Synthesis of Amphoteric Superabsorbent Polymer Modified by Wheat Straw Cellulose

WANG Dan

WANG Dan, SONG Zhan-qian, SHANG Shi-bin *

(Institute of Chemical Industry of Forest Products, CAF; Key and Open Lab. on Forest Chemical Engineering, SFA, Nanjing 210042, China)

Abstract: Superabsorbent polymers (SAPs) were prepared from wheat straw cellulose (WSC), acrylic acid (AA), acrylamide (AM) and [2-(methylacryloyloxy) ethyl] trimethylammonium chloride (MAETAC) through graft copolymerization. Factors affecting water-absorbent capacity of SAPs, such as monomers ratio, WSC dosage, contents of initiator and crosslinking agent, and neutralization degree of AA were investigated and discussed in detail. Amphoteric SAPs, with absorbent capacity of 853 times their own weight in distilled water and 118 times in 0.9 % saline solution under optimized synthesis condition, were obtained.

Key words: amphoteric superabsorbent polymer; wheat straw cellulose; water absorbency

CLC number: TQ35; TQ32 **Document code**: A **Article ID**: 0253 - 2417(2006)02 - 0033 - 05

麦秸秆纤维改性两性高吸水树脂合成及性能研究

王 丹, 宋湛谦, 商士斌

(中国林业科学研究院 林产化学工业研究所;国家林业局 林产化学工程重点开放性实验室, 江苏 南京 210042)

摘 要:利用麦秸秆、丙烯酸、丙烯酰胺和甲基丙烯酰氧乙基三甲基氯化铵(DMC)为原料,通过接枝共聚合成高吸水性树脂。对影响反应的因素,如麦秸秆用量、单体丙烯酸、丙烯酰胺、DMC的用量和配比、引发剂及交联剂用量、丙烯酸中和度等进行了详细研究,得到了最佳制备工艺条件。制备的两性高吸水性树脂吸蒸馏水达853 g/g、吸生理盐水为118 g/g。

关键词:两性高吸水性树脂;麦秸秆;吸水性

As a new type of material developing fast in polymeric science in recent years, superabsorbent polymers (SAPs) are moderately crosslinked functional polymer-based material which contain strong hydrophilic groups, and can absorb a large amount of water during a short time and the absorbed water is hardly removable even under pressure. Therefore, SAPs have great advantages over traditional water-absorbing materials such as cotton, pulp, and sponge, and have found a variety of valuable applications[1-2]. From different sources of raw materials, SAPs can be generally classified into three classes: synthetic, starch-based and cellulose-based. Synthetic SAPs are slightly crosslinked homopolymers of hydrophilic vinyl monomers, but in this kind of SAPs remains unreacted acrylic acid that is harmful to people, and it is nonbiodegradable. Starch-based and cellulose-based SAPs are produced by graft copolymerization of various hydrophilic vinyl monomers onto starch and cellulose[3-5]. Cellulose-based SAPs have attracted great attention because of their excellent gel strength and stability, low soluble component, high mildew resistance, etc.

In this paper, the authors reported synthesis of superabsorbent polymers by graft copolymerization of AA, AM and MAETAC onto WSC using N,N′-methylenebisacrylamide (NMBA) as crosslinking agent and sodium

Received date: 2005 - 09 - 21

Foundation item: 国家自然科学基金资助项目(30471362)

Biography: 王 丹(1979 -),男,山东龙口人,博士生,从事纤维素化学利用研究与开发

* **Correspondence Auther**: 商士斌,研究员,从事天然资源化学利用研究与开发; **E-mail**: shangsb@ hotmail. com。

bisulfite (SBS) and ammonium persulfate (APS) as initiator in aqueous solution. The effects on water absorbency of such factors as monomers ratio, WSC dosage, neutralization degree of AA, content of initiator and crosslinking agent were investigated. This is an innovated research never reported in previous articles. Using renewable and agriculturally-derived wheat straw as extender and replacement for synthetic, petroleum-based superabsorbent polymers not only reduces our dependence on petrochemical derivatives, but also provides improved material in which carbohydrate portion can be biodegraded rapidly in environment, and would produce great economic and social benefits.

1 Experimental

1.1 Materials

WSC was prepared in lab. AA (chemically pure) was distilled under reduced pressure and stored at −8℃ until it was used. MAETAC (76.12 %, aqueous solution) was purchased from Xinyu Chemical Industry Co. Ltd, China, and was used without purification. AM, NMBA, SBS and APS were all chemically pure and used as purchased.

