CELLULOSE CHEMISTRY AND TECHNOLOGY

PHOTO-INDUCED SYNTHESIS AND CHARACTERIZATION OF POLY(METHYL ACRYLATE) GRAFTED SODIUM SALT OF PARTIALLY CARBOXYMETHYLATED SODIUM ALGINATE

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Photo-induced graft copolymerization of methyl acrylate (MA) onto sodium salt of partially carboxymethylated sodium alginate (Na-PCMSA, $\overline{DS}$ = 1.10) was carried out in an aqueous medium using ceric ammonium nitrate (CAN) as photoinitiator to synthesize a novel graft copolymer, Na-PCMSA-g-PMA, which may find its potential application in the removal of the toxic metals from aqueous solution. By studying the influence of concentrations of nitric acid, photoinitiator (CAN), monomer (MA), as well as reaction time, temperature and amount of substrate, on the grafting yields, the reaction conditions for optimum grafting were evaluated. Under optimized conditions, the maximum values of the grafting yields achieved were %G = 303.57 and %GE = 98.32. The experimental results were found to be in very good agreement with the kinetic scheme proposed earlier by us. The grafting process was confirmed and the products were characterized by FTIR, TGA and SEM techniques.

Keywords: photo-induced grafting, methyl acrylate, sodium salt of partially carboxymethylated sodium alginate, optimum reaction conditions, characterization

INTRODUCTION

Chemical modification of polymers with the aim of imparting specific desirable properties is one of the main directions of development of modern macromolecular chemistry. 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. Among the grafting methods used, photo-grafting polymerization is widely known due to its significant advantages: less degradation of the backbone polymer, control over the grafting reaction in addition to attaining higher grafting efficiency, low cost of operation and selectivity to absorb UV light.

Sodium alginate (SA) is a linear, unbranched naturally occurring colloidal hydrophilic polysaccharide containing various properties of β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues. The M and G monomers are linked by 1→4 glycosidic bonds, forming either homogeneous or heterogeneous sequences.[1] SA has been widely used in food processing, medical and pharmaceutical industries, as well as in textile industries, due to its excellent physical and chemical properties. Even though SA finds a wide range of industrial applications, it also has some drawbacks like biodegradability which limits its uses considerably. These drawbacks can be improved through grafting of vinyl monomers onto it. As a part of our research programme, therefore, we have successfully carried out ceric-induced[2,3] as well as Fenton's reagent initiated[4,5] grafting of acrylonitrile onto sodium alginate and investigated the biodegradable behaviour of the graft copolymer SA-g-PAN, by studying its interactions with various microorganisms.[6] We also reported for the first time grafting of ethyl acrylate (EA),[7] methyl acrylate (MA) and methyl methacrylate (MMA)[8] onto SA in the presence of Ce^{+4} and studied the thermal behaviour of the different graft copolymers of SA.[9] Yinghai *et al.* have also carried out graft copolymerization of methyl acrylate[10] and methyl methacrylate[11] onto SA, using potassium diperiodatocuprate (III) and potassium ditelluratoargentate (III) as initiating system, respectively.

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The evaluation of optimum conditions for grafting of N-vinyl-2-pyrrolidone onto SA, using potassium peroxymonosulphate/glycolic acid, has also been reported by Arpit Sand *et al.*[12]

In the present investigation, we have modified SA by carboxymethylation, as the introduction of carboxymethyl groups in the SA molecule will enhance the behaviour of SA towards photo-grafting. Literature survey reveals that there are no reports on the modification of sodium salt of partially carboxymethylated sodium alginate (Na-PCMSA) through photo-grafting. Therefore, the present work aims to determine the optimization reaction conditions for photo-grafting of methyl acrylate onto Na-PCMSA ($\overline{DS}$ = 1.10), using ceric ammonium nitrate as photoinitiator. The photo-grafting process has also been confirmed and the effects of reaction conditions on the extent of grafting have been investigated. This has been done not only to develop specialty polymeric materials, but also to elucidate the photo-grafting mechanism over a range of values for the reaction variables studied in the present work. The synthesized graft copolymer, Na-PCMSA-g-PMA, has also been successfully evaluated for its potential application as a Pb (II) metal adsorbent by treating it with hydroxylamine in the presence of alkaline solution. The effects of initial lead ion concentration, adsorbent dosage, contact time, pH and temperature on the removal of Pb (II) have been studied systematically. The interesting results obtained in this regard will be published elsewhere.

EXPERIMENTAL

Materials and methods

Sodium alginate (SA) used in the present work was kindly supplied by Loba Chemie, Mumbai. Methyl acrylate (Fluka) was purified by treating with alkali solution in the usual manner. CAN (Qualigens, Glaxo India, India) was used as received. Analar grade nitric acid was used. Fresh solutions of the photoinitiator were used, prepared by dissolving the required amount of CAN in nitric acid. All other reagents and solvents used were of reagent grade. Nitrogen gas was purified by passing through fresh pyrogallol solution. Low conductivity water was used for the preparation of solutions, as well as for graft copolymerization reactions. The methods of preparation and purification, as well as the measurement of degree of substitution ($\overline{DS}$) of the sodium salt of partially carboxymethylated sodium alginate (Na-PCMSA), were followed as described earlier.[13] The $\overline{DS}$ of Na-PCMSA was found to be 1.10.

Photo-graft copolymerization

Graft copolymer of Na-PCMSA ($\overline{DS}$ = 1.10)

The photo-graft copolymerization reactions were carried out in a photochemical reactor supplied by Scientific Aids and Instrument Corp. (SAIC, Madras, India) as per the procedure described earlier.[14] A weighed amount of Na-PCMSA ($\overline{DS}$ = 1.10, 0.2-3.0 g, dry basis) was dissolved in 144.28 mL of low conductivity water in the reaction flask and the solution was stirred with continuous bubbling of a slow stream of nitrogen gas for one hour at 55 °C and thereafter for twenty minutes at room temperature. 2.5 mL of freshly prepared CAN solution (0.5 x 10^{-3}-10 x 10^{-3} mol/L) in nitric acid (nil – 0.5 mol/L) was added to the reaction flask, and the contents were then flushed with purified nitrogen gas, which was followed by the addition of the purified methyl acrylate (MA) (0.051-0.506 mol/L). The reaction flask was then assembled with an immersion well containing a 125W medium pressure mercury lamp. The whole assembly (photochemical reactor) was placed in a dark cabinet after covering it completely with aluminum foil. The lamp was then illuminated. Water from a constant-temperature water circulation bath was circulated over the immersion well and the reaction flask. The solution then was irradiated with continuous stirring for different time intervals (0.5-10 h) in the temperature range of 15-45 °C. After the completion of the grafting reaction, the irradiated sample solution was removed carefully, and the crude graft copolymer was isolated by centrifugation. It was then purified by repeated washings with 95% methanol and finally with pure methanol. The crude copolymer sample of Na-PCMSA-g-PMA thus obtained was dried in vacuum at 40 °C. The homopolymer, polymethylacrylate (PMA), was separated from the crude graft copolymer by carrying out Soxhlet extraction with acetone for 48 h. After the complete removal of the homopolymer, the pure graft copolymer was dried at 40 °C in vacuum until a constant weight was obtained. The synthetic route for the photo-synthesis of the graft copolymer, Na-PCMSA-g-PMA, is shown in Scheme 1.

