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Synthesis and characterization of hydroxypropyl methylcellulose and ethyl acrylate graft copolymers

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Abstract

The synthesis of hydroxypropyl methylcellulose-*g*-poly (ethyl acrylate) was carried out by potassium persulfate induced graft copolymerization in homogeneous aqueous medium. By varying the reaction conditions, graft copolymers with different percentage of grafting were prepared. These graft copolymers were characterized by fourier transform infrared spectra (FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermogravimetric analyses (TGA), X-ray diffraction analysis (XRD), and dynamic light scattering (DLS) methods. The molecular weight of grafted and ungrafted polymer chains determined by gel permeation chromatography (GPC) increased with increasing monomer and matrix concentration but decreased with increasing initiator concentration and reaction temperature. The mechanical properties of graft copolymers were measured as function of the percentage of grafting. In addition, the equilibrium humidity adsorption behavior and the disintegration time of the grafted copolymer films were also studied.

Keywords: Graft copolymer; Hydroxypropyl methylcellulose; Ethyl acrylate; Cellulose derivatives; Characterization; Property

1. Introduction

Graft copolymerization is a useful technique for modifying the properties of the most abundant natural cellulose and cellulosics polymers (Bianchi, Bonazza, Marsano, & Russo, 2000; Bikkullova, Druzhinina, & Abronin, 2005; Canche-Escamilla, Rodriguez-Trujillo, Herrera-Franco, Mendizabal, & Puig, 1997; Chauhan, Guleria, & Sharma, 2005b; Coskun & Temuz, 2005; Elisabetta et al., 2005; Estella, Enrico, Laura, & Saverio, 1998; Khan, 2005; Mishra & Bajpai, 2005; Okieimen, 1998; Okieimen, Sogbaike, & Ebhoaye, 2005; Pradeep, Saikia, & Dass, 2004; Roman-Aguirre, Marquez-Lucero, & Zaragoza-Contreras, 2004; Trivedi, Kalia, Patel, & Trivedi, 2005). It is important to mention that not only pure cellulose have been modified but also several cellulose derivatives, either in pure or raw form. In recent years, Chauhan et al. reported the graft copolymerization of certain vinyl monomers onto hydroxypropyl cellulose (HPC) in order to obtain new polymeric materials for environmental management and investigated the optimum grafting conditions as well as the utilization as the sorption agent of some metal ions (Chauhan, Guleria, & Mahajan, 2001; Chauhan & Mahajan, 2002a, 2002b; Chauhan, Mahajan, Sddiqui, & Gupta, 2004b, 2004a; Chauhan, Singh, Chauhan, Verma, & Mahajan, 2005a, 2005b). They used pine needles from the huge forest of the Western Himalayas as a source of cellulose. Cellulose was derivatized to HPC, the useful water-soluble cellulose ether, and then, HPC was graft-copolymerized with the vinyl monomers. In addition, some reports on cellulose derivatives focus on the graft copolymerization of vinyl monomers onto ethyl cellulose (EC) in homogeneous organic solvent medium (AbdelRazik, 1990, 1992, 1994, 1996a, 1996b, 1997a; AbdelRazik, 1997b; Aggour, 1999; Aggour & AbdelRazik, 1999; Shen, Yu, & Huang, 2005). In some studies (Biswal & Singh, 2004; Vasile, Bumbu,

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Dumitriu, & Staikos, 2004; EI-Hady & Ibrahim, 2004; Okieimen & Ogbeifun, 1996; Zhang, Tan, & Li, 2000), carboxymethyl cellulose (CMC) has also been grafted with vinyl monomers in a homogeneous solution system, and the grafted copolymer obtained has been used as membrane substrates (Ibrahim, Flefel, & EI-Zawawy, 2002).

Among the cellulose derivatives, hydroxypropyl methylcellulose (HPMC) is an important potential material with a wide range of applications in drugs, textiles, foods, and paper. HPMC is formed by its reaction with chloromethane and epoxy propane. The structure of HPMC is shown in Fig. 1. It has a number of hydroxypropyl groups, introduced into the cellulose molecule, which promote its water solubility. HPMC is also easily available and very cheap. However, there are few reports on the graft copolymerization of HPMC in homogeneous aqueous medium. In our previous paper (Wang & Xu, 2006), the graft copolymerization of ethyl acrylate (EA) onto HPMC initiated by potassium persulfate (KPS) was carried out in an aqueous homogeneous medium under various conditions to determine the optimum conditions for the graft copolymerization. In this paper, we focus on the characterization and the properties of the HPMC and EA graft copolymer, and the results obtained were also used to elucidate the relationship between the structure of the graft copolymer and the properties of it. Furthermore, the grafted chains on the HPMC backbone can hinder the penetration and the absorption of water molecules onto cellulose chains.The decreasing of absorbed water is an indicator of the protective effect given to HPMC by grafting copolymerization, and the graft copolymers obtained could have utility in applications of the tablet coating materials.

2. Experimental

2.1. Materials

Hydroxypropyl methylcellulose (Taian Ruitai Cellulose Co., Ltd, Shandong, China) was dried in a vacuum desiccator on calcium chloride. Ethyl acrylate (Tianjin Chemical Reagent Co., Inc., Tianjin, China) was washed with 5% sodium hydroxide and stored below 5 °C after vacuum distillation. The potassium persulfate was reagent grade chemicals and used after recrystallization. All other reagents were laboratory grade chemicals and were used as such.

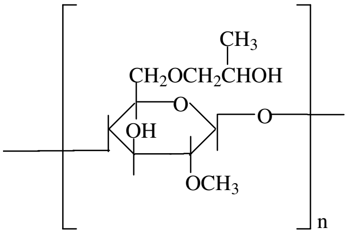

Fig. 1. Structure of hydroxypropyl methylcellulose.

2.2. Graft copolymerization

The graft copolymerization of EA onto HPMC was carried out by adding a calculated amount of HPMC (6 g) in a three-necked round-bottom flask containing a known amount of distilled water. The flask was fitted with an electrically operated stirrer and kept in a water bath maintained at 60 ± 1 °C. The solution was purged with nitrogen gas for about 30 min before adding KPS (0.15 g) into the flask. Then, EA (6 g) was charged into the flask to initiate the graft copolymerization after KPS interacting with HPMC for 5 min. The reaction mixture was stirred at a constant rate to avoid the adverse effect of stirring on graft copolymerization. The reactants were allowed to react about 4 h before the reaction was terminated.

2.3. Isolation of the grafted and ungrafted polymer chains

The rough product contained the HPMC graft copolymer and the PEA homopolymer was dried to a constant weight at 60 °C in a vacuum. The HPMC graft copolymer was separated from the PEA homopolymer by extraction (72 h) with acetone utilizing a Soxhlet apparatus. The PEA homopolymer (ungrafted PEA chains) was recovered from the acetone solution by reprecipitation into distilled water. Then, the two separated products were dried again under a vacuum. Finally, the purified copolymer HPMC-g-PEA obtained was hydrolyzed in 72% H_2SO_4 solution at 30 °C for 4 h to obtain the grafted PEA chains.

