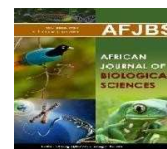


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PHOTO-INDUCED SYNTHESIS AND CHARACTERIZATION OF POLY(BUTYL ACRYLATE) GRAFTED SODIUM SALT OF PARTIALLY CARBOXYMETHYLATED SODIUM ALGINATE

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Abstract

In this article, photo-induced synthesis of poly (butyl acrylate)-grafted sodium salt of partially carboxymethylated sodium alginate (Na-PCMSA-g-PBA) using ceric ammonium nitrate (CAN) as a photo-initiator has been reported for the first time. In order to optimize the photo-graft copolymerization reaction, the reaction variables such as concentrations of butyl acrylate (BA) monomer, photo-initiator, and nitric acid (HNO₃) as well as the amount of backbone, reaction time, and temperature have been varied systematically and studied their influence on grafting yields viz. percent grafting (%G) and grafting efficiency (%GE). Under the optimum reaction conditions, the grafting yields obtained are %G = 220.85 and %GE = 97.81, and %Hp 2.19. Evidence of grafting has been examined spectroscopically, thermally and morphologically. The photo-synthesized novel graft copolymer (Na-PCMSA-g-PBA) may find its potential applications as metal adsorbent.

Keywords: *butyl acrylate, characterization, optimal reaction conditions, photo-induced grafting, sodium salt of partially carboxymethylated sodium alginate*

1. Introduction

Graft copolymerization initiated by ultraviolet (UV) irradiation is a well-known technique employed for significantly modifying the properties (chemical as well as physical) of natural polymers which are abundantly available in nature as well as they are renewable, hydrophilic and modifiable (Hebeish & Guthrie, 1981; Grajek & Andrzejewska, 2017). However, the UV- induced or photo-induced grafting technique has several advantages (Trivedi & Chourasia, 2023): less degradation of the backbone polymer, more control over the grafting reaction, lower operational cost, and UV-light absorption.

Sodium Alginate (SA) is an industrially important natural polysaccharide consisting of β -D-mannuronate (M) and α -L-guluronate (G) and is derived mainly from brown algae. SA is a biocompatible, non-toxic, biodegradable, and nonimmunogenic macromolecule and therefore it is widely used in food, textile, paints, leather, pharmaceutical and cosmetic industries (Szekalska et al., 2016). Thus, although SA has got its industrial importance but being biodegradable it is unsuitable for most uses as a plastic due to its poor dimensional stability and mechanical properties. Therefore, these drawbacks may be overcome through graft copolymerization of different vinyl monomers onto SA (Akin & Isiklan, 2016; Liu et al., 2005; Pal et al. 2010; Salisu et al. 2016; Staikos et al. 2018; Real et al. 202; Liu et al. 2019).

In our laboratory, as a part of our research programme, we have modified carboxymethylated derivatives of guar gum (Trivedi et al., 2015), psyllium (Trivedi et al. 2015) and tamarind kernel powder (Trivedi et al. 2021) and sodium alginate (Trivedi & Chourasia, 2023; Trivedi et al. 2015; Trivedi & Chourasia, 2023) by grafting different vinyl monomers onto them using low energy radiation and evaluating some of them for their potential applications as superabsorbents (Trivedi & Chourasia, 2023). In the present investigation, the photo-induced synthesis of poly(butyl acrylate) grafted sodium salt of partially carboxymethylated sodium alginate (herein after called as Na-PCMSA-g-PBA) has been optimized through the systematic variation of different reaction variables. The influence of these reaction variables on %G and %GE has been studied and the results are clearly presented and deeply discussed. The products have been characterized by FTIR, TGA/DTG, and SEM techniques. The scope of the present work is based on the evaluation of the synthesized graft copolymer, Na-PCMSA-g-PBA, for its application as a Pb(II) metal adsorbent by treating it with hydroxylamine in the presence of an alkaline solution which is in progress.

2. Materials and Methods

2.1 Materials

Loba Chemie Pvt. Ltd., Mumbai (India) supplied SA. The home-made sample of Na-PCMSA ($\overline{DS} = 1.10$) was used. BA (Aldrich make) was washed with 2% sodium hydroxide solution to remove the stabilizer. After treating the monomer with an alkali solution, it was washed repeatedly with distilled water, till it was freed from alkali and finally dried over anhydrous sodium sulphate. CAN was obtained from Qualigens, Glaxo India, India and used as received. A fresh solution of CAN was prepared in analar grade nitric acid supplied by Qualigens, Glaxo India, India. All other reagents and solvents used were of reagent grade. Nitrogen gas was purified by passing through a fresh pyrogallol solution. Low-conductivity water was employed for the photo-graft copolymerization reactions.

2.2.Methods

2.2.1. Synthesis of carboxymethylated derivative of sodium alginate (Na-PCMSA)

The procedures for carrying out the synthesis, purification and measurement of degree of substitution of sodium salt of partially carboxymethylated sodium alginate (Na-PCMSA) were followed as described earlier (Trivedi & Prajapati, 2015). The value of the average degree of substitution (\overline{DS}) of Na-PCMSA sample was found to be 1.10.

2.2.2.Photo-initiated synthesis and purification of Na-PCMSA-g-PBA

In order to carry out photo-induced synthesis of the graft copolymer, Na-PCMSA-g-PBA, a photo-chemical reactor supplied by Scientific Aids and Instruments Corporation (SAIC, Madras, India) was employed. The complete experimental set up for carrying out the photo-induced graft copolymerization reaction is represented in Figure 1.

