

Viscoelastic behavior of ceramic suspensions with carrageenan

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Received 3 November 2004; received in revised form 13 January 2005; accepted 23 January 2005

Available online 26 February 2005

Abstract

Aqueous gelcasting of ceramic suspensions with carrageenan is one of the novel ceramic shaping techniques that have received considerable attention during the last few years. The ability of carrageenans to form cold-setting reversible gels in aqueous media is responsible for the body formation step. In this work the rheology and viscoelastic behavior of these systems is studied. Zirconia (TZ-3YE) suspensions with a solids loading of 67 wt.% (i.e. approximately 25 vol.%) and three different carrageenan concentrations (0.7, 1.0 and 1.3 wt.%, related to the free water content in the suspension) were prepared. The temperature dependence of the dynamic storage and loss moduli is determined by oscillatory shear rheometry. The concentration dependence of melting and cooling cycles (ranges 50–63 and 29–37 °C, respectively) is considered and analyzed. The results are interpreted in terms of linear viscoelasticity and the gelation step is discussed in relation to the mechanism of body formation.

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Keywords: Shaping; Slip-casting; Suspensions; Sol–gel processes; ZrO₂

1. Introduction

With the advance of new shaping methods for ceramic suspensions, using organic or bioorganic components, there is an increased interest in the viscoelastic behavior of these systems. Knowledge of the viscoelastic behavior is necessary because gelation, i.e. a continuous change in the rheological behavior from viscous to viscoelastic or elastic, is the essential body-forming step in many of the new shaping processes, such as casting of ceramic suspensions with polypeptides (e.g. gelatine^{1–5}) or polysaccharides (e.g. agarose, agar or carrageenan^{5–17}), including starch consolidation casting.^{5,18–26} For the latter it has been shown, that starch swelling alone cannot be the only mechanism of body formation, since the (independently measured) starch swelling kinetics is too rapid compared to the time necessary for body formation.²⁴ Thus, in addition to the steric effect due to swelling (excluded volume effect) a subsequent change in

the rheological properties is required to account for the full time needed to produce rigid green bodies. In the case of carrageenan and similar polysaccharides (agaroids), rheology has been thoroughly studied for silicon nitride suspensions with solids loadings of 43 vol.% (70 wt.%)^{9,10} and for alumina suspensions usually with a solids loadings of 50 vol.% (80 wt.%).^{8,11,12,14,16}

As far as the concentration measures are concerned, it has to be emphasized, however, that they are meant to be concentrations of the as-prepared stock suspensions before mixing with the (bio-)organic components. The final solids volume fractions after mixing, for all alumina suspensions whose rheology has been characterized so far, are considerably lower, e.g. between 25 and 45 vol.% for alumina suspensions with agaroids.^{8,11,12,14,16} As a consequence of the low solids volume fractions and the fact that casting is performed into non-porous molds, the shrinkage is high. Reported drying shrinkage values range from 5 to 26% (linear),¹⁵ but the total shrinkage after firing (sintering) can be expected to be much higher. Of course, these high shrinkage values have to be kept in mind when these methods, at the current

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state-of-the-art, are called “near-net” shaping techniques.¹² Although bulk densities close to the theoretical density can be achieved, such high shrinking values bear considerable danger of geometrical deformation and impede a precise control of dimensional tolerances.

Only one paper,⁶ dealing with alumina suspensions containing agar and locust bean gum (galactomannan), covers a concentration range of 40–60 vol.% (73–86 wt.%) of alumina after mixing with the polysaccharide. In that work, linear drying shrinkage could be reduced from 4 to 6% for alumina green bodies prepared from the 40 vol.% suspensions to 0.4–1.3% for those prepared from the 60 vol.% suspensions. Total shrinkage after sintering was 14–17% and approximately 10% (linear) for alumina green bodies prepared from the 40 vol.% and the 60 vol.% suspensions, respectively. These are acceptable values for a net-shaping technique.

As far as rheology is concerned, the majority of published work applies only rotational viscometry (using a double-cone sensor system) with controlled shear rate,^{8–10,12–14,16} resulting in flow curves covering a shear rate range of approximately 0–1000 s⁻¹. In these works shear-thinning behavior (with or without hysteresis, i.e. a certain degree of thixotropy) has been found in most cases. Apparent viscosities have been determined for constant shear rates ranging from 5 to 500 s⁻¹, with a preference for the value 100 s⁻¹. The order-of-magnitude of the apparent viscosities of alumina suspensions with polysaccharides exhibits a range from approximately 5 to 50 Pa s for shear rates of 5 s⁻¹^{11,16} and a range between <100 and 2000 mPa s for shear rates of 100 s⁻¹,^{12,14} depending on composition (type of polysaccharide or polysaccharide mixture), concentration (solids volume fraction and polysaccharide concentration) and temperature. Interestingly, the latter viscosity range is not significantly different from the viscosity range covered for pure polysaccharide solutions (without alumina powder).¹³ This, of course, can in principle be a consequence of the fact that either the influence of alumina on the overall rheological behavior of the suspension is small (due to the relatively low concentration) or the measuring range of the double-cone sensor system is exceeded or the measured viscosities after gelling are artifacts due to wall-slip errors.

