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Graft copolymerization of chitosan with acrylic acid under microwave irradiation and its water absorbency

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Abstract

Acrylic acid was grafted onto chitosan by using the ceric ion as an initiator in the presence of *N*,*N*′-methylenebisacrylamide (MBA) as a crosslinker under microwave irradiation based on our modified apparatus. The effects of some grafting variables on the water absorbency were investigated by orthogonal tests, and the optimal conditions were described. The structure of the graft copolymer was confirmed by IR spectrum and TGA. The influence of microwave power and the amounts of the initiator and crosslinker on the reaction were further studied. The result shows that the microwave irradiation method can increase the reaction rate by eight times over the conventional method. The graft copolymer is an effective superabsorbent resin (SAR) and can absorb water 704 times its own dry weight.

Keywords: Graft copolymerization; Chitosan; Acrylic acid; Microwave irradiation; Superabsorbent

1. Introduction

Chitosan is a highly deacetylated derivative of chitin, one of the most abundant natural and biodegradable polymers. It has been widely applied in the biomedical, pharmaceutical, cosmetic, and agricultural fields (Goosen, 1997). It has both reactive amino and hydroxyl groups that can be used to chemically alter its properties under mild reaction conditions. It is a bio-adsorber with gel forming ability. The superabsorbent resins grafted with chitosan can absorb aqueous solutions up to hundreds of times their own dry weight (Nge, Hori, Takemura, & Ono, 2004) and should have the antibacterial activities (No, Park, Lee, Hwang, & Meyers, 2002). Therefore, the superabsorbent resin can be used in infant diapers, feminine hygiene products, agriculture, and other specialized areas (Dutkiewicz, 2002). An effective approach to modify swelling behavior of chitosan resin in various pHs is graft polymerization of vinylic monomers such as acrylic acid, acrylamide, acrylonitrile onto chitosan (Borzacchiello et al., 2001; Mahdavinia, Pourjavadi, Hosseinzadeh, & Zohuriaan, 2004; Yazdani-Pedram, Retuert, & Quijada, 2000). Among the recently developed superabsorbents, acrylic acid (AA)-based superabsorbents have been extensively studied because AA is cheap and easily polymerized to a higher molecular weight polymer (Raju & Raju, 2001). Many investigators (Qiu, Yu, & Zhu, 2005; Sashiwa & Shigemasa, 1999) have prepared the AA-based superabsorbents to enhance absorbency.

Microwave irradiation using the commercial household microwave oven has received increasing interest in organic synthesis due to the remarkable enhancement of the rates of some organic reactions over conventional reaction (Cao, Ge, & Lai, 2001; Shao, Yang, & Zhong, 2003). Microwave energy can be directly and uniformly absorbed throughout the entire volume of an object, causing it to heat up evenly and rapidly (Danks, 1999). The microwave irradiation has been successfully used in the synthesis of the superabsorbent resin of starch-sodium acrylate graft and the water-absorbent rate of the resin synthesized is much higher than that of the resin by traditional polymerization (Xu et al., 2004). It has been also used in the synthesis of chitosan-graft-poly (acrylonitrile) without any radical

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initiator in a very short time of 1.5 min (Vandana, Devendra, Ashutosh, & Rashmi, 2005). However, the reaction system based on the household microwave oven usually can't control the temperature and has no stirring which may cause some trouble reproducing the reaction results such as conversion and yield (Nüchter, Ondruschka, Bonrath, & Gum, 2004). Recently, we have modified the household microwave oven to control the temperature (Ge & Luo, 2005a). By using this apparatus, we have carried out some studies on the chemical modification of chitosan and obtained some significant results (Ge & Luo, 2005b; Zheng & Ge, 2003). In this paper, the microwave apparatus has been further modified with stirring and used to study the graft copolymerization reaction with acrylic acid onto chitosan to prepare the superabsorbent chitosan resin.

