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# Rheology of dispersions of xanthan gum, locust bean gum and mixed biopolymer gel with silicon dioxide nanoparticles

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ABSTRACT

Mixed xanthan gum (XG) and locust bean gum (LBG) biopolymers form thermally reversible gels of interest in tissue engineering and drug delivery. 1% solutions of XG, LBG and 1:1 ratio XG/LBG mixed gels (LX) containing silicon dioxide ($SiO_2$) nanoparticles were rheologically characterized with respect to nanoparticle concentration and temperature. 10% nanoparticles in XG created larger domains of associated polymer, resulting in enhanced viscosity and viscoelastic moduli. In LBG with 10% particles, transient viscosity and a gel–sol transition occurred due to particle bridging and aggregation. In the LX gel, 10% $SiO_2$ particles caused an increase in elasticity. When ramping temperature from 25 °C to 85 °C, the complex modulus for all solutions containing 10% $SiO_2$ was relatively constant, indicating that nanoparticles counteracted the effect of temperature on the material properties. Understanding the influence of nanoparticle loading on material properties is necessary for biopolymer material development where property prediction and control are critical.

## 1. Introduction

In aqueous polymer solutions containing nanoparticles, polymer–particle dispersions, the interaction of nanoparticles with polymer chains under shear can have a strong influence on material properties. The formation of nano- and micro-structures within the fluid results in complex rheological behavior such as shear thickening, shear thinning or gelation. The properties of polymer nanocomposites with controlled optical, electrical or mechanical properties have been of significant interest for materials science applications [1] and polymer–particle dispersions are prevalent in paints and coatings, oil recovery, wastewater treatment, and industrial separation processes [2–4].

Biopolymers are also attractive options in biomedical, biotechnology and food processing applications due to factors such as cost, sustainability and biocompatibility. Understanding the impact of molecular interactions between polymer and particulates on the mechanical response is of significant interest [4–7], for example in drug delivery, where biopolymers interact with nanoparticulate drugs. Hydrogels formed from biopolymers are being developed as materials for tissue engineering applications [6], as models for the extracellular matrix of biofilms [8] and as biomaterials with antibacterial properties [9]. Solution rheology impacts processing of the solution and the resulting gel properties. Therefore, design of novel polymer hydrogels and biomaterials depend on characterization and understanding of molecular level interactions and their influence on material properties in the solution phase.

Particle size is an important factor in predicting the material response to deformation, as nano- versus micro-particulate interactions with the polymer can be quite different [10–12]. The rheology of particle suspensions is well known [13–15] going back to Einstein's classic relationship between viscosity and particle volume fraction [16]. Experimental and theoretical work has looked at the interactions of polymer chains with colloidal particles [2], however, the nature of interactions, the molecular structures formed under shear and their impact on the mechanical response are significantly different for particles on the nanoscale [17–19] and depending upon the nature of the interaction between the polymer chain and the particle surface (i.e. adsorbing, non-adsorbing), the impact on material properties can vary drastically. The formation of soft deformable secondary structures in solution due to polymer bridging changes the size of the fundamental “particle” and with high enough particle concentrations may form a percolated network causing elastic effects [18].

In this work, we explore the impact of silicon dioxide nanoparticles on the material properties of two biopolymers with varying conformations in solution. Xanthan gum, a semi-rigid rod-like molecule, and locust bean gum, a random coil, are polysaccharide biopolymers often exploited in food and cosmetic industries as thickeners [20–22]. When mixed, the two biopolymers interact to form a firm thermally reversible gel of interest as tissue scaffolds and in drug delivery systems [23,24]. Mixed polymer gels in general have applications in pharmaceutical and food industries [25] and the properties of xanthan/galactomannan hydrogels as well as their mechanisms of formation have been studied extensively [26–28]. With the addition of silicon dioxide ($SiO_2$) nanoparticles to polymer solutions, novel behaviors and material properties

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have been observed for use in drug delivery systems [29], and $SiO_2$ particles have been shown to carry high loads of poorly soluble drugs while being relatively non-toxic. Previous studies of silicon dioxide nanoparticles in polysaccharide solutions have observed gel formation mediated by the nanoparticulate silica [30,31]. For colloidal silica gels formed in concentrated biopolymer solutions, the network structure was found to be impacted by the elasticity of the suspending medium [32].

Xanthan gum (XG) is an anionic polysaccharide made through fermentation of glucose by the bacterium *Xanthomonas campestris* with a backbone of β-(1,4)-D-glucose. Alternate glucose residues have a charged trisaccharide side chain consisting of two mannose residues with a glucuronic acid residue between them. The terminal mannose moiety may carry pyruvate residues linked to the 4- and 6-positions. The internal mannose unit is frequently acetylated at O-6 [33]. In its native state, XG exists as a double-stranded, right-handed five-fold helix. As a polyelectrolyte, it's conformation in solution is a function of ionic strength and pH [31,34]. Locust bean gum (LBG) is a nonionic polysaccharide biopolymer derived from the seed of the Carob tree and exists in solution with water as a random coil [30]. It consists of a linear (1,4) linked β-D-mannose backbone where every fourth mannose is substituted with a (1,6) linked α-D-galactose unit. The mannose units are randomly dispersed throughout the polymer chain and multiple units in a row can allow for self-association, while the galactose units prevent strong chain interactions. When combined, XG and LBG form a thermally reversible gel (LX) [27].

Here, we characterize the rheological response for xanthan gum solutions, locust bean gum solutions and their synergistic mixed gel in the presence of silicon dioxide nanoparticles and analyze the impact of polymer–particle interactions with respect to nanoparticle concentration. XG is known to undergo a conformational change at higher temperatures that impacts the rheological response. In biomedical applications, specific fluid behaviors may be desired at different temperature, therefore viscoelastic fluid parameters were also monitored with respect to temperature.

