Graft Copolymerization Onto Tamarind Kernel Powder: Ceric(IV)-initiated Graft Copolymerization of Acrylonitrile

Puja Goyal, Vineet Kumar, Pradeep Sharma

Chemistry Division, Forest Research Institute (ICFRE), Dehradun 248006, India

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ABSTRACT: Tamarind Kernel Powder (TKP) is derived from the seeds of *Tamarindus indica* Linn., a common and most important tree of India. It is extensively used in cotton sizing, as a wet-end additive in the paper industry, as a thickening, stabilizing, and gelling agent in the food industry. However, because of its fast biodegradability there is a need to prepare graft copolymers of TKP. The graft copolymerization of acrylonitrile (AN) onto TKP with ceric ammonium nitrate as a redox initiator in an aqueous medium has been studied. The reaction conditions were optimized to afford maximum percent grafting and percentage grafting efficiency of AN onto TKP, which was found to be 86% and 64%, respectively. Fourier Transform Infrared Spectrum of the grafted products showed an additional sharp absorption band at 2244 cm^{-1} due to $-C\equiv N$ stretching, thereby confirming the grafting of AN onto TKP. Scanning electron microscopy studies indicated change in contour of the polysaccharide on grafting and the thick polymeric coating of AN on its surface alongwith grafting of AN such that all the gap between polysaccharide particles have been closed. Thermal studies using thermogravimetric and differential gravimetric analyses confirmed that TKP-*g*-AN has overall high thermal stability than pure TKP. Reaction mechanism of grafting of acrylnitrile onto TKP is also proposed. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 377–386, 2009

Key words: tamarind kernel powder; graft copolymerization; acrylonitrile; ceric ammonium nitrate; free-radical initiator; scanning electron microscopy

INTRODUCTION

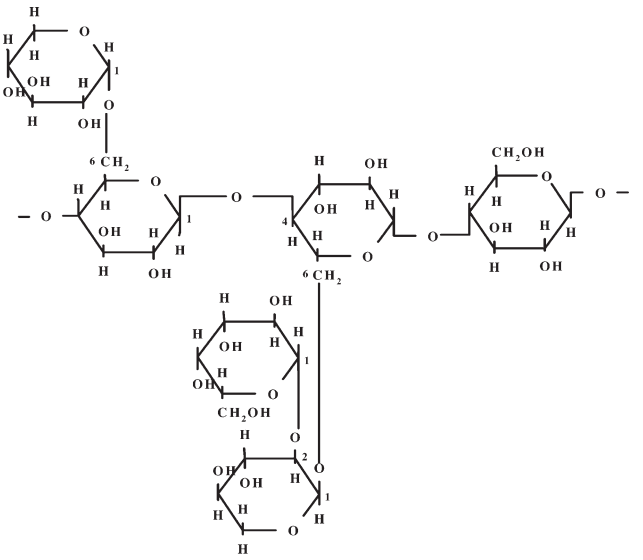
Tamarind (*Tamarindus indica*) is an economically most important and common tree cultivated throughout India and is particularly abundant in Madhya Pradesh and South India especially in Tamil Nadu, Karnataka, and Andhra Pradesh. The timber from the tree is very valuable. The wood is used as fuel and for making agricultural implements. Almost every part of it finds some use, but the most useful is its fruit. Fruit in the form of large pods is composed of 55% pulp, 34% seeds, and 11% shell and fibers. The pulp is acidic in nature, which is widely used in India as a souring agent in culinary preparations. The seed is a by-product of the tamarind pulp industry, which is an agricultural waste; it is cheaper indigenous product when compared with other gums or synthetic mucilagenous substances.[1]

The seed is exalbuminous and has about 70% kernel or endosperm enclosed by about 30% testa, which is rich brown in color. Tamarind Kernel Powder (TKP) is obtained from the seed kernel after dehusking of the brown testa and pulverizing creamy white kernel. The analysis of the seed kernels gave the following range of values: protein 17.1–20.1%; fat 6.0–8.5%; carbohydrates 65.1–72.2%; crude fiber 0.7–4.3%; and ash 2.3–3.2%.[1] The dark brown fatty oil from the kernels is used in the preparation of paints, varnishes, and for burning lamps.

TKP, a crude extract of tamarind seeds has been used as a replacement for starch in cotton sizing and as a wet-end additive in the paper industry, where it replaces starches and galactomannans.[2] It also finds application as a creaming agent for rubber latex, as a soil stabilizer, in medical and pharmaceutical application and oil-field applications.[3] Refined tamarind seed polysaccharide is used as a thickening, stabilizing, and gelling agent in the food industry, particularly in Japan where it is a permitted food additive.[2,4]

The proposed structure of the polysaccharide is composed of (1→4)-β-linked D-glucan backbone, substituted by single unit, (1→6)-linked α-D-xylopyranosyl side chains, some of which are further substituted by D-galactopyranosyl residues linked (1→2)-β.[4] Exact composition of polysaccharide is not fully known till date. The ratio of glucose : xylose : galactose in the polysaccharide has been reported by number of workers as approximately 3 : 2 : 1, 3 : 2.25 : 1, 2.25 : 1.25 : 1, 4 : 2 : 1, and 2.8 : 2.25 : 1.0.[2,4,5] Arabinose residues are frequently reported for tamarind seed polysaccharide but these probably arise from contaminating arabinans.[4]

Correspondence to: V. Kumar (drvineet@gmail.com).



Structure of TKP

Solution properties of TKP are mainly because of polysaccharide components. It disperses rapidly in cold water, but a uniform solution is obtained on heating or dispersing the powder in hot water.[1] In aqueous solution, powder behaves as a simple thickener, but it can form gels with sugar similar to fruit pectins and is therefore a good substitute in the preparation of jams, jellies, and related products. In contrast to pectins, TKP does not gel with calcium ions.[6] In India, TKP is perhaps one of the cheapest gum available. However, because of several drawbacks, such as unpleasant odor, dull color, presence of water insolubles, low solubility in cold water, and fast biodegradability, it is wanting in several speciality end-use properties.

