Ceric Ammonium Nitrate-Initiated Graft Copolymerization of Acrylamide onto *Cassia tora* Gum

Brij Raj Sharma, Vineet Kumar, P. L. Soni

Centre of Advance Studies in Chemistry of Forest Products, Forest Research Institute, Dehradun-248006, India

ABSTRACT: Graft copolymerization of acrylamide onto *Cassia tora* gum was studied in an aqueous medium using ceric ammonium nitrate-nitric acid as the redox initiator. To optimize the reaction conditions for obtaining maximum percent grafting, the concentrations of *Cassia tora* gum, ceric ammonium nitrate, acrylamide, and nitric acid, time, and temperature were varied. Results are discussed and a reaction mechanism is proposed. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3250–3255, 2002

INTRODUCTION

Natural polysaccharides are frequently modified with chemicals to give them new properties for broader applications. In recent years, chemical modification of natural polymers by grafting has received considerable attention because grafted copolymers have improved physicochemical properties and industrial applications. Among chemical methods, redox-initiated grafting offers advantages because, in the presence of redox systems, grafting can be carried out under milder conditions with minimum side reactions. Grafting of vinyl monomers onto natural polymers like guar gum,[1,2] starch,[3,4] and cereal flour[5] with different redox initiators has been studied. *Cassia tora* gum (CTG) is derived from the seeds of *Cassia tora* Linn, a common herbaceous annual occurring weed throughout India. The pods are 15–22.5 cm long, up to 0.625 cm in diameter, and contain flattened dark seeds. The *Cassia tora* seed is composed of hull (27%), endosperm (32%), and germ (41%). Methylation studies showed that backbone of the polysaccharide has a fundamental structure consisting of linear chain of β-D-(1→4) linked mannopyranosyl residues substituted by α-D-galactopyranosyl groups mainly at O-6.[6] There are very few reports on the modification of CTG and its use.[7–9] However, no work has been reported on grafting of vinyl monomers onto CTG. With a view that grafted CTG may find better applications in comparison to native CTG, this work of graft copolymerization of acrylamide (AA) onto CTG is investigated in the presence of ceric ammonium nitrate (CAN) as

redox initiator and with the reaction conditions for graft copolymerization optimized.

The use of CAN for chemical initiation of vinyl polymerization has been shown in the possible modification of biopolymers such as starch, cellulose, guar gum, etc.[4,10–14] The formation of free radicals on these biopolymers by cerium(IV) has been demonstrated by electron spin resonance.[15] The mechanism by which cerium(IV) generates free radicals is believed to involve the formation of coordination complex between the oxidant (i.e., CAN) and the hydroxyl group of biopolymer. The ceric(IV)–biopolymer complex then disproportionates, forming a free radical on the biopolymer chain and cerium (III).[16] Model compound studies of cerium(IV) oxidation of monohydric alcohol and 1,2-glycols support the postulated mechanism and suggest that the C_2—C_3 glycol and the C_6 hydroxyl of anhydro-D-glucose unit may be preferred site for free radical generation.[17–20] Evidence for the formation of stable coordination complex has been obtained by kinetic and spectroscopic methods for cerium(IV) oxidation of many compounds in perchloric and nitric acids.[20–22]

Relative reactivity of the C_6 hydroxyl and C_2—C_3 glycol was estimated by comparing tetrahydropyran-2-methanol and cyclohexanemethanol as models for the C_6 hydroxyl and with *trans*-1,2-cyclohexanediol for C_2—C_3 glycol units. The results show that the relative rate of the ceric ion oxidation of *trans*-1,2-cyclohexanediol was six times higher than the primary hydroxyl.[20]

Furthermore, equilibrium constants for *trans*-1,2-cyclohexanediol and *cis*-1,2-cyclohexanediol are consistent with chelate complex formation. In the stable conformations of these compounds, the separation of the hydroxyl groups is almost the same, and the relatively large Ce(IV) can easily bridge this distance. The formation of a five-membered chelate ring fused to the

cyclohexane ring results in a relatively rigid system with the trans isomer, whereas the complex with cis isomer is relatively flexible because conformation interconversion can occur as readily in the complex as in the uncomplexed diol. The greater flexibility of the complex with the cis isomer thus contributes to its somewhat greater stability (more positive entropy of formation).[20]

