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Rheological characterization of C-S-H phases–water suspensions

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Abstract

The aim of this experimental work was to investigate the performance of microsilica–calcium hydroxide–water suspensions. Interactions between the raw material particles and between water and the raw material particles lead to the formation of gelatinous structures in this suspension. It is essential to use oscillation methods to examine the structure without destruction. The characterization of the tests is made by the storage modulus G' in dependence of the frequency. The tests show an unexpectedly strong elastic behaviour. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Calcium silicate hydrate plays an important role in the building material industry. The characterization of the variety of different phases which can be crystalline, semicrystalline or amorphous are of interest in the basic research in addition to its great practical relevance.

The investigations are performed with diluted suspensions of the commonly used raw materials especially microsilica and calcium hydroxide. Microsilica is an industrial deposit product with outstanding properties and many different applications. It is separated from the waste air of the silicon metal or silicon alloy production in the form of dust and is used for the past few decades. A large amount of microsilica is used in the concrete construction sector. Special concretes with outstanding properties are revolutionizing the building and construction industry [1]. Besides this, amorphous SiO_2 raw material can also be used in other sectors like the refractory industry or for the production of thermal insulation. A slight change in the amount of the microsilica can change the properties of the product drastically.

At any rate, the great reactivity of the microsilica is primarily used at the conversion of calcium hydroxide in the pozzolanic reaction [2]. This is due to its high content of amorphous SiO_2 and large surface area.

The recording or modelling of the kinetic of this reaction is difficult because of the overlapping of different partial reactions. The progress of the reaction is generally determined using various methods, for example, the concentration of the calcium hydroxide or the amount of chemically bound water in dependence of the reaction time.

These methods are also suitable to characterize the reaction of pozzolana after longer periods [3]. Immediately after mixing, the reaction of microsilica with calcium hydroxide starts and shows a noticeable progress of the reaction under definite circumstances within a short time.

It is expected that the rheological properties of the diluted suspensions of the raw materials and the newly formed solid substances are influenced by the formation of the fine and voluminous C-S-H phases and the change of the microstructure of the solid substance phases.

These changes shall be recorded in our experiments by using suitable rheological measurements. A broader motivation to investigate the rheology of C-S-H suspensions is that these suspensions are stirred, pumped, and formed in the industrial production of thermal insulation materials. Here, the rheological properties have a great significance [4].

2. Gel formation

During the gel formation, a three-dimensional network is formed and a colloidal liquid–solid system is built up. The gel formation is related with a change of the properties like

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viscosity, elasticity, and distribution of the clusters. At this time, the gel formation is far away from an equilibrium. Finally, thick structures are built up due to the condensation reactions between the different silicate building units. Gel formation is also an important step in the hydration of cement.

The reaction of calcium hydroxide with microsilica in the cement results first in the formation of water-rich hydrate phases, which release a part of the water after a few hours similar to the water-rich silica gels [5].

In addition, if sufficient amount of $Ca(OH)_2$ is present, the final C-S-H phases do not form directly, but lime-poor and water-rich gels are produced intermediately. The gel formation starts a few minutes after mixing. In the following reaction of SiO_2 with $Ca(OH)_2$ or C-S-H (lime rich), the final C-S-H phases are formed and water is released between 12 and 24 h. Therefore, microcracks as a result of shrinkage can occur in concrete with microsilica [6]. It cannot be decided from the curves of the thermal gravimetric analysis whether C-S-H gels, silica gels, or both have been formed.

Large clusters associated by a strong bonding exist and separate from the suspension. They do not fill the space totally, as liquid and solid phases in colloidal structures are still present in a heterogeneous mixture. They have a layer structure with stored water and can absorb and release water [7].

3. Materials and techniques

We used a molar CaO/SiO_2 ratio of 1:1 in our experiments. The raw materials were taken from a defined batch of microsilica and the calcium hydroxide was produced from $CaCO_3$ (p.a. quality) by burning and hydrating.

Table 1 contains details of the microsilica used.

