

Solid State Mechano-Chemical Grafting Copolymerization of Hydroxyethyl Cellulose with Acrylic Acid

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ABSTRACT: The effects of mechanochemical treatment on hydroxyethyl cellulose (HEC) and its grafting reaction with acrylic acid (AA) under solvent-free conditions were studied through a vibratory ball-milling machine, which was developed in our laboratory. Fourier transform infrared (FTIR) spectroscopy and ^{13}C -NMR analysis were used to investigate the structural development of HEC during vibromilling and the grafting mechanism. Further development of the structure and properties of the graft copolymer was characterized by viscosity measurement, wide-angle X-ray diffraction (WAXD), and thermal gravity (TG) analysis. The FTIR results showed a new peak at 1720 cm^{-1} , corresponding to the C=O absorbance peak of AA, which indicated that AA

was successfully grafted onto HEC during the high-energy vibromilling of the HEC/AA mixture at ambient temperature in the absence of a solvent and a catalyst. The WAXD showed the destruction of crystals of HEC during the milling, and the TG analysis demonstrated the improvement of the thermal stability of the copolymer. The effects of the processing conditions on the grafting rate and grafting efficiency were studied by chemical titration to determine the optimum grafting conditions. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3537–3542, 2009

Key words: graft copolymers; polysaccharides; degradation; structure

INTRODUCTION

In recent years, an increased demand for renewable materials has been induced by environmental concerns in many industrial applications. As one of most plentiful natural polymers on Earth, cellulose can be obtained from various plants as a principal component of cell walls, microorganisms, and animals.¹ Because of their renewability, biodegradability, and avirulence, increasing attention has been paid to novel composites of cellulosic materials. However, the poor solubility of cellulose in common solvents limits its applications to only a few areas; thus, chemical modification is necessary to prepare cellulose derivatives by the introduction of polar and/or functional moieties onto the cellulose backbone.²

Hydroxyethyl cellulose (HEC), one important cellulose derivative, is used extensively in the pharmaceutical industry,³ painting,⁴ and emulsion polymerizations.⁵ Because of its wonderful water-solution properties and its chemical composition, with a large amount of relatively easily accessible hydroxyl units that can be attached by a number of functional

groups,⁶ more and more studies have focused on the modification of HEC. Because of the β -D-glucose rings of the main chain of HEC and the strong hydrogen bonds among the hydroxyl groups,⁷ these chemical modifications have mainly been realized through the solution process instead of through traditional technologies such as extrusion and internal mixing.^{8,9} The grafting reaction of acrylic acid (AA) on HEC has been widely investigated because of its wonderful superabsorbent and environment-dependent abilities.¹⁰ Of the solution methods reported, there are advantages and disadvantages. In these processes, HEC is dissolved in an appropriate solvent at a certain temperature. Reactants are added along with an initiator, such as ceric ammonium nitrate,¹¹ or a treatment, such as ultrasound.¹² The reactants are more easily mixed to obtain a better interaction with HEC because of the relatively homogeneous system formed in the solution. The resultant copolymer is sedimented by another solvent to be purified. The process is expensive and relatively complex, and it is difficult to avoid byproducts. The recycling of a large quantity of the solvent is needed, which also makes it impractical for large-scale production.¹³

Therefore, the development a new modification under solvent-free condition is necessary and significant. Nowadays, mechanochemical modifications has been paid more and more attention.¹⁴ Here, we focused on the process of vibratory ball milling, which has been used in comprehensive fields and

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applications, such as the fine grinding of minerals¹⁵ and polymers,¹⁶ surface modification of materials,¹⁷ and preparation of dry-blending systems.¹⁸ As a result of the prolonged milling action, when the transferred energy during the hit is enough to overcome the activation barrier, chemical reactions may occur.¹⁹ For example, grafting reactions were performed.²⁰ Mechanochemical degradation²¹ and the modification^{22,23} of poly(vinyl chloride) and polyethylene²⁴ were investigated in our laboratory. Meanwhile, the mechanochemical effects on cellulosic materials were also studied. Endo²⁵ prepared a novel blend of cellulose and poly(ethylene glycol) by improving their compatibility through the formation of hydrogen bonds between the two composites. Qiu et al.²⁶ prepared a cellulose-maleated polypropylene composite through the formation of ester bonds between them. The structural degradation and recrystallization of cellulose were also studied by a ball-milling process.^{27,28} However, grafting reactions, especially AA-grafted cellulosic materials under solvent-free conditions, have rarely been mentioned.

