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Preparation of oxidized agar and characterization of its properties

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ABSTRACT

A series of oxidized agars with different carboxyl content were prepared, and their properties were determined and analyzed. The results showed that the gelling temperature, the optical rotation and the apparent viscosity of the agar solution, and the melting temperature, the strength, the hardness, the fracturability, the springiness, the chewiness and the gumminess of agar gel all decreased except that the cohesiveness increased after oxidation. The gel skeleton structures of agar before and after oxidation were all of the porous network structures, but the pores of gel skeleton structure became smaller and denser after oxidation.

1. Introduction

Agar is a kind of gel-forming polysaccharide extracted from seaweed, which is widely used for pharmaceutical, food and biomaterial due to its combination of gelling property, biocompatibility and biodegradability (García-González, Alnaief, & Smirnova, 2011; Wijesekara, Pangestuti, & Kim, 2011).

The properties of agar have been studied in detail. Its properties including gelling temperature, gel melting temperature, gel strength and apparent viscosity varied with different seaweed source and extraction conditions (Freile-Pelegrín & Murano, 2005). The skeleton structure of agar gel was compact and regular polymeric network with well-defined pores (Sousa, Borges, Silva, & Gonçalves, 2013). By means of X-ray (Foord & Atkins, 1989), NMR (Dai & Matsukawa, 2012), rheological methods (Nordqvist & Vilgis, 2011) and temperature dependence of the optical rotation (Arnott et al., 1974), the mechanism of agar solution from sol to gel has been investigated, and the results showed that agar molecules turned from random coil into double helix at first when agar solution cooled, then double helix gathered and generated the hard gel with further cooled. However, the literatures on the physicochemical properties of agar derivatives were precious few. In this research, a series of oxidized agar with different carboxyl content were prepared, and their properties were determined and analyzed.

2. Experiment

2.1. Materials

Gracilaria agar (3,6-anhydro-L-galactose content: 32.12%; sulfate content: 3.64%; gel strength: 1420 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 oxidized agar

30.0 g raw agar, 240 mL water and suitable amount of ferrous sulfate were mixed with stirring. Keeping the temperature at 30 °C and pH within 7.5–7.8, hydrogen peroxide solution (30%) in different dosages were added dropwise within 30 min, and then continued to react for another 3 h. Adjusting pH to 6.5–7, filtering, washing, and drying, a series of oxidized agars with different carboxyl content were obtained. The carboxyl content of oxidized agar was determined according to the procedure of Chattopadhyay, Singhal, and Kulkarni (1997).

3. Characterizations

The gelling temperature, gel melting temperature and gel strength were measured as described by Freile-Pelegrín and Robledo (1997). Sulfate content and 3,6-anhydrogalactose content (3,6-AG) were determined based on the method described by Sousa, Alves, Morais, Delerue-Matos, and Gonçalves (2010). The determination of the apparent weight-average molecular weight was measured according to the method of Suzuki, Sawai,

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and Takada (2001). The FT-IR spectra were obtained from samples in KBr pellets using a Nicolet 200 FT-IR spectrophotometer (Nicolet, Madison, WI, USA). Apparent viscosity, optical rotation and texture profile analysis (TPA) of sample gels were made as described by Braudo, Muratalieva, Plashchina, and Tolstoguzov (1991), Plashchina, Muratalieva, Braudo, and Tolstoguzov (1986) and Lau, Tang, and Paulson (2000) respectively. Thermogravimetric analyses (TG) were carried out on a thermal analyzer Perkin–Elmer TG7 using the temperature program 30–600 °C at a heating rate of 5 °C/min in a nitrogen atmosphere. The drying gel samples, removed water by a vacuum freeze dryer, were sputtered with a layer of gold and examined by scanning electron microscopy (JSM-840, Jeol, Japan).

4. Results and discussion

4.1. Physicochemical properties

Table 1 showed that the apparent molecular weight, sulfate content and 3,6-AG content of agar were all slightly reduced after oxidation, and the gelling temperature, gel melting temperature and gel strength of oxidized agar were all decreased with the increase of carboxyl content. The results indicated that the molecular chain of agar was less broken after oxidation under the chosen reaction conditions, and the introduction of carboxyl group in little quantity could affect the gelling properties of agar.

4.2. Analysis of IR and Cryo-SEM

Fig. 1 indicated that the IR spectra of agar before and after oxidation were almost the same. This result meant that the introduction of carboxyl content into agar molecule was small. Fig. 2 indicated that the gel skeleton structures of agar before and after oxidation were all of the porous network structures, and the pores of gel skeleton structure became smaller and denser after oxidation. This result meant that the gel skeleton structure of oxidized agar would have much higher capillary force to hold the water in gels than that of raw agar according to the capillary effect, i.e., the oxidized agar would have the higher gel water holding capacity than raw agar.

