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Synthesis, characterization, and applied properties of carboxymethyl cellulose and polyacrylamide graft copolymer

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ABSTRACT

The synthesis of carboxymethylcellulose (CMC)-g-polyacrylamide (PAM) was carried out in an aqueous medium by using a redox system as an initiator. The effects of reactive conditions on the weigh-average molecular weight of the copolymers (such as initiator concentrations, monomer concentrations, initial reaction temperature, and pH value) were investigated, and the optimal conditions for the grafting reaction were established. The obtained graft copolymers were characterized by Fourier transform infrared spectroscopy, thermal analysis, X-ray diffractometry, intrinsic viscosity, and radius of gyration. An equation relating the radius of gyration of the copolymer influenced by the radius of gyration of PAM and CMC was obtained. The experimental results show how the salt-resistance and heat-resistance of graft copolymers are improved remarkably.

1. Introduction

Among soluble polymers, both carboxymethyl cellulose (CMC) and partially hydrolyzed polyacrylamide (HPAM) are very important chemicals used in oilfield production. CMC, a filtrate reducer in drilling fluid and the viscosifier in fracturing operation, is a chemical derivative of cellulose. Its aqueous solution has the predominant salt-resistance performance, but the intrinsic viscosity, strength, and heat-resistance of CMC are limited by its low weigh-average molecular weight (Benke, Takács, Wojnárovits, & Borsa, 2007; Hossam, Safaa, & Abdel, 2004; Lin, Kumar, Rozman, & Noor, 2005; Sabaa & Moktar, 2002; Zhang, 1999). Partially HPAM is known to employ aqueous media rendered more viscous than ordinary water in the enhanced oil recovery (EOR) of petroleum. By water-flooding, although all of the soluble polymers solution perform the shear-thinning non-Newtonian behavior, the partially HPAM solution could be easily diluted with brine (contains sodium ions) which are generally encountered in production formation and water. Fresh water is necessary for the effective use of partially HPAM in EOR applications as viscosifiers (Bicak, Sherrington, & Senkal, 1999; Biswal & Singh, 2004; Singh et al., 2000). Because partially HPAM is sensitive to salts, it is therefore necessary to study modified partially HPAM which will improve its salt-tolerance.

Recently, grafting of polyacrylamide (PAM) onto CMC were studied by different methods (Biswal & Singh, 2004; Nayak & Singh, 2001; Singh et al., 2000) in order to improve the salt-tolerance of partially HPAM. The molecular weights of graft copolymers are not remarkably increased, which means the intrinsic viscosity and heat-resistance of copolymers are low. In order to improve the molecular weights of graft copolymers, the graft copolymerization of PAM onto CMC was investigated in an aqueous medium using the ammonium persulphate and sodium sulfite redox system as an initiator. The graft copolymers were characterized by various techniques such as infrared spectroscopy, thermal analysis, X-ray diffractometry, intrinsic viscosity, and radius of gyration of graft copolymers.

2. Experimental

2.1. Materials

CMC was chemically pure and purchased from the Chinese Changqing Reagent Factory. It was extracted by the solvent extraction method using a mixture of water and ethanol (80:20 by volume). Its weigh-average molecular weight was 1.92×10^5. The content of the carboxyl groups was found using acid base titration which was 0.65 carboxyl groups per anhydroglucose unit. Chemically pure acrylamide was supplied by Chinese Fushun Reagent Factory. Ammonium persulphate, sodium sulfite, ethanol, acetone, and sodium chloride were analytical reagent grade and supplied by Chinese Tianjin Chemical Reagent Factory.

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2.2. Synthesis of graft copolymers

The appropriate amount of CMC was first placed in a beaker while stirred in distilled water under an inert nitrogen atmosphere, and then a predetermined quantity of acrylamide (AM) was added and stirred for 30 min to fully dissolve. At a certain temperature, the sodium sulfite and ammonium persulphate were successively added to the solution and the graft polymerization proceeded being thermally insulated for 8–10 h, until the reaction ended. After the product was cooled to room temperature (25 °C), it was separated by precipitation using ethanol and extracted by soxhle extraction with acetone for 10 h to remove the homopolymers, and then dried at 35 °C under vacuum and finally retrieved the powdered copolymer samples. The graft percentage was determined by the percent increase in weight as follows (Sabaa & Moktar, 2002):

$$\%\mathrm{Graft} = (W_g - W_o) \times 100/W_o \qquad (1)$$

where W_o and W_g represent the weights of the initial and the grafted CMC, respectively.

