Synthesis and Characterization of Polyacrylonitrile Pregelled Starch Graft Copolymers Using Ferrous Sulfate-Hydrogen Peroxide Redox Initiation System as Surface Sizing Agent

Chunyan Wang, Xiaorui Li, Jingqian Chen, Guiqiang Fei, Haihua Wang, Qin Liu

Key Laboratory of Chemistry and Technology for Light Chemical Industry, Ministry of Education, Shaanxi University of Science and Technology, Xi'an, Shaanxi Province 710021, People's Republic of China

ABSTRACT: A graft copolymer was synthesized by graft copolymerization of starch with styrene (St) and butyl acrylate (BA), using ferrous sulfate-hydrogen peroxide redox initiation system. The starch was pregelled in the presence of acrylonitrile (AN) in aqueous alkali at high temperature before graft polymerization. Major factors affecting the polymerization reaction were investigated. It was found that a graft copolymer with higher percentage conversion (PC), graft efficiency (GE) and graft percentage (GP) was obtained by controlling the initiator concentration, concentration, and ratio of monomers and polymerization temperature. The optimum conditions were as follows: H_2O_2 concentration, 12%; monomer concentration, 120%; St/BA ratio, 1 : 1; polymerization temperature, 65°C. Fourier transform infrared spectroscopy and NMR analyses were used to gain information on the structure of the products. It was demonstrated that St, BA, and AN had been successfully grafted onto starch and ─CN had been saponified into ─CONH$_2$ and ─COO$^-$ to a certain degree when pregelling. Scanning electron microscope micrographs showed the coarse structure and broad network. The graft polymerization took place on the surface of starch granule and led to amorphization of the starch structure. Graft polymer had better thermal stability and was endowed with pseudo-plasticity. It was observed that the starch graft copolymer offers good properties such as water resistance as surface-sizing agent. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2630–2638, 2011

Key words: graft copolymers; starch; pregel; copolymerization; surface sizing; initiators

INTRODUCTION

With increasing concerns about environmental protection and green chemistry, starch has gained academic attraction as well as industrial interest because of its natural abundance, low cost, renewability and biodegradability.[1] During the past decades, it has been extensively used in many technical fields such as agricultural, pharmaceutical, cosmetic, textiles, and papermaking industries.[2–6] However, their inherent drawbacks in mechanical properties limited their application to some extent. Therefore, various physical or chemical modification of the starch molecules via oxidation, dextrinization, esterification, etherification, and grafting has been accordingly adopted to minimize these defects.[7–15] Vinyl monomers graft copolymerization onto starch was

demonstrated to be one of the most effective way to improve the properties of starch.

Grafting method and monomer category played an important role in the properties of the final product. Although most of grafting polymerization is radical initiated reaction, classica chemical-initiating systems for the formation of starch radicals are permanganates in the presence of acids, the Fenton agent, ceric ammonium nitrate/nitric acid, and persulfates.[16–19] Fenton agent obtained more attention due to its higher reactivity and environmental friendly properties.[17] It was reported that vinyl monomers such as acrylonitrile (AN), methacrylonitrile, acrylate, methyl methacrylate, styrene (St), and acrylamide have been successfully grafted onto starch.[20–26] However, their copolymer onto starch was seldom reported.

Furthermore, pregelatinized starch was often used for graft polymerization owing to its large molecular weight and indissolubility. Mechanical stirring together with heating was conventionally certified to be a good method to pregel starch.[27] In addition, strong aqueous alkali was also used as solvent to expedite starch dissolution and inhibit molecular aggregation.[28–30] In this work, AN was added when pregelling starch in aqueous alkali at high

temperature, which was never reported before. The polar nitrile (CN) groups of polyacrylonitrile can be partly hydrolyzed to amide ($CONH_2$) and carboxyl (COO^-) groups, which provide higher binding interaction between polymer and fiber in the presence of aluminum sulfate. At the same time, it was beneficial for the enhancement of emulsifying capacity and was able to decrease the particle size, which can accelerate their penetration into the fiber network.

In this work, systematic investigation on starch graft copolymerization was discussed. The starch was pregelled in the presence of AN in aqueous alkali at high temperature and then grafted with mixed St and butyl acrylate initiated by ferrous sulfate-hydrogen peroxide redox system. The physicochemical properties of the products were characterized as well as its application in the papermaking industry as a surface-sizing agent.

EXPERIMENTAL

Reagents and materials

Cassava starch (14–15% moisture content) was obtained from Redflag Starch Plant (Tianjin, China). St (98%), butyl acrylate (BA, 99%), and ferrous sulfate ($FeSO_4 \cdot 7H_2O$) were purchased from Tianjin Fuchen Chemical Reagent Plant (Tianjin, China). AN (98%) and hydrogen peroxide (H_2O_2, 30%) were from Paini Chemical Reagent Plant (Zhengzhou, China). Sodium hydroxide (NaOH) was purchased from Tianjin Zhiyuan Chemical Reagent Co. (Tianjin, China). Glacial acetic acid (HAc, 99.5%) was from Xi'an Sanpu Fine Chemical Plant (Xi'an, China). All chemicals except starch were analytical grade and used as received without further purification. Distilled water was used for all experiments.

