Synthesis of Wheat Straw Composite Superabsorbent

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ABSTRACT: A novel wheat straw composite superabsorbent was prepared by graft polymerization with acrylic acid (AA), acrylamide (AM), and maleic anhydride-modified wheat straw in aqueous solution, using *N,N*-methylene-*bis*-acrylamide (MBA) as a cross-linker and ammonium persulfate (APS) and sodium bisulfite (SBS) as redox initiators. Factors influencing the degree of carboxylation, such as reaction time, reaction temperature, and the amount of maleic anhydride, were investigated. Morphologies and structure of the wheat straw composite superabsorbent were characterized by fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), and X-ray diffraction (XRD). Water absorption of wheat straw composite superabsorbent was rapid, requiring 13.1 min to reach 63% of equilibrium absorbency (781 g/g). FTIR spectra indicate that maleic anhydride has been reacted onto the wheat straw backbone and the structure of wheat straw graft copolymer is formed. SEM data show that the fibrous morphology of wheat straw disappears and gel aggregates with many large microporous holes are formed after wheat straw graft modification. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 3404–3410, 2013

INTRODUCTION

Superabsorbent polymers (SAPs) are lightly cross-linked networks of flexible polymer chains and can absorb a large amount of water compared with general water-absorbing materials in which the absorbed water is hardly removable even under some pressure. Because of excellent properties to traditional water-absorbing materials such as cotton, pulp, or sponges, SAPs are widely used in many specialized applications including hygienic products,[1] agriculture,[2–4] waste water treatment,[5,6] and drug-delivery systems.[7,8]

Recently, much attention has been paid to the superabsorbents prepared with natural material, such as cellulose,[9,10] starch,[11,12] chitosan,[13,14] guar gum[15] and gelatin[16] because of their abundant resources, low production cost, and biodegradability.

As by-product of wheat crops, wheat straw (WS) is an abundant biodegradable resource whose main components are cellulose, hemicellulose, and lignin. Up to now, most of the crop residues have been focused on burying them back to improve the fertility of the soil, using them as the materials for paper industry, and producing protein feed, alcohol, and methane by microbial fermentation.[17]

WS can be modified through chemical method, such as acid and base treatment, and used as skeletal material, on which