Graft copolymer of SA

In order to understand the influence of introducing the carboxymethyl groups (in SA molecule) on the grafting yields, we have also carried out the photo-grafting of MA onto SA, using the established optimal reaction conditions obtained in the case of photo-grafting of MA onto Na-PCMSA ($\overline{DS}$ =1.10) with CAN as photoinitiator. The experimental procedure followed for the synthesis of the graft copolymer, SA-g-PMA, is the same as discussed above.

Dark method

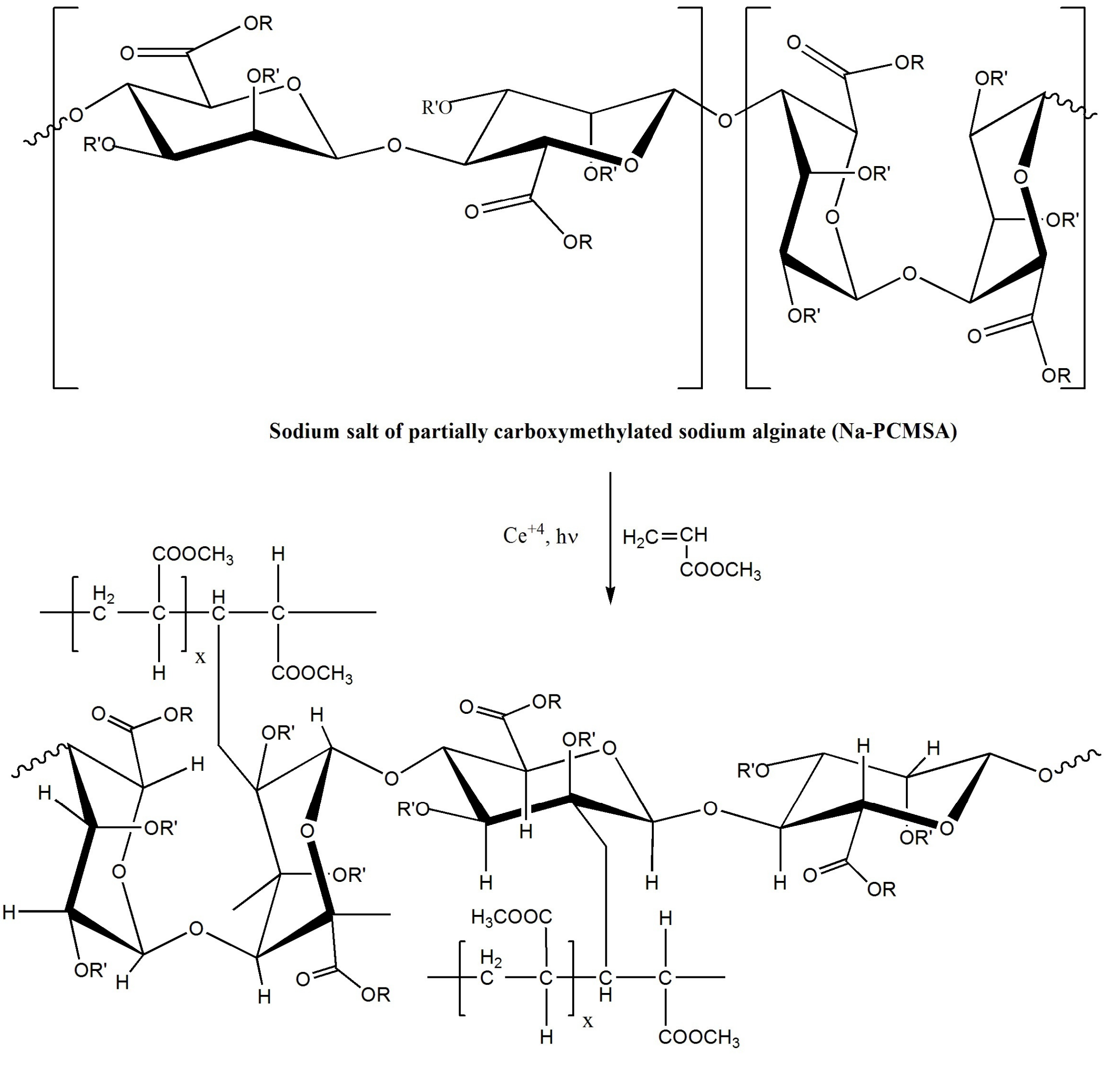
To compare the efficiency of CAN as photoinitiator, the grafting of MA onto Na-PCMSA ($\overline{DS}$ =1.10) was carried out in the absence of the ultraviolet radiation (dark method) by following the above mentioned procedure using the following reaction conditions: Na-PCMSA (dry basis) = 0.6 g, $[HNO_3]$ = 0.10 mol/L, [CAN] = 1.0 x 10^{-3} mol/L, [MA] = 0.101 mol/L, Time = 0.5-10 h, Temperature = 35 °C and Total volume = 150 mL.

Isolation of grafted chains

The graft copolymer of Na-PCMSA ($\overline{DS}$ =1.10) containing PMA was hydrolyzed by refluxing for 12 h in 1N HCl, as suggested by Brockway and Seaberg.[15] After all the Na-PCMSA went into the solution, a resinous mass was obtained, which was characterized with IR spectroscopy.

