Graft Copolymerization of *N*-Vinyl-2-Pyrrolidone onto Sodium Carboxymethylcellulose with Azobisisobutyronitrile as the Initiator

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ABSTRACT: Graft copolymers of sodium carboxymethylcellulose with *N*-vinyl-2-pyrrolidone were prepared in aqueous solutions with azobisisobutyronitrile as the initiator. The graft copolymers [sodium carboxymethylcellulose-*g*-poly(*N*-vinyl-2-pyrrolidone)] were characterized with Fourier transform infrared spectroscopy, elemental analysis, nuclear magnetic resonance spectroscopy, differential scanning calorimetry, and scanning electron microscopy. The grafting parameters, including the graft yield of the graft copolymer and the grafting efficiency of the reaction, were evaluated comparatively. The effects of reaction variables such as the time, temperature, and monomer and initiator concentrations on these parameters were studied. The graft yield and grafting efficiency increased and then decreased with increasing concentrations of *N*-vinyl-2-pyrrolidone and azobisisobutyronitrile and increasing polymerization temperatures. The optimum temperature and polymerization time were 70°C and 4.30 h, respectively. Further changes in the properties of grafted sodium carboxymethylcellulose, such as the intrinsic viscosity, were determined. The overall activation energy for the grafting was also calculated to be 10.5 kcal/mol. J Appl Polym Sci 104: 936–943, 2007

Key words: graft copolymers; hydrophilic polymers; radical polymerization; copolymerization

INTRODUCTION

Carboxymethylcellulose (CMC) is the most important water-soluble cellulose derivative and is broadly used because of its low cost, biodegradability, biocompatibility, and lack of toxicity.[1–4] The food industry, cosmetics, pharmaceuticals, suspension agents, tablet excipients, viscosity-increasing agents, formulation agents for the controlled release of drugs and pesticides, paper and paper products, adhesives, and ceramics provide a small compilation of the numerous applications in which CMC is used in an acidic or sodium salt form.[5]

In recent years, the chemical modification of CMC by the grafting of hydrophilic vinyl monomers (nonionic, anionic, or cationic), such as acrylamide,[6] acrylonitrile,[7] acrylic acid,[8] and trimethylallylammonium choloride,[9] has gained considerable attention and has been proved to have value in preparing new polymeric materials with special properties and enlarging the range of its utilization. However, grafting hydrophilic *N*-vinyl-2-pyrrolidone (N-VP) onto CMC has not been studied.

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N-VP is a hydrophilic and nonionic monomer, the polymerization of which is easily initiated through radicals, thermal irradiation, or photoirradiation.[10] Poly(*N*-vinyl-2-pyrrolidone) (PVP) is a polymer with great potential applications in different biomedicines. The principal reason for successful PVP application is its excellent biocompatibility with living tissues and extremely low cytotoxicity.[11] Many workers have carried out grafting reactions of N-VP onto silica,[12] polypropylene film,[13] gelatin,[14] and low-density polyethylene.[15]

In a previous study,[16] N-VP was grafted onto poly (ethylene terephthalate) (PET) films, and the reaction conditions for grafting were optimized. In this work, we successfully carried out the grafting of N-VP onto sodium carboxymethylcellulose (NaCMC) with azobisisobutyronitrile (AIBN), and we evaluated the optimized reaction conditions for grafting. The graft copolymer was also characterized with different techniques.

EXPERIMENTAL

Materials

NaCMC with a viscosity of 400–800 cps (2% aqueous solution at 25°C) was purchased from Sigma (St. Louis, MO). N-Vinyl-2-pyrrolidone was supplied by Fluka Chemie AG (Buchs, Switzerland) and purified by vacuum distillation at 2 mmHg and 65°C. AIBN,

obtained from Merck AG (Steinheim, Germany), was used after purification by recrystallization with methanol and dried in a vacuum oven for 2 days. Other reagents were Merck products and used as supplied.

Graft copolymerization

The grafting reactions were carried out under a nitrogen atmosphere in a 250-mL, three-necked flask equipped with a reflux condenser, a stirrer, and a gas inlet system and immersed in a constant-temperature bath. In a typical reaction, NaCMC (0.5–1.5 g) was dissolved in distilled water (50 mL) at room temperature with constant stirring and bubbling of a slow stream of nitrogen for 30 min. The mixture was immediately placed into the water bath adjusted to the polymerization temperature. N-VP was dissolved in 25 mL of distilled water and mixed with the NaCMC solution; the mixture was stirred for 10 min. Then, AIBN at the required concentration in 2 mL of acetone was added slowly to the reaction mixture, and the total volume of the reaction mixture was made up to 100 mL with distilled water. A continuous supply of nitrogen was maintained throughout the reaction period. The grafting reactions were carried out for various times (1–6 h) and temperatures (55–80°C). At the end of the predetermined polymerization time, the reaction was terminated by the addition of a saturated solution of hydroquinone. The products were precipitated in an excess of acetone, separated by filtration, and then extracted with ethyl alcohol to remove the homopolymer (PVP) for 24 h. After the complete removal of PVP, the pure graft copolymer was dried at 40°C *in vacuo* to a constant weight. The grafting parameters, including the graft yield (GY) and grafting efficiency (GE), were calculated as follows:

