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Rheometric and ultrasonic investigations of viscoelastic properties of fresh Portland cement pastes

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Abstract

The paper investigates the possibility of using a shear wave reflection technique to monitor the viscoelastic behavior (represented by storage shear modulus and viscosity) of Portland cement paste at very early age. Three cement pastes with water/cement ratios equal to 0.4, 0.5 and 0.6 cured under water at a constant temperature of 25 °C were studied. By measuring the wave reflection coefficients and the phase angles of reflected ultrasonic waves, the dynamic storage shear moduli and the viscosity of the cement paste can be calculated. The calculated results of the storage modulus were compared with the results obtained directly from the oscillatory rheometric measurement. In addition, the viscosity calculated from the wave reflection measurements was compared with results obtained directly from the step rheometric method and a qualitative agreement was found. The results show that as a non-destructive method, the ultrasonic wave reflection method provides useful information about both the elastic and viscous behavior of cement pastes at very early age.

Keywords: Viscoelastic behavior; Ultrasonic wave reflection coefficient; Oscillatory rheology; Storage modulus; Viscosity

1. Introduction

When cement paste is subjected to an external force, it responds in a manner intermediate between an elastic material and a viscous material. This viscoelastic behavior changes during the hydration process of the cement particles [1]. A better understanding of the viscoelastic properties of cementitious materials can help to control the volume stability of the material at later ages.

Viscoelastic properties are important not only for cement-based materials at later ages; it is also a factor that affects the workability of the material in the very early age. The knowledge of viscoelastic properties can provide fundamental information about the physical status of a solid particle suspension system transforming to a viscous semi-solid flowable and subsequently to a solid system.

This study will mainly focus on the viscoelastic properties of Portland cement pastes at very early age, namely before the initial setting time. The methods used in the research to investigate the viscoelastic properties of the cement pastes at early age are based on the theory of dynamic rheology [2].

In 1950s, Mason [3] introduced the concept of non-invasive ultrasound viscometry. He measured ultrasonic wave reflections from a liquid–quartz interface and used this data to determine the viscosity response of the fluid. Since then, ultrasonic shear waves have been used to characterize the viscosity of the fluid in several ways. Parameters such as wave amplitude, phase angle and the frequency of the wave were used to monitor the viscous or viscoelastic properties of thick fluids [4–7]. By using shear waves, the measurements can be correlated to viscosity, which is the parameter of interest for most engineers and researchers.

The ultrasonic wave reflection technique was first applied to the area of cementitious materials by Stepišnik et al. in 1981 [8]. This method can be used to monitor the setting and hardening behavior [9] and can also be adopted to mimic the strength development of cementitious materials at early age [10–13]. In a recent study, more attention was paid to the application of this method to monitor the viscoelastic properties of cement pastes [14]. It was shown that when cement paste is in solid state, the

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material behavior can be approximated by neglecting the phase shift measured by the wave reflection technique [8,15]. But few results on fresh cement paste in flowable status were reported.

In this study, the application of the ultrasonic shear wave reflection technique was explored. The technique was used to monitor the viscoelastic properties of cement pastes at very early age by observing the evolution of the storage shear modulus and the viscosity. The calculated storage shear modulus, which represents the elastic properties of the materials were compared to the results measured directly from the oscillatory rheometric method, which is from a micro-structural point of view also a non-destructive testing method. In this oscillating rheometric method [16–18], the storage and loss shear moduli of the cement paste can directly be measured by applying oscillating shear strain according to a sine function and measuring the corresponding shear stress. By controlling the value of oscillatory shear strain and the frequency within the linear viscoelastic region of the material, the microstructure of the cement paste will not be destroyed during the oscillations, and the evolution of the material properties during hydration can be observed.

2. Theory background

2.1. Material properties

If mechanical energy acting on a body is partly stored in deformation and partly dissipated in other forms, then such behavior is defined as viscoelastic behavior [19]. Concrete is a typical viscoelastic material. The porous structure of the paste matrix and the interfacial transition zone between cement paste and aggregates make the properties of concrete more complex. Understanding the viscoelastic properties of Portland cement paste can be helpful to better understand the behavior of concrete.

The deformation of a viscoelastic material is not proportional to the applied force because of the energy dissipation. In this context, dynamic methods can help to distinguish between the elastic and viscous properties of the material. When a linear viscoelastic body is subjected to stress varying sinusoidally with time at a certain frequency, the corresponding strain is not in the same phase as applied stress, which results in a phase lag between strain and stress as shown in Fig. 1(a) [19]. The applied stress can be separated into two independent components: one is exactly in phase with strain, the other is $\pi/2$ out of phase as shown in Fig. 1(b) [19].

The viscosity, which represents the resistance of the fluid to flow, can also be calculated through the wave reflection technique. The calculated results were compared to the viscosity measured directly from the step rheometric method [20]. In the step rheometric method, the strain rate varied within a certain range in uniformly changing steps and the corresponding stresses at each strain rate step were measured. The comparison of the viscosities obtained with the two methods is discussed in a later part of this paper.

