Carbohydrate Polymers 98 (2013) 542–545

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Short communication

Effects of sucrose and urea on soy hull pectic polysaccharide gel induced by D-glucono-1,5-lactone

He Liu*, Qinghua Li, Danshi Zhu, Jun Li, Junshan Liu, Ping Geng, Yutang He

School of Chemistry & Chemical Engineering and Food Safety, Food Science Research Institute, Bohai University, 19 Keji Road, Jinzhou 121013, China

ARTICLE INFO

Article history:
Received 3 May 2013
Received in revised form 20 June 2013
Accepted 22 June 2013
Available online 29 June 2013

Keywords:
Soy hull pectic polysaccharide
D-Glucono-1,5-lactone
Sucrose
Urea
Water molecule state
Low field NMR
Rheology

ABSTRACT

Gelation properties of pectic polysaccharide extracted with ammonium oxalate from soybean hulls assisted by microwave were seldom studied. Water mobility in soy hull pectic polysaccharide (SHPP) was firstly studied by low field NMR. D-Glucono-1,5-lactone (GDL) and sucrose both could decrease spin–spin relaxation times (T_2) of SHPP solutions which indicated the SHPP network formed. Rheological analysis conformed that SHPP gel was formed induced by GDL and enhanced by sucrose. Urea can increase T_2 and collapse the network of SHPP. TGA was used to draw the profiles of water desorption from SHPP solutions or gels, during heating at a controlled rate. It was found that sucrose increased the bound water content and urea acted a conversely role. Hydrogen bond is the main force to maintain SHPP gel network.

1. Introduction

Soy hulls are major by-products in the soybean processing industry, and the insoluble carbohydrate fraction contains 30% pectin, 50% hemicelluloses, and 20% cellulose. So the soy hulls were potentially inexpensive commercial sources of pectin (Monsoor & Proctor, 2001). The structure of the cell wall polysaccharides from soybean was first investigated in 1960s (Huisman, Schols, & Voragen, 1999). In the recent publications, we had studied the gelation properties of soy hull pectic polysaccharide (SHPP) (Liu, Guo, et al., 2010; Liu, Liu, Guo, & Zhu, 2010; Liu, Guo, Hu, Liu, & Zhu, 2011; Liu, Guo, Li, Zhu, & Li, 2013).

The pectin molecules as hydrocolloids affect the water behavior. Near their surface pectin can bind, immobilize, and interact with water molecules. Thus, the analysis of the NMR water proton longitudinal (spin–lattice) T_1 and the transverse (spin–spin) T_2 relaxation processes can indirectly provide valuable information about the dynamics and pectin structure in the water medium. NMR proton spin–spin relaxation time measurements had been found useful for monitoring the mobility and state of aggregation of biomolecules (proteins and polysaccharides) in solution and gelled systems (Dobies, Kuśmia, & Jurga, 2006).

Therefore, in this paper we used 1H NMR method to study gelation of SHPP solution induced by GDL in the present of sucrose and urea. In addition, the rheological methods were used in order to check the difference of the gel network formed as different dispersions.

2. Materials and methods

2.1. Materials

Soy hulls were purchased from local market, and were grounded to a particle size of 60 meshes with grinder. All chemical reagents used were analytical grade. Deionized water was used throughout.

2.2. Extraction and purification of SHPP

SHPP was extracted with ammonium oxalate from soybean hulls assisted by microwave. Soy hulls (30 g) were dissolved in 750 ml deionized water with 0.6 wt% ammonium oxalate at 85 °C, solutions were irradiated at 450W of microwave oven (Midea Corp., PJ23C-SC1, China) maintaining at 95 °C for 10 min. The hot samples were then filtered through four layer filter cloth; then the solution pH was adjusted to 4.5; then the solution was centrifuged at 4500 × *g* (Backman, Avanti J-25, USA) for 10 min in order to precipitate soybean protein, then the liquid supernatant was concentrated by vacuum evaporating with rotatory evaporator (Shanghai Yarong, RE-3000A, China). The SHPP solution was precipitated by absolute ethanol; afterwards the precipitate was washed by 70% ethanol. The sediment was separated and dried with air dry oven at 65 °C and the SHPP was obtained in the end.