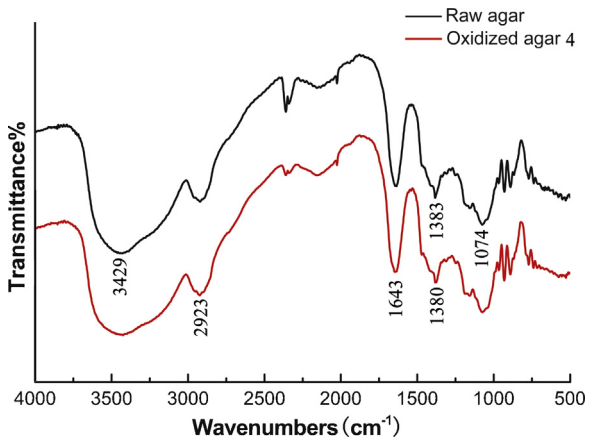

Fig. 1. The FT-IR spectra of raw agar and oxidized agar.

As shown in Fig. 3, the oxidation of agar did not change variation trend of solution optical rotation of agar on cooling, but lowered its solution optical rotation value. The temperatures of the transition beginning point (from coil to helix) of both raw agar and oxidized agar were same and about 60 °C. However, the temperatures of the transition end point (Braudo et al., 1991) of oxidized agars were lowered with the increase of its carboxyl content. Fig. 3 also indicated that the solution apparent viscosity values of the all samples increased gradually as the temperature decreased, and all increased sharply at the range of 35–50 °C. This result meant that all solutions were gelling in this range of temperature. The temperatures of gel formation point of samples, calculated from Fig. 3 (Plashchina et al., 1986), were about 40 °C (raw agar), 39 °C (oxidized agar 2), 37 °C (oxidized agar 4) respectively, which were in almost perfect agreement with corresponding values of gelling temperature in Table 1.

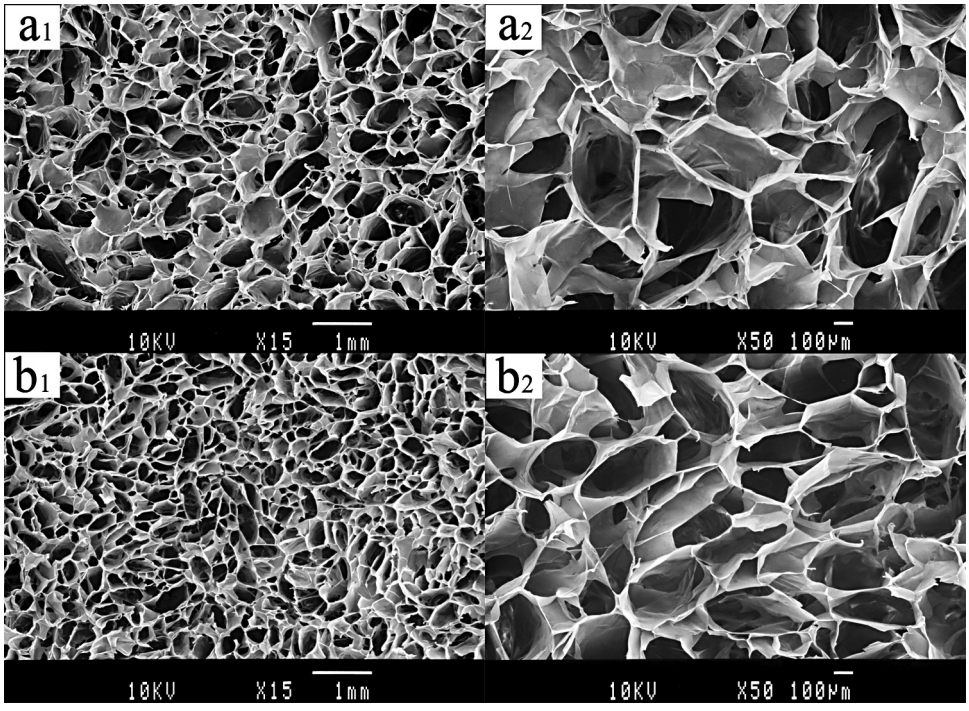

Fig. 2. Cryo-SEM images of the gel skeleton structures of raw agar and oxidized agar, (a_1, a_2): raw agar; (b_1, b_2): oxidized agar 2.

Table 1
Physicochemical properties of the oxidized agars.

