Trends in Carbohydrate Research

Graft copolymerization of Carboxymethylcellulose: An Overview

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Abstract

The modification of Carboxymethylcellulose (CMC) through vinyl monomers containing different functional groups to increase its functionality has attracted the attention of researchers. Among the various methods for modifying polymers, graft copolymerization appears to be highly attractive and has made a paramount contribution towards improved industrial and biomedical applications. In recent years, the polymer functionalization of CMC has greatly benefited from advances in polymerization techniques. Graft copolymerization technique provides different functionalities onto CMC surface, where CMC and its modified graft copolymers have multifunctional characteristics and known for their potentially wider range of applications. In addition to the conventional grafting techniques, we highlight the recent developments in graft copolymerization process that allows increase control over the grafting and permits the production of functional cellulose which possess improved physical and chemical properties**.**

Keywords: Carboxymethylcellulose, graft copolymer, vinyl monomers, biodegradability, FTIR, Thermal analysis

Introduction

Among the various methods for modifying polymers, graft copolymerization seems to be highly attractive and has made a paramount influence towards improved industrial and biomedical applications.[13] Carboxymethylcellulose (CMC) is a polysaccharide consisting of substituted anhydroglucose units and is also known as cellulose gum. Carboxymethyl group increases the swellability of cellulose,[4] which leads to their unique applications in various industries, such as the paper[5] and textile processing industries.[6] Usually, water-based mud for oil-field drilling is effective water-soluble polymers used to perform such main functions as shale inhibition, viscosity, and filtration control.[7-8] Up to now, conventional anionic polymers such as Carboxymethylcellulose and partially hydrolyzed polyacrylamide and recently developed cationic polymers such as quaternary polyamine and cationic polyacrylamide have been widely used for this purposes.[911] The anionic polymers possess good filtration control and viscosity-building properties but weak shale inhibition. The cationic polymers exhibit effective shale inhibition but suffer from weak mud performance, bad compatibility, and high toxicity to aquatic organisms. Therefore, there has been increasing demand in the oil-field industry to develop environmentally acceptable polymeric additives that can combine cationic and anionic polymer behavior advantageously and overcome the limitations inherent
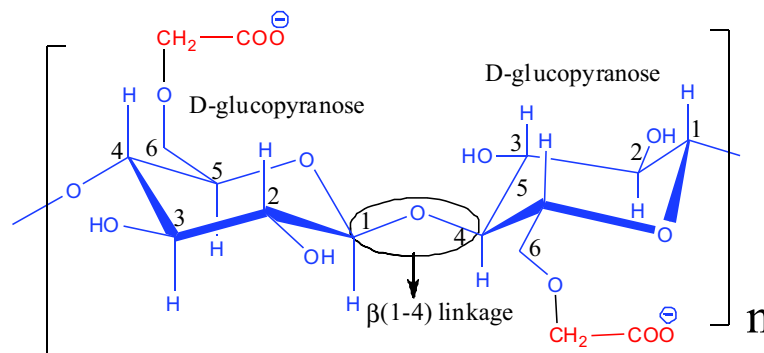
Figure 1. Carboxymethylcellulose polysaccharide

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in the aforementioned additives.[1214] On the other hand, polymers based on acrylamide are the most widely commercially used water-soluble products.[15] Their uses range from paper manufacturing[16] and water treatment[17] to oil recovery,[18] soil modification,[19] and medical applications.[20] Thus, polysaccharide (sodium Carboxymethyl cellulose)- based graft copolymers have been found to have multifunctional characteristics as oil-field-drilling mud additives with respect to shale inhibition, viscosity building, and filtration control.[21-22]

Source and Structural unit

Carboxymethylcellulose (CMC) is a derivative of cellulose formed by its reaction with alkali and chloroacetic acid. The CMC structure is based on the β-(14)-D-glucopyranose polymer of cellulose (**Fig. 1**). It is often used as its sodium salt, sodium carboxymethyl cellulose. Different preparations may have different degrees of substitution, but it is generally in the range 0.6 - 0.95 carboxymethyl group per monomer unit. CMC molecules are most extended (rod-like) at low concentrations but at higher concentrations the molecules overlap and coil up and then, at high concentrations, entangle to become a thermo-reversible gel. Increasing ionic strength and reducing pH both decrease the viscosity as they cause the polymer to become more coiled.[23]

Carboxymethylation of cellulose

As we know cellulose (cotton) fiber as raw material for carboxymethyl cellulose (CMC), which is ether in which the hydroxyl group of anhydrous glucose is replaced by the carboxymethyl group of monochloroacetate. The fiber was tattered and grinned enough to make contact with chemical solution. The main step in carboxymethylation is the formation of alkali cellulose, which has modified the crystalline structure of cellulose and increased the accessibility of fibers to chemicals by swelling.[24] The cellulose fibers were treated for 5-6 hours with NaOH solution. Under alkaline conditions, the hydroxyl group of cellulose shows high activity. The excess sodium hydroxide from the pretreated fibers was removed by filter press. Highly purified monochloroacetic acid (MCA) was dissolved in distilled water. The pretreated alkali cellulose was reacted with MCA. The mixture was stirred at 600-800 rpm on a magnetic hot-plat stirrer at constant temperature of 75°C for four hours. Isopropanol and water were used as solvents. The CMC gel product was filtered from solvent. The pH was adjusted to 7. The product was purified with methanol, dried at 70°C in a conventional oven for one hour.[25-28] The product was filtered, washed for several times with a mixture of $CH_3OH:H_2O$ (1:1), and dried. General mechanism comes by production of CMC which required two consecutive steps of reactions.[29-30] These reactions are summarized as basification (1) and etherification (2) as shown in **Fig. 2**.

The above reaction can be carried out with or without solvents.[31] The first reaction is endothermic as the
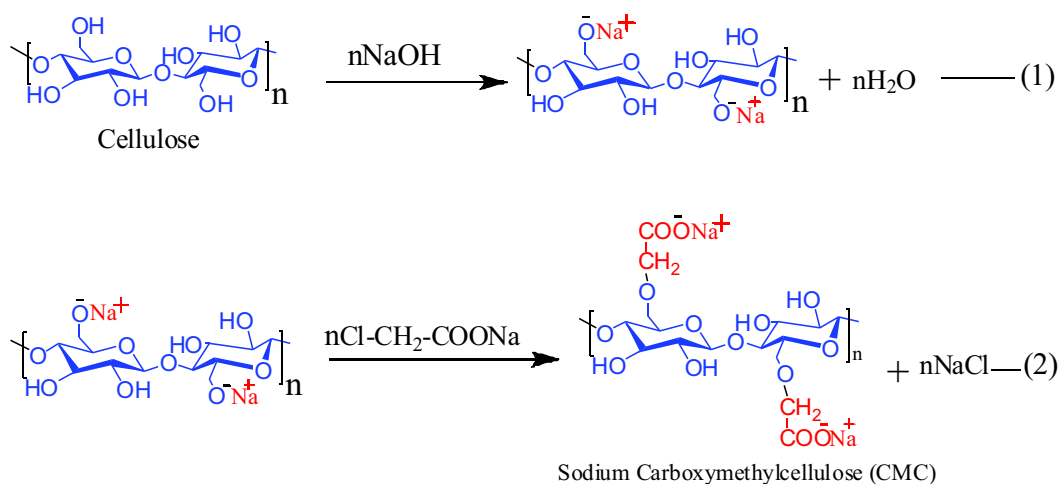
Figure 2. General mechanism for Carboxymethylation of Cellulose

second reaction is exothermic. Therefore, the removal of emitted heat to out of the reaction vessel *via* a jacket was required. The product is known as sodium Carboxymethyl cellulose.