* Corresponding author. Tel.: +86 416 3400326.
E-mail address: liuhe2069@163.com (H. Liu).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.06.048

2.3. SHPP dispersions preparation

SHPP was slowly added to deionized water, and vigorously mixed for 30 min at 70 °C, sodium azide was added to inhibit bacterial degradation (the concentration of sodium azide was 0.2 mg/ml). SHPP solutions were centrifuged at 10,000 g (Sigma, 3-18K, Germany) for 10 min to obtain clear supernatant solution. To prepare the SHPP-GDL (sucrose or urea) systems, the required GDL, sucrose, and urea were added to stock solutions as dry powder. Concentration of SHPP was fixed at 4 wt% in all samples, the specific experiment formulations were shown in the Table 1.

2.4. Rheological analysis

Controlled stress rheometer (TA instrument, AR-1500, USA) was used for the rheological analysis. The SHPP dispersions with different reagents were loaded on the plate (parallel-plate geometry, 40 mm diameter, 0.5 mm gap) of rheometer at 25 °C and stay equilibrium for 10 min. In the linear viscoelastic region, stress was controlled at 0.1 Pa and angular frequency was set as 0.628 rad/s, the small deformation oscillatory of time sweep determination was carried out at 25 °C for 2.5 h. The complex modulus (G^*) that represents the resistance of SHPP gel network to deformation or the total energy needed to induce changes in the samples was calculated as $G^* = (G'^2 + G''^2)^{1/2}$ (Mahammad, Comfort, Kelly, & Khan, 2007). The sample periphery was covered with light silicone oil during the rheological analysis to minimize water evaporation.

2.5. NMR measurements

NMR relaxation measurements were performed on a Niumag Benchtop Pulsed NMR Analyzer PQ001 (Niumag2.5 Electric Corporation, Shanghai, China) at a resonance frequency for protons of 22.6 MHz. Approximately 2 g of sample was placed in a 15 mm glass tube and inserted in the NMR probe. Spin–spin relaxation time, T_2, was measured using the Carr–Purcell–Meiboom–Gill sequence.

2.6. Thermogravimetry (TG) analysis

A classical assay of TG (TGA/DSC1, Mettler Toledo, Switzerland) method was used to measure the water states in three-dimensional network of gels. Approximately of 20 mg sample was placed in porcelain crucible, dynamic temperature sweep from 25 to 300 °C at 5 °C/min was adopted to tracking the weight loss process of SHPP dispersions.

3. Results and discussion

3.1. NMR proton relaxation

Nuclear magnetic resonance (NMR) had been used to characterize the state, mobility and distribution of water in polymer systems. Typically, the signal decay could be fitted into a distributed exponential consisting of one or two separate peaks. Fig. 1 shows distributed T_2 relaxation times in different samples. If there is not interaction between water and solute, the enhancement in relaxation time was proportional to the water concentration. The reverse is also true; increasing the water concentration in a solution decreases the relaxation rate and increases the relaxation time (Oztop, Rosenberg, Rosenberg, McCarthy, & McCarthy, 2010). But the T_2 of 4 wt% SHPP solution is much lower than that of solution with 30 wt% sucrose and 2 mol/L urea. This indicates that the interaction of SHPP and water molecule hinders the mobility of water molecule and decrease the relaxation time. When GDL was added, T_2 decreased significantly from 533.76 to 132.19 ms. Sucrose addition to the SHPP + GDL system decrease T_2 to 114.97 ms which

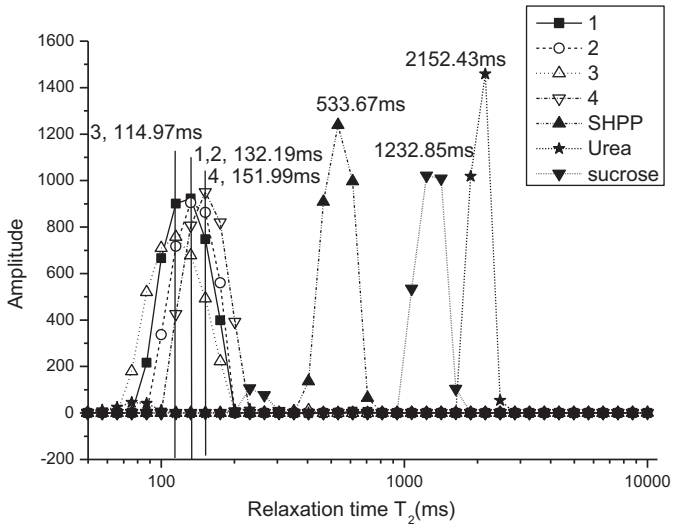

Fig. 1. Spin–spin relaxation times (T_2) of 4 wt% SHPP dispersions with 3 wt% GDL (■), 30 wt% sucrose (○), 3 wt% GDL + 30 wt% sucrose (△), 3 wt% GDL + 2 mol/L urea (▽) and 4 wt% SHPP (△), 30 wt% sucrose (▽), 2 mol/L urea alone (★).

reveals that the water mobility is further restricted. But SHPP with 3 wt% GDL or 30 wt% sucrose show no difference for the relaxation time though the water content of former is higher than the latter. It can be deduced that GDL induced SHPP molecular interaction and water is embedded in the SHPP network. When urea, which is a kind of hydrogen broken reagent was added in the SHPP + GDL system, the water mobility increased as its relaxation time increase from 132.19 to 151.99 ms. So it is illustrated that hydrogen bond plays an important role for the interaction of SHPP molecule and between SHPP and water molecule.

