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Dynamic mode rheology of cement and tricalcium silicate pastes from mixing to setting

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Abstract

Dynamic mode rheometry was used to study the evolution of the structure of cement and pure tricalcium silicate pastes from mixing up to setting and even after setting, together with the nature of the forces responsible for the mechanical properties of the pastes. A special mixer-type tool was used to study rheology during the very first minutes following the end of mixing, which are out of reach with classical tools. Both kinds of pastes have the same behavior. It was found that the main evolution of the structure of the pastes occurs during the very first minutes following the end of mixing, while there is no change in interparticular forces up to setting and even a few hours later. Setting, as defined by the Vicat needle, is not related to any particular change of the nature of the forces or structural transition within the paste. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Rheology; Bond strength; Ca_3SiO_5; Cement paste

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1. Introduction

The evolution of the rheological properties of cement pastes up to setting has been the subject of numerous studies but most of them were made in shear mode, giving information related to practically interesting problems such as workability [1,2]. However, such studies do not allow to obtain information concerning more fundamental phenomena, such as the evolution of the structure of the paste and of the forces responsible of its mechanical properties. Dynamic mode rheology has also been used [3–12] to study the mechanical properties of cement pastes from mixing up to setting. The ability to realize nondestructive measurements in the linear viscoelastic domain (LVD) is especially interesting and it provides useful information concerning structure or forces acting inside the paste. Yet, in most of the published literature, it is either impossible to determine whether the measurements were made within the LVD or clear from the figures that the strain used was above the critical strain. Since dynamic mode rheology results can be interpreted only within this linear domain, it is very difficult to conclude about most of these results. This problem has already been stressed by Schultz and Struble [5].

The present study is therefore devoted to dynamic mode rheology of cement and tricalcium silicate pastes. By using two different measurement tools, it has been possible to follow the evolution of the properties of these pastes from the first minute after the end of mixing to after setting.

2. Materials and methods

2.1. Materials

The two products used during this study were a silica-rich Portland cement and pure tricalcium silicate, both provided by Lafarge LCR (L'Isle d'Abeau). The composition of the cement is detailed in Table 1. The tricalcium silicate had a mean diameter (volume) of 6.5 μm, with 90% of the particles smaller than 13.7 μm.

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Table 1
Chemical composition of clinker (mass percent) from X-ray analyses

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SO_3
66.48	22.91	3.24	2.20	0.83	0.19	0.12	2.90

2.2. Methods

We will briefly outline the main features of dynamic mode rheometry. Detailed descriptions can be found in many textbooks [13–15]. In our study, the measurements were made with a controlled strain rheometer (RDA II Rheometric Scientific, USA). In this case, the sample is submitted to a sinusoidal strain, $\gamma(t) = \gamma_0 \cos(\omega t)$, and the resulting stress is recorded: $\tau = \tau_0 \cos(\omega t + \delta)$. The complex modulus of the material studied is $G^* = \tau/\gamma$. This complex number can be written as $G^* = G' + iG''$, where G' is the storage modulus and G'' is the loss or viscous modulus. The limiting cases for the behavior of a material are:

- Hookean solid: stress and strain are in phase: $\tau = G\gamma$, i.e., $G^* = G' = G$ and $G'' = 0$.
- Newtonian liquid: stress and strain rate are in phase, $\tau = \eta\gamma$, i.e., $G^* = iG'' = i\omega\eta$ and G'.

A real material has a viscoelastic behavior, G' and G'' are finite. The material can exhibit a solid-like behavior, with $G' \gg G''$, or a liquid-like one, with $G' \ll G''$ (in low frequency range).

It must be noted that the sample is in fact submitted to a sinusoidal angular displacement, and that the resulting torque is measured. The classical rheological parameters (strain, stress, G^*, G', G'' ...) are calculated from these values and the geometrical characteristics of the measurement tool.

Two different measurement tools were used (Fig. 1): a classic parallel plate geometry, and a mixer-type tool. The former has been modified in order to keep the sample in water-saturated air. The surface of the plates has also been roughened in order to avoid wall slippage [16]. The sample is a disk of paste, with a diameter of 8 mm and a thickness of 2 mm. With these dimensions and the characteristics of the rheometer, the lowest strain possible is 0.01% (10^{-4}). For the measurements made with this geometry, the paste was prepared by mixing the powder (cement or tricalcium silicate) and water by hand in a beaker, then transferred to the measurement tool. This results in a delay (about 2 min) between the end of mixing and the beginning of the dynamic mode measurement. Moreover, despite the care taken, additional stress can be added to the sample during this transfer, in particular, during the gap adjustment. In such concentrated systems, it is well known that stresses are very long to relax. The measurements would then not be made on the paste in the state it has reached immediately after mixing.

The second tool used is a mixer-type geometry, which consists of a helical ribbon in a cylindrical bowl. The ribbon has an inner diameter of 10 mm and an outer diameter of 18 mm. Its height is 15 mm, and its width is 1 mm.

Another type of nonconventional geometry, in this case, an interrupted impeller, was used by Banfill and colleagues [17–19] to study cement pastes under continuous shear. Their results show that this alternative geometry can yield results equivalent to those obtained with a classical geometry, with the advantage of being much less sensitive to segregation. The purpose of the present study is quite different, since it is limited to dynamic mode rheometry, on paste whose liquid-to-solid ratio has been chosen to ensure that no segregation takes place.

