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Radiation induced degradation of xanthan gum in the solid state

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HIGHLIGHTS

- Radiation-induced degradation of xanthan gum (XG) described.
- The influences of dose rate on the radiation degradation of XG were examined.
- G(S) and degradation rate of XG were calculated by using molecular weights data.

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ABSTRACT

In this study, the effect of ionizing radiation on xanthan gum was investigated. Xanthan samples were irradiated with gamma rays in air at ambient temperature in the solid state at different dose rates and doses. Change in their molecular weights was followed by size exclusion chromatography (SEC). Chain scission yield (G(S)), and degradation rate constants (k) were calculated. The calculated G(S) values are 0.0151 ± 0.0015, 0.0144 ± 0.0020, 0.0098 ± 0.0010 μmol/J and k values are $1.4 \times 10^{-8} \pm 1.4 \times 10^{-9}$, $1.3 \times 10^{-8} \pm 2.0 \times 10^{-9}$, $8.7 \times 10^{-9} \pm 1.0 \times 10^{-9}$ Gy^{-1} for 0.1, 3.3 and 7.0 kGy/h dose rates, respectively. It was observed that the dose rate was an important factor controlling the G(S) and degradation rate of xanthan gum.

Considering its use in food industry, the effect of irradiation on rheological properties of xanthan gum solutions was also investigated and flow model parameters were determined for all dose rates and doses. Rheological analysis showed that xanthan solution showed non-Newtonian shear thinning behaviour and ionizing radiation does not change the non-Newtonian and shear thinning flow behaviour of xanthan gum solutions in concentration ranges of this work. It was determined that, Power Law model well described the flow behaviour of unirradiated and irradiated xanthan solutions.

1. Introduction

Xanthan gum, a heteropolysaccharide produced from the fermentation of corn sugar by bacterium *Xanthomonas campestris*, is widely used as food additive and rheology modifier; thickener, stabilizer, emulsifier, gelling agent and water-binding agents in the food, textile, cosmetic, pharmaceutical and oil industry (Barrére et al., 1986; Cottrell et al., 1980). Its very high molecular weight (2×10^6–2×10^7 g/mol) and its chemical structure makes it a highly stable polysaccharide against enzymolysis and acidolysis. The main chain consists of trisaccharide side chains containing a D-glucuronic acid unit between two D-mannose units linked at the O-3 position of every other glucose residue in the main chain, (Cottrell et al., 1980; Katzbauer, 1998; Garcia-Ochoa et al., 2000). Approximately one-half of the terminal D-mannose contains a pyruvic acid residue linked via keto group to the 4 and 6 positions, with an unknown distribution. The presence of acetic and pyruvic acids produces an anionic polysaccharide type (Sandford and Baird, 1983).

In recent years, there has been growing interest in understanding the effect of ionizing radiation on the chemical structure of polysaccharides such as chitin, chitosan, sodium alginate, and kappa carrageenan due to their versatile food and non-food applications (Choi et al., 2002; Nagasawa et al., 2000). The research in this field is mostly concentrated on the degradative effect of radiation to produce polysaccharides with desired low molecular weight ranges. We have carried out numerous studies on radiation induced degradation of polysaccharides in our research group. In

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2007 radiation-induced degradation of galactomannan polysaccharides such as locust bean gum (LBG), guar gum (GG) and tara gum (TG) have been investigated by Şen et al. (2007). It was concluded that G/M (galactose/mannose) ratio did not change the chain scission yield of galactomannans, whereas, initial molecular weight was more important in affecting degradation rate of galactomannans under gamma rays. On the other hand, it was found that G/M (guluronic acid/mannuronic acid) ratio was an important factor affecting chain scission yield of sodium alginate (Şen et al., 2010). In 2014 Şen et al. found that one of the important parameters of radiation-induced degradation of chitosan is its degree of deacetylation value (Taşkın et al., 2014).

It is well known that the main effect of ionizing radiation on polysaccharides is chain scission of C–O bond connecting the glycoside groups on the main chain (Kume and Takehisa, 1982; Qin et al., 2003; Fei et al., 2000). However, there is no sufficient information about the effect of ionizing radiation on xanthan gum in the literature. In this research, we have investigated the chain scissioning effect of ionizing radiation on xanthan gum in solid state at different dose rates and doses and determined the flow behaviour of xanthan solutions before and after the irradiation.

2. Experimental

A commercial xanthan sample (food grade, Batch number: M1207A G48 1207007, produced by Jungbunzlauer, Austria) in the powder form was used. Waters 2000-1000-500 ultrahydrogel columns were used for molecular weight analyses and universal calibration was constructed by using narrow molecular weight pullulan standards obtained from Shodex Company. NaCl (0.1 M) was used as the eluting solvent. The Mark–Houwink parameters used for pullulan standards and xanthan gum were $K=2.31\times10^{-4}$ dL/g, $a=0.65$ and $K=1.7\times10^{-6}$ dL/g, $a=1.14$, respectively (Mendichi and Scieroni, 1998; http://www.ampolymer.com/Mark-HouwinkParameters.html).

