Instability of low-moisture carrageenans as affected by water vapor sorption at moderate storage temperatures

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Abstract

Isothermal microcalorimetry was used to study the exothermic heat flow caused by the absorption of water into carrageenans and a furcellaran, leading to their thermodynamic instability under moderate storage conditions (35 °C, $\tau = 12$ h), where τ is the reaction time (h). The net heats evolved by furcellaran, ι -carrageenan, κ -carrageenan, and a mixture of κ/λ -carrageenan were 43.5 J/g, 45.9 J/g, 31.6 J/g, and 28.1 J/g, respectively. The pronounced exothermic behavior of furcellaran was attributed to the enthalpic association of water molecules with the thermally degraded carbohydrate matrix. The responses of a heat treatment of carrageenans at 55 °C, 85 °C, and 105 °C for 15 min on exothermic heat Q (J/g) at different water activities ($a_w = 0.26, 0.51, 0.76$, and 1.0) were measured. The dependence of the net recorded heat Q on water activity can be satisfactorily approximated by the equation $Q = a[1 - (1 - a_w)^b]$, where a and b are the coefficients found by the nonlinear least-squares method. It was concluded that carrageenans affected by excessive heat treatment should be preferably stored with limited water access.

Keywords Carrageenan · Instability · Water sorption · Isothermal microcalorimetry

1 Introduction

The success of any new product depends on the quality of its flavor, color, and texture, its stability under various storage conditions and its safety. These factors are intimately related to the ingredients in the food product and to the physical processes and handling procedures to which it has been subjected [1]. Particularly organic materials may involve problems because of the liability of macromolecules to structural alterations, resulting in different physical responses of the material: mechanical, thermal, optical, etc. This leads to the diminished functionality and undesired failure of the product [2].

The physical properties of any food are dictated by the complex behavior of its macromolecular constituents in

their natural forms and as modified during processing and storage [3].

Industrial gums, which for the most part are water-soluble polysaccharides, are well-known ingredients in the marketplace and are used increasingly for both food and nonfood processing [4, 5]. Carrageenans, one of the most important algae polysaccharides originating from various Florideophyceae species, form a family of linear sulfated galactans built up of alternating 3-linked β -D-galactopyranose and 4-linked α -D-galactopyranose residues with a variable 3,6-anhydro ring [6]. The three main types of carrageenans are kappa (κ -), iota (ι -), and lambda (λ -) carrageenan. They have one, two, and three sulfate ester groups per dimer, respectively. κ - and ι -carrageenans contain 3,6-anhydrogalactose units, whereas λ -carrageenan has no 3,6-anhydrogalactose

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group [7]. Furcellaran is a type of κ -carrageenan whose major structural difference is a smaller degree of sulfation (17–18%) [8].

The principal property of these polysaccharides is their easy hydration to produce aqueous solutions possessing high viscosities and/or steady gels at low concentrations. The development of the desired properties, in general, is controlled by their structure–water associations in high-moisture systems [9].

Under normal humidity, galactans generally equilibrate to contain 8–12% moisture. With such limited water access, various food polysaccharides exist in an amorphous, metastable state, which has an effect on stability and rates of deteriorative changes [10, 11]. It is well recognized that the state diagram showing relationships between glass transition temperature T_g and water content W_{H_2O} (g/100 g of solids), depending on water activity a_w , has a fundamental significance in the characterization of the physical state of such materials [12]. In general, the sorption isotherms ($W_{H_2O} = f(a_w)$) are recorded thermogravimetrically without a need for heat transferring ($\pm$) evaluation. If such an evaluation becomes necessary, e.g., for sorption isosteric heat (Q^{st}) determinations, the Clausius–Clapeyron equation has been applied in most of the studies previously cited [13, 14].

Recently, it was noticed that some batches of the stored furcellaran powder showed an exothermic heat flow resulting in a local self-browning and limited burning as well.

In general, the pronounced exothermic behavior is attributed to the onset of pyrolytic degradation, which in fact takes place under very abusive conditions [15, 16]. Typically, differential scanning calorimetry (DSC) has been used to probe the thermal properties of polysaccharides at low moisture, whereas the primary thermal output has been registered as an endothermic event controlled by T_g [17, 18]. To the contrary, Mitsuiki and coworkers [19] found a clear shift in exothermic heat flow and observed corresponding peaks in the derivative of the heat flow curve ($dDSC$) at $\sim 90^\circ\text{C}$ and 40°C for agar containing 22.8% of water and carrageenan with 25.1% of water, respectively. It has also been reported that galactans have no glass transition behavior [20]. Later it was proved that gel-derived agars exhibit a small endotherm in the range of 55 – 70°C ; at higher temperatures, a larger endotherm with an associated enthalpy change (32 J/g ; 15.9% water) was observed. In contrast to the gel-derived agars, the roller-dried samples showed no corresponding endothermic transitions above 100°C , while a small endotherm at 50 – 70°C was still monitored [21].

