

RHEOLOGY OF CERAMIC SUSPENSIONS WITH ORGANIC OR BIOPOLYMERIC GELLING ADDITIVES PART 2. SUSPENSIONS WITH CARRAGEENAN

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Carrageenan, a polysaccharide biopolymer of the agaroid group, can be used as a gelling agent in ceramic shaping techniques. Its function is based on the ability to form elastic hydrogels from viscous aqueous solutions upon cooling. In this paper the performance of carrageenan systems is studied by oscillatory shear rheometry. It is shown that aqueous solutions with 2.2, 3.1 and 3.9 wt.% carrageenan undergo reversible gelation within a temperature range of approx. 5°C at gelation temperatures of 46, 51 and 56°C, respectively. The resulting storage moduli of the gels are approx. 5, 15 and 20 kPa, respectively, thus exhibiting a strong dependence on the carrageenan concentration. The rheology of zirconia suspensions, containing 67 wt.% zirconia (Tosoh TZ-3YE) and effective carrageenan concentrations of 0.7, 1.0 and 1.3 wt.% in the aqueous phase, is briefly summarized as well. In contrast to pure carrageenan solutions, which are purely viscous at elevated temperatures, the mixed suspensions (containing zirconia and carrageenan) are viscoelastic at 80°C and exhibit lower gelation temperatures on cooling (29, 33 and 37°C, respectively). The resulting storage moduli after cooling to room temperature are in the range 2-25 kPa, i.e. of the same order as for pure carrageenan hydrogels. This green rigidity guarantees easy demolding and further handling of the as-shaped ceramic green bodies.

INTRODUCTION

During the last two decades several new shaping techniques have been developed for ceramic suspensions. A common feature of most of these techniques is the possibility to perform casting into non-porous molds, e.g. polymer or metal molds with impermeable walls. Due to the fact that no dewatering is necessary across a semipermeable interface (in contrast e.g. to traditional slip casting of ceramic suspensions using plaster molds or polymer sieves), the body formation proceeds essentially without gradients, so that potentially great microstructural uniformity can be achieved.

Many of these new shaping techniques are designed for aqueous suspensions, i.e. essentially water-based systems, containing varying amounts of organic agents and / or biopolymers. Among the most thoroughly studied processes are casting with polysaccharides, including agaroids (agarose, agar and carrageenan) [1-16] and starch [17-25]. All these processes exploit the ability of the mentioned polysaccharides to undergo, in combination with water and induced by temperature changes, a phase transformation from a viscous suspension or sol

(macromolecular solution) into an elastic or viscoelastic gel. For example, starch exhibits swelling in water at moderately elevated temperatures, while the agaroids in general (and carrageenan in particular) undergo a coil-to-helix transition and transform to an elastic gel upon cooling. Generally speaking, carrageenans are sulphonated galactans extracted from various species of red algae (seaweed). They are extensively used in the food industry as gelling agents. For basic general information on polysaccharides in general, and carrageenan sources, types, composition, structure and properties in particular, the reader can refer to [26-28] and the references cited therein. Selected aspects with special relevance to ceramic processing have recently been summarized in [16].

Concomitantly with the advance of new shaping techniques based on ceramic suspensions containing polysaccharides there is an increased interest in the rheological characterization of these systems not only by rotational viscometry (one of the traditional methods in ceramic technology) but also by oscillatory rheometry (which is a standard method in food technology). In particular, concerning carrageenan a considerable amount

of work has been done for suspensions of silicon nitride and alumina [3-11]. The rheological behavior of carrageenan-water mixtures and its temperature dependence, however, is rather unknown within the ceramic community, and carrageenan-containing zirconia suspensions have not been investigated until very recently [16]. In the present paper, which is part of a series concerning rheological characterization of ceramic suspensions with biopolymers, we present the rheological characterization of aqueous carrageenan systems and carrageenan-containing zirconia suspensions. For an adequate assessment of the results presented herein and their interpretation, the reader is assumed to be familiar with the basic theory of linear viscoelasticity as outlined in the first paper (Part I) of this series [29].