Through graft copolymerization of vinyl monomers, desirable properties can be imparted to natural and synthetic polymers without altering the other properties. Among chemical methods, redox-initiated grafting is advantageous because in the presence of redox systems, grafting can be carried out under milder conditions with minimum side reactions. The grafting of acrylonitrile (AN) onto natural polymers like starch,[7–12] guar gum,[13,14] chitosan,[15] and *Cassia tora* gum[16] with different redox systems has been reported.

In our laboratory seed gums (*Cassia occidentalis*/*Cassia tora*/*Cyamopsis tetragonoloba*/TKP) were modified via carboxymethylation,[17–20] carbamoylethylation,[21–23] cyanoethylation,[24,25] and grafting.[16,26–28] A number of chemical modifications of tamarind seed polysaccharide have been described including acetyl,[29] hydroxyalkyl,[30,31] carboxymethyl derivatives,[6,17,20,31–35] and grafting.[26,36] However, no work has been reported on grafting of AN onto TKP. With a view that grafted TKP may find better applications in comparison with native TKP, the work of graft copolymerization of AN onto TKP was investigated in the presence ceric ammonium nitrate (CAN) as redox initiator and the reaction conditions for graft copolymerization were optimized.

EXPERIMENTAL

Materials and methods

TKP was obtained from M/s Sooraj Trading Co., Kolar Gold Fields, Karnataka, India. CAN, dimethylformamide, and methanol were of laboratory grade (S. D. Fine-Chem., Mumbai, India), nitric acid (AR grade, Ranbaxy Laboratories, India) and AN (Aldrich Chemical Company) were freshly distilled before use. The infrared spectrum of grafted sample was measured in KBr pellets using a JASCO FTIR-5300 spectrophotometer in the range 4000–650 cm^{-1}.

Graft copolymerization

The grafting reaction was carried out under nitrogen atmosphere in a 500 mL, four-necked flask equipped with a reflux condenser, a stirrer, dropping funnel, and a gas inlet system immersed in a constant temperature water bath. In a typical reaction, TKP (0.006–0.025 mol; 1–4 g) was dispersed in a definite volume of water with constant stirring and bubbling of a slow stream of nitrogen for 30 min at the desired temperature (20–40°C). After 30 min, a freshly prepared 10 mL solution of CAN (0.02–0.06 mol, 0.11–0.33 g) in nitric acid (0.1–0.4*N*) was added and stirred for 10 min. Nitrogen gas was continuously passed through the reaction mixture and AN (0.091–0.152 mol, 6–10 mL) was added. In all the reactions, total volume of the reaction was kept constant. The grafting reaction was carried out for varying time intervals (1–4 h). The zero time of the reaction was at the time of monomer addition. After completion of the reaction, the reaction mixture was immediately poured into methanol in the ratio of 1 : 5 of material to liquor for precipitation. The precipitated product was recovered by centrifugation and washed with pure methanol (2 × 50 mL). The crude copolymer thus obtained was dried till constant weight under vacuum (7.6 mm Hg) for 24 h at 40°C. The dried product was extracted with dimethylformamide for 48 h and washed with methanol to remove the homopolymer (polyacrylonitrile). The grafted TKP (TKP-*g*-AN) was dried to a constant weight under vacuum (7.6 mm Hg) for 24 h at 40°C. The percentage grafting (%G) and percentage grafting efficiency (%GE) were determined from the increase in the weight of TKP after grafting in the following manner:

$$\% \text{ G} = \frac{\text{Weight of polymer grafted}}{\text{Initial weight of backbone}} \times 100$$

$$\% \text{ GE} = \frac{\text{Weight of polymer grafted}}{\text{Weight of polymer grafted} + \text{Weight of homopolymer}} \times 100$$

Infrared analysis

The Fourier Transform Infrared Spectrum (FTIR) of grafted samples was measured in KBr pellets using a JASCO FTIR-5300 spectrophotometer in the range 4000–650 cm^{-1}.

Scanning electron microscopy studies

Scanning electron microscopy images at 500 magnifications were obtained for TKP and TKP-*g*-AN using Zeiss EVO 40 EP Scanning Electron Microscope (Cambridge, England). The sample was laid on the aluminum stub using double-sided conducting adhesive tape and was sputter coated with gold.

Thermogravimetric analysis and differential thermogravimetric analysis

Thermogravimetric (TGA) and differential thermogravimetric (DTG) analyses were conducted using a Perkin-Elmer Thermal Gravimetric Analyzer under nitrogen atmosphere at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

CAN has been used extensively as the redox initiator for effecting grafting of a variety of vinyl monomers onto biopolymers viz. guar gum,[14,28,37] cellulose,[38] and chitin.[39] Ce(IV) ion enters into complex formation with biopolymers, and on disproportionation, the complex generates free radicals on the backbone polymer where grafting of the appropriate vinyl monomer can occur. The formation of free radicals in Ce(IV)-treated biopolymers has been confirmed by electron spin resonance.[40] The mechanism by which Ce(IV) interacts with biopolymer to form free radical involves the formation of a coordination complex between the Ce(IV) and the hydroxyl group of biopolymer. The Ce(IV)-biopolymer complex then disproportionates forming a free radical on the biopolymer chain and Ce(III).[40,41]