According to the decomposed stress components, the relationship between stress and strain of a viscoelastic material

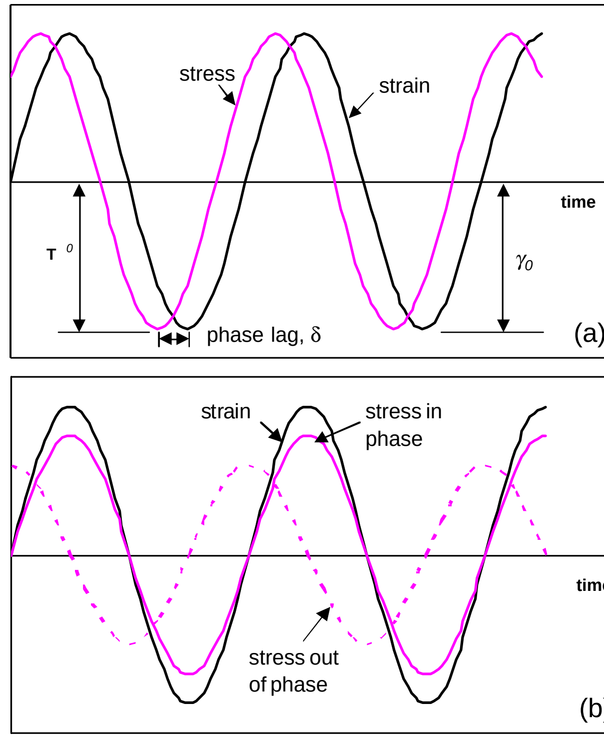

Fig. 1. Stress and strain relation in a viscoelastic material [3].

can be established by using the modulus of rigidity in a complex format. If a material is subjected to a shear deformation, the shear modulus can be expressed as follows,

$$G^* = \frac{\tau}{\gamma} = G' + iG'' \tag{1}$$

$$G' = \frac{\tau_0}{\gamma_0}\cos\delta \tag{2}$$

$$G'' = \frac{\tau_0}{\gamma_0}\sin\delta = \omega\eta' \tag{3}$$

where G^* is the complex shear modulus, G' is the storage shear modulus, which represents the elastic behavior or the energy storage of the material, and G'' is the loss shear modulus, which represents the viscous behavior or energy dissipation of the material. If the physical status of the viscoelastic material is in flowable status, the loss shear modulus can also be related to the in-phase viscosity of the material [8,14,15] as shown in the second part of Eq. (3), where ω is the angular frequency of the applied oscillating strain (stress). The phase lag(δ) between stress and strain, which changes between 0 and $\pi/2$ can also be used to describe the material behavior. When a material is ideally elastic, the phase lagδ equals to zero; when a material is ideally viscous, parameter δ equals to $\pi/2$.

2.2. Linear viscoelastic region (LVER)

Generally speaking, the elastic moduli of a viscoelastic material are time dependent. However, there is a specific region, called linear viscoelastic region (LVER) [21], under which the elastic moduli of such a viscoelastic material are independent of time, amplitude of the oscillating strain or stress, and applied oscillating frequency.

To define the LVER of a certain material, two aspects need to be considered. First, a critical maximum value of the strain needs to be found [16–19,22,23]. There is a linear part of the stress–strain curve, where the shear modulus is independent of the applied strain (or stress). And the loading and unloading paths within this linear region are identical. The critical strain (γ_{0cr}), which marks the ending of the linear stress–strain relation, is defined as the limit strain of LVER. Beyond this region, loading and unloading paths are different, which means that there will be a residual stress in the cement particles during the oscillation test.

Second, a critical frequency (f_{cr}) of the applied oscillating strain needs to be found in order to define the LVER. The structure of the material requires sufficient time to relax and release residual energy during oscillating, so that particles in the microstructure can elastically recover to their equilibrium status. This requires the applied frequency to be lower than a certain level so that there will not be any residual stress or energy from the previous oscillation during the whole period of testing.

2.3. Acoustic shear impedance

The propagation of shear waves in a material is governed by its acoustic shear impedance [24], which can be considered as a material property. Generally, the shear impedance can be related to the shear modulus of the material by using Eq. (4) [24].

$$Z = \rho v_s = \sqrt{\rho G} \tag{4}$$

where ρ is the mass density of the material and v_s is the shear wave velocity. If the viscoelastic property is concerned, shear modulus G should be replaced by the complex shear modulus, which makes the shear impedance also a complex quantity (Eq. (5)) [8,15], where R and X are the real and the imaginary parts of the complex shear impedance, respectively. By linking Eqs. (1) and (5), both the storage and loss shear modulus can be expressed as a function of the real and imaginary part of the shear impedance as shown in Eqs. (6) and (7). By considering the angular frequency of the transmitted wave, the viscosity of the material can be determined as shown in the Eq. (7).

$$Z = R + iX \tag{5}$$

$$G' = \frac{R^2 - X^2}{\rho} \tag{6}$$

$$\eta' = \frac{G''}{\omega} = \frac{2RX}{\omega\rho} \tag{7}$$

If the acoustic shear impedance of the tested material is known, the complex shear modulus can be calculated. According to Whorlow [7], several methods, such as the audio-frequency or high-frequency impedance method can be applied to measure the shear impedance of the material. The method used in this study is an ultrasonic shear wave reflection method, which will be discussed in a later part of this paper.

3. Experimental program

3.1. Materials

Ordinary Type I Portland cement provided by Lafarge was used for all the experiments. The Blaine surface area is 365 m^2/kg. The chemical composition of the cement is listed in Table 1.

Plain cement pastes with water/cement ratios of 0.4, 0.5 and 0.6 were tested. The specification of ASTM C305 [25] was followed during the mixing of the cement pastes to be tested by the wave reflection method. All specimens tested by the wave reflection technique and the rheometric methods were cured at a constant temperature of 25 °C.

