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The physicochemical property characterization of agar acetate

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ABSTRACT

A series of agar acetates with different degree of substitution (DS) were prepared, and their properties were determined and analyzed. The results showed that the gelling temperature, the gel melting temperature, the gel strength, the gel hardness, the gel fracturability, the gel springiness and the solution apparent viscosity of agar acetates all decreased except that their gel cohesiveness increased with the increase of DS. The variation process of agar molecules in solution from coil to helix could be also observed by measuring solution optical rotation in a lower concentration at which even the solution could not form a gel. The gel skeleton structures of agar acetates were of porous network structures, and the pores became smaller and denser with the increase of DS. After acetylation, the water holding capacity of the agar was improved, but its thermal stability was lowered.

1. Introduction

Agar, the gel-forming polysaccharides extracted from Gelidiaceae and Gracilariaceae species (Freile-Pelegrín & Robledo, 1997), is linear polymers based on a disaccharide repeat structure of 1,3-linked β-D-galactopyranose and 1,4-linked 3,6 anhydro-α-L-galactopyranose units (Arnott et al., 1974; Labropoulos, Niesz, Danforth, & Kevrekidis, 2002). Agarose and agaropectin are the two components of agar, the former consisting of neutral polysaccharides with a high gelling ability and the latter consisting of ionic polysaccharides with a low gelling ability (Arnott et al., 1974; Yaphe, 1984). Agar is widely used for medical, pharmaceutical, food and electronic industrial and laboratory experimental purposes due to its combination of renewability, biological activities, biocompatibility, biodegradability and nontoxicity (Cayre, Chang, & Velev, 2007; García-González, Alnaief, & Smirnova, 2011; Scholten & Pierik, 1998; Wijesekara, Pangestuti, & Kim, 2011; Wu, Geng, Chang, Yu, & Ma, 2009).

In recent years, the esterification of different polysaccharides has gained great interest. As described by Sweedman, Tizzotti, Schäfer, and Gilbert (2012), starches modified with octenyl succinic anhydride had been used in a range of industrial applications, particularly as a food additive. Superabsorbent hydrogels were prepared from native celluloses by esterification crosslinking with 1,2,3,4-butanetetracarboxylic dianhydride (Kono & Fujita, 2012). Poplar wood fibers were chemically modified by esterification (acetate, propionate, benzoate), and the properties were shown to be more thermally stable and hydrophobic than unmodified fibers (Wei, McDonald, Freitag, & Morrell, 2013). However, the literature and reports on agar esterification were very few. Acetylation of agar was firstly patented by Kenneth and Guiseley (1976), but no more properties of the agar acetates were described except the gelling temperature. In this research, a series of agar acetates with different DS were prepared, and their properties were determined and analyzed.

2. Experiment

2.1. Materials

Gracilaria agar (3,6-anhydro-L-galactose content: 35.5%; sulfate content: 3.2%; gel strength: 1930 g/cm^2) was purchased from Qingdao Agar Manufacturing Company, Shandong Province, China. All reagent used in this research were purchased from Laiyang Chemical Reagent Plant, Shandong province, China.

2.2. The preparation of agar acetates with different DS

Agar acetates were prepared by the method of Kenneth and Guiseley (1976) described in US3956273. Degree of substitution (DS) was determined by titration according to the method of Tupa, Maldonado, Vázquez, and Foresti (2013).

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2.3. FT-IR spectroscopy

The FT-IR spectra were obtained from samples in KBr pellets using a Nicolet 200 FT-IR spectrophotometer (Nicolet, Madison, WI, USA).

2.4. Physicochemical properties

The gelling temperature and the gel melting temperature were measured as described by Freile-Pelegrín and Robledo (1997). The gel strength was measured using a Nikkansui-type gel tester (Kiya Seisakusho Ltd., Tokyo, Japan). The measurements above were performed on a 1.5 wt% sample solution. Sulfate content was determined based on the method described by Matos, Fortunato, Velizarov, Reis, and Crespo (2008), using a Dionex ion exchange chromatography system (Dionex Corporation, USA). The 3,6-anhydro-L-galactose content (3,6-AG) was determined by the colorimetric method of Yaphe and Arsenault (1965) using the resorcinol-acetal reagent and with fructose as standard.

2.5. Test of apparent viscosity

Apparent viscosity was measured by using a Brookfield Synchrolectric Viscometer (USA). This viscometer could permit deformation to be measured at a constant stress and allowed gel samples to be tested at stress below the rupture point. The gel formation point, Tg, was taken as the temperature at which $\partial\eta/\partial T \rightarrow \infty$, i.e. when a yield stress appears, as described in the study of Plashchina, Muratalieva, Braudo, and Tolstoguzov (1986). The solution (1.5 wt%) was kept in the viscometer cell for 10 min at 80 °C, and then the temperature was lowered at a rate of 0.3 °C/min.

