



# PHOTO-INDUCED SYNTHESIS AND CHARACTERIZATION OF GRAFT COPOLYMER OF SODIUM SALT OF PARTIALLY CARBOXYMETHYLATED SODIUM ALGINATE AND METHYL METHACRYLATE

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## Abstract

Photo-induced graft copolymerization of Sodium Salt of Partially Carboxymethylated Sodium Alginate (Na-PCMSA,  $\overline{DS} = 1.10$ ) with methyl methacrylate (MMA) using ceric ammonium nitrate (CAN) as a photo-initiator was carried out under nitrogen atmosphere in an aqueous medium. The reaction conditions for maximum photo-grafting were optimized by varying the reaction time, temperature, amount of substrate, concentrations of nitric acid, photo-initiator (CAN) and monomer (MMA) to study their influence on grafting yields. The optimal reaction conditions were obtained with amount of Na-PCMSA 0.4g (dry basis), CAN concentration of  $4 \times 10^{-3}$  mol/L,  $\text{HNO}_3$  concentration of 0.3 mol/L, MMA concentration of 0.152 mol/L, reaction time of 4h and reaction temperature of 30°C. Under the optimum reaction conditions, the maximum grafting yields achieved were %G = 284.12 and %GE = 98.44. The characterization of grafted products by means of FTIR, thermal analysis and scanning electron microscopy provided the evidence of photo-grafting of poly(methyl methacrylate) onto Na-PCMSA. The synthesized novel graft copolymer, Na-PCMSA-g-PMMA, may find its potential applications as a metal adsorbent.

**Keywords:** Photo-induced grafting, Methyl Methacrylate, Sodium salt of Partially Carboxymethylated Sodium Alginate, Optimum Reaction Conditions, Characterization

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## 1. Introduction

Various routes to the modification of natural polymers exist. One which has received particular attention is that of graft copolymerization [1]. The synthesis of graft copolymers mainly involves the usage of chemical and radiation (high-, and low-energy) methods [1,2]. However, the photo-grafting method has several advantages [2-4].

Among an industrially important natural and renewable polymers, Sodium Alginate [SA,  $(C_6H_7O_6Na)_n$ ] is a straight-chain, biodegradable, non-toxic, hydrophilic polyanionic copolymer which is composed of two 1→4 glycosidically linked monomers: β-D-mannuronic acid (M) and α-L-guluronic acid (G) [5]. It has been widely used in various industrial applications like textile, food, cosmetics, pharmaceuticals, and medical etc.[6-8]. Thus, SA finds wide range of industrial applications even though it is prone to enzymatic degradation and suffers from limitations in fabrication. These drawbacks can be improved through the development of chemically modified matrices by grafting. There are several reports on the graft copolymerization of vinyl monomers onto sodium alginate [9-14].

As a part of our research programme we have successfully modified carboxymethylated derivatives of guar gum [15,16], psyllium [17-20], tamarind kernel powder [21-23] and sodium alginate [24] by grafting different vinyl monomers onto them using low energy radiation. In this study, the photo-induced synthesis of poly(methyl methacrylate) grafted sodium salt of partially carboxymethylated sodium alginate has been optimized through the variation of different reaction variables in terms of the determination of the highest grafting yields (%G = 284.12 and %GE = 98.44). In addition, photo-graft copolymerization has been characterized by FTIR, TGA/DTG and SEM methods. The synthesized graft copolymer, Na-PCMSA-g-PMMA, is expected to hold better properties of metal ion uptake and therefore its potential application as a Pb(II) metal adsorbent has been evaluated by treating the graft copolymer with hydroxylamine in the presence of alkaline solution and characterized by using FTIR, EDAX and SEM techniques. However, the obtained encouraging results will be communicated elsewhere.

## 2. Experimental

### 2.1. Materials

Sodium alginate (SA) was kindly supplied by Loba Chemie Pvt. Ltd., Mumbai (India). The methods of preparation, purification and measurement of degree of substitution of the sodium salt of carboxymethylated sodium alginate (Na-PCMSA) were followed as described earlier [25]. The  $\overline{DS}$  of Na-PCMSA sample was found to be 1.10. Methyl Methacrylate (MMA) (Fluka, Switzerland make) was purified as per the usual procedure by treating with alkali solution. CAN (Qualigens, Glaxo India, India) was used as received. Analar grade nitric acid was used. Fresh solutions of the photo-initiator (CAN) were prepared by dissolving the required amount of it 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 and for photo-graft polymerization reactions.

### 2.2. Methods

#### 2.2.1. Photo-Induced Synthesis of Poly(methyl methacrylate) grafted Na-PCMSA (Na-PCMSA-g-PMMA)

A photo-chemical reactor supplied by Scientific Aids and Instruments Corporation (SAIC, Madras, India) was employed to carry out photo-induced graft copolymerization reactions for the synthesis of the graft copolymer, Na-PCMSA-g-PMMA as per the procedure described earlier [24]. The complete experimental set up for carrying out the photo-graft copolymerization reaction is represented in Fig. 1.

However, the reaction conditions which were varied in the present study for establishing the optimal reaction conditions are: Wt. of Na-PCMSA = 0.2 g to 3.0 g (dry basis); [CAN] =  $0.5 \times 10^{-3}$  to  $10 \times 10^{-3}$  mol/L; [HNO<sub>3</sub>] = Nil to 0.5 mol/L; [MMA] = 0.051 to 0.506 mol/L; Temperature = 15°C to 45°C; Reaction Time = 0.5 h to 10.0 h and Total Volume = 150mL. After completion of the photo-grafting reaction, the irradiated sample solution was removed carefully and the crude graft product was isolated by centrifugation. It was then purified by repeated washings with 95% methanol and finally

with pure methanol. The crude graft copolymer sample of Na-PCMSA-g-PMMA thus obtained was dried in vacuum at 40°C. The homopolymer, poly(methyl methacrylate) was isolated from the crude graft copolymer sample by carrying out soxhlet extraction with acetone for 48h. After the complete removal of the homopolymer (PMMA), the pure graft copolymer sample was dried at 40°C under vacuum until a constant weight was obtained. The synthetic pathway for the preparation of the photo-graft copolymer, Na-PCMSA-g-PMMA, is shown in Scheme 1.