vinyl monomers and cross-linking agents can graft to form superabsorbent composite.[18–22] Liu[18] prepared a novel superabsorbent composite having semi-interpenetrating polymer networks (semi-IPNs) through polymerization of WS cellulose-g-poly (potassium acrylate) (WSC-g-PKA) in the presence of polyvinyl alcohol (PVA). The structure and morphology of semi-IPNs SAR were characterized by fourier transform infrared spectroscopy (FTIR), SEM, and thermogravimetric analysis (TGA), which confirmed that WS cellulose (WSC) and PVA participated in the graft polymerization reaction with acrylic acid (AA). The semi-IPNs SAR prepared under optimized synthesis condition gave the best water absorption of 266.82 g/g in distilled water and 34.32 g/g in 0.9 wt % NaCl solution. Li[19] prepared a WS-based superabsorbent (WS-SAB) by graft copolymerization of acrylic acid, acrylic amide, and dimethyl diallyl ammonium chloride onto the cellulose of WS. The product had a water absorbency of 133.76 g/g in distilled water and 33.83 g/g in 0.9 wt % NaCl solution. The swelling capacity did not change after several times of water absorption and release. Liu[20] prepared a superabsorbent composite by graft copolymerization through AA and chemically modified pulverized WS (CMPWS). The product had maximum absorbencies of 417 g/g in distilled water and 45 g/g in 0.9 wt % NaCl solution. Xie[21]
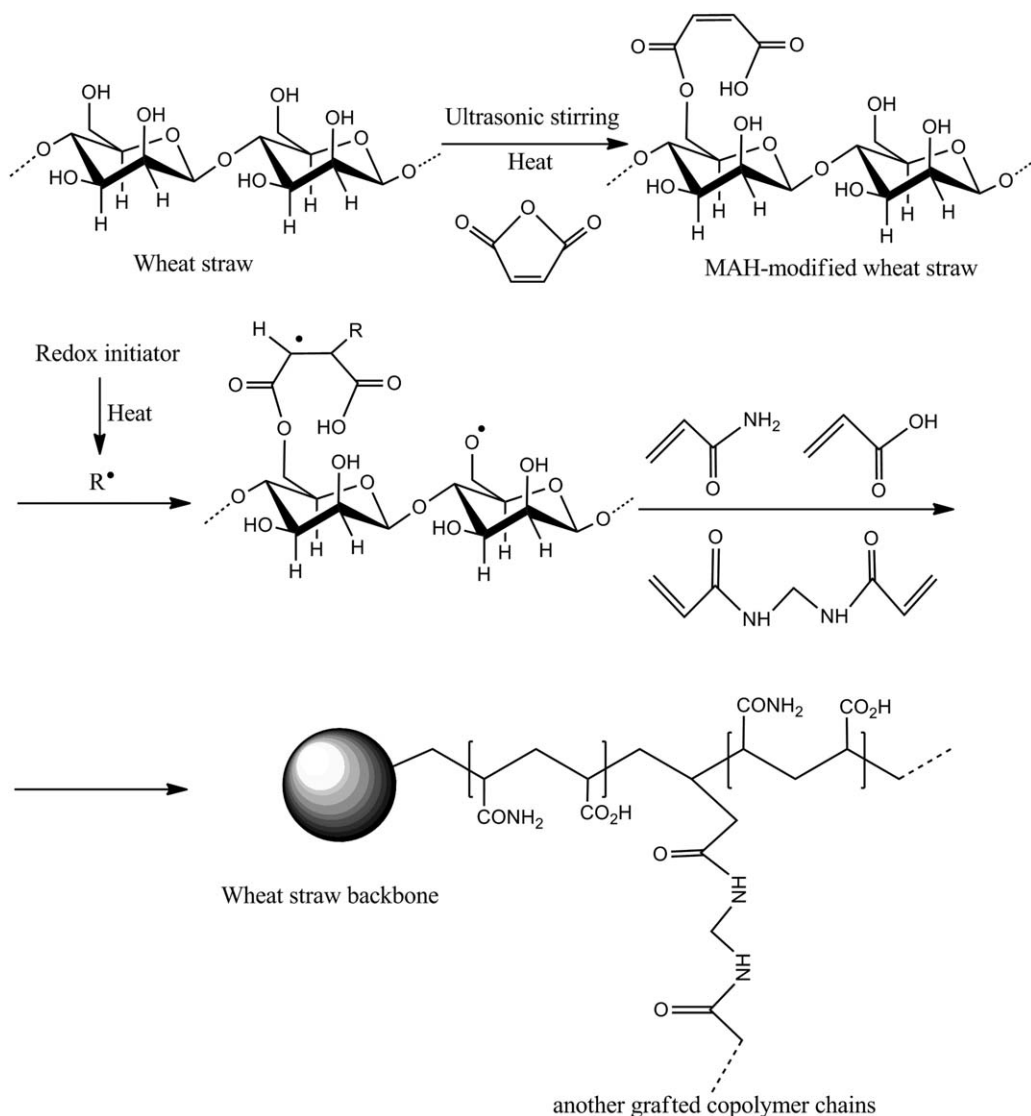
Scheme 1. Proposed mechanism for the formation of WS composite superabsorbent.

prepared a functional superabsorbent possessing a core/shell structure, whose core was urea in attapulgite and alginate matrix, and shell was chemically modified WS-*g*-poly(acrylic acid)/attapulgite (CMWS-*g*-PAA/APT) superabsorbent composite containing urea and borax. The results showed that the product with slow-release and water-retention capacity, being economical, nontoxic in soil, and environment friendly, could be found good application in agriculture and horticulture. Ma[22] prepared a novel superabsorbent composite by graft copolymerization through AA, acrylic amide (AM), dimethyl diallyl ammonium chloride (DMDAAC), and pretreated WS (PTWS). The SAR has the best water absorbency of 133.76 g/g in distilled water and 33.83 g/g in 0.9 wt % NaCl solution.

On the basis of our previous research on superabsorbent[23,24] and superabsorbent composite,[25,26] in this article, WS was first modified by maleic anhydride (MAH), and then a novel WS composite superabsorbent was synthesized by redox polymerization in AA and AM aqueous solutions with modified WS used as an organic additive. Effects of reaction time, reaction

temperature, and the amount of MAH on the degree of carboxylation were investigated. Morphologies and structure of the WS composite superabsorbent were characterized by FTIR, SEM, and X-ray diffraction (XRD).