Graft polymerization

Certain amounts of cassava starch and distilled water were placed in a round-bottomed flask with constant stirring and nitrogen atmosphere at room temperature. After 10 min, monomer AN and NaOH solution were poured into the system at an elevated temperature (80°C) for 1 h. Then, decreasing the temperature to desired point, pregelled starch can thereby be obtained after adjusting the pH to 4.0–5.0 with HAc. Ferrous sulfate and hydrogen peroxide were used as initiator for the graft polymerization of pregelled starch. Ten minutes later, mixture of St and BA, simultaneously with hydrogen peroxide solution, was added dropwise into the polymerizing microemulsion with vigorous stirring in 2 h, and then the reaction was kept for another 1h. The product was precipitated with acetone, filtered, and dried at 60°C in circulated air oven to a constant weight.

The homopolymers were separated by Soxhlet extraction with acetone as the solvent for 24 h.

Isolation of grafted polymer by starch hydrolysis

To separate the grafted polymer from starch backbone, the starch-grafted polymer was subjected to acid hydrolysis. Four grams of acetone-extracted and dried starch-grafted polymer was suspended and stirred in 200 mL of 3N hydrochloric acid at 90–100°C for 2 h under reflux. The nonaqueous-grafted polymer was filtered and washed with distilled water until pH reached 7. The final product was dried in the oven at 60°C. The percentage conversion (PC), graft efficiency (GE), graft percentage (GP), and graft yield (GY) were calculated as follows:

$$PC\ (\%) = w_1/w_2 \times 100\% \qquad (1)$$

$$GE\ (\%) = w_3/w_1 \times 100\% \qquad (2)$$

$$GP\ (\%) = w_3/w_4 \times 100\% \qquad (3)$$

$$GY\ (\%) = w_5/w_4 \times 100\% \qquad (4)$$

where w_1 is the weight of polymer (i.e., starch-grafted polymer and homopolymer), w_2 is the weight of monomer, w_3 is the weight of grafted polymer, w_4 is the weight of pure starch, and w_5 is the weight of starch-grafted polymer.

Characterization of starch-grafted polymers

Fourier transform infrared spectroscopy (FTIR) spectra of samples were recorded on a VECTOR-22 FTIR spectrometer (Bruker, German) using KBr pellets in the frequency of 4,000–400 cm^{-1} at 1 cm^{-1} resolution, signal-averaged over 32 scans, and baseline corrected.^{1}H-NMR and ^{13}C-NMR were performed on a Germany Bruker Avance 400MHZ Spectrometer with DMSO-d_6 as solvent.

A Jeol JSM-6700F scanning electron microscope (SEM) with an accelerating voltage of 5 kV was used to study the surface morphology of the samples.

Thermogravimetric analysis (TGA) of samples was performed on TGA Q500 under nitrogen atmosphere in the temperature range of 20–600°C, using a heating rate of 5°C min^{-1}.

The wide-angle X-ray diffraction (WAXD) analysis of the samples was performed on D8 discover X-ray diffractometer (Bruker axs, Germany) in the range of $2\theta = 3°–17.3°$, and the degree of crystallinity was accordingly calculated by the software.

The rheological properties of emulsions were analyzed in an AR2000ex Rheometer (TA, American). Steady-state flow tests (shear rate from 0.01 to 100 s^{-1}) were carried out at 25°C using DIN concentric cylinders geometry.
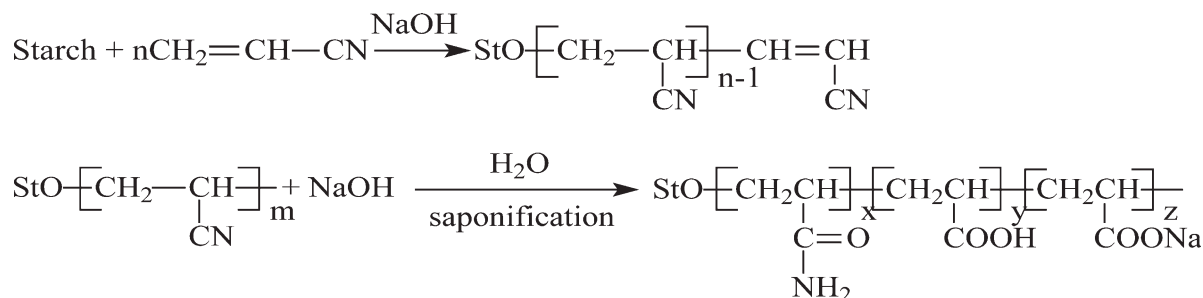
Figure 1 The reaction mechanisms of starch pregelling.

RESULTS AND DISCUSSION

Tentative mechanism of grafting

Starch pregelling

The nitrile (CN) groups of polyacrylonitrile grafted on starch can be partly hydrolyzed to amide (CONH$_2$) and carboxyl (COO$^-$) groups. The reaction mechanisms are summarized as Figure 1.

