



Graft Copolymerization of butyl acrylate onto sodium salt of partially Carboxymethylated Psyllium by Photopolymerization

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ABSTRACT

The graft copolymerization of butyl acrylate onto sodium salt of partially carboxymethylated psyllium (Na-PCMPsy) in an aqueous medium was investigated, using ceric ammonium nitrate (CAN) as a photo initiator. The reaction variables including concentration of initiator, nitric acid, monomer and amount of the backbone as well as time and temperature have been varied for establishing grafting. The influence of these reactions conditions on the grafting yield has been discussed. Fourier transforms infrared spectra analysis and scanning electron microscopy characterized the graft copolymer.

Key words: photo-polymerization, carboxymethylated psyllium, graft copolymers, optimized reaction conditions, SEM.

INTRODUCTION

Psyllium is a natural polysaccharide obtained from plantago ovata which is composed of neutral arabinoxylan (arabinose 22.6%, xylose 74.6%) having straight chain of xylose with arabinose branches at 2 or 3 position randomly attached [1]. Psyllium is highly viscous in an aqueous medium and it is natural biodegradable polymer which decomposes before its melts, in order to overcome this difficulty the carboxymethylated derivative of it [2,3]. Polysaccharide graft copolymers have been prepared to add new properties to the natural polymers with a minimum loss of native properties. Since last seven to eight years, grafting of various vinyl monomers onto psyllium has been the most frequently attempted method to impart desirable properties to the polysaccharide without degradation [4-8]. Several techniques have been reported for graft copolymerization such as chemical treatment, plasma treatment, gamma radiation but the UV-radiation techniques most promising and practical method because of its simplicity [9-13]. The photo-induced graft copolymerization by low energy UV-radiation possesses certain advantages like less degradation of the native polymer chain [14-23]. Moreover, the UV-radiation equipment is most cost effective than the high energy radiation equipments.

In present work, psyllium was carboxymethylated, then photo-induced grafted with butyl acrylate in an aqueous medium using ceric ammonium nitrate as a photo-initiator and optimized the reaction conditions. The graft copolymers have been characterized by FT-IR spectroscopy and scanning electron microscopic (SEM) techniques.

MATERIALS AND METHODS

Psyllium was supplied by Gujarat Sat–Isabgol Factory, Unjha (Gujarat/India). Sodium salt of Partially Carboxymethylated Psyllium was prepared from Psyllium and purification as well as the measurement of degree of substitution were followed as discussed earlier. The \overline{DS} was found to be 0.13. Butylacrylate (BA) (Fluka) was washed with 2% NaOH aqueous solution, followed by washing with distilled water, then dried over anhydrous calcium chloride and finally purified with usual procedure. Ceric ammonium nitrate, CAN (Analar grade, Qualigens, Glaxo India Ltd) was used as photo-initiator. All other reagents and solvents used were of reagent grade. Nitrogen gas was purified by passing through freshly prepared alkaline pyrogallol solution. The double distilled water was used for the preparation of solutions as well as in polymerization reactions.

2.2 Photo-induced Graft Copolymerization

The grafting reactions were carried out in a photochemical reactor. A weighed amount of Na-PCMPsy (0.2 - 1.0 g) was dissolved in double distilled water and the solution was stirred for an hour at 55°C and there after certain time interval at room temperature 2.5 mL of freshly prepared CAN solution (0.5×10^{-3} – 10.0×10^{-3} mol/L) in nitric acid (NiL–0.5 mol/L) was added to the reaction flask and contents were then flushed with purified nitrogen gas for half an hour followed by addition of a known concentration of freshly distilled BA (0.037 – 0.369 mol/L). The reaction flask was then assembled with immersion well containing 125 W medium pressure mercury lamp. The whole assembly (photochemical reactor) was placed in a dark cabinet. The lamp was then illuminated. Water from constant temperature water circulation bath was circulated over immersion as well as the reaction flask. The solution then was irradiated with continuous stirring for different time intervals (0.5 – 10 h) in the temperature range 20-45°C. After completion of the grafting reaction, the irradiated sample solution was removed carefully and the crude graft product was isolated by centrifugation. It was then purified by 95% methanol and finally washed with pure methanol. The crude copolymer sample of Na-PCMPsy-g-PBA thus obtained was dried under vacuum at 40°C. The homopolymer was removed from the crude graft copolymer by exhaustive soxhlet extraction with acetone for 48 h.

