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Viscosifying properties of corn fiber gum with various polysaccharides

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ABSTRACT

The effect of corn fiber gum (CFG) on the aqueous solutions of a series of widely-used commercial polysaccharides has been studied by rheological techniques using a shear stress synergism index I_S to evaluate its viscosifying action. While CFG solution exhibited Newtonian fluid behavior with a very low viscosity even at a high concentration, the aqueous mixtures of CFG and some non-gelling polysaccharides (hyaluronan, guar gum, carboxymethylcellulose, hydroxyethylcellulose, konjac glucomannan, pectin and chitosan) showed a pseudoplastic fluid behavior. Furthermore, the addition of CFG showed a remarkable viscosifying action for the aqueous solutions of these non-gelling polysaccharides likely due to their interaction by hydrogen bonding. However, the viscosity behavior of CFG with some gelling polysaccharides such as methylcellulose, gellan gum, carrageenan, xanthan, may be based on a different mechanism. A proper model of intermolecular interaction between CFG and these gelling and non-gelling polysaccharides has been discussed and proposed.

1. Introduction

Corn fiber gum (CFG) is an alkaline hydrogen peroxide extract of corn fiber, an abundant low-priced by-product of corn kernel milling process. It has a highly branched structure with a β-(1-4)-xylopyranose backbone and α-L-arabinofuranose residues as side chains on both primary and secondary hydroxyl groups with some D-glucuronic acid residues linked to the O-2 position of xylose residue of the backbone. Galactose and some xylose residues are attached to the arabinofuranosyl branches (Yadav, Johnston, & Hicks, 2009). According to reports by various groups (Doner, Chau, Fishman, & Hicks, 1998; Hespell, 1998; Saulnier, Marot, Chanliaud, & Thibault, 1995; Sugawara, Suzuki, Totsuka, Takeuchi, & Ueki, 1994; Whistler & BeMiller, 1956), CFG has the following glycosyl composition: D-xylose (48–54%), L-arabinose (33–35%), galactose (7–11%), and glucuronic acid (3–6%). CFG shows a good emulsification ability for oil-in-water emulsions system which is related to its protein and lipid contents (Yadav et al., 2009). It has several useful properties, e.g., adhesive, stabilizing (Wolf, MacMasters, Cannon, Rosewell, & Rist, 1953), film forming and emulsifying (Mikkonen et al., 2008; Woo, 2001). CFG contains some proteins similar to gum arabic (Yadav, Cooke, Johnston, & Hicks, 2010; Yadav, Parris, Johnston, Onwulata, & Hicks, 2010) and regarded as an anionic, highly branched polysaccharide with a long xylopyranose backbone.

Mixing two or more gums to formulate a food or non food products has recently attracted a great interest, since such blending produces a dispersed system, which can combine the advantage of each component and sometime even bring some additional excellent properties (Gruber & Konish, 1997; de Jong & van de Velde, 2007; Kaletunc-Gencer & Peleg, 1986; Zhang & Zhou, 2006). Many pharmaceutical and cosmetics products also contain different types of gums to modify viscosity or even as the matrix of such products. These gums often act as thickeners, stabilizers or emulsifiers. The presence of different types of gums may give rise to different viscosity behavior. For example, the mixture of locus bean gum and carrageenan makes a more viscous solution than the sum of their individual viscosity (Hernández, Dolz, Dolz, Delegido, & Pellicer, 2001), while the addition of gum arabic into konjac glucomannan solution leads to a decrease in its viscosity (Liang et al., 2011). The study of rheological properties of various mixed systems is essentially important for both scientific and industrial aspects (Rinaudo & Moroni, 2009; Williams, Day, Langdon, Phillips, & Nishinari, 1991). For example, the stabilization of emulsion systems used either in food or cosmetics is greatly related to the viscosity of the mixture in the aqueous solution (Behrend, Ax, & Schubert, 2000; Hemar, Tamehana, Munro, & Singh, 2001). The

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mixing of different types of polysaccharides in water can form either a uniform solution or a multiphasic system. Phase separation in aqueous system containing different polysaccharides is a common phenomenon and has been studied for a long time (Antonov, Pletenko, & Tolstoguzov, 1987; Boyd et al., 2009; Tolstoguzov, 2000). The influence of phase behavior on the flowing behavior of the mixed system is also of primary importance as it is one of the basic factor for food formulation and processing to provide good texture and flavor in food products (Tolstoguzov, 2000).

Taking into account that CFG has an excellent emulsifying ability and makes a low viscous solution at a high concentration, the study of viscosifying action of CFG in aqueous solution of many different polysaccharides or their derivatives is important to broaden its applications for many food and non-food uses. As far as we know, most of the published reports on CFG are on its isolation (Doner et al., 1998; Singh, Doner, Johnston, Hicks, & Eckhoff, 2000), structural characterization (Yadav, Fishman, Chau, Johnston, & Hicks, 2007; Yadav, Johnston, & Hicks, 2007; Yadav, Parris, Johnston, & Hicks, 2008), and emulsifying properties (Yadav, Cooke, et al., 2010; Yadav, Johnston, Hotchkiss, & Hicks, 2007; Yadav, Parris, et al., 2010; Yadav et al., 2008, 2009). Studies on the viscosity and viscosity behavior of the aqueous mixture of CFG with other polysaccharides have not been done and reported. The objective of the present work is to study the viscosifying action of CFG in its aqueous mixture with several kinds of widely-used commercial carbohydrate polymers and propose a possible model of their interaction in aqueous solution.

