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To cite this article: Xiaowei Du *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **562** 012044

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Synthesis and Properties of 2-Acrylamide-2-Methyl Propane Sulfonic Acid -Graft-Guar

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Abstract. 2-acrylamide-2-methyl propane sulfonic acid (AMPS) was grafted onto guar macromolecules using biodegradable guar as raw material, persulfate potassium ($K_2S_2O_8$) and sodium sulfite (Na_2SO_3) redox system as initiators. The different influence factors on graft reaction were investigated to determine the ideal reaction conditions. The sulfonated guar with high viscosity has good salt resistance, compatibility and stability with the toothpaste components, which can improve toothpaste tailing phenomenon and meet the requirements of water-based adhesive and thickening agent in other industries.

1. Introduction

With the development of economy, more and more attention has been paid to environmental pollution in global. GG, starch and other natural polymer materials have gradually attracted attention [1]. Guar (GG) is natural extracted from guar seed endosperm non-ionic galactomannan. Structurally it has a back bone of b-1, 4-linked mannose units with a-1, 6-linked galactose units attached as side chains to almost every alternate mannose unit. It is a non-toxic side effects, biodegradable, edible and renewable resource [2-5]. Aiming at its characteristics of large molecular weight, low solubility, weak acid resistance and freezing resistance, poor antimicrobial performance, unstable viscosity [6], easy degradation and odor, the study on chemical and physical modification is more active, such as carboxymethylation, hydroxypropyl, sulfuric acid esterification, phosphoric acid esterification, carboxymethyl, hydroxypropyl and quaternary ammonium salt type etc [7-10]. In comparison, domestic research on GG is relatively few [11], but foreign research is more active, such as India, Pakistan, the United States, France, Germany, Japan and other developed countries. Many articles were published in famous magazines every year. Both application research and application field expansion are indicators.

Due to its stable property, nonionic hydroxypropyl guar is widely used as thickening agent in toothpaste industry [12]. The demand of hydroxypropyl guar in toothpaste industry is about 500 tons every year. Concerning epoxy propane, the modifying ether agent, is a kind of dangerous chemical goods. There is a big potential safety hazard in the process of actual production operation, especially higher risk in the summer. When used as toothpaste thickening agent, the trailing phenomenon appear during sealing process and greatly affect the production efficiency of the toothpaste. Currently, carrageenan and hydroxyethyl cellulose commonly used in senior toothpaste are expensive [13]. So it's necessary to develop a new GG derivative instead of hydroxypropyl GG, carrageenan or hydroxyethyl cellulose to meet the demand of toothpaste industry.

The chemical modification method of GG mainly has four kinds, respectively functional derivative method, grafting polymerization, crosslinking and enzyme degradation [14]. The method grafting monomer with a particular functional group onto the guar molecule structure can make the products



with all the performance of the polymer and monomer, increase the molecular chain length and relative molecular weight and improve its thickening effect. At present, more researches focus on guar grafting reaction with the acrylamide [15], acrylonitrile[16], acrylate[17] and methyl acrylate[18] etc. But the reaction with 2-acrylamide-2-methyl propane sulfonic acid (AMPS) is rarely reported.

The main aim of the paper is to prepare a new guar derivative containing sulfonic acid group. The addition of new sulfonic acid group can improve the stability of guar solution and increase the salt resistance performance. The probability used as new thickening agent of toothpaste is explored through comparison with other polysaccharides.

2. Experiment

2.1. Materials

Guar, carboxymethyl guar, hydroxypropyl guar were supplied by Shangqiu yiyuan technology Co., Ltd; AMPS, persulfate potassium ($K_2S_2O_8$) and sodium sulfite(Na_2SO_3), were obtained from Sigma-Aldrich and used as received. All other chemicals were commercially available products used without further purification.