2.4. Definition of the grafting parameters

The monomer conversion was obtained gravimetrically. Percentage of grafting (G) and grafting efficiency (G_E) were calculated with the following equation after the HPMC-g-PEA, grafted PEA chains, and the HPMC were weighed

$$G(\%) = \frac{\text{Weight of PEA Grafted}}{\text{Weight of HPMC}} \times 100$$

$$G_{\mathrm{E}}(\%) = \frac{\text{Weight of PEA Grafted}}{\text{Weight of EA Reacted}} \times 100$$

3. Characterization and properties testing

FTIR spectra analyses were used to identify the graft copolymerization. The FTIR spectra of HPMC, PEA, and the grafted HPMC after 72 h of acetone extraction samples were recorded on KBr pallets using Nicolet 5DX Fourier transform infrared spectrophotometer.

Water dispersion samples for transmission electron microscopy (TEM JEOL CX-100II) were prepared by diluting in distilled water, dispersing, and depositing on perforated carbon films supported on copper grids.

Scanning electron microscopy (SEM) was utilized to examine the surface morphology of the grafted HPMC film samples. For this, the film samples were coated with a thin layer of electrically conductive material. The coating is achieved by sputtering of a heavy metal (Au). Samples were glued with an electrically conductive adhesive to a metal-base specimen holder to achieve good electrical contact with the grounded electrode. The micrographs were obtained on a Philips XL30 SEM.

Thermal analysis of HPMC and grafted HPMC have been carried out by recording thermogravimetric (TG) curve using Perkin-Elmer Pyris 6 system at a heating rate of 10 °C/min under nitrogen atmosphere.

X-ray diffraction patterns of samples of pure HPMC and pure HPMC-g-PEA were recorded at ambient conditions on an X-ray diffractometer, model X'Pert Pro (Philips), using CoKα radiation.

The weight-average molecular weight ($\overline{M_W}$ g/mol) of grafted and ungrafted PEA chains were measured by gel permeation chromatography (GPC) on a system equipped with a Agilent 1100 pump, three columns (79911GP-510, 79911GP-MXC, and 79911GP-504), and a BI-DNDC differential refractometer detector. The eluent was THF, and the flow rate was 1.0 mL/min. Monodispersed polystyrene (PSt) was used as the standard to generate the calibration curve.

Laser light scattering was performed with a commercial spectrometer (BI-200SM equipped with a 9000AT digital time correlation) and a solid-state laser (Changchun New Industries Optoelectronics Tech Co., Ltd. MGL 100; out power = 30 M_W at $\lambda = 532$ nm) as the light source was used. The graft copolymer solutions were equilibrated for 30 min before the measurements. The hydrodynamic radius (R_h) of the graft copolymer was measured with dynamic light scattering at 90°.

Mechanical properties tests were carried out at ambient conditions using a microprocessor-controlled material-testing machine (Testometric M350-10KN) loaded with a data analysis software package (WinTest Analysis 1.36 version). Measurements were performed using a calibrated load cell of 1 kN at a crosshead speed of 10 mm/min with an internal extensometer with automatic break detector having a constant gage length (30 mm) throughout the tests. Parameters such as the tensile strength and the corresponding elongation were determined. The numerical values were calculated as an average of the five measurements for each type of sample.

The graft copolymer free films were obtained by the casting of the HPMC-g-PEA copolymer water dispersion samples onto smooth glass plates. The films were dried in vacuum at room temperature for 48 h. The free films (20–30 μm in thickness) produced were tailored to 1 × 1 cm square samples, and put into the certain mount of simulated gastric fluid with moderate rotate speed at 37 °C. The time for the free films beginning to disintegrate was recorded.

Humidity resistance behaviors of studied by putting the known weight films of pure HPMC and pure HPMC-g-PEA in a desiccator with relative moisture 80% at room temperature for 72 h to reach the equilibrium humidity adsorption. The films were removed and weighed quickly. The percentage of equilibrium humidity adsorption was determined as follows:

$$\text{Percent of equilibrium humidity adsorption} = \frac{M_1 - M_2}{M_2} \times 100$$

where M_1 and M_2 represents the weights of the films after and before swelling moisture, respectively.

4. Results and discussion

4.1. Fourier transform infrared spectra (FTIR)

Infrared spectral analysis has been utilized to prove the grafting. For this purpose, the FTIR spectra of HPMC, PEA, and HPMC-g-PEA are shown in Figs. 2–4. From the spectra of HPMC (Fig. 2), it shows a strong absorption band at 3457.18 cm^{-1}, due to the stretching frequency of the –OH group. The band at 2928.28 cm^{-1} is the result of C–H stretching vibration. The bands around 1457.81 and 1378.06 cm^{-1} are assigned to –CH$_2$ scissoring and –OH bending vibration, respectively. The band at 1063.57 cm^{-1} is due to C–O stretching vibration.

In the case of PEA (Fig. 3), the absorption band at 2937.30 cm^{-1} is for the C–H stretching vibration. The absorption band at 1736.55 cm^{-1} corresponds to an ester carbonyl group (>CO) of the ethyl acrylate. Other bands at 1251.66 and 1171.16 cm^{-1} are attributed to C–O antisymmetric and symmetric stretching vibration, respectively.

The FTIR spectrum of HPMC-g-PEA grafted copolymer (Fig. 4) shows all the characteristic absorption of HPMC and also an obvious absorption band at 1739.22 cm^{-1} corresponding to the >CO group of the ethyl acrylate which was initially absent in pure HPMC (Fig. 2). As homopolymerization PEA was initially

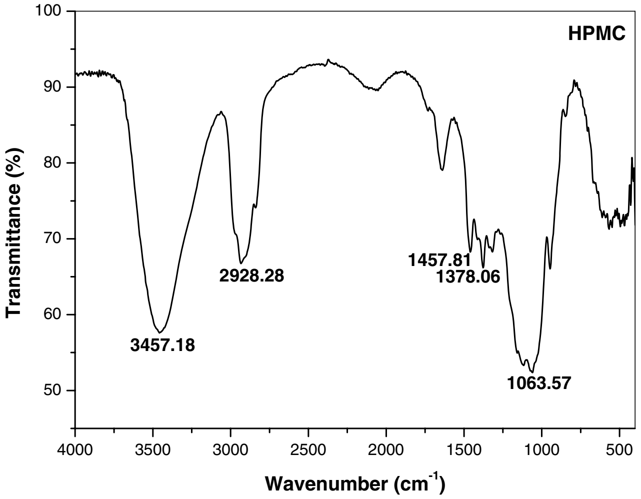

Fig. 2. FTIR spectra of HPMC.

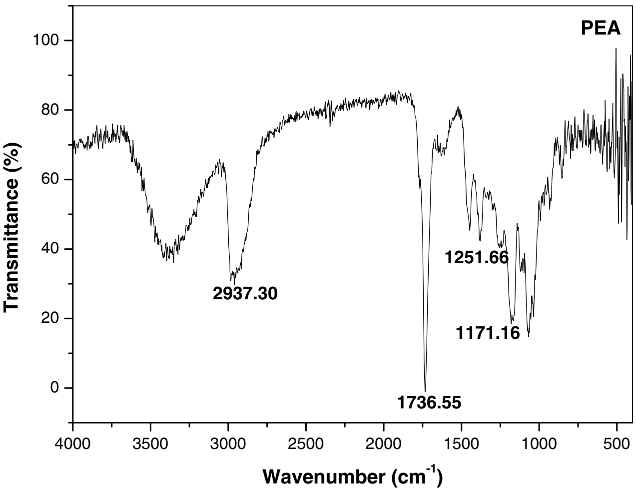

Fig. 3. FTIR spectra of PEA.