2.3 UV-Radiation Source

The UV-radiation source was purchased from Scientific Aids and Instruments Corporation (SAIC), Madras. The UV-reactor was then assembled with immersion well containing 125 W medium pressure mercury lamps. The medium pressure lamps have much more intense arcs and radiate predominantly 254, 365, or 425 nm radiation.

2.4 IR Spectra

IR spectra of Psyllium, Na-PCMPsy (\overline{DS} = 0.13), Na-PCMPsy-g-PBA and PBA were taken in KBr pellet using Nicolet Impact 400 D Fourier Transform Infra Red Spectrophotometer.

2.5 Scanning Electron Microscopy (SEM)

Model ESEM TMP + EDAX, Philips make has been used to obtain the micrographs of Psyllium, Na-PCMPsy (\overline{DS} = 0.13) and Na-PCMPsy-g-PBA graft copolymer samples.

RESULTS AND DISCUSSION

The reaction variables including concentrations of initiator (CAN), nitric acid, monomer (BA) and amount of the backbone as well as time and temperature have been varied for establishing the optimized reaction conditions for grafting.

3.1 Effect of backbone concentration

Fig.1 represents the effect of backbone concentration on percentage grafting (%G) and percentage grafting efficiency (%GE). It is seen from these figure that with increasing Na-PCMPsy concentration, the values of %G and %GE are found to be decreases from the very beginning. 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 increase in Na-PCMPsy concentration, the decrease in the monomer-to-backbone ration lowers %G. Secondly, high Na-PCMPsy macroradicals, which can interact with each other to terminate the reaction as a result termination rate of graft copolymerization becomes faster than the rate of initiation thereby also lowering %G. The value of %GE also decreases with increase in the amount of Na-PCMPsy as well as it decreases due to increase the rate of homopolymer formation (PBA).

3.2 Effect of photoinitiator concentration

It Can be observed from the figure 2 that initially both %G and %GE are found to be increased with increase in photoinitiator concentration reached maximum values of %G and %GE at $[CAN] = 6.0 \times 10^{-3}$ mol/L. At this optimum value of the photoinitiator concentration, the value of %G is found to be 229.31%. Beyond this optimum value of the photoinitiator concentration, %G and %GE are found to be decreased. The observed increase in %G within the photoinitiator concentration (CAN) range 0.5×10^{-3} - 3.00×10^{-3} may be due to the fact that within these concentration ranges, the complex formation between the -OH groups as well as carboxylate anion of Na-PCMPsy and Ce^{+4} is facilitated and the photo decomposition of the complex leads to the formation of more active sites. The observed decrease in the grafting yields (%G and %GE) beyond optimum concentration may be attributed to fast termination of the growing grafted chains. Furthermore, homopolymer (PBA) formation at higher initiator concentration which competes with the grafting reaction for the available monomer (BA) could also lead to a decrease in %G as well as %GE.

3.3 Effect of acid concentration

The photo-grafting of BA onto Na-PCMPsy at different nitric acid concentrations are shown in Figure 3. It can be observed from this figure that there exists an optimum concentration of nitric acid at 0.20 mol/L which affords maximum percentage of grafting and grafting efficiency. The values of %G and %GE are found to be decrease beyond the respective optimum concentration of nitric acid. It is interesting to note that even at zero concentration of nitric acid, an appreciable value of percentage of grafting is observed this may be due to the possibility that, even in absence of acid, in an aqueous medium Na-PCMPsy ionizes fully to a greater extent which facilitates the diffusion of monomer as well as photoinitiator leading to appreciable values of grafting. The values of %G and %GE increase in the beginning with increase in nitric acid concentration may be due to decrease 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 and %GE could be attributed to a corresponding reduction in ceric-Na-PCMPsy complex formation, as well as an increase in termination rates.