2.2. Grafting Reaction

The grafting procedure adopted was as follows. The guar gum flour (10 g) was slowly dispersed to form a 30% (w/v) solution in a hydro-alcoholic mixture of isopropyl alcohol (30 mL) in a clean round bottom flask (100 mL) maintained at 25 °C, with constant stirring (600±10 rpm, overhead mechanical stirrer). The resulting heterogeneous mixture was heated to a certain temperature and purged with nitrogen. Then the calculated amount of Na_2SO_3 and $K_2S_2O_8$ was added to the slurry at regular intervals, the required amount of AMPS neutralized slowly with 15%(w/w) NaOH water solution bringing the pH to 7, was then added dropwisely under constant stirring. The reaction continued for required time and then the reaction mixture was cooled gradually, dispersed in acetone.

2.3. Purification of Samples

Graft samples synthesized were washed with three successive portions of acetone, filtered and then dried under vacuum. The weight growth efficiency and weight growth rate were calculated according to formula (1), (2).

$$\text{Weight Growth Efficiency} = \frac{W_1 - W_0}{W_2} \times 100\% \quad (1)$$

$$\text{Weight Growth Rate} = \frac{W_1 - W_0}{W_0} \times 100\% \quad (2)$$

where: W_0 is the weight of guar powder, g

W_1 is the mass of the grafted product, g

W_2 is the weight of the AMPS, g

2.4. Viscosity Measurements

The viscosities of aqueous solutions of polysacchride were determined using a Brookfield viscometer (American). The temperature of the thermostat was controlled within 25±0.1°C.

2.5. Stability and Salt Resistance Test of Grafted Products

Three grafted samples with different viscosity were selected and prepared into 1%wt. aqueous solution and saline solution (KCl mass fraction is 2%wt.). The viscosity was measured with a rotary viscometer at different time. The stability and salt resistance of the gel solution were also determined.

3. Results and Discussion

Guar is a natural polymer material. Even under cold water can form a high viscosity glue. So

depending on its nature, it can be used as a green thickener. And the introduction of sulfonate groups on polysaccharide molecular structure can endow the adhesive with stability and high salt resistance.

