



## Study of effects and conditions on the solubility of natural polysaccharide gum karaya

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### ABSTRACT

Natural polysaccharide gum karaya (GK, *Sterculia urens*) is a plant exudates widely available and relatively cheap biomaterial, which is used in food industry. However, GK is insoluble in water and it limits subsequent processing and broader utilization in medicine. Different conditions for the solubilization of GK were evaluated in this work (e.g. type and concentration of hydroxide, concentration of GK dispersion and time of solubilization process) which were not published before. GK samples were compared using different types of characterization techniques such as ATR-FTIR, NMR, TGA-FTIR, DSC, SEM and rheology. Optimized conditions for successful GK solubilization proceeded with 1 mol l<sup>-1</sup> of sodium or potassium hydroxide and 2 wt% dispersion of GK at room temperature. A novel mechanism was suggested and by this mechanism the complex plant based biopolymer can be solubilized through the careful control of its ionic environment and degree of deacetylation. Resulted water soluble GK seems to be promising biomaterial forming hydrogels useful in regenerative medicine.

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### 1. Introduction

Natural gums are widely available and relatively cheap material with interesting properties. Gums are commonly utilised in commercial food additives, pharmaceutical industry and in medicine e.g. in development of hydrogels for wound dressings and drug delivery systems (Mirhosseini & Amid, 2012). However, some gums are naturally insoluble in water. For example gum karaya (also *Sterculia gum*) is insoluble in water which could restrict its further use. Thus, complex study of different solubilisation conditions and comparison of insoluble and soluble material is desirable.

GK is a natural gum exudate of the *Sterculia urens* tree belonging to the family *Sterculiaceae* (Singh & Vashishtha, 2008; Singh, Sharma, & Pal, 2011). It is a branched and partially acetylated

polysaccharide which is hydrophilic, anionic nature and it is obtained as a calcium and magnesium salt (Babu, Prasad, & Ramana Murthy, 2002; Silva, Brito, de Paula, Feitosa, & Paula, 2003; Singh et al., 2011). GK is a tree sap (Panda, 2010) and contains β-D-galactose, L-rhamnose, β-D-glucuronic acid and D-galacturonic acid and other residues (Verbeken, Dierckx, & Dewettinck, 2003).

The wide interest in GK-based biomaterials is due to the unique combination of features such as biocompatibility, high swelling and water retention capacity, high viscosity, gel and film forming, adhesion abilities and high molecular mass (Le Cerf, Irinei, & Muller, 1990; Singh & Sharma, 2008). GK is also resistant to hydrolysis by mild acid and it is partly resistant to bacterial and enzymatic degradation (Verbeken et al., 2003).

Original gum karaya (OGK) is insoluble and only swells in water. The swelling behaviour of GK is caused by the presence of the acetyl groups (8 wt%) (Le Cerf et al., 1990; Verbeken et al., 2003). GK powder absorbs water and swells up to 60–100 times of the original volume, producing a viscous dispersion (Verbeken et al., 2003). Previous works showed increasing solubility of GK by alkali treatment (most commonly are used sodium hydroxide (NaOH),

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potassium hydroxide (KOH) and ammonium hydroxide (NH<sub>4</sub>OH) attributed to the GK deacetylation resulted in soluble form (SGK) similarly as for other acetylated polysaccharides.

NH<sub>4</sub>OH treatment of OGK was used by Le Cerf et al. (1990). OGK dispersion (2 g l<sup>-1</sup>) was stirred for 5 h in cold water and then treated by NH<sub>4</sub>OH for one hour at pH 10. This method was taken over by Vinod, Sashidhar, Suresh, et al. (2008) and Vinod, Sashidhar, Sarma, & Vijaya Saradhi, 2008 for the deacetylation of OGK and gum kondagogu, respectively. Different reaction temperature and time for OGK deacetylation by NH<sub>4</sub>OH was studied in work by (Patra, Vojtova, & Martinova, 2015).

Solubilisation of OGK by NaOH was used in study by (Zhang, Du, Xu, & Zhang, 2009). OGK (100 g) was added into 1000 ml of NaOH solution (4 wt%) and gently shaken for 24 h at 60 °C. NaOH was also used for the treatment of *Sterculia striata* (Brito, Sierakowski, Reicher, Feitosa, & de Paula, 2005; Brito, Silva, de Paula, & Feitosa, 2004). Equal volume of a 1 mol l<sup>-1</sup> NaOH solution was added to 1% polysaccharide solution and the system was stirred for 20 min at room temperature. Study by Vinod & Sashidhar (2010) used NaOH for solubilisation of gum kondagogu dispersion (1 g l<sup>-1</sup>). Three volumes of this solution were mixed with one volume of 1 mol l<sup>-1</sup> NaOH solution for 20 min at room temperature with gentle agitation. Deacetylation of OGK was also carried out by (Patra et al., 2015) by adjusting pH of 1 wt% GK dispersion by NaOH at 40 °C.

KOH has not been utilised for OGK deacetylation. However, 0.2 mol l<sup>-1</sup> KOH was used for example for dissolving rhamnsan gum at room temperature for 12 h under nitrogen atmosphere (Tako, Tohma, Taira, & Ishihara, 2003) and by (Khouryieh, Herald, Aramouni, Bean, & Alavi, 2007) for deacetylation of xanthan gum (0.2% w/v) with adding 0.025 mol l<sup>-1</sup> KOH and 0.1% (w/v) KCl for 2.5 h at room temperature under nitrogen atmosphere. Finally, the effect of NaOH and KOH (0.0025; 0.005 and 0.01 mol l<sup>-1</sup>) on the deacetylation process of xanthan solution (0.5 and 1%) for 3 h at 25 °C was compared in (Pinto, Furlan, & Vendruscolo, 2011).