Evidence for complex formation has been obtained by kinetic and spectrophotometric methods for the oxidation of various alcohols and substrates containing alcohol groups by Ce(IV) ions in perchloric and nitric acids.[42–44] The postulated mechanism has been supported by the model compound studies of Ce(IV) oxidation of monohydric alcohols and 1,2-glycols and suggest that the C_2—C_3 glycol and the C_6 hydroxyl of an anhydro-D-glucose unit may be preferred sites for free-radical generation.[44–46]

The relative rates of oxidation of the C_6 hydroxyl and the C_2—C_3 glycol were examined. Model compounds such as cyclohexanemethanol and tetrahydropyran-2-methanol were used for the C_6 hydroxyl, and *trans*-1,2-cyclohexanediol for C_2—C_3 glycol. The results indicate that diol group oxidized about six times faster than the C_6 hydroxyl. Thus, Ce(IV) oxidation will occur mainly at the C_2—C_3 glycol unit and to some extent at the C_6 primary hydroxyl.[44]

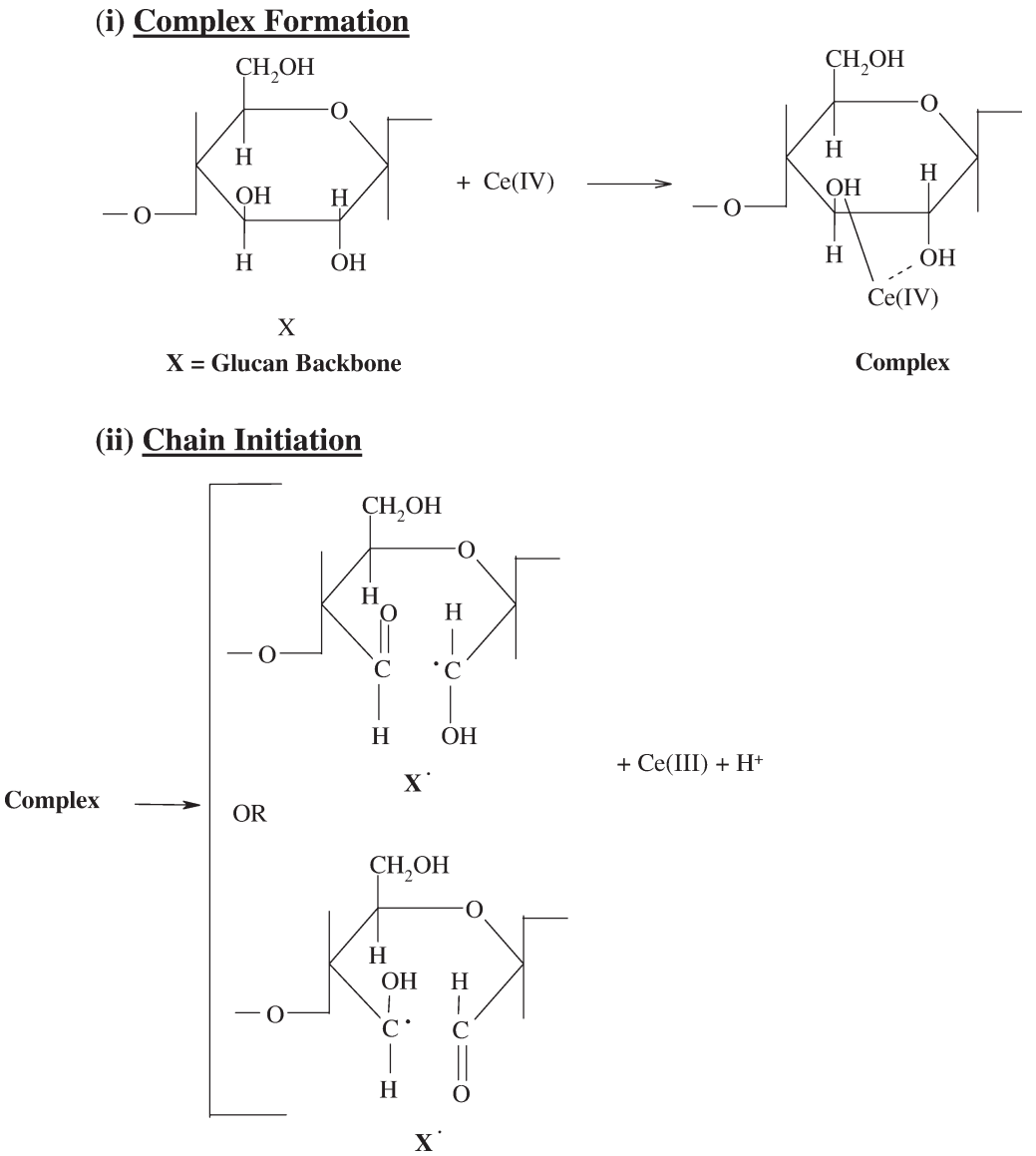
The equilibrium constants for complex formation show that the presence of adjacent hydroxyl groups in the organic substrate causes a substantial increase in the stability of the complex compared with compounds with only one hydroxyl. Thus, the equilibrium constants for *cis*- and *trans*-1,2-cyclohexanediols are considerably larger than that for the monohydric alcohols. The greater stability of the complexes with 1,2-glycols indicate that these compounds form a chelate complex with Ce(IV).[44]

Furthermore, the equilibrium constants for the *cis*- and *trans*-1,2-cyclohexanediols are consistent with chelate complex formation. In the stable conformations of these compounds, the separation of the hydroxyl groups is about the same, and a relatively large Ce(IV) ion 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 the *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.[44]

In view of the above, it is proposed that in the Ce(IV)-initiated graft copolymerization onto TKP, the oxidation reaction of Ce(IV) with TKP will occur preferably at the C_2—C_3 glycol unit and to a lesser extent at the C_6 primary hydroxyl as a result of one electron transfer process. The Ce(IV) ion initially forms a Ce(IV)-xyloglucan complex. This complex is then reduced to Ce(III) ion with the formation of free radical at either C_2 or C_3 on the backbone as shown in Scheme 1.[40] The free radical then reacts with the vinyl monomer, which is present in the reaction mixture to initiate graft copolymerization. The grafting occurs mainly at C_2—C_3 as discussed above. The grafting was also confirmed by the IR spectrum of the grafted sample, which showed an additional sharp absorption band at 2244 cm^{-1} due to —CN stretching confirming the grafting of AN onto TKP (Fig. 7).

