

The study of foodstuff rheological and thermal properties

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Doctoral Thesis Summary



Tomas Bata University in Zlín
Faculty of Technology

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Studium reologických a termických vlastností potravin

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SUMMARY

The Doctoral Thesis deals with the issue of rheological and thermal properties of foodstuffs and additives based on polysaccharides and proteins which are widely used as food hydrocolloids.

Rheological analysis was used to determine intrinsic viscosity and flow parameters of polysaccharide solutions (guar gum, κ -carrageenan, xanthan gum) and gelatin/polysaccharide blends. Using suitable rheological models (Ostwald-de Waele and Herschel-Bulkley model), it was possible to define temperature and concentration dependency of flow parameters, the effect of solvent used and to examine the conformational transition of the dissolved polymers.

Rheological analysis of polysaccharides solutions both in distilled water and 0.07M KCl in the temperature range from 20 to 45 °C confirmed the concentration and temperature dependency of the solutions viscosities as reflected in observed changes of flow parameters. The transition from double helical polysaccharide structure to single coil conformation (in salt solution) and the disentanglement of coils' chains (in distilled water) promoted by elevating temperature were proved at temperature about 30 °C by a detectable change of the Kraemer constant temperature dependency.

Gelatin/polysaccharide blends in 0.07M KCl and 0.07M NaCl solutions were studied in the temperature range 25-45 °C by the same rheological models. Flow parameters of the blends were affected by the conformational change of the polysaccharide (helix-coil transition), as well as by the conformational ordering of gelatin, characterized by the dissociation of gelatin triple helices into flexible coils, and gel-sol transition. There was an evident change of the parameters at temperature about 35 °C.

Thermogravimetric analysis and differential thermal analysis were employed to determine thermal properties of powder polysaccharides. The results of thermal analysis showed that powder samples exhibit varying ability to bind moisture depending on their structure. The temperature of the endothermic process (polysaccharide order-disorder transition) was determined at different heating rates. Peak temperature of the endotherm was found in the range 50-85°C, influenced by the applied heating rate and moisture content of the sample. Activation energy (E_a) of the phase transition associated with the kinetics of water evaporation was calculated by several kinetic models (Friedman model, Kissinger model, and Model-free kinetics).

The Arrhenius model was used to evaluate the temperature resistance of the molecular structure of hydrocolloid water and salt solutions, prepared from the powders. Results of the Arrhenius model indicate that energy necessary to promote viscous flow of solutions is higher for samples in distilled water than in 0.07M KCl, suggesting the ion-induced assembly of molecular chains in salt solution. In both cases, E_a was substantially reduced by application of higher shear rate.

ABSTRAKT

Disertační práce se zabývá problematikou reologických a termických vlastností potravinářských látek a aditiv na bázi polysacharidů a proteinů, jež jsou hojně využívány jako potravinářské hydrokoloidy.

Reologická analýza byla využita ke stanovení vnitřní viskozity a tokových parametrů roztoků polysacharidů (guarové gummy, κ -karagenanu, xanthanové gummy) a směsí želatiny a polysacharidu. S využitím vhodných reologických modelů (Ostwald-de Waeleho a Herschel-Bulkleyho modelu) bylo možné určit teplotní a koncentrační závislost tokových parametrů roztoků, vliv použitého rozpouštědla a stanovit konformační přechod rozpuštěných polymerů.

Reologická analýza roztoků polysacharidů v destilované vodě a 0,07M KCl v teplotním rozmezí od 20 do 45 °C potvrdila závislost viskozity roztoků na jejich koncentraci a teplotě, což se projevilo v pozorování změn tokových parametrů. Přechod polysacharidové struktury dvojšroubovic na konformaci jednoduchých klubek (v solném roztoku) a proces rozplétání řetězců klubek (v destilované vodě) stimulované zvýšením teploty byly prokázány při teplotě kolem 30 °C nárůstem teplotní závislosti Kraemerovy konstanty.

Pomocí stejných reologických modelů byly v teplotním rozmezí 25 až 45 °C studovány směsi želatiny a polysacharidu v 0,07M KCl a 0,07M NaCl. Tokové parametry směsí byly ovlivněny konformační změnou polysacharidu (přechod dvojšroubovice-klubko) i konformačním uspořádáním želatiny (přechodem z uspořádané do neuspořádané struktury, tj. disociací želatinových trojšroubovic do pružných klubek), a také gel-sol přechodem želatiny. Změna tokových parametrů byla patrná při teplotě kolem 35 °C.

Pro stanovení tepelných vlastností práškových polysacharidů byla použita termogravimetrická analýza a diferenciální termická analýza. Výsledky termické analýzy ukázaly, že práškové vzorky mají různou schopnost vázat vlhkost v závislosti na jejich struktuře. Teplota endotermního procesu (přechodu polysacharidu z uspořádané do neuspořádané struktury) byla stanovena při různých rychlostech ohřevu. Teplota endotermního píku byla zjištěna v rozmezí 50-85 °C, a byla ovlivněna aplikovanou rychlostí ohřevu a vlhkostí vzorků. Aktivační energie (E_a) fázového přechodu spojená s kinetikou odpařování vody byla vypočtena na základě několika kinetických modelů (Friedmanova modelu, Kissingerova modelu a Model-free kinetics).

Arrheniův model byl použit k vyhodnocení teplotní rezistence molekulární struktury vodných a solných roztoků hydrokoloidů, připravených z příslušných práškových polysacharidů. Výsledky Arrheniova modelu naznačují, že energie potřebná pro viskózní tok roztoků je vyšší u hydrokoloidů v destilované vodě než v 0,07M KCl, což by mohlo implikovat vznik iontově-indukované struktury molekulárních řetězců v solném roztoku. V případě obou typů roztoků byla E_a podstatně redukována aplikací vyšší smykové rychlosti.

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INTRODUCTION

Rheological and thermal properties of food products and additives have a major impact on the food functional properties, shelf life, quality and sensory attributes. Rheological and thermal properties play an important role in the production and storage of many different foods and beverages, and these properties are also important in view of the consistency and overall attractiveness of the products for consumers.

In recent years, many studies have reported on the functional aspects of hydrocolloids and their application within food systems. Many hydrocolloids are widely used in the food industry to extend food shelf life, improve rheological properties of food products and encapsulate flavour compounds. The principal reason for the extensive use of hydrocolloids in the food industry is their ability to bind with water and to modify the properties of food ingredients (Mohammadi et al., 2014; Varela & Fiszman, 2011).

From a chemical point of view, hydrocolloids are mainly polysaccharides obtained from different sources. They are present in various parts of edible plants (starch, guar gum), of algae (carrageenan), of fungi and microorganisms (xanthan gum) (Rhein-Knudsen et al., 2017; Tomasik, 2004). In general, food hydrocolloids are a diverse group of long-chain polymers that are readily dispersive, fully or partially soluble, and prone to swell in water. Although food hydrocolloids are usually present in the final products at concentration less than 1 % (w/w), they may significantly affect the rheological, textural, organoleptic and other properties of many different foods. For example, guar gum provides relatively high viscosity to the liquid foods even at low concentrations, and this fact can be a limiting factor in the relevant production (Cevoli et al., 2013; Nor Hayati et al., 2016; Williams & Phillips, 2009).

1. THE CURRENT STATE OF ART

1.1 Rheology of food products and additives

Rheology of biopolymer solutions, particularly in a dilute form, has been extensively examined to gain insight into the structure and conformation of polymers in the solutions. In many technologies, (bio)polymers are nowadays used to control solution rheology, which provides information on the dynamics of individual polymer chains (Bock et al., 1994). The conformational properties play also an important role in food technology, and an increasing rheological research of the biopolymers, especially polysaccharides and proteins, can be expected in the following years.

The quality control of raw material and food products (including shelf life testing) and the evaluation of sensory attributes involve the rheological measurements. The investigation of rheological behaviour of food structure and

conformation of its molecular components is very important aspect of the present research (McKenna & Lyng, 2003).

Overall, many areas of food industry require valuable scientific data on rheological behaviour of different food products and additives. Therefore, there is a great value in extending scientific research on the rheology of various solutions and mixtures, based on hydrocolloids. For instance, the assessment of structure and conformational changes of polysaccharide/proteins solutions (the biopolyelectrolyte complexes) seems to be a promising research area.