In any case, the rheological characterization of ceramic suspensions containing polysaccharides by rotational viscometry is inadequate from a principal point of view. However, despite the fact that viscoelasticity is quite common among polysaccharide systems, and in particular the viscoelastic behavior of gelling carrageenans is well known and widely used in food technology,^{27–30} it seems that but a few researchers in the field of ceramic technology have recognized this fact recently as serious as it should be taken. Actually, up to now, only two works have drawn the unavoidable consequence and have used oscillatory rheometry for the characterization of ceramic suspensions containing carrageenan.^{6,11} Elastic moduli (shear or storage moduli) measured for gelled suspensions (ready for demolding) are of the order 1–10 kPa.

Far from being only an additional source of information—as it might seem to traditional ceramists accustomed to classical viscometric measurements—it has to be recalled that rheometry has to *replace* viscometry in the case of viscoelastic systems, because from the viewpoint of the theory of materials, e.g. an (apparent) viscosity is not even defined for viscoelastic materials. Rotational viscometry is absolutely sufficient for purely viscous ceramic suspensions without polysaccharides. It can be used as an auxiliary tool to roughly assess, e.g. the castability of ceramic suspensions with polysaccharides or to perform a qualitative and relative comparison between the rheological behavior of these systems when only one parameter (e.g. solids volume fraction, polysaccharide concentration or temperature) is changing. It is, however, absolutely inadequate for the quantitative characterization of the rheological behavior of viscoelastic systems or systems exhibiting a sol–gel transition from viscous to elastic. In this case rheometry, at least in its simplest variant (oscillatory rheometry), is an indispensable tool.

The theory of viscoelasticity, especially in its non-linear parts, is rather complex. There are of course many excellent textbooks and monographs on this topic. A rather representative and comprehensive bibliographical list has been given recently.³¹ For a routine characterization of gelation processes, however, it is usually not necessary to invoke the general theory. In many cases it is sufficient to know the rheological behavior in the range of small stresses, deformations or deformation rates, i.e. in the range where the linear theory of viscoelasticity is approximately valid. For this range of applications the theory has been concisely summarized in.³¹

It is the aim of the present contribution to present and comment the results of oscillatory shear measurements obtained for carrageenan-containing zirconia suspensions, which have not been studied so far. In the first part of the theoretical section the structure and rheology of gelling carrageenans is summarized. In the second, the linear theory of viscoelasticity is briefly outlined (to the degree necessary to adequately interpret oscillatory shear measurements). The experimental section gives material characteristics and experimental details. Finally, the results are critically discussed and compared to the findings of other authors on related systems.

2. Theoretical

2.1. Carrageenans as body-forming agents in ceramic suspensions

Carrageenans are linear, water-soluble, sulfated polysaccharides extracted from various species of the *Rhodophyta* (marine red algae). Their structure is generally based on repeating, glycosidically linked, disaccharide units of 1-3-linked β -D-galactose (galactopyranose, “A units”) and 1-4-linked α -D-galactose (galactopyranose, “B units”), but with the different carrageenans having different degrees of sulfa-

tion (H substituted by SO_3^- groups) of the monosaccharide residues and different extents of conversion of the 1-3-linked B units to the anhydride (3,6-anhydro) ring-form.^{32,33} Carrageenans are distinguished from the closely related agars in that the B units occur in the D form in carrageenans and in the L form in agars. Commonly, one distinguishes four ideal structural types: λ -carrageenan, ι -carrageenan, κ -carrageenan and β -carrageenan. The most highly sulfated type is λ -carrageenan, which does not form ordered helices and, thus, does not gel. The ideal β -carrageenan type is sulfate-free. All gelling, i.e. helix-forming, carrageenans contain large proportions of ι -, κ - and β -blocks, which all contain the 3,6-anhydro form of the B unit.

Being a raw material of biological origin, native carrageenans are quite polydisperse with respect to molecular weight and the residue composition varies with the algal source and from batch to batch. However, it is usually possible to obtain more homogeneous fractions by salt precipitation. This is the basis of the original definitions of λ -carrageenan and κ -carrageenan as the fractions that are soluble or insoluble, respectively, in a 0.25 M KCl solution. Fractions of nearly pure κ -carrageenan may be obtained from the algae *Eucheuma cottonii*.^{34,35} Similarly pure fractions of β -carrageenan have not been obtained. Typically, β -blocks occur together with κ -blocks. *Eucheuma gelatinae* yields a gelling carrageenan with a particularly low sulfate content.³⁶ A special, but thoroughly studied, gelling carrageenan type is furcellaran, a mixture of κ - and β -types with a κ - β -ratio of approximately 3:2, extracted from *Furcellaria lumbricalis*,³⁷ cf. also.³³