Determination of the optimum reaction conditions

To optimize the conditions for grafting of AN onto TKP, the concentration of nitric acid, free-radical



Scheme 1 Grafting mechanism.

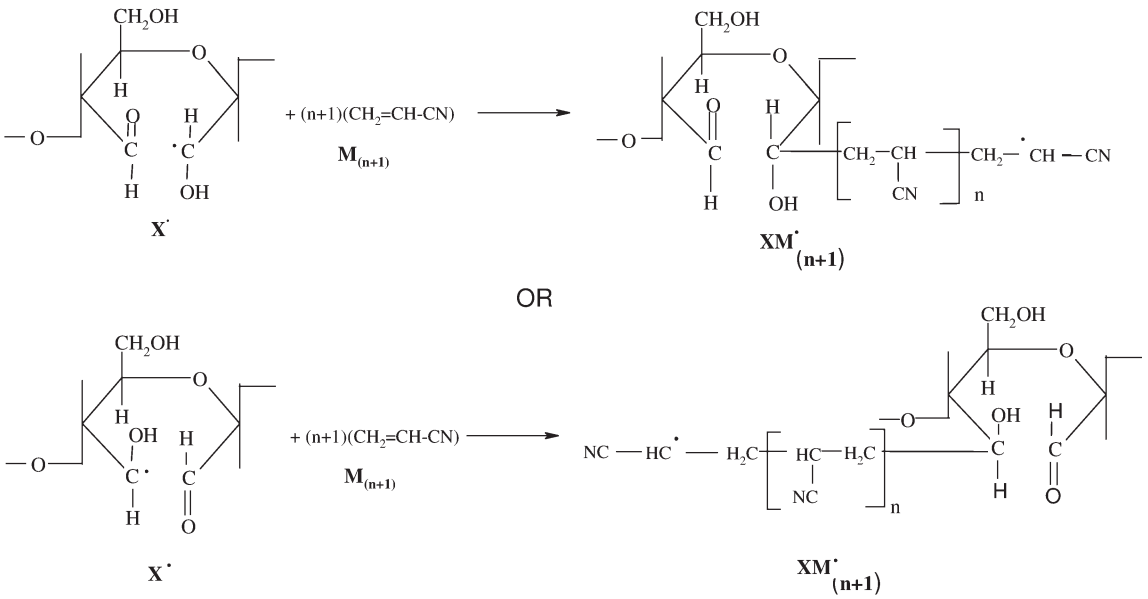
initiator, monomer, TKP, time, and temperature were varied.

Effect of CAN concentration

The effect of variation in CAN concentration on %G and %GE is shown in Figure 1. CAN concentration was varied from 0.02 to 0.06 mol. It is evident from the data that the %G increases with an increase in the initiator concentration, and reaches a maximum value of 70.3% at 0.05 mol of CAN. Further increase in CAN concentration (0.06 mol) is accompanied by a decrease in the %G (65%). The observed increase in %G, with the CAN concentration ranging from 0.02 to 0.05 mol, may be due to the fact that in this concentration range, the increase in concentration of Ce(IV) ion results in an increase in the total number of Ce(IV)-xyloglucan complex that decomposes to give more active sites. Thus, this activation along the backbone is immediately followed by graft copolymerization of monomer onto the backbone. At relatively higher concentration of the initiator, the number of backbone radicals increases. This will enhance the possibility of termination of the backbone radicals before grafting takes place. Furthermore, homopolymer formation at higher initiator concentration competes with the grafting reaction for available monomer thereby leading to a decrease in %G.

Figure 1 also shows a decrease in %GE with increase in the CAN concentration. The fast dissociation of CAN may account for higher %GE in the initial stages, since the total amount of Ce(IV) would be available for initiation. The higher the concentration of Ce(IV), the greater will be the termination of

(iii) Chain propogation



(iv) Chain termination

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

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

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

Scheme 1 (*Continued*)

growing grafted chains, resulting in the reduction of %G as well as %GE.[16,26–28]

Effect of nitric acid concentration

The concentration of nitric acid was varied from 0.1 to 0.4*N*, keeping fixed the concentrations of all other reagents, time, and temperature. The effect of acid concentration on %G and %GE is shown in Figure 2. It is observed that there exists an optimum concentration of nitric acid, which affords maximum percent grafting (71.4%). This corresponds to 0.3*N* in present case.

The role of nitric acid in grafting of AN onto TKP is explained by the fact that ceric ion in water is believed to react in the following manner:

$$Ce^{4+} + H_2O \leftrightarrow [Ce(OH)_3]^{3+} + H^+ \quad (1)$$

$$2[Ce(OH)_3]^{3+} \leftrightarrow [Ce—O—Ce]^{6+} + H_2O \quad (2)$$

Thus, ceric ion exists as $[Ce]^{4+}$, $[Ce\ (OH)_3]^{3+}$, and $[Ce—O—Ce]^{6+}$ in aqueous solution. The concentration of these species is found to vary with the concentration of nitric acid. The %G and %GE increases with increase in acid concentration upto 0.3*N*. This is attributed to the increase in the concentrations of $[Ce(OH)_3]^{3+}$and $[Ce]^{4+}$ at the expense of $[Ce—O—Ce]^{6+}$. Ceric ion $[Ce]^{4+}$ and $[Ce\ (OH)_3]^{3+}$, being smaller in size, are more effective in their ability to form complexes with TKP than $[Ce—O—Ce]^{6+}$. With further increase in acid concentration beyond 0.3*N*, it was observed that %G and %GE decreases. This is explained by the fact that as $[H^+]$ increases, the equilibria, eqs.(1) and (2) shift toward the formation of more and more $[Ce]^{4+}$ and $[Ce\ (OH)_3]^{3+}$. These species, at higher concentration of acid, affect the grafting adversely. Instead of propagating the polymeric chain, these species at higher concentration affect the termination steps, thus lowering the %G and %GE. Moreover, ceric ion has been reported to be involved in oxidative termination of growing monomeric chain as shown in eq. (3).[16,26–28]

