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Article

Synthesis and Characterization of Sodium Carboxymethyl Cellulose Graft Copolymers with 2-Acrylamido-2-methyl-1-propanesulfonic Acid and Sodium 4-Vinylbenzene Sulfonate

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ABSTRACT

Sodium carboxymethyl cellulose was graft copolymerized with sulfonic acid and sulfonate functionalized monomers (2-acrylamido-2-methyl-1-propanesulfonic acid [AMPS] and sodium 4-vinylbenzene sulfonate [SVBS]) in aqueous medium persulfate as an initiator. Grafting parameters such as percentage of grafting, grafting efficiency, conversion, and yield of SA-g-AMPS and SA-g-SVBS were investigated gravimetrically as a function of time, monomer concentration, temperature, and initiator concentration. The synthesized graft copolymers were characterized by Fourier transform infra-red, differential scanning colorimetry, and X-Ray diffraction.

Key words: Graft copolymers, Polysaccharides, Cellulose, Vinylbenzene sulfonate, 2-Acrylamido-2-methyl-1-propanesulfonic acid

1. INTRODUCTION

Polysaccharides are biodegradable polymers, nowadays, these are replacing pure synthetic polymers in concern with the environmental pollution and development of biomaterials [1-4]. Various attempts have been made to overcome the issues of like biodegradability biocompatibility and physicochemical properties through functional modification of either synthetic or natural polymers [5]. Cellulose and its derivatives are easily functionalized by grafting with different monomers, and the resultant derivatives are employed in a variety of applications. Numerous grafting methods for graft polymerization of cellulose derivatives have been explored; however, free-radical polymerization is one of the easiest and fastest for cellulose derivatives due to the facile radical production of hydroxyl groups present on the glucan unit [6].

Sodium carboxymethyl cellulose (CMC) is one of the potential biopolymers due to the presence of two hydroxyl groups one carboxymethyl group on D-anhydroglucopyranose unit [7]. Hence, the free hydroxyl groups are readily available for further modification of CMC, that is, based on the required property or targeted martials [8]. Grafted with various vinyl monomers obtained by free radical polymerization methods and have been used in the fields of drug delivery, toxic metal ion removal, organic dye removal, and flocculant [8,9].

Polymer electrolyte membranes (PEM) and polymeric matrices are useful for various applications such as drug delivery, toxic metal ion removal, dye adsorption, water desalination, electrodialysis, and fuel cell applications [4,10-14]. There are huge reports on fabrications of PEMs from pure polymer blends, graft copolymers, and incorporation of inorganic additives in the polymer matrix. However, sulfonated polymers, that is, poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) and poly(sodium 4-vinylbenzene sulfonate) based (PSVBS) more significant in preparation of PEMs, it is due to the presence of -SO_3H, which enhance the hydrophilicity of the membrane and transport of cations through the membrane.

The current study describes the graft copolymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and sodium 4-vinylbenzene sulfonate (SVBS) onto the CMC using simple free-radical polymerization with ammonium persulfate (APS) and potassium persulfate (KPS) as initiators. Using various grafting parameters, the authors evaluated the effect of reaction time, reaction temperature, initiator concentration, and monomer concentration on graft copolymerization. To the best of the authors' knowledge, this is the first study of its sort to be published in the literature, involving the preparation of CMC graft copolymers by KPS and APS in the grafting of AMPS and SVBS, respectively.

2. EXPERIMENTAL

2.1. Materials

AMPS and SVBS are purchased from the Aldrich chemicals. Sodium carboxymethaly cellulose (CMC), APS, KPS, Acetone received from the Merk. All experiments are carried with double distilled water.

2.2. Synthesis of CMC-g-AMPS and CMC-g-SVBS

Graft copolymers of CMC-g-AMPS and CMC-g-SVBS were synthesized as per the procedure adopted from our earlier work [15]. Briefly, known quantities of polymer (0.5 g of CMC) was transferred to

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three necked round bottomed flask containing 50 mL of distilled water; the flask was fitted with the reflux condenser with nitrogen line and placed the flask into the water bath under 200 rpm stirring for 12 h and raised the temperature up to 65°C. Nitrogen was purged for 12 min, then added KPS or APS was added and allowed for 30 min to generate free radicals. 3 mmol of monomers (SVBS or AMPS) were dissolved in distilled water separately in 10 mL water, resulting solution was equilibrated to water bath temperature, then added to the CMC solution dropwise and reaction was allowed for the pre-determined duration. Resulting graft copolymer was precipitated from excess of acetone and purified as shown in Scheme 1. Finally, the product was dried at constant temperature (40°C) for 24 h and stored in desiccator for further applications.