## 2. Materials and methods

### 2.1. Sample preparation

Locust bean gum (LBG, Sigma Aldrich) was purified before use in a two-step process, consisting of centrifugation and filtration. A 1 wt.% solution of LBG in de-ionized water was first centrifuged at 17,500 rpm for 1 h at 4 °C. The supernatant was then removed and filtered using vacuum filtration through 8 μm MF membrane filters (Millipore). After filtration, the clear and colorless solution was lyophilized. Xanthan gum (XG, MP Biomedical) was purified by centrifuging a 2 wt.% solution at 12,500 rpm for 1 h at 4 °C. The supernatant was then removed and lyophilized. The resulting purified LBG and XG polymers were used to make solutions for all rheological tests.

In order to get dissolution of LBG in water, polymer was added to water at 1% (w/v) and mixed at ~600 rpm. The solution was initially heated to 325 °C for ~5 min and temperature was decreased by increments of 5 °C every 5–10 min until reaching 260 °C. At this point, the solution was mixed for about 2 h or until the polymer was completely dissolved into the solution. The solution was weighed and any water lost to evaporation was added back into the solution. To create homogeneous polymer–particle dispersions with locust bean gum, silicon dioxide particles with a diameter of 10–20 nm (Sigma-Aldrich) were added at concentrations from 1% to 10% by weight to the dissolved polymer solution and mixed vigorously with a stir bar. The solutions were mixed at room temperature for approximately 30 min or until no clumps of silicon dioxide nanoparticles remained.

XG was mixed in water with a stir bar at 1% (w/v) at 45 °C for ~30 min to 1 h or until fully dissolved. To create homogeneous polymer–particle dispersions with xanthan gum, $SiO_2$ nanoparticles were first added to distilled water at concentrations from 1% to 10% by weight and mixed vigorously and then the XG was added. The dispersion was mixed at 45 °C until the XG was fully dissolved and no clumps of silicon dioxide particles remained, approximately 30 min to 1 h. Solutions with air bubbles were degassed under a vacuum.

To prepare LX gels, the same procedures described above were used to make XG and LBG solutions with and without nanoparticles. The two solutions were then mixed in a 1:1 ratio of XG to LBG to form a gel with 1% (w/v) total polymer concentration and the desired 1 and 10% $SiO_2$ particle concentrations. Measurements of pH were performed with a standard pH meter.

### 2.2. Rheology methods

Rheological measurements were conducted at 25 °C with an AR-G2 rheometer (TA Instruments) equipped with a 60 mm diameter stainless steel parallel plate geometry and 60 mm diameter cone-and-plate with a 2° cone angle. Temperature was controlled to within 0.1 °C by a Peltier plate. For nonlinear rheology, flow curves were collected under a controlled strain for shear rates ranging from 0.1 to 1000 $s^{-1}$. In the case where transient effects were present, peak holds were performed at fixed shear rate for 4 h or until such time as the viscosity plateaued with time. For linear rheology, a strain sweep was performed to determine the linear viscoelastic region. The values were typically 3% for XG, but for LBG and LX ranged from 0.5% (1% LX with 10% $SiO_2$) to 0.6% (1% LBG with 10% $SiO_2$) to 10% (1% LBG with 1% $SiO_2$). Oscillatory measurements were made for frequencies ranging from 0.5 to 500 rad $s^{-1}$ at a fixed strain. To check for transient effects, time sweeps were performed with fixed strain and frequency for 1% LBG with 10% $SiO_2$ nanoparticles. Temperature sweeps were performed at a strain within the linear viscoelastic region for each sample and 6.28 rad $s^{-1}$ frequency, ramping from 25 °C to 85 °C at a rate of 1 °C/min. For samples where dehydration could be an issue, mineral oil was added in a thin layer along the outside of the sample.

## 3. Results and discussion

In this work, no additional salt was added to the polyelectrolyte polymer solutions and the pH was neutral at ~7. The XG chains under these conditions can be considered semi-rigid rods with weak electrostatic screening. For polyelectrolyte solutions, the polymer chains would be expected to become more flexible with increasing ionic strength since the persistence length decreases with the Debye screening length. The Debye screening length is the distance beyond which counterions neutralize charge and the Coulomb potential decays exponentially [35]. For XG however, the polymer chains become more rigid with increasing salt due to collapse of the side chains along the polymer backbone [31]. With decreasing pH, the polymer chains would become more flexible due to weaker electrostatic repulsion and self-association between the carboxylic groups on the XG trisaccharide side chains would occur more strongly due to larger availability of sites for hydrogen bonding.

The 1% (w/v) XG solution exhibits shear thinning over the entire range of accessible shear rates, shown in Fig. 1a. This behavior has been previously characterized in the literature as a "weak gel" behavior, due in part to the self-association [27] via hydrogen bonding. For the weak gel at rest, "domains" of associated XG molecules are present that, unlike in a "true" gel, do not span the entire sample in three dimensions. Under shear however, these domains are broken down, causing shear-thinning. If modeled as a power law [13], $\eta = \mu_o \dot{\gamma}^{n-1}$, the apparent viscosity trends as $n = 0.193$ with a zero shear viscosity $\mu_o = 14.9$ Pa·s. The zero shear viscosity is the value of apparent viscosity in the limit of zero shear rate. Indications of a true gel formation, such as hysteresis and a change in viscosity with sample aging [31], were not observed. Hence we describe the 1% XG solution in this work as a "weak" gel. The addition of 1% (w/v) nanoparticles to the XG solution