2.3. Calculation of the approximate molecular weight

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

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

where M_w is the weigh-average molecular weight.

The graft copolymers were synthesized by opening the monomer rings of polysaccharide backbone, and grafting PAM onto the free radicals generated. The opening imparts are slight flexibility to the backbone. Moreover, the percentage of polysaccharide in the molecular chain constitution of the copolymer was still smaller in comparison with the PAM. Hence, in case of the grafted polysaccharides, several workers (Erciyes et al., 1992; Hartley, 1959; Swarson, Shogren, Fanta, & Lmam, 1993; Tripathy, Karmakar, & Singh, 2000) had used the Mark–Houwink equation to estimate an approximate molecular weight, which is applicable for linear polymers. The same has been done in the present case.

2.4. Measurement of the intrinsic viscosity

Intrinsic viscosity measurements of CMC, PAM, and CMC-g-PAM were carried out using a capillary viscometer with Ubberlohde geometry at 25 °C. All of those samples were dissolved in distilled water and allowed to stand two hours to fully hydrate before being diluted in the sodium chloride solution to meet the required concentration. The final polymer concentrations of CMC, PAM, and CMC-g-PAM were the same values of 2.0% (wt.). The typical five concentrations of sodium chloride from 0.4×10^4 to 1.6×10^4 mg/L were individually measured to yield the regression line of reduced viscosity vs. concentration from which the intrinsic viscosity was extracted by extrapolating to zero concentration.

3. Characterization

The CMC, PAM, and synthesized graft copolymers, were individually characterized by Fourier Transform Infrared spectroscopy, Thermogravimetric analysis, and X-ray diffractometry.

3.1. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of CMC, PAM, and the graft copolymers were recorded using KBr pellets. A Perkin-Elmer-630 FTIR spectrophotometer was used to record the spectra in the range of 4000–400 cm^{-1}.

3.2. Thermogravimetric analysis (TGA)

The TGA studies were carried out on a Shimadzu-50 instrument (Japan) at a heating rate of 10 °C min^{-1} under nitrogen flow (20 ml min^{-1}) over a temperature range from room temperature up to 500 °C.

3.3. X-ray diffractometry (XRD)

The CMC and all the graft copolymers 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 Kα radiation. The scattering angle (2θ) was varied from 0 to 70°.

4. Results and discussion

4.1. Optimal synthesis conditions on the molecular weights of graft copolymers

The relationship between molecular weights of graft copolymers and synthesis conditions was studied (Table 1). The results reveal that the maximum molecular weight of the graft copolymer is 7.5×10^6. This is higher than the molecular weights of graft copolymers from CMC synthesized by other means. The corresponding optimal synthesis conditions are established, the initiator

Table 1
Effect of synthesis conditions on the molecular weight (M_w).

Ratio of materials	M_w at different conditions				
w(CMC):w(AM) = 1:4 Monomer concentrations: 20% pH: 7	Initiator concentrations (mg/L) M_w ($\times 10^6$)	100 0.45	200 2.55	300 4.65	400 3.12
w(CMC):w(AM) = 1:4 Initiator concentrations: 300 mg/L pH: 7	Monomer concentrations (%) M_w ($\times 10^6$)	10 1.85	20 5.26	30 4.32	40 3.55
w(CMC):w(AM) = 1:4 Monomer concentrations: 20% Initiator concentrations: 300 mg/L	pH M_w ($\times 10^6$)	6 1.55	7 4.32	8 7.5	9 5.28
Monomer concentrations: 20% Initiator concentrations: 300 mg/L pH: 7	w(CMC):w(AM) M_w ($\times 10^6$)	1:01 0.25	1:02 1.05	1:04 4.58	1:06 3.25

