Thermochimica Acta 596 (2014) 63–69

Contents lists available at ScienceDirect

Thermochimica Acta

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

Gel–sol–gel transition of kappa-carrageenan and methylcellulose binary systems studied by differential scanning calorimetry

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ARTICLE INFO

Article history:
Received 30 May 2014
Received in revised form 8 September 2014
Accepted 30 September 2014
Available online 5 October 2014

Keywords:
κ-Carrageenan
Methylcellulose
Binary system
Hydrogel
DSC

ABSTRACT

Kappa-carrageenan (κC) was mixed with methylcellulose (MC) with various mixing ratios. Phase transition behaviour of the above mixed solutions with 1 and 2% concentration was investigated by visual observation and differential scanning calorimetry (DSC). Three regimes showing unique transition behaviour were observed: Regime I which is an MC rich region where only sol–gel transition is found, Regime II an intermediate mixing range of κC and MC where sinusoidal change of gel–sol–gel transition was observed, and Regime III a κC rich region where only gel–sol transition was detected. A phase diagram of κC/MC binary systems was established based on transition temperatures obtained by visual observation and DSC.

1. Introduction

It is well known that gelation of polysaccharides is markedly affected by addition of another polysaccharide. Child and Pryce [1] reported nuclear magnetic relaxation times of water restrained by agarose gel. Molecular mobility of water molecules increases when locust bean gum (LBG) is added to agarose. This indicates that junction zone formation of agarose is disturbed by the introduction of LBG [1]. In contrast, it has been shown that xanthan gum forms firm gel when galactomannan or glucomannan is mixed [2–8]. We have reported an ion-complex formation between xanthan gum and chitosan molecules. It was found that the hydrophobic field in the junction zone increases by complex formation [9].

Among various combinations of bi-component polysaccharide systems, binary systems κ-carrageenan (κC) and galactomannan have received particular attention. Many research papers on rheological and thermal properties of binary systems report that functional properties of κC are controllable by addition of galactomannans [10–14]. It is noted that the binary system of κC and xanthan gum [15] and κC and konjac glucomannan [16,17] forms synergistic binary gels. The above studies indicate that functional properties of polysaccharide hydrogels are affected by the introduction of other polysaccharides through specific networks or interpenetrating structures.

κC extracted from red seaweed is a representative polysaccharide and the aqueous solution easily forms rigid gel by cooling. Carrageenans are composed of alternating 3-linked β-D-galactopyranose and 4-linked α-D-galactopyranose or 4-linked 3,6-anhydrogalactose, forming the disaccharide repeating unit of carrageenans [18]. The sulphated galactans are categorized according to the presence of the 3,6-anhydrogalactose on the 4-linked residue and the position and number of sulfate groups. Most major types of carrageenans are classified into three types, known as κ-, ι- and λ-carrageenans. Aqueous solutions of κ- and ι-carrageenans form hydrogel with or without the presence of salt, however, the aqueous solution of λ-carrageenan shows no gelation. It is reported that κC hydrogel is formed after a conformational change of molecular chains from coil to helix in aqueous solution. Molecular conformation of κC aqueous solution and complex transition mechanism have extensively been discussed in order to establish a reasonable molecular model [19,20]. Gel–sol transition temperature of κC is observed at around 30–60 °C, although the temperature depends on molecular mass, concentration and other factors [21,22]. Carrageenans are widely used as viscosity intensifiers in the food and cosmetic industries.

Methylcellulose (MC) is a water soluble cellulose derivative. The hydroxyl groups of cellulose are substituted with methoxyl groups. Degree of substitution (DS) of MC is defined as number of hydroxyl group substituted by methoxyl group in a glucose unit. MC shows unique characteristics and MC gel is formed when aqueous solution is heated. It is reported that MC gel is formed through hydrophobic interaction between adjacent molecular chains with

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http://dx.doi.org/10.1016/j.tca.2014.09.021

methoxyl groups. MC is a thermoreversible hydrogel, accordingly, MC maintains a sol state at room temperature. MC is extensively used as a binder or thickener in pharmaceutical, cosmetic and food applications [23–32].

In this study, κC sol was mixed with MC sol with various mixing ratios and hydrogels were prepared. Phase transition behaviour of the above mixed gels was investigated by visual observation, and DSC. When two kinds of gel-forming polymers, such as MC and gelatin are mixed, a unique and complex phase behaviour, gel–sol–gel transition, is observed [33,34]. Recently, gel–sol and sol–gel thermal transitions of the MC and κC systems at the mixing ratio MC/κC = 1/1 is investigated by small angle X-ray diffractometry (SAX), DSC and rheology [35,36]. The purpose of this study is to establish a phase diagram of MC and κC systems based on the results obtained by thermal measurements in order to control gelation as a function of temperature in a wide range of mixing ratios.

2. Experimental

2.1. Sample preparation

κC in powder form was purchased from Sigma (C1013, commercial grade, Type I). MC in 4000 cP powder form was purchased from Wako Pure Chemical Industries Ltd. DS is 26–33% according to the manufacturer's report. MC was dissolved in deionised water and solutions with concentrations of 1% and 2% were prepared. The solutions were kept at 4 °C for 1 week. κC was dissolved in deionised water and solutions with concentration 1% and 2% were prepared. The solutions were annealed at 105 °C for 2 h. Binary solutions with concentration of 1% and 2% with different mixing mass ratios (MC/κC) = 0/1.0, 0.1/0.9, 0.2/0.8, 0.3/0.7, 0.4/0.6, 0.5/0.5, 0.6/0.4, 0.7/0.3, 0.8/0.2, 0.9/0.1 and 1.0/0 were prepared. Binary solutions were kept at 4 °C before measurements.