2. Materials and methods

2.1. Materials

Hyaluronan (HA) was obtained from Freda Biochemistry (China) in the form of sodium salt. Methyl cellulose (MC) (SM4000, DS 1.8 and M_w 3.8 $\times$ 10^5 Da, determined by light scattering method at pH 7) was purchased from Shin-Estu Chemical Co. Ltd., Japan. Chitosan (CTS) (viscosity 550 mPa s in water and degree of deacetylation 85) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Carboxymethylcellulose (CMC) (DS 0.9 and M_w 7.0 $\times$ 10^5, determined by light scattering method at pH 7) was purchased from Acros Organics (China). Hydroxyethylcellulose (HEC) (viscosity 95 cps and DS 1.8) was obtained from Aladdin Reagent Co., Ltd (China). Guar gum, xanthan gum, κ-carrageenan and pectin were purchased from Danisco USA Inc. Gellan gum was supplied by CP Kelco Corporation. Konjac glucomannan was supplied by Shimizu. Chemical Co., Tokyo, Japan. Three generation polyamidoamine (PAMAM) dendrimers with carboxyl end groups (M_w 4856 g/mol) were synthesized following the procedure reported by Tomalia et al. (1985). All the other chemicals used in the study were purchased from Sinopharm Chemical Reagent Co., Ltd., China and they were of analytical grade.

2.2. Preparation of solutions

The polysaccharide samples were dispersed in distilled water and then mixed on a roller mixer for 24 h. The suspension of MC sample was transferred to a refrigerator at 4 °C until completely dissolved as it was not completely soluble at room temperature. The solution of CTS was prepared in 1% acetic acid. The solutions of gellan gum, konjac glucomannan and carrageenan were prepared by heating at 80 °C for 1 h.

The aqueous mixture of CFG with gellan gum or carrageenan was prepared by mixing gellan gum or carrageenan with CFG solution in 1:1 ratio at 80 °C and then cooling to the room temperature. For preparing mixture of CFG with other polysaccharides, its solution at different concentrations was mixed with the polysaccharide solution in 1:1 ratio at room temperature and mixed gently on a roller mixer. In all these solutions, no phase separation was seen even after their storage at 4 °C for a week.

2.3. Size exclusion chromatography (SEC)

The molecular characterization of CFG, HA and a tailored HA (HA-C) was done using a Viscotek TDA 305 instrument (Malvern Instruments, USA) equipped with two Viscotek A6000M columns, two light scattering (Low Angle Light Scattering, LALS, 7° and Right Angle Light Scattering, RALS, 90°), one refractive index (RI) and one on-line viscometer (VIS) detectors. HA sample was tailored to get its M_w comparable to CFG for performing a comparative molecular characterization. The concentrations of CFG and HA were 2 and 0.5 mg/mL, respectively. The experimental conditions for chromatography consisted of 0.15 M $NaNO_3$ as the mobile phase, 30 °C temperature, 0.7 mL/min flow rate and 100 μl injection volume. Data were collected and analyzed by OmniSEC software.

2.4. Rheological measurements

The study of rheological properties was carried out using a rotational rheometer AR G2 (TA Instruments, USA) with a 2°1′8″ cone plate geometry (60 mm diameter and 58 μm gap). The temperature was regulated by a circulating water bath using Peltier system. A thin layer of low-viscosity silicone oil was placed on the periphery surface of the solution held between the plates to reduce the evaporation of water from the samples during the measurement. Steady shear viscosity was measured over a shear rate range of 0.01–1000 s^{-1} at 25 °C. Steady shear state was assumed to be attained, when the variation of torque was less than 5% throughout three consecutive sampling periods (20 s). The maximum point time was set to 6 min. Stress–shear rate measurement and viscoelastic measurement were also conducted using the same rheometer. Oscillatory measurement of storage modulus G', loss modulus G'', and complex dynamic viscosity η^* were performed at a strain of 1%, which is within the region of linear viscoelastic response in the range from 10^{-2} to 10^2 rad/s.

All measurements were performed three times. The biggest variance of the measurement is below 10%.

3. Results and discussion

The rheological properties of an aqueous mixture of CFG and HA (using HA as a model polysaccharide) at different mixing ratios, were first studied and the viscosifying action of CFG on HA solution was evaluated in detail. Fig. 1a and b show the effect of shear rate on the steady shear viscosity and the steady shear stress of individual CFG, HA and their (HA + CFG) mixture at 25 °C. The steady shear viscosity of CFG solution at different concentrations was almost independent of the shear rate without any remarkable shear thinning phenomenon even at a very high shear rate of up to 1000 s^{-1}, showing a typical Newtonian fluid behavior. Moreover, the steady shear viscosity of CFG solution increased with increase in its concentration. But still it was as low as 0.3 Pa s even at a relatively high concentration of 60 mg/mL, indicating its behavior to form a low viscous solution at its high concentration. The viscosifying action of CFG in its solution with HA (10 mg/ml) became more effective as the concentration of CFG increased from 10 to 60 mg/ml. The curves for zero shear viscosity of individual HA (10 mg/ml), CFG (10, 30 and 60 mg/ml) and HA mixture with each three concentration of CFG are shown in Fig. 1c. It is very clearly seen that the zero shear viscosity of the HA/CFG mixture containing 60 mg/ml CFG increased more than 5 times (above 35 Pa s from