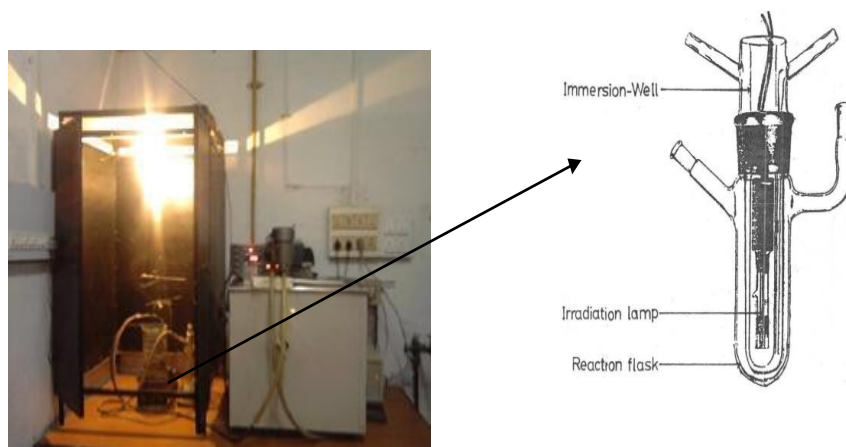


Figure 1. Detailed experimental setup for carrying out photo-graft copolymerization reaction.

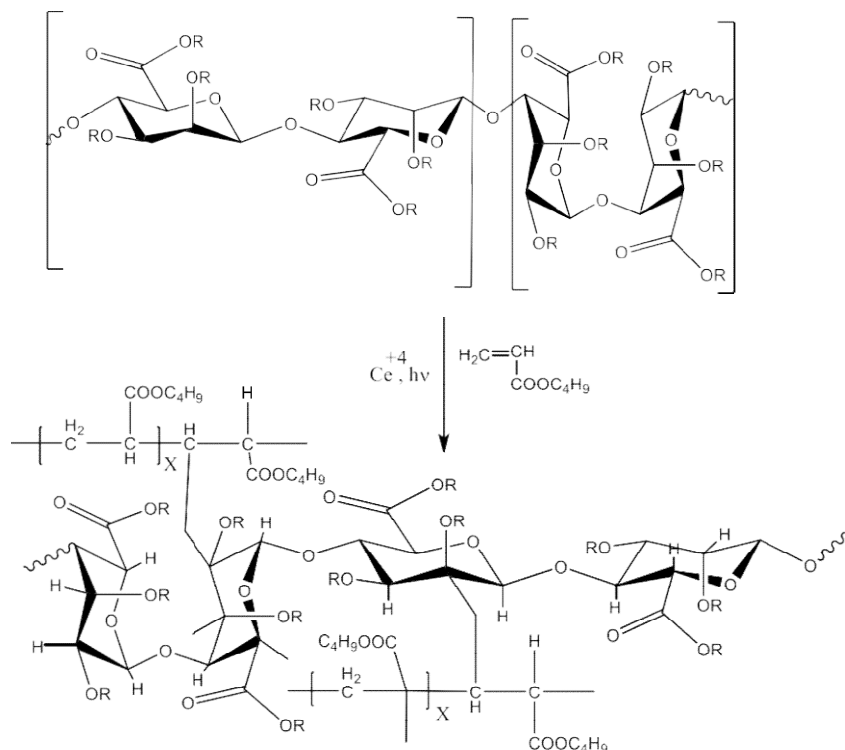
The procedure followed for carrying out the synthesis of the graft copolymer (Na-PCMSA-g-PBA) was the same as described earlier (Trivedi & Chourasia, 2023). However, in the present work, the reaction conditions which were varied for establishing the optimal reaction conditions are represented in Table 1. The crude graft copolymer obtained at the end of the

Table-1. Photo-grafting of butyl acrylate (BA) onto Na-PCMSA ($\overline{DS} = 1.10$): Reaction Conditions varied and Optimized Reaction Conditions.

Reaction Conditions Varied	Optimized Reaction Conditions*
Wt of Na-PCMSA : 0.2 to 3.0g (dry basis)	0.4 g (dry basis)
[CAN] : 0.5×10^{-3} to 10×10^{-3} mol/L	4×10^{-3} mol/L
[HNO ₃] : Nil to 0.5 mol/L	0.3 mol/L
[BA] : 0.051 to 0.506 mol/L	0.152 mol/L
Temperature : 15 to 45°C	35°C
Reaction Time : 0.5 to 10h	4h
Total Volume : 150mL	150mL

*Under Optimal Reaction Conditions: %G = 220.85, %GE = 97.81. %H_p = 2.19

photo-grafting reaction was isolated by centrifugation and purified by repeated washings with 95% methanol and finally with pure methanol. The crude graft copolymer (Na-PCMSA-g-PBA) sample thus obtained was dried in a vacuum at 40°C. The dried crude graft copolymer produced was then extracted with acetone exhaustively in a Soxhlet apparatus in order to remove the PBA homopolymer. The pure graft copolymer 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-PBA, is shown in Scheme 1.



where $R = \text{Na}$ or $-\text{CH}_2\text{COONa}$, $R' = \text{H}$ or $-\text{CH}_2\text{COONa}$

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

2.3. Grafted Chains Isolation

In order to isolate the grafted chains (PBA), the graft copolymer (Na-PCMSA-g-PBA) sample was hydrolyzed by refluxing it for 12h in 1N HCl (Brockway & Seaberg, 1987). After all the Na-PCMSA went into the solution, a resinous mass was obtained, which was characterized with FTIR spectroscopy.

2.4.Characterization of Na-PCMSA-g-PBA

2.4.1. FTIR Analysis

The Fourier transform infrared (FTIR) spectra of Na-PCMSA ($\overline{DS} = 1.10$), Na-PCMSA-g-PBA ($\%G = 220.85$), and PBA were recorded on Nicolet Impact 400D FTIR Spectrophotometer in the wavelength region between 400 and 4000 cm^{-1} using KBr pellets.

2.4.2. Thermogravimetric Analysis (TGA)

A Perkin Elmer Pyris 1 TGA, STA 8000 was used to perform TGA of Na-PCMSA ($\overline{DS} = 1.10$), Na-PCMSA-g-PBA ($\%G = 220.85$), and PBA samples. The sample was heated at a rate of 10°C/min from room temperature up to 800°C under nitrogen atmosphere.

2.4.3. Scanning Electron Microscopy (SEM)

In order to examine the morphology and surface structure of Na-PCMA ($\overline{DS} = 1.10$) and Na-PCMSA-g-PBA (%G = 220.85), a scanning electron microscope ESEM TMP + EDAX, Philips model was used.