The percentage of grafting (%G), percentage of grafting efficiency (%GE), percentage of conversion (%C), and percentage of yield were calculated using

$$\text{Percentage of Grafting}(\%G) = \left(\frac{W_1 - W_0}{W_0}\right)100 \quad (1)$$

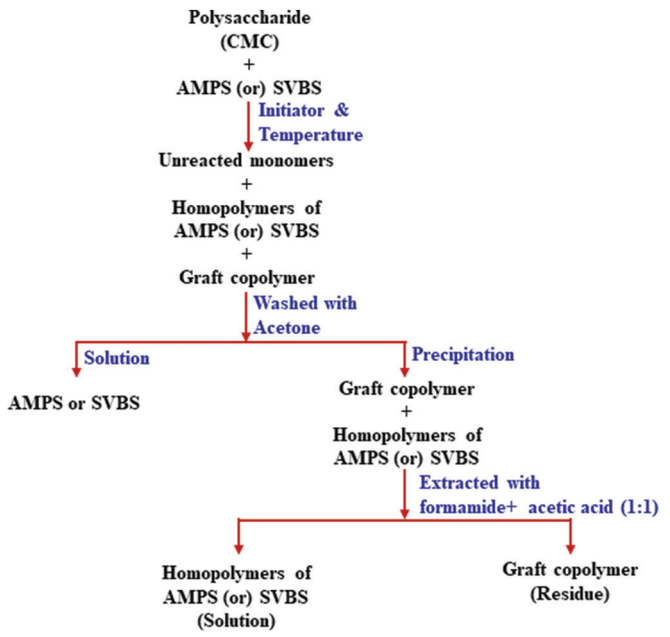
$$\text{Percentage of Grafting Efficiency}(\%GE) = \left(\frac{W_1 - W_0}{W_2}\right)100 \quad (2)$$

$$\text{Percentage of Coversion}(\%C) = \left(\frac{W_1}{W_2}\right)10 \quad (3)$$

Where, W_0, W_1, and W_2 are the weight of the CMC, CMC graft copolymer and AMPS/SVBS monomer, respectively.

2.3. Characterization

CMC, CMC-g-AMPS, and CMC-g-SVBS polymers were characterized by the Fourier transform infrared (FTIR) spectrometer, Perkin Elmer (Spectrum 2, UK), X-ray diffraction (XRD) (Rigaku instrument (model miniflex 600), Japan) and differential scanning colorimetry (DSC) (TA instruments (model STA Q600) USA)).



Scheme 1: Purification of CMC graft copolymer.

3. RESULTS AND DISCUSSION.

The synthesis of CMC graft copolymers of AMPS and SVBS is a single step reaction as shown in Scheme 2. The plausible free radical polymerization (persulfate) reaction mechanism of graft copolymers is presented in Scheme 3. Water is a universal solvent, here, it helps in transportation and diffusion of monomer units to reach the hydroxyl groups of CMC. However, among available polymerization techniques, free-radical polymerization reaction is well known and simple radical polymerization. In specific, free-radical formation occurs due to the homolytic decomposition of KPS/APS under the required temperature, which led the reaction ignition on the CMC surface, followed by chain propagation and termination which are the crucial steps influenced by the external parameters such as, initiator concentration, monomer concentration, time duration, and temperature.

3.1. FTIR Studies

FTIR spectra for the pure CMC, CMC-g-AMPS, and CMC-g-SVBS copolymers were analyzed to determine the functionality and grafting of monomers onto CMC (Figure 1). The significant FTIR peaks of CMC at 3400, 1720 and 1637, 1430, 1320, 1163, 1057, and 897 cm^{-1} attributed to -OH stretching vibrations, $-COO^-$ asymmetric starching vibrations, $-CH_2$ bending vibrational modes, C-O-C glycosidic bonds, and -C-O stretching vibrational modes of saccharide units, respectively. In the case of graft copolymers, sulfonic acid and sulfonate groups hydrates absorption peaks are detected around 2000–2400 and 1230–1240 cm^{-1}. In specific, FTIR spectra of CMC-g-AMPS are shown in Figure 1a, in addition the CMC bands a new peak can be assigned for -C=O stretching vibrations of amide, N-H bending vibrations and S-O stretching vibrations ($-SO_3H$) of AMPS at 1695 1540 and 620 cm^{-1}, respectively. FTIR spectra of CMC-g-SVBS is shown in Figure 1b, in addition the CMC bands the new peaks can be assigned for para-substituted benzene ring and S-O stretching vibrations ($-SO_3H$) were confirmed by the peaks 1445, 1015, 770, and 620 cm^{-1}.