The special process parameters are equal to those of the production of thermal insulation materials based on calcium silicate. The so-called prereaction of the raw materials is accelerated by increased temperatures and is aimed at a pumpable suspension that can be used at the filter presses. In the industrial process, temperatures of 60 to 95 °C are realized in order to achieve this maturation. This range of the temperature is also applied to our examinations.

Diluted suspensions with a solid content of 30% and a constant C/S ratio were produced with tempered and distilled water. In the next step, the samples were transferred to a thermal bath and were stirred at a constant low speed. Samples were taken and examined after definite periods of time.

4. Rheological examinations

Suspensions of microsilica and calcium hydroxide interactions as well between the raw material particles as between water and the raw material particles lead to the formation of gelatinous structures. The gel consists of solid and liquid phases and the mechanical response of the gel depends on the amounts of both phases and their interaction. Furthermore, the gel shows time-dependent response to an external force.

Quantitative evidence about the progress of the pozzolanic reaction between microsilica and calcium hydroxide can be achieved by the measurement of the viscosity as pointed out in our pretests. The progress of the reaction using common shear viscometry is influenced by the shear and it results primarily in a strong difference in the viscosity development between the sample volume in the shear gap and outside the gap (above and below the cylinder). Practical experience showed that the shear has great influence on the viscosity development of the suspension. The suspension must be moved in a suitable way during the maturation time of the prereaction. Therefore, rotor design was based on empirical knowledge and the rotors are turning slowly in a definite time regime. It is important that the complete volume is moved to avoid the danger of the hardening, however, it must not be stirred too fast and too frequently to prevent a crushing of the formed gel structures.

At shear viscometric experiments, viscosity normally increases depending on the rate of the pozzolanic reaction. However, the unsheared areas of the sample are already more solid and it can be assumed that a destruction of these gels also takes place in the shear gap besides the formation of gels. The disadvantages of the shearing tests lie in the destruction of the network. The viscosity at a given shear rate is used to characterize an immediate structure, however, the C-S-H material is not inelastic but viscoelastic. The structure that shall be measured is destroyed by the measuring.

According to these reasons, either nondestructive measuring methods shall be used or a characteristic value has to be determined for the measurement of the strength of the gel structure. Material structures can nondestructively be observed under different loads with oscillating measuring

Table 1
Properties of the used microsilica

		Density (g/cm^3)		Specific surface (m^2/g) BET		d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
Microsilica A		2.58 ± 0.04		24.4		0.138	0.564	1.692
Chemical analysis	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOW
Mass (%)	95.93	0.21	0.12	0.36	0.30	0.19	0.68	2.04