2.2. Visual observation of gel–sol–gel temperature

Visual observation of gel–sol–gel temperature was carried out by tilted test tube method. A glass bottle with 10 ml solution was placed in a water bath. A thermometer was inserted in the bottle and the water bath was heated from 5 to 90 °C at the heating rate of 2 °C min^{-1}. The temperatures at which the transparent hydrogel became transparent sol (T_{g-s}), the transparent sol started to become turbid (T_{s-ts}), the turbid sol became a completely rigid turbid hydrogel (T_{s-g}) and phase separation occurred (T_{ps}) were noted. In order to confirm the repeatability of each experiment, the same sample was cooled and heated twice.

2.3. DSC measurement

DSC measurement was carried out as previously reported [21,22]. A Seiko Instruments Inc., highly-sensitive differential scanning calorimeter (DSC) DSC 120 equipped with a cooling apparatus was used. Temperature and enthalpy calibrations were carried out using water. The sol sample was poured into a silver sealed type sample pan. Sample mass was ca. 50 mg and a 70 μl aluminium sealed type sample pan was used. Distilled water was used as a reference. The sample pan was hermetically sealed and the total mass of the sample recorded. The scanning rate was 2 °C min^{-1}. The sample was heated from 25 °C to 100 °C at homogeneous sol state in the sample pan. Then the sample was cooled from 100 °C to 0 °C and heated from 0 °C to 100 °C (first-run measurement). Next, the sample was cooled from 100 °C to 0 °C and heated from 0 °C to 100 °C (second-run measurement). Liquid nitrogen was used as a coolant. A Sartorius ultramicro-balance ($\pm 1.0 \times 10^{-5}$ g) was used for sample mass measurements.

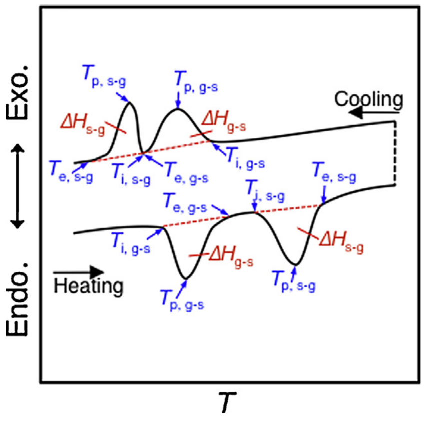

Fig. 1. Schematic DSC curves of κC/MC systems.

Fig. 1 shows a schematic DSC curve of sol–gel and gel–sol transition of samples. From heating curves, the starting temperature of gel–sol transition ($T_{i,g-s}$), peak ($T_{p,g-s}$), end temperature of gel–sol transition ($T_{e,g-s}$), starting temperature of sol–gel transition ($T_{i,s-g}$), peak ($T_{p,s-g}$) and end temperature of sol–gel transition ($T_{e,s-g}$) were defined. $T_{i,g-s}$ was defined as the temperature where DSC curves deviate from the baseline. $T_{e,g-s}$ was defined as the temperature where DSC curves return to the baseline. From cooling curves, the starting temperature of gel–sol transition ($T_{i,g-s}$), peak ($T_{p,g-s}$), end temperature of gel–sol transition ($T_{e,g-s}$), starting temperature of sol–gel transition ($T_{i,s-g}$), peak ($T_{p,s-g}$) and end temperature of sol–gel transition ($T_{e,s-g}$) were defined. The gel–sol transition enthalpy (ΔH_{g-s}) and sol–gel transition enthalpy (ΔH_{s-g}) were calculated from the area of gel–sol transition peak and that of sol–gel transition peak, respectively.

3. Results

Transition behaviour of MC was observed visually revealing (1) transparent sol transforms to turbid sol at 5 °C (T_{s-ts}), (2) turbid sol transforms to clear gel (T_{ts-g}) (3) phase separation occurs by further heating [29]. In κC/MC binary systems, three regimes were found as schematically shown in Fig. 2. Mixing ratios where transparent sol is formed and no gelation observed at 5 °C were categorized into Regime I. κC/MC = 0.1/0.9 system (concentration 1%) and 0.1/0.9 and 0.2/1.8 systems (concentration 2%) correspond to Regime I. By heating, the above binary systems transformed into turbid sol and rigid gel. It is noted that no gelation was observed,

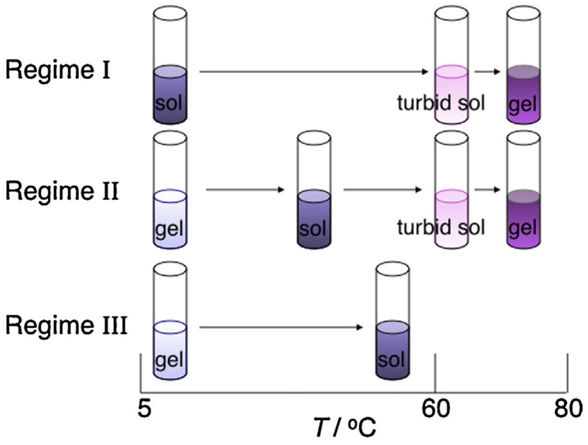

Fig. 2. Illustration of visual observation of κC/MC binary systems as a function of temperature.