Graft polymerization

Hydroxide ion (OH$^-$) and hydroxyl-free radical ($\cdot$OH) were first produced with ferrous sulfate-hydrogen peroxide redox initiation system, then inducing the formation of pregelled starch macroradicals (St-O$\cdot$), followed by chain propagation of grafting. The termination was carried out by the initiator, coupling, disproportionation. The detailed reaction mechanisms are elucidated as Figure 2.

Effect of reaction parameters

Effect of initiator concentration

Ferrous sulfate was selected as catalyst and hydrogen peroxide as an oxidant to initiate the polymerization under acidic condition. Effects of initiator concentration on PC, GE, and GP were investigated by changing the concentration of hydrogen peroxide (based on weight of starch, ows), as shown in Figure 3 and Table I. The optimum H$_2$O$_2$ concentration was found to be 12%. As shown in Figure 2 (initiation of grafting), the reaction was reversible, Fe^{2+} could be produced in a cycle way. As the H$_2$O$_2$ concentration increased, more radical sites were produced, resulting in the simultaneous occurrence of both graft copolymerization and homopolymerization. However, the hydroxyl radicals can recombine themselves or with other radicals to terminate chain propagation as well as initiating homopolymeriaztion with further increase in H$_2$O$_2$ concentration. Therefore, great reduction in GP and GE was detected after optimum point. While PC kept almost constant when H$_2$O$_2$ concentration was greater than 12%, which suggested that most free radicals were mainly confined to

initiation of polymerization when initiator concentration was comparatively low, but the contribution of initiator in initiation reaction was balanced with its contribution in termination reaction when initiator concentration was higher than 12%.

Effect of the concentration and ratio of two monomers

Effects of monomer concentration (ows) on PC, GE, and GP were presented in Figure 4 and Table I. The increment in PC, GE, and GP with increasing monomer concentration could be ascribed to enhanced diffusion opportunities of monomer into starch molecules. As a result, it was easier for the reaction to take place among reactants. However, when monomer concentration was greater than 120%, the PC and GE decreased while GP tended to level off. The decline in PC was mainly because the free radical sites on starch backbone were gradually occupied with reaction, and there was not adequate initiator for either copolymerization or homopolymerization of monomers. The decrease in GE can be attributed to the transfer of radicals to extra monomer molecules, resulting in the increase of homopolymer and P(St-BA) copolymer, whereas those polymers blocked the reaction between monomers and starch macroradicals, which caused further decrease in GE and increase in GP.

In addition, effects of St/BA ratio on PC, GE, and GP were investigated, as shown in Figure 5 and Table I. It was observed that GE and GP declined as St/BA ratio increased and PC achieved the optimum when St/BA ratio was 1 : 1. The main reasons were that: compared to St, butylacrylate had higher polarity. So, it was easier for butylacrylate to approach starch and diffuse into the starch molecules to induce graft polymerization. Furthermore, it was difficult for homopolymerization to take place in butylacrylate due to its longer branched chain.
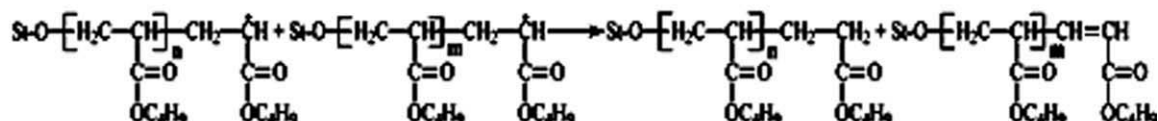
Effect of polymerization temperature

As shown in Figure 6 and Table I, polymerization temperature exerted a significant effect on PC, GE, and GP. Initially, the increment of the three

1. Initiation of grafting:
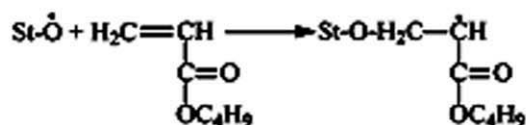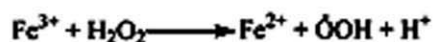
2. Propagation of grafting
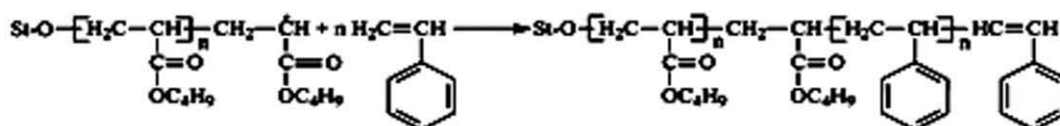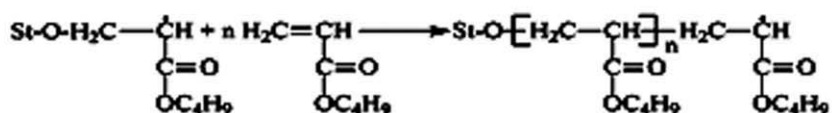
3. Termination of grafting:
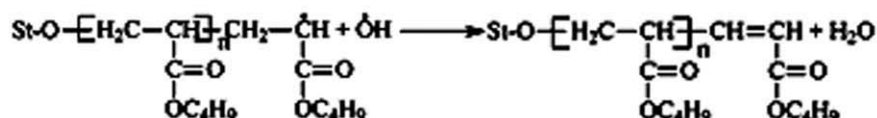
(Graft termination by initiator)
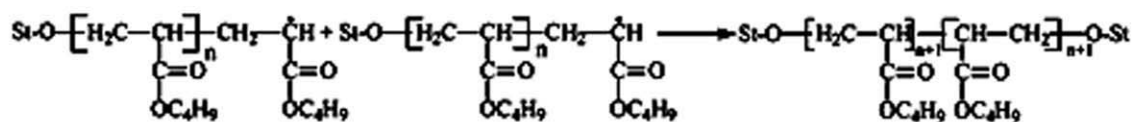
(Graft termination by coupling)