EXPERIMENTAL

Materials
AA, analytical grade, was purified by distillation under vacuum. Acrylamide (AM), analytical grade, was purified by recrystallization. *N*,*N*-methylene-*bis*-acrylamide (MBA), analytical grade, was purified by recrystallization. MAH, ammonium persulfate (APS), and sodium bisulfite (SBS), analytical grade, were used without further purification. WS used in this study was agricultural residue of Chengdu, China. WS were crushed by disintegrator first and then ground to a 100 mesh particle size prior to use. All solutions were prepared with distilled water.

Modification of Wheat Straw with Maleic Anhydride
WS was cut into pieces and washed several times with distilled water and then dried at 70°C to a constant weight. The

dried WS was milled and screened, with a particle size of 100–200 mesh. A weight quantity of dried WS powder and N,N-dimethyl formamide (DMF) were added into a 250-mL flask and stirred by ultrasonic wave for 40–60 min, and then MAH was added into the above slurry and heated to 75–115°C for about 5 h under ultrasonic stirring. Finally, the resulting product was cooled to room temperature, filtered, and washed several times with distilled water and ethanol and then dried at 70°C to a constant weight. The dried MAH-modified WS was milled and screened, with a particle size of 100–200 mesh.

Determination of the Degree of Carboxylation of Maleic Anhydride-Modified Wheat Straw

Degree of carboxylation (D_c) was determined by using titration method. A sample of about 1.0 g MAH-modified WS was dissolved in 10 mL of benzyl alcohol, and then 10 mL 0.5 mol/L NaOH was added to the slurry and the solution was occasionally shaken for 72 h to complete saponification at room temperature. The excess alkali in the solution that leached from the sample was titrated with 0.5 mol/L HCl using phenolphthalein as an indicator. Blank runs were carried out for correction.

Degree of carboxylation (D_c) was calculated according to the following equations:

$$W_{ma} = \frac{98c(V_0 - V)}{1000 \times W} \qquad (1)$$

$$D_c = \frac{162W_{ma}}{98(1 - W_{ma})} \qquad (2)$$

where W_{ma}, content of MAH group; W, mass of MAH-modified WS powder; c, HCl concentration (mol/L); V_0, volume (mL) of HCl used to titrate blank; V, volume (mL) of HCl used to titrate sample; 162, molecular weight of the anhydroglucose unit; 98, molecular weight of MAH.

Preparation of Wheat Straw Composite Superabsorbent

A series of WS composite superabsorbents with different amounts of MAH-modified WS powder, cross-linker, and different AA/AM mass ratio were prepared by the following procedure: (1) typically, a weight quantity of dried MAH-modified WS powder and distilled water were put in a 250-mL three-necked flask equipped with a stirrer, a condenser, and a thermometer. The slurry was heated to 55–65°C and then redox initiator APS (88 mg) and SBS (28 mg) were added into the slurry under nitrogen atmosphere. After 30 min, 8 g of AA with 55–75% neutralization degree (neutralized with 20% sodium hydroxide solution in an ice bath), 6 g of AM, and 48 mg of MBA were added into the flask. After reaction for 3 h at 55–65°C, the resulting product was washed several times with distilled water and ethanol and then dried at 70°C to a constant weight. The dried product was milled and screened, with a particle size of 100 mesh.

Water Absorbency Using Filtration Method

Approximately 50 mg of dried superabsorbents with a particle size of 100 mesh were dispersed in 100 mL of deionized water for 30–60min. Then, excess water was allowed to drain through a 300-mesh wire gauze. The weight of the superabsorbent
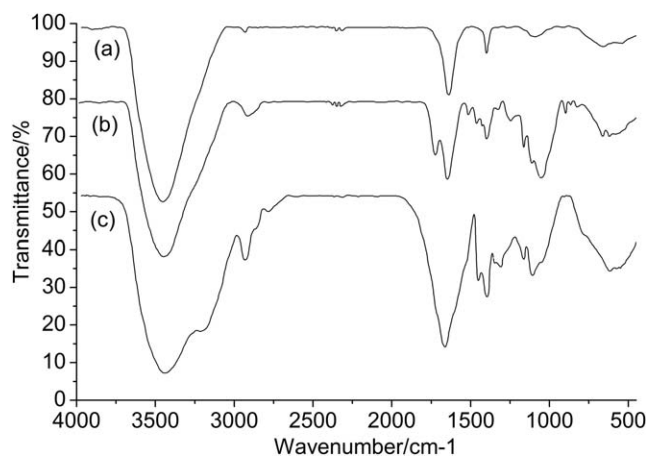

Figure 1. FTIR spectra of the raw WS (a), MAH-modified WS (b), and WS composite superabsorbent (c).

containing absorbed water was measured after draining for 1 h and water absorbency were calculated according to the following equation:

$$Absorbency\left(\frac{g}{g}\right) = \frac{W_2 - W_1}{W_1} \qquad (3)$$

where W_1 and W_2 are the weight of the dry and swollen superabsorbent, respectively.