Molecular Structure

CMC molecules are somewhat shorter, on average, than native cellulose with uneven carboxymethylation giving areas of high and low substitution. This substitution is mostly 2-*O*- and 6-*O*-linked, followed in order of importance by 2,6-di-*O*- then 3-*O*-, 3,6-di-*O*-, 2,3-di-*O*- lastly 2,3,6-tri-*O*-linked.[32]

Physico-Chemical properties of Carboxymethylcellulose in terms of viscosity, stability and compatibility

CMC is cellulose ether, produced by reacting alkali cellulose with sodium monochloroacetate under rigidly controlled conditions. CMC absorbs moisture from the air. The amount absorbed and the rate of absorption depend on the initial moisture content and on the relative humidity and temperature of the surrounding air. The elemental analysis of Carboxymethylcellulose constitutes only 35% carbon, 5.40% Hydrogen, 52.53% Oxygen, 7.07% sodium.[33]
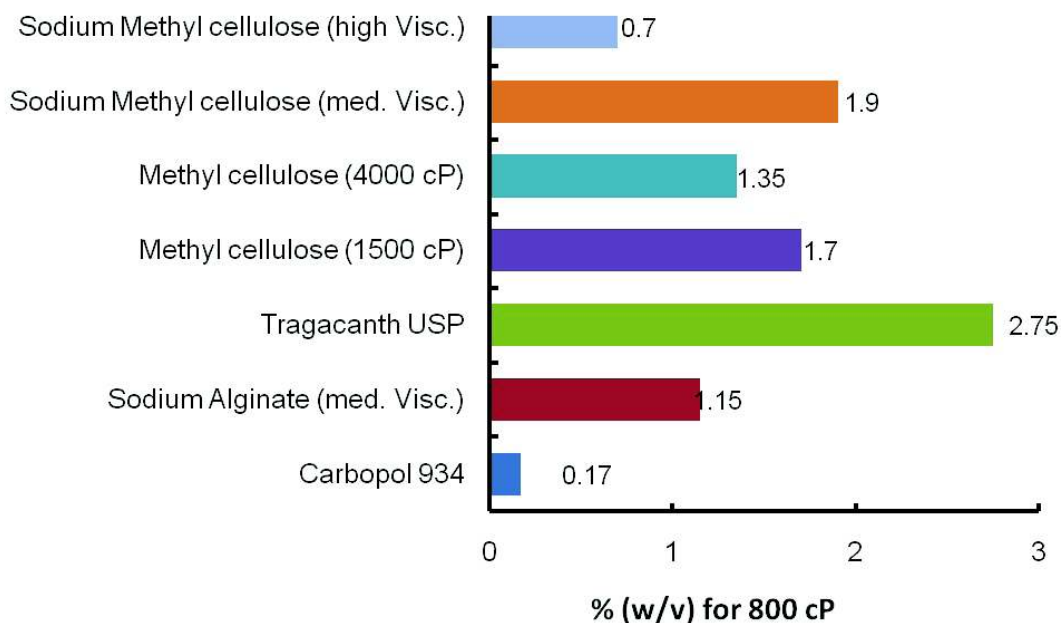
Fig. 3 indicating concentrations of various hydrocolloids required to produce an apparent viscosity of 800 cP at 20°C shows that a brand of Carboxymethylcellulose is in that respect a runner up to Carbopol.[34]

Grafting of Vinyl Monomers onto Carboxymethylcellulose

Polymer chains are grafted on polysaccharides through three main strategies: the 'grafting through', the 'grafting on' and the 'grafting from' processes.[35] The 'grafting through' technique involves copolymerizing pre-made vinyl functionalized polysaccharide material with comonomers. Besides the conventional free radical processes, the 'grafting from' technique involving the growth of grafts directly from the polysaccharide backbones is the most extensively studied and used technique. The methods of graft copolymerization (**Fig. 4**) are based on one or more of three approaches, "grafting-to", "grafting-from" and "grafting-through".

In the "grafting-to" approach, an end functional pre-formed polymer with its reactive end-group is coupled with the functional groups that are located on the CMC backbone. In the "grafting-from" approach, the growth of polymer chains occurs from initiating sites on the CMC backbone. In the "grafting-through" approach, a macromonomer, usually a vinyl macromonomer is copolymerized with a low molecular weight co-


Figure 3. Concentrations of various hydrocolloids or gum

monomer. Among these three approaches of grafting, the "grafting-from" approach is the most commonly used procedure. One of the major advantages of this approach is that a high graft density can be achieved due to the easy access of the reactive groups to the chain ends of the growing polymers. The "grafting-to" approach is inherently limited by the crowding of chains at the surface. This hinders the diffusion of chain ends to the surface for further attachment and consequently limits the final graft density.[36] Although the "grafting-through" approach is relatively convenient, it still requires the synthesis of cellulose-derived macromonomers.

Radicals can be conveniently generated along the polysaccharide backbone in the presence of chemical initiators.[37-40] The synthesis of grafted polymers (**Fig. 5**) essentially involves free radical which are generated *in situ* by radical/redox initiators such as ethylenediamine

tetraacetic acid/ceric ammonium nitrate,[41] ferrous ammonium sulfate/potassium persulfate,[42] ceric ammonium nitrate/HNO_3,[43] potassium persulfate (KPS)/*N,N,N',N'*-tetramethylethylene diamine[44] and $K_2S_2O_8$/ascorbic acid.[45] The radical-initiated functionalization of polysaccharides has received considerable attention in recent years and has been proven to be a useful method for the industrial production of modified polysaccharides. However, these transformations mostly require inert working conditions and are tedious and time consuming. In these conventional procedures the copolymer products are often accompanied by homopolymer formation which besides decreasing the yield and also contaminates the copolymeric product. Other than by the use of radical initiators,[46-51] free radicals are generated through γ-rays,[52-54] UV radiations,[55] electron beam[56] and microwave irradiation.[57-60]
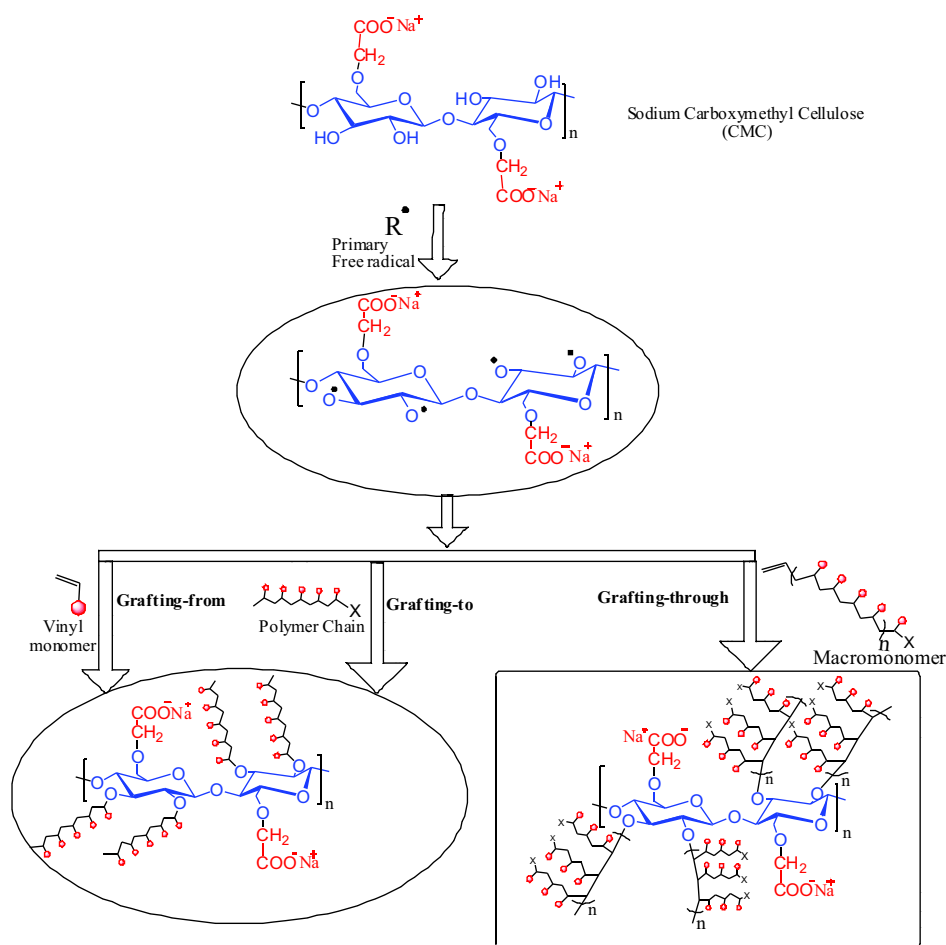
Figure 4. Grafting -through, -from- and -to techniques

Conventional grafting procedures may lead to polysaccharide backbone degradation and are not amenable to block copolymer formation. Their use may often be detrimental for some applications as they have limited control over graft molecular weight distribution. These problems have been tackled from beginning to end by the use of controlled/ living radical polymerizations[35,61-63] to obtain graft-functionalized polysaccharide based macromolecular materials.

