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Preparation and characterization of graft copolymerization of ethyl acrylate onto hydroxypropyl methylcellulose in aqueous medium

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Abstract

Graft copolymerization of ethyl acrylate (EA) onto water-soluble hydroxypropyl methylcellulose (HPMC) was investigated with potassium persulfate (KPS) as initiator in an aqueous medium. The effects of monomer concentration, initiator concentration, matrix concentration, reaction temperature, reaction time and pre-interacting time in terms of percentage of grafting (G) and grafting efficiency (G_E) are discussed. The graft copolymers were characterized by Fourier transform infrared spectra (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction analysis (XRD) and differential scanning calorimetry (DSC). In addition, equilibrium humidity adsorption behavior of the pure grafted copolymers was also studied.

Abbreviations: DSC – Differential scanning calorimetry; EA – Ethyl acrylate; FTIR – Fourier transform infrared spectra; HPMC – Hydroxypropyl methylcellulose; KPS – Potassium persulfate; SEM – Scanning electron microscopy; TEM – Transmission electron microscopy; XRD – X-ray diffraction analysis

Introduction

Cellulose is one of the most abundant of the naturally occurring polymers. It has been the subject of a great deal of research in recent times, mainly with respect to attempts to modify its physical and chemical structure as a means of improving its properties and broadening its industrial applications. Many investigators (Padma et al. 1980; Canche-Escamilla et al. 1997; Liu and Hsieh 2003; Bikkullova et al. 2005; Mehmet and Temuz 2005) have reported modifications by means of the graft copolymerization of vinyl monomers onto cellulose, often using different initiator systems (Gupta and Sujata 2000; Pradeep et al. 2004; Roman-Aguirre et al. 2004). The properties of the grafted copolymers produced can then be tailored by the chemical structure of the monomers, the length of the grafted segment and the grafting parameters. Various vinyl monomers, such as methyl methacrylate (Saikia and Ali 1999; Ferdous 2005), 4-vinylpyridine (Ghanshyam et al. 2000), acrylonitrile (Estella et al. 1998; Gupta and Sujata 2001) and styrene (Inderjeet et al. 2005), have been used for effecting cellulose modifications, but only a few studies have been reported on the graft copolymerization of ethyl acrylate onto cellulose (Gupta et al. 2002; Elisabetta et al. 2005). In addition, many of the results reported were obtained for heterogeneous graft copolymerization systems in which the partitioning of the reactants

between the polymeric substrate-aqueous phase and the transfer of the reactants across phase boundaries could affect grafting characteristics (Okieimen and Ogbeifun 1996). The homogeneous aqueous system for graft copolymerization is consequently considered to be environmental friendly with no resulting organic solvent pollution and an area of research worth further study. Kislenko (1999, p 199) has reported that stable water dispersions can be formed during the graft polymerization of vinyl monomers onto water-soluble polymers (polysaccharides and their derivatives) and that the valuable colloid chemical properties of water dispersions formed allow these to be used as film-forming dispersions, lubricants and metal working fluids, soil conditioners and flocculants. In the investigation reported here, an effort has been made to study the grafting copolymerization of ethyl acrylate (EA) onto the water-soluble, cellulose-derivative hydroxypropyl methylcellulose (HPMC) using potassium persulfate (KPS) as the initiator in aqueous medium, and the grafting parameters have been determined. In addition, the graft copolymerization was characterized by the FTIR, SEM, TEM, XRD and DSC methods. The equilibrium humidity adsorption behavior was also studied.

Experimental

Materials

Hydroxypropyl methylcellulose (Taian Ruitai Cellulose, Shandong, China) was dried in a vacuum desiccator on calcium chloride. Ethyl acrylate (Tianjin Chemical Reagent, Tianjin, China) was washed with 5% sodium hydroxide and stored below 5 °C following vacuum distillation. The potassium persulfate was a reagent-grade chemical and used after recrystallization.