IR spectra

IR spectra of SA, Na-PCMSA ($\overline{DS}$ =1.10), Na-PCMSA-g-PMA and PMA (isolated by hydrolysis) were taken in KBr with a Perkin Elmer FT-IR Spectrophotometer (Model: Spectrum GX).



where R = Na or -CH_2COONa, R' = H or -CH_2COONa

Scheme 1: The synthetic route of photo-graft copolymer, Na-PCMSA-g-PMA

Thermogravimetric analysis (TGA)

The thermal behaviour of Na-PCMSA ($\overline{DS}$ =1.10), Na-PCMSA-g-PMA (%G = 303.57) and PMA has been examined in an inert atmosphere at a heating rate of 10 °C/min with the help of a Perkin Elmer Thermal Analyzer (Model: Pyris1).

Scanning Electron Microscopy (SEM)

A Scanning Electron Microscope (JEOL JSM-6380LV) was used to obtain micrographs of Na-PCMSA ($\overline{DS}$ =1.10) and Na-PCMSA-g-PMA (%G = 303.57).

Grafting yields and kinetic parameter

The percentage of grafting (%G), percentage of grafting efficiency (%GE), and rate of polymerization (R_p) were evaluated as follows:[16]

$$\%\,G = \frac{\text{Wt. of polymer grafted}}{\text{Initial wt. of backbone}} \text{ x } 100 \qquad (1)$$

$$\%\,GE = \frac{\text{Wt. of polymer grafted}}{\text{Wt. of polymer grafted} + \text{Wt. of homopolymer}} \text{ x } 100 \qquad (2)$$

$$\text{Rate of polymerization } R_p\ (\text{mol. } L^{-1}.\, s^{-1}) = \frac{\text{Weight of polymer grafted} + \text{Weight of homopolymer}}{\text{Mol. wt. of monomer} \text{ x } \text{Reaction time (s)} \text{ x } \text{Volume of reaction mix. (mL)}} \text{ x } 10^3$$

RESULTS AND DISCUSSION

In the present study of photo-induced graft copolymerization, the reaction conditions were varied to discover the optimum ones for grafting.

Effect of backbone concentration

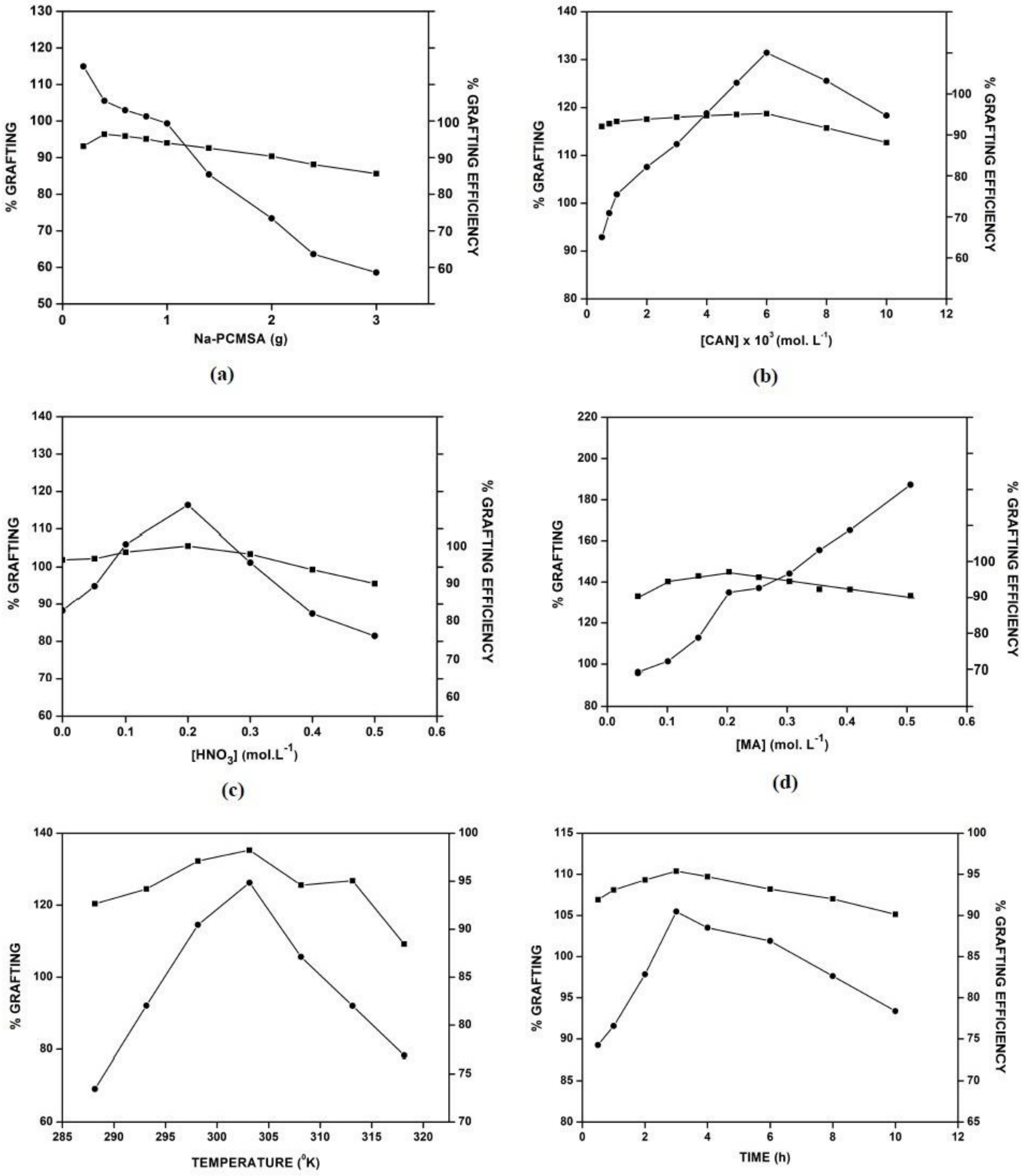
The influence of varying the amount of Na-PCMSA on the grafting yields (%G and %GE) is shown in Fig. 1(a). It can be seen from the figure that the value of %G decreases with increasing the amount of Na-PCMSA. However, %GE in the beginning increases very slowly and thereafter decreases continuously. The observed decrease in the grafting yields may be attributed to the fact that as the concentration of Na-PCMSA is increased, the viscosity of the reaction medium increases, which hinders the movement of free radicals causing a less efficient initiation and leading to a decrease in the grafting yields. Similar results are reported in the literature.[14,17]

