RHEOLOGY OF CERAMIC SUSPENSIONS WITH ORGANIC OR BIOPOLYMERIC GELLING ADDITIVES PART 1. THEORY OF LINEAR VISCOELASTICITY

EVA GREGOROVÁ, WILLI PABST, JIŘÍ ŠTĚTINA*

*Department of Glass and Ceramics, Institute of Chemical Technology Prague,
Technická 5, 166 28 Prague 6, Czech Republic*
**Department of Dairy and Fat Technology, Institute of Chemical Technology Prague,
Technická 5, 166 28 Prague 6, Czech Republic*

E-mail: gregoroe@vscht.cz

Many new ceramic shaping methods, in particular those involving casting of ceramic suspensions into non-porous molds, are based on gelation steps and sol-gel transitions. For these systems, usually containing an aqueous phase with organic or biopolymeric ingredients, rotational viscometry is insufficient and oscillatory shear rheometry becomes an indispensible tool to characterize the rheological changes during processing, particularly the body-formation step. In this introductory paper, the theory of linear viscoelasticity is summarized for ceramic scientists and engineers to the degree necessary for a basic understanding of the rheological behavior of sol-gel systems and gelation processes. This shortcut should provide a handy reference for subsequent papers dealing with the rheology of ceramic suspensions containing carrageenan and other organic or biopolymeric ingredients.

INTRODUCTION

The recent development of new shaping methods for ceramic suspensions, using organic or biopolymeric components [1-24], has led to an increased interest in the viscoelastic behavior of these systems. Except for inorganic sol-gel systems, this mode of rheological behavior has been widely neglected in ceramic science and technology so far. Therefore knowledge on viscoelasticty is mostly quite rudimentary among ceramic scientists and engineers. However, a certain knowledge of the viscoelastic behavior is necessary because gelation, i.e. a continuous change in the rheological behavior from viscous to elastic (with a viscoelastic transition region) is the essential body-forming step in many of the new shaping processes.

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 and the reader can refer to these for more detailed information and further reading [25-29]. 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.

It is the aim of this paper to summarize and explain the linear theory of viscoelasticity to the degree necessary to correctly interpret small amplitude oscillatory shear experiments on gelling systems, in particular aqueous ceramic suspensions containing organic or biopolymeric ingredients. Thus the paper provides a concise shortcut through the linear theory of viscoelasticity and should serve as a sufficient theoretical background for the interpretation of rheological measurements in subsequent papers.

Linear elasticity and linear viscosity

The constitutive equation of perfectly elastic, linear (i.e. Hookean) isotropic solids, after physical and geometrical linearization, cf. e.g. [30], is

$$\mathbf{T} = \lambda\,(\mathrm{tr}\,\mathbf{E})\,\mathbf{1} + 2\,\mu\,\mathbf{E} \tag{1}$$

where $\mathbf{T}$ is the Cauchy stress tensor, λ and μ the Lamé constants (moduli), $\mathbf{E}$ the small strain tensor, defined as the symmetric part of the displacement gradient $\nabla\mathbf{u}$,

$$\mathbf{E} \equiv \frac{1}{2}\,[\nabla\mathbf{u} + (\nabla\mathbf{u})^T] \tag{2}$$

tr denotes the trace and tr$\mathbf{E}$ is approximately equal to the relative change of volume, i.e. tr$\mathbf{E} \approx \Delta V/V_0$. Instead of the Lamé constants λ and μ other elastic constants can

be used, e.g. the shear modulus G and the Poisson ratio v. Hooke's law in this case is

$$T = \frac{2Gv}{1-2v}(\text{tr }\mathbf{E})\,\mathbf{1} + 2G\mathbf{E} \qquad (3)$$