2. Experimental

2.1. Materials and equipments

Biochemical reagent grade chitosan (deacetylation degree > 90%, viscosity < 100 cps) from Shanghai Yuanju Biology Technology Ltd, Shanghai, China, was used. All other chemicals were of reagent grade and were used without further purification. A Galanz microwave oven (WP700L17), produced by Shunde Galanz Electric Appliances Factory, Ltd, China, was employed in these studies after modification as outlined below. IR spectra were recorded on a Bruker FT-IR spectrometer (Vector 33). Thermogravimetric analysis (TGA) was carried out on a Universal V4.1D TA Instruments (SDT Q600) in N_2 atmosphere.

2.2. Modification of microwave oven

A diagram of the microwave oven used in these studies is shown in Fig. 1 which has been further modified on the our previous work (Ge & Luo, 2005a). Five holes were drilled into the oven to provide the inlet and outlet for recycling thermostat water, the inlets for nitrogen gas, kerosene thermometer and the branch tube with the glass stirrer, reflux condenser, and drop funnel. The holes were jacketed with copper tubing to avoid microwave leakage. The thermostat recycling water was provided by a thermostat water bath. The kerosene thermometer was used to avoid the influence of microwave. Using this apparatus, the highest reaction temperature was 100 °C and temperature variation could be controlled under low or middle microwave power.

2.3. Grafting of chitosan with acrylic acid under microwave irradiation with Ce^{4+} as an initiator

Certain amounts (0.3 g) of chitosan and 10 ml of 5%(w/w) acetic acid solution were added to a three-neck reactor with swirling to get the chitosan solution. After completely dissolving and stewing for 2 h, some volume of 0.01 mol/L ammonium cerous sulfate (ACS) as the initiator was added to the solution. The reactor with stirring under nitrogen gas was placed in a thermostated water bath preset at the desired temperature (60 °C) to pretreat for 30 min. And then, 10 ml of 5 mol/L sodium hydroxide solution were added dropwise to the stirred acrylic acid solution (8 ml) in a 50 ml beaker cooled with an ice bath for partial neutralization. The partially neutralized acrylic acid and some volume of 0.01 mol/L *N*,*N*′-methylenebisacrylamide (MBA) solution as the crosslinker were added to the reactor, respectively. Finally, the reactor was transferred inside the water bath of the modified microwave oven preset at desired temperature (60 °C) and radiated by microwave for 30 min under nitrogen gas. In order to compare with the microwave method, the traditional heating method is used that let the reactor continue to place in the thermostated water bath at 60 °C to react for 4 h. After completing the reaction, the product was allowed to cool to room temperature and neutralized to pH 8 by addition of 1 mol/L NaOH solution. The product was filtered and washed with distilled water to remove the ungrafted molecules and monomer. The washed product was dehydrated with absolute ethanol. The dehydrated specimen was vacuum dried at 60 °C until the weight became constant. After being grounded and sieved with a 100-mesh steel screen, a powdered superabsorbent resin was obtained. The probable reaction route is given in Scheme 1.

2.4. Grafting degree and grafting efficiency

Grafting degree and grafting efficiency were calculated according to the following equations:

$$\text{Grafting degree} = (W_2 - W_0)/W_0,$$

$$\text{Grafting efficiency} = W_2/W_1,$$

where W_0, W_1, and W_2 are the weight of the raw chitosan, the product, the grafted copolymer that the homopolymers of the product were removed by extracting with dimethylformamide solvent, respectively.

