Rheological properties of kuzu starch pastes with galactomannans

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Abstract The paper describes the effects of galactomannans on viscoelastic properties of commercial Japanese white kuzu starch pastes. The study included morphological, thermal and rheological analyses of the biopolymer. The results obtained in the form of storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ were described by the modified fractional Kelvin–Voigt model with two springpot-type elements, created on the basis of differential calculus of fractional order and Fourier transform. It allowed to determine 17 material parameters providing a lot of additional information about structure and viscoelastic properties of the biopolymer in comparison to the classical analysis of oscillatory and creep tests. The study led to the conclusion that commercial Japanese white kuzu starch was so-called type II starch with a high pasting temperature of 75 °C and an average granule diameter equal to 10.9 μm . Rheological properties of the pastes depended on the galactose-to-mannose ratio in galactomannan molecule. The larger substitution degree, the higher viscosity, characteristic relaxation times, polydispersity index, gel stiffness, and the lower cross-linking density and average molecular weights. The presence of galactose side groups favored the hydration and immobilization of water molecules.

Keywords Kuzu starch · Galactomannan · Pasting process · Rheological properties · Fractional modelling

Introduction

Kuzu (kudzu) is a plant of *Pueraria* genus from Southeast Asia. Its root is a medical raw material which has been used in natural medicine since ancient times (Wong et al. 2011). Kuzu is used to treat diabetes, flu, fever, nausea, migraines, allergies, and diseases of upper respiratory tract. Plant has strongly alkaline properties, so it deacidifies and detoxifies the body, and helps to regulate metabolism. Kuzu raises the level of hormones—serotonin and dopamine—which are responsible for good mood and reduction of stress. It also affects the cardiovascular system by lowering blood pressure, increasing economization of heart beat and reducing the risk of heart attack. In problems with digestion and stomach-intestinal ailments, kuzu is often served in the form of paste. The components present in kuzu root are able to penetrate intestines, to fight bacterial infections, and to prevent contractions of smooth muscles. The studies conducted at many scientific centers indicated that eating kuzu root can reduce alcohol craving as much as 80% (Lukas et al. 2005). This is mainly because of daidzein—a compound from the group of isoflavones, also known as phytoestrogen. Daidzein has antioxidant properties, mitigates the effects of alcohol intoxication, and improves the functioning of organs already damaged by alcohol. Furthermore, consumption of powdered kuzu root has positive effect in the treatment of nicotine addiction (Meletis and Zabriskie 2008). The unquestionable advantage of this method is that the treatment does not cause any side effects.

Inside the kuzu root there is 15–35% of starch from which 19–24% is the amylose fraction (Van Hung and Morita 2007). Starch granules have an irregular polygonal shape and a diameter from 3 to 23 μm (Hoover 2001). Kuzu starch is a polysaccharide with high pasting

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temperature of 70–76 °C (Van Hung and Morita 2007; Geng et al. 2007). It contains a number of micronutrients, including phosphorus, iron, and calcium, thus it provides a valuable alternative to thickening and binding agents, such as gelatin or potato starch.

Galactomannans are hydrocolloids extracted from the seeds of leguminous plants. The main chain of galactomannans is composed of mannose units, and side groups in the form of galactose molecules. The literature distinguishes 4 basic galactomannans depending on the galactose-to-mannose ratio also known as the substitution degree (Mathur 2011): fenugreek gum (1:1), guar gum (1:2), tara gum (1:3), and locust bean gum (1:4). Starch–galactomannan mixtures in food industry have been used for over 50 years. One of the reasons is the ability to reduce starch content of at least 50%, allowing a reduction in caloric value of food (Imeson 1997). Hydrocolloid additives provide product stability during storage, prevent crystallization and separation of phases, and allow adjustment of its rheological properties (Saha and Bhattacharya 2010).

In the literature, there is lack of comprehensive information about rheological properties of kuzu starch, despite the considerable possibilities of its practical application. Until now, only a few papers on this subject were published (Van Hung and Morita 2007; Geng et al. 2007). So far, there have been no oscillatory or creep tests of kuzu starch pastes in mixture with hydrocolloid gelling/thickening agents. Therefore, the aim of research was a comprehensive description of structure and rheological properties of pastes obtained from kuzu starch and galactomannans.

