ARCHIVES OF ACOUSTICS
25, 1, 83–92 (2000)

THE POSSIBILITY OF APPLYING OF ACOUSTIC METHODS FOR THE MONITORING OF SOL-GEL PROCESSES

J. RZESZOTARSKA

Department of Chemistry, University of Warsaw
(02-093 Warszawa, ul. Pasteura 1, Poland)

J. RANACHOWSKI

Polish Academy of Sciences
Institute of Fundamental Technological Research
(00-049 Warszawa, Świętokrzyska 21, Poland)

Models simulating the propagation of acoustic waves in the successive stages of the gelation process are presented. The early stage of gelation has been considered with scattering theory for very low concentrations of suspensions. The system may be simulated by the line of the independent Maxwell elements. When concentration of the suspension increases, the interaction of the particles can be presented by an acoustic model, which consist of a chain of coupled Maxwell elements. After the gelation point, the system becomes rigid, and three dimensional tensoral fields distribution of stress and strain was used.

1. Introduction

This paper is aimed at the presentation of the possible applications of the ultrasonic methods to the monitoring of the gelation process. New trends in material science of the last years concern, among other things, the manufacturing of materials and composites arranged in a nanometric scale. The application of nanotechnology has opened perspectives of manufacturing materials of unique mechanical, electrical, optical and catalytic properties. The application of the sol-gel method enabled the creation of materials of parameters that can not be obtained by traditional methods, e.g. the titanic-silica glass. Ceramic materials produced by this method are similar to the natural ones, e.g. to bones and shells.

The gelation process has not been fully known so far, therefore its monitoring is essential for both the practical and scientific reasons. The application of acoustic methods to this purpose requires an improvement of both the measuring methods and the theoretical analyses.

The peculiarity of the problem lies in the fact that during the separate stages of the gelation process, the two-phase medium changes its structure continually. Beginning from the nuclei present in the liquid, growing agglomerates of fractal structure are formed. After reaching the gelation point, the system becomes a rigid spatial structure immersed in a liquid. The knowledge of the propagation of acoustic waves in such a system is still incomplete and requires further research.

This paper is confined to the general presentation of models simulating the propagation of acoustic waves in the separate stages of gelation.

2. Stages of the gelation process

Gelation may be defined as a secondary phase transition of the sol to a gel. In the sol phase, there exist molecules or particles consisting of several monomers in the solution. Approaching the gelation point, aggregation of the particles occurs and the measured physical values achieve critical sizes.

After this phase of the transformation, an unique state of matter arises characterised by a spatial expanded lattice filled up with gel. Macroscopically, the medium shows elastic properties similar to solid bodies. The liquid phase contained in gel enables, after exceeding a critical point, comparatively a relatively fast transport of ions. It means that the diffusion coefficients are only slightly lower than in a liquid.

After the transition, the transport of the liquid phase contained in the gel is relatively fast. This means that the diffusion coefficients of the ions in the gel are only a little smaller than in a liquid. The evaporation velocity of the liquid from the system is so fast as if there were only a liquid in the vessel. The energy of this transition is rather small, for example, for silica gel it equals 10–20 kcal/mole depending on the conditions under which the process occurs.

Together with the progress in the aging process, after crossing the gelation point the rigidity increases, because residual oligomers of the gel present in the solvent, are bonded in the main lattice, forming additional cross-links. This phenomenon is responsible for the appearance of the elasticity of the system. The elastic properties of the gel on the molecular level depend on the structure of the network, especially on the cross-links.

The sol-gel transitions discussed occur in several consecutive stages listed below:

- molecular aggregation and forming of clusters; the cluster is defined as a collection of mutually connected bonds and nodes,
- further aggregation and growing of clusters; the life time of this stage depends on the distribution and expansion of the clusters,
- proper transformation of the sol to gel, i.e. the formation of a large cluster that consists of a continuous network filling the whole volume of the vessel; a space structure of the system is formed,
- the formed extensive cluster becomes dense as the result of the formation of new cross-linking bonds; this stage is named ageing during which the elastic properties of the medium increase significantly.