With this geometry, the mixing and the measurements in dynamic mode can be done with the same tool, without any transfer. It thus suppresses the problems of delay and additional supplied stress mentioned above. The water was placed in the bowl and the powder (cement or tricalcium silicate) poured in about 30 s, while the bowl was turning at a constant rate. The rotation was maintained for a total duration of 2 min. At this time, the torque recorded had reached a constant value. The measurements in dynamic mode where started at once.

It has been shown on several different types of material that this geometry allows to obtain the same rheological information or signature than conventional parallel plate geometry [20–22]. Recent literature is available that gives the procedure in order to transform the equivalent (or relative) quantities into absolute quantities. This procedure is based on a Couette analogy and is described elsewhere [23]. Yet, at the time when this study was realized, the exact values of the conversion factors were not available. This is why the results will be reported in terms of equivalent stress, equivalent strain, equivalent moduli, even if the symbols used where those of classical stress, strain, and moduli. The

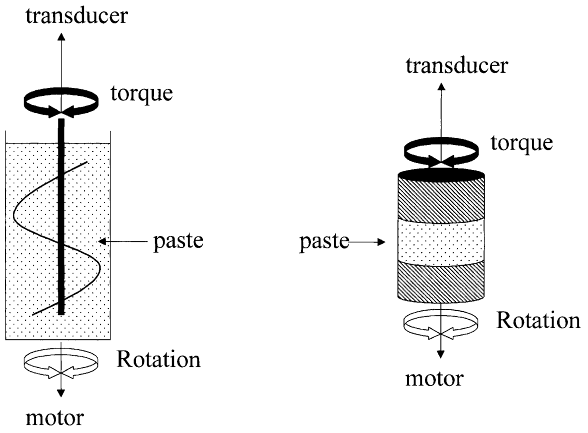

Fig. 1. Tools used for dynamic mode rheometry. Parallel plate (right) and mixer-type tool (left). Both geometries were used with the same rheometer, i.e., same motor and transducer. The amount of cement or tricalcium silicate used is about 2 g with parallel plates and 25 g with the mixer-type tool.

comparison between the helical ribbon and the parallel plates is presented in Fig. 2. The signatures obtained by the two tools are equivalent: the strain sweep show an LVD with a critical strain close to the limit of the rheometer used, and the frequency sweep show similar evolutions of *G*′ and *G*″ (or equivalent *G*′ and *G*″) with frequency. We can thus use the results of either tool to study the evolution of the structure of the paste, except during the very first minutes