2.5. Measurement of water absorbency

The powdered superabsorbent resin (0.1 g) was dispersed in distilled water (100 ml) for at least 2 h at room temperature to reach swelling equilibrium, which resulted in the absorption of water inside the network of the resin and the formation of swelled sample. The residual water was removed by filtrating with 100-mesh stainless steel screen and until water ceased to dropped. The weight of the resin containing absorbed water was measured after draining for 1 h, and the water absorbency was calculated according to the following equation:

$$\text{Absorbency(g/g)} = (W' - W)/W,$$

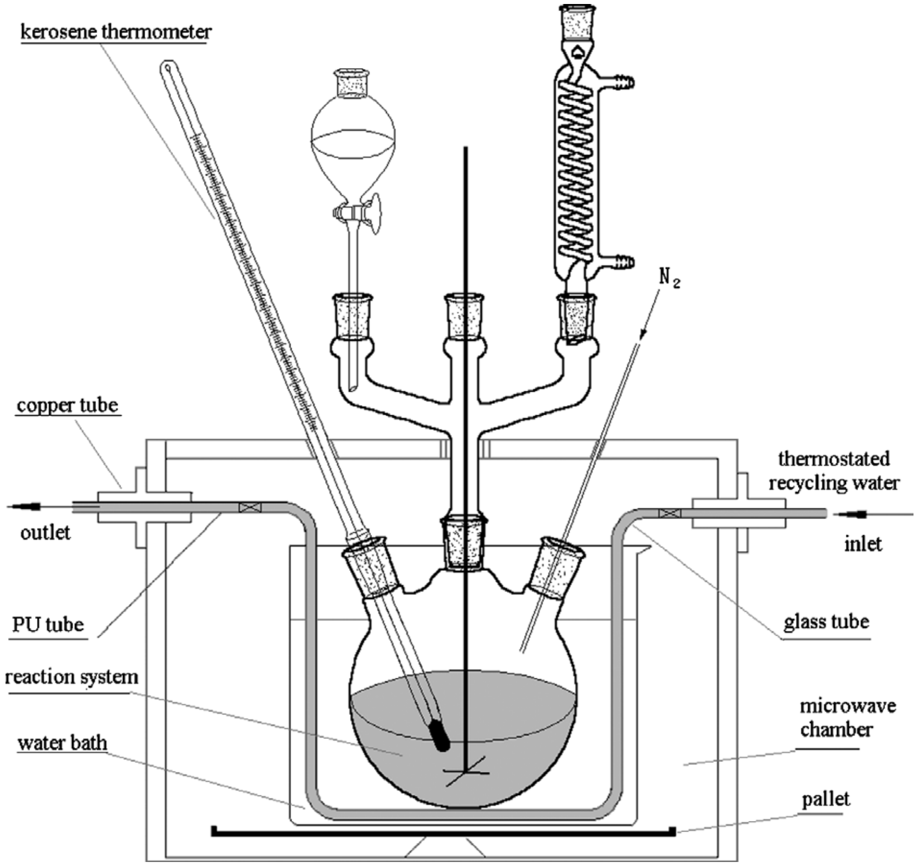
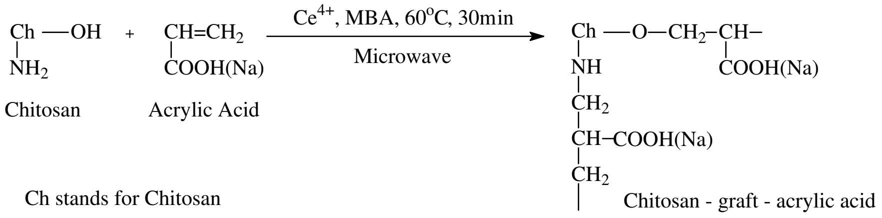


Fig. 1. Schematic of modified microwave oven.



Scheme 1.

where W and W' are the weight of the dry and swollen superabsorbent resin, respectively.

3. Result and discussion

3.1. Optimization of reaction condition

In order to select the optimization factor of reaction, we have carried out several preliminary experiments. The experimental results show that the mixture solution of chitosan and initiator must be pretreated at least 30 min under nitrogen atmosphere and the microwave radiation time needs 30 min to obtain the higher grafting degree and water absorbency of the chitosan resin.

The best condition of the grafting reaction was selected from the orthogonal tests. Four independent variables: amount of chitosan (g), volume of 0.01 mol/L MBA crosslinker (mL), volume of 0.01 mol/L ACS initiator (mL) and microwave irradiation power (W) were chosen, each at three levels. The investigated variables and their test levels are listed in Table 1. Reference to the experimental design theory, the orthogonal array $L_9(3^4)$ was selected to arrange the test program. The water absorbency of the grafting resin was a criterion of each test. The test results are listed in Table 2.

