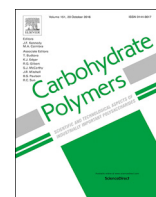




Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpolMolecular structure and properties of κ -carrageenan-gelatin gelsS.R. Derkach^{a,*}, N.G. Voron'ko^a, Yu. A. Kuchina^a, D.S. Kolotova^a, A.M. Gordeeva^{b,c}, D.A. Faizullin^{b,c}, Yu. A. Gusev^c, Yu. F. Zuev^{b,c,d}, O.N. Makshakova^{b,*}^a Murmansk State Technical University, Sportivnaya str. 13, 183010 Murmansk, Russia^b Kazan Institute of Biochemistry and Biophysics, FRC Kazan Scientific Center of RAS, Lobachevsky Str., 2/31, 420111 Kazan, Russia^c Kazan (Volga region) Federal University, Kremlevskaya str. 18, 420111 Kazan, Russia^d Kazan State Power Engineering University, Krasnoselskaya str. 51, 420066, Kazan, Russia

ARTICLE INFO

Chemical compounds studied in this article:

 κ -Carrageenan (PubChem CID: 11966249)

Gelatin i.e., Collagen I, alpha chain (PubChem

CID: 6913668)

Distilled water (PubChem CID: 962)

Keywords:

Gelatin

 κ -Carrageenan

Gel structure

Rheology

IR spectroscopy

Molecular docking

ABSTRACT

Rheological studies, FTIR spectroscopy and a molecular docking approach were used to explore the structural basis of the peculiar physicochemical properties of gelatin gels modified with a κ -carrageenan admixture. Mixed gel properties are affected by the polysaccharide-to-gelatin ratio, Z, and can be divided into two categories. At low ratios, the strength of mixed gels varies insignificantly compared to gelatin due to the similar structures of the gels. Above the threshold content of κ -carrageenan ($Z > 0.1$), the storage modulus and yield stress of mixed gels are significantly enhanced. The nonadditivity and threshold character of the rheological properties could be the result of conformational ordering of both gelatin and κ -carrageenan, leading to the formation of additional junction zones in the gel network. According to molecular docking studies, the junctions could be formed as a result of complementary interactions between the gelatin triple helix and the κ -carrageenan double helix. The stack formation increases the interaction energy, which explains the strengthening of the gel network.

1. Introduction

Gelatin occupies a very important place among the hydrocolloids that are used widely in modern food technologies and is a structure-forming agent that gives products a desired shape and consistency (Haug & Draget, 2009). A large amount of data regarding the formation of structures in gelatin and the properties of gelatin hydrogels has been summarized in reviews (Izmailova et al., 2004; Johnston-Banks, 1990). However, in many cases when developing new food products, the gel strength, melting temperature, T_m , and gelling temperature, T_g , of gelatin might be below the required values. One of the budding methods for altering the physicochemical properties of gelatin is the admixture of polysaccharides as co-gelators. In multicomponent food systems, the interaction between these ingredients, in addition to their individual properties, plays a significant role in creating a structure that determines the quality of the final product (Le, Rioux, & Turgeon, 2017; Schmitt & Turgeon, 2011). In accordance with the compatibility conditions, the interactions of biopolymers in aqueous mixtures can result in the formation of polyelectrolyte complexes (Schmitt, Sanchez, Desobry-Banon, & Hardy, 1998), which have specific effects on gelling in mixed systems.

Numerous studies have been devoted to the effect of

polysaccharides on the rheological properties and thermal stability of gelatin gels. The type of polysaccharide and the polysaccharide/gelatin weight ratio in the mixture determine the degree of modification of the gelatin properties. Thus, guar gum, dextran, carboxymethyl cellulose, and inulin do not significantly affect the melting temperature and strength of gelatin gels (Harrington & Morris, 2009). In contrast, under conditions that inhibit the formation of polyelectrolyte complexes with gelatin, β -glucan (Sinthusamran & Benjakul, 2018), alginate (Panouille & Larreta-Garde, 2009), and agar (Saxena, Kaloti, & Bohidar, 2011) exhibit a plasticizing effect, reducing both the strength and gelling temperature of gelatin gels. Conversely, under conditions that provoke a complex formation in aqueous mixtures with gelatin, sodium alginate (Boanini, Rubini, Panzavolta, & Bigi, 2010), chitosan (Derkach, Voron'ko, & Sokolan, 2017; Wang, Qiu, Congrove, & Denbow, 2009), ι -carrageenan (Michon, Cuvelier, Launay, & Parker, 1996), and κ -carrageenan (Derkach, Voron'ko, Maklakova, & Kondratyuk, 2014; Haug, Draget, & Smidsrod, 2004; Pranoto, Lee, & Park, 2007) improve the physicochemical properties of gelatin gels. These modified gels exhibit increases in strength, elasticity modulus and melting point.

Previously, several mechanisms explaining the modification of the physicochemical properties of gelatin as a gelator have been evaluated (de Kruijff, Weinbreck, & de Vries, 2004; Wang, Virgilio, Wood-Adams, &

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