(Graft termination by disproportionation)

Figure 2 The reaction mechanisms of graft polymerization.

parameters with increase in temperature up to 65°C probably can be due to the enhanced diffusion and mobility of monomer molecules, which contributed to more opportunities of collision with starch macromolecules and increased propagation of grafted chains. However, PC, GE, and GP decreased when temperature exceeded 65°C. This can be attributed to (1) the faster termination and chain transfer reaction; (2) higher probability of homopolymerization

instead of the graft copolymerization; and (3) an increase in the oxidation rate of starch.

Charaterization of starch-grafted polymers

Evidence of grafting

FTIR spectra of pure starch, pregelled starch in the presence of AN, and starch-grafted copolymers were
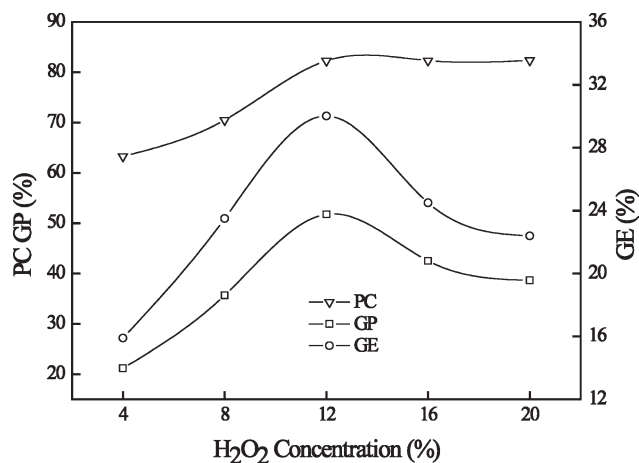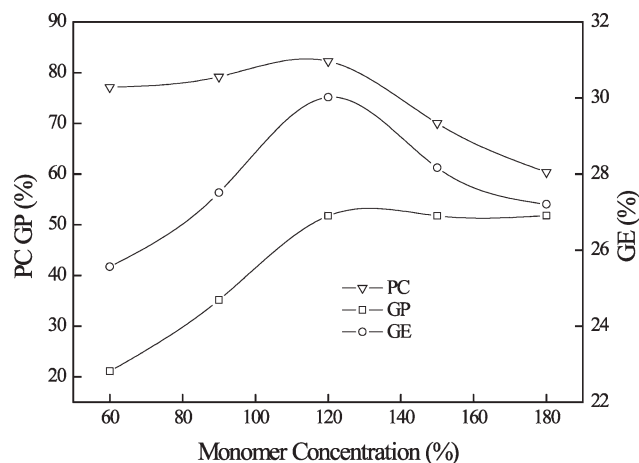
Figure 3 Effect of H_2O_2 concentration on PC, GE, and GP.

Figure 4 Effect of monomer concentration on PC, GE, and GP.

shown in Figure 7. The spectrum of the grafted starch showed the abroad characteristic absorption of starch at 3,000–3,800 cm^{-1}, which is due to O—H stretching vibration. The sharp absorption band at 2254 cm^{-1} was attributed to —CN stretching, indicating the occurrence of grafting of AN onto starch. However, the new weak absorption peaks at 1670 cm^{-1}, 1618 cm^{-1}, and 1603 cm^{-1}, resulting from C=O, N—H stretching vibrations in —$CONH_2$ group, and C=O stretching vibration in carboxylate, respectively, suggest that —CN had been saponified into —$CONH_2$ and —COO^- to a certain degree. The strong characteristic absorption peaks at 758 cm^{-1} and 698 cm^{-1} due to C—H out-of-plane bending vibration and peaks at 3100–3000 cm^{-1} and 1500–1400 cm^{-1} attribute to C—H stretching vibration and breathing vibration of benzene ring. Therefore, it

was demonstrated that the polystyrene had been successfully grafted onto starch. The appearance of new peak at 1731 cm^{-1} associated with the presence of ester carbonyl group (C=O) indicated the grafting of polybutyl acrylate onto starch molecules.