The order of influence of each variable on the water absorbency appears to be $A >> C \sim B > D$. Thus, the amount of chitosan has the greatest influence and the irradiation power has the smallest influence. The optimum level of each variable is A-3, B-2, C-1, D-3. Therefore, the optimum reaction conditions were as follows: amount of chitosan, 0.3 g; volume of 0.01 mol/L crosslinker, 5 mL; volume of 0.01 mol/L initiator, 2.5 mL; microwave

Table 1
Investigated variables and their levels

Levels of each variables	*A*: Amount of chitosan (g)	*B*: volume of crosslinker (mL)	*C*: volume of initiator (mL)	*D*: microwave irradiation power (W)
1	0.9	2.5	2.5	0 (Traditional heating)
2	0.6	5	5	120
3	0.3	10	10	260

Table 2
Orthogonal experimental arrangement and test result

Experiment number	*A*	*B*	*C*	*D*	Absorbency (g/g)
1	1	1	1	1	105
2	1	2	2	2	150
3	1	3	3	3	77
4	2	1	2	3	260
5	2	2	3	1	250
6	2	3	1	2	260
7	3	1	3	2	450
8	3	2	1	3	680
9	3	3	2	1	490
Average					
Levels 1	111	272	348	282	Total average = 302
Levels 2	257	360	300	287	
Levels 3	540	276	259	339	
Variance (average)	429	88	89	57	

irradiation power, 260 W. Under these conditions, the product can absorb water 680 times its own dry weight.

3.2. FT-IR and TGA analyses of graft chitosan resin

The IR spectra of the raw chitosan and the graft chitosan resin prepared under the optimal conditions are shown in Fig. 2. Fig. 2(a) shows that the main characteristic peaks of chitosan are at 3455 $\mathrm{cm^{-1}}$ (O–H stretch), 2879 $\mathrm{cm^{-1}}$ (C–H stretch), 1600 $\mathrm{cm^{-1}}$ (N–H bend), 1327 $\mathrm{cm^{-1}}$ (C–N stretch), 1155 $\mathrm{cm^{-1}}$ (bridge O stretch), and 1092 $\mathrm{cm^{-1}}$ (C–O stretch). In the spectrum of grafted chitosan, in addition to the chitosan characteristic peaks, some new absorption peaks appear. The peak at 1719 $\mathrm{cm^{-1}}$ corresponds to the carboxy absorption from grafted poly (acrylic acid) and the peaks at 809 and 620 $\mathrm{cm^{-1}}$ are also characteristic of poly (acrylic acid). Furthermore, the bands at 1560 and 1403 $\mathrm{cm^{-1}}$ correspond to the sodium carboxy group. These indicate that acrylic acid in polymer has been grafted onto chitosan.

The grafting was also supported by thermogravimetric analysis (Fig. 3). TGA of chitosan (a) shows a weight loss in two stages. The first stage ranges between 10 and 100 °C and shows about 12% loss in weight. This may correspond to the loss of adsorbed and bound water. The second stage of weight loss starts at 210 °C and continues up to 360 °C during which there was 44% weight loss due to the degradation of chitosan. However, the TGA of the grafted product is different. The latter has three stage of weight loss between 10 and 550 °C. The first stage of weight loss starts at 180 °C and continues up to 340 °C, during which there was 22% weight loss due to the degradation of chitosan. The second stage from 340 to 420 °C and the third stage from 420 to 500 °C may contribute to the decomposition of different structure of the graft copolymer. Below 430 °C the copolymer had lower weight loss than chitosan. These mean that the grafting of chitosan increases the thermal stability of chitosan in some extent.

