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Graft Copolymerization of Artemisia Seed Gum with Acrylic Acid under Microwave and its Water Absorbency

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A super-absorbent polymer was prepared by grafting copolymerization of acrylic acid onto Artemisia seed gum, using microwave irradiation and ammonium persulfate as an initiator. The effect of various preparation conditions on its water absorbency, such as the ratio of acrylic acid to Artemisia seed gum, degree of acrylic acid neutralization, amount of initiator and microwave irradiation time, was investigated by orthogonal tests. The optimal reaction conditions were 3 min (irradiation time), 70% neutralization degree of acrylic acid and 2% initiator on the basis of the mass of acrylic acid used. When the mass ratio of acrylic acid to Artemisia seed gum is 5:0.5, the product has a water absorbency close to 400 times at room temperature in distilled water, this indicated that is has a high water absorbency. The structure of the graft copolymer was confirmed by Fourier transform infrared spectrometer (FT-IR) and thermogravimetric analysis (TGA). Further more, this microwave irradiation processing method to prepare water absorbent materials has no industrial cast off produced, that is to say, this method is environmentally friendly.

Keywords: graft copolymerization; super-absorbent; acrylic acid; Artemisia seed gum; microwave irradiation

1 Introduction

Super-absorbent polymers can absorb, swell and retain aqueous solutions up to hundreds of times their own weight compared with general water absorbing materials in which the absorbed water is hardly removable even under some pressure (1). Super-absorbent polymers have great advantages over traditional water-absorbing materials such as cotton, pulp, sponge, etc. Such materials were used widely in artificial snow, agriculture, horticulture, and drug delivery (2–7).

Microwave irradiation, using commercial household microwave ovens, has received increasing interest in organic synthesis due to the remarkable enhancement of the rates of some organic reactions over conventional thermal reaction. Microwave energy can be directly and uniformly absorbed throughout the entire volume of an object, causing it to heat up evenly and rapidly. Microwave irradiation has been successfully used in the synthesis of superabsorbent resins, made from starch-sodium acrylate grafting, where the water-absorbent rate of the resin synthesized is much higher than that of the resin by traditional polymerization. Microwave utilization enables rapid synthetic transformations at ambient pressure, thus providing unique chemical processes with special attributes, such as ease of manipulation, decreased costs and high yield (8–10).

In recent years, harmful sand and dust storms often occur in the spring in the northwest area in China. The causes are very complex. One of the best counter measures is to plant grasses and trees as much as possible. In such dry regions, the water resource is very valuable. The crops and green plants eagerly need a good and effective measure to address the need of a water resource. One way is using crop-irrigation. But, this way has some disadvantages such as the increase of salinity in the soil, after water evaporation. Another way is focused on using super-absorbent polymers. However, high cost slows the latter type materials use in this region.

In this paper, a high water-absorbent polymer is prepared by intercalated polymerization under the condition of microwave radiation. Optimum conditions for preparation are studied through orthogonal experiments. The effects of the degree of neutralization, initiator content and irradiation time on water absorbency are investigated. As a result, water absorbency of the polymer is up to 394 g/g for distilled water.

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2 Experimental

2.1 *Materials and Equipments*

Artemisia seed gum was obtained from Yuhuan (Zhejiang, China). Acrylic acid was purified by distillation. Ammonium persulfate, used as received, was employed as the polymerization initiator. All other chemicals were of analytical grade and no further purification was required. A Galanz microwave oven (WP700L17), produced by Shunde Galanz Electric Appliances Factory, China, and a centrifuge (GL-20G-dα), produced by Anting Apparatus Factory, China, were employed in these studies.

2.2 *Grafting of Artemisia Seed Gum with Acrylic Acid under Microwave Irradiation*

Controlled amounts of 4.5 mol/L sodium hydroxide were added dropwise to the acrylic acid solution (5 mL) in a three-neck reactor cooled with an ice bath for partial neutralization. Ammonium persulfate initiator, controlled amount, was then added to the reactor. Artemisia seed gum (1.0 g) was then added to the reactor, with vigorous stirring. Finally, the reactor was placed inside the microwave oven, preset at the desired power (180W) and radiated by microwave for some set time. After completing the reaction, the products were dried in a vacuum drying oven at 20°C. The probable reaction route is given in Scheme 1.