3.2. Ultrasonic shear wave reflection measurement (WR-method)

The wave reflection coefficient was calculated from the information obtained from the ultrasonic wave reflection tests. The apparatus used is shown in Fig. 2. A fused quartz plate with a thickness of 10 mm was used as a buffer material. Two transducers with 2.25 MHz central frequency were coupled to the quartz plate. The transducers are connected to pulsers, which in turn are connected to a personal computer. The two trans-ducers collect the wave reflection data independently from each other, which means that the described setup is capable to perform simultaneous measurements at two different specimens. The data collection was controlled by a computer program.

According to the theory of wave reflection [24], for the normal incidence of shear waves at a boundary, the reflection coefficient can be defined as:

$$r = \frac{A_r}{A_i} = \frac{Z_2 - Z_1}{Z_2 + Z_1} \tag{8}$$

where r is the wave reflection coefficient, defined as the amplitude ratio between the reflected (A_r) and incident (A_i) waves, which can be obtained directly from experimental measurements. Parameter r is also a function of the mechanical properties of the buffer and tested material, which is reflected in the second part of Eq. (8). Here, Z_1 and Z_2 are the shear impedance of the buffer material and the measured material, respectively.

If the viscoelastic property of the tested material is concerned, the reflection coefficient can be expressed in a complex format as shown in Eq. (9).

$$r^* = r_0 e^{i\phi} = r_0(\cos\phi + i\sin\phi) \tag{9}$$

where ϕ is the phase shift between the incident and reflected waves, and r_0 is the magnitude of the reflection coefficient. The

Table 1
Chemical compositions of Portland cement Type I- Lafarge

Chemical data	SiO_2	CaO	Al_2O_3	Fe_2O_3	C_3S	C_3A
Percent	20.4	65.3	4.8	2.8	68	8

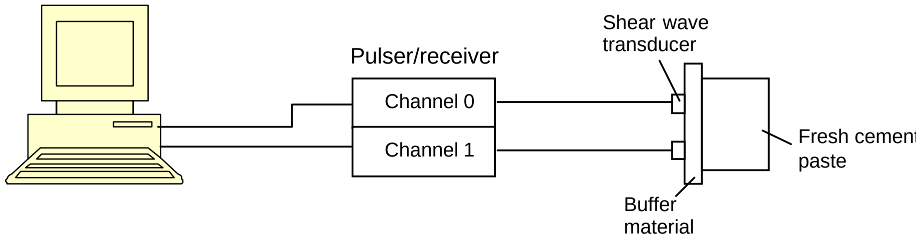

Fig. 2. Experimental apparatus for wave reflection measurements.

phase shift equals to π at $t=0$ and it decreases during the hydration process of the cement paste.

The shear impedance of the buffer material is considered to be constant with $Z_1=8.25\times10^6$ kg/m^{2}s for fused quartz. The real (R) and imaginary part (X) of the shear impedance of the viscoelastic material given in Eqs. (10) and (11) can be obtained by solving Eqs. (5) and (9)

$$R = Z_1\frac{1-r_0^2}{1-2r_0\cos\phi+r_0^2} \tag{10}$$

$$X = Z_1\frac{2r_0\sin\phi}{1-2r_0\cos\phi+r_0^2} \tag{11}$$

The storage shear modulus (Eq. (12)) and the viscosity (Eq. (13)) of the measured cement paste can be calculated by substituting Eqs. (10) and (11) in Eqs. (6) and (7).

$$G' = \frac{R^2-X^2}{\rho} = Z_1^2\frac{\left(1-r_0^2\right)-4r_0^2\sin^2\phi}{\rho\left(1-2r_0\cos\phi+r_0^2\right)^2} \tag{12}$$

$$\eta' = \frac{2RX}{\omega\rho} = Z_1^2\frac{4r_0\left(1-r_0^2\right)\sin\phi}{\omega\rho\left(1-2r_0\cos+r_0^2\right)^2} \tag{13}$$

3.3. Strain sweep and frequency sweep rheometric methods

In order to define the LVER of the cement pastes, a two-step procedure was applied. First, a strain sweep was used to determine the magnitude of the critical strain. During the strain sweep test, a small frequency at the level of 1 Hz was used for all of the three pastes with water cement ratios changing from 0.4 to 0.6. The shear strain was swept from 3.87×10^{-5}, which is the lowest capacity of the machine [26], to 1.00×10^2. The shear moduli were measured during the strain sweep tests and the critical strain values were determined using the value at which the shear moduli began to decrease.

Second, the critical value of the applied frequency was determined by frequency sweep. During the frequency sweep, the cement paste is subjected to an oscillatory strain with constant amplitude at a value smaller than the critical strain determined by step one. The frequency was swept from 0.1 Hz to 100 Hz for all three pastes. The critical value of the applied frequency is defined as the frequency at which the measured shear modulus begins to decrease. The effect of the applied shear strain and frequency on the material behavior will be discussed in the appendix of this paper. An example of the measured results with strain and frequency sweep is also given in the appendix (Figs. A3 and A4).

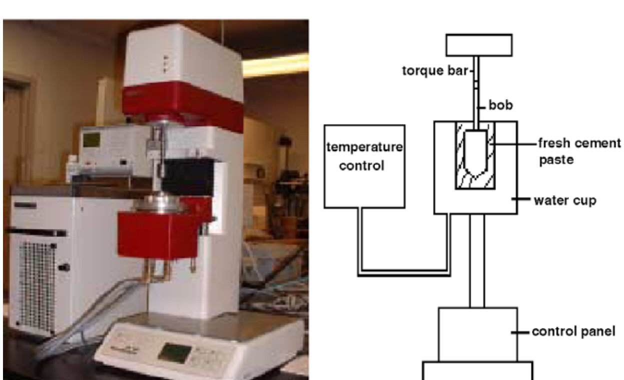

Fig. 3. Sketch of HAAKE RS150 rheometer.

