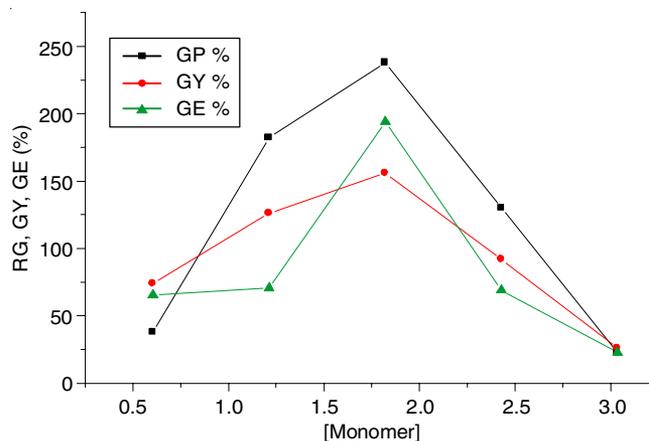


Fig. 2. Effect of monomer concentration on %RG, %GY and %GE {[Ce(IV)] = 5 × 10<sup>-3</sup> mol/dm<sup>3</sup>, [H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>] = 0.5 × 10<sup>-2</sup> mol/dm<sup>3</sup>, [HNO<sub>3</sub>] = 5 × 10<sup>-2</sup> mol/dm<sup>3</sup>, banana cellulose = 0.5 g, temperature = 90 °C, duration of grafting = 2 h}

**Effect of initiator concentration:** The variation of ceric ammonium nitrate was found to be 2.0 × 10<sup>-3</sup> mol/dm<sup>3</sup>–12.0 × 10<sup>-3</sup> mol/dm<sup>3</sup> at 90 °C. The %RG, %GY and %GE increases with the increase of CAN concentration, up to 5.0 × 10<sup>-3</sup> mol/dm<sup>3</sup> and then decreases with further increase of CAN. The molar ratio of the initiator (CAN – OA) plays an important

TABLE-1  
EFFECT OF MONOMER CONCENTRATION ON GRAFTING OF ACRYLONITRILE ONTO BANANA CELLULOSE  
[Banana cellulose – 0.5 g, temperature – 90 °C (363 K), duration of grafting – 2 h]

[Ce(IV)] × 10 <sup>3</sup> (mol dm <sup>-3</sup> )	[H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	[HNO <sub>3</sub> ] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	[AN] (mol dm <sup>-3</sup> )	Grafting polymerization (%)	Grafting yield (%)	Grafting efficiency (%)
5	0.5	5	0.606	38.0	73.8	65.54
5	0.5	5	1.213	182.4	126.0	70.76
5	0.5	5	1.820	238.0	156.0	194.2
5	0.5	5	2.427	130.0	92.0	69.07
5	0.5	5	3.034	22.6	26.0	22.60

role in obtaining high %RG, %GY and %GE (Table-2). The optimum molar ratio of the maximum graft yield was 0.005 M. It has been observed that with a further increase in molar ratio, the %RG, %GY and %GE were found to be decreased. This is attributed to the generation of more  $Ce^{4+}$  ions at the higher molar ratio, which results in the termination of growing chains. Further, it has been observed that if the CAN-OA molar ratio is lower than the critical value, then there is a decrease in %RG because of a lesser generation of free radicals. The increasing trends of the grafting parameters indicated that ceric ions exclusively participate in the formation of active sites on the cellulose up to this concentration of ceric ions and beyond it, no more active sites are formed on the cellulose. Further increase in CAN concentration is accompanied by a decrease in the %RG, %GY and %GE. The decreasing trend in %RG and %GE beyond  $5.0 \times 10^{-2}$  mol  $dm^{-3}$  concentration of ceric ions may be assumed to be due to its participation in the termination reactions with growing homopolymer and propagation chains on the cellulose. The observed increase in %RG, %GY and %GE with the concentration of CAN range, maybe because, under such conditions, activation along the backbone takes place immediately, followed by graft co-polymerization of the monomer onto the backbone. A relatively high concentration of initiator may cause a reduction of grafting, due to an increased number of backbone radicals terminated before acrylonitrile addition. Furthermore, homopolymer formation at a higher initiator concentration, which is complete with the grafting reaction for the available monomer, could lead to a decrease in grafting yield. The fast dissociation of CAN may account for its higher GE in the initial stages since the total amount of  $Ce(IV)$  would be available for initiation. In ceric ion initiated graft co-polymerization, the termination of the growing grafted chain increases as the concentration of  $Ce(IV)$  increases. This is due to the increasing initiator concentration, which results in a gradual decrease in grafting. The grafting yield was increased with increasing initiator (CAN) concentration from 0.002-0.005 M. The increase in the %RG and %GY occurred due to the generation of more active grafting sites on the banana cellulosic backbone. The increase in initiator concentration above  $5.0 \times 10^{-3}$  M decreased the %RG, %GY and %GE. The decrease in trend at higher concentrations may be due to the filling of active sites of cellulose by the initiator instead of monomers and the monomers from bulk polymers *i.e.* homopolymers [39,40]. It was also observed that with increasing the initiator concentration the %RG, %GY and %GE increases in the initial stages up to  $5.0 \times 10^{-3}$  M, with further increase of initiator all these parameters decrease drastically (Fig. 3). These increasing trends of the parameters indicated that ceric ions exclusively participate in the formation of free

