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Chemical and physical characterization of galactomannan extracted from guar cultivars (*Cyamopsis tetragonolobus* L.)

Sumedha Liyanage [a], Noureddine Abidi [a,*], Dick Auld [b], Hanna Moussa [c]

[a] Fiber and Biopolymer Research institute, Department of Plant and Soil Science, Texas Tech University, Lubbock, TX, USA
[b] Department of Plant and Soil Science, Texas Tech University, Lubbock, TX, USA
[c] Department of Mechanical Engineering, Texas Tech University, Lubbock, TX, USA

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ABSTRACT

Guar gum, known as galactomannan, is a heteropolysaccharide of galactose and mannose. Because of its unique rheological properties, guar gum has a diverse range of applications in various industries (hydraulic fracturing, paper, textiles, pharmaceuticals, and food). Chemical and physical characterization of guar gum using different analytical techniques is very important to understand the gum chemistry, optimize its applications, and investigate the impact of the purification. Therefore, galactomannan extracted from two guar cultivars planted in West Texas was characterized using different analytical tools to elucidate the variation in the physical and chemical properties with various levels of impurities. The gum was extracted with minimal contamination with continuous sample assessment using Fourier transform infrared spectroscopy (FTIR) and was purified using ethanol precipitation. The purified and unpurified gum samples were characterized using high-performance liquid chromatography, thermogravimetric analysis, X-ray diffractometry, and FTIR spectroscopy to determine the mannose to galactose ratio, thermal stability, level of crystallinity and chemical composition, respectively. Pure guar galactomannan and food-grade guar gum were used as reference materials. The effect of sodium chloride and potassium chloride on guar gum was also investigated. Scanning Electron Microscopy was employed to visualize the morphology of guar seeds.

1. Introduction

Guar, also known as Cluster bean (*Cyamopsis tetragonolobus* L.), has been cultivated for generations, particularly in India and Pakistan (Chudzikowski, 1971; Whistler and Hymowitz, 1979), as a green manure, vegetable (Watt, 1908), and a forage crop (Chudzikowski, 1971). Currently, guar gum, the endosperm polysaccharide of guar seed, serves as one of the most important water soluble gums, with an estimated annual world market of 150,000 t (Gong et al., 2011) due to its unique rheological properties. There is a diverse range of industrial applications of guar gum such as in food (Bourriot et al., 1999), pharmaceuticals (Crescenzi et al., 2004), paper (Chudzikowski, 1971), cosmetics (Chudzikowski, 1971), mining (Chudzikowski, 1971; Crescenzi et al., 2004), and mineral processing industries (Bulatovic, 2007). The hydraulic fracturing industry utilizes a considerable quantity of guar gum and its derivatives in commonly used fracturing fluids (Coveney et al., 2000; Weaver et al., 2003). In fact, guar gum is the most popular polymer in aqueous-based fracturing fluids (Kyaw et al., 2012).

Galactomannan is a common endosperm polysaccharide found in most legume seeds (Dea and Morrison, 1975; Sandolo et al., 2007), including locust bean (Srivastava and Kapoor, 2005), fenugreek, and alfalfa (Whistler and Hymowitz, 1979). It is a hetero-polysaccharide of galactose (Gal) and mannose (Man). Guar gum, chemically known as guar galactomannan, consists of a linear chain of (1→4)-linked β-D-mannopyranosyl sugar units with (1→6)-linked α-D-galactopyranosyl sugars as single unit side chains (Dea and Morrison, 1975; McClear, 1985; Miyazawa and Funazukuri, 2006). Although galactomannan extracted from different species shares the same basic structure, it varies in molecular weight (Miyazawa and Funazukuri, 2006), in the molecular weight distribution (Miyazawa and Funazukuri, 2006), in the mannose/galactose ratio, and in the distribution of the galactose side branches along the mannose backbone (Miyazawa and Funazukuri, 2006; Srivastava and Kapoor, 2005). These variations impact the solubility, thermal stability, and rheological properties of the gum.

* Corresponding author.
E-mail address: n.abidi@ttu.edu (N. Abidi).

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The mannose/galactose ratio of guar galactomannan has been estimated to be 1.8 (Srivastava and Kapoor, 2005), 1.67 (Cunha et al., 2007), 1.55 (Dressler et al., 2003), and 1.44 (Miyazawa and Funazukuri, 2006). The mannose/galactose ratio influences the solubility (Weaver et al., 2003), the chain stiffness, the spatial extension, and the polymer association (Dressler et al., 2003). The galactose side branches keep the chains far apart (Srivastava and Kapoor, 2005), preventing the formation of helical structures, which reduces the polymer solubility (Weaver et al., 2003). Therefore, the nature of the galactose substitution along the polymer chain plays a major role in solubility (Srivastava and Kapoor, 2005). Regions without galactose side branches form partially crystalline domains due to inter- and intramolecular associations, which reduce the solubility (Dressler et al., 2003). The mannose/galactose ratio is influenced by the method of purification (Cunha et al., 2007) and climate variations (Bocchinfuso et al., 2010; Cheng et al., 2002). The mannose/galactose ratio can be determined using high-performance liquid chromatography (HPLC). To this end, the gum must be fully hydrolyzed into its monomers, generally through treatment with trifluoroacetic acid (Cunha et al., 2007), sulfuric acid (Miyazawa and Funazukuri, 2006), or hydrochloric acid (Cheng et al., 2002).