Graft copolymerization

The first step of the graft copolymerization of EA onto HPMC was the addition of a calculated amount of HPMC (9.57–38.28 g/l) into 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 the desired temperature (50–70 °C). This solution was first purged with nitrogen gas for about 30 min before KPS (1.772–5.316 mmol/l) was added to the flask. After the KPS had pre-interacted with the HPMC for varying time intervals (0–20 min), EA (0.097–0.376 mol/l) was then added into the flask to initiate the graft copolymerization. The reaction mixture was stirred at a constant rate to avoid the adverse effect of stirring on graft copolymerization. The grafting reaction was allowed to continue for varying time intervals (0.33–4 h) before the reaction was terminated and the rough product dried to a constant weight at 60 °C in a vacuum. The dried product was extracted with acetone in a Soxhlet apparatus for 72 h in order to remove the PEA homopolymer, and the extracted product was finally dried and weighed. Since the factors that were varied determine the relative population of various reactants species generated in the reaction system that was used, the effects of these reaction conditions on grafting parameters were obtained by varying one reaction condition at a time.

Definition of grafting parameters

Percentage of grafting (G) and grafting efficiency (G_E) were calculated using the following equation after the HPMC-g-PEA, PEA chains, and the HPMC were weighed:

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

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

Characterization

The FTIR spectra of HPMC and grafted HPMC were recorded on KBr pallets using a Nicolet 5DX Fourier transform infrared spectrophotometer. FTIR spectra analyses were used to identify the graft copolymerization of EA onto HPMC. Surface micrographies of grafted and ungrafted HPMC films were obtained by SEM (Philips XL30 SEM) in which the films were covered with gold before the analysis in order to avoid elec-

trostatic charge. Water dispersion samples for transmission electron microscopy (JEOL CX-100II) were prepared by diluting the graft copolymerization product in distilled water, then dispersing and depositing it on perforated carbon films supported on copper grids. 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 CoKa radiation. The thermograms of the pure HPMC and Pure HPMC-g-PEA were obtained by using differential scanning calorimetry (DSC) in a NETZSCH 204 SYSTEM under a nitrogen atmosphere at a heating rate of 10 °C per minute.

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:

$$\text{Percent of equilibrium humidity adsorption} = \frac{W_1 - W_2}{W_2} \times 100$$

where W_1 and W_2 represents the weights of the films after and before swelling moisture, respectively.

Results and discussion

Graft copolymerization mechanism

In a system consisting of KPS, EA and HPMC, a possible explanation for the mechanism of graft copolymerization might be as follows:
Initiation

$$K_2S_2O_8 \rightarrow 2SO_4^{\cdot-}$$
$$\text{Cell-OH} + SO_4^{\cdot-} \rightarrow \text{Cell}\cdot$$
$$\text{Cell}\cdot + M \rightarrow \text{CellM}\cdot$$
$$M + SO_4^{\cdot-} \rightarrow M\cdot$$

Propagation:

$$\text{Cell } M\cdot + nM \rightarrow \text{Cell} - (M)_n - M\cdot$$
$$M\cdot + nM \rightarrow (M)_n - M\cdot$$

Termination:

$$\text{Cell}-(M)_n-M\cdot + \text{Cell-}(M)_m-M\cdot \rightarrow \text{Graft-copolymer}$$
$$(M)_n-M\cdot + (M)_m-M\cdot \rightarrow \text{Homopolymer}$$

in which Cell-OH represents the reactive group in the HPMC backbone, M is the monomer and CellM· and M· are the corresponding growing radicals.

Investigations on grafting parameters

Effect of monomer concentration

Figure 1 represents the effect of monomer concentration on G and G_E at 60 °C. G and G_E can be seen to have an increasing trend with increasing monomer concentration. In the EA concentration range of 0.097–0.376 mol/l, G and G_E apparently increased with increasing EA concentration; the clarification for this would be that the local EA concentration in or around the HPMC increases, and this helps the diffusion of the monomer molecules to the macroradical sites on the HPMC backbone. Secondly, the molecular weights of the grafted PEA chains increase with increasing monomer concentration, which would enhance the G as well as the G_E values. Thirdly, the apparent acceleration in G and G_E can also be attributed to the gel effect (Ighodalo et al. 1993), resulting from an enhanced solubility of PEA in its monomer with increasing EA concentration. This would