The first term is responsible for volumetric changes (isotropic deformation, i.e. hydrostatic dilation or compression), the second for shape changes (shear deformations or shear strains). In almost complete analogy to equation (1) the constitutive equation of purely viscous, linear (i.e. Newtonian) isotropic fluids is

$$T + p\mathbf{1} = \zeta(\text{tr }\mathbf{D})\,\mathbf{1} + 2\eta\mathbf{D} \qquad (4)$$

where p is the pressure (for incompressible fluids, i.e. liquids, an arbitrary hydrostatic pressure), $\zeta + {}^2\!/_3\eta$ the bulk viscosity (for incompressible fluids, i.e. liquids, not defined), η the shear viscosity, $\mathbf{D}$ the strain rate tensor (stretching tensor, rate of deformation tensor), defined as the symmetric part of the velocity gradient

$$\mathbf{D} \equiv \frac{1}{2}[\nabla\mathbf{v} + (\nabla\mathbf{v})^T] \qquad (5)$$

cf. e.g. [31]. Compressible fluids are gases and bubbly liquids. They exhibit both viscous and elastic behavior. Perfect fluids are gases without viscosity. For incompressible fluids, i.e. gas-free liquids, $\text{tr}\mathbf{D} = \text{div }\mathbf{v} = 0$, as a consequence of mass conservation.

When only shear deformations are considered (one-dimensional case) and these are additionally assumed to be small, the constitutive equations of Hookean solids and Newtonian fluids are

$$\tau = G\gamma \qquad (6)$$

and

$$\tau = \eta\dot{\gamma} \qquad (7)$$

respectively, where τ is the shear stress, γ the shear strain, $\dot{\gamma}$ the shear strain rate, often simply called shear rate (with the superimposed dot denoting the time derivative), G the shear modulus and η the shear viscosity.

Linear viscoelasticity - qualitative features
and simple models

Viscoelastic materials can be characterized by a dimensionless number, the so-called Deborah number De, which is the ratio between a characteristic time intrinsic to the material (relaxation or delay time) $t_{material}$ and a characteristic time related to the process (deformation time or inverse strain rate) $t_{process}$:

$$\text{De} = \frac{t_{material}}{t_{process}} \qquad (8)$$

For fluids De $\ll$ 1 (purely viscous fluids De $\rightarrow$ 0), while for solids De $\gg$ 1 (perfectly elastic solids De $\rightarrow\infty$). Materials for which De $\approx$ 1 (in the process under consideration) are called viscoelastic. Viscoelastic materials exhibit a number of typical rheological features,

among them e.g. normal stress effects (rod-climbing or Weissenberg effect in Couette flow, die-swell or Barus effect in Poiseuille flow), stress relaxation, delayed response, recoil and creep, cf. [25-29].

The simplest (one-dimensional) models of viscoelastic materials are the Maxwell model (more fluid-like)

$$\dot{\gamma} = \frac{\dot{\tau}}{G} + \frac{\tau}{\eta} \qquad (9)$$

and the Kelvin model (more solid-like)

$$\tau = G\gamma + \eta\dot{\gamma} \qquad (10)$$

The mechanistic analog of the Hooke model, equation (6), is a spring and of the Newton model, equation (7), a dashpot, cf. figure 1 (a and b). In the language of these mechanistic analogs the Maxwell model corresponds to a spring and a dashpot in series (figure 1c), and the Kelvin model corresponds to a parallel arrangement of a spring and a dashpot (figure 1d).
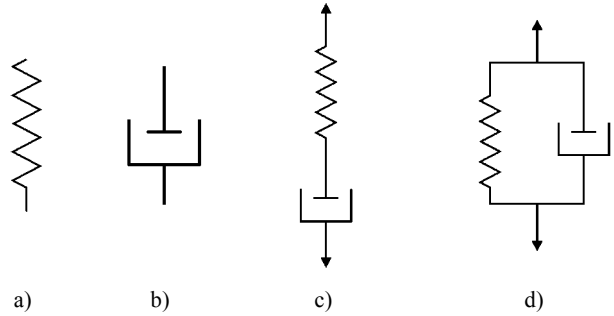

Figure 1. Mechanistic analogs of the Hooke model, a spring (a), the Newton model, a dashpot (b), the Maxwell model, a spring and a dashpot in series (c) and the Kelvin model, a spring and a dashpot in parallel arrangement (d).