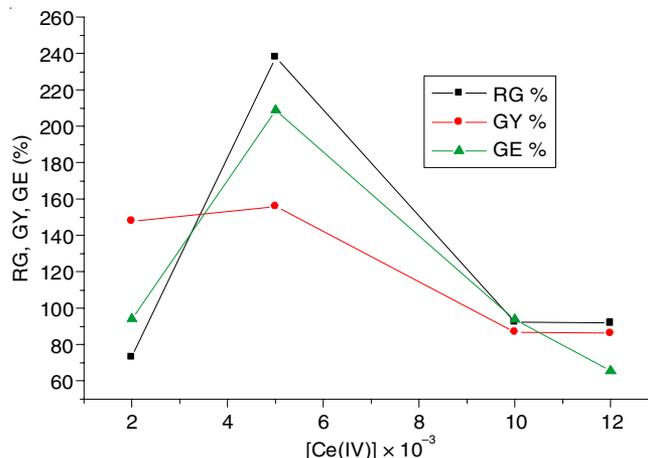


Fig. 3. Effect of concentration of  $Ce(IV)$  on %RG, %GY and %GE

radical active sites on the banana cellulosic backbone up to this concentration of ceric ions and beyond it, no more active sites are formed on the banana cellulosic backbone. This may be because with a high concentration of initiator more and more homopolymers are formed thereby decreasing both %GY and %GE of graft co-polymerization. It is evident that the ceric ion, due to its strong oxidizing properties and high oxidation potential, reacts with acrylonitrile to yield the homopolymer instead of the graft copolymer when present in higher concentrations. This observation is in close agreement with the results obtained by other investigators [1,10,11,41]. The order of the reaction is found to be fractional order.

**Effect of accelerator concentration:** The graft copolymerization was carried out by varying the concentration of accelerator from  $0.2$  to  $4 \times 10^{-2}$  mol/ $dm^3$ , keeping all variables constant. The % of grafting yield increases with an increase in accelerator concentration and for  $2 \times 10^{-2}$  mol/ $dm^3$  oxalic acid concentration maximum % grafting yield was observed and after that the % grafting yield decreases (Fig. 4). Similarly, the %GE also increases with the increase of oxalic acid concentration up to  $2 \times 10^{-2}$  mol/ $dm^3$  and thereafter, there is a decrease in %GE with an increase in oxalic acid concentration (Table-3).

**Effect of acid concentration:** The graft copolymerization was carried out by varying the concentration of nitric acid from  $2$  to  $15 \times 10^{-2}$  mol/ $dm^3$ , keeping all other reaction conditions constant. Table-4 shows the dependence of percentage grafting and percent grafting efficiency on  $HNO_3$  concentration at  $90^\circ C$ , CAN concentration of  $5.0 \times 10^{-2}$  M, acrylonitrile concentration of  $1.820$  M for  $2$  h. The concentration of nitric acid varied between  $0.02$ -  $0.15$  M. A critical concentration of nitric acid ( $0.02$  M), which permits the maximum percent grafting maybe also observed. The % of grafting yield decreases

