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Carbohydrate Polymers 57 (2004) 379–387

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Characterisation of carboxymethyl cellulose and polyacrylamide graft copolymer

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Received 1 September 2003; revised 7 April 2004; accepted 21 April 2004

Abstract

The synthesis of carboxymethyl cellulose-g-polyacrylamide was carried out by a ceric ion induced solution polymerization technique. By varying the amount of catalyst and monomer, six different grades of graft copolymers were synthesized. These graft copolymers were characterized by elemental analysis, infrared spectroscopy, rheological studies, scanning electron microscopy, thermal analysis, viscosity measurement and X-ray diffractometry. They exhibit distinguished flocculation characteristics in various suspensions and effluents. Their flocculation and viscosifying characteristics are drastically enhanced on their hydrolysis.

Keywords: Carboxymethyl cellulose; Graft copolymer; Flocculation; Polyacrylamide

1. Introduction

Carboxymethyl cellulose (CMC) is an important industrial polymer with a wide range of applications in flocculation, drag reduction, detergents, textiles, paper, foods, drugs, and oil well drilling operation. CMC is a derivative of cellulose and formed by its reaction with sodium hydroxide and chloroacetic acid. It has a number of sodium carboxymethyl groups (CH_2COONa), introduced into the cellulose molecule, which promote water solubility. The various properties of CMC depend upon three factors: molecular weight of the polymer, average number of carboxyl content per anhydroglucose unit, and the distribution of carboxyl substituents along the polymer chains (Baar & Kulicke, 1994; Kamide et al., 1985; Reuben & Conner, 1983). The most important properties of CMC are viscosity building and flocculation. Among all the polysaccharides, CMC is easily available and it is also very cheap. It has high shear stability. The structure of CMC is shown in Fig. 1.

Polymeric flocculants are progressively being used more and more due to their low dose, ease in handling, non-interference with pH of the suspensions and larger floc forming capability (Bratby, 1980). Among the two types of polymeric flocculants natural and synthetic; natural polymers are fairly shear stable, biodegradable and cause drag reduction and flocculation at relatively higher concentration. The synthetic polymers are much more effective than natural ones due to their versatile tailorability. However, they are not shear resistance. Several attempts have been made in the past to combine the best properties of both by grafting synthetic polymers onto natural ones (Singh, 1995; Swanson, Shogren, Fanta, & Imam, 1993). One of the great advantages thus obtained is the consequent reduced biodegradability because of the drastic change of the original structure of the natural polymer as well as the increased synthetic polymer content within the product.

Recently, a new class of flocculating agents based on graft copolymers (Nayak & Singh, 2001; Rath & Singh, 1997; Singh et al., 2000; Tripathy, Panday, Karmakar, Bhagat, & Singh, 1999) of natural polysaccharides and synthetic polymers such as polyacrylamide (PAM) has been reported. The graft copolymers have also been found to be reasonably shear stable (Ungeheur, Bewersdorff, & Singh, 1989) because of the attachment of flexible synthetic polymers onto the rigid polysaccharide backbones. The study of flocculation characteristics of the graft copolymers of polyacrylamide and various polysaccharides such as amylose, amylopectin (Rath & Singh), guar gum/hydroxylpropyl

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doi:10.1016/j.carbpol.2004.04.020

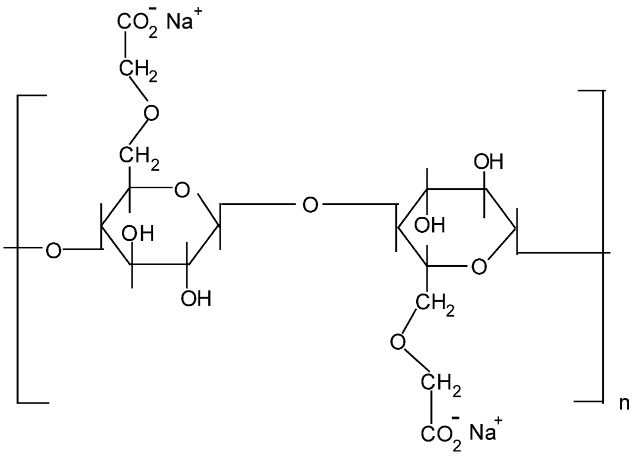

Fig. 1. Structure of CMC.

guar gum (Nayak & Singh), starch (Singh et al., 2000), sodium alginate (Tripathy et al.) has established that each of the graft copolymer is a better flocculating agent than PAM and the corresponding polysaccharides. It has been observed that the graft copolymers having fewer but longer PAM branches are fairly shear stable and exhibit better flocculation characteristics. Among all the graft copolymers, PAM grafted amylopectin exhibits the best performance than the others (Singh et al., 2000). This is due to the highly branched structure of amylopectin, the approachability to the colloidal particles increases, as per Singh's model (Singh, 1995; Singh & Karmakar et al., 2000; Singh & Tripathy et al., 2000).