So, no clear evidence of exothermic heat flow for galactans at moderate temperatures was found. However, it is known that the amorphous sugars may sorb large amounts of water from their surroundings, resulting

in crystallization during storage above a critical, temperature-dependent relative humidity [22]. An exotherm occurring in DSC scans has been attributed to the instant crystallization of sugars [23]. Therefore, considering that a feature of the reported furcellaran was its dehydration by the roller (drum)-drying procedure, contrary to a typical gel-processed technique, the pronounced exothermic behavior was attributed to an enthalpic association of water molecules with the thermally modified carbohydrate matrix.

The purpose of the present study was to determine the effect of the exothermal phenomenon in isothermal conditions, considered here to be due to the structural transformation and following water interaction with the affected furcellaran/carrageenan powders, resulting in subsequent wetting and crystallization of the sugars.

2 Materials and methods

2.1 Materials

Commercial furcellaran was supplied by Est-Agar AS (Kärle, Estonia). It is a typical product extracted from *Furcellaria lumbicalis* (Gigartinales), with subsequent drum-drying in the final step. The three various carrageenan samples analyzed in this study were obtained from Sigma-Aldrich (USA).

High-purity standards of sodium chloride NaCl 6.0 molal in H_2O ($a_w = 0.76$) and lithium chloride LiCl 8.57 molal in H_2O ($a_w = 0.51$) and LiCl 13.41 molal in H_2O ($a_w = 0.26$) were purchased from Decagon Devices, Inc. (USA). For $a_w = 1.0$ distilled water was used. Values of water activities are given at temperature 35°C .

2.2 Preparation of samples for measurement

The delivered samples of furcellaran and carrageenan were stored in sealed plastic containers at room temperature (20°C) until used either for direct microcalorimetric measurements or optional preheating before the thermal analysis.

The water content of each sample was determined by loss on drying (L_D , %) after heating at 105°C to constant weight. The measurements were carried out at least twice; when values were different by $> 1\%$, the number of measurements was increased.

The optional preheating was carried out according to the method described by [24] with a Halogen Moisture Analyzer HR 73 (Mettler Toledo, Switzerland). The selected temperature range was 55 – 105°C , and the time of treatment 15 min. The residual moisture content of the samples

was expressed by L_D if necessary. The preheated samples were stored in a desiccator over P_2O_5 until used, within 6 h.

2.3 The microcalorimetric measurement of heat flow

The calorimetric experiments were performed using a Thermal Activity Monitor TAM IV built up as an isothermal heat conduction microcalorimeter (TA Instruments, Delaware, USA). The furcellaran or carrageenan sample (of 100 mg) was quantitatively transferred into a standard 3 ml glass ampule. Additionally, a small glass container (*microhygrostat*) with a saturated salt solution was placed inside the glass ampule immediately before sealing it. The operated sample maintained well-defined relative humidity ($a_w = RH/100$) all through the reaction time of 12 h. The heat flow due to any changes in the powder as a consequence of the humidity was recorded. Four parallel experiments under various RH against blank with deionized water (2 ml) were run simultaneously at 35 °C. Power–time curves were registered using the data acquisition program Digitam 3.0 (TA Instruments, Delaware, USA).

Minimum duplicated measurements for each testing sample were made, and mean values were used for further analysis.

2.4 Statistical analysis

Curve fitting was performed with a brute force nonlinear least-squares method from an R 3.6.0 (R Foundation for Statistical Computing, Vienna, Austria) package “nls2” version 0.2.

3 Results and discussion

The measuring principle of TAM is based on registering heat flow rate between the sample vessel and heat sink detected by Peltier effect plates [25, 26].