TABLE-2  
EFFECT OF INITIATOR ( $Ce(IV)$ ) CONCENTRATION ON GRAFTING OF ACRYLONITRILE ONTO BANANA CELLULOSE

[Ce(IV)] × 10 <sup>3</sup> (mol dm <sup>-3</sup> )	[H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	[HNO <sub>3</sub> ] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	[AN] (mol dm <sup>-3</sup> )	Grafting polymerization (%)	Grafting yield (%)	Grafting efficiency (%)
2	0.5	5	1.820	73.20	148.0	94.15
5	0.5	5	1.820	238.00	156.0	208.96
10	0.5	5	1.820	92.40	87.0	93.80
12	0.5	5	1.820	91.86	86.2	65.54

TABLE 3  
EFFECT OF ACCELERATOR (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) CONCENTRATION ON GRAFTING OF ACRYLONITRILE ON TO BANANA CELLULOSE

[Ce(IV)] × 10 <sup>3</sup> (mol dm <sup>-3</sup> )	[H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	[HNO <sub>3</sub> ] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	[AN] (mol dm <sup>-3</sup> )	Grafting polymerization (%)	Grafting yield (%)	Grafting efficiency (%)
5	0.2	5	1.8200	80.8	65.2	80.70
5	1.0	5	1.8200	282.0	71.2	90.00
5	2.0	5	1.8200	125.0	98.0	86.82
5	4.0	5	1.8206	60.2	59.6	78.40

TABLE-4  
EFFECT OF ACID (HNO<sub>3</sub>) CONCENTRATION ON GRAFTING OF ACRYLONITRILE ONTO BANANA CELLULOSE

[Ce(IV)] × 10 <sup>3</sup> (mol dm <sup>-3</sup> )	[H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	[HNO <sub>3</sub> ] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	[AN] (mol dm <sup>-3</sup> )	Grafting polymerization (%)	Grafting yield (%)	Grafting efficiency (%)
5	0.5	2	1.820	93	78.6	90.0
5	0.5	5	1.820	80	72.0	88.2
5	0.5	8	1.820	68	60.0	85.0
5	0.5	15	1.820	66	56.0	84.2

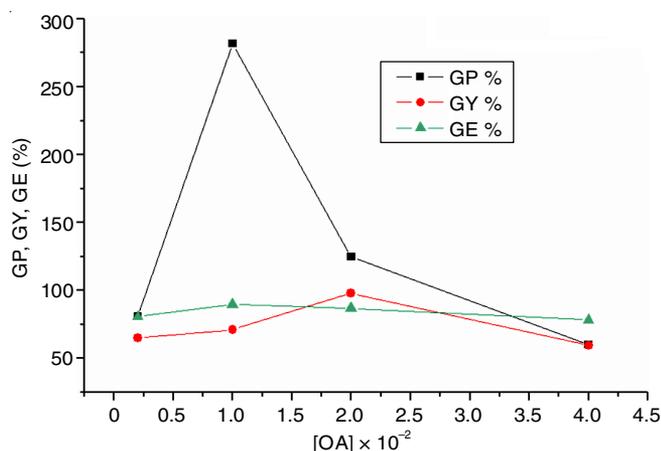


Fig. 4. Concentration of oxalic acid vs. % GP, % GY and % GE {[H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>] = 0.5 × 10<sup>-2</sup> mol/dm<sup>3</sup>, [AN] = 1.820 mol/dm<sup>3</sup>, [HNO<sub>3</sub>] = 5 × 10<sup>-2</sup> mol/dm<sup>3</sup>, banana cellulose = 0.5 g, temperature = 90 °C, duration of grafting = 2 h}

with an increase in acid concentration and for 2 × 10<sup>-2</sup> mol/dm<sup>3</sup> acid concentration maximum % grafting yield was observed and after that the % grafting yield decreases (Fig. 5).

