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Short Communication

Chemical modification of xanthan gum to increase dissolution rate

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Abstract

Xanthan gum is modified with formaldehyde to improve the dissolution rate. The FT-IR spectra and the X-ray diffraction spectra both show that chemical modification reduces intermolecular interactions and crystallinity. Viscosity measurements show that the chemically modified gum dissolves more rapidly than before.

Keywords: Xanthan gum; Chemical modification; Intermolecular interaction; Dissolution rate

1. Introduction

Xanthan gum (XG) is a high molecular weight natural exopolysaccharide produced by the bacterium *Xanthomonas campestris*. Because of its wide applications in the oil, food, textile, cosmetic and pharmaceutical industries, the output of XG is now the largest of the natural exopolysaccharides. A limit to its use is its slow dissolution rate although some physical means have been used to improve dispersibility. (Sandford, Baird, & Cottrell, 1981). Like that of other polymers, the dissolution process of XG includes two steps (Van Krevelen, 1976): firstly solvent penetrates the solute, causing the solute to swell, secondly the solute dissolve into the solvent phase. Hydrocolloids such as, xanthan gum can form 'fish-eyes' (Sandford et al., 1981) during dissolution. That is to say, when gum particles begin to hydrate, a gelatinous layer of partially hydrated gum forms on the outside of the particle. In the gelatinous layer, the molecule of gum cannot leave the particle surface rapidly and this prevents water from penetrating to complete hydration and from dissolving the particle. The objective of the work is to modify xanthan to reduce intermolecular interactions so that the gelatinous later cannot form, or even if it forms, the molecules in the layer can leave the surface of the particle rapidly to increase the rate of dissolution compared with the unmodified gum.

2. Experimental

2.1. Materials

XG was produced in an automatic fermenter (Model NLF22, 10L, Switzerland) by the bacterium *Xanthomonas campestris* obtained from Shandong Food and Fermentation Engineering Research Major Laboratory, and the fermentation liquor was precipitated in ethanol. The crude XG was hydrated in a water–ethanol mixture, centrifuged, precipitated and washed. The wet gum was then dried and ground into particles with surface areas ranging from 7×10^{-8} to 1×10^{-7} m^2. Formaldehyde was obtained from the Shanghai Chemical Reagent Plant.

2.2. Methods

FT-IR spectra. FT-IR spectra were recorded on a Nicolet 5DX spectrometer (USA). The dry sample power was mixed with KBr and pressed into pellets under reduced pressure. The FT-IR spectra were obtained by scanning between 4000 and 450 cm^{-1}.

X-ray diffraction spectra. X-ray diffraction spectra were recorded on a D/max-ra spectrometer (Japan). The dry sample powder was pressed into pellets. The X-ray

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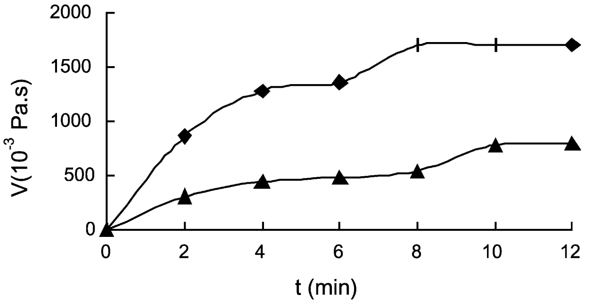

Fig. 1. Changes of viscosity with time when 2.0 g sample XGM (a) and XG (b) dissolves in 200 ml distilled water.

Table 1
Viscosity (10^{-3} Pa · s) and concentration of XGM at different dissolution instant

t_{int} (min)	2	4	6	8	10	12
V (10^{-3} Pa s)	860	1280	1360	1700	1700	1700
C% (w/v)	0.71	0.88	0.91	1.02	1.02	1.02

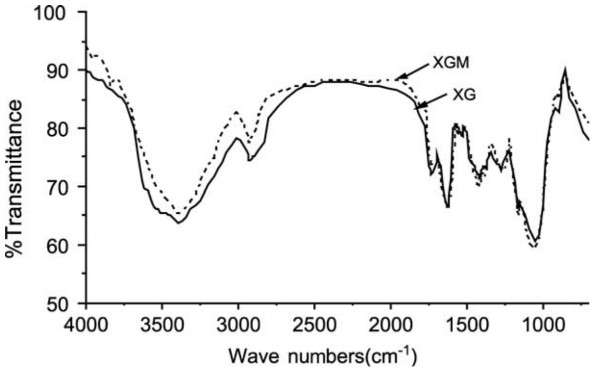

Fig. 2. FT-IR spectra of XG and XGM.

diffraction spectra were recorded using Cu Kα radiation, (40 Kv, 60 mA).

2.3. Modification of XG

At pH values between 1.6 and 2.0, formaldehyde (10 ml) was added to 1000 ml fermentation liquor (containing XG about 3%) in a 2000 ml round flask. The solution was mechanically stirred at 40 °C for 6 h, after which the solution was precipitated in ethanol. The crude modified gum was purified as for XG, and was then dried and ground into particles with surface areas ranging from 7×10^{-8} to 1×10^{-7} m^2 to give the purified modified gum (XGM).

2.4. Viscosity measurements

Equilibrium viscosity (V_{eq}) of 1.0% (W/V) XG or XGM solution was measured with rotational viscometer (Model NDJ-1, Shanghai) fitted with No. 3 spindle at shear rate 1 s^{-1} after XG or XGM had dissolved in water for 24 h.

Viscosity measurements were made with an NDJ-1 rotation-viscometer fitted with a No. 3 spindle at a shear rate of 1 s^{-1}.