3. The fractal concept of gelation

The classical Flory's theory of gelation has been applied until now to answer the following question: what is the fraction of all bonds (p_c) that must formed before continuous network structure appears. The general equation is

$$p_c = \frac{1}{z-1}\,, \tag{1}$$

where p_c — gel point, z — number of bonds in the monomer. This model predicts that $p_c = 1/3$ when $z = 4$ (for silica). This means that the point of gelation occurs when one third of all the possible bonds are formed. The disadvantage of this theory is that it neglects the formation of rings within the growing clusters and that it does not consider the kinetics of gelation. Thus, the classical model does not provide a realistic image of the cluster growth. These properties are considered in the fractal growth model of gelation.

A fractal is a paradigm for describing the morphology and evolution of the shape and the growth processes. A fractal dimension of 1.0 which defines the cluster growth (D) represents a linear growth. If the fractal dimension is equal to 3, the cluster density is uniform (nonfractal growth). A fractal growth imply a decrease in the density with increasing radius of the cluster ($D < 3$).

The mass (M) in the gelation process with fractal radius (r) is growing according to the relation

$$M = kr^D, \tag{2}$$

where k is a constant.

The rate of the cluster growth and the cluster–cluster aggregation growth for silica gels, according to Connel and Aubert, increases exponentially

$$\begin{aligned} r &= r_0 \exp(q_r t), \\ M &= M_0 \exp(q_r t), \end{aligned} \tag{3}$$

where t is time and q_r is a constant, M is the fractal mass or the average molecular weight, M_0 is the mass (molecular weight) of the monomer, r_0 is the radius of the monomer (core radius).

Below the gel point, the molecular weight and cluster size can be calculated from the viscosity as a function of time.

The decrease in density (ρ), as the fractal increases in size, can be calculated from the relation

$$F = \frac{\rho}{\rho_0} = \left(\frac{r_0}{r}\right)^{3-D}. \tag{4}$$

In the evolution of solids from solutions, a different type of structures, depending on the degree of cross-linking, can be formed. Recently, various experimental techniques of microscopy, small-angle X-ray scattering, small-angle neutron scattering and rheology have been applied to elucidate fractal structures in the aggregation and gelation of systems. According to the fractal theories, the network structure of gels is a collection of

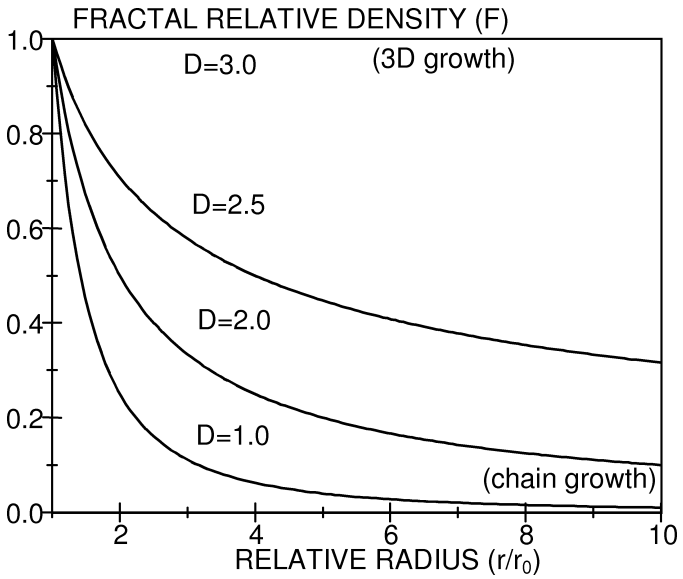

Fig. 1. Fractal relative density versus relative radius as a function of variations in the fractal dimension. From E.J.A. Pope [2].

fractal aggregates closely packed throughout the system. The rheologic measurements are easy, especially in the high concentration range of the clusters.