Characterization of the Water Superabsorbent

The micrographs of superabsorbents were taken using SEM (JSM-5600LV, JEOL, Ltd). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold. FTIR spectrum was carried out on a Perkin–Elmer 1750 spectrophotometer, equipped with an Epson Endeavour II data station. The samples were prepared as KBr pellets or as liquid films interposed between KBr discs. XRD measurements were performed using an X-ray diffractometer, Bruker AXS Model D8 Discover (Cu Kαradiation, 40 kV, 40 mA, with $\lambda = 0.15406$ nm, and $n = 1$) at a scanning range from 10° to 60°and a scanning rate of 0.0258 min^{-1}.

RESULTS AND DISCUSSION

FTIR Spectra of the Composite Superabsorbent

WS composite superabsorbent was synthesized by simultaneous graft copolymerization of AA and AM onto MAH-modified WS by using APS and SBS as redox initiators and MBA as a cross-linker. The possible mechanism for cross-linking graft copolymerization is shown in Scheme 1. Redox initiators decompose to generate sulfate anion radicals and sulfite radicals under heating. These radicals either abstract hydrogen from the hydroxyl group of the WS backbone to form alkoxy radicals on the WS backbone or attack the double linkage of MAH to form free radicals on the WS backbone. These macroradicals initiate AA/AM grafting onto WS backbone and lead to a graft copolymer. Because a cross-linking agent, for example, MBA, is presented in the system, the copolymer comprises a cross-linked structure. FTIR
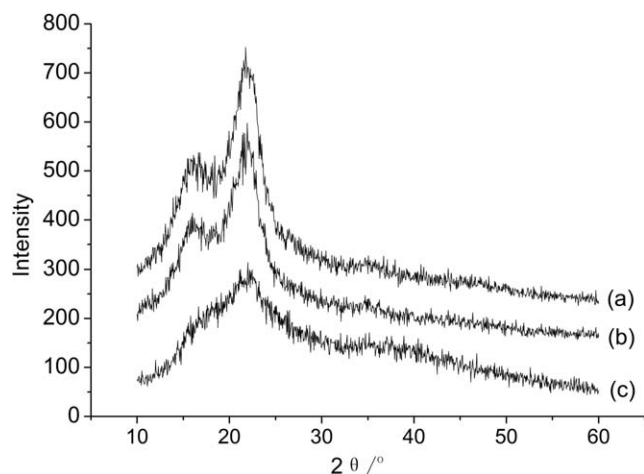
Figure 2. XRD patterns for the raw WS (a), MAH-modified WS (b), and WS composite superabsorbent (c).

Figure 3. SEM of WS (a) and WS composite superabsorbent (b).

spectroscopy was used to confirm the chemical structure of composite superabsorbent.

The infrared spectra of WS, modified straws, and WS composite superabsorbent containing 10 wt % WS are shown in Figure 1. The main components of WS are cellulose, hemicelluloses, and lignin. The raw WS displays the following bands, namely, the band at 3445 cm^{-1} is attributed to OH stretching in hydroxyl functional groups. The band at 2932 cm^{-1} is ascribed to C–H stretching absorption bands that might be present in methylene groups in cellulose. The bands at 1640 and 1401 cm^{-1} are ascribed to the skeletal C=C stretching vibrations in the aromatic ring bands. In the infrared spectrum of MAH-modified WS, the new absorption bands at 1718 and 1282 cm^{-1} are attributed to carboxylic acid.[27,28] This confirms that MAH have reacted onto WS backbone. In the infrared spectrum of WS composite superabsorbent, the absorption bands at 1663 cm^{-1} represents amide group stretching,[29] and 1563 cm^{-1} is ascribed to asymmetric –COO stretching; the band at 1401 cm^{-1} (the skeletal C=C stretching vibrations in the aromatic rings) indicates the existence of WS in the composites. Therefore, the resulting product is a composite based on poly(AA/AM) incorporated with WS.