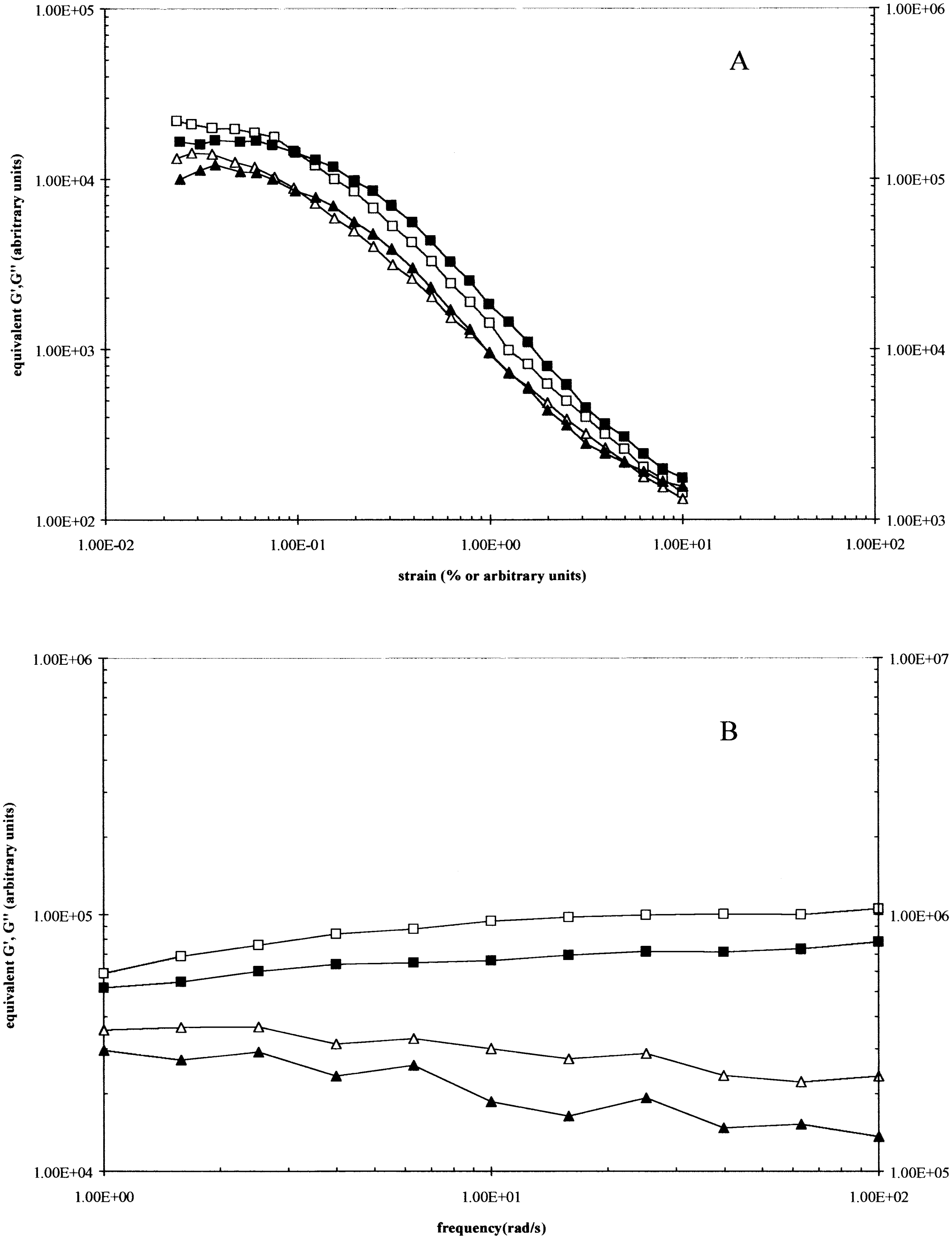

Fig. 2. Comparison between mixer-type tool and parallel plates for strain sweep (A) and frequency sweep (B). The sample was in each case a paste of pure clinker, w/c = 0.35, or the strain sweep, the frequency was 5 rad/s. The measurements were made between 7 and 11 min after the end of mixing. Black symbols: parallel plates, hollow symbols: mixer-type tool. Squares: *G*′ or equivalent *G*′ (see text). Triangles: *G*″ or equivalent *G*″ (see text).

following the end of mixing, where only the mixer-type tool can be used.

The liquid-to-solid ratio (or water-to-cement: w/c) used was chosen in order to ensure good mixing and easy placement in the measurement tool when the parallel plates were used. The value of w/c is thus different for the two geometries and for the two materials. It was limited to a small range in each case: lower w/c result in poor mixing and/or problems while placing the sample in the measurement tool, whereas higher w/c result in sedimentation or samples too liquid to be placed easily within the parallel plates. All the measurements were made at 25°C.

Several different tests are used in dynamic mode rheology. The first of them is a strain sweep. The sample is submitted to an increasing strain. For small strains, the moduli are independent of the strain. When the strain exceeds a critical value (critical strain), the moduli decreases as the strain increases. This is the end of the LVD of the material. Dynamic mode rheometry results can be interpreted only within this linear domain. When the applied strain exceeds the critical strain, the structure of the material (that may correspond to well-defined interparticle distances [24]) is destroyed. This test is thus needed in order to determine the conditions under which the dynamic mode measurements can be done and are nondestructive.

Another kind of test is the frequency sweep. The sample is submitted to a strain smaller than the critical strain determined by the previous test, with an increasing or decreasing frequency. This test provides information about the structure of the material through its mechanical spectrum. In the case of evolving structure, the kinetics of rheological evolution has to be relatively slow with respect to the experimental time needed for a mechanical spectrum determination t_{exp}. If F is defined as an appropriate rheological function to be recorded, the mutation number [25] defined by $N_{\mathrm{mu}}=(t_{\mathrm{exp}}/F)(\partial F/\partial t)$ has to be not more than a few percent.

This raises difficulties in the case of fast reactive systems, such as cement pastes. The duration of the measurement of a single point is at least the period of the sinusoidal strain, which, if $\omega=1$ rad/s, is about 6 s. For lower frequencies, each reading can last 1 min or more. A complete frequency sweep, covering several decades in frequency with five or more points per decade, will then last several minutes. This is hardly usable with a material where changes occur very rapidly, which is the case of cement and C_3S pastes, especially during the first minutes after mixing, as it will be shown later. For that reason, the frequency sweeps were recorded at frequencies higher than 1 rad/s with the usual method. When needed (i.e., during the first minutes), the lower frequencies were reached with another kind of test, namely Fourier transform mechanical spectroscopy [26,27]. The use of this technique in the case of cement pastes is however limited, as it will be shown later.

The last kind of dynamic mode test is a time sweep: the sample is submitted to a strain with constant frequency, and a constant amplitude smaller than the critical strain. This enables to follow the evolution of the mechanical properties of the paste with time.

3. Results and discussion

All the tests made during this study (presented here or not) show that the general rheological behavior of the pastes is the same for C_3S and cement. By general behavior, we mean that we consider the shape of the evolutions of G' and G'' vs. time, strain, or frequency rather than the absolute values of these parameters. These evolutions carry information about the structure of the pastes or the nature of the forces (see below). The w/c ratio has no influence on this general behavior either, at least within the range studied. We thus believe that the results of this study are relevant to the evolution of Portland cement or tricalcium silicate pastes from mixing up to setting and later.

3.1. Preliminary results: Linear Viscoelastic Domain

As mentioned above, the critical strain must be determined before any other dynamic mode rheometry experiment. The results obtained with strain sweeps and frequency on cement and tricalcium silicate pastes are reported in Figs. 3 and 4.