Literature survey reveals that no living radical graft copolymerization process has been handled onto sodium carboxymethyl cellulose, till date. This technique is tolerant to moisture, can be performed with the polymers having a range of functional groups, and thus is very useful to precisely tailor the properties of the polysaccharide-based materials where the synthetic graft length, chemical composition and product topology can be controlled and tailored. All these techniques use the concept of significantly reducing the concentration of propagating radical chain ends so as to minimize the irreversible termination reactions which form 'dead' polymer chains. This is done by addition of species that can reversibly trap the 'active' propagating radical species through reversible termination or reversible transfer.

Zhang et. al.[64] developed amphoteric graft copolymers of CMC with 2-(dimethylamino)ethyl methacrylate in aqueous solution using ammonium persulfate and N,N,N',N'-tetramethylethylenediamine as the initiation system and also prepared effective water-soluble polymers as clay-stabilizing agents for oilfield drilling and modified CMC by the grafting of diallyldimethylammonium chloride[65] in aqueous medium using the $KMnO_4/H_2SO_4$ initiation system and a hydrophobically modified water-soluble graft copolymer of Na CMC with acrylamide and dimethyloctyl(2-methacryloxyethyl)ammonium bromide using potassium persulfate and dimethylaminoethyl methacrylate as initiators in aqueous solution.[66]

Carboxymethylcellulose grafted polyacrylic acid (CMC-g-PAA) was synthesized by using different groups such as Kubota et al.,[67] Kuwabara, Kubota et al.[68] El-Sherbiny et al.[69] and Mishra et. al.,[70] in different conditions, using photo initiators, Photo-grafting, ammonium persulfate (APS) and microwave radiation, respectively. The application of the grafted product was found as flocculent for river water clarification, towards augmentation of drinking water.

Okieimen et al.[71] prepared graft copolymers of acrylonitrile, ethyl acrylate, methyl acrylate, ethyl methacrylate, and methyl methacrylate and of acrylonitrile/ethyl methacrylate and acrylonitrile/methyl methacrylate monomer mixtures

on CMC by use of ceric ion initiator in aqueous medium.

CMC grafted polyacrylamide (CMC-g- PACM) also synthesized by Yang et al using sodium sulfite/APS redox system[72] and El-Hady by using sodium bisulfate/APS[73] in an aqueous medium and Kumar et al used ferrous sulfate and potassium bromate[74] as redox initiator. Wunderlich,[75] Biswal and Singh,[76] Okieimen[77] and Deshmukh et al.[78] grafted polyacrylamide onto CMC sodium salt backbones by using ceric ammonium nitrate (CAN) as an initiator. Furthermore, Tripathy et al. synthesized CMC-g-PACM and sodium alginate-g-polyacrylamide which were prepared in aqueous solution using Ce^{4+} as initiator.[79] Graft copolymers of starch or CMC with polyacrylamide were tested for their aqueous drag-reduction, shear stability, effectiveness, and biodegradability.

A new superabsorbent polymer (CMC-g-poly(acrylic acid-co-acrylamide) onto CMC by both the above monomers acrylic acid (AA) and acrylamide (ACM) prepared through the free-radical grafting solution polymerization with a redox couple of potassium persulfate and sodium metabisulfite as an initiator in the presence of N,N'-methylenebisacrylamide as a crosslinker.[80]

The homogeneous graft polymerization of N-vinylpyrrolidone onto a 3:1 mixture of CMC and hydroxyethyl cellulose was carried out in an aqueous system.[81] Graft copolymers of CMC and hydroxyethyl cellulose with N-vinyl-2-pyrrolidone and acrylamide have been synthesized by grafting copolymer of N-vinyl-2-pyrrolidone and acrylamide onto a mixture of CMC and hydroxyethyl cellulose through a solution polymerization technique using a redox initiation system.[82]

Pourjavadi et al.[83] grafted polyacrylonitrile (PAN) and Castellano et al.[84] grafted polymethylmethacrylate (PMMA) onto CMC sodium salt backbones by using ceric ammonium nitrate (CAN) as an initiator. Wang and Wang[85] grafted several vinyl monomers onto CMC and then incorporated inorganic nano-scale clays to derive superabsorbent because it afforded unique environmental and commercial advantages.

Poly(N-isopropyl acrylamide) grafted onto CMC[86] and studied the enzymic degradation of poly(N-isopropyl acrylamide) (PNIPAM) grafted to CMC. The enzymic activity of the cellulosic preparation against CMC and the grafted copolymers was determined by the Petterson-Porath method. While as CMC-g-PNIPAM also prepared by some other group of Bokias et al.[87] using ammonium per sulfate and 2-aminoethanethiol hydrochloride (AET) and block copolymer of PNIPAM and polyacrylic acid (AA) by Kubota et al.[88] using hydrogen peroxide and

Table 1: Available graft copolymers from Carboxymethyl Cellulose

S. No.	Graft Copolymer [1]	Author	Initiator [2]	Ref.
1.	CMC-g-ACM-co-DMAEMA	Zhang et al	APS/TMEDA	[22, 64]
2.	CMC-g- DADMAC	Zhang et al	$KMnO_4/H_2SO_4$	[65]
3.	CMC-g- DMOAAB-co-ACM	Zhang et al	APS	[66]
4.	CMC-g-PAA	Kubota et al	photo initiators	[67]
5.	CMC-g-PAA	Kuwabara, Kubota	Photografting	[68]
6.	CMC-g-PAAs	El-Sherbiny et al	APS	[69]
7.	CMC-g-PAA	Mishra,et al	Microwave initiated	[70]
8.	CMC-g-MA and CMC-g-EA	Okieimen, Ogbeifun	CAN	[71]
9.	CMC-g-EMA	Okieimen, Ogbeifun	CAN	[71]
10.	CMC-g-PACM	Yang et al	sodium sulfite/APS	[72]
11.	CMC-g-PACM	El-Hady, Ibrahim	sodium bisulfate/APS	[73]
12.	CMC-g-PACM	Kumar et al	$Fe^{+2}/KBrO_3$	[74]
13.	CMC-g-PACM	Wunderlich et al	CAN	[75]
14.	CMC-g-PACM	Biswal, Singh	CAN	[76]
15.	CMC-g-PACM	Okieimen	CAN	[77]
16.	CMC-g-PACM	Deshmukh et al	CAN	[78]
17.	CMC-g-PACM	Tripathy	CAN	[79]
18.	CMC-g-Poly(AA-co-ACM)	Suo et al	PMS/ sodium metabisulfite	[80]
19.	CMC-g-PACM	Ibrahim et al	KPS/Sodium metabisulfite	[81]
20.	CMC-g-NVP	Flefel et al	PMS/sodium metabisulfite	[82]
21.	CMC-g-PAN	Pourjavadi et al	CAN	[83]
22.	CMC-g-PMMA	Castellano et al	CAN	[84]
23.	CMC-g-PNaA	Wang, Wang	APS	[85]
24.	CMC-g-PNIPAM	Vasile et al	EDC	[86]
25.	CMC-g-PNIPAM	Bokias et al	APS/AET	[87]
26.	CMC-g-PNIPAM-AA	Kubota et al	H_2O_2/MSA	[88]
27.	CMC-g-PNVF	Tripathy et al	PMS/TU	[89]
28.	CMC-g-Poly (AAm-co-AMPS)	Pourjavadi et al	APS	[90]
29.	CMC-g-poly(N,N-DHACM)	Vidal et al	PMS	[91]
30.	CMC-g-PVSA	Sand et al	PDP/TU	[92]
31.	CMC-g-BMC	Sadeghi et al	CAN	[93]
32.	poly(NVP-co-AMPS)	Sadeghi et al	CAN	[95]
33.	CMC-g-PMMA	Han et al	potassium persulfate	[96]
34.	CMC-g-PAMPS	Behari, Pandey	H_2O_2/Fe^{+2}	[100]
35.	CMC-*g*-PVA	El-Zawawy, Waleed	BA	[103]