2.3 *Grafting Degree and Grafting Efficiency*

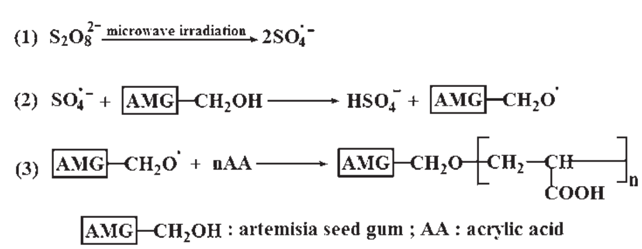
Grafting degree and grafting efficiency were calculated according to the following equations: Grafting degree = $(W_2-W_0)/W_0$; Grafting efficiency = $(W_2-W_0)/(W_1-W_0)$, Where W_0, W_1 and W_2 are the weight of the Artemisia seed gum, the product and the grafted copolymer, respectively, where the homopolymers in the reaction vessel were removed by exacting with acetone solvent.

2.4 *Measurement of Water Absorbency*

The powdered superabsorbent resin (0.1000 g) was dispersed in distilled water (100 mL) for 24 h at room temperature to reach swelling equilibrium, which resulted in the absorption of water inside the resin network and the formation of a swelled sample. The residual water was removed by filtrating with 100-mesh stainless steel screen and until water ceased to be released. The weight of the resin containing absorbed water was measured according to the following equation:

$$\text{Absorbency (g/g)} = (W_3 - W)/W$$

where W and W_3 are the weight of the dry and swollen superabsorbent resin, respectively.



Sch. 1. The mechanism of graft copolymerization.

3 Results and Discussion

3.1 *Optimization of Reaction Conditions*

The best condition of the grafting reaction was selected from the orthogonal tests. Four independent variables: ratio of acrylic acid (mL) to Artemisia seed gum (g), neutralization degree of acrylic acid (%), amount of initiator (%) and microwave irradiation time (min) were chosen, each at four levels. The investigated variables and their test levels are listed in Table 1. Reference to the experimental design theory, the orthogonal array $L_{16}(4^4)$ 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 appeared to be B > A > C > D. Thus, the neutralization degree of acrylic acid had the greatest influence and the microwave irradiation time had the smallest influence. The optimum level of each variable was A-1, B-2, C-1, D-2. Therefore, the optimum reaction conditions were as follows: ratio of acrylic acid (mL) to Artemisia seed gum (g), 5:0.5; neutralization degree of acrylic acid (%), 70%; amount of initiator (%), 2%; microwave irradiation time (min), 3 min. Under these conditions, the product can absorb water 394 times its own dry weight.

3.2 *FT-IR and TGA Analyses of Graft Artemisia Seed Gum Resin*

The IR spectra of the raw Artemisia seed gum and the graft Artemisia seed gum prepared under optimal conditions were shown in Figure 1. Figure 1(a) showed that the main characteristic peaks of Artemisia seed gum are at 3424 cm^{-1} (O-H stretch), 2926 cm^{-1} (C-H stretch) and

Table 1. Investigated variables and their levels

Levels of each variables	A: Ratio of acrylic acid to Artemisia seed gum (mL: g)	B: Neutralization degree of acrylic acid (%)	C: Amount of Initiator (%)	D: Microwave Irradiation time (min)
1	5:0.5	60	2	2
2	5:1	70	3	3
3	5:1.5	80	4	4
4	5:2	90	5	5

Table 2. Orthogonal experiment arrangement and test result

Experiment number	A	B	C	D	Absorbency (g/g)
1	1	1	1	4	350
2	1	2	2	3	330
3	1	3	3	2	312
4	1	4	4	1	200
5	2	1	2	2	276
6	2	2	1	1	380
7	2	3	4	4	220
8	2	4	3	3	250
9	3	1	3	1	271
10	3	2	4	2	260
11	3	3	1	3	248
12	3	4	2	4	180
13	4	1	4	3	193
14	4	2	3	4	208
15	4	3	2	2	280
16	4	4	1	1	200
Average					
Level 1	298	272	294	263	Total average =260
Level 2	282	295	267	282	
Level 3	240	265	260	255	
Level 4	220	208	218	240	
Variable (average)	78	87	76	42	

1640 cm^{-1} (C═O stretch). In the spectrum of grafted Artemisia seed gum, in addition to the Artemisia seed gum characteristic peaks, some new absorption peaks appeared. The peak at 1719 cm^{-1} corresponded to the carboxyl absorption from grafted poly(acrylic acid) and the peaks at 809 cm^{-1} and 620 cm^{-1} were also characteristic of poly(acrylic acid). Furthermore, the bands at 1565 cm^{-1} and 1409 cm^{-1} corresponded to the sodium carboxyl group. These indicated that acrylic acid in polymer had been grafted onto Artemisia seed gum.