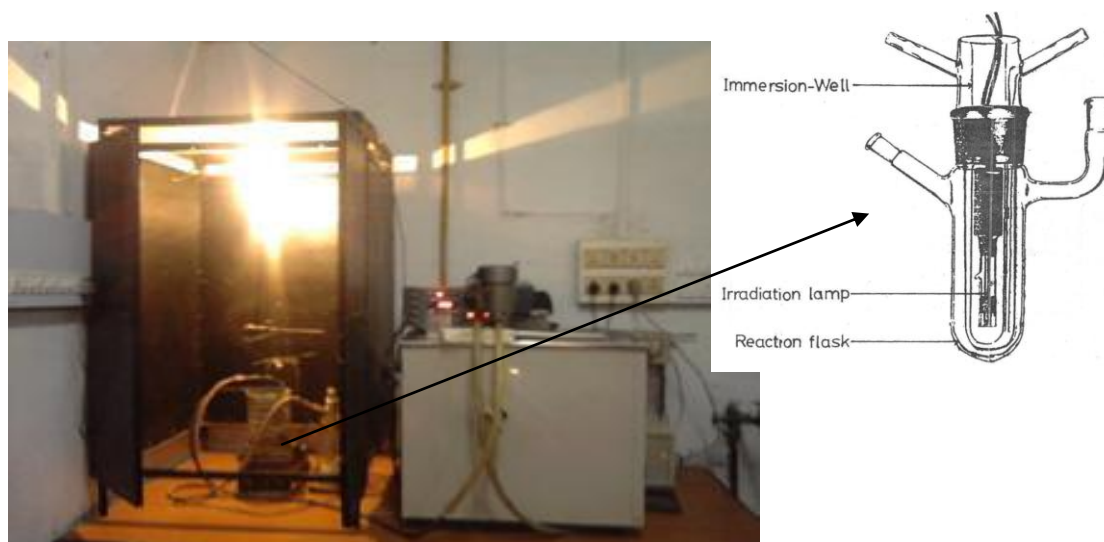
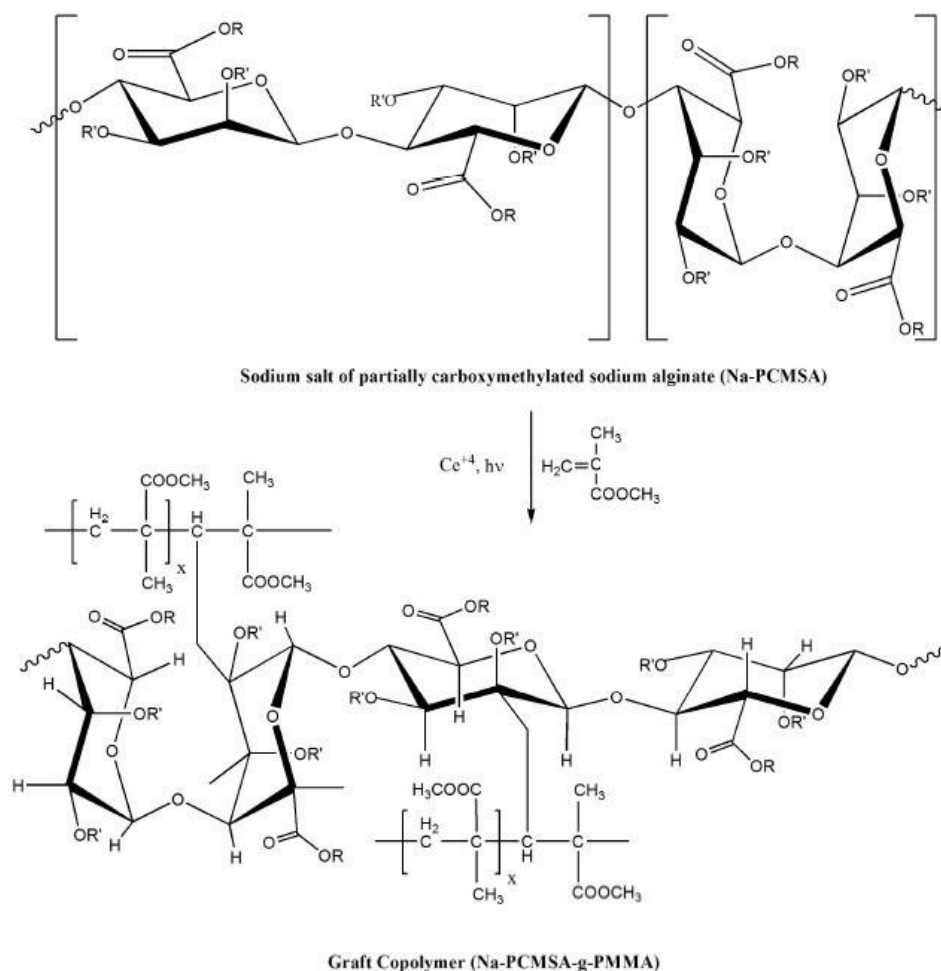


Fig.1. Detailed experimental setup for carrying out photo-graft copolymerization reaction.



where R = Na or -CH<sub>2</sub>COONa, R' = H or -CH<sub>2</sub>COONa

Scheme 1. The synthetic route of photo-graft copolymer, Na-PCMSA-g-PMMA.

### 2.2.2. Photo-Initiated synthesis of SA-g-PMMA

The photo-initiated synthesis of poly(methyl methacrylate) grafted sodium alginate (SA-g-PMMA) was carried out using the optimal reaction conditions established in the case of the synthesis of Na-PCMSA-g-PMMA with a view to study the influence of introducing the carboxymethyl groups in SA molecules on the grafting yields.