[1]CMC-g-ACM-co-DMAEMA (i.e. CMC -g-acrylamide-co-2(Dimethylamino)ethyl methacrylate); CMC-g-DADMAC (i.e. CMC-g-diallyldimethylammonium chloride); CMC-g-PAMPS (i.e. Carboxymethylcellulose -g-polyacrylamido-2-methylpropanesulfonic acid); CMC -g-EMA (i.e. Carboxymethylcellulose -g-polyethylmethacrylate); CMC -g-EA(i.e. Carboxymethylcellulose-g- polyethylacrylate); CMC -g-PMMA (i.e. Carboxymethylcellulose -g-polymethylmethacrylate); CMC-g-AAs (i.e. Carboxymethylcellulose -g-polyacrylic acids); CMC -g-ACM (i.e. Carboxymethylcellulose -g-polyacrylamide); CMC-g-DMOAAB-co-ACM (i.e. Carboxymethylcellulose -g-polyethylmethacrylate); CMC -g-Poly(AAm-co-AMPS) (i.e. Carboxymethylcellulose -g- polyacrylamide-co-acrylamido-2-methylpropanesulfonic acid); CMC -g-Poly (N,N-DHACM) (i.e. Carboxymethylcellulose -g-poly(N,N-dihexylacrylamide); CMC -g-NVP (i.e. Carboxymethylcellulose -g-poly(N-Vinylpyrrolidone); CMC -g-MA (i.e. Ca Lrboxymethylcellulose-g-polymethacrylate); CMC -g-PNaA (i.e. Carboxymethylcellulose-g-polysodiumacrylate); CMC -g-AA(i.e. Carboxymethylcellulose -g-polyacrylic acid); CMC -g-PVSA(i.e. Carboxymethylcellulose -g-poly (N -vinylsulfonicacid); CMC -g-PAA(i.e. Carboxymethylcellulose -g-polyacrylic acid); CMC -g-PVA(i.e. Carboxymethylcellulose -g-polyvinylalcohol); CMC -g-PNVF(i.e. Carboxymethylcellulose -g-poly (N-vinylformamide); CMC -g-(AA-co-ACM) (i.e. Carboxymethylcellulose -g-polycrylic acid -co-acrylamide); CMC -g-PNIPAM -co-AA(i.e. Carboxymethylcellulose -g- poly(N-isopropylacrylamide)-co-acrylate); CMC -g-PAN(i.e. Carboxymethylcellulose-g-polyacetonitrile); CMC-g-BMC (i.e. Carboxymethylcellulose -g- poly(Butylmethacrylate); CMC-g-PNIPAM (i.e. Carboxymethylcellulose -g-poly(N-isopropylacrylamide)); CMC -g-PACM (i.e. Carboxymethylcellulose -g-polyacrylamide).

[2]Ammonium persulfate (APS); potassium persulfate or potassium peroxymonosulphate (PMS)/ sodium metabisulfite; Ammonium persulfate (APS); Ceric Ammonium Nitrate (CAN); N,N,N',N'-tetramethylethylene diamine (TMEDA); sodium sulfite; sodium bisulfate; ferrous sulfate (Fe^{+2}); potassium bromate (KBrO$_3$); hydrogen peroxide (H$_2$O$_2$); 1 -3-(3-dimethylaminopropyl)-3ethylcarbodiimide hydrochloride (EDC);2 -aminoethanethiol hydrochloride (AET); methanesulfonic acid (MSA), Thiourea (TU); Boric acid (BA); Potassium peroxydiphosphate (PDP).

methanesulfonic acid.

Tripathy et al.[89] reported the graft copolymerization of N-vinylformamide onto sodium CMC by free radical polymerization using potassium peroxymonosulfate/thiourea redox system in an inert atmosphere. Pourjavadi et al.[90] have developed a series of biopolymer-based superabsorbent hydrogels based on CMC free-radical graft copolymerization of acrylamide and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) in aqueous solution using methylenebisacrylamide as a crosslinking agent and ammonium persulfate as an initiator. Vidal et al.[91] studied the intra and/or intermolecular associations of CMC-g-poly(N,N-dihexylacrylamide) copolymers in aqueous systems. Sand et al.[92] presented graft copolymerization of vinyl sulfonic acid onto sodium CMC by free radical polymerization using potassium peroxydiphosphate/thiourea redox system in an inert atmosphere.

Sadeghi et al.[93,94] applied this initiation technique for Graft copolymerization of Butyl methacrylate (BMC) and Acrylic acid (AA) onto CMC under argon atmosphere in a homogeneous aqueous medium by using ceric ammonium nitrate (CAN) as an initiator. They developed a novel superabsorbent hydrogel and developed novel biopolymer-based superabsorbent hydrogels[95] by grafting and crosslinking of poly(NVP-co-AMPS) chains onto CMC backbones through a free radical polymerization method. Han et al.[96] synthesized CMC-g-PMMA using potassium persulfate. This graft copolymer has finds an effective additive, for reinforcing the rice-hull-cement composite. It can reinforce the rice-hull-cement composite and expands the application of the composite in building industries. Kulkarni et al.[97] synthesized novel pH-sensitive interpenetrating network hydrogel beads of polyacrylamide-grafted-xanthan (PACM-g-XG) and sodium CMC loaded with ketoprofen were prepared and evaluated for pH sensitivity and drug release characteristics. Bumbu et al.[98] has been studied the dilute aqueous solution behavior of the grafted CMC-g-PNIPAM copolymers as a function of their components, temperature and pH. Li et al.[99] synthesized two kinds of super absorbent resins from CMC with potassium persulfate and methylene bisacrylamide as initiator and crosslinker respectively, by radical polymerization in aqueous solution. They found that absorption capacities of CMC-g-PAA are better in the water-keep capability being heated, while CMC-g-PAA-co-PVP is better in the water absorbency and salt resistance.

Graft copolymer of 2-acrylamido-2-methyl-1-propanesulfonic acid[100] prepared using H$_2$O$_2$/Fe^{+2} redox pair and graft copolymer of N-vinyl-2-pyrrolidone (NVP)[101] with sodium CMC was synthesized under nitrogen using the potassium peroxymonosulphate/thiourea redox pair and found good flocculation property for coal.

Wang et al.[102] prepared a super absorbent material with the super absorbent resin (SAR) of the CMC grafting acrylic acid (CMC-AA) and inorganic gel. Conducting hydrogel copolymer by graft copolymerization of CMC and boric acid onto

poly(vinyl alcohol) (PVA) was prepared by El-Zawawy and Walled.[103] The dielectric properties of CMC-g-PVA/prehydrolyzed banana blend have been investigated. Lin et al.[104] subjected to a grafting reaction to introduce photoreactive epoxide groups onto the CMC chain. Glycidyl methacrylate (GMA) was grafted onto the sodium CMC using ceric ammonium nitrate (CAN) as initiator in a homogeneous reaction system and induced cationic photoinitiators and UV light for further reaction. Zohuriaan-Mehr et al.[105] modified CMC sodium salt (CMC) to prepare a novel poly(acrylamidoxime) chelating resin.