The Maxwell model allows for stress relaxation on deloading

$$\tau = \tau_0 \cdot \exp\left(-\frac{t}{t_{relax}}\right) \qquad (11)$$

with a relaxation time

$$t_{relax} = \frac{\eta}{G} \qquad (12)$$

The Kelvin model allows for delayed response. On deloading the deformation relaxes slowly, i.e.

$$\gamma = \gamma_0 \cdot \exp\left(-\frac{t}{t_{delay}}\right) \qquad (13)$$

while on loading the final deformation γ_{final} is attained only after a certain time, i.e.

$$\gamma = \gamma_{final} \cdot \left[1 - \exp\left(-\frac{t}{t_{delay}}\right)\right] \qquad (14)$$

The time lag (delay time) is in both cases

$$t_{delay} = \frac{\eta}{G} \qquad (15)$$

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,

$$\gamma = \gamma_0 \cos \omega t \qquad (16)$$

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

$$\tau = \tau_0 \cos (\omega t + \delta) = \tau_0 \cos \delta \cos \omega t - \tau_0 \sin \delta \sin \omega t \qquad (17)$$

where τ_0 is the shear stress amplitude and δ the phase angle (phase shift). Equation (17) 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

$$\gamma = \frac{d\gamma}{dt} = -\omega\gamma_0 \sin \omega t \qquad (18)$$

cf. figure 2. Therefore the material behaves partly as an elastic solid and partly as a viscous liquid, and the stress-strain relation (17) can be written as

$$\tau = \gamma_0 (G' \cos \omega t - G'' \sin \omega t) \qquad (19)$$

where the storage modulus G' is

$$G' = \frac{\tau_0}{\gamma_0} \cos \delta \qquad (20)$$

and the loss modulus G'' is

$$G'' = \frac{\tau_0}{\gamma_0} \sin \delta \qquad (21)$$

The ratio

$$\frac{G''}{G'} = \tan \delta \qquad (22)$$

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 $i = \sqrt{-1}$)

$$\cos \omega t + i \sin \omega t = \exp(i \omega t) \qquad (23)$$

the strain and stress cycles (16) and (17) can be represented by the real parts of

$$\gamma^* = \gamma_0 \exp(i\omega t) \qquad (24)$$

and

$$\tau^* = \tau_0 \exp[i(\omega t + \delta)] \qquad (25)$$

Then the complex modulus G^* is

$$G^* = \frac{\tau^*}{\gamma^*} = \frac{\tau_0}{\gamma_0} \exp(i \delta) = \frac{\tau_0}{\gamma_0} (\cos \delta + i \sin \delta) =$$
$$= G' + iG'' = G' (1 + i \tan \delta) \qquad (26)$$

In complete analogy a complex viscosity can be defined via equations (17) and (18), where the shear rate is the real part of

$$\dot{\gamma}^* = i \omega \gamma_0 \exp(i \omega t) \qquad (27)$$

The complex viscosity η^* is then

$$\eta^* = \frac{\tau^*}{\dot{\gamma}^*} = \frac{\tau_0}{i\omega\gamma_0} \exp(i \delta) = \frac{\tau_0}{i\omega\gamma_0} (\cos \delta + i \sin \delta) =$$
$$= \frac{G'}{i \omega} + \frac{iG''}{i \omega} = \frac{G''}{\omega} - i \frac{G'}{\omega} = \eta' - i\eta'' \qquad (28)$$

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

$$G^* = i \omega \eta^* \qquad (29)$$

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

$$G' = \omega \eta'' \qquad (30)$$

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

$$G'' = \omega \eta' \qquad (31)$$

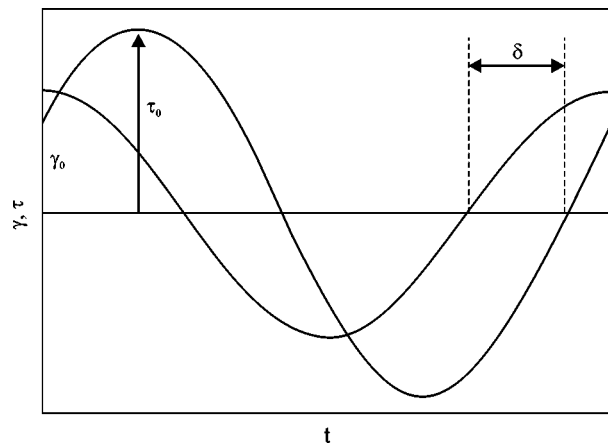Of course both the complex modulus and the complex viscosity are frequency- and temperature dependent.