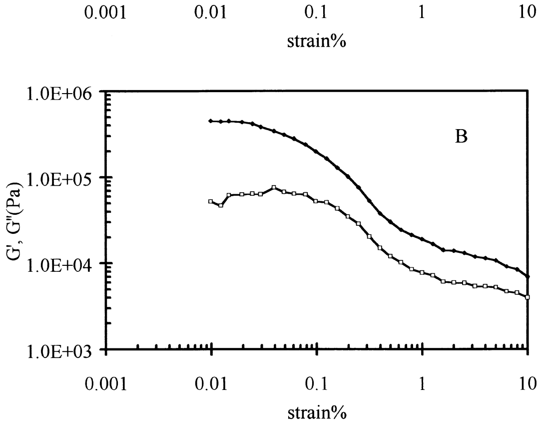

Fig. 3. Strain sweeps on cement (A) and C_3S (B) pastes. ■: G', △: G''. Liquid-to-solid ratios are 0.28 for cement and 0.39 for C_3S. The frequency is 1 rad/s. Both tests were carried out with the parallel plate geometry. The measurement was made 1 h after mixing for the cement sample and 10 min for tricalcium silicate.

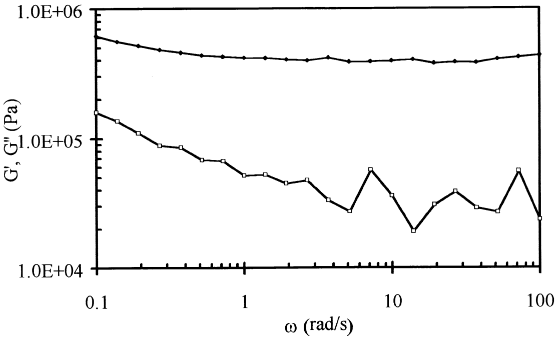

Fig. 4. Frequency sweep on tricalcium silicate. ■: G', △: G''. The strain was 0.02%. The points were recorded with decreasing frequency: the last reading (lowest frequency) was thus taken 7 min after the first one. The measurement was made 10 min after the end of mixing.

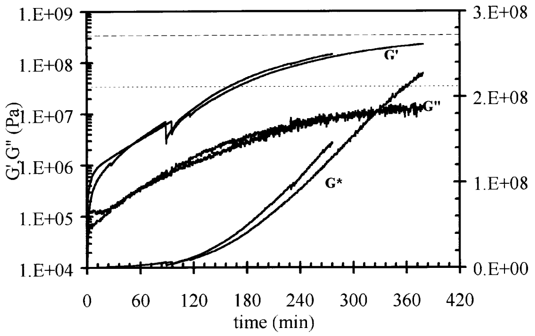

Fig. 5. Evolution of complex, storage, and loss modulus with time for two tricalcium silicate pastes (w/c = 0.39). Strain = 0.02%, frequency = 1 rad/s. The lower horizontal dotted line represents the end of the working zone, the upper dotted line represents the end of the transition zone (see text). Both dotted lines are on the logarithmic scale.

All the samples exhibit a limited linear viscoelastic domain (LVD). The end of the LVD occurs for a critical strain (γ_c) of about 0.03%. The same order of magnitude for the critical strain has been found by Schultz and Struble [5].

Dynamic mode measurements are thus possible, provided the strain is kept lower than 0.03%. This value is very low, only three times higher than the lowest strain that can be imposed on the sample with the rheometer and tools used (0.01% in our case). This probably explains most of the problems encountered during previous studies, where dynamic measurements were made above the critical strain (see Introduction).

3.2. Working zone

Once the measurement conditions have been fixed, it is possible to follow the evolution of the mechanical properties of the paste with nondestructive tests. It can be done as long as the stiffness of the sample is lower than the transducer's stiffness (Instrument compliance: 1.43×10^{-6} rad/g cm) [28]. With the parallel plate tool, the complex modulus corresponding to this limit can be calculated. For the time sweeps recorded at $\omega = 1$ rad/s, with the parallel plate tool (gap: 2 mm, diameter: 8 mm) the transition zone (corresponding to a sample stiffness equal to 10% of transducer stiffness) is reached when $G^* = 3.4 \times 10^7$ Pa. The end of the transition zone (corresponding to a sample stiffness equal to 100% of transducer stiffness) corresponds to $G^* = 3.4 \times 10^8$ Pa. The results obtained with this geometry must be taken with caution within the transition zone.

It is found that during the time period of interest, the sample remains in the working zone of the rheometer. Measurement can thus be made from mixing up to a certain time after setting in our case. This is shown on Figs. 5 and 6. The rate of the evolution of G' and G'' vs. time seems to decrease 3 h after the beginning of the measurements, but it corresponds to the limit of the working zone. At this time, the rheometer can no longer take into account the torsion of the transducer. The actual strain imposed on the sample is then lower than the strain selected, but this decrease is not corrected by the rheometer. This results in an apparent modulus lower than the actual value. The change in the evolution rate may therefore not be linked to changes in the sample properties, but in changes in the measurement conditions.

From a chemical point of view, the hydration reaction is slowing down around this period of time, which could lead to a lower rate of modulus evolution. It can be seen on Fig. 6 that the sample enters the transition zone shortly before the heat flux reaches a maximum, i.e., shortly before the reaction slows down. The apparent decrease in the rate of evolution of G^* vs. time is clear on the longest experiment in Fig. 5. Yet, even if the moduli were increasing at a constant rate, the results obtained outside the working zone of the rheometer would anyway show a slowing down of the evolution. Thus, it is not possible to link the change observed on the time sweeps to any change within the paste.

It can be seen that the setting time, defined by the Vicat needle, lies within the working zone defined earlier. It is also found that at the working zone limit, the degree of hydration, which can be calculated from the heat flux evolution, remains very low, around 1%.