3.2. Rheological properties

Complex modulus G^* describes the total resistance to deformation of a material that it is considered as an elastic solid and it is expressed in Pa (Dimitreli & Thomareis, 2008). Fig. 2 showed G^* of different SHPP solutions, respectively, as a function of time. All G^*

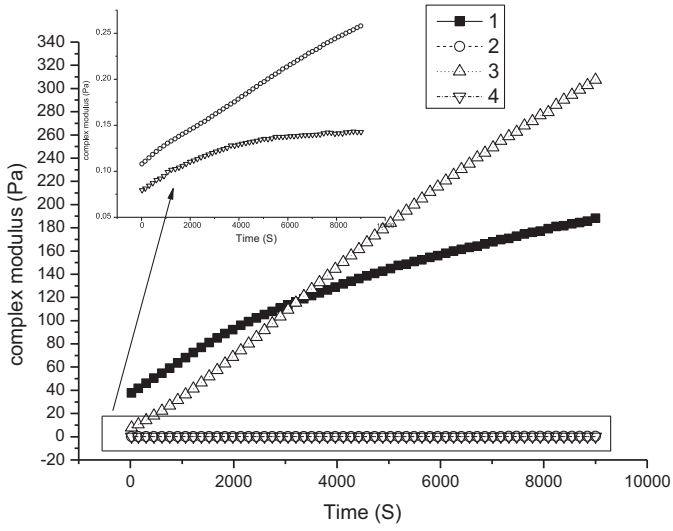

Fig. 2. Complex modulus (G^*) showing the time-dependence (recorded after the hot solution was loaded on plate of rheometer) of 4 wt% SHPP dispersions with 3 wt% GDL (■), 30 wt% sucrose (○), 3 wt% GDL + 30 wt% sucrose (△), 3 wt% GDL + 2 mol/L urea (▽).

Table 1
Compositions of SHPP dispersion systems.

No	SHPP (wt%)	GDL (wt%)	Sucrose (wt%)	Urea (mol/L)	Water content (%)
1	4	3	–	–	93.46
2	4	–	30	–	74.63
3	4	3	30	–	72.99
4	4	3	–	2	91.74

values increased gradually after systems were put on the plate of rheometer. G^* of 4 wt% SHPP + 3 wt% GDL + 30 wt% sucrose system increased more apparent than that of others. Sucrose addition to 4 wt% SHPP + 3 wt% GDL solutions strengthen the elasticity of SHPP gel. Sucrose solely cannot induce the gelation of 4 wt% SHPP. 2 mol/L urea can collapse the SHPP network formed by hydrogen bond and decrease the complex modulus significantly (Fig. 2, line 4). And when the network of SHPP was collapsed, the water obtained freedom and the mobility increased just coincides with NMR analysis above.

3.3. Thermogravimetric analysis

The TGA curves for different SHPP solutions were shown in Fig. 3. By analysis of the first derivatives of the thermogravimetric curves (Fig. 3, line part), some representative stages of mass loss were