THEORETICAL

Concerning the interpretation of measured stress response data in terms of linear viscoelasticity the reader is referred to Part 1 of this series [29]. In particular, it has to be remembered that viscoelastic systems in small amplitude oscillatory shear are characterized by a complex viscosity or, alternatively, a complex modulus

$$G^* = G' + iG'' \quad (1)$$

where G' is the storage modulus and G'' the loss modulus and the ratio

$$G''/G' = \tan \delta \quad (2)$$

is termed the loss factor (damping factor, loss tangent). Note that G' , G'' and $\tan \delta$ depend on the test frequency and on temperature. In the special case of purely elastic systems there are no dissipative losses; therefore the loss modulus G'' is small compared to the storage modulus G' , the loss factor $\tan \delta$ approaches zero and the phase angle δ is close to 0° , i.e. the stress response is in phase with the strain. On the other hand, in the special case of purely viscous systems no elastic energy can be stored; in this case the storage modulus G' is undefined and the phase angle (phase shift) between strain and stress response is 90° .

Carrageenans are linear biopolymers with high molecular weight and regular but imprecisely defined structures, containing small amounts of sulphur (in amounts depending on the algae source) and potassium (as a residual from extraction). Figure 1 shows the structure unit of kappa carrageenan. Dry carrageenan powder consists of xerogel fragments, which exhibit low solubility in water at room temperature but readily dissolve at slightly elevated temperatures. Of course, it can be expected that the dissolution of carrageenan (formation of hydrated random coils from partially order double-helix aggregates) will be accompanied by

changes in the apparent viscosity of the system. Moreover, the apparent viscosity of carrageenan solutions can be expected to be dependent on the concentration of carrageenan, and power laws can be used to describe this concentration dependence [30].

Upon cooling the carrageenan molecules in solution undergo a coil-to-helix transition, possibly accompanied by the formation of double-helix bundles, agglomerates and network structures, resulting in a more or less elastic, water-saturated gel (hydrogel) [26]. Similar to the concentration dependence of the (apparent) viscosities of carrageenan solutions, also the concentration dependence of the storage moduli of kappa carrageenan gels can be described by power laws of the form

$$G' = k \cdot C^n \quad (3)$$

where the fit parameters k and n depend on the concentration measure adopted. As emphasized in [29], the storage modulus is also a measure of gel strength, i.e. a relevant quantitative measure to assess the "strength" (or, more precisely, the rigidity) of as-molded ceramic green bodies in the state ready for demolding.

Note that the gelation of carrageenan solutions (coil-to-helix transition and network formation) with decreasing temperature is a reversible process. It can therefore be reversed via thermal network destruction a helix-to-coil transition initiated by heating (so-called "melting" of the hydrogel).

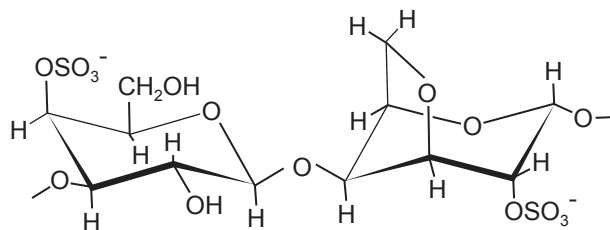


Figure 1. Structure unit of kappa-carrageenan.

EXPERIMENTAL

Material characteristics and sample preparation

Carrageenan solutions were prepared using a commercially available kappa carrageenan (*Secogel TCP*, *Hispangar*, Spain), obtained by alkaline extraction with KCl. It is supplied in the form of granules $< 250 \mu\text{m}$ with a moisture content of $< 12 \text{ wt.}\%$. Carrageenan stock solutions were prepared with 2.2, 3.1 and 3.9 wt.% carrageenan in distilled water by mixing and heating in a closed glass vessel up to approx. 80°C to ensure complete dissolution.