3.3. Effect of microwave power on grafting reaction

To study the effect of microwave radiation on the reaction, the other reaction variables were adopted as the optimal levels: amount of chitosan, 0.3 g; volume of 0.01 mol/L crosslinker, 5 mL; volume of 0.01 mol/L initiator, 2.5 mL and the microwave power was adjusted. In addition, distilled water (12.5 mL) was added to reaction mixtures. Because higher microwave power might cause the temperature of reaction system to be difficult to control, the highest power used was 260 W. Relationships between grafting degree, grafting efficiency, water absorbency of the product resin and microwave power are given in Fig. 4. The results of microwave power 0 W were obtained by the traditional heating method to react for 240 min. Fig. 4 shows a clear effect of microwave irradiation on the reaction. Under traditional heating conditions, the reaction time needs 240 min and the water absorbance is 665 g/g. Under microwave irradiation, however, the reaction time is only about 30 min. The grafting degree and water absorbance of the product resin approach or exceed ones of the resin by the traditional heating method. This means the microwave irradiation can enhance eight times reaction rate over the traditional heating method. On the other hand, the grafting degree and grafting efficiency of the chitosan resin decrease slightly with the increase of the microwave power. These may attribute to more homopolymerization while increasing microwave power. Therefore, the more proper microwave power used should be 120 W. Under these conditions, the grafting degree and grafting efficiency of the resin are 0.896 and 0.865, respectively. The resin can absorb water 704 times its own dry weight that is larger than that of the resin prepared by Nge et al. (2004).

3.4. Effect of amount of ACS initiator on grafting reaction

We examined the effect of amount of 0.01 mol/L ACS initiator on grafting reaction, while keeping the other reaction variables on the above mentioned conditions: amount of chitosan, 0.3 g; volume of 0.01 mol/L crosslinker, 5 mL and the microwave power, 120 W. In order to keep the same concentration of the other reactants under various volume of initiator, the distilled water of 15 ml-Volume(initiator) was added to the reactor. The relationship between grafting degree, grafting efficiency, water absorbency of the product resin and the volume of initiator used are given in Fig. 5.