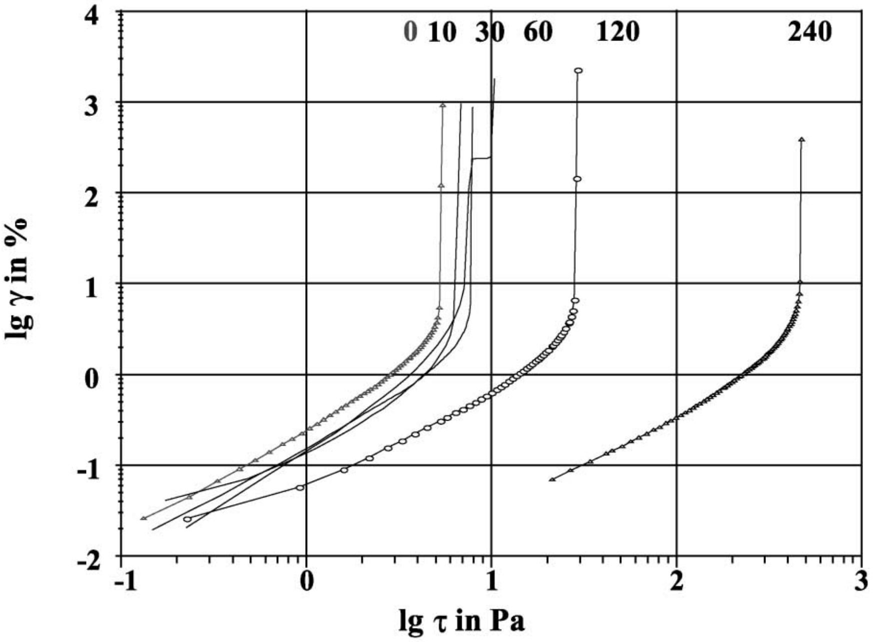

Fig. 1. Development of the yield point of the C-S-H gels at a temperature of 45 °C after different times (time in min as parameter).

methods. With the determination of the yield point, a characteristic value is given for the characterization of the gels.

A Rheometer RS150 (ThermoHaake) is available for the rheological measurements. Different systems were tested as measuring facilities. The only practicable solution was to use a profiled plate–plate system. The formation of a water-rich gliding layer, which can lead to measurement faults (such phenomena are, e.g., also known in cementitious suspensions), is prevented with such system.

4.1. Determination of the yield point

One possible method to observe the development of the particle structures is the measuring of the yield point. The yield point is the minimum force required to induce the flowing of the sample. There are different methods to determine the yield point. The most accurate one consists of a suitable shear stress ramp where the resulting deformation is measured. A significant change of the deformation is to remark in a double logarithmic presentation. The

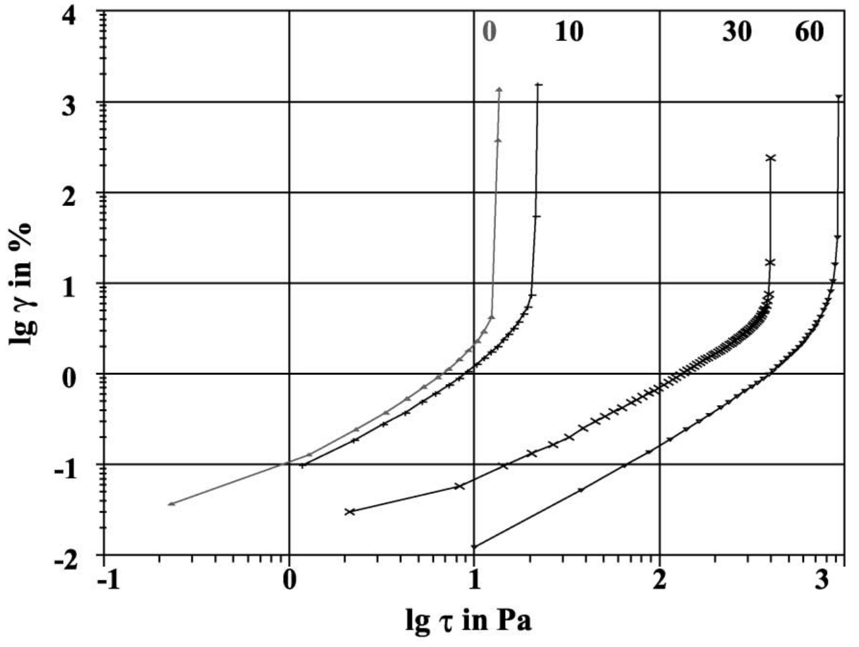

Fig. 2. Development of the yield point of the C-S-H gels at a temperature of 65 °C after different times (time in min as parameter).

yield point is obtainable from the crossover point of the tangents applied.

With less shear stress, the samples react like a solid matter and after exceeding a significant shear stress, the yield point τ_0, they start to flow like a liquid. The yield point test always delivers a relative value since the measuring conditions, e.g., duration of the measuring, can have an influence on the result.

At the pozzolanic reaction between microsilica and calcium hydroxide, a gelatinous structure occurs in which water is stored. At the beginning of the measurement, this gel structure retains the induced tensions. Then glide layers build up in the gel by excessive water after exceeding the yield point, and a strong increase in the deformation with increasing shear stress is observed. The stress τ_0 and the corresponding deformation γ have to be considered for a more precise characterization of this yield point.