3. Results and Discussion

3.1 Grafting yields

The graft copolymer (Na-PCMSA-g-PBA) has been characterized according to Fanta's definition (Fanta et al. 1978):

$$(i) \% G = \frac{\text{Wt. of polymer grafted}}{\text{Initial wt. of backbone}} \times 100 \quad (1)$$

$$(ii) \% GE = \frac{\text{Wt. of polymer grafted}}{\text{Wt. of polymer grafted} + \text{Initial wt. of backbone}} \times 100 \quad (2)$$

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

3.2. Optimization of Photo-graft Copolymerization Reaction

In the present study to optimize the reaction conditions for the photo-graft copolymerization reaction, the concentrations of nitric acid, photo-initiator (CAN), monomer (BA), as well as reaction time, temperature, and amount of substrate, were varied. The results regarding the influence of these reaction conditions on the grafting yields are discussed as under:

3.2.1. Effect of amount of substrate (Na-PCMSA)

The variation of the grafting yields (%G and %GE) as a function of the amount of Na-PCMSA was studied by the variation of the amount of Na-PCMSA from 0.2 to 3.0g and results obtained are represented in Figure 2(a). As it becomes evident from this figure that %G decreases continuously while %GE increases very slowly in the beginning up to 0.4g of Na-PCMSA, beyond which it decreases very slowly with further increase in the amount of Na-PCMSA. The observed continual decline in %G and %GE (beyond 0.4 g of Na-PCMSA) may be due to the fact that with the increase in the amount of substrate, Na-PCMSA, the viscosity of the reaction medium increases which hinders the movement of the photo-initiator, CAN, thereby reducing the grafting yields. Additionally, as the amount of Na-PCMSA is increased, more and more macroradicals are formed, speeding up the termination rate of photo-graft copolymerization relative to the rate of initiation. In the literature, similar outcomes are also observed (Trivedi et al. 1995; Trivedi et al 1994; Trivedi & Chourasia, 2023; Keles & Sacak, 2003).

3.2.2. Effect of photo-initiator (CAN) concentration

The photo-graft copolymerization was studied at various photo-initiator concentrations (0.50×10^{-3} to 10×10^{-3} mol/L) at fixed monomer, BA concentration (0.101 mol/L), reaction time (3h) and temperature (35°C) and the results are depicted in Figure 2(b). It can be observed from this figure that with an increase in ceric ion concentration, the value of %G increases and reaches a maximum value (126.68%) at $[Ce^{4+}] = 4 \times 10^{-3}$ mol/L. However, the value of %GE varies in the similar way and achieves a maximum value of 96.28% at the optimum concentration of $Ce^{4+} = 4 \times 10^{-3}$ mol/L [cf. Figure 2(b)]. Beyond the optimum value of the photo-initiator concentration, both the values, %G and %GE are found to be decreased,

as it becomes evident from Figure 2(b). Thus, the observed increase in %G and %GE within the photo-initiator concentration range of 0.50×10^{-3} to 4×10^{-3} mol/L may be explained due to the fact that in this concentration range, the activation along the backbone takes place immediately, followed by photo-graft copolymerization of BA onto Na-PCMSA ($\overline{DS} = 1.10$). However, the retarding effect of the grafting yields with photo-initiator concentration beyond its optimum value (4×10^{-3} mol/L) may be ascribed to (i) predominance of homopolymerization over photo-grafting; and (ii) termination of growing grafted chains by excess of primary radicals formed from photo-initiator. The literature also contains reports of similar observations (Trivedi & Chourasia, 2023; Guo et al. 2019, Sharma et al., 2020; Masry et al. 2022).

3.2.3. Effect of acid (HNO₃) concentration

In order to study the dependence of the grafting yields (%G and %GE) on the nitric acid concentration, the concentration of nitric acid was varied from nil to 0.5 mol/L, keeping other variables constant. From the results as shown in Figure 2(c), interestingly it can be noted that even at zero concentration of nitric acid, an appreciable value of the percentage of grafting (%G = 97.37) is observed. This may be due to the possibility that, even in absence of acid, in an aqueous medium, Na-PCMSA ionizes fully to a greater extent which facilitates the diffusion of monomer (BA) and photo-initiator (CAN) leading to the appreciable value of %G. It can be further noticed from this figure that there exists an optimum concentration of nitric acid (0.3 mol/L) for which the maximum value of percentage of grafting (%G = 116.05) was achieved. Beyond the optimum concentration of acid, the observed decrease in the grafting yields may be explained due to the fact that as the nitric acid concentration increases, the formation of more and more $[Ce^{4+}]$ and $[Ce(OH)_3]^{3+}$ species takes place which in turn accelerates the termination of the growing polymeric grafting chains resulting in the decrease in the grafting yields. Moreover, $[Ce^{4+}]$ ion has been reported to be involved in the oxidative termination of the growing monomeric chains (Kumar et al. 2011). Similar results are also reported in the literature (Trivedi & Chourasia, 2023; Trivedi & Chourasia 2023; Kaur et al. 2010).

3.2.4. Effect of monomer (BA) concentration

Grafting yields are impacted by monomer concentration. As a result, the monomer (BA) concentration was changed from 0.051 to 0.506 mol/L at constant concentration of the CAN (1.0×10^{-3} mol/L) and constant amount of Na-PCMSA (0.6 g. dry basis) at 35°C. The results are shown in Figure 2(d). It can be seen from this figure that %G increases rapidly up to $[BA] = 0.152$ mol/L, beyond which the value of %G increases gradually. However, the grafting efficiency (%GE) increases slowly up to 0.152 mol/L and then decreases with a further increase in the monomer concentration.