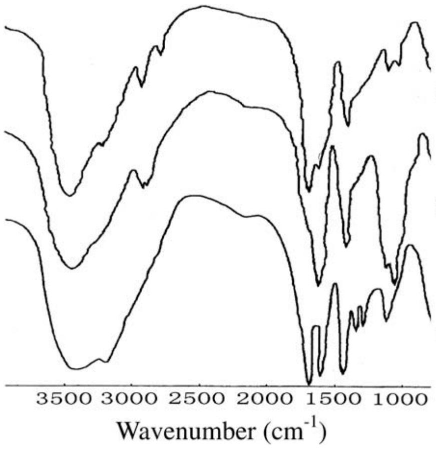

Fig. 1. FT-IR spectra of (a) PAM; (b) CMC; (c) CMC-g-PAM (w(CMC):w(AM) = 1:4).

concentrations are 300 mg/L, the monomer concentrations are 20% (wt.%), the ratio of CMC and AM on weight is 1/4, and the solution pH value is 8.

4.2. FTIR spectroscopy

The graft copolymer structure was confirmed by FTIR spectroscopy. The FTIR spectra of (a) PAM, (b) CMC, and (c) CMC-g-PAM (w(CMC):w(AM) = 1:4) are showed in Fig. 1. The peak at 3444 cm^{-1} in the CMC-g-PAM copolymer is the overlap of hydroxyl group of CMC and amine group of PAM. The peak at 1625 cm^{-1} in the CMC-g-PAM is the overlap resulting from the carboxyl group 1592 cm^{-1} of CMC and amide group (1625 cm^{-1}) of PAM, which could be seen in Fig. 1a–c, respectively. There are a set of similar peaks at 1068 cm^{-1} in Fig. 1c and b which is the CH–O–CH$_2$ group resulting from grafting reaction between the hydroxyl group located in anhydroglucose C$_2$ position and the π band of PAM. The primary peaks existed in the CMC-g-PAM, suggesting formation of aether (>CH–O–CH$_2$) during the grafting copolymerization. The molecular formula of CMC-g-PAM could be shown in Fig. 2. The main chain of graft copolymer is CMC, and the side chains of graft copolymer are PAM.

4.3. Thermal analysis

In the case of CMC-g-PAM (382% the graft percentage, seen Fig. 3c), the degradation of the polymer occurs in two stages. The first thermogravimetry (TG) stage referring mainly to degradation of the CMC main chain takes place in the 240–260 °C temperature range, with a mass loss of 12 wt.%. However, the mass loss of CMC is 40 wt.% in the temperature range of 240–300 °C (see Fig. 3a). The second TG stage, occurs in the 260–450 °C temperature range with a mass loss of 46 wt.% which could be ascribed to the decomposition of the PAM side chains. However, the mass loss of PAM is 85 wt.% in the temperature range of 260–440 °C (see Fig. 3b).On the basis of the above results, we can conclude that anti-heat decomposition could be improved by the grafting of PAM to CMC. Furthermore, the ratio of mass loss on side chains and main chain (3.83) is comparable with the graft percentage (382%).

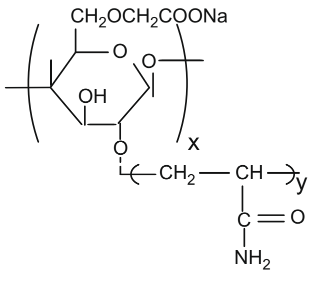

Fig. 2. The structural formula of CMC-g-PAM.