3.1. Effect of Monomer Dosage on Graft Reaction

The effect of 10 g of guar powder on graft reaction is shown in Figure 1

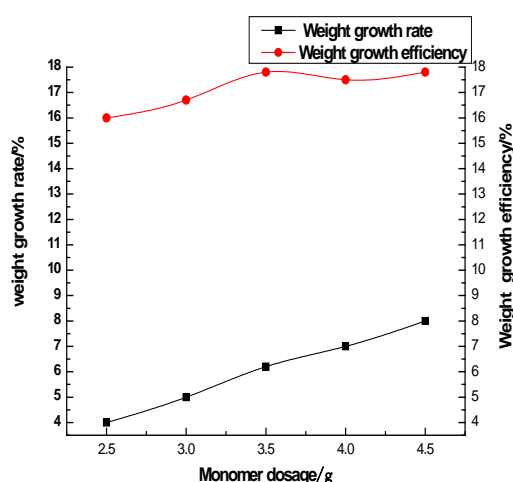


Figure 1. Effect of monomer content on graft reaction

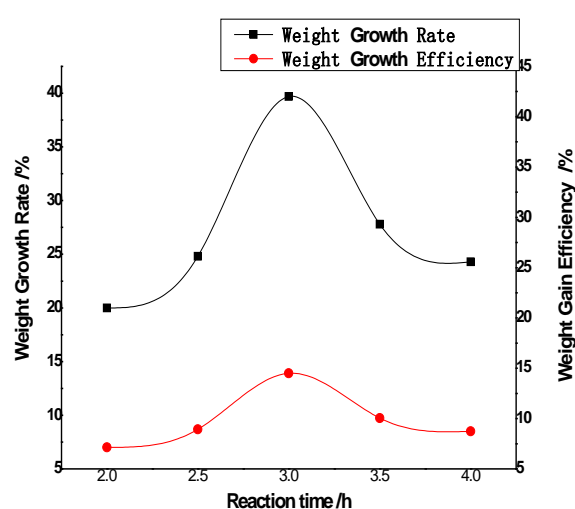


Figure 2. Influence of reaction time on graft reaction

It is known from Figure 1 that with the increase of monomer dosage, the weight growth rate and weight growth efficiency increase, and the weight growth efficiency reaches its maximum at 3.5g, and then tends to be stable. This is because the monomer concentration increases, the number of grafted monomers per free radical increases, and the molecular weight of grafted branched-chain increases, thus the weight gain efficiency increases. When the monomer quantity is large, on one hand, the reaction speed is accelerated, resulting in the increase of the viscosity of the system, preventing the monomer from diffusing in the system. The monomer diffusion to the graft chain free radical is blocked, which is not conducive to the continuation of graft copolymerization. Therefore, the weight gain efficiency decreases. On the other hand, monomers are prone to homopolymerization, and the growth rate of homopolymer chain is higher than that of grafted chain. Homopolymerization of monomers may play a leading role. When the total mass of the monomer was 3.5g and the mass of guar was 10g, better grafting effect was obtained. Therefore, in this study, the mass ratio of guar to monomer was 3:1.

3.2. Effect of Initiator Dosage on Graft Reaction

The effects of dose-induced graft reaction were shown in Table 1 after fixation of other conditions.

Table 1. Influence of initiator dosage on graft reaction

Initiator dosage /‰	1.5	2.0	3.0
Weight growth rate /%	4.0	6.2	4.6
Weight growth efficiency /%	11.4	17.6	13.1
Viscosity/Pa.s	5.6	5.4	5.2

It can be seen from table 1 that the weight gain rate and weight gain efficiency are the maximum when the amount of initiator is 2‰. At first, as the amount of initiator increased, the free radicals generated on guar backbone increased, and thus more monomers were involved in the reaction,

resulting in increased weight gain rate and weight gain efficiency. After reaching a certain amount, the probability of monomer homopolymerization induced by the initiator also increases, thus reducing the weight gain rate and weight gain efficiency.

3.3. Effects of Initiator Reaction Time on Graft Reaction

When other conditions remain unchanged, the effect of the initiator reaction time on graft reaction is shown in table 2.

Table 2. Influence of initiator reaction time on viscosity of products

t/min	8	11	13	15
Weight growth rate/%	4.3	5.9	6.8	5.3
Weight growth efficiency/%	12.3	16.9	19.4	15.1
Viscosity/Pa.s	4.3	3.5	3.2	3.7

It can be seen from table 2 that when the initiator reaction time is relatively short and monomer is added, the weight gain rate and weight gain efficiency are relatively small. With the increase of reaction time, the weight gain rate and weight gain efficiency increase, and the maximum value occurs at 13min. And then with the increase of time, the weight gain rate and weight gain efficiency begin to decline.

In the first short time, the initiator decomposes less free radicals, the monomers react to generate less free radicals, and the activity points generated on the guar molecular chain are less, so the chances of grafting are small. The rapid growth of free radical polymerization forces monomers to polymerize on a limited number of active chains, resulting in the formation of polymers with too high molecular weight, therefore, higher viscosity of the product. With the extended reaction time, the increase of free radicals generated in the system and monomer free radicals generated by the monomer reaction, there are more active points on the molecular chain of guar, more chances of grafting, shorter molecular chain and less entanglement, so the product viscosity is small. When the time is too long and the free radical concentration is too large in the system, some of the side reaction that are easy to induce decomposition or cage effect are consumed. Too many free radicals accelerate the termination of the active chain, leading to the termination of the macromolecular chain containing free radical guar, thus reducing the weight gain rate and weight gain efficiency.

3.4. Effect of Reaction Time on Weight Growth Rate

The effect of the reaction time on the graft reaction is shown in Figure 2.

It can be seen from Figure 2 that the maximum values of weight growth efficiency and weight growth rate occur when the reaction time is 3 h. Because at the initial stage of the reaction, the monomer initiator concentration is higher and the reaction is faster, and then the monomer concentration decreases. At the same time, as the grafting chain grows, the viscosity of the reaction system also increases, hindering the free diffusion of monomer, resulting in slow reaction. With the extension of time, the dissolution of guar is improved. So, the appropriate time is 3 h.