Effect of photoinitiator concentration

Fig. 1(b) shows the effect of the photoinitiator (CAN) concentration on the grafting yields. It should be noted that the value of %G increases very rapidly up to [CAN] = 6 x 10^{-3} mol/L compared to that of %GE. Thus it is clear that there exists a critical concentration of ceric ion (6 x 10^{-3} mol/L) up to which both the %G as well as %GE increase and decrease thereafter. The initial increasing trend in the grafting yields is due to the sufficient numbers of ceric (IV) ions in the reaction mixture at 0.1 mol/L concentration of nitric acid, which have been ultimately consumed in the formation of active sites onto Na-PCMSA, thereby facilitating the photo-graft copolymerization of MA. The observed decrease in the grafting yields at higher photoinitiator concentration, i.e. beyond [Ce^{+4}] = 6 x 10^{-3} mol/L, may be attributed to the fast termination of the growing grafted chains. Further, homopolymer (PMA) formation at higher photoinitiator concentrations, which competed with the photo-grafting reaction for the available monomer (MA), could also lead to a decrease in %G and %GE. Our observations are in line with those reported elsewhere.[18-21]

Effect of acid concentration

The results of the grafting yields (%G and %GE) in the case of photo-grafting of MA onto Na-PCMSA ($\overline{DS}$ = 1.10) at different nitric acid concentrations are depicted in Fig. 1 (c). It is evident from this figure that there exists an optimum concentration of nitric acid (0.2 mol/L), which affords maximum %G as well as %GE. Beyond the optimum concentration of nitric acid, both values, %G and %GE, are found to decrease. Interestingly, even at zero concentration of nitric acid, the value of %G is found to be 88.3% [cf. Fig. 1 (c)], which may be due to the possibility that, even in the absence of acid, in an aqueous medium Na-PCMSA ionizes fully to a greater extent, which facilitates the diffusion of monomer as well as photoinitiator leading to higher value of grafting. Below the optimum concentration, the observed increase in the values of %G and %GE with the increase in nitric acid concentration may be attributed to an increase in the initiation rate of photo-grafting. On the other hand, the tendency of grafting yields to decrease with the increase in nitric acid concentration, beyond the optimum value (0.2 mol/L), could be associated with a fast rate of termination because of the increased rate of generation of free radical species as well as abundance of hydrogen protons. In addition, the coagulation of colloidal homopolymer in solution at lower pH values would also retard the diffusion of both monomer and photoinitiator, thereby leading to decreased grafting yields. Similar observations are reported in literature.[14,22]



(e) (f)

Figure 1: Influence of (a) amount of sodium salt of partially carboxymethylated sodium alginate (Na-PCMSA), (b) photoinitiator (CAN) concentration, (c) nitric acid concentration, (d) methyl acrylate (MA) concentration, (e) reaction temperature and (f) reaction time on: (●) -%G; or (■) -%GE

Effect of monomer concentration

The influence of monomer concentration on the grafting yields is shown in Fig. 1(d). It becomes evident that %G is directly related to the concentration of MA since it increases significantly as MA concentration increases within the range studied. However, the increase in %G with the concentration of MA is rapid up to

0.203 mol/L, but beyond this concentration the increment in %G is observed to have a slower rate. Probable explanations for this finding might be the following: (i) with increasing monomer (MA) concentration, the complexation between Ce^{+4} and monomer is enhanced, (ii) at higher monomer concentration, a large amount of the growing polymeric chains that are formed are involved in generating additional active sites onto Na-PCMSA by the chain transfer reaction, and (iii) the molecular weight of the grafts increase with increasing monomer concentrations.

On the other hand, as is evident from Fig. 1(d), the %GE increases with the increase in MA concentration up to 0.203 mol/L, but decreases with further increase in monomer concentration, unlike the trend exhibited by the results of %G. The results of Fig. 1(d) suggest that homopolymerization remained minimal when MA was used at a concentration of 0.203 mol/L. Above this concentration, homopolymerization is more favoured. Similar results are also reported in the literature.[23-26]

Effect of temperature

For studying the influence of temperature on the grafting yields, the photo-grafting reactions were carried out at seven different temperatures, ranging from 15-45 °C. The results are presented in Fig. 1(e). The grafting yields gradually increase with the increase in temperature, reach a maximum value at 30 °C and then decrease. The favourable effect of temperature on grafting could be attributed to (a) enhanced diffusion of monomer molecules into the Na-PCMSA structure, (b) increase in mobility of monomer molecules and their collisions with Na-PCMSA macroradicals, and (c) increased propagation of the graft chains. However, the negative effect on grafting at and above 35 °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 in the grafting yields. Similar results are also reported in the literature.[24,27-29]

Effect of reaction time

The effect of duration of the grafting reaction was studied by varying the time period from 0.5 h to 10 h and results are shown in Fig. 1(f). It can be seen from this figure that in the beginning the value of %G increases with the increase in reaction time and reaches the maximum value of 105.48% within 3 h, beyond which it decreases. The value of %GE also varies in the same way. Thus, the observed increase in the grafting yields up to 3 h can be explained on the basis of the fact that with the increase in reaction time, the number of grafting sites on the Na-PCMSA backbone increases as a result of which the extent of initiation and propagation of photo-graft copolymerization also increases with reaction time, leading to the increase in the grafting yields. On the other hand, the observed decrease in the grafting yields beyond the optimum reaction time may be presumably due to the detrimental effect of UV radiation on the grafted side chains of PMA at longer irradiation time intervals in the presence of the photoinitiator. Besides, beyond the optimum reaction time, the depletion of monomer and photoinitiator concentrations, as well as shortage of the available grafting sites may lower the grafting yields. Similar time dependency of grafting yields was reported by other researchers.[18,19,22,30,31]

Effect of liquor ratio

The influence of liquor ratio on %G is presented in Table 1. It can be seen from this table that there is a continuous increase in %G from 58.54% to 114.95% at a slow rate with the increase in the liquor ratio from 50 to 750 mL solution per g of Na-PCMSA. This observation can be explained on the basis of the fact that as the value of the liquor ratio decreases, the viscosity of the medium increases which, in turn, hinders the movement of free radicals, thereby decreasing %G.

From the foregoing discussion, the optimized reaction conditions evaluated in the present study of photo-graft copolymerization of MA onto Na-PCMSA ($\overline{DS}$ = 1.10) are: Na-PCMSA (dry basis) = 0.4 g, [CAN] = 6.0×10^{-3} mol/L, [HNO_3] = 0.20 mol/L, [MA] = 0.203 mol/L, Time = 3 h, Temperature = 30 °C and Total volume = 150 mL. The maximum values of grafting yields achieved are %G = 303.57 and %GE = 98.32.