XRD Analysis of the Composite Superabsorbent

XRD patterns of raw WS, MAH-modified straws, and WS composite superabsorbent are shown in Figure 2. As indicated in Figure 2, raw WS shows two distinct diffraction peaks, an indicative of polycrystalline structure of WS. MAH-modified WS still has these two characteristic diffraction peaks. This conforms that MAH reacts with hydroxyl groups only in the amorphous regions of WS without destroying its polycrystalline structure. However, after graft copolymerizing of MAH-modified WS with AA and AM, these diffraction peaks almost disappear and are transformed into a large and wide dispersion peak. This might demonstrate the successful grafting of AA and AM onto WS backbones, which destroys the crystal structure of WS under ultrasonic irradiation and transforms the polycrystalline structure of WS into amorphous structure.
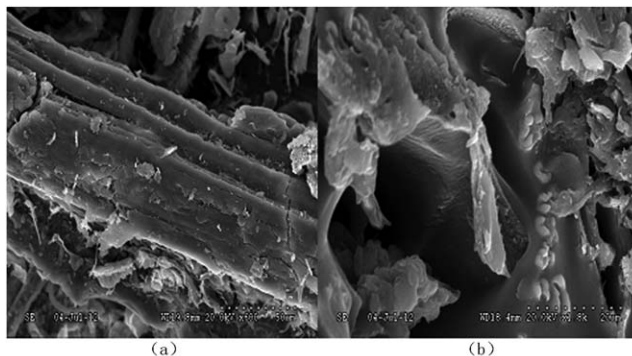
Morphologies of the Composite Superabsorbent

SEM micrographs of dried WS and dried WS composite superabsorbent are depicted in Figure 3. It can be observed that dried WS displays a porous and fibrous morphology. However, composite superabsorbent presents an undulant and coarse surface with many microporous holes after WS graft modification, which can facilitate the permeation of water into the polymeric network.[30] This indicates that WS composite superabsorbent has good water absorption.

Effects of Reaction Temperature on the Degree of Carboxylation of Maleic Anhydride-Modified Wheat Straw

In this article, MAH was selected to react with hydroxyl groups on WS under ultrasonic wave and different temperatures, using DMF as solvent. Effects of reaction temperature on the degree of carboxylation are presented in Figure 4. From Figure 4, it is clear that reaction temperature has great influence on the degree of carboxylation. Degree of carboxylation increases rapidly as temperature increases from 75°C to 95°C, while decreases considerably with further increase in temperature.

Higher temperature will favor higher reaction rate between anhydride and hydroxyl groups on WS because of the enhanced diffusion of MAH toward reactive sites on WS, enhanced swellability of WS, and enhanced mobility of the
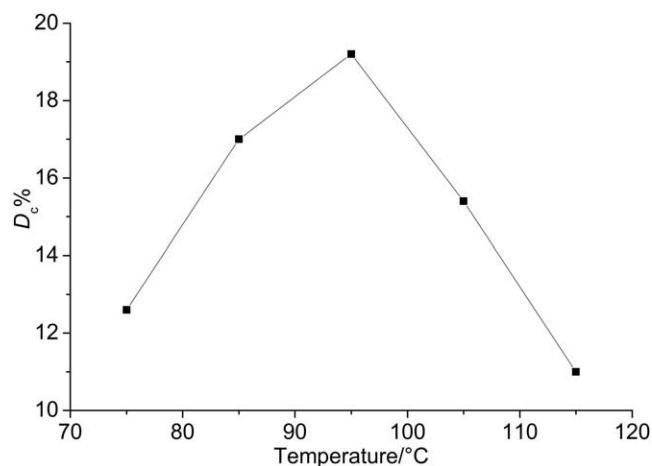

Figure 4. Effect of temperature on the degree of carboxylation of MAH-modified WS.
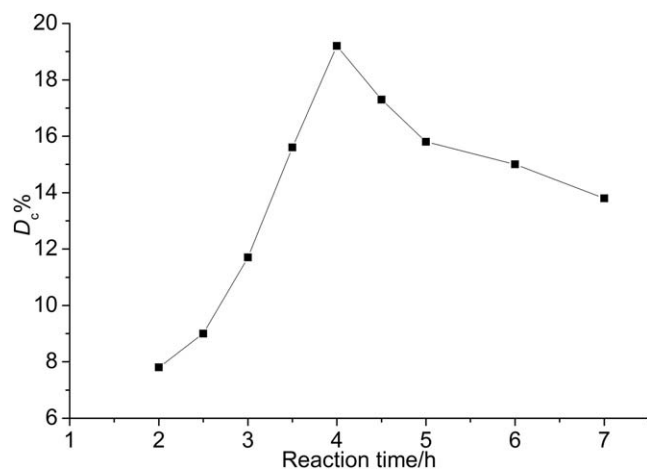
Figure 5. Relationship between the degree of carboxylation and reaction time of MAH-modified WS at 95°C.

