

Cellulose Membranes Grafted with Vinyl Monomers in Homogeneous System

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ABSTRACT: The homogeneous grafting of a hydrophilic monomer onto cellulose derivatives was carried out in an aqueous system at 30, 50, 70, and 90°C during reaction periods of 30–180 min. The graft polymer was isolated by ethanol from the reaction mixture, dried, and weighed. The grafted polymer was characterized by the IR method, as well as the microscopic sample morphology detected by scanning electron microscopy. The water absorption capacities and grafting values of the grafted cellulose derivatives were also determined. The maximum grafting yield was obtained at 30°C. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2629–2638, 2002

Key words: hydrophilic monomer; cellulose derivatives; grafted polymer; absorption capacity; grafting yield

INTRODUCTION

Cellulose is somewhat unique when compared with many other high polymers in that it contains so many functional hydroxyl groups, both primary and secondary.¹ It is a naturally occurring complex polysaccharide and the most abundant renewable organic raw material in the world.² The properties of cellulose may be modified by changing both the physical and chemical structures. The graft polymerization method has gained importance in modifying the chemical and physical properties of pure cellulose and has been investigated in the last few decades.² Grafting onto cellulose is possible by growing a polymer chain on active sites of the cellulose backbone.²

In a series of studies^{3–9} cellulose was grafted with vinyl monomers in a homogeneous solution system and was used as a membrane substrate

using different types of initiators.^{10–24} The modified cellulose membranes indicated an interesting specificity of solute permeability, depending on the monomers that were grafted.²⁵ According to the nature of the vinyl monomer grafted on the cellulose, it gains different physical and/or chemical properties. To increase the hydrophilicity, monomers containing hydrophilic groups must be grafted onto cellulose.² The use of a hydrophilic vinyl monomer, *N*-vinyl pyrrolidone (NVP), is expected to increase the affinity of the membranes for water and improve the solute permeability through them.²⁵ It also has good properties such as biocompatibility, low toxicity, and film-forming and adhesive characteristics.²⁶

However, unmodified cellulose is neither useful for selective binding nor dissolution in the usual solvents.²⁷ This is why cellulose derivatives, which are chemically modified celluloses with (active) functional groups installed prior to bead formation, offer the advantages of the formation of preactivated separation materials with a uniform distribution of active sites and the formation of a simple solvent system.²⁸

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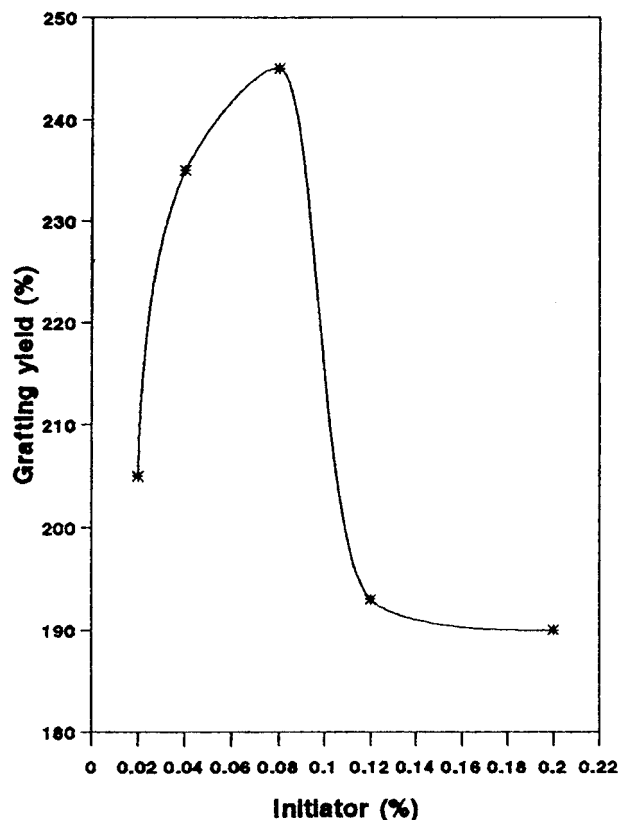


Figure 1 The effect of the percentage of CAS on the grafting yield using 3 : 1 CMCNa/HEC, 3 : 1 NVP-CMCNa/HEC, and a reaction time of 3 h at 30°C.

Therefore, it was the objective of the current study to explore the feasibility of producing hydrogel beads by grafting NVP to cellulose derivatives. A mixture was made of carboxymethyl cellulose in its sodium salt form (CMCNa) and hydroxyethyl cellulose (HEC) using ceric ammonium sulfate (CAS) as an initiator at 30, 50, 70, and 90°C during reaction periods of 30–180 min. We used the mixture of CMCNa with HEC because CMC cannot be used by itself because it tends to form intramolecular rather than intermolecular crosslinks, as reported in the literature²⁹; hence, the introduction of HEC avoids the formation of intramolecular crosslinks.

EXPERIMENTAL

Chemicals

All reagents, NVP (Merck, 98%), CMCNa [degree of substitution (DS) = 0.7–0.85, Fluka], and HEC (DS = 2.5, Merck) were used as received. The

CAS (Fluka AG, Buchs SG) was used as the initiator. Distilled water was used for the swelling.