Furthermore, the graft copolymers were characterized by NMR spectroscopy. The ^{1}H-NMR and ^{13}C-NMR spectra of starch-grafted copolymers were presented in Figures 8 and 9, respectively. As shown in Figure 8, the characteristic peaks between 4.3 and 5.7 ppm were assigned to four protons, namely, the proton bound to C_1 (δ = 5.5 ppm) and those bound in the three hydroxyl groups of the AGU of starch. The resonance at δ = 7.1 ppm was attributed to the proton of benzene ring, and accordingly, the observed multiplet was assigned tentatively to the methyl of an end unit of structure CH_3—CH_2—CH_2—CH_2— in grafted poly(BA). As shown in Figure 9, the typical pattern of the AGU units of starch was easily identified between 58 and 102 ppm. The peak at δ = 120 ppm was assigned to —CN group of AN and peak at 128 ppm was

TABLE I
Effect of Reaction Parameters

Reaction parameters		PC	GP	GE
H_2O_2 concentration (%)	4	63.30	21.20	15.90
	8	70.50	35.70	23.50
	12	82.31	51.78	30.02
	16	82.35	42.50	24.50
	20	82.36	38.70	22.40
Monomer concentration (%)	60	77.13	21.12	25.56
	90	79.23	35.20	27.51
	120	82.31	51.78	30.02
	150	70.01	51.80	28.17
	180	60.37	51.81	27.21
St/BA ratio	1:3	77.52	57.34	35.16
	1:2	80.47	55.21	32.62
	1:1	82.31	51.78	30.02
	2:1	79.64	44.45	26.54
	3:1	76.38	38.73	24.11
Temperature (°C)	55	67.32	37.44	26.44
	60	75.47	43.21	27.22
	65	82.31	51.78	30.02
	70	76.34	45.51	28.34
	80	69.48	39.72	27.18

Figure 5 Effect of St/BA ratio on PC, GE, and GP.
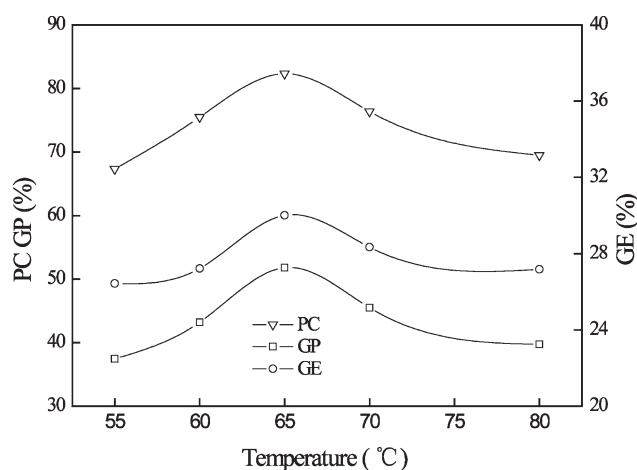
Figure 6 Effect of polymerization temperature on PC, GE, and GP.

Figure 8 ^{1}H-NMR spectrum of starch-grafted copolymers.
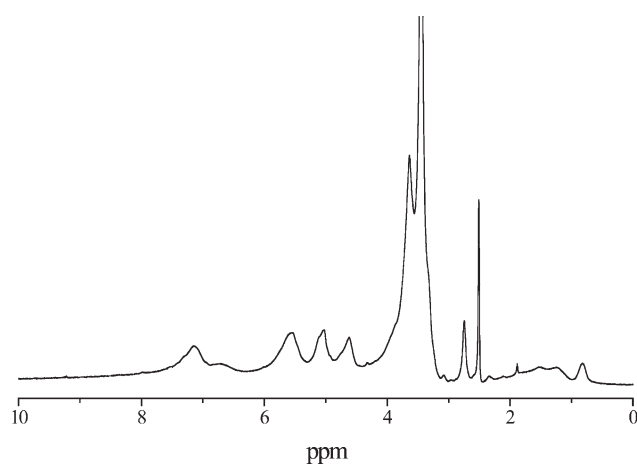
attributed to the carbon of benzene ring, and the peak at $\delta = 175$ ppm was assigned to the carbonyl group. ^{1}H-NMR and ^{13}C-NMR spectroscopy confirmed the fact that the graft copolymerization took place.

grafting reaction occurred at the surface of the starch particle, and the grafted chains were surrounded and attached to the whole surface area of the particle.

Morphology observation

The effect of polymer grafting upon the surface morphology of starch was studied by SEM (Fig. 10). The surface morphology of pure starch granules was of different sizes, and the surface was very smooth with oval particle shape [Fig. 10(a)]. After pregelled, the granule surface became rough and covered with a thick layer of polymers, but the major part of the starch granules was still intact [Fig. 10(b)], because the AN may has been partly grafted onto the starch. Figure 10(c) indicated great changes, and the granular structure was totally destroyed, because the

Thermogravimetric analysis

The comparative TGA–DTG data were illustrated in Figure 11. And different thermal behaviors for pure starch and starch-grafted polymer were observed. The first stage, occurring in the range from 20 to 150°C, displayed about 11.09% and 4.65% loss in weight for pure starch and starch-grafted polymer, respectively. The initial slight loss in weight was due to the loss of moisture. Two decomposition peaks at 290 and 396°C were detected for starch-grafted polymer, which can be attributed to degradation of pure starch and grafted polymer. And it was also obvious that the peaks shifted to higher temperature ranges compared to their corresponding