Zirconia suspensions were prepared using a commercially available submicron tetragonal zirconia powder type (*TZ-3YE*, *Tosoh*, Japan). These powder contains > 99.7 wt.% ZrO_2 (tetragonal phase stabilized by 3 mol.%, i.e. 5 wt.%, Y_2O_3) and 0.25 ± 0.1 wt.% Al_2O_3 . The median particle size is approx. $0.6 \mu m$ and the specific surface area approx. $16 \pm 3 m^2/g$. Aqueous suspensions with a solids loading of 75 wt.% (i.e. approx. 35 vol.%) were prepared using 1.1 wt.% (based on solids) of a commercial deflocculant (*Dolapix CE 64*, *Zschimmer & Schwarz*, Germany). After mixing, agitation and ultrasonication the zirconia suspensions were heated up to approx. $60^\circ C$ and were ready for mixing with the as-prepared carrageenan stock solutions (approx. at the same temperature).

The resulting zirconia concentration in the final suspensions with carrageenan was 67 wt.% (i.e. approx. 25 vol.%) in all cases. The fluidity of the suspension at this concentration is comparable to that of slips used in conventional slip casting of ceramic suspensions. Table 1 lists the concentration of zirconia in the zirconia stock suspensions W_Z , the concentration of the carrageenan stock solutions W_C as well as the carrageenan concentration in the final suspensions (related to the total free water available) W_{CF} and the zirconia concentration in the final suspensions W_{ZF} .

Table 1. Zirconia concentration in the zirconia stock suspensions W_Z , concentration of the carrageenan stock solutions W_C , carrageenan concentration in the final suspensions (related to the total free water available) W_{CF} and zirconia concentration in the final suspensions W_{ZF} .

W_Z (wt.%)	W_C (wt.%)	W_{CF} (wt.%)	W_{ZF} (wt.%)
75	2.2	0.7	67
75	3.1	1.0	67
75	3.9	1.3	67

Measurement details

Rheological measurement were performed using a *RS 80* rheometer (*Haake*, Germany) with a coaxial cylinder sensor system (*Z 40*, gap 8 mm), connected to a thermostatic heater (*DC 30*) and a cooling unit (*K 15*). A cover plate was used to prevent evaporation and to guarantee uniform heating. If not mentioned otherwise, the oscillatory mode has been applied (frequency 1 Hz). Only exceptionally, viz. for the pure carrageenan systems during the first heating-up phase (dissolution step), the rotational mode was used (at $10 s^{-1}$). Stress sweep tests and frequency sweep tests were performed for carrageenan solutions with lowest (2.2 wt.%) and highest (3.9 wt.%) concentration at $20^\circ C$ (after cooling) to assess the frequency dependence of the viscoelastic moduli and the phase angle and to confirm the applicability of linear viscoelasticity theory. It was found that

the frequency dependence of the viscoelastic moduli and the phase angle was reasonably small between 0.1 and 10 Hz and that for stresses between 1 and 10 Pa the viscoelastic moduli and the phase angle remained reasonably constant.

For routine measurements a frequency of 1 Hz and a strain amplitude of 1% was chosen. The rheological behavior of the pure carrageenan systems was characterized in the rotational mode during first heating and in the oscillatory mode during cooling (repeated cooling cycles). The rheological behavior of the carrageenan-containing zirconia suspensions (as-cooled) was characterized in the oscillatory mode during both the heating cycle (gel melting) and the subsequent cooling cycle (gelation). The temperature range was from 20 to $80^\circ C$ for all measurements. The heating and cooling rate was $0.5^\circ C$ per minute, if not mentioned otherwise.

RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the viscosity accompanying the dissolution of as-delivered carrageenan powder (2.2, 3.1 and 3.9 wt.%) in water. The data were recorded with the rheometer *RS 80* in the rotational mode, using a shear rate of $10 s^{-1}$ and a heating rate of $0.5^\circ C/min$. The rotational mode of measurement is adequate in this case since the system can be expected to be almost purely viscous at room temperature (suspension of carrageenan xerogel fragments) and at $80^\circ C$ as well (carrageenan solution). It is evident that, apart from the temperature dependence of the baseline viscosity (dashed line), which is listed in table 2 (and which exhibit a reasonable concentration dependence in comparison to that of water), the temperature dependence of the viscosity exhibits a strong anomaly at intermediate temperatures, the position and amplitude of which again correlate well with the carrageenan concentration, cf. table 3. Moreover, the maximum viscosi-