3.5. Influence of Reaction Temperature on Graft Reaction

Although the decomposition temperature of redox initiator is relatively low, the gel solution is relatively stable in the polymerization process and can be initiated at room temperature. However, in the early stage of the gel solution polymerization, the formation of colloidal particles and the initial chain growth require certain energy, so it still needs heating.

When other conditions remain unchanged, the influence of reaction temperature on the graft reaction is shown in Figure 3.

It can be seen from Figure 3 that the weight growth rate and weight growth efficiency increases firstly and then decreases with the increase of temperature. When the temperature is 45°C, the both values reach the maximum. Since persulfate is a thermal initiator, when the temperature is low, the decomposition rate of $K_2S_2O_8$ is low, the generation of free radicals is less, and the weight growth rate

and weight growth efficiency are low as well. The high temperature is beneficial to the swelling of guar particles and the collision of free radicals and monomers, which increases the above two parameters. However, if the temperature is too high, the monomers' movement ability will be strengthened, which will easily cause the free radicals to collide with each other and deactivate. Meanwhile, the chain transfer rate, the homopolymerization rate and the chain termination rate will increase correspondingly, thus reducing the grafting efficiency. Therefore, the optimal reaction temperature is 45°C.

3.6. Effect of Liquor Ratio on Graft Reaction

Table 3. Influence of Liquor ratio on graft reaction

Liquor ratio /g.g-1	2.2	2.6	2.8
Weight growth rate /%	21.0	23.0	8.0
Weight growth efficiency /%	60.0	65.7	22.9
Viscosity/Pa.s	2.3	2.9	3.7

It can be seen from table 3 that with the increase of the liquor ratio the weight growth rate and weight growth efficiency increase first and then decrease. The reason is that when the reaction solution is relatively viscous in the liquor ratio of the system, the system viscosity increases, which prevents the initiator and monomer from diffusing, and is not conducive to the continuation of graft copolymerization, the monomer homo-polymerization may play a leading role. When the system liquor ratio is relatively large, the amount of solvent contained in the solution is large, the monomer concentration in the solution is small, the probability of collision with free radicals is small, and the graft reaction is not easy to occur.

3.7. Effect of Dispersant Concentration on Graft Reaction

Fixed guar powder with 10g, 3.5g of monomer content, 18g of disperse dose, 45°C of reaction temperature, change the mass concentration of ethanol in the dispersant, and test the weight growth rate and weight growth efficiency. The results are shown in Figure 4.