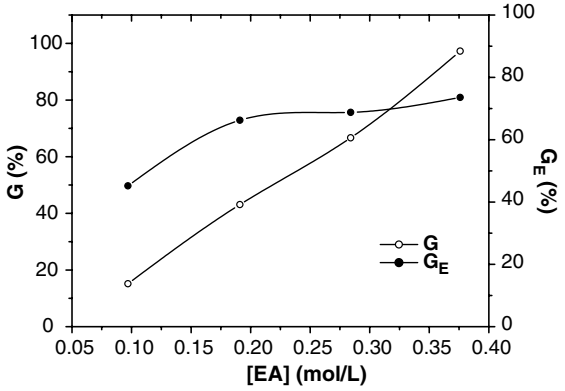

Figure 1. Effect of monomer concentration on %G (*white circle*) %G_E or (*black circle*). Reaction conditions: [KPS] = 2.658 mmol/l, [HPMC] = 28.710 g/l, reaction temperature = 60 °C, reaction time = 4 h, pre-interacting time = 5 min.

consequently increase the viscosity of the reaction medium and result in a reduced rate of termination by the coupling of growing polymer chains. In addition, with the higher monomer concentration, there are larger amounts of the growing polymeric chains that are formed which are in turn involved in generating additional active sites on HPMC by the chain transfer reaction. Similar results are reported by Subasini et al. (1981).

Effect of initiator concentration

The effect of KPS concentration on the grafting parameters was studied at a fixed monomer concentration and a fixed matrix concentration (see Figure 2). G and G_E were then recorded at different KPS concentrations ranging from 1.772–5.316 mmol/l. G and G_E were observed to have an appreciable increasing trend up to 4.430 mmol/l KPS; however, as the levels of KPS rose higher than 4.430 mmol/l, G and G_E values showed a corresponding decreasing trend. The increasing trend shown by G and G_E with increasing KPS concentration up to 4.430 mmol/l indicates that within this concentration range, KPS actively participates in the formation of reactive sites on the HPMC backbone (Gupta and Sujata 2000) and that more reactive sites on the HPMC backbone are formed with increasing initiator concentrations, which in turn enhances the G and G_E; this process is clear from the curves shown in Figure 2. With increases in KPS concentration beyond 4.430 mmol/l, the KPS starts to participate in the termination of the growing chains of the homocopolymers and grafted copolymers, which in turn lowers the G and G_E. Similar trends can also be seen in experiments described by Subasini et al. (1981).

Effect of matrix concentration

The influence of varying amount of HPMC on G as well as G_E is shown in Figure 3. It can be observed from this figure that, within the backbone concentration range studied, G consistently decreases with increasing amounts of HPMC but that G_E increases only slightly over the full range of HPMC content studied. The results of Figure 3 can be explained on the basis of the fact that although the weight of the grafted PEA chains may increase with increasing HPMC concentrations, the decrease in the monomer-to-backbone ratio lowers G. In addition, the number of HPMC macroradicals that can interact with each other to terminate the reaction increases with increasing HPMC, which can make the termination rate of graft copolymerization surpass the rate of initiation, thereby also lowering G. Similar results have also been reported in the case of ethyl methacrylate being grafted onto polyvinyl alcohol (Chowdhury 1998).

Effect of reaction temperature

Figure 4 shows the influence of the reaction temperature on G and G_E: G increases with increases in the reaction temperature from 50 to 65 °C but decreases with as the reaction temperature surpasses 65 °C, while G_E decreases

