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Depolymerization of guar gum solution using different approaches based on ultrasound and microwave irradiations

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ABSTRACT

The present work investigates the application of ultrasound and microwave operated individually or in combination for depolymerization of aqueous solution of guar gum. In addition, intensification aspects due to the use of an initiator, potassium persulfate (KPS), has been investigated. The extent of depolymerization has been analyzed in terms of the reduction in intrinsic viscosity. Also, the effectiveness of treatment approach has been analyzed on the basis of kinetic rate constant, limiting intrinsic viscosity and the time required for the desired extent of viscosity reduction. The kinetic rate constant has been found to increase with an increase in the temperature and KPS loading. For the individual operation involving irradiations, the rate was found to be higher in the case of ultrasound as compared to the microwave irradiations. In the case of sequential approach, microwave followed by ultrasound was more effective as compared to the approach of ultrasound followed by microwave. The obtained results clearly established that ultrasound in combination with KPS was the most effective approach for depolymerization. The work has also enabled to understand the effective role of KPS and operating temperature in intensifying the viscosity reduction of guar gum polysaccharides.

1. Introduction

Guar gum (GG) is a water-soluble and naturally occurring poly galactomannan derived from the seeds of *Cyamopsis tetragonolobus* (guar) plant [1]. It is mainly comprised of a linear backbone of β (1-4)-linked D-mannose units (M) with randomly attached side chains of α (1-6)-linked galactose units (G) [2]. Due to the low cost and capacity to impart high viscosities at relatively low concentrations, guar gum has been used in different industrial applications including food and pharmaceutical sectors. Guar gum is used as a food supplement [3] and also as additive in many food products such as sauces, syrups, ice cream, instant foods, beverages, confectionaries and baked goods. GG is also used as a thickening and gelling agent [4,5]. Considering the pharmaceutical sector applications, GG is used in tablet manufacturing as a binder and disintegrating agent and also for drug micro-encapsulation [6]. Furthermore, GG has been reported to be useful in the therapy of hypercholesterolemia and hyperglycemia as well as an indigestible sugar in obesity treatment [7]. Another important use of guar gum has been reported in the gas and oil sector as a hydraulic fracturing fluid [8,9]. All these industrial applications of guar gum are feasible because of the capability to form hydrogen bonding with water molecules. For all above applications, guar gum needs to be depolymerized in a controlled manner giving lower molecular weight fractions as desired for the specific application.

The important properties of polysaccharides depend on their molecular weight, which can be expressed as a function of the intrinsic viscosity. For obtaining the desired molecular weight of the polymers in an efficient manner, development of fast and inexpensive methods for depolymerization of native polysaccharides is very important. Depolymerization of polysaccharides has been studied using various methods though acid based [10] and enzymatic [11] methods have been most common. Even though the acidic and enzymatic methods are convenient, these methods suffer from important drawbacks as higher treatment time, higher treatment costs especially in the case of enzymatic methods and difficulty in achieving an uniform molecular weight distribution after degradation [8,12]. Some of the newer methods for depolymerization include methods based on the use of ultrasound [13,14] and irradiation (treatment with ionizing radiation) [15] as well as free radical induced degradation [12]. Use of ethylene dibromide or ethylene oxide for degradation of polysaccharides is associated with the problems related to the handling of hazardous chemicals. Irradiation is a simple method for controlled

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degradation of polysaccharides but a major limitation of this technique is the possibility of some radicals being trapped in crystalline regions of polymer, which can lead to slow but uncontrollable degradation [16,17]. The present work will concentrate on the use of ultrasound based methods for intensification of depolymerization of polysaccharides.

Ultrasound has been used as intensifying approach in different fields such as synthesis [18], electrochemistry [19], water disinfection [20], material science [21] etc. Use of ultrasound can possibly lead to greener intensified processing with considerable economic savings [21–23]. Ultrasound can also be effectively applied for polymer degradation [13,24] based on the splitting of the most liable chemical bond without inducing any changes in the chemical nature [25]. Ultrasound based approach for polymer degradation is unique and fast because of the fragmentation at the center of polymer chain. Ultrasound creates physical effects in terms of acoustic streaming which is liquid circulation associated with intense turbulence and shear. The shear field generated due to the movement of the wall of violently collapsing bubble [22,23,25,26] is mainly responsible for the polymer degradation. Effect of ultrasound on polysaccharides has been investigated in the past with studies dealing with guar gum [14,27], carboxymethyl cellulose (CMC) [13], chitosan and starch [28], pullulan and dextran [29] etc. Ansari et al. [14] studied the effect of ultrasound on the guar gum solution at different treatment time (1, 3, 5, 10, 20 and 30 min) at 25 °C with an objective of getting improved physicochemical properties. It was reported that the intrinsic viscosity reduced with an increase in the irradiation time. Tiwari et al. [27] investigated the changes in rheological properties of guar gum solution due to the use of ultrasound at varying intensity levels (3.7, 6.3, 8.1 and 10.1 W/cm^2) for fixed treatment time as 5 min at 25 °C and reported significant reduction in the apparent viscosity. The decrease in the apparent viscosity was permanent with almost no recovery being observed for treated guar gum after a 24 h storage period. It can be seen that the earlier studies dealing with application of ultrasound have been limited to quantifying the extent of decrease in the viscosity as a function of treatment time or intensity of irradiation. The present work highlights the novel combination of ultrasound with KPS as an initiator as well as compares the efficacy of ultrasound based approach with microwave based approach. Use of combined treatment schemes based on microwave and ultrasound has also been investigated which is the first such depiction for depolymerization of polysaccharides to the best of our knowledge.