3.4. Oscillatory rheometric method (OR-method)

The OR-method was used to study the microstructural evolution of cement pastes by several researchers in the recent decade [16–18,22,23,27,28]. In this study, a strain control rheometer, Haake RS150, was used (Fig. 3). Co-axial cylinders with diameters of 20 mm and 21.6 mm were used. A gap between the outer and inner cylinder of 0.8 mm allows assuming that the shear stress is uniformly distributed across the gap [16]. A sample of approximately 25 g of cement paste was mixed by hand for 90 s. After transferring the cement paste into the rheometer, a high shear rate of 600 s^{-1} was used for 30 s to initiate the irreversible structural breakdown of the cement particles [28]. Hand mixing followed by pre-shearing in the rheometer at a high strain rate provides a standard pre-shearing treatment. Then the cement paste was allowed to rest for 600 s to let the particles achieve their structural equilibrium and by this to reach the same stress status before the oscillating testing. During the oscillatory testing, the strain-control mode was used. According to the values of critical strains listed in Table 2, the used strain amplitudes were 1×10^{-4} for w/c=0.4 and 0.5, and 7×10^{-5} for w/c=0.6 for the OR-method. The

Table 2
Linear viscoelastic region for cement pastes (T=25 °C)

w/c ratio	$\gamma_{0\mathrm{cr}}$	f_{cr} (Hz)
0.4	5.67×10^{-4}	7.46
0.5	2.99×10^{-4}	15.40
0.6	1.37×10^{-4}	17.03

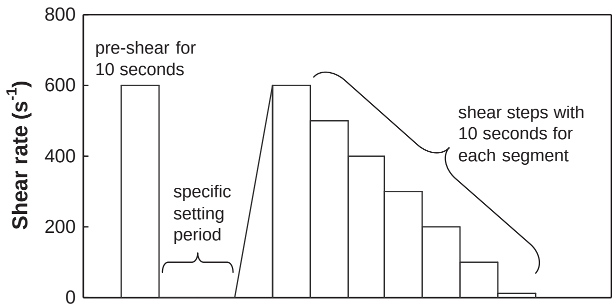

Fig. 4. Sketch of the procedure for SR-method.

frequency used was 1 Hz for all the cement pastes. The in-phase and out-of-phase shear stresses can be traced during the measurements. The temperature of the specimens was maintained at 25 °C by controlling the circulating water in the water cup in which the outer cylinder is embedded. All the samples were covered by non-seepage oil during the oscillating test to prevent the moisture loss. Non-seepage oil has a very high viscosity, prevents the oil of being absorbed by the cement paste.

3.5. Step rheometric method (SR-method)

The step rheometric [20] method was used in this study to investigate the evolution of the viscosity. The experimental setup used in this method is exactly the same as that used in the oscillatory rheometric method. After transferring the cement paste to the rheometer, a high shear rate at 600 s^{-1} was applied to bring the cement particles to a stress status that can easily be reproduced during repetitive measurements. The cement paste was allowed to set for a specific period of time so that the cement particles are in equilibrium position. After the settling period, segmented shear tests were employed. The applied shear rate decreased from 600 s^{-1} to 10 s^{-1} based on a uniform step and for each shear strain rate, the shear stress was measured. The sketch of the procedure used in the SR-method is shown in Fig. 4. Based on the Bingham model, the viscosity of the cement paste at that specific age can be defined as the slope of the obtained stress–strain rate curve. In order to investigate the evolution of viscosity, different specimens at certain hydration ages were tested.

4. Results and discussions

4.1. Linear viscoelastic region

The strain and frequency sweep tests were applied for plain Portland cement paste with water/cement ratios equal to 0.4, 0.5 and 0.6. Each test was repeated for three times. The mean values of the critical strain and the critical frequency for the LVER of these three pastes under a constant temperature (T=25 °C) are listed in Table 2. The magnitude of the critical strain increases with the decrease of water/cement ratio. It is believed that this effect is caused by the different amount of solid particles (cement) in the pastes with different water/cement ratios. A higher concentration of solids in a suspension increases the stress resistance of the suspension, which is reflected by a longer linear portion in the stress–strain relationship. This phenomenon can also be explained via shear stress. In suspension rheology, the yield stress increases with solid content. Critical stress can be regarded equivalent to yield stress. So, the dependency of the critical strain on water/cement ratio can be correlated directly with the critical stress since the modulus does not change with LVER. Similarly, because of the higher solid volume in a cement paste with lower water/cement ratio, it may take longer for the solid particles to return to their initial status and to prevent residual energy during the oscillating test. This can help to explain that the value of the critical frequency is smaller for the cement paste with a lower water cement ratio as shown in Table 2. Examples of strain sweep and frequency sweep measurements are given in the appendix of this paper. The influences of the oscillating strain amplitude and applied frequency on the material behavior are also discussed.

4.2. Oscillatory rheometric measurement (OR-method) via strain-control

One of the major advantages of the OR-method is that time-dependent changes of the material properties can be observed and analyzed. Fig. 5 shows the continuous development of storage and loss shear moduli of plain cement paste with w/c=0.4 during the first 3 h of hydration. The storage modulus increases with time from an initial value of 1 kPa to above 1300 kPa at about 2.5 h. Different from storage modulus, the loss modulus increases from 10 kPa to around 70 kPa during the first hour and then decreases. Struble et al. [18] reported similar curves for the storage and loss moduli. The reason for the decrease of the loss modulus was not illustrated.