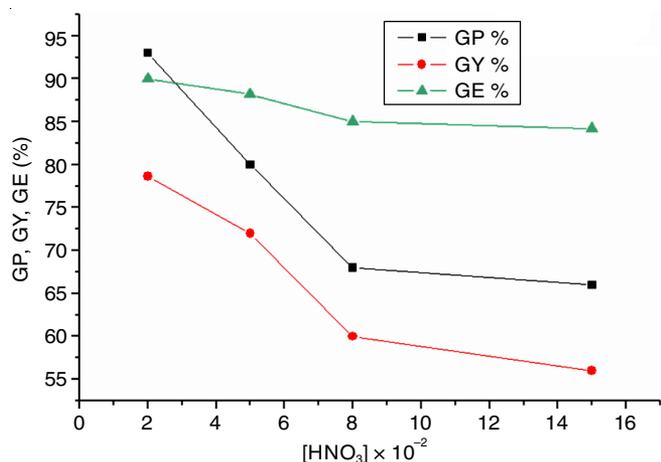


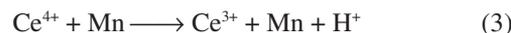
Fig. 5. Concentration of HNO<sub>3</sub> vs. % GP, % GY and % GE {[Ce(IV)] = 5 × 10<sup>-3</sup> mol/dm<sup>3</sup>, [AN] = 1.820 mol/dm<sup>3</sup>, [H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>] = 0.5 × 10<sup>-2</sup> mol/dm<sup>3</sup>, banana cellulose = 0.5 g, temperature = 90 °C, duration of grafting = 2 h}

The observed low grafting for 0.15 M HNO<sub>3</sub> can be explained as follows:

In aqueous medium, Ce(IV) is believed to combine with water in the following manner:



In the absence of acid, Ce<sup>4+</sup> primarily exists as [Ce]<sup>4+</sup>, [Ce(OH)<sub>3</sub>]<sup>3+</sup> and [Ce-O-Ce]<sup>6+</sup>. Due to its large size, [Ce-O-Ce]<sup>6+</sup> is incapable of entering the complex formation with banana cellulose. Thus, with the increase in acid concentration, equilibria (1) and (2) shift towards the formation of more [Ce(OH)<sub>3</sub>]<sup>3+</sup> and Ce<sup>4+</sup>, at the expense of [Ce-O-Ce]<sup>6+</sup>, ceric [Ce]<sup>4+</sup> and [Ce(OH)<sub>3</sub>]<sup>3+</sup> which being smaller in size, are more effective in forming complexes with banana cellulose molecules than with [Ce-O-Ce]<sup>6+</sup>, a higher percentage of grafting thus resulting. A decrease in the grafting percentage beyond 0.15 M HNO<sub>3</sub> could be attributed to the termination of the increasing grafted chains due to the presence of a higher concentration of this species:



Thus, nitric acid plays a definite role in grafting acrylonitrile onto banana cellulose.

**Effect of duration on grafting:** The graft yield increases up to 2 h, where the equilibrium was established as shown in Fig. 6. Initially, the monomers interact with the cellulosic skeleton to form co-polymers and the active site of the cellulosic skeleton fully saturates in 2 h. Further increase in reaction time does not affect grafting yield as the available active sites have saturated and the equilibrium has been established after 2 h [42,43]. In other words, it can be seen that %RG, %GY and %GE increase rapidly with an increase in time up to 120 min after which it decreased. Reaction time allows the ceric solution to diffuse into the banana cellulosic backbone before grafting reaction, thereby allowing initiation of free radicals on a cellulose sample by oxidation with Ce(IV) ions. Initially increase in %RG, %GY and %GE can be attributed to this factor. The decrease of these parameters in prolonging this reaction time beyond 120 min could be attributed to the decay of free radical activity of Ce(IV) oxidized cellulose resulting from the free radical

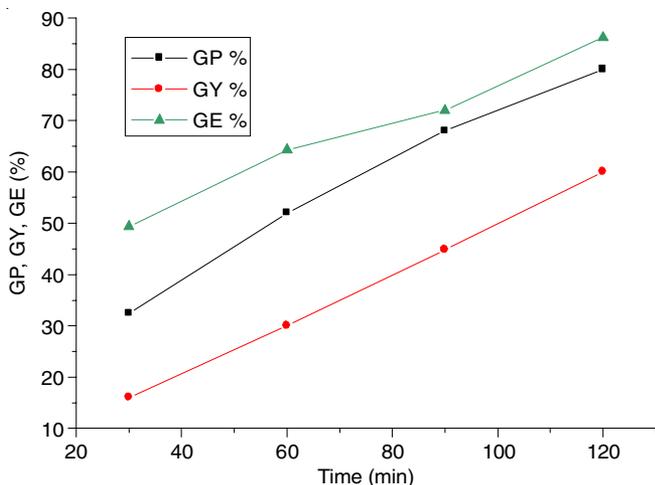


Fig. 6. Time vs. % GP, % GY and % GE { $[Ce(IV)] = 5 \times 10^{-3} \text{ mol/dm}^3$ ,  $[AN] = 1.820 \text{ mol/dm}^3$ ,  $[HNO_3] = 5 \times 10^{-2} \text{ mol/dm}^3$ , banana cellulose = 0.5 g, temperature = 90 °C,  $[H_2C_2O_4] = 0.5 \times 10^{-2} \text{ mol/dm}^3$ }