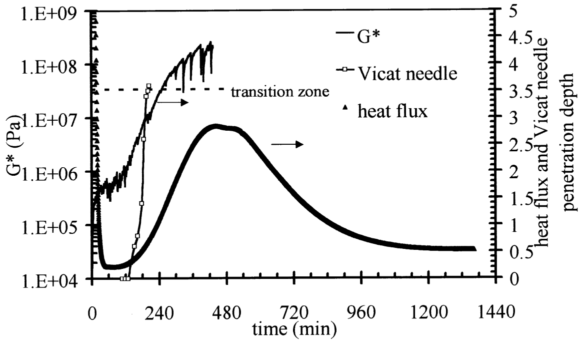

Fig. 6. Evolution of complex modulus, heat flux, and Vicat needle penetration depth for a cement paste (w/c = 0.28). Three samples of the same paste were used. Rheological properties were recorded with the parallel plate tool (strain = 0.02%, frequency = 1 rad/s). The heat flux was recorded with a conduction calorimeter (Setaram, Tian–Calvet-type). The transition zone is defined in the text and in Fig. 5.

For the rest of this study, all the measurements considered were made within the working zone.

It must be noted that Schultz and Struble [5] observed value of G' and G'' about 10 times lower than the results of the present study. Yet, it is clear that the type of product, the w/c ratio, and the time after mixing at which the measurement is performed have a major effect on the value of these parameters. For instance, we find rather similar values of modulus for the tricalcium silicate paste at w/c = 0.39 and for cement at w/c = 0.28 In their study, Schultz and Struble [5] observed also a decrease of G' by more than 35% when the w/c ratio was increased from 0.40 to 0.50. We consider therefore that the difference in absolute value between these two study has no major significance.

3.3. Structure

The different rheological tests provide information about the structure of the paste [24,29,30]. In this domain, it is the general trend of the evolution of G' and G'' vs. time, strain, or frequency that are most relevant. The results obtained with the mixer-type tool, though not in fundamental units, can therefore be used in the same way as the ones obtained with the parallel plate geometry.

Ten minutes after mixing up to setting, all the tests are characteristic of a structured material: the strain sweeps (Figs. 3, 8, and 9) show an LVD with a very small critical strain (0.03%), the frequency sweeps (Figs. 4 and 7) show that G' and G'' have parallel evolution vs. frequency, and the time sweep (Fig. 5) shows that G' is about 10 times higher than G'' during the entire measurement. The only evolution is the increase in moduli. Thus, it seems that there is no major change in the structure of the paste during this time period.

The effect of the strain sweeps on the sample is shown in the lower part of Fig. 8: strain above the critical one destroys the structure of the paste, resulting in a decrease in modulus. By comparing Figs. 5 and 8, and it can be seen that the structure is restored rapidly: 1 h after the strain sweep, the moduli have almost reached the values they would have reached without strain sweeps, i.e., without destruction of the structure. The strain sweeps performed every hour (Fig. 8) are similar to the strain sweep performed 2 h and 30 min after mixing without external modification of the sample (Fig. 9).

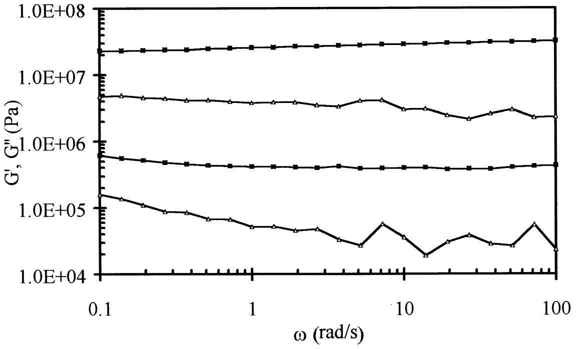

Fig. 7. Frequency sweeps on a tricalcium silicate paste at w/c = 0.39. Parallel plates: strain = 0.02%. ■: G', △: G''. The readings were taken by decreasing frequency. The lower spectrum was obtained 10 min after the end of mixing, the upper one 2 h and 25 min after the end of mixing. At this time, the set defined by the Vicat needle has already occurred.

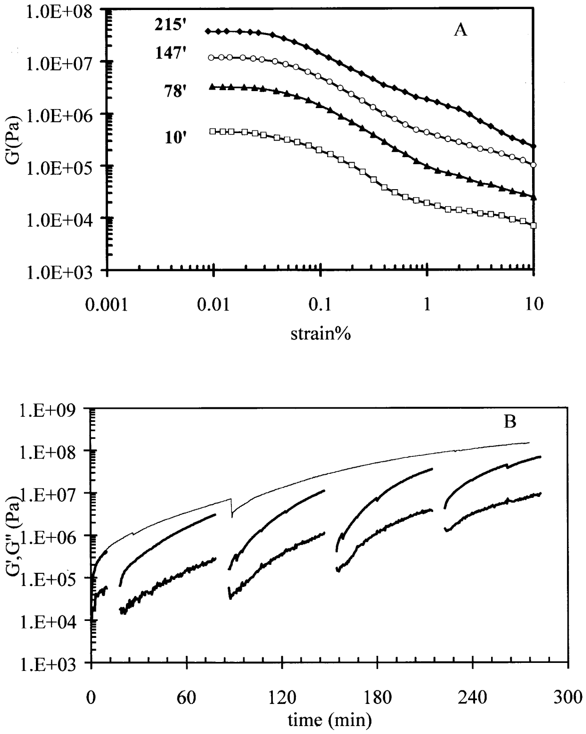

Fig. 8. (A) Strain sweeps on tricalcium silicate paste at w/c = 0.39 (G' only). Parallel plates: frequency = 1 rad/s. ■: G', △:G''. (B) Time sweeps conducted between the strain sweeps (strain = 0.02%, frequency = 1 rad/s). The continuous line represents the elastic modulus (G') of one of the time sweeps shown in Fig. 4.