### 2.2.3. Dark Method

In order to compare the efficiency of CAN as a photo-initiator, the grafting of MMA onto Na-PCMSA ( $\overline{DS} = 1.10$ ) was carried out at different times (0.5h to 10h) in the absence of the ultra-violet radiation (Dark Method) by following the same procedure, as mentioned in the above section 2.2.1. The following reaction conditions were used: Na-PCMSA (dry basis) = 0.6 g, [CAN] =  $1 \times 10^{-3}$  mol/L, [HNO<sub>3</sub>] = 0.1 mol/L, [MMA] = 0.101 mol/L, Temperature = 35°C and Total Volume = 150 mL.

### 2.3. Isolation of Grafted Chains

The graft copolymer of Na-PCMSA containing PMMA was hydrolyzed by refluxing it with 12 h in 1N HCl [26]. After all the Na-PCMSA went into the solution, a resinous mass was obtained which was characterized with FTIR spectroscopy.

### 2.4. Calculation of Grafting Yields

The percentage of grafting (%G), percentage of grafting efficiency (%GE) and percentage of homopolymer (%H<sub>p</sub>) were evaluated by using the following expressions [24]:

$$(i) \%G = \frac{\text{Wt.of polymergrafted}}{\text{Initial wt. of backbone}} \times 10^2 \quad (1)$$

$$(ii) \%GE = \frac{\text{Wt.of polymergrafted}}{\text{Wt.of polymer grafted} + \text{Wt.of homopolymere}} \times 10^2 \quad (2)$$

$$(iii) \%H_p = 100 - \%GE \quad (3)$$

### 2.5. Characterization Methods

#### 2.5.1. FTIR Spectroscopy

The FTIR spectra of Na-PCMSA ( $\overline{DS} = 1.10$ ), Na-PCMSA-g-PMMA (%G = 284.12) and PMMA (isolated by hydrolysis) were recorded by KBr pellet method using Nicolet Impact 400D Fourier Transform Infrared Spectrophotometer between 400 and 4000 cm<sup>-1</sup>.

#### 2.5.2. Thermogravimetric Analysis (TGA)

The TGA traces of Na-PCMSA ( $\overline{DS} = 1.10$ ), Na-PCMSA-g-PMMA (%G = 284.12) and PMMA were obtained with the help of Perkin Elmer Thermal Analyzer (Model: Pyris 1), in an inert atmosphere at a heating rate of 10°C/min.

#### 2.5.3. Scanning Electron Microscopy (SEM)

Surface morphology of Na-PCMSA ( $\overline{DS} = 1.10$ ) and Na-PCMSA-g-PMMA (%G = 284.12) samples were analyzed with the help of ESEM TMP +EDAX, Philips make model.

### 3. Results and Discussion

#### 3.1. Optimization of Photo-induced Graft Copolymerization

As photo-graft copolymerization reaction variables determine the extent of grafting and homopolymer amount, the reaction variables including the concentrations of nitric acid, photo-initiator (CAN), monomer (MMA), as well as reaction time, temperature and amount of substrate were varied to achieve the optimal grafting conditions. The results of this investigation are discussed as under.

##### *Effect of amount of Na-PCMSA*

The influence of amount of Na-PCMSA on %G and %GE was studied by varying the amount of Na-PCMSA (0.2 g to 3.0g) keeping other variables constant. The results are shown in Fig.2 (a). As it is reflected from this figure, the value of %G decreases continuously with increasing amount of Na-PCMSA while the value of %GE increases very slowly in the beginning but beyond Na-PCMSA = 0.4g it decreases with further increase in the amount of Na-PCMSA. The observed decreasing trends in the values of %G and %GE may be due to the fact that with increase in the amount of Na-PCMSA, the viscosity of the medium increases thereby obstructing the movement of photo-initiator (CAN) which ultimately reduces the grafting yields (%G & %GE). In addition, with increasing the amount of Na-PCMSA, more and more Na-PCMSA macroradicals will be produced leading to the faster rate of termination of photo-graft copolymerization, thereby lowering both %G and %GE values. Similar results are also reported in the literature [10,15,18,24,27].

##### *Effect of Photo-initiator concentration*

The photo-initiator (CAN) concentration has a remarkable influence on the grafting yields. Fig.2(b) shows the effect of CAN concentration on the grafting yields changing from  $0.50 \times 10^{-3}$  mol/L to  $10 \times 10^{-3}$  mol/L at constant temperature ( $35^{\circ}\text{C}$ ), reaction time (3h) and MMA concentration (0.10 mol/L). As is seen from the figure, both %G and %GE increased as the CAN concentration increased from  $0.50 \times 10^{-3}$  mol/L to  $4.00 \times 10^{-3}$  mol/L. The optimum values of %G and %GE were obtained to be 146.17% and 94.82% respectively at the  $[\text{Ce}^{4+}] = 4 \times 10^{-3}$  mol/L. The observed increase in %G with the CAN concentration ranging from  $0.50 \times 10^{-3}$  mol/L to  $4.00 \times 10^{-3}$  mol/L, may be attributed to the fact that in this concentration range, the increase in concentration of ceric ion results in the increase in the total number of Ce(IV)-Na-PCMSA complex which decompose to give more active sites on the backbone. Thus, this activation along the backbone is immediately followed by photo-graft copolymerization of MMA onto Na-PCMSA giving rise to higher %G (146.17%) and lower homopolymer formation ( $\%H_p = 5.18$ ). However, beyond the optimum concentration of CAN ( $4 \times 10^{-3}$  mol/L), the reduction of grafting is observed which may be due to an increase in the number of backbone radicals terminated prior to MMA addition. Further, homopolymer formation at higher photo-initiator concentration which competes with the photo-grafting reaction for available monomer could lead to a decrease in %G and %GE. Similar observations have also been reported in the literature [28-31].

