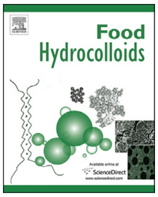
Food Hydrocolloids 41 (2014) 44–52

Contents lists available at ScienceDirect

Food Hydrocolloids

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



# Impact of sucrose and trehalose on different agarose-hydrocolloid systems

Natalie Russ*, Birgitta I. Zielbauer, Thomas A. Vilgis

*Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany*

ARTICLE INFO

*Article history:*
Received 31 October 2013
Accepted 18 March 2014
Available online 29 March 2014

*Keywords:*
Agarose
Alginate
Xanthan
Disaccharide
Viscoelasticity
Water holding capacity

ABSTRACT

Adding high amounts of sugar influences the physical properties of hydrocolloid systems enormously, due to their mutual interactions with each other as well as with water molecules. The impact of the two disaccharides sucrose and trehalose on the thermo-mechanical properties of agarose based hydrogels is investigated. Agarose, a typical gelling agent, is combined with the nongelling agents sodium-alginate and xanthan, two polyelectrolytes which differ significantly in their flexibility. Material properties, such as viscoelasticity, water holding capacity, gelling temperature and thermal stability can be adapted by the controlled addition of sugar. These properties are investigated by strain and temperature dependent oscillatory rheological measurements as well as by controlled drying experiments. The experiments clearly indicate the competition of the different carbohydrates for water. The differences in water binding of sucrose and trehalose are clearly visible. A phenomenological model is presented and illustrates the different effects of the sugar molecules on the hydrocolloid systems. It is suggested that hydrate shells and the differences in local water binding on atomistic and nano scales have strong effects on macroscopic properties.

## 1. Introduction

Hydrocolloids are widely used in daily life and especially in the food industry to improve the quality and to adjust the texture of different food products. They are well established as thickening additives, as gelling agents or to stabilize dispersions and solutions. Additionally, their applications in different food products are often affected by the presence of high sugar concentrations, which are used as sweeteners or to change the texture of the resulting product to produce an overall acceptable mouth feel. For many products such as confectionery, candies and bakery products, high sugar concentrations are essential since they define the local physical interactions of proteins, starches and hydrocolloids, which may have been added as stabilizers and texturizers. In this study the impact of the disaccharides sucrose and trehalose on the thickening properties of well-defined model systems, rather than on real foods, which are multicomponent materials with many competing interactions, is investigated. Nongelling hydrocolloids such as alginate (in the absence of bivalent calcium ions) and xanthan have been chosen, and the impact of sugar addition on the gelling properties of agarose and the composite gels agarose–alginate and agarose–xanthan is studied.

For some basic information about the chemical and physical properties of the hydrocolloids agarose (Imeson, 2010; Stanley, 2006), xanthan (Sworn, 2010; Urlacher & Noble, 1999) and alginate (Clare, 1993; Onsøyen, 1999) the reader is referred to the literature. The gelation mechanism and final gel properties of agarose and its modification by additions of non-gelling hydrocolloids with different flexibility have been the main topic of previous work (Russ, Zielbauer, Koynov, & Vilgis, 2013). The gelation of agarose consists of a two-step mechanism with an initial helix formation and subsequent aggregation of the helices (Nordqvist & Vilgis, 2011; Normand, Lootens, Amici, Plucknett, & Aymard, 2000). The addition of the nongelling agents xanthan and alginate influences this gelation mechanism in different ways. Xanthan molecules in solution behave as charged and very stiff, almost rigid rods which undergo above a critical concentration, a so-called non-equilibrium jamming transition (Edwards & Vilgis, 1986), resulting in an immobilization of the rods at random positions with random orientations. This rigid and randomly oriented structure of the ensemble of xanthan rods reduces the mobility and diffusion of the dissolved and homogeneously distributed agarose chains. Consequently, the gelation of agarose under spatial restrictions limits the elasticity and stability of the network. Alginate in contrast, consists

---

* Corresponding author. Tel.: +49 6131 379149.
*E-mail addresses:* russ@mpip-mainz.mpg.de (N. Russ), zielbauer@mpip-mainz.mpg.de (B.I. Zielbauer), vilgis@mpip-mainz.mpg.de (T.A. Vilgis).

http://dx.doi.org/10.1016/j.foodhyd.2014.03.020

as well as agarose of entangled and flexible polymer coils, which hardly hinder the diffusion of the agarose chains and the gel formation. Additionally the flexible alginate coils get incorporated into the meshes of the agarose network where they act as reinforcing fillers, resulting in a more stable and elastic network. Most of these effects are ruled by large scale conformational chain properties, long range interactions between charges and short range dipolar interactions, in contrast to other properties induced by low molecular weight sugars.

The addition of low molecular weight sugars to hydrocolloid solutions or gels influences the physical properties of those by competing effects on local length scales. It will be shown below, that local interactions (hydrate shells, additional hydrogen bonding) have a strong effect in macroscopic quantities like moduli and viscosity (Fioretto et al., 2013). Adding sugar to hydrocolloid systems at constant polymer concentrations leads to a "replacement" of free water by sugar molecules, leading to an effectively increased hydrocolloid concentration with respect to the amount of solvent. Therefore the distance between the polymer chains decreases, and the mean intermolecular polymer–polymer interactions increase. Moreover, the sugar molecules compete with the hydrocolloids for the available water to form hydrate shells. On the other hand, the sugar molecules can interact with the polymer chains of the hydrocolloids via hydrogen bonds or minimalize the electrostatic repulsion in polyelectrolytes.