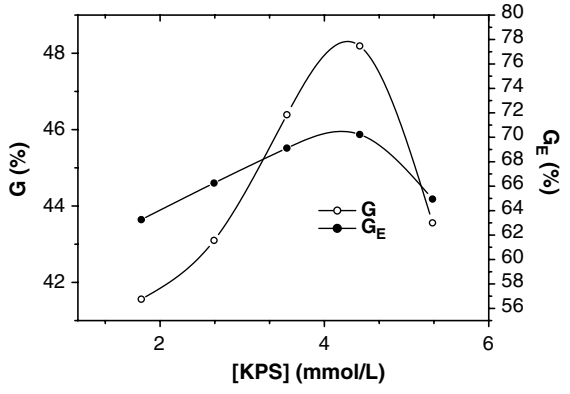

Figure 2. Effect of initiator concentration on %G (*white circle*) or %G_E (*black circle*). Reaction conditions: [EA] = 0.191 mol/l, [HPMC] = 28.710 g/l, reaction temperature = 60 °C, reaction time = 4 h, pre-interacting time = 5 min.

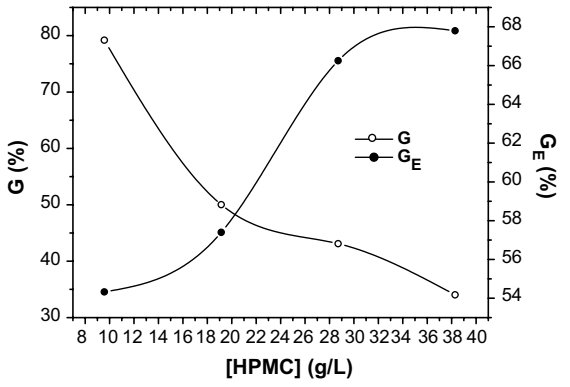

Figure 3. Effect of matrix concentration on: %G (*white circle*) or %G_E (*black circle*). Reaction conditions: [EA] = 0.191 mol/l, [KPS] = 2.658 mmol/l, reaction temperature = 60 °C, reaction time = 4 h, pre-interacting time = 5 min.

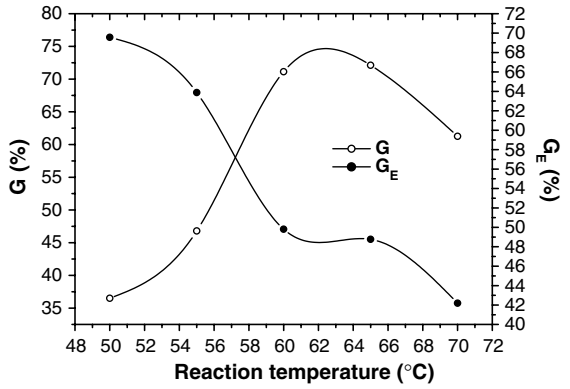

Figure 4. Effect of reaction temperature on: %*G* (*white circle*) or %G_E (*black circle*). Reaction conditions: [EA] = 0.395 mol/l, [KPS] = 3.704 mmol/l, [HPMC] = 26.67 g/l, reaction time = 2 h, pre-interacting time = 5 min.

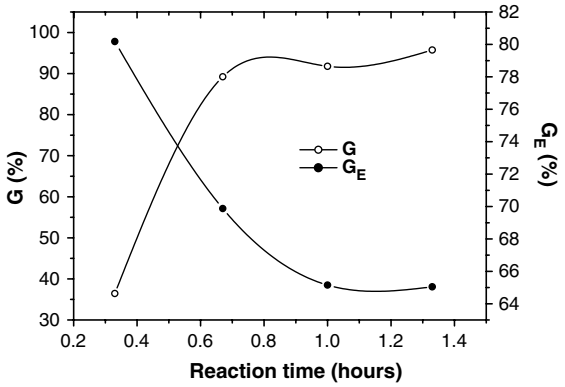

Figure 5. Effect of reaction time on: %*G* (*white circle*) or %G_E (*black circle*). Reaction conditions: [EA] = 0.395 mol/l, [KPS] = 4.873 mmol/l, [HPMC] = 26.32 g/l, reaction temperature = 60 °C, pre-interacting time = 5 min.