The observed increase in %G and %GE may be explained by the fact that with the increase in the monomer concentration, the formation of a larger amount of the growing polymeric chains leads to the formation of more grafting sites onto Na-PCMSA by the chain transfer reaction leading to a higher graft yields. However, with further higher monomer concentration, the concentration of PBA macroradicals increases, and the rates of their combination and disproportionation is faster than the rate of their combination with Na-PCMSA molecules. Therefore, due to formation of the homopolymers, the gradual increase in %G is observed beyond the optimal value of the monomer concentration. In addition, these homopolymers hinder the rate of penetration of BA molecules to the polysaccharide

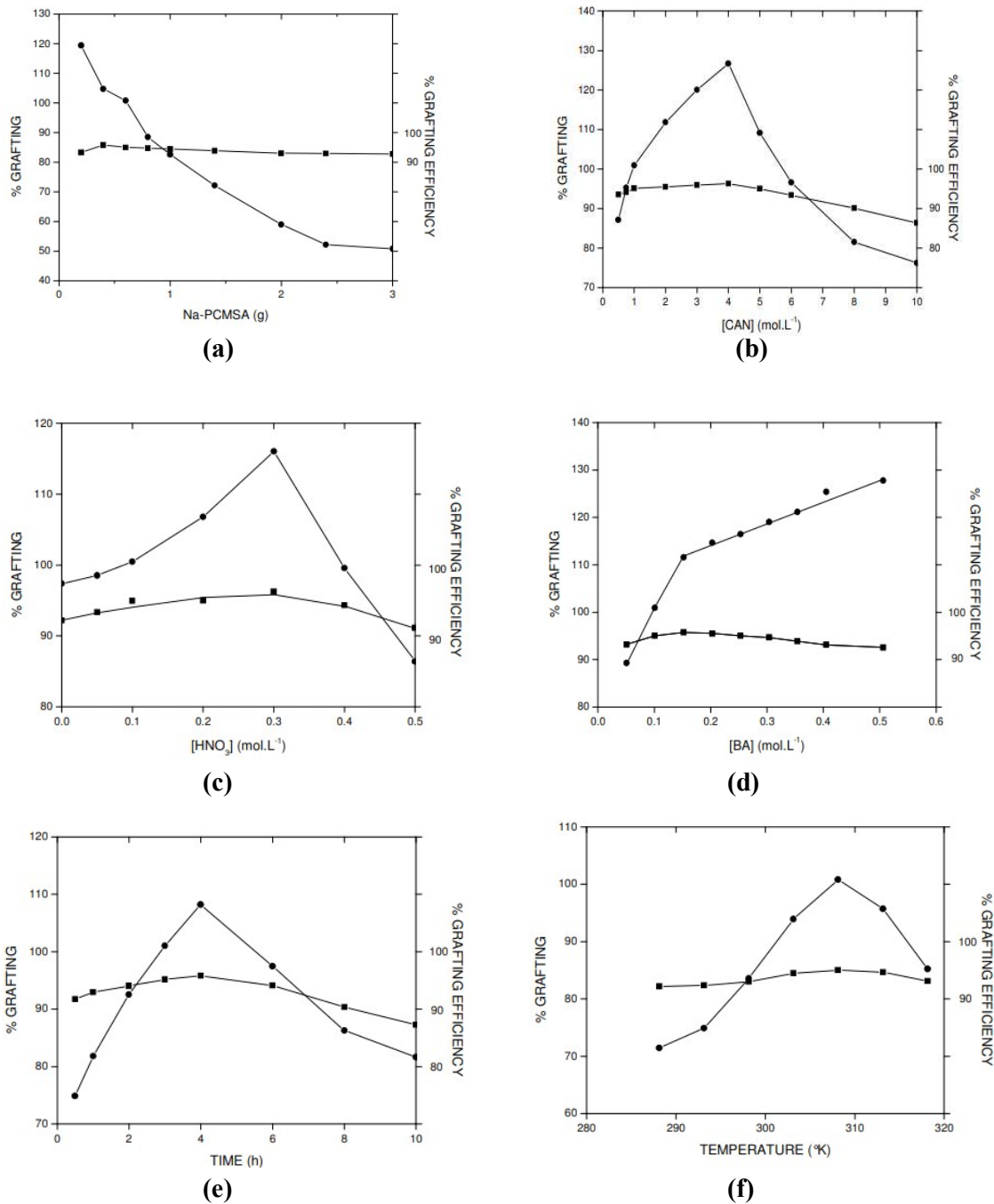


Figure 2. Influence of (a) amount of sodium salt of partially carboxymethylated sodium alginate (Na-PCMSA), (b) ceric ammonium nitrate (CAN) concentration, (c) nitric acid (HNO₃) concentration, (d) butyl acrylate (BA) concentration, (e) reaction time and (f) reaction temperature on: -●- %G; or -■- %GE.

(Na-PCMSA) free radicals, resulting in a decrease in %GE. Similar behaviors were also seen in the previous research (Trivedi et al. 2015; Trivedi & Chourasia, 2023; Akkaya & Usulan, 2010).

3.2.5. Effect of Reaction time

To investigate the effect of reaction time on the grafting yields, the photo-graft copolymerization reaction was carried out by varying the duration of the reaction from 0.5h to

10 h with the temperature (35°C), BA monomer (0.101 mol/L) and initiator (1.0×10^{-3} mol/L) concentrations kept constant. The results are depicted in Figure 2(e). It can be seen from this figure that the values of %G and %GE increased with increase in photo-polymerization time up to 4h and achieved respective maximum values of 108.21 % and 95.82%. However, beyond the optimum value (4h), the values of %G and %GE are found to be decreased with further increase in time. The observed increase in the grafting yields may be due to the increase in the number of grafting sites on the Na-PCMSA backbone and subsequent addition of the monomer molecules to the growing grafted chains. However, beyond 4h, as the reaction proceeds, the observed decrease in the grafting yields could be attributed to the decrease in the concentrations of monomer and initiator as well as the reduction in the number of active sites on the Na-PCMSA backbone accessible for grafting. Besides, the longer UV irradiation time has a detrimental effect on the grafted chains of PBA in the presence of a photo-initiator which is also responsible for the observed decrease in the grafting yields values. Similar results have been obtained by many researchers (Trivedi & Chourasia, 2023, Sadeghi et al. 2012).