Methods

Two grams of a mixture of CMCNa with HEC in a weight ratio of 3:1 was added to 50 mL of distilled water in a flask fitted with a mechanical stirrer, condenser, and dropping funnel. Then 0.02, 0.04, 0.08, 0.12, and 0.2% CAS and NVP in cellulose derivative/NVP ratios of 1 : 1, 1 : 2, 1 : 3, 1 : 4, and 1 : 5 were added to the reaction mixture. The reaction was carried out by placing the flask in a water bath at 30, 50, 70, and 90°C for 30, 60, 90, 120, and 180 min. After the desired reaction time had elapsed, the product was dewatered with ethanol and filtered, and the residue was air dried and weighed. The percentage of grafting level is reported as the weight of the graft polymer divided by the weight of the mixture of CMCNa/HEC used and multiplied by 100.

Characterization

Fourier transform IR (FTIR) spectroscopy was performed using a Jasco FTIR-300E spectropho-

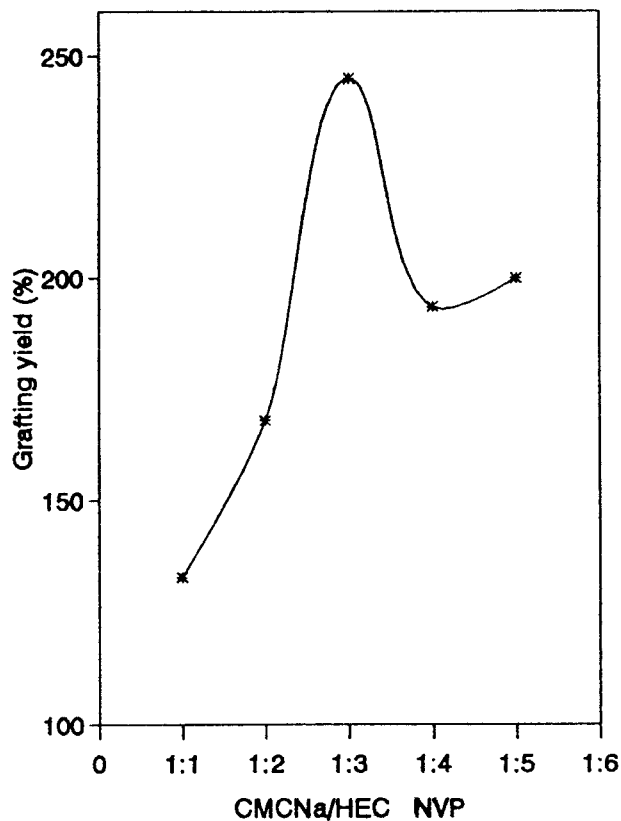


Figure 2 The effect of the NVP ratio on the grafting yield using 3 : 1 CMCNa/HEC, 0.08% CAS, and a reaction time of 3 h at 30°C.

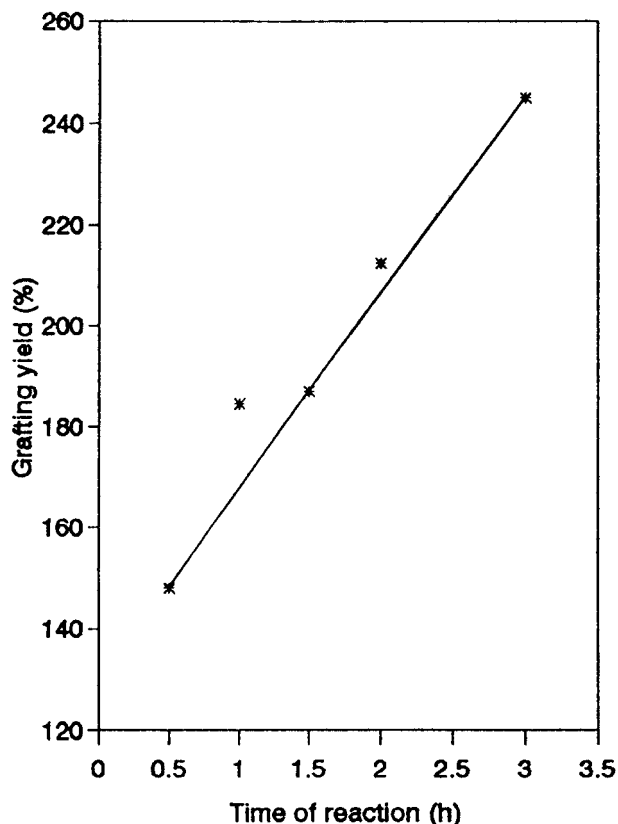


Figure 3 The effect of the reaction time on the grafting yield using 3 : 1 CMCNa/HEC, 3 : 1 NVP-CMCNa/HEC, 0.08% CAS, and a reaction temperature of 30°C.

tometer to characterize the grafted polymer. The grafted sample was ground, mixed with KBr in a ratio of 1:200 mg (cellulose/KBr), and pressed under a vacuum to form pellets. The absorption was measured over a range of 4000–400 cm^{-1} . A scanning electron microscope was also used (JSM-T20), and the elemental analysis for the grafted polymer products was analyzed using a Vario el Elementar.