In view of the information just presented, it is proposed that the oxidation reaction of CTG will occur preferably at the C_2—C_3 glycol unit and to a very less extent at the C_6 hydroxyl because the mannan backbone of CTG contains a *cis*-OH group at C_2—C_3. The proposed mechanism is as follows: In the presence of ceric salts, like CAN [$Ce(NH_4)_2(NO_3)_6$], as initiator on graft polymerization onto CTG, a ceric ion–CTG complex is initially formed as a result of electron transfer. The ceric ion (IV) is reduced to cerous ion (III) and a free radical is created on the galactomannan backbone,[13] as shown in Scheme 1. The radical site on the galactomannan chain then initiates graft copolymerization of a polar vinyl monomer, which is present in the reaction mixture. The grafting occurs mainly at C_2—C_3, as already discussed.
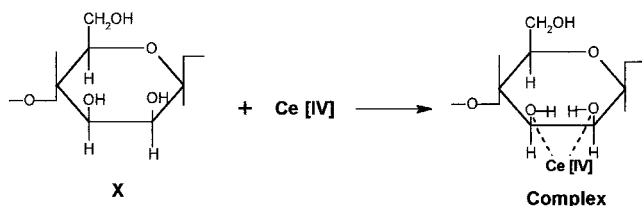
EXPERIMENTAL

Materials and methods

Gum from *Cassia tora* seed (CTG) was isolated as per method described by Soni and Pal.[23] Acrylamide (for synthesis, Loba Chemie), ceric ammonium nitrate (Aldrich Chemical Company), and nitric acid (AR grade, Ranbaxy Laboratories Ltd., India) were used in this study.

Graft copolymerization

The grafting reaction was carried out under nitrogen atmosphere in a 500-mL, three-necked flask equipped with a stirrer, a gas inlet system, and a reflux condenser immersed in a constant-temperature water bath. In a typical reaction, CTG (3–5 g) was dissolved in water (200 mL) with constant stirring and bubbling of a slow stream of nitrogen at the desired temperature. The freshly prepared 10-mL solution of ceric ammonium nitrate (0.005–0.03 mol) in nitric acid (0.1–0.3 M) followed by acrylamide (0.07–0.56 mol) in water (90 mL) was added and a continuous supply of nitrogen was maintained throughout the reaction pe-

riod. The grafting reaction was carried out for varying period of time intervals (3–6 h). After the reaction was over, the reaction mixture was poured in methanol for precipitation. Centrifugation, washing with methanol, and filtration processes were carried out, and the product was dried in the vacuum dessicator. The dried product was extracted with dimethylforamide: acetic acid mixture (1:1) for 48 h. After complete removal of homopolymer (polyacrylamide), the grafted CTG was dried to a constant weight. The percent grafting, percent total conversion, and percent grafting efficiency were calculated from the increase in weight of CTG after grafting, in the following manner:

$$\% \text{ Grafting} = \frac{\text{Wt. of polymer grafted}}{\text{Initial wt. of backbone}} \times 100 \quad (1)$$

% Conversion

$$= \frac{\text{Wt. of grafted polymer} - \text{Wt. of backbone}}{\text{Wt. of monomer}}$$

$$\times 100 \quad (2)$$

% Grafting Efficiency

$$= \frac{\text{Wt. of polymer grafted}}{\text{Wt. of polymer grafted} + \text{Wt. of homopolymer}}$$