The aim of this study was to develop a novel method for preparing AA-grafted HEC through the process of vibratory ball milling at ambient temperature in the absence of a solvent and a catalyst. Compared with traditional solution processes, it has obvious advantages, such as the lack of a solvent, a low reaction temperature, and a low amount of energy consumed. The influence of the processing conditions on the grafting rate and efficiency were investigated by chemical titration. A grafting mechanism is proposed on the basis of the results of ¹³C-NMR. The crystalline structure and thermal stability of AA-grafted HEC during ball milling were also investigated.

EXPERIMENTAL

Materials

Commercial HEC (HEC) powder was obtained from Xiangtai Corp. (Zhongxiang, China). Its molecular weight was 4.43×10^5 g/mol (H₂O, 25°C), as determined by a viscosity method.²⁹ AA and acetone were analytical grade and were obtained from Bodi Chemical Corp. (Tianjin, China).

Graft copolymerization

The graft copolymerization was carried out in a vibratory ball-milling machine, which was developed in our laboratory. HEC powder (300 g) and certain amounts of AA were added to the jar, with varied milling times, rotational speeds, and charge ratios. The temperature of the powder mixture was measured with a DM-6902 K-type thermometer (Victor Hi-tech Co., Shenzhen, China). The temperature

before milling was approximately 25°C and rose to nearly 34°C after the completion of the process.

Purification

The milled mixture was extracted by acetone in a Soxhlet extractor to remove excessive monomer for 48 h and then stored at 80°C in a vacuum oven for 48 h to a constant weight.

Characterization

KBr pellets of pure HEC and the copolymer were prepared for Fourier transform infrared (FTIR) measurement. The FTIR spectra was recorded on a Nicolet-560 spectrometer (Nicolet Co., USA) at a resolution of 2 cm⁻¹ with accumulation of 32 scans in the spectral range 4000–400 cm⁻¹.

The grafting degree (G_d) and grafting efficiency (G_e) were determined by chemical titration. Purified HEC-g-AA powder (0.2 g) was dissolved completely in 20 mL of deionized water at 80°C. Then, we added 25.0 mL of a 0.05 mol/L KOH solution, and the mixture was refluxed at 100°C for 2 h to ensure complete reaction with AA groups. With 0.1 mL of a 1.0% phenolphthalein ethanol solution as an indicator, the cooled solution was titrated with a 0.05-mol/L HCl solution. G_d and G_e were calculated as follows³⁰:

$$G_d(\text{wt}\%) = \frac{(V_0 - V_1) \times C}{W \times 1000} \times M \times 100\% \quad (1)$$

$$G_e(\%) = \frac{G_d}{\text{AA content}} \times 100\% \quad (2)$$

where C is the concentration of HCl solution (mol/L); V_0 and V_1 are the volumes (mL) of HCl solution added to the blank and HEC-g-AA solutions, respectively; M is the molecular weight of AA (72 g/mol); W is the weight of HEC-g-AA powder (0.2 g); and AA content is the weight of AA added to the HEC powder before milling. The titration was repeated three times for each sample.

The grafting mechanism was confirmed through ¹³C-NMR measurements by a DRX-400 Bruker spectrometer (Bruker Co., Germany). The HEC and the graft copolymer were dissolved overnight in D₂O at 40°C.