3.2.6. Effect of Reaction temperature

The influence of temperature on the grafting yields was studied by carrying out the photo-graft copolymerization of BA onto Na-PCMSA ($\overline{DS} = 1.10$) at seven different temperatures, ranging 15-45°C. The results are presented in Figure 2(f). As it can be seen from the figure, both %G and %GE values are increased with increasing the temperature from 15 to 35°C and then decreased with further increase in the temperature. The highest %G and %GE values obtained were 100.81% and 95.01% respectively at 35°C. The results of the figure may be explained on the basis of the fact that with increasing the reaction temperature, the rate of redox reaction between the photo-initiator CAN and Na-PCMSA will be increased. Besides, the mobility of the Na-PCMSA backbone, monomer and initiator molecules will also get enhanced with increase in reaction temperature leading to the increase in the rates of grafting. However, the lowering of grafting yields by an increase in the temperature above 35°C could be due to the favored chain termination reactions, chain transfer reactions and increase in the formation of homopolymer (PBA). Similar results have been obtained by many researchers (Trivedi et al. 2021; Taskin et al. 2011).

From the foregoing discussion the optimal reaction conditions evaluated in the present study of photo-graft copolymerization of BA onto Na-PCMSA ($\overline{DS} = 1.10$) are tabulated in Table-1. The maximum values of the grafting yields achieved are: %G = 220.85, %GE = 97.81. %H_p = 2.19.

4. Characterization

4.1. Spectral Characterization of Na-PCMSA-g-PBA

In the FTIR spectrum of Na-PCMSA ($\overline{DS} = 1.10$) (not shown), the strong absorption peak appeared at 1745 cm^{-1} is due to C = O stretching, indicating the presence of -COO moiety in the Na-PCMSA. The absorption bands appeared at 1647 cm^{-1} (due to asymmetric stretching of the moiety) and 1417 cm^{-1} (due to symmetric stretching) also provide proof of the presence of -COO moiety (Trivedi & Chourasia 2023). Figures 3(a) & (b) represent the FTIR spectra of Na-PCMSA-g-PBA and PBA (isolated by hydrolysis) respectively. Figure 3(a) showed absorption bands of Na-PCMSA as well as an additional strong absorption band at $\sim 1737\text{-}1745 \text{ cm}^{-1}$ assigned to C=O stretching of ester group (-COOCH₃), characteristics of

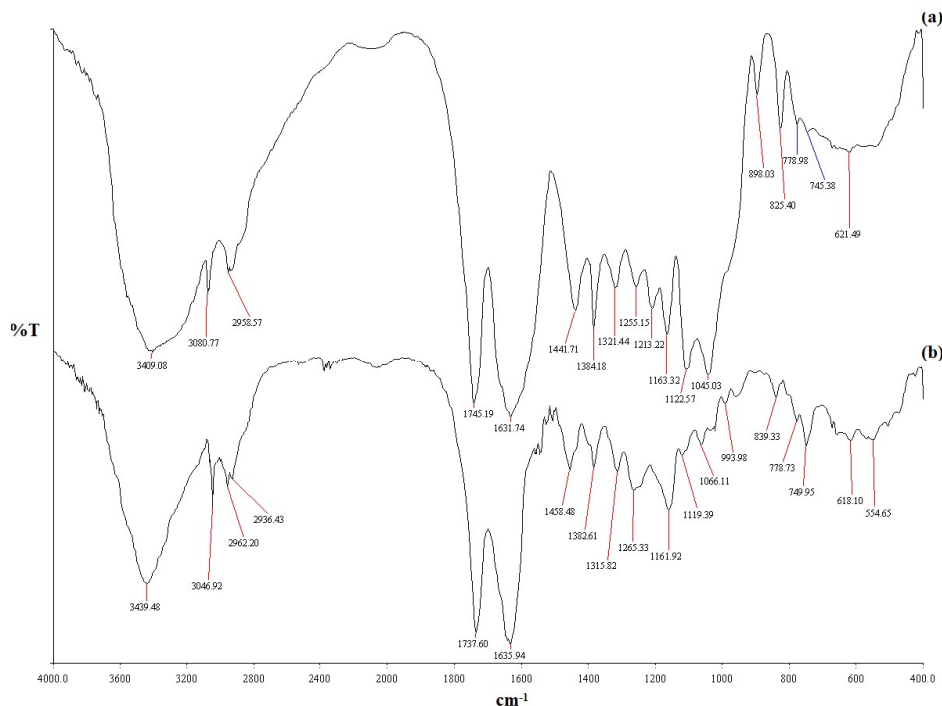


Figure 3. FTIR Spectra of (a) Na-PCMSA-g-PBA (%G = 220.85) and (b) PBA.

methacrylates. The FTIR spectrum of PBA [Figure 3(b)] indicated the presence of C = O stretching at $\sim 1732\text{-}1738\text{cm}^{-1}$ which may be due to the fact that the hydrolysis of the graft copolymer, Na-PCMSA-g-PBA, gives back the grafted PBA chains. In conclusion, the results of Figures 3(a) & 3(b) provide substantial evidence of the photo-grafting of PBA onto Na-PCMSA ($\overline{DS} = 1.10$).

4.2. Thermal Characterization of Na-PCMSA-g-PBA

Figure 4 represents the primary thermograms and derivatograms obtained at a scan rate of $10^\circ\text{C}/\text{min}$ for Na-PCMSA (S_1), Na-PCMSA-g-PBA (S_2) and PBA (S_3) samples in an inert atmosphere. As it can be seen from the Figure 4(S_1) that the overall degradation of Na-PCMSA sample involves only two steps of degradation. The first step in the temperature range $135.95\text{-}280.85^\circ\text{C}$ involves about 40.64% weight loss with a maximum weight loss occurring at 212.88°C [cf. Figure 4(S_1)]. The second step of degradation exhibits the temperature range $552.40\text{-}795.81^\circ\text{C}$ involving 19.35% weight loss with a maximum weight loss at 701.51°C . Beyond 225°C the sample degrades very slowly with a char yield value of 28.80% at 700°C .