As shown in Figs. 5 and 10, the main evolution seems to occur during the first minutes after the end of mixing: there is a sharp increase in G' and G'' during the very first minutes, together with an evolution of the ratio G'/G''. This evolution is obvious on a logarithmic scale, which is the most relevant choice to follow the evolution of moduli that are increasing by four orders of magnitude during the test (Fig. 5). As mentioned above, the first 2 min following the end of mixing can be studied only with the mixer-type tool. Later tests show the same kind of results, i.e., parallel evolution of G' and G'' vs. frequency, with G' about 10 times higher than G''.

The most appropriate test to study the evolution of the structure of the sample is the frequency sweep. Since the evolution of the rheological properties of the sample is rapid in this period (Fig. 10), the duration of a single sweep cannot exceed 1 min. For this reason, the measurements at frequencies higher than 2 rad/s were performed by the classical method, while the two points corresponding to lower frequencies were recorded with the multiwave test of the RDA II. This test is a Fourier transform mechanical

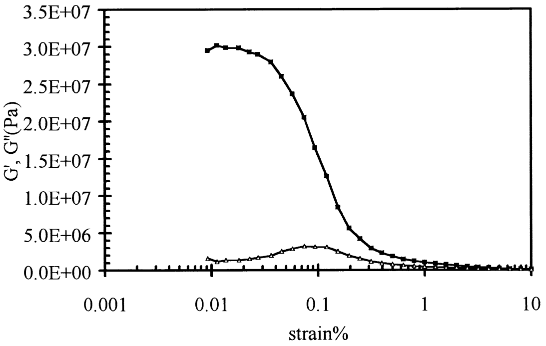

Fig. 9. Strain sweep on tricalcium silicate paste at w/c = 0.39. Parallel plates: frequency = 1 rad/s. ■: G', △: G''. The measurement was made 2 h and 30 min after the end of mixing. Between mixing and the strain sweep, the sample was submitted to a time sweep (not shown) with strain = 0.02% and frequency = 1 rad/s, i.e., within the LVD. This time sweep was thus nondestructive.

spectroscopy. In this test, the strain is the sum of several sinusoidal strains. For technical reasons, the frequencies must be in the form $\omega_i = 2^n\omega_0$. It is possible then to make measurements at up to eight frequencies, in the time needed to perform the measurement at the lowest frequency, which results in an appreciable gain of time. Another requirement is that the sum of the strains used at all frequencies must be smaller than the critical strain of the material tested. In the case of cement pastes, with a very small critical strain, this is the main limit of this method. It is limited to two modes only, since the sum of the strains used must be lower than the critical strain of the sample (here 0.03%) while every strain must be higher than the lowest command strain (here 0.01%). In order to achieve a suitable sensitivity, only two frequencies were used. The results of these measurements are presented on Fig. 11.

They show that both G' and G'' depend strongly on frequency during this time period. There is a cross-over between G' and G'' within the frequency range studied from 1 to 3 min after the end of mixing (no results are available for earlier period). Then, 4 min after mixing or later, the evolutions of G' and G'' vs. frequency are parallel, and both become quickly independent of frequency (Fig. 4). These tests evidence the fact that the sample is undergoing an important structural change during this period, from rather dispersed state to structured state. Its rheological behavior changes from slightly liquid-like ($G'' > G'$) to strongly solid-like ($G' > G''$). In this period of time, very shortly after the end of mixing, the parallel plate geometry cannot be used and all the results are obtained with the mixer-type tool.

The evolution of the structure of the paste is thus occurring during the first minutes after the end of mixing. Despite the very high solid concentration, the sample is initially in a dispersed state. It evolves spontaneously within a few minutes to a structured state, with the formation of an "infinite" aggregate (i.e., of the size of the sample under test), that is of a connected network of particles. Previous studies have already shown this fast coagulation of cement particles in dilute suspension [31,32]. It was found that this reversible coagulation of particles occurs in dilute as well as in concentrated suspensions (pastes). This structure was also detected by previous rheological studies, but no measurement was made while it was forming [5]. From the present results, it appears that it is established after mixing or restored after high strain shear very quickly, in a matter of minutes (see Figs. 10 and 11 for the evolution after mixing and Fig. 8 for the evolution after destruction of the structure by high strain shear).

During the next hours, and at least up to after setting (as defined by the Vicat test), there is no sign of any structural evolution within cement (or tricalcium silicate) paste.

