Grafting of Methyl acrylate onto Sodium Salt of Partially Carboxymethylated Guar Gum Initiated by Potassium Persulphate as a redox initiator

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ABSTRACT

Using potassium persulfate as a redox initiator in an aqueous medium, a previously unknown graft copolymer of poly methyl acrylate (PMA) and the sodium salt of partially carboxymethylated guar gum (Na-PCMGG) was created. By gradually changing different reaction parameters, the best reaction conditions for providing the highest proportion of grafting were assessed. (viz. concentrations of potassium persulphate, monomer as well as reaction time, temperature, and amount of substrate). Maximum grafting efficiency and percentage under ideal reaction circumstances [Na-PCMGG (g) = 0.25 (dry basis); [KPS] = 0.03 mol.L^{-1}; [MA] = 0.037 mol.L^{-1}; Time = 2h; Temperature = 40^{o}C and Total Volume = 150mL] %GE = 98.31 and %G = 203.40. The kinetic scheme that we had previously proposed was found to be in excellent agreement with the experimental findings. Scanning electron microscopy and spectroscopic analysis were used to describe every sample. Thermal technique characterizations are currently being worked on. The Na-PCMGG-g-PMA graft copolymer that was created may be used as a metal absorbent.

Keywords: Sodium salt of Partially Carboxymethylated Guar Gum, Graft Copolymerization, Methyl Acrylate, Optimal Reaction Conditions, Characterization.

1. INTRODUCTION

Graft copolymerization, a method of chemically altering a polymeric material made from renewable resources, is generally recognized as an efficient way to give the backbone polymer useful properties without significantly changing the original ones. Because the activation energy of redox initiation is so much lower than that of the other methods, chemical initiation of grafting is the simpler of the different methods [1]. However, the grafting outcome is significantly influenced by the choosing of redox initiating system.

A naturally occurring galactomannan polysaccharide, guar gum (GG) has a continuous chain of β-D-mannopyranosyl units linked (1→4) and single member α-D-galactopyranosyl units (1→6) as side branches [2]. Due to the incomplete hydration of GG at ambient temperature and poor solution clarity as well as the desire for products with modified or special properties, we have used the carboxymethylated derivative of guar gum i.e. sodium salt of partially carboxymethylated guar gum (Na-PCMGG) in the present work.

Petroleum, textile, paper, food, explosives, mining, minerals, pharmaceuticals, medicines, and drugs are just a few of the sectors that use guar gum and its derivatives [3]. As a result, even though guar gum and its derivatives have a broad range of uses, they are also easily biodegradable like other polysaccharides [4] which could be prevented by attaching vinyl monomers to them.

To date many investigations have been carried out on grafting of vinyl monomers onto guar gum [5,6,7] and sodium salt of partially carboxymethylated guar gum [8,9,10,11,12] using various redox initiating systems. We attempted to modify Na-PCMGG in the present study by methyl acrylate free radical graft copolymerization, and we evaluated the best reaction conditions to enable the greatest percentage of grafting. This was done in order to clarify the grafting process as well as to produce specialized polymeric materials. The newly developed Na-PCMGG-g-(polyhyrdoxamic acid) ion exchange resin can be made by treating the optimally synthesized graft copolymer, Na-PCMGG-g-PMA (%G = 203.40), with hydroxylamine hydrochloride, which has the potential to be used as an adsorbent material to remove heavy metal ions from industrial and other waste materials.

2. EXPERMINETAL

2.1 *Materials and Methods*

Encore Natural Pvt. Ltd. Naroda, Ahmedabad, Gujarat, India graciously provided a sample of sodium salt of partly carboxymethylated guar gum (Na-PCMGG, $\overline{DS}$ = 0.15) for this study. It was purified using the precipitation technique, and the salt was eliminated by repeatedly washing the sample in 95% aqueous methanol before washing it in pure methanol and ether, respectively. It was dried at 40°C in a vacuum furnace. MA (Sigma Aldrich, USA) was washed with 2% sodium hydroxide solution to remove the stabilizer. After treating it with alkali solution, it was washed repeatedly with distilled water. It was freed from alkali and dried over anhydrous sodium sulphate and then distilled at atmospheric pressure, the middle fraction was used. KPS of reagent grade was used as received. 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 to for the preparation of all the solutions as well as for polymerization reactions.