consistently with increases in the reaction temperature. The significant increase in *G*, especially in the 50–65 °C range where the amount of *G* increases by approximately twofold, is a consequence of an increase in the reaction rate. Firstly, the higher temperature accelerates the decomposition rate of KPS so that more reactive sites are generated on the HPMC backbones; as the same time, the initiation rate and propagation rate of grafting copolymerization can also be accelerated. Secondly, the solubility of monomer molecules and the diffusion and mobility of the monomer from the aqueous phase to the HPMC backbone are enhanced. The observed decrease in *G* beyond 65 °C can be ascribed to the fact that there are more PEA homopolymers formed at higher reaction temperature. In addition, various hydrogen abstraction and chain transfer reactions may also be accelerated at higher temperatures, thereby leading to decreased *G*. The significant decrease in G_E depicted in Figure 4 may be attributable to the extremely low chain transfer to the monomer in the graft copolymerization system and the increased number of homopolymers formed at the higher temperature. These results are in agreement with observations reported by Zheng et al. (2005).

Effect of reaction time

The influence of reaction time on *G* and G_E are shown in Figure 5. The increase in *G* is due to the increase in the number of reactive sites on the HPMC backbones as the reaction progresses. However, G_E values decrease during the course of the reaction, indicating that with graft copolymerizations processing gradually, nearly all of the reactive sites are occupied and that no additional reactive sites are formed.

Effect of pre-interacting time

Figure 6 shows the effect of pre-interacting time on *G* and G_E values. *G* and G_E increase with increasing duration of the pre-interacting time. The reason for this may be that with prolongation of the pre-interacting time, there will be increasingly more reactive sites generated from the interactions between KPS and HPMC in the aqueous graft copolymerization system that can accelerate and enhance the graft copolymerization of EA onto HPMC.

Characterization of graft copolymerization

Fourier transform infrared spectra

Figure 7 shows the FTIR spectra of HPMC and purified HPMC-g-PEA. The A spectrum of HPMC shows the characteristic absorption at 2900–3500 cm^{-1}. The B spectrum of the grafted copolymer shows the characteristic absorption of HPMC at 2900–3500 cm^{-1} and also an absorption band at 1739.22 cm^{-1} that corresponds to an ester carbonyl group (>CO) of the ethyl acrylate which was initially absent in pure HPMC (spectrum A). The presence of a new absorption band at 1739.22 cm^{-1} has provided evidence for the grafting of EA onto the HPMC.

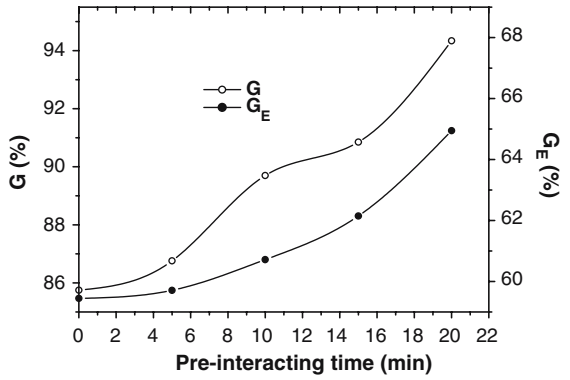

Figure 6. Effect of pre-interacting time on: %*G* (*white circle*) or %G_E (*black circle*). Reaction conditions: [EA] = 0.395 mol/l, [KPS] = 3.704 mmol/l, [HPMC] = 26.67 g/l, reaction temperature = 60 °C, reaction time = 3 h.

Scanning electron microscopy

Figure 8 shows two electron micrographs of HPMC – taken before and after the grafting process – which clearly show that there are evident differences in HPMC depending on the experimental stage. Figure 8a shows the pure HPMC before the graft copolymerization and Figure 8b shows the same HPMC following the graft copolymerization process. Prior to the graft copolymerization process (Figure 8a) the surface of pure HPMC is relatively smooth; following 72 h of acetone extraction (Figure 8b) well-defined agglomerates are present, the texture of which is different from that of the pure HPMC. These agglomerations are found on the surface of the grafted HPMC and, of course, not on the ungrafted ones. This result indicates that a considerable amount of PEA is grafted on HPMC.