Therefore, it seems possible to indicate the progress of the pozzolanic reaction at constant parameters (temperature, raw material, type of rheometer and measuring procedure). In addition, it will also be possible to test various charges of microsilica regarding their influence on the reaction and to check the suitability for the specific use.

Fig. 1 represents the measurements carried out at 45 °C at different reaction times. The yield points at 75 °C are given in Fig. 2. In the evaluation of the measurements, it could be noticed that the deformation at the yield point only varied in a relatively narrow range. This is an indication that the structure of the formed gel does not change with time. From this, it can be concluded that the C-S-H phase is built up uniformly in the diluted suspension and the adhesion forces between the particles are similar.

The shear stress τ_0 increases both with temperature and time. This can be understood as an equivalent increasing in the number of entanglements in the network structure and can be seen as a degree of the progress of the reaction between microsilica and $Ca(OH)_2$ or for the amount of C-S-H phase formed. The amount of C-S-H phase, which has equal-type properties, increases with time and temperature.

Table 2 lists the yield points development of the C-S-H suspensions at certain temperatures after different periods of time. The influence of the temperature and the maturation time on the shear stress value of the yield point as a measure for the formation of the gel structure are very obvious to recognize. Immediately after mixing, considerable values for the shear stress τ_0 is observed. At higher temperatures, the τ_0 values already multiply themselves after a short maturation time. The deformation γ is 2.4% on the average and lies at all measurements in a relatively narrow range between 1.1% and 4.2%.

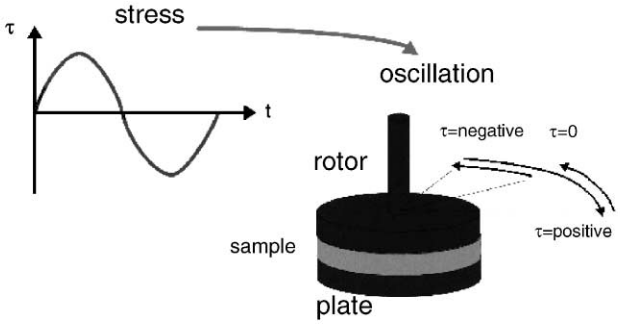

Fig. 3. Principle of the oscillation method.

4.2. Oscillation methods

To prevent the destruction of the gelatinous structures during the measurement, it is necessary to change from the shear viscosimetry to an oscillating method. This means, at a given shear stress with a sinus temporal function, the resulting time-dependent deformation will be measured. The deflection angles of the rotor are about 1°. Fig. 3 illustrates the oscillation measuring principle.

The complex module G^* stands for the total resistance of the sample against the deformation forced (Eq. (1)).

$$|G^*| = \tau_0/\gamma_0 \tag{1}$$

The rheological "answer" of the sample can be divided into a viscous and an elastic part. In this way, samples with viscoelastic properties, in other words, with a flow behaviour which lies between the solid matter and Newtonian fluid, can be described (Eqs. (2) and (3)).

$$G' = G^*\cos\delta \tag{2}$$

$$G'' = G^*\sin\delta \tag{3}$$

The elastic modulus G' describes the part of the energy of deformation which can be retained and gained back after decrease of the stress. The viscous modulus G'' shows the part of deformation energy which is consumed by viscous flow and is changed into shear heat. The applied deformation and the resulting shear stress are displaced at the phase angle δ. The angle size gives information about the amount

Table 2
Development of the yield points of the C-S-H suspension at various temperatures and after different periods of time (stress τ_0 in Pa and deformation γ in %)

	Time (min)				
T (°C)	0	10	30	60	120
45	5.1 Pa/2.0%	6.1 Pa/1.1%	6.9 Pa/2.4%	7.9 Pa/2.0%	27.0 Pa/2.1%
65	14.5 Pa/2.1%	19.8 Pa/4.2%	360 Pa/2.6%	820 Pa/2.1%	–
75	13.0 Pa/1.1%	28.6 Pa/2.1%	900 Pa/3.5%	7943 Pa/3.5%	–