The graft copolymers were synthesized by using ceric ammonium nitrate (CAN) as initiator. Ceric ion initiates free radical sites on the polysaccharide backbone (Hartley, 1959; Mino & Kaizerman, 1958; Mino, Kaizerman, & Rasmusen, 1959; Ogiwara, Ogiwara, & Kubota, 1968), and therefore minimize the formation of homopolymers. The graft copolymers of carboxymethyl cellulose and PAM were synthesized by using CAN (Singh, Tripathy, & Biswal, 2001). In this article, we report the characterization of grafted and ungrafted carboxymethyl cellulose by various techniques such as elemental analysis, infrared (IR) spectroscopy, rheological studies, scanning electron microscopy (SEM), viscometry and X-ray diffraction.

2. Experimental

2.1. Materials

CMC was procured from Supertex Ltd, Mumbai, India. Acrylamide was purchased from E. Merck, Germany. CAN was obtained from Loba Chemie, Bombay, India. Acetone and hydroquinone were supplied by S.D. Fine Chemicals, Bombay India. CMC was used after purification by soxhlet extraction for 60 h using ethyl alcohol, as suggested by Whitcomb and Macoskow (1978). All other chemicals were used as supplied by the companies.

2.2. Synthesis of graft copolymers

The graft copolymers of CMC and PAM were synthesized by ceric ion induced solution polymerization techniques (CMC-g-PAM 1 to CMC-g-PAM 6). The details of the synthetic procedure are given elsewhere (Singh et al., 2001). The synthetic details of the parameters of the graft copolymers are summarized in Table 1.

2.3. Extraction of homopolymers

The small amount of the homopolymer present in the graft copolymers was extracted by solvent extraction method using a mixture of formamide and acetic acid (1:1 by volume) (Fanta, 1973).

3. Characterisation

The synthesized graft copolymers, CMC and PAM were characterized by elemental analysis, IR spectroscopy, rheological studies, SEM, thermal analysis, viscometry, and X-ray diffractometry (XRD).

3.1. Elemental analysis

The elemental analysis of CMC and all the graft copolymers (CMC-g-PAM 1 to CMC-g-PAM 6) was performed using a Carlo Erba 1108 Elemental Analyzer. The estimation of only three elements, that is, carbon,

Table 1
Synthetic details of graft copolymers

Sl no.	Polymer	Parameter 'X'	Parameter 'Y'	Intrinsic viscosity (dl/g)	$M_n \times 10^6$	$M_w \times 10^6$
I	CMC-g-PAM 1	1.046	0.1796	8.65	1.65	2.63
II	CMC-g-PAM 2	0.837	0.1832	8.23	1.53	2.47
III	CMC-g-PAM 3	0.698	0.1917	7.46	1.32	2.19
IV	CMC-g-PAM 4	1.246	0.2097	9.11	1.78	2.81
V	CMC-g-PAM 5	1.395	0.2314	10.15	2.10	3.22
VI	CMC-g-PAM 6	0.697	0.1263	7.12	1.23	2.06

Parameter 'X' = acrylamide (mole)/CAN (mole × 10^3). Parameter 'Y' = acrylamide (mole) × conversion efficiency. Conversion efficiency = (wt of graft copolymer − wt of polysaccharide)/wt of acrylamide.

Table 2
Elemental analysis results of CMC and graft copolymers

Polymer	Carbon%	Hydrogen%	Nitrogen%
CMC	29.30	4.44	0.12
CMC-g-PAM 1	41.66	7.04	14.77
CMC-g-PAM 2	42.55	6.79	14.90
CMC-g-PAM 3	41.44	7.00	14.46
CMC-g-PAM 4	41.71	6.66	14.87
CMC-g-PAM 5	42.60	6.84	15.16
CMC-g-PAM 6	42.47	6.73	14.48

hydrogen, and nitrogen was undertaken. The results are shown in Table 2.

3.2. Infrared spectroscopy

The IR spectra of CMC, PAM, and the graft copolymers (CMC-g-PAM 5) were recorded in solid state using KBr pellet. A Perkin–Elmer-630 IR spectrophotometer was used to record the spectra in the range of 4000–400 cm^{-1}.

3.3. Intrinsic and absolute viscosity

Viscosity measurements of the aqueous solutions of CMC and the graft copolymers (CMC-g-PAM 1 to CMC-g-PAM 6) were carried out with the help of Ubbelohde viscometer (CS/S: 0.003867) at 27 ± 0.1 °C as reported earlier (Nayak & Singh, 2001).

3.4. Rheological studies

The rheological measurements of aqueous solutions of CMC and the graft copolymer (CMC-g-PAM 5) were carried out in controlled stress AR-1000 Advanced Rheometer. For these measurements, a 2° cone of diameter 4 cm and with truncation of 46 μm was used. The temperature of the system was maintained at 30 °C throughout the experiment.

3.5. Scanning electron microscopy (SEM)

A CAM SCAN SERIES-2 (Cambridge Scanning Company, UK) was used. For this study CMC was used in the powder form, whereas PAM and all graft copolymers were in the form of small granules.

3.6. Thermogravimetric analysis

The thermal analysis of CMC, PAM and CMC-g-PAM 1 to CMC-g-PAM 6 was carried out with a Stanton Redcroft (STA 625) thermal analyzer. Both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of all the samples were performed up to a temperature of 600 °C, starting from room temperature in nitrogen atmosphere. A heating rate of 10°/min was maintained in all cases.