During the thermal treatment at small oscillatory deformation with shear strains of frequency (ω), the shear modulus (G^*), which is a complex number with a real part G' (stiffness modulus) and an imaginary part G'' corresponding to shear losses, is measured for gels. The G' values are larger that the G'' this generally only one of the characteristic properties of gel is described.

4. Models simulating the propagation of acoustic waves in the successive stages of the gelation process

From the acoustical point of view, the whole gelation process can be divided in several stages. For each of them, somewhat different models of the acoustic wave propagation give the best simulation. These stages correspond to the stages of the cluster nucleation and the particles aggregation presented in Sec. 2 of this work.

There are no sharp limits between the ranges of evolution where the acoustic model fits best, except the rapid change of the system at the gelation point. The models simulate the behaviour of the propagation velocities and the attenuation of acoustic waves. The generation of acoustic emission was beyond the scope of the present investigations.

The main problem is the dependence of the parameters of the acoustic wave propagation on the elastic or visco-elastic moduli of the two-phase network in the sol-gel system.

The following consecutive models are taken into account.

4.1. A fluid with very low concentration of suspensions

This case corresponds to an initial state of the sol with few suspended particles (nuclei) per volume unit of very small size (compared with the acoustic wave length). The system can be considered to be homogeneous; if is a liquid phase with a volume elasticity (bulk elasticity modulus) K and the viscosity η related to the imaginary part G'' of the shear modulus G^*. The imaginary part of the modulus, K^*, which corresponds to the volume viscosity, K'', and the real part of the shear modulus related to the shape stiffness can be omitted. The system has the same parameters as a pure liquid not affected by the suspension. The usual classical model of a homogeneous fluid is valid.

4.2. A fluid with the increasing concentration of suspensions

The system becomes a two phase system, its viscosity depends on the number and size of particles according to the Einstein formula. The formula is applicable for a uniform concentration and size of particles when the volume concentration is less then 0.1. When the formation of the surface fractal structure of the clusters takes place, this process can be expressed in the acoustic model by assuming a change in the size and density of the particles, as already shown.

The main feature of the system at this stage is that the vibrations of the particles are independent from each other, and there is no mutual interaction between the particles.

The system may be simulated by the line of the independent Maxwell elements (Fig. 2).

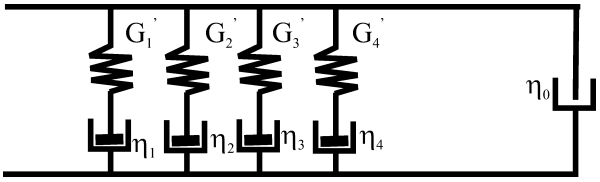

Fig. 2. The line of the independent Maxwell elements, as a model of a fluid with concentration of suspensions less than 0.1.

Each element has its own relaxation time with a random spectral distribution, however the previous, still valid, assumption of a uniform size of the particles suggest that the distribution has a distinct maximum. The shear modulus is treated here as a complex number, $G^* = G' + jG''$, and the system viscosity is $\eta = G''/\omega$, but its real part G' is still not significant.

The bulk viscosity K'' and the scattering of the longitudinal wave on the suspended particles can be neglected. The system should be analyzed as a inhomogeneous visco-elastic liquid.

4.3. The beginning of the interaction between particles

When the concentration of the suspension increases, the appearance of the mutual links is caused by changes of the particles structure. They are no longer uniform balls

but mass fractals of very complicated shape connected by chemical bonds. An exact theoretical evaluation of the scattering and attenuation of an acoustic wave is impossible in this case, however acoustic measurements provide valuable information about changes in the behaviour of the whole system. The interaction of the particles can be presented by an acoustic model which consist of a chain of coupled Maxwell elements, i.e. the so-called "ladder" model (Fig. 3) equivalent to a delay-line model used in electronics. Due to the interacting particles, the discrete spectrum of relaxation times (DRS) is an ordered one, in contrast to the random spectrum as in the previous stage. The links between the particles (clusters) has still a large compliance, nevertheless the shear modulus should be count as a complex number, $G^* = G' + jG''$, and the measurements of velocity and attenuation of the shear wave are relevant for the evaluation of the viscosity. The system is a two-phase system but the solid state phase is not yet stiff enough to be treated as a solid framework, rather the presentation as a visco-elastic-liquid with the "bounded" mass fractals is more correct. The scattering of the longitudinal wave on the clusters is now perceptible. The general theory of the acoustic wave scattering is applicable. The particle is considered to be an inclusion of defined cross-section. The calculation of the size and number of the cross-sections as complex units enable the evaluation of the attenuation and dispersion of the acoustic wave.