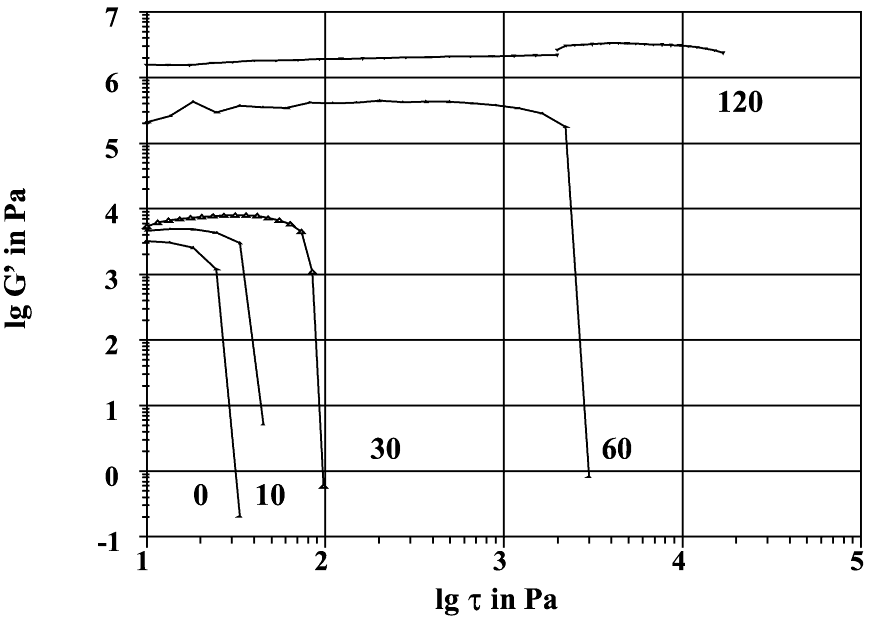

Fig. 4. Alterations of the linear viscoelastic range of the C-S-H gels at a temperature of 65 °C and the frequency of 1 Hz (time in min as parameter).

of the viscous or elastic part of the sample. Only viscous substances present a phase displacement of 90°; at a phase displacement of 0° the substance reacts purely elastically. Viscoelastic samples are characterized by a value between 0° and 90°.

The strain of the sample must be in the range of the linear viscoelasticity during the measurements. This means, that the material functions (elastic modulus G' and viscosity modulus G'') are independent from the predefined shear stress. This range was determined in tests as function of the shear stress. A strong change of this linear viscoelastic range appeared at the examined suspensions (time: 0–120 min; temperature: 45–90 °C). The consequence is that reliable measurements can only be achieved if the measuring conditions are adjusted accurately.

Fig. 4 shows the alteration of the viscoelastic range at a constant temperature of 65 °C in dependence of the time with assistance of G'. The elastic modulus G' is constant within the linear viscoelastic range. The modulus decreases after exceeding this range. Simultaneously, the deformation γ increases steeply. The linear range changes quickly with the maturation time. While after a few minutes a small force is already sufficient to exceed the linear viscoelastic range, the maximum tension is insufficient to leave this range after