$$Ce^{4+} + M_n^{\bullet} \rightarrow Ce^{3+} + M_n + H^+ \quad (3)$$

Thus, nitric acid plays a definite role in promoting grafting of poly(acrylonitrile) onto TKP.

Effect of monomer concentration

The effect of monomer concentration on the grafting yields is represented in Figure 3. It is observed from

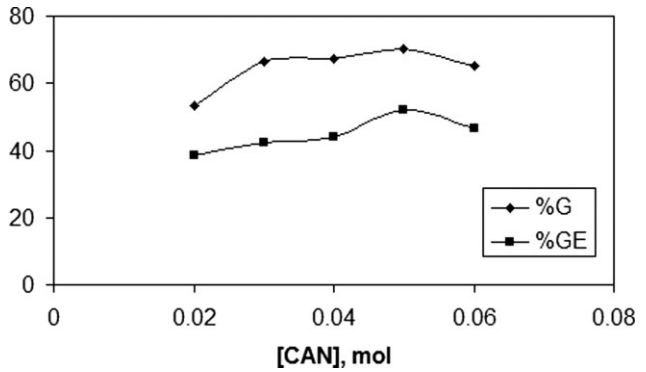


Figure 1 Effect of CAN concentration on %G and %GE. Reaction conditions: [TKP] 0.019 mol; [AN] 0.091 mol; [HNO_3] 0.2*N*; reaction time 3 h; reaction temperature 30°C; total reaction volume 100 mL.

the results that with increase in monomer concentration, %G increases and reaches the maximum value 85% at 0.12 mol. A further increase in monomer concentration leads to decrease in %G and %GE. The enhancement of grafting by increasing the monomer concentration could be ascribed to the greater availability of grafting sites on TKP macroradicals to monomer molecules. However, at higher monomer concentration, i.e., beyond 0.12 mol there is a decrease in %G and %GE. This decrease can be attributed to the higher affinity of AN monomer for its homopolymer (polyacrylonitrile) over the TKP macroradicals. Thus, most of the monomer is preferentially used up in the formation of homopolymer on increasing the AN concentration, which is evident from the rise in viscosity of the reaction medium at higher concentration.[16,26]

Effect of concentration of TKP

The effect of concentration of TKP on %G and %GE was studied by varying the amount of TKP (0.006–0.025 mol) and keeping other variables fixed. It can

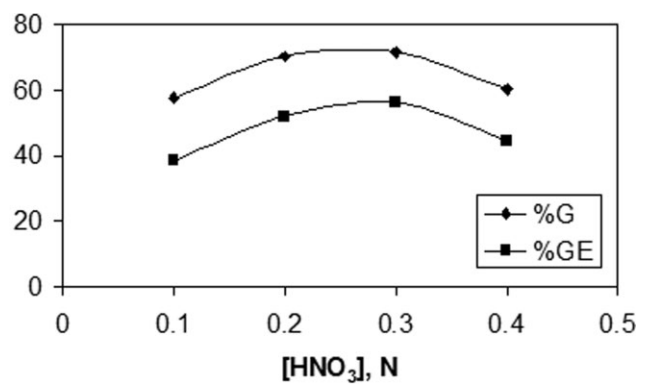


Figure 2 Effect of nitric acid concentration on %G and %GE. Reaction conditions: [TKP] 0.019 mol; [CAN] 0.05 mol; [AN] 0.091 mol; reaction time 3 h; reaction temperature 30°C; total reaction volume 100 mL.

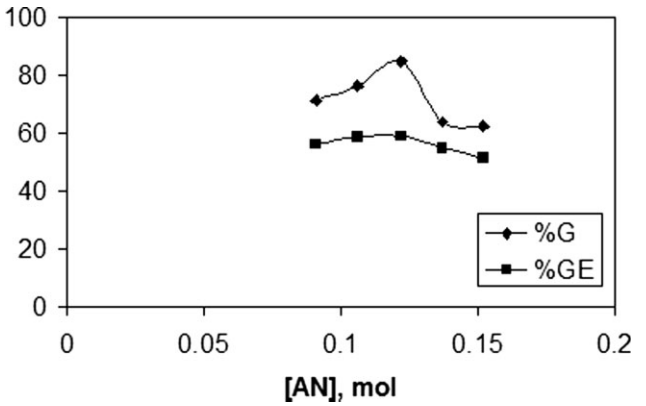


Figure 3 Effect of monomer concentration on %G and %GE. Reaction conditions: [TKP] 0.019 mol; [CAN] 0.05 mol; [HNO_3] 0.3*N*; reaction time 3 h; reaction temperature 30°C; total reaction volume 100 mL.

be seen from Figure 4 that %G and %GE increased initially with an increase in TKP concentration and reached a maximum value (86% and 64%, respectively) at 0.012 mol. With a further increase in TKP concentration, both %G and %GE were found to be decreased. The initial rise may be due to an increase in the reactive sites with increasing concentration of the TKP. The decrease is due 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. Similar results have also been reported in the literature.[16,26–28]