1.2 Synthesis procedure

A series of amphoteric SAPs were prepared by the following procedure: Reactions were conducted in a three-necked flask equipped with a mechanical stirrer, condenser, and nitrogen line. A weighed quantity of AA was dissolved in distilled water and then neutralized at 5 ℃ with sodium hydroxide solution (6 mol/L) in the flask. A predetermined ratio of WSC and other monomers (AM, MAETAC) along with crosslinking agent (NMBA) dissolved in distilled water were put into reaction vessel under nitrogen flushing. After 15 min, initiator(SBS and APS) was added to the reaction mixture and then the whole system was put in a thermostat water bath at constant temperature. After graft copolymerization, gel was formed. The resulting product was washed with ethanol and then dried in vacuum oven at 60 ℃ to constant weight. After drying, reweighing, and milling through screen, amphoteric SAPs were obtained.

1.3 Water-absorbency measurement

A weighted quantity of copolymer was immersed in distilled water at room temperature until swelling equilibrium was reached. Swollen gel was then separated from unabsorbed water by filtering through a 200-mesh screen. Water absorbability of the copolymer was determined by weighing the swollen gel, and absorbency was calculated by the following formula:

$$A = (m_2 - m_1)/m_1$$

Where m_1 and m_2 denote weights of dried and water-swollen copolymers, respectively, g; A denotes absorbency which was calculated as grams of water per gram of dried copolymer, g/g.

Absorbency in saline solutions of the copolymer sample was evaluated in 0.9 % NaCl solution, according to the former method described for water-absorbency measurement in distilled water.

2 Results and discussion

2.1 Effect of weight ratio of AA to MAETAC for WSC-graft-poly (AA-co-MAETAC)

Effect of ratio of AA to MAETAC on water absorbency was investigated (Fig. 1). At the beginning when AA is less than 40 % of both monomers, water absorbency decreased with increase of AA content and tended to disappear. This is possibly because of the interaction between anion of AA and cation of MAETAC. When AA is about 40 %, amounts of positive and negative charge tended to be equal, and the combination of positive and negative ions induced contraction of polymeric chain, therefore hydrophilic property of copolymers was lowered. Subsequently, absorbency increased with further increasing of AA content until 80 %. Experiments show that an ideal ratio of AA to MAETAC is 4 : 1.

2.2 Effect of weight ratio of AA to AM for WSC-graft-poly (AA-co-AM)

Influence of weight ratio of AA to AM on water absorbency was showed in Fig. 1. When content of WSC and total amount of AA and AM were kept constant, water absorbency increased with increase of weight ratio of AA to AM for the gels until the percentage of AA is 65 %. Sorption capacity decreased with further increase of AA. This phenomenon is explained by the decrease of hydrophilic group (—COOH) along with increase of content of AM in gels. Experiments show that appropriate ratio of AA to AM is 1.86 : 1.

2.3 Effect of weight ratio of AM to MAETAC for WSC-graft-poly (AM-co-MAETAC)

Influence of weight ratio of AM to MAETAC on water absorbency can be seen in Fig. 1. It is clearly seen that equilibrium swelling capacity of gel increases with percentage of MAETAC monomer when it is less than 35 % of two monomers. Further increase of MAETAC causes decrease in water absorbency. This is attributed to the cooperation of nonionic and cationic groups. Therefore the best ratio of AM to MAETAC is 1 : 1.86 as shown in Fig. 1.

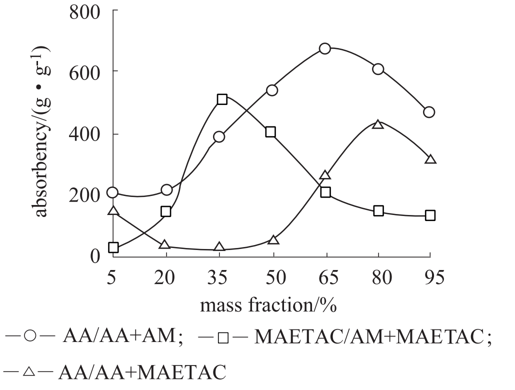

Fig. 1 Effects of composition of monomers on absorbency of WSC graft copolymers

2.4 Effect of weight ratio of three monomers for WSC-graft-poly (AA-co-AM-co-MAETAC)

In order to find the best ratio of AA, AM and MAETAC for copolymers, the amount of total monomers and wheat straw cellulose and two monomers' ratio were kept constant, and the application of other one was changed. Table 1 summarized the effect of ratio of three monomers on water absorbency. It can be seen that different ratio caused different sorption capacity. Experiments showed higher absorbency than other two situations for copolymers when ratio of AA and AM was constant. As ratio of three monomers was m(AA) : m(AM) : m(MAETAC) = 1.86 : 1 : 0.31, 1 g of gel can absorb 553 g of distilled water. It is the optimal ratio for the copolymer, which can furthest improve the cooperation of different hydrophilic ions.