The biopolyelectrolyte complexes (PECs), which are formed by oppositely charged polysaccharides and proteins, were largely investigated in the last years. The research was particularly focused on the physicochemical properties of the complexes, including rheological and gelation behaviour of food biopolymers employed in PECs (Derkach et al, 2015b; Viebke et al., 1994). Gelatin in food production is limited by its rheological properties, thermal stability, etc., but the formation of polyelectrolyte complexes allows the compatibility of gelatin with different ionic polysaccharides, such as xanthan gum and κ -carrageenan. Moreover, the specific hydrophilic and polydisperse character of gelatin provides the electrostatic complexes a great nutritional value, favourable in the production of dietary food (Derkach et al., 2015a).

1.2 Thermal analysis of food products and additives

The application of thermal analysis (TA) in food technology is relatively new. Thermal analysis has been mainly used as a standard method for investigation of polymers. As found, TA techniques provide good performance standards. At present time, thermal analysis became generally accepted scientific method of food research and development. Above all, differential scanning calorimetry (DSC) is now being used in the food industry even for routine process analysis and quality control. Nowadays, thermal analysis of food products is managed to reliably determine thermal stability of particular food complexes. Additionally, TA techniques enable to investigate the influence of changing heating/cooling rate, atmosphere, stress and storing conditions on the transitions of individual food components (Behlau & Widmann, 2003).

In recent years, thermal properties of food hydrocolloids have been intensively studied. In particular, thermal behaviour of starch was characterized in detail (Bogracheva et al., 2002; Gryszkin et al., 2014).

However, there is a lack of knowledge about phase transition, thermal kinetics and temperature dependency of several food additives. First of all, there is a great value to extend previous studies about thermal properties of pure powder polysaccharides and the molecular sensitivity of their solutions to temperature.

The determination of transition temperatures becomes increasingly important in food technology. For instance, the glass transition temperature is closely connected to the stability considerations of amorphous dried foods and deep-

freeze processes (Behlau & Widmann, 2003). An increasing number of scientific publications, which are focused on the evaluation of reaction kinetics, also indicate the applicability of TA in the production processes (Cai et al., 2018).

2. FOOD RHEOLOGY

Rheology is the branch of physics focused on the way in which materials deform or flow in response to applied forces or stresses. For liquids, the simplest rheological equation is Newton's law of viscosity, according to which the stress is proportional to the rate of straining:

$$\tau = \eta \cdot \dot{\gamma} \quad (2.1)$$

where τ is the shear stress, η - the dynamic viscosity, $\dot{\gamma}$ - the shear rate (velocity gradient) (Macosko, 1994).

The Newtonian fluid is the basis for classical fluid mechanics. Most small molecules liquids like water and oils are Newtonian. However, many colloidal suspensions and (bio)polymer solutions do not obey the simple linear relation between shear stress and shear rate. Nearly all these non-Newtonian fluids provide a viscosity that decreases with increasing velocity gradient in shear. This *shear-thinning* (*pseudoplastic*) behaviour occurs in a wide range of materials, including hydrocolloid solutions. Some concentrated suspensions (e.g., starch-water suspensions) show *shear-thickening* (*dilatant*) behaviour, which is characterized by an increasing viscosity with increasing $\dot{\gamma}$.

Many important kinds of food products lie between the ideal elastic solid and ideal viscous fluid. For instance, mayonnaise is a typical example of shear-thinning substance. If mayonnaise is left on a piece of bread subject only to gravity stresses, it will barely move, but when sheared by a knife it spreads easily. In contrast, honey, which is more viscous than mayonnaise at high stresses, will slowly run through holes in the bread. The viscosity of honey is relatively constant, but the viscosity of mayonnaise is strongly dependent on the shear stress (Macosko, 1994). A number of food products exhibit a rheological property called yield stress τ_0 which must be overcome in order to flow or to deform a substance. Also, τ_0 represents a minimum shear stress needed to be exceeded before the liquid (material) is able to flow (Figura & Teixeira, 2007).

3. THERMAL ANALYSIS

Thermal analysis is a term used for a range of thermoanalytical techniques which involve the measurement of physical and chemical properties of a sample as a function of temperature or time. The sample is subjected to a temperature program, which consists of a series of preselected segments in which the sample is heated or cooled at a constant rate or held at a constant temperature. In many experiments, the atmosphere of inert or oxidizing gases plays also an important role (Behlau & Widmann, 2003; Kloužková et al., 2012).

Thermogravimetric analysis (TGA) is a method based on recording of sample mass as a function of temperature and time. For that reason, TGA is useful for the investigation of effects which involve mass changes, such as dehydration, decomposition, oxidation and others.

Differential thermal analysis (DTA) measures the difference in temperature between the sample and an inert reference material as a function of temperature, and detects changes in heat content. It is used to characterise thermal events, such as melting, decomposition, oxidation, phase transition, glass transition, etc. During these changes, the sample temperature either lags behind (if the change is *endothermic*) or leads (if the change is *exothermic*) the temperature of the reference (Gorodylová et al., 2015).

Thermal analysis enables to monitor the kinetics of a physico-chemical reaction and determine its kinetic constants. Assuming that the course of a reaction can be expressed by formal kinetic equation, it is possible to state the following relationship:

$$\frac{d\alpha}{dt} = k_i(1 - \alpha)^{n_i} \quad (3.1)$$

where α is the degree of conversion, t - the time, k_i - the rate constant, n_i - the reaction order.

The temperature dependency of the rate constant k_i can be expressed on the basis of the Arrhenius equation:

$$k_i = A \exp\left(-\frac{E_a}{RT}\right) \quad (3.2)$$

where A is the preexponential factor (having the meaning of the kinetic process parameter), E_a - the activation energy, T - the thermodynamic temperature, R - the universal molar gas constant ($8.3144598 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) (Kejnar, 2009).

Kinetic transitions (evaporation, thermal decomposition, etc.) shift the temperature peaks to higher values at higher heating rates. Higher heating rates enhance the sensitivity, but, on the other hand, reduce the possibility to distinguish the simultaneous physico-chemical reactions within the sample (Kloužková et al., 2012).

4. AIMS OF THE THESIS

The aim of the Doctoral Thesis is to examine rheological and thermal properties of selected food matrices, particularly polysaccharide and protein hydrocolloids which are used as food additives. The methods of the rheological and thermal analysis will be employed in this study.

The flow properties of model solutions of food hydrocolloids and their blends will be investigated using rheological analysis. Based on the rheological models, the flow parameters of the samples will be determined in relation to the concentration of the solutions, temperature and shear rate used. The influence of conformational transition of the dissolved polymers (polysaccharides, proteins)

on flow properties of aqueous and salt solutions will be examined. The intrinsic viscosity (limiting viscosity number) of the solutions will also be determined, dependent on the specific physico-chemical conditions, and the temperature sensitivity of the samples will be evaluated by Arrhenius model.

Another aim of the Doctoral Thesis is to determine thermal properties of food samples, particularly of powder polysaccharides. As typical for food matrices, thermal analysis of the samples will be focused on the determination of their moisture content, on water release process, conformation and phase transition of individual chemical components, as well as components interaction with each other. In this context, the relationship between water (moisture) content, nature of interactions within the sample and observed endo/exothermic effects, i.e., the relationship between temperature peaks and weight loss of the sample during the thermal treatment (heating procedure) will be studied. Thermal analysis methods will also be used to evaluate the reaction kinetics, i.e., the evaporation of water from powder polysaccharide samples. On the basis of the most appropriate kinetic models, the reaction mechanism will be assessed, with a special focus on the activation energy of the thermal process.

5. MATERIALS AND METHODS

5.1 Materials and solutions

Powder samples of shear-thinning polysaccharides, guar gum (No. G4129), κ -carrageenan (No. 22048, viscosity of 0.3% solution at 25 °C reported as 5-25 mPa.s) and xanthan gum (No. G1253, viscosity of 1% solution reported as 800-1200 mPa.s) were purchased from Sigma-Aldrich Co. (St. Louis, USA). Gelatin of analytical grade (No. 2111104) was obtained by the company IPL (Uherský Brod, Czech Republic). Samples were stored in a dry laboratory place at room temperature (ca. 25 °C) and relative humidity (RH) of about 40 % (vol.). To adjust a constant moisture level of powder polysaccharides, one set of samples was conditioned in an desiccator at 25 °C for 72 hours, using potassium acetate (Sigma Aldrich, USA) as water activity standard which was dissolved at 25 °C to prepare saturated aqueous solution of defined water activity (saturated vapours of 22.5 % RH). Another set of samples was conditioned in a desiccator at the same conditions using potassium chloride (Sigma Aldrich, USA) as saturated solution to equilibrate the moisture level of powders at 84.3 % RH.

