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Carbohydrate Polymers 60 (2005) 117–125

Carbohydrate Polymers

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Ceric-induced grafting of acrylonitrile onto sodium salt of partially carboxymethylated guar gum

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Received 5 April 2004; revised 18 November 2004; accepted 30 November 2004
Available online 28 January 2005

Abstract

The optimum reaction conditions for affording maximum percentage of grafting have been established in the case of grafting of acrylonitrile (AN) onto Na-PCMGG ($\overline{\mathrm{DS}} = 0.497$) using ceric ammonium nitrate (CAN) as a redox initiator, in an aqueous medium, by successively varying reaction conditions such as concentrations of nitric acid, ceric ammonium nitrate, monomer (AN) as well as reaction time, temperature and amount of substrate. The influence of these reaction conditions on the grafting yields have been discussed. The overall activation energy of grafting has been calculated. The IR-spectroscopic, thermal (TGA/DSC) and scanning electron microscopic (SEM) techniques have been used for the characterization of the graft copolymer.

Keywords: Sodium salt of partially carboxymethylated guar gum; Graft copolymerization; Acrylonitrile; Optimized reaction conditions; The overall activation energy of grafting (E_g); IR; TGA; DSC; SEM

1. Introduction

Considerable interests have been shown on the chemical modification of natural macromolecules for imparting desirable properties onto them. In recent years, chemical modification of natural polymers through grafting has received considerable attention and has made paramount contribution towards better industrial and biomedical applications. In previous papers, we reported ceric-induced (Shah, Patel, & Trivedi, 1992, 1993) and Fenton's reagent initiated (Shah, Patel, & Trivedi, 1994a,b) grafting of acrylonitrile onto sodium alginate (SA) and investigated the biodegradable behaviour of SA graft acrylonitrile by studying its interactions with various microorganisms (Shah, Ramesh, Patel, & Trivedi, 1994c). We have also grafted ethyl acrylate (Shah, Patel, & Trivedi, 1994d), methyl acrylate (MA) and methyl methacrylate (MMA) (Shah, Patel, & Trivedi, 1995) onto SA in the presence of Ce^{+4} and studied the thermal behaviour of the graft copolymers (Shah, Patel, & Trivedi, 1996). We have also reported ceric-induced grafting of methyl acrylate onto sodium salt of partially carboxymethylated sodium alginate (Patel, Patel, & Trivedi, 1999) and synthesis, characterization and evaluation of sodium salt of partially carboxymethylated starch graft poly(methyl methacrylate) copolymers as a New Biodegradable Plastics (Rex, Datta, & Trivedi, 2002) as well as the evaluation of the graft copolymers of Agar for sustained release of Diclofenac sodium from tablet (Umatt, Patel, & Trivedi, 2001).

In the present investigation we have modified Guar Gum (GG), a naturally occurring plant-derived polysaccharide of great commercial importance, by carboxymethylation, as the derivatization enhances the behaviour of GG toward grafting due to the combined influence of the following factors: (a) carboxymethyl groups increase the swellability of GG, thereby facilitating diffusion of the monomer and initiator, and (b) the ionization of carboxyl groups along the guar gum chains introduces negative charges which attract ceric ions to the GG molecules leading to the formation of more active sites, available for the monomer, thus increasing the reactivity of GG.

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doi:10.1016/j.carbpol.2004.11.027

Literature survey reveals that recently a good amount of work on grafting of various vinyl monomers onto guar gum using different initiating systems has been carried out (Chowdhary, Samui, Kundu, & Nandi, 2001; Kamel, El-Thalouth, & Abd, 2000; Kunj, Taunk, & Tripathi, 1999; Kunj, Taunk, Tripathi, & Kumar, 2000; Kunj, Kumar, Tripathi, & Pandey, 2001; Taunk, 2000). However, the data on the grafting of vinyl monomers onto sodium salt of partially carboxymethylated guar gum are scanty. As a part of our research programme, we have therefore successfully carried out the modification of sodium salt of partially carboxymethylated guar gum (Na-PCMGG, $\overline{\mathrm{DS}}=0.497$) by graft copolymerization with methyl acrylate (MA) (Trivedi, Kiran, Patel, & Trivedi, 2004a), methyl methacrylate (MMA) (Trivedi, Kiran, Patel, & Trivedi, 2004b), ethyl methacrylate (EMA) (Trivedi, Kiran, Patel, & Trivedi, 2004c) using ceric ammonium nitrate (CAN) as a redox initiator as well as using CAN as a Photoinitiator (Thaker & Trivedi et al.,2004 a,b). Recently, we have also compared the reactivity of different vinyl monomers towards grafting (Trivedi, Kiran, Patel, & Trivedi, 2004d) and studied the effects of substrate structure and liquor ratio on percent grafting (Trivedi, Kiran, Patel, & Trivedi, 2004e) using the optimum reaction conditions established for affording maximum percentage of grafting of different vinyl monomers onto Na-PCMGG ($\overline{\mathrm{DS}}=0.497$).

This paper presents the results of the evaluation of the optimized reaction conditions of grafting of acrylonitrile onto the sodium salt of partially carboxymethylated guar gum (Na-PCMGG) by using the tetravalent cerium ion as well as the characterization of the graft copolymer by using different techniques. The studies on the potential application of the graft copolymer (Na-PCMGG-g-PAN) as super absorbent is in progress and the results will be published elsewhere.