3.7. X-ray diffractometry (XRD)

Carboxymethyl cellulose, polyacrylamide and all the graft copolymers (CMC-g-PAM 1 to CMC-g-PAM 6) were subjected to XRD analysis. The powdered polymer sample was packed into a hole of 2 mm diameter in a small container made of perspex (poly(methyl methacrylate)) about 1.5 mm thick. A PW 1840 diffractometer and PW 1729 X-ray generator (Philips, Holland) were used for this study producing Cu K_α radiation. The scattering angle (2θ) was varied from 10 to 45°.

4. Results and discussion

4.1. Synthesis

Table 1 shows the synthesis details of the graft copolymers based on carboxymethyl cellulose and polyacrylamide The amount of acrylamide and CAN were varied in order to observe the effect with varying number and length of grafted PAM chains. Two series of graft copolymers, a total of six grades of graft copolymer (CMC-g-PAM 1 to CMC-g-PAM 6) were synthesized by grafting polyacrylamide onto the CMC backbones. In the first series (I–III), the amounts of CMC and acrylamide were kept constant, only the CAN concentration was changed. The ratio of acrylamide to CAN (parameter *'X'*) decreases from I to III. As the concentration of acrylamide was the same in this series, by increasing the CAN concentration the parameter *'Y'* (concentration of acrylamide × conversion efficiency) increases, because of the increase in conversion efficiency from I to III. In the second series (IV–VI), the amounts of CMC and CAN were kept constant whereas the amount of acrylamide was changed. As there is more acrylamide in V, the parameters *'X'* and *'Y'* is more in CMC-g-PAM 5. So, it has been observed that with increasing the acrylamide amount, the parameter *'Y'* increases. This is achieved by ceric ion induced redox polymerization technique. The mechanism of ceric ion initiation involves the formation of chelate complex that decomposes to generate free radical sites on the polysaccharide backbone. These active free radical sites in the presence of acrylic monomers generate graft copolymers. The average number of grafting sites per backbone molecule depends on the ratio of concentration of ceric ion to polysaccharide, CMC. A low concentration of catalyst should initiate a few grafting sites resulting in longer polyacrylamide chains as against a high concentration of catalyst that will initiate a larger number of grafting sites thus making the average polyacrylamide chains shorter for the same acrylamide concentration. This is reflected in the graft copolymers in the series.

4.2. Elemental analysis

The results of elemental analysis of CMC and all the graft copolymers are given in Table 2. CMC does not show any significant presence of nitrogen. However, the negligible amount of nitrogen may be because of the trace quantities of unisolated proteins in the polysaccharides. It has been found that there is a considerable percentage of nitrogen in the graft copolymers, which is accounted for the presence of grafted PAM chains. In the series of graft copolymers based on CMC, the variation in the nitrogen content, although not much, is significant in case of CMC-g-PAM 5. The higher percentage of nitrogen may be due to the increased PAM content in the graft copolymer, which is also due to the higher moles of acrylamide in the reaction feed. Among other graft copolymers CMC-g-PAM 6 has the smallest percentage of nitrogen, which has lowest polyacrylamide content compared to other graft copolymers in the series.

4.3. IR spectroscopy

The graft copolymer structure is confirmed by IR spectroscopy The IR spectra of CMC, PAM, and CMC-g-PAM 5 are shown in Figs. 2–4. From the IR spectra of CMC (Fig. 2), it is evident that it shows a broad absorption band at 3432 cm^{-1}, due to the stretching frequency of the –OH group. The band at 2909 cm^{-1} is due to C–H stretching vibration. The presence of a strong absorption band at 1603 cm^{-1} confirms the presence of COO^{-} group. The bands around 1423 and 1325 cm^{-1} are assigned to $-CH_2$ scissoring and –OH bending vibration, respectively. The band at 1061 cm^{-1} is due to $>CH-O-CH_2$ stretching.

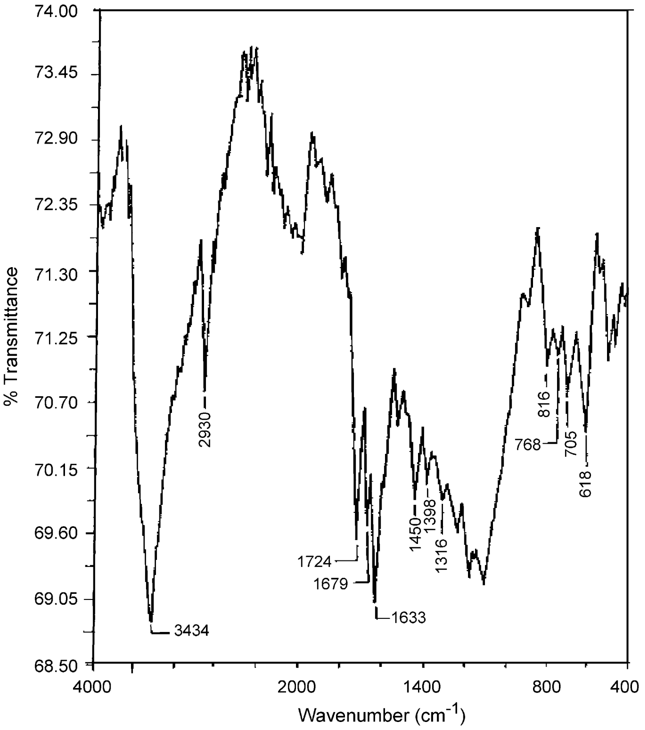

Fig. 3. IR spectra of PAM.

