International Journal of Biological Macromolecules 72 (2015) 687–691

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

Dynamic and shear stress rheological properties of guar galactomannans and its hydrolyzed derivatives

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ARTICLE INFO

Article history:
Received 15 June 2014
Received in revised form 4 August 2014
Accepted 9 September 2014
Available online 23 September 2014

Keywords:
Guar galactomannans
Hydrolysis
Rheology
Viscoelastic properties
SIM

ABSTRACT

Guar galactomannan from seed of *Cyamopsis tetragonolobus* was hydrolyzed using acid (HCl), base [$Ba(OH)_2$] and enzyme (mannanase) method to obtain depolymerized substances with possible functional applications as soluble dietary fiber. Rheological behavior of crude, purified, and depolymerized guar gum solutions was studied at 25 °C, using shear stress and dynamic oscillatory measurements, performed with controlled stress rheometer Bohlin CVO (Malvern Instruments) fitted with cone-and-plate geometry. The various guar gums solutions with different viscosities exhibited shear-thinning behavior at high shear rate and Newtonian behavior at low shear rate. At low shear rate, sigma crude guar gum (SCGG), crude guar gum (CGG), acid hydrolyzed guar gum (AHGG) and enzyme hydrolyzed guar gum (EHGG) exhibited viscosities of 18.59, 1.346, 0.149 and 0.022 Pa s, respectively. Oscillatory experiments (G'', G') of gums solutions showed typical behavior of weak viscoelastic gel. All investigated guar gums were further used for glucose bio-accessibility using a novel in vitro small intestinal model (SIM). All gums solutions resulted in 20% reduction in simulated glucose absorption, indicating a non-significant functionality difference between various guar gums. So, it can be concluded that hydrolyzed guar gums without disturbing their rheological and physiological behavior would be useful for incorporation in various food products as soluble dietary fiber.

1. Introduction

Guar gum (GG) belongs to the wide family of galactomannans, which occur in nature in the endosperm of guar (*Cyamopsis tetragonolobus* L.) seeds and act as food reserve materials for germination. It consists of a main chain of 1,4-β-D-mannose and a side group of 1,6-α-linked D-galactose units [1,2]. Guar galactomannan is composed of galactose and mannose units in 1:2 ratios (Fig. 1) [3]. The galactose:mannose ratio is important in determining the viscoelastic properties of the solutions [2,4]. The galactomannans have been widely used in the food industry as ingredients to enhance viscosities in processing [5].

The functional properties of polysaccharide hydrocolloids are directly related with their structure [6]. Degraded galactomannan with reduced molecular weight and viscosity could be applied as soluble dietary fiber in functional foods [7]. Hydrolyzed guar galactomannans have the same chemical structure and physiological functions with crude guar gum. In addition, they are stable against low pH, heat, acid and digestive enzymes [8]. Consumption of depolymerized guar galactomannans has apparently enhanced growth of intestinal flora good for human health, and has also been associated with reduction in serum cholesterol and plasma glucose levels [9].

Rheological studies of polysaccharide gums in aqueous solutions are useful to understand the polysaccharide structure and to investigate its potential functionalities in a wide range of food applications and pharmaceutical industry for drug release formulations [4,10,11]. Galactomannan solutions typically exhibit shear thinning non-Newtonian behavior, where the viscosity reduces with increase of shear rate [12].

However, the rheological behavior of guar gum solutions is still object of debate and incompletely understood, due to the complex associations of the chains that cannot be related to a single specific model [13]. In the present work, the rheological behavior of

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http://dx.doi.org/10.1016/j.ijbiomac.2014.09.019
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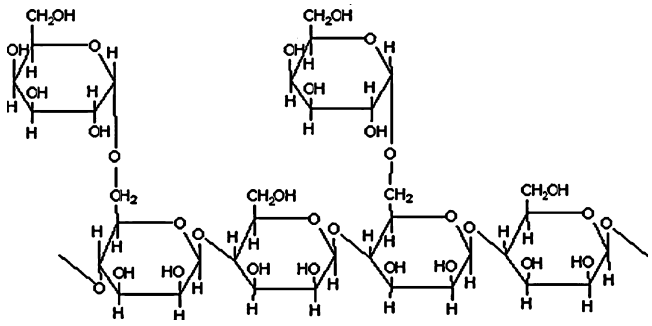

Fig. 1. Structure of guar: guar has a linear backbone of α-1,4-linked mannose units with β-1,6-linked galactose units randomly attached as side chains

guar galactomannans and its hydrolytic forms in aqueous solutions were investigated in shear stress and dynamic oscillatory conditions at 25 °C. Guar gum solutions were further used to study the effect of formulation on simulated glucose absorption using a novel dynamic small intestinal model that mimics flow and mixing in the gut.