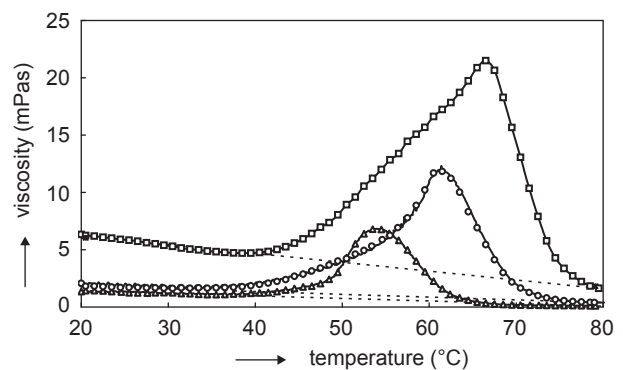


Figure 2. Temperature dependence of the viscosity accompanying the dissolution of carrageenan (2.2, 3.1 and 3.9 wt.%) in water (measured with rheometer *RS 80* in the rotational mode, shear rate $10 s^{-1}$, heating rate $0.5^\circ C/min$).

ty achieved (in mPas) can be plotted against concentration W_C (in wt.%) and fitted with a power law relation (correlation coefficient 0.995) to give $\eta = 1.35 \cdot W_C^{2.02}$

Figures 3 and 4 show the results of four oscillatory measurements of pure carrageenan solutions with the lowest concentration (2.2 wt.%) during cooling (two different samples). It is evident that the high-temperature behavior of G' , G'' and δ as well as the gel transition temperature T_H (defined here as the start temperature of the coil-to-helix transition on cooling) show excellent reproducibility and precision so that even such small effects as the shift of the gel transition tempera-

Table 2. Room temperature viscosity and temperature coefficient of the baseline viscosity (dashed line in figure 1) for pure carrageenan solutions during the first heating cycle.

Carrageenan concentration (wt.%)	Viscosity at 20°C (mPas)	Temperature coefficient of viscosity (mPas/°C)
0	1.00	-10.8
2.2	1.43	-22.7
3.1	1.84	-24.5
3.9	6.23	-77.5

Table 3. Maximum viscosities, temperatures corresponding to the maximum viscosities and temperatures where dissolution is complete (pure carrageenan solutions during the first heating cycle).

Carrageenan concentration (wt.%)	Maximum viscosity (mPas)	Temperature (°C) of	
		maximum viscosity	complete dissolution
2.2	7	54	66
3.1	12	61.5	74
3.9	21.5	66.5	77

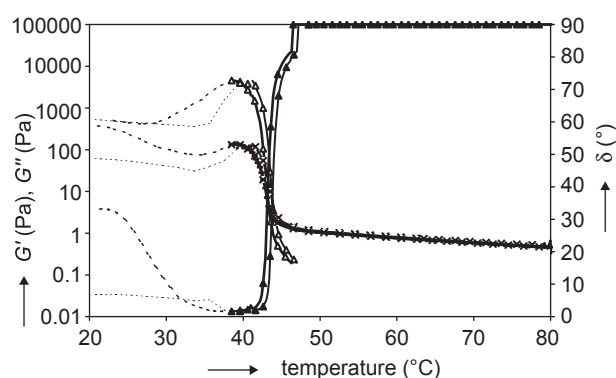


Figure 3. Temperature dependence of the storage modulus G' (Δ), loss modulus G'' (\times) and phase angle δ (\blacktriangle) for carrageenan solutions with 2.2 wt.% carrageenan (comparative sample of the same composition and preparation history as the sample in figure 4, measured to check reproducibility) during cooling (thin dotted line - first cooling cycle with cooling rate 0.2°C/min, thick line - second cooling cycle with cooling rate 0.5°C/min).

ture with cooling rate can be detected. For these carrageenan solutions the gel transition temperature T_H is 47.5°C for a cooling rate of 0.1°C/min, 47°C for a cooling rate of 0.2°C/min and 46°C for a cooling rate of 0.5°C/min. At temperatures higher than 48°C these solutions are purely viscous, i.e. the phase shift is 90° and the storage modulus is undefined. Upon cooling below that temperature the system is transformed (within a few °C) into a purely elastic hydrogel, characterized by zero phase shift ($\delta = 0^\circ$) and high values of the storage modulus. After passing through a maximum value the storage modulus decreases with further decrease of temperature (concomitantly, the phase shift goes through a minimum and then increases), as a consequence of wall slip effects. The observed maximum in G' , due to slippage at the wall, is well documented in the literature [26].

