Food Chemistry 256 (2018) 419–426

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Review

Modifications of konjac glucomannan for diverse applications

Fan Zhu

School of Chemical Sciences, University of Auckland, Private Bag 92019, Auckland 1142, New Zealand

ARTICLE INFO

Keywords:
Film
Encapsulation
Biodegradable
Chemical and physical modifications
Super absorbent
Konjac glucomannan
Underutilized species

ABSTRACT

Konjac glucomannan (KGM) is a major polysaccharide from the corm of *Amorphophallus konjac*. Native KGM has limited uses and has been chemically/physically/enzymatically modified to expand the range of functional properties. This mini-review summarises the recent advances of modifying KGM for diverse food and nonfood applications, focusing on the chemical and physical modifications. The chemical methods include substitution, grafting, cross-linking, oxidation, and deacetylation, whereas the physical modifications are electrospinning, microfluidic spinning, γ-irradiation, extrusion, and electric field processing. The modified KGM has been used in a range of different applications, including biodegradable film, emulsion, medical and pharmaceutical material, encapsulation and controlled release, fish feed and functional food ingredient, separation medium, aerogel, liquid crystal, absorbent for removal of pollutants in waste water, and so on. These KGM-based products tend to be biodegradable, biocompatible, and non-toxic with improved functional performance.

1. Introduction

Konjac (*Amorphophallus konjac*) of the Araceae (aroid) family is native to warm subtropical and tropical Asia. It is widely grown as a cash crop with high yields in countries such as China, India, and Japan (Behera & Ray, 2017). Apart from starch, glucomannan is the major component of the konjac corm which may accounts for ~70% of the dry weight of refined flour (Behera & Ray, 2017; Huang, Jin, Ye, Hu, & Wang, 2016; Zhu, 2016). Konjac glucomannan (KGM) is consisted of D-mannose and D-glucose residues (linked by β-1,4 bonds) with a ratio of 1.6:1 or 1.4:1, depending on the genotypes (Behera & Ray, 2017; Zhang, Chen, & Yang, 2014). On average, there is an acetyl group on the C-6 position of the backbone per every 9–19 sugar residues. Side chains may exist with a degree of branching of ~8%. The molecular weight of KGM ranges from 500 k to 2000 k, depending on the plant source and processing methods. KGM tends to have a homogeneous size distribution with a polydispersity (M_W/M_n) of 1.21 (Behera & Ray, 2017; Zhang et al., 2014).

KGM has good water binding and gelation capacity as well as film forming property (Zhang et al., 2014). These functional properties make konjac corm powder and KGM excellent food ingredients. Konjac powder has been a food item in China and Japan since ancient times. There are a few KGM based food products from the markets such as noodles and cakes which are locally popular. KGM is a GRAS (generally regarded as safe) food additive as approved by Health Canada in Canada and FDA (Food and Drug Administration) in USA. It is also approved by European Union as E425 (Tester & Al-Ghazzewi, 2016). There are various health effects associated with the consumption of KGM and related products. The health effects include weight loss and satiety, oral health, enhancing the growth and viability of beneficial organisms in colon, binding of nutrients (e.g., cholesterol), and so on (Tester & Al-Ghazzewi, 2016). There has been increasing interest in using KGM for the formulation of functional foods.

Apart from food applications, KGM has been used in other areas such as for biomedical and environmental uses. Compared with synthetic and fossil oil based polymers, natural polysaccharides including KGM tend to be renewable, environmentally friendly (biodegradable), and biocompatible (Zia, Zia, Zuber, Ahmad, & Muneer, 2016). KGM has been a research focus in the last few years. This is partially reflected by some recent reviews on various aspects of KGM (Behera & Ray, 2017; Tester & Al-Ghazzewi, 2016; Zhang et al., 2014; Zia et al., 2016). For example, Zhang et al. (2014) reviewed the modifications of KGM for the uses in oral colon targeting drug delivery systems. Zia et al. (2016) reviewed the properties and applications of KGM based polyurethanes. The nutritional properties and health effects of KGM and the hydrolyzed products have also been reviewed lately (Behera & Ray, 2017; Tester & Al-Ghazzewi, 2016). These reviews pointed out that native KGM has a very limited range of functionalities. It is commonly modified to expand the functional variation for diverse applications (Zhang, Xie, & Gan, 2005). During the last few years, many different types of chemical and physical modification methods such as grafting and electrospinning have been used to create new properties of KGM for desired applications (e.g., as wound dressing hydrogel and for the removal of heavy metals from waste water) (Chen, Zhang, Ding, Lin, &