In this study, two disaccharides, sucrose and trehalose, are investigated. Sucrose consists of glucose and fructose combined by a (1, 2)-linkage, whereas trehalose is composed of two glucose rings with a (1, 1)-bond. These two disaccharides strongly differ in their interactions with water molecules, due to differences in their chemical structure regarding the positions and orientation of their hydroxyl groups (Gharsallaoui, Rogé, & Mathlouthi, 2008). The dynamic state of water molecules around the sugar molecules in solution depends on the polar interaction between water and sugar molecules, which is affected by the number of equatorial hydroxyl groups ($n(e\text{-OH})$). Uedaira, Ikura, and Uedaira (1989) proposed that the sugar molecules, possessing a higher number of $e$-OH groups per molecule have a stronger stabilizing effect on the water structure. Sucrose has a high solubility in water, whereas the trehalose molecules with their higher $n(e\text{-OH})$ interact very strongly with the water molecules via hydrogen bonds, resulting in a higher water holding capacity (Branca et al., 2001). The differences between mono- and disaccharides in affecting hydrocolloid properties have been addressed elsewhere (Maurer, Junghans, & Vilgis, 2012).

In order to evaluate the impact of sucrose and trehalose on the mechanical and thermal properties of the different hydrocolloid systems, amplitude and temperature dependent oscillatory rheology measurements have been performed. Additionally, the water holding capacity of the different gels was examined by drying them under defined conditions. Based on these results, simple models are proposed to describe the impact of sucrose and trehalose on the gelling and thickening properties of agarose, xanthan and alginate as well as on their mixtures agarose–xanthan and agarose–alginate.

## 2. Materials and methods

### 2.1. Materials

Agarose (CAS No. 9012-36-6) was purchased as fine white powder from Fisher Scientific GmbH with a specific gelling temperature ($T_{\text{gel}}$) between 34 and 45 °C and a gel strength of >1000 g/cm$^2$ as given by the producer. Na-alginate (CAS No. 9005-38-3) was purchased from Sigma–Aldrich Chemie GmbH. Xanthan gum (reinst, E-415, CAS-No. 11138-66-22) was from Carl Roth GmbH & Co. KG. Sucrose (CAS No. 57-50-1) and trehalose (CAS No. 99-20-7) were purchased from Theka Analytical and Acros Organics (Thermo Fisher Scientific Inc.), respectively. Sucrose had a purity of ≥99.0% and D-trehalose was about 99% anhydrous.

### 2.2. Sample preparation

1%, 1.25% and 1.7% w/w of agarose was dispersed in distilled water or in the appropriate sugar (sucrose or trehalose) solutions with 20% and 40% w/w. For the moisture content analysis, sugar solutions with 10 and 30% w/w were used additionally. The dispersion was heated up to 90 °C and kept there for 5 min while stirring (200 rpm). By using a contact thermometer and a snap-cap vial, a constant temperature of 90 °C and minimal water evaporation could be assured. After 5 min the hot clear solution was poured into moulds with a defined geometry. For the amplitude-sweep tests, moulds with a diameter of 25 mm and a height of 3 mm and for the moisture content analysis moulds with 50 mm diameter and a height of 1 mm were used. Excess solution was wiped off with a broad razor blade. The solution was allowed to cool down to room temperature for 15 min, then the moulds were removed and the set gels hardened in the refrigerator at 4 °C for 24 h. To produce the 1-1 mixtures of agarose–alginate and agarose–xanthan, the pure xanthan or alginate dispersions have been prepared first. For this, 1%, 1.25% and 1.7% w/w of the xanthan and alginate powder were dispersed in distilled water or sugar solutions and stirred for 24 h at room temperature at 200 rpm. Then 1% w/w agarose was dispersed in distilled water or sugar solution like before and mixed in a 1-1 ratio with the hydrocolloid dispersions. The mixture was shaken by hand and heated up again to 90 °C for 5 min while stirring at 200 rpm. Afterward the gels hardened as described above, first at room temperature and then in the refrigerator.

### 2.3. Dynamic viscoelastic measurements

The measurements of the viscoelastic properties as well as the sol–gel transition of the hydrocolloids were carried out with a stress controlled rheometer (Bohlin Gemini 200, Malvern, UK). Two different tests were performed: amplitude-sweep test and temperature-sweep test.

Amplitude tests were performed for $\gamma = 0.001$-1 at a constant frequency $f = 1$ Hz and temperature $T = 25$ °C. Five periods per point were measured with a delay time of 0.5 s and an integration time of 5 s. Measurement of five different samples were averaged and the standard deviation taken as error. The plateau modulus $G'$ has been extracted from these averaged curves at a strain well in the linear viscoelastic region. Alginate solutions and xanthan dispersions were measured with a stainless steel coaxial cylinder (C25, Malvern, UK) while for gelled agarose samples a plate–plate geometry of stainless steel with a diameter of 25 mm was used. For the latter, an adequate contact between samples and measuring system without significant compression of the sample had to be ensured. Therefore the gap size for each sample was set manually. After inserting the sample, the upper plate was set to a gap of 3000 μm and lowered in steps of 100 μm until the contact between sample and plate was distinct and visible. To avoid slippage of the samples at high deformations, sandpaper with a grain size 80 was glued onto both plates.

The temperature-sweep test yields information about the sol–gel transition and the thermal stability of the hydrocolloid gels. Storage $G'$ and loss $G''$ modulus are measured as a function of temperature with $f = 1$ Hz and strain $\gamma = 0.001$ or 0.01. Integration and delay time were the same as for the amplitude-sweep. Here three different samples for each system investigated were measured and the results were averaged. 1350 μL of the hot and