$$\text{GY } (\%) = [(w_g - w_o)/w_o] \times 100 \quad (1)$$

$$\text{GE } (\%) = [(w_g - w_o)/(w_g - w_o) + w_h] \times 100 \quad (2)$$

where w_o, w_g, and w_h denote the weights of the original (ungrafted) NaCMC, grafted NaCMC, and homopolymer, respectively.

The rate of grafting (R_g) was calculated with the formula as follows:

$$R_g = [(w_g - w_o) \times 1000]/[M \times t \times V] \quad (3)$$

where M is the molar weight of the monomer, t is the polymerization time (s), and V is the volume (mL) of the overall reaction medium.

Fourier transform infrared (FTIR) measurements

FTIR spectra of NaCMC and grafted NaCMC were taken in the wavelength region between 400 and 4000 cm^{-1} at the ambient temperature with a Mattson (Cambridge, United Kingdom) model 1000 FTIR spectrophotometer with KBr discs.

Elemental analysis

Elemental analysis of the graft copolymers with various GYs was performed with a Leco (St. Joseph, MI) CHNS-932 CHN analyzer.

Nuclear magnetic resonance (^{1}H-NMR) spectroscopy

^{1}H-NMR spectroscopy of NaCMC and sodium carboxymethylcellulose-*g*-poly(*N*-vinyl-2-pyrrolidone) (NaCMC-*g*-PVP) was performed with a Bruker (Rheinstetten, Germany) DPX FT-NMR (400 MHz) in D_2O.

Differential scanning calorimetry (DSC)

Thermal analyses were performed with DSC (Sapphire differential scanning calorimeter, PerkinElmer, Shelton, CT). The sample weights ranged from 3.0 to 9.0 mg. The samples were heated from 30 to 300°C at a heating rate of 10°C/min. The intercept points of the slopes were taken as the glass-transition temperatures.

Scanning electron microscopy (SEM)

SEM photographs were taken with JSM (Tokyo, Japan) 5600 scanning microscope to examine the morphology and surface structure of NaCMC and N-VP grafted NaCMC at the required magnification at room temperature. The polymers were deposited onto a brass hold and sputtered with a thin coat of gold *in vacuo*. The acceleration voltage was 20 kV with the secondary electron image as a detector.

Determination of the intrinsic viscosity

Intrinsic viscosity measurements were carried out for grafted NaCMC in distilled water with an Ubbelohde capillary flow viscometer mounted in a water bath maintained at 25.0 ± 0.1°C.

RESULTS AND DISCUSSION

Effect of the polymerization time

The grafting of NaCMC was carried out at various polymerization times, with the monomer and initiator concentrations and temperature kept constant, and the results are shown in Figure 1. GY and GE progressively increased with an increase in the polymerization time up to 4.30 h and then leveled off when a 229% saturation grafting value was reached. The increase in the grafting parameters could be attrib-

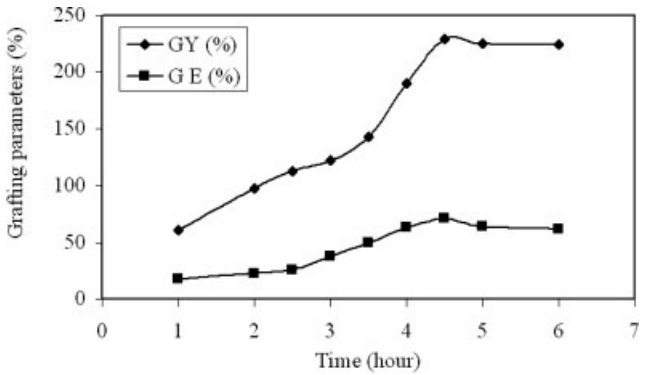

Figure 1 Variation of the grafting parameters with the polymerization time ([NaCMC] = 1.0 g/dL; [N-VP] = 0.46*M*; [AIBN] = 4.2×10^{-3} *M*; temperature = 70°C).

uted to the increase in the number of grafting sites on the NaCMC backbone and the addition of monomer molecules to the growing grafted chains. The following trend of almost leveling off was due to the decrease in the monomer initiator concentrations, a reduction in the number of active sites on the NaCMC backbone, and an increase in the medium viscosity and thus the formation of a diffusion barrier. Similar results were found for the graft copolymerization of acrylamide onto cellulose with ceric ammonium nitrate.[17]

Liu et al.[18] studied the grafting of methyl methacrylate onto another polysaccharide sodium alginate with potassium ditelluratoargentate(III). They reported the same trend for the effect of the reaction time on the grafting parameters.