Materials and methods

Materials

Research materials included: pure commercial Japanese white kuzu starch (KS) (Terrasana, Netherlands) and galactomannans extracted from seeds of leguminous plants: fenugreek gum (FG), guar gum (GG), tara gum (TG) and locust bean gum (LBG) (Phayno Industry Limited, China). According to the data provided by manufacturer/distributor, commercial Japanese white kuzu starch contained 83.8% of polysaccharides (including 23.1% of amylose), 0.5% of lipids, 0.2% of proteins, 0.07% of ash, 0.03 of micronutrients (calcium, phosphorous, iron), 0.002 of daidzein, and 15.4% of moisture.

Morphological characteristics

Particle size distribution of Japanese white kuzu starch was conducted using laser diffraction analyzer SALD-2300

(Shimadzu, Japan), according to the methodology described by Rafiq et al. (2015) and Jan et al. (2015).

Thermal properties

Pasting temperature of Japanese white kuzu starch was determined using starch cell C-ETD160/ST (Anton Paar, Austria). 20 ml samples of 3% (w/v) aqueous suspensions of starch were kept at 25 °C for 5 min, heated from 25 to 95 °C with heating rates of 5 and 10 °C/min, kept at 95 °C for 75 min, cooled from 95 to 25 °C with cooling rates of 5 and 10 °C/min, and kept at 25 °C for 10 min; while stirring with a constant rotation speed of 300 rpm.

Rheological properties

Samples of 3% (w/v) aqueous kuzu starch suspensions with 0.3% (w/v) galactomannan additives were heated at 95 °C for 75 min, while stirring with a magnetic stirrer Yellow Line MAG HS 7 (IMLAB, France) at constant rotation speed of 300 rpm. The obtained pastes were cooled, stored at 5 °C for 24 h, and then subjected to the rheological tests at constant temperature of 25 °C, using rotary rheometer Physica MCR 301 (Anton Paar, Austria) with plate–plate system (plate diameter—50 mm, gap width—1 mm). The range of linear viscoelasticity was determined by strain sweep at oscillation frequency equal to 1 Hz (6.28 rad s^{-1}).

The main rheological measurements included the determination of:

- Storage modulus G' , loss modulus G'' and tangent of loss angle δ , for oscillation frequency ω in the range of 6.3×10^{-4} –450 rad s^{-1} , for specified sinusoidal shear strain with 3% amplitude within the linear viscoelastic region;
- Shear creep compliance $J(t)$ as a function of time t in the range of 0–2000s, for specified constant shear stress of 1 Pa, also within the range of linear viscoelasticity.

Fractional modelling

The experimental data from oscillatory tests were described by means of the modified fractional Kelvin–Voigt model with two built-in springpot-type elements (Jóźwiak et al. 2015)—Eqs. (1) and (2). The model was derived on the basis of differential calculus of fractional order and Fourier transform. Generally, each springpot can be understood as a component having intermediate properties between ideal elastic Hooke element (spring) and perfect viscous Newton element (dashpot) (Lewandowski and Chorązyczewski 2010). The first springpot in the modified fractional Kelvin–Voigt model represented friction

between adjacent chains, and the second springpot characterized elastic deformations of statistical segment of biopolymer chain.

$$G'(\omega) = G_N^0(\tau_0\omega)^\alpha \cos\left(\alpha \frac{\pi}{2}\right) + G_e(\tau_m\omega)^\beta \cos\left(\beta \frac{\pi}{2}\right) \quad (1)$$

$$G''(\omega) = G_N^0(\tau_0\omega)^\alpha \sin\left(\alpha \frac{\pi}{2}\right) + G_e(\tau_m\omega)^\beta \sin\left(\beta \frac{\pi}{2}\right) + \frac{(G_N^0)^2}{\eta_0\omega} \quad (2)$$

where G' is storage modulus, G'' is loss modulus, ω is oscillation frequency, G_N^0 is plateau modulus, G_e is equilibrium modulus, τ_0 and τ_m are characteristic relaxation times, α and β are fractional exponents, η_0 is Newtonian steady-state shear viscosity.