Swelling Measurement

To determine the water absorption capacity of NVP-grafted CMCNa/HEC, an accurately weighed 0.100-g sample was allowed to soak for 30 min in 100 mL of distilled water at 25°C. The swollen polymer was then separated from the unabsorbed water by pouring it into a sintered glass filter (porosity 2) under pressure. The sintered glass filter was weighed to determine the weight of the water-swollen gel. The swelling characteristic is expressed as

$$\text{absorption capacity} = A = \frac{(W_1 - W_2)}{W_2}$$

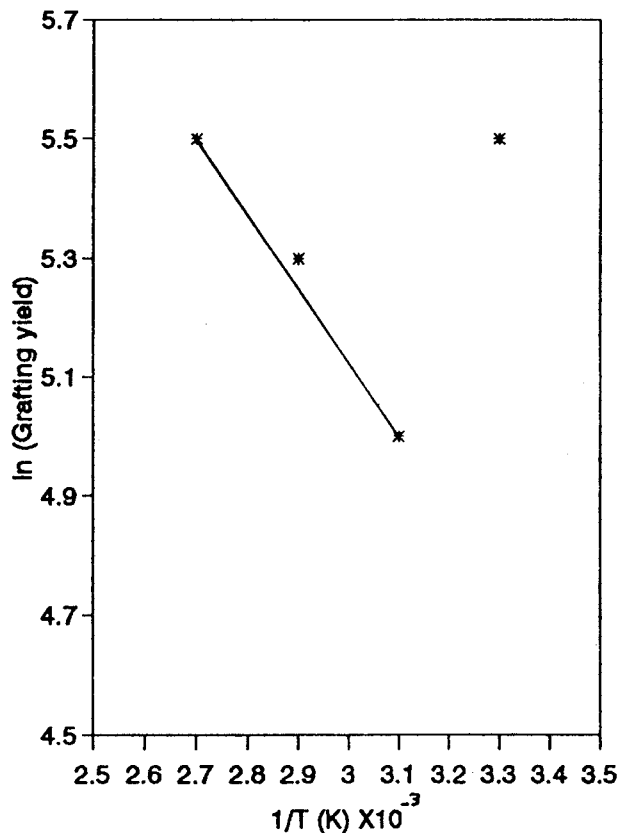


Figure 4 The natural log of the percentage of grafting yield versus $1/T$ using 3 : 1 CMCNa/HEC, 3 : 1 NVP-CMCNa/HEC, 0.08% CAS, and a reaction time of 3 h.

where W_1 and W_2 are the weights of the water-swollen gel and the dry absorbent, respectively. The absorption capacity was calculated as grams of water per gram of NVP-grafted CMCNa/HEC.

RESULTS AND DISCUSSION

The goal of our work was to provide a comparison of the grafted polymerization of NVP on CMCNa/HEC at different reaction temperatures. Reactions

Table I Elemental Analysis of NVP-g-CMCNa/HEC Sample

CMCNa/ HEC-NVP Ratio	Elemental Analysis (N%)	Grafting Yield (%)
1 : 1	2.55	133
1 : 2	3.29	168
1 : 3	5.12	245
1 : 4	4.25	193.5
1 : 5	4.47	200

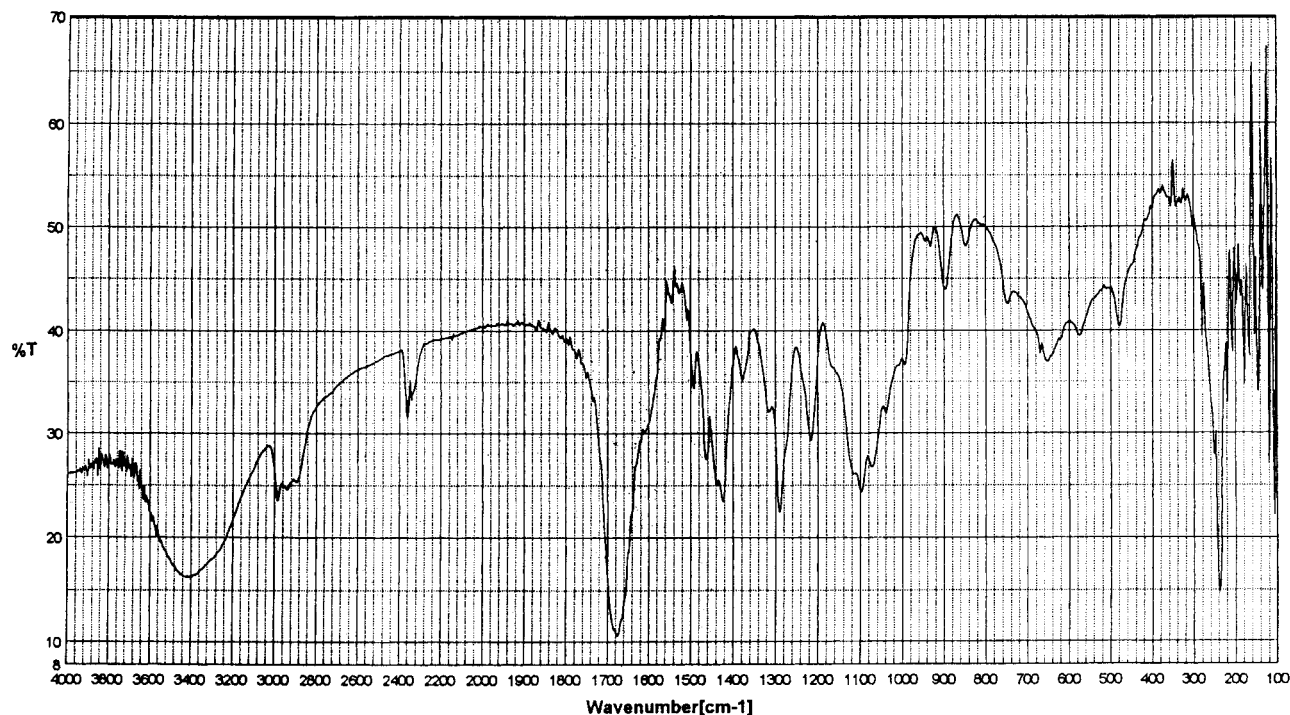


Figure 5 The IR spectrum of CMCNa/HEC grafted *N*-vinyl-2-pyrrolidone.

were conducted at 30, 50, 70, and 90°C for 30, 60, 90, 120, and 180 min using 0.02, 0.04, 0.08, 0.12, and 0.2% CAS and different cellulose derivatives/NVP ratios. The results are presented below for the grafting, characterization, and water absorption capacity under the different conditions.