Solutions of polysaccharides were prepared in the concentration range of 0.25 %, 0.50 %, 0.75 % and 1.00 % (w/w) in two different solvents (distilled water and 0.07M KCl). The salt mixtures of gelatin/polysaccharide (in 0.07M KCl or 0.07M NaCl) were prepared by blending the equal amounts of 1.0% gelatin and 1.0% polysaccharide to achieve the final concentration of 0.5% (w/w).

All of the liquid samples were stored in a refrigerator at temperature about 4 °C.

5.2 Rheological analysis

Viscosimetric analysis of the solutions was performed using laboratory rheometer HAAKE RheoStress 1 (Thermo Scientific, USA). The model type of measuring geometry cylinder-cylinder was used (volume 40.1 mL). Thermal control was ensured by Thermostat HAAKE AC 200 (Thermo Scientific, USA).

Prior to testing, the solutions were carefully mixed and gently shaken to ensure the homogeneous consistency and thermally equilibrated in the water bath. Values of shear stress and dynamic viscosity were determined at specific temperatures (20 °C, 25 °C, 30 °C, 35 °C, 40 °C and 45 °C) which were kept constant with an accuracy of ± 0.5 °C. Viscometric properties were measured in the range of shear rate between 2 and 200 s^{-1} with the duration of one cycle 180 s. Measurement was performed three times for each sample. Experimental data were statistically analysed using ANOVA testing (analysis of variability) and fitted by suitable rheological models.

The Ostwald-de Waele model describes the effect of hydrocolloid concentration on apparent viscosity of the solution (Marcotte et al., 2001b) and the model has the following form:

$$\tau = k \cdot \gamma^n \quad (5.1)$$

where τ is the shear stress (Pa), k the consistency coefficient ($Pa \cdot s^n$), γ the shear rate (s^{-1}), n the flow behaviour index (dimensionless).

The Herschel-Bulkley model was used to describe the flow properties of the solutions above some yield point. This model has the following form:

$$\tau = \tau_0 + k \cdot \gamma^n \quad (5.2)$$

where τ_0 is the yield stress (Pa).

The solutions were characterized by viscosity intensifying effect, i.e., by the intrinsic viscosity of the solutions. The relationship of natural logarithm of relative viscosity divided by concentration ($\ln \eta_r/c$) against concentration c , i.e., the Kraemer equation, was used to determine the intrinsic viscosity $[\eta]$:

$$\frac{\ln \eta_r}{c} = [\eta] - k_K [\eta]^2 c \quad (5.3)$$

where k_K is the Kraemer constant (Figura & Teixeira, 2007).

5.3 Thermal analysis

Thermal properties of powder samples were evaluated by automatic simultaneous thermal analyser DTG/60 (Shimadzu, Japan). Thermal effects characterized by reaction enthalpy were analysed by software ta60 Version 1.40 (Shimadzu, Japan). An equivalent amount of each polysaccharide was placed into an aluminium measuring pan (10 mg \pm 0.5 mg), an empty pan was employed as reference. Measurement was realized under nitrogen atmosphere (the flow rate of 50 mL/min). Thermal stability of powders was tested at 10 °C/min heating rate from 30 °C to 600 °C. For kinetic parameters evaluation

samples were heated from 30 °C to 200 °C at several different heating rates (5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min). All experiments were conducted three times for each sample and statistically analysed by ANOVA method.

Based on TGA data, activation energy (E_a) was determined for thermally treated powder samples. Three different kinetic models (Friedman model, Kissinger model, and Model-free kinetics) which represent specific types of thermal kinetic evaluation were chosen to calculate the values of E_a . The activation energy was related to the water evaporation and phase transition of the polysaccharide samples occurred in the specified temperature range.

Degree of conversion α can be defined as the degree of sample transition or degradation during thermal treatment at a time t . The form of the Friedman model (differential model) is presented by Eq. (5.4):

$$\ln \frac{d\alpha}{dt} = \ln A + n \cdot \ln(1 - \alpha) - \frac{E_a}{RT} \quad (5.4)$$

where A is the pre-exponential factor (min^{-1}), E_a the activation energy ($\text{J}\cdot\text{mol}^{-1}$), R the molar gas constant ($8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), and T the thermodynamic temperature (K) (Cai et al., 2018).

Kissinger model (integral model) is described by Eq. (5.5):

$$\ln \frac{\beta}{T_m^2} = \ln \left[\frac{n \cdot (1 - \alpha_m)^{n-1}}{E_a} \cdot RA \right] - \frac{E_a}{R} \cdot \frac{1}{T_m} \quad (5.5)$$

where β is the heating rate ($^{\circ}\text{C}\cdot\text{min}^{-1}$), T_m the peak temperature (K) recorded on the derivative thermogravimetric curve ($\text{mg}\cdot\text{min}^{-1}$), and α_m the degree of conversion corresponding to T_m .

The last method, which was used to calculate the activation energy, was Model-free kinetics. Using this model, E_a was determined at various degrees of conversion, as stated by Eq. (5.6):

$$\ln \beta + \ln g(\alpha) = \ln k(T) + \ln \frac{RT^2}{E_a \alpha} - \frac{E_a}{RT} \quad (5.6)$$

where $g(\alpha)$ is the value integrated up to α ; it provides following relation (Eq. 5.7):

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta} \int_{T_0}^T e^{-E_a/RT} dT \quad (5.7)$$

where T_0 is an arbitrary temperature at which a given conversion (α) will be reached (Ramajo-Escalera et al., 2006).

5.4 Arrhenius model

Influence of temperature on the viscosity of hydrocolloid solutions and blends was evaluated by the Arrhenius model shown in Eq. (5.8):

$$\eta = A \cdot e^{\left(\frac{E_a}{RT}\right)} \quad (5.8)$$

where η is the dynamic viscosity ($\text{Pa}\cdot\text{s}$), A the pre-exponential factor (min^{-1}), E_a the activation energy ($\text{J}\cdot\text{mol}^{-1}$), R the molar gas constant ($8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), and T the thermodynamic temperature (K) (Marcotte et al., 2001a).

6. RESULTS AND DISCUSSION

6.1 Rheological properties of hydrocolloid solutions and blends

The flow behaviour of polysaccharide solutions was different due to relatively strong inter- and intra-molecular hydrogen bonding present between individual macromolecular coils in distilled water, and, on the other hand, due to the presence of chaotropic cations in 0.07M KCl which eliminated the contributions to the viscosity from hydrogen bonding system and from intramolecular electrostatic repulsion (polyelectrolyte effect) of the polymer chains (Kupská et al., 2014).

Thus, it was possible to follow concentration effect of expanded stiffed macromolecular coil transition to random coil conformation, as well as temperature effect of conformational transition, as induced by external stimuli, i.e., by changing temperature, polymer concentration and type of solvent.

Concentration (c) had an obvious effect on the flow behaviour of polysaccharide solutions. The consistency coefficient (k) calculated by the rheological models increased with c , whereas flow behaviour index (n) decreased, both for samples in water and KCl. In the case of guar gum and κ -carrageenan solutions, n was decreasing with concentration and increasing with temperature (T). On the contrary, the consistency coefficient was increasing with c and decreasing with temperature. In sum, temperature had an opposite effect to that of concentration. However, the solutions of xanthan gum, particularly at lower concentrations (0.25 %, 0.50 %), exhibited a different behaviour of n versus T , as compared to other samples.

Xanthan gum exhibited a significant yield stress (τ_0) within the whole studied temperature range. This fact is probably related to the ability of xanthan solutions to retain their stable viscosity and gel network three dimensional structure at higher temperatures until reaching a specific "melting temperature". The viscosity stability at elevated temperatures (relatively high at low-shear conditions) and the non-negligible value of yield stress result from the weak intermolecular associations of xanthan structure, even at very low hydrocolloid concentration. This rheological behaviour of xanthan gum is a consequence of the progressive alignment of the rigid xanthan molecules with the shearing force (Marcotte et al., 2001b).