2.5. XG and XGM dissolution

XG or XGM (2.0 g) sample was added to 200 ml distilled water in a 400 ml beaker and stirred at a shear rate of 3.3 s^{-1}.

3. Results and discussion

3.1. Comparison of the viscosity of XGM and XG during dissolution

The viscosities of XGM and XG were measured at different dissolution times for 2.0 g solid dissolved in 200 ml distilled water. It was found that the XGM dispersed very rapidly to give lump free solution. The viscosity of XGM solutions was higher than that of XG at any time as shown in Fig. 1. The rate of viscosity increase of XGM was very fast from 0 to 4 min, and the viscosity reaches the equilibrium viscosity (V_{eq}) when the interval between the beginning of dissolution and measurement (t_{int}) was 8 min. In contrast, the rate of viscosity increase of XG was slow, and the viscosity was about 40% of V_{eq} when $t_{\text{int}} = 10$ min. It therefore appears that chemical modification can improve the dissolution properties of XG.

3.2. Measurement of the rate of dissolution of XGM

The rate at which a solid dissolves is governed by many factors, but under given conditions, the rate of dissolution can be measured. Because there is no way of separating the particle phase from the solution, it is difficult to measure the quantity of XG or XGM that dissolves. The viscosity is an important physical parameter, which is governed primarily

Table 2
FT-IR spectral data (cm^{-1}) of XGM and XG

Assignment	–OH	–CH$_2$	–C=O	–C=O of pyruvate	–COO$^-$		–C–H	–C–O–C–	–C–O–C–O–C– acetal		C$_1$–H of β-pyranose
XG	3386.0	2923.3	1733.3	1627.0	1529.1	1416.3	1377.9	1255.9	1160.1	1056.4	897.8
XGM	3397.7	2923.3	1728.3	1625.0	1541.9	1416.5	1378.9	1276.0	1160.5	1056.9	895.8

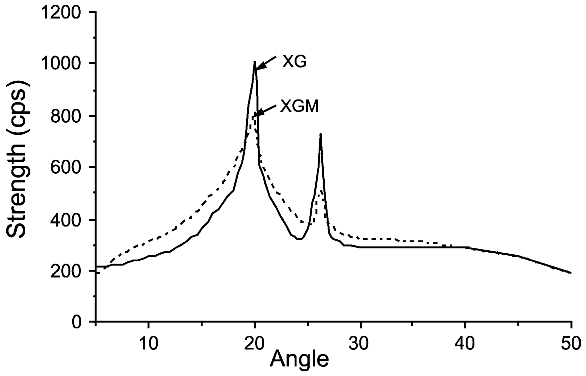

Fig. 3. X-ray diffraction spectra of XG and XGM.

by the number of molecule of XG in solution and can be measured easily.

The equilibrium viscosity of XGM solutions as a function of concentration was measured, in the concentration range 0.2–1.0%. It is found that there is a linear relation between log V and log C. The linear equation is

$$\lg V = 1.89 \lg C + 3.21 \qquad (1)$$

with a correlation coefficient of $R = 0.9994$. The viscosity of XGM solution is measured at different dissolution times when 2.0 g solid dissolve in 200 ml distilled water, and the corresponding concentration is calculated according to Eq. (1), and shown in Table 1. Table 1 shows that the rate of dissolution is very fast between 0 and 2 min, about 0.36 g/100 ml · min. The rate decreases as the concentration increases, and the XGM dissolves completely when $t_{\text{int}} = 8$ min. The dissolution time is shortened greatly, compared with XG considering that it took 30 min to dissolve 0.5 g of XG in 100 ml distilled water completely (Fenglai, 1987).

3.3. FT-IR spectra of XGM and XG

The FT-IR spectra of XGM and XG recorded under the same conditions are showed in Fig. 2. The spectra are summarized in Table 2. It is found that the vibration peak of –OH at 3397.7 cm^{-1} appears in the spectra of XGM. Compared with that of XG (3386.0 cm^{-1}), the peak of XGM shifts to high wave number with 10 cm^{-1}, suggesting that the intermolecular interaction between XG molecules is stronger than that between XGM molecules (Yongcheng, 1989). The vibration peaks of the acetal at 1160.5 and 1056.9 cm^{-1} of XGM are stronger than those of XG at 1160.1 and 1056.4 cm^{-1}, inferring that the chemical modifier reacts with the –OH of the XG to form the acetal. These results indicate that when XGM dissolves in water, the attraction of the molecular cluster of the solid phase to the XGM surface molecules at the surface of the swollen layer is much weaker, causing the XGM surface molecules which swell completely to diffuse into the water phase more easily.

3.4. X-ray diffraction spectra of XGM and XG

Fig. 3 shows the X-ray diffraction spectra of XGM and XG. It is obvious that the diffraction peaks of XG are sharper than those of XGM, and the ratio of peak area to curve area of XG is bigger than that of XGM, suggesting that XG has a higher crystallinity (Ewing, 1975). Because in the crystalline state the interaction between molecules is stronger than the amorphous state, the solvent molecules penetrate into XG with more difficultly than into XGM during the process of dissolution.

The result is consistent with that obtained from FT-IR spectra. The FT-IR spectra indicate that the chemical modifier reacts with –OH of pyranose ring, which interferes with the regularity of the polymer chain making it difficult for XGM to crystallize.

4. Conclusion

Chemical modification can increase the dissolution rate of XG. The FT-IR and X-ray diffraction spectra, show that the XG molecular structure changes, causing intermolecular interactions and structure of XG to change. The changes hasten the process of swelling and dissolution.

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