Figure 7 FTIR spectra of (a) pure starch, (b) pregelled starch in the presence of AN, and (c) starch-grafted copolymers.
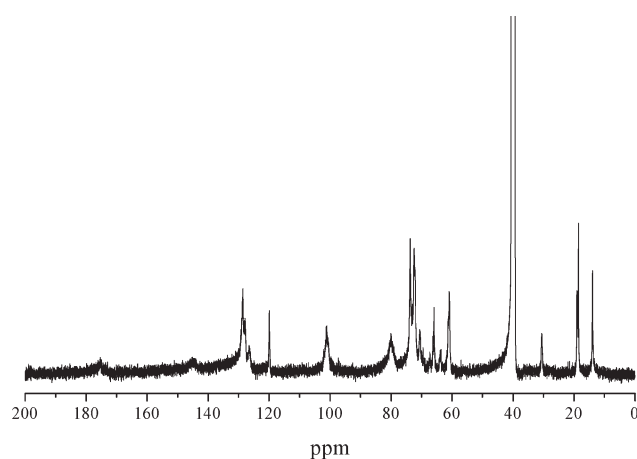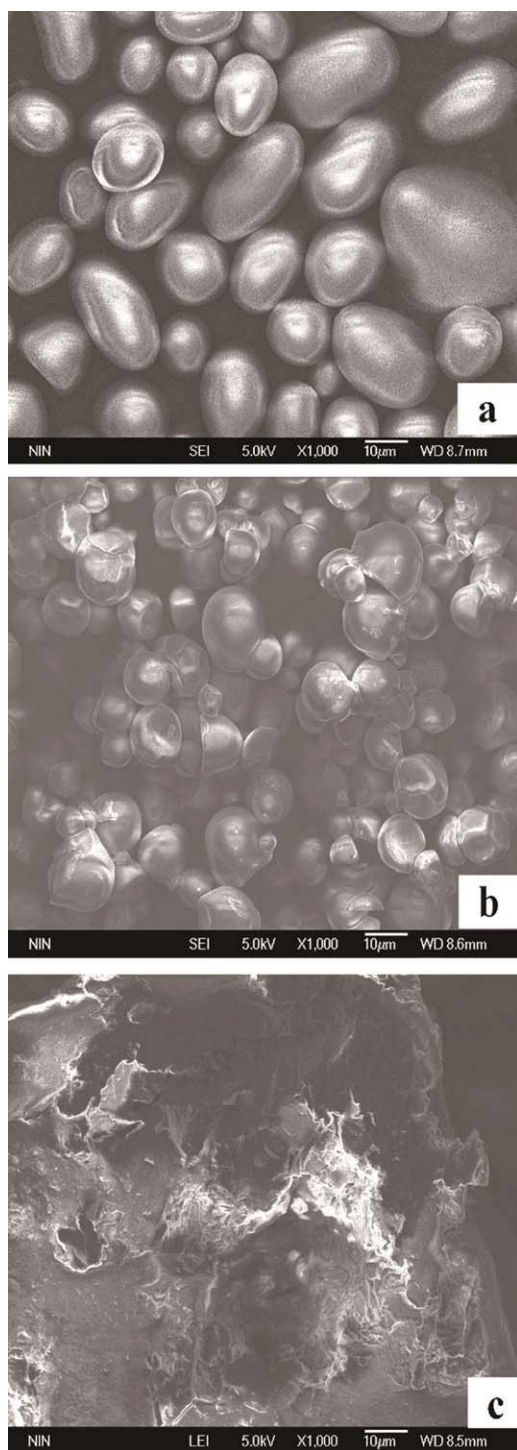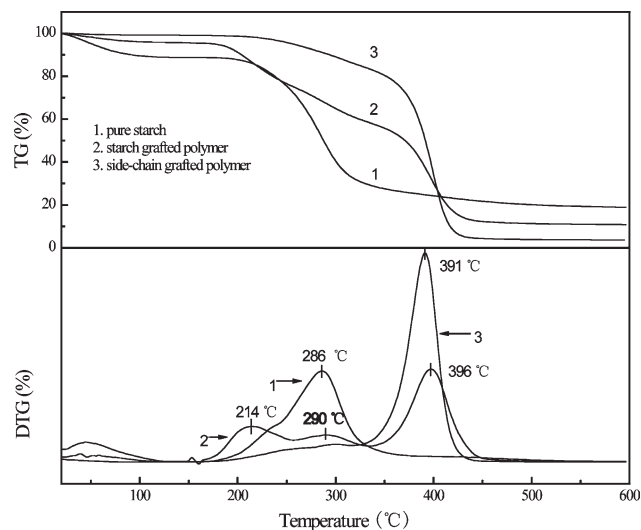

Figure 9 ^{13}C-NMR spectrum of starch-grafted copolymers.

Figure 11 TGA–DTG curves for pure starch, starch-grafted polymer with %GY = 139.5 and side-chain grafted polymer.

mum grafting condition). It was also found that the decomposition temperature of grafted starch increased; thus, it was concluded that the starch-grafted polymer was endowed with improved thermal stability compared to pure starch.