##### *Effect of Nitric acid Concentration*

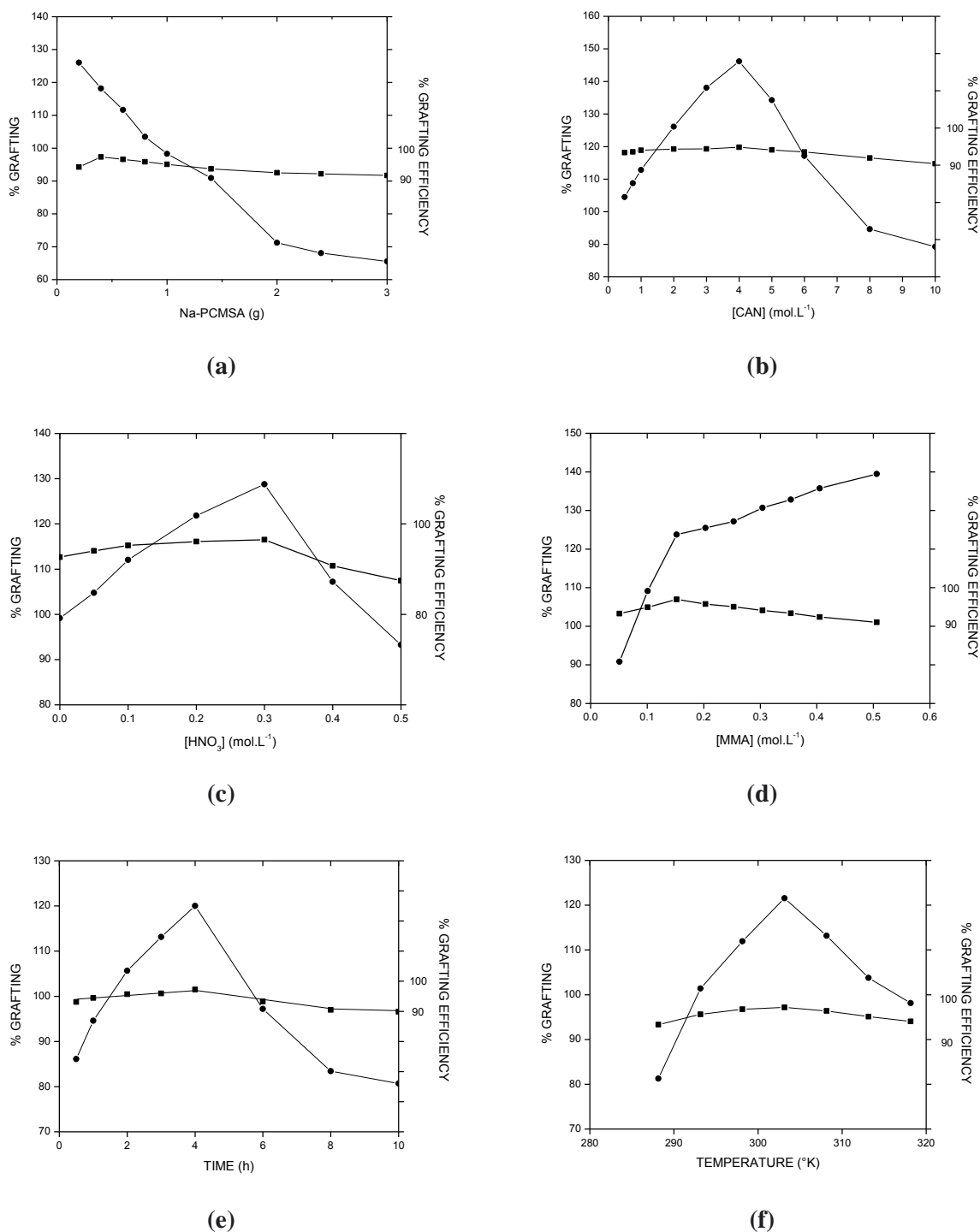
The effect of the nitric acid concentration on the grafting yields was studied by the variation of the concentration of nitric acid from nil to 0.50 mol/L, keeping fixed the concentrations of all other reagents, time and temperature. The results obtained are presented in Fig.2(c). Initially, the values of the grafting yields are found to be increased with increase in nitric acid concentration up to 0.30 mol/L. This is attributed to the increase in the concentrations of  $[\text{Ce}^{4+}]$  and  $[\text{Ce}(\text{OH})_3]^{3+}$  at the expense of  $[\text{Ce-O-Ce}]^{6+}$ . The size of  $[\text{Ce}^{4+}]$  and  $[\text{Ce}(\text{OH})_3]^{3+}$  ions is smaller than that of  $[\text{Ce-O-Ce}]^{6+}$  ion and therefore they are more effective in their ability to form complexes with the Na-PCMSA backbone than  $[\text{Ce-O-Ce}]^{6+}$  ion. It is observed from Fig.2(c) further that beyond  $[\text{Ce}^{4+}] = 0.30$  mol/L, the grafting yields decrease. This may be explained due to the fact that as the nitric acid concentration increases, the formation of more and more  $[\text{Ce}^{4+}]$  and  $[\text{Ce}(\text{OH})_3]^{3+}$  takes place which in turn accelerates the termination of the growing polymeric grafting chains resulting in the decrease in the grafting yields. Moreover,  $[\text{Ce}^{4+}]$  ion has been reported to be involved in the oxidative termination of the growing monomeric chains [32,33]. Similar observations are also reported in the literature [25,34].