Effect of the temperature

The effect of the temperature on the graft copolymerization of N-VP onto NaCMC was studied by the variation of the temperature between 55 and 80°C, and the results are presented in Figure 2. GY increased as the temperature increased from 55 to 70°C; a further increase in the temperature reduced it. On the other hand, GE increased very slowly in the beginning and then decreased with a further increase in the temperature. The highest GY and GE values obtained were 229 and 71%, respectively, at 70°C. The enhancement in the grafting with the rising polymerization temperature could be ascribed to a higher rate of AIBN decomposition and a possible reaction between the growing homopolymer chain radical and NaCMC. The increase in the reaction temperature also enhanced the mobility of the NaCMC backbone, monomer, and initiator molecules. Hence, the diffusion of the monomer and initiator into the NaCMC backbone increased with increasing temperature. Therefore, R_g increased. However, the lowering of grafting parameters by an increase in the temperature above 70°C could be due to the favored chain-termination reactions, chain-transfer reactions, and an increase in the formation of the homopolymer, as reflected by the GE curve in Figure 2. Similar results have been obtained by many workers who have studied graft copolymerization.[18–21]

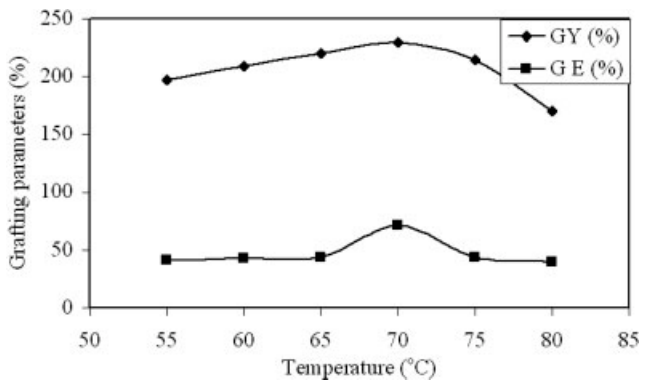

Figure 2 Variation of the grafting parameters with the temperature ([NaCMC] = 1.0 g/dL; [N-VP] = 0.46*M*; [AIBN] = 4.2×10^{-3} *M*; time = 4.30 h).

Zhang and Tan[19] studied the graft copolymerization of 2-(dimethylamino)ethyl methacrylate onto carboxymethylated cellulose and reported that the grafting parameters increased with an increase in the temperature up to 35°C and then decreased up to 60°C.

The overall activation energy for grafting was determined to be 10.5 kcal/mol from an Arrhenius plot of log R_g versus the reciprocal of the temperature ($1/T$), as shown in Figure 3. In our previous work,[16] the overall activation energy was calculated similarly to be 11.5 kcal/mol for the grafting of N-VP onto PET. The small value of the obtained activation energy shows that the grafting reaction between N-VP and NaCMC is thermodynamically favored and needs little energy.

Effect of the monomer concentration

The variation of the grafting parameters with the monomer concentration was studied in the range of

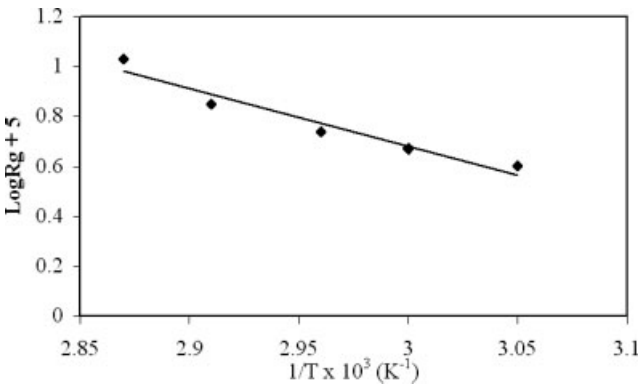

Figure 3 Arrhenius plot of log R_g versus $1/T$.