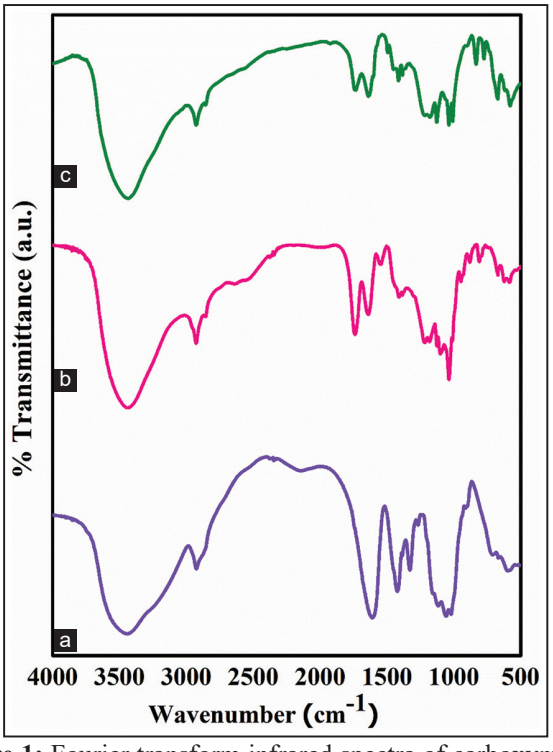
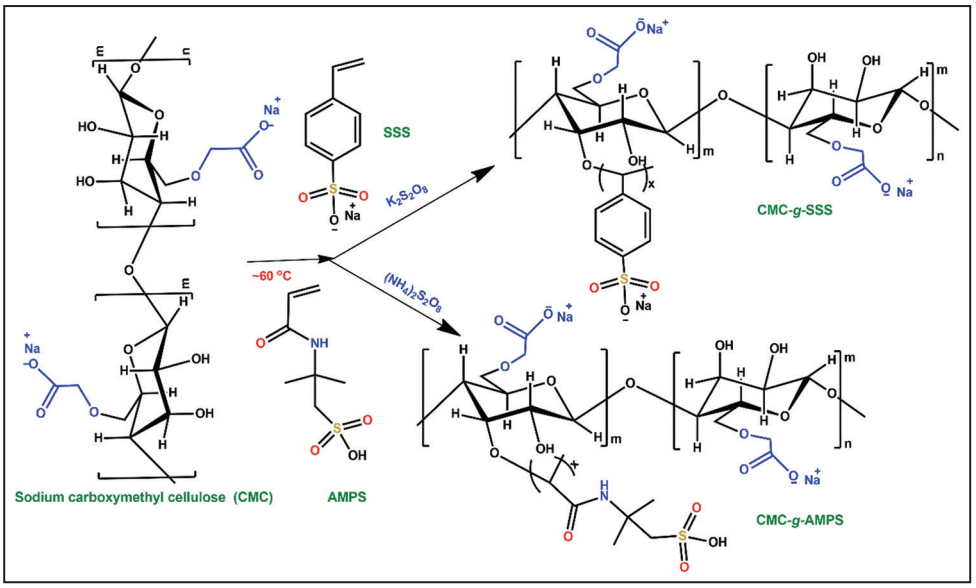


Figure 1: Fourier transform infrared spectra of carboxymethyl cellulose (CMC) (a), CMC-g-2-Acrylamido-2-methyl-1-propanesulfonic acid (b) and CMC-g-sodium 4-vinylbenzene sulfonate (c).



Scheme 2: Plausible schematic chemistry of graft copolymerization of AMPS and SVBS on to CMC.