termination by charge transfer [1,2,5]. Also, since there is a large excess of acrylonitrile monomer even after the longer reaction times, the decrease after 120 min is presumably due to initiator exhaustion. These observations are in accordance with those observed by several researchers [5,10,11,44].

**Effect of temperature on the rate of grafting:** The rate of grafting (RG) increases with an increase in temperature. The energy of activation was found to be  $47.8884 \text{ kJ mol}^{-1}$  for graft co-polymerization of banana cellulose with acrylonitrile. This can be well explained on the basis of the fact that an increase in temperature causes faster diffusion of monomer molecules toward active grafting sites present on the banana cellulose. In addition, as the temperature increases, the rate of production of primary radicals also increases, this causes an increase in the rate of grafting %RG. The increase in temperature seems to cause a higher rate of initiator dissociation, as well as diffusion and mobility of the monomer from the aqueous phase to the backbone, with a considerable improvement in grafting yield that result.

The effect of reaction temperature on the graft copolymerization was carried out at different temperatures between 80 °C and 100 °C and keeping the other variables constant. As shown in Table-5, it is found that %RG and % GE increase initially up to 100 °C and then decrease to some extent with further increase in temperature. This is attributed to the fact that increasing the temperature favours the activation of macro radicals as well as accelerates the diffusion and mobility of the monomers from the aqueous phase to the cellulose phase. However, a further increase in temperature decreases %RG and %GE parameters, which can be ascribed both to the acceleration of termination reaction and to the increased chance of chain transfer reaction, accounting for the increase in the number of homopolymers.

This observation indicates that the optimal reaction temperature is 100 °C. Similar behaviour was also observed by other several researchers [2,3,10,11,45]. The effect of temperature on grafting copolymerization (Fig. 7) indicated that increasing the temperature up to 100 °C increases the diffusion of monomers through cellulose chains, swelling of cellulose as well as the rate of initiation and propagation of the grafting reaction. Above 100 °C, the grafting copolymerization decreases due to the oxidation of free radicals and mutual termination of growing macro radicals favours more homopolymer formation [46,47].

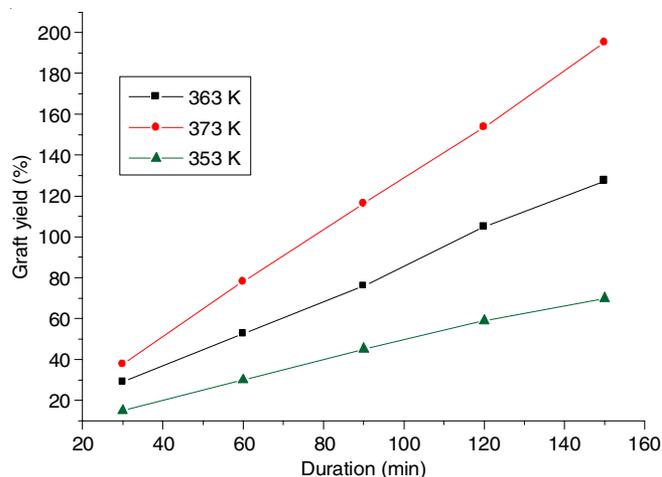


Fig. 7. Plot of % GY vs. duration of grafting at different temperatures { $[Ce(IV)] = 5 \times 10^{-3} \text{ mol/dm}^3$ ,  $[AN] = 1.820 \text{ mol/dm}^3$ ,  $[HNO_3] = 5 \times 10^{-2} \text{ mol/dm}^3$ , banana cellulose = 0.5 g,  $[H_2C_2O_4] = 0.5 \times 10^{-2} \text{ mol/dm}^3$ , duration of grafting = 2 h}

**Activation parameters:** The activation energy ( $E_a$ ) was calculated from the Arrhenius plot of  $\log RG$  vs.  $1/T$  at 353 K, 363 K and 373 K (Fig. 8). Activation energy ( $E_a$ ) =  $47.8884 \text{ kJ mol}^{-1}$ , while the calculated other activation parameters were  $\Delta H = 44.870 \text{ kJ mol}^{-1}$ ;  $\Delta S = -51.178 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $\Delta G = 18.622 \text{ kJ mol}^{-1}$ .