Viscosity measurements of HEC before and after milling in deionized water were carried out with an Ubbelohde viscometer (Liangjing Co., Shanghai, China) at $25 \pm 0.5^\circ\text{C}$. For each sample solution, the flow time was measured at four different concentrations, and then, the intrinsic viscosity ($[\eta]$) was obtained. The viscosity-average molecular weight (M_η) was determined with the following empirical equation²⁹:

$$[\eta] = 4.70 \times 10^{-4} [M_\eta]^{0.8} \quad (3)$$

The crystalline structures of the samples were measured by wide-angle X-ray diffractometry (Philip X'pert Pro MPD, Cu K α at 40 kV and 20 mA with 2θ from 7 to 40°).

The thermal stability of purified HEC-*g*-AA was examined with a TGA Q500 analyzer (TA Instruments, USA). The measurements were taken in a nitrogen flow at a heating rate of 10°C/min with the temperature ranging from 35 to 450°C.

RESULTS AND DISCUSSION

Effects of ball milling on G_d and G_e

Figure 1 shows the effect of the AA content on G_d and G_e . G_d passed through a maximum with the increase of AA content. The higher AA concentration increased the probability that AA monomers reacted with the HEC macroradicals to graft AA onto HEC. On the other hand, redundant AA may have promoted the mobility of the HEC chains under the mechanochemical effects of steel-polymer impacting, shearing, and pressing and thereby decreased the number of initial HEC macroradicals. Therefore, G_d in the AA content range of 1–5 phr almost increased linearly and then decreased after a critical concentration of AA at about 5 phr.

Figure 2 shows that the G_d and G_e increased with the milling time. G_d and G_e were very small within 1 h and increased linearly during 1–8 h. Thereafter, the increase became slow. The very small G_d within 1 h may have been due to the bad blending between HEC and AA at the beginning of the milling, and the size reduction effects of HEC happened mainly, instead of the induction of macroradicals. With increasing milling time, the marked increase of G_d indicated the formation of more HEC macroradicals and better mixing between the two components. The slower improvement in G_d beyond 8 h may have been due to the consuming of AA to form homo-

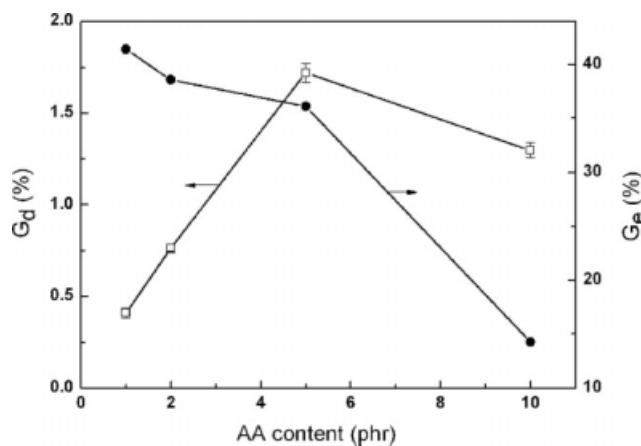


Figure 1 Effect of the AA content on (\square) G_d and (\bullet) G_e .

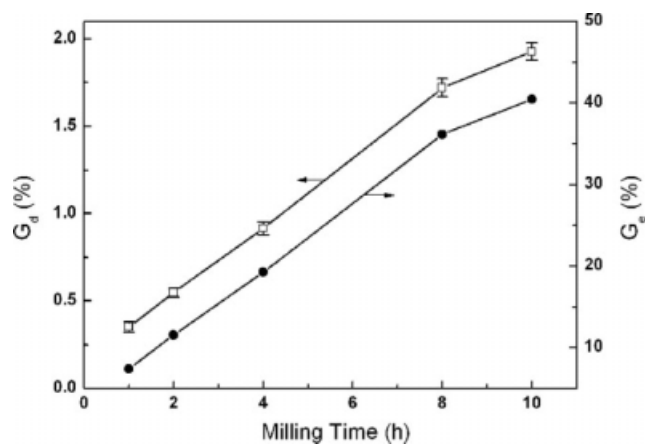


Figure 2 Effect of the milling time on (\square) G_d and (\bullet) G_e .

polymers and the recombination reactions of HEC macroradicals, which is discussed later.