Primary Free Radical Formation

$$S_2O_8^{2-} \xrightarrow{\Delta} 2SO_4^{\bullet-}$$

$$SO_4^{\bullet-} + H_2O \longrightarrow HSO_4^{-} + OH^{\bullet}$$

Initiation

$$SO_4^{\bullet-} \text{ or } OH^{\bullet} + M \longrightarrow IM^{\bullet}$$
$$(I)$$

$$CMCOH + IM^{\bullet} \longrightarrow CMCO^{\bullet} + IHMH$$

$$CMCO^{\bullet} + M \longrightarrow CMCOM_1^{\bullet}$$

Propagation

$$CMCOM_1^{\bullet} + M \longrightarrow CMCOM_2^{\bullet}$$

$$CMCOM_2^{\bullet} + M \longrightarrow CMCOM_3^{\bullet}$$

$$CMCOM_{n-1}^{\bullet} + M \longrightarrow CMCOM_n^{\bullet}$$

$$IM_1^{\bullet} + M \longrightarrow IM_2^{\bullet}$$

$$IM_2^{\bullet} + M \longrightarrow IM_3^{\bullet}$$

$$IM_{n-1}^{\bullet} + M \longrightarrow IM_n^{\bullet}$$

Termination

$$CMCOM_n^{\bullet} + CMCOM_m^{\bullet} \longrightarrow \text{Graft copolymer}$$

$$IM_n^{\bullet} + IM_m^{\bullet} \longrightarrow \text{Homo polymer}$$

where **CMC**: Sodium Carboxymethyl Celluloce
M: Monomer (SVBS or AMPS)

Scheme 3: Plausible reaction path way (reaction mechanism) for the synthesis of graft copolymers (CMC-g-AMPS and CMC-g-SVBS).

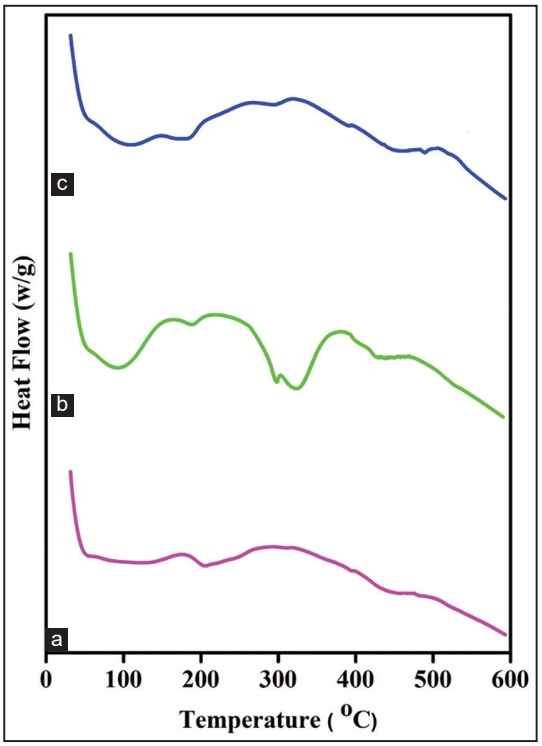


Figure 2: Differential scanning colorimetry thermograms of carboxymethyl cellulose (CMC) (a), CMC-g-2-Acrylamido-2-methyl-1-propanesulfonic acid (b) and CMC-g-sodium 4-vinylbenzene sulfonate (c).

3.2. DSC Studies

DSC study is one of the useful techniques to explain the functionalization or modification polymers. DSC thermograms of CMC (A) CMC-g-AMPS (B) and CMC-SVBS(C) are recorded from 30 to 600°C and are shown in Figure 2. The initial weigh loss of the 30–180°C is related to the evaporation of water molecules. The endothermic peak of CMC observed at 180–280°C.

3.3. XRD Studies

XRD patterns of CMC, CMC-g-AMPS, and CMC-g-SVBS are displayed in Figure 3. The diffractions of CMC indicate that the