$$\times 100 \quad (3)$$
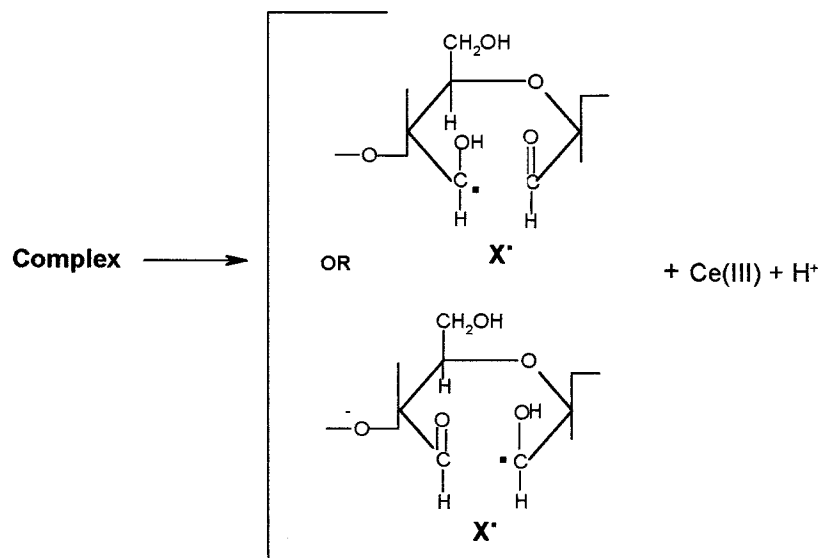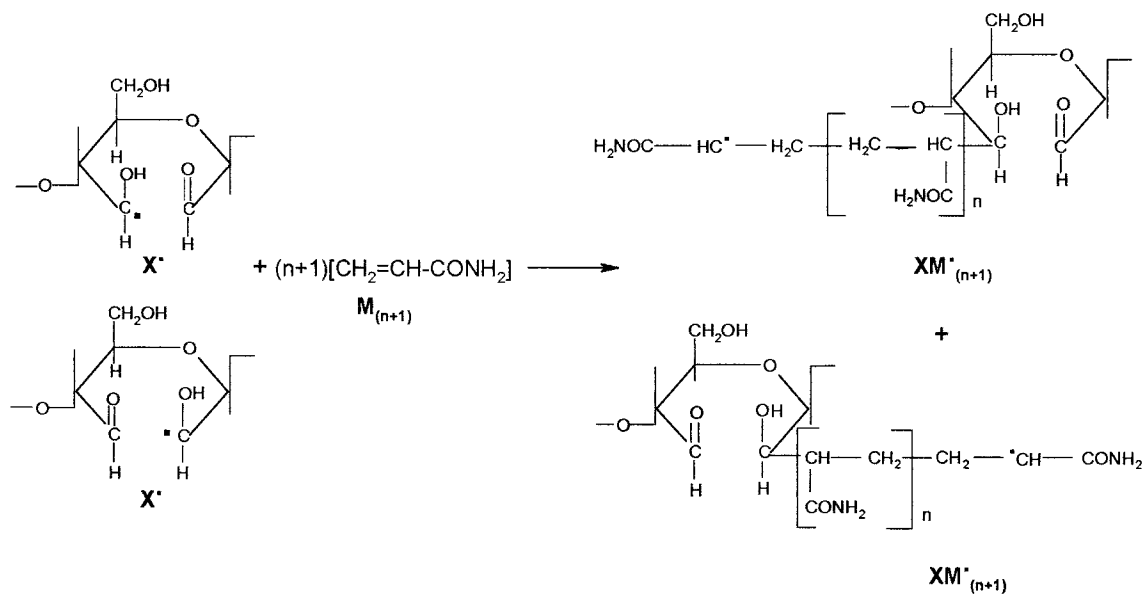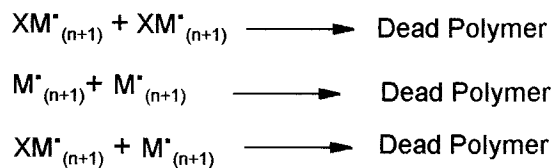
RESULTS AND DISCUSSION

Determination of optimum reaction conditions

To optimize the conditions for grafting of acrylamide onto CTG, the concentrations of nitric acid, free radical initiator, and monomer, time, and temperature were varied.

Effect of reaction time

The effect of polymerization time on percent grafting and percent grafting efficiency is shown in Figure 1. The percent grafting increases rapidly with time up to 5 h, after which it levels off. The increase in percent grafting is accounted for by the increase in number of grafting sites in the initial stages of the reaction.[24] The leveling off of grafting with time could be attributed to a decrease in concentration for both initiator and monomer as well as to a reduction in the number of sites on the backbone accessible for grafting as the reaction proceeds.