Effect of reaction time

The effect of polymerization time on %G and %GE is shown in Figure 5. It can be seen from Figure 5 that the percent grafting exhibits progressive improvement with the increase in reaction time and showed maximum %G (86%) at 3 h. The effect of

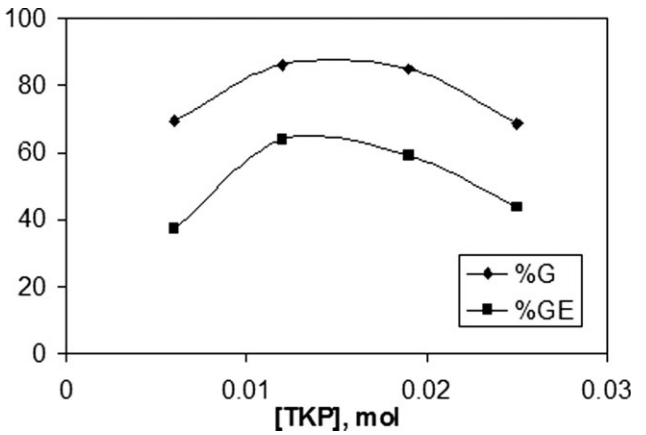


Figure 4 Effect of TKP concentration on %G and %GE. Reaction conditions: [CAN] 0.05 mol; [AN] 0.122 mol; [HNO_3] 0.3*N*; reaction time 3 h; reaction temperature 30°C; total reaction volume 100 mL.

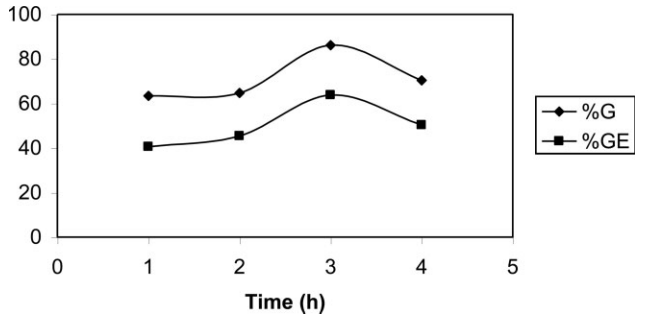


Figure 5 Effect of reaction time on %G and %GE. Reaction conditions: [TKP] 0.012 mol; [CAN] 0.05 mol; [AN] 0.122 mol; [HNO_3] 0.3*N*; reaction temperature 30°C; total reaction volume 100 mL.

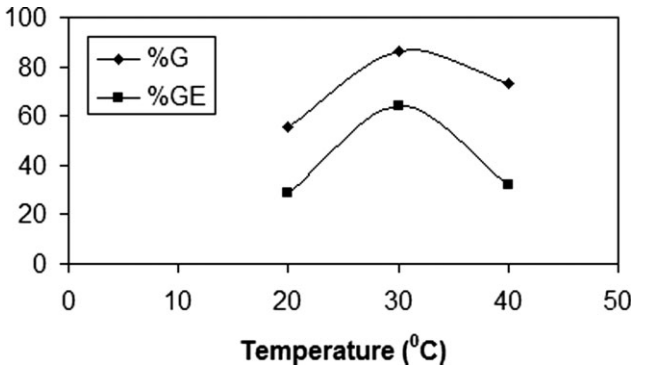


Figure 6 Effect of temperature on %G and %GE. Reaction conditions: [TKP] 0.012 mol; [CAN] 0.05 mol; [AN] 0.122 mol; [HNO_3] 0.3*N*; reaction time 3 h; total reaction volume 100 mL.