2. Experimental

2.1. Materials

Guar gum (GG) was kindly supplied by H.B. Gum Industries Pvt. Ltd; Kalol (Gujarat/India). The method of preparation and purification, as well as the measurement of degree of substitution ($\overline{\mathrm{DS}}$) of the sodium salt of partially carboxymethylated guar gum (Na-PCMGG) were followed as described earlier (Joshi, Sinha, Patel, & Trivedi, 1995; Trivedi, Patel, & Patel, 1978). The $\overline{\mathrm{DS}}$ of Na-PCMGG was found to be 0.497. AN (Samir Tech. Chem.) was distilled out at atmospheric pressure and the middle fraction was collected and used. CAN of reagent grade (Chiti Chem; Baroda) was used as received. Analar grade nitric acid was used. Fresh solutions of the initiator were used, made by dissolving the required amount of CAN in nitric acid. All other reagents and solvents used in the present work were of reagent grade. N_2 gas was purified by passing through fresh pyrogallol solution. Deionized water was used for the preparation of solutions as well as for polymerization reactions.

2.2. Graft copolymerization

A 500 ml three-necked flask equipped with mechanical stirrer, a reflux condenser and a glass inlet system was immersed in constant temperature bath for grafting reactions. In a typical reaction, varying amount (0.5×10^{-3}–3.0×10^{-3} kg, dry basis) of Na-PCMGG ($\overline{\mathrm{DS}}=0.497$) was dissolved in low conductivity water (100 ml) with constant stirring and bubbling a slow stream of nitrogen for 1 h at the desired temperature (20–45 °C). Freshly prepared 10 ml solution of CAN (2.5×10^{-3}–8.0×10^{-2} M) in nitric acid (nil to 1.0 M) was added and stirred for 20 min. Nitrogen gas was continuously passed through the reaction solution and freshly distilled AN (0.037–0.370 M) was added. The grafting reactions were carried out for varying time intervals (0.5–10 h). After completion of the reaction, the mixture was immediately poured into excess of methanol to precipitate out the polymer. The crude copolymer product was filtered, repeatedly washed with nitric acid as well as 90% methanol and finally washed with pure methanol. The crude copolymer thus obtained was dried under vacuum at 40 °C. The homopolymer poly (acrylonitrile) (PAN) was separated from the crude graft copolymer by extraction with dimethyl formamide for 48 h. After complete removal of the homopolymer, the pure graft copolymer was dried at 40 °C under vacuum to a constant weight.

The percentage of grafting (%G), percentage of grafting efficiency (%GE) as well as rates of polymerization (R_P), graft copolymerization (R_g) and homopolymerization (R_h) were evaluated by using expressions as mentioned earlier (Vijaykumar, Reddy, & Joseph, 1985).

2.3. IR spectra

IR spectra of Guar Gum, Na-PCMGG ($\overline{\mathrm{DS}}=0.497$), Na-PCMGG-g-PAN and PAN were taken in KBr pellets using Nicolet impact 400D Fourier Transform Infra Red Spectophotometer.

2.4. Thermogravimetric analysis (TGA)

The thermal behaviour of Guar Gum, Na-PCMGG ($\overline{\mathrm{DS}}=0.497$), Na-PCMGG-g-PAN and PAN has been examined in an inert atmosphere at a heating rate of 10 °C/min with the help of the Dupont 951 thermogravimetric analyzer.

2.5. Differential scanning calorimetry (DSC)

The DSC scans of Guar Gum, Na-PCMGG ($\overline{\mathrm{DS}}=0.497$), Na-PCMGG-g-PAN and PAN have been recorded in nitrogen atmosphere at a scan rate of 10 °C/min on DSC 2920 TA instrument.

2.6. Scanning electron microscopy (SEM)

Model ESEM TMP+EDAX, Philips make has been used to obtain the micrographs of Guar Gum, Na-PCMGG ($\overline{DS}=0.497$) and Na-PCMGG-g-PAN.

3. Results and discussion

3.1. Determination of optimum reaction conditions

In order to optimize the conditions for grafting, the amount of Na-PCMGG, concentrations of monomer (AN), initiator (CAN), nitric acid and also temperature and time were varied.

3.1.1. Effect of amount of Na-PCMGG

The influence of varying amount of Na-PCMGG on %G as well as %GE is shown in Fig. 1. It can be observed from this figure that, with the backbone concentration range studied, %G consistently decreases by increasing the amount of Na-PCMGG but %GE remains almost constant over the full range of Na-PCMGG content studied. The results of this figure can be explained on the basis of the fact that although the weight of the grafted side chains may increase with the increase in Na-PCMGG concentration, the decrease in the monomer-to-backbone ratio lowers %G. Secondly, high Na-PCMGG macroradicals, which can interact with each other to terminate the reaction as a result of Na-PCMGG $\times 10^3$ kg which the termination rate of graft copolymerization becomes faster than the rate of initiation thereby also lowering %G. Similar results are also reported in the case of grafting of butyl acrylate onto gelatin (Chong, Fong, Fu, Huang, & Lian, 1988), methyl methacrylate onto jute fibre (Nayak, Das, & Singh, 1991) and ethyl methacrylate onto polyvinyl alcohol (Chowdhury et al., 1998).