As it can be observed from Figure 4(S_2) that the graft copolymer, Na-PCMSA-g-PBA (%G = 220.85) sample involves two steps of degradation. The first step encompasses the temperature ranges from 128.46°C to 305.71°C involving about 25.90% weight loss with a maximum weight loss at 261.49°C . On the other hand in the temperature range $305.71\text{-}529.56^\circ\text{C}$, the second step of degradation involves 31.86% weight loss with a maximum weight loss at 370.58°C leaving behind 33.64% char yield at 700°C . The homopolymer sample (PBA) also exhibits two steps of degradation [cf. Figure 4(S_3)]. The first step of degradation in the temperature range $166.29\text{-}248.51^\circ\text{C}$ involves only 5.92% weight loss with a maximum weight loss at 224.76°C . In the temperature range $248.51\text{-}446.41^\circ\text{C}$, the second

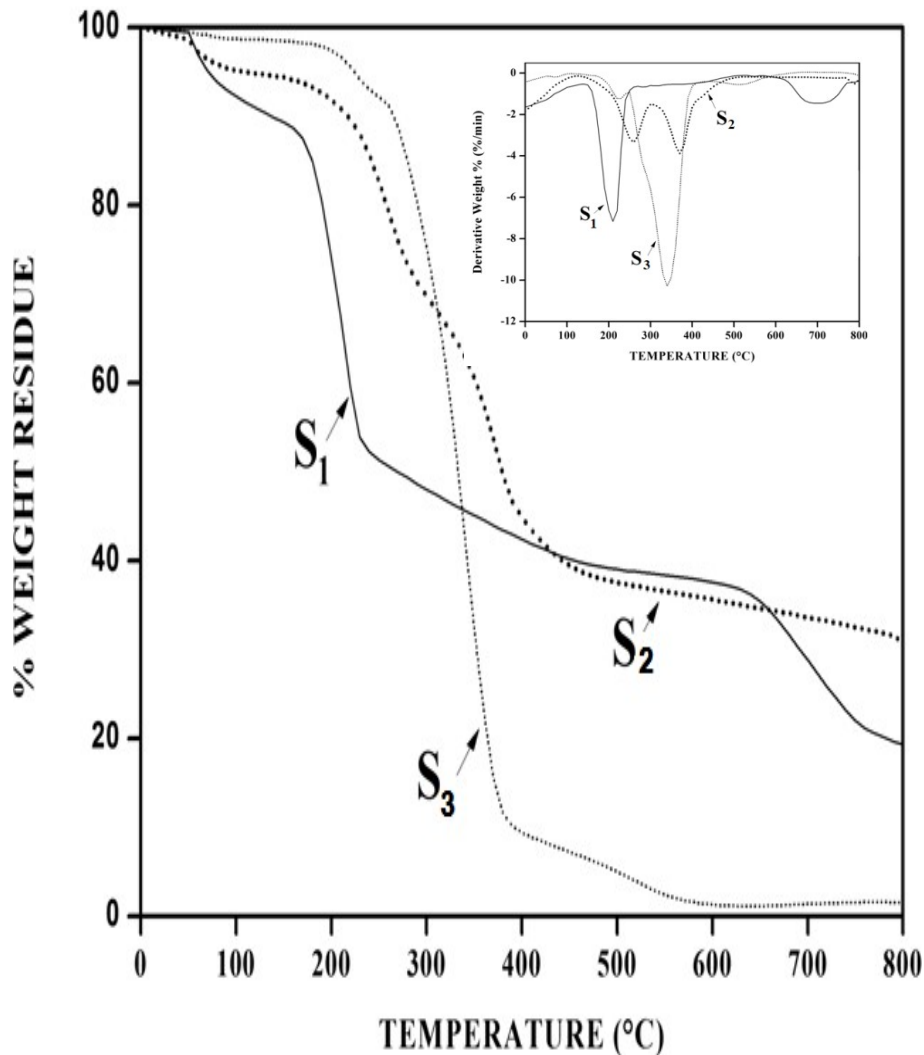


Figure 4. TG thermograms for (—) Sodium salt of Partially Carboxymethylated Sodium Alginate [Na-PCMSA ($\overline{DS} = 1.10$)] (S_1), (•••••) Na-PCMSA-g-PBA (%G = 220.85) (S_2), and (.....) PBA (S_3) at $10^\circ\text{C}/\text{min}$. The inset shows the first derivatives of the curves shown in the figure.

step of degradation involves 85.04% weight loss with a maximum weight loss at 340.43°C leaving behind only 1.37% char yield at 700°C indicating that the graft copolymer, Na-PCMSA-g-PBA is more stable in comparison with the homopolymer, PBA. However, the comparison of the char yield values of the graft copolymer with that of Na-PCMSA sample at 700°C lead to conclude that the thermal stability of the Na-PCMSA sample increased upon grafting of high molecular weight, hydrophobic long PBA chains (Wang et al. 2017):

4.3. Morphological Characterization of Na-PCMSA-PBA

The scanning electron micrographs of ungrafted (Na-PCMSA) and PBA grafted Na-PCMSA (Na-PCMSA-g-PBA, %G = 220.85) are shown in Figure 5. By comparing the surface morphology of the grafted Na-PCMSA [Figure 5(b)] with ungrafted Na-PCMSA [Figure 5(a)], it can be observed that the morphology of Na-PCMSA was changed by the

grafted chains, and this is an additional proof of photo-grafting.