KINETICS AND MECHANISM

The mechanism of the free radical photo-grafting of MA onto Na-PCMSA ($\overline{DS}$ = 1.10) is expected to proceed according to the following proposed scheme:[14]

Radical generation:

$$\text{X-H} + \text{Ce}^{+4} \underset{}{\overset{K}{\rightleftharpoons}} [\text{Complex}] \underset{k_d}{\overset{h\nu}{\longrightarrow}} \text{X}^\bullet + \text{Ce}^{+3} + \text{H}^+$$

$$\text{Ce}^{+4} + \text{H}_2\text{O} \xrightarrow{h\nu} \text{Ce}^{+3} + {}^\bullet\text{OH} + \text{H}^+$$

Initiation:

$$\text{X}^\bullet + \text{M} \xrightarrow{k_i} \text{XM}^\bullet$$

$$^\bullet\text{OH} + \text{M} \xrightarrow{k_i} \text{OH-M}^\bullet$$

$$\text{Ce}^{+4} + \text{M} \longrightarrow \text{M}^\bullet + \text{Ce}^{+3} + \text{H}^+$$

Propagation:

$$\text{XM}^\bullet + \text{nM} \xrightarrow{k_p} \text{XM}^\bullet_{n+1}$$

$$\text{OH-M}^\bullet + \text{nM} \longrightarrow \text{OH-M}^\bullet_{n+1}$$

$$\text{M}^\bullet + \text{nM} \longrightarrow \text{M}^\bullet_{n+1}$$

Termination:

$$\text{XM}^\bullet_{n+1} + \text{XM}^\bullet_{n+1} \xrightarrow{k_t} \text{Graft copolymer}$$

$$\text{XM}^\bullet_{n+1} + \text{OHM}^\bullet_{n+1} \longrightarrow \text{Graft copolymer}$$

$$\text{OHM}^\bullet_{n+1} + \text{OHM}^\bullet_{n+1} \longrightarrow \text{Homopolymer}$$

$$\text{M}^\bullet_{n+1} + \text{M}^\bullet_{n+1} \longrightarrow \text{Homopolymer}$$

$$\text{XM}^\bullet_{n+1} + \text{M}^\bullet_{n+1} \longrightarrow \text{Graft copolymer}$$

$$\text{XM}^\bullet_{n+1} + \text{Ce}^{+4} \longrightarrow \text{XM}^\bullet_{n+1} + \text{Ce}^{+3} + \text{H}^+$$

$$\text{M}^\bullet_{n+1} + \text{Ce}^{+4} \longrightarrow \text{M}^\bullet_{n+1} + \text{Ce}^{+3} + \text{H}^+$$

Here, X–H denotes the reactive groups of Na-PCMSA and M is the monomer (MA). With a steady state assumption, the following expressions [eqs. (4) and (5)] were derived for the value of R_p:

$$R_p = k_p \left[\text{XM}^\bullet_{n+1}\right] \left[\text{M}\right] \tag{4}$$

$$R_p = k_p \left[\frac{k_d \bullet k_i}{k_t}\right]^{1/2} \left[\text{Ce}^{+4}\right]^{1/2} \left[\text{M}\right] \tag{5}$$

$$R_p = R_g + R_h \tag{6}$$

The values of R_p evaluated for various monomer (MA) and photoinitiator (CAN) concentrations, for the photo-grafting of MA onto Na-PCMSA ($\overline{DS} = 1.10$) are presented in Tables 2 and 3, respectively.

The effects of the concentration of the monomer (MA) and photoinitiator (CAN) on R_p, as expected from the previous equations, are shown in Fig. 2. The plots of R_p versus the monomer concentration and R_p versus $[\text{Ce}^{+4}]^{1/2}$ were found to be linear with a good correlation coefficient, supporting the previous scheme.

Evaluation of energy of activation

The natural log of % grafting (ln %G) versus 1/T was plotted for the initial portion of the curve, i.e. 15-30 °C [cf. Fig. 1(e)], as shown in Fig. 3, and these values are found to fall on a straight line with a good correlation coefficient value. The least square value of the overall activation energy of grafting (E_g) was calculated and was found to be 29.42 kJ/mol. Leza *et al.*[32] have also reported the value of E_g to be 32.6 kJ/mol in the case of grafting of 4-vinyl pyridine (4-VP) onto partially carboxymethylated cotton (PCMC). Trivedi *et al.*[33] have also grafted methyl acrylate onto sodium salt of partially carboxymethylated guar gum ($\overline{DS}$ = 0.497) using CAN as initiator and reported the E_g value to be 16.74 kJ/mol.

Table 1
Effect of liquor ratio (mL sol/g Na-PCMSA) on %G, in the case of photo-grafting of methyl acrylate (MA) onto sodium salt of partially carboxymethylated sodium alginate (Na-PCMSA, $\overline{DS}$ =1.10)[a]

Liquor ratio (mL sol/g Na-PCMSA)	% Grafting (%G)
750 : 1	114.95
375 : 1	105.51
250 : 1	102.97
187.5 : 1	101.26
150 :1	99.35
107.1 : 1	85.41
75 :1	73.39
62.5 : 1	63.68
50 :1	58.54

[a]Reaction conditions: Na-PCMSA: varied as shown (dry basis); [CAN]: 1.0 x 10^{-3} mol/L; [HNO_3]: 0.10 mol/L; [MA]: 0.101 mol/L; Time: 3 h; Temperature: 35 °C and Total volume: 150 mL

Table 2
Rate of polymerization (R_p) for photo-graft copolymerization of methyl acrylate (MA) onto sodium salt of partially carboxymethylated sodium alginate (Na-PCMSA, $\overline{\text{DS}}$ = 1.10) at various ceric ammonium nitrate (CAN) photoinitiator concentrations[a]

[CAN] x 10^3 (mol/L)	$[\text{CAN}]^{1/2}$ $(\text{mol/L})^{1/2}$	R_p x 10^5 $(\text{mol.L}^{-1}.\text{s}^{-1})$
0.50	0.022	0.43
0.75	0.027	0.45
1.00	0.032	0.47
2.00	0.045	0.49
3.00	0.055	0.51
4.00	0.063	0.54
5.00	0.071	0.57
6.00	0.077	0.59
8.00	0.089	0.59
10.00	0.100	0.58

[a]Reaction conditions: Na-PCMSA: 0.60 g (dry basis); [CAN]: varied as shown; [HNO_3]: 0.10 mol/L; [MA]: 0.101 mol/L; Time: 3 h; Temperature: 35 °C and Total volume: 150 mL