Values of intrinsic viscosity $[\eta]$ of guar gum and xanthan gum in KCl solutions are moderately lower in comparison with $[\eta]$ of these polymers in distilled water at the same temperature. As stated by Ma and Pawlik (2007) for dilute guar gum solutions, the chaotropic electrolytes such as KCl are able to accelerate the dissolution of colloidal aggregates which are present in polysaccharide solutions under ambient conditions. This dissolution of polymer aggregates consequently results in a decrease of intrinsic viscosity. Intrinsic viscosity of xanthan gum is strongly dependent on its macromolecular structure. Xanthan is relatively rigid, probably due to the interactions between the

trisaccharide side chains and the polymer backbone, resulting in a greater conformational constraint. The presence of ionizable groups on side chains, which dissociate in water, affects xanthan solution properties. The addition of salt causes the collapse of side chains onto the backbone because of the charge screening effect, and the xanthan chains tend to adopt a stable helical conformation. This screening effect leads to a decreased intrinsic viscosity in the salt solution (Brunchi et al., 2014). κ -carrageenan in 0.07M KCl provided hard gels, except at 0.25% concentration which exhibited an unstable gelation at room temperature. Intrinsic viscosity of these polymer-salt solutions was evidently higher than that of samples in water, particularly at lower shear rates. The less negative values of Kraemer constant (k_K) determined for κ -carrageenan in KCl also indicate a better affinity of carrageenan chains to this solvent as compared to distilled water (Fig. 6.1).

There was a detectable change of rheological behaviour of gelatin/polysaccharide blends reflecting the conformational transition (helix-coil) at temperature about 35 °C. The change corresponds to the conformational ordering of hydrocolloid chains in the complex (leading to the enhancement of gelatin/polysaccharide electrostatic complexation) and gelatin gel-sol transition upon heating.

Temperature had an obvious effect on the flow behaviour of studied blends; the consistency coefficient (k) of guar gum/gelatin and κ -carrageenan/gelatin blends was predominantly decreasing with temperature, whereas the flow behaviour index (n) was increasing in the studied temperature range (25-45 °C). However, xanthan gum/gelatin blends exhibited an opposite behaviour of n versus temperature, as compared to other samples. For xanthan gum/gelatin blend in NaCl, the flow behaviour index was predominantly decreasing, whereas the consistency coefficient increasing with temperature. Both for xanthan gum/gelatin in KCl and NaCl, there was an evident change of n at temperature about 35 °C, demonstrating a conformational transition of hydrocolloid chains, as shown in Fig. 6.2.

Overall, xanthan gum provided more viscous blends at higher temperatures, in contrast to guar gum and κ -carrageenan blends which tend to less pseudoplastic behaviour at elevated temperatures. The blends of xanthan gum also exhibited a significant yield stress (τ_0) within the whole temperature range.

Overall, the values of k and n are comparatively different for the blends in KCl and NaCl, respectively. The presence of chaotropic cations (K^+) and kosmotropic cations (Na^+) leads to the reduction of electrostatic complex coacervation of gelatin/polysaccharide system (Cao et al., 2016), but the mechanism of their action is opposite. The chaotropic electrolytes (KCl) suppress the electrostatic repulsion effect on the polymer chains. On the other hand, the kosmotropic electrolytes (NaCl) promote interactions between water molecules and thus stabilize intramolecular interactions in protein macromolecules such as gelatin (Moelbert et al., 2004).

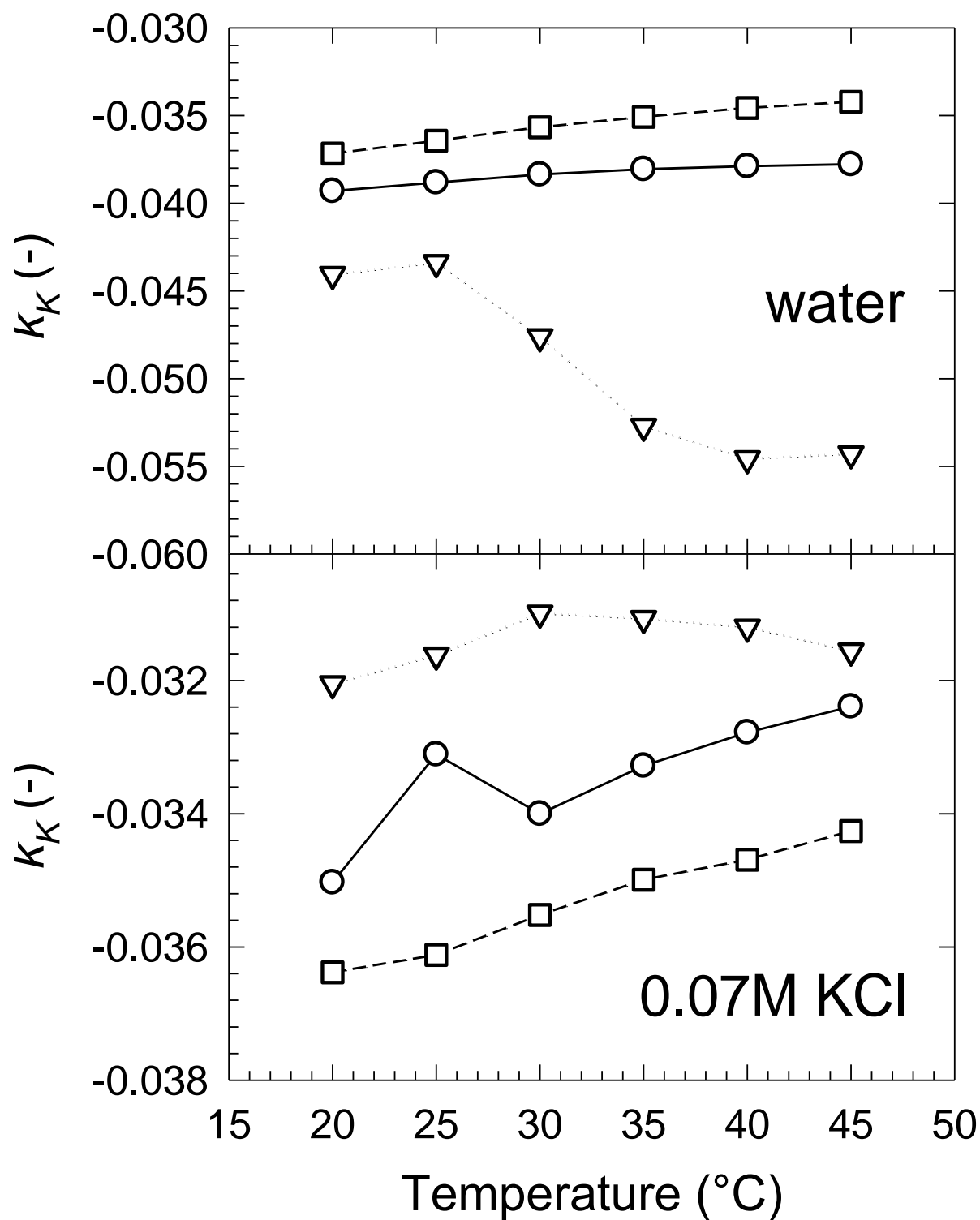


Fig. 6.1. Temperature dependency of the Kraemer constant (k_K) of studied samples in water and in 0.07M KCl (at shear rate 20 s^{-1}): circle – guar gum, triangle – κ -carrageenan, square – xanthan gum.