Table 1 Effect of monomer ratio on absorbency of WSC-graft-poly (AA-co-AM-co-MAETAC)

samples No.	m(AA) : m(AM) : m(MAETAC)	absorbency / ($g \cdot g^{-1}$)	samples No.	m(AA) : m(AM) : m(MAETAC)	absorbency / ($g \cdot g^{-1}$)
1	1.86 : 1 : 0.12	452	9	4 : 5.00 : 1	335
2	1.86 : 1 : 0.31	553	10	4 : 11.67 : 1	279
3	1.86 : 1 : 1.23	421	11	4 : 45.00 : 1	268
4	1.86 : 1 : 2.86	49	12	0.31 : 1.86 : 1	171
5	1.86 : 1 : 6.67	305	13	1.23 : 1.86 : 1	65
6	1.86 : 1 : 25.74	364	14	2.86 : 1.86 : 1	264
7	4 : 0.56 : 1	331	15	6.67 : 1.86 : 1	352
8	4 : 2.14 : 1	391	16	25.74 : 1.86 : 1	433

2.5 Effect of WSC dosage

Fig. 2(a) shows the influence of content of WSC on water absorbency of copolymers. Increasing WSC/monomers ratio up to 15 % caused a slight increment in water absorbency. However, further increase of WSC caused a decrease in water absorbency, which could be explained by that with the increasing of WSC, viscosity of the reaction system increased and collisions between monomers and radicals were blocked, so speed of copolymerization was lowered, grafted chain was shorted, and effective three-dimensional network cannot be built, therefore sorption capacity decreased. It is appropriate that WSC dosage is 5 %–15 % of total amount of monomers.

2.6 Effect of neutralization degree of AA

Effect of neutralization degree of AA on water absorbency is shown in Fig. 2(b). It is obvious that water absorbency increased from 40 % to 70 % and decreased with further increases in the neutralization degree of AA. When AA was neutralized with sodium hydroxide, negatively charged carboxyl groups attached to the polymer chains to set up an electrostatic repulsion that tended to expand the network. In a certain range of neutralization degree, electrostatic repulsion increased with increase of neutralization degree, resulting in the increase of water absorbency. In addition, with lower neutralization degree, monomer AA was more active and also played the role of crosslinking agent, which resulted in higher crosslinking density of the gel and lower water absorbency. Furthermore, low neutralization degree also caused less ion concentration of copolymer network and lower osmotic pressure, which resulted in the decrease of water absorbency. However, further increase in neutralization degree led monomer AA to be less active, which caused increase of chain transfer reaction and proportion of short-grafted polymeric chain, so soluble part of the product increased and water absorbency declined[6-8]. Under our experimental conditions, neutralization degree of 70 % of AA possesses the highest water absorbency.

2.7 Effect of initiator content

Influence of initiator content on absorbent capacity of gel was studied by varying initiator content from 1 % to 4 % of monomers (Fig. 2(c)). Initiator concludes SBS and APS, and molar ratio of them is 1 : 1. Maximum absorbency (560 g/g) was obtained at 2.5 % of initiator content. More or less than this content gave gel with decreased absorbent capacity. The number of active free radicals on WSC backbone was decreased at content of initiator lower than 2.5 %, which resulted in lower graft polymerization extent and consequently in lower final water absorbency. Subsequent absorbency loss is due to increase in number of radicals produced as concentration of initiator increases. The increase in the production of radicals promotes rate of polymerization, thereby lessening the crosslinking density, and is further responsible for a decrease in water absorbency.

2.8 Effect of crosslinking agent content

Fig. 2(d) demonstrates the effect of crosslinking agent content on absorbent capacity of product. Water absorbency increases as NMBA content increases from 0.1 % to 0.2 % and decreases considerably when NMBA content is higher than 0.2 % of total amount of monomers. This is due to decrease in the space between copolymer chains as crosslinking agent content increases. The absorbed water is constrained among polymer networks so that it can hardly be removed even under some pressure. With low content of crosslinking agent, the absence of crosslinked networks limits the amount of water that can be absorbed, which was shown in Fig. 2(d). More crosslinking agent causes higher crosslinking density and decreases the space between copolymer chains and consequently, the resulting highly crosslinked rigid structure cannot be expanded and hold a large quantity of water. From Fig. 2(d), it is clear that maximum absorbency is found when content of NMBA reaches 0.2 % of the total amount of monomers.