3.4 Effect of monomer concentration

Figure 4 shows the effect of monomer concentration on the grafting parameters. The grafting yields (%G and %GE) are found to be increased sharply with the increase in monomer concentration from 0.037 to 0.258 mol/l. However, further increase in monomer concentration did not improve %G further and decreased %GE. It is well known that the rate of grafting reaction depends on the rate of availability of monomer to substrate. The initial increase in the grafting reaction was due to increasing supply of monomers to backbone macroradicals, however, the decline in %GE at higher concentration of BA could be ascribed to the chain transfer to excess monomer molecules in the vicinity of growing ends of grafted chains.

3.5 Effect of temperature

The effect of reaction temperature on graft parameters is shown in Figure 5. It is found that %G and %GE are affected by the reaction temperature between 20 and 40°C. This is attributed to the fact that the viscosity of the medium is maintained low without gel effect all through the reaction. When temperatures exceed 40°C, the termination reaction and radicals speed up, thereby decreasing the graft parameters [%G and %GE]. The observed decrease in grafting efficiency with rising temperature may also be attributed to the solubility of monomer in the aqueous phase at higher temperatures, thus increasing the possibility of the monomer to contact Ce(IV), hence more Ce(IV) will be available to initiate the homopolymerization.

3.6 Effect of time

It can be observed from the figure 6 that the values of %G and %GE are found to be increased in the beginning and achieved the maximum value of the grafting 250.95% at 2 h. However, beyond these optimum value, %G and %GE are found to be decreased with further increase in time. The result of this figure may be explained on the basis of the fact that with 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. But beyond the optimum value of reaction time as the available sites for photo-grafting of the corresponding monomer on the Na-PCMPsy backbone get reduced, the decrease in the value of % G as well as the decrease in % GE values is observed. The observed decrease in the values of grafting yields is also may be presumably due to the detrimental effect of UV-radiation onto the grafted side chains PBA at longer irradiation times in the presence of the photoinitiator.

Characterization

FT-IR Spectroscopy

The FT-IR spectrum of pure psyllium (Fig. 7) shows the characteristic peak at 3407 cm⁻¹ due to -OH stretching, -C=O of -COOH at 1640 cm⁻¹ and ether linkage at 1465 cm⁻¹. FT-IR spectrum of Na-PCMPsy (Fig.8) shows characteristic peaks at 1605 and 1423 cm⁻¹ respectively due to asymmetric and symmetric vibration of -COOH group. This can be attributed to the incorporation of carboxymethyl groups in psyllium. FT-IR spectrum of Na-PCMPsy-g-PBA (Fig. 9) shows characteristic strong adsorption band about 1730-1750 cm⁻¹ assigned to -C=O stretching of ester group (-COOCH₃) characteristics of acrylates.