Figure 3 gives the effect of the charge ratio of the steel ball/mixture (charge ratio for short) on grafting. The weight of HEC was fixed at 300 g with an AA content of 5 phr. When the charge ratio was lower, fewer HEC macroradicals were formed because the energy transmitted to each particle was lower during the milling, and the contacts between the steel ball and reaction powder were less frequent, whereas the contacts of polymer particles, which were inefficient in the graft polymerization, were increased.³¹ With increasing charge ratio from 13 to 20, more HEC macroradicals were formed, which led to a higher G_d . However, a further increase in the charge ratio caused a slower increase in G_d , which may have been because a high filling ratio would have restricted the mobility of the steel ball and then resulted in a poor milling effect. Therefore, a smaller amount of HEC macroradicals caused a slower increase in G_d .

Figure 4 shows that G_d and G_e increased with rising rotational speed. Under the lowest rotational speed of 300 rpm, the probability of the contacts

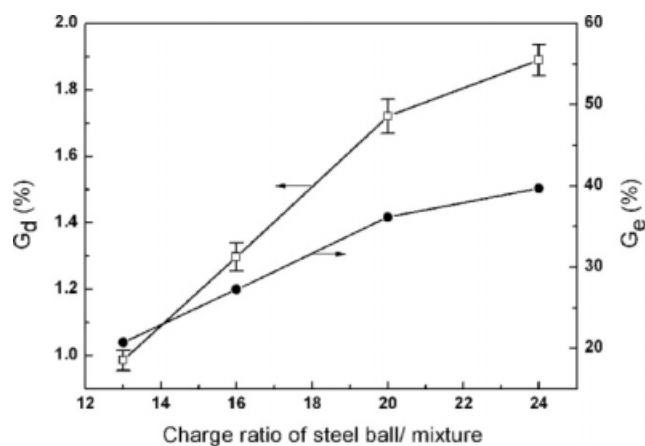


Figure 3 Effect of the charge ratio on (\square) G_d and (\bullet) G_e .

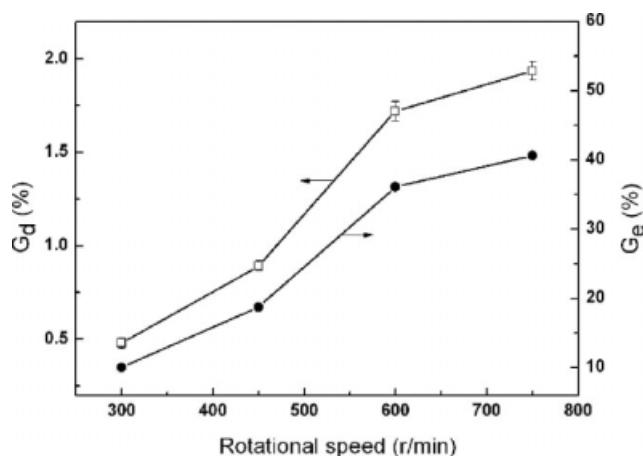


Figure 4 Effect of the rotation speed on (\square) G_d and (\bullet) G_e .

between the steel balls and the polymers were lower, which led to a less effective milling of the polymeric particles. The higher rotational speed caused a higher shear force, which could result in the formation of more HEC macroradicals. Meanwhile, a higher rotational speed improved the diffusion of AA in HEC, which was also helpful in increasing G_d and G_e . When the rotational speed was beyond 600 rpm, a slower increase in G_d was observed, which may have been because of the consumption of AA to form homopolymers and the recombination reactions of HEC macroradicals.