Figure 2. Shear strain γ, shear stress τ and shear strain rate (shear rate) $\dot{\gamma}$, δ denotes the phase shift (phase angle) between strain and stress, subscript 0 indicates amplitudes.

Suspensions, gels and the significance of viscoelastic behavior in sol-gel systems and gelation processes

Suspensions are multiphase mixtures, i.e. heterogeneous on the microscopic level. In classical suspensions it is understood that the typical particle size is larger than 0.1 μm, i.e. > 100 nm. On the other hand, solutions are single-phase, i.e. homogenous on the microscopic level. Suspensions with nanosized (1–100 nm) particles of isometric shape, i.e. the colloidal counterparts of suspensions, are called sols. Similar to liquid solutions, which are purely viscous (often even linear, i.e. Newtonian), also most suspensions and their colloidal counterparts (sols) are purely viscous up to relatively high particle concentrations as long as the dispersed particles are rigid and of isometric shape. Suspensions and sols with deformable and/or anisometric particles (e.g. fiber and platelet suspensions), including polymer solutions and liquid crystals, often exhibit non-Newtonian behavior, from non-linear flow curves to typical viscoelastic behavior such as normal stress effects and relaxation phenomena.

Many organic polymers, in particular those of biological origin, when dispersed or dissolved in aqueous media, are capable of forming viscoelastic systems (e.g. water with swelling starch [1-4,10-16] or elastic gels with water (hydrogels). The formation of elastic gels from purely viscous systems (sol-gel transition) can be chemically induced or thermally induced. In the latter case we can distinguish gel formation on cooling or on heating (so-called thermogelling). The former applies e.g. to gelatine [5,6,10,12,16] and agaroids such as agarose, agar or carageenan [7,8,16-24], the latter e.g. to methylcellulose [9]. Gelling is not restricted to organic systems, of course. Examples of inorganic gels are silica gel, titania gel, boehmite gel and zirconia gel, the preparation of which is well known [32]. Often they are prepared from precursor solutions, which are mixed to form sols at room temperature (chemically induced) or at elevated temperature and subsequently transform into gels. Typically, even suspensions with anisometric particles nanosized (< 100 nm) in only one direction are capable of gelling (e.g. suspensions of flaky montmorillonite or other smectic clays, with a platelet thickness of approx. 1 nm) [33,34].

It is clear that the mechanism of the sol-gel transition is a polymerization reaction (formation of chemical bonds) whose kinetics is triggered by the chemical environment and the external conditions, in particular temperature. Due to the viscoelastic behavior in the transition region, relaxation times characterizing the material $t_{material}$, cf. equation (8), are large. For this reason the sol-gel transition is not a well-defined phase transition (of the first kind) but depends on the rate of temperature change. Concerning the difficult question whether the sol-gel transition has an underlying thermodynamic phase transition (of the second kind) or not, one may invoke the same reasoning as in the case of the glass transition, cf. e.g. [35]. In any case the result of a sol-gel transition is a gel, usually isotropic (amorphous). On the microscopic level it consists of a gel network, i.e. a cellular solid formed by the new chemical bonds. As long as the open-cell pores are filled with water the (water-saturated) material is a two-phase mixture called hydrogel. Note that, although such a hydrogel is highly compliant (non-rigid) with respect to shear deformations, it can nevertheless be purely elastic, i.e. characterized by a zero phase shift ($\delta = 0°$) and loss factor (tan $\delta = 0$), cf. equations (17), (20)-(22), (25)-(26), (28). In this case the small amplitude shear experiment measures directly the shear modulus G (which corresponds to the measured storage modulus G'). Of course, viscosity is not defined for such a system, i.e. the complex viscosity η^* defined via equation (29) has only an imaginary part. Since the shear modulus G is connected to the tensile modulus (Young's modulus) E via the standard relation

$$G = \frac{E}{2(1 + v)} \tag{32}$$

cf. e.g. [30], and the tensile modulus is - via the Griffith theory (linear fracture mechanics) - connected to the theoretical strength σ