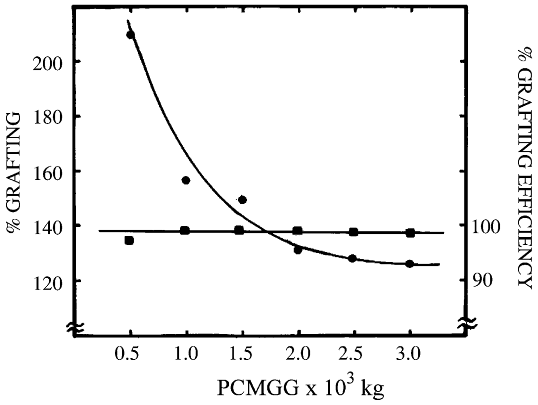

Fig. 1. Influence of amount of sodium salt of partially carboxymethylated guar gum (Na-PCMGG) on: (●) % G; or (■) % GE.

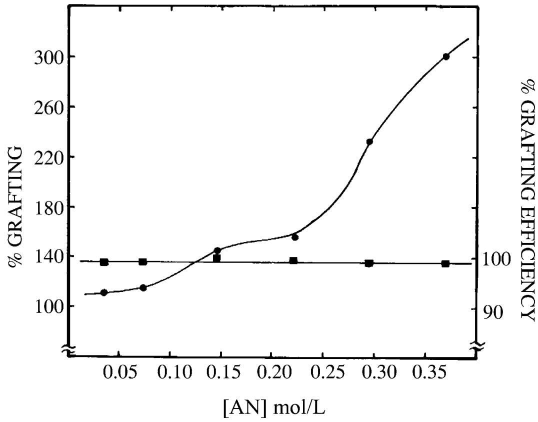

Fig. 2. Effect of acrylonitrile (AN) concentration on: (●) % G; or (■) % GE.

3.1.2. Effect of monomer concentration

Fig. 2 represents the influence of monomer (AN) concentration on the grafting yields. It is interesting to note from this figure that there is a marked increase in %G with increase in monomer concentration. The probable explanation for this finding might be due to the following: (i) with increasing monomer (AN) concentration, the complexation between Ce^{+4} and monomer is enhanced, (ii) gel effect (Lenka, Nayak, & Mishra, 1980) i.e. increase in viscosity of the medium owing to the solubility of PAN in its own monomer, which could be more pronounced with increase of monomer concentration. This hinders termination particularly by coupling (bimolecular termination) of growing polymer chains, whereas the other steps in the graft polymerization process viz. initiation, propagation and radical chain processes are not affected in the same degree by increasing viscosity because the mobility of the grafted polymer chains is restricted by the Na-PCMGG structure. In addition, the gel effect also causes swelling of Na-PCMGG, thus facilitating the diffusion of monomer to the growing chains and active sites on the backbone, thereby enhancing grafting, (iii) at higher monomer concentration, a large amount of the growing polymeric chains that are formed are involved in generating additional active sites onto Na-PCMGG by the chain transfer reaction, and (iv) the molecular weight of the grafts increase with increasing monomer concentrations.

The influence of monomer concentration onto R_p, R_g and R_h is shown in Figs. 3 and 4. It can be observed from Fig. 3 that an increase in monomer concentration in the system increases the rate of polymerization (R_p). Thus, observed increase in R_p may be due to either in the rate of graft copolymerization (R_g) or the rate of homopolymerization (R_h) or both. This is evidenced by the increase in the rate of graft copolymerization (R_g) (cf. Fig. 4). However, grafting efficiency (%GE) remains steady (cf. Fig. 2) with increasing monomer concentration showing that even where %G and R_g are increased, they have not contributed to a progressive increase in %GE. This may be due to the grafted chains acting as diffusion barriers, which may impede diffusion of

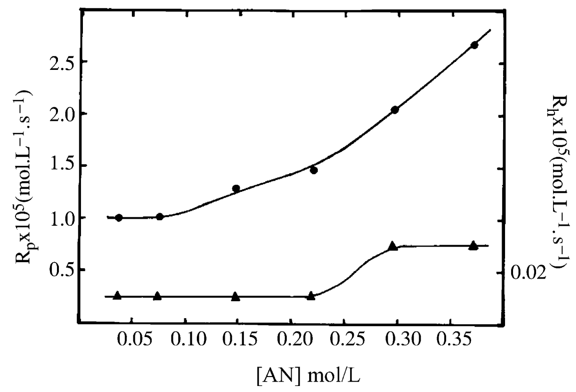

Fig. 3. Effect of acrylonitrile (AN) concentration on: (●) $R_p \times 10^5$; or (▲) $R_h \times 10^5$.

monomer into the backbone. As a result, less monomer would be available for grafting and more of it may be used for homopolymerization. Similar results are also reported in the literature (AbouZeid, Anwar, & Hebeish, 1982; Hebeish, Kantouch, Khalil, & El-Rafie, 1973; Ghosh et al., 1983, Leza et al., 1988).

3.1.3. *Effect of initiator concentration*

The effect of the concentration of Ce^{+4} ion on the grafting yields is shown in Fig. 5. It can be seen from this figure that with increasing ceric-ion concentration, %G increases and reaches a maximum value of 291.75% at $[Ce^{+4}] = 0.05$ mol/L, however, with further increase in $[Ce^{+4}]$, the value of %G decreases. On the other hand, %GE increases in the beginning upto $[Ce^{+4}] = 0.013$ mol/L beyond which it decreases slowly with further increase in $[Ce^{+4}]$, as observed from Fig. 5. Thus, the observed increase in %G within the CAN concentration range of 0.0025–0.05 mol/L may be interpreted on the basis of the fact that the increasing concentration of ceric-ions results in an increase in the total number of the complex Na-PCMGG-ceric ions which decompose to give more active sites. Thus this activation along the backbone which has taken place is immediately followed by the graft copolymerization of AN onto the Na-PCMGG backbone.