Grafting

Numerous methods were developed for the grafting of vinyl monomers to cellulose. These are reviewed in a number of articles and a recent monograph.^{30–32} Among the most promising and practical of these is the ceric ion technique.^{33,34} Figure 1 summarizes the variations of the CAS percentage with the grafting yield percentage of NVP-grafted CMCNa/HEC. The percentage of grafting increased with increasing ceric concentration and reached a maximum value at about 0.08%. After this concentration the percentage of grafting decreased and began to level off. Schwab et al.³⁴ and Cumberbirch and Holker³⁵ previously observed this effect for other cellulosic systems. The decrease in grafting with the increased ceric ion concentration is believed to be due to an increase in the radical termination step involving the Ce^{4+} ion.

The same observation was noticed with the variation of the CMCNa/HEC to NVP ratio versus the percentage of grafting yield. This result is

examined in Figure 2. The grafting increases with the concentration of NVP and reaches a maximum at around a 1 : 3 CMCNa/HEC to NVP ratio. Further increases in the ratios lead to decreases and finally a leveling off of the grafting values. Although the reasons for this trend are not clear, there may be an association into micelles of the NVP in the aqueous medium at higher ratios, which possibly reduces the effective monomer concentration accessible for grafting.

On the other hand, using toluene instead of ethanol in dewatering the grafting polymer yielded higher grafting results (i.e., 300%). It is well known that during the graft polymerization onto cellulose with a redox type of initiator, some of the radicals resulting from decomposition of the initiator create active centers on the cellulose to initiate graft polymerization in the aqueous medium.² Therefore, the graft yield depends on the cellulose. The ceric ion initiator tends to produce grafting in the surface regions,³⁶ and toluene appeared to be sufficiently polar to remove surface CAS solution yet hydrophobic enough to not remove that sorbed into the fibers.

Figure 3 shows the effect of the reaction time on the percentage of grafting yield. One observes that the rate of grafting increased during the period of the reaction, and this is may be due to

the presence of a large excess of NVP available even after the longer reaction times.

As the temperature rose from 30 to 70°C for 180 min of grafting, the grafting decreased from 245 to 213.5%. The grafting yield remained almost the same at a reaction temperature of 90°C after the initial period, and higher grafting degrees were generally obtained at 30°C. Moreover, the natural log of the percentage of grafting after 3 h versus $1/T$ may be plotted³⁷ for the portion of 30–90°C. These values fall on a straight line, as seen in Figure 4. The calculated activation energy was 2.4×10^4 J/mol (5.7 kcal/mol). This overall activation energy reflects initiation, termination, and propagation, together with degradation.

Elemental Analysis

The nitrogen contents of the polymer products were analyzed. The results are summarized in Table I. It can be seen that the increase of the NVP content in the polymer results in the increase of the nitrogen content in the polymers until a CMCNa/HEC to NVP ratio of 1 : 3. This can be explained by the fact that a lower conversion of polymer was obtained at a higher NVP ratio. For instance, 245% graft yield can be obtained for a CMCNa/HEC to NVP ratio of 1 : 3; however, only 193.5 and 200% graft yields can be obtained for ratios of 1 : 4 and 1 : 5, respectively.

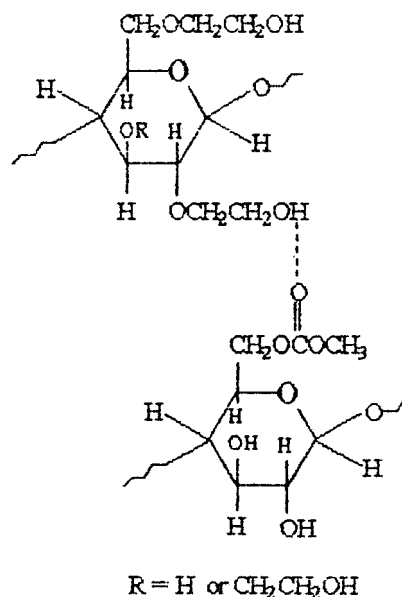
IR Spectra Analysis

The IR spectra of the CMCNa/HEC graft polymer of the NVP monomer (Fig. 5) showed absorption bands at 2360 and 1000–1100 cm^{-1} , which are characteristic of CMC,³⁸ and bands at 3400 cm^{-1} for the OH band, and 2983 cm^{-1} for the CH band, which are characteristic for both CMC and HEC.

