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Kinetic study of κ-carrageenan degradation and its impact on mechanical and structural properties of chitosan/κ-carrageenan film

Mahdiyar Shahbazi[a], Ghadir Rajabzadeh[a,*], Rammile Ettelaie[b], Ali Rafe[a]

[a] Research Institute of Food Science and Technology (RIFST), Mashhad, Iran
[b] Procter Department of Food Science, University of Leeds, Leeds LS29JT, United Kingdom

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ABSTRACT

The purpose of the current research was to study κ-carrageenan degradation behavior under thermal treatment, and its influence on chitosan κ-carrageenan film properties. A pseudo-first-order reaction equation was applied by using reciprocal plots of κ-carrageenan molecular mass versus heating time, which showed a strong dependence on heating time. Incorporation of thermally treated κ-carrageenan into the chitosan had diminished both water resistance and water vapor permeability of the blend, in contrast to those for intact or untreated κ-carrageenan. A dramatic decrease of equilibrium moisture content and tensile strength were noticed, and these parameters were more affected by the longer times. Furthermore, the contact angle of the films was found to be a function of the heating time. Scanning electron microscopy revealed apparent agglomeration of κ-carrageenan through the thermal process. Atomic force microscopy demonstrated that the intact blend had the flattest surface, whilst the blend containing treated κ-carrageenan had high roughness.

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1. Introduction

The application of petroleum based packaging materials has a serious environmental pollution due to the fact that they are non-degradable (Hoagland & Parris, 1996). As an alternative, biodegradable materials from the natural sources like carbohydrates can be employed (Sanchez-Garcia, Hilliou, & Lagaron, 2010). However, a packaging based on carbohydrates suffers from poor physico-mechanical and weak barrier properties (Parris, Coffin, Joubran, & Pessen, 1995).

One way to resolve these problems is to blend the biopolymers to improve the film properties. These improvements could be ascribed to the strengthening of the mechanical parameters (Zhu, Sheng, & Tong, 2014; Zivanovic, Li, Davidson, & Kit, 2007), increasing the surface hydrophobicity (Zhu et al., 2014), decreasing the water vapour permeability (Zhu et al., 2014; Zivanovic et al., 2007) and relative water resistance (Xiao, Gao, Wang, & Zhang, 2000).

Chitosan is distinguished as a natural polymer with wide applications in the food and pharmaceutical industries. Chitosan is one of the most abundant carbohydrates in the nature. It is obtained through the process of alkaline N-deacetylation of chitin,

which is mainly extracted from the shellfish (Hoagland & Parris, 1996). This biopolymer has a semi-crystalline structure and high hydrophilic characteristics, which can form hydrogen bonds with water molecules. A special feature of chitosan is the formation of uniform films with the potential applications in food industry (Xu, Kim, Hanna, & Nag, 2005). Chitosan becomes soluble and cationic when it is dissolved in acidified solutions, whereas most other hydrocolloids display anionic property in aqueous media. So, there is a notable affinity between these hydrocolloids and chitosan in the blend mixture (Park, Lee, Jung, & Park, 2001).

Carrageenan is the sulfated form of D-galactan obtained from the red algae (Lobban, 1994). Carrageenan consists of repeating galactose units and 3,6-anhydrogalactose joined by alternating α-(1,3) and β-(1,4) glycosidic links. All three kinds of carrageenan (iota, kappa and lambda) produce high viscosity when incorporated in the aqueous systems (Imeson, Phillips, & Williams, 2000). The kappa carrageenan (KC) is widely used for the synthesis of the blend films, where the physical and mechanical properties of the films are amended in the presence of KC.

Park et al. (2001) prepared the blend film based on chitosan and KC in the presence of several organic acids, and found that the physical and mechanical properties of the blend film demonstrated strong dependency on the organic acid solvent. Their results showed that the tensile strength and water barrier property of a blend of chitosan and KC involved acetic acid and ascorbic acid was significantly improved than other organic acid solutions.

In a study conducted by Rodrigues, da Costa, and Grenha (2012), the chitosan and KC was crosslinked through tripolyphosphate, and the effect of the cross-linker in the particles properties was investigated.

Bratskaya et al. (2007) synthesized two type films include covalently grafted chitosan and chitosan/KC films, to decrease initial bacterial deposition rates and the number of bacteria adhering on the film.

There are several methods for preparing the biodegradable films based on the thermal processes, including thermo-compression, blow molding and solvent casting method (Fakhouri et al., 2013; Teixeira et al., 2012). The solvent casting, in particular, is widely used for the synthesis of the biodegradable films (Fakhouri et al., 2013). The temperature history of the biofilm has a great effect on the features of the film; however this effect has almost been completely ignored. More specifically, the depolymerisation kinetic by the thermal degradation during the preparation of the biodegradable films has rarely been evaluated.

In the aforementioned methods, whenever high temperatures were employed, the hydrolysis reaction occurred. Under these circumstances, degradation and scission of the chain caused a decrease in the molecular weight of polysaccharide chain (Bradley & Mitchell, 1988). In addition, the heat treatment highly affected the other dispersion parameters. It was proven that the degradation rates of the polysaccharides were related to their molecular conformation, in which the concentrated regions, in comparison with dilute regions, had a higher resistance to heat, and generally were more capable of hindering the chain degradation (Hjerde, Smidsrød, & Christensen, 1996).