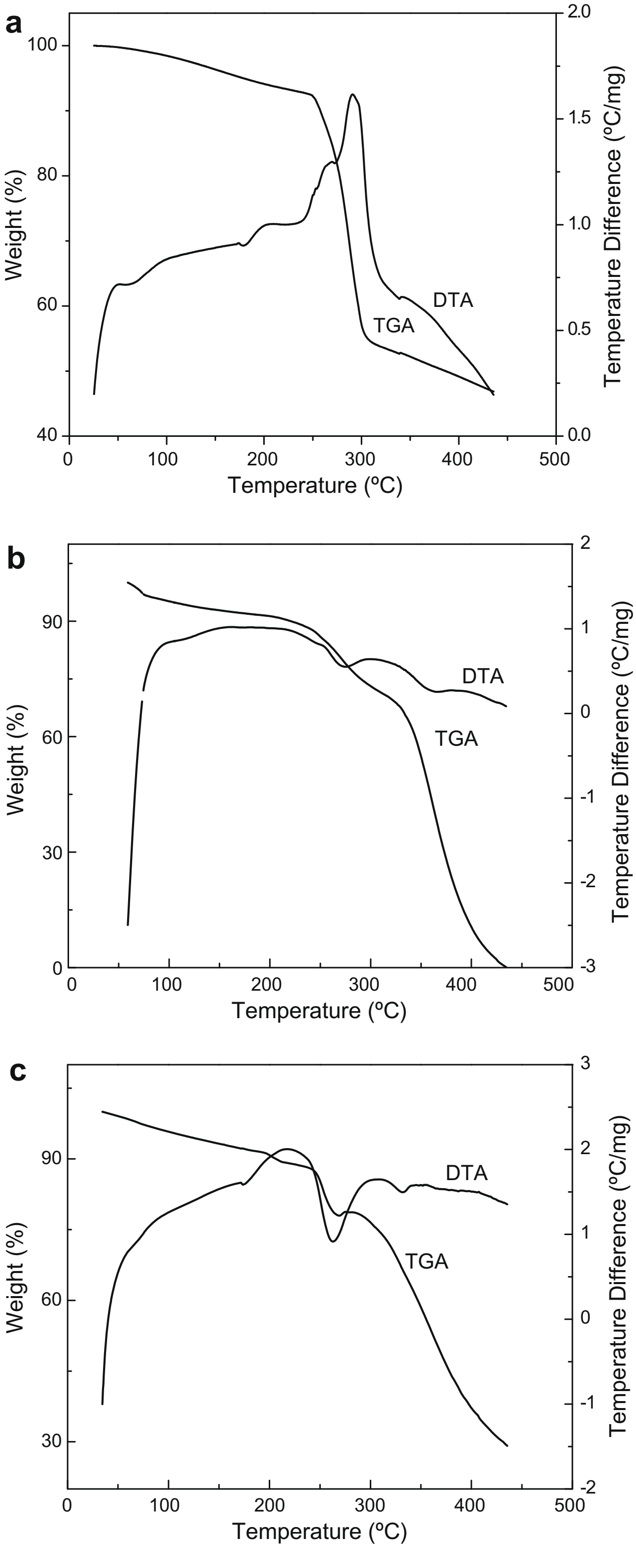

Fig. 3. DTA–TGA curve of (a) CMC, (b) PAM, and (c) CMC-g-PAM (the graft percentage: 382%).