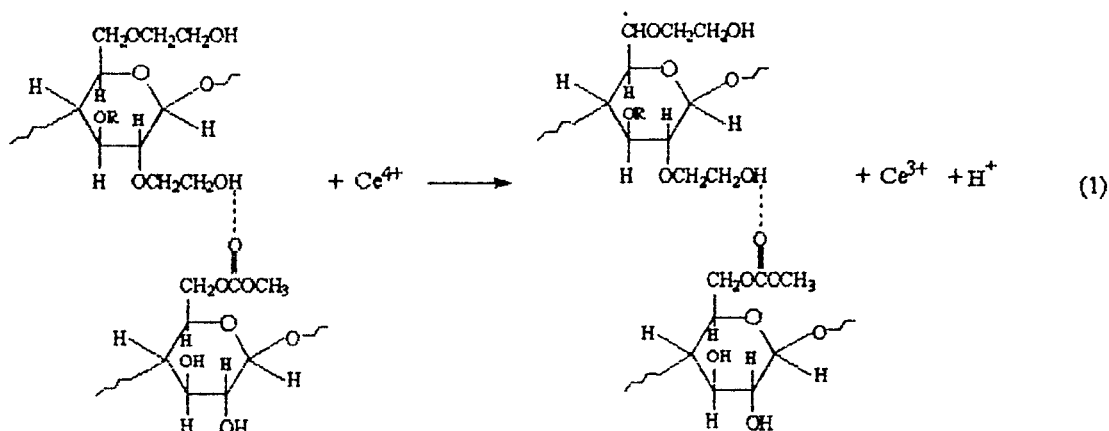
An additional band at 1675 cm^{-1} for the C=O band appears.

Polymer Characterization

As mentioned previously, the reason for using a mixture of CMCNa and HEC was to avoid the formation of intramolecular crosslinks.²⁹ Hence, one can suggest the following crosslinks between them:

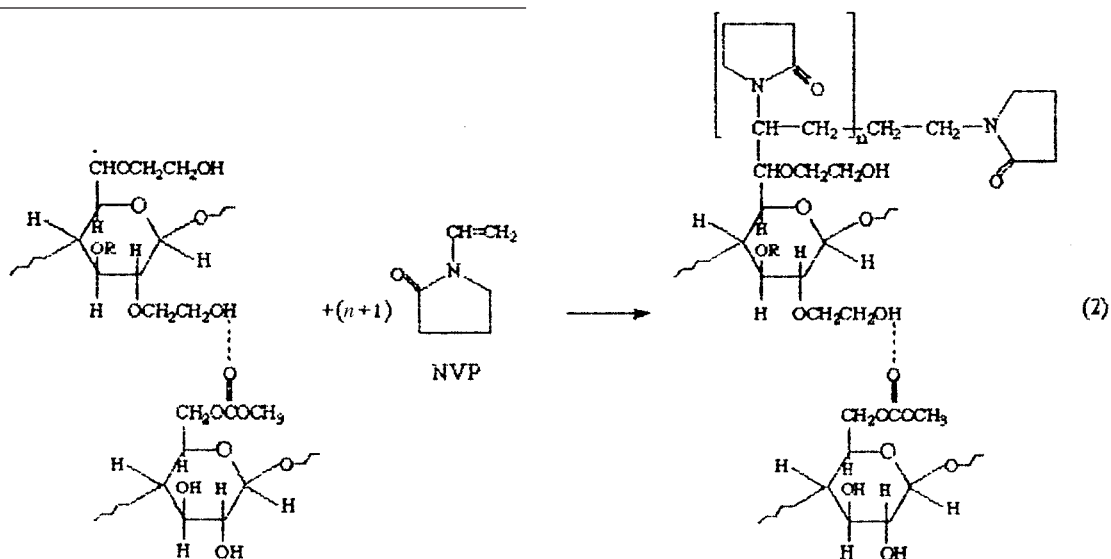


When ceric salts, such as CAS, were used as the initiator in the graft polymerization onto cellulose, it is proposed that a ceric ion–cellulose complex is initially formed as a result of one electron transfer. Then the ceric ion is reduced to cerous ion, and a free radical is created on the cellulose backbone.³⁹ According to this, one can consider the following mechanism:



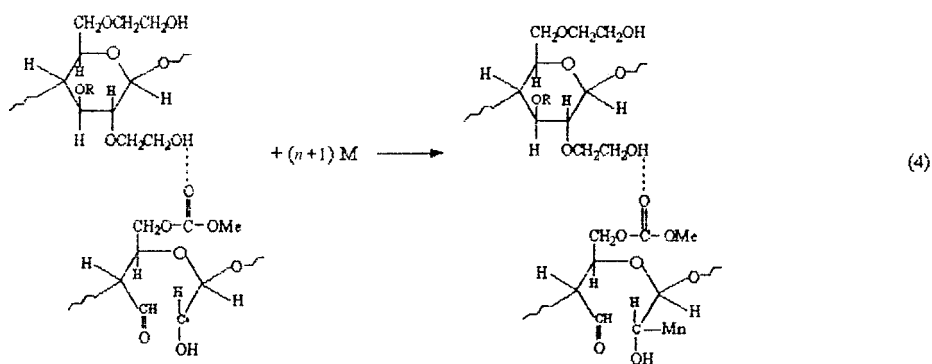
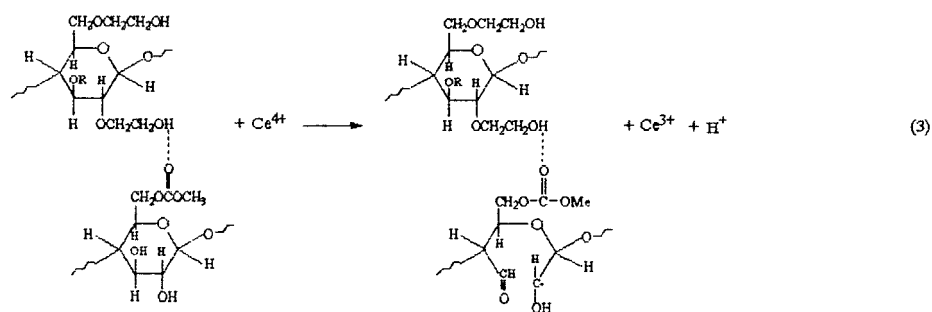
The radical site on the cellulose derivative then initiates graft polymerization of a polar vinyl

monomer, which is present in the reaction mixture.