3.4. Forces between particles

From the results of the strain sweeps, it is possible to make some inferences concerning the characteristics of the forces between particles from mixing to shortly after setting. These attractive forces are responsible for the structural evolution of the cement paste during the first minutes after the end of mixing, discussed above. The repulsive forces between tricalcium silicate or clinker particles have been identified as electrostatic forces linked to electrical double layer around particles. In the medium considered here

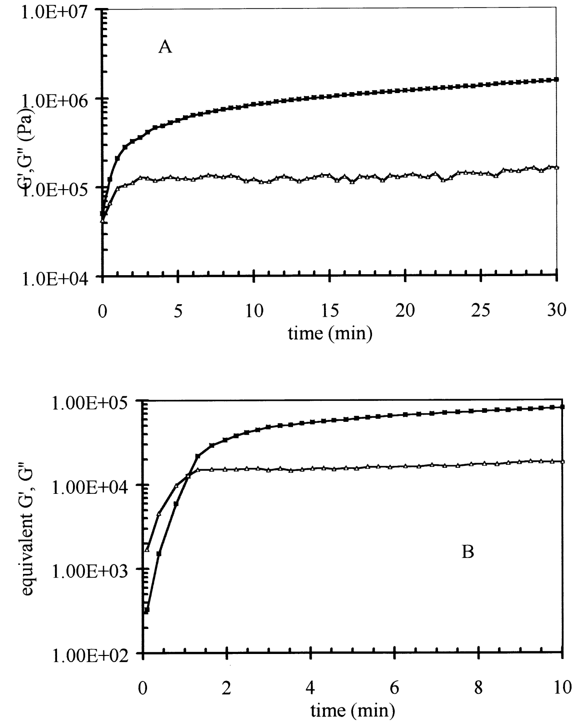

Fig. 10. Origin of time = beginning of the measurement. (A) Sweep on a tricalcium silicate paste, w/c = 0.39. Parallel plates: strain = 0.02%. The measurement started 150 s after the end of mixing. This is the first part of the time sweep represented in Fig. 5. (B) Sweep on a cement paste, w/c = 0.48. Mixer-type tool: The measurements started 15 s after the end of mixing. The (equivalent) strain is within the LVD. ■: equivalent storage modulus, △: equivalent loss modulus. Frequency = 1 rad/s for both tests.

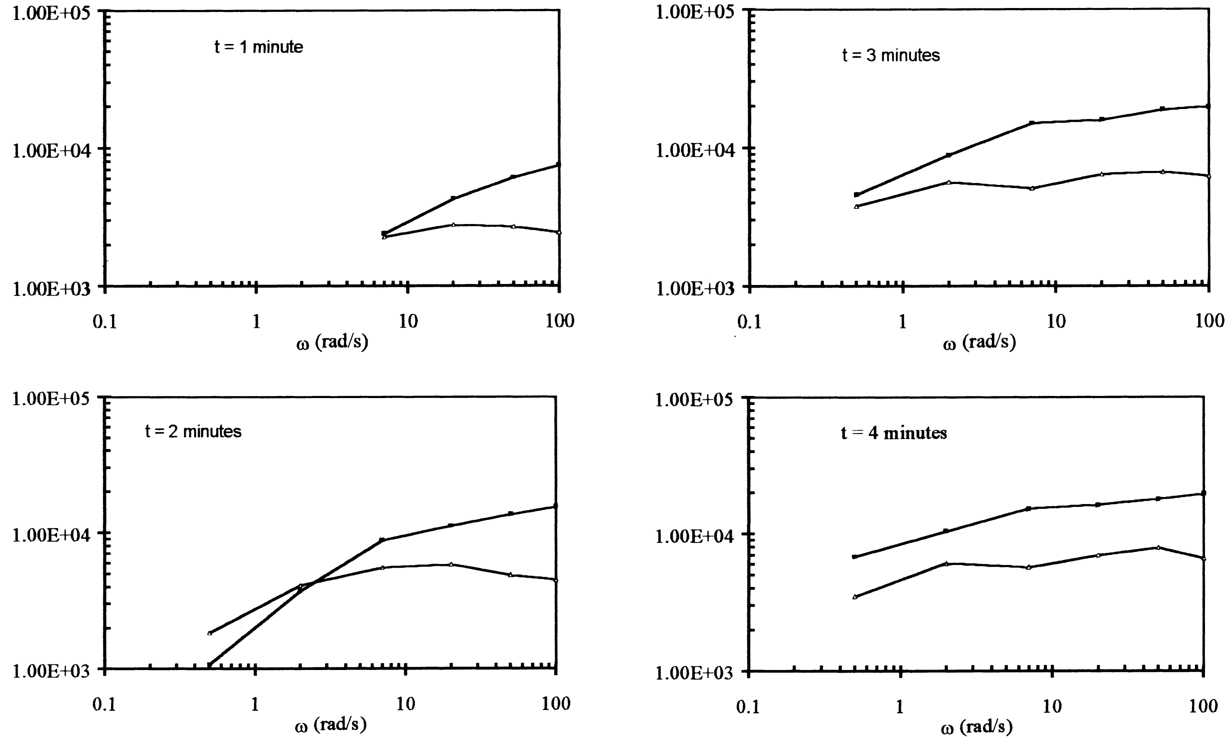

Fig. 11. Series of frequency sweeps on a cement paste, w/c = 0.37. Mixer-type tool: The (equivalent) strain is within the LVD. ■: equivalent storage modulus, △: equivalent loss modulus. The readings at 0.5 and 2 rad/s were taken with the multiwave test (see text).