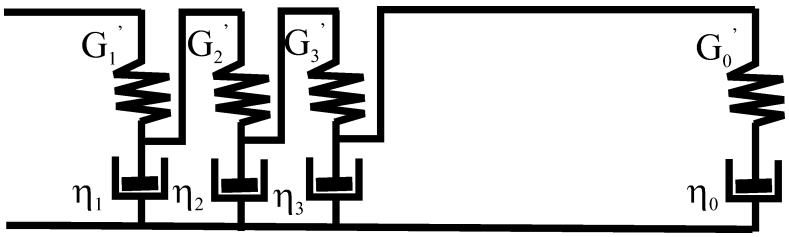

Fig. 3. The chain of coupled Maxwell elements, i.e. the "ladder" model of a fluid with interacting clusters of a mass fractal structure.

4.4. Increase of the bonds stiffness between the clusters

The two-phase system is now similar to a solid elastic space framework plunged in the liquid. The large number of the relaxation times τ, has a statistical distribution H_τ, and the resultant viscosity can be evaluated from the formula

$$\eta = \int_0^\infty H_\tau(\ln \tau). \tag{5}$$

To take into account both the solid state and fluid parameters of the system, an acoustic model similar to that of Mervin seems to be most convenient (Fig. 4).

The model can be applied to transverse (shear) waves and to longitudinal ones. For this reason, it can be considered, assuming certain simplifications, as the joint Maxwell–Voigt model (Burgers model).

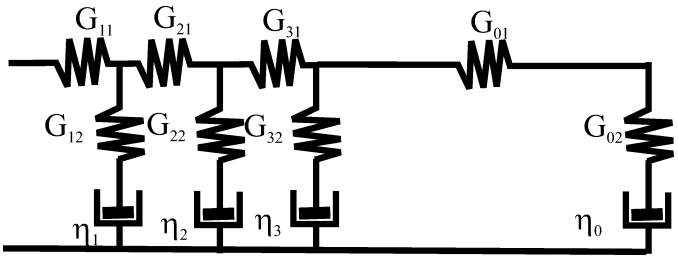

Fig. 4. The chain of Burgers elements; the completed Mervin model of the solid elastic network planged in a fluid.

4.5. The rigid porous structure saturated by the fluid

This case corresponds to the system after crossing the gelation point. The pores of the solid structure are partially open; thus the flow of the fluid is possible. The previous one-dimension models are not applicable, because it is necessary to analyze three dimensional tensoral fields of stress and strain. The approach, presented first by Biot completed by Willis, is used as the basis of the following investigation. The idea consist in a stepwise consideration of the quasistatic and dynamical system treated first as a purely elastic one and than as a viscoelastic one.

The quasistatic case. When the system is treated as a homogeneous two-phase one, its elastic properties are determined by four constants: λ and μ — the Lamé coefficients, B — the penetration volume coefficient defined as the pressure required to force a certain volume of the fluid into the porous structure while the total volume remain constant. Q — the coefficient characterizing the coupling between the volume change of the solid and that of the fluid. The second Lamé constant, μ, is equivalent to the shear modulus G, but for the description of the continuous medium it is more convenient.

An important parameter is also the porosity. The mass porosity β is defined by the formula

$$\rho_1 = (1-\beta)\rho_s\,, \qquad \rho_2 = \beta\rho_f\,, \qquad \rho = \rho_1 + \rho_2\,, \tag{6}$$

where ρ_s — solids state density, ρ_f — fluid density, ρ_1 and ρ_2 the solid and fluid parts of the resultant density of the system ρ, respectively.