In aqueous solution, at low temperatures and in the presence of potassium-ions, κ -carrageenan forms double helical structures with a pitch of 2.5 nm.^{32,33} On heating, these structures “melt”. The molecules undergo a helix-to-coil transition, passing from an ordered state containing double-helices to the random-coil state at a well-defined temperature T_C . This process is reversible. On cooling, the κ -carrageenan reverts to the helical structure, again at a well-defined transition temperature T_H . Typically, such systems exhibit hysteresis, with a significant difference between T_C and T_H .³² For other carrageenans than κ -carrageenan, as well as for low-molecular-weight fractions of κ -carrageenan, the transitions are not sharp.³³ Below, a certain critical molecular weight ($M \approx 3 \times 10^4$), no gel is formed. Above this value, the elastic modulus (shear modulus G or storage modulus G') of potassium-containing κ -carrageenan gels increases steeply with the molecular weight (up to $M \approx 2 \times 10^5$), above which it is independent of molecular weight.^{38,39} The dependence of the gel properties on carrageenan concentration has been studied by a number of groups.^{33,38–41} Rochas et al.³⁹ found that the critical concentration for gelation C_0 was of the order of a fraction of a percent. At higher concentrations $C > C_0$, the elastic modulus of κ -carrageenan gels follows a power law of the form

$$G = KC^n, \quad (1)$$

where K is a fit parameter and the exponent n adopts values between 2 and 2.4. Hermansson⁴² studied the influence of cooling rate and salt ion effects on the elastic modulus (and thus gel strength) of κ -carrageenan gels. He found that for a 1% sample in 0.1 M KCl the elastic modulus obtained with a cooling rate of 0.5 °C/min was three times higher than with a rate of 1.5 °C/min. Usually, increasing salt concentration (for κ -carrageenan especially that of potassium ions) enhances the elastic modulus (as long as the salt concentration is not too high).³³

The coil-to-helix transition on cooling proceeds according to second-order kinetics and is generally more rapid for κ -carrageenan than for ι -carrageenan.³³ With respect to potential applications in ceramic shaping technologies it is important to note that, apart from the sulfate content, potassium is usually contained in carrageenan as a result of the extraction process. Far from being an impurity only, this potassium content is essential from a functional point of view in that it increases the stability of the ordered (i.e. helical) conformation, promotes gelation and aggregation (into chain dimers or “superstrands”) and enhances gel strength, especially in κ -carrageenan.^{32,33,43} Similar ion sensitivity is a striking feature of all gelling carrageenans.

Although not much is known about the gel structure itself, it is highly probable that the mechanism of gelation consists not only in the formation of helices but, at least for κ -carrageenan, involves the formation of junction zones (i.e. helix aggregation) as well.³³

From the viewpoint of chemical purity (relatively low sulfate content), gel-forming ability, coil-to-helix transition kinetics and temperatures, commercial availability and price (especially compared to agarose, which is sulfate-free) κ -carrageenan can be a reasonable compromise for use in ceramic shaping technologies.

2.2. Linear viscoelasticity in small amplitude oscillatory shear

When an isotropic, linearly viscoelastic material is subjected to a sinusoidally varying shear strain γ (at a frequency below that required to induce resonance vibrations),

$$\gamma = \gamma_0 \cos \omega t, \quad (2)$$

where γ_0 is the shear strain amplitude, t , time and ω , angular frequency, the shear stress response is

$$\tau = \tau_0 \cos(\omega t + \delta) = \tau_0 \cos \delta \cos \omega t - \tau_0 \sin \delta \sin \omega t, \quad (3)$$

where τ_0 is the shear stress amplitude and δ the phase angle (phase shift). Eq. (3) demonstrates that the shear stress consists of two components. One component is of magnitude $\tau_0 \cos \delta$ and is in phase with the strain, the other (of magnitude $\tau_0 \sin \delta$) is 90° ahead of the strain and thus in phase with the shear rate

$$\dot{\gamma} = \frac{d\gamma}{dt} = -\omega \gamma_0 \sin \omega t. \quad (4)$$