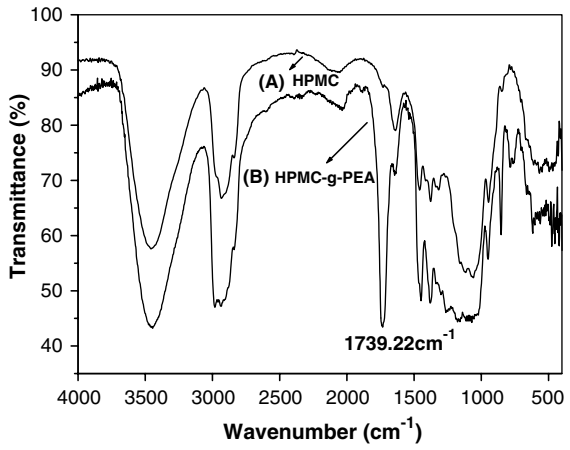

Figure 7. FTIR spectra of HPMC and HPMC-g-PEA.

Transmission electron microscopy

The TEM technique was utilized to observe the morphology of the stable water dispersion of HPMC-g-PEA. It is evident from Figure 9 that large numbers of spherical particles are present; these particles are not very stable and are not agglomerated to one another. The size of these particles ranges from 200 nm (Figure 9a) to 500 nm (Figure 9b), indicating a narrow size distribution. Kislenko (1999, p 199) reported that graft polymerization of vinyl monomers onto water-soluble polymers occurs according to the mechanism of emulsion polymerization. During the graft polymerization, a water dispersion of the graft copolymers with spherical particles is formed. Each particle consists of the core of the hydrophobic graft polymer and the hydrophilic shell of the backbone polymer, and the stability of the water dispersions is derived from amphyphility of the graft copolymer.

X-ray diffraction analysis

The X-ray diffraction patterns of pure HPMC and pure HPMC-g-PEA at room temperature from $2\theta = 5$ to 80 °C are shown in Figure 10a, b. The XRD pattern of pure HPMC (Figure 10a) shows that it, like all other natural polymers, has a partial crystalline nature (Anuradha and Malvika 2005). The XRD pattern of pure HPMC-g-PEA (Figure 10b) is similar to that of pure HPMC in keeping the specific crystal plane diffraction (101) and (002) of the pure HPMC, however the peaks seem to become more dispersive than those of pure HPMC, and the 2θ and d values observed in both cases are different. It is well known that heterogeneities in the bulk structure of the cellulose give rise to accessible and inaccessible regions and that reactions of cellulose hydroxyls first take place in the more accessible amorphous regions and then on the surface of elementary crystallites. The XRD results provide evidence that grafted PEA chains are formed after graft copolymerization, which enlarges the proportion of amorphous regions and makes the peaks more dispersive.

Differential scanning calorimetry

The DSC curves of pure HPMC and pure HPMC-g-PEA are shown in Figure 11. Curves of pure

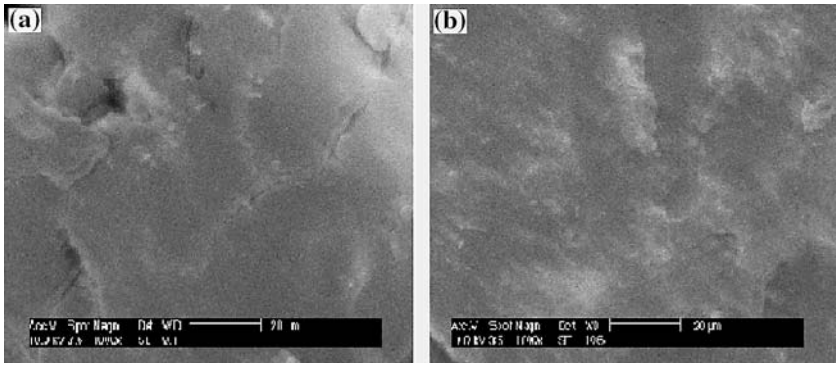

Figure 8. Scanning electron micrographies of pure HPMC (**a**) and pure HPMC-g-PEA (**b**) (15.17 *G*%).