It has been observed that percent grafting efficiency does not change appreciably during the course of reaction. The grafting efficiency pattern of CTG shows the similarity to the grafting efficiency pattern of vinyl monomers onto cellulose[25] and starch[3] with ceric ion

Chain Initiation

Complex $\longrightarrow$ [...] $+ Ce(III) + H^+$

Chain Propagation

$$X^\bullet + (n+1)[CH_2=CH-CONH_2] \longrightarrow XM^\bullet_{(n+1)}$$

$$M_{(n+1)}$$

$$+ \quad XM^\bullet_{(n+1)}$$

Chain Termination

$$XM^\bullet_{(n+1)} + XM^\bullet_{(n+1)} \longrightarrow \text{Dead Polymer}$$

$$M^\bullet_{(n+1)} + M^\bullet_{(n+1)} \longrightarrow \text{Dead Polymer}$$

$$XM^\bullet_{(n+1)} + M^\bullet_{(n+1)} \longrightarrow \text{Dead Polymer}$$
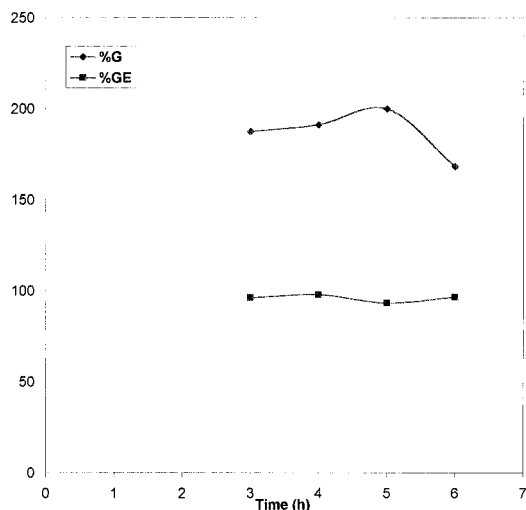
Scheme 1

Figure 1 Effect of reaction time on percent grafting and percent grafting efficiency.

as an initiator. Thus, to obtain the maximum percent grafting, the optimum time duration is 5 h.

Effect of ceric ammonium nitrate (CAN) concentration

The effect of variation in CAN concentration on percent grafting is shown in the Figure 2. CAN concentration was increased from 0.005 to 0.03 mol. Results show that optimum percent grafting was achieved at 0.01 mol concentration, after which it decreases drastically. The results in Figure 2 also show that at a reasonably low initiator concentration, the percent grafting is significantly higher compared with percent grafting at higher concentration. This difference is due to the increasing participation of ceric ion in the termination of growing grafted chains[16] by the following reaction:
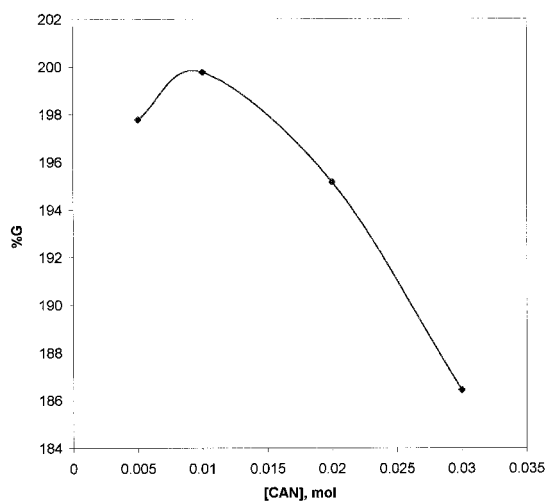