The TAM IV responses for a commercial furcellaran containing 11.2% w/w water and equilibrated at $a_w = 0.26$, 0.51, 0.76, and 1.0 are shown in Fig. 1. The absorption of the samples at water activity of 0.51, 0.76, and 1.0 produced exothermic responses, and the curves showed similar shapes. It could also be proposed that the absorption response is the sum of two exotherms, the absorption and the blank response, as is common for some salt solutions [27]. In the latter case, the hydration of water-binding sites along furcellaran polymer chains will dominate in the subsequent processes. The effect of increasing the water activity is clearly related to an increase in the amount of heat released during absorption process. The increase in the heat flow of absorption ranged from about 45 to 310 μW

Fig. 1 Typical calorimetric curves on TAM for furcellaran at four different water activities. Experiment conditions: temp. 35 °C, $m = 0.890$ g

for water activity of 0.51 and 1.0, respectively. However, the sample at water activity 0.26 produced a slight endothermic response indicating the desorption process.

Although the calorimetric response for isothermal water sorption studies is balanced between the exotherm(s) and endotherm(s), heat emitted by furcellaran was evident. The released heat Q (J/g) was expressed as Eq. (1) [28]:

$$Q = \int \Phi d\tau \quad (1)$$

where Φ —heat flow rate (μW) and τ —reaction time (h) are equal to the net area under the curve. The total heat evolved during an experiment is large enough to be detected and shows variation between furcellaran samples at different water activities. The value ranges from 0 to 43.5 J/g depending on applied a_w (Table 1).

In order to compare the calorimetric response for furcellaran with other glycans, three carrageenan samples (three replicates for each one) were examined under the same experimental conditions ($a_w = 0.26$, 0.51, 0.76, and 1.0). The example of corrected calorimetric response (the thermal power within the first 0.52 h was not registered) is shown in Fig. 2, in which the power–time curves for furcellaran and all carrageenan samples were found to be described by Eq. (2):

$$dQ/d\tau = a \cdot e^{b\tau} \quad (2)$$

where $dQ/d\tau$ is the heat flow rate (μW), τ is the reaction time (h), a and b are the coefficients (Table 2) for each sample found by the least-squares method.

For example, the heat flow rate for κ -carrageenan monitored at $a_w = 0.51$ was described by $dQ/d\tau = 132.91 \times e^{-0.38\tau}$.

Most of the experimental curves were well approximated by the simple exponential decay function (Eq. 2). However, it should be noted that in some samples, small

Table 1 Water content of furcellaran and carrageenans for isothermal calorimetry measurement (12 h at 35 °C) at different water activities and the net heat evolved

Sample	Water content L_D , % (w/w)	Experimental net heat evolved Q , J/g			
		$a_w=0.26$	$a_w=0.51$	$a_w=0.76$	$a_w=1.0$
Furcellaran	11.2	0	6.3	29.3	43.5
ι-carrageenan	9.4	0.41	15.1	37.5	45.9
κ-carrageenan	6.7	0	10.6	28.6	31.6
κ/λ-carrageenan	9.9	0	4.7	22.6	28.1

Fig. 2 Corrected calorimetric curves on TAM for κ-carrageenan ("blue circle" denotes experimental data; "red solid line" denotes calculated curve). Experiment conditions: temp. 35 °C, $a_w=0.51$, $m=0.1004$ g

deviations were observed indicating that potentially more complex processes are taking place and can be investigated further.

Carrageenans have different thermal outputs depending on their specific compositions. As is evident from data in Table 1, no heat release was observed at $a_w=0.26$, except for ι-carrageenan. The thermal outputs of all samples at higher water activities increased in the same shape of the curve; the highest values were obtained for ι-carrageenan. The thermal outputs of κ- and the mixture of κ/λ-carrageenan were similar, which was expected, as κ-carrageenan dominates the mixture.

It should be emphasized that in our research there were no strict criteria for the selection of carrageenans; for example, no processing or composition varieties were taken into account.

It is also important to stress that the experimentally measured net heat values shown in Table 1 form ca 85% of those calculated by fitting $dQ = (a \times e^{bt})dt$ because at the beginning of an experiment (0.52 h = 31 min) (Fig. 1) the heat flow cannot be recorded until the system has stabilized. The final moisture content in the sample was determined by moisture equilibrium with atmosphere at a given temperature. Practically, this means that if the sample was previously dehydrated below its equilibrium water content, it would ultimately absorb some water at the same relative humidity until equilibrium was reached. But it could also be expected that the equilibrium water content would depend on the thermal history relevant to the process of studied material. One possible explanation is that the furcellaran ($L_D=11.2\%$) used in this study had more pronounced water uptake in comparison with carrageenans ($L_D=6.7\text{--}9.9\%$) under the same environmental conditions, considering that it had passed through a previous severe heat treatment in drum-drying.