2.2 Graft Copolymerization

A 500 ml three-necked flask equipped with mechanical stirrer, reflux condenser and a gas inlet system was immersed in a constant temperature bath for grafting reactions. In a typical reaction, varying amount (0.25-30g) of Na-PCMGG ($\overline{DS}$ = 0.15) was dissolved in low conductivity water (100 mL) with constant stirring and bubbling a slow stream of nitrogen gas for 1h at the desired temperature (20^o –80^oC). Freshly prepared KPS (5 x 10^{-3} M to 45 x 10^{-3} M) solution was added and stirred for 20 min. Nitrogen gas was continuously passed through the reaction solution and freshly distilled methyl acrylate (MA) monomer (0.036 M to 0.295 M) was added. The grafting reactions were carried out for varying time intervals (0.5 to 10 h). After completion of the reaction, the mixture was immediately poured into excess of methanol to coagulate 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^oC. The homopolymer poly(methyl acrylate) (PMA) was separated from the crude graft copolymer by extraction with acetone for 48h. After complete removal of the homopolymer, the pure graft copolymer was dried at 40^oC under vacuum to a constant weight.

2.3 Isolation of Grafted Chains

The graft copolymer of Na-PCMGG ($\overline{DS}$ = 0.15) containing PMA was hydrolyzed by refluxing for 12 h in 1N HCl as suggested by Brockway and Seaberg [13]. After all the Na-PCMGG went into the solution, a resinous mass was obtained which was characterized with IR spectroscopy.

2.4 FTIR Spectra

The IR Spectra of Na-PCMGG ($\overline{DS}$ = 0.15), Na-PCMGG-g-PMA and PMA were taken in KBR pellets using Nicolet Impact 400D Fourier Transform Infra Red Spectrophotometer.

2.5 Scanning Electron Microscopy (SEM)

Model ESEM TMP + EDAX, Philips make was used to obtain the micrographs of Na-PCMGG ($\overline{DS}$ = 0.15) and Na-PCMGG-g-PMA (%G = 203.40).

2.6 Grafting Yields and Kinetic Parameters

The percentage of grafting, grafting efficiency, percentage homopolymer and rates of polymerization (R_p), graft copolymerization (R_g) and homopolymerization (R_h) were evaluated by the help of the following expressions :

$$\text{(i) Percentage Grafting } (\%G) = \frac{\text{Wt.of Polymer grafted}}{\text{Wt.of homopolymer}} \text{ X } 10^2 \quad (1)$$

$$\text{(ii) Percentage Grafting Efficiency } (\%GE) = \frac{\text{Wt.of Polymer grafted}}{\text{Wt.of Polymer grafted + Wt.of Homopolymer}} \text{ X } 10^2 \quad (2)$$

$$\text{(iii) \% Homopolymer } (\%Hp) = 100 - \%GE \quad (3)$$

$$\text{(iv) } R_p\ (mol.L^{-1}.s^{-1}) = \frac{\text{Wt. of Polymer Grafted + Wt. of Homopolymer}}{\text{Mol.wt.of monomer x Reaction time (sec) x Vol. of the reaction mix.(mL)}} \text{ x } 10^3 \quad (4)$$

$$\text{(v) } R_g\ (mol.L^{-1}.s^{-1}) = \frac{\text{Wt. of Polymer Grafted}}{\text{Mol.wt.of monomer x Reaction time (sec) x Vol. of the reaction mix.(mL)}} \text{ x } 10^3 \quad (5)$$

$$\text{(vi) } R_h\ (mol.L^{-1}.s^{-1}) = \frac{\text{Wt. of Homopolymer}}{\text{Mol.wt.of monomer x Reaction time (sec) x Vol. of the reaction mix.(mL)}} \text{ x } 10^3 \quad (6)$$

3. RESULTS AND DISCUSSION

Determination of optimum reaction conditions

The optimal reaction conditions for affording maximum percentage of grafting in the case of grafting of MA onto Na-PCMGG ($\overline{DS}$ = 0.15) have been evaluated by varying various reaction parameters.