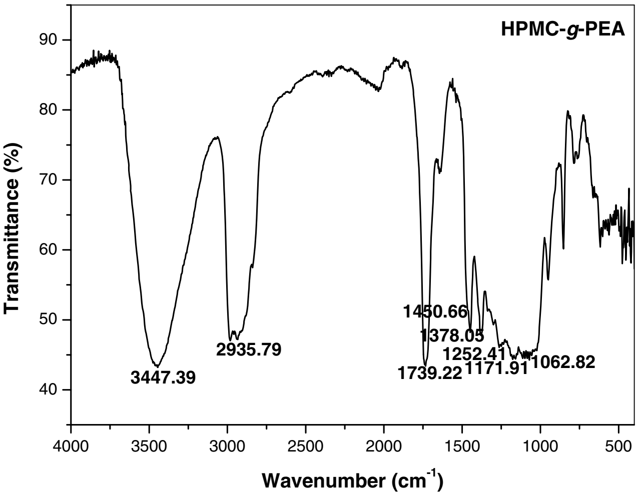

Fig. 4. FTIR spectra of HPMC-g-PEA.

removed from the reaction product, the presence of new absorption band at 1739.22 cm^{-1} has confirmed the presence of >CO group and provided evidence for grafting of EA onto the HPMC.

4.2. Transmission electron microscopy (TEM)

Fig. 5 is the morphology micrographs of the water dispersions of HPMC-g-PEA obtained by TEM technique. It was evident from the Fig. 5 that there are large numbers of spherical particles, which were very stable and were not agglomerated to one another. The size of the spherical particles ranges from 200 nm (a) to 500 nm (b). Kislenko (1999) has reported that graft polymerization of vinyl monomers onto water-soluble polymers occurs according to the mechanism of emulsion polymerization. During the graft polymerization, water dispersion of HPMC-g-PEA graft copolymer with spherical particles is formed. Each particle consists of the core of the hydrophobic PEA grafted chains and the hydrophilic shell of the HPMC backbone, and the stability of the water dispersion comes from the amphiphilicity of the graft copolymer.

4.3. Thermogravimetric analyses (TGA)

Thermogravimetric analyses (TGA) were carried out in order to evaluate the effect of the chemical modification on the thermal stability of HPMC. Fig. 6 shows the thermograms for (a) HPMC and (b) HPMC-g-PEA, respectively. Primary thermograms were obtained by plotting the percentage residual weight against the temperature. The initial decomposition temperature (IDT) was calculated from the end of the initial straight-line portion of the curve from where the actual decomposition is believed to have occurred. It can be observed that IDT of HPMC is raised from 320 to 335 °C upon grafting copolymerization. Increasing in IDT of HPMC after grafting copolymerization indicates that the chemical change in HPMC has occurred upon grafting and the thermal stability of the PEA grafted HPMC has been found to be higher in comparison to the pure HPMC as clear from the TGA curves.

4.4. X-ray diffraction analysis (XRD)

The X-ray diffraction patterns of pure HPMC and pure HPMC-g-PEA at room temperature from $2\theta = 5°$ to $80°$ are shown in Fig. 7, and the crystallinity calculated were listed in Table 1. It can be seen that the XRD pattern

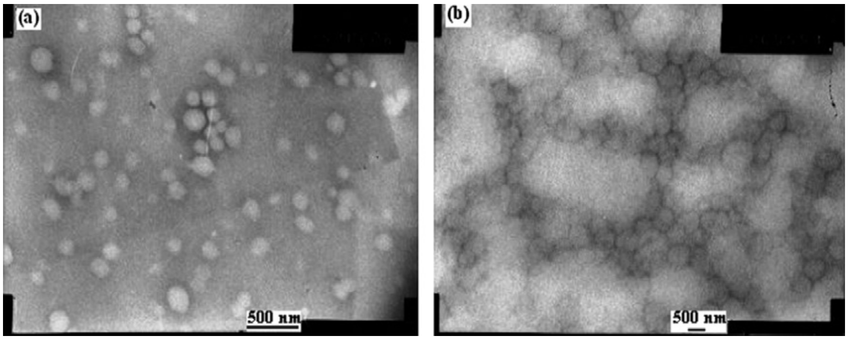

Fig. 5. Transmission electron micrograph of the HPMC-g-PEA water dispersions.

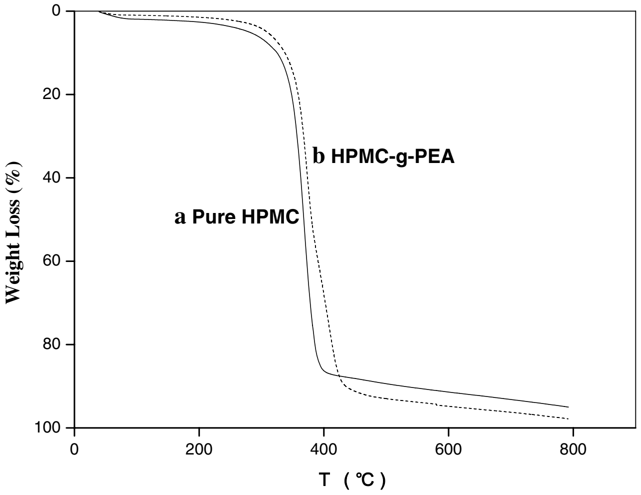

Fig. 6. Primary thermograms of (a) pure HPMC and (b) HPMC-g-PEA.

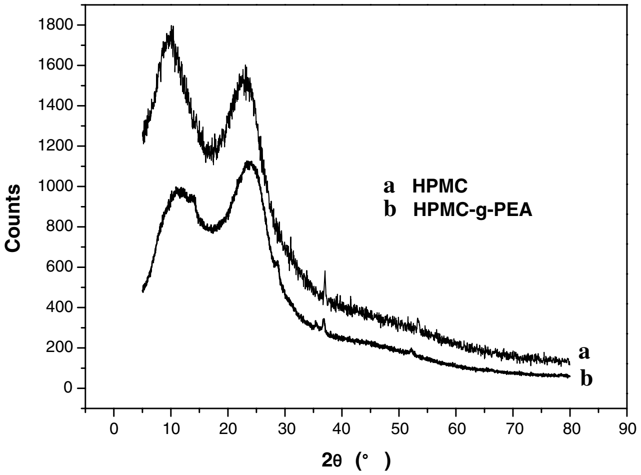

Fig. 7. X-ray diffraction pattern of (a) HPMC and (b) HPMC-g-PEA.

Table 1
The crystallinity calculated by XRD analysis of HPMC and HPMC-g-PEA samples

Sample	Crystallinity (%)
HPMC	28.39
HPMC-g-PEA	24.65

of pure HPMC shows, like all other natural polymers, partial crystalline nature (Mishra & Bajpai, 2005), and the percentage crystallinity calculated (Yang, Su, & Gao, 1990) is 28.39%. Furthermore, the XRD pattern of pure HPMC-g-PEA is similar to that of pure HPMC, which keeps the specific crystal plane diffraction (1 0 1) and (0 0 2) of the pure HPMC. However, the peaks seem to become more dispersive than those of pure HPMC and the percentage crystallinity calculated is 24.65%. It is well known that heterogeneities in the bulk structure of the cellulose give rise to accessible and inaccessible regions where reactions of cellulose hydroxyl take place first in more accessible amorphous regions and then on the surface of elementary crystallites. XRD results evidence that grafted PEA chains were formed after graft copolymerization, which enlarges the proportion of amorphous regions and makes the percentage crystallinity smaller.