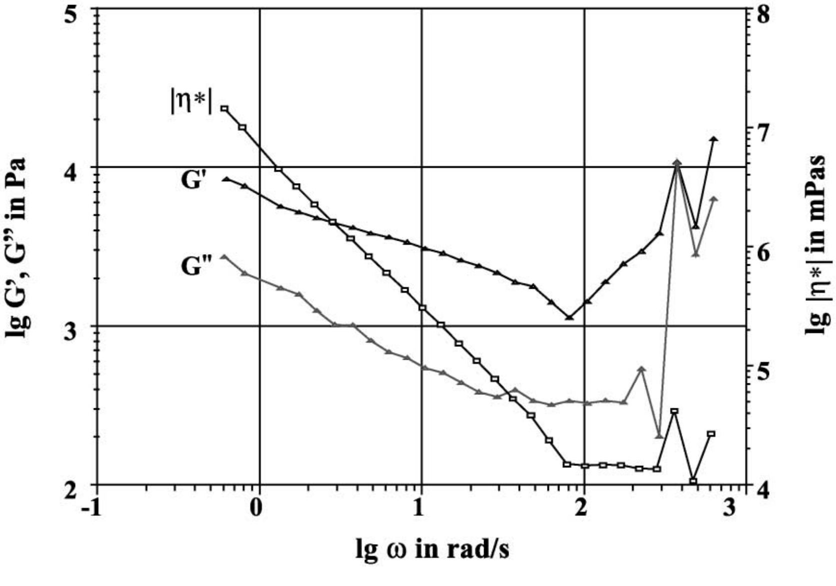

Fig. 5. Frequency dependence of the viscoelastic values G', G'' and $|\eta^*|$; C-S-H gel at a temperature of 75 °C after maturation time 10 min.

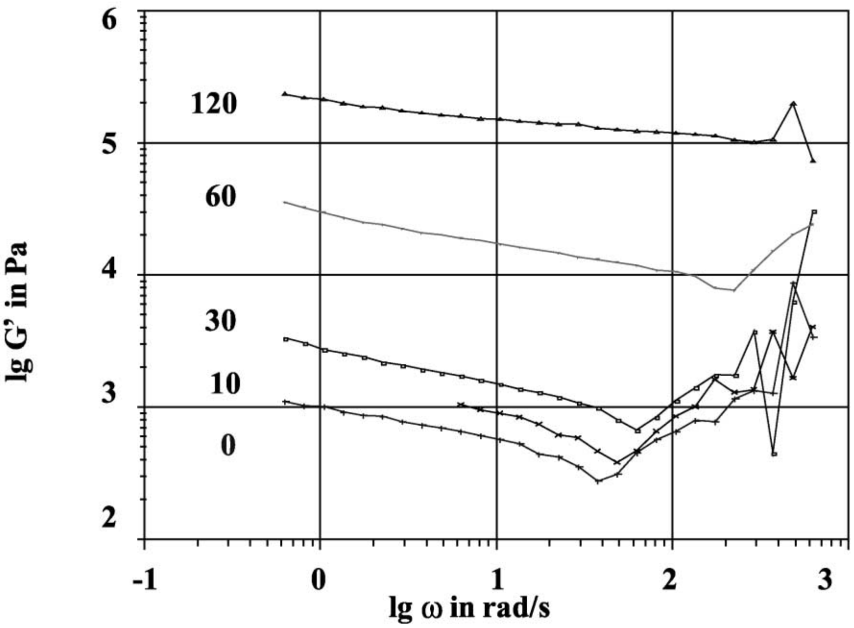

Fig. 6. Alteration of the storage modulus of the C-S-H gels at a temperature of 65 °C (time in min as parameter).

120 min. This means that the network structure is so stable that linear viscoelastic behaviour exists at all applying stresses. These experiments were carried out with different frequencies since the linear viscoelastic range depends also on the frequency.

The characterization of the samples is made by the moduli in dependence of the frequency. At this either the shear stress or the deformation is given. For a characterization of the gel structures, a present constant deformation is suitable in order to compare the loading status.

The large frequency range was consciously chosen especially at high frequencies in order to obtain information about the stability of the network. When exceeding a certain frequency, the steady course of the curve changes and the data are no longer reproducible.