Abbreviations: CKGM, carboxymethyl KGM; DS, degree of substitution; DP, degree of polymerization; KGM, konjac glucomannan; TEMPO, 2,2,6,6-tetramethyl-1-piperidiny-1-oxyl

E-mail address: fzhu5@yahoo.com.

https://doi.org/10.1016/j.foodchem.2018.02.151
Received 6 September 2017; Received in revised form 21 November 2017; Accepted 27 February 2018
Available online 06 March 2018
0308-8146/

Lu, 2017; Shahbuddin, Bullock, MacNeil, & Rimmer, 2014). A review on the recent progress in this field would greatly support the current exploitation of KGM as versatile biomaterial.

The present mini-review summarises the chemical and physical modifications of KGM and the various applications, focusing on the literatures from the past 5 years. The basics of KGM such as extraction, structure, and physicochemical properties have been reviewed previously (Behera & Ray, 2017; Zhang et al., 2014), and thus, are not covered in this review. Readers are encouraged to refer to the previous publications to gain the basic background information on KGM. There has been a rather large number of publications on the chemical and physical modifications of KGM from the last 5 years or so. Therefore, only representative papers have been intentionally selected in the current review in order to comprehensively cover the various modifications and applications of KGM, while not exceeding the word limit of the Journal. The applications of the modified KGM, instead of the modification/synthesis process (e.g., reaction conditions), are emphasized to give the paper a focus. In some of the reported cases, combined modifications were employed (e.g., both physical and chemical), which, in this review, is categorised according to the major and emphasized type of modification. In general, this review is categorised into subsections primarily based on the types of modifications. For example, within the chemical modification section, subsections on substitution-, chain elongation-, and depolymerisation-type modifications are produced. Readers are also encouraged to refer to the Supplementary material (figures and tables) for much increased readability and clarity. The enzymatically modified KGM, which has been recently reviewed (Tester & Al-Ghazzewi, 2016), is not covered here. This review may provide a basis to further develop konjac as a sustainable crop.

2. Chemical modifications

Many types of chemical modification methods and the combinations have been conducted on KGM (Supplementary Table 1 and Fig. 1). The major modifications include substitution, chain elongation, and degradation with some examples of the themes illustrated (Supplementary Fig. 1). These modified KGM have been used in diverse applications as described below.

2.1. Substitution

2.1.1. Acetylation for film formation

Environmental concerns require the production of biodegradable films to replace the fossil oil based products. KGM triacetate and acetate with different degrees of substitution (DS) were prepared for thermoplastic film production (Enomoto-Rogers, Ohmomo, & Iwata, 2013). At a DS of 3, the number based molecular weights of the KGM triacetate was 3×10^5 and the degree of polymerisation (DP) was 1×10^3. Increasing DS of both acetates increased the decomposition temperatures of KGM. Increasing DS also decreased the glass transition temperature of the acetates (e.g., from 219 °C at DS of 1.3 to 178 °C at DS of 3), probably due to the effect on hydrogen bonding. The KGM acetate was made into films by casting the solution. The films were transparent. Increasing DS decreased the elongation at break and the tensile strength of the films as illustrated in Supplementary Fig. 2A, which may be due to the effect of acetylation on hydrogen bond formation and intermolecular interactions of KGM molecules (Enomoto-Rogers et al., 2013). Huang, Takahashi, Kobayashi, Kawase, and Nishinari (2002) studied the effect of acetylation on the gelation properties of KGM and found that increasing DS increased the elasticity of KGM gel. This appeared to be similar to the result that increasing DS decreased the tensile strength of KGM film (Enomoto-Rogers et al., 2013), though it should be noted that film and gel are different structural systems. Only one study so far reported the production of KGM acetate based film (Enomoto-Rogers et al., 2013).