$$\sigma = \sqrt{\frac{E \cdot y}{d}} \tag{33}$$

where y is the specific surface energy and d the dimension of typical inhomogeneities (e.g. pore or cell size), cf. e.g. [36], it may be expected that the measured shear modulus of an elastic gel is connected to the gel strength by a relation of the type

$$\sigma \propto \sqrt{G} \tag{34}$$

or a similar one. Therefore oscillatory rheometry, apart from characterizing the viscosity of purely viscous liquids (e.g. mixtures in the sol state) and both viscoelastic moduli (storage and loss modulus) in the viscoelastic transition region, can potentially be used as a tool to provide a quantitative measure of gel strength. In ceramic technology a quantitative knowledge of gel strength would be very useful, since gel strength is a critical parameter to be controlled when new shaping methods have to be optimized: although it is a common aim to keep the concentration of organic / biopolymeric additives as low as possible it must be high enough to guarantee at least a minimum gel strength to ensure defect-free demolding, handling and transport before the drying step. It must be noted, however, that the above arguments are only qualitative, since the Griffith theory (linear fracture mechanics) assumes brittle materials. Further, clearly, it can be expected that the theoretical strength may be orders of magnitude away from experimentally measured strength values. It seems that a rigorous theory of gel strength is not available so far.

At the moment, of course, other methods are commonly used to measure gel strength, e.g. penetrometry [37]. All these methods are more or less empirical and deliver relative values. A stringent derivation of the relation between shear modulus (storage modulus) and gel strength, preferentially based on rational mechanics or micromechanics, would be highly desirable.

After drying, the remaining solid and water-free[1] skeleton is called a xerogel. It is also purely elastic, but of course its shear modulus cannot be measured by oscillatory rheometry anymore, since it is almost rigid and there is no pore liquid available that would ensure coupling of the measured sample to the solid walls of the rheometer's measuring cylinders. In other words when the gel is dry, the so-called "no-slip condition" at the wall, which is the basic condition of all viscometric and rheometric measurements, cannot be fulfilled. In such a case only solid-solid friction is measured. When the gel is water-saturated the no-slip condition may or may not be fulfilled, depending on the circumstances. In rotational viscometry it cannot be fulfilled as long as the gel structure remains intact. Complete rotation (i.e. a turn by 360°) either destroys the gel structure (when the gel-wall interaction, or, more precisely, the interaction of the pore-filling liquid with the walls, is stronger than the gel strength) or else leads to slip of the gel sample as a whole (when the gel-wall interaction is weaker than the gel strength). In oscillatory rheometry the no-slip condition is fulfilled, at least for some time, for elastic hydrogels in a similar way as for ordinary viscous liquids or viscoelastic materials, as long as the oscillations are chosen to be of a sufficiently small amplitude.

Drying of multiphase solids, especially particulate solids (i.e. humid solids with separate particles held together by capillary forces or elastic gels with a flexible network) is usually connected with shrinkage. Shrinkage is of course connected with demixing, i.e. during drying one of the phases (constituents), usually the pore fluid, disappears from the system (either by seepage or by evaporation). At the end of the drying step the remaining mixture has changed its volume and is usually one phase (when the empty pores are considered as voids). In this sense the mixture as a whole can be considered as compressible, although both of its constituents are (practically) incompressible, cf. the discussions on this point in rational multiphase mixture theory [38]. It has been shown earlier [39] that, according to the Coussy model [40], the kinetics of drying shrinkage can be described by the equation

$$\varepsilon = \varepsilon_{final} \cdot \left[1 - \exp\left(- \frac{t}{t_C} \right) \right] \qquad (35)$$

where $\varepsilon = \mathrm{tr}\mathbf{E} \approx \Delta V / V_0$ is the relative volume change (total shrinkage), cf. the comment to equation (2) above, ε_{final} can be interpreted as the final asymptotic shrinkage