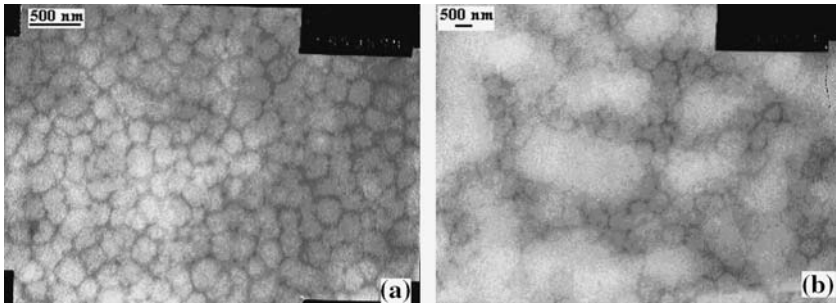

Figure 9. Transmission electron micrograph of the HPMC-g-PEA water dispersions.

HPMC-g-PEA samples are different from those of pure HPMC and PEA. For pure PEA and HPMC, the glass transition temperatures (T_g) appear at −24 °C (James 1999) and 194 °C (McPhillips et al. 1999), respectively. While the pure grafted HPMC samples with lower *G* (13.50%) or higher *G* (73.67%) both have two endothermic peaks: the first one at the lower temperature corresponds to the T_g of PEA; the second one at the higher temperature corresponds to the T_g of HPMC. The two endothermic peaks shift towards each other with the increase in *G*. To be more specific, the T_g of PEA shifts from −22 to −18 °C, and the T_g of HPMC shifts from 165 °C to about 160 °C. The results indicate that the grafted PEA chains affect and enhance the internal plasticization role by increasing the amount of grafted PEA chains. In addition, the endothermic peaks around 50–100 °C may be due to the loss of moisture absorbed by the samples (Trivedi et al. 2005), and it can be seen that this peak becomes smaller with increasing *G* values. The reason for this is that the hydrophilic ability decreases with increasing amounts of hydrophobic grafted PEA chains.

Equilibrium humidity adsorption behavior

Equilibrium humidity adsorption behavior of pure HPMC-g-PEA samples was investigated as a function of the amount of grafted PEA, and the results are listed in Table 1. It is observed from the data that the percentage of equilibrium humidity adsorption decreases significantly with increasing amounts of grafted PEA chains. The reason is that the grafted chains of PEA are hydrophobic and consequently the lower percentage of equilibrium humidity adsorption is observed.

Conclusion

The grafting of HPMC to prepare its EA-grafted copolymers has been carried out successfully using the KPS initiator system. The grafting parameters