Nachbaur et al. [22,23] also reported oscillatory rheometric measurements on cement pastes. Similar results were obtained for the storage modulus, while those for the loss modulus were different. Parallel plates were used during the oscillating test, and both the storage and loss moduli increased with time. This indicates that the development of the storage modulus measured by the oscillatory rheometer is independent of the instrument, which agrees with the results shown by Saak [29], where it is reported that the storage moduli measured by the co-axial cylinder, the parallel plate and the vane rheometer

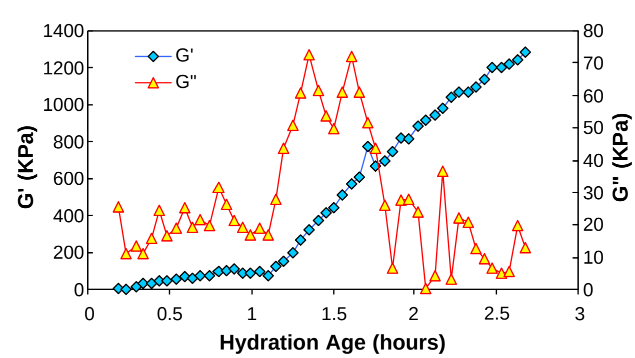

Fig. 5. Storage and loss modulus as a function of hydration time (w/c=0.4, T=25 °C).

correspond to each other very well. However, the loss modulus development curve was found to be affected by the instrument type. The loss modulus tends to be very sensitive to the stress status and stress distribution applied to the material. The stress distribution in the cement paste measured with a co-axial rheometer and a parallel-plate rheometer are very likely to lead to the different shape of the loss modulus curve due to the geometry of the rheometer. Because of these discrepancies, the loss modulus from the OR-method will not be further included in the discussion of this paper.

The development of the storage shear modulus of Portland cement pastes with different water/cement ratios is plotted in Fig. 6. The storage modulus curve starts with a flat part, which can be related to the dormant period of cement hydration [30], followed by a steeply increasing part. At a given hydration age it is found that the lower the water/cement ratio is, the faster is the increase of the storage modulus. The storage shear modulus can be considered as closely related to the volume fraction of solid particles in the cement paste, which contributes the most to the elastic property of the measured material.

4.3. Viscosity obtained through step rheometric method (SR-method)

The SR-method can be considered as a suitable method to measure the viscosity. In this method, the applied shear rate decreases in uniform steps from high to low value. An example of results obtained with the SR-method for the paste with w/c = 0.5 at the age of 0.5 h is shown in Fig. 7(a). Based on the Bingham model, the viscosity is defined as the slope of the measured stress–strain rate curve.

The viscosity of the three Portland cement pastes was measured at different hydration ages by using different specimens prepared according to the same procedure. For each hydration age, the measurements were repeated three times and average values were used for the evaluation of the results. The development of the viscosity of the pastes in time is shown in Fig. 7(b). It can be seen from the figure that for a given age the cement pastes with higher water/cement ratios exhibits significant lower values of the viscosity. The high content of solid cement particles in a paste with the low water/cement ratio densifies the suspension, which reduces the flowability of the material. It should also be noted that the increase of the viscosity with time is not linear. The viscosity increases at a very slow rate at very early age, whereas at later ages the plotted data exhibit a much more rapid change. This could also be attributed to the dormant period of the hydration process.

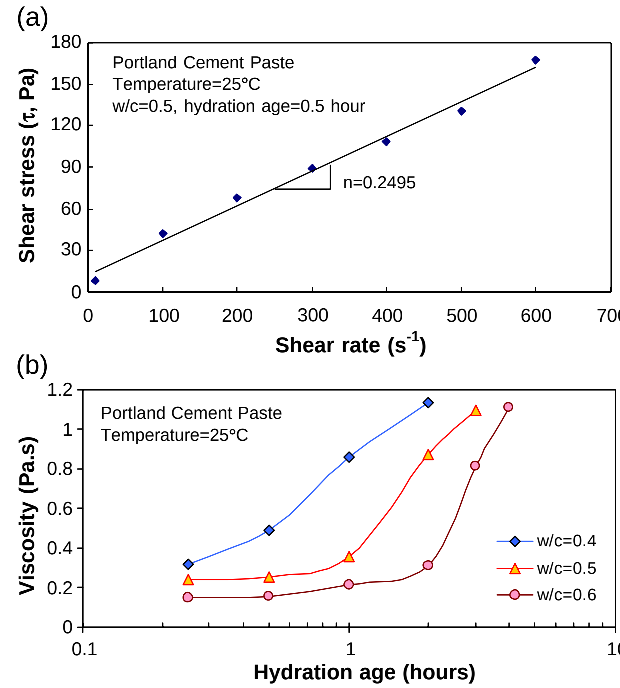

Fig. 7. (a) Viscosity obtained with Bingham Model. (b) Time development of the viscosity.

4.4. Shear modulus calculated from WR-measurement

The supplementary angle of the phase shift $(\pi - \phi)$ obtained from the WR-measurement increases from a value, which is less than 1° to about 10°. By combining the phase shift with the reflection coefficient measured with the WR-technique, the correspondent storage modulus and the viscosity can be calculated by using Eqs. (12) and (13). An example of calculated results for storage and loss shear moduli of the cement paste with w/c = 0.6 is shown in Fig. 8. It can be seen that both, storage and loss moduli, increase with time.