Therefore, the material behaves partly as an elastic solid and partly as a viscous liquid, and the stress–strain relation (3) can be written as

$$\tau = \gamma_0(G' \cos\omega t - G'' \sin\omega t), \quad (5)$$

where the storage modulus G' is

$$G' = \frac{\tau_0}{\gamma_0} \cos\delta \quad (6)$$

and the loss modulus G'' is

$$G'' = \frac{\tau_0}{\gamma_0} \sin\delta. \quad (7)$$

The ratio

$$\frac{G''}{G'} = \tan\delta \quad (8)$$

is termed the loss factor (damping factor, loss tangent). It should be emphasized that G' , G'' and $\tan\delta$ depend on the test frequency and on temperature. An alternative formulation of linear viscoelasticity is possible via complex numbers. Making use of the Euler relation (with the complex unity $i = \sqrt{-1}$)

$$\cos\omega t + i \sin\omega t = \exp(i\omega t) \quad (9)$$

the strain and stress cycles (2) and (3) can be represented by the real parts of

$$\gamma^* = \gamma_0 \exp(i\omega t) \quad (10)$$

and

$$\tau^* = \tau_0 \exp[i(\omega t + \delta)]. \quad (11)$$

Then the complex modulus G^* is

$$\begin{aligned} G^* &= \frac{\tau^*}{\gamma^*} = \frac{\tau_0}{\gamma_0} \exp(i\delta) = \frac{\tau_0}{\gamma_0} (\cos\delta + i\sin\delta) = G' + iG'' \\ &= G'(1 + i\tan\delta). \end{aligned} \quad (12)$$

In complete analogy a complex viscosity can be defined via Eqs. (3) and (4), where the shear rate is the real part of

$$\dot{\gamma}^* = i\omega\gamma_0 \exp(i\omega t). \quad (13)$$

The complex viscosity η^* is then

$$\begin{aligned} \eta^* &= \frac{\tau^*}{\dot{\gamma}^*} = \frac{\tau_0}{i\omega\gamma_0} \exp(i\delta) = \frac{\tau_0}{i\omega\gamma_0} (\cos\delta + i\sin\delta) \\ &= \frac{G'}{i\omega} + \frac{iG''}{i\omega} = \frac{G''}{\omega} - i\frac{G'}{\omega} = \eta' - i\eta''. \end{aligned} \quad (14)$$

Between the complex modulus and the complex viscosity the following relation holds:

$$G^* = i\omega\eta^*. \quad (15)$$

In other words, the real part of the complex modulus (the storage modulus, a measure of the elasticity of a fluid, for

perfectly elastic solids equal to the shear modulus) is connected to the imaginary part of the viscosity via

$$G' = \omega\eta'', \quad (16)$$

while the imaginary part of the complex modulus (the loss modulus, a measure of energy dissipation) is connected to the real part of the viscosity via

$$G'' = \omega\eta'. \quad (17)$$

Of course both the complex modulus and the complex viscosity are frequency- and temperature-dependent.

3. Experimental

3.1. Material characteristics and sample preparation

Zirconia suspensions were prepared using a commercially available submicron tetragonal zirconia powder type (TZ-3YE, Tosoh, Japan). These powder contain >99.7 wt.% ZrO₂ (tetragonal phase stabilized by 3 mol%, i.e. 5 wt.%, Y₂O₃) and 0.25 ± 0.1 wt.% Al₂O₃. The median particle size is approximately 0.6 μm and the specific surface area approximately 16 ± 3 m²/g. Similar to other zirconia powders, the solids volume fractions which can be achieved with this powder type are considerably lower than those achievable, e.g. with alumina powders. Aqueous suspensions with a solids loading of 75 wt.% (approximately 35 vol.%) were prepared using 1.1 wt.% (based on solids) of a commercial deflocculant (Dolapix CE 64, Zschimmer & Schwarz, Germany). After mixing in polyethylene bottles the zirconia suspensions were agitated with zirconia balls in a laboratory shaker (HS 206 B, IKA Werke, Germany) for 90 min, followed by 30 s ultrasonic treatment (UP 200S, Dr. Hielscher, Germany). Subsequently, the as-prepared zirconia suspensions were heated up to approximately 60 °C and were ready for mixing with the as-prepared carrageenan stock solutions.

The carrageenan stock solutions were prepared using a commercially available κ-carrageenan (Secogel TCP, Hispangar, Spain) obtained by alkaline extraction from different red seaweeds of the order *Gigartinales*, purified by filtration and reprecipitated with KCl. It is supplied in the form of granules <250 μm with a moisture content of <12 wt.%. The heavy metal content is <20 ppm (As 3 ppm, Pb 5 ppm, Cd 2 ppm and Hg 1 ppm). According to the supplier it should be used in concentrations of approximately 0.5–1.2% (depending on the purpose), results in solutions with a pH range of 7–11 and its gels should exhibit a “strength” of approximately 130–190 Pa (the physical meaning or determination method of this “strength” is not given, however). RFA measurements (X-ray fluorescence analysis) revealed in the detectable fraction (i.e. without light elements H, C and O) a preponderance of K (59%), Cl (23%) and S (16%), apart from a small content of Na (1.1%) and Ca (0.8%). Carrageenan stock solutions were prepared with 2.15, 3.05 and 3.92 wt.% carrageenan in

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	2.15	0.7	67
75	3.05	1.0	67
75	3.92	1.3	67

distilled water by mixing and heating in a closed glass vessel up to approximately 80 °C to ensure complete dissolution.