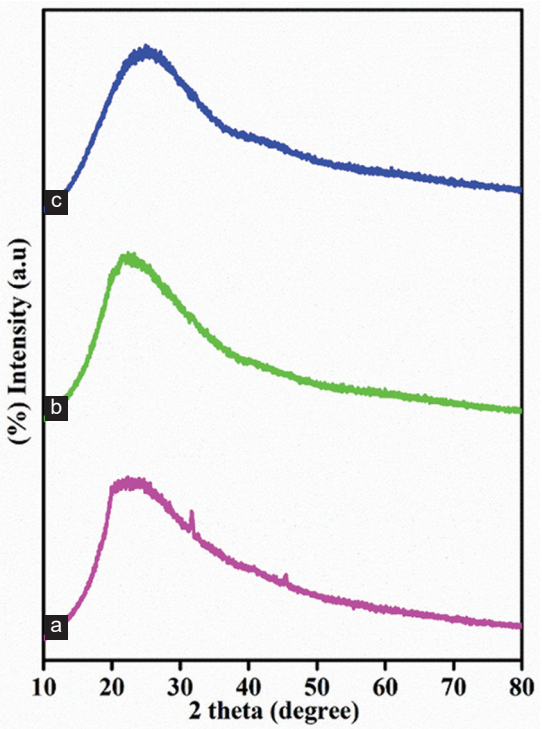


Figure 3: X-ray diffraction patterns of carboxymethyl cellulose (CMC) (a), CMC-g-2-Acrylamido-2-methyl-1-propanesulfonic acid (b) and CMC-g-sodium 4-vinylbenzene sulfonate (c).

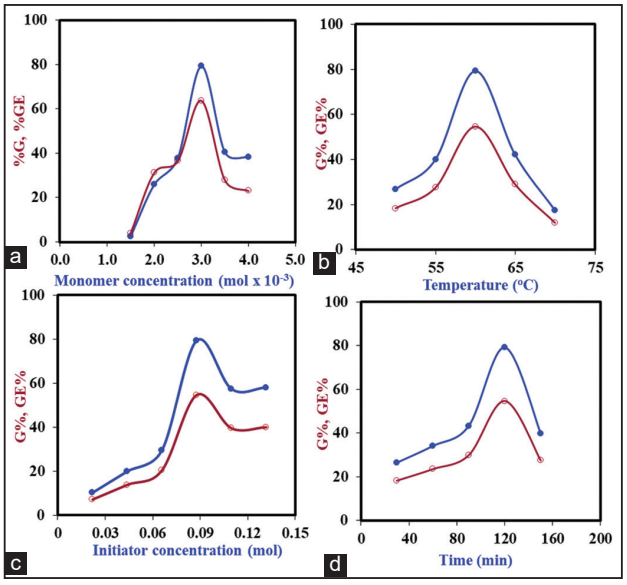


Figure 4: Effect of various reaction conditions on the grafting of 2-Acrylamido-2-methyl-1-propanesulfonic acid onto the carboxymethyl cellulose (CMC), prepared by ammonium persulfate as initiator. (a) Effect of monomer concentration (Other reaction conditions: 0.5 g of CMC; temperature: 60°C; time: 120 min; initiator concentration 0.088 mol). (b) Effect of reaction temperature (Other reaction conditions: 0.5 g of CMC; Monomer concentration: 3 mmol; time: 120 min; initiator concentration 0.088 mol) (c) Effect of initiator concentration (Other reaction conditions: 0.5 g of CMC; Monomer concentration: 3 mmol; time: 120 min; temperature: 60°C) (d) Effect of reaction time. (Other reaction conditions: 0.5 g of CMC; Monomer concentration: 3 mmol; initiator concentration 0.088 mol; temperature: 60°C).

Table 1: %Grafting, %grafting efficiency, %conversion, and %yield of CMC-g-AMPS graft copolymer prepared by APS as initiator based on effect of various reaction conditions.

	% grafting	% Grafting efficiency	% Conversion	% Yield
Temperature (°C)	**Effect of temperature on grafting**			
50	26.40	18.20	87.13	51.58
55	34.04	23.46	92.39	54.69
60	43.30	29.85	98.78	58.47
65	79.30	54.66	123.59	73.16
70	39.82	27.45	96.38	57.05
Time (min)	**Effect of time on grafting**			
30	26.68	18.39	87.32	51.69
60	39.90	27.50	96.43	57.08
90	79.30	54.66	123.59	73.16
120	42.06	28.99	97.92	57.97
150	17.30	11.92	80.85	47.86
APS concentration (mmol)	**Effect of initiator concentration on grafting**			
0.022	10.24	7.06	75.99	44.98
0.044	19.94	13.74	82.67	48.94
0.066	29.56	20.38	89.31	52.87
0.088	79.30	54.66	123.59	73.16
0.110	57.34	39.52	108.45	64.20
0.131	58.02	39.99	108.92	64.48
AMPS concentration (mmol)	**Effect of monomer concentration on grafting**			
1.5	2.49	4.00	164.84	63.20
2.0	25.86	31.19	151.82	68.81
2.5	37.80	36.48	132.98	67.67
3.0	79.30	63.77	144.19	79.92
3.5	40.42	27.86	96.79	57.30
4.0	38.28	23.09	83.40	52.02