4.5. Gel permeation chromatography (GPC)

The weight-average molecular weights of grafted and ungrafted polymer chains are the important parameters for the graft copolymerization. The molecular weight of grafted chain was investigated by isolating the grafted PEA chains (after hydrolyzing the anhydroglucose chains of HPMC in the graft copolymers), determining the molecular weight by GPC and comparison with the molecular weight of ungrafted PEA chains formed in the homopolymerization. Furthermore, the effects of reaction conditions on the molecular weight of graft and ungrafted PEA polymer chains are studied, and the results are given in Figs. 8–15.

Figs. 8 and 9 show the variation of $\overline{M_{\mathrm{W}}}$ for grafted and ungrafted PEA chains, respectively. The results showed that $\overline{M_{\mathrm{W}}}$ of both grafted and ungrafted PEA chains increase gradually with increasing the monomer concentration and reaction time. Higher monomer concentration and longer reaction time could lead to the formation of higher-molecular weight polymer chains because there is a higher amount of available monomer for the graft copolymerization and homopolymerization simultaneously, and a longer time is needed to consume all the monomer. And, the increasing trend of $\overline{M_{\mathrm{W}}}$ has indicated that the frequency of chains termination was not increased on increasing the concentration of the monomer in the reaction mixture (Gupta, Sahoo, & Khandekar, 2002). In addition, all $\overline{M_{\mathrm{W}}}$ of grafted PEA chains are larger than those of ungrafted PEA chains, which is agree with the results of the report (Bianchi et al., 2000). Especially, the reaction condition with higher monomer concentration (0.35 mol/L) favors the homopolymerization, which can lower the difference between $\overline{M_{\mathrm{W}}}$ of the grafted PEA chains and $\overline{M_{\mathrm{W}}}$ of the ungrafted PEA chains.

The effects of initiator concentration and reaction time on $\overline{M_{\mathrm{W}}}$ of grafted and ungrafted PEA chains are given in Figs. 10 and 11. As expected, molecular weight decreases as the initiator concentration increases, which indicates that the grafting reaction follows the classical free-radical polymerization kinetics (Canche-Escamilla et al., 1997). The results in Figs. 10 and 11 are consistent with this expectation. The declining trend in the molecular weight at higher KPS concentration is ascribed to the saturation of radical concentration, since a further increase in KPS concentration would lead to termination of the primary radicals. Furthermore, the decreasing trend in molecular weight of grafted and ungrafted PEA chains on increasing the concentration of KPS has suggested the primary radicals participation in a chain-termination process. This premature termination of growing chains has resulted in

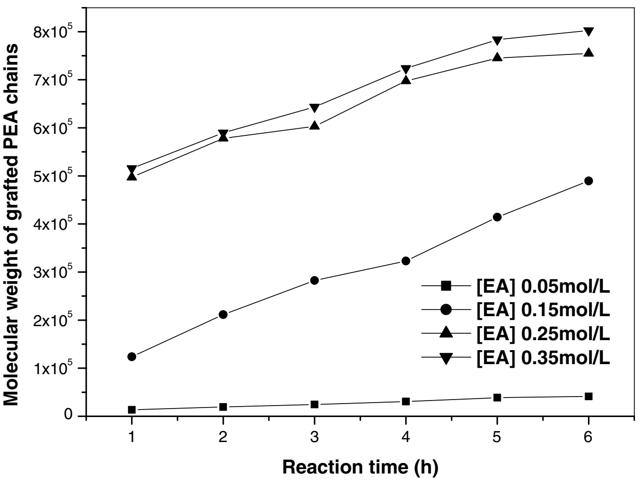

Fig. 8. Effect of monomer concentration on molecular weight of grafted PEA chains.

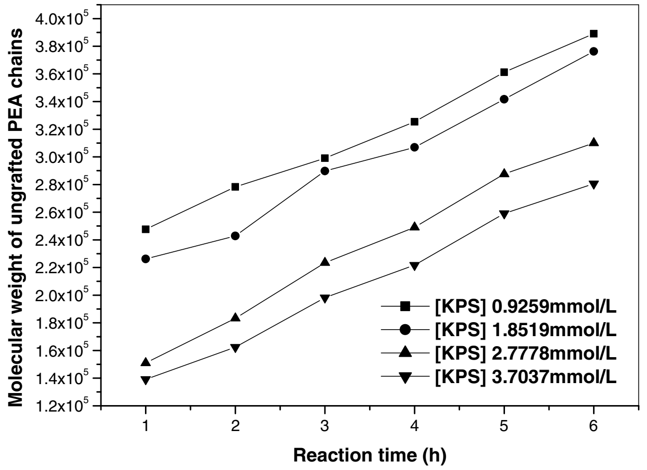

Fig. 11. Effect of initiator concentration on molecular weight of ungrafted PEA chains.

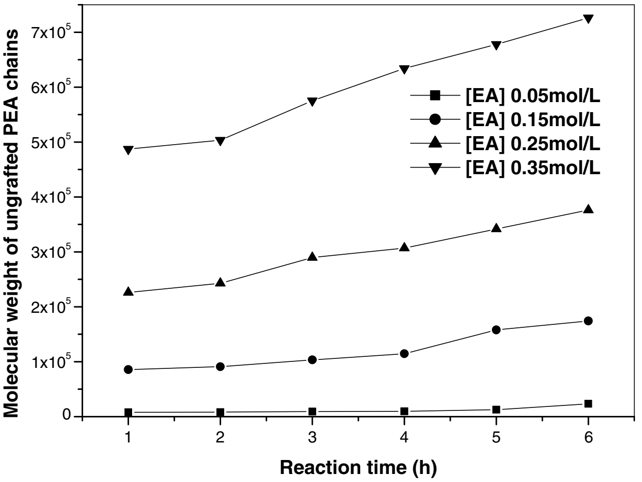

Fig. 9. Effect of monomer concentration on molecular weight of ungrafted PEA chains.

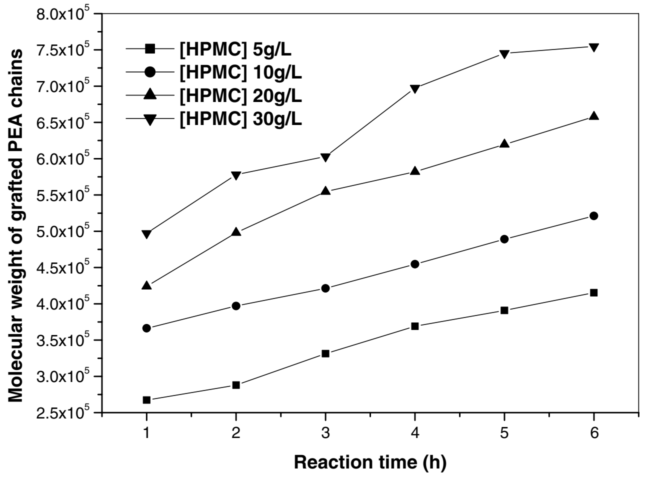

Fig. 12. Effect of matrix concentration on molecular weight of grafted PEA chains.