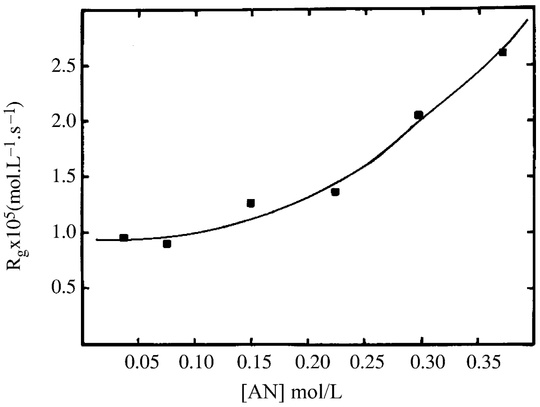

Fig. 4. Effect of acrylonitrile (AN) concentration on: (■) $R_g \times 10^5$.

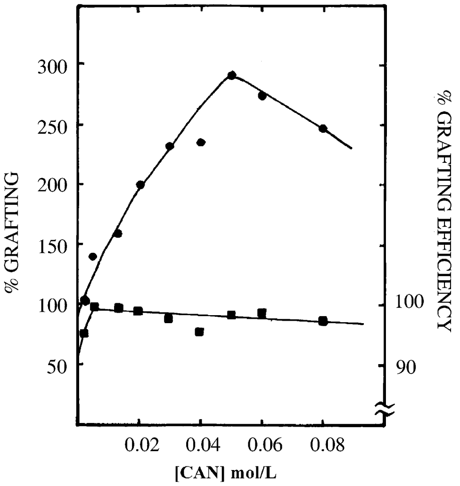

Fig. 5. Effect of ceric ammonium nitrate (CAN) concentration on: (●) % G; or (■) % GE.

The observed decrease in %G as well as %GE at higher concentration of the initiator may be due to the efficiency of Ce^{+4} to take part in the termination of growing grafted chains. Secondly, at higher ceric ion concentration, the complex formation between the monomer and ceric ions assumes predominance over that between Na-PCMGG and ceric-ion. This would favour the formation of homopolymer at the cost of grafting. Similar results are also reported in the case of grafting of allyl methacrylate onto cotton cellulose (El-Alfty, Khalil, & Hebeish, 1981), methyl methacrylate onto starch (Egboh et al., 1988) and ethyl acrylate onto sodium alginate (Shah et al., 1994d).

3.1.4. *Effect of nitric acid concentration*

Fig. 6 shows the dependence of percent grafting as well as percent grafting efficiency on the nitric acid concentration. It is quite interesting to note from this figure that at zero concentration of acid, very high value of %G is observed which may be attributed to the fact that, even in absence of acid, in an aqueous medium Na-PCMGG swells to a greater extent which makes the functional groups of Na-PCMGG more accessible towards grafting. However, it

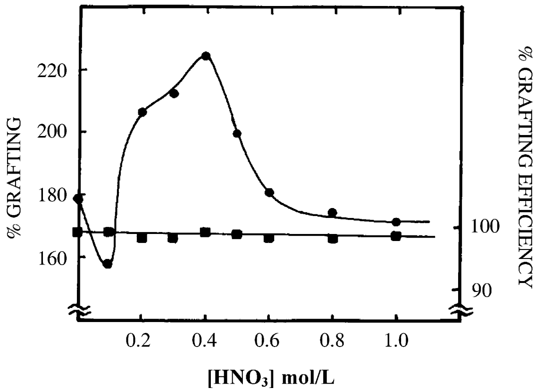

Fig. 6. Effect of nitric acid concentration on: (●) % G; or (■) % GE.

is observed that there exists an optimum concentration of nitric acid (0.40 mol/L) which affords maximum percent grafting. Beyond this concentration of nitric acid, %G decreases and reaching value, which is even, lower than in the absence of the acid. The initial increase in grafting with an increase in acid concentration may be due to a decrease in the termination rate of the growing polymer chain, or an increase in the initiation rate. However, beyond the optimum concentration of acid, the decrease in %G could be attributed to a corresponding reduction in ceric-Na-PCMGG complex formation, as well as an increase in termination rates. Rao et al., (1969) and Shah et al. (1992) have made similar observations.

3.1.5. *Effect of temperature*

Fig. 7 shows the influence of temperature on %G and %GE. It can be seen from this figure that %G increases with rise of temperature from 20 to 30 °C but decreases with further increase in temperature. The value of %GE remains almost constant initially upto about 30 °C and then decreases with further increase in temperature.

The observed increase in %G with temperature can be interpreted in terms of the favourable influence of temperature on: (i) the faster decomposition of Na-PCMGG-Ceric complex so that more active sites are generated on the Na-PCMGG chains, (ii) the swellability of Na-PCMGG, (iii) the solubility of monomer molecules, (iv) the diffusion and mobility of the monomer from the aqueous phase to the Na-PCMGG backbone and (v) the rates of initiation and propagation of grafting.

The observed decrease in %G beyond 30 °C can be ascribed to the fact that at higher temperature graft copolymerization occurs with poor selectivity. In addition, various hydrogen abstraction and chain transfer reactions also might be accelerated at higher temperature leading to the decrease of percent grafting. The decrease in %GE, as can be seen from this figure may be attributed to the solubility of AN in the aqueous phase at higher temperatures, thus increasing the possibility of the monomer to contact Ce^{+4}, hence more Ce^{+4} will be available to initiate the homopolymerization. Similar results are also reported in the literature (Leza, Casions, & Guzman, 1989; Shah et al., 1994d; Vijaykumar et al., 1985).