Xanthan samples irradiated in powder and in dilute solution form to obtain various molecular weight fractions by using Co-60 gamma source in air at ambient temperature, at different dose rates (0.1, 3.3 and 7.0 kGy/h) and doses (2,5, 5.0, 10, 20, 30 and 50 kGy). Irradiations were carried out in the Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering (IFIN-HH), Romania by using Gamma Chamber 5000 for the 3.3 and 7.0 kGy/h dose rates and Gamma Irradiator SVSTCo-60/B for the 0.1 kGy/h dose rate.

Spectroscopic characterization of unirradiated and irradiated xanthan gum samples were performed by recording their Nuclear Magnetic Resonance (NMR) and Fourier Transform Infra-red (FT-IR) spectra. The changes in the ratio of hydrogen atoms in methyl groups of pyruvate and acetate were followed with Bruker 400 MHz ultrashield model digital FT-NMR model spectrometer operated at 90 °C in which trimethylsilane (TMS) was used as an internal standard. The possible functional groups formed after irradiation of xanthan gum were followed with Spectrum 100 model, Perkin Elmer FT-IR spectrometer in Attenuated Total Relectance (ATR) mode with a resolution of 4 cm^{-1} in a range of 4000–600 cm^{-1}.

Rheological properties of xanthan gum solutions were determined by using a Thermo-Haake Modular Advanced Rheometer System (MARS) equipped with a cone-plate fixture with a radius of 35 mm, cone angle of 4° and a gap size of 0.139 mm. All measurements were performed at a fixed temperature (30 °C) and concentration (1% w/v) over a wide range of shear rates from 0.01 to 500 s^{-1}.

3. Results and discussion

3.1. Effect of gamma rays on the chemical structure of xanthan gum

Spectroscopic characterization of xanthan samples was performed by recording their FTIR and ^{1}H-NMR spectra. The minor increases in the area of –OH group region (3000–3500 cm^{-1}) was observed while no change in finger print region indicates the lack of formation of carbonyl and carboxylic acid groups. It is suggested that degradation of xanthan proceeds by main chain scission on glycosidic bonds and ended with –OH termination. ^{1}H-NMR spectra confirms the scission on main chain of xanthan. On the other hand, there is no effect on side groups after irradiation, while the ratio of number of protons in pyruvate group to acetate group is 0.77 in pure xanthan, it is 0.65–0.85 for xanthans irradiated to 2.5–50 kGy.

3.2. Effect of gamma rays on the molecular structure of xanthan gum

It is very well known that polysaccharides in dry form or in solution degrade when exposed to ionizing radiation (Kume and Takehisa, 1982; Qin et al., 2003; Fei et al., 2000). For the investigation of the effect of gamma rays on the molecular weight of xanthan, weight ($\bar{M}_w$) and number average molecular weight ($\bar{M}_n$) values of the polymers were determined by size exclusion chromatography (SEC) analysis. SEC chromatograms obtained for 7.0 and 0.1 kGy/h dose rates are given in Fig. 1. As seen in Fig. 1, there are two main peaks observed for xanthan in the high and low molecular weight regions. As the absorbed dose increased, the main peak the xanthan sample at low retention volumes shifted to higher retention volumes indicating a decrease in the molecular weight of the samples as a function of irradiation. As can be seen in Fig. 1 this shift is much higher at 0.1 kGy/h dose rate than 7.0 kGy/h. A slight increase on the intensity of low molecular weight peak was also observed. Changes in $\bar{M}_w$ and $\bar{M}_n$ with absorbed dose are given in Figs. 2 and 3, respectively. As can be seen from these figures, both average molecular weights decreased rapidly up to 50 kGy and this decrease is more effective for low dose rate irradiations. Fast decrease in molecular weight was attributed to longer irradiation period of samples in the presence of oxygen i.e enhancing of oxidative degradation at low dose rates.

3.3. Radiation stability of xanthan gum

The efficiency of radiation-induced events is expressed by G-value. The G-value is defined as the number of events as mol per J, and has been customarily used to measure radiation – chemical yield. The molecular weight values of the xanthan were used for the determination of G(S) and degradation rate. If scission is the only mode of action of radiation then the radiation – chemical yield of degradation (scission) G(S) is determined from the Alexander–Charlesby–Ross equation given below for polymers irradiated in dry and solid form (Charlesby, 1960):

$$\frac{1}{\bar{M}_n}-\frac{1}{\bar{M}_{n0}}=G(S)D \tag{1}$$

where, the absorbed dose D is in J/kg (Gy) and $\bar{M}_n$ and $\bar{M}_{n0}$ (kg/mol) are the number average molecular weights of the polymer before and after irradiation.

For the determination of the G(S) (mol/J) values, $1/\bar{M}_n-1/\bar{M}_{n0}$ was plotted against dose for all irradiations and given in Fig. 4. Then, the $G(S)$ values were calculated by using the relevant slopes (Table 1).

The equation given by Jellinek (1955) modified by Şen et al. (2010) is used for the determination of degradation rate constants (Eq. (2)):