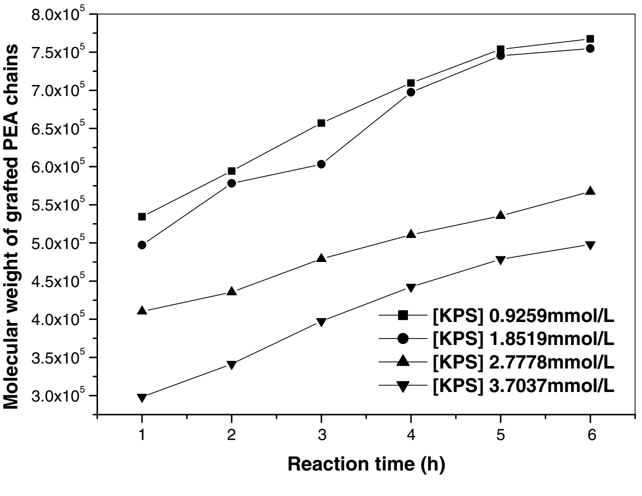

Fig. 10. Effect of initiator concentration on molecular weight of grafted PEA chains.

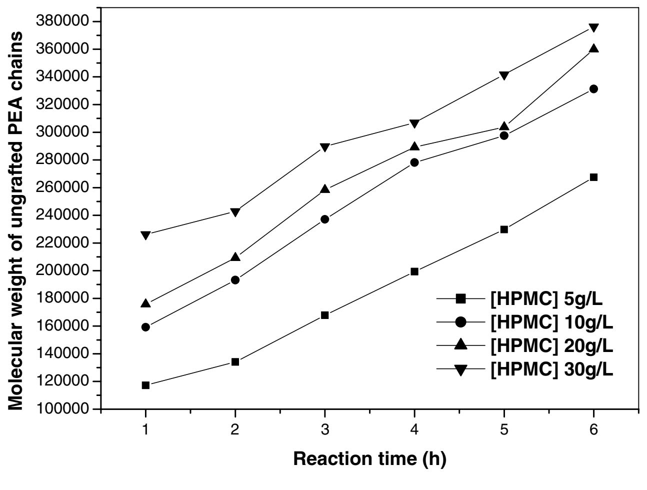

Fig. 13. Effect of matrix concentration on molecular weight of ungrafted PEA chains.

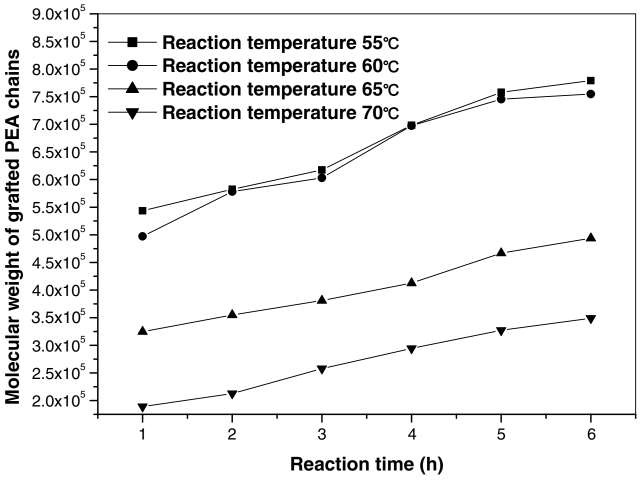

Fig. 14. Effect of reaction temperature on molecular weight of grafted PEA chains.

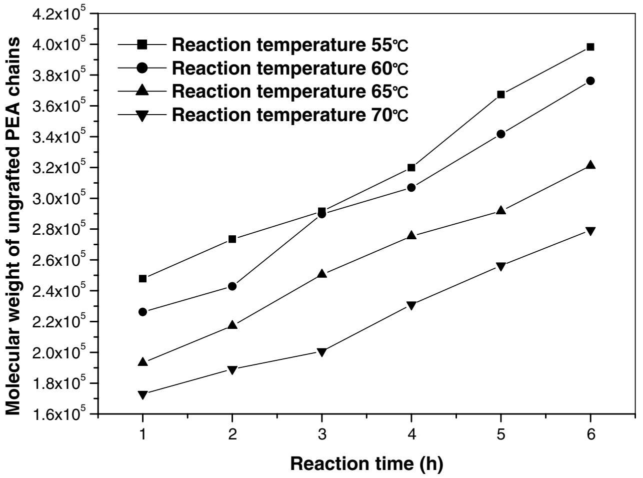

Fig. 15. Effect of reaction temperature on molecular weight of ungrafted PEA chains.

decrease in molecular weight of grafted and ungrafted PEA chains (Gupta et al., 2002). Finally, higher initiator concentration yields a higher number of reactive sites on the HPMC backbone, which lowers the number of EA molecules grafted onto average per reactive site on the basis of fixing monomer concentration. As a result, the molecular weights of the PEA polymer chains could be decreased at higher initiator concentration, and the similar results are also reported in the literature (Canche-Escamilla et al., 1997; Nishioka, Matsumoto, Yumen, Monmae, & Kosai, 1986).

The results of effect of the matrix concentration on $\overline{M_W}$ of grafted and ungrafted PEA chains are listed in Figs. 12 and 13. The data obtained showed that the molecular weight increased with increasing the matrix concentration. An increase in matrix concentration would facilitate the formation of cellulose macroradicals because of an increase in the relative ratio of cellulose to primary radicals, leading to an increase in molecular weight. On the other hand, an increase in solution viscosity with increasing matrix concentration would lead to the gel effect (Eromosele & Hamagadu, 1993), which also causes an increase in the molecular weight of the PEA polymer chains. The results in Figs. 12 and 13 are consistent with the discussions above.

Figs. 14 and 15 show the reaction temperature and reaction time dependence of $\overline{M_W}$ for grafted and ungrafted PEA chains. As can be seen from the Figs. 14 and 15, the molecular weight of grafted and ungrafted PEA chains decrease with increasing reaction temperature, and increase with increasing reaction time. This result is consistent with expectation based on the kinetics of radical polymerization (Nishioka et al., 1986). With increasing the reaction temperature, the rate of chain transfer and chain termination reactions between grafted chains and monomer molecules is faster than that of the graft copolymerization, which reduces the molecular weight of grafted chains as well as ungrafted PEA chains. In addition, higher reaction temperature favors the homopolymerization (Gupta et al., 2002), which makes the values of grafted and ungrafted molecular weight of the PEA chains close.

4.6. Dynamic light scattering (DLS)

As can be seen from Fig. 5, water dispersion of HPMC-g-PEA graft copolymer consists of large number of spherical particles. Since the varying factors determine the relative population of various reactants species generated in the graft copolymerization system, after the molecular weight being discussed, effects of reactants concentration on the particle size were also investigated here.