2. Materials and methods

2.1. Purification of guar gum

Fine powder of crude guar gum (100 g) was dissolved in 2 L of distilled water and allowed to stand for 24 h with intermittent stirring. The gum mucilage was strained with calico to remove any insoluble debris or impurities and precipitated with 500 mL of 96% ethanol. The precipitated gum was re-filtered, washed with diethyl ether and freeze dried (CHRIST, Alpha 1–4 LD Plus, version 1.26, Germany) at −55 °C. The dried purified gum was milled to fine powder [14].

2.2. Hydrolysis of guar gum

2.2.1. Acid hydrolysis

Guar gum (10 g) was taken in 80% aqueous methanol (200 mL) containing 5% w/v HCl. The reaction mixture was heated for 2.5 h at 65 °C. The depolymerized guar gum was neutralized with 1.0 N NaOH solution and filtered under suction, washed with ethanol, freeze dried and milled to fine powder [15].

2.2.2. Base hydrolysis

Guar gum (5 g) was hydrolyzed with a saturated barium hydroxide [$Ba(OH)_2$] solution (200 mL) at 100 °C for 8 h. The hydrolyzed gum was neutralized with 1 M H_2SO_4, filtered, freeze-dried and milled to fine powder [16].

2.2.3. Enzyme hydrolysis

Guar gum powder was also hydrolyzed with the enzyme mannanase (Novozyme, UK) by the method with some modifications as described by Cheng and Prud'homme [17]. Guar powder 1.5 g was sprinkled slowly onto 198.5 mL of deionized water. The mixture was stirred through magnetic stirrer during the reaction. A 0.04 mg (0.04 units/200 mL) of mannanase enzyme was diluted in 2 mL of 0.1 M sodium acetate/acetic acid buffer solution (6.0 pH) and mixed thoroughly for 60 min. The solution pH was adjusted to 7.0 using 0.1 N HCl (37%, sp. gravity, 1.19 g/mL). Finally, the polymer solution was transferred to a container and placed for approximately 20–24 h at 25 °C to complete hydration. The mixture was magnetically stirred during the reaction. Guar and enzyme mixture was immediately heated to 100 °C for 20 min to denature the enzyme and stop the reaction. Mixture was filtered and residues were freeze-dried and ground to fine powder.

2.3. Rheological properties of aqueous guar solution

2.3.1. Preparation of solutions

The required amount of the powdered gum (1% w/v) was gradually added to the appropriate amount of distilled deionized water. The dispersion was vigorously stirred for 1 h, at room temperature, followed by heating the dispersion at 80 °C in a water bath for 30 min, under continuous stirring.

2.3.2. Shear stress properties

Shear stress and viscosity measurements were performed at 25 °C using a controlled stress rheometer (Bohlin CVO, UK) fitted with a cone and plate geometry (4° cone angle, 40 mm diameter) with controlled shear rate [4].

2.3.3. Oscillatory properties

Dynamic measurements and frequency sweeps measurements were performed at 25 °C using a controlled stress rheometer (Bohlin CVO, UK) fitted with a cone and plate geometry (4° cone angle, 40 mm diameter, 54 μm gap) with controlled shear stress in the 0.1–100 $rads^{-1}$ range [4].

2.4. Glucose absorption in simulated small intestinal model (SIM)

Glucose absorption measurement with respect to various guar gum solutions through in vitro small intestinal model was assessed with the method adopted by Tharakan et al. [18]

2.4.1. Preparation of solution

To prepare the guar–glucose (1% w/v) solutions, a known quantity of glucose (1 g) and then guar gum powder (1 g) was slowly added to the distilled deionized water (100 mL) in a beaker being stirred using a magnetic stirrer. Once the material had been added, the container was weighed and the solution heated to 80 °C and kept for 10 min at this temperature. Stirring continued for 12 h to ensure complete hydration of the guar gum; the final concentration was calculated after finding the weight loss through evaporation. The formulations were used within 24 h of preparation to avoid microbial growth induced changes in the properties of solutions.

2.4.2. Effect of mixing and flow rate on glucose absorption

Guargum–glucose solution (500 mL) was placed in the luminal part of the dialysis membrane (8.5 kDa MWCO). Glucose, being small molecule, passed through the membrane and was collected in the recipient side. Distilled deionized water (500 mL) was used as recipient fluid. Experiments were conducted at room temperature for a total of 90 min, taking samples every 5 min. Two processing conditions were investigated to study the effect of mixing on the glucose absorption:

(i) Mixing induced by segmentation contractions. In this case net flow was induced with peristaltic pump (3 rpm, 12 mL/min) and local mixing was induced by squeezing of the membrane, thus simulating gut segmentation contractions.
(ii) No mixing or segmentation (stationary flow). Net flow was induced using a peristaltic pump as previously but with no segmentation contractions.

The overall flow in the recipient side (outside of the membrane) was constant during experiments and was generated from a variable speed peristaltic pump. Each experiment was carried out in triplicate.