Microwave (MW) irradiation has also been a well-known approach for process intensification resulting in uniform heating of the reaction mixture and selective absorption of thermal energy by polar molecules [30–32]. The important advantages of microwave based processing over conventional systems [21] are reduction in reaction time, enhanced yields, localized higher energy densities, homogeneous and selective heating as well as clean and greener processing. Microwave can also be applied for inducing polymer degradation and there have been some studies depicting the application for guar gum [12], chitosan [33], xyloglucan [34] and xanthan pectin [27]. Reddy and Tammishetti [12] studied the effect of microwave power (200, 400, 600 and 800 W) over different time periods as 5, 10 and 15 min on the degradation of 2% guar gum solution. It has been reported that the viscosity reduction generally increased with an increase in the power dissipation and time of treatment.

Persulfate is a strong oxidizing agent which can be also used as an initiator for polymerization or depolymerization reactions. The decomposition kinetics of persulfate is pH-dependent and in an alkaline medium, typically sulfate and bisulfate anions are formed, which on heating produce radicals [35]. Use of irradiations such as ultrasound can produce a similar activation effect for the dissociation reaction producing radicals.

The present work has focused on investigating the depolymerization of guar gum solution using different approaches based on ultrasound and microwave irradiation. The extent of depolymerization has been monitored in terms of the change in the intrinsic viscosity of the polymer solution, which is an easy method to quantify the rate of depolymerization. The work also reports the effect of potassium persulphate (KPS) as an initiator in combination with ultrasound and microwave irradiations. A novel approach of using sequential combination of ultrasound and microwave irradiations has also been investigated. As the study concentrated on use of ultrasound and microwave in sequence, the medium composition being subjected to microwave can change and hence the dielectric constants may be different, which has not been considered in the present work.

2. Materials and methods

2.1. Materials

Guar gum was obtained from Premcem Gums Pvt., Ltd., Mumbai, as a gift sample and has particle size of 200 mesh and viscosity of 3500 cps. Potassium persulphate (KPS) was obtained from S.D. Fine Chemicals Ltd., Mumbai, India. All the chemicals were used as received from the supplier. Deionised water has been used to prepare different solutions of required concentrations and was prepared freshly in the laboratory.

2.2. Hydration method

For the hydration experiments, guar gum solutions with varying concentrations over the range 0.3–1% (w/v) were prepared by carefully sprinkling the required amount of guar gum powder into a rapidly swirling vortex of 100 ml deionised water in a glass beaker obtained using magnetic stirrer. The time of addition of the powder was about 60–90 s and proper care was taken to avoid any lump formation so that a homogeneous polymer solution is obtained. The prepared guar gum samples were dispersed in water for 30 min and kept in the refrigerator. The viscosity measured using an Ubbelohde glass capillary viscometer, after keeping the samples overnight in refrigerator, was considered to be the initial viscosity. Aqueous solutions (0.3%, 0.5%, 0.7%, 1%) of the guar gum were also used for viscosity measurement at ambient temperature so as to obtain a calibration chart between the known concentrations of the prepared solutions and the measured viscosity. All the measurements were performed in triplicate and the mean value was taken for the analysis. At lower concentration of guar gum powder the hydration was not observed due to complete dissolution of guar powder within short time period while above 1% concentration, guar gum behaves as thixotropic and required more time for guar dissolution. Based on the hydration study results, 0.5% concentration has been selected for the actual study of effect of different operating parameters.

2.3. Ultrasonic horn

Experiments involving ultrasonic irradiations were performed using ultrasonic horn operated with 5 s ON and 5 s OFF pulse at power dissipation of 100 W. The ultrasonic horn obtained from M/s Dakshin, Mumbai had a fixed frequency of 20 kHz, tip diameter of 2.1 cm and rated power dissipation as 240 W. Using calorimetric measurements [36], the actual power dissipated in the system was observed to be 15.7 W for a supplied power of 100 W giving an energy efficiency of 15.7%. Calorimetric measurements for each run also indicated that the actual power dissipated into the solution was same for all the solutions with varying initial viscosities as investigated in