Fig. 16 represents the effect of monomer concentration on the particle size at 60 °C. The particle size has shown the increasing trend on increasing the monomer concentration. In the EA concentration range of 0.13–0.51 mol/L, the particle size apparently increased as the EA concentration grew because the local EA concentration in or

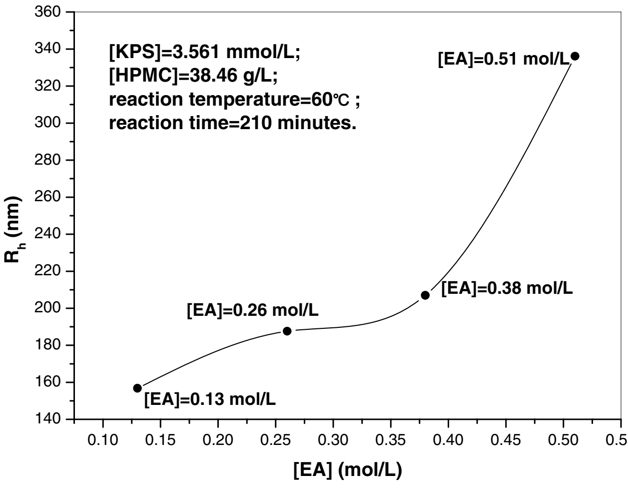

Fig. 16. Effect of monomer concentration on particle size.

around the HPMC backbone increased, and this helped the diffusion of the monomer molecules to the macroradical sites on the HPMC backbone. As a result, the EA molecules continuously graft onto the HPMC backbone, and the molecular weight of grafted PEA chains consequently increases with increasing the monomer concentrations (see Fig. 8), which makes the particle size become larger.

Effect of KPS concentration on the particle size has been studied at the fixed monomer concentration and the fixed matrix concentration (Fig. 17). The particle sizes were recorded at different KPS concentrations ranging from 1.187 to 5.935 mmol/L. The particle sizes have shown an appreciable decreasing trend within the whole KPS concentration range studied. The declining trend of the particle sizes on increasing the KPS concentration has indicated that within this concentration range, KPS actively participate in the formation of reactive sites on the HPMC backbone (Gupta & Sahoo, 2000), and the more reactive sites at HPMC backbone were formed with increase in the initiator concentrations, which lowers the number of EA molecules grafted onto average per reactive site on the basis of fixing monomer concentration. Therefore, the molecular weight of grafted PEA chains decreases with increasing the KPS concentration (see Fig. 10), which causes the particle size to be smaller as is clear from the curve shown in Fig. 17.

The influence of varying amount of HPMC on the particle size is shown in Fig. 18. It can be observed from this figure that, within the matrix concentration range studied, the particle size consistently increases by increasing the amount of HPMC. As discussed above, the increasing matrix concentration would favor the formation of cellulose macroradicals due to an increase in the relative ratio of cellulose to primary radicals, which leads to an increase in molecular weight. In addition, the gel effect produced with increasing matrix concentration would also cause an increase in the molecular weight of the PEA polymer chains. Consequently, the increasing molecular weight of grafted PEA chains makes the particle size larger.

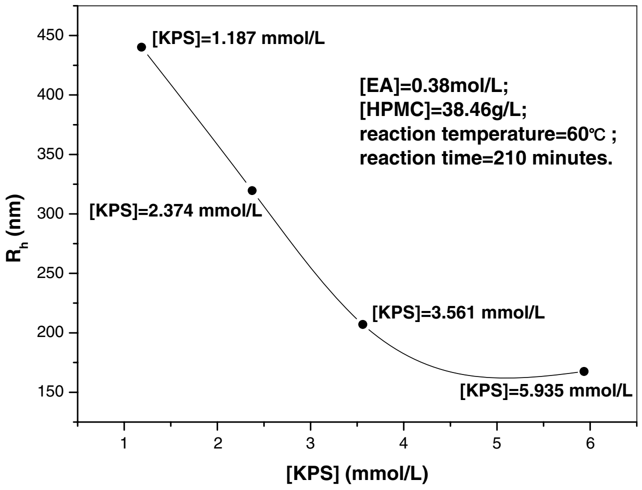

Fig. 17. Effect of initiator concentration on particle size.

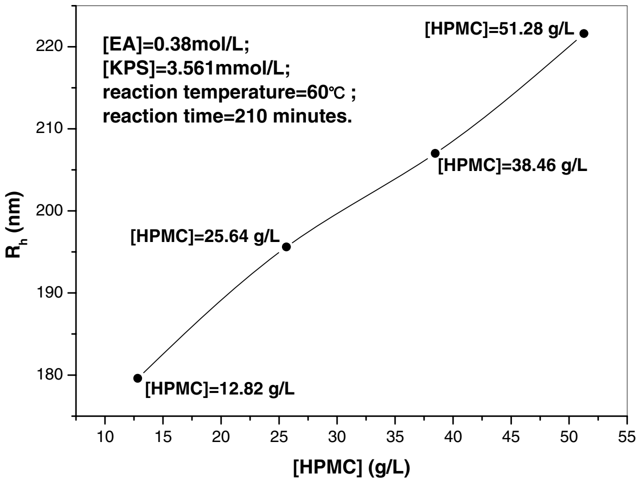

Fig. 18. Effect of matrix concentration on particle size.

4.7. Mechanical properties

The tensile strength and percent elongation were evaluated from the load versus extension curves. The load versus extension curves followed a similar pattern for both HPMC and grafted HPMC samples. The results of the relative mechanical parameters were plotted as a function of the percentage of grafting (*G*) as shown in Fig. 19. The results show that the tensile strength decreases and the percent elongation increases with increasing the percentage of EA grafting onto HPMC. Grafting copolymerization of EA onto HPMC backbone obviously affects the mechanical properties of the HPMC. This could be attributed to the dead weight of the graft PEA chains attached to the cellulose backbone. The reason for the decreasing tensile strength is likely that a greater disruption of the strong hydrogen bonds in the HPMC main structure cannot compensate for the relatively weaker bonds produced by the graft copolymer with EA (Khan, 2004). This is brought about by the difference in the position of the grafted chain with the HPMC backbone relative to the

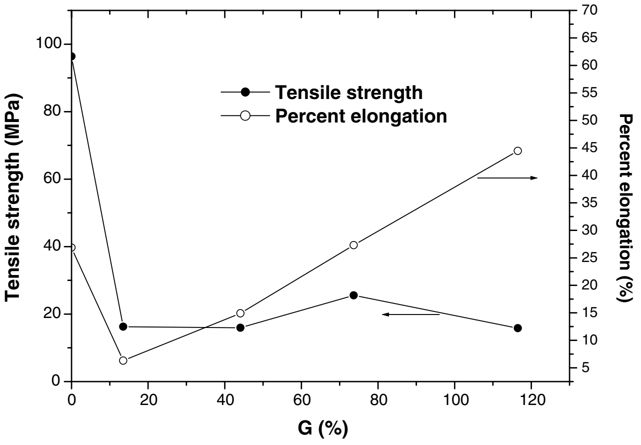

Fig. 19. Variation of the mechanical properties with the percentage of grafting.

