SILANIZATION OF GUAR GUM TO IMPROVE THE TEMPERATURE RESISTANCE

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Abstract: For a widely used gelating agent in hydraulic fracturing fluid, the temperature resistance is required. To improve the temperature resistance of Guar gum (GG), it was modified by silanization. The reaction conditions were investigated, and the optimized conditions were as following: the reaction temperature of 85 °C, 5:1 molar ratio of guar gum to TMS-C1 and 4-6 h of reaction time. The viscosity of silanized guar gum (SGG) aqueous gel was greatly improved even high temperature at 80 °C.

Key words: guar gum, temperature resistance, silanization, modify

Introduction

Guar gum (GG) is a natural non-ionic polysaccharide produced from the seeds of two annual leguminous plants, *Cyamopsis tetragonalobus* and *psoraloides*. The guar gum macromolecule is a chain of $(1\rightarrow 4)$ -linked β -D-mannopyranose units with α -D-galactopyranose units connected to the mannose backbone through $(1\rightarrow 6)$ glycosidic linkages (shown as Figure 1).^[1-3] The poly-mannose chain is randomly substituted with galactose units at a mannose-to-galactose ratio of 1.8-1.0. Because of these associations, guar gum possesses remarkable rheological properties and is widely used in food, personal care, textile printing and water based paints and oil recovery.^[4] Under normal conditions, aqueous solutions of guar gum contain a small fraction of undissolved colloidal aggregates and only a combination of high temperatures and pressures during the solution preparation stage results in a complete (or nearly complete) dissolution and hydration of the polymer.

In the field of oil recovery, hydraulic fracturing is a widely used method for stimulating petroleum producing subterranean formations and is commonly performed by contacting the formation with a viscous fracturing fluid with propping agents. Guar gum has been utilized to increase the viscosity of aqueous solutions. However, the gels produced with such gelling agents generally have limited stability at elevated temperatures, and the viscosity of the gelled aqueous solutions decreases substantially after only a short period of time. So many efforts have been tried

to improve the viscosity, such as borate cross-linked guar and zirconium (IV) cross-linked guar.^[5,6] In this paper we will report a simple chemical method to improve the temperature resistance of guar gum and investigated the modification conditions.

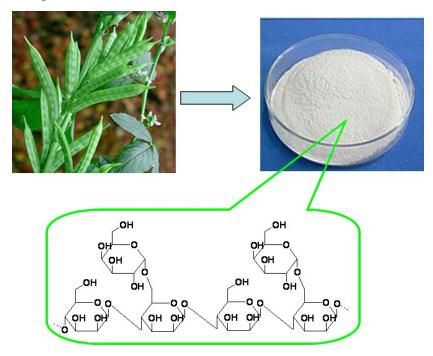
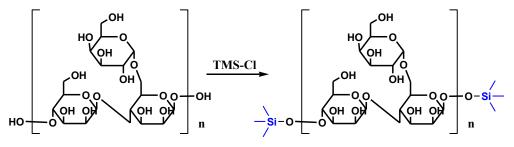


Figure 1. Cyamposis tetragonolobus, guar gum powder and the chemical component

Experiment

5 g of guar gum was loaded in a flask, 20 ml toluene was added, and the mixture was stirred for 30 min under room temperature. A certain amount of trimethylsilyl chloride (TMS-Cl) solution was added dropwise, and the mixture was heated to a certain temperature by a water bath and was stirred for a certain time. After the reaction finished, the pH value of the mixture was adjusted to 7 by a NaOH solution. The product was filtrated, washed and obtained after vacuum drying. The reaction and the structure of guar gum (GG) solution and silanized guar gum (SGG) were shown in Scheme 1. The viscosity of GG solution and SGG solution were tested using a RheolabQC rotating viscometer.