Mixing of zirconia stock suspensions and carrageenan stock solutions was performed at approximately 60 °C in such a way that the resulting zirconia concentration in the final suspensions with carrageenan was 67 wt.% (i.e. approximately 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} .

3.2. Measurement details

The rheological behavior of the suspensions was characterized via small amplitude oscillatory shear measurements using the rheometer RS 80 (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. Stress sweep tests and frequency sweep tests were performed for carrageenan solutions with lowest (2.15 wt.%) and highest (3.92 wt.%) concentration at 20 °C (after cooling) to assess the frequency dependence of the vis-

coelastic 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. Reproducibility and time independence of the measured values (during 300 s) was tested (and confirmed) for the 3.92 wt.% carrageenan solution.

For measuring the final suspensions a frequency of 1 Hz and a strain amplitude of 1% was chosen. The rheological behavior of the final suspensions (as-cooled) was characterized during the heating cycle (gel melting) and during the subsequent cooling cycle (gelation) in the temperature range from 20 to 80 °C. The heating and cooling rate was 0.5 °C/min.

4. Results and discussion

Figs. 1, 2 and 3 show the storage modulus G' (empty symbols), loss modulus G'' (full symbols) and phase angle δ (crosses) for final suspensions with carrageenan concentrations (W_{CF}) of 0.7 wt.% (triangles), 1.0 wt.% (circles) and 1.3 wt.% (squares), respectively, during the heating cycle. Figs. 4, 5 and 6 show the corresponding data for the cooling cycle.

At room temperature (20 °C) all investigated systems consist in a gel matrix with embedded zirconia particles and exhibit purely elastic behavior, as indicated by the almost zero value of the phase angle. At this temperature the storage modulus G' (corresponding to the usual elastic shear modulus G in this case) attains values of approximately 2–3, 10–12 and 20–26 kPa for carrageenan concentrations (W_{CF}) of 0.7, 1.0 and 1.3 wt.%, respectively, cf. also Fig. 7, which compares the temperature dependence of G' for all three systems during a second heating cycle (with linear ordinate). Of course, these values can be considered as rela-

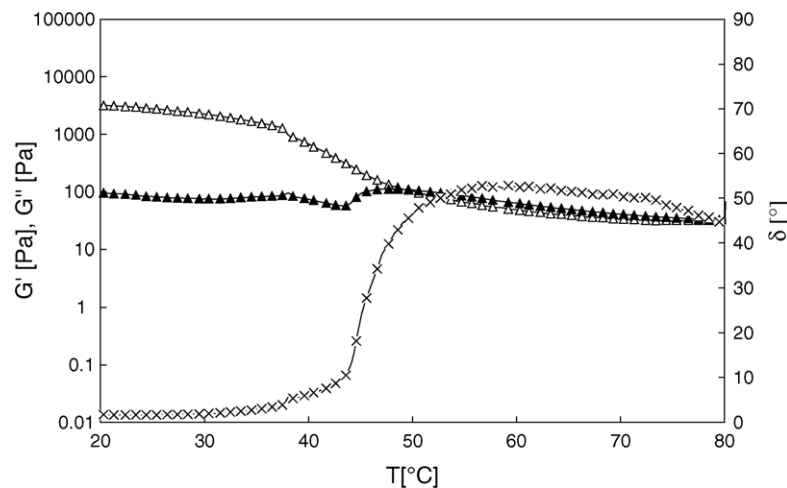


Fig. 1. Temperature dependence of the storage modulus G' (empty triangles), loss modulus G'' (full triangles) and phase angle δ (crosses) for zirconia suspensions with 0.7 wt.% carrageenan (W_{CF}) during the heating cycle.

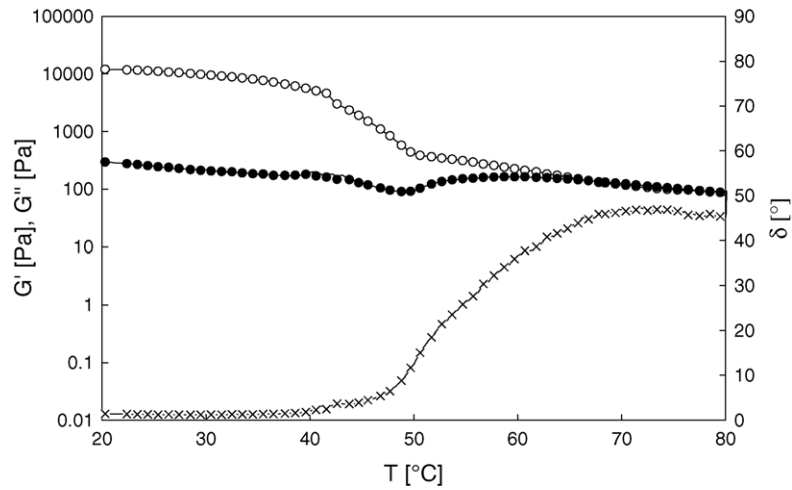


Fig. 2. Temperature dependence of the storage modulus G' (empty circles), loss modulus G'' (full circles) and phase angle δ (crosses) for zirconia suspensions with 1.0 wt.% carrageenan (W_{CF}) during the heating cycle.