This approach allowed the description of dynamic behavior of biopolymer, in a wide range of oscillation frequency, by 2 algebraic equations which contained 7 parameters characterizing viscoelastic properties of the given material. Using the formulas presented in the previous publication (Jóźwiak et al. 2015), it was possible to determine another 10 material constants: relaxation strength ΔG , plateau compliance J_N^0 , steady-state compliance J_e , dispersion modulus f , coefficient of network vibration damping k , dimensionless width of viscoelastic plateau L , cross-linking density ω_0 , gel stiffness S , average entanglement molecular weight M_e , and average molecular weight between cross-links M_c .

Results and discussion

Morphological characteristics

Granulometric analysis of kuzu starch indicates its particle size distribution. Figure 1 shows the normalized particle fractions and the cumulative curve. Starch granules had a size distribution ranging from 0.7 to 70 μm , an average diameter of 10.9 μm , and a median equal to 11.5 μm .

Thermal properties

Based on the pasting curves determined for two heating/cooling rates of 5 and 10 $^\circ\text{C}/\text{min}$ (Fig. 2), it was concluded that investigated material was so-called type II starch (Le Thanh-Blicharz et al. 2011) with a high pasting temperature of 75 $^\circ\text{C}$. Starches of this kind indicate an increase in viscosity during heating, no change in viscosity during thermostating, and then again an increase in viscosity during cooling. Increased pasting temperature of commercial Japanese white kuzu starch was associated with a higher content of lipids and proteins which formed

complexes with amylose and hindered its passage to the solution.

Rheological properties

The analysis of dynamic moduli G' and G'' (Fig. 3) has shown that across the entire oscillation frequency range ω the investigated biopolymer was located in viscoelastic plateau region. This area is a highly flexible physical state, where even a small stress can cause a significant deformation. The dynamic curves were approaching each other for the highest oscillation frequencies ω . However, they did not intersect themselves. The point above which viscous properties would dominate over the elastic properties, and which represents the upper limit of the viscoelastic plateau region, was not achieved. The addition of galactomannans increased the disruption of starch granules. Interactions could occur between the hydrocolloids and the low-molecular-weight amylose and amylopectin, separated from damaged granules (Imeson 1997). Generally, the increase in galactose-to-mannose ratio in galactomannan molecule caused that the curves of storage modulus G' and loss modulus G'' were lying closer to each other which meant the flattening of viscoelastic plateau region. The curves determined by the modified fractional Kelvin–Voigt model with two springpot-type elements were characterized by a very precise description of experimental data. Determination coefficient in each case was close to unity $R^2 = 0.99$, mean percentage error was equal to 2.6%, and maximum fitting error—observed only for a few measurement points—did not exceed 11%.

In the literature concerning a synergism of various starch–galactomannan mixtures (Bahnassey and Breene 1994; Shi and BeMiller 2002; Kim and Yoo 2011), these substances were considered as composite materials consisting of swollen granules (mainly amylopectin) dispersed in a continuous biopolymer matrix (mostly amylose). During pasting process, the galactomannan had to remain in the continuous phase—its diffusion inside granules was impossible for hydrodynamic reasons. Hence, as soon as kuzu starch granules swell above the pasting temperature ($> 75^\circ\text{C}$), the volume available to hydrocolloid molecules decreased which led to a drastic elevation in concentration of the galactomannan in continuous phase and subsequent high viscosity of the paste (Sikora and Krystyan 2008).

Generally, two mechanisms could take place during rheological oscillatory tests of starch–galactomannan pastes: phase separation (incompatibility phenomena between unlike polysaccharides) and interactions between like and unlike polysaccharides. Smaller change in storage modulus G' compared with loss modulus G'' in kuzu starch–galactomannan pastes (Fig. 3) indicated a

Fig. 1 Particle size distribution of commercial Japanese white kuzu starch (Terrasana, Netherlands)

Fig. 2 Pasting curves of commercial Japanese white kuzu starch (Terrasana, Netherlands)

thermodynamically incompatible network structure where interactions between biopolymers of the same type are favored energetically compared with interactions between different biopolymers (Eidam et al. 1995; Kim and Yoo 2011; BeMiller 2011).