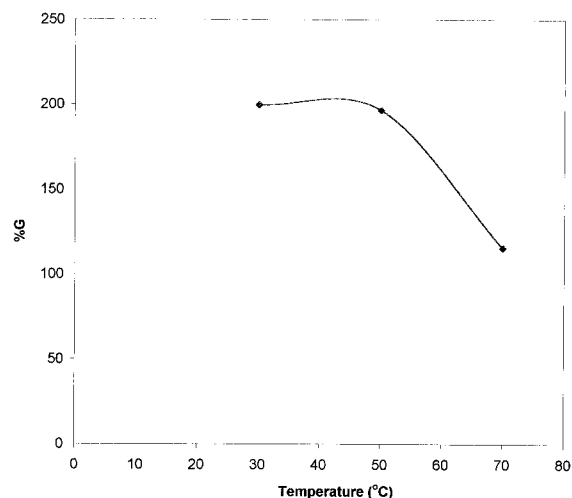**Figure 2** Effect of CAN concentration on percent grafting.

Figure 3 Effect of temperature on percent grafting.

$$CTG\text{-}M^{\cdot} + Ce(IV) \rightarrow CTG\text{-}M + Ce(III) + H^{+} \quad (4)$$

Furthermore, at higher initiator concentration, the formation of homopolymer competes with the grafting reaction and thus decreases the percent grafting.

Effect of temperature

The graft copolymerization of acrylamide onto CTG was studied at different temperatures (30–70°C). The effect of temperature on percent grafting is shown in Figure 3. Results show that maximum grafting was obtained at 30°C and grafting decreased with further increase of temperature. The dependence of percent grafting on temperature can be ascribed to the enhancement of the rate of diffusion of monomer. Beyond the optimum increase of temperature, the graft copolymerization occurs with poor selectivity, and various hydrogen abstraction and chain transfer reactions may be accelerated, leading to the decrease of percent grafting.

Effect of nitric acid concentration

The concentration of nitric acid was varied from 0.1–0.3 M, keeping fixed the concentrations of all other reagents, time, and temperature. The effect of acid concentration on percent grafting is shown in Figure 4. The percent grafting increases with increase of acid concentration up to 0.2 M and decreases beyond this concentration. This result is because there exists an optimum concentration of nitric acid that affords maximum grafting, which corresponds to 0.2 M in the present case. Beyond the optimum concentration of nitric acid, the percent grafting decreases in each case. The role of nitric acid in grafting of vinyl monomers onto CTG is explained by the fact that ceric ion in water is believed to react in the following manner:
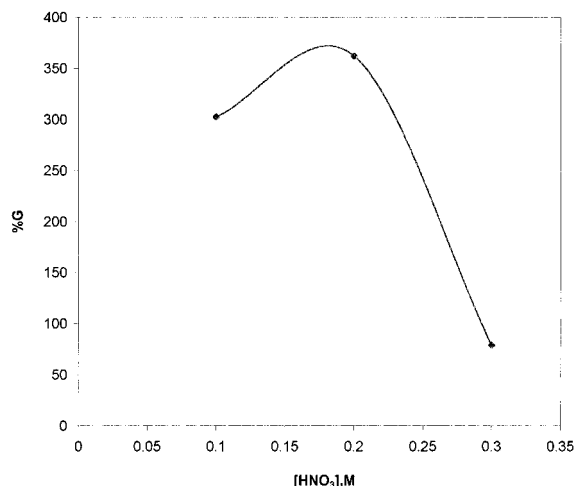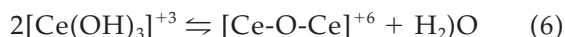
Figure 4 Effect of nitric acid concentration on percent grafting.

$$Ce^{+4} + H_2O \leftrightharpoons [Ce(OH)_3]^{+3} + H^+ \qquad (5)$$

$$2[Ce(OH)_3]^{+3} \leftrightharpoons [Ce\text{-}O\text{-}Ce]^{+6} + H_2O \qquad (6)$$

Thus ceric ion exists as Ce^{+4}, $(Ce[OH]_3)^{+3}$, and $[Ce\text{—}O\text{—}Ce]^{+6}$ in aqueous solution. The concentration of these species varies with the concentration of nitric acid.[26]

In the beginning, the percent grafting increase with increase in $[H^+]$. This result is attributed to the increase in concentration of Ce^{+4} and $(Ce[OH]_3)^{+3}$ at the expense of $(Ce\text{—}O\text{—}Ce)^{+6}$. Ceric ions $(Ce)^{+4}$, being smaller in size, are more effective in their ability to form complexes with CTG than $(Ce\text{—}O\text{—}Ce)^{+6}$. Further increase in nitric acid concentration, beyond 0.2 M, decreases percent grafting. This result may be explained by the fact that as $[H^+]$ increases, the equilibria (eqs. 5 and 6) shifts towards formation of more $(Ce\text{—}O\text{—}Ce)^{+6}$.