As regards the systematic studies on the variables effect of the polysaccharide heat degradation and its influence on the film, these are scanty. The alteration of molecular mass and the mechanism of degradation via thermal casting method need to be explored in more details to fully understand their effects on the film properties.

Accordingly, the aim of this study is to investigate the changes in the molecular size of KC (using intrinsic viscosity as an indicator) occurring during being heated in aqueous media, and the incorporation of this biopolymer into the chitosan solution to evaluate the final resulting blend properties. For degradation rate of KC, our initial hypothesis is based on the fact that the chain scission of sulfate esters on the KC follows a *pseudo* first-order kinetics.

2. Materials and methods

2.1. Materials

The commercial potassium KC salt and chitosan were provided from Sigma–Aldrich Chemical Co. (St. Louis, MO, USA).

2.2. KC thermal treatment

Thermal treatment of biopolymers at 80 °C is commonly used in the laboratory and industry for the preparation of their films (Lai, Lii, Hung, & Lu, 2000). To investigate the degradation kinetic in this condition, KC (0.275 g, in accordance with critical overlap concentration) was completely dissolved in deionized water (0.275 g/dL) and heated at 80 °C in a thermostatically controlled chamber under continuous stirring. This was followed by the thermal treatment at 60, 120, 180, and 240 min.

2.3. Rheological study of KC

After heat treatment, an Ostwald viscometer (Ubbelohde-type, Germany) equipped with a temperature control system was used to determine the coil overlap concentration (c^*) of the KC chains and their intrinsic viscosity ($[\eta]$) (40 ± 0.1 °C). The intrinsic viscosity ($[\eta]$) of

KC was determined under the coil overlap concentration (in the dilute region). The sample viscosity (η) was converted to relative viscosity (η_{rel}), reduced viscosity (η_{red}) and inherent viscosity (η_{inh}) defined by Eqs. (1), (2) and (3), respectively:

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t}{t_0} \cdot \frac{\rho}{\rho_0} \tag{1}$$

$$\eta_{red} = \frac{(\eta_{rel} - 1)}{C} \tag{2}$$

$$\eta_{inh} = \frac{\ln(\eta_{rel})}{C} \tag{3}$$

where, t and t_0 are the efflux times of the solution and the solvent, ρ/ρ_0 is the ratio of the density of the solution to the used solvent, $\eta_{rel} - 1$ is specific viscosity (η_{sp}), and C is the concentration of KC.

The $[\eta]$ is usually obtained from the mean intercept of $\ln(\eta_{rel})/C$ and η_{sp}/C to the infinite dilution limit according to the Huggins (Eq. (4)) and Kraemer (Eq. (5)) empirical expressions:

$$\frac{\eta_{sp}}{C} = [\eta] + K_1[\eta]^2 C \tag{4}$$

$$\frac{\ln \eta_{rel}}{C} = [\eta] + K_2[\eta]^2 C \tag{5}$$

where, K_1 is the Huggins constant, which is 0.35 for KC (Harding, Day, Dhami, & Lowe, 1997; Huggins, 1942). K_2 is the Kraemer constant (Kraemer, 1938). Theoretically $K_1 + K_2 = 0.5$, so the Kraemer constant is 0.15 for KC (Morris & Ross-Murphy, 1981). All determinations were carried out in triplicate.

2.4. Theoretical basis: degradation rate

Masson (1955) and Bradley and Mitchell (1988) illustrated that the chain scission of the glycosidic linkage of KC, for short-term heat treatment, is a first-order reaction. Based on this concept, the rate constant (r) of scission of KC can be determined upon heating process.

The degradation rate can be ascertained by using plots of reciprocal molecular mass against heating time. The rate constant of the degradation reaction can be determined by Eq. (6) (Bradley & Mitchell, 1988; Masson & Caines, 1954):

$$\left(\frac{1}{M_t}\right) - \left(\frac{1}{M_0}\right) = \left(\frac{r}{m}\right) t \tag{6}$$

where, M_t and M_0 (kDa) are the molecular weights at times t and t_0; r (min^{-1}) is the *pseudo* first-order rate constant; t is the heating time (min); and m (kDa) is the average molecular weight of monosaccharide units. On the hypothesis of Hjerde et al. (1996) and Tanford (1961), $\alpha(1 \rightarrow 3)$ and $\beta(1 \rightarrow 4)$ glycoside bonds on KC have a similar susceptibility to scission.

It is known that the intrinsic viscosity is correlated to molecular weight according to Marck–Houwink equation (Rao, 1999):

$$[\eta] = K M_w^\alpha \tag{7}$$

Combining Eqs. (6) and (7) provides a relationship between the time and intrinsic viscosity:

$$\left(\frac{1}{[\eta]_t^{1/\alpha}}\right) - \left(\frac{1}{[\eta]_0^{1/\alpha}}\right) = \left(\frac{r}{m} \times K^{1/\alpha}\right) t \tag{8}$$

where, $[\eta]_t$ and $[\eta]_t$ are intrinsic viscosity at t and t_0; K and α are Marck–Houwink parameters, and $((r/m) \times K^{1/\alpha})t$ is the slope of the curve.