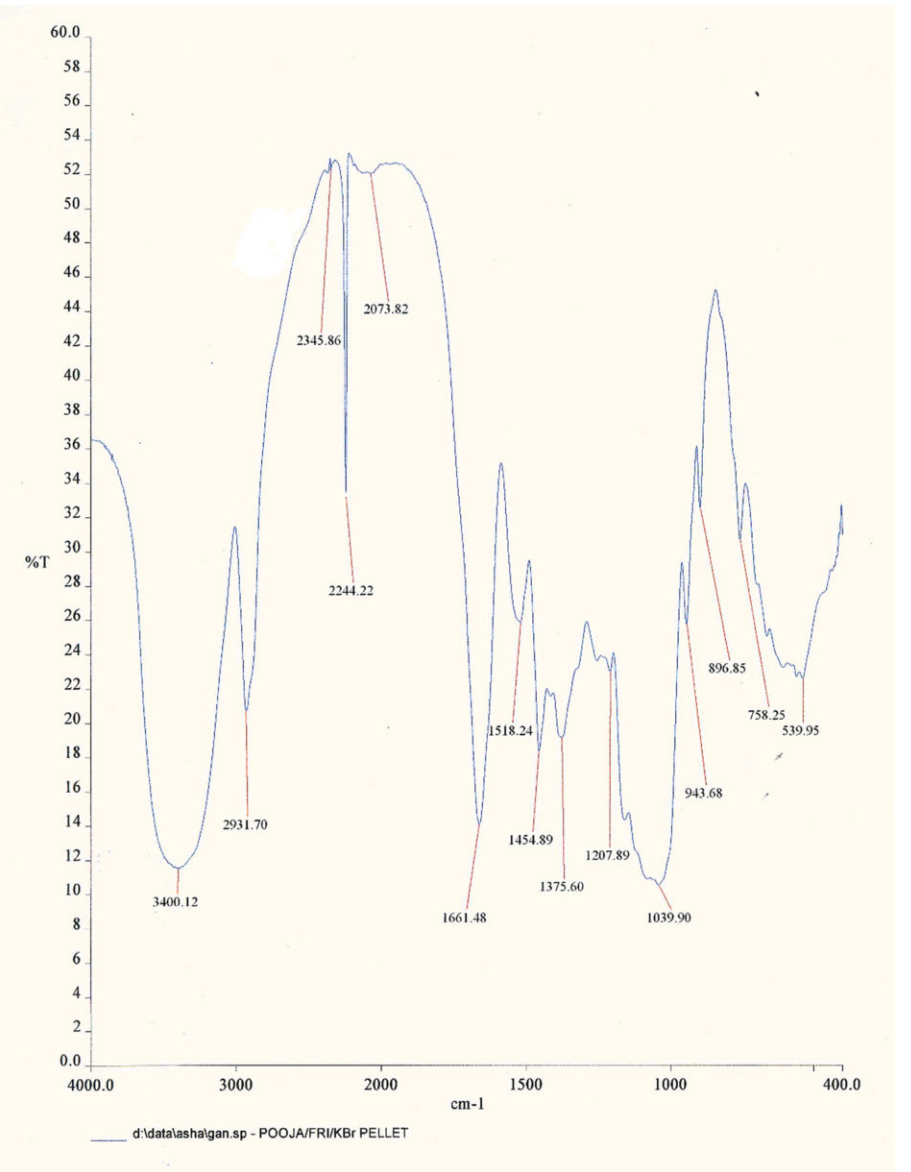


Figure 7 IR spectrum of TKP-*g*-AN [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

time on grafting can be explained by the fact that more the contact time of monomer molecules with the TKP macroradicals sites, the higher will be the grafting, but the decrement in %G and %GE occurs beyond 3 h, which can be rationalized on account of depletion of monomer and initiator concentration with the progress of the reaction. Further, with an increase in the reaction time, mutual annihilation of growing grafted chains also occurs and leads to a decrease in %G and %GE.[16,26–28]

Effect of temperature

The graft copolymerization of AN onto TKP has been studied at different temperatures (20–40°C), keeping other variables constant. The effect of temperature on %G and %GE is shown in Figure 6. It is seen from Figure 6 that the %G as well as %GE increases with the increase in temperature from 20 to 30°C, but decreases with further increase in temperature. The maximum %G (86) was obtained at 30°C. The dependence of %G on temperature can be ascribed to the enhancement of the rate of diffusion of monomer. Increase in temperature beyond the optimum temperature (30°C in this case) leads to the graft copolymerization with poor selectivity, and various hydrogen abstraction and chain transfer reactions might be accelerated, leading to the decrease in %G and %GE.

Further at higher temperature, there may also be the acceleration of the termination process, which leads to the formation of more homopolymer. Similar results have been reported in the literature.[16,26–28]

IR characterization

The IR spectrum of the grafted samples showed an additional sharp absorption band at 2244 cm^{-1} due to $-C\equiv N$ stretching, thereby confirming the grafting of AN onto TKP (Fig. 7).

Surface morphology

Scanning electron micrograph of TKP [Fig. 8(a)] clearly exhibits the polysaccharide nature having varied particle sizes with rough surface. Even the polysaccharide seems completely scattered alongwith larger particles. A change in contour of the polysaccharide on grafting and the thick polymeric coating of AN on their surface alongwith grafting of AN such that all the gap between polysaccharide particles have been closed indicate the effect of grafting [Fig. 8(b)]. It can be seen that individual polysaccharide molecules of TKP have joined through these surface coatings during grafting process.

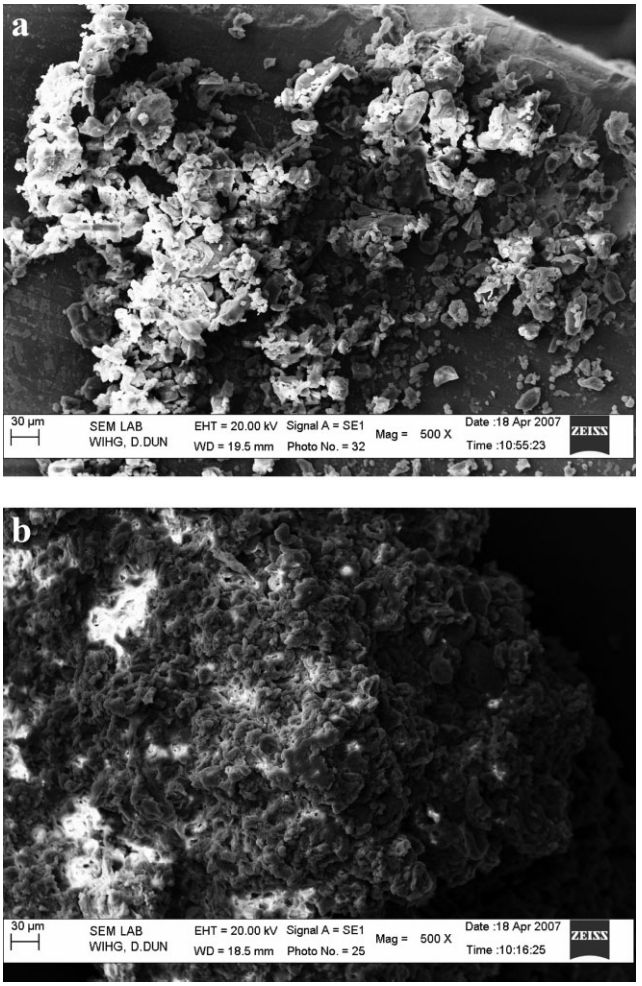


Figure 8 a) Scanning electron micrographs at 500 magnification of TKP. (b) Scanning electron micrographs at 500 magnification of TKP-*g*-AN.

Thermal characterization

Understanding the behavior of TKP-*g*-AN under the influence of thermal load is important to study its properties for different applications. DTG and TGA were used to study the thermal properties of native TKP and its grafted derivative.