Table 3
Rate of polymerization (R_p) for photo-graft copolymerization of methyl acrylate (ma) onto sodium salt of partially carboxymethylated sodium alginate (Na-PCMSA, $\overline{\text{DS}}$=1.10) at various monomer concentrations[a]

[MA] (mol/L)	R_p x 10^5 $(\text{mol.L}^{-1}.\text{s}^{-1})$
0.051	0.46
0.101	0.46
0.152	0.51
0.203	0.60
0.253	0.62
0.304	0.66
0.354	0.72
0.405	0.77
0.506	0.89

[a]Reaction conditions: Na-PCMSA: 0.60 g (dry basis); [CAN]: 1.0 x 10^{-3} mol/L; [HNO_3]: 0.10 mol/L; [MA]: varied as shown; Time: 3 h; Temperature: 35 °C; Total volume: 150 mL

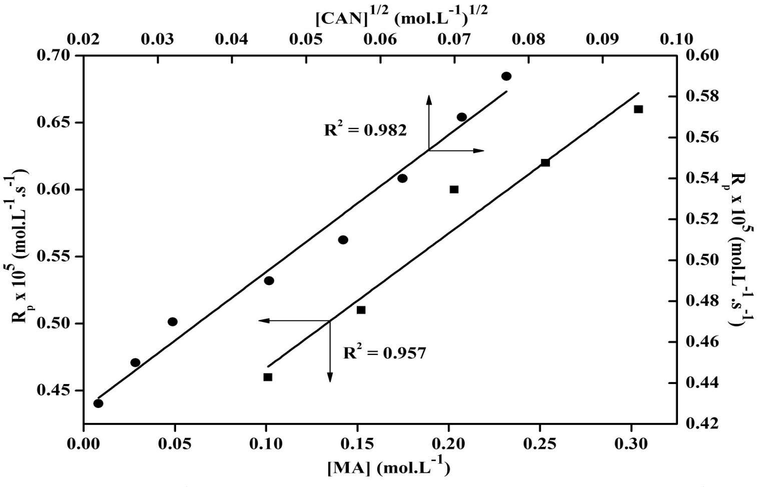


Figure 2: Plots of (●) R_p x 10^5 versus monomer concentration and (■) R_p x 10^5 versus $[\text{CAN}]^{1/2}$

Comparison of CAN efficiency

The results of the grafting yields obtained with the photo and dark methods are depicted in Fig. 4. The grafting yields were found to be higher when the grafting of MA was carried out onto Na-PCMSA ($\overline{DS}$ = 1.10) at various reaction time intervals using ultraviolet radiation, in comparison with the dark method. The observed higher grafting yields may be due to the fact that the complex, which formed from the reaction between the functional groups of Na-PCMSA and ceric ions, may have dissociated to a greater extent in the presence of ultraviolet radiation (photo method) than in the absence of radiation (dark method), as a result, a greater number of free radical sites may have been produced for grafting to occur with the photo method, leading to higher values of the grafting yields.

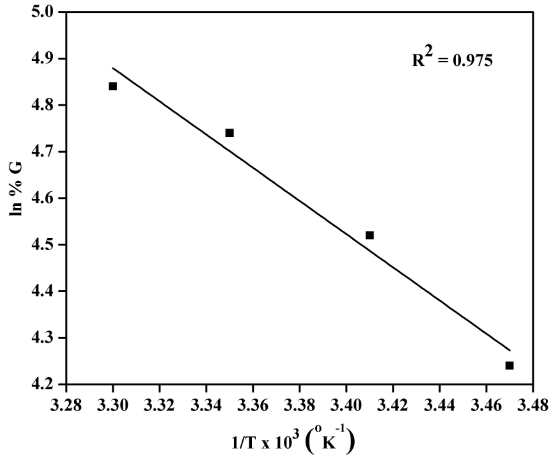


Figure 3: Plot of ln %G versus T^{-1}

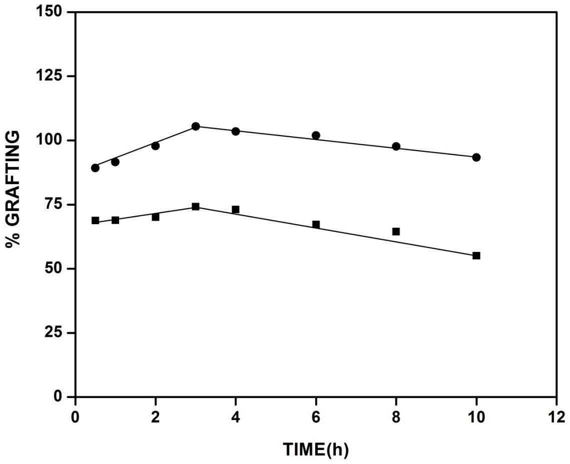


Figure 4: Effect of reaction time on %G: (●) photo method and (■) dark method

Table 4
Grafting yields obtained in the case of photo-grafting of MA onto SA and Na-PCMSA

Structure	%G	%GE
Na-PCMSA[a]	303.57	98.32
SA[a]	240.83	86.54

[a] Optimum reaction conditions: SA/Na-PCMSA (dry basis) = 0.4 g, [CAN] = 6.0 x 10^{-3} mol/L, [HNO_3] = 0.20 mol/L, [MA] = 0.203 mol/L, Time = 3 h, Temperature = 30 °C and Total volume = 150 mL

Effect of substrate structure

In order to investigate the influence of introducing functional group(s) like carboxymethyl in the SA molecule on its susceptibility toward grafting, ceric ion initiated photo-grafting of MA onto SA was also carried out using the optimized reaction conditions (Table 4) evaluated for grafting of MA onto Na-PCMSA ($\overline{DS}$ = 1.10) and the results of the grafting yields are indicated in Table 4.

As shown in Table 4, the introduction of carboxymethyl groups in SA enhances the behaviour of SA toward grafting of MA. As a result of this, the values of %G and %GE are found to be higher in the case of grafting of MA onto Na-PCMSA ($\overline{DS}$ = 1.10) compared to SA. This could be attributed to the combined influence of the following factors. First, the carboxymethyl groups increase the swellability of SA, thereby facilitating the diffusion of the monomer (MA) and initiator (CAN); second, the ionization of carboxyl groups along the SA chains introduces negative charges, which attract ceric ions to the SA molecules leading to the formation of more active sites on the SA backbone, available for the monomer (MA), thus increasing the reactivity of SA. Similar results are reported in the case of the grafting of 4-vinyl pyridine[34] and vinyl monomers (acrylonitrile, methyl methacrylate and acrylamide)[35] onto partially carboxymethylated cotton.

