Graft copolymerization is a technique for modifying the chemical and physical properties of natural and synthetic polymers. Applications of these modification reactions are useful in the field of polymer science. Chemical grafting is one of the most effective method for modifying structure and properties of biopolymers. Graft copolymerization of natural polysaccharides is becoming an important resource for developing advanced materials as it can improve the functional properties of natural polysaccharides. Sodium alginate an industrially important marine polysaccharide has drawn attention of a large number of researches worldwide because of easy availability, ease of modification and potential for use in various industrial applications. In the present work, modification of sodium salt of partially carboxymethylated sodium alginate (Na-PCMSA, $\bar{DS} = 0.605$) has been carried out via grafting.

A brief chapter wise summary of results of study and important conclusions are discussed below:

**Chapter-1:**

In this chapter a general introduction to sodium alginate and its derivatives as well as to graft copolymers, including modes and methods of synthesis along with the importance of grafting has been reported.

**Chapter-2:**

In this chapter the optimal reaction conditions in the case of grafting of different vinyl monomers (AN, MMA, MA, EA, EMA and BA) onto Na-PCMSA ($\bar{DS} = 0.605$) using ceric ammonium nitrate (CAN) as a redox initiator, in an aqueous medium by successively varying various reaction parameters viz. concentrations of nitric acid, ceric ammonium nitrate (CAN), monomer (AN or MA or MMA or EA or EMA or BA) as well as reaction time, temperature and amount of substrate have been established.

The optimized reaction conditions established in the case of graft copolymerization of (i) **AN are**:

Na-PCMSA ($\bar{DS} = 0.605$) = 0.5g (dry basis); [CAN] = 0.04 mol.L$^{-1}$; [HNO$_3$] = 0.50 mol.L$^{-1}$; [AN] = 0.203 mol.L$^{-1}$; Time = 4.5 h; Temperature = 35°C and Total Volume = 150 mL;
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(ii) MA are:
Na-PCMSA ($\overline{DS} = 0.605$) = 1.5 g (dry basis); [CAN] = 0.05 mol.L$^{-1}$; [HNO$_3$] = 0.30 mol.L$^{-1}$; [MA] = 0.304 mol.L$^{-1}$; Time = 2 h; Temperature = 40$^\circ$C and Total Volume = 150 mL;

(iii) MMA are:
Na-PCMSA ($\overline{DS} = 0.605$) = 1.0 g (dry basis); [CAN] = 0.03 mol.L$^{-1}$; [HNO$_3$] = 0.30 mol.L$^{-1}$; [MMA] = 0.203 mol.L$^{-1}$; Time = 3 h; Temperature = 30$^\circ$C and Total Volume = 150 mL;

(iv) EA are:
Na-PCMSA ($\overline{DS} = 0.605$) = 1.5 g (dry basis); [CAN] = 0.04 mol.L$^{-1}$; [HNO$_3$] = 0.40 mol.L$^{-1}$; [EA] = 0.304 mol.L$^{-1}$; Time = 5 h; Temperature = 40$^\circ$C and Total Volume = 150 mL;

(v) EMA are:
Na-PCMSA ($\overline{DS} = 0.605$) = 1.0 g (dry basis); [CAN] = 0.03 mol.L$^{-1}$; [HNO$_3$] = 0.30 mol.L$^{-1}$; [EMA] = 0.203 mol.L$^{-1}$; Time = 3 h; Temperature = 30$^\circ$C and Total Volume = 150 mL; and

(vi) BA are:
Na-PCMSA ($\overline{DS} = 0.15$) = 1.0 g (dry basis); [CAN] = 0.03 mol.L$^{-1}$; [HNO$_3$] = 0.30 mol.L$^{-1}$; [BA] = 0.203 mol.L$^{-1}$; Time = 4 h; Temperature = 40$^\circ$C and Total Volume = 150 mL.

At the optimum reaction conditions, the respective maximum values of the percent grafting (%G) achieved are 376.82 %, 364.94%, 352.37%, 340.45%, 290.45% and 254.94 % in the case of grafting of AN, MA, MMA, EA, EMA and BA onto Na-PCMSA ($\overline{DS} = 0.605$). The influence of the various reaction parameters on the grafting yields (% G and %GE) as well as on the rates of polymerization ($R_p$), graft copolymerization ($R_g$) and homopolymerization ($R_h$) have been studied and the results are interpreted scientifically.