Effect of monomer concentration

Effect of monomer concentration was studied keeping other variables fixed. The effect of monomer (AA) concentration on percent grafting as well as percent conversion are shown in Figure 5. The percent grafting increases as the monomer concentration increases from 0.035 to 0.49 mol, and thereafter, it decreases with further increase of monomer concentration. The rapid increase of grafting by increasing monomer concentration up to 0.49 mol could be ascribed to the greater availability of grafting sites to monomer. However, the decreasing trend of percent grafting beyond optimum monomer concentration is probably due to the competition between homopolymerization and graft copolymerization, where the former prevails over the latter at higher AA concentration. The effect

of AA concentration on the percent conversion, when CTG copolymerized with AA, is also shown in Figure 5. The results signify that the percent conversion displays outstanding increment when AA concentration increases from 0.07 to 0.14 mol. However, further increase in AA concentration enhances percent conversion, but to a lesser extent. Enhancement in percent conversion at higher AA concentration could be associated with greater availability of monomer molecules in the vicinity of CTG molecules as well as in the polymerization medium. This greater availability would favor greater opportunity for AA to graft CTG as well as allow greater collision of initiated AA molecules with its own molecules, thereby promoting homopolymerization. This analysis is in agreement with the results obtained in the grafting of AA onto starch.[27]

Effect of concentration of *cassia tora* gum

The effect of concentration of CTG on percent grafting and on percent conversion was studied by varying the amount of CTG (3–5 g), keeping other variables fixed. The results in Figure 6 show that percent grafting and percent conversion increases with increase in amount of CTG up to 4 g and then decreases with increase in amount of CTG. The initial increase may be because the reactive sites increase with increase in the concentration of CTG. The decrease beyond the amount of 4 g may be attributed to the destruction of radical activity on the backbone soon after it is formed due to the termination between backbone–backbone and backbone–primary radicals. This result is in agreement with the results obtained in the grafting of acrylonitrile onto starch[28] and grafting of poly(acrylonitrile) onto guar gum.[2]
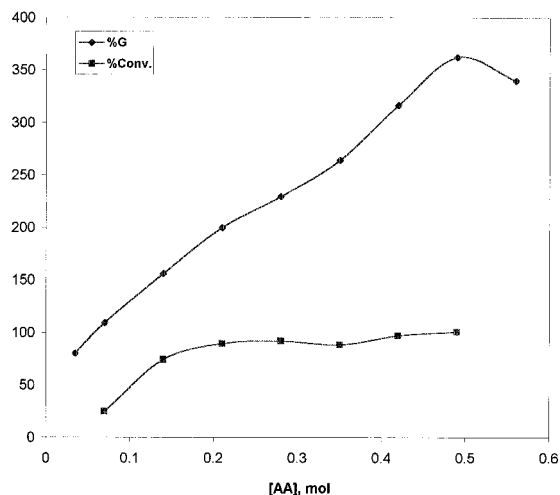

Figure 5 Effect of monomer concentration on percent grafting and percent conversion.
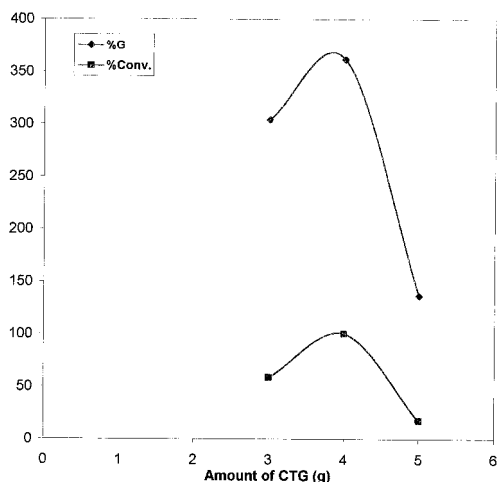
Figure 6 Effect of amount of CTG on percent grafting and percent conversion.