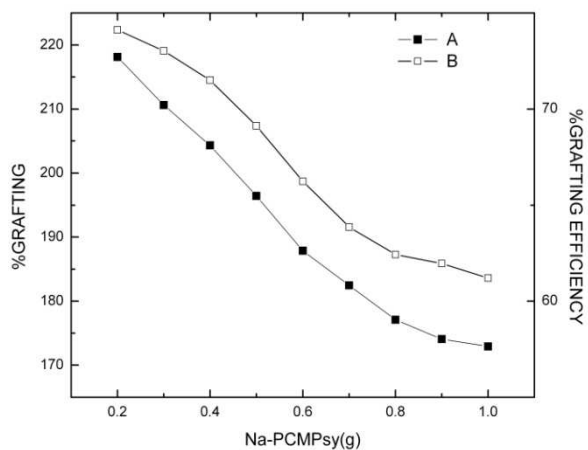


Figure 1: Effect of amount of Na-PCMPsy on: (A)-%G; or (B)-%GE

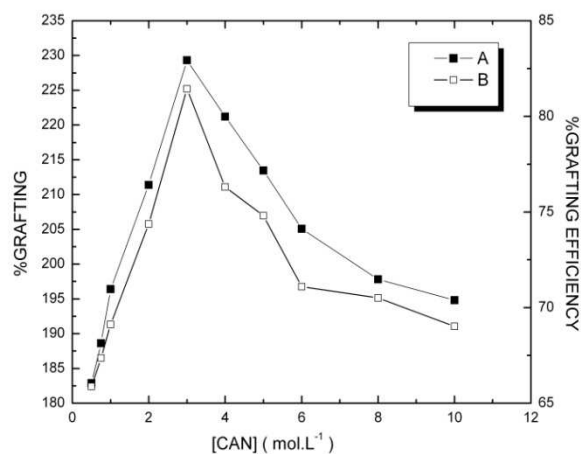


Figure 2: Effect of ceric ammonium nitrate concentration on: (A)-%G; or (B)-%GE

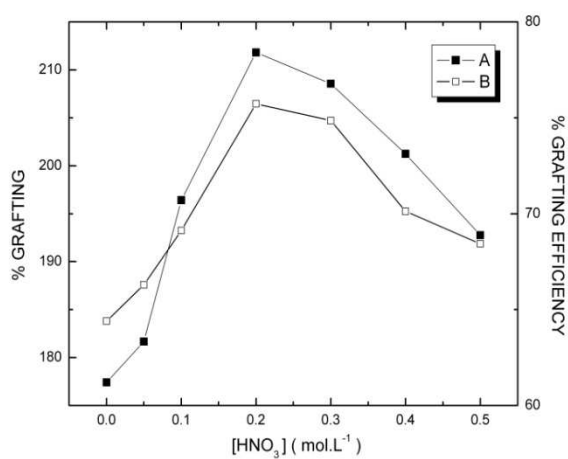


Figure 3: Effect of nitric acid concentration on: (A)-%G; or (B)-%GE

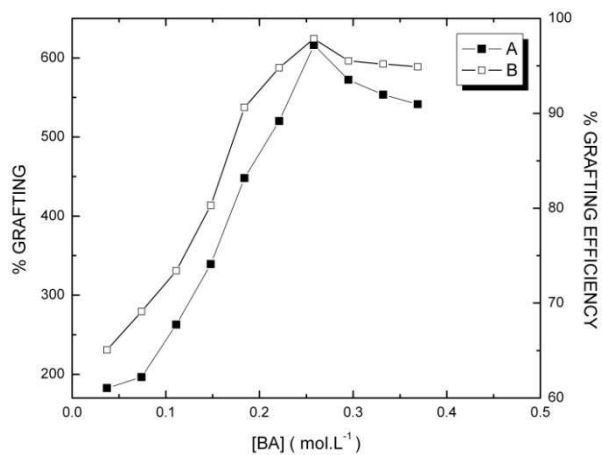


Figure 4: Effect of monomer concentration(BA) on: (A)-%G; or (B)-%GE

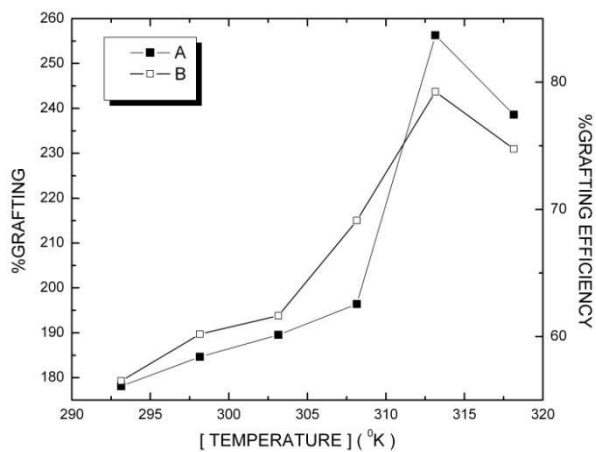