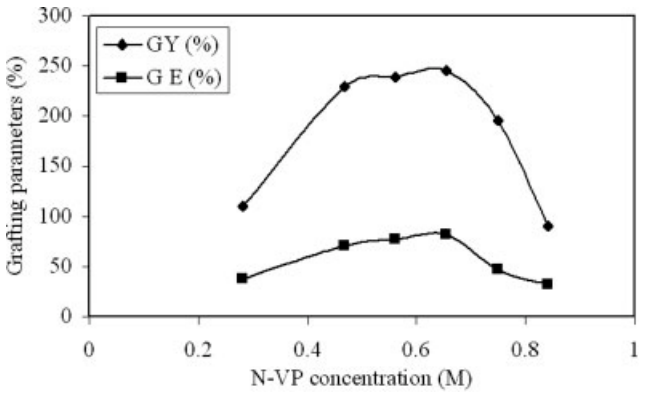

Figure 4 Effect of the monomer concentration on the grafting parameters ([NaCMC] = 1.0 g/dL; [AIBN] = 4.2 $\times$ 10^{-3} *M*; time = 4.30 h; temperature = 70°C).

0.28–0.84*M*, with all the other conditions kept constant. The results are presented in Figure 4. The grafting parameters increased steadily with the monomer concentration up to 0.66*M* and then decreased with a further increase in the N-VP concentration. As the monomer concentration increased, the diffusion of the monomer molecules into the NaCMC backbone increased, and this led to a higher grafting yield. The decrease in the grafting after this value could be associated with the depletion of available N-VP due to the simultaneous increase in the homopolymerization rate (as shown by the GE values) with the growing N-VP concentration in the polymerization medium. With a higher monomer concentration, the concentration of PVP macroradicals increased, and the rates of their combination and disproportionation were faster than the rate of their combination with NaCMC molecules. Therefore, the homopolymer and a lower percentage of grafting were produced. In addition, the homopolymer that accumulated in the reaction medium increased the medium viscosity, and the monomer diffusion into the NaCMC backbone became more difficult. Such behaviors were also obtained in other studies in the literature.[14,19,20,22–24] In the study of Shah et al.,[22] they investigated the grafting of acrylonitrile onto a sodium alginate polymer and observed that the grafting percentage increased as the monomer concentration increased from 0.272 to 0.679*M* and after that decreased with a further increase in the monomer concentration.

Effect of the initiator concentration

Another parameter that affects the grafting parameters is the initiator concentration. Figure 5 shows the effect of the AIBN concentration on R_g as the AIBN concentration increased. GY and GE increased significantly as the AIBN concentration increased up to 3.2 $\times$ 10^{-3} *M* and then fell down upon a further increase in the initiator concentration. The enhancement of the grafting as the AIBN concentration increases to a certain limit implies that primary free-radical species may participate essentially in the direct abstraction of a hydrogen atom from the NaCMC backbone to yield an NaCMC macroradical capable of initiating the grafting. Above this limit, the termination process with the growing polymer chains instead of the propagation process, the combination of the free-radical species, and the termination process with the NaCMC macroradicals prevail over the initiation process. A decrease in the grafting parameters were observed with a further increase in the initiator concentration, and this was consistent with the results of our previous studies[16,25] and others' studies.[18,22,23,26] Gupta and Sahoo[26] studied the Co(III) acetylacetonate complex initiated grafting of N-VP on cellulose in aqueous media and observed that the yield percentage increased up to 15 $\times$ 10^{-5} *M* initiator and then decreased with an increase in the initiator concentration.

Effect of the NaCMC concentration

The effect of the NaCMC concentration on the grafting parameters was studied by the variation of the concentration of NaCMC from 0.5 to 1.5 g/dL and is presented in Figure 6. As the concentration of NaCMC was increased, the grafting parameters decreased continuously. This trend can be explained by the fact that as the concentration of NaCMC increased, the viscosity of the reaction medium also increased, and this hindered the movement of free radicals, thereby reducing the grafting parameters. Moreover, a high NaCMC concentration could produce more NaCMC macroradicals, which could interact with one another to terminate the reaction, thus lowering both the GY and GE values. Similar findings were reported by Banerjee et al.[27] They grafted 2-acrylamido-2-methyl-1-propanesulfonic acid onto NaCMC with a bromate/

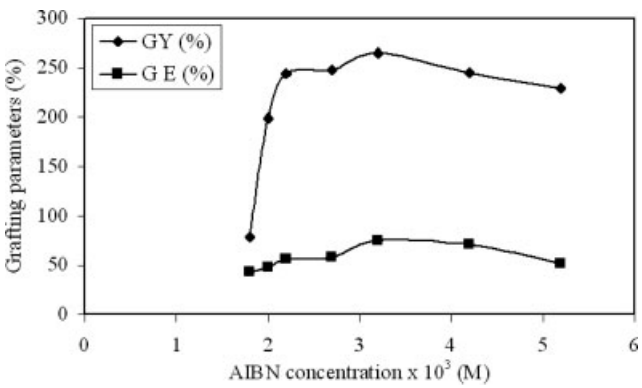

Figure 5 Effect of the initiator concentration on the grafting parameters ([NaCMC] = 1.0 g/dL; [N-VP] = 0.66*M*; time = 4.30 h; temperature = 70°C).