Effect of Backbone Concentration

Figure 1(a) illustrates how the quantity of Na-PCMGG affects grafting yield. It is clear from the findings that as Na-PCMGG concentration rises, %G continuously declines. This is due to a decline in the MA to Na-PCMGG ratio's value. However, the grafting efficiency immediately rises to the substrate amount's ideal value before falling. The reason for the early rise in %GE is that Na-PCMGG is easily accessed by both monomer and initiator molecules, leading to the production of an increasing number of graft side chains. (PMAs). However, as

Na-PCMGG concentration is further increased, the reaction medium's viscosity rises, eventually restricting macroradical migration and reducing grafting yield.

Effect of Initiator Concentration

Figure 1(b) illustrates the concentration range where the impact of KPS concentration on grafting yields was investigated. The findings show that the percentage of grafting is found to be fairly appreciable at a relatively low initiator concentration. This can be explained by the fact that the ionization of the carboxyl groups on the backbone increased the initiator concentration's attraction to the backbone, which in turn causes the formation of more active centers and, as a result, results in a typically higher number of %grafting. A higher initiator concentration was found to enhance the value of grafting yields (% G and %GE), which peaked at 149.80 at [KPS] = 30 x 10^{-3} mol/L but decreased at higher concentrations. Because more primary radicals are produced during polymerization, more propagating radicals are produced, which increases the number of grafting sites on the Na-PCMGG backbone and results in a rise in the proportion of grafts within the cited range. Beyond the ideal number, however, the rate of termination rises and the percentage of grafting yields falls.

Monomer Concentration

Figure 1(c) findings demonstrate that as concentration rises up to 0.037 mol/L, %G grows quickly. Additionally, at greater monomer concentrations, %G exhibits a tendency to plateau. However, %GE also starts off very slowly and then starts to decline once more. While the decline in %GE at higher MA concentrations is linked to excess monomer molecules may be due to movement which eventually proximal end of the graft chain, the observed initial increase in grafting yield is ascribed to the increased supply of monomer (MA) to the Na-PCMGG macroradicals. The decrease in grafting sites on the Na-PCMGG molecule may be the cause of the grafting tapering off after saturation. As a result, the ungrafted MA has a propensity to make Homopolymer (PMA).