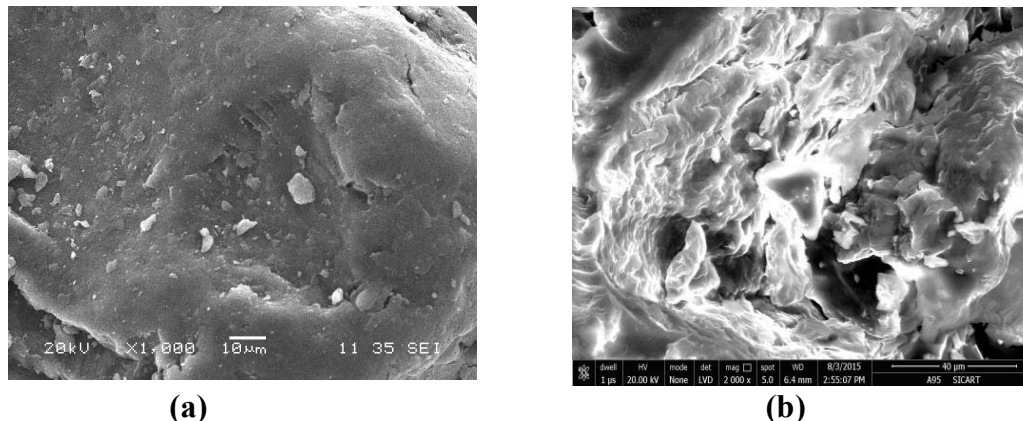


Figure 5. Scanning Electron Micrographs of (a) Sodium salt of Partially Carboxymethylated Sodium Alginate [(Na-PCMSA ($\overline{DS} = 1.10$))] (1000X) and (b) Na-PCMSA-g-PBA (%G = 220.85)(2000X)

5. Conclusions

In this study, first time the photo-grafting of Na-PCMSA to prepare its BA-grafted copolymer (Na-PCMSA-g-PBA) has been carried out successfully using the CAN/HNO₃ redox initiator system. The photo-grafting synthesis has been optimized through the variation of different reaction variables in terms of the determination of the highest grafting yields (%G = 220.85, %GE = 97.81 and %H_p = 2.19). The grafting yields (%G and %GE) have been found to be strongly dependent on variations in photo-graft copolymerization reaction conditions and the results of such dependency have been explained. The graft copolymer has been characterized by using FTIR, TGA/DTG and SEM techniques. Fourier Transform Infrared (FTIR) spectral analysis provided the evidence of the photo-grafting of BA onto Na-PCMSA. Finally, the thermal stability of Na-PCMSA has been increased after being grafted with BA. The scanning electron microscopy (SEM) micrographs showed that the photo-grafting also affected the smooth surface structure of Na-PCMSA. The synthesized novel graft copolymer (Na-PCMSA-g-PBA) after treatment with hydroxylamine in the presence of alkaline solution may find potential application as a novel ion-exchange resin.

6. Acknowledgments

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References

- Hebeish, A., & Guthrie, J. T. (Eds). (1981). *The Chemistry And Technology of Cellulosic Copolymers*, Springer-Veriag, Berlin, Heidelberg, New York.
- Grajek, K., & Andrzejewska, E. (2017). Recent advances in photo-induced free radical polymerization, *Moj Polymer Science*, 1(2), 58-60. <https://doi.org/10.15406/mojps.2017.01.00009>.
- Trivedi, J. H., & Chourasia, A. V. (2023). Sodium Salt of Partially Carboxymethylated Sodium Alginate-g-Poly(acrylonitrile): I. Photo-Induced Synthesis, Characterization, and Alkaline Hydrolysis. *Gels*, 9(5), 1-14. <https://doi.org/10.3390/gels9050410>.

- Szekalska, M., Puciłowska, A., Szymańska, E., & Ciosek, P. (2016). Alginate: Current Use and Future Perspectives in Pharmaceutical and Biomedical Applications. *International Journal of Polymer Science*, 8, 1-17. <https://doi: 10.1155/2016/ 7697031>
- Akın, A., & Işıklan, N. (2016). Microwave assisted synthesis and characterization of sodium alginate-graft-poly(N,N'-dimethylacrylamide). *International Journal of Biological Macromolecules* 82(4), 530-540. <https://doi: 10.1016/j.ijbiomac.2015.10.050>
- Liu, Y., Yang, L., Li, J., & Shi, Z. (2005). Grafting of methyl methacrylate onto sodium alginate initiated by potassium doperiodatocuprate (III). *Journal of Applied Polymer Science*. 97(4), 1688–1694. <https://doi:10.1002/app.21626>
- Sen, G., Singh, R. P., & Pal, S. (2010). Microwave-initiated synthesis of polyacrylonitrile grafted sodium alginate: Synthesis and characterization. *Journal of Applied Polymer Science*. 115(1), 63–71. <https://doi: 10.1002/app.30596>
- Salisu, A., Sanagi, M., Naim, A., Karim K., Ibrahim, W. & Abdulganiyu, U. (2016). Alginate graft polyacrylonitrile beads for the removal of lead from aqueous solutions. *Polymer Bulletin*.73(2), 519–537. <https://doi: 10.1007/s00289-015- 1504-3>
- Ciocoiu, O. N., Staikos, G., & Vasile, C. (2018). Thermoresponsive behavior of sodium alginate grafted with poly(N-isopropylacrylamide) in aqueous media. *Carbohydrate Polymers*.184, 118–126. <https://doi: 10.1016/j.carbpol.2017.12.059>
- Flores, C. G., Cornejo, M. d. L. A., Moreno, A., & Real, A. D. (2021). Synthesis of a Biodegradable Polymer of Poly (Sodium Alginate/Ethyl Acrylate). *Polymers* 13(4), 1-12. <https://doi: 10.3390/polym13040504>
- Sun, F., Guo, J., Liu, Y., & Yu. Y. (2019) Preparation, characterizations and properties of sodium alginate grafted acrylonitrile/polyethylene glycol electrospun nanofibers. *International Journal of Biological Macromolecules*. 137(6), 420–425. <https://doi: 10.1016/j.ijbiomac.2019.06.185>.
- Trivedi, J. H., Thaker, M. D., & Trivedi, H. C. (2015). Photo-Induced Graft Copolymerization of Acrylonitrile onto Sodium salt of Partially Carboxymethylated Guar Gum. *Journal of Applied Polymer Science*, 132(5), 1-10. <https://doi: 10.1002/app.41371>
- Trivedi, J. H., Min, W., Huang, Y., & Trivedi, H. C. (2015). Photo-Induced Sodium salt of Partially Carboxymethylated Psyllium-g-Polyacrylonitrile: I. Synthesis and Characterization. *International Journal of Scientific and Research Publications*, 5(5), 1-10. <https://www.ijsrp.org/research-paper-0515.php?rp=P414131>
- Trivedi, J. H., Joshi, H. A., & Trivedi, H. C. (2021). Synthesis and Characterization of Photo- Graft Copolymers of Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder. *Macromolecular Symposia*, 398(1), 1-13. <https://doi: 10.1002/masy.202000014>.
- Trivedi, J. H., Chourasia, A. V., & Trivedi, H. C. (2015). Photo-Induced Synthesis and Characterization of Poly(Methyl Acrylate) Grafted Sodium salt of Partially Carboxymethylated Sodium Alginate. *Cellulose Chemistry and Technology*, 49(1), 7–19. [https://cellulosechemtechnol.ro/pdf/CCT1\(2015\)/p.7-19.pdf](https://cellulosechemtechnol.ro/pdf/CCT1(2015)/p.7-19.pdf)