AMPS: 2-Acrylamido-2-methyl-1-propanesulfonic acid, APS: Ammonium persulfate, CMC: Carboxymethyl cellulose

significant crystalline peaks of pristine CMC are appeared at 2θ values 19° and 25°. However, the diffractions of the graft copolymers, that is, CMC-g-AMPS and CMC-g-SVBS are not exhibited the significant peaks of CMC, it may be due the disorientation of the CMC crystals and reduced crystallinity by incorporation of AMPS and SVBS side chains on backbone of the CMC.

3.4. Grafting Parameters

The optimum reaction conditions were determined by varying reaction conditions, such as monomer concentration, initiator concentration, time, and temperature.

3.4.1. Effect of temperature

Temperature is one of the important parameters in chemical reaction, which is plays key role in increment of product yield until a limiting value reached. However, in the present case, temperature helps

in decomposition of the initiator; enhances the solubility of the CMC, AMPS and SVBS; in addition, enhances the rate of initiation and propagation of graft reaction; finally, it increases the rate of termination. As shown in Tables 1 and 2, grafting reaction temperature increased 50–70°C for both AMPS and SVBS (Figures 4 and 5); at low temperature %G is low, but increase the temperature grafting is significantly affected from 50 to 60°C and 50 to 65°C for AMPS and SVBS monomer, respectively. However, further increase in temperature, due to rapid collisions between CMC and APS/KPS, an increase in CMC macro radicals, in addition there may be formation monomer free-radical led to the homopolymer, results in the formation reduction in the %G.

3.4.2. Effect of monomer

Free radical polymerization method is best suitable for graft copolymerization acrylic monomers on to the carbohydrate polymers; it is due to its easy reaction initiation by the free radicals of monomers. However, the reaction efficiency purely depends on the monomer concentration, that is, more amount of monomer present in the reaction led to the trigger free radical formation that activate the grafting reaction. In addition, there is a gel effect, that is, the solubility of homopolymer in monomer solution reduces the rate of reaction termination and increases monomer diffusion to the active site of CMC. In theory, grafting rises with increasing monomer concentration, but there is always a constraint, namely a reaction environment in which grafting is not preferred.

The effect of AMPS and SVBS monomer concentration (1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 mmol.) on grafting parameters is presented in Tables 1 and 2, respectively. The percentage of grafting is increased with increase of AMPS concentration (1.5–4.0 mmol) (Figures 4 and 5). The %G and %GE are reaching maximum value 82.04 and 56.55, respectively, at the SVBS concentration 3.5 mmol. The %G and %GE are reaching maximum value 94.24 and 85.27 respectively, at the SVBS concentration 3.0 mmol.

Table 2: %Grafting, %grafting efficiency, %conversion, and %yield of CMC-g-SVBS graft copolymer prepared by KPS as initiator based on effect of various reaction conditions.

	% Grafting	% Grafting efficiency	% Conversion	% Yield
Temperature (°C)	**Effect of temperature on grafting**			
50	26.42	23.90	114.38	60.05
55	33.24	30.07	120.55	63.29
60	67.12	60.73	151.20	79.38
65	94.24	85.27	175.74	92.26
70	30.48	27.58	118.05	61.98
Time (min)	**Effect of time on grafting**			
30	26.66	24.12	114.60	60.16
60	38.18	34.54	125.02	65.64
90	55.42	50.14	140.62	73.82
120	60.46	54.70	145.18	76.22
150	94.24	85.27	175.74	92.26
180	32.64	29.53	120.01	63.00
KPS concentration (mmol)	**Effect of initiator concentration on grafting**			
0.02	24.70	22.35	112.82	59.23
0.04	51.24	46.36	136.84	71.84
0.06	71.24	64.46	154.93	81.34
0.07	94.24	85.27	175.74	92.26
0.09	50.64	45.82	136.29	71.55
SVBS concentration (mmol)	**Effect of monomer concentration on grafting**			
1.5	14.37	26.00	206.96	73.66
2.0	46.70	63.38	199.09	84.46
2.5	78.22	84.92	193.50	92.77
3.0	94.24	85.27	175.74	92.26
3.5	93.20	72.28	149.83	84.39
4.0	92.02	62.44	130.30	77.63