Figure 6. Influences of MAH amount (based on WS mass) on the degree of carboxylation of MAH-modified WS.

reactant molecules. Therefore, the degree of carboxylation increases with increasing temperature. However, when temperature exceeds 95°C, the degree of carboxylation decrease rapidly because of some side reactions, such as oxidation of hydroxyl groups and degradation of some amount of cell wall polymers at higher temperatures.[31]

Effects of Reaction Time on the Degree of Carboxylation of Maleic Anhydride-Modified Wheat Straw

Relationship between the degree of carboxylation and reaction time of MAH-modified WS at 95°C is shown in Figure 5. It can be seen that the degree of carboxylation increases considerably with increasing reaction time up to 4 h, and then decreases gradually with a further increase in reaction time.

Recently, ultrasound techniques have been reported to improve the isolation of cell wall polymers. The mechanical action of the ultrasound on the cell walls results in an increased accessibility and enhanced penetration of solvent into cellular materials and improved mass transfer.[32–35] Besides, the solid surface in contact with the liquid might be enhanced through ultrasonic irradiation because of acoustic cavitation.[36] Therefore, longer reaction time will promote reaction between anhydride and hydroxyl groups on WS. However, when reaction time exceeds 4 h, the degree of carboxylation decreases gradually because of some side reactions, such as oxidation of hydroxyl groups and degradation of some amount of cell wall polymers at temperature as high as 95°C.[31]

Effects of Maleic Anhydride Amount on the Degree of Carboxylation of Maleic Anhydride-Modified Wheat Straw

WS is an abundant biodegradable resource and its main components are cellulose, hemicellulose, and lignin. Three free hydroxyl groups on C2, C3, and C6 of the anhydroglucose unit of the WS can react with anhydride group, although these three free O–H groups have different reactivities. MAH amount has great influence on the degree of carboxylation and the results are indicated in Figure 6. It is interesting to observe that the degree of carboxylation increases with MAH amount
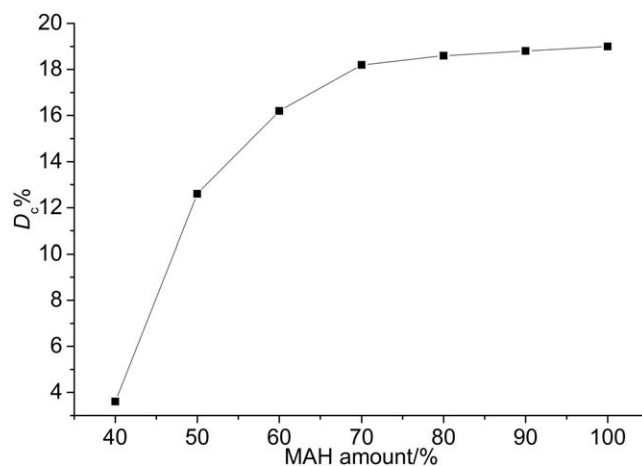
nonlinearly and then levels off when the MAH amount surpasses about 70%.

More MAH will accelerate reaction rate between anhydride and hydroxyl groups on WS because of an increase in availability of anhydride molecules in the proximity of WS reactive sites. Consequently, the degree of carboxylation increases with MAH amount. WS has crystalline and amorphous regions, where MAH can only react with hydroxyl groups residing in the amorphous regions. Besides, large branched chains formed by reaction between anhydride and hydroxyl groups may impede the further reaction between anhydride and hydroxyl groups because of their steric hindrance. Therefore, the degree of carboxylation changes slightly when MAH amount exceeds 70%.