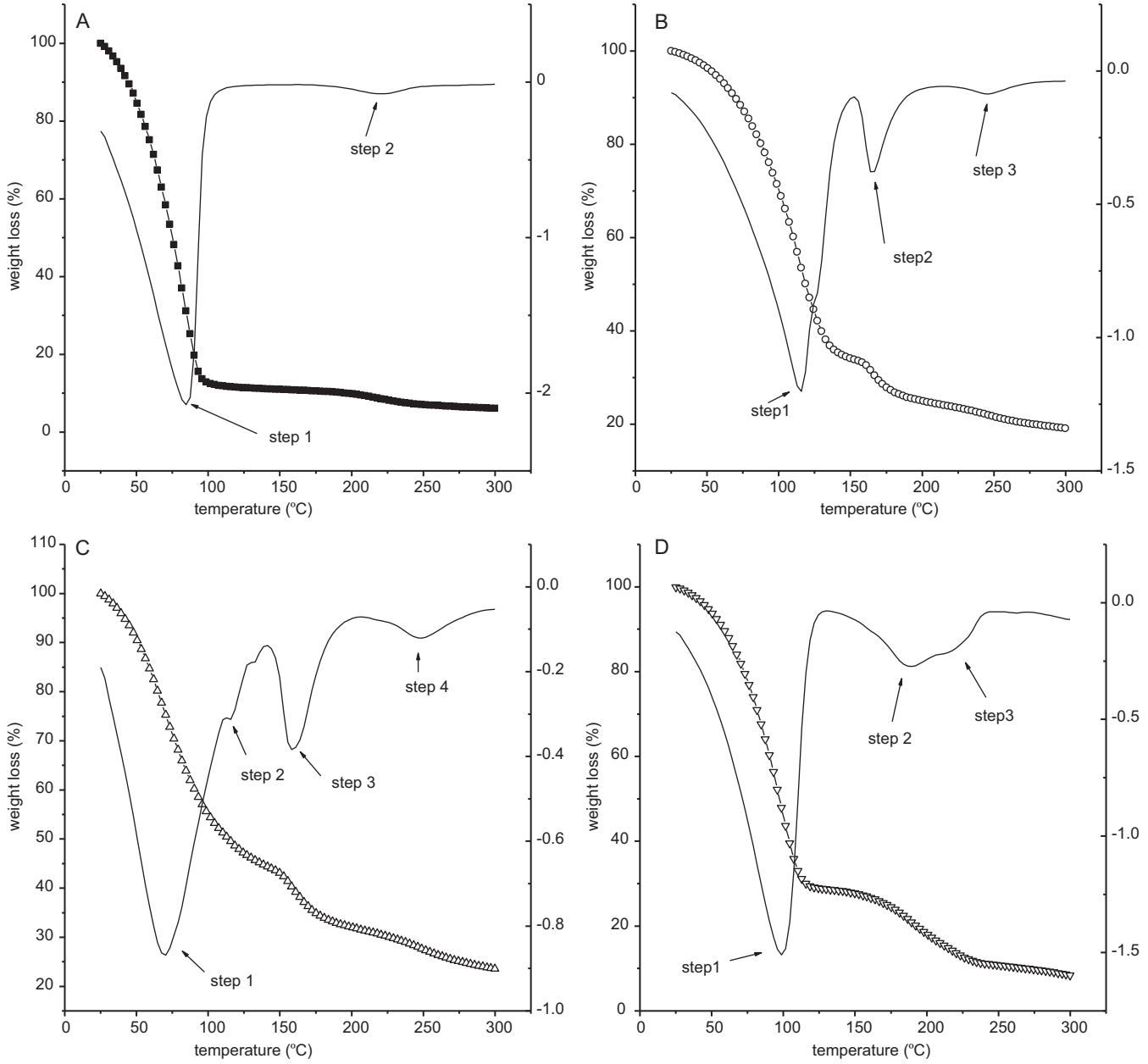

Fig. 3. TG (scatter) and derivative thermogravimetric analysis (DTG, line) curves of 4 wt% SHPP dispersions with 3 wt% GDL (■), 30 wt% sucrose (○), 3 wt% GDL + 30 wt% sucrose (△), 3 wt% GDL + 2 mol/L urea (▽).

Table 2
Thermogravimetric data obtained during heating at 10 °C/min under nitrogen atmosphere (15 mL/min) from 25 to 300 °C.

Sample	Step	Temperature domain (°C)	Weight loss at step end (%)	Residues at 300 °C (%)
1	1	25–100	88	6
	2	200–250	6	
2	1	25–150	66	19
	2	150–190	8	
	3	240–260	7	
3	1	25–100	46	23.5
	2	100–125	7	
	3	175–200	15	
	4	200–300	8.5	
4	1	25–125	71	8.5
	2	125–225	11	
	3	225–300	9.5	