Figures 5 and 6 show the corresponding data for carrageenan solutions with higher concentration (3.1 and 3.9 wt.%). It is evident that with increasing concentration the solutions tend to exhibit a certain, albeit small, degree of elasticity even at temperatures above the gel transition temperature T_H , i.e. $\delta < 90^\circ$. Again, upon cooling below that temperature this viscoelastic system is transformed into a purely elastic hydrogel ($\delta = 0^\circ$, high G' values) and after passing through a maximum value the storage modulus apparently decreases, due wall slip effects.

In table 4 the gel transition temperatures T_H are compared for all three carrageenan solutions for cooling rates of 0.1°C/min (first cooling) and 0.5°C/min (second cooling after reheating). It is evident that there are systematic differences of 1.5-2°, with the higher temperature referring to the slower cooling rate, in full accordance with what can be expected from the kinetics of this viscoelastic transition region (which is determined by temperature and relaxation times). In accordance with the aforementioned fact that wall slip effects

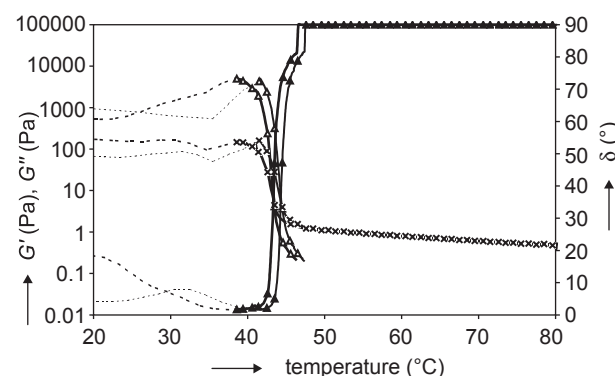


Figure 4. Temperature dependence of the storage modulus G' (Δ), loss modulus G'' (\times) and phase angle δ (\blacktriangle) for carrageenan solutions with 2.2 wt.% carrageenan during cooling (thin line - first cooling cycle with cooling rate 0.1°C/min, thick line - second cooling cycle with cooling rate 0.5°C/min).

Table 4. Gel transition temperatures (coil-to-helix) T_H for carrageenan solutions during the cooling cycle in dependence of the cooling rate.

Carrageenan concentration (wt.%)	T_H for cooling rate	
	0.1°C/min (°C)	0.5°C/min (°C)
2.2	47.5	46
3.1	53	51
3.9	57.5	56

Table 5. Gel transition temperatures (coil-to-helix) T_H and storage moduli G' at room temperature for zirconia suspensions with carrageenan concentrations (W_{CF}) of 0.7, 1.0 and 1.3 wt.% for two cooling cycles (both with cooling rate 0.5°C/min).

Carrageenan concentration (wt.%)	T_H (°C)	T_H (°C)	G' (kPa)	G' (kPa)
	first cooling	second cooling	first cooling	second cooling
0.7	29	28	3.1	2.1
1.0	33	32	12.1	9.9
1.3	37	36	25.8	21.2

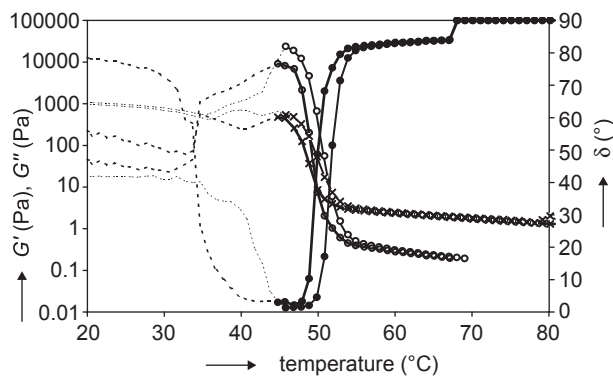


Figure 5. Temperature dependence of the storage modulus G' (○), loss modulus G'' (×) and phase angle δ (●) for carrageenan solutions with 3.1 wt.% carrageenan during cooling (thin line - first cooling cycle with cooling rate 0.1°C/min, thick line - second cooling cycle with cooling rate 0.5°C/min).