Wide-angle X-ray diffraction studies

Wide-angle X-ray diffraction (WAXD) patterns of pure starch and 139.5% polymer grafted starch were displayed in Figure 12. Starch granules are semicrystalline by nature. The crystallinity is essentially due to amylopectin fraction. XRD pattern of pure starch comprises mainly four sharp diffraction peaks at 2θ = 15.0°, 17.3°, 20.1°, and 22.8°. However, the four

Figure 10 SEM micrographs at a magnification of ×1000: (a) pure starch, (b) pregelled starch in the presence of AN, and (c) 139.5% polymer grafted starch. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pure components. This demonstrated the occurrence of grafting of polymer onto starch. Furthermore, it can be calculated from the TGA results that grafting percent was 47.02%, which was in coincidence with the previous study (the GP was 51.78% in the opti-
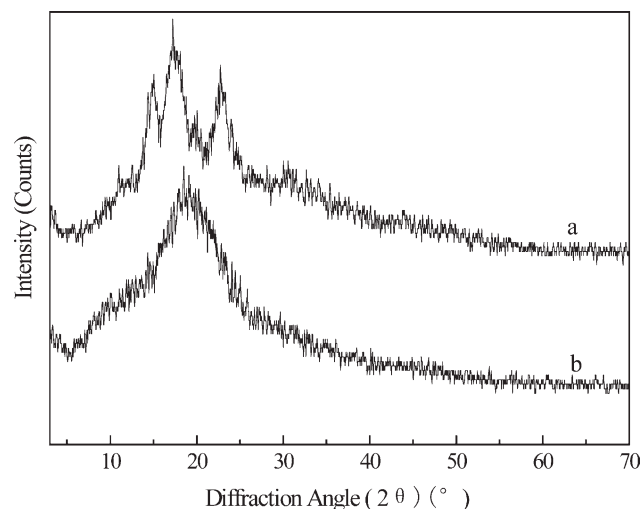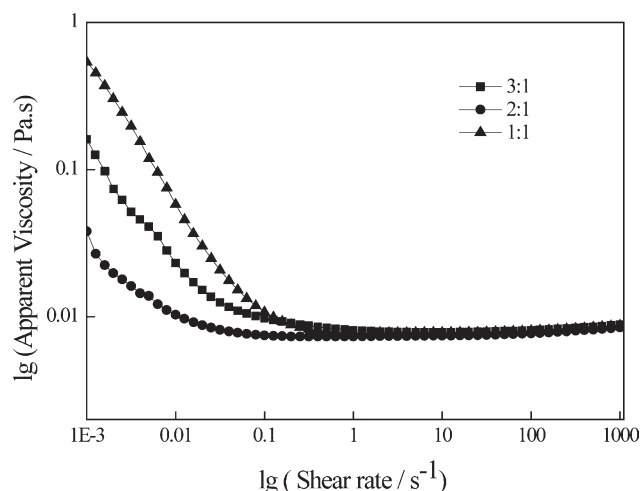

Figure 12 Wide angle X-ray diffraction patterns of (a) pure starch and (b) 139.5% polymer-grafted starch.

Figure 13 Shear rate versus viscosity with variation in St/BA ratio (H_2O_2 concentration = 12%, monomer concentration = 120%, and polymerization temperature = 65°C).

crystal peaks were merged into a broad smoothened peak around 19.3° after graft polymerization, and the crystallinity decreased from 18.12% to 0.82%, confirming that the crystal phase was destroyed due to the graft polymerization.

The rheological properties

Rheological behaviors of starch grafted polymer were shown in Figure 13. Non-Newtonian shear-thinning (pseudo-plastic) behavior was observed for all samples, that is, the apparent viscosity decreased greatly with increasing the shear rate at the beginning and then leveled off. It was also found that the apparent viscosity decreased with the increase of St/BA ratio. This may be due to the increased viscosity with an increase in grafting percentage within the range studied.

Surface sizing of paper

The starch-grafted polymer was adopted to be used as surface-sizing agent in papermaking industry. Ta-

TABLE II
Physical Properties of Paper Sized with Starch-Grafted Polymer by Varying the St/BA Ratio

Paper sample	St/BA ratio	Water absorption (%)	Ring crush index (N m/g)	Bursting strength (kPa)
Unsized	–	98.10	3.97	107.5
Sized with pregelled starch	–	88.05	4.50	165.5
Sized with	3 : 1	50.41	6.32	239.5
starch	2 : 1	35.04	6.63	240.5
grafted	1 : 1	30.02	6.77	241.5
polymer	1 : 2	34.07	7.24	243.5
	1 : 3	40.14	7.09	242.5

ble II presented physical properties of paper sized with starch-grafted polymer by varying the St/BA ratio. The results indicated that (1) paper sized with pregelled starch exhibited higher ring crush index and bursting strength while water absorption decreased; (2) paper sized with starch grafted polymer had higher ring crush index and bursting strength but lower water absorption than paper sized with pregelled starch; (3) the lowest water absorption of paper sized with starch grafted polymer was observed to be 30.02% when St/BA ratio was 1 : 1 and then increased with further increase in St/BA ratio. On the contrary, the ring crush index and bursting strength increased with the increase of St/BA ratio and then decreased when St/BA ratio greater than 1 : 2, and the highest ring crush index and bursting strength were 7.24 N m/g and 243.5 KPa, respectively.