**Water absorbency:** Water absorbency of ungrafted and grafted banana cellulose was determined by measuring the water retention value (WRV). It was found that the WRV of AN grafted banana cellulose was reduced with the increase in %GY thereby increasing the hydrophobic nature of the banana cellulose (Table-6). The decrease in WRV might be due to the occupancy of the active sites of banana cellulose by acrylonitrile polymer.

## Conclusion

The  $\alpha$ -cellulose extracted from banana cellulose exhibits the characteristic physico-chemical properties of dissolving cellulose. Graft copolymerization of acrylonitrile onto  $\alpha$ -cellulose pulp by ceric ion can be carried out in the presence of nitrogen,

TABLE-5  
EFFECT OF TEMPERATURE ON GRAFTING OF ACRYLONITRILE ONTO BANANA CELLULOSE

Parameter	318 K	328 K	333 K	353 K	363 K	373 K
Graft polymerization (RG%)	–	–	32.4	82	90.0	123.80
Graft yield (GY%)	–	–	16.0	60	105.0	152.96
Graft efficiency (GE%)	–	–	49.3	75	86.8	184.00

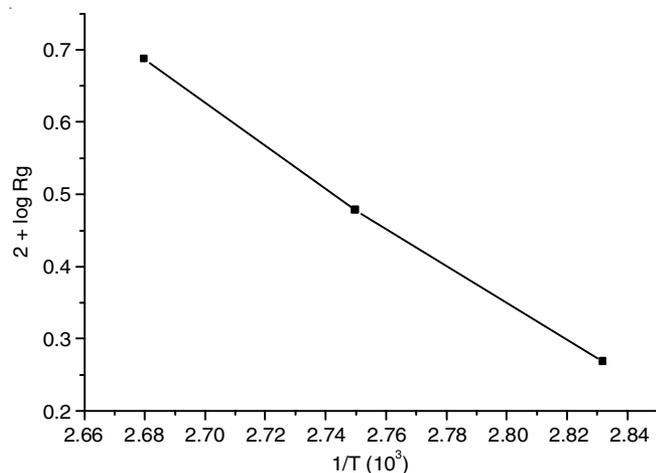


Fig. 8. Effect of temperature on the rate of grafting

TABLE-6  
WRV OF UNTREATED AND GRAFTED BANANA CELLULOSE

Samples	GY (%)	WRV (%)
Ungrafted banana cellulose	0	114.28
Grafted banana cellulose	73.8	12.8
	126	4.57

under an optimized set of conditions *viz.*, 0.1 M concentration of CAN,  $6 \times 10^{-3}$  mol/dm<sup>3</sup> of acrylonitrile, 0.1 N HNO<sub>3</sub> in 100 mL water; 2 h of grafting time and at 90 °C for grafting cellulose. The water retention value of grafted  $\alpha$ -cellulose pulp was obtained as 4.57 g/g, which is much lower than that obtained with ungrafted  $\alpha$ -cellulose pulp. Banana cellulose, therefore, seems to be a potential feedstock for the production of  $\alpha$ -cellulose, which can be subsequently converted into grafted cellulose for several applications.

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#### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