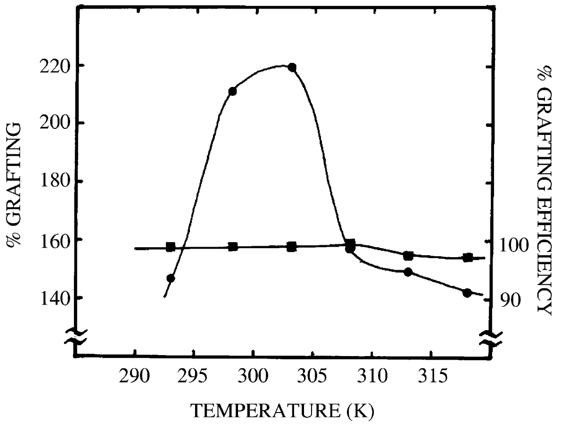

Fig. 7. Influence of reaction temperature on: (●) % G; or (■) % GE.

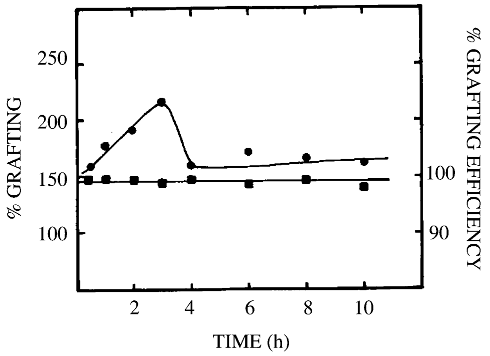

Fig. 8. Influence of reaction time on: (●) % G; or (■) % GE.

3.1.6. *Effect of reaction time*

The influence of reaction time on the grating yields is shown in Fig. 8. It is interesting to note from this figure that a value of 159% has been obtained for %G in the first half an hour only. However, %G further increases upto a maximum of 216.33% within 3 h. The initial increase in %G is due to the increase in the number of grafting sites on the Na-PCMGG backbone as reaction progresses. But beyond 3 h, the decrease in %G is due to the depletion in monomer and initiator concentration as well as shortage of the available grafting sites. However, %GE does not change appreciably during the course of the reaction indicating that after optimum grafting, all the sites are occupied and no more active sites are formed. Similar results are also reported by Shah et al. (1994d) in the case of grafting of ethyl acrylate onto sodium alginate.

Thus, from the above discussion the optimized reaction conditions obtained in the graft copolymerization of AN are: Na-PCMSA, $\overline{DS}=0.497)=0.5\times10^{-3}$ kg (dry basis); $[AN]=0.147\ mol\ L^{-1}$; $[CAN]=0.05\ mol\ L^{-1}$; $[HNO_3]=0.40\ mol\ L^{-1}$; Temp. = 30 °C; Time = 3 h; Volume of water = 139.27 mL; and Total volume = 150 mL.

3.2. *Evaluation of energy of activation*

The natural log of % grafting (ln %G) versus 1/*T* is plotted for the initial portion of the curve, i.e. 20–30 °C (cf. Fig. 7) as shown in Fig. 9 and these values are found to fall on a straight line as is evident from this figure. The least square value of the overall activation energy of grafting (E_g) is calculated from the results of Fig. 9 and is found to be 30.29 kJ/mol. Leza et al. (1989) have calculated similarly the overall activation energy to be 8.70 kJ/mol in the case of grafting of 4-vinyl pyridine (4-VP) onto cotton and 32.60 kJ/mol in the case of partially carboxymethylated cotton (PCMC) using ceric ammonium nitrate as an initiator. Mc Dowall, Gupta, and Stanett (1982) have also grafted acrylic acid onto rayon filaments using ceric

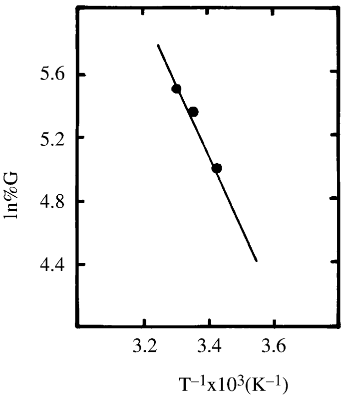

Fig. 9. Plot of natural log of percentage grafting versus T^{-1}.

ammonium sulfate as initiator and the activation energy calculated was 38 kJ/mol. Gita Patel et al. (1999) have also reported $E_g = 32.29$ kJ/mol in the case of grafting of methyl acrylate onto sodium salt of partially carboxymethylated sodium alginate (Na-PCMSA, $\overline{DS} = 1.625$).

3.3. Evidence of grafting

3.3.1. IR-spectra

Fig. 10 shows the IR spectrum of Guar Gum. The presence of a very strong and broad absorption band at ~3415 cm^{-1} is assigned to OH stretching. Reasonably sharp absorption band ~2930 cm^{-1} may be attributed to the –CH stretching. The absorption band appeared at ~1650 cm^{-1} is due to hydration of water. The –CH$_2$ bending in GG is assigned to an absorption at ~1440 cm^{-1} and the frequency at ~1380 cm^{-1} is attributed to CH bending. The bending of OH is probably distributed at ~1300 and ~1250 cm^{-1} frequencies.