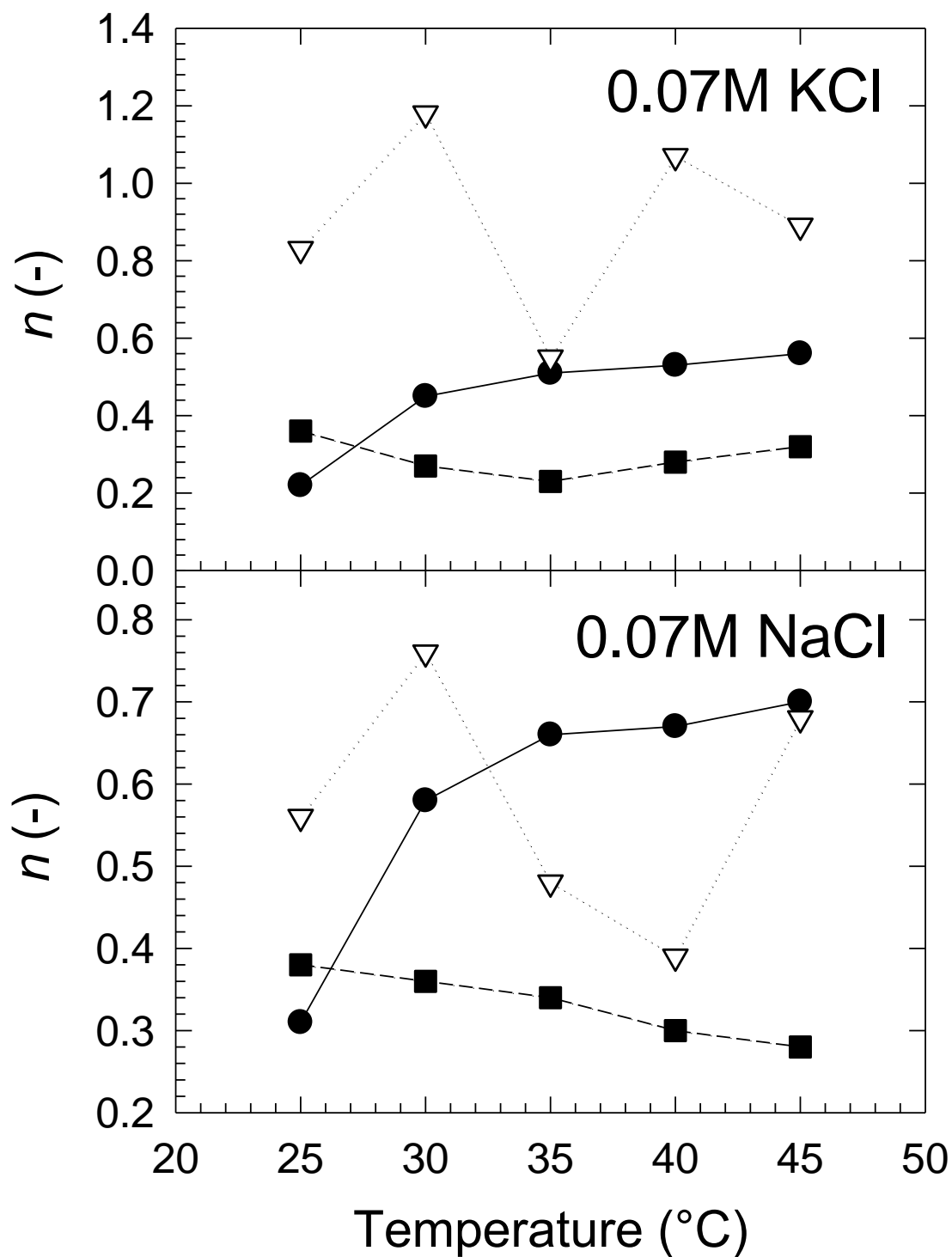


Fig. 6.2. Temperature dependency of flow behaviour index (n) (Herschel-Bulkley model) of 0.5% (w/w) gelatin/polysaccharide blends in 0.07M KCl and 0.07M NaCl (at shear rate 20 s^{-1}): full circle – guar gum/gelatin, empty triangle – κ -carrageenan/gelatin, full square – xanthan gum/gelatin.

6.2 Thermal analysis of polysaccharide powders

Different moisture content of powders after their conditioning proved the ability of hydrocolloids to bind water to different extent, i.e., the role of polysaccharide structure to equilibrate the moisture content of powders was evident. After the conditioning by saturated vapours of defined RH, guar gum was able to bind relatively low moisture content, as compared to other hydrocolloid samples (e.g., 27.3 % w/w by potassium acetate conditioning). This fact can be related to the unique structure of guar gum, consisting of galactomannan chains of various mannose to galactose ratio (Gupta et al., 2015). On the other hand, xanthan gum was able to bound relatively high moisture content (38.7 % w/w using potassium acetate standard) which indicates the higher affinity of its polymeric structure to water molecules. Character of xanthan order-disorder transition is dependent on the degree of ionization of xanthan carboxyl and acetyl residues (Bilanovic et al., 2015; Pelletier et al., 2001), and this fact may be related to the obtained values of thermal parameters, including moisture content (i.e., corresponding weight loss) of the sample.

In sum, observed results confirmed the ability of powder hydrocolloids to bind moisture in varying degrees, depending on their chemical configuration and higher-order conformational structure. As shown in Table 6.1, the hydrocolloids with higher moisture content provided larger values of reaction enthalpy, suggesting that the reaction of endothermic transition is fully completed at higher moisture level in the system. The first thermal transition is an endothermic process initialized at the beginning of heating procedure (30 °C), analogous to the gelatinization of starch. Reaction enthalpy provides energy required to change the structure of powder samples, thus ΔH illustrates the order-disorder transition reflecting changes on molecular scale of tested samples. This fact is in accordance with the moisture weight loss at temperatures ranging between 30 to 200 °C. This was demonstrated by the first step on TGA curves in the above mentioned temperature range, corresponding to the phase transition observed on DTA curves. Reaction enthalpy, related to the order-disorder transition and water evaporation, was evidently affected by the moisture content of the sample, as well as by the heating rate used.

Three different kinetic models were used to evaluate the process of water evaporation and order-disorder phase transition as induced on heating of powder samples (in the temperature range from 30 to 200 °C after room conditioning). Values of activation energy (E_a), representing the energy barriers which has to be overcome to attain sample transition, were determined based on TGA results. According to the kinetic model used, E_a values varied in a specific range. Using Friedman model, E_a was found to range between 10 and 30 kJ/mol. In the case of guar gum, activation energy fluctuated in the range about 25 to 30 kJ/mol. For κ -carrageenan, E_a was generally increasing with rising heating rate until 15 °C/min. By Kissinger model, E_a was determined in the range from 25 to 45 kJ/mol.

Model-free kinetics was used to provide information about the relation between degree of conversion and activation energy which may not be constant at the same heating rate and is a function of sample conversion (Ramajo-Escalera et al., 2006). Model-free kinetics for the calculation of E_a values of κ -carrageenan is illustrated in Fig. 6.3. This method demonstrated an evident decrease of activation energy (from 180 to 60 kJ/mol) during heating of powders with increasing degree of conversion, particularly between 5 and 20 % of α . The largest decrease of E_a values was obtained for κ -carrageenan, the lowest for xanthan gum. The decrease of activation energy with α can be related to the loss of moisture and increasing disordering of powder system. The energetic associations between water molecules and polysaccharide chains (hydrophilic moieties) are disrupted during thermal treatment (Dranca & Vyazovkin, 2009) and the energy necessary to overcome the energy barriers of the system drop continually until 60 % of sample conversion.

Table 6.1. Thermal analysis of powders (conditioned at room conditions) in the temperature range 30-200 °C at different heating rates.

Sample	β (°C.min ⁻¹)	TGA	DTA	
		Weight loss (% w/w) (30-200 °C)	Temperature T_p (°C)	Enthalpy ΔH (Endo) (J.g ⁻¹)
Guar gum	5	10.9	52.4	169.0
	10	10.0	64.4	216.0
	15	9.9	72.1	236.3
	20	9.4	77.4	221.1
κ -carrageenan	5	9.5	49.6	94.0
	10	9.0	64.5	139.3
	15	8.7	70.7	137.9
	20	8.4	82.1	154.4
Xanthan gum	5	11.3	56.7	171.7
	10	12.1	69.2	259.6
	15	11.9	76.6	264.0
	20	11.9	83.1	298.5

Note: β – heating rate; TGA – thermogravimetric analysis; DTA – differential thermal analysis; T_p – peak transition temperature; ΔH – reaction enthalpy.

