Effects of micronization on microstructure and rheological properties of guar gum

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Abstract. Micronized guar gum was prepared by a vibrating superfine mill with different micronization time of 15, 30, 45 and 60 min, and its microstructures and rheological properties were investigated. Untreated guar gum had a smooth and dense surface, and the surface of guar gum became loose and rough after micronization, which indicated the microstructure of guar gum was destroyed. Rheological behavior analysis showed that micronization treatment decreased the viscosity of guar gum, and the treated samples were more solid like than untreated guar gum. Due to agglomeration, the viscosity of guar gum reached the minimum value when the micronization time was 60 min.

1. Introduction
Guar gum is made from the endosperm part of the seed of guar bean. Its main origins are dry areas in Pakistan and India or in the southeastern United States. Its main component is galactomannan, whose main chain is D-mannose linked by β-1,4-glycosidic bonds, and the side chain is composed of single D-galactose whose α-1,6-glycosidic bonds are unequally linked to some C6 positions of the backbone [1]. Guar gum is commonly used as a food thickener and stabilizer to improve the organization of ice cream, and adjust the viscosity of seasonings. Because of its excellent performance, guar gum has a wide range of applications in the mining industry, paper industry, textile industry and pharmaceutical industry [2]. Micronization refers to the use of mechanical or hydrodynamic methods to overcome the solid internal cohesion and break it up, thereby crushing material particle whose diameter is over 3 mm into 10-25 μm [3]. Native guar gum does not fully hydrate at room temperature, and the solution clarity is poor [4]. Therefore, the objective of this study is to investigate the microstructure and rheological properties of micronized guar gum prepared by vibrating superfine mill with different micronization time from 15 to 60 min, which broaden the application of vibrating superfine mill in guar gum modification.

2. Materials and Methods

2.1. Materials
Guar gum (food grade) Shandong Yousuo Chemical Technology Corporation
2.2. Micronization sample preparation
Micronized tapioca starch was prepared by a VSM (WZJ6, Pele powder Co., Ltd, Jinan, China) with micronization time of 15, 30, 45, and 60 min.

2.3. Microstructure observation
The guar gum sample (dry base) was adhered to the sample holder with a conductive adhesive, and placed in an ion sputter. A platinum film was deposited on the sample surface and observed and photographed under a scanning electron microscope [5].

2.4. Flow behavior analysis

2.4.1. Steady shear analysis. The sample was equilibrated 30 s at 25°C. Thereafter, the sample was sheared from 0.1 to 300 s⁻¹, and then from 300 to 0.1 s⁻¹ at 25°C to determine steady state flow behavior.

2.4.2. Frequency sweep analysis. Guar gum suspension was conditioned at 25°C for 30 s. A frequency sweep was conducted from 0.1 to 20 Hz with a strain of 2%, and then took a frequency sweep at 20 Hz for 60 s at 25°C. The frequency sweep was conducted from 20 to 0.1 Hz with a strain of 2%.

3. Results and analysis

3.1. Microstructure Analysis
The morphology of guar gum is shown in Fig. 1. From Fig. 1, it can be seen that the microstructure of guar gum markedly changed after micronization. Untreated guar gum had a smooth, dense and irregular surface [6]. When the micronization time was 15 min, the surface of guar gum became rough, and the morphology of the particles slightly changed. However, the granule surface of guar gum became loose, and the structural obviously damaged as the micronization time increased. Also, the particle size became larger and gradually agglomerated. This may be due to the internal structure of guar gum became loose after micronization, favoring the entry of water molecules, and enhancing the cross-linking effect. Another reason may be that the samples were hard to get physical dispersion after micronization, resulting the guar gum aggregation.