The IR spectrum of Na-PCMGG ($\overline{DS} = 0.497$) (Fig. 11) shows somewhat reduced intensity of the absorption at ~3408 cm^{-1}, due to OH stretching, indicating that some of the OH groups present in GG sample are involved in carboxymethylation. The presence of a band at ~2930 cm^{-1} is due to –CH stretching. The band due to water (bending of water) appeared at ~1650 cm^{-1} in GG sample (cf. Fig. 10) is absent in the Na-PCMGG sample. The asymmetric and symmetric vibrations due to moiety are assigned to 1615–1427 cm^{-1}, respectively. This can be attributed to the incorporation of carboxymethyl groups in guar gum. In the GG sample the –CH$_2$ bending was assigned to ~1440 cm^{-1} (cf.. Fig. 10). On the other hand in the case of Na-PCMGG sample (Fig. 11) the band appeared at ~1427 cm^{-1} is a split band and one of them may be assigned to bending of –CH$_2$.

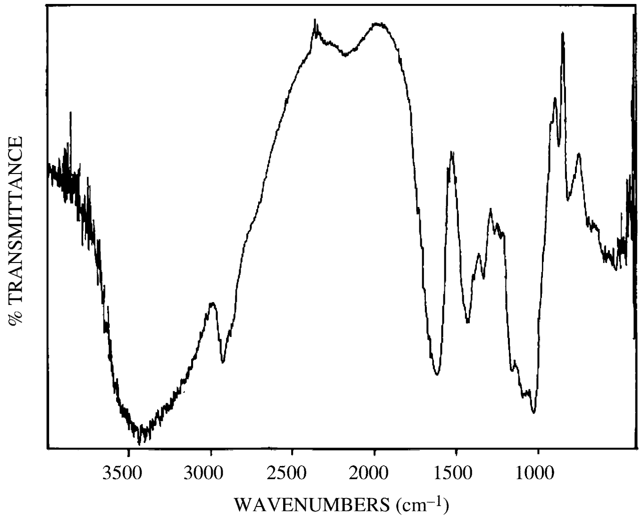

Fig. 11. IR spectrum of Na-PCMGG ($\overline{DS} = 0.497$) sample.

Figs. 12 and 13 show the IR spectra of Na-PCMGG-g-PAN and PAN (isolated by hydrolysis method) samples, respectively.

The spectra of the graft copolymer (Fig. 12) showed absorption bands of Na-PCMGG ($\overline{DS} = 0.497$) (Fig. 11) as well as an additional band at ~2247 cm^{-1}, which has been

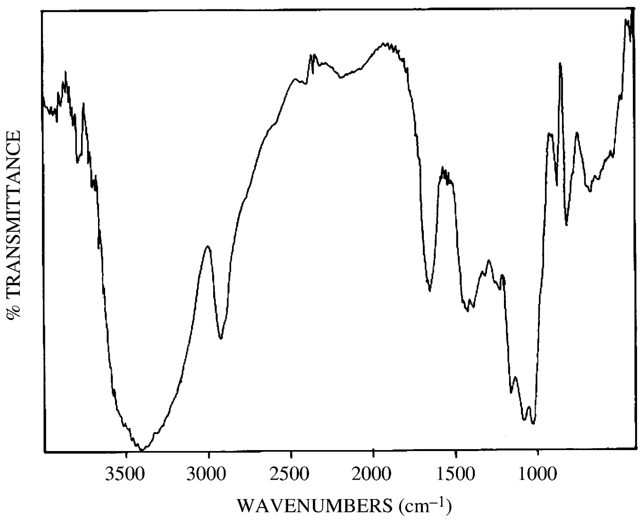

Fig. 10. IR spectrum of Guar Gum sample.

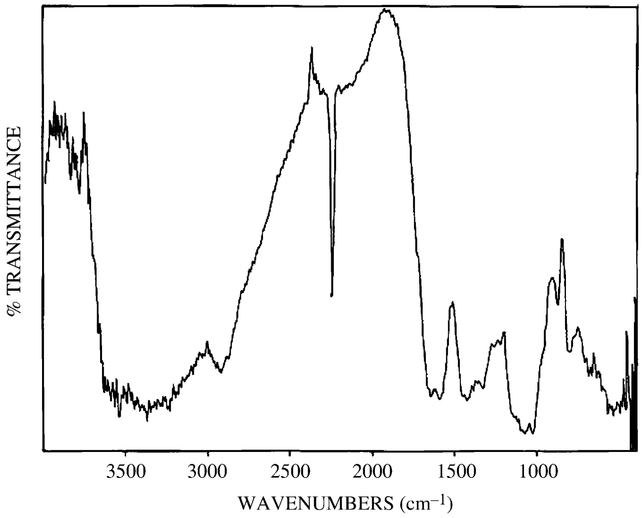

Fig. 12. IR spectrum of Na-PCMGG-g-PAN sample.

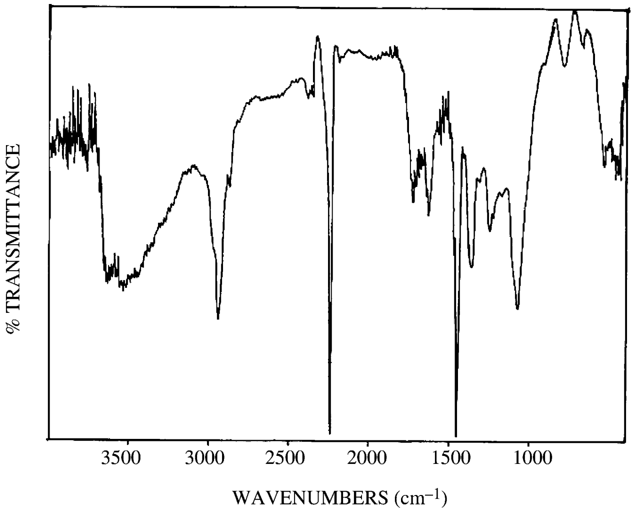

Fig. 13. IR spectrum of PAN sample.

attributed to $-C\equiv N$ stretching mode, characteristic of the spectra of PAN (Fig. 13). Thus, the presence of an additional band at $\sim 2247\ \mathrm{cm}^{-1}$ in the graft copolymer, i.e. Na-PCMGG-g-PAN indicates beyond doubt that grafting of AN onto Na-PCMGG has taken place.