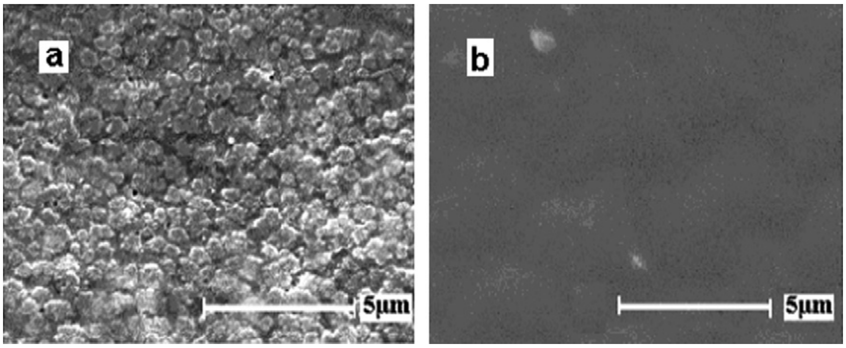

Fig. 20. SEM micrographs of grafting copolymers (a) $G = 13.50\%$; (b) $G = 73.67\%$.

equivalent cellulose-substrate-based copolymer, thus reducing the hydrogen bonding or the degree of chain entanglements. The increase in percent elongation suggests that the degree of molecular chain mobility becomes higher by PEA graft copolymer add-on with the HPMC sample. All the results indicate that the grafted PEA chains play and enhance the internal plasticization role through increasing the amount of grafted PEA chains. Especially, the tensile strength and the percent elongation reach the minimum with the lowest G (13.5%) value, which can be attributed to the phase separation phenomenon owing to the low G value. Canche-Escamilla et al. (1997) have reported that there will be a better adhesion between the matrix and the reinforcing agent when the grafted cellulose is used because the monomer grafted to the cellulose acts as a compatibilizer with the matrix. The graft copolymer cannot play the compatibilizer role with a little amount of grafted PEA chains at the lowest G value. While, with increasing the G values, this phase separation phenomenon would be lightened, which can be proved from the scanning electron micrographs shown in Fig. 20 (with the same magnification).

4.8. Equilibrium humidity adsorption behavior and disintegration property testing

Equilibrium humidity adsorption behavior and the disintegration property of the HPMC and pure HPMC-g-PEA samples were investigated as a function of the G values and the results are shown in Fig. 21. It is observed from the data that the percent of equilibrium humidity adsorption decreases about five times with the increase in the G values, while the disintegration time increases gradually with increasing the G values. The results of the percent of equilibrium humidity adsorption for HPMC-g-PEA samples suggest that the grafted PEA chains admixed molecularly throughout the HPMC matrix, thus the hydrophilic ability of HPMC matrix was decreased with increasing the amount of hydrophobic grafted PEA chains. Furthermore, introducing hydrophobic grafted PEA chains makes the graft copolymer samples insoluble and the disintegration time becomes longer with the increase in G values.

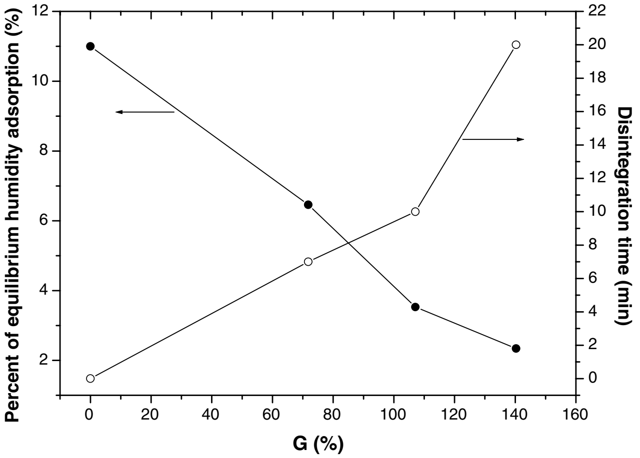

Fig. 21. Effect of G values on the percent of equilibrium humidity adsorption and the disintegration time.

5. Conclusions

Grafting of HPMC to prepare its EA-grafted copolymers has been carried out successfully in an aqueous homogeneous medium. FTIR spectra of the HPMC-g-PEA confirmed the existence of a chemical link between the HPMC and the PEA. Water dispersion of graft copolymer with spherical particles is formed during the graft polymerization. Grafting PEA chains enhanced the thermal stability of the HPMC backbone. XRD results evidence that grafted PEA chains enlarge the proportion of amorphous regions of HPMC. The molecular weight of grafted and ungrafted PEA chains and the particle sizes were strongly dependent on the variations in graft copolymerization conditions. The tensile strength decreases and the percent elongation increases with increasing the percentage of EA grafting onto HPMC. In addition, the hydrophilic ability of HPMC was decreased with increasing the amount of grafted PEA chains.

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References

AbdelRazik, E. A. (1990). Homogeneous graft copolymerization of acrylamide onto ethylcellulose. *Polymer, 31*, 1739–1744.

AbdelRazik, E. A. (1992). Photoinduced graft-copolymerization of dichlorodimethylsilane onto ethyl cellulose in homogeneous media. *Journal of Photochemistry and Photobiology A-Chemistry, 63*, 75–86.

AbdelRazik, E. A. (1994). Thermal graft copolymerization of 4-vinyl pyridine onto ethyl cellulose in homogeneous media. 1. Influence of ammonium persulfate. *Acta Polymerica, 45*, 50–54.

AbdelRazik, E. A. (1996a). Aspects of thermal graft copolymerization of methyl methacrylate onto ethyl cellulose in homogeneous media. *Carbohydrate Polymers, 31*, 23–27.

AbdelRazik, E. A. (1996b). Grafting of dichlorodimethylsilane onto cellulose acetate as a model system in homogeneous media. *Polymer International, 40*, 207–211.

AbdelRazik, E. A. (1997a). Aspects of thermal graft copolymerization of methyl methacrylate onto ethyl cellulose in homogeneous media. *Polymer-Plastics Technology and Engineering, 36*, 891–903.

AbdelRazik, E. A. (1997b). Photoinduced graft copolymerization of ethyl acrylate, methyl methacrylate and methyl acrylate onto ethyl cellulose in homogeneous media. *Journal of Photochemistry and Photobiology A-Chemistry, 107*, 271–274.

Aggour, Y. A. (1999). Homogeneous graft copolymerization of 2-acrylamido-2-methylpropanesulphonic acid onto ethyl cellulose. *Journal of Polymer Materials, 16*(1), 1–6.

Aggour, Y. A., & AbdelRazik, E. A. (1999). Graft copolymerization of end allenoxy polyoxyethylene macromonomer onto ethyl cellulose in a homogeneous system. *European Polymer Journal, 35*, 2225–2228.

Bianchi, E., Bonazza, A., Marsano, E., & Russo, S. (2000). Free radical grafting onto cellulose in homogeneous conditions. 2. Modified cellulose-methyl methacrylate system. *Carbohydrate Polymers, 41*, 47–53.

Bikkullova, A. R., Druzhinina, T. V., & Abronin, I. A. (2005). Characteristics of heterophase radical graft polymerization of methyl methacrylate on polymer fibers. *Fibre Chemistry, 37*(1), 11–17.

Biswal, D. R., & Singh, R. P. (2004). Characterisation of carboxymethyl cellulose and polyacrylamide graft copolymer. *Carbohydrate Polymers, 57*, 379–387.

Canche-Escamilla, G., Rodriguez-Trujillo, G., Herrera-Franco, P. J., Mendizabal, E., & Puig, J. E. (1997). Preparation and characterization of henequen cellulose grafted with methyl methacrylate and its application in composites. *Journal of Applied Polymer Science, 66*, 339–346.