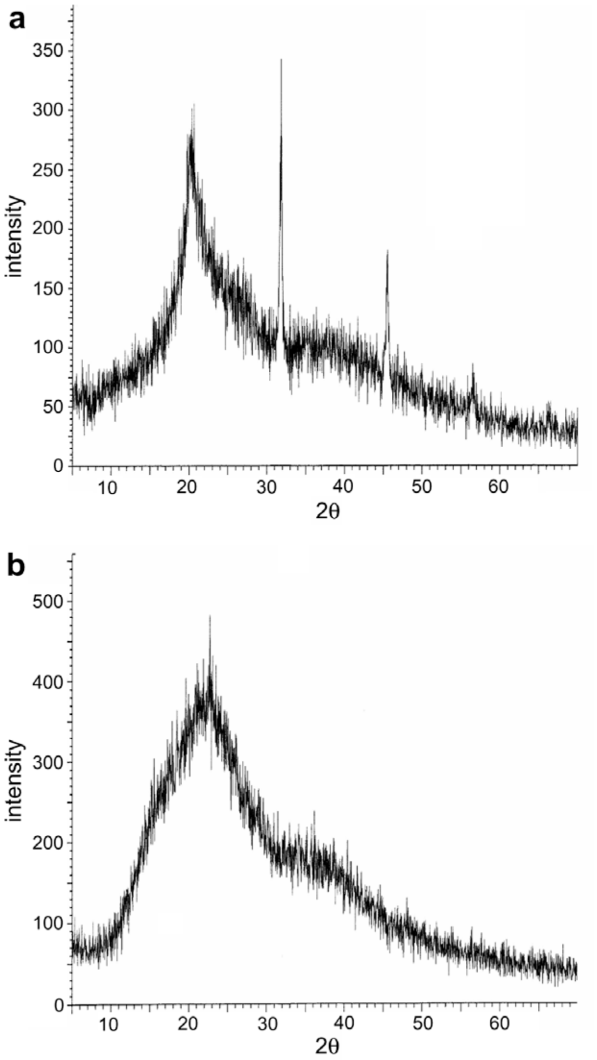

Fig. 4. X-ray diffraction pattern of (a) CMC and (b) CMC-g-PAM (w(CMC):w(AM) = 1:4).

4.4. XRD analysis

The X-ray diffraction patterns of CMC and CMC-g-PAM are depicted in Fig. 4a and b, respectively. There is a shift peak at $2\theta = 23^\circ$ in CMC-g-PAM corresponding to the position at $2\theta = 20^\circ$ observed in CMC pattern. This could be explained by a rearrangement in the morphology of the polymeric chain after grafting of PAM to CMC. Moreover, it is clearly seen that there are two peaks disappearing at the position $2\theta = 32^\circ$ and $2\theta = 46^\circ$ in CMC-g-PAM contrasted to CMC pattern. This phenomena could be partially explained from the grafting molecular structure of CMC-g-PAM showed in Fig. 2. This indicates the reduction power of H-bonding connection between the grafting cellulosic chains due to the hydroxyl group in anhydroglucose translating into the aether group during the grafting copolymerization.

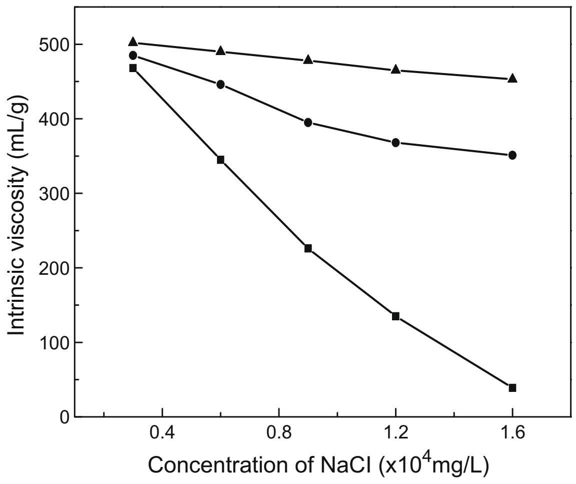

Fig. 5. Effect of concentration of NaCl on the intrinsic viscosity. ■, Partially hydrolyzed PAM; ●, NaCMC; ▲, partially hydrolyzed CMC-g-PAM.

4.5. The relationship between intrinsic viscosity and radius of gyration of graft copolymers

4.5.1. Effect of sodium chloride concentration on the intrinsic viscosity

The relationship between intrinsic viscosity of CMC, PAM, CMC-g-PAM, and sodium chloride concentration is shown in Fig. 5. The intrinsic viscosity of CMC-g-PAM solution slowly decreases with increasing in concentration of sodium chloride, and its retention rate is 91% within testing range. However, the intrinsic viscosity of PAM and CMC solution drastically decreases, and the retention rate is 73% and 11%, respectively. Then the mean-square radius of polymer could be estimated according to the Eq. (3) (Okano, 1998):

$$r_m = (0.237 \times 10^{-10}[\eta]M_w)^{1/3} \tag{3}$$

where M_w is the weigh-average molecular weight and $[\eta]$ is the intrinsic viscosity.