The grafting was also supported by thermogravimetric analysis (Figure 2). TGA of Artemisia seed gum showed a weight loss in two stages. The first stage ranged between 20 and 90°C and showed about 12% loss in weight. This may correspond to the loss of absorbed and bound water. The second stage of weight loss started at 225°C and continued to 340°C, during which there was 45% weight loss due to the degradation of the Artemisia seed gum. However, the TGA of the grafted Artemisia seed gum is different. The latter has three stages of weight loss between 10 and 500°C. The first stage of weight loss starts 180°C and continues up to 250°C, during which there was 12% weight loss due to the degradation of the Artemisia seed gum. The second stage from 250°C to 350°C and the third stage from 350°C to 500°C may be attributed to the decomposition of different structures of the graft copolymer.

3.3 *Effect of Neutralization Degree of Acrylic Acid on Grafting Reaction*

To study the effect of neutralization degree of acrylic acid on the reaction, the other variables were adopted as the optimal levels: ratio of acrylic acid to Artemisia seed gum, 5 mL:0.5 g; amount of initiator, 2%; microwave irradiation time, 3 min and the neutralization degree of acrylic acid was adjusted. Relationship between grafting degree and grafting efficiency of the product resin and neutralization degree of acrylic acid are given in Figure 3.

3.4 *Effect of Amount of Initiator on Grafting Reaction*

We examined the effect of the amount of initiator on the grafting reaction, while keeping the other reaction variables per the above mentioned conditions: ratio of acrylic acid to Artemisia seed gum, 5 mL:0.5 g; neutralization degree of acrylic acid, 70% and microwave irradiation time, 3 min. The relationship between grafting degree, grafting efficiency,

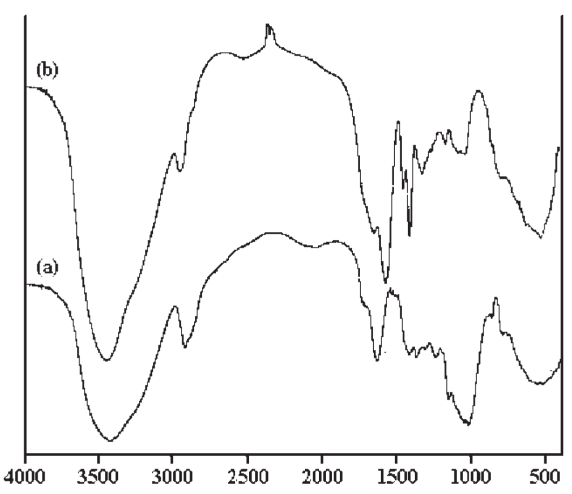


Fig. 1. FT-IR spectra of the raw Artemisia seed gum (a) and grafted Artemisia seed gum (b) with acrylic acid.

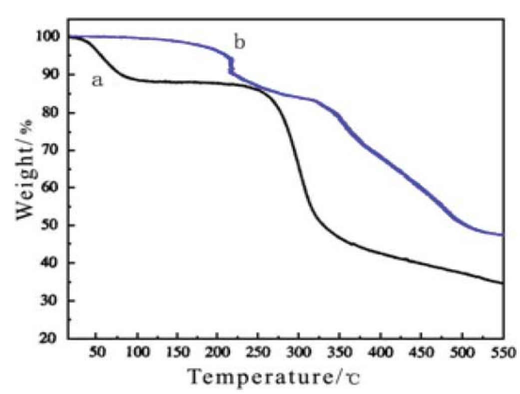


Fig. 2. TG of Artemisia see gum (a) and grafted Artemisia seed gum resin (b).