#### REFERENCES

1. A.-A.M.A. Nada, Y.A. Mohammed and M.F. Hesham, *BioResearch*, **3**, 46 (2007).
2. A.N. Nakagaito and H. Yano, *Appl. Phys. A*, **78**, 547 (2004); <https://doi.org/10.1007/s00339-003-2453-5>
3. D. Klemm, B. Heublein, H.-P. Fink and A. Bohn, *Angew. Chem.*, **44**, 3358 (2005); <https://doi.org/10.1002/anie.200460587>
4. R. Khullar, V.K. Varshney, S. Naithani and P.L. Soni, *Express Polym. Lett.*, **2**, 12 (2008); <https://doi.org/10.3144/expresspolymlett.2008.3>
5. A.S. Singha and A.K. Rana, *J. Polym. Environ.*, **20**, 361 (2012); <https://doi.org/10.1007/s10924-011-0370-9>
6. Kh.M. Mostafa, *J. Appl. Sci.*, **5**, 341 (2005); <https://doi.org/10.3923/jas.2005.341.346>
7. F. Soleimani and H. Shahsavani, *Indian J. Sci. Technol.*, **5**, 2041 (2012).
8. G. Raju, C.T. Ratnam, N.A. Ibrahim, M.Z. AbRahman and W.Z.W. Yunus, *Polym. Plast. Technol. Eng.*, **46**, 949 (2007); <https://doi.org/10.1080/03602550701582710>
9. I. Kaur, R. Kumar and N. Sharma, *Carbohydr. Res.*, **345**, 2164 (2010); <https://doi.org/10.1016/j.carres.2010.06.018>
10. P. Purohit, A. Bhatt, R.K. Mittal, M.H. Abdellattif and T.A. Farghaly, *Front. Bioeng. Biotechnol.*, **10**, 1044927 (2022); <https://doi.org/10.3389/fbioe.2022.1044927>
11. M. Kumar, P.S. Gehlot, D. Parihar, P.K. Surolia and G. Prasad, *Eur. Polym. J.*, **152**, 110448 (2021); <https://doi.org/10.1016/j.eurpolymj.2021.110448>
12. Y. Onishi, G.B. Butler and T.E. Hogen-Esch, *J. Appl. Polym. Sci.*, **92**, 3022 (2004); <https://doi.org/10.1002/app.20261>
13. M. Sadeghi and H. Hosseinzadeh, *J. Chil. Chem. Soc.*, **55**, 123 (2010); <https://doi.org/10.4067/S0717-97072010000400019>
14. F.E. Okieimen, *J. Appl. Polym. Sci.*, **89**, 913 (2003); <https://doi.org/10.1002/app.12014>
15. M. Sadeghi and H. Hosseinzadeh, *Turk. J. Chem.*, **32**, 375 (2008).
16. G. Mino and S. Kaizerman, *J. Polym. Sci.*, **31**, 242 (1958); <https://doi.org/10.1002/pol.1958.1203112248>
17. R.F. Storey, D. Sudhakar and L.J. Goff, *J. Macromol. Sci.*, **24**, 1051 (1987); <https://doi.org/10.1080/0022338708078142>
18. G. Zhang, Z. Zhang, F. Xie, X. Hu, X. Luo and X. Chen, *J. Appl. Polym. Sci.*, **75**, 977 (2000); [https://doi.org/10.1002/\(SICI\)1097-4628\(20000222\)75:8<977::AID-APP1>3.0.CO;2-6](https://doi.org/10.1002/(SICI)1097-4628(20000222)75:8<977::AID-APP1>3.0.CO;2-6)
19. J. Retuert and M. Yazdani-Pedram, *Polym. Bull.*, **31**, 559 (1993); <https://doi.org/10.1007/BF00297892>
20. S. Kataoka and T. Ando, *J. Polym. Sci. Technol.*, **37**, 85 (1980); <https://doi.org/10.1295/koron.37.375>
21. M. Yazdani-Pedram and J. Retuert, *J. Appl. Polym. Sci.*, **63**, 1321 (1997); [https://doi.org/10.1002/\(SICI\)1097-4628\(19970307\)63:10<1321::AID-APP11>3.0.CO;2-7](https://doi.org/10.1002/(SICI)1097-4628(19970307)63:10<1321::AID-APP11>3.0.CO;2-7)
22. Y. Wang, J.X. Yang and K.Y. Qiu, *Acta Polym. Sinica*, **2**, 188 (1994).
23. C.H. Peng, Y.T. Wang, G. Cheng and Y.R. Tang, *Environ. Sci.*, **19**, 29 (1998).
24. L. Yu, Y. He, L. Bin and F. Yue'e, *J. Appl. Polym. Sci.*, **90**, 2855 (2003); <https://doi.org/10.1002/app.13011>
25. I. Casinos, *Polymer*, **35**, 606 (1994); [https://doi.org/10.1016/0032-3861\(94\)90519-3](https://doi.org/10.1016/0032-3861(94)90519-3)
26. T. Fang, J. Liu, J. Yu, L. Wang and S. Xu, *Polym. Bull.*, **29**, 71 (1992); <https://doi.org/10.1007/BF00558038>
27. C.H. Bamford, A.D. Jenkins and R. Johnston, *J. Appl. Polym. Sci.*, **29**, 355 (1958); <https://doi.org/10.1002/pol.1958.1202912003>
28. B.R. Sharma, V. Kumar and P.L. Soni, *J. Appl. Polym. Sci.*, **90**, 129 (2003); <https://doi.org/10.1002/app.12593>
29. V.D. Athawale and V.L. Vidyagauri, *Starch-Starke*, **50**, 426 (1998); [https://doi.org/10.1002/\(SICI\)1521-379X\(199810\)50:10<426::AID-STAR426>3.3.CO;2-R](https://doi.org/10.1002/(SICI)1521-379X(199810)50:10<426::AID-STAR426>3.3.CO;2-R)
30. A. Hebeish, M.H. El-Rafie, A. Higazy and M. Ramadan, *Starch-Starke*, **48**, 175 (1996); <https://doi.org/10.1002/star.19960480505>
31. A.S. Sinha, A. Shama and V. Thakur, *Bull. Mater. Sci.*, **31**, 7 (2010); <https://doi.org/10.1007/s12034-008-0002-8>
32. M.J. Zohuriaan, A. Pourjavadi and M. Sadeghi, *Iran. Polym. J.*, **14**, 131 (2005).
33. J. Zhang, H. Chen and A. Wang, *Polym. Compos.*, **28**, 208 (2007); <https://doi.org/10.1002/pc.20384>
34. M.T. Taghizadeh and M.A. Darvishi, *Iran. Polym. J.*, **10**, 283 (2001).
35. G.F. Fanta, R.C. Burr, W.M. Doane and C.R. Russel, *J. Polym. Sci.: Symposia*, **45**, 89 (1974); <https://doi.org/10.1002/polc.5070450108>
36. J.-P. Gao, R.-C. Tian, J.-G. Yu and M.-L. Duan, *J. Appl. Polym. Sci.*, **53**, 1091 (1994); <https://doi.org/10.1002/app.1994.070530811>
37. L.M. Zhang and L.Q. Chen, *J. Appl. Polym. Sci.*, **83**, 2755 (2002); <https://doi.org/10.1002/app.10191>