Figure 5: Effect of temperature on: (A)-%G; or (B)-%GE

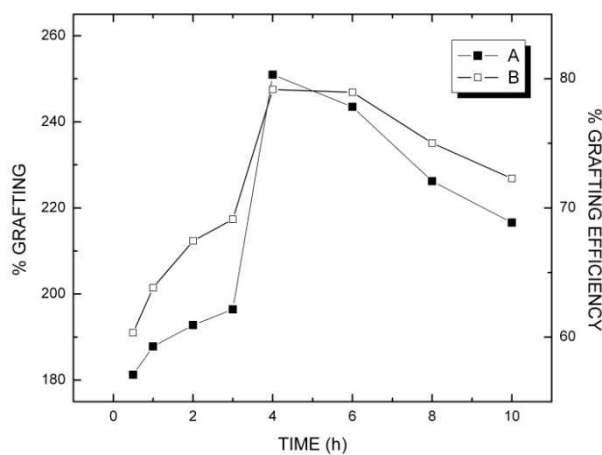


Figure 6: Effect of reaction time on: (A)-%G; or (B)-%GE

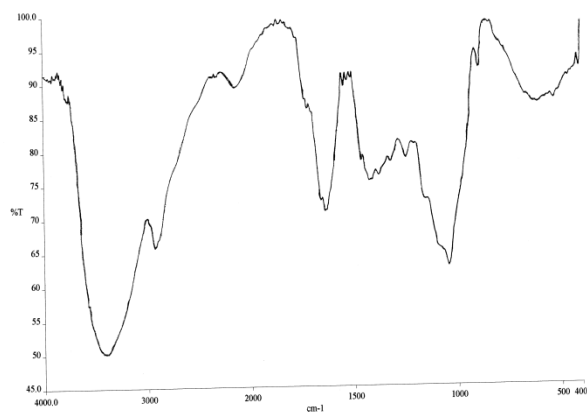


Figure 7. IR spectrum of psyllium

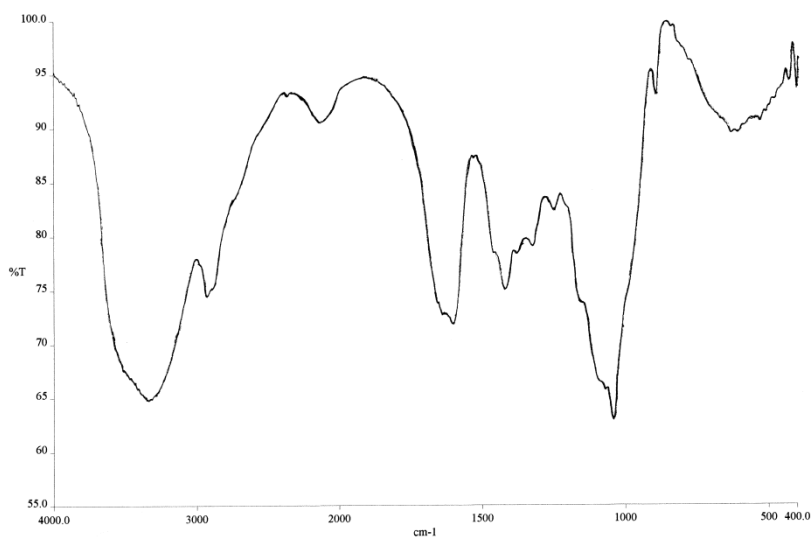


Figure 8. IR spectrum of Na-PCMPsy

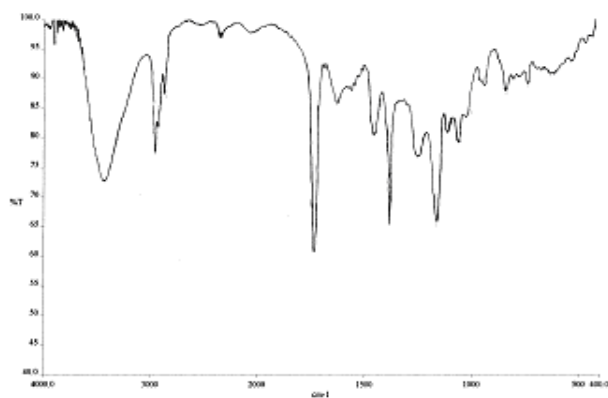


Figure 9. IR spectrum of Na-PCMPsy-g-PBA

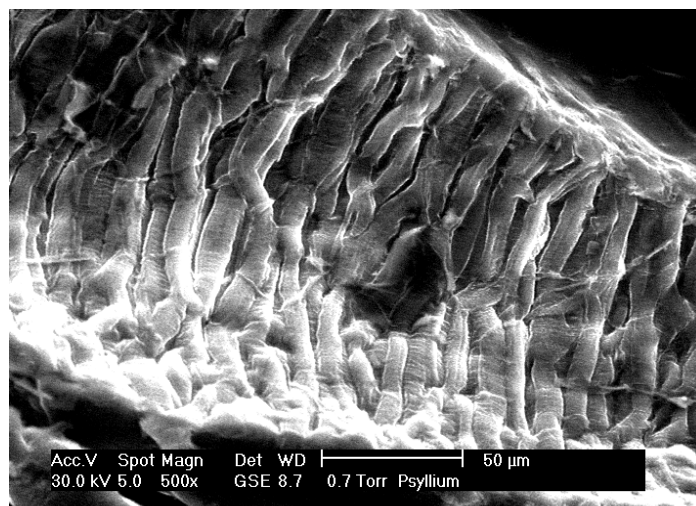


Figure 10. Scanning Electron Micrograph of Psyllium (500X)