2.6. Test of optical rotation

Optical rotation was measured with an ATAGO polarimeter (POL-1/2, Japan) at 589 nm. The measurement was taken in a thermostated silica cell. The optical path length was 1 dm. The measurements were performed on 0.05 wt% and 0.25 wt% solutions, respectively. The solution was kept in cell for 10 min at 80 °C, and then the temperature was lowered at a rate of 0.3 °C/min.

2.7. Texture profile analysis of gels

The gels (1.5 wt% samples in water, cooling for 12 h) were subjected to an instrumental texture profile analysis (TPA). The gel specimens were placed between parallel flat plate fixtures fitted to a TA.XT2 Texture Analyzer (Stable Micro Systems, Surrey, UK). The gels were compressed twice at 1 mm/s to 50% of their original height. The results were reported by TPA as the means of duplicate tests. The TPA parameters, namely hardness (peak force on first compression (N)), fracturability (first bite, the force required to produce the first fracture (N)), cohesiveness (ratio of the active work done under the second force–displacement curve to that done under the first compression curve (dimensionless)) and springiness (distance that the sample recovered after the first compression (mm)) were computed.

2.8. Thermogravimetric analyses

Thermogravimetric analyses were carried out on a thermal analyzer Perkin-Elmer TG7. The measurements were used the temperature program 30–600 °C at a heating rate of 5 °C/min in a nitrogen atmosphere. The samples with equal actual moisture content were prepared by the method of Zeleznak and Hoseney (1987).

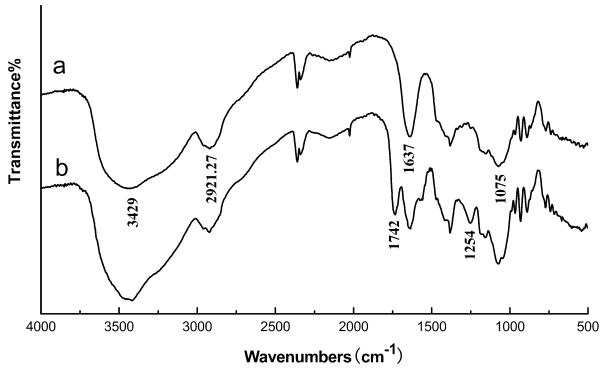

Fig. 1. The FT-IR spectra of raw agar and agar acetate, (a) raw agar; (b) agar acetate (DS = 0.365).

2.9. Cryo scanning electron microscopy (Cryo-SEM)

Gel samples (1.5 wt%) were placed into ultra-low temperature freezer for 3 h. The vacuum freeze dryer (FD1, Boyikang Company, Beijing, China) was used to remove water in the gel (about 36 h). The drying samples were cut into small pieces and fixed onto metallic sample holders with conducting silver glue and then sputtered with a layer of gold. The ready samples were examined by scanning electron microscopy (JSM-840, Jeol, Japan).

3. Results and discussion

3.1. FT-IR spectroscopy

The FT-IR spectra of raw agar and agar acetate with DS = 0.365 are shown in Fig. 1. Compared with the FT-IR spectrum of raw agar (curve a), the FT-IR spectrum of agar acetate (curve b) was almost the same as the one of raw agar except for the appearance of new absorption peaks at 1742 cm^{-1} and at 1254 cm^{-1}. The absorption peak at 1742 cm^{-1} indicated the presence of carbonyl group, corresponding to C=O of acetic ester. The absorption peak at 1254 cm^{-1} in the fingerprint region could be attributed to the C—O—C (acetic ester group) bond stretching vibration.

3.2. Physicochemical properties

Physicochemical properties of the prepared agar acetates were tested and shown in Table 1. It could be seen from Table 1 that the gelling temperature, the gel melting temperature and the gel strength of agar acetates were all decreased with the increase of DS. Among which, the variation trend of the gelling temperatures with the increase of DS was in agreement with the data reported in the patent by Kenneth and Guiseley (1976). It was worthwhile to note that the relationship between gel strength and DS values (in the range from 0 to 0.365) was in good linear correlation (correlation coefficient $R = -0.99834$) as it could be seen in Fig. 2.

3.3. Optical rotation analysis

Studies had shown that the mechanism of agar solution from sol to gel was due to the double helix structure formed between molecules (Arnott et al., 1974; Nordqvist & Vilgis, 2011). When agar water solution cooled, agar molecules turned into double helix, further cooled, the double helix was gathered and generated the hard gel. Temperature dependence of the optical rotation for solutions of raw agar and agar acetate (DS = 0.365) on cooling was shown in Fig. 3.