In the case of PAM (Fig. 3), a broad absorption band at 3434 cm^{-1} is for the N–H stretching frequency of

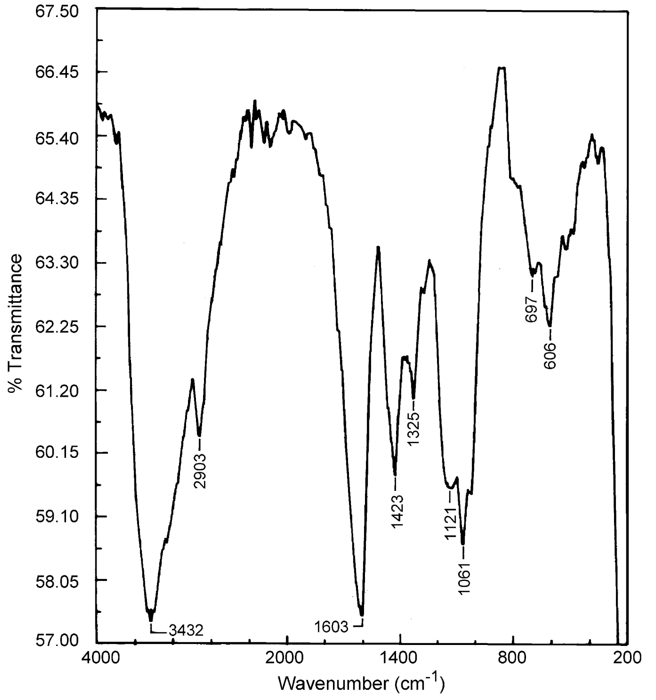

Fig. 2. IR spectra of CMC.

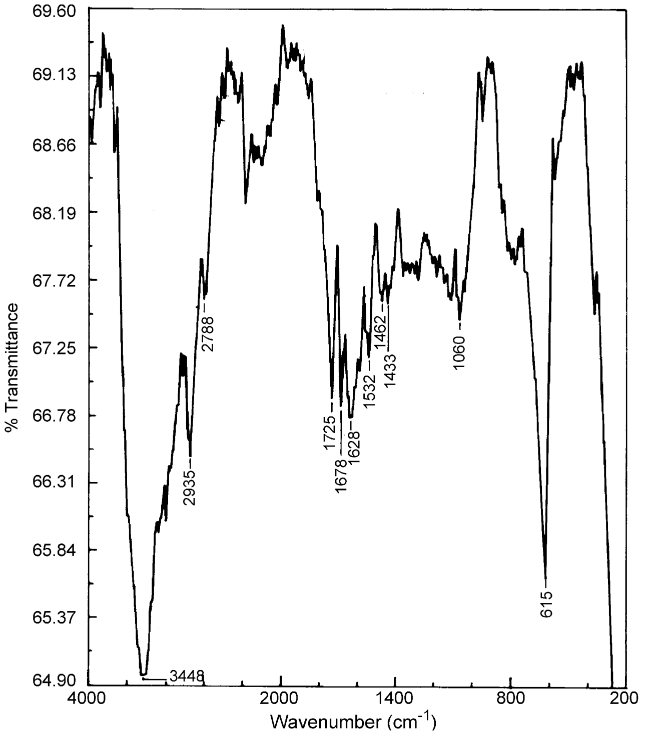

Fig. 4. IR spectra of CMC-g-PAM 5.

the NH_2 group. Two strong bands around 1679 and 1633 cm^{-1} are due to amide-I (C=O stretching) and amide-II (NH bending). Another band at 1724 cm^{-1} is due to the presence of free acid groups. The bands around 1398 and 2930 cm^{-1} are for the C–N and C–H stretching vibrations. Other bands at 1450 and 1318 cm^{-1} are attributed to CH_2 scissoring and CH_2 twisting. NH wagging vibrations occurring at 618, 705, 768 and 816 cm^{-1}, respectively.

Fig. 4 shows the IR spectrum of CMC-g-PAM 5. The presence of a broad absorption band at 3448 cm^{-1} is due to the overlap of –OH stretching band of CMC and –NH stretching band of PAM. A band at 1678 cm^{-1} is due to the amide-I band of the amide group of PAM. The band at 1603 $cm^{-1}$of CMC and amide-II band of PAM overlap with each other and lead to a broad band at 1628 cm^{-1}. The presence of a band at 1724 cm^{-1} is due to free acid groups. The above-mentioned bands of CMC-g-PAM 5 are also present in CMC and PAM, but at slightly different frequencies. As PAM was initially removed from the reaction products, the presence of the above bands in the graft copolymer gives strong evidence of grafting.