Physicochemical properties	Raw agar	Oxidized agar 1	Oxidized agar 2	Oxidized agar 3	Oxidized agar 4
Carboxyl content (%)	–	0.072	0.128	0.184	0.218
Gelling temperature (°C)	40	39.5	39	38	37
Melting temperature (°C)	83	82.5	81.5	80	79
Gel strength (g/cm^2)	1420	1360	1300	1120	1020
3,6-AG content (%)	32.12	32.11	32.09	32.08	32.07
Sulfate content (%)	3.640	3.638	3.637	3.636	3.635
Apparent molecular weight ($\times 10^5$)	2.16	2.14	2.12	2.09	2.07

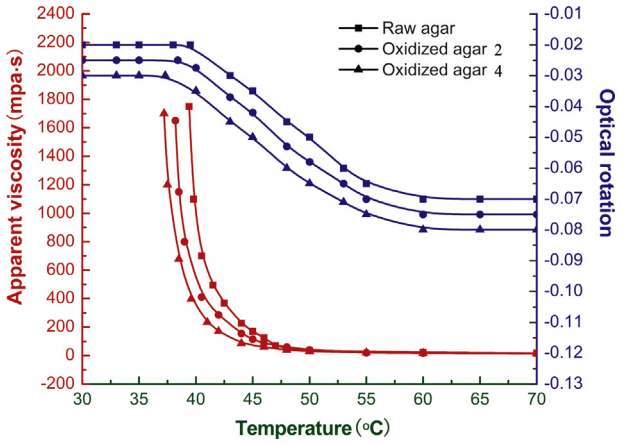

Fig. 3. Temperature dependence of the optical rotation and apparent viscosity for solutions of raw agar and oxidized agars on cooling.

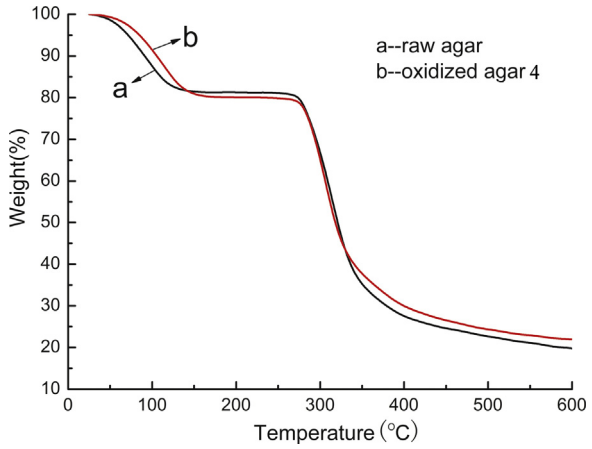

Fig. 5. TG curves of raw agar and oxidized agar.

4.3. Textural properties

TPA is a very useful method for analyzing the gel textural properties (Charoenrein, Tatirat, Rengsutthi, & Thongngam, 2011; Chung, Olson, Degner, & McClements, 2013; Hajidoun & Jafarpour, 2013). As shown in Fig. 4, the hardness, the fracturability, the springiness, the chewiness, the gumminess of oxidized agar gels all decreased except that the cohesiveness increased with the increase of the oxidized degree, there into, the results that the decrease of the springiness and the increase of the cohesiveness could be attributed to that the pores of porous skeleton structures of oxidized agar gels tended to be smaller and denser (see Fig. 2).

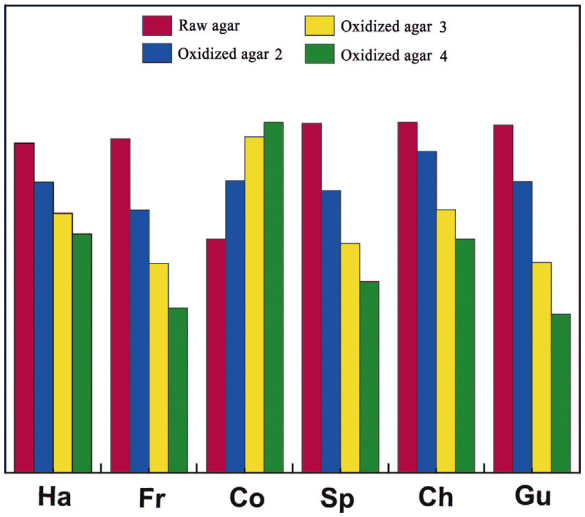

Fig. 4. The hardness (Ha), fracturability (Fr), cohesiveness (Co), springiness (Sp), chewiness (Ch) and gumminess (Gu) of agar and oxidized agar gels.

4.4. TG analysis

TG curves (see Fig. 5) showed that the loss of free water presented in raw agar and oxidized agar 4 were 18% and 20% respectively. The water loss rate of raw agar was obviously larger than that of oxidized agar in moisture drying region, which indicated that water holding capacity of oxidized agar was better than that of raw agar. The degradation temperature of both raw agar and oxidized agar were all around 270 °C, which indicated the thermal stability of agar molecule had no obvious change after oxidation.

5. Conclusions

A series of oxidized agars with different carboxyl content were prepared, and their properties were determined. The results showed that the gelling temperature, the optical rotation and the apparent viscosity of the agar solution, the melting temperature, the strength, the hardness, the fracturability, the springiness, the chewiness and the gumminess of agar gel all decreased except that the cohesiveness increased after oxidation. Cryo-SEM images indicated that the gel skeleton structures of agar before and after oxidation were all of the porous network structures, but the pores of gel skeleton structure became smaller and denser after oxidation. TG curves indicated that water holding capacity of oxidized agar was better than that of raw agar.

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