Effects of ball milling on the molecular structure of HEC

The FTIR spectra of HEC, milled HEC, and HEC-g-AA are shown in Figure 5; these were consistent with

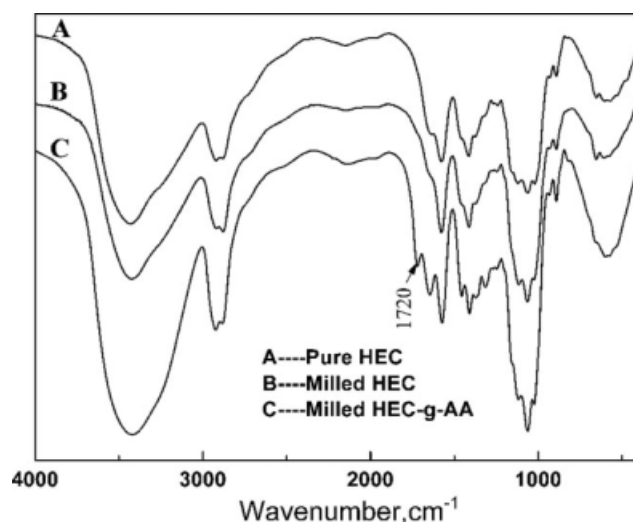


Figure 5 FTIR spectra of (A) HEC, (B) milled HEC, and (C) HEC-g-AA under the following milling conditions: AA content = 5 phr, milling time = 8 h, charge ratio = 20, and rotation speed = 600 rpm.

the data reported earlier by Khutoryanskaya and Khutoryanskiy.³² No new absorption peak appeared for pure HEC after milling, which indicated that this process did not produce a novel structure of HEC. The appearance of an absorption peak at 1720 cm^{-1} in purified milled HEC/AA samples was attributed to C=O stretching vibrations of the carboxyl group in AA, which demonstrated the success of grafting. The introduction of AA to the HEC chains was further confirmed by the ^{13}C -NMR spectrum of the copolymer. Furthermore, the absorption peak at 1051 cm^{-1} , which characterized C—O—C asymmetric stretching vibrations, shifted little after ball milling, which demonstrated that the mechanochemical degradation of HEC hardly occurred at the glucose rings. The main degradation point should have been at the glycosidic bonds,¹⁴ which was also demonstrated by ^{13}C -NMR analysis.

Grafting mechanism

The data listed in Table I shows the changes in $[\eta]$ and M_w of HEC during the milling. M_w of HEC decreased sharply with the effects of injecting, shearing, and pressing of the steel ball onto the powder. These effects caused a large amount of chain destruction of HEC, and a number of HEC macroradicals were formed, which indicated that the grafting reactions were initiated through HEC macroradicals formed during vibromilling. The structure change was also confirmed from ^{13}C -NMR analysis.

As shown in Figure 6, the peaks at 60–110 ppm in the ^{13}C -NMR spectrum of pure HEC were related to the ring carbons of HEC, which was consistent with related results in the literature.^{33,34} The peak at about 22 ppm corresponded to the carbons of end groups and was weaker than those in the milled HEC [Fig. 6(b)] and the graft copolymer [Fig. 6(c)]. It is well understood that degradation during ball milling mainly occurs in the skeleton structure. The structural analysis of the HEC/AA system [Fig. 6(c)] revealed the success of the grafting of AA onto HEC by the peaks at 34, 43, and 181 ppm, which were related to the carbons in AA.

Effects of ball milling on the crystalline structure of HEC and the copolymer

Wide-angle X-ray diffraction diagrams of HEC and HEC/AA are shown in Figure 7. The diffraction peak of the original HEC appeared at $2\theta = 22^\circ$,