The dynamic case. The system parameters are evaluated when an acceleration of the system as a whole occurs. In general case, when the mobilities of the solid and fluid are different, the corresponding displacements are u_s and u_f. This is caused by the additional force, F, caused by the flow resistance of the fluid through the solid framework

$$F = \rho_{12}\frac{\partial^2 u}{\partial t^2}\,, \tag{7}$$

when $u = u_f - u_s$.

The factor ρ_{12} corresponds to the apparent additional density (with positive of negative sign) of the parts ρ_{11} and ρ_{22} of the resultant density ρ; this means:

$$\rho_{11} = \rho_1 + \rho_{12} \qquad \text{and} \qquad \rho_{22} = \rho_2 + \rho_{12}\,. \tag{8}$$

The substitutional dynamic moduli of the system can be calculated by usual method of the theory of elasticity.

Acoustic wave propagation in the lossless system. The velocity of the acoustic wave propagation is calculated from the dynamic parameters of the system described above. The shear waves excite the rotational acoustic fields in the coupled fluid and solid; the apparent density of the system is smaller than in the quaststatic case. The velocity of the transverse (shear) wave is equal to

$$c_T^2 = \frac{\mu}{\rho_{11}} \left(\frac{1}{1 - \dfrac{\rho_{12}^2}{\rho_{11}\rho_{12}}} \right). \tag{9}$$

The dilatational wave can be described approximately as a longitudinal plane wave propagating in the x-direction. It is convenient to introduce a reference velocity c_{0L}, calculated for the dilatational wave in the system when the so-called "dynamic compatibility" is fulfiled, and the mutual solid-fluid displacements are equal to zero

$$c_{0L} = \frac{\lambda + 2\mu + B + 2Q}{\rho}\,. \tag{10}$$

In the general case, the bulk dilatations of the solid, ε_s, and of the fluid, ε_f, are different for the longitudinal wave

$$\varepsilon_s = C_s \exp(kx + \omega t) \qquad \text{and} \qquad \varepsilon_f = C_f \exp(kx + \omega t). \tag{11}$$

The expression for the wave velocity should fulfil the usual equations of motion for a solid and fluid. This condition yield to the complicated second order equation for the variable

$$w = \left(\frac{c_{0L}}{c_L} \right)^2.$$

The two roots of this equation define the two dilatation waves having the different velocities

$$c_{1L} = w_1^{-1/2} c_{0L} \qquad \text{and} \qquad c_{2L} = w_2^{-1/2} c_{0L}\,. \tag{12}$$

The terms of the high-velocity or first kind wave for c_{1L} and the low-velocity or second kind wave for c_{2L} are admitted.

Acoustic wave propagation in the visco-elastic system. The energy dissipation depend only on the relative motion of the solid framework in relation to the saturated fluid and can be expressed by the formula

$$D = b(v_f^2 - v_s^2). \tag{13}$$

The coefficient b is a measure of the degree of viscosity of the system and has the value

$$b = \frac{\eta \beta^2}{q}\,, \tag{14}$$

where η — viscosity of the fluid, β — mass porosity of the solid framework, q — the coefficient of permeability.

It is worth introducing several reference values and to express the acoustic wave parameters as relative magnitudes.

a) For the shear wave the reference velocity

$$c_{0T}^2 = \frac{\mu}{\rho} \tag{15}$$

corresponds to the condition $v_f = v_s$.

b) The reference frequency of the acoustic sinusoidal wave corresponds to the coefficient b

$$f_c = \frac{b}{2\pi\rho}\,. \tag{16}$$

c) The reference attenuation coefficient results from the preceding quantities

$$\alpha_{0T} = \frac{2\pi f_c}{c_{0T}}\,. \tag{17}$$

For given values of the reference velocity and the reference frequency, the numerical solution of the complicated theoretical formula are calculated by M.A. Biot. It enables the evaluation of the frequency dependence of the shear wave velocity. The attenuation coefficient for this wave versus frequency is equal approximately to

$$\frac{\alpha_T}{\alpha_{0T}} = \frac{1}{2}(\rho_{22} + \rho_{12}) \left(\frac{f}{f_0}\right)^2. \tag{18}$$

However, the assumed here exponent is for some systems less than 2.