4.4. Intrinsic viscosity and absolute viscosity

Keeping the other factors constant, for two polymers of approximately similar molecular weight, a branched polymer will have lower hydrodynamic volume and hence a lower intrinsic viscosity as compared to its linear counterpart. For a series of branched polymers, the longer the branches, the higher will be the intrinsic viscosity and vice versa. This has been observed in practice. In the first series of graft copolymers (CMC-g-PAM 1 to CMC-g-PAM 3), the intrinsic viscosity values gradually decrease. The intrinsic viscosity value of CMC-g-PAM 5 is higher because of the presence of longer PAM chains. The acrylamide concentration of CMC-g-PAM 6 is lower than that of CMC-g-PAM 1, the intrinsic viscosity of the former is lower than that the latter. However, the intrinsic viscosity of CMC-g-PAM 3 was found to be higher than CMC-g-PAM 6, which indicates that CMC-g-PAM 3 contains longer PAM chains than CMC-g-PAM 6. The intrinsic viscosities of all graft copolymers are reported in Table 1. The intrinsic viscosity of CMC was found to be 6.7 dl/g, which is consistent with the value observed by Gómez-Díaz and Navaza (2002). Intrinsic viscosity plots of CMC and CMC-g-PAM 5 are shown in Fig. 5.

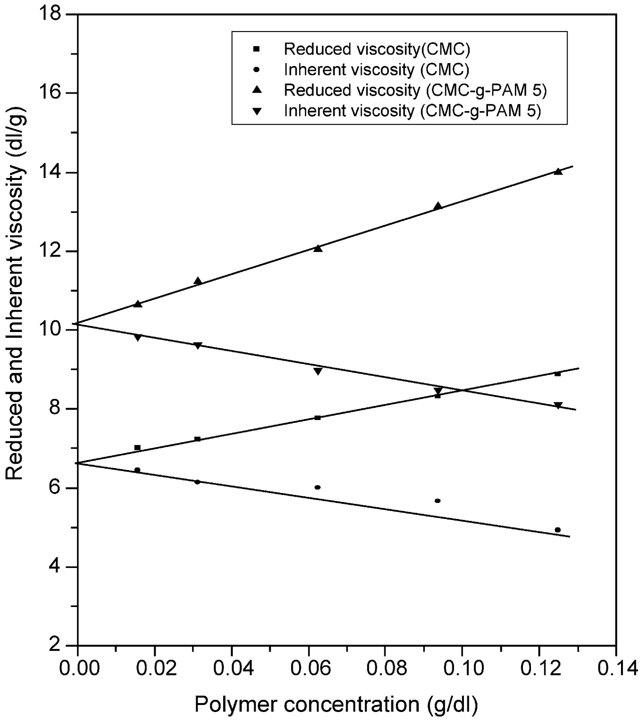

Fig. 5. Reduced/inherent viscosity versus concentration curves of CMC and CMC-g-PAM 5 for measurement of intrinsic viscosity.

4.5. Calculation of the approximate molecular weight

Molecular weight of the polymer samples can be estimated from the intrinsic viscosity $[\eta]$ values. The Mark–Houwink equation, $[\eta] = KM^{\alpha}$ is generally employed for the estimation of molecular weight of linear polymers, where K and α are constants for a given polymer/solvent/temperature system. For polyacrylamide the values of K and α are given below (Erciyes, Erim, Hazer, & Yagci, 1992).

$$[\eta] = 6.8 \times 10^{-4}\ (M_{\rm n})^{0.66} \qquad (1)$$

$$[\eta] = 6.31 \times 10^{-5}\ (M_{\rm w})^{0.80} \qquad (2)$$

Where $M_{\rm n}$ is the number-average molecular weight and $M_{\rm w}$ is the weight-average molecular weight.

Graft copolymers are synthesised by opening the monomer rings of polysaccharide backbone and grafting of polyacrylamide onto the free radicals generated. The opening imparts slight flexibility to the backbone. Moreover, the percentage of polysaccharide is small in comparison with the polyacrylamide. Hence, in case of the grafted polysaccharides, several workers (Erciyes et al., 1992; Tripathy, Karmakar, & Singh, 2000) have used the Mark–Houwink equation to estimate approximate molecular weight, which is applicable for linear polymers. The same has been done in the present case. The approximate molecular weights of the graft copolymers are given in Table 1.

4.6. Rheological studies

The rheological studies of aqueous solution of CMC and CMC-g-PAM 5 were carried out at the concentration of 0.5-wt%. We plotted the shear stress and shear rate on two axes in logarithmic scales. Similarly, plots of viscosity versus shear rate of the polymer solutions were drawn.

Fig. 6 shows the relationship between viscosity and shear rate γ. All the aqueous solutions of the polymers show