Extraction of homopolymers from Graft copolymers

The small amount of the homopolymers present in the graft copolymers can be separated. To remove homopolymer and unreacted Carboxymethylcellulose by using alternate extractions with benzene and 1:1 methylene chloride-methanol mixture can be done. Sometimes, it is not successful; therefore, a fractional precipitation method or solvent extraction method may also be adopted. The graft copolymer was dissolved in a methylene chloride-methanol mixture (80:20). Methanol was very slowly added to the solution to precipitate homopolymer and true graft copolymer. Dissolution in the methylene chloride-methanol mixture and precipitation with methanol were repeated four times. The final solution contained 45-46% methanol or extracted by solvent extraction method using a mixture of formamide and acetic acid (1:1 by volume). The above precipitate was extracted with boiling benzene to remove homopolymers and finally true graft copolymer was isolated.

Determination of grafting parameters in Graft Copolymerization reaction

Different parameters such as percentage of grafting or grafting ratio (%G), percentage grafting efficiency (%E), percentage addon (%A), percentage conversion (%C) and percentage homopolymer (%H) are usually determined as functions of different variables that influence graft copolymerization, according to Fanta's definition.[106]

$$\text{Grafting ratio (\%G)} = \frac{\text{Grafted polymer}}{\text{Weight of substrate}} \times 100$$

$$\text{Grafting Efficiency (\%E)} = \frac{\text{Grafted polymer}}{\text{Polymer formed}} \times 100$$

$$\text{Add on (\%A)} = \frac{\text{Synthetic polymer}}{\text{Grafted copolymer}} \times 100$$

$$\text{Conversion (\%C)} = \frac{\text{Polymer formed}}{\text{Monomer charged}} \times 100$$

$$\text{Homopolymer (\%H)} = (100 - \% \text{ Grafting efficiency})$$

$$\text{Rate of polymerization (Rp) (mol.s}^{-1}.\text{m}^{-3}) = \frac{\text{Weight of total polymer formed}}{\text{Molecular weight of monomer} \times [\text{Reaction time (s)}] \times \text{volume (m}^3)}$$

$$\text{Rate of graft copolymerization (Rg) (mol.s}^{-1}.\text{m}^{-3}) = \frac{\text{Weight of grafted copolymer}}{\text{Molecular weight of monomer} \times [\text{Reaction time (s)}] \times \text{volume (m}^3)}$$

These parameters give the quantitative measurement of the grafting reactions.

Mechanism of Graft Copolymerization

The general mechanism is presented in scheme-1. It is found that the reaction containing sodium Carboxymethylcellulose (CMC), vinyl monomer, redox pair, oxidant reacted with reductant to give a primary free radical (**Scheme 1**) in the case of "grafting from" approach. This radical abstracts hydrogen atom from the CMC molecule to produce sodium Carboxymethylcellulose macroradicals. The monomer radicals, which were in close proximity to the reaction sites, became acceptors of the sodium Carboxymethylcellulose radicals; this resulted in chain initiation. Thereafter, they became free-radical donors to neighboring molecules. In this way, the grafted chain propagated in "grafting from" approach. These grafted chains terminated by coupling to give the graft copolymers, as shown in **Scheme 1**.

FTIR Studies

From the FTIR spectrum of CMC (**Fig. 5**), it has been observed that a small peak at 3126-3606 cm^{-1} is due to stretching vibration due to O-H. The peak due to C-H stretching vibrations observed around 2900 cm^{-1}. The band at 1061 cm^{-1} is attributed to the COC stretching vibrations. After grafting with vinyl monomers (**Fig. 5**), stretching vibration due to O-H is absent; this might be the grafting site. In many cases where thermal grafting was carried out, the C-C bond cleavage has been observed, but in microwave condition, the more polar 'OH' bond excites, leading to its cleavage resulting in the free radical site for grafting. The peak around 1700 cm^{-1} is due to C=O stretching vibration. The peak around1600 cm^{-1} is due to asymmetrical stretching vibrations of COO− groups. Smaller peaks around 1400 cm^{-1} and 1300 cm^{-1} are assigned to symmetrical stretching vibrations of COO− groups.[72] The
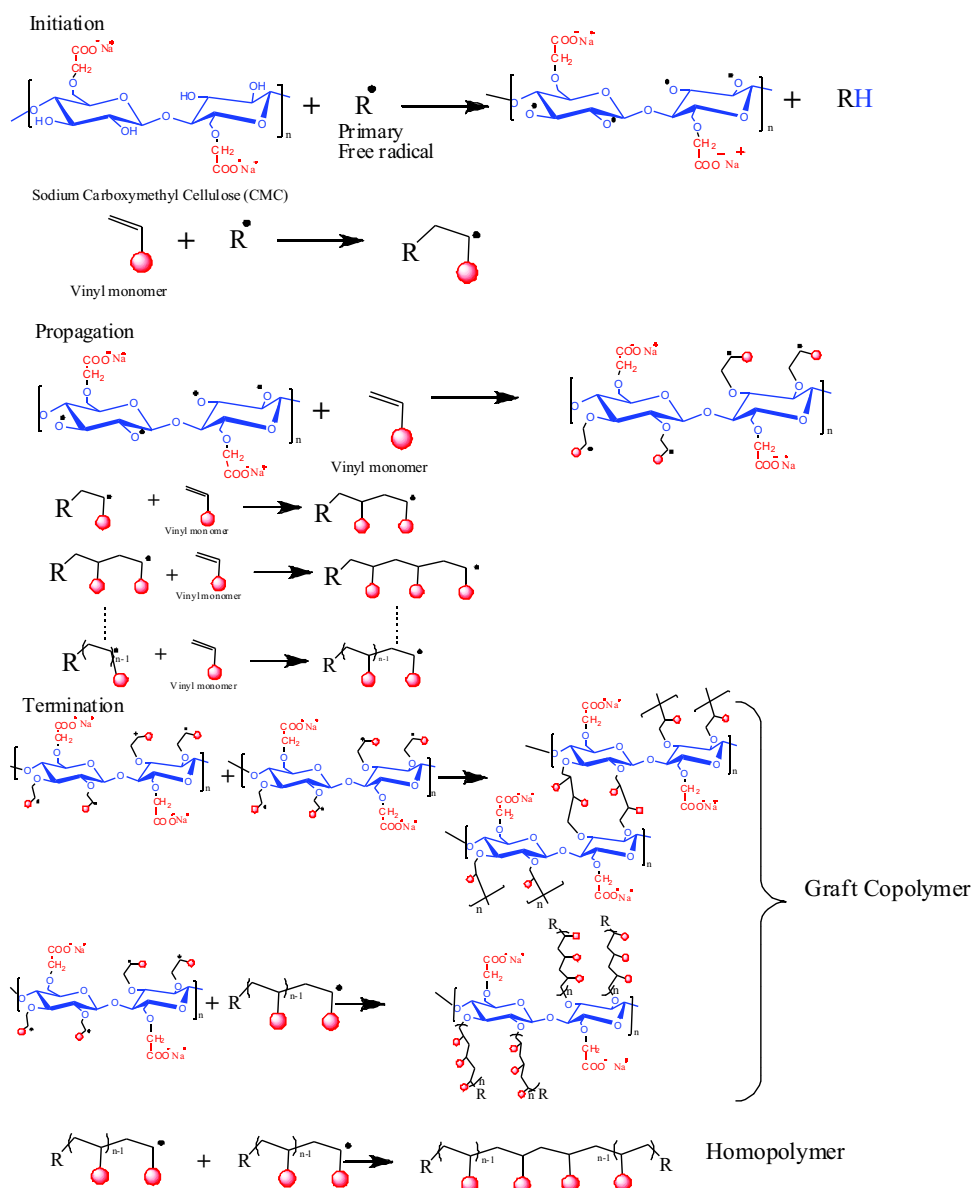
Scheme 1. Schematic Mechanism of Conventional free radical graft copolymerization of Sodium Carboxymethylcellulose (CMC)