KPS: Potassium persulfate, SVBS: Sodium 4-vinylbenzene sulfonate, CMC: Carboxymethyl cellulose

3.4.3. Effect of reaction time

The data effect of reaction time on grafting is presented in Tables 1 and 2. The reaction time was varied by changing the reaction period 30–150 min for CMC-g-AMPS and 30–180 min for CMC-g-SVBS (Figures 4 and 5). The grafting parameters %G and %GE increased with increasing reaction time; it may be due to increasing addition of monomer free radicals to the growing grafted chains. However,

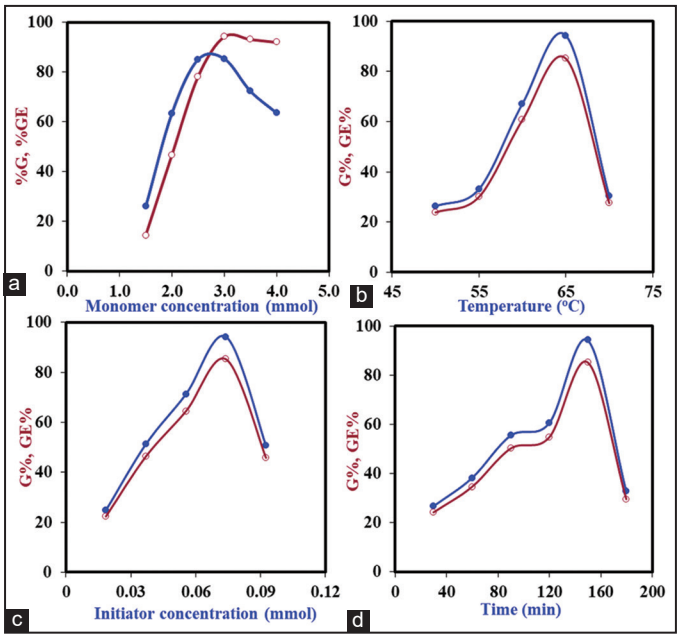


Figure 5: Effect of various reaction conditions on the grafting of sodium 4-vinylbenzene sulfonate (SVBS) onto the carboxymethyl cellulose (CMC), prepared by potassium persulfate as initiator. (a) Effect of monomer (SVBS) concentration (Other reaction conditions: 0.5 g of CMC; temperature: 65°C; time: 150 min; initiator concentration 0.07 mmol). (b) Effect of reaction temperature (Other reaction conditions: 0.5 g of CMC; Monomer concentration: 3 mmol; time: 150 min; initiator concentration 0.07 mmol) (c) Effect of initiator concentration (Other reaction conditions: 0.5 g of CMC; Monomer concentration: 3 mmol; time: 150 min; temperature: 65°C) (d) Effect of reaction time (Other reaction conditions: 0.5 g of CMC; Monomer concentration: 3 mmol; initiator concentration 0.07 mmol; temperature: 65°C).

the maxim %G is observed for 120 min for the CMC-g-AMPS and 150 min for the CMC-g-SVBS. After reaching the maximum reaction time the %G is lowered for both graft copolymers it may be due to the decreasing monomer and catalyst content in the reaction.

3.4.4. Effect of initiator concentration

CMC grafted with AMPS and SBVS using APS and KPS, respectively; grafting reactions were planned with varying initiator concentrations, keeping other parameters constant. The maximum grafting percentage obtained for CMS graft copolymer with AMPS and SBVS are and 79.30 (at 0.088 mmol APS) and 94.24 (at 0.07 mmol KPS), respectively. The obtained results are presented in Tables 1 and 2.

4. CONCLUSION

In the present study, sodium CMC was grafted with 2-acrylamide-2-methyl-1-propanesulphonic acid and SVBS using APS and KPS as initiators. Grafting reaction conditions such as time, monomer concentration, temperature, and initiator concentration have shown significant influence on grafting parameters percentage of grafting, grafting efficiency, conversion and yield by in aqueous medium persulfate as an initiator. Grafting percentages were achieved up to 82.04 and 94.24 for AMPS and SVBS, respectively. The highest grafting percentage for AMPS achieved using APS at 60°C, 120 min of reaction time, 3.0 mmole of monomer and 0.088 mmol of initiator. The highest grafting percentage for SVBS achieved using KPS at 60°C, 150 min of reaction time, 3.0 mmole of monomer and 0.07 mmol of initiator.