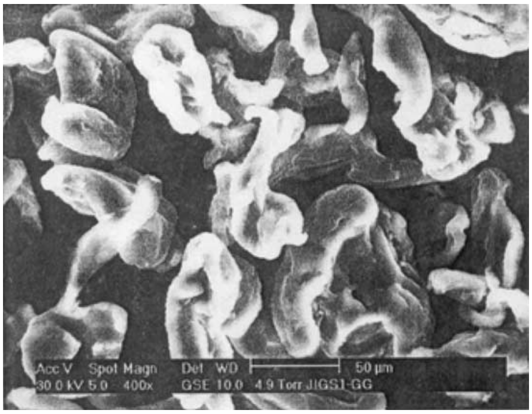

Fig. 14. Scanning Electron Micrograph of Guar Gum (400×) sample.

Fig. 15. Scanning Electron Micrograph of Na-PCMGG ($\overline{DS}=0.497$) (400×) sample.

Fig. 16. Scanning Electron Micrograph of Na-PCMGG-g-PAN (%G = 157.21) (400×) sample.

3.3.2. Scanning electron microscopy (SEM)

The scanning electron micrograph of Guar Gum (Fig. 14) shows discrete elongated granular structures separated from one another. Upon carboxymethylation of Guar gum, the structure of Guar gum gets improved as shown in Fig. 15 wherein the topology of the granules (Fig. 14) is modified in such a way that some of the granules get attached by adhering themselves. However, the clustering of the granules seems to be poor and the granules could be distinguished from one another.

The surface topology of Na-CMGG-g-PAN (%G = 157.21) is seen in Fig. 16. Upon comparing the morphology of the grafted sample (Fig. 16) with ungrafted material [GG (Fig. 14), Na-PCMGG (Fig. 15)] it is clearly evident that the grafted chains have drastically changed the topology of the Na-PCMGG ($\overline{DS}=0.497$) sample. As seen from Fig. 16

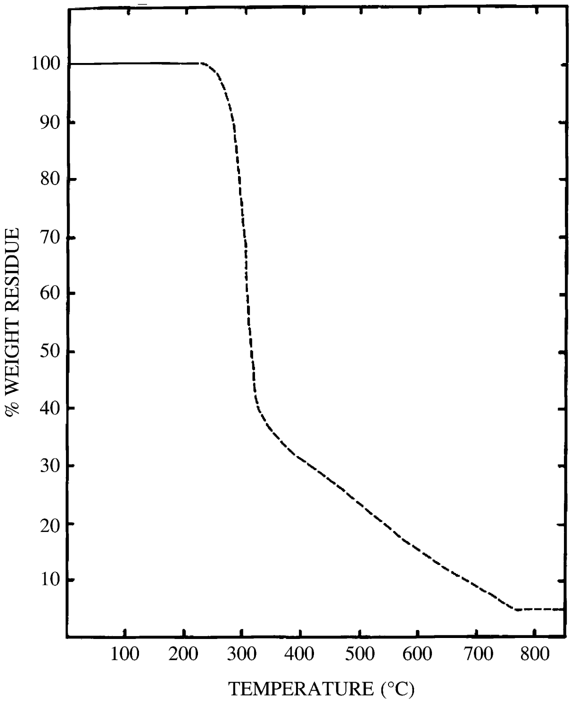

Fig. 17. TG thermogram for Guar gum.

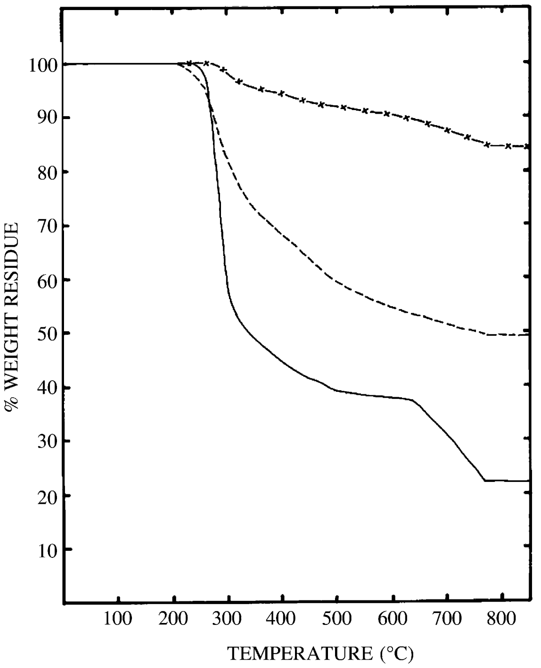

Fig. 18. TG thermograms for (—) Na-PCMGG ($\overline{\text{DS}}=0.497$), (– – –) Na-PCMGG-g-PAN (%G = 157.21) and (-×-×-) PAN.

the stiff morphology with lower adhering characteristics is observed with AN. The scanning electron micrograph of Na-PCMGG-g-PAN (Fig. 16) further reveals the additional surface deposits indicating that grafting has taken place.