The analysis of shear creep compliance $J(t)$ (Fig. 4) allowed to compare flowing abilities of the material. Compliance $J(t)$ is defined as the ratio of deformation γ at time t to specified constant shear stress σ . In general, shear creep compliance $J(t)$ was increasing with the decline in

substitution degree—curves were becoming increasingly similar to pure kuzu starch paste. The same tendency was observed for oscillatory tests (Fig. 3).

Figure 5 shows a summary list of the rheological parameters of kuzu starch pastes determined by the modified fractional Kelvin–Voigt model with two springpots, depending on the type of galactomannan. With an increasing substitution degree, it was observed a significant increase in the strength of biopolymer cross-linking G_N^0 combined with a slight increase in total network elasticity

Fig. 3 Experimental and model values of storage modulus G' and loss modulus G'' in a function of oscillation frequency ω , depending on the type of galactomannan

Fig. 4 Experimental values of shear creep compliance $J(t)$ in a function of creep time t , depending on the type of galactomannan

G_e . It resulted from the galactomannan–starch interactions giving a thickening effect—the effective increase of amylose concentration in the continuous phase (Sikora and Krystyjan 2008). The difference between modules G_N^0 and G_e was the strength of stress relaxation ΔG —its linear

growth was visible. The inverses of plateau modulus and equilibrium modulus were so-called plateau compliance J_N^0 and steady-state compliance J_e , respectively. Plateau compliance represented the strength of suppression of long-range configurational rearrangements caused by

Fig. 5 Rheological parameters of kuzu starch pastes determined by the modified fractional Kelvin–Voigt model with two springpots, depending on the type of galactomannan

entanglements of biopolymer network, while steady-state compliance indicated the energy stored during steady-state flow of the biopolymer under low stress (Ferry 1980).

Along with the increase in substitution degree, both characteristic relaxation times τ_0 and τ_m were also extended. Taking into consideration fractional exponents α and β , it was noticed that the value of parameter α dropped below 0.5, which indicated a reduction in friction between adjacent biopolymer chains probably due to the enhanced water retention. Dumitriu (2004) and Mathur (2011) reported that intra- and interchain hydrogen bonding between linear galactomannan molecules could result in time-durable junction zones. It required a minimum of continuously unsubstituted 6 or more mannose groups on backbone. More frequent occurrence of galactose groups on mannose backbone (higher substitution degree) reduced strong chain–chain hydrogen bonding interactions and improved water retention. Such immobilization of water molecules, combined with a local increase in galactomannan concentration caused by swelling of starch granules during pasting, resulted in increased Newtonian steady-state shear viscosity η_0 and stretched region of viscoelastic plateau L (Pilarska and Gawalek 2016).

Reduction in cross-linking density ω_0 and average molecular weights M_e and M_c as well as the increase in dispersion modulus f , also resulted from a growing number of galactose groups, which effectively limited the formation of intra- and interchain hydrogen bonds (Lee and Chang 2015). It was noticed that the longer hydrocolloid chain, the greater changes in those parameters. In addition, the increase in substitution degree reduced flexibility,

overall extensibility, and gyration radius of galactomannan chains (Petkowicz et al. 1998; Mathur 2011). This resulted in the higher gel stiffness S and coefficient of network vibration damping k .

Conclusion

The study led to the conclusion that commercial Japanese white kuzu starch was so-called type II starch with a high pasting temperature of 75 °C. The investigated material was a highly polydisperse polysaccharide with an average granule diameter equal to 10.9 μm .

The modified fractional Kelvin–Voigt model with two springpots described experimental data in the form of storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ in the range of over 6 logarithmic decades, with mean percentage error equal to 2.6%. This approach allowed to determine 17 rheological parameters providing a lot of additional information about structure and viscoelastic properties of kuzu starch pastes with galactomannans in comparison to the classical analysis of oscillatory and creep tests.

Rheological properties of the biopolymer depended on the galactose-to-mannose ratio. The larger substitution degree, the higher viscosity, characteristic relaxation times, polydispersity index, gel stiffness, and the lower cross-linking density and average molecular weights. The presence of galactose side groups prevented the formation of hydrogen bonds and favored the hydration and immobilization of water molecules.

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