CONCLUSION

Graft copolymerization of acrylamide onto CTG in aqueous medium can be initiated effectively with CAN. The optimum reaction conditions obtained for grafting of AA onto CTG were: CTG = 4 g, [CAN] = 0.01 mol, [AA] = 0.49 mol, [HNO$_3$] = 0.2 M, reaction time = 5 h, and temperature of reaction = 30°C.

References

1. Raval, D.K.; Patel, R.G.; Patel, V.S. Starch/Stärke 1988, 40 (2), 66–69.
2. Bajpai, U.D.N.; Mishra, V.; Rai, S. J Appl Polym Sci 1993, 47, 717–722.
3. Athawale, V.D.; Vidyagauri, Starch/Stärke 1998, 50 (10), 426–431.
4. Athawale, V.D.; Lele, V. Carbohydr Polym 2000, 41, 407–416.
5. Patil, D.R.; Crookston, M.N.; Fanta, G.F.; Peroria, I.L. Starch 1995, 47 (3), 110–115.
6. Soni, P.L.; Pal, R. Trends Carbohydr Chem 1996, 2, 33.
7. Soni, P.L. Process for the modification of *Cassia tora* gum. Indian Pat. No. 1542/ DEL/99 (1999).
8. Soni, P.L.; Singh, S.V.; Naithani, S. In Paper International, Oct.–Dec.; 2000; Vol. 5, Issue 1.
9. Soni, P.L.; Naithani, S.; Singh, S.V.; Kapoor, S.K. IPPTA Convention Issue 2001, 97–107.
10. Ren, L.; Tokura, S. Carbohydr Polym 1994, 23, 19–25.
11. Carr, M.E.; Peroria, I.L. Starch/Stärke 1992, 44, 219–223.
12. Chinnaswamy, R.; Hanna, M.A. Starch/Stärke 1991, 43 (10), 396–402.
13. Gurdag, G.; Yasar, M.; Gurkaynak, M.A. J Appl Polym Sci 1997, 66, 929–934.
14. Deshmukh, S.R.; Singh, R.P. J Appl Polym Sci 1987, 33, 1963–1975.
15. Reyes, Z.; Rist, C.E.; Russell, C.R. J Polym Sci 1966, A-1, 4, 1031.
16. McCormick, C.L.; Park, L.S. J Polym Sci, Polym Chem Ed 1981, 19(9), 2229–2241.
17. Mino, G.; Kaizerman, S.; Rasmussen, E. J Am Chem Soc 1959, 81, 1494.
18. Iwakura, Y.; Kurosaki, T.; Imai, K. J Polym Sci, Part A: Polym Chem 1965, 3, 1185.
19. Cumberbirch, R.J.E.; Holker, J.R. J Soc Dyers Colourists 1966, 82, 59.
20. Hintz, H.L.; Johnson, D.C. J Org Chem 1967, 32, 556.
21. Guilbault, G.G.; McCurdy Jr., W.H. J Phys Chem 1963, 67, 283.
22. Venkatakrishna, S.; Santappa, M. Z Physik Chem (Frankfurt) 1958, 16, 73.
23. Soni, P.L. Indian Patent 1108 / DEL / 94, 1994.
24. Nagabhushanam, T.; Joseph, K.T.; Santappa, M. J Polym Sci, Polym Chem Ed 1978, 16, 3287.
25. McDowall, D.J.; Gupta, B.S.; Stanett, V.T. Prog Polym Sci 1984, 10, 1.
26. Trivedi, H.C.; Patel, C.P.; Shah, S.B. Trends Carbohydr Chem 1996, 2, 1–24.
27. Hebeish, A.; El-Rafie, M.H.; Higazy, A.; Ramadan, M.; Doki, Starch/Stärke 1996, 48 (5), 175–179.
28. Mehrotra, R.; Ranby, B. J Appl Polym Sci 1977, 21, 3407.