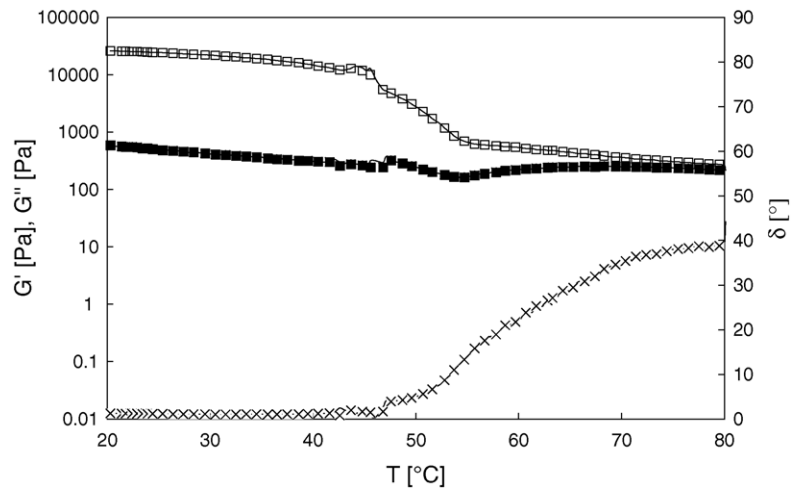


Fig. 3. Temperature dependence of the storage modulus G' (empty squares), loss modulus G'' (full squares) and phase angle δ (crosses) for zirconia suspensions with 1.3 wt.% carrageenan (W_{CF}) during the heating cycle.

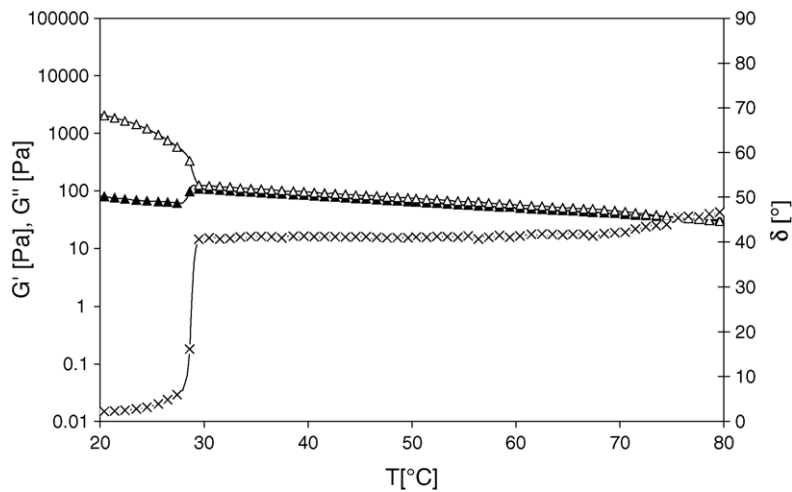


Fig. 4. Temperature dependence of the storage modulus G' (empty triangles), loss modulus G'' (full triangles) and phase angle δ (crosses) for zirconia suspensions with 0.7 wt.% carrageenan (W_{CF}) during the cooling cycle.

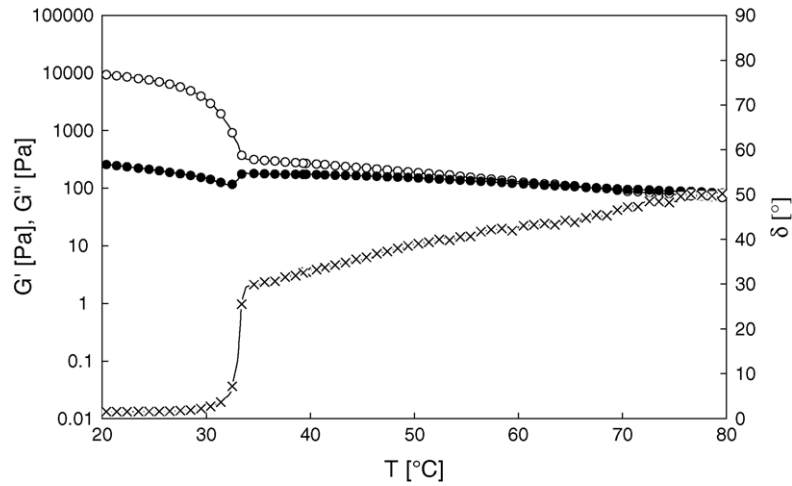


Fig. 5. Temperature dependence of the storage modulus G' (empty circles), loss modulus G'' (full circles) and phase angle δ (crosses) for zirconia suspensions with 1.0 wt.% carrageenan (W_{CF}) during the cooling cycle.