Evidence of grafting

FTIR spectroscopy

Fig. 5(a) shows the IR spectrum of SA. The absorption bands appeared at 1613 cm^{-1} and 1416 cm^{-1} are due to the asymmetric and symmetric vibrations of –COO- moiety. The bands appeared at 1125 cm^{-1} and 2927 cm^{-1} are assigned to C-O stretching and –CH stretching, respectively. The broad peak appeared at 3437 cm^{-1} is due to the stretching of the hydroxyl groups. The IR spectrum of Na-PCMSA ($\overline{DS}$ = 1.10) [Fig. 5(b)] showa a strong absorption peak at ~1744 cm^{-1}, which is assigned to –CO stretching of the partially carboxymethylated sodium alginate. The absorption bands appeared at ~1616 cm^{-1} and at ~1412 cm^{-1} are assigned to the asymmetric and symmetric vibrations due to –COO- moiety, which is present in Na-PCMSA. Figs. 5(c) and 5(d) show the IR spectra of Na-PCMSA-g-PMA and PMA samples (isolated by the hydrolysis method), respectively. The spectrum of the graft copolymer [Fig. 5(c)] shows absorption bands of Na-PCMSA, as well as an additional band at ~1739 cm^{-1} due to C=O stretching of the ester group (-COOCH$_3$), characteristic of the spectrum of PMA [Fig. 5(d)]. Thus, the presence of an additional band at ~1739 cm^{-1} in the graft copolymer, i.e. Na-PCMSA-g-PMA, indicates beyond doubt that photo-grafting of MA onto Na-PCMSA ($\overline{DS}$ = 1.10) has taken place.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a simple and accurate method for studying the decomposition pattern and the thermal stability of the polymers. Fig. 6 shows the primary thermograms and derivatograms for Na-PCMSA (S$_1$), Na-PCMSA-g-PMA (S$_2$) and PMA (S$_3$) samples. It becomes evident from the thermogram of Na-PCMSA [Fig. 6 (S$_1$)] that the decomposition process in N$_2$ for Na-PCMSA occurs in three stages. The initial slight loss in weight is merely due to evaporation of the absorbed moisture. Rapid decomposition occurs in the second stage, with the onset of the decomposition temperature (IDT) at 137.84 °C, resulting in a major weight loss of 49.90% (Table 5). The derivatogram clearly exhibits the temperature for the maximum decomposition for this stage as 209.10 °C. Beyond 271.35 °C, the sample degrades slowly and gradually up to 575 °C and thereafter it degrades somewhat rapidly with a maximum rate of weight loss at 698.79 °C involving 17.63% weight loss. The final decomposition temperature (FDT) was found to be 780.40 °C. The char yield of 29.32% was obtained at 700 °C.

The graft copolymer Na-PCMSA-g-PMA (%G = 303.57) shows a four stage decomposition pattern [Fig. 6 (S2)]. Obviously, the first stage is due to dehydration showing about 5.73% weight loss, while about 23% weight loss occurs in the second stage of decomposition in the temperature range of 112.64-262.52 °C (Table 5).

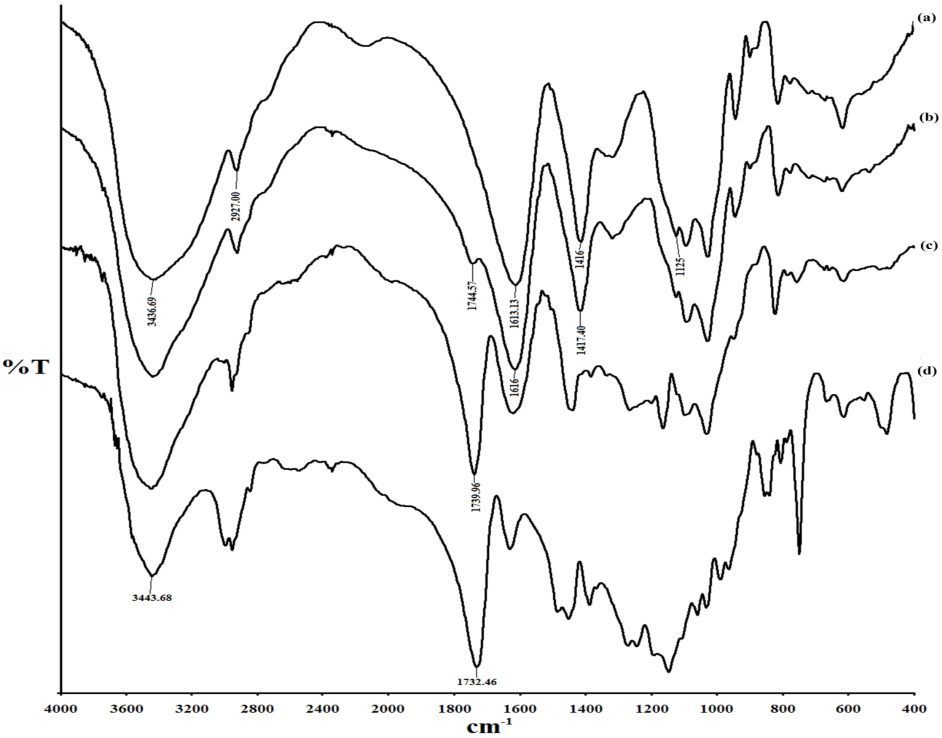


Figure 5: IR spectra of (a) sodium alginate (SA), (b) Na-PCMSA, (c) Na-PCMSA-g-PMA and (d) PMA

The maximum rate of weight loss achieved in this stage is at 204.60 °C. The third stage of degradation (262.52-418.22 °C) involves 47.46% weight loss, while the fourth stage involves only 11.92% weight loss during the temperature range 525.22-667.57 °C. The maximum rates of weight loss occur at 330.78 °C and 593.48 °C for the third and fourth decomposition steps, respectively. A char yield of only 4.58% is obtained at 700 °C.