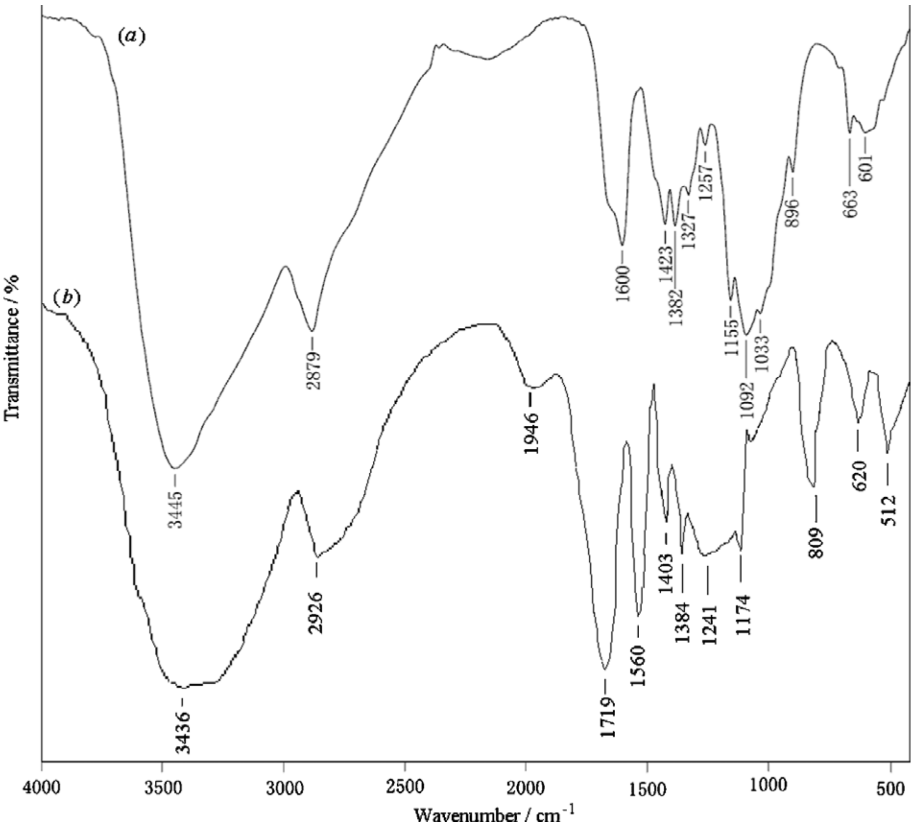


Fig. 2. FT-IR spectra of the raw chitosan (a) and grafted chitosan resin (b) with acrylic acid.

The results indicate the increase of amount of initiator cause the slight increase of grafting degree and the remarkable decrease of grafting efficiency and water absorbency. These can be explained that increase of mount of initiator cause the increase of the homopolymerization reaction of acrylic acid. However, the influence effect of water absorbency is more complicated. Therefore, the more proper amount of 0.01 mol/L ACS initiator should be 2.5 mL and the water absorbency of the product resin is 704 g/g.

3.5. *Effect of amount of crosslinker on grafting reaction*

The effect of amount of MBA crosslinker used on grafting reaction was also investigated while the other variables were kept on the above mentioned conditions: amount of chitosan, 0.3 g; volume of 0.01 mol/L initiator, 2.5 mL and the microwave power, 120 W. In order to keep the same concentration of the other reactants under various volume of crosslinker, the distilled water of 17.5 mL-Volume(crosslinker) was added to the reactor. The relation-

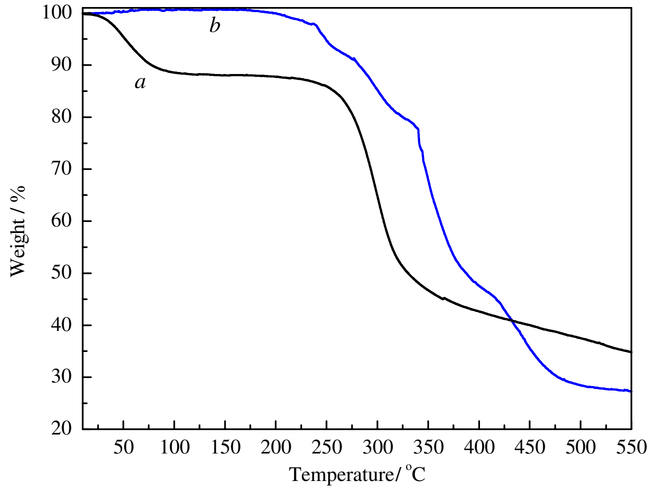


Fig. 3. TGA of chitosan (a) and grafted chitosan resin (b).

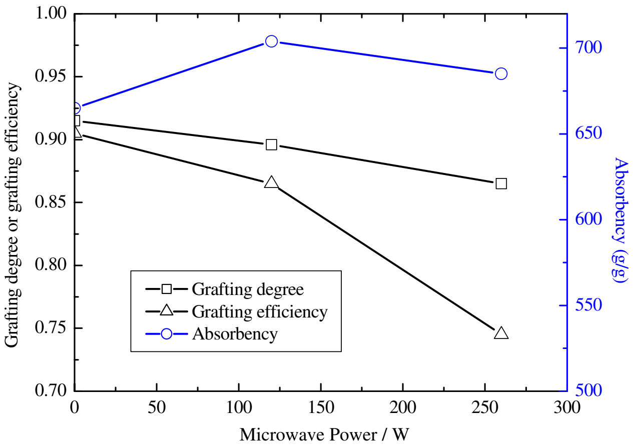


Fig. 4. Effect of microwave power on grafting reaction.