In the next series of experiments, furcellaran and carrageenans were subjected to optional heat treatment at 55 °C, 85 °C, and 105 °C for 15 min. The processed samples were monitored by isothermal microcalorimetry depending on a_w (Fig. 3). It became apparent that the calorimetric response depended on the depth of the applied optional heat treatment. The mathematical evaluation of the results expressed in Fig. 3 showed that the dependence of the total heat Q (J/g) on water activity a_w could be satisfactorily approximated by Eq. (3):

$$Q = a \left[1 - (1 - a_w)^b \right] \quad (3)$$

where a and b are the coefficients found by the nonlinear least-squares method.

Table 2 Coefficients a and b of furcellaran and carrageenans samples for Eq. 2

Sample	$a_w=0.26$		$a_w=0.51$		$a_w=0.76$		$a_w=1.0$	
	a	b	a	b	a	b	a	b
Furcellaran	–	–	44.30	–0.26	221.52	–0.32	303.80	–0.30
ι-carrageenan	–	–	158.23	–0.35	424.05	–0.43	613.92	–0.56
κ-carrageenan	–	–	132.91	–0.38	322.78	–0.42	449.37	–0.51
κ/λ-carrageenan	–	–	88.61	–0.62	170.87	–0.26	284.81	–0.36

Fig. 3 Heat evolved as a function of water activity for furcellaran and different carrageenans at optional heat treatment temperatures for 15 min. “dashed lines” denote fitted curves; symbols “blue square,” “green triangle,” “red circle” denote experimental data: “blue square” 55 °C, “green triangle” 85 °C, “red circle” 105 °C. Values of the coefficients a and b from Eq. 3 obtained by curve fitting are shown with the corresponding colors. $Q_{55\text{ }^{\circ}\text{C}} = 81.17 [1 - (1 - a_w)^{1.34}]$, $Q_{85\text{ }^{\circ}\text{C}} = 111.44 [1 - (1 - a_w)^{1.79}]$, $Q_{105\text{ }^{\circ}\text{C}} = 117.49 [1 - (1 - a_w)^{1.95}]$

Curves of this type begin from the point [0,0] and asymptotically approach the maximum value a at water activity $a_w = 1$. Visual observation of the regression lines confirmed the goodness-of-fit of the proposed model.

The additional heat treatment reduced the moisture content in the examined samples to the level of 0–3.5%. Therefore, a joint contribution (structural rearrangement and lowered moisture level) to the exothermal heat effect was perhaps possible. But considering that $Q_{85\text{ }^{\circ}\text{C}} = f(a_w)$ and $Q_{105\text{ }^{\circ}\text{C}} = f(a_w)$ still had distinguishing curves, the influence of thermal disordering was probably dominant.

Water activity a_w was closely related to the chemical potential μ determining system at equilibrium, Eq. (4) [29]:

$$\mu = \mu_0 + RT \ln(a_w) = \mu_0 + RT \ln(p/p_0) \quad (4)$$

where μ is the actual chemical potential (kJ mol^{-1}), μ_0 reference state chemical potential (kJ mol^{-1}), R universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T temperature (K), p vapor pressure of water in the headspace above the sample at T (Pa), and p_0 vapor pressure of water in the headspace above the water at T (Pa).

It was predicted that applying heat for the additional processing of carrageenan would destabilize the galactans, thus opening more binding sites for water. Consequently, at higher a_w , the increase in actual chemical potential μ would lead to increased absorption energy. In general, the binding sites included hydroxyl groups of polysaccharides, carbonyl and amino groups of proteins, and other polar sites [2, 30]. Thus, the high-temperature heat treatment of low-moisture carrageenans leads to product instability, increasing water vapor absorption and causing significant increase in heat release even at moderate storage conditions. This process can lead to the possibility of temperature rise over product critical self-ignition temperature.

4 Conclusions

In conclusion, there was a noticeable similarity in the water absorption behavior of carrageenans and furcellaran monitored by the microcalorimeter. The results are: (1) furcellaran and carrageenans are affected by the excessive heat

treatment, so they should be preferably stored with limited water access, and (2) considering the structural similarities between furcellaran and carrageenan, the microcalorimetric assay is proposed as a potential method for the evaluation of the thermal history of the processed samples.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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