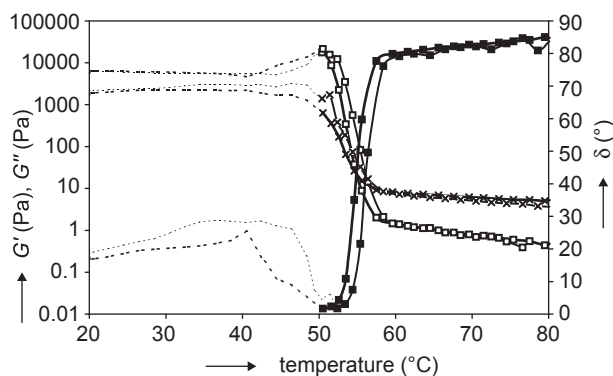


Figure 6. Temperature dependence of the storage modulus G' (□), loss modulus G'' (×) and phase angle δ (■) for carrageenan solutions with 3.9 wt.% carrageenan during cooling (thin line - first cooling cycle with cooling rate 0.1°C/min, thick line - second cooling cycle with cooling rate 0.5°C/min).

are responsible for the apparent decrease in the storage modulus G' (and concomitant artifacts in the phase angle δ) with decreasing temperature below T_H , it is clear that only the maximum values of G' have physical significance. These are 4.7, 15 and 20 kPa for carrageenan concentrations of 2.2, 3.1 and 3.9 wt.%, respectively. Fitting with the power law relation (3) yields $G' = 1.48 \cdot W_C^{1.93}$, where the storage modulus G' is in kPa (correlation coefficient 0.963).

Figures 7 through 9 show the temperature dependence of G' and δ for the three zirconia suspensions upon cooling. From the δ values around 45° at 80°C it is evident that even at these high temperatures the carrageenan-containing zirconia suspensions exhibit a rather large degree of elasticity. In other words, they are not completely viscous but viscoelastic, in contrast to the pure carrageenan solutions (especially those with low concentration of carrageenan). During cooling the degree of elasticity increases continuously until at the gel transition temperature T_H the phase angle δ exhibits a steep final decrease to values very close to zero, i.e. the completely elastic state is attained within a few °C. Table 5 lists the gel transition temperatures T_H and the resulting storage moduli G' at room temperature. A comparison of the data from the first cooling cycle with those of the second shows that, although the high-temperature behavior is different in a characteristic way (obviously due to a memory effect in the material), both the gel transition temperatures T_H and the storage moduli G' at room temperature are very well reproducible (T_H within approx. 1°C, G' within 1-5 kPa). Figure 10 shows that the temperature of the helix-to-coil transition during heating is not well defined (covering a range of approx. 10 - 25°C) and shifted towards significantly higher values (mean values 50, 58 and 63°C), compared to the cooling cycle (29, 33 and 37°C, respectively). The hysteresis between the average helix-to-coil transition temperature T_C on heating and the gel transition temperature T_H on cooling (coil-to-helix transition temperature) is approx. 20-25°C, cf. [16]. The dependence of the room temperature storage modulus G' (in kPa) of zirconia green bodies on the carrageenan concentration W_{CF} related to the aqueous phase (in wt.%) can be expressed via the power law $G' = 9.82 \cdot W_{CF}^{3.17}$, obtained by fitting the arithmetic means of the values in table 5 (correlation coefficient 0.998). The value of the exponent (3.17) is considerably higher than for pure carrageenan gels (1.93), indicating a synergetic effect of zirconia powder in combination with carrageenan: although the zirconia concentration is identical in all three systems, the elastic modulus increases faster with carrageenan concentration than expected from the increase of the matrix storage modulus (G' of the carrageenan gel) alone. Note that for all three suspensions the storage moduli (2-26 kPa) are high enough for the green bodies to be demolded and handled without danger of deformation.