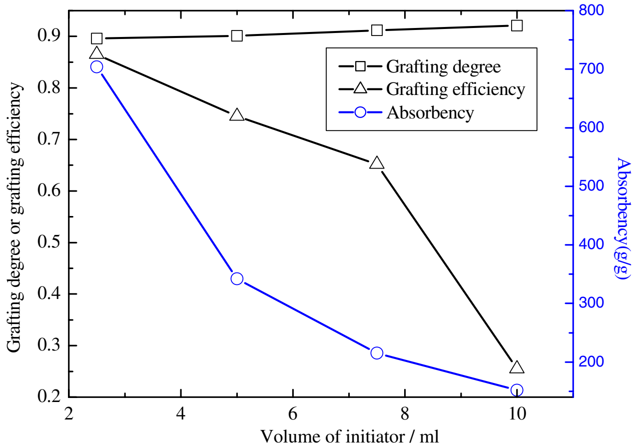


Fig. 5. Effect of amount of initiator ACS on grafting reaction.

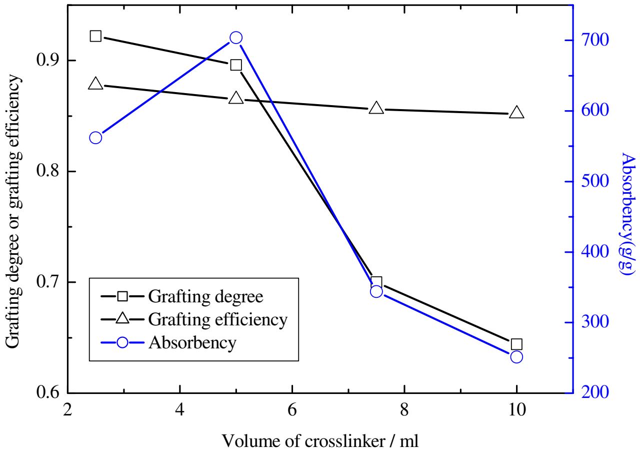


Fig. 6. Effect of amount of crosslinker on grafting reaction.

ship between grafting degree, grafting efficiency, water absorbency of the product resin and the volume of 0.01 mol/L crosslinker used are given in Fig. 6. The results indicate that the effects of amount of crosslinker on relative quantities of the grafting reaction are very different. With the increase of amount of crosslinker, grafting efficiency, and grafting degree decrease slightly, however, the grafting degree deceases remarkably when the amount of crosslinker exceeds 5 mL. As for the water absorbency of the product resin, it increases when the amount of crosslinker is below 5 mL. However, it decreases remarkably when the amount of crosslinker exceeds 5 mL. These Similar observations have been reported and explained by Mahdavinia et al. (2004). Therefore, the more proper amount of the crosslinker should be 5 mL and grafting degree, grafting efficiency, and water absorbency of the product resin are 0.896, 0.865, and 704 g/g, respectively.

4. Conclusion

A superabsorbent chitosan resin was synthesized by a graft copolymerization reaction of chitosan with the partially neutralized acrylic acid under microwave radiation. The optimum reaction conditions were as follows: amount of chitosan, 0.3 g; volume of 0.01 mol/L initiator ACS, 2.5 mL; volume of 0.01 mol/L initiator MBA, 5 mL; microwave power, 120 W; reaction time, 30 min. At these conditions under microwave irradiation, the grafting degree and grafting efficiency of the resin were 0.896 and 0.865, respectively, which approached to the ones obtained by the traditional heating method. However, the reaction rate under this microwave irradiation method was increased by eight times over the conventional method and the resin can absorb water 704 times its own dry weight. Therefore, this is a valuable synthesized method and the chitosan resin synthesized is an effective superabsorbent material.

References

Borzacchiello, A., Ambrosio, L., Netti, P. A., Nicolais, L., Peniche, C., Gallardo, A., et al. (2001). Chitosan-based hydrogels: synthesis and characterization. *Journal of Materials Science-Materials in Medicine, 12*, 861–864.

Cao, Z.-Y., Ge, H.-C., & Lai, S.-L. (2001). Studies on synthesis and adsorption properties of chitosan cross-linked by glutaraldehyde and Cu(II) as template under microwave irradiation. *European Polymer Journal, 37*, 2141–2143.