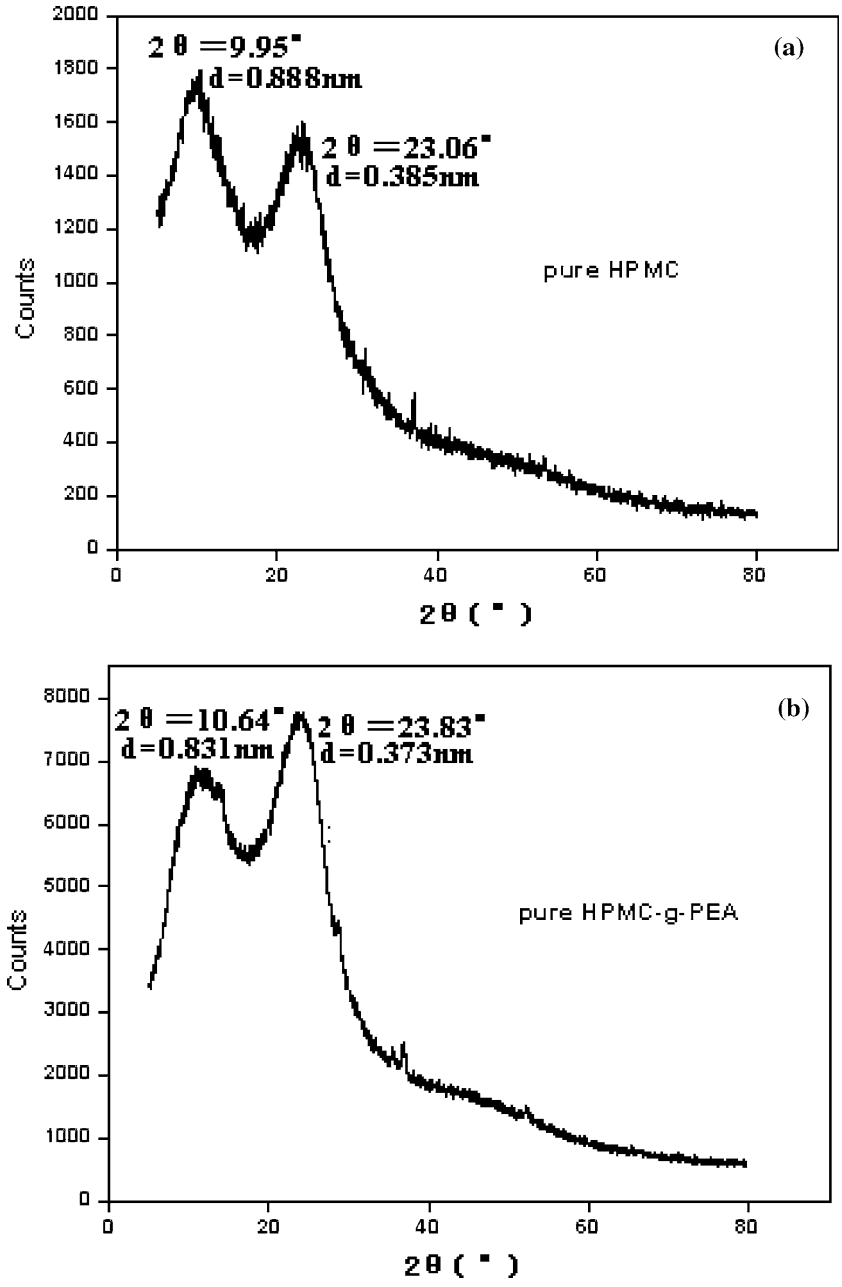

Figure 10. X-ray diffraction pattern of HPMC (**a**) and HPMC-g-PEA (**b**).

were strongly dependent on variations in graft copolymerization conditions. FTIR spectra of the HPMC-g-PEA confirmed the existence of a chemical link between the HPMC and the PEA. Characterization through SEM, XRD and DSC revealed that the grafted and ungrafted HPMC samples were quite clearly different. The glass transition temperature (T_g) peaks of HPMC and PEA shift towards each other with increases in the percentage of grafting. The percentage of equilibrium humidity adsorption decreases with increasing amounts of grafted PEA chains.

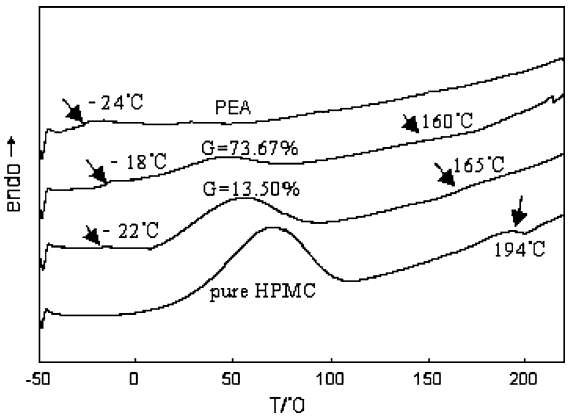

Figure 11. DSC scans of pure HPMC, PEA and pure HPMC-g-PEA ($G = 13.50\%$, $G = 73.67\%$).

Table 1. Effect of the amount of grafted PEA on percentage of equilibrium humidity adsorption.

Sample no.	Grafted PEA/HPMC (g/g)	Percentage of equilibrium humidity adsorption (%)
1	0	11.00
2	1.2	4.52
3	1.5	3.90
4	1.7	2.65
5	2.0	2.32

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