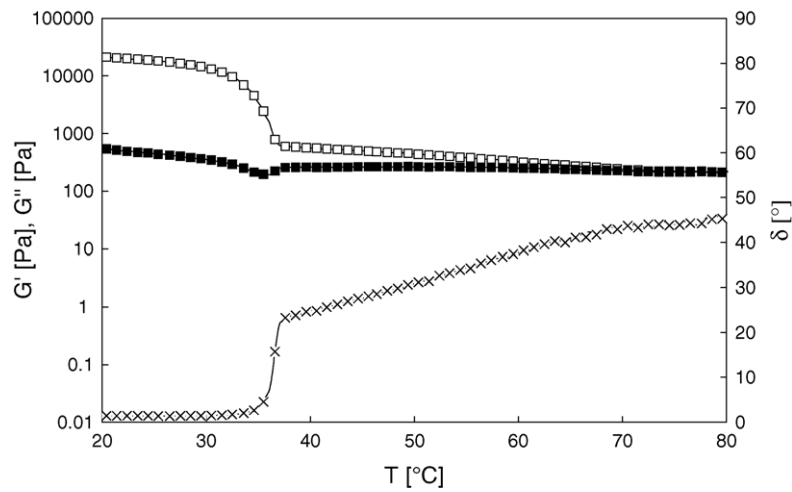


Fig. 6. Temperature dependence of the storage modulus G' (empty squares), loss modulus G'' (full squares) and phase angle δ (crosses) for zirconia suspensions with 1.3 wt.% carrageenan (W_{CF}) during the cooling cycle.

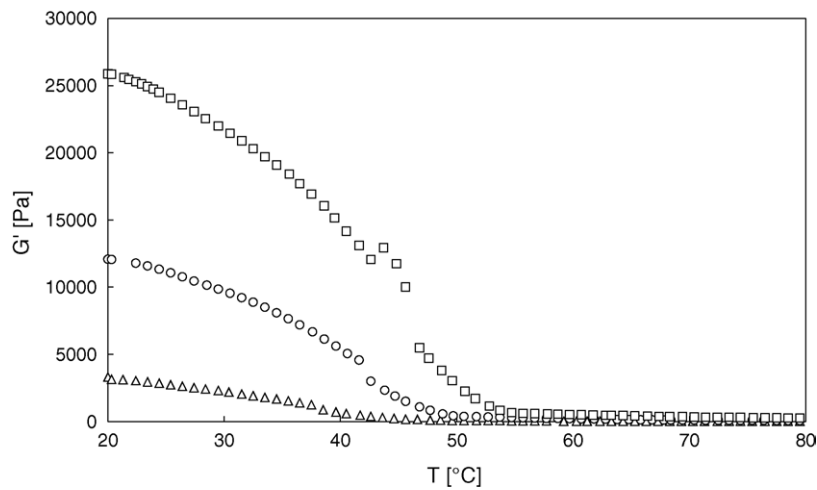


Fig. 7. Temperature dependence of the storage modulus G' compared for all three systems, i.e. for carrageenan concentrations (W_{CF}) of 0.7 (triangles), 1.0 (circles) and 1.3 wt.% (squares), respectively (second heating cycle).

Table 2

Temperatures and temperature differences characterizing the carrageenan-containing zirconia suspensions or gels during heating and cooling; T_C^- and T_C^+ denote start and end temperature, respectively, of the transition region during heating, $\Delta T_C = T_C^+ - T_C^-$ their difference, $\langle T_C \rangle$ the average transition temperature, T_H the onset of transition during cooling and $\langle T_C \rangle - T_H$ the hysteresis between the helix-to-coil transition on heating and the coil-to-helix transition on cooling

W_{CF} (wt.%)	T_C^- (°C)	T_C^+ (°C)	ΔT_C (°C)	$\langle T_C \rangle$ (°C)	T_H (°C)	$\langle T_C \rangle - T_H$ (°C)
0.7	44	56	12	50 ± 6	29	21
1.0	49	67	18	58 ± 9	33	25
1.3	51	75	24	63 ± 12	37	26

tive measures of the strength of the ceramic green bodies.³¹ Thus, compared to the gel strength of pure carrageenan gels the strength of the resulting ceramic green bodies is higher by at least 1–2 orders of magnitude. Such a strength is more than sufficient for successful demolding and subsequent handling.