The mean-square radius of large molecules in sodium chloride solution is listed in Table 2. Having analyzed the data in Table 2 with the software of Statistics Analysis System (SAS company), the equation on the radius of gyration of copolymer influenced by the radius of gyration of PAM, and CMC is obtained

$$y = 0.174525 + 0.416036x_1 + 2.005714x_2 + 0.201334x_1^2 - 4.226451x_1x_2 \quad r^2 = 0.9984$$

where y, x_1, and x_2 are the radius of gyration of large molecules of copolymer, PAM, and CMC, respectively.

The equation shows that the radius of gyration of copolymer is the synergetic effect result on the radius of gyration of PAM, and the radius of gyration of CMC.

It can be seen from the Fig. 5, Table 2, and the equation that not only the intrinsic viscosity and radius of gyration of CMC-g-PAM are higher than that of PAM and CMC, but also the salt-resistance of CMC-g-PAM has been improved remarkably.

Table 2
The mean-square radius of large molecules in NaCl solution.

r_m (nm)	NaCl (0.3 × 10^4 mg/L)	NaCl (0.6 × 10^4 mg/L)	NaCl (0.9 × 10^4 mg/L)	NaCl (1.2 × 10^4 mg/L)	NaCl (1.6 × 10^4 mg/L)
HPAM	0.4058	0.3607	0.3175	0.2644	0.1923
CMC	0.1297	0.127	0.1211	0.119	0.1157
P(AM–CMC)	0.4142	0.4119	0.4073	0.4043	0.4

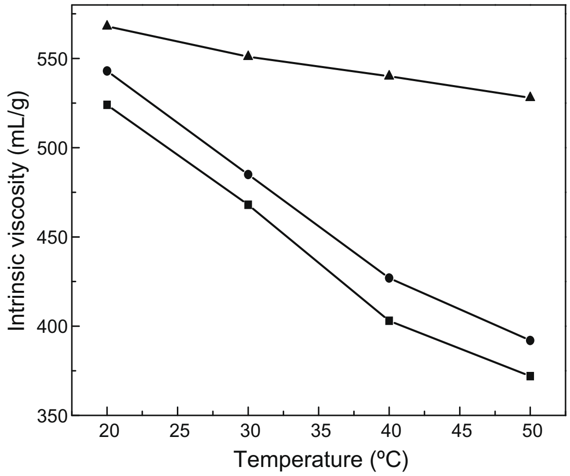

Fig. 6. Effect of temperature on the intrinsic viscosity. ■, Partially hydrolyzed of PAM; ●, NaCMC; ▲, partially hydrolyzed CMC-g-PAM.

4.5.2. Effect of temperature on the intrinsic viscosity

The studies of intrinsic viscosity on aqueous solution of CMC, PAM, and CMC-g-PAM were carried out at the same concentration of 2.0 wt.%. The relationship between temperature (20–50 °C) and intrinsic viscosity is shown in Fig. 6. The intrinsic viscosity of the CMC-g-PAM solution slowly decreases with increasing temperature, and its retention rate is 93% within the test range. However, the intrinsic viscosity of PAM and CMC solution presents the temperature effect of common polyelectrolyte and its retention rate is 72%. Therefore, with increasing temperature, the extent on the change of intrinsic viscosity of CMC-g-PAM solution will be lower than that of PAM, and CMC solutions. It is certain that heat-resistance of CMC-g-PAM is better than that of PAM and CMC.

5. Conclusions

PAM has been successfully grafted onto CMC polymer chain by using redox system as initiator in aqueous medium. The optimal conditions for the grafting are established, and the maximum molecular weight of graft copolymer is found to be about 7.5×10^6. The IR spectra of the extraction of graft copolymer provide proof of grafting. The thermogravimetric analysis results give further proof of grafting. X-ray diffraction patterns show the presence of crystallinity in case of CMC, which reduce grafting due to disruption of the original ordered structure. The equation on the radius of gyration of copolymers influenced by the radius of gyration of PAM and CMC is obtained. Furthermore, the viscosity, salt-resistance, and heat-resistance of the aqueous solution of the graft copolymer are improved remarkably.

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