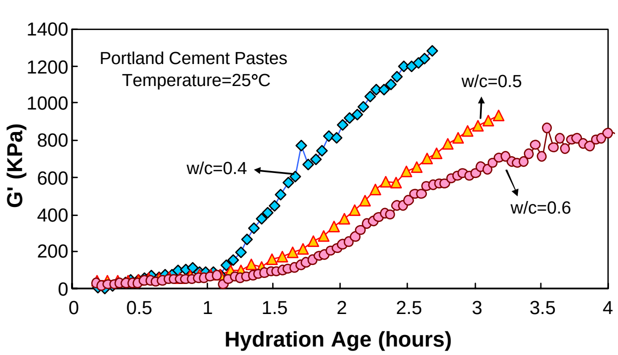

Fig. 6. Storage shear modulus of as a function of hydration time with different water/cement ratio.

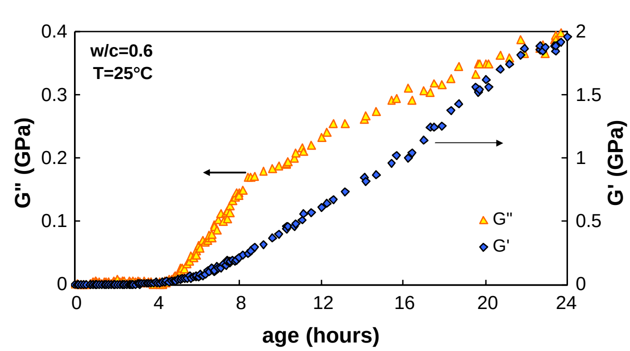

Fig. 8. Storage and loss shear moduli calculated from wave reflection measurement.

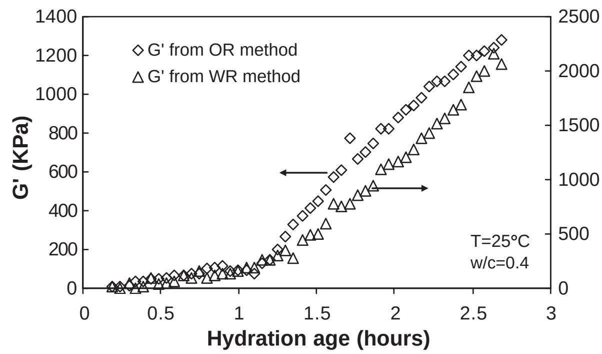

Fig. 9. Comparison of storage shear moduli from WR- and OR-methods.

However, the storage modulus increases with at much higher rate than the loss modulus, which means the elastic property of the material becomes the dominant part that affects the material behavior at later age.

4.5. Comparison of elastic shear moduli with WR- and OR-methods

A comparison of the storage shear moduli for cement paste with w/c = 0.4 determined with the WR- and OR-methods is shown in Fig. 9. It can be seen that at a given hydration age, the absolute value of the storage modulus calculated from the WR-measurement is bigger than that obtained from the OR-method. This systematic difference could be due to the different methods applied (e.g. different frequency and experimental procedure). However, it can also be noted that both moduli develop after a very similar trend. In Fig. 10, the evolution of G' for all three cement pastes is plotted. In the figure, the moduli values obtained from the OR- and WR-methods are normalized with respect to their values at the end of the OR-measurements. The moduli first exhibit a moderate increase followed by a steeply increasing part. The time of the sharp increase of the moduli can be considered as the end of the dormant period in the hydration process [30]. It is obvious that the storage shear moduli obtained with the two different methods develop after very similar trends for all tested water/cement ratios, which shows that the WR-method can monitor the elastic behavior of cementitious materials in fresh state.

4.6. Validation of monitoring the elastic properties with WR-method

Because of the systematic difference between the absolute values of the storage shear moduli obtained with the WR- and OR-methods, it is necessary to further investigate the validity of using the WR-method for monitoring the elastic properties of cementitious materials. The storage shear modulus data calculated from results of the WR-method were compared with the results measured directly from the resonant frequency method (RF-method) [31] with the cement paste in a solid state. An example of this comparison is given in Fig. 11. First, it can be noted that the curves of the two moduli have a similar shape. The moduli start to increase at approximately the same time and the time when the moduli start to approach their final values is also similar. Furthermore, it can be seen that the shear moduli G_{RF} and G_{WR} are almost equal. The good correspondence between the data obtained with these two methods indicates that WR-method is an efficient method, which can trace the development of the elastic property of the material during hydration.

4.7. Comparison of viscosity obtained with WR- and SR-methods

The viscosity of the tested cement paste can be calculated from the results of the WR-measurements according to Eq. (13). Fig. 12(a) shows the viscosity data determined from WR-measurements performed at the three cement pastes at the age of 15 min. In general, it can be stated that the plotted data follow the expected trend that the viscosity increases with a decrease in water/cement ratio. This observation shows that the WR-method can give a qualitative indication of the viscosity of fresh Portland cement pastes.