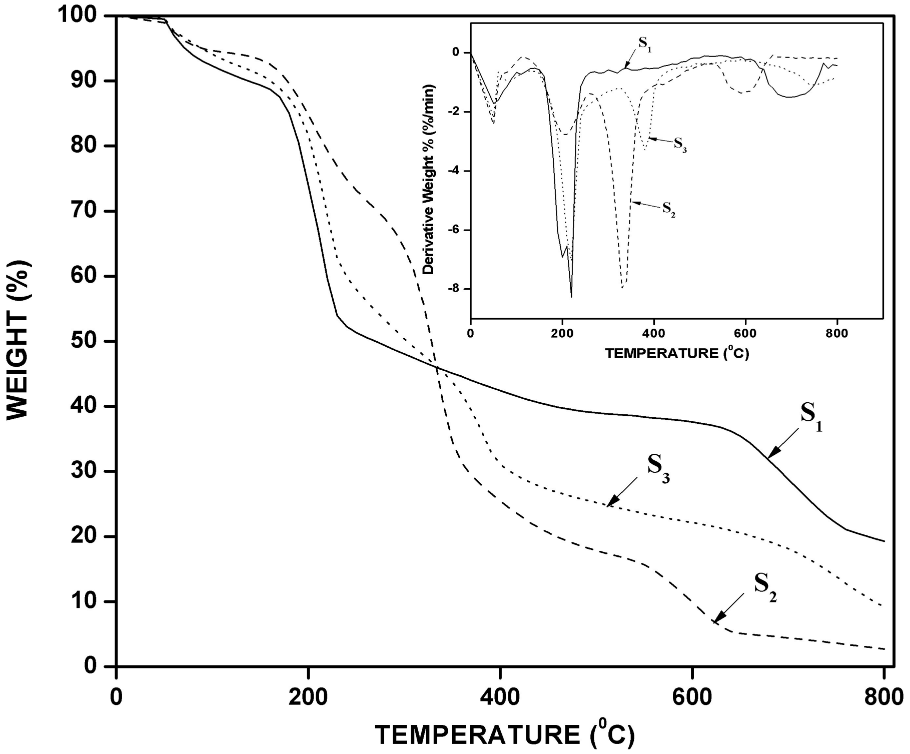


Figure 6: TG thermograms for (——) Na-PCMSA (S_1), (----) Na-PCMSA-g-PMA (%G = 303.57) (S_2) and (….) PMA (S_3) at 10 °C/min. The inset shows the first derivatives of the curves shown in the figure

Table 5
Values of percent weight loss of Na-PCMSA ($\overline{DS}$ = 1.10), Na-PCMSA-g-PMA and PMA at different temperature ranges

Sample	Temperature range (°C)	T_{max} (°C)	Weight loss (%)	Char yield at 700 °C (%)
S_1	0-100.61	—	7.69	29.32
	137.84-271.35	209.10	49.90	
	575-780.40	698.99	17.63	
S_2	0-112.64	—	5.73	4.58
	112.64-262.52	204.60	22.93	
	262.52-418.22	330.78	47.46	
	525.22-667.57	593.48	11.92	
S_3	0-63.56	—	2.70	18.49
	121.81-323.25	220.96	44.66	
	323.25-476.14	381.17	21.52	

S_1 = Na-PCMSA; S_2 = Na-PCMSA-g-PMA (% G = 303.57); S_3 = PMA

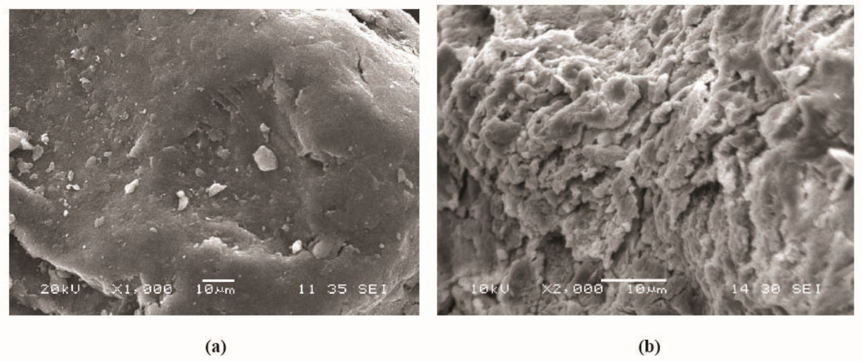


Figure 7: Scanning electron micrographs of (a) Na-PCMSA (1000X) and (b) Na-PCMSA-g-PMA (%G = 303.57) (2000X)

PMA shows a three stage decomposition pattern [Fig. 6 (S3)]. In the first stage, a slight loss in weight is due to evaporation of the absorbed moisture. The degradation appears to be a two stage process, i.e. from 128.81-323.25 °C and from 323.25 to 476.14 °C, involving about 44.66% and 21.52% weight loss, respectively. The maximum decomposition for the second and third stages occurs at 220.96 °C and 381.17 °C, respectively. The char yield at 700 °C amounts to about 18.49%. Thus, it can be concluded that the overall thermal stability of Na-PCMSA has got decreased after photo-grafting of MA onto it. However, PMA has higher thermal stability than Na-PCMSA-g-PMA. The results of TGA [Fig. 6 and Table 5] thus also provide additional evidence of photo-grafting.

Morphological studies (SEM)

A comparative study of the scanning electron micrographs [Figs. 7(a) and 7(b)] of Na-PCMSA ($\overline{DS}$ = 1.10) and Na-PCMSA-g-PMA (%G = 303.57) is used as supportive evidence for grafting, indicating that grafting has indeed taken place. A considerable amount of grafted polymer is found to be deposited [Fig. 7(b)], which appears to have a different structure from Na-PCMSA [Fig. 7(a)].

CONCLUSION

In summary, we have reported for the first time on the optimum reaction conditions in the case of photo-induced graft copolymerization of MA onto Na-PCMSA ($\overline{DS}$ = 1.10), using CAN as photoinitiator. The influence of various reaction conditions on the grafting yields has been discussed. Under the optimized reaction conditions, the maximum percentage of grafting yields achieved are %G = 303.57 and %GE = 98.32. The experimental results have been analyzed in terms of the earlier proposed kinetic scheme and are found to be in good agreement with it. The overall activation energy for photo-grafting has been found to be 29.42 kJ/mol. The efficiency of the photoinitiator (CAN) has also been studied by carrying out graft copolymerization of MA onto Na-PCMSA ($\overline{DS}$ = 1.10) in the presence and absence of the ultraviolet radiation. The influence of the introduction of carboxymethyl groups in SA molecule on its behaviour toward photo-grafting with MA has also been investigated. Various analytical techniques, such as FTIR, SEM and TGA, have been successively used in order to confirm the photo-grafting of poly(methyl acrylate) on the Na-PCMSA chains. The synthesized graft copolymer (Na-PCMSA-g-PMA), after treating it with hydroxylamine in an alkaline medium, may find potential applications as an adsorbent for metal ion sorption.

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