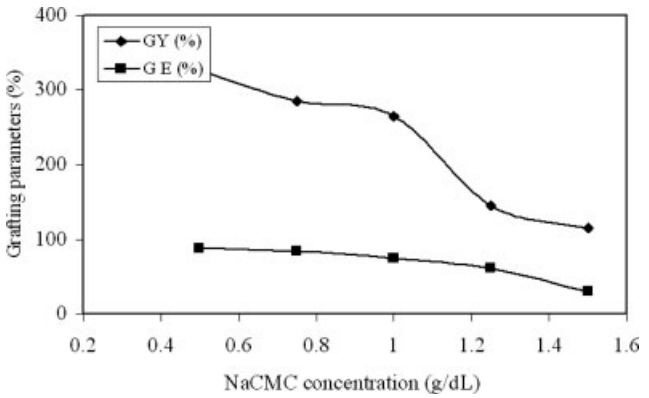

Figure 6 Effect of the NaCMC concentration on the grafting parameters ([N-VP] = 0.66*M*; [AIBN] = 3.2×10^{-3} *M*; time = 4.30 h; temperature = 70°C).

thioure redox pair and observed the same trend concerning the NaCMC concentration. Similar results can also be found in the literature.[19,21,28,29]

Characterization of the graft copolymers of NaCMC with N-VP

The FTIR spectra of NaCMC and its graft copolymer with a grafting yield of 122% are shown in Figure 7. Grafted and ungrafted NaCMC showed a broad band between 3000 and 3700 cm^{-1}, which was attributed to O—H stretching vibrations. The strong band of NaCMC at 1618 cm^{-1} was assigned to the carboxyl group. Interestingly, the carboxyl group band for grafted NaCMC shifted from 1618 to 1680 cm^{-1} because of the carbonyl stretching vibration of vinylpyrrolidone.[10,13] Grafted NaCMC showed two peak at 1423 and 1289 cm^{-1} due to C—N stretching and C—N bending of PVP, respectively, which confirmed the grafting of the monomer.[30,31]

Other evidence of the grafting includes the ^{1}H-NMR spectra of NaCMC and NaCMC-*g*-PVP, as shown in Figure 8. Compared with NaCMC, grafted NaCMC showed additional signals between 1.5 and 2.5 ppm due to CH and CH_2 protons of poly(vinyl pyrrolidone).

Elemental analysis results for NaCMC-*g*-PVP with three different GYs are presented in Table I. The presence of nitrogen in the grafted NaCMC and its increasing content with GY confirmed the grafting reaction. Figure 9 shows a possible reaction between NaCMC and N-VP.

DSC analyses were performed to understand the thermal behavior of the graft copolymers, and the results are illustrated in Figure 10. The temperature of the end points of the endotherm peaks shifted to lower temperatures with the grafting of the N-VP monomer. The glass-transition temperatures of the NaCMC-*g*-PVP copolymers were lower than that of NaCMC, as shown in Table II. This is attributed to the fact that grafted chains might act as internal