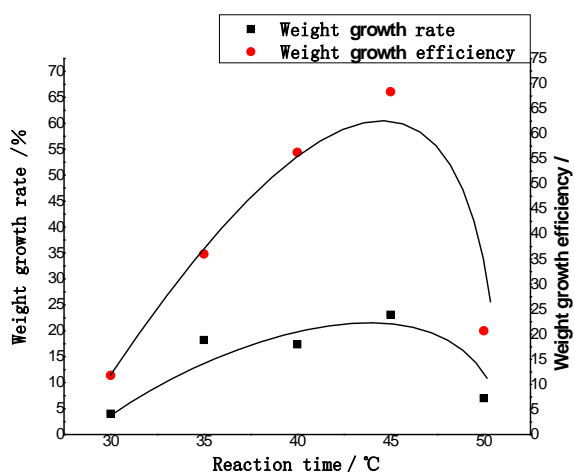


Figure 3. Influence of reaction temperature on graft reaction

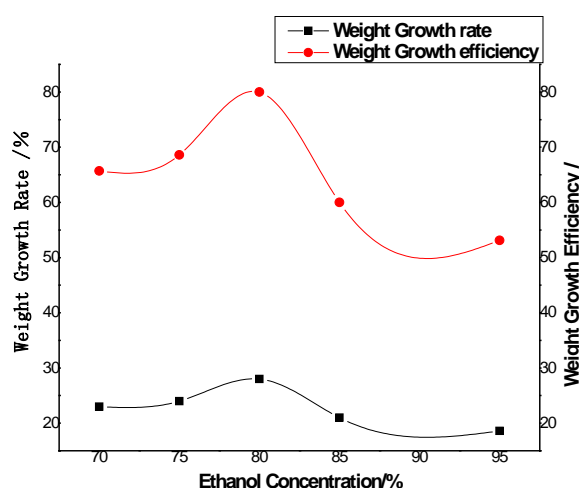


Figure 4. Influence of concentration of dispersant on graft reaction

It can be seen from Figure 4 that when the concentration of dispersant ethanol is 80%, it is favorable for grafting reaction. When the concentration is low, guar expands, and the viscosity of the

system increases, which prevents the monomer from diffusing in the system. It is not conducive to the continuation of graft reaction. Therefore, the weight growth efficiency decreases. When the initiator is added, it cannot disperse well, resulting in poor initiator effect. When the concentration is high, the concentration of ethanol is high, the water content is low, the guar particles are not easy to swell, and the initiator and monomer cannot enter the particles, resulting a low weight growth rate.

3.8. Stability of Sulfonated Guar Solution

1%(w/w) guar and sulfonated guar samples solution were prepared. The rotary viscosity was measured at different time and the results are shown in Table 4. The viscosity of sulfonated guar solution showed little change even after 65h, while guar solution had corrupted. The grafted guar improved the defects of guar aqueous solution.

Table 4. Stability comparison of sulfonated guar with guar

storage period/h	Viscosity/Pa.s			
	guar	Sample 1	Sample 2	Sample 3
2	7.48	3.70	1.78	5.1
24	7.42	3.75	1.82	5.5
49	3.07	3.81	1.84	5.7
65	corruption	3.39	1.69	5.4

Table 5 listed the viscosity of sulfonated guar, carboxymethyl guar and hydroxypropyl guar aqueous solution and 2 % KCl saline solution after 2h. Table 5 shows that the sulfonated guar derivatives have better salt resistance than the commercially available carboxymethyl guar and hydroxypropyl guar.

Table 5. Salt resistance of sulfonated guar and other modified guar

solvent	Viscosity/Pa.s			
	Sample 2	Sample 3	carboxymethyl guar	hydroxypropyl guar
water	1.78	5.1	2.86	2.58
2% KCl salt water	1.69	4.88	1.47	1.69

Two sulfonated guar samples with different viscosity were selected and sent to Chongqing Lengsuanling Toothpaste Factory, where they were mixed with toothpaste ingredients in a certain proportion. Compared with the modified guar used in toothpaste at present, the solution stability and paste stability are shown in Table 6.

Table 6. Stability comparison among different guar derivatives

guar derivatives	Sample 2	Sample 3	carboxymethyl guar	hydroxypropyl guar
appearance	light yellow fine powder			
dissolution rate in water	moderate	fast	moderate	slow
transparence	semitransparent	semitransparent	semitransparent	semitransparent
18h	no change	no change	thinning	thinning
6d	no change	no change	thinning	thinning
wire drawing	drawing a short	drawing a short	normal	normal
stability	normal, no separation	normal, no separation	normal, no separation	some separation

The results showed that the sulfonated guar derivatives had high stability, good compatibility with

the toothpaste components, stable paste and improved smearing.

4. Conclusions

The process and formula of guar-graft-AMPS were optimized and the following conclusions were obtained. Under the condition of nitrogen protection, the mass ratio of AMPS to guar powder is 1:3, the total liquor ratio of the system is 1:2.2, the concentration of dispersant ethanol is 80%, the reaction time is 3h and the reaction temperature is 45°C. Thus, the weight gain rate can reach above 70% and the grafted product has high viscosity. The stability and salt resistance of the grafted guar aqueous solution were improved apparently. Compared with carboxymethyl guar and hydroxypropyl guar used in toothpaste, the synthesized sulfonated guar exhibited compatible with the toothpaste components. The paste was stable and the tailing phenomenon was improved.

5. References

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