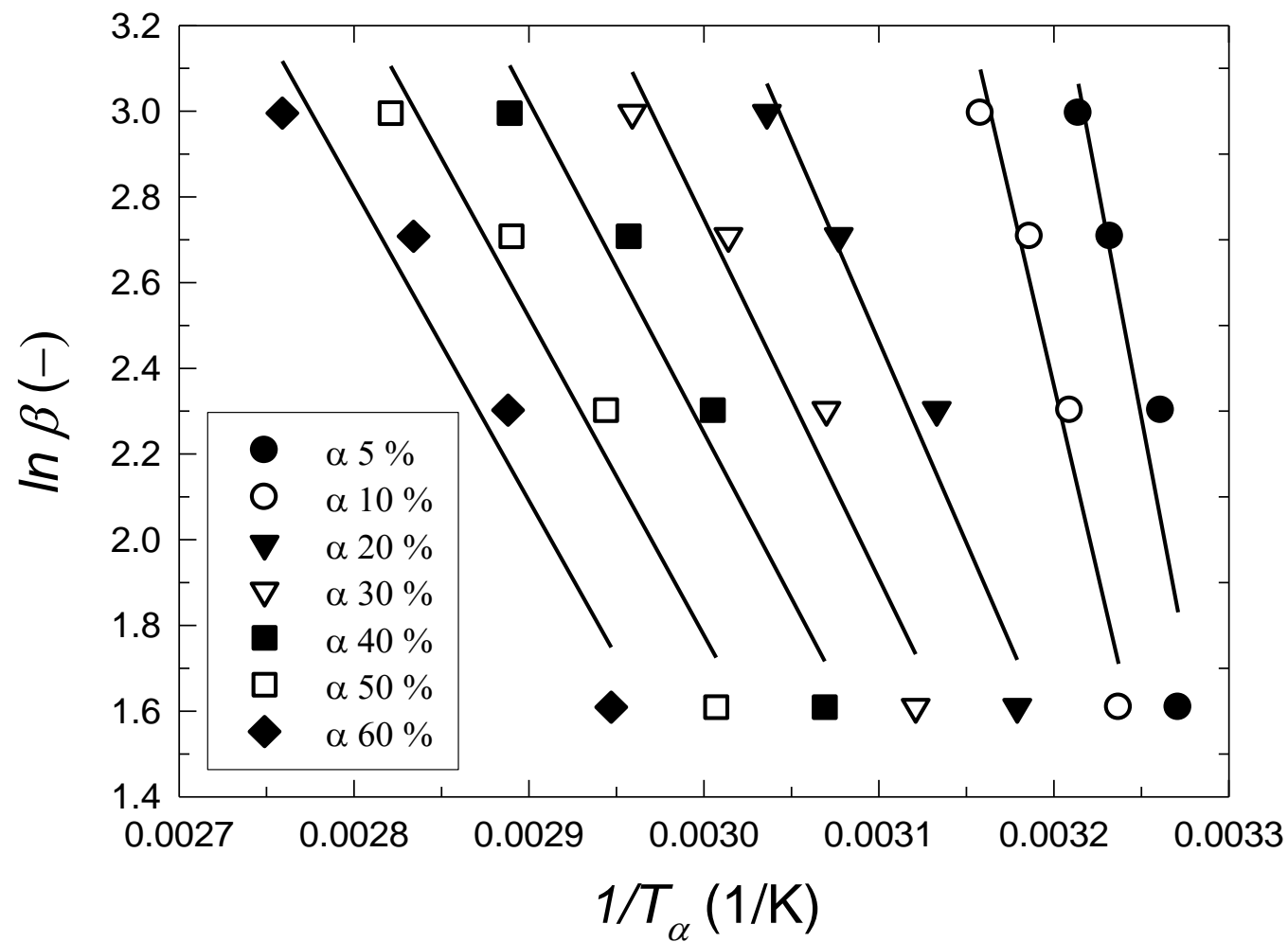


Fig. 6.3. Model-free kinetics plot of κ -carrageenan (conditioned at room conditions) in the temperature range 30-200 °C: β – heating rate; T_α – thermodynamic temperature at the degree of conversion α . Full line – linear regression curve.

6.3 Arrhenius model

As determined by the Arrhenius model, polysaccharides in water generally exhibited higher values of activation energy (E_a) and higher values of pre-exponential factor (A), than samples in KCl (except E_a values for xanthan gum). This behaviour can be explained by the presence of chaotropic cations K^+ in KCl solution, which partially shield the ionic charges along the polymer chains via electrostatic adsorption. As a result, this leads to a decrease in polymer bulk viscosity. In accordance with this fact, a lower activation energy has to be overcome to achieve the disentanglement of higher-order polymer structure in a salt solvent, and thus, to promote viscous flow of the solution exhibiting a less temperature-dependent behaviour. This is very important technological aspect in the manufacturing of food products modified by the hydrocolloids.

Obtained results of the present study confirmed the fact that the activation energy of hydrocolloid solutions, both in water and KCl, decreases with increasing shear rate. It suggests that the energy necessary for reorientation of solvent molecules is substantially reduced by higher shear rate. However, the energy intake at 100 s^{-1} is still relatively high, which indicates a possible reorganisation of hydrocolloid chain structure during the solution shearing process.

In the case of gelatin/polysaccharide blends, relatively high values of E_a were determined for guar gum/gelatin blends both in KCl and NaCl, and for κ -carrageenan/gelatin blend in NaCl; these blends are relatively high temperature-dependent samples indicating a higher resistance of their molecular structure to temperature. On the other hand, the lowest values of E_a were calculated for xanthan gum/gelatin mixtures which were less affected by the temperature changes. This fact proves that xanthan gum/gelatin blends have the ability to retain their polymer network and viscosity at higher temperatures. Overall, the activation energy of samples in 0.07M NaCl was higher than that of samples in KCl; it means that the blends in NaCl need higher amount of activation energy to promote viscous flow than the samples in KCl, probably due to more complex structure of hydrocolloids in NaCl solution. Samples in KCl provided lower values of E_a and higher values of pre-exponential factor (A), indicating a less stabilized structure, as compared to Arrhenius parameters for NaCl blends, regardless of the polysaccharide type.

The activation energy read at 20 s^{-1} was higher than E_a read at 100 s^{-1} for all samples. This is in accordance with the fact that the structure of a hydrocolloid and its change with the shearing plays an important role in the temperature dependency of the solutions (Marcotte et al., 2001a). The observations indicate that energy necessary for reorientation of water (solvent) molecules in gelatin/polysaccharide blends is obviously influenced by the type of hydrocolloid and salt solution, as well as by the applied shear rate.

7. CONTRIBUTION TO SCIENCE AND PRACTICE

The study of rheological and thermal properties of food hydrocolloids is very perspective area. The research on this field is promising new approaches how to understand the effect of these hydrocolloids on the functional character of food products and how to optimize their amount in selected food matrices.

The main contributions of this Doctoral Thesis in the field of hydrocolloid rheology can be summarized into the following points:

- Structural change of food hydrocolloids in aqueous and salt solutions (semi-dilute regime) can be detected by appropriate rheological models (Ostwald-de Waele model and Herschel-Bulkley model), i.e., by temperature and concentration dependency of the flow parameters. The transition of hydrocolloid chains (order-disorder transition) with changing temperature obviously influences the flow behaviour of hydrocolloid solutions.
- Conformational ordering of gelatin/polysaccharide blends (polyelectrolyte complexes) induced by temperature changes has an effect on their rheological behaviour and other functional properties of the blends.
- Presence of specific ions (chaotropic cations K^+ , kosmotropic cations Na^+) in the solvent used affects the flow behaviour and gelation of the hydrocolloid solutions.

Thermal and temperature dependency of food hydrocolloids can characterize endothermic and exothermic events in these materials, and also the resistance of their molecular structure to the changes in temperature, concentration, shear rate and other physico-chemical factors. The key points determined during the study of hydrocolloids' thermal and temperature properties are stated here:

- The ability of powder samples to bind moisture in varying degrees depends on the chemical and higher-order structure of each polysaccharide studied. The moisture content is related to the values of reaction enthalpy and peak temperature upon thermal treatment of powders.
- In dependence of the kinetic approach used (Friedman model, Kissinger model, Model-free kinetics), the values of activation energy (E_a) vary in a specific range. The largest values of E_a determined at low conversions (at the onset of powder thermal treatment) suggest that energy barriers of powders originate from cooperative disruption of energetic associations between water molecules and hydrophilic groups on the polymer matrix.
- There was found a reverse dependency between activation energy of polysaccharide solutions and reaction enthalpy of powder samples. The highest resistance of κ -carrageenan solution molecular network to temperature changes was related to the lowest energy intake needed to dissociate the polymeric structure of κ -carrageenan powder sample. Vice versa, xanthan gum with the highest sensitivity of its solution structure to temperature changes provided the largest reaction enthalpy during thermal treatment of powders.