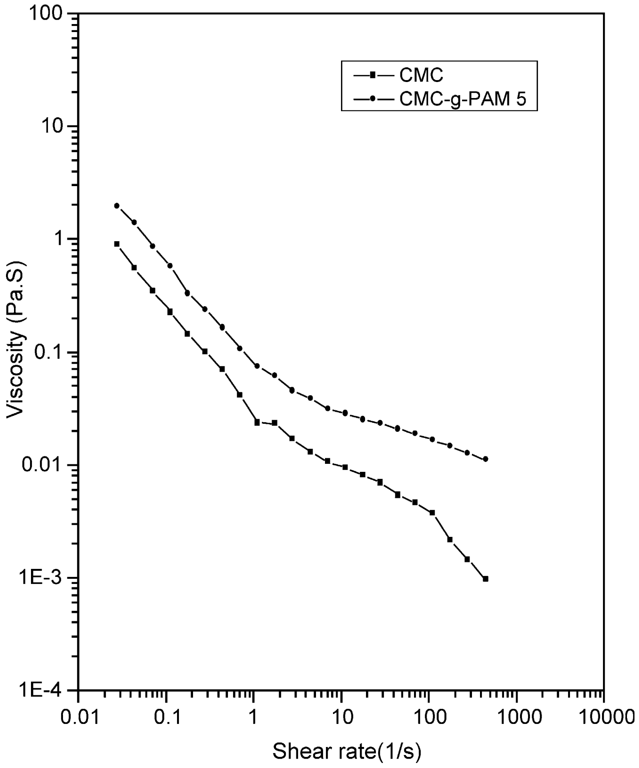

Fig. 6. Viscosity versus shear rate curves of CMC and CMC-g-PAM 5.

non-Newtonian behaviour. The viscosity of the polymer solutions decreases with increase in shear rate. Similar results are observed by Cheng, Takai and Ekong (1999); Gómez-Díaz and Navaza (2003). Both the aqueous solutions of CMC and CMC-g-PAM show strong pseudo-plastic behaviour. At low and high shear rate, the viscosity of the solutions of graft copolymer is found to be higher than that of CMC. The changes in viscosity are due to the presence of the grafted chains in the graft copolymer. This marked shear thinning behaviour of polysaccharide and the graft copolymer solution may be explained by the conformational states of polymer molecules. Domains of associated polysaccharide and the graft copolymer chains exist at rest or low shear, which are stabilized by hydrogen bonds. On shearing, the extent of aggregation is reduced resulting in a lower solution viscosity.

4.7. Scanning electron micrographs

Fig. 7 shows the scanning electron micrographs of CMC, PAM, and graft copolymers (CMC-g-PAM 6). Surface morphology of CMC before grafting shows a granular structure, which has been changed to fibrillar form after grafting. PAM morphology is also changed drastically when grafted onto CMC. Thus, comparison of these figures reveals that grafting has taken place.

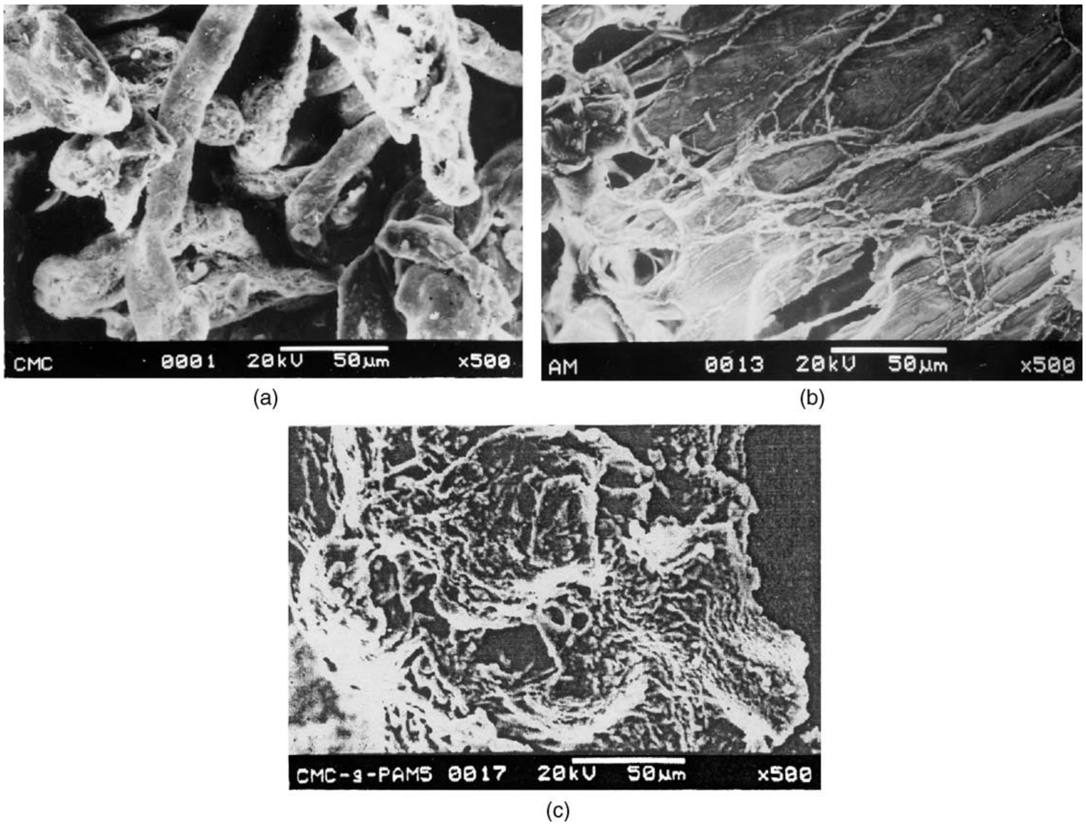

Fig. 7. Scanning electron micrographs of: (a) CMC, (b) PAM, (c) CMC-g-PAM 5.