(denoting the state where the skeleton, although possibly still porous, has lost the flexibility necessary for further volume deformation) and t_C as a characteristic drying time (shrinkage time), i.e. the time after which ε equals $\varepsilon = (1 - 1/e) \cdot \varepsilon_{final} = 0.632 \cdot \varepsilon_{final}$, i.e. after which 63.2 % of the final shrinkage has been attained. Evidently, equation (35) is formally identical to the constitutive equation of a Kelvin model material, equation (14). Note, however, that in the derivation of equation (35) no assumption has been made concerning the viscoelastic character of the material, cf. [39,40]. In particular, in Coussy's model the material has not been assumed to be a viscoelastic gel. Thus it can as well be applied to describe the drying of a water-saturated particulate solids, e.g. a humid clay body. Nevertheless the governing differential equation

$$t_C \frac{d\varepsilon}{dt} + \varepsilon = \varepsilon_{final} \qquad (36)$$

and its solution, equation (35), are identical to the differential equation of the mechanistic analog of the Kelvin model, cf. figure 1d. This might indicate a certain analogy between poroelasticity and viscoelasticity, similar to the well-known analogy of poroelasticity and thermoelasticity [41,42].

Finally a few words on other rheological phenomena would seem useful. Although purely viscous up to relatively high concentrations, suspensions exhibit a blocking phenomenon at concentrations close to a critical concentration (volume fraction) ϕ_C, i.e. viscous flow is impeded in close proximity to ϕ_C, cf. [31]. For suspensions this critical volume fraction can be interpreted in terms of a maximum particle packing fraction. The maximum particle packing fraction is the volume fraction of (solid, more or less rigid) particles at which strong repulsive particle-particle interactions (sometimes called "excluded volume effects", in common rigid-particle suspensions de facto simply "mechanical contacts") prevent further densification under compressive forces (due to sterical constraints). Moreover, close to ϕ_C shear flow is prevented as well (due to immensely high interparticle friction). Ideal suspensions of monodisperse rigid spheres should exhibit a critical volume fraction ϕ_C of approx. 0.64, i.e. at 64 vol.% the effective viscosity would attain an infinite value [31]. In practice, this value is often a good approximation also for polydisperse systems as long as the particles are isometric. For suspensions of anisometric particles, e.g. fibers or platelets, however, the critical volume fraction attains much lower values, cf. [43]. Many systems with nanosized particles (i.e. particles with at least one dimension < 100 nm), including concentrated colloidal sols with anisometric particles and clay suspensions and pastes, exhibit so-called viscoplastic behavior, described by a flow curve with a yield stress, either linear (Bingham materials) or non-linear (Herschel-Bulk-

ley materials). Although the existence of the yield stress has been questioned from a fundamental point of view [44], it certainly is a useful engineering tool to describe the phenomenology of certain deformation and flow processes quite well. As long as loaded below the yield stress, these materials behave as elastic solids (with a linear stress-strain curve up to a certain – small – value of strain), above the yield stress the material responds by viscous flow. In small amplitude oscillatory shear experiments viscoplastic materials would usually appear purely elastic. Consequently, a material cannot be classified as viscoplastic by means of oscillatory rheometry. On the other hand, in order to characterize viscoelastic behavior oscillatory shear rheometry is the most common tool. With respect to the new shaping methods for ceramic suspensions, which are continuously being developed [1-24], it is a desideratum to apply oscillatory rheometry, widely used in polymer and biopolymer science and technology, routinely in ceramic science and technology as well and to include a more detailed knowledge of viscoelasticity into the education schedules not only of glass technologists but also of ceramic engineers.

CONCLUSION

The linear theory of viscoelasticity has been summarized for ceramic scientists and engineers to the degree necessary for a basic understanding of the rheological behavior of sol-gel systems and gelation processes. Starting with the two extreme modes of material behavior, i.e. those of linearly elastic (Hookean) solids and linearly viscous (Newtonian) fluids, the two simplest models of viscoelastic materials (Maxwell fluid and Kelvin solid) were briefly recalled. With a view on oscillatory rheometry the basic treatment of the viscoelastic response to small amplitude shear oscillations has been given in elementary (trigonometrical) and in complex formulation. Storage modulus G', loss modulus G'' and phase shift δ or its tangent, the loss factor, have all been defined and it has been recalled that only two of these three quantities are independent. The temperature and frequency dependence of these quantities as well as the interrelation between real and imaginary parts of the complex modulus and the complex viscosity (two complementary quantities) has been emphasized. The general significance of viscoelastic behavior in sol-gel systems and gelation processes has been discussed in a qualitative way. Practical aspects of the rheology of suspensions and their colloidal counterparts (sols) have also been addressed, including critical volume fractions and the effect of anisometric particle shape. The sol-gel transition has been explained and for elastic gels slip phe-