##### *Effect of monomer concentration*

As the monomer concentration has a remarkable influence on the grafting yields, the effect of



monomer (MMA) concentration on the photo-grafting reaction was studied by changing the monomer concentration from 0.051 mol/L to 0.506 mol/L with all other conditions kept constant. Results obtained are displayed in Fig.2(d). It can be seen from the figure that there is a sharp increase in the value of %G with the monomer concentration up to 0.152 mol/L, beyond which the %G shows a tendency to level off. However, on the other hand the value of %GE increases steadily with the monomer concentration up to 0.152 mol/L and then decreases with further increase in the monomer concentration. The results can be explained by the fact that as the monomer concentration increases, the diffusion of the monomer



**Fig. 2. Influence of (a) amount of sodium salt of partially carboxymethylated sodium alginate (Na-PCMSA); (b) photo-initiator (CAN) concentration; (c) nitric acid (HNO<sub>3</sub>) concentration; (d) methyl methacrylate (MMA) concentration; (e) reaction time and (f) reaction temperature on: -●- %G; or -■- %GE.**

molecules into the Na-PCMSA backbone increases leading to higher %G and %GE. The decrease in %GE after the optimum monomer concentration (0.152 mol/L) could be associated with the depletion of the available MMA due to the simultaneous increase in the homopolymerization rate with the increasing MMA concentration in the polymerization medium. Such behaviors have also been obtained in other studies [24, 35, 36].

#### *Effect of Reaction Time*

In order to study the influence of reaction time on the grafting yields, the photo-graft copolymerization of MMA onto Na-PCMSA has been recorded at different reaction times ranging from 0.5h to 10h while other variables were kept constant. The results are shown in Fig. 2(e). As to the time dependence of photo-grafting reaction, %G increased rapidly in the beginning and achieved a maximum value of the grafting 120.02% within the first 4h of the process. The value of the %GE also increased very slowly and the highest value obtained was 97.22% at 4h. The results of this figure may be explained due to fact that with an increase in reaction time, the number of grafting sites on the backbone increases as a result of which the extent of initiation and propagation of photo-graft copolymerization also increases with time leading to the increase in the grafting yields. After the optimum reaction time (4h), the decrease in the values of %G and %GE is due to the decreased number of available active free radical sites for photo-grafting and retardation of diffusion of reactants. In addition, the longer UV irradiation time has a detrimental effect on the grafted chains of PMMA in the presence of a photo-initiator which is responsible for the decrease in the grafting yield values. A similar time dependency on grafting yields has been reported in the literature [15,17,23,37].

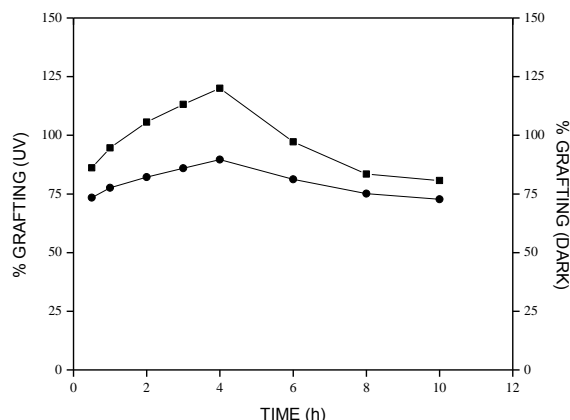
#### *Effect of Temperature*

The photo-grafting reaction was carried out at different temperatures (15°C-45°C) keeping other variables constant and the results are presented in Fig. 2(f). As can be seen from the figure that the value of %G increased with the rise of temperature from 15°C to 30°C and then with a further increase in temperature it decreased. The value of %GE also behaved in a similar fashion. At the optimum value of the temperature, 30°C [cf. Fig. 2(f)], the maximum values of the grafting yields, %G =121.56 and %GE = 97.15 were achieved. The increase in %G up to 30°C could be attributed to the increased rate of photolysis of the Na-PCMSA-Ceric complex so that more number of active sites are generated on to the Na-PCMSA backbone resulting in the increased propagation of the photo-graft copolymerization reaction. The enhanced rate of diffusion of monomer (MMA) and photo-initiator (CAN) into and onto Na-PCMSA backbone as well as the increased mobility of the monomer (MMA) molecules and their higher collision probability with the backbone (Na-PCMSA) macroradicals also resulted in the increase in %G up to 30°C. However, the observed decrease in the grafting yield values beyond 30°C may be attributed to the formation of the homopolymer (PMMA). Similar results have been obtained by many researchers [25, 38,39].

Thus, the optimal reaction conditions evaluated in the photo-graft copolymerization of MMA onto Na-PCMSA were: Na-PCMSA = 0.4 g (dry basis), [CAN] =  $4 \times 10^{-3}$  mol/L, [HNO<sub>3</sub>] = 0.3 mol/L, [MMA] = 0.152 mol/L, Time = 4h, Temperature = 30°C and Total Volume = 150 mL. The highest values of %G = 284.12 and %GE = 98.44 were achieved under the optimum reaction conditions evaluated.

### *3.2. Comparison of Photo-Initiator Efficiency*

With a view to compare the efficiency of the photo-initiator (CAN) the grafting of MMA onto Na-PCMSA ( $\overline{DS} = 1.10$ ) has been carried out in the presence as well as in the absence of the ultra-violet radiation (dark method) at various reaction times under identical reaction conditions. Thus, the results of the %G obtained with the photo and dark methods are shown in Fig. 3. It becomes evident from this figure that the values of %G are found to be higher when the grafting of MMA was carried out onto Na-PCMSA ( $\overline{DS} = 1.10$ ) at various time intervals using ultra-violet radiation, in comparison with the dark method. The reason for the observed higher %G values may be due to the fact that the complex, which has been formed by the reaction between functional groups of Na-PCMSA and ceric ions, may have dissociated to a greater extent in the presence of ultra-violet radiation (photo method) than in the absence of radiation (dark method), as a result of which a greater number of free radical sites may have been produced for grafting to occur with photo method, giving rise to higher values of %G.