SUMMARY AND CONCLUSIONS

With the advance of new shaping techniques the rheology of aqueous carrageenan systems, in particular their viscoelastic behavior, has become a point of inte-

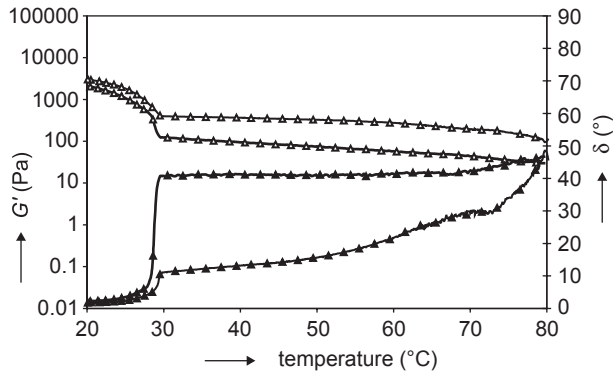


Figure 7. Temperature dependence of the storage modulus G' (Δ) and phase angle δ (\blacktriangle) for zirconia suspensions with 0.7 wt.% carrageenan (W_{CF}) for two cooling cycles (thin line - first cooling, thick line - second cooling).

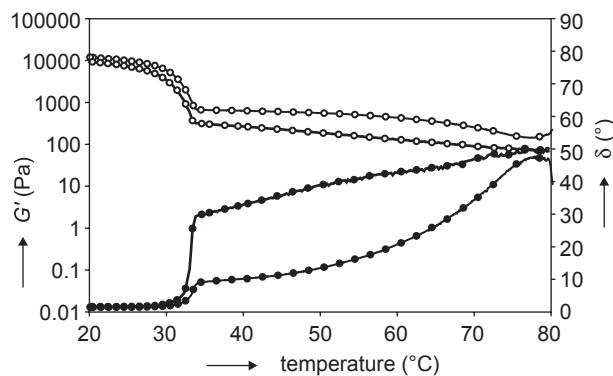


Figure 8. Temperature dependence of the storage modulus G' (\circ) and phase angle δ (\bullet) for zirconia suspensions with 1.0 wt.% carrageenan (W_{CF}) for two cooling cycles (thin line - first cooling, thick line - second cooling).

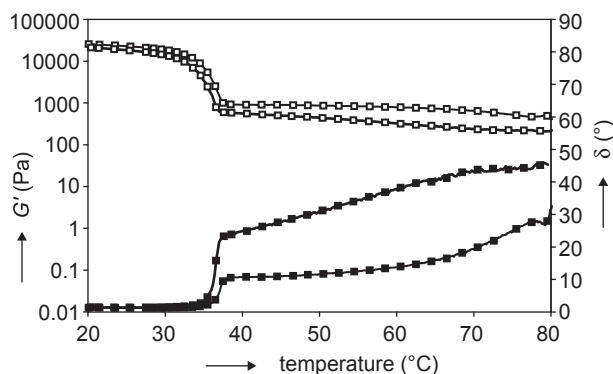


Figure 9. Temperature dependence of the storage modulus G' (\square) and phase angle δ (\blacksquare) for zirconia suspensions with 1.3 wt.% carrageenan (W_{CF}) for two cooling cycles (thin line - first cooling, thick line - second cooling).