(electrolytic solution of very high ionic strength, about 5×10^{-2}·mol kg^{-1} for tricalcium paste and 5×10^{-1}·mol mol kg^{-1} for a cement with 0.7% of alkali, in a paste at w/c = 0.3), these forces are smaller than attractive forces, resulting in coagulation of particles [33]. There is no change in the shape of the strain sweeps during this period: there is an LVD, with a very low critical strain (0.03%). The forces responsible for the mechanical properties of the paste are thus highly dependent of the interparticle distance. Very small critical strains are associated to strong interparticle forces [4,34].

The paste shows some kind of cohesion immediately after mixing and, as mentioned above, the rheological characteristics are the same from 10 min after mixing to after setting. From a chemical point of view, the degree of hydration of the material 10 min after mixing is negligible, especially in the case of pure tricalcium silicate pastes. There are discrepancies between different studies about the length of hydration after which a C_3S surface gets covered by C-S-H: less than 10 min according to Sujata and Jennings [35], 1 h according to Gauffinet et al. [36]. Anyway, in the experiments presented here, these surfaces are either C_3S then C-S-H or C-S-H. The mechanical properties observed are therefore due to forces between surfaces of tricalcium silicate then C-S-H, since no other solid phase is present in the system.

The critical strain remains constant from 10 min after mixing to after setting. Its value can be compared to the strain at rupture observed on aged concrete, about 10^{-4} [37]. The measurement methods are different, but the order of magnitude of the maximum strain that the cement paste (fresh or hardened) can withstand, remains the same.

It seems thus that the same type of forces is responsible of the cohesion of cement or tricalcium silicate pastes during this period. The increase in modulus (and cohesion) is then due to the increase in facing surfaces, following the formation of C-S-H, at the contact points between particles, the specific surface of C-S-H being very high [38]. It has already been noted that the surfaces of C_3S and C-S-H have similar electrokinetic properties [33].

The increase in storage modulus has previously been associated to the formation of hydrates by Lei and Struble [39]. The present study gives detail about the mechanism of this evolution: the results obtained on tricalcium silicate pastes show that the hydrates responsible for this evolution are C-S-H, since none of the other products mentioned in this reference forms during the first hours of reaction. These authors associated setting, as defined by the Vicat needle, to a fundamental difference in the mechanism of the suspension, resulting in a sudden acceleration in the rate of increase of the moduli. On the contrary, we consider that our results show that no particular evolution occurs at the time of setting. The linear scale is not appropriate to represent the evolution of modulus during several hours, with an increase of four orders of magnitude, since it gives a much higher weight to the later evolution, and hides the evolution during the first minute. The setting time of cement paste is a technological parameter, defined according to standards. Any change in these standards (for instance, choosing the Gillmore needle instead of the Vicat apparatus) will lead to changes in the setting time of a given paste. Moreover, it is very difficult to define the setting time of concrete, and a criterion based on compressive strength (high enough to allow removal of formworks) could be used as well [40]. The possibility that setting time depends on the choice of the standard used is incompatible with the assumption that it is linked to a major transition in the mechanisms responsible of the rheological properties of the paste.

These results on the nature of attractive forces in fresh cement or C_3S pastes can be compared to previous studies on the nature of forces on hardened concrete. The importance of interparticle forces ("physical" forces, by opposition to "chemical" forces implying some kind of chemical bonds) was stressed by Czernin [41] on sand particles. According to Powers [42], physical forces (between surfaces) are responsible for the main part of the strength of cement, but chemical forces contribute to some extend. But the results of Sereda and Soroka [43] on compacts of hydrated cement show that the strength of hardened cement paste is due to physical forces and that chemical forces are negligible.

It could seem surprising that the modulus of the materials increases by three to four orders of magnitude within a few hours without changes in the nature of the forces. Yet, Rueb and Zukoski [34] have shown that the modulus depends strongly on the geometry of the aggregates of particles, and very little on the strength of the interparticle bonds, and that it is possible to observe an increase in modulus at almost constant interparticle forces.

Dynamic mode rheometry appears to be a valuable tool for the nondestructive study of the evolution of the structure of cement pastes and of the forces between particles from mixing to setting.

4. Conclusion

The fast evolution of the paste during the first hours following mixing causes specific problems that must be taken into account in a rheological study, especially the time gap between the end of mixing and the beginning of measurements with classical tools, and the ratio between the stiffness of the sample and the stiffness of the transducer used for the measurements.

The evolution of cement and pure tricalcium silicate pastes are similar, and the liquid-to-solid ratio has no effect on the general trends of these evolutions within the range studied.

The main evolution of the structure of the paste occurs within a few minutes after the end of mixing. This period of time is beyond the possibilities of classical rheological tools such as parallel plate. In this study, a mixer-type tool was used. This nonconventional tool has proved extremely valuable to study the early evolution of the pastes. During the very first minutes after the end of mixing, the spontaneous coagulation of the particles, initially in a dispersed state despite the high solid concentration, leads to the formation of a structure within the paste. This structure does not change during the next hours, until at least after setting.

The critical strain of the pastes is very small (0.03%), which suggests that particles are held together by strong short-range interparticle forces. These attractive forces, which overcome the repulsive forces between particles in cement pastes, are physical interparticle forces. The same forces are responsible for the mechanical properties of the pastes from mixing to after setting, and even later.

Setting, as defined by the Vicat needle, does not correspond to changes in structure or forces.

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