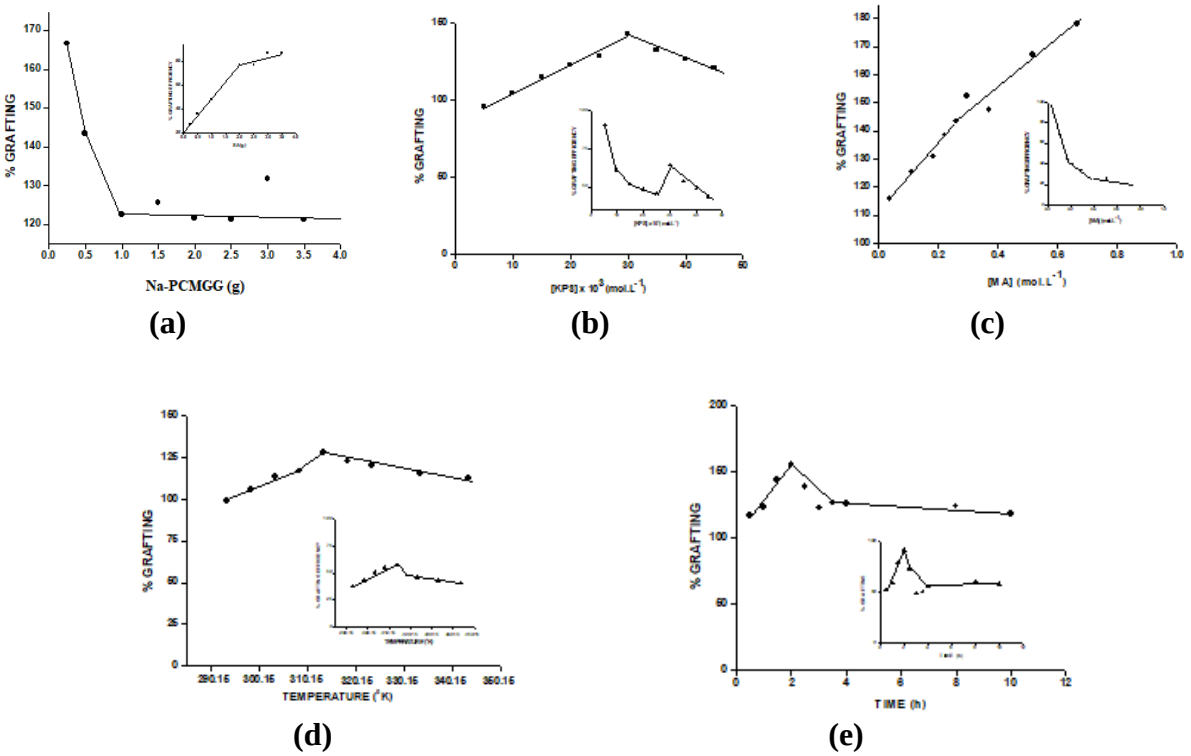


Figure 1. Influence of **(a)** amount of sodium salt of partially carboxymethylated Guar Gum (Na-PCMGG); **(b)** KPS concentration; **(c)** MA concentration; **(d)** Temperature and **(e)** Time on: (•) %G ; or (▲) %GE.

Effect of Temperature

The grafting reaction was conducted between 20 and 80°C while holding the other variables fixed. Figure 1(d) illustrates how climate affects %G and %GE. The maximum %G attained at the optimum point and its value are shown by the results to decrease with increasing temperature. The increase in the rate of monomer diffusion is the cause of the reliance of % G on temperature. Graft copolymerization happens with poor selectivity at temperatures above the optimal range, and various hydrogen abstraction and chain transfer reactions may also be accelerated at higher temperatures, resulting in a reduction in grafting yields.

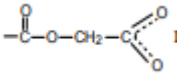
Effect of Reaction Time

The influence of reaction time on the grafting yields (%G and %GE) is represented in Figure 1(e). It can be seen from this figure that the values of %G and %GE increased with increase in reaction time up to 2h and thereafter they are found to be decreased. The increase in the values of the grafting yields is attributed to the increase in the number of grafting sites on the Na-PCMGG backbone as reaction progresses. But after 3h, the observed decrease in the values of the grafting yields is due to the depletion of monomer and initiator concentration as well as shortage of the availability of the grafting sites.

Thus, from the above discussion, the optimized reaction conditions obtained for grafting of PMA onto Na-PCMGG : Na-PCMGG (g) = 0.25 (dry basis); [KPS] = 0.03 mol.L^{-1}; [MA] = 0.037 mol.L^{-1}; Time = 2h; Temperature = 40°C and Total Volume = 150mL The highest percentage of grafting (203.40) and percentage of grafting efficiency (98.31) were achieved under the above referred optimized reaction conditions.

4. EVIDENCY OF GRAFTING

4.1 FTIR Spectra

Figures 2 represent the IR spectra of Na-PCMGG ($\overline{DS}$ = 0.15), Na-PCMGG-g-PMA (%G =203.40) and PMA respectively. It is evident from Figure 2(a) that the absorption peak appeared at 1744 cm^{-1} is a strong one and is assigned to C=O stretching, suggesting the presence of moiety  in the Na-PCMGG. The presence of –COO moiety present in Na-PCMGG is also evident from the absorption bands appeared at ~1613 cm^{-1} and ~1416 cm^{-1} [cf. Figure 2(a)]. The IR spectrum of the graft copolymer, Na-PCMGG-g-PMA [Figure 2(b)] shows absorption bands of the Na-PCMGG as well as an additional strong ~1745 cm^{-1} absorption band at assigned to C=O stretching of ester group (-$COOCH_3$), characteristic of the methacrylates. The IR spectrum of PMA [Figure 2(c)] indicates the presence of C=O stretching at ~1745 cm^{-1}. This may be attributed to the fact that the hydrolysis of the graft copolymer, Na-PCMGG-g-PMA, gives back methyl acrylate. Thus, the results of Figures 2(a) to 2(c) provide a substantial evidence of grafting of MA onto Na-PCMGG ($\overline{DS}$ = 0.15).