CONCLUSION

This Doctoral Thesis was focused on the rheological and thermal properties of several food hydrocolloids (shear-thinning polysaccharides and gelatin) which find growing use in the food industry.

Rheological analysis of polysaccharides solutions in distilled water and 0.07M KCl provided information about their hydrodynamic properties as a function of polymer concentration, type of solvent and temperature. Flow parameters of the solutions were described by suitable rheological models (Ostwald-de Waele and Herschel-Bulkley models). The transition from double helical polysaccharide structure to conformation of single coils at temperature about 30 °C (in salt solution) and the disentanglement process of polymer coils (in distilled water) were proved by the temperature dependency of the Kraemer constant (k_K). The intrinsic viscosity of the solutions was dependent on the hydrocolloid type and solvent used. Overall, the intrinsic viscosity at lower shear rate (20 s⁻¹) was higher than that at higher shear rate (100 s⁻¹) owing to the breakdown of the original molecular structure. For all solutions, based on the k_K results, KCl seems to be a better solvent as compared to distilled water.

The same rheological approach was used for gelatin/polysaccharide blends, dissolved in 0.07M KCl and 0.07M NaCl. The functional properties of the blends were influenced by the conformational transition of hydrocolloid chains. A noticeable change of flow parameters upon heating, determined about 35 °C, corresponds to the order-disorder transition of the hydrocolloids, as well as to the gel-sol transition of gelatin. The flow behaviour and gelation properties of the blends were affected by the type of hydrocolloid and solvent used.

Thermal properties of powder polysaccharides were assessed by thermal analysis techniques (TGA and DTA). The powders were able to bind moisture to different extent, dependent on the chemical and higher-order structure of the polysaccharides, as well as on their conditioning. On the basis of the latter water binding ability, samples showed different values of reaction enthalpy and peak temperature. The order-disorder phase transition (endothermic process) occurred in the temperature range 50-85 °C. Different kinetic models (Friedman model, Kissinger model, and Model-free kinetics), were used to assess the kinetics of phase transition and water evaporation, providing information about the energy barriers which has to be overcome during thermal treatment of the powders. Model free kinetics revealed a significant decrease in activation energy (E_a) with increasing degree of conversion (α), in the highest extent between 5 and 20 % of α , probably due to the release of water molecules from polymer matrix at the onset of powder thermal treatment.

Temperature dependency of the solutions was evaluated using the Arrhenius model. Higher values of pre-exponential factor (A) and E_a determined for samples in water can be explained by a more complicated (less ordered) structure of aqueous solutions, in comparison to polysaccharides in salt solvents.

REFERENCES

- BEHLAU, L. & WIDMANN, G. (2003). *Collected Applications: Thermal Analysis. Food Handbook*. Mettler-Toledo.
- BILANOVIC, D., STAROSVETSKY, J. & ARMON, R. H. (2015). Cross-linking xanthan and other compounds with glycerol. *Food Hydrocolloids*. Vol. 44, p. 129-135. ISSN 0268-005X.
- BOCK, J., VARADARAJ, R., SCHULZ, D. N. & MAURER, J. J. (1994). Solution Properties of Hydrophobically Associating Water-Soluble Polymers. In: DUBIN, P., BOCK, J., DAVIS, R., SCHULZ, D. N. & THIES, C. (eds.). *Macromolecular Complexes in Chemistry and Biology*. 1st ed., p. 33-50. Berlin: Springer Verlag. ISBN 978-3-642-78471-2.
- BOGRACHEVA, T. Y., WANG, Y. L., WANG, T. L. & HEDLEY, C. L. (2002). Structural Studies of Starches with Different Water Contents. *Biopolymers*. Vol. 64, p. 268-281. ISSN 0006-3525.
- BRUNCHI, C.-E., MORARIU, S. & BERCEA, M. (2014). Intrinsic viscosity and conformational parameters of xanthan in aqueous solutions: Salt addition effect. *Colloids and Surfaces B: Biointerfaces*. Vol. 122, p. 512-519. ISSN 0927-7765.
- CAI, J., XU, D., DONG, Z., YU, X., YANG, Y., BANKS, S. W. & BRIDGWATER, A. V. (2018). Processing thermogravimetric analysis data for isoconversional kinetic analysis of lignocellulosic biomass pyrolysis: Case study of corn stalk. *Renewable and Sustainable Energy Reviews*. Vol. 82, p. 2705-2715. ISSN 1364-0321.
- CAO, Y., FANG, Y., NISHINARI, K. & PHILIPS, G. O. (2016). Effects of conformational ordering on protein/polyelectrolyte electrostatic complexation: Ionic binding and chain stiffening. *Scientific Reports - Nature*. Vol. 6, p. 1-11. ISSN 2045-2322.
- CEVOLI, C., BALESTRA, F., RAGNI, L. & FABBRI, A. (2013). Rheological characterisation of selected food hydrocolloids by traditional and simplified techniques. *Food Hydrocolloids*. Vol. 33, p. 142-150. ISSN 0268-005X.
- DERKACH, S. R., ILYIN, S. O., MAKLAKOVA, A. A., KULICHIKHIN, V. G. & MALKIN, A. Y. (2015a). The rheology of gelatin hydrogels modified by κ -carrageenan. *LWT - Food Science and Technology*. Vol. 63, p. 612-619. ISSN 0023-6438.
- DERKACH, S., ZHABYKO, I., VORON'KO, N., MAKLAKOVA, A. & DYAKINA, T. (2015b). Stability and the rheological properties of concentrated emulsions containing gelatin- κ -carrageenan polyelectrolyte complexes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. Vol. 483, p. 216-223. ISSN 0927-7757.

DRANCA, I. & VYAZOVKIN, S. (2009). Thermal stability of gelatin gels: Effect of preparation conditions on the activation energy barrier to melting. *Polymer*. Vol. 50, p. 4859-4867. ISSN 0032-3861.

FIGURA, L. O. & TEIXEIRA, A. A. (2007). *Food Physics: Physical Properties - Measurement and Applications*. Berlin, Heidelberg, New York: Springer-Verlag. ISBN 978-3-540-34194-9.

GORODYLOVÁ, N., ŠULCOVÁ, P., DOHNALOVÁ, Ž., BOSACKA, M. & FILIPEK, E. (2015). Application of DTA/TG method for investigation of solid state reaction mechanisms. In: ŠULCOVÁ, P. & DOHNALOVÁ, Ž. (eds.). *Sborník příspěvků termoanalytického semináře TAS 2015*. 1st ed., p. 90-94. Pardubice: Univerzita Pardubice. ISBN 978-80-7395-888-6.

GRYSZKIN, A., ZIEBA, T., KAPELKO, M. & BUCZEK, A. (2014). Effect of thermal modifications of potato starch on its selected properties. *Food Hydrocolloids*. Vol. 40, p. 122-127. ISSN 0268-005X.

GUPTA, S., SAURABH, CH., VARIYAR, P. S. & SHARMA, A. (2015). Comparative analysis of dietary fiber activities of enzymatic and gamma depolymerized guar gum. *Food Hydrocolloids*. Vol. 48, p. 149-156. ISSN 0268-005X.

KEJNAR, Z. (2009). *Kinetické modely degradace v termální analýze*, diploma thesis. Zlín: Univerzita Tomáše Bati ve Zlíně.

KUPSKÁ, I., LAPČÍK, L., LAPČÍKOVÁ, B., ŽÁKOVÁ, K. & JUŘÍKOVÁ, J. (2014). The viscometric behaviour of sodium hyaluronate in aqueous and KCl solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. Vol. 454, p. 32-37. ISSN 0927-7757.

KLOUŽKOVÁ, A., ZEMENOVÁ, P., KLOUŽEK, J. & PABST, W. (2012). *Termická analýza* [online]. Praha: Vysoká škola chemicko-technologická v Praze [cit. 2017-12-30]. Available from:

<http://tresen.vscht.cz/sil/sites/default/files/Termick%C3%A1%20anal%C3%BD%20za.pdf>

MA, X. & PAWLIK, M. (2007). Intrinsic viscosities and Huggins constants of guar gum in alkali metal chloride solutions. *Carbohydrate Polymers*. Vol. 70, iss. 1, p. 15-24. ISSN 0144-8617.