Swelling Kinetics of the Composite Superabsorbent

The swelling capacity of WS composite superabsorbent was measured in distilled water at consecutive time intervals. Figure 7 represents the dynamic swelling behavior of the WS composite superabsorbent with the composition of 10 wt % WS, 1.6 wt % initiator, 0.3 wt % cross-linker, and AA/AM mass ratio of 60:40. Initially, the rate of water absorbency sharply increases
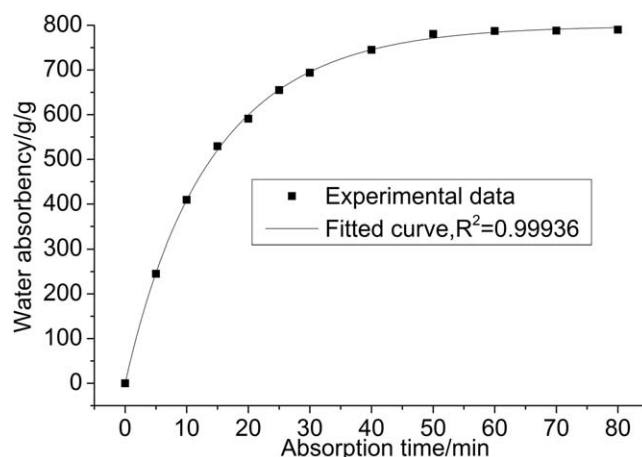

Figure 7. Water absorbency rate of WS composite superabsorbent.

and then begins to level off. The equilibrium swelling with water absorbency of 781 g/g, is achieved after 50 min. A power law behavior is obvious from Figure 7. The swelling kinetics can be expressed by the Voigt-based viscoelastic model (eq. (4))[37]:

$$Q_t = Q_e(1 - e^{-t/r}) Q_t = Q_e(1 - e^{-t/r}) \tag{4}$$

where Q_t (g/g) is the degree of swelling at time t, Q_e is the equilibrium swelling (power parameter, g/g), t is time (min) for swelling Q_t, and r (min) stands for the " rate parameter," denoting the time required to reach 0.63 of equilibrium water absorbency.

The data obtained from the equilibrium water absorbency and the swelling rate is fitted into the eq. (4) to obtain the rate parameter r and power parameter Q_e. The rate parameter and power parameter for the composite superabsorbent are found to be 13.1 min and 791 g/g, respectively. Because the rate parameter r is a measure of resistance to water permeation, a low calculated r value (13.1 min) reflects a high swelling rate of the composite superabsorbent.[38]

CONCLUSIONS

WS was first carboxylated by MAH under ultrasonic stirring and then the WS composite superabsorbent was prepared by graft copolymerization among MAH-modified WS, AM, and AA in aqueous solution. Effects of reaction time, reaction temperature, and the amount of MAH on the degree of carboxylation were investigated. The superabsorbent composite has water absorbency of 781 g/g within 50 min with the composition of 10 wt % WS, 1.6 wt % initiator, 0.3 wt % cross-linker, and AA/AM mass ratio of 60:40. FTIR spectra confirm the formation of MAH-modified WS and WS composite superabsorbent by exhibiting all the characteristic bands of both WS and monomer units. Composite superabsorbent has an undulant and coarse surface with many large microporous holes.

ACKNOWLEDGMENTS

REFERENCES

1. Kosemund, K.; Schlatter, H.; Ochsenhirt, J. L.; Krause, E. L.; Marsman, D. S.; Erasala, G. N. *Regul. Toxicol. Pharm.* **2009**, *53*, 81.

2. Liang, R.; Yuan, H. B.; Xi, G. X.; Zhou, Q. X. *Carbohyd. Polym.* **2009**, *77*, 181.

3. Liu, M. Z.; Liang, R.; Zhan, F. L.; Liu, Z.; Niu, A. Z. *Polym. Int.* **2007**, *56*, 729.

4. Puoci, F.; Iemma, F.; Spizzirri, U. G.; Cirillo, G.; Curcio, M.; Picci, N. *Am. J. Agric. Biol. Sci.* **2008**, *3*, 299.

5. Mishra, D. K.; Tripathy, J.; Srivastava, A.; Mishra, M. M.; Behari, K. *Carbohyd. Polym.* **2008**, *74*, 632.

6. Duan, J. C.; Lu, Q.; Chen, R. W.; Duan, Y. Q.; Wang, L. F.; Gao, L.; Pan, S. Y. *Carbohyd. Polym.* **2010**, *80*, 436.