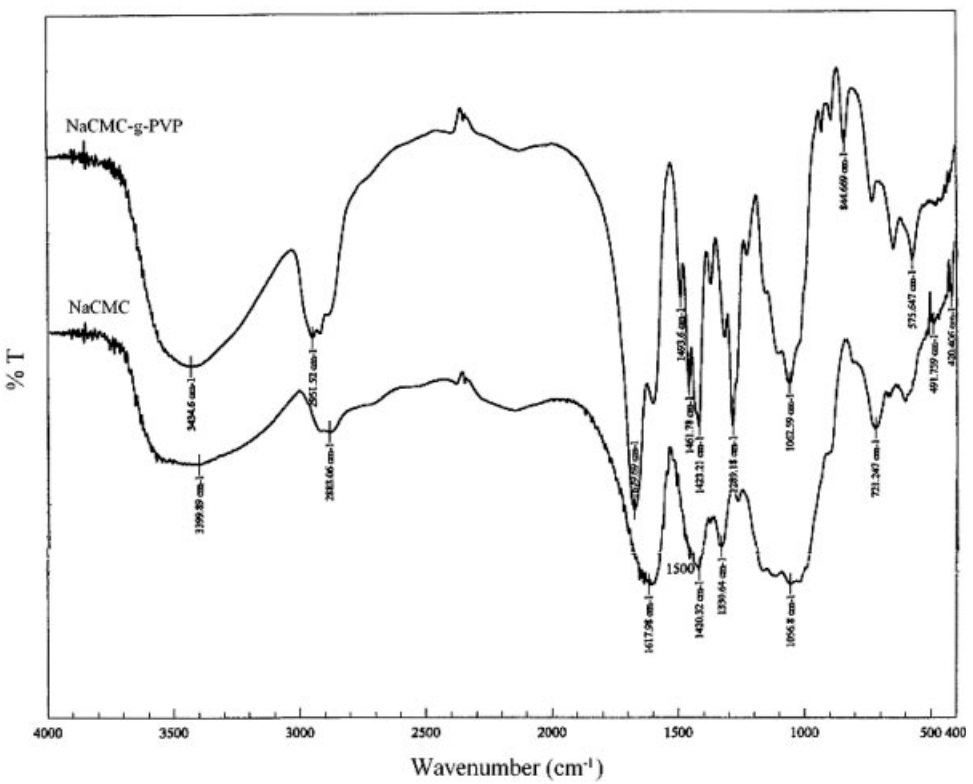

Figure 7 FTIR spectra of NaCMC and NaCMC-*g*-PVP (GY = 122%).

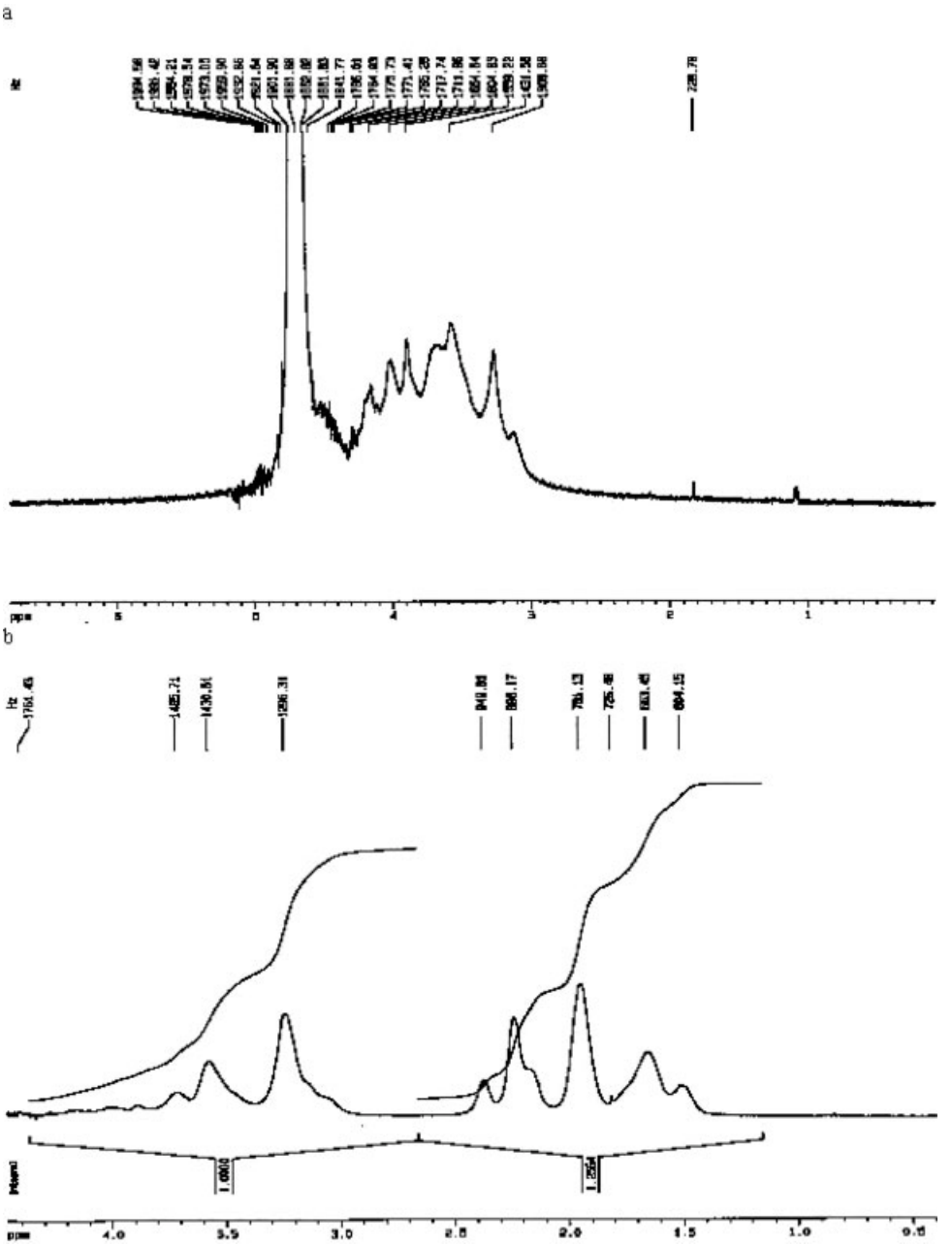

Figure 8 ^{1}H-NMR spectra of NaCMC and grafted NaCMC (GY = 122%).