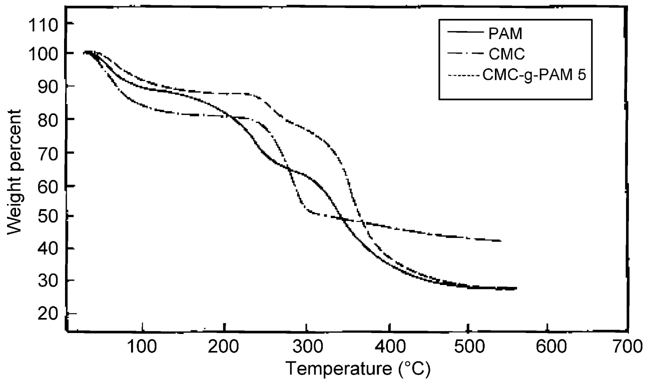

Fig. 8. TGA curves of CMC, PAM, and CMC-g-PAM 5.

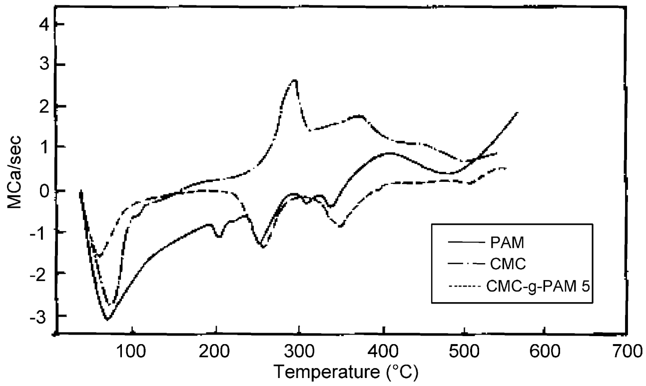

Fig. 9. DSC curves of CMC, PAM, and CMC-g-PAM 5.

4.8. Thermal analysis

Both TGA and DSC were carried out for CMC, PAM and all the graft copolymers (CMC-g-PAM 1 to CMC-g-PAM 6).

4.8.1. Thermogravimetric analysis (TGA)

The TGA curves of CMC, PAM, and CMC-g-PAM 5 in nitrogen atmosphere are shown in Fig. 8. In the case of CMC two distinct zones are observed where the weight is being lost. The initial weight loss is due to the presence of small amount of moisture in the sample. The second loss is due to the loss of CO_2 from the polysaccharide. As there are COO^- group in the case of CMC, it is decarboxylated in this temperature range. The rate of weight loss is increased with increase in temperature. In case of PAM, the initial weight loss is followed by a continuous weight loss with increasing temperature. The degradation after that is due to the loss of the NH_2 group in the form of ammonia as observed in corresponding DSC curves followed by endothermic peaks. However, in the case of CMC-g-PAM 5, the degradation of the polymer takes place in two stages. The first decomposition is for the degradation of both CMC and PAM. The second degradation is due to the decomposition of the cyclised product. From the TGA curves, it is obvious that CMC-g-PAM 5 is thermally more stable as compared to CMC and PAM. So, from the TGA results we concluded that the grafting of PAM chains onto the polysaccharide backbone enhances the thermal stability of the polysaccharides. While studying the TGA curves of all the graft copolymers (CMC-g-PAM 1 to CMC-g-PAM 6). It has been observed that for each graft copolymer different percent of weight is lost at a constant temperature. Among the graft copolymers, CMC-g-PAM 5 contains highest percent of PAM. Therefore; it has a higher thermal stability than the other graft copolymers.

4.8.2. Differential scanning calorimetry (DSC)

The DSC curves of CMC, PAM, and CMC-g-PAM 5 are shown in Fig. 9. CMC shows a distinct feature in the DSC curve having one endotherm (76 °C) and others at relatively higher temperatures due to the decomposition of the main chain. This step is followed by depolymerisation, which proceeds due to the cleavage of glycosidic linkages. The other small exothermic peaks at about 380 °C and above are due to the combustion of the degraded products. In the DSC curve of PAM, four endothermic peaks are observed.

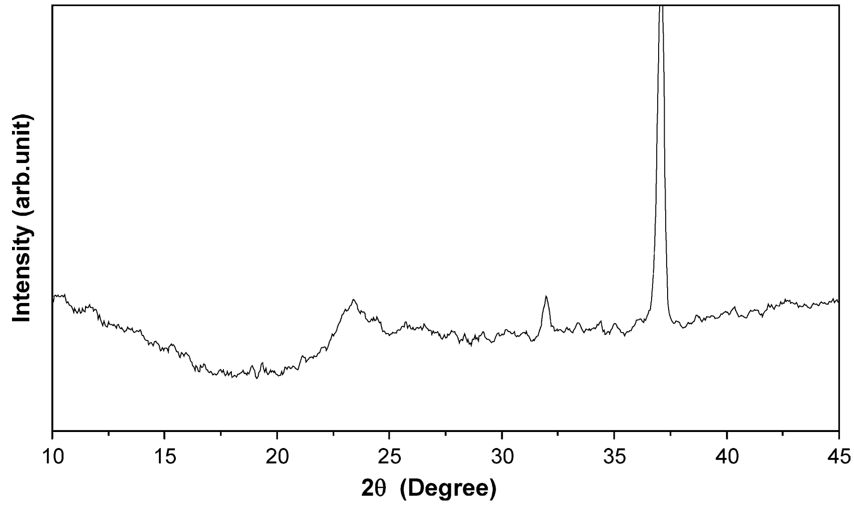

Fig. 10. X-ray diffractograms of CMC.