The kinetic scheme of free radical graft copolymerization of AN, MA, MMA, EA, EMA and BA onto Na-PCMSA ($\overline{DS} = 0.605$) has been proposed and the equations relating the values of $R_p$, $R_g$ and $R_h$ are also suggested. The experimental results obtained in the present work have been analyzed in light of the proposed reaction scheme and are found to agree very well with the scheme.
Under the established optimum reaction conditions, the reactivity of different vinyl monomers towards grafting has been compared and observed the following reactivity order: AN > MA > MMA > EA > EMA > BA

The plausible explanation has been furnished for the observed reactivity order of monomers towards grafting. The value of the overall activation energy of grafting ($E_g$) has also been evaluated in the case of all the monomers and the following reactivity pattern for the higher members of methacrylate homologous series has been suggested:

MA > MMA > EMA

The lowest value of $E_g$ (22.85 kJ/mole) obtained in the case of MA, compared to that of MMA (32.79 kJ/mole) and of EMA (62.78 kJ/mole) indicates the ease of occurrence of grafting reaction as a result of which higher value of the %G is observed in MA (%G = 364.94) compared to MMA (%G = 352.37) and EMA (%G = 290.45).

The grafting of ethyl acrylate (EA) onto Na-PCMSA ($\bar{D_S} = 0.605$) has also been studied in different water/solvent mixtures. The solvents used include methanol, ethanol, n-propanol, n-butanol and carbon tetrachloride. From the results it has been observed that the magnitude of grafting differs significantly with the type and ratio of solvent used in the mixture. Of the water/solvent mixtures used, water/methanol at a ratio of 75/25 is found to constitute the most favourable medium for graft copolymerization of EA onto Na-PCMSA ($\bar{D_S} = 0.605$) giving rise to highest value of percentage of grafting.

The influence of liquor ratio on %G in the case of grafting of AN, MA, MMA, EA, EMA and BA onto Na-PCMSA ($\bar{D_S} = 0.605$) has been studied and the results have been interpreted. The effect of introducing functional group(s) like carboxymethyl in sodium alginate molecules on its susceptibility towards grafting with different vinyl monomers has been investigated and the percentage of grafting has been found to be greatly enhanced after carrying out carboxymethylation of sodium alginate.

The proof of the etherification of sodium alginate has been provided by the help of the spectroscopic (FTIR and $^1$H-NMR) methods. The evidence of grafting has also been ascertained by using FTIR and SEM techniques.

Chapter-3

This chapter describes the thermal behaviour of sodium alginate, Na-PCMSA and its different graft copolymers (viz. Na-PCMSA-g-PAN, Na-PCMSA-g-PMA, Na-PCMSA-g-PMMA, Na-PCMSA-g-PEA, Na-PCMSA-g-PEMA and Na-PCMSA-g-
Summary

PBA) as well as the corresponding homopolymers (viz. PAN, PMA, PMMA, PEA, PEMA and PBA) in an inert atmosphere at a heating rate of 10°C/min by thermogravimetric analysis (TGA). The results of the primary thermograms for all these samples have been discussed in detail. The temperature characteristic values have been reported for all the samples. The thermal behaviour of Na-PCMSA-g-PMMA (%G = 352.37) has also been studied at four different heating rates by TGA and the results obtained have been analyzed by employing Osawa as well as Freeman-Carroll methods (multiple heating rate methods) for the evaluation of the activation energy.

Chapter-4:

A novel superabsorbent hydrogel, H-Na-PCMSA-g-PAN has been prepared by grafting of AN onto Na-PCMSA (DS = 0.15), followed by alkaline hydrolysis of the Na-PCMSA-g-PAN graft copolymer to achieve an in-situ crosslinked hydrogel network, H-Na-PCMSA-g-PAN, with high capability of water absorption (absorbency in water, 245.03 g/g gel; absorbency in 0.15M NaCl, CaCl₂ and AlCl₃ solutions respectively to be 81.17 g/g gel, 77.89 g/g gel and 56.80 g/g gel). The synthesized hydrogel also exhibited the maximum swelling capacity of the order of 79.71 g/g gel in simulated urine. These promising results make it worth to prepare hydrogel suitable for utilization as diaper as well as adsorbent material. The results regarding the absorbency measurements of the hydrogel in low conductivity water, 0.15M different salt (NaCl, CaCl₂ and AlCl₃) solutions and simulated urine have been explained successfully on the basis of “charge screening” effect and “ionic crosslinking” phenomenon. The experimental data suggested clearly that the swelling process of the hydrogel obeys second-order kinetics in different swelling media. The swelling characteristics as well as equilibrium water contents have also been investigated for the superabsorbent hydrogel, H-Na-PCMSA-g-PAN in different swelling media.