An additional group (butyryl) was attached to the KGM acetate to produce mixed esters varying in the DS (Danjo, Enomoto-Rogers, Takemura, & Iwata, 2014). The mixed esters had number based molecular weights of 3–6 $\times 10^5$ and DP of $> 1 \times 10^3$. The mixed esters had a much higher decomposition temperature (~360 °C) than KGM (274 °C). The acylation of hydroxyl groups of KGM much decreased the intramolecular dehydration, improving the thermostability. The mixed esters of KGM were made into transparent films (Danjo et al., 2014). Increasing DS of acetylation increased the tensile strength of the films, whereas increasing DS of butyrylation enhanced the elongation at break. This is possibly due to the plasticizing effect of butyryl group. The resulting films had comparable mechanical properties to those of commonly used polymers such as PMMA, suggesting the potential commercial applications of KGM based films (Danjo et al., 2014).

2.1.2. Acylation with acyl carbon chains for film formation

Apart from KGM acetate and butyrate as described in the previous section, KGM was acylated with acyl carbon chains (n from 2 to 12) (Enomoto-Rogers, Ohmomo, Takemura, & Iwata, 2014), which has been the only systematic study on KGM acrylated with different carbon chain lengths so far. DS of these KGM esters reached 3 with DP varying from 0.9×10^3 (KGM laurate) to 2.6×10^3 (KGM propionate). Increasing carbon number of acyl chains decreased the glass transition temperature (T_g) of the samples. KGM acetate (described in the above section) was also acylated with acyl carbon chains (n from 3 to 18). These mixed esters had DS ranging from 0.7 (KGM acetate stearate) to 2.2 (KGM acetate propionate) and DP varying from 100 (KGM acetate palmitate) to 330 (KGM acetate butyrate). Therefore, KGM was partially degraded during the synthesis of the mixed esters. The mixed esters of KGM had higher T_g than those of respective homoesters. The acyl groups introduced onto KGM may disrupt the molecular interactions and the hydrogen bond formation. The esters were insoluble in ethanol and water but soluble in tetrahydrofuran, ethyl acetate, and chloroform. The esters were dissolved in chloroform and casted into transparent and colorless films (Enomoto-Rogers et al., 2014). Increasing chain length of acryl groups increased the elongation at break, while decreasing the Young's moduli and tensile strengths of the films. Overall, it becomes obvious that the functional properties of the films of KGM esters could be mostly controlled by the type and DS of acryl groups (Danjo, Enomoto-Rogers, Takemura, & Iwata, 2014; Enomoto-Rogers et al., 2013, 2014).

2.1.3. Carboxymethylation for film formation, paper strengthening, and controlled release

Carboxymethyl KGM (CKGM) is one of the most commonly used modified KGM. The introduced carboxymethyl group decreased the interactions (intermolecular hydrogen bonding) among KGM, rendering the KGM more liquid like (Kobayashi, Tsujihata, Hibi, & Tsukamoto, 2002). The effect of carboxymethylation on the water binding properties of KGM was further studied (Xiao, Dai, Wang, Ni, & Yan, 2015). The modification decreased the equilibrium moisture content (25 °C), water absorption, and solubility of KGM. Atomic force microscopy (AFM) analysis showed that the modification increased the folding of the KGM molecules, possibly making them less interactive with water molecules (Xiao et al., 2015).

CKGM was mixed with soy protein isolate (SPI) to produce biodegradable films (Wang et al., 2014). Both hydrogen bonding and Maillard reactions occurred between CKGM and SPI, making the two components compatible. The interactions increased the tensile strength and elongation at break, while decreasing the oxygen permeability of the composite films. Increasing CKGM proportion decreased the surface roughness and water adsorption, while increasing the surface wettability of the films (Wang et al., 2014). The decreased water adsorption could be attributed to the increased hydrophobicity of KGM by carboxymethylation as described by Xiao et al. (2015).

CKGM has been used as a paper strengthening agent (Wang, He, Wang, & Song, 2015). Addition of CKGM (0.9%) increased the density,