This work reports the effects of different parameters on the solubilisation process of GK such as type and concentration of hydroxide, concentration of GK dispersion and time of solubilisation process evaluated by extensive characterisation of prepared samples by ATR-FTIR, NMR, TGA-FTIR, DSC, SEM and rheology. This work originally compares different types of used hydroxide such as NaOH, KOH, lithium hydroxide (LiOH) and NH<sub>4</sub>OH, optimizes conditions for solubilisation of GK and proposes mechanism of solubilisation process, which is important for example for the gelation mechanism understanding and hydrogels preparation useful in many biomedical applications.

## 2. Materials and methods

### 2.1. Chemicals

Gum karaya was purchased from Sigma-Aldrich ( $M_w$  of approx. 9 500 000 g mol<sup>-1</sup>), NaOH, KOH, LiOH, NH<sub>4</sub>OH and hydrochloric acid were purchased from Lach-Ner, s.r.o., Czech Republic, ethanol (96%) was obtained from Moravian distillery of Kojetín, Czech Republic, ultrapure water type II (ISO 3696) was prepared by Millipore Elix 5 instrument.

### 2.2. Solubilisation and purification of original gum karaya

Powder of OGK was stirred in ultrapure water at a speed of 300 rpm for 24 h at room temperature to obtain dispersion. Solubilisation was carried out following the deacetylation method

described in (Lee, Ashby, & Day, 1996). Briefly, dispersion of OGK was solubilised by NaOH, KOH, LiOH and NH<sub>4</sub>OH. Three volumes of OGK dispersion were mixed with one volume of hydroxide solution and stirred for certain time (from 5 min up to 24 h) at room temperature. Conditions of solubilisation are described in Table 1.

Diluted hydrochloric acid (1 and 0.1 mol l<sup>-1</sup>) was used for the neutralisation of hydroxide excess after OGK solubilisation. The solubilised samples were filtered through polypropylene filters (pore size of 42 µm) and centrifuged (MPW-350R Med. Instruments) for 40 min at 40 °C, 15 000 rpm to remove impurities. After that the samples were filtered again through paper filter MN 616 md (pore size 4–7 µm). Samples were precipitated with ethanol in ratio of 2:1 and air-dried for 24 h. Dry samples were powdered and stored in a glass vial.

Names of samples have been created in order to distinguish easier among different samples and their solubilisation parameters. First number belongs to the concentration of GK dispersion, letters refer to type of hydroxide, number in brackets is connected with concentration of hydroxide and last number is time of process. If there is no number in brackets, the concentration is always 1 mol l<sup>-1</sup>.

### 2.3. Characterisation

#### 2.3.1. Attenuated total reflectance - Fourier transform infrared spectroscopy

Infrared spectra were recorded with Fourier transform infrared spectrometer (FTIR) Tensor 27 (Bruker) between 4000 and 650 cm<sup>-1</sup>. Samples were analysed in powder form in attenuated total reflection mode (ATR) with diamond crystal. The number of scans was 32 and the resolution was 4 cm<sup>-1</sup>.

#### 2.3.2. Carbon nuclear magnetic resonance

Carbon nuclear magnetic resonance (<sup>13</sup>C NMR) spectrum of OGK was recorded on a 500 MHz Bruker AVANCE III spectrometer, equipped with 10 mm selective dualprobe C–H–D PASEX (frequency 125.78 MHz for <sup>13</sup>C nuclei). <sup>13</sup>C NMR spectra of two solubilised samples were measured on a 700 MHz instrument Bruker AVANCE III HD using 5 mm high sensitive cryoprobe CP TXO C/N–H–D (frequency 176.08 MHz for <sup>13</sup>C). All spectra were measured in mixture D<sub>2</sub>O/H<sub>2</sub>O (10:90) solutions (OGK in form of gel) at 45 °C. Chemical shifts are reported in ppm relative to standard tetramethylsilane (TMS).

#### 2.3.3. Asymmetrical flow field-flow fractionation

An asymmetrical flow field flow fractionation (A4F) system Eclipse AF4 coupled with an Agilent 1260 chromatographic system was used for the characterisation of sample 2NaOH\_05. The sample was prepared in ultrapure water at the concentration of 2 mg mL<sup>-1</sup> and left to dissolve overnight and then filtered with a 0.45 µm filter. The carrier was 0.1 mol l<sup>-1</sup> NaNO<sub>3</sub> at a detector flow of 1 ml min<sup>-1</sup>. A 25 cm long channel with spacer of 350 µm and the cross flow gradient was used for the separation. The detectors were a MALS photometer HELEOS II and a refractive index detector Optilab T-REX. The Eclipse AF4 and the detectors are manufactured by Wyatt Technology Corporation.

#### 2.3.4. Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy

Thermogravimetric analysis (TGA) was taken on a thermogravimeter Discovery TGA (TA Instruments) under nitrogen atmosphere (25 ml min<sup>-1</sup>) at heating rate of 10 °C·min<sup>-1</sup>. Platinum pans

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