CONCLUSIONS

With the assistance of $Fe_2(SO_4)_3$—H_2O_2 redox initiation system, St and BA can be grafted efficiently onto cassava starch, which was pregelled with AN in alkali solution at high temperature in advance. It is concluded that initiator concentration, concentration, and ratio of the two monomers and polymerization temperature have great effects on PC, GE, and GP. The optimum conditions were as follows: H_2O_2 concentration, 12%; monomer concentration, 120%; St/BA ratio, 1 : 1; polymerization temperature, 65°C. FTIR and NMR demonstrated the formation of the graft copolymer. The SEM indicates the occurrence of grafting on the surface of starch granule, and granular structure was totally destroyed after graft polymerization. The thermal stability of starch was found to get improved after grafting, and the WAXD confirmed that the crystal phase was destroyed by graft polymerization. It was found that the emulsion displayed non-Newtonian behavior, and the apparent viscosity increased with the increase of GP. As a surface-sizing agent, the lowest water absorption was obtained when St/BA ratio was 1 : 1, and highest ring crush index and bursting strength were observed when St/BA ratio was 1 : 2.

References

1. Sugahara, Y.; Ohta, T. J Appl Polym Sci 2001, 82, 1437.
2. Massicotte, L. P.; Baille, W. E.; Mateescu, M. A. Int J Pharm 2008, 356, 212.
3. Lehmann, A.; Volkert, B.; Fischer, S.; Schrader, A.; Nerenz, H. Colloid Surf A 2008, 331, 150.
4. Mesharam, M. W.; Patil, V. V.; Mhaske, S. T. Carbohydr Polym 2009, 75, 71.
5. Svetlana, B.; Simona, S.; Gudrun, P. Ind Eng Chem Res 2006, 45, 7374.
6. Poraj-Kozminski, A.; Hill, R. J.; Van de Ven, T. G. M. J Colloid Interf Sci 2007, 309, 99.

7. Chan, H. T.; Bhat, R.; Karim, A. A. J Agric Food Chem 2009, 57, 5965.
8. Wang, Y. J.; Wang, L. F. Carbohydr Polym 2003, 52, 207.
9. Kato, Y.; Matsuo, R.; Isogai, A. Carbohydr Polym 2003, 51, 69.
10. Kiatkamjornwong, S.; Thakeow, P.; Sonsuk, M. Polym Degrad Stab 2001, 73, 363.
11. Mostafa, K. M. Carbohydr Polym 2003, 51, 63.
12. Wu, J. H.; Wei, Y.; L; Lin, J. M.; Lin, S. B. Polymer 2003, 44, 6513.
13. Zhu, Z. F.; Li, M. L.; Jin, E. Q. J Appl Polym Sci 2009, 112, 2822.
14. Li, A.; Liu, R. F.; Wang, A. Q. J Appl Polym Sci 2005, 98, 1351.
15. Ma, Y. G. C.; Manolache, S.; Sarmadi, M.; Denes, F. S. Starch/Stärke 2004, 56, 47.
16. Pourjavadi, A.; Zohriaan-Mher, M. J Starch/Stärke 2002, 54, 482.
17. Tolvanen, P.; Maki-Arvela, P.; Sorokin, A. B. Chem Eng J 154: 52 2009.
18. Teli, M. D.; Waghmare, N. G. Carbohydr Polym 2010, 81, 695.
19. Kaewta, K.; Varaporn, T. Carbohydr Polym 2008, 73, 647.
20. Tong, Q. Y.; Zhang, G. W. Carbohydr Polym 2005, 62, 74.
21. Çelik, M.; Saçak, M. J Appl Polym Sci 2002, 86, 53.
22. Pimpan, V.; Thothong, P. J Appl Polym Sci 2006, 101, 4083.
23. Mostafa, K. M.; EI-Sanabary, A. A. J Appl Polym Sci 2003, 88, 959.
24. Cao, Y. M.; Qing, X. S.; Zhou, F. M.; Lin, S. G. Eur Polym J 2002, 38, 1921.
25. Ge, X. C.; Xu, Y.; Meng, Y. Z.; Li, R. K. Y. Compos Sci Technol 2005, 65, 2219.
26. Zhang, L.; M; Gao, JP; Tian, RC; Yu, J G; Wang, W J Appl Polym Sci 2003, 88, 146.
27. Guan, J. J.; Hanna, M. A. Biomacromolecules 2004, 5, 2329.
28. Cardoso, M. B.; Putaux, J. L.; Samios, D.; Da Silveira, N. P. Carbohydr Polym 2007, 70, 160.
29. Nor Nadiha, M. Z.; Fazilah, A.; Bhat, R.; Karim, A. A. Food Chem 2010, 121, 1053.
30. Lee, H. J.; Han, J. A.; Lim, S. T. Food Hydrocolloid 2009, 23, 1935.