Chauhan, G. S., Guleria, L. K., & Mahajan, S. (2001). A study in sorption of some metal ions on novel hydrogels based on modified cellulosics and 2-acrylamido-2-methyl propane sulphonic acid. *Desalination, 141*, 325–329.

Chauhan, G. S., & Mahajan, S. (2002a). Use of novel hydrogels based on modified cellulosics and methacrylamide for separation of metal ions from water systems. *Journal of Applied Polymer Science, 86*, 667–671.

Chauhan, G. S., & Mahajan, S. (2002b). Structural aspects and nature of swelling medium as equilibrium swelling determinants of acrylamide and cellulosic-based smart hydrogels. *Journal of Applied Polymer Science, 85*, 1161–1169.

Chauhan, G. S., Sharma, R., & Lal, H. (2004a). Synthesis and characterization of graft copolymers of hydroxypropyl cellulose with acrylamide and some comonomers. *Journal of Applied Polymer Science, 91*, 545–555.

Chauhan, G. S., Mahajan, S., Sddiqui, K. M., & Gupta, R. (2004b). Immobilization of lipase on hydrogels: structural aspects of polymeric matrices as determinants of enzyme activity in different physical environments. *Journal of Applied Polymer Science, 92*, 3135–3143.

Chauhan, G. S., Singh, B., Chauhan, S., Verma, M., & Mahajan, S. (2005a). Sorption of some metal ions on cellulosic-based hydrogels. *Desalination, 181*, 217–224.

Chauhan, G. S., Guleria, L., & Sharma, R. (2005b). Synthesis, characterization and metal ion sorption studies of graft copolymers of cellulose with glycidyl methacrylate and some comonomers. *Cellulose, 12*, 97–110.

Coskun, M., & Temuz, M. M. (2005). Grafting studies onto cellulose by atom-transfer radical polymerization. *Polymer International, 54*, 342–347.

EI-Hady, B. A., & Ibrahim, M. M. (2004). Graft copolymerization of acrylamide onto carboxymethylcellulose with the xanthate method. *Journal of Applied Polymer Science, 93*, 271–278.

Elisabetta, P., Silvia, V., Enrico, P., Alessandro, M., Enrico, F., Giorgio, L., et al. (2005). Thermal analysis and characterization of cellulose grafted with acrylic monomers. *Thermochimica Acta, 425*, 173–179.

Eromosele, I. C., & Hamagadu, T. J. (1993). Graft copolymerization of methylmethacrylate onto caesarweed fibers by the potassium permanganate-toluene redox system. *Journal of Applied Polymer Science, 50*, 645–649.

Estella, B., Enrico, M., Laura, R., & Saverio, R. (1998). Free radical grafting onto cellulose in homogeneous conditions. 1. Modified cellulose-acrylonitrile system. *Carbohydrate Polymers, 36*, 313–318.

Gupta, K. C., & Sahoo, S. (2000). Ceric ion initiated grafting on cellulose from binary mixture of acrylonitrile and methylacrylate. *JMS Pure and Applied Chemistry, A37*(5), 447–468.

Gupta, K. C., Sahoo, S., & Khandekar, K. (2002). Graft copolymerization of ethyl acrylate onto cellulose using ceric ammonium nitrate as initiator in aqueous medium. *Biomacromolecules, 3*, 1087–1094.

Ibrahim, M. M., Flefel, E. M., & EI-Zawawy, W. K. (2002). Cellulose membranes grafted with vinyl monomers in a homogeneous system. *Polymers for Advanced Technologies, 13*, 548–557.

Khan, F. (2004). Photoinduced graft-copolymer synthesis and characterization of methacrylic acid onto natural biodegradable lignocellulose fiber. *Biomacromolecules, 5*, 1078–1088.

Khan, F. (2005). Characterization of methyl methacrylate grafting onto preirradiated biodegradable lignocellulose fiber by γ-radiation. *Macromolecular Bioscience, 5*, 78–89.

Kislenko, V. N. (1999). Emulsion graft polymerization: mechanism of formation of dispersions. *Colloids and Surface A: Physicochemical and Engineering Aspects, 152*, 199–203.

Mishra, A., & Bajpai, M. (2005). Synthesis and characterization of polyacrylamide grafted copolymers of kundoor mucilage. *Journal of Applied Polymer Science, 98*, 1186–1191.

Nishioka, N., Matsumoto, Y., Yumen, T., Monmae, K., & Kosai, K. (1986). Homogeneous graft copolymerization of vinyl monomers onto cellulose in a dimethyl sulfoxide-paraformaldehyde solvent system IV. 2-Hydroxyethyl methacrylate. *Polymer Journal, 18*(4), 323–330.

Okieimen, F. E., & Ogbeifun, D. E. (1996). Graft copolymerization of modified cellulose, grafting of acrylonitrile, and methyl methacrylate on carboxy methyl cellulose. *Journal of Applied Polymer Science, 59*, 981–986.

Okieimen, F. E. (1998). Graft copolymerization of vinyl monomers on cellulosic materials. *Die Angewandte Makromolekulare Chemie, 260*, 5–10.

Okieimen, F. E., Sogbaike, C. E., & Ebhoaye, J. E. (2005). of cadmium and copper ions from aqueous solution with cellulose graft copolymers. *Separation and Purification Technology, 44*, 85–89.

Pradeep, D., Saikia, C. N., & Dass, N. N. (2004). Thermal behavior of some homogeneously polymethyl methacrylate (PMMA)-grafted high α-cellulose products. *Journal of Applied Polymer Science, 92*, 3471–3478.

Roman-Aguirre, M., Marquez-Lucero, A., & Zaragoza-Contreras, E. A. (2004). Elucidating the graft copolymerization of methyl methacrylate onto wood-fiber. *Carbohydrate Polymers, 55*, 201–210.

Shen, D. W., Yu, H., & Huang, Y. (2005). Densely grafting copolymers of ethyl cellulose through atom transfer radical polymerization. *Journal of Polymer Science: Part A: Polymer Chemistry, 43*, 4099–4108.

Trivedi, J. H., Kalia, K., Patel, N. K., & Trivedi, H. C. (2005). Ceric-induced grafting of acrylonitrile onto sodium salt of partially carboxymethylated guar gum. *Carbohydrate Polymers, 60*, 117–125.

Vasile, C., Bumbu, G. G., Dumitriu, R. P., & Staikos, G. (2004). Comparative study of the behavior of carboxymethyl cellulose-g-poly(*N*-isopropylacrylamide) copolymers and their equivalent physical blends. *European Polymer Journal, 40*, 1209–1215.

Wang, L. L., & Xu, Y. S. (2006). Preparation and characterization of graft copolymerization of ethyl acrylate onto hydroxypropyl methylcellulose in aqueous medium. *Cellulose, 13*, 191–200.

Yang, Z. L., Su, M. Y., & Gao, G. (1990). *Cellulose ether foundation and application*. Guangzhou, China: South China University of Technology Press (chapter 6).

Zhang, L. M., Tan, Y. B., & Li, Z. M. (2000). New amphoteric graft copolymers of sodium carboxymethyl cellulose with acrylamide and dimethylaminoethyl methacrylate: aqueous solution properties. *Journal of Applied Polymer Science, 76*, 305–310.