plasticizers. Similar observations can also be found in the literature.[32]

SEM micrographs of ungrafted and N-VP grafted NaCMC (with 61% GY) are shown in Figure 11. By comparing the surface morphology of grafted NaCMC [Fig. 11(b)] with that of ungrafted NaCMC [Fig. 11(a)], we found that the grafted chains drastically changed the morphology of NaCMC. As shown in Figure 11, the surface of the NaCMC-*g*-PVP copolymer was more uneven than that of NaCMC, and this is another proof of grafting.

TABLE I
Elemental Analysis Results for Grafted NaCMC

Copolymer	GY (%)	C (%)	H (%)	N (%)
NaCMC-*g*-PVP1	61	45.26	7.37	5.40
NaCMC-*g*-PVP2	98	48.29	7.20	7.51
NaCMC-*g*-PVP3	113	52.95	7.26	8.90

Intrinsic viscosity measurements

Intrinsic viscosity data obtained from N-VP-grafted NaCMC with various GYs are plotted in Figure 12. The intrinsic viscosity increased with increasing GY. The intrinsic viscosity of a polymer, though greatly

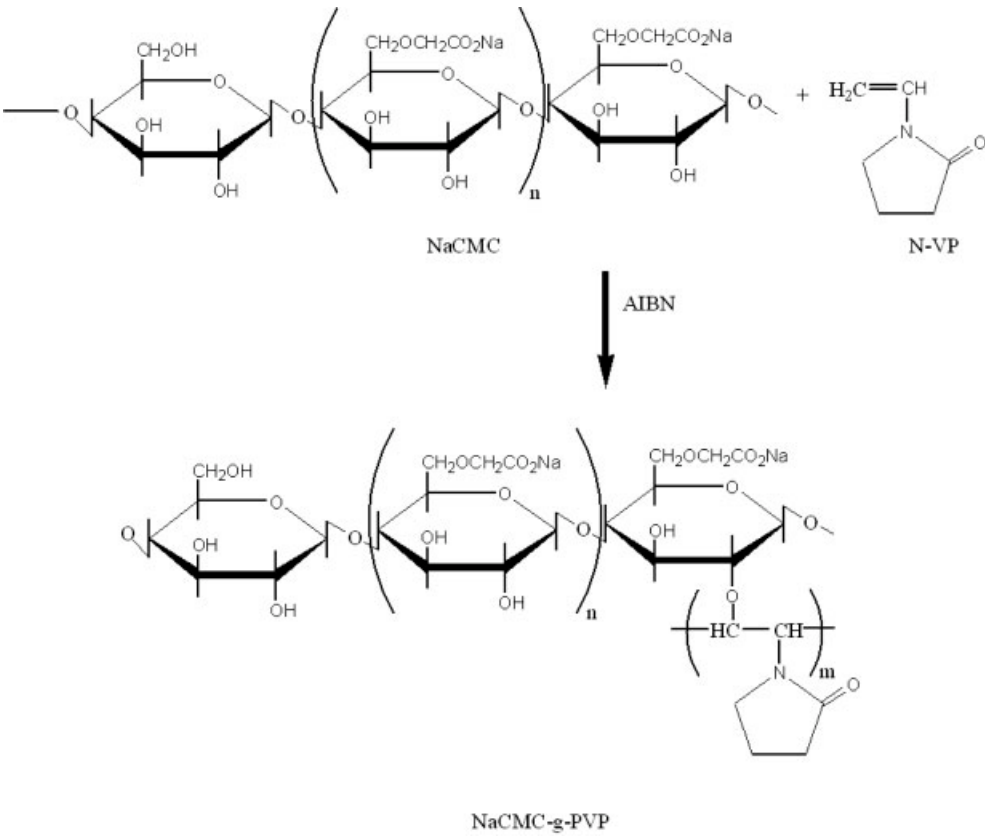

Figure 9 Possible reaction of NaCMC with N-VP.

dependent on its molecular weight, is also significantly influenced by the structure of the polymer solution.[33] It is a measure of the hydrodynamic volume of the polymer in solution. The longer the grafted chains are, the higher the hydrodynamic volume will be of the polymer in solution, and hence the higher the intrinsic viscosity will be. Therefore, the fact that the intrinsic viscosity increased with increasing GY suggests that the length of the grafted PVP chains increased. Similar results were observed during the grafting of N-VP[16] and 4-vinylpyridine onto PET films.[25]