To further validate the ability of the WR-method in providing information about the viscosity of cementitious materials, the viscosity of the three cement pastes was measured with the step rheometric method at different ages. The comparison of these results with viscosity values calculated from the WR-measurements is given in Fig. 12(b). It can be seen that the viscosity values obtained from the two different methods are related by a strong linear trend. The trend line has a high statistical significance (R^2 = 0.9688) and is valid

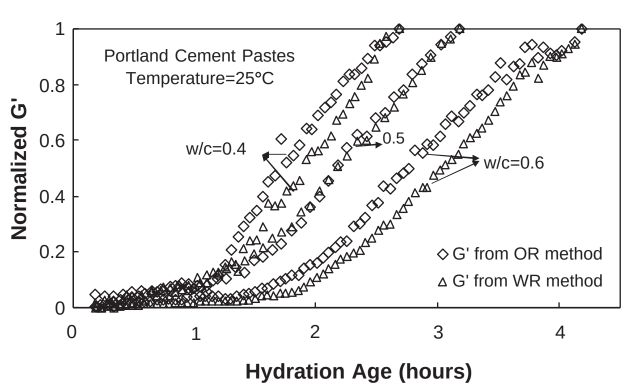

Fig. 10. Comparison of normalized storage moduli from WR- and OR-methods.

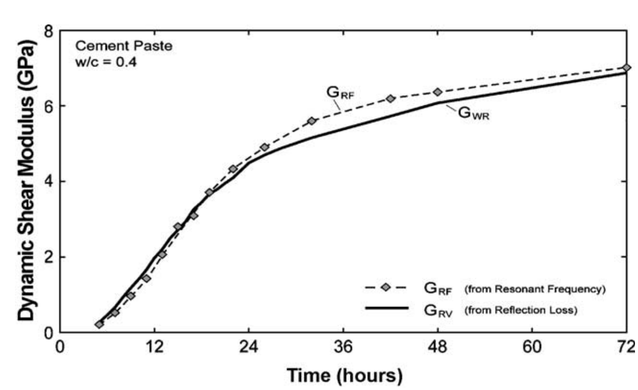

Fig. 11. Comparison of shear modulus obtained with WR- and RF-methods.

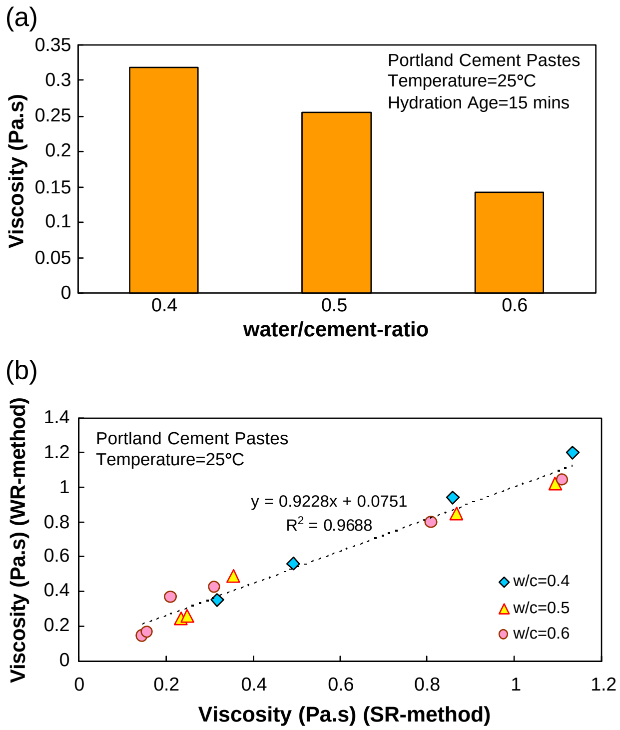

Fig. 12. Comparison of the viscosity through two methods.

for the viscosity values measured on pastes with different w/c ratios at different ages. This indicates that the WR-method and SR-method yield very similar information about the viscosity of the tested cement pastes. Based on these results it can be concluded that the wave reflection technique provides reliable information about the viscous properties of fresh cement pastes.

The authors emphasize that the storage modulus and the viscosity determined with the WR-method should be regarded as a function of the frequency of the ultrasonic shear waves that are used for the measurements. By using different frequencies, the absolute values of storage modulus and viscosity will be affected. However, the general trend of the measured parameters can be considered to remain the same.

5. Conclusions

1. Based on the theory of shear wave propagation in elastic and viscoelastic media, the wave reflection technique can be used to monitor the viscoelastic properties of cement pastes at very early ages. By considering the wave reflection coefficient and the phase shift between the incident and reflected waves, the storage shear modulus and the viscosity of fresh cement paste can be calculated.
2. The storage moduli calculated from the wave reflection measurements exhibit similar trends as the moduli values measured with the oscillatory rheology method. This shows that the wave reflection method has the ability to reflect the evolution of solid phases in the microstructure of cement paste. This finding is validated by the good agreement between the dynamic shear moduli of cement paste measured with the wave reflection method and the torsional resonant frequency method.
3. The wave reflection measurements were successfully used to qualitatively observe the influence of the water–cement ratio on the viscosity of fresh cement paste. At a given hydration age, the viscosity increases with the decrease of the water/cement ratio. At a given water/cement ratio, the viscosity increases with increasing hydration age. The wave reflection technique can reproduce these trends correctly. The comparison of viscosity values measured with the wave reflection method and the step rheometric method has shown that both methods yield results that follow very similar trends. Based on this finding, the wave reflection method can be regard as an efficient tool to monitor the viscous properties of cementitious materials at very early age.

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Appendix A. Effect of the applied shear strain and frequency on the material behavior in OR-measurement

Strain sweep and frequency sweep procedures are used to define the LVER of the investigated Portland cement pastes. The amplitude of the oscillating strain was changed from 3.87×10^{-5} to 100 during the strain sweep test. The effect of the amplitude of oscillating strain on the material behavior is shown in Fig. A1. For the paste with w/c = 0.5, the phase lag between the strain and the stress equals to 9.99° when $\gamma_0 = 0.0004$, and it increases to 77.6° when γ_0 equals to 1.064. This shows that the cement paste exhibits a more liquid behavior at higher strains and becomes more flowable during the strain sweep.