MACOSKO, C. W. (1994). *Rheology. Principles, Measurements, and Applications*. New York: Wiley-VCH. ISBN 1-56081-579-5.

MARCOTTE, M., TAHERIAN, A. R. & RAMASWAMY, H. S. (2001a). Rheological properties of selected hydrocolloids as a function of concentration and temperature. *Food Research International*. Vol. 34, p. 695-703. ISSN 0963-9969.

MARCOTTE, M., TAHERIAN, A. R., TRIGUI M. & RAMASWAMY, H. S. (2001b). Evaluation of rheological properties of selected salt enriched food hydrocolloids. *Journal of Food Engineering*. Vol. 48, p. 157-167. ISSN 0260-8774.

McKENNA, B. M. & LYNG, J. G. (2003). Introduction to food rheology and its measurement. In: McKENNA, B. M. (ed.). *Texture in food. Volume 1: Semi-solid foods*. 1st ed., p. 131-160. Cambridge: Woodhead Publishing Ltd. ISBN 1-85573-673-X.

MOELBERT, S., NORMAND, B. & DE LOS RIOS, P. (2004). Kosmotropes and chaotropes: modelling preferential exclusion, binding and aggregate stability. *Biophysical Chemistry*. Vol. 112, p. 45-57. ISSN 0301-4622.

MOHAMMADI, M., SADEGHNIA, N., AZIZI, M., NEYESTANI, T. & MORTAZAVIAN, A. M. (2014). Development of gluten-free flat bread using hydrocolloids: Xanthan and CMC. *Journal of Industrial and Engineering Chemistry*. Vol. 20, iss. 4, p. 1812-1818. ISSN 1226-086X.

NOR HAYATI, I., WAI CHING, C. & ROZAINI, M. Z. H. (2016). Flow properties of o/w emulsions as affected by xanthan gum, guar gum and carboxymethyl cellulose interactions studied by a mixture regression modelling. *Food Hydrocolloids*. Vol. 53, p. 199-208. ISSN 0268-005X.

PELLETIER, E., VIEBKE, C., MEADOWS, J. & WILLIAMS, P. A. (2001). A Rheological Study of the Order-Disorder Conformational Transition of Xanthan Gum. *Biopolymers*. Vol. 59, p. 339-346. ISSN 0006-3525.

RAMAJO-ESCALERA, B., ESPINA, A., GARCÍA, J. R., SOSA-ARNAO, J. H. & NEBRA S. A. (2006). Model-free kinetics applied to sugarcane bagasse combustion. *Thermochimica Acta*. Vol. 448, p. 111-116. ISSN 0040-6031.

RHEIN-KNUDSEN, N., ALE, M. T., AJALLOUEIAN, F., YU, L. & MEYER, A. S. (2017). Rheological properties of agar and carrageenan from Ghanaian red seaweeds. *Food Hydrocolloids*. Vol. 63, p. 50-58. ISSN 0268-005X.

TOMASIK, P. (2004). Saccharides and Polysaccharides: An Introduction. In: TOMASIK, P. (ed.), *Chemical and Functional Properties of Food Saccharides*. P. 1-18. Boca Raton, London, New York, Washington, D.C.: CRC Press LLC. ISBN 0-8493-1486-0.

VARELA, P. & FISZMAN, S. M. (2011). Hydrocolloids in fried foods. A review. *Food Hydrocolloids*. Vol. 25, iss. 8, p. 1801-1812. ISSN 0268-005X.

VIEBKE, C., PICULELL, L. & NILSSON, S. (1994). On the mechanism of gelation of helix-forming biopolymers. *Macromolecules*. Vol. 27, p. 4160-4166. ISSN 0024-9297.

WILLIAMS, P. A. & PHILLIPS, G. O. (2009). Introduction to food hydrocolloids. In: PHILLIPS, G. O. & WILLIAMS, P. A. (eds.). *Handbook of Hydrocolloids*. 2nd ed., p. 1-22. Cambridge: Woodhead Publishing. ISBN 978-1-84569-414-2.

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LIST OF SYMBOLS AND ABBREVIATIONS

A	pre-exponential factor
c	concentration
E_a	activation energy
$f(\alpha)$	reaction model
ΔH	reaction enthalpy
k	consistency coefficient
k_i	rate constant
k_K	Kraemer constant
Δm_w	weight loss (moisture content)
n	flow behaviour index
n_i	reaction order
R	molar gas constant
R^2	determination coefficient
T	temperature
T_m	peak temperature on derivative thermogravimetric curve
T_p	peak temperature
T_α	temperature at the degree of conversion α
t	time
α	degree of conversion (conversion rate)
α_m	degree of conversion corresponding to T_m (Kissinger model)
β	heating rate
γ	shear rate
η	dynamic viscosity
η_{sp}	specific viscosity
$[\eta]$	limiting viscosity number (intrinsic viscosity)
τ	shear stress
τ_0	yield stress
ANOVA	analysis of variability
DSC	differential scanning calorimetry
DTA	differential thermal analysis
PECs	biopolyelectrolyte complexes
RH	relative humidity
TA	thermal analysis
TBU	Tomas Bata University
TGA	thermogravimetric analysis

LIST OF PUBLICATIONS

Articles in international journals with impact factor (Web of Science)

VALENTA, T., LAPČÍKOVÁ, B. & LAPČÍK, L. (2018). Determination of kinetic and thermodynamic parameters of food hydrocolloids/water interactions by means of thermal analysis and viscometry. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. Vol. 555, p. 270-279. ISSN 0927-7757.

LAPČÍKOVÁ, B., VALENTA, T. & LAPČÍK, L. (2017). Rheological Properties of Food Hydrocolloids based on Polysaccharides. *Journal of Polymer Materials*. Vol. 34, iss. 3, p. 631-645. ISSN 0970-0838.

LAPČÍK, L., VAŠINA, M., LAPČÍKOVÁ, B. & VALENTA, T. (2016). Study of bread staling by means of vibro-acoustic, tensile and thermal analysis techniques. *Journal of Food Engineering*. Vol. 178, p. 31-38. ISSN 0260-8774.

Articles in journals indexed in Scopus database

LAPČÍKOVÁ, B., VALENTA, T., LAPČÍK, L., FUKSOVÁ, M. (2018). Thermal aging of edible oils: spectrophotometric study. *Potravinárstvo: Slovak Journal of Food Sciences*. Vol. 12, iss. 1, p. 372-378. ISSN 1337-0960.

VALENTA, T., LAPČÍKOVÁ, B., LAPČÍK, L., LI, P. (2017). The effect of conformational transition of gelatin-polysaccharide polyelectrolyte complex on its functional properties. *Potravinárstvo: Slovak Journal of Food Sciences*. Vol. 11, iss. 1, p. 587-596. ISSN 1337-0960.

Conference proceedings

VALENTA, T., LAPČÍKOVÁ, B., LAPČÍK, L. (2016). Thermal properties of food hydrocolloids. In: JAMPÍLEK, J. & MARVANOVÁ, P. (eds.). *8th Central European Conference "Chemistry towards Biology"*. *Book of Abstracts*. P. 162. Brno: University of Veterinary and Pharmaceutical Sciences Brno. ISBN 978-80-7305-777-0.

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2006 – 2009 **Bachelor's Degree** at TBU in Zlín, Degree course: Chemistry and Food Technology. Bachelor topic: *Enzymatic hydrolysis of carbohydrates and proteins*

Language skills:

English (level B2)
German (level B1)
Chinese (level A1)

2016 – 2018 Chinese Language and Culture Course (public course), Faculty of Humanities, TBU in Zlín

Computer skills:

MS Office (Word, Excel, PowerPoint)
TA-60 software (Shimadzu, Japan)
SigmaPlot (Systat Software, USA)

Other skills:

Food Handler Card of the worker in the food industry

Ing. Tomáš Valenta, Ph.D.

The study of foodstuff rheological and thermal properties

Studium reologických a termických vlastností potravin

Doctoral Thesis Summary

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