TABLE I
[η] and M_w Values of HEC Before and After Milling

Sample	$[\eta]$ (L/g)	M_w (g/mol)
HEC	1.55	4.43×10^5
Milled HEC	0.30	5.8×10^4

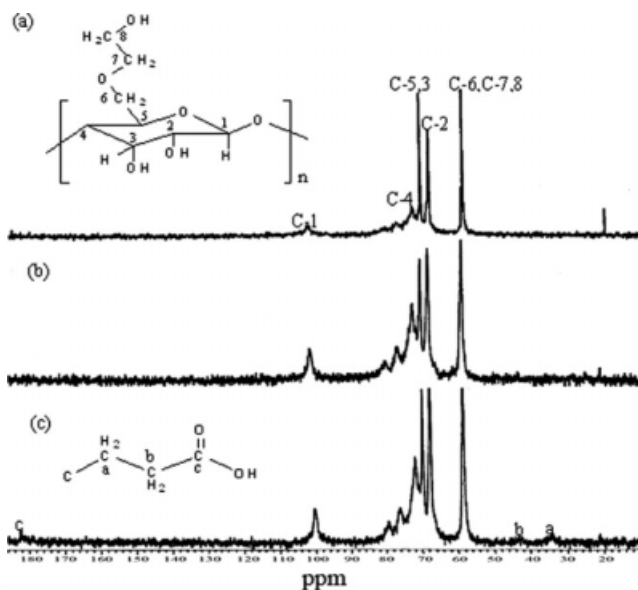


Figure 6 ^{13}C -NMR spectra of (a) HEC, (b) milled HEC, and (c) HEC-g-AA under the following milling conditions: AA content = 5 phr, milling time = 8 h, charge ratio = 20, and rotation speed = 600 rpm.

which was characterized as cellulose I.³⁵ Curve B (milled HEC) and C (milled HEC/AA) were in an almost amorphous state, which indicated the destruction of the crystalline region during milling. These data demonstrated the obvious effect of ball milling on HEC powders, such as injecting, shearing, and pressing. However, the XRD pattern still showed identical peaks of cellulose I, which indicated that the crystal type of the cellulose did not change after milling.

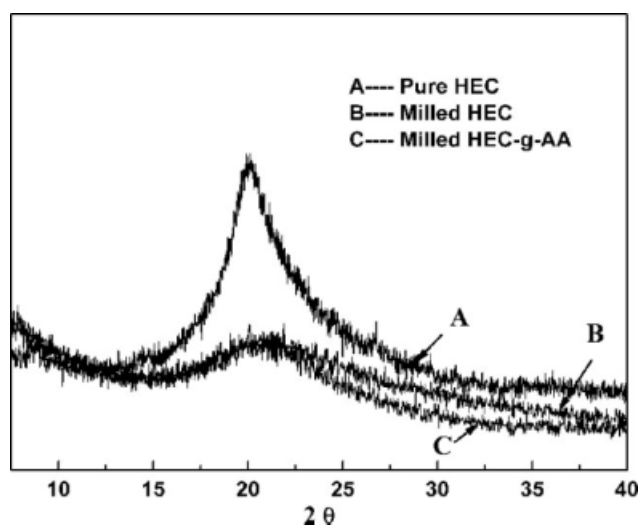


Figure 7 Crystal structure of (A) HEC, (B) milled HEC, and (C) HEC-g-AA under the following milling conditions: AA content = 5 phr, milling time = 8 h, charge ratio = 20, and rotation speed = 600 rpm.

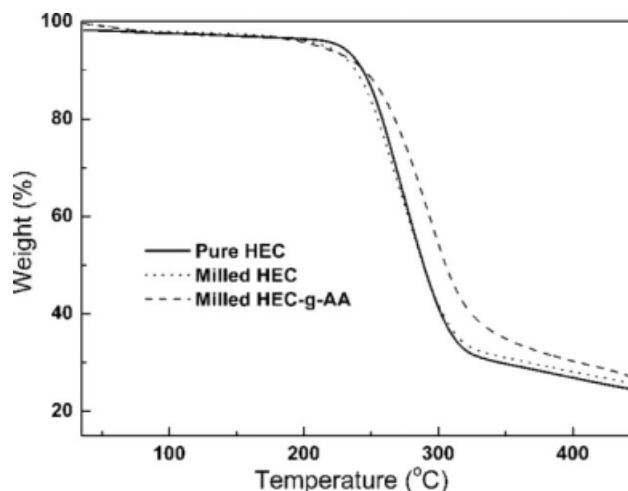


Figure 8 TG curves of (—) HEC, (···) milled HEC, and (---) HEC-g-AA under the following milling conditions: AA content = 5 phr, milling time = 8 h, charge ratio = 20, and rotation speed = 600 rpm.