Scheme 1 Silanization of guar gum

Results and Discussion

Trimethylsilyl chloride (TMS-Cl) is a well known protect agent for the hydroxyl group in organic synthesis projects. Besides, in order to overcome the inherent disadvantage of alditol acetates derivatization, trimethylsilyl (TMS) derivatization has been developed to quantify neutral sugars in soils by GC,^[7-8] which improve the temperature resistance of sugars preventing the decomposing. Naturally, the TMS derivatization of GG resulted in SGG can be expected to improve the temperature resistance. In the silanization of guar gum the trimethylsilyl tends to react with the un-etherized hemiacetal hydroxyl group of mannose, which can prevent the hydrolysis under high temperature.

The effect of reaction temperature on the viscosity of SGG gel was investigated firstly with a reaction time of 2h and the 5:1 molar ratio of guar gum to TMS-Cl, and the results were shown in Figure2, in which the number behind SGG indicates the reaction temperature (°C). From this figure, it can be found that the SGG gels are all viscouser than that of GG under different test temperature. The gel intensity declines along with the test temperature and reach around 10 mPa·s at 80°C. Compared the gel intensity under 60-70°C, it can be found the SGG prepared under 85°C displays the highest temperature resistance.

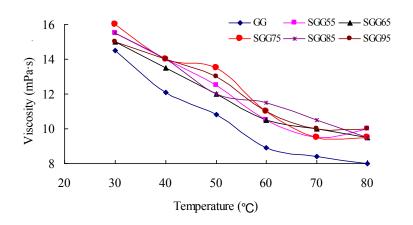


Figure 2 The effect of reaction temperature on the viscosity of SGG gel

The effect of molar ratio of guar gum to TMS-Cl on the viscosity of SGG gel was investigated with reaction time of 2h and reaction temperature of 85°C, and the results were shown in Figure 3, in which the number behind SGG indicates the molar ratio of guar gum to TMS-Cl. From this figure, it can be found that the SGG gels are all viscouser than that of GG under different test temperature. The gel intensity declines along with the test temperature and reach around 9.5 mPa·s at 80°C. Compared the gel intensity under 30-80°C, it can be found the SGG prepared with the molar ratio of 5:1 displays highest temperature resistance.

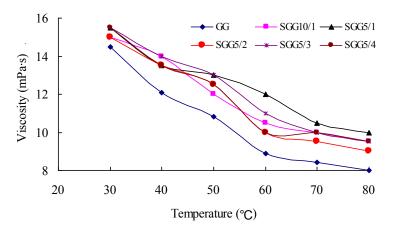


Figure 3 The effect of molar ratio of guar gum to TMS-Cl on the viscosity of SGG gel

The effect of reaction time on the viscosity of SGG gel was investigated with the 5:1 molar ratio of guar gum to TMS-Cl and reaction temperature of 85 °C, and the results were shown in Figure 4, in which the number behind SGG indicates the reaction time. From this figure, it can be found that the SGG gels are all viscouser than that of GG under different test temperature. The gel intensity declines along with the test temperature and reach 8.0-11.5 mPa·s at 80°C. Compared the gel intensity under 30-80°C, it can be found the SGG prepared with the reaction time of 4-6 h displays highest temperature resistance.

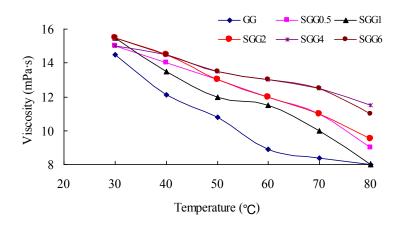


Figure 4 The effect of reaction time on the viscosity of SGG gel

Conclusion

To improve the temperature resistance, GG was modified by silanization using TMS-C1. The modification conditions were investigated, and the optimized conditions were as following: the

reaction temperature of 85°C, 5:1 molar ratio of guar gum to TMS-Cl and 4-6 h of reaction time.

The viscosity of SGG gel was improved much in the temperature range from 30 to 80°C, which indicates the SGG has potential to be used as thermo tolerant gelating agent.

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