38. R. Bouhdadi, S. Benhadi, S. Mplina, B. George, M.E. Moussaouiti and A. Merlin, *Maderas: Cienc. Technol.*, **13**, 105 (2011); <https://doi.org/10.4067/S0718-221X2011000100009>
39. M.M. Ibrahim, E.M. Flefel and W.K. El-Zawawy, *Polym. Adv. Technol.*, **13**, 548 (2002); <https://doi.org/10.1002/pat.224>
40. F. Yang, G. Li, Y.G. He, F.X. Ren and J.X. Wang, *Carbohydr. Polym.*, **78**, 95 (2009); <https://doi.org/10.1016/j.carbpol.2009.04.004>
41. M.M. Ibrahim, E.M. Flefel and W.K. El-Zawawy, *J. Appl. Polym. Sci.*, **84**, 2629 (2002); <https://doi.org/10.1002/app.10425>
42. C. Routray and B. Tosh, *Cellulose*, **19**, 2115 (2012); <https://doi.org/10.1007/s10570-012-9762-9>
43. A. Batacharia and B.N. Misra, *Prog. Polym. Sci.*, **29**, 767 (2004); <https://doi.org/10.1016/j.progpolymsci.2004.05.002>
44. A. Jideonwo and H.A. Adimula, *J. Appl. Sci. Environ. Manage.*, **10**, 51 (2006); <https://doi.org/10.4314/jasem.v10i3.17336>
45. S.C. Hsu, T.M. Don and W.Y. Chiu, *Polym. Degrad. Stab.*, **75**, 73 (2002); [https://doi.org/10.1016/S0141-3910\(01\)00205-1](https://doi.org/10.1016/S0141-3910(01)00205-1)
46. T. Hajeeth, T. Gomathi and P.N. Sudha, *Int. J. Front. Sci. Technol.*, **1**, 1 (2013).
47. N. Bhatt, P.K. Gupta and S. Naithani, *Cell. Chem. Technol.*, **45**, 321 (2011).