With increasing temperature the storage modulus decreases and as soon as the phase angle increases to values significantly above zero, the material becomes viscoelastic and G' cannot be interpreted as an elastic modulus any more. At a certain temperature the gel matrix starts to melt. The underlying helix-to-coil transition is accompanied by a steep increase in the phase angle, i.e. viscoelastic behavior. In contrast to what is reported for pure carrageenan gels, however, the transition is not sharp for zirconia suspensions with carrageenan. Instead of a well-defined temperature T_C we have a broad temperature range $\Delta T_C = T_C^+ - T_C^-$ (with T_C^- and T_C^+ denoting the start and the end of the transition region) around an average temperature $\langle T_C \rangle$, cf. Table 2. The final values of the phase angle (δ approximately $45 \pm 5^\circ$) indicate that even at the highest temperatures achieved (80°C), none of the suspensions attains purely viscous behavior (which would be characterized by $\delta = 90^\circ$), in contrast to what should be expected for pure carrageenan solutions.

The coil-to-helix transition occurring in the matrix phase on cooling is much sharper. Based on the abrupt change of the phase angle on cooling, its onset expresses itself in a significant change of the suspension rheology and can be characterized by a well-defined transition temperature T_H . Table 2 lists all these characteristic temperatures, together with the hysteresis $\langle T_C \rangle - T_H$ between the helix-to-coil transition on heating and the coil-to-helix transition on cooling.

It is evident that all characteristic temperatures are strongly dependent on the carrageenan concentration, so that process control is possible by fine-tuning the carrageenan concentration. With respect to the casting process and the body formation step it should be noted that the suspensions are all viscoelastic even at the highest temperature (80°C). Usually, viscoelastic behavior (which, of course, is a kind of time-dependent behavior) is not advantageous in casting processes. Preferably, the “ideal” casting suspension should be purely viscous. This drawback, however, is compensated by the fact that the interval of “workability” is quite large, viz. from 80°C , say, down to 29, 33 and 37°C for suspensions with carrageenan concentrations (W_{CF}) of 0.7, 1.0 and 1.3 wt.%, respectively.

5. Summary, conclusions and outlook

The rheology and viscoelastic behavior of zirconia suspensions with carrageenan have been investigated in the temperature range relevant for the green body formation step. While carrageenan-containing silicon nitride and alumina suspensions have been studied before, this is the first investigation related to the zirconia system. Also it is the first characterization of the rheological and viscoelastic behavior of ceramic suspensions with carrageenan, which compares suspensions with identical weight or volume fraction of solids (67 wt.% or approximately 25 vol.%). Thus, for the first time it was possible to compare the effect of different carrageenan concentrations (0.7, 1.0 and 1.3 wt.% in the water available) under otherwise identical conditions.

It has been shown that all characteristic temperatures and temperature differences are strongly dependent on the carrageenan concentration. The as-prepared, cooled and reheated suspensions are viscoelastic at 80°C (phase angle approximately 45°). On cooling, no significant rheological changes occur down to temperatures (coil-to-helix transition temperatures T_H) of 29, 33 and 37°C for suspensions with carrageenan concentrations (W_{CF}) of 0.7, 1.0 and 1.3 wt.%, respectively. Thus, although the suspensions are not purely viscous (which would be the ideal case for casting), in practice this is a sufficiently wide temperature interval to perform the casting step conveniently. After cooling down to room temperature, the matrix has gelled and the green bodies are purely elastic, with a strength of the order 2–20 kPa. Of course, this green body strength (which is a synergistic result of the gel strength of the pure carrageenan system and the “reinforcing” zirconia particles) can easily be controlled by fine-tuning the carrageenan concentration to match the respective requirements for demolding and subsequent handling.

Because of the very low volume fraction of zirconia attainable in suspensions, total shrinkage after firing will be immense. The preparation of highly concentrated zirconia suspensions, of course, is a well-known problem also for conventional slip-casting and can only be solved by selecting a powder with an appropriately low surface area and a precise control of particle–particle interactions. It has been explained, however, that similar arguments refer also, e.g. to silicon nitride and alumina. This might principally question the status of the carrageenan casting method for near-net shaping purposes when precise dimensional tolerances have to be met. Further, it can be asked to what degree is

the method really generic (in the sense of being applicable to any powder system). Apart from that, impurities contained in carrageenan and the fact that it is a natural raw material of biological origin (which naturally shows scatter in composition and properties) set certain natural limits to the range of applicability and process control. On the other hand, it may be mentioned that results concerning ceramic bodies after firing¹⁷ have shown that defect-free zirconia bodies with a bulk density >98% of theoretical can readily be attained, indicating that de-airing is not a too critical issue in gel-casting with carrageenan.

In any case this work can be read as a general recipe of how the rheological and viscoelastic behavior of ceramic suspensions containing organic or bioorganic gelling additives should be characterized. Although currently not widely used in ceramic technology, in the near future such a characterization will become indispensable to assess the effectivity of new gelling additives and to model the body formation step in the new casting methods.

Acknowledgement

This work was part of the frame research program “Preparation and properties of advanced materials—modeling, characterization, technology”, supported by the Czech Ministry of Education, Youth and Sports (Grant no. MSM 223100002). The support is gratefully acknowledged. Further we are indebted to Hispangar S.A. (Burgos, Spain) for supplying free samples of carrageenan.

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