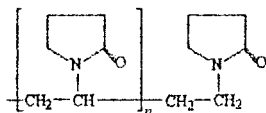


Another grafting site subsequently proposed⁴⁰ involves the oxidation of the anhydroglucose

unit. Thus, one can consider the following mechanism:

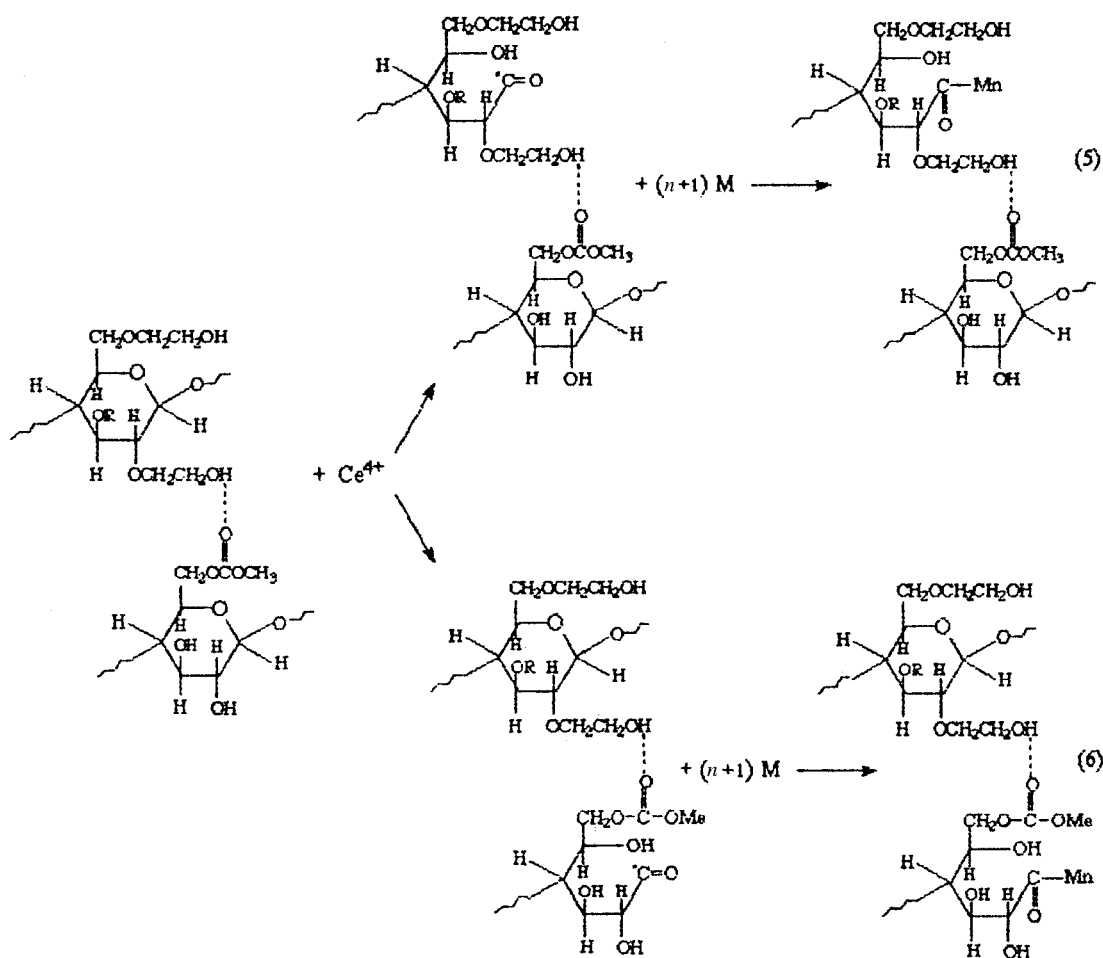


where Mn



The following initiation mechanism was also proposed, causing the formation of a block copol-

mer⁴⁰ as shown below:



Water Absorption Capacity

Liquid water sorption tests were performed on a total of 14 types of samples to assess the effect of the chemical composition (CMCNa/HEC–NVP ratio), initiator concentration, polymerization temperature, and manufacturing precipitation on the water-swelling properties of these cellulose-based materials.

It is generally known that the water retention properties of cellulosic materials are the result of

the interaction through bonding of the hydroxyl groups on the cellulose with water molecules.² We focused our attention on samples differing in their manufacturing precipitation (using either ethanol or toluene) but characterized by the same chemical composition (CMCNa/HEC ratio of 3 : 1, 0.08% Ce^{4+}) and polymerization procedure (CMCNa/HEC–NVP ratio of 1 : 3 at 30°C for 3 h). The degree of swelling in distilled water for samples A (CMCNa/HEC), B (NVP-grafted CMCNa/

Table II Swelling Degree of Samples A–C in Distilled Water

Sample	Type	Precipitation	Absorption Capacity (g/g)
A	CMCNa/HEC	Ethanol	382
B	NVP- <i>g</i> -CMCNa/HEC	Ethanol	138
C	NVP- <i>g</i> -CMCNa/HEC	Toulene	75

HEC, precipitated with ethanol), and C (NVP-grafted CMCNa/HEC, precipitated with toluene) is summarized in Table II.