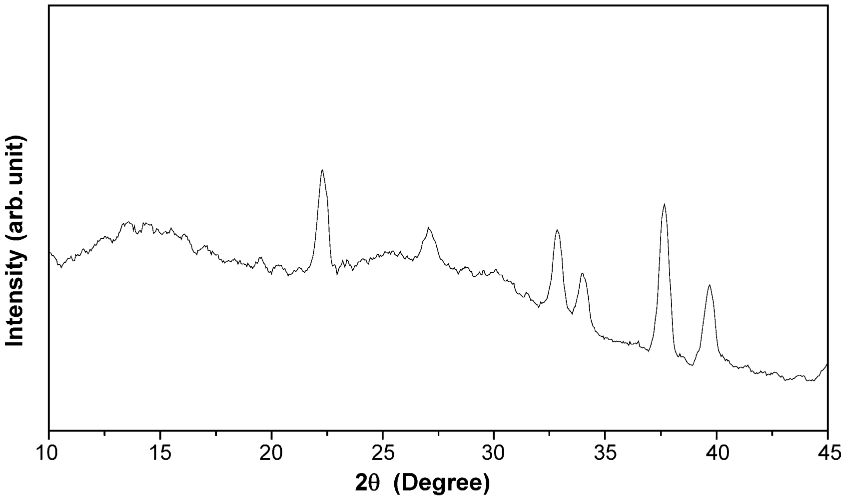

Fig. 11. X-ray diffractograms of PAM.

The first peak at temperature 68.9 °C is due to the loss of absorbed moisture in the sample. The second peak at 203 °C is for crystalline melting of PAM. The third peak at 258 °C is due to loss of ammonia. As has been reported (Convely, 1970) that PAM degrades in the temperature range of 175–300 °C by the formation of imide group via cyclization. The peak at 360.5 °C is for the decomposition of cyclized imide groups. In the grafted product, the characteristic peaks are very similar to that of PAM, but at slightly different temperatures.

4.9. XRD

XRD analysis showed that CMC exhibits a very small crystallinity (Fig. 10). In the case of PAM, the crystalline peaks appear in the 2θ range 21–42° (Fig. 11). The percentage crystallinity calculated (Blundell & Osborn, 1983) is 36%. However, the grafted products (Fig. 12) do not have any peak indicating crystallinity. It is thus concluded that grafting leads to disruption in the original crystalline structure of PAM.

5. Conclusions

The aim of this study was to prove the occurrence of grafting by various techniques. Variation of the synthetic parameters resulted in a series of graft copolymers with variation in the length and number of PAM chains. With increase in PAM chains of the graft copolymer, the viscosities of the graft copolymers gradually increase. Elemental analysis results provide further proof of grafting. The IR spectra of the graft copolymer after extraction of homopolymer also provide strong proof of grafting. Shear viscosity of the aqueous solution of the graft copolymer is much more than that of

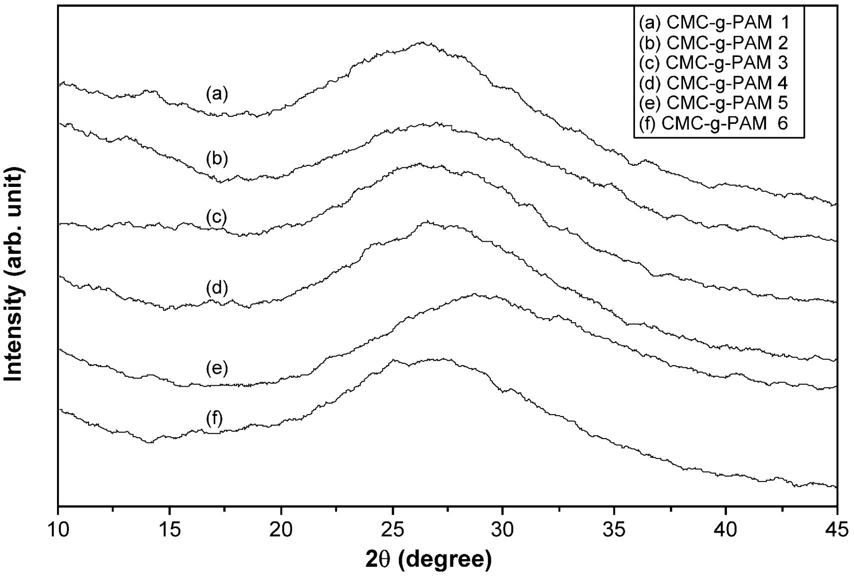

Fig. 12. X-ray diffractograms of CMC based graft copolymers (CMC-g-PAM 1 to CMC-g-PAM 6).

the corresponding polysaccharides. Morphological studies of the graft copolymers, CMC and PAM also support grafting. TGA results show different thermal decomposition patterns for the base polysaccharides and the corresponding graft copolymers. X-ray diffraction patterns show the presence of crystallinity in case of CMC and PAM, which reduces on grafting due to disruption of the original ordered structure.

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