The mannose/galactose ratio and the substitution pattern of galactose branches depend not only on the plant source but also on the extraction conditions (Dressler et al., 2003). Crude guar gum contains proteins and fibers (Srivastava and Kapoor, 2005) from the seed coating and the germ residues as impurities, which may affect the gum properties. For example, it has been reported that the presence of cellulose and protein residues reduces the conductivity within the proppant pack in fracturing fluids (Weaver et al., 2003). Moreover, the endosperm itself contains impurities, and the pure gum accounts for approximately 86% of the endosperm (Chudzikowski, 1971). Guar gum is purified by precipitation into polar solvents (Srivastava and Kapoor, 2005) such as ethanol (Dea and Morrison, 1975) or by complexation with Cu^{2+} or Ba^{2+} (Dea and Morrison, 1975; Srivastava and Kapoor, 2005). The purification improves the behavior of the gum, such as solubility, development of viscosity, and thermal stability.

In this paper, we report the chemical and physical characterization of guar gum extracted from currently cultivated guar germplasm in West Texas (Monument and Matador) using different analytical tools. The guar gum extracted was purified using ethanol precipitation and characterized to investigate the effect of purification on the properties of the gum. Pure guar galactomannan purchased from Magazyme (Megazyme International Ireland, Ireland) and food-grade guar gum purchased from a local food store were used as standards.

2. Materials and methods

2.1. Materials

Four different guar gum samples were used: guar galactomannan medium viscosity (Megazyme International Ireland, Ireland) was used as received. Food-grade guar gum was purchased from Sprouts Farmers Market, (Lubbock, Texas) and sieved using a USA standard testing sieve (No 60 – Fisher Scientific Company, USA) prior to storing. The endosperm powder was extracted from two different cultivars, Matador and Monument, grown at Texas Tech University Quaker research farm with supplemental irrigation of 0.15 inches of water per day during the growing season. Trifluoroacetic acid (TFA), methanol, and sodium hydroxide (NaOH) were purchased from Sigma–Aldrich (Sigma–Aldrich Corporation, USA). Sulfuric acid (H_2SO_4), and potassium chloride (KCl) were purchased from Fisher Scientific (Fisher Scientific Company, USA).

2.2. Extraction of endosperm powder from guar seeds

The guar endosperms were separated using the protocol reported by Sabahelkheir and coworkers (Sabahelkheir et al., 2012) with a slight modification. Instead of soaking raw guar seeds in water, guar seeds were subjected to an initial heat treatment at 100 °C for 30 min using an isotemp oven (Fisher Scientific Company, USA) to kill the germ and deactivate the enzymes. The treated seeds were then soaked in water at 80 °C following a reported protocol (Sabahelkheir et al., 2012). Then, the dried endosperm samples were ground into a 20 mesh size using a Willey mill and sieved using a standard sieve. All samples were stored in a refrigerator (4 °C) and conditioned at 65 ± 2% relative humidity and 21 ± 1 °C for at least 24 h prior to analysis.

2.3. Purification of Matador and Monument endosperm powder

Samples of Matador and Monument endosperm powders (500 mg) were sprinkled separately into 150 mL of MilliQ water at 80 °C and kept on a laboratory hotplate with a magnetic stirrer. The mixtures were continually stirred using a glass rod while the powder was sprinkled. The heater was then turned off, and the mixtures were magnetically stirred for a further 6 h to ensure maximum dissolution. The solutions were filtered through filter paper (P8, Fisher Scientific Company, USA) to remove any insoluble material. An equal volume of ethanol was then added to each filtrate followed by mixing using a glass rod to facilitate the precipitation of guar gum. Then, each filtrate was recovered by filtering through a perforated funnel, washed with excess ethanol and dried at 30 °C in an Isotemp oven overnight and then stored in a refrigerator (4 °C) prior to analysis.

2.4. Characterization of guar gum

2.4.1. Images of guar seed cross-sections

Raw seeds from both cultivars were immersed in 80 °C distilled water for 1.5 h, and thin manual sections of fully imbibed seeds were made carefully using a sharp razor blade. The cross-sections were dried for 24 at 65 ± 2% relative humidity and 21 ± 1 °C. The cross-sections were mounted on carbon discs prior to visualization, and no coating was performed. Then, scanning electron micrographs were collected using a Hitachi Scanning Electron Microscope (TM-1000, Hitachi, Japan) at an accelerating voltage of 15 kV.

2.4.2. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of all the samples (guar galactomannan, food-grade guar gum, Matador endosperm powder, Monument endosperm powder, ethanol precipitate of Matador endosperm powder, and ethanol-precipitated Monument endosperm powder) were collected using a Spectrum-400 equipped with a universal attenuated total reflectance (UATR) accessory (Spectrum-400, PerkinElmer, USA). The spectra were collected in the mid IR range (4000–650 cm^{-1}) with a spectrum resolution of 4 cm^{-1}. Thirty two co-added scans were collected from each sample. The sample was placed on the ZnSe-Diamond crystal without further sample preparation. A constant pressure, which was monitored by the software, was applied on the sample to ensure good contact between the sample and the Infrared beam and to prevent any loss of IR radiation. The ZnSe-Diamond crystal was cleaned with MilliQ water before recording each spectrum, and a background scan of the clean crystal was collected. The spectra normalization and baseline correction were performed using Spectrum software (PerkinElmer, USA).