5. ACKNOWLEDGMENTS

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6. REFERENCES

1. A. Sood, A. Gupta, G. Agrawal, (2021) Recent advances in polysaccharides based biomaterials for drug delivery and tissue engineering applications. ***Carbohydrate Polymer Technologies and Applications***, **2:** 10006.
2. K. S. V. Krishna Rao, B. V. K. Naidu, M. C. S. Subha, T. M. Aminabahvi, (2006) Novel carbohydrate polymeric membranes in pervaporation dehydration of acetic acid, ***Carbohydrate Polymers***, **66:** 345-351.
3. K. S. V. Krishna Rao, B. V. K. Naidu, M. C. S. Subha, and T. M. Aminabhavi, (2006) Novel Chitosan-based pH-Sensitive Interpenetrating Network Microgels for the Controlled Release of Cefadroxil, ***Carbohydrate Polymers***, **66:** 333-344.
4. T. J. S. Vani, N. S. Reddy, P. R. Reddy, K. S. V. Krishna Rao, J. Ramkumar, A. V. R. Reddy, (2014) Synthesis, characterization and metal uptake capacity of new polyaniline and poly (acrylic acid) grafted sodium alginate/gelatin adsorbent, ***Desalination Water Treatment***, **52:** 526-535.
5. J. Mergy, A. Fournier, E. Hachet, R. Auzély-Velty, (2012) Modification of polysaccharides via thiol-ene chemistry: A versatile route to functional biomaterials. ***Journal of Polymer Science Part A: Polymer Chemistry***, **50**:4019-4028.
6. D. R. Biswal, R. P. Singh, (2004) Characterisation of carboxymethyl cellulose and polyacrylamide graft copolymer. ***Carbohydrate Polymers***, **57:** 379-387.
7. C. G. Lopez, S. E. Rogers, R. H. Colby, P. Graham, J. T. Cabral, (2015). Structure of sodium carboxymethyl cellulose aqueous solutions: A SANS and rheology study. ***Journal of Polymer Science Part B: Polymer Physics***, **53:** 492-501.
8. A. Pettignano, A. Charlot, E. Fleury, (2019) Carboxyl-functionalized derivatives of carboxymethyl cellulose: Towards advanced biomedical applications. ***Polymer Reviews***, **59:** 510-560.
9. K. M. Rao, B. Mallikarjuna, K. S. V. Krishna Rao, M. N. Prabhakar, K. C. Rao, M. C. S. Subha, (2012) Preparation and characterization of pH sensitive poly (vinyl alcohol)/sodium carboxymethyl cellulose IPN microspheres for *in vitro* release studies of an anti-cancer drug. ***Polymer Bulletin***, **68:** 1905-1919.
10. N. S. Reddy, S. Eswaramma, K. S. V. Krishna Rao, A. V. R. Reddy, J. Ramkumar, (2014) Development of hybrid hydrogel networks from poly (acrylamide-co-acrylamido glycolic acid)/ cloisite sodium for adsorption of methylene blue. ***Indian Journal of Advances in Chemical Science***, **2:** 107-110.
11. N. S. Reddy, K. S. V. Krishna Rao (2016) Polymeric hydrogels: Recent advances in toxic metal ion removal and anti-cancer drug delivery applications, ***Indian Journal of Advances in Chemical Science***, **4:** 214-234.
12. B. P. Tripathi, N. C. Dubey, M. Stamm, (2013) Functional polyelectrolyte multilayer membranes for water purification applications. ***Journal of Hazardous Materials***, **252:** 401-412.
13. Q. Zhao, Q. F. An, Y. Ji, J. Qian, C. Gao, (2011) Polyelectrolyte complex membranes for pervaporation, nanofiltration and fuel cell applications. ***Journal of Membrane Science***, **379:** 19-45.
14. X. Meng, F. Tian, J. Yang, C. N. He, N. Xing, F. Li, (2010) Chitosan and alginate polyelectrolyte complex membranes and their properties for wound dressing application, ***Journal of Materials Science: Materials in Medicine***, **21**, 1751-1759.
15. S. S. Prasad, K. M. Rao, P. R. S. Reddy, N. S. Reddy, K. S. V. Krishna Rao, M. C. S. Subha (2012) Synthesis and characterisation of guar gum-g-poly(acrylamidoglycolic acid) by redox initiator, ***Indian Journal of Advances in Chemical Science***, **1:** 28-32.