The thermal stability of TKP and TKP-*g*-AN can be compared on the basis of the onset temperature of decomposition, % weight loss for the different stages of decomposition, and the % weight residue at maximum temperature of decomposition. Figure 9(a,b) shows the primary thermogram (TG) and derivatogram (DTG) for TKP and TKP-*g*-AN, respectively.

Pure TKP [Fig. 9(a)] shows characteristic three-step thermogram. The first stage is from 24 to 100°C, which has initial weight 100% at 24°C. At 100°C the weight is 93%, indicating a weight loss of 7%. The initial loss in weight (7%) is merely due to evaporation of absorbed moisture. The rapid decomposition

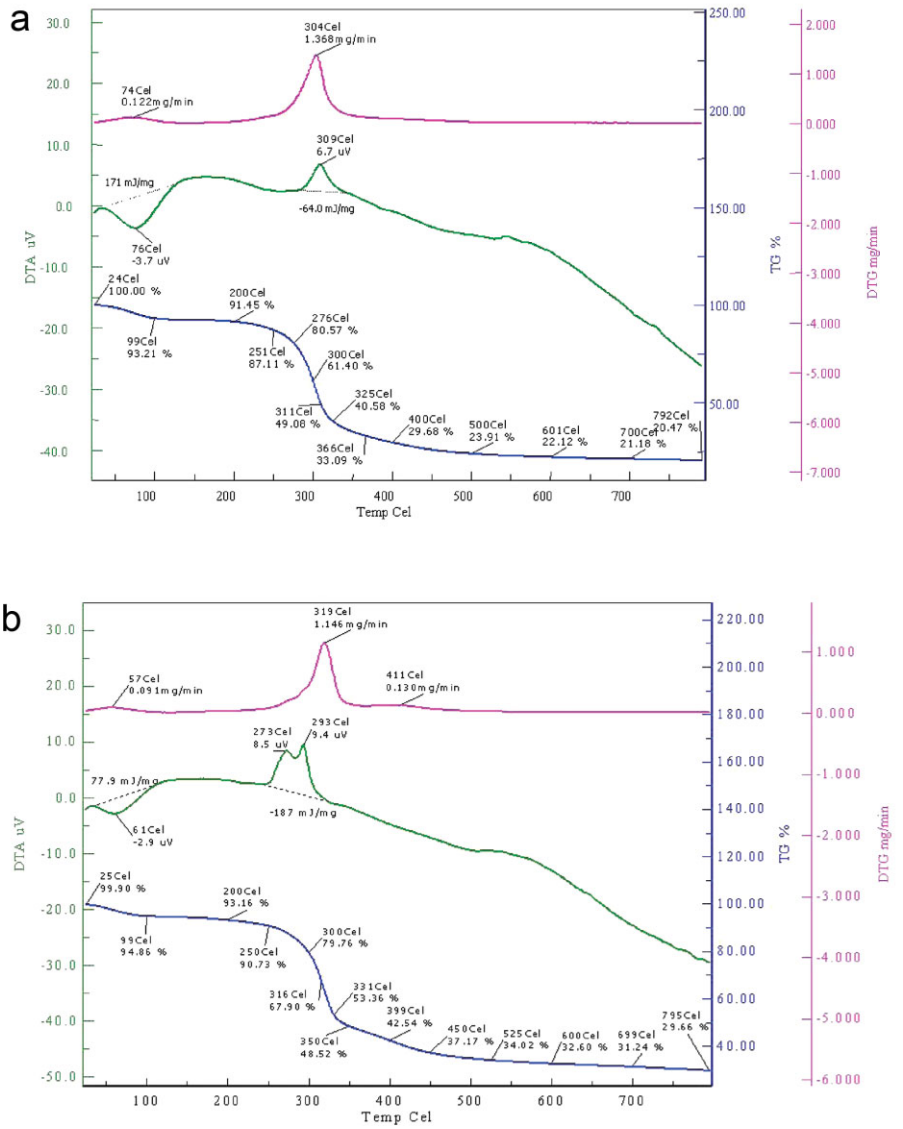


Figure 9 a) TGA and DTG curves of TKP. (b) TGA and DTG curves of TKP-*g*-AN [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

occurs in second stage (251–325°C) resulting in the onset of major weight loss of about 47% at 251°C (T_o) and T_{max} = 325°C due to the degradation of TKP. The DTG clearly exhibits the temperature for maximum decomposition for this stage at 304°C. The final stage of decomposition (400–800°C) is due to the formation and evaporation of some volatile compounds, hence is rather slow and results in about 10% weight loss. A char yield of 21.18% was observed at 700°C and 20.47% at 800°C.

Figure 9(b) shows four-stage decomposition pattern between 25 and 800°C. The first stage (25–100°C) is due to loss of moisture showing about 6% weight loss, while 42.2% loss occurs in second stage of decomposition in the temperature range of 250–350°C due to degradation of grafted copolymer (TKP-*g*-AN). The DTG clearly exhibits the temperature for maximum decomposition for this stage at 319°C. The third stage from 399 to 450°C during which there was 5.37% weight loss may contribute to the decomposition of different structure of TKP-*g*-AN. Below 450°C, the copolymer had low weight loss than TKP. The char yield of 31.24% was obtained at 700°C and 29.66% at 800°C. Thus, TKP-*g*-AN has overall high thermal stability than pure TKP.

CONCLUSION

The graft copolymerization of AN onto TKP in aqueous medium was initiated effectively with CAN. The reaction conditions were optimized for grafting of AN onto TKP by varying the concentration of TKP, CAN, AN, HNO_3, polymerization time, and reaction temperature. The characterization of the grafted products by means of FTIR, scanning electron

microscopy, and thermal analysis furnished evidence of grafting of AN onto TKP. TKP-*g*-AN has overall high thermal stability than pure TKP.

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