**Fig. 3. Effect of reaction time on %G : (■) - photo method; and (●) - dark method.**

### 3.3 Influence of Incorporation of Carboxymethyl groups in SA molecules

In order to investigate the influence of introducing the functional group(s) like carboxymethyl in the sodium alginate (SA) molecule(s) on its behavior toward photo-grafting, the ceric-ion initiated photo-grafting of MMA onto SA was carried out using the optimized reaction conditions established in the case of photo-grafting of MMA onto Na-PCMSA ( $\overline{DS} = 1.10$ ). The results of the grafting yields (%G, %GE and %Hp) obtained are tabulated in Table 1. It becomes evident that the values of %G and %GE are found to be higher in the case of photo-grafting of MMA onto Na-PCMSA ( $\overline{DS} = 1.10$ ) compared to sodium alginate. The results could be explained on the basis of the following two aspects: (i) the introduction of carboxymethyl groups further increase the swellability of sodium alginate, thereby facilitating the diffusion of monomer (MMA) and photo-initiator (CAN) and (ii) the ionization of carboxymethyl groups along the SA chains introduces negative charges, which in turn attract ceric ions to the SA backbone leading to the formation of more active sites on the SA backbone which are available to the monomer (MMA) thereby increasing the reactivity of SA towards photo-grafting.

**Table 1. Grafting yields obtained in the case of photo-grafting of MMA onto SA as well as Na-PCMSA ( $\overline{DS} = 1.10$ ).**

Structure	%G	%GE	%Hp
SA <sup>a</sup>	210.22	87.03	12.97
Na-PCMSA <sup>a</sup>	284.12	98.44	1.56

<sup>a</sup>Optimum Reaction Conditions: SA/Na-PCMSA (dry basis) = 0.4g, [CAN] =  $4 \times 10^{-3}$  mol/L, [HNO<sub>3</sub>] = 0.3 mol/L, [MMA] = 0.152 mol/L, Time = 4h, Temperature = 30°C and Total Volume = 150 mL

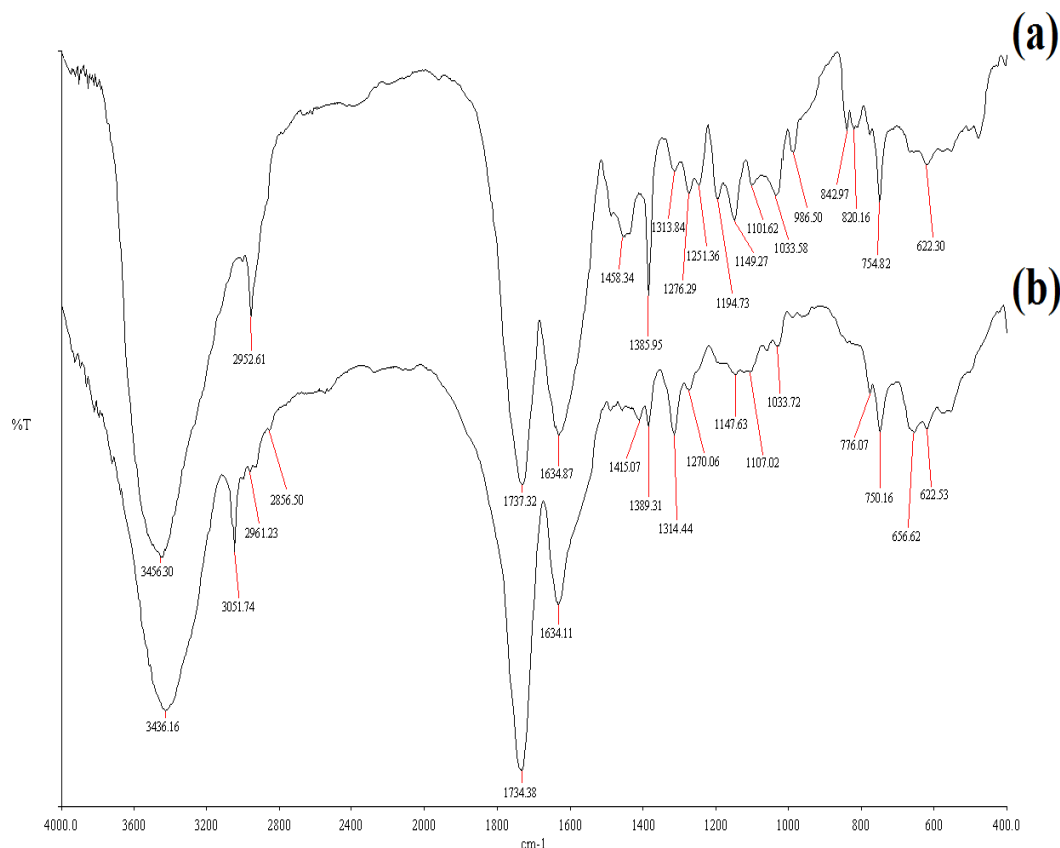
## 4. Characterization

### 4.1. FTIR Spectroscopy

In the IR spectrum of Na-PCMSA ( $\overline{DS} = 1.10$ ) (not shown), the strong absorption peak observed at 1745 cm<sup>-1</sup> is assigned to C=O stretching, suggesting the presence of -COO moiety in Na-PCMSA. The presence of -COO moiety is also evident from the absorption bands appeared at 1617 cm<sup>-1</sup> (due to asymmetric stretching of the moiety) and 1417 cm<sup>-1</sup> (due to symmetric stretching) of the moiety [24]. The IR spectra of Na-PCMSA-g-PMMA and PMMA (isolated by hydrolysis) are presented in Figs. 4(a) and 4(b) respectively. In addition to the absorption bands of Na-PCMSA, an additional strong absorption band appeared at ~1737-1745 cm<sup>-1</sup> is assigned to C=O stretching of ester group (-COOCH<sub>3</sub>), characteristic of the methacrylates [Fig.4(a)]. The PMMA isolated from the graft copolymer (Na-PCMSA-g-PMMA) also showed an absorption band at ~1732-1738 cm<sup>-1</sup> indicating the presence of C=O stretching [Fig.4(b)]. This may be attributed to the fact that the hydrolysis of the graft copolymer



gives back the grafted chains of PMMA. Thus, the results of Figs. 4(a) & 4(b) provide a substantial evidence of the photo-grafting of MMA onto Na-PCMSA ( $\overline{DS} = 1.10$ ).