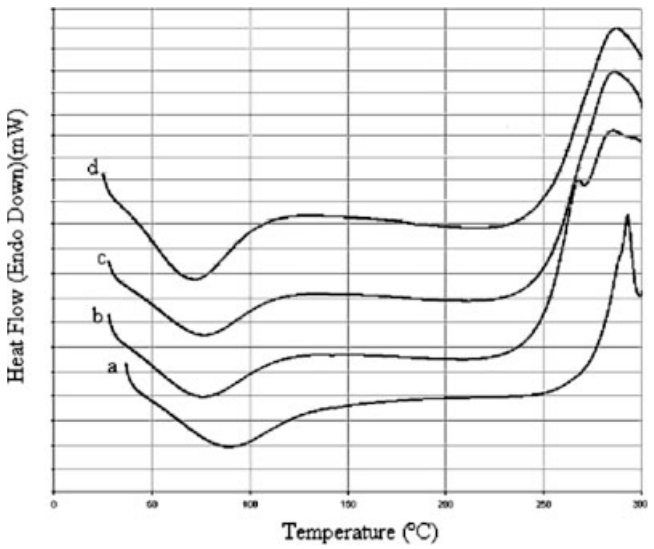

Figure 10 DSC thermograms of (a) NaCMC, (b) NaCMC-*g*-PVP with 61% GY, (c) NaCMC-*g*-PVP with 98% GY, and (d) NaCMC-*g*-PVP with 113% GY.

CONCLUSIONS

N-VP was successfully grafted onto CMC with AIBN as the initiator. The graft copolymerization was confirmed with FTIR, ^{1}H-NMR, elemental analysis, DSC, and SEM. The optimum conditions for the maximum grafting parameters (376% GY and 88% GE) were obtained when the polymerization was carried under the following conditions: [AIBN] = 3.2×10^{-3} *M*,

TABLE II
Glass-Transition Temperature (T_g) Values of NaCMC and Grafted NaCMC Obtained from DSC Analysis

Polymer	GY (%)	T_g (°C)
NaCMC	—	69.5
NaCMC-*g*-PVP1	61	59.1
NaCMC-*g*-PVP2	98	57.9
NaCMC-*g*-PVP3	113	52.0

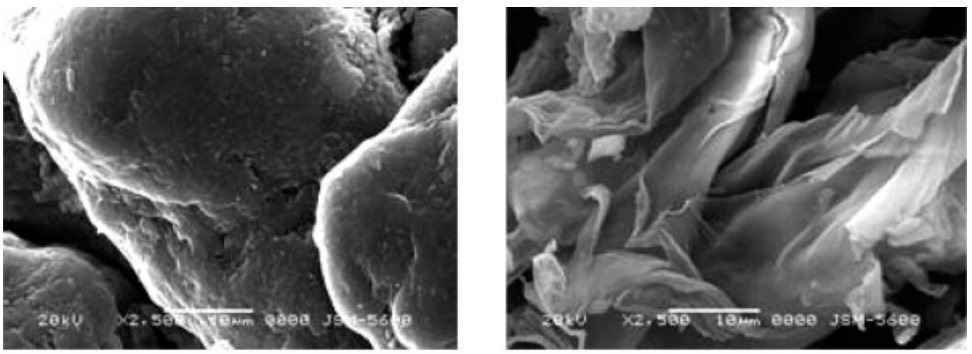

Figure 11 SEM micrographs of (a) ungrafted and (b) N-VP-grafted NaCMC with an original magnification of 2500×.

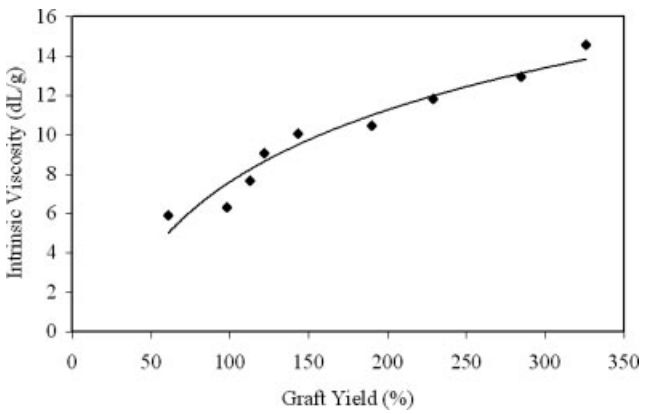

Figure 12 Variation of the intrinsic viscosity with GY.

[N-VP] = 0.655*M*, [NaCMC] = 0.5 g/dL, time = 4.30 h, and temperature = 70°C. The overall activation energy for grafting was calculated to be 10.5 kcal/mol. Furthermore, the intrinsic viscosity of grafted NaCMC increased with an increase in the grafting yield.

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