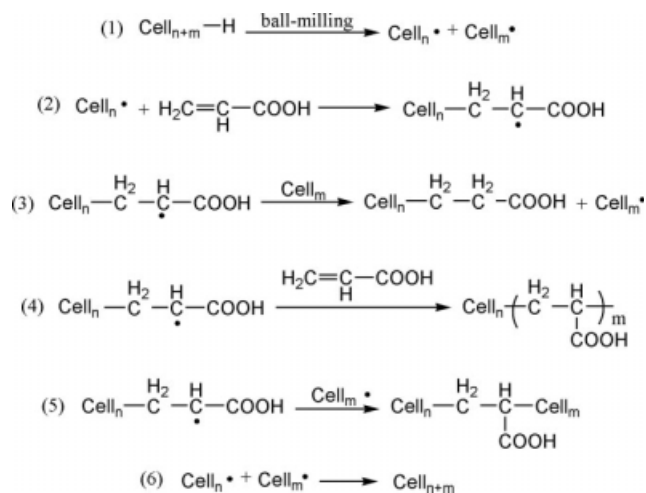
Effects of ball milling on the thermal stability of HEC and the copolymer

Figure 8 gives the thermal gravity (TG) curves for the thermal degradation of HEC and its graft copolymer at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. The TG curve of the original HEC had three distinct stages, which was consistent with related results in the literature.³⁶ The slight weight loss of HEC in the first stage was due to the physical desorption of water (intermolecular and intramolecular dehydration). In the second stage, the weight loss started at 180°C and continued to about 350°C with a 67% weight loss, which was due to the removal of CO_2 or hydrocarbons.

The third stage started because of the reactions of pyrolysis and carbonization. Table II shows the values of the initial decomposition temperature (T_d) and the temperature at the maximum rate (T_{dm}). The thermal decomposition parameters showed that the grafting copolymer exhibited a better thermal stability than original HEC. On the other hand, the difference between the original and milled HEC could be explained as the reduction of the crystalline phase and the increase in the amorphous phase in HEC during milling. However, the reason for the higher degradation temperature of the grafting copolymer is still unknown. It possibly indicated a higher

TABLE II
 T_d and T_{dm} Values of Pure HEC, Milled HEC, and HEC-g-AA

Sample	T_d ($^\circ\text{C}$)	T_{dm} ($^\circ\text{C}$)
HEC	243	269
Milled HEC	236	264
HEC-g-AA	251	293



Scheme 1 Proposed reactions for the preparation of HEC-g-AA through vibratory ball milling.

degree of thermal resistance due to the grafted carboxyl groups.

Proposed reactions

On the basis of the previous results and discussions, the main reactions are proposed in Scheme 1.

First of all, HEC macroradicals were formed by ball milling (reaction 1), and AA molecules were grafted onto the macroradical chain (reaction 2). Then, the macroradical abstracted hydrogen from the HEC chain to form a new HEC macroradical (reaction 3) or homopolymerized with AA molecules to form an oligomeric grafting (reaction 4). In the presence of radicals, the corresponding reactions competed with each other, and the termination reactions were very complex and difficult to determine. The main possible termination reactions are proposed in reactions 5 and 6 for combination, along with some possible disproportionation, although other reactions may exist through both combination and disproportionation.

CONCLUSIONS

A new method of ball milling to prepare HEC-g-AA was developed with the advantages of being solvent free, having a lower process temperature, being energy efficient, having a low cost, and being easily run. AA molecules were successfully grafted onto HEC chains, whose macroradicals were formed through the effects of high-energy vibromilling. G_d and G_e were determined by chemical titration,

increasing with increases in AA content, milling time, charge ratio of the steel ball/mixture, and rotational speed and then leveling off. The sharp decrease in the crystallinity of HEC was found because of the obvious effect of ball milling on HEC powders, such as injecting, shearing and pressing, whereas crystal type of HEC did not change after milling. Meanwhile, the grafting copolymer exhibited a better thermal stability than original HEC, which was in opposition to the milled HEC.

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