Similar result was also found by Wang S et al. [7], who reported that guar gum was tangled and firmly interpenetrating to form a network structure after pressure cracking. And this high degree of association or overlap makes the gap between the molecules smaller, which is conducive to improving the processing performance of guar gum.
3.2. Flow behavior analysis

The frequency sweeping and steady state shearing results of the micronized guar gum were shown in Fig. 2. As shown in Fig. 2(a), the flow curves (shear stress and shear rate) of native and treated guar gum behaved as pseudoplastic with shear-thinning. These results were consistent with those previously finding for Guar gum solutions [8]. As shown in Fig. 2(b), the viscosity of native guar gum was the largest and the viscosity of guar gum gradually decreased with the increase of superfine micronization time, indicating the treated guar gum was more liquid like. When the treatment time reached 60 minutes, the viscosity of guar gum had a minimum value. This may be due to the fact that after micronization reached a certain degree, the intermolecular cross-linking effect enhanced and water molecules were difficult to enter, causing the guar gum agglomerates. Therefore, its viscosity gradually decreased.

As shown in Fig. 2(c) and (d), the $G'$ value of guar gum gradually decreased as the micronization time increased, indicating the structure of native guar gum is destroyed. The treated samples were more solid alike than the native guar gum. The $G'$ value of guar gum reached a minimum, probably due to agglomeration of guar gum. This was similar to the findings of Rohart A, who revealed that thermomechanical treatment could reduce the viscosity of guar gum [9].

As shown in Fig. 2(e), the $\tan\delta$ value ($G''/G'$) of the guar gum gradually increased as the micronization treatment time increased, reaching a maximum value when the treatment time was 60 min. The results indicated that guar gum showed more and more solid similarity after micronization treatment, which was consistent with the results obtained by SEM analysis.
Figure 2. Effect of Micronization on shear rate-shear stress plots (a), viscosity (b), $G'(c)$ and $G''$ (d) of native guar gum

4. Conclusion
The SEM results of guar gum showed that the surface of native guar gum was smooth, dense and then became coarse and loose after micronization. And when the superfine grinding time reached 45 min, guar gum agglomerated, indicating that the superfine grinding treatment destroyed the microstructure of guar gum. The rheological analysis demonstrated that guar gum showed pseudoplastic with shear-thinning. The viscosity of guar gum decreased first, and then slightly increased after micronization treatment. This may be due to the fact that micronization increased the cross-linking effect between guar gum and exhibited certain solid similarities. In a word, micronization can change the structure and rheological properties of guar gum to a certain extent, which provides a certain theoretical basis for the application of guar gum.
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References
[1] Li D, Yang N, Zhang Y, et al. Structural and physicochemical changes in guar gum by alcohol-acid treatment[J]. Carbohydr Polym, 2018, 179:2-9.
[2] Mudgil D, Barak S, Patel A, et al. Partially hydrolyzed guar gum as a potential prebiotic source.[J]. International Journal of Biological Macromolecules, 2018, 112:207-210.
[3] Ren G Y, Dong L, Wang L J, et al. Morphological properties and thermoanalysis of micronized cassava starch.[J]. Carbohydrate Polymers, 2010, 79(1):101-105.
[4] Hong C H, Zhang K, Choi H J, et al. Mechanical degradation of polysaccharide guar gum under turbulent flow[J]. Journal of Industrial & Engineering Chemistry, 2010, 16(2):178-180.
[5] Xia W, He D N, Fu Y F, et al. Advanced technology for nanostarches preparation by high speed jet and its mechanism analysis.[J]. Carbohydrate Polymers, 2017, 176:127.
[6] Gong H, Liu M, Chen J, et al. Synthesis and characterization of carboxymethyl guar gum and rheological properties of its solutions[J]. Carbohydrate Polymers, 2012, 88(3):1015-1022.
[7] Wang S, Zhang Y, Guo J, et al. A study of relation between suspension behavior and microstructure and viscoelastic property of guar gum fracturing fluid[J]. Journal of Petroleum Science & Engineering, 2014, 124:432-435.
[8] M.D. Torres, Hallmark B, Wilson D I. Effect of concentration on shear and extensional rheology of guar gum solutions[J]. Food Hydrocolloids, 2014, 40(10):85-95.
[9] Rohart A, Michon C. Effect of thermomechanical treatment on microstructure of guar gum/acid milk gels[J]. Journal of Food Engineering, 2016, 171:14-21.