For the dilatational wave, a similar method can be applied. The reference velocity is the same as for the lossless system, c_{0L}, the reference frequency is equal to f_0, and the reference attenuation coefficient

$$\alpha_{0L} = \frac{2\pi f_0}{c_{0L}}\,. \tag{19}$$

However, the problem is much more complicated, because the two kinds of waves have different frequency dependences and the variable w in the second order equation of motion has roots with the complex magnitudes for the second kind wave; the attenuation coefficient and propagation velocity are both proportional to the factor $(f/f_0)^{1/2}$. For the wave of the first kind the attenuation coefficient is, similarly as for the shear wave, proportional to $(f/f_0)^2$, but the reduced velocity is proportional to the term $\left[1 - A(f/f_0)^2\right]$, while the factor A can be either positive or negative.

The present theoretical investigation serves for the evaluation of the general behaviour of the acoustic wave propagation during the consecutive stages of the gelation process. An exact quantitative evaluation of the velocity and attenuation of those waves (usually ultrasonic waves) can be achieved only by experiment.

Acknowledgement

The research was supported by the National Committee of Scientific Research (KBN) under the grant Nr 7 T07B 047 15.

References

[1] C.J. Brinker and G.W. Schere, *Sol-gel science*, Academic Press, New York 1990.

[2] *Chemical processing of ceramics*, B.J. Lee, E.J.A. Pope [Eds.], New York 1994.

[3] D. Stauffer, *Gelierungstheorie — Versäumte Zusammenarbeit von Physik und Chemie*, Ber. Bunsenges. Phys. Chem., **102**, 1672–1678 (1998).

[4] Farady Discussions-Gels, **101** (1995).

[5] J. Ranachowski and T. Łaś, *Non-destructive testing of some dielectric solids materials* [in Polish], [in:] The Present Problems of the High Voltage Technology, PWN, Warszawa 1965, 365–397.

[6] J. Ferguson and Kembłowski, *Applied rheology of fluids*, MARCUS, Łódź 1995.

[7] R. De Boer and W. Ehlery, *A historical review of the formulation of porous medies theories*, Acta Mech., **74**, 1–8 (1998).

[8] M.A. Biot, *Theory of propagation of elastic waves in a fluid-saturated porous solid*, J. Acoust. Soc. Am., **28**, 168–191 (1956).

[9] M.A. Biot and D.G. Willis, *The elastic coefficients of the theory of consolidation*, J. Appl. Mech., **24**, 594–601 (1957).

[10] W. Phillipoff, *Relaxations in polymer solutions. Liquids and gels*, Physical Acoustics, P. Mason [Ed.], New York, Vol. II, part B (1965), 1–90.

[11] R.S. Marvin and H. Oeser, *Distribution of relaxation times*, J. Research Nat. Bur. Standards, **B66**, 171–177 (1962).

[12] J. Lewandowski, *Acoustic and effective material parameters of heterogeneous viscoelastic bodies*, Acta Mech., **57**, 143–158 (1985).

[13] J. Lewandowski, *Acoustic and dynamic properties of two-phase media with non-spherical inclusions*, Ultrasonics, **33**, 61–68 (1995).

[14] J.J. McCoy, *A theory of stress wave propagation through inhomogeneous solids*, J. Appl. Mech., **44**, 462–471 (1977).

[15] I. Malecki and J. Ranachowski, *The acoustic cross-section method for evaluation of porous material parameters*, Bull. Pol. Ac. Sci., Ser. Tech. Sci., **45**, 43–56 (1997).

[16] P.R. Williams and R.L. Williams, *Rheometrical aspects of the viscoelastic dispersion of shear waves in gel-like mechanical network*, J. Non-Newtonian Fluid Mech., **78**, 203–225 (1998).