polysodiumacrylate (PNaA) grafted CMC in place of polyacrylic acid (PAA), the characteristic absorption bands of CMC at 1061, 1115 and 1159 cm^{-1} (stretching vibrations of COH) were obviously weakened after reaction. The new bands around 1700cm^{-1} (C=O stretching of COOH) and 1580cm^{-1} (asymmetric stretching of COOgroups) and at 1450 and 1400 cm^{-1} (symmetric stretching of COO− groups) appeared in the spectra of CMC-gPNaA (**Fig. 5**). The position of these bands is close to that of PNaA, which revealed that PNaA was grafted onto CMC backbone. The asymmetric stretching vibration of COONa groups on CMC at 1600 cm^{-1} can be observed, which overlapped with the characteristic absorption of COOgroups of grafted PNaA chains and formed a broad band.[77] Whereas in the case of IR spectrum of CMCg-PAM,
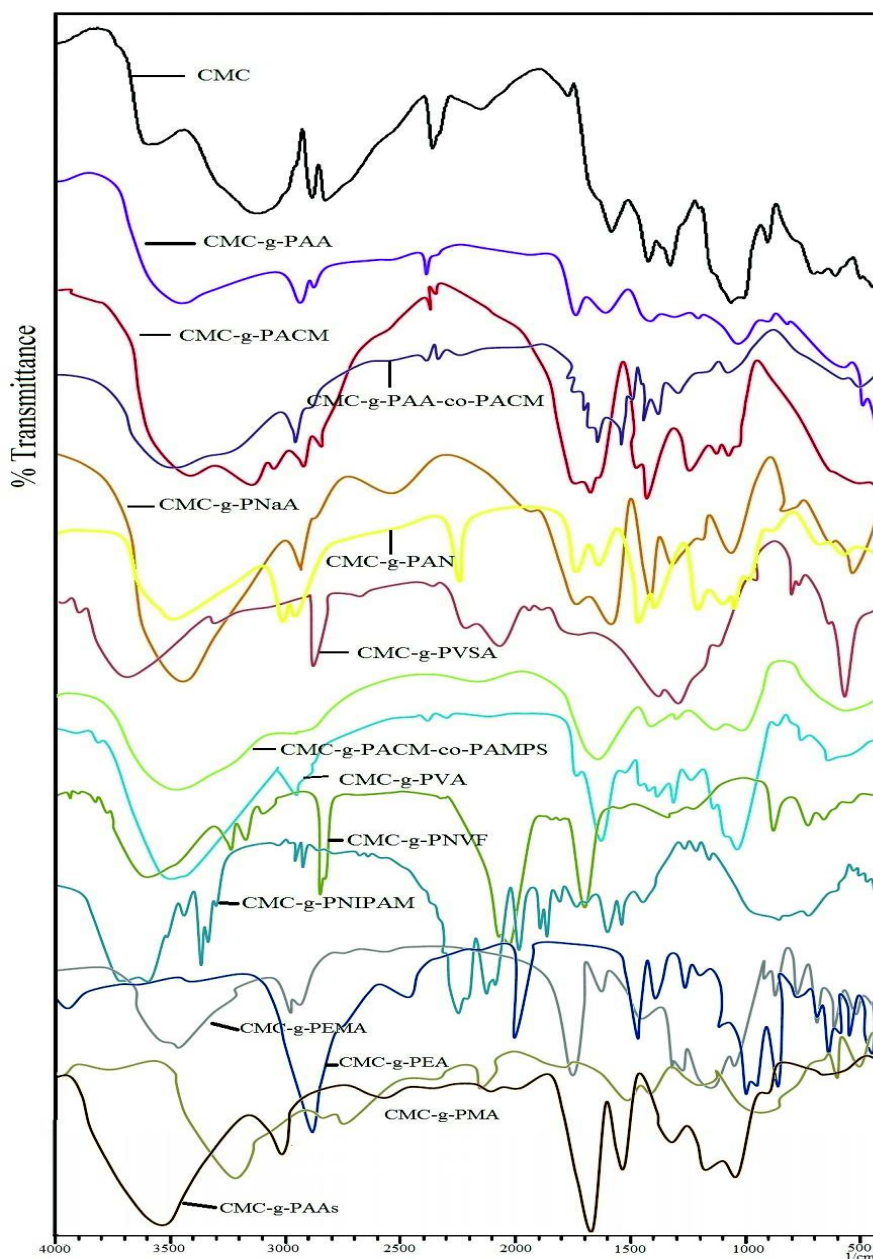
Figure 5. FTIR spectra of different graft copolymers of CMC by vinyl monomers.

additional peaks around 3160 and 3050 cm^{-1} for amide, around 1650 cm^{-1} for C-O, around 1400 cm^{-1} for C-N, and around 1220 cm^{-1} for COO- can be seen. The peak around 3450 cm^{-1} in the CMC-g-PAM copolymer is the overlap of hydroxyl group of CMC and amine group of PAM. The peak around 1630 cm^{-1} in the CMC-g-PAM is the overlap resulting from the carboxyl group 1600 cm^{-1} of CMC and amide group (1630 cm^{-1}) of PAM, which could be seen in Figure 6, respectively. There are a set of similar peaks around 1070 cm^{-1} in **Fig. 6**, which is the $CHOCH_2$ group resulting from grafting reaction between the hydroxyl group located in anhydroglucose C2 position and the band of PAM. The characteristics of polysaccharide backbone of carboxymethyl cellulose totally changed when vinylsulfonic acid is grafted onto it. The characteristic absorption band of SO_2O stretching vibration around 1200 cm^{-1} confirmed the graft copolymerization of vinylsulfonic acid onto CMC. While in place of polyacrylic acid or polysodiumacrylate, the grafting of other acids derivatives such as methyl acrylate, ethyl acrylate and ethyl methacrylate, additional absorption bands appeared at 2300 and 1600 cm^{-1} due to poly(methyl acrylate), at 3000 and 1650 due to the spectrum of poly(ethyl acrylate), and around 3000, 2900 and 1650cm^{-1} which belong to the spectrum of poly(ethyl methacrylate). Whereas, when the combination of two monomers, acrylamide (ACM) with acrylic acid (AA) were grafted together as co-monomer, the band observed in the IR spectrum of CMC-g-poly(AA-co-ACM) around 1700 cm^{-1} is attributed to the carbonyl stretching of the carboxylic acid groups. The peak around 1650 cm^{-1} is assigned to the characteristic absorption bands of the carboxamide-functional groups of the amide moiety of the ACM unit.[107-108] The very intense characteristic band around 1550 cm^{-1} is due to the C=O asymmetric stretching in the carboxylate anion that is reconfirmed by another sharp peak around 1406 cm^{-1}, which is related to the symmetric stretching mode of the carboxylate anion.[109-110] In addition, peaks around 1458 and 1179 cm^{-1} corresponding to the CO-O- and OH coupling interactions of the carboxylic group and C-N stretching vibrations can also be observed.[111] The peak around 1100 cm^{-1}, ascribed to the C-O-C stretching interactions, can also be observed. While, when the combination of acrylamide (ACM) was taken with acrylamido-2-methylpropane-1-sulfonic acid (AMPS), it carries carboxamide functional groups that are evidenced by a new characteristic absorption band around 1650cm^{-1} (**Fig. 5**). A new characteristic absorption band in the spectrum of the hydrogel at 1700 cm^{-1} may be attributed to the C=O stretching mode of amide groups and justifying the grafting of AAm and

AMPS onto CMC. The stretching band of -NH overlapped with the -OH stretching band of the CMC portion of the copolymer.