A scanning electron microscope analysis was performed to elucidate the effects of different water sorption behaviors. The scanning electron micrographs of the desiccated gel surfaces reported in Figure 6(a–c) clearly evidence the morphological differences. The NVP-grafted CMCNa/HEC precipitated with toluene [Fig. 6(c)] is more dense and compact compared to the ungrafted CMCNa/HEC sample that is characterized by a microporous structure [Fig. 6(a)]. In the NVP-grafted CMCNa/HEC precipitated with ethanol an intermediate structure was observed [Fig. 6(b)]. Therefore, differences in the sorption behavior can be explained in terms of the different macroscopic morphologies obtained. In fact, the structures characterized by a higher microvoid size show remarkably higher sorption uptakes, which is attributable to the fact that part of the water condenses in the microvoids.

Effect of Polymerization Temperature

In radical polymerization started by the thermal decomposition of an initiator where transfer reactions are negligible, it is well known that as the temperature is increased, the rate of polymerization is strongly enhanced and the molecular weight of the polymer is reduced because of the increase of the rate termination and transfer reactions.⁴¹ The effect of the polymerization temperature on the absorption capacity of NVP-grafted CMCNa/HEC was investigated. Figure 7 shows that the absorption capacity of the polymer is decreased when the polymerization temperature is increased. This is because an increase in the temperature decreases the molecular weight, and there is an increase of the relative amount of polymer chain ends. Polymer chain ends do not contribute to the absorption capacity. Therefore, increasing the polymerization temperature results in a decrease in the absorption capacity of NVP-grafted CMCNa/HEC.

Effect of NVP Ratio in Grafted Polymer

Figure 8 shows that the swelling properties of NVP-grafted CMCNa/HEC are drastically affected by changing the NVP contents, indicating that the absorption capacity is increased as the NVP ratio is increased till a CMCNa/HEC to NVP ratio of 1 : 3. After this the absorption capacity of the polymer is reduced, and this may be because

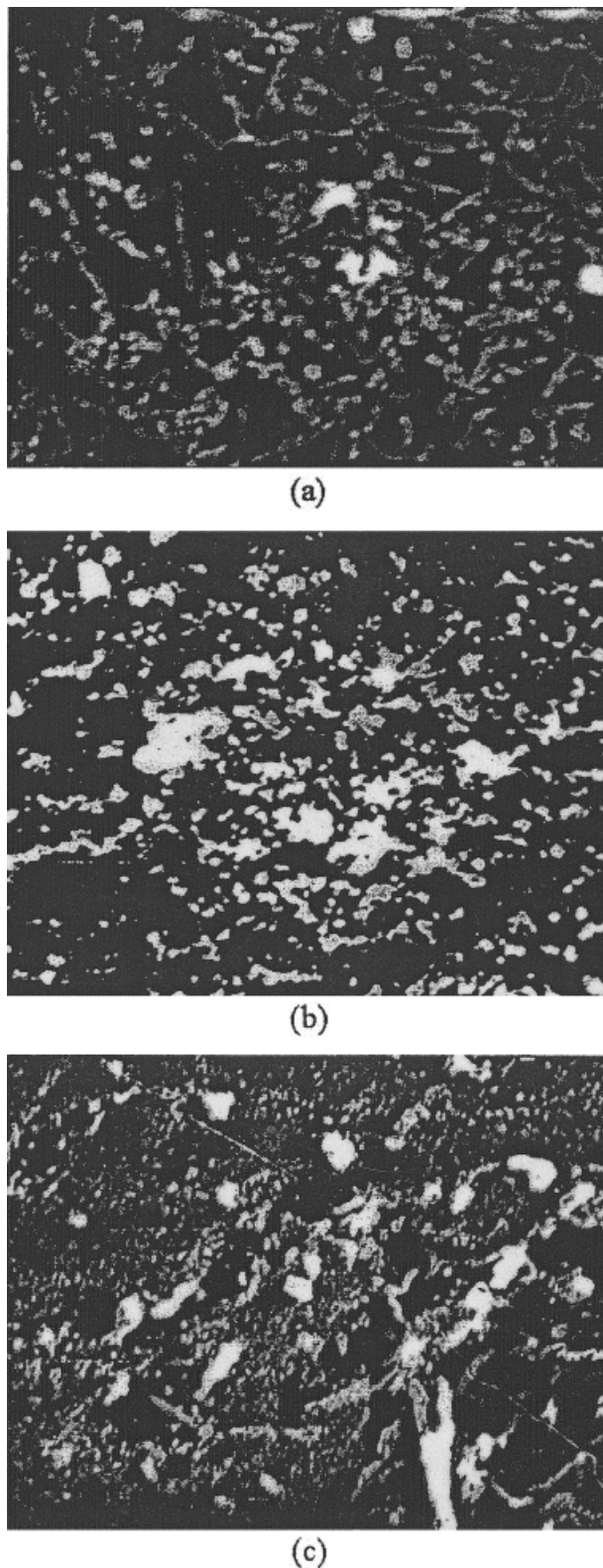


Figure 6 Electron micrographs of samples with a CMCNa/HEC ratio of 3 : 1 and 0.08% CAS : (a) ungrafted, (b) NVP-*g*-CMCNa/HEC (3 : 1), and (c) precipitated with ethanol.