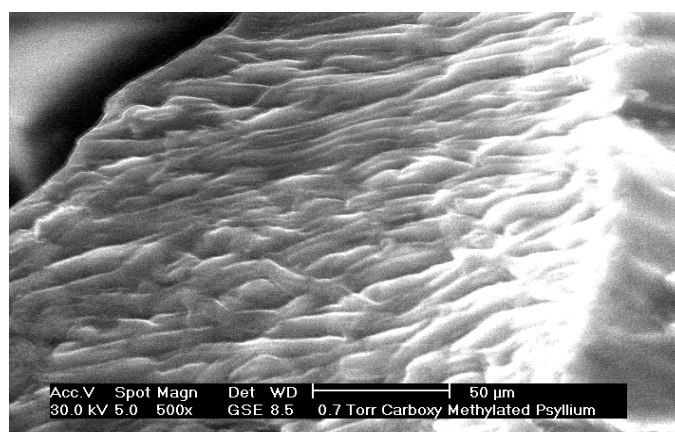


Figure 11. Scanning Electron Micrograph of Na-PCMPsy (DS = 0.13) (500X)

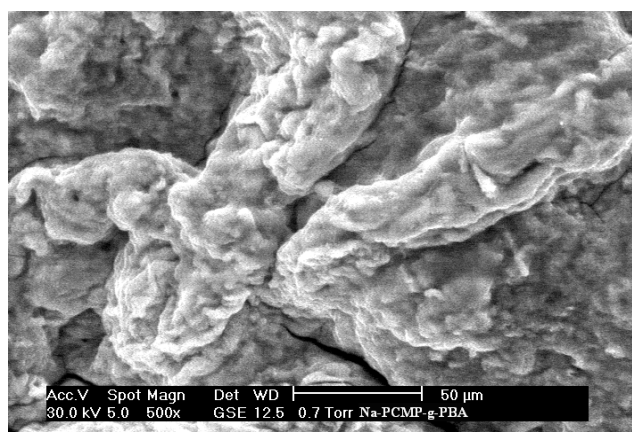


Figure 12. Scanning Electron Micrograph of Na-PCMPsy-g-PBA (500X)

Scanning Electron Microscopy (SEM)

The scanning electron micrograph of psyllium (Figure 10) shows fiber-like appearance structure. Upon carboxymethylation of psyllium, the structure of psyllium gets improved as shown in (Figure 11), wherein the morphology of the fiber-like structure is modified in such a way that because of the introduction of the hydrophilic groups onto psyllium, the fibers seem to have got

swollen and exhibited smooth surface. The surface topology of Na-PCMPsy is shown in Figure 11. Upon comparing the morphology of the grafted sample (Figure 12) with ungrafted material, it is clearly evident that the grafted chains have drastically changed the topology of the Na-PCMPsy. As shown in Figure 12, globule-like morphology is observed with BA. It is clearly indicate that grafting has been taken place.

CONCLUSION

Photo-grafting of BA has been successfully carried out onto Na-PCMPsy (\overline{DS} = 0.13) using CAN as a photo-initiator and the optimized reaction conditions have been evaluated. Evaluated optimize reaction condition is Na-PCMPsy: 0.2g (dry basis), $[HNO_3]$: 0.2 mol /L, $[BA]$: 0.259 mol/L, $[CAN]$: 3.0×10^{-3} mol/L, Time: 4.0h and Temperature: 40°C. The maximum values of the grafting yields (%G= 329.46 and %GE= 90.69) achieved at optimize reaction condition. The FT-IR spectra and SEM techniques have been employed successfully as the evidence of photo-grafting.

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