Danks, T. N. (1999). Microwave Assisted Synthesis Of Pyrroles. *Tetrahedron Letters, 40*, 3957–3960.

Dutkiewicz, J. K. (2002). Superabsorbent materials from shellfish waste – A review. *Journal of Biomedical Materials Research, 63*, 373–381.

Ge, H.-C., & Luo, D.-K. (2005a). Temperature – controlling microwave reaction apparatus and its application to carboxymethylation of chitosan. *Chemical Research and Application (Chinese), 17*, 835–836.

Ge, H.-C., & Luo, D.-K. (2005b). Preparation of carboxymethyl chitosan in aqueous solution under microwave irradiation. *Carbohydrate Research, 340*, 1351–1356.

Goosen, M. F. A. (Ed.). (1997). *Applications of Chitin and Chitosan*. Lancaster, PA: Technomic Publishing.

Mahdavinia, G. R., Pourjavadi, A., Hosseinzadeh, H., & Zohuriaan, M. J. (2004). Modified chitosan 4. Superabsorbent hydrogels form poly(actylic acid-co-acrylamide) grafted chitosan with salt- and pH-responsiveness properties. *European Polymer Journal, 40*, 1399–1407.

Nge, T. T., Hori, N., Takemura, A., & Ono, H. (2004). Swelling behavior of chitosan/poly(acrylic acid) complex. *Journal of Applied Polymer Science, 92*, 2930–2940.

No, H. K., Park, N. Y., Lee, S. H., Hwang, H. J., & Meyers, S. P. (2002). Antibacterial activities of chitosans and chitosan oligomers with different molecular weights on spoilage bacteria isolated from tofu. *Journal of Food Science, 67*, 1511–1514.

Nüchter, M., Ondruschka, B., Bonrath, W., & Gum, A. (2004). Microwave assisted synthesis – a critical technology overview. *Green Chemistry, 6*, 128–141.

Qiu, H.-X., Yu, J.-G., & Zhu, J.-L. (2005). Polyacrylate/(chitosan modified montmorillonite) nanocomposite: water absorption and photostability. *Polymers and Polymer Composites, 13*, 167–172.

Raju, M. P., & Raju, K. M. (2001). Design and synthesis of superabsorbent polymers. *Journal of Applied Polymer Science, 80*, 2635–2639.

Sashiwa, H., & Shigemasa, Y. (1999). Chemical modification of chitin and chitosan 2: preparation and water soluble property of N-acylated of N-alkylated partially deacetylated chitins. *Carbonhydate Polymers, 39*, 127–138.

Shao, J., Yang, Y.-M., & Zhong, Q.-Q. (2003). Studies on preparation of oligoglucosamine by oxidative degradation under microwave irradiation. *Polymer Degradation and Stability, 82*, 395–398.

Vandana, S., Devendra, N. T., Ashutosh, T., & Rashmi, S. (2005). Microwave promoted synthesis of chitosan-graft-poly(acrylonitrile). *Journal of Applied Polymer Science, 95*, 820–825.

Xu, K., Song, C.-L., Zhang, W.-D., Luo, Y. X., Dong, L.-S., & Wang, P. (2004). Synthesis of super-absorbent resin of starch-sodium acrylate graft copolymer by the method of microwave polymerization. *Journal of Functional Polymer (Chinese), 17*, 473–478.

Yazdani-Pedram, M., Retuert, J., & Quijada, R. (2000). Hydrogels based on modified chitosan, 1. Synthesis and swelling behavior of poly (acrylic acid) grafted chitosan. *Macromolecular Chemistry and Physics, 201*, 923–930.

Zheng, D. -F., & Ge, H. -C. (2003). Preparation of chitosan grafted by vanillin under microwave radiation and its adsorption property. *Huanan Ligong Daxue Xuebao/Journal of South China University of Technology* (Natural Science, Chinese), 12, 51–54.