differentiated. Weight loss process depends on the water contents and additive kind. The SHPP + GDL system showed weight loss in two stages, the first one (88%) (Table 2) occurred in the range of 25–100 °C probably due to the loss of free water, that is, water integrated within the SHPP matrix but with a low binding energy just as in cheese matrix (Oliveira et al., 2011). The subsequent weight losses were 6%, and occurred in temperature ranges of 180–300 °C might be degradation of GDL. In the case of SHPP + sucrose system, the weight loss contain three stages, the first one (66%) occurred in the range 25–150 °C probably due to the loss of free and bound water related to the more strongly associated water with SHPP or sucrose. The subsequent weight losses were 8%, and 7% occurred in temperature ranges of 150–190 °C and 240–260 °C might be degradation of sucrose. When GDL was added into the SHPP + sucrose system, TG profile was more complicated, showing mass losses in four stages. However, at the first stage temperature investigated (25–100 °C), only 46% mass loss was observed. This indicates GDL made more bound water formed in SHPP + sucrose system by induce gelling of SHPP. The last three mass loss stages contain the bound water releasing or sucrose decomposition. When urea was added, the free water content increased significantly (71% in the first mass loss stage); it would mean that SHPP did not form any matrix capable of inclusion of water, which indicated that urea induced the collapse of SHPP gel network. It agrees with findings from the NMR and rheological analysis.

4. Conclusions

The ^{1}H NMR dispersion of spin–spin relaxation time (T_2) measurements was applied to study SHPP solutions or gels. Results suggested that the average mobility of water was largely dependent on the agent added to the aqueous SHPP solution. Water proton NMR findings for the GDL added were indicative of a decreasing mobility of SHPP molecules mainly due to the cross-linking process because GDL and sucrose. Urea break hydrogen bond and restrained their associations, thereby the gel network could not be formed. This result was conformed by rheological analysis. It was found that sucrose increased the bound water content and urea acted conversely role through TGA. In conclusion, hydrogen bond is the main force to maintain SHPP gel network.

Acknowledgements

The authors acknowledge the support of the National Natural Science Foundation of China (NSFC, No. 31201385) and the Program for Liaoning Excellent Talents in University (No. LJQ2011123). We thank Dr. Chao Zhang (Beijing Academy of Agriculture and Forestry Sciences) for the help of rheological analysis.

References

Dimitreli, G., & Thomareis, A. S. (2008). Effect of chemical composition on the linear viscoelastic properties of spreadable-type processed cheese. *Journal of Food Engineering*, *84*(3), 368–374.
Dobies, M., Kuśmia, S., & Jurga, S. (2006). 1H NMR and rheological studies of the calcium induced gelation process in aqueous low methoxyl pectin solutions. *Acta Physica Polonica A*, *108*(7), 33–46.
Huisman, M. M. H., Schols, H. A., & Voragen, A. G. J. (1999). Enzymatic degradation of cell wall polysaccharides from soybean meal. *Carbohydrate Polymers*, *38*(4), 299–307.
Liu, H., Guo, X., Gao, H., Liu, J., Liu, H., & Zhu, D. (2010). Optimizing the parameters of microwave assisted extraction of pectin from soy hull through uniform design. *Food and Fermentation Technology (China)*, *46*(5), 37–40.
Liu, H., Guo, X., Hu, Y., Liu, H., & Zhu, D. (2011). The preliminary study on the embedding *Lactobacillus bulgaricus* by utilizing soy hull pectin gel. *Journal of Dairy Science and Technology (China)*, *34*(1), 50–53.
Liu, H., Guo, X., Li, J., Zhu, D., & Li, J. (2013). The effects of $MgSO_4$, D-glucono-δ-lactone (GDL), sucrose, and urea on gelation properties of pectic polysaccharide from soy hull. *Food Hydrocolloids*, *31*(2), 137–145.
Liu, H., Liu, H.-d., Guo, X.-f., & Zhu, D.-s. (2010). Water-holding capacity and mechanical and optical characteristics of soy hull low and high methoxyl pectin complex gel. *Food Science (China)*, *31*(19), 111–114.
Mahammad, S., Comfort, D. A., Kelly, R. M., & Khan, S. A. (2007). Rheological properties of guar galactomannan solutions during hydrolysis with galactomannanase and α-galactosidase enzyme mixtures. *Biomacromolecules*, *8*(3), 949–956.
Monsoor, M., & Proctor, A. (2001). Preparation and functional properties of soy hull pectin. *Journal of the American Oil Chemists' Society*, *78*(7), 709–713.
Oliveira, N., Dourado, F., Peres, A., Silva, M., Maia, J., & Teixeira, J. (2011). Effect of guar gum on the physicochemical, thermal. rheological and textural properties of green edam cheese. *Food and Bioprocess Technology*, *4*(8), 1414–1421.
Oztop, M. H., Rosenberg, M., Rosenberg, Y., McCarthy, K. L., & McCarthy, M. J. (2010). Magnetic resonance imaging (MRI) and relaxation spectrum analysis as methods to investigate swelling in whey protein gels. *Journal of Food Science*, *75*(8), E508–E515.