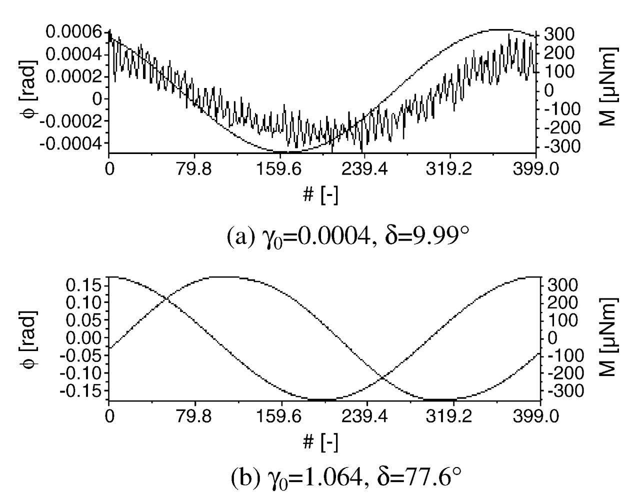

Fig. A1. Changing of phase lag during strain sweep (f = 1 Hz, w/c = 0.5).

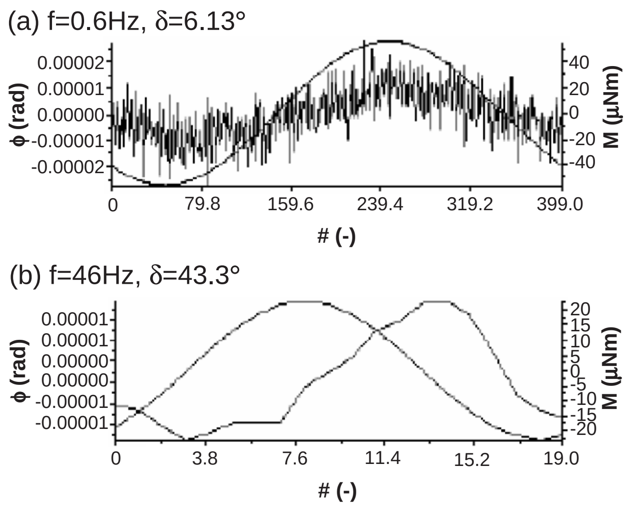

Fig. A2. Changing of phase lag during frequency sweep (γ_0=0.0001, w/c=0.5).

The same effect can be observed when the frequency increases from a low to a high value during the frequency sweep test as shown in Fig. A2. The applied shear strain was fixed on a level of 1×10^{-4} during this test. The measured phase lag increased from 6.13° to 43.3° when the applied frequency increased from 0.6 Hz to 46 Hz. The material exhibits more liquid behavior at high frequencies even when the applied shear strain is on a low level. This proves again that the amplitude and the frequency of the oscillating strain are two important factors, which affect the material behavior.

The critical amplitudes of the oscillating strains (γ_{0cr}) were determined for cement pastes with water/cement ratios equal to 0.4, 0.5 and 0.6 via the strain sweep test. The storage modulus (G') was measured during the test. With cement paste with w/c=0.5 as an example, the development of the storage modulus is plotted in Fig. A3. In order to determine the critical strain, the changing rate of the storage modulus with respect to the strain amplitude was calculated. The strain value at which the modulus starts to decrease by at least 10% is defined as the critical strain. For each paste, tests were repeated three times and the average values of these three measurements were used. Similarly, the development of the storage modulus during frequency sweep is shown in Fig. A4. The changing rates of the modulus with respect to applied frequency were calculated. The frequency at which the modulus starts to decrease by more than 10% is defined as the critical frequency. Again, the values of the critical frequencies for three cement pastes were determined from the average values of three measurements.

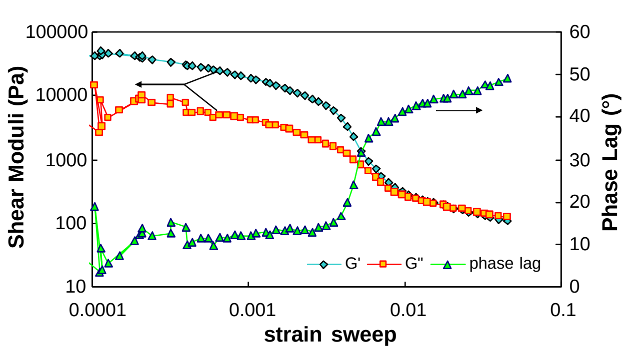

Fig. A3. Shear moduli vs. strain sweep (w/c=0.5, T=25 °C).

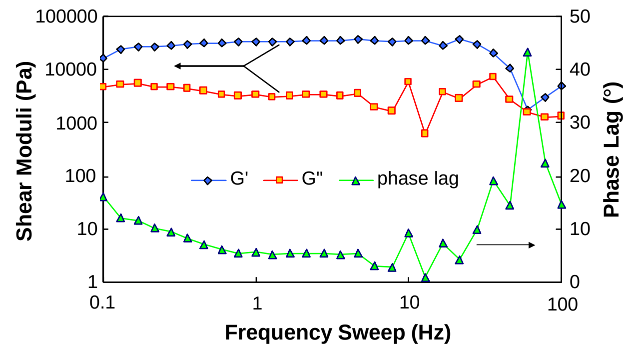

Fig. A4. Shear moduli vs. frequency sweep (w/c=0.5, T=25 °C).

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