- Trivedi, J. H., Chourasia, A. V. (2023). Photo-induced Synthesis and Characterization of Graft Copolymer of Sodium salt of Partially Carboxymethylated Sodium Alginate and Methyl Methacrylate. *European Chemical Bulletin*, 12(4), 2159-2172. [https://doi: 10.48047/ecb/2023.12.4.143](https://doi.org/10.48047/ecb/2023.12.4.143)
- Trivedi, J. H., & Chourasia, A. V. (2023). Sodium Salt of Partially Carboxymethylated Sodium Alginate-Graft-Poly(Acrylonitrile): II Superabsorbency, Salt Sensitivity and Swelling Kinetics of Hydrogel, H-Na-PCMSA-g-PAN. *Gels*. 9(5), 1-17. [http://doi: org/10.3390/gels9050407](http://doi.org/10.3390/gels9050407)
- Trivedi, J. H., & Prajapati, M. K. (2015). Carboxymethyl Sodium Alginate: Synthesis and Characterization. *Journal of Pure and Applied Sciences-Prajna*. 22 & 23, 24-28. https://www.spuvvn.edu/publication/prajna/prajna_2015/chemistry/05-QQ-Chemistry.
- Brockway, C. E., & Seaberg, P. A. (1987). Grafting of polyacrylonitrile to granular corn starch, *Journal of Polymer Science Part A-1: Polymer Chemistry*, 5(6), 1313-1326. <https://doi:10.1002/pol.1967.150050614>
- Fanta, G. F., Burr, R. C., Doane, W. M., & Russel, C. R. (1978). Absorbent Polymers from Starch and Flour Through Graft Polymerization of Acrylonitrile and Comonomer Mixtures. *Starch/Starke*, 30(7), 237–242. <https://doi: 10.1002/star.19780300706>
- Keles, H., & Sacak, M. (2003). Graft copolymerization of methyl methacrylate onto gelatin using $\text{KMnO}_4\text{-H}_2\text{SO}_4$ redox system. *Journal of Applied Polymer Science*, 89(10), 2836-2844. <https://doi: 10.1002/app.12482>
- Shi, Z., Jia, C., Wang, D., Deng, J., Xu, G., Wu, C., Dong, M., & Guo Z. (2019). Synthesis and characterization of porous tree gum grafted copolymer derived from *Prunus cerasifera* gum polysaccharide. *International Journal of Biological Macromolecules*, 133,964-970. <https://doi: 10.1016/j.ijbiomac.2019.04.128>
- Sharma, G., Kumar, A., Naushad, Mu., Al.Misned, F. A., El-Serehy, H. A., Ghfar, A. A., Sharma, K. R., Si, C., & Stadler, F. (2020). Graft Copolymerization of Acrylonitrile and Ethyl Acrylate onto Pinus Roxburghii Wood Surface Enhanced Physicochemical Properties and Antibacterial Activity. *Journal of Chemistry*, 1–16. <https://doi.10.1155/2020/6285354>
- Masry, B. A., Shahr, A. M., & Al-Aidy., H. A. (2022). Ceric-ions redox initiating technique for Zirconium and Niobium separation through graft copolymerization of natural polysaccharides. *Separation Science and Technology*, 57(4), 603–618. <https://doi: 10.1080/ 01496395.2021.1919708>
- Kumar, V., Naithani, S., & Pandey, D. (2011). Optimization of reaction conditions for grafting of α -cellulose isolated from *Lantana camara* with acrylamide. *Carbohydrate Polymers*, 86(2), 2011, 760–768. <https://doi: 10.1016/j.carbpol.2011.05.019>
- Kaur, I., Kumar, R., & Sharma, N. (2010) A comparative study of the graft copolymerization acrylic acid onto rayon fiber by a ceric ion redox system and γ -radiation method. *Carbohydrate Research*, 345(15), 2164–2173. <https://doi: 10.1016/j.carres.2010.06.018>
- Akkaya, A., & Uslan, A. H. (2010). Sequential immobilization of urease to glycidyl methacrylate grafted sodium alginate. *Journal of molecular catalysis. B:Enzymatic*.67 (3&4), 195-201. <https://doi: 10.1016/j.molcatb.2010.08.005>

- Sadeghi, M., Shafief, F., & Mohammadasab, E. (2012). Optimization Effective Parameters on Gamma Radiation Polymerization Copolymer based on Collagen. *Oriental Journal of Chemistry*, 28(2), 829-834. <https://www.orientjchem.org/vol28no2/optimization-effective-parameters-on-gamma-radiation-polymerization-copolymer-based-on-collagen/>.
- Taskin, G., Sanli, O., & Asman, G. (2011). Swelling assisted photografting of itaconic acid onto sodium alginate membranes. *Applied Surface Science*, 257(22), 9444-9450. [https://doi: 10.1016/j.apsusc.2011.06.030](https://doi:10.1016/j.apsusc.2011.06.030).
- Wang, S., Xu, J., Wang, Q., Fan, X., Yu, Y., Wang, P., Zhang, Y., & Yuan, J. (2017). Cavaco-Paulo, A. Preparation and rheological properties of starch-*g*-poly(butyl acrylate) catalyzed by horseradish peroxidase. *Process Biochemistry Part A*, 59, 104-110. [http://doi: 10.1016/j.procbio.2017.01.014](http://doi:10.1016/j.procbio.2017.01.014).