3.3.3. Thermogravimetric analysis (TGA)

(a) Guar Gum, Na-PCMGG and its graft copolymer as well as homopolymer:

Fig. 17 shows the primary thermogram of Guar gum obtained at a scan rate of 10 °C/min in an inert atmosphere. The overall degradation of Guar gum (Fig. 17) involves only single step. The sample begins to decompose at 225 °C, rapidly loses 60% of its weight upto 325 °C. Beyond 325 °C, the weight loss is slow and gradual upto about 765 °C leaving 5% residual weight. In the temperature range 325–765 °C, the sample loses 35% of its original weight. The maximum rate of weight loss occurs at 315 °C.

Fig. 18 shows the primary thermograms obtained at a scan rate of 10 °C/min for Na-PCMGG ($\overline{\text{DS}}=0.497$), Na-PCMGG-g-PAN (%G = 157.21) and PAN in an inert atmosphere. It can be observed from this figure that Na-PCMGG sample shows single step of degradation. The decomposition starts at 215 °C and proceeds at a faster rate up to 310 °C and at this temperature, the sample loses 45% of its original weight. However, beyond this temperature, degradation proceeds at a very slow rate up to 625 °C. This temperature range, i.e. 310–625 °C, involves about 17.5% weight loss. With further increase in temperature, the proceeds at a very slow rate up to 625 °C. This temperature range, i.e. 310–625 °C, involves about 17.5% weight loss. With further increase in temperature, the degradation is found to occur at a relatively fast rate up to 765 °C, compared to the degradation proceeded in the earlier temperature range. The temperature at which the maximum rate of weight loss occurs is 300 °C. The overall degradation leaves about 22% residue.

The overall thermal degradation of Na-PCMGG-g-PAN (%G = 157.21) involves only single step of degradation. The decomposition begins at 205 °C and proceeds slowly up to 780 °C involving about 51% weight loss with a maximum rate of weight loss at 340 °C. The degradation is complete at about 780 °C leaving about 49% residual weight. In the case of PAN (Fig. 18) the overall degradation involves only a single step. The degradation occurs in the temperature range 270–780 °C involving about 16% weight loss with a maximum rate of weight loss at 460 °C. The final residue at 780 °C amounts to about 84%.

The temperature characteristic values as well as the value of the integral procedural decomposition temperature (IPDT) of Guar gum, Na-PCMGG ($\overline{\text{DS}}=0.497$), Na-PCMGG-g-PAN (%G = 157.21) and PAN are tabulated in Table 1. The examination of IPDT values indicates that not only the overall thermal stability of Guar gum has been increased upon its carboxymethylation but the overall thermal stability of Na-PCMGG has also been increased to a greater extent upon grafting of AN onto it.

The observed increase in the value of IDPT of Guar gum from 477.72 to 531.80 °C upon carrying out its carboxymethylation is attributed to the introduction of the polar groups into it leading to the increased inter-molecular and intra-molecular interactions which ultimately imparts higher thermal stability to it.

The increased ring formation at higher temperatures may be responsible for the observed higher value of IPDT for the Na-PCMGG-g-PAN sample compared to that of Na-PCMGG ($\overline{\text{DS}}=0.497$). Similar observations are also made by Varma and Ravisankar (1973) and Lokhande, Varadarajan, and Iyer (1992).

Table 1
Thermal analysis of Guar Gum, Na-PCMGG ($\overline{\text{DS}}=0.497$), Na-PCMGG-g-PAN (%G = 157.21) and PAN samples

Sample	Thermogravimetric analysis data						Transition data from DSC	
	T_i (°C) (IDT)	T_f (°C) (FDT)	T_{max} (°C)	T_{10} (°C)	T_{50} (°C)	IPDT (°C)	T_1 (°C)	T_2 (°C)
Guar Gum	225	765	315	280	315	477.72	115.88 (endo)	313.53 (exo)
Na-PCMGG	215	765	300	270	340	531.80	177.50 (endo)	282.18 (exo)
Na-PCMGG-g-PAN	205	780	340	275	750	619.58	150.50 (endo)	304 (exo)
PAN	270	780	460	600	—	745.83	279.94 (exo)	—

3.3.4. Differential scanning calorimetry (DSC)

The transition data of Guar gum, Na-PCMGG ($\overline{\mathrm{DS}} = 0.497$), Na-PCMGG-g-PAN and PAN samples obtained from their respective DSC thermograms (not shown) are also represented in Table 1. It can be seen from this table that Guar gum shows an endothermic peak at 115.88 °C and an exothermic peak at 313.53 °C. The endotherm may be due to the loss of residual moisture and the exotherm is attributed to the decomposition of the sample. On the other hand, in the case of Na-PCMGG sample, the endothermic transition appeared at 177.50 °C is due to the melting of Na-PCMGG but the exothermic transition observed at 282.18 °C is attributed to the decomposition of the sample.

The endothermic transition appeared at 150.50 °C and an exothermic peak appeared at 304 °C may be attributed respectively to the gross melting and gross decomposition of the Na-PCMGG-g-PAN (%G = 157.21) sample. The sharp exothermic transition appeared at 279.94 °C, as observed in the case of PAN sample, is due to pyrolytic decomposition of the sample.

Acknowledgements

One of us (JHT) is grateful to University Grants Commission (UGC), New Delhi for the financial assistance. This project work was financed by UGC, New Delhi, under scheme No.F.12-21/2002 (SR-1).

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