2.9 An orthogonal experiment

SAPs synthesized under the above individual optimal conditions did not possess high water absorbency. This may due to the neglect of interactions of those factors. For example, proportion of hydrophilic groups, which greatly influences absorbent capacity of copolymers, depends on not only the proportion of monomers but also on neutralization degree of AA; structure of three-dimensional network relates to nearly all factors. The former optimal conditions were obtained respectively when only one factor was alterable and others were fixed values. Therefore, it is necessary to carry out an orthogonal experiment in which relevant factors on water

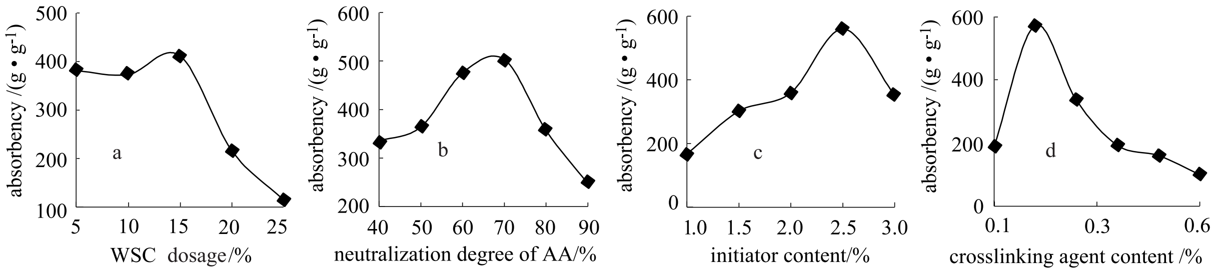

Fig. 2　Effects of WSC dosage(a), meutralization degree of AA(b), initiator content (c) and crosslinking agent content (d) on absorbency of WSC-graft-poly (AA-co-AM-co-MAETAC)

absorbency, including monomers ratio, neutralization degree of AA, WSC dosage, initiator content and crosslinking agent content, can be investigated together. According to orthogonal experiment, maximum absorbency (water absorbency 853 g/g and w 0.9 % NaCl solutions 118 g/g) was achieved under optimum conditions that were found to be weight ratio of monomers m(AA) : m(AM) : m(MAETAC) = 1.86 : 1 : 0.31, neutralization degree of AA 75 %, WSC dosage 5 %, initiator content 2.5 % and crosslinking agent content 0.1 % of the total amount of monomers.

3　Conclusion

Amphoteric superabsorbent polymers with anionic, cationic, and nonionic hydrophilic groups were prepared by graft copolymerization of AA, AM and MAETAC onto cellulose chain of wheat straw. Monomers ratio, WSC dosage, contents of initiator and crosslinking agent, and neutralization degree of AA have important influences on water absorbency of SAPs. Under optimum conditions, amphoteric SAPs have the absorbent capacity of 853 times its own weight in distilled water and 118 times in 0.9 % saline solution.

References:

[1] YOSHIDA M, ASANO M, SUAKURA M. A new temperature-sensitve hydrogel with α-amino acid group as side chain of polymer [J]. Eur Polym J, 1989, 25(10): 1197-1202.

[2] SHIGA T, HIROSE Y, OKADA A, et al. Bending of poly (vinyl alcohol)-poly(sodium acrylate) composite hydrogel in electric fields [J]. J Appl Polym Sci, 1992, 44(2): 249-253.

[3] CHEN J W, ZHAO Y M. An efficient preparation method for superabsorbent polymers [J]. J Appl Polym Sci, 1999, 74: 119-124.

[4] WEI L, WEI'AN Z, PENG C, et al. Synthesis and properties of starch grafted poly [acrylamide-co-(acrylic acid)]/montmorillonite nanosuperabsorbent via γ-ray irradiation technique [J]. J Appl Polym Sci, 2005, 96(4): 1341-1346.

[5] GULTEN G, GAMZE G. Graft copolymerization of acrylic acid onto cellulose: Effects of pretreatments and crosslinking agent [J]. J Appl Polym Sci, 2001, 80: 2267-2272.

[6] AN L, AIQIN W, JIANMIN C. Studies on poly(acrylic acid)/ attapulgite superabsorbent composite. I. Synthesis and characterization [J]. J Appl Polym Sci, 2004, 92(3): 1596-1603.

[7] ARDESHIR S, KATBAB A A, VASHEGHANI-FARAHANI E, et al. Formulation design, optimization, characterization and swelling behaviour of a cationic superabsorbent based on a copolymer of [3-(methacryloylamino) propyl] trimethylammonium chloride and acrylamide [J]. Polym Int, 2004, 53(1):92-100.

[8] POURJAVADI A, SADEGHI M, HOSSEINZADEH H. Modified carrageenan. 5. Preparation, swelling behavior, salt- and pH-sensitivity of partially hydrolyzed crosslinked carrageenan-graft-polymethacrylamide superabsorbent hydrogel [J]. Polym Adv Technol, 2004, 15(11): 645-653.