**Fig. 4. FTIR Spectra of (a) Na-PCMSA-g-PMMA (%G = 284.12) and (b) PMMA.**

#### 4.2. Thermogravimetric Analysis (TGA)

The traces of TGA and DTG for Na-PCMSA ( $S_1$ ), Na-PCMSA-g-PMMA ( $S_2$ ) and PMMA ( $S_3$ ) are represented in Fig.5. The values of the temperature characteristics (IDT, FDT,  $T_{10}$ ,  $T_{50}$  and  $T_{max}$ ) as well as the values of percent weight loss of all the samples at different temperature ranges including their char yield values at 700°C are derived from the corresponding primary thermograms (Fig.5) and recorded in Table 2. It is evident from the TGA/DTG traces of Na-PCMSA [Fig. 5( $S_1$ )] sample involves only two steps of degradation. The first step encompasses the temperature range from 135.95°C to 280.85°C involving about 40.64% of the weight loss of the sample. The temperature at which the maximum weight loss occurs is 212.88°C [cf. Fig. 5( $S_1$ )]. The second step of degradation exhibits the temperature range 552.40-795.81°C involving about 19.35% weight loss with a maximum weight loss occurring at 701.51°C. This sample also degrades very slowly beyond 225°C. The chain yield of Na-PCMSA sample is found to be 28.80% at 700°C.

The graft copolymer, Na-PCMSA-g-PMMA (%G = 284.12) sample involves only single step of degradation [Fig. 5( $S_2$ )]. The graft copolymer sample in the temperature range 140.34-477.66°C involves about 87.76% weight loss with a maximum weight loss occurring at 325.26°C [cf. Fig.5( $S_2$ )]. On the other hand the homopolymer (PMMA) exhibits two steps of degradation [Fig. 5( $S_3$ )]. The first step in the temperature range 165.19-250.91°C involves 7.61% weight loss with a maximum weight loss at 220.37°C. The second step of degradation for this sample involves 84.38% weight loss in the temperature range 250.71-497.21°C [cf. Fig. 5( $S_3$ )].

The char yield values for the graft copolymer, Na-PCMSA-g-PMMA and PMMA samples are found to be 8.6% and 4.51% respectively at 700°C. The results of the char yield values lead to conclude that the thermal stability of Na-PCMSA ( $\overline{DS} = 1.10$ ) sample gets decreased upon photo-grafting of MMA onto it. This observed decrease in the thermal stability of the graft copolymer of Na-PCMSA containing PMMA is expected since polyacrylates are known to depolymerize upon pyrolysis [17, 40, 41].

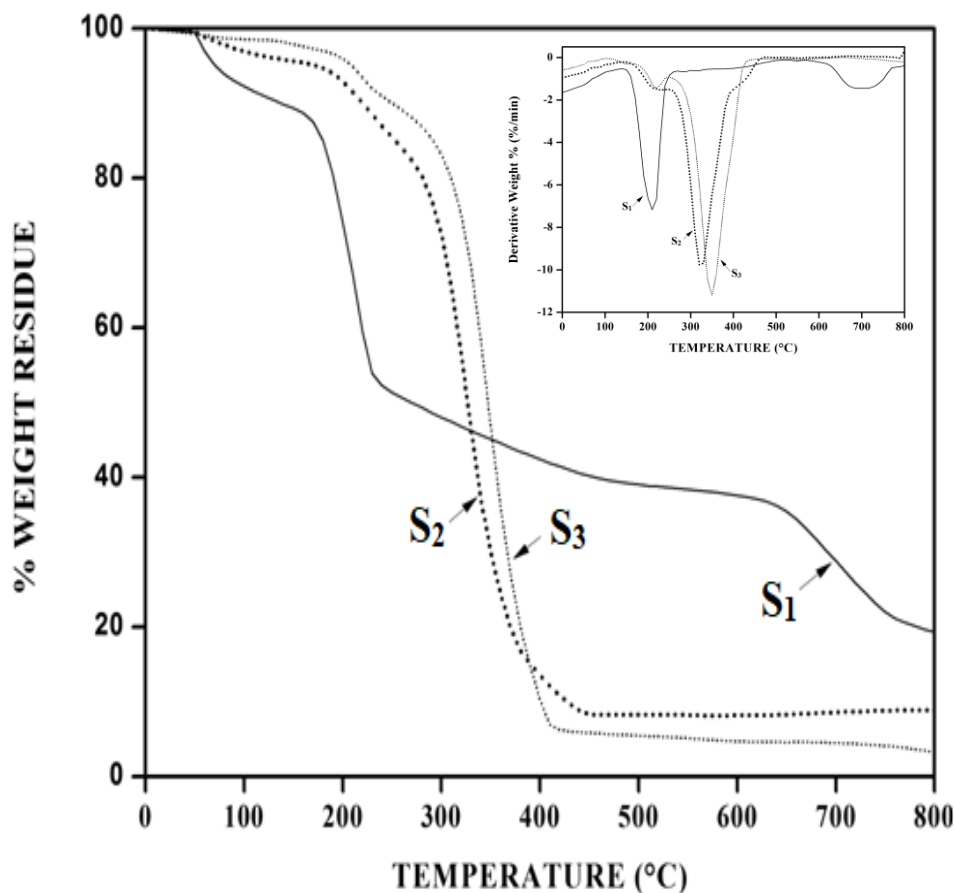


Fig. 5. TG thermograms for (—) Sodium salt of Partially Carboxymethylated Sodium Alginate (Na-PCMSA,  $\overline{DS} = 1.10$ ) ( $S_1$ ), (•••••) Na-PCMSA-g- PMMA (%G = 284.12) ( $S_2$ ) and (.....) PMMA ( $S_3$ ) at  $10^\circ\text{C}/\text{min}$ . The insert shows the first derivatives of the curves shown in the figure.