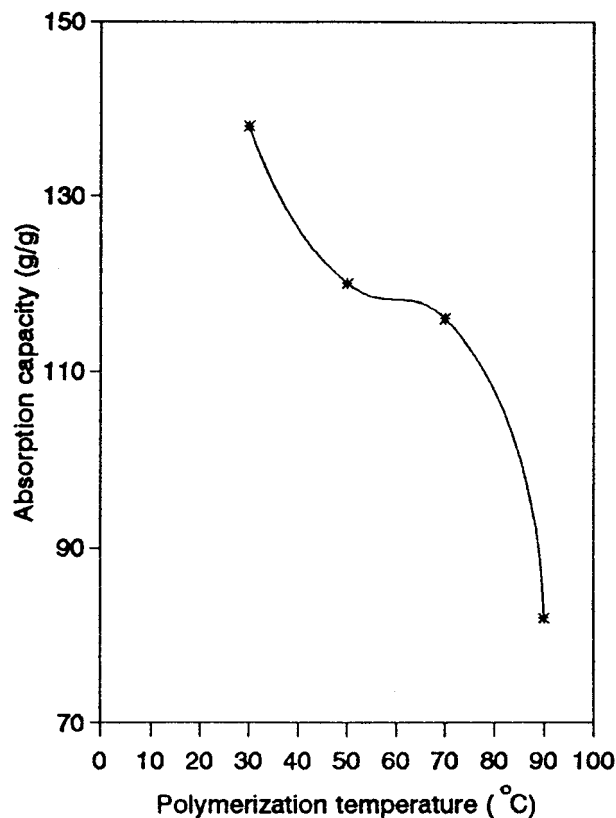


Figure 7 The Effect of the polymerization temperature using 3:1 CMCNa/HEC, 3:1 NVP-CMCNa/HEC, 0.08% CAS, and a reaction time of 3 h.

an increase of the NVP content affected the average molecular weight. It is well known that a decrease of the average molecular weight is accompanied by a decrease of the swelling ratio.⁴²

Effect of Initiator Concentration

Seymour and Carraher⁴³ demonstrated that the number-average degree of polymerization is inversely proportional to the square root of the concentration of the initiator. It is suggested that at a given monomer concentration, polymerization temperature, and crosslinking agent concentration the higher the initiator concentration the smaller the molecular weight of the polymer obtained. A decrease of the molecular weight causes the relative amount of polymer chain ends to increase. As mentioned, the polymer chain ends do not contribute to the absorption capacity. Therefore, increasing the initiator concentration results in the decrease in the absorption capacity of NVP-grafted CMCNa/HEC. The results of this study are shown in Table III.

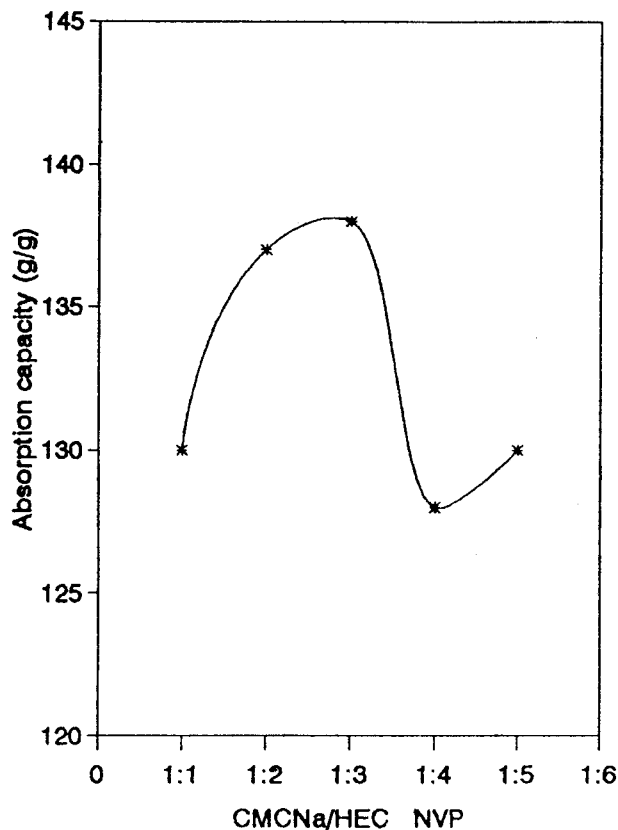


Figure 8 The effect of the NVP content using 3:1 CMCNa/HEC, 0.08% CAS, and a reaction time of 3 h at 30°C.

CONCLUSIONS

In this work NVP-grafted CMCNa/HEC was prepared using CAS as the initiator. The absorption behavior is related to their chemical composition and the precipitated solvent used. The decrease of the absorption capacity is due to the formation of a more dense and compact structure. The effects of the initiator concentration, polymerization temperature, and amount of NVP in the polymer were investigated. It was found that the absorption capacities decrease with increasing initiator

Table III Effect of Initiator Concentration on Absorption Capacity

Ce ⁴⁺ (%)	Absorption Capacity (g/g)
0.02	209
0.04	149
0.08	138
0.12	133
0.20	131

concentration, polymerization temperature, and amount of NVP in the grafted polymer.

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