The IR spectra of CMC graft copolymer of PVA (**Fig. 5**) showed absorption bands around 3420, 2360, 1650, and 1120 cm^{-1}, characteristic of CMC,[112] and additional bands around 3000, 1000950 cm^{-1} (-COH stretch and out-of-plane), and 14301400 cm^{-1} (CH_2 stretch) that belong to the spectrum of PVA. Kolboe and Ellefsen[113] suggested that the bands in the 1630 cm^{-1} region of cellulose may be attributed to C-O stretching vibration of the carbonyl group. The bands from 1450 to 1320 cm^{-1} are associated with CH in the plane deformation of CH_2 groups. The bands in the region 12501056 cm^{-1} involve the C-O stretching vibrations of alcohols in cellulose. The peak around 897 cm^{-1} is due to glucosidic linkage,[114-116] while peaks around 666 -610 cm^{-1} are due to out-of-plane bending vibration of intermolecular H-bonded O-H group.[114117]

The spectrum of the original CMC-g-PAN, a sharp absorption peak shown around 2220 cm^{-1} is attributed to stretching of -CN groups. After alkaline hydrolysis, the absorption modes around 1720 and 1690 cm^{-1} can be attributed to carbonyl stretching of COO-Na+ and $CONH_2$ groups, respectively (**Fig. 5**), that is reconfirmed by a broad bond around 24003600 cm^{-1} due to absorption of the N-H stretching of carboxamide group. Moreover, sharp band of -CN groups completely disappeared after hydrolysis.

The IR spectrum of sodium carboxymethyl cellulose-g-N-vinylformamide (**Fig. 5**) confirmed grafting by characteristic absorption band around 3650 cm^{-1} due to appearance of NH stretching vibration (Amide II) of pendant chain of N-vinylformamide molecule results from the interaction between NH bending vibration and CN stretching vibration, respectively. A band around 1109 cm^{-1} is due to CN stretching vibration of secondary amide present in pendant chain attached to sodium carboxymethylcellulose.

The FTIR spectra of graft copolymer of CMC with acrylamide and DMAOAB, C-O manifest the peaks of CMC (cycloether,1060 cm^{-1}; -COO-, 1590 cm^{-1}, and 1410 cm^{-1}), AM (3200 cm^{-1}, 1650 cm^{-1}, 1330cm^{-1}), and DMAOAB [-$(CH_2)_nCH_n$- 4720cm^{-1}; -COO- 1180 cm^{-1}, weak peaks], confirming that CAO consists of the components of CMC, AM, and DMOAAB. In the IR spectra of the graft copolymers carboxymethyl cellulose-g-poly(N-isopropylacrylamide) one can observe almost all the characteristic bands of both partners CMC (COO- around 1600, 1430 cm^{-1}, acid groups 900, 1280 cm^{-1}, ether groups 1080, 1120 cm^{-1} and OH groups: 1430, 1340 cm^{-1}) and PNIPAM (mono substituted amide group at 1650, 1550, 1470, 1280 cm^{-1},

primary amine moieties at 1180, 1140, 1070 cm^{-1}and isopropyl group at 2950, 1395, 1375, 1340, 1180, 1140 cm^{-1}), with the exception of the characteristic bands of primary amine from PNIPAM spectra, that vanished (bands 1180, 1140, decrease drastically). This indicates that the grafting reaction took place. The IR spectra of the two graft copolymers do not present significant differences in the shape being only slowly dependent on the content of the grafted polymer. This could be an indication that there are no physical interactions between the two partners of the copolymer. The main characteristic bands of both components PNIPAM and PAA: COO- around 1600, 1430 cm^{-1}, of COOH groups at 900 and 1280 cm^{-1}, of OH around 1430, 1340, 1170 cm^{-1} and of the ether groups at 1080, 1120 cm^{-1}.

Thermal analysis

The rate of weight loss of CMC[118] (**Fig. 6**) increases with increase in temperature from 200°C, attains a maximum at 286 °C, thereafter, decreases and attains a constant value. About 60% of CMC has been degraded around 388 °C, therefore, the final decomposition temperature was not much high i.e. at 444°C. The polymer decomposition temperature has been found as 250°C and temperature at which maximum degradation occurs *i.e.* T$_{max}$ has been found at 287 °C. This T$_{max}$ might be occurred due to the loss of pendent carboxymethyl group from CMC. Integral procedural decomposition temperature of CMC has been found to be 237°C and about 21% char yield occurs at 1000°C.

The rate of weight loss of carboxymethyl cellulose-g-vinyl sulfonic acid (**Fig. 6**) increases with increase in temperature from 100°C to 180°C. First T$_{max}$ at 263°C might be due to elimination of CO$_2$ molecule from the polymeric backbone, Second T$_{max}$ at 324°C might be due to elimination of OCH$_3$ group from pendent chain attached of the polymeric backbone. The third T$_{max}$ 768°C at might be due to elimination of SO$_2$ molecule from pendent chain attached to the polymeric backbone, which is also confirmed by the exothermic peak present in DTA curve of graft copolymer at 775°C. The fourth T$_{max}$ 1088°C at might be due to elimination of OH group from pendent chain attached to the polymeric backbone.
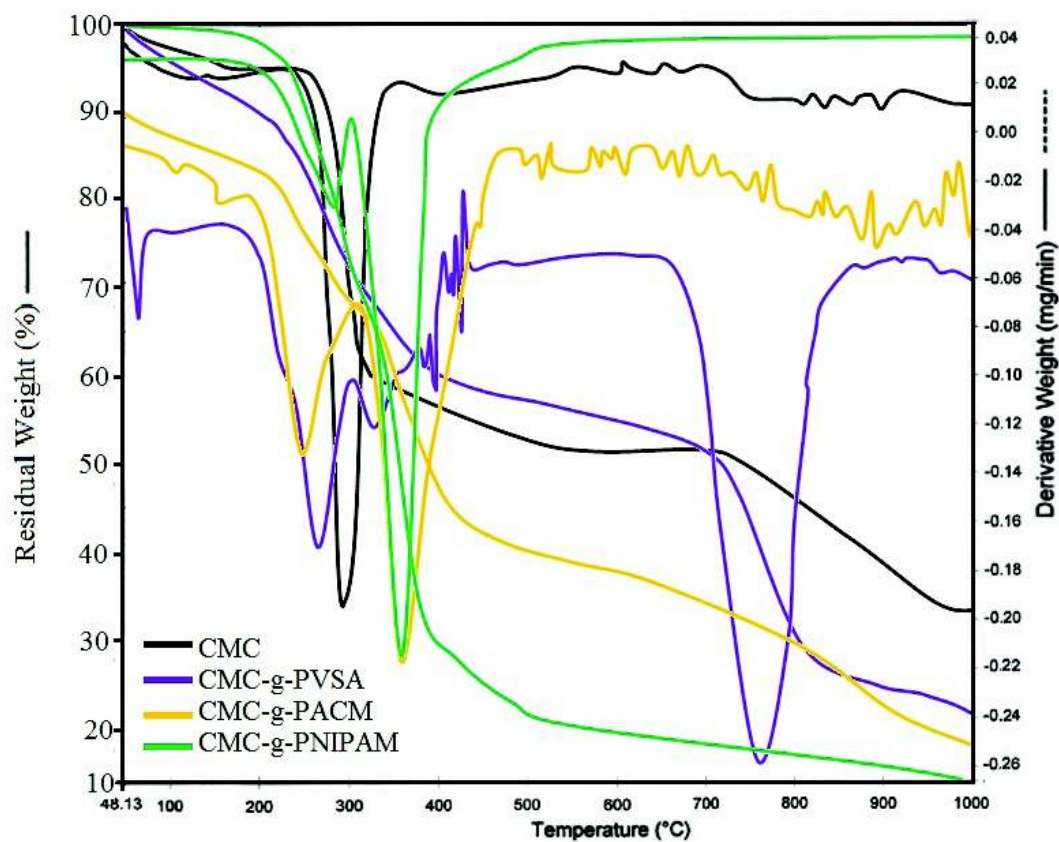
Figure 6. Thermogravimetric analysis of CMC and their graft copolymers.

The final decomposition temperature and integral decomposition temperature have been found to be around 1131°C and 361°C, respectively. The high value of Polymer decomposition temperature, final decomposition temperature, integral procedural decomposition temperature and three steps degradation indicate that graft copolymer is more stable than parent polymer backbone.