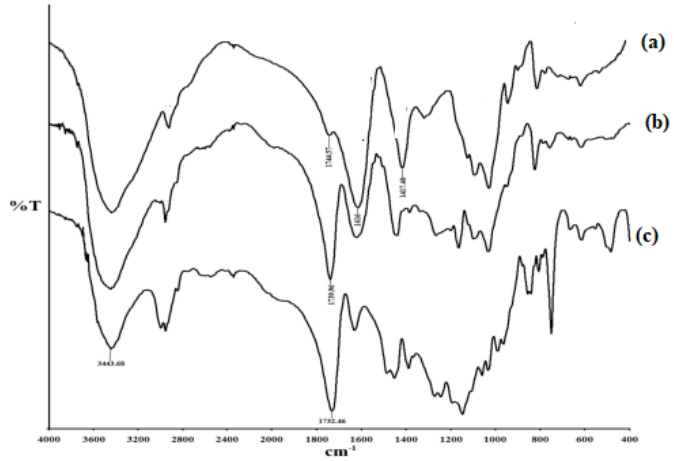
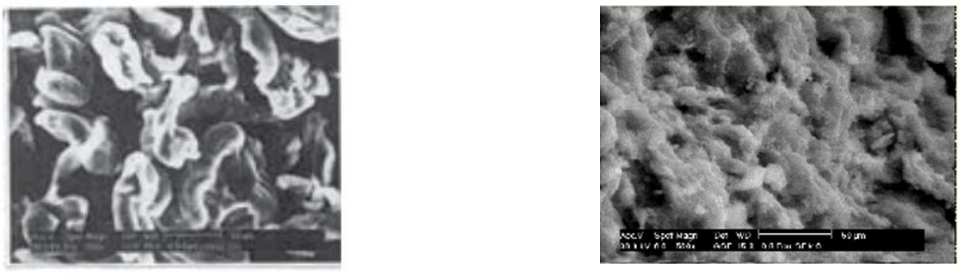


Figure 2. FT-IR spectra of **(a)** Na-PCMGG ($\overline{DS}$ = 0.15), (b) Na-PCMGG-g-PMA (%G = 203.40) and (c) PMA samples.

4.2 Scanning Electron Microscopy (SEM)

Figure 3 (a) and Figure 3(b) represents the scanning electron micrographs obtained for Na-PCMGG ($\overline{DS}$ = 0.15) and its graft copolymer, Na-PCMGG-g-PMA (%G = 203.40) respectively. Upon comparing the morphology of the grafted samples [Figure 3(b)] with ungrafted sample [Figure 3(a)] it reveals that additional surface deposits indicating that grafting has taken place.



(a) **(b)**

Figure 3. Scanning Electron Micrograph of **(a)** Na-PCMGG (500x) and **(b)** Na-PCMGG-g-PMA (500X).

CONCLUSION

The current findings demonstrate that PMA occurs onto Na-PCMGG (= 0.15), with potassium persulfate acting as the redox activator. Both spectral and scanning electron microscopy were used to analyze the Na-PCMGG-g-PMA copolymer, revealing the structural differences from the Na-PCMGG. The highest graft yields (%G = 203.40 and %GE = 98.31) and the best reaction conditions were achieved when the graft copolymerization was done under the following circumstances: Na-PCMGG (g) = 0.25 (dry base); [KPS] = 0.03 mol.L^{-1}; [MA] = 0.037 mol.L^{-1}; Temperature = 40^{o}C, Time = 2h, and Total Volume =150mL. After being treated with hydroxylamine hydrochloride, the current work's perfectly synthesized graft copolymer, Na-PCMGG-g-PMA, may find use as a novel metal adsorbent. There is already more work being done in this area.

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