nomena and gel strength have been mentioned, including their consequence for materials characterization and processing, respectively. An interesting analogy has been shown between the mathematical description of drying shrinkage kinetics and the Kelvin model for viscoelastic materials. With respect to the recent developments of new shaping methods for ceramic suspensions, the wider use of oscillatory rheometry in ceramic science and technology is advocated. This introductory paper should provide a handy reference for subsequent experimental papers dealing with the rheology of ceramic suspensions containing carrageenan and other organic or biopolymeric ingredients in an aqueous medium. Part 2 with concern the viscoelastic behavior of zirconia suspensions with carrageenan. Part 3 will concern the rheology of starch-containing suspensions.

Notes:

[1] Water-free except for structural, i.e. chemically bonded, water in the form of OH groups. In contrast to absorbed or physically adsorbed water, this chemically bonded water cannot be eliminated by conventional drying, but only during firing.

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REOLOGIE KERAMICKÝCH SUSPENZÍ S OBSAHEM ORGANICKÝCH RESP. BIOPOLYMERNÍCH GELUJÍCÍCH ADITIV
ČÁST 1. LINEÁRNÍ TEORIE VISKOELASTICITY

EVA GREGOROVÁ, WILLI PABST, JIŘÍ ŠTĚTINA*

*Ústav skla a keramiky,
Vysoká škola chemicko-technologická v Praze,
Technická 5, 166 28 Praha 6*

**Ústav technologie mléka a tuků,
Vysoká škola chemicko-technologická v Praze,
Technická 5, 166 28 Praha 6*

V tomto článku je shrnuta lineární teorie viskoelasticity v míře nezbytné pro moderní keramickou vědu a technologii. Umožňuje porozumění alespoň základům reologického chování sol-gelových soustav a gelovacích procesů. Vycházíme ze dvou takřka extrémních typů materiálového chování, tj. z lineárně elastických (Hookových) pevných látek a z lineárně viskózních (Newtonských) tekutin a dále ze dvou nejjednodušších (základních) modelů viskoelastických materiálů (Maxwellovy a Kelvinovy hmoty). S ohledem na aplikaci v oscilační reometrii je shrnut (jednak pomocí elementárních trigonometrických funkcí, jednak v komplexním vyjádření) základní formalismus popisující viskoelastickou odezvu na smykové oscilace s malou amplitudou. Jsou definovány akumulační modul *G'*, ztrátový modul *G''* a fázový posun (fázový úhel) *δ* resp. ztrátový faktor tan *δ*, avšak pouze dva z nich jsou nezávislé. Je zdůrazněna teplotní a frekvenční závislost těchto veličin a také vztah mezi reálnou a imaginární částí komplexního modulu resp. komplexní viskozity. Obecný význam viskoelastického chování v keramických sol-gelových soustavách a gelovacích procesech je diskutován spíše kvalitativně. Jsou diskutovány praktické aspekty reologie suspenzí a solů, včetně kritických objemových frakcí a vlivu anizometrického tvaru částic. Je popsán přechod sol-gel a u elastických gelů jsou zmíněny skluz a pevnost, včetně jejich praktických konsekvencí pro měření resp. pro technologii. Zmíněna je také zajímavá analogie mezi matematickým popisem kinetiky smrštění sušením a Kelvinovým modelem viskoelastických materiálů. S ohledem na nedávný razantní vývoj nových tvarovacích metod pro keramické suspenze je zdůrazněna nutnost širšího použití oscilační reometrie v keramické vědě a technologii. Tento úvodní článek má sloužit jako stručná reference pro další navazující experimentální články zabývající se reologií keramických suspenzí s obsahem karagenanu a jiných organických resp. biopolymerních složek ve vodném prostředí. Druhá část se bude zabývat viskoelastickým chováním suspenzí oxidu zirkoničitého s obsahem karagenanu. Třetí část bude zaměřena na reologii suspenzí s obsahem škrobu.