rest in ceramic technology. The function of carrageenan as a gelling agent is based on the ability to form elastic hydrogels from viscous aqueous solutions upon cooling. In this paper the rheology of carrageenan solutions and carrageenan-containing ceramic suspensions has been studied by oscillatory shear rheometry. It has been shown that aqueous solutions with 2.2, 3.1 and 3.9 wt.% carrageenan undergo reversible gelation within a temperature range of approx. 5°C at gelation temperatures of 46, 51 and 56°C, respectively. The resulting storage moduli of the gels are approx. 5, 15 and 20 kPa, respectively, thus exhibiting a strong dependence on the carrageenan concentration. Results concerning the rheology of zirconia suspensions, containing 67 wt.% zirconia (Tosoh TZ-3YE) and effective carrageenan concentrations of 0.7, 1.0 and 1.3 wt.% in the aqueous phase, have been summarized as well. In contrast to pure carrageenan solutions, which are purely viscous at elevated temperatures the mixed suspensions (containing zirconia and carrageenan) are viscoelastic at 80°C and exhibit lower gelation temperatures on cooling (29, 33 and 37°C, respectively). The resulting storage moduli after cooling to room temperature are in the range 2-25 kPa, i.e. of the same order as for pure carrageenan hydrogels. This green rigidity guarantees easy demolding and further handling of the as-shaped ceramic green bodies. Finally, it has been shown that the concentration dependences of viscosities and storage moduli can be conveniently described by power law relations.

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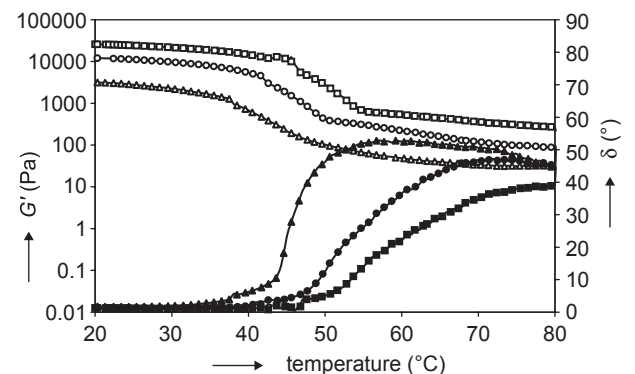


Figure 10. Temperature dependence of the storage modulus G' (Δ , \square , \circ) and phase angle δ (\blacktriangle , \blacksquare , \bullet) for zirconia suspensions with 0.7 (Δ , \blacktriangle), 1.0 (\circ , \bullet) and 1.3 wt.% (\square , \blacksquare) carrageenan (W_{CF}) during the heating cycle.

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REOLOGIE KERAMICKÝCH SUSPENZÍ S OBSAHEM ORGANICKÝCH RESP. BIOPOLYMERNÝCH GELUJÍCÍCH ADITIV
ČÁST 2. SUSPENZE S OBSAHEM KARAGENANU
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V souvislosti s novými tvarovacími metodami keramických suspenzí roste v keramické technologii zájem i o reologii vodných soustav s obsahem karagenanu, včetně jejich viskoelastického chování. Funkce karagenanu jakožto gelující přísady je založena na schopnosti tvořit elastické hydrogely z viskózních vodných roztoků během chlazení. V tomto článku je pomocí oscilační reometrie studována reologie karagenanových roztoků a keramických suspenzí obsahujících karagenan. Je ukázáno, že vodné roztoky s obsahem 2.2, 3.1 a 3.9 hm.% karagenanu vykazují reverzibilní gelaci v poměrně úzkém teplotním intervalu cca. 5 °C při teplotách 46, 51 a 56 °C. Výsledné akumulární moduly gelů jsou cca. 5, 15 a 20 kPa, v závislosti na použité koncentraci karagenanu. Kromě viskoelastického chování čistých karagenanových roztoků jsou shrnuty výsledky týkající se reologie zirkoničitých suspenzí obsahujících karagenan, tj. suspenzí s obsahem 67 hm.% oxidu zirkoničitého (TZ-3YE, Tosoh) a výslednými koncentracemi karagenanu 0.7, 1.0 a 1.3 hm.% (vztaheno k vodné fázi). Na rozdíl od karagenanových roztoků, které jsou při zvýšených teplotách čistě viskózní, jsou tyto suspenze při 80 °C viskoelastické a vykazují nižší gelovací teploty během chlazení (29, 33 a 37°C). Výsledné akumulární moduly po chlazení na pokojovou teplotu jsou v oblasti 2-25 kPa, tzn. řádově stejně velké jako pro karagenanové gely. Takovéto hodnoty zaručují bezdefektní vyjímání vzorků z forem a bezproblémovou manipulaci s takto zhotovenými syrovými tělesy.