In the case of CMC-g-PAM (**Fig. 6**), the degradation of the polymer occurs in two stages. The first stage referring mainly to degradation of the CMC main chain in the 240260°C temperature range, with a mass loss of 12%. The second stage occurs in the 260450°C temperature range with a mass loss of 46% which is due to the decomposition of the PAM side chains. The thermal degradation of the grafted copolymer CMC-g-PNIPAM occurs in two stages. The first TG stage referring mainly to degradation of the CMC main chain takes place in the 150330°C (maxim at 290°C) temperature range, with a mass loss of 28 %. The second TG stage occurred in the 340450°C (maxima at 360°C) temperature range with a mass loss of 35% which could

be ascribed to the decomposition of the PNIPAM side chains.

In the case of the graft copolymers of CMC-g-PNIPAM, the first DTG peak is shifted to a higher temperature than that of CMC, while the second DTG peak is shifted to a lower temperature with respect to the corresponding peak of PNIPAM; these changes indicate an influence of the decomposition of one of the components on the decomposition of the other one. Therefore, the graft copolymers are more thermally unstable than the homopolymers. The TG/DTG curves of the physical mixtures are completely different to that of the components; this indicates interactions between components that could lead to a new structure. Physical mixtures are more instable than the components and the corresponding graft copolymers; their TG/ DTG curves are shifted to lower temperatures (**Fig. 6**).

Viscosity potential of carboxymethylcellulose

Viscosity is often taken as a common denominator and performance Index in comparing different grades of carboxymethyl cellulose.
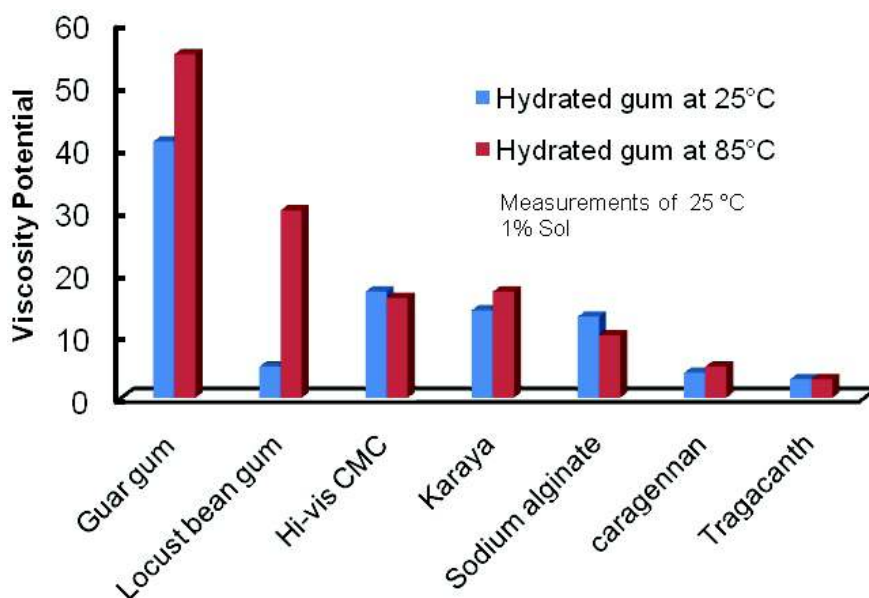
Figure 7. Viscosity potential of some water soluble gums.

There are five variables that determine the pattern of viscosity development and the behavior of a given of Carboxymethylcellulose grade in an aqueous system, *viz*. concentration, dispersion, temperature, pH, and presence of foreign substances. Understanding their implications is of great help in formulating with of Carboxymethylcellulose or processing (**Fig. 7**).

Biodegradation Studies

Relative viscosity is a value derived from timing the efflux of a fixed amount of hydraulic fluid as it moves through a standard-sized oral cavity at a fixed temperature. Relative viscosity $\eta_{rel} = (\eta/\eta_0)$ was obtained from efflux time of polymer solution (t) and that of

solvent 1.0M NaNO$_3$ (t$_0$). CMC (DS 0.7-0.85), CMC with hexyl ethyl cellulose (DS 2.5) (CMC/HEC=3:1), and all their grafted copolymers were tested for their biodegradability. Solutions, 0.6%, were prepared in single-distilled water, and the viscosity measurements were performed using an Ostwald Viscometer (Figure 9). It has been observed that relative viscosity of CMC-g-vinyl sulfonic acid is lower than sodium CMC (Figure 8) where as relative viscosity of CMC-g-N-vinyl pyrrolidone and CMC-g-polyacrylamide is found lower than mixture of CMC and hexyl ethyl cellulose. This might be due to the incorporation of copolymers into the polysaccharides which make the molecule more

flexible and reduce the viscosity drastically and change in the structure due to grafting.[110] CMC like other polysaccharide solutions, is highly prone to biodegradation, and it was found that its solution after 3days of its preparation starts degrading and during 10 days the solution showed considerable loss of viscosity (figure 9). These results show that the CMC is less susceptible than the mixture of sodium CMC with hexylethylcellulose (CMC+HEC). The graft copolymer of vinyl sulfonic acid (CMC-g-PVSA) is less susceptible to biodegradation and results have also been reported.[111]
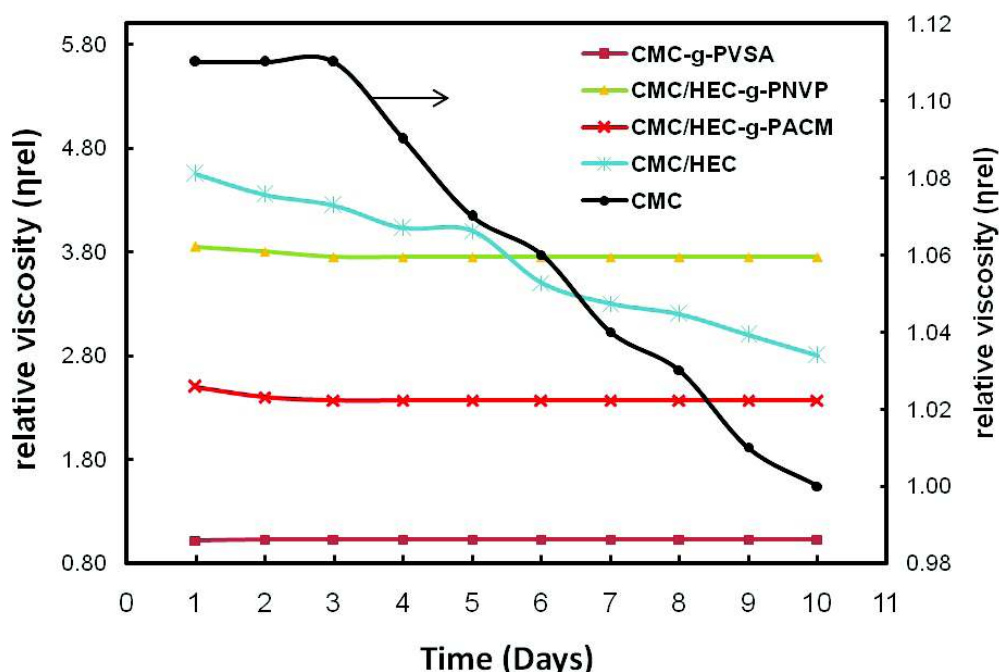
Figure 8. Relative viscosity *vs*. time period to study biodegradation of sodium Carboxymethylcellulose and their water soluble graft copolymers

This shows that by incorporation of poly (vinyl sulfonic acid) chains in graft copolymer CMC becomes less susceptible to bacterial attack.[119] The graft copolymer of N-vinyl pyrrolidone (CMC-g-PNVP) and graft copolymer of polyacrylamide (CMC-g-PACM) with the mixture of CMC and hexylethylcellulose were also found less susceptible to biodegradation i.e. less susceptible to bacterial attack. Moreover, the graft copolymers (CMC-g-PVSA, CMC/HEC-g-PNVP and CMC/HEC-g-PACM) were found more active against fungi, which caused diseases to the plants, rather than bacteria and yeast. Thus, the grafting of NVP and ACM

onto CMC/HEC resulted in systems that are less susceptibility to biodegradation.

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