The samples show an unexpectedly strongly distinctive elastic behaviour. The elastic modulus lies approximately an order of magnitude over the parallel going viscosity modulus. The change of the moduli is relatively little over a large frequency domain. The phase moving angle δ lies between

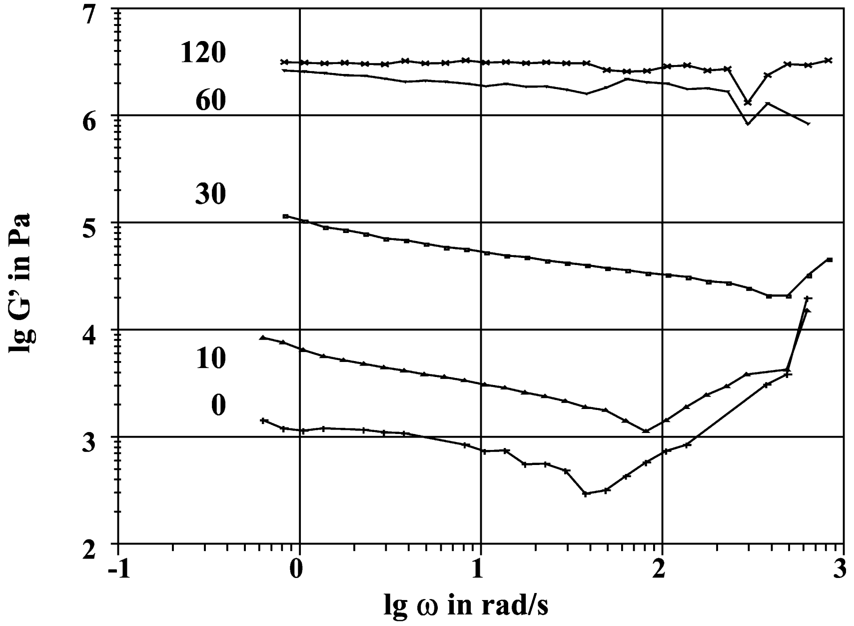

Fig. 7. Alteration of the storage modulus of the C-S-H gels at a temperature of 75 °C (time in min as parameter).

6° and 12°. A strong 3-D structure builds up despite the high water fraction of 70%. The complex viscosity shows a linear course up to or exceeding the critical frequency. The results of the measurements by variation of the parameter temperature and maturation time, respectively, show a very similar run of the curves. The results for a suspension at 75 °C after 10 min of maturation time are presented in Fig. 5 exemplary.

For the evaluation of different samples, the comparison of the curves of G' is very useful. In Figs. 6 and 7, the temporal change of the elastic modules for different temperatures is shown. The curves run nearly parallel, therefore the dependence of the formation of the gel structure from the time is obvious. The critical frequency, above which the structure is no longer stable, rises with the time and consequently with the strength of the structure.

5. Results and discussion

Rheological measurements are suitable for studying particle interactions in the $CaO-SiO_2-H_2O$ system from structural changes up to the formation of products (Tobermorit, Xonotlit), and the time dependence of these interactions. A possibility to observe the development of the particle structures is the measuring of the yield point. At the beginning of the measurement, the gel structure absorbs the induced tensions. Glide layers are built after exceeding the yield point, and a very strong increase of the deformation with increasing shear stress can be observed. The deformation at the yield point varies only in a relatively narrow range. This is an indication that the structure of the gel formed from different charges is similar and does not change with time. Contrary, the shear stress τ_0 increases not only with the temperature, but also with the maturation time. This can be explained by the increasing number of equal-type connections of the net structure.

It is necessary to change from the shear viscometer to the oscillation viscometer to measure nondestructively. The tensions during the measurements have to lie in the range of the linear viscoelasticity to obtain reproducible results. From the suspensions examined a strong change of this linear viscoelastic range arises in the considered frame of parameters. Exact adjusting of the measuring conditions is necessary for the measurements.

The characterization of the samples are made with the moduli in dependence of the frequency. The samples show an unexpected strong distinctive elastic behaviour. The elastic modulus lies approximately an order of magnitude over the viscosity modulus, which passes parallel. For comparison of different samples, we use the curves of the elastic modulus G'. The curves run nearly parallel, therefore the dependence of the construction of the gel structure on time is obvious. The critical frequency, above which the structure is no longer stable, rises with time that means, with the strength of the structure. The absolute values and the course of curves of the elasticity module G' give an information about the strength of the structure in dependence of the maturation time and the temperature.

Acknowledgments

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