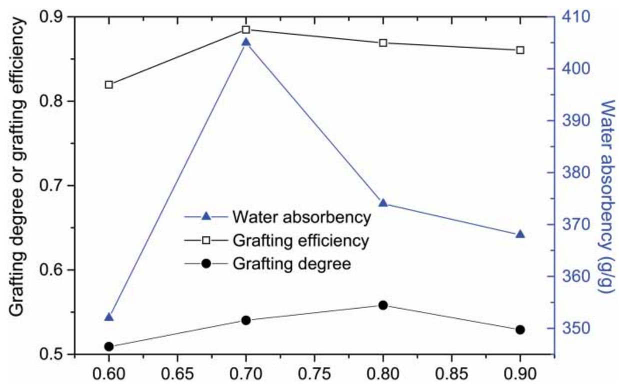


Fig. 3. Neutralization degree of acrylic acid (%).

water absorbency of the product resin and the amount of initiator used are given in Figure 4. The results indicate that the increase of initiator causes a slight increase of grafting degree and the slight decrease of grafting efficiency, but a remarkable decrease of water absorbency. The latter can be explained by noting that an increase in the amount of initiator can cause an increase of the acrylic acid homopolymerization. However, the influence on water absorbency is more complicated. Therefore, the optimum amount of initiator should be 2% and the water absorbency of the product resin is 405 g/g.

3.5 *Effect of Microwave Irradiation Time on Grafting Reaction*

The effect of microwave irradiation time on the grafting reaction was also investigated while the other variables were kept constant, per the above mentioned conditions: ratio of acrylic acid to Artemisia seed gum, 5 mL:0.5 g; neutralization degree of acrylic acid, 70% and amount of initiator, 2%. Relationships between grafting degree, grafting efficiency, water absorbency of the product resin and microwave irradiation time are shown in Figure 5.

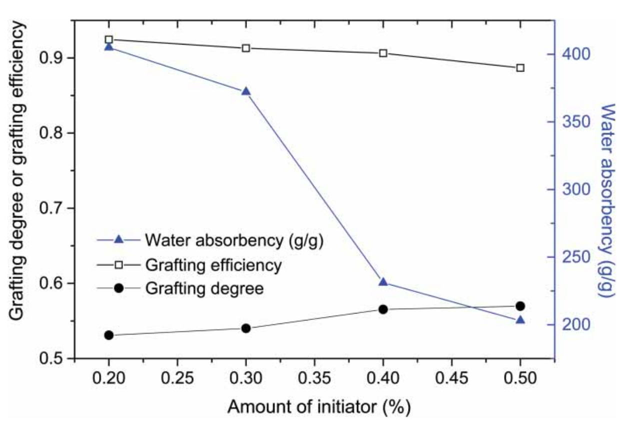


Fig. 4. Amount of initiator (%).

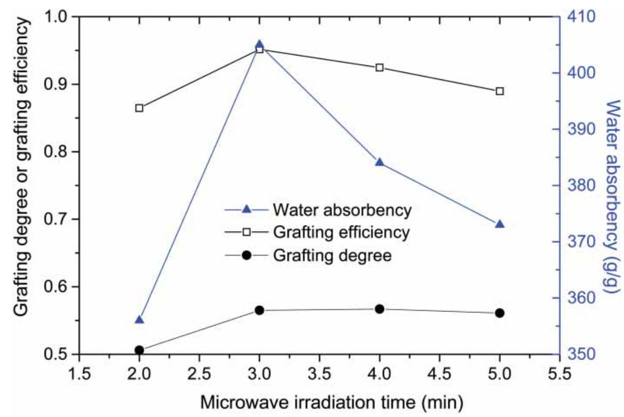


Fig. 5. Microwave irradiation time (min).

Figure 5 shows a clear effect of microwave irradiation time on the reaction. The grafting efficiency of the Artemisia seed gum resin decreases slightly with the increase of the microwave irradiation time. On the other hand, when the microwave irradiation time is lower than 3 min, the water absorbency of the product increases acutely as the microwave irradiation time increased. But when the microwave irradiation time was longer than 3 min, the water absorbency decreased. The latter results may be attributed to more homopolymerization, upon increasing the microwave irradiation time. Therefore, the more proper microwave irradiation time used should be 3 min. Under these conditions, the resin can absorb water 405 times its own dry weight.

4 Conclusions

A superabsorbent Artemisia seed gum resin was synthesized by a graft copolymerization reaction of Artemisia seed gum with partially neutralized acrylic acid under microwave radiation. The optimum reaction conditions were as follows: ratio of acrylic acid to Artemisia seed gum, 5 mL:0.5 g; neutralization degree of acrylic acid, 70%; amount of ammonium persulfate, 2%; microwave irradiation time, 3 min. Using these conditions for microwave irradiation, the resin can absorb water 405 times its own dry weight. Therefore, this is a valuable synthesis method and the Artemisia seed gum resin synthesized is an effective superabsorbent material.

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