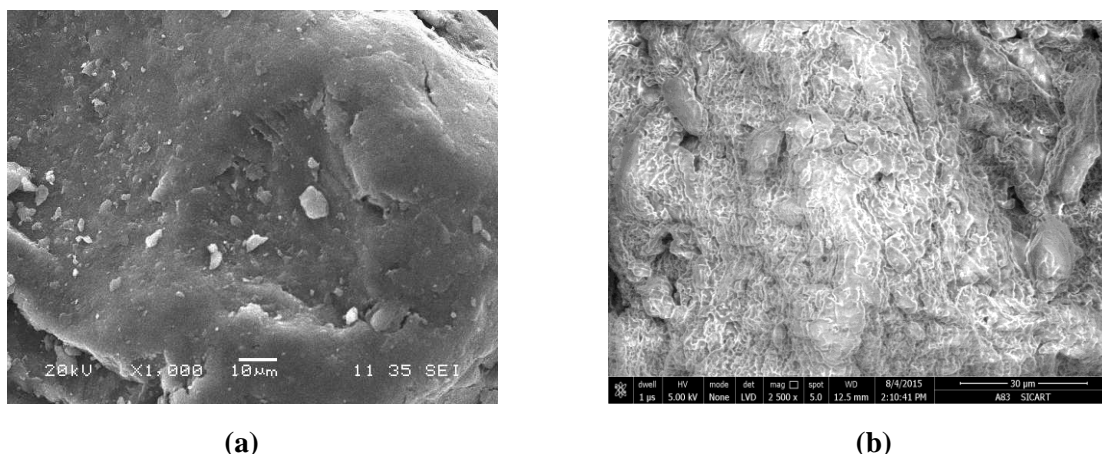
Table 2. Thermogravimetric data of Sodium Salt of Partially Carboxymethylated Sodium Alginate [Na-PCMSA, ( $\overline{DS} = 1.10$ )] ( $S_1$ ), Na-PCMSA-g-PMMA (%G = 284.12) ( $S_2$ ) and PMMA ( $S_3$ ) samples.

Sample	$T_i^0$ (°C) (IDT)	$T_f^0$ (°C) (FDT)	$T_{10}$ (°C)	$T_{50}$ (°C)	Temperature (°C) at weight loss				Temperature range (°C)	$T_{max}$ (°C)	Weight loss (%)	Char yield at $700^\circ\text{C}$ (%)
					20%	50%	60%	80%				
$S_1$	140	796.53	138.14	271.17	191	219	459	--	50-100	--	7.193	28.80
									135.95-280.85	212.88 (34.52) <sup>a</sup>	40.64	
									552.40-795.81	701.51 (71.12) <sup>a</sup>	19.35	
$S_2$	145.27	505.24	221.47	328.37	280.86	316.49	337.14	371.68	50-100	--	2.657	8.6
									140.34-477.66	325.26 (47.91) <sup>a</sup>	87.76	
$S_3$	161.72	443.13	251.80	349.01	311.19	338.24	357.79	382.64	50-100	--	0.746	4.51
									165.19-250.71	220.37 (6.21) <sup>a</sup>	7.61	
									250.71-497.21	350.11 (53.64) <sup>a</sup>	84.38	

<sup>a</sup>the values correspond to respective weight loss.

#### 4.3. Scanning Electron Microscopy (SEM)

The scanning electron micrographs obtained for Na-PCMSA ( $\overline{DS} = 1.10$ ) and Na-PCMSA-g-PMMA (%G = 284.12) samples are represented in Figs. 6(a) and 6(b) respectively. It appears from the SEM of Na-PCMSA [Fig. 6(a)] sample, that it has got smooth surface. However, upon photo-grafting of MMA onto it, the morphology of the Na-PCMSA sample has got changed drastically. The lumpy morphology is obtained [Fig. 6(b)] due to the grafted PMMA chains. Thus in comparison of the morphology of the grafted sample with that of the ungrafted sample provided supportive evidence of a photo-grafting.



**Fig. 6. Scanning Electron Micrographs of (a) Sodium salt of Partially Carboxymethylated Sodium Alginate (Na-PCMSA,  $\overline{DS} = 1.10$ ) (1000X) and (b) Na-PCMSA-g-PMMA(%G = 284.12) (2500X).**

#### 5. Conclusion

In the present study, an unreported photo-induced graft copolymerization of methyl methacrylate (MMA) onto Na-PCMSA ( $\overline{DS} = 1.10$ ) has been carried out using ceric ammonium nitrate (CAN) as a photo-initiator to synthesize a novel graft copolymer, Na-PCMSA-g-PMMA. The synthesis of the graft copolymer has been optimized through the variation of different reaction variables such as concentrations of photo-initiator (CAN), nitric acid, and monomer (MMA) as well as reaction time, temperature and amount of the backbone in terms of the determination of the highest grafting yields (%G = 284.12, %GE = 98.44, and %H<sub>p</sub> = 1.56). The dependence of reaction variables on the grafting yields has been explained. The evaluated optimum reaction conditions are: Na-PCMSA = 0.4g (dry basis), [CAN] =  $4 \times 10^{-3}$  mol/L, [HNO<sub>3</sub>] = 0.3 mol/L, [MMA] = 0.152 mol/L, Time = 4h, Temperature = 30°C, and Total Volume = 150mL. The grafting of MMA onto Na-PCMSA ( $\overline{DS} = 1.10$ ) has also been carried out in the presence as well as the absence of the ultraviolet-radiation (dark method) with a view to study the efficiency of photo-initiator (CAN). The influence of introducing the functional groups like carboxymethyl in the sodium alginate molecule on its susceptibility toward photo-grafting with MMA has been investigated and it has been observed that changing the chemical structure of SA by carboxymethylation has enhanced its behavior toward photo-grafting. The plausible explanation for the observation has also been furnished. The photo-grafting process has been confirmed and the products are characterized by employing FTIR, TGA/DTG and SEM techniques. The synthesized novel graft copolymer (Na-PCMSA-g-PMMA) after treating with hydroxylamine in the presence of alkaline solution may find potential application as a novel ion-exchangeable resin.

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#### Conflicts of Interest

The authors declare no conflict of interest.

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