7. Sadeghi, M.; Hosseinzadeh, H. J. *J. Bioact. Compat. Pol.* **2008**, *23*, 381.

8. Wang, Q.; Zhang, J. P.; Wang, A. Q. *Carbohyd. Polym.* **2009**, *78*, 731.

9. Chang, C. Y.; Duan, B.; Cai, J.; Zhang, L. N. *Eur. Polym. J.* **2010**, *46*, 92.

10. Suo, A. L.; Qian, J. M.; Yao, Y.; Zhang, W. G. *J. Appl. Polym. Sci.* **2007**, *103*, 1382.

11. Pourjavadi, A.; Jahromi, P. E.; Seidi, F.; Salimi, H. *Carbohyd. Polym.* **2010**, *79*, 933.

12. Kiatkamjornwong, S.; Mongkolsawat, K.; Sonsuk, M. *Polymer.* **2002**, *43*, 3915.

13. Zhang, J. P.; Wang, Q.; Wang, A. Q. *Carbohyd. Polym.* **2007**, *68*, 367.

14. Mahdavinia, G. R.; Zohuriaan-Mehr, M. J.; Pourjavadi, A. *Polym. Adv. Technol.* **2004**, *15*, 173.

15. Wang, W. B.; Wang, A. Q. *Carbohyd. Polym.* **2009**, *77*, 891.

16. Pourjavadi, A.; Hosseinzadeh, H.; Sadeghi, M. *J. Compos. Mater.* **2007**, *41*, 2057.

17. Bertrand, I.; Prevot, M.; Chabbert, B. *Bioresour. Technol.* **2009**, *100*, 155.

18. Liu, J.; Li, Q.; Su, Y.; Yue, Q. Y.; Gao, B. Y.; Rui Wang, R. *Carbohyd. Polym.* **2013**, *94*, 539.

19. Li, Q.; Ma, Z. H.; Yue, Q. Y.; Gao, B.Y, Li, W. H.; Xu, X. *Bioresour. Technol.* **2012**, *118*, 204.

20. Liu, Z. X.; Miao, Y. G.; Wang, Z. Y.; Yin, G. H. *Carbohyd. Polym.* **2009**, *77*, 131.

21. Xie, L. H.; Liu, M. Z.; Ni, B. L.; Zhang, X.; Wang, Y. F. *Chem. Eng. J.* **2011**, *167*, 342.

22. Ma, Z. H.; Li, Q.;Yue, Q. Y.; Gao, B. Y.; Xu, X.; Zhong, Q. Q. *Bioresour. Technol.* **2011**, *102*, 2853.

23. Wan, T.; Yao, J.; Ma, X. L. *J. Appl. Polym. Sci.* **2008**, *110*, 3859.

24. Wan, T.; Wang, L.; Yao, J.; Ma, X. L.; Yin, Q. S.; Zang, T. S. *Polym. Bull.* **2008**, *60*, 431.

25. Wan, T., Wang, X. Q.; Yuan, Y.; He, W. Q. *Polym. Int.* **2006**, *55*, 1413.

26. Wan, T.; Wang, X. Q.; Yuan, Y.; He, W. Q. *J. Appl. Polym. Sci.* **2006**, *102*, 2875.

27. Chen G.; Zhang Y.; Zhou X. *Appl. Surf. Sci.* **2006**, *253*, 1107.

28. Schwanninger, M.; Rodrigues, J. C.; Pereira, H.; Hinterstoisser, B. *Vib. Spectrosc.* **2004**, *36*, 23.

29. Krishnan, M.; Flanagan, D. R. *J Control Release* **2000**, *69*, 273.

30. Omidian, H.; Hashemi, S. A.; Sammes, P. G.; Meldrum, I. *Polymer.* **1999**, *40*, 1753.

31. #P.; Konwar, D. *Org. Biomol. Chem.* **2005**, *3*, 3473.

32. Aliyu, M.; Hepher, M. J. *Ultrason. Sonochem.* **2000**, *7*, 265.

33. Mason, T. J.; Paniwnyk, L.; Lorimer, J. P. *Ultrason. Sonochem.* **1996**, *3*, 253.

34. Ebringerova, A.; Hromadkova, Z. *Ultrason. Sonochem.* **1997**, *4*, 305.

35. Liu C. F.; Sun R. C.; Qin M. H.; Zhang A. P.; Ren J. L.; Xu F.; Ye J.; Wu S. B. *Ind. Crops. Prod.* **2007**, *26*, 212.

36. Mason, T. J.; Joyce, E.; Phull, S. S.; Lorimer, J. P. *Ultras. Sonoch.* **2003**, *10*, 319.

37. Hosseinzadeh, H.; Pourjavadi, A.; Zohuriaan-Mehr, M. J. *J. Biomater. Sci. Polym Ed.* **2004**, *15*, 1499.

38. Pourjavadi, A.; Mahdavinia, G. R. *Turk. J. Chem.* **2006**, *30*, 595.