A MICROMECHANIC MODEL FOR CHARACTERIZATION OF CEMENT PASTE AT EARLY AGE VALIDATED WITH EXPERIMENTS

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Abstract
The gradual evolution of the material properties of a cement-based material, i.e. the stiffness of cement paste, is the result of the continuous change of the microstructure with the progress of the hydration process. Based on an existing micromechanical model for the simulation of the shear and elastic modulus of cement paste, this paper is orientated to experimentally determine the structure parameter $k$ in this model. The dynamic elastic modulus, shear modulus, the degree of hydration and the ultrasonic pulse velocity were determined for cement pastes with water/cement ratios of 0.50 and 0.60. The structure parameter $k$ was determined and applied to the micromechanical model, where the evolution of the modulus of elasticity is predicted and compared with experimental results.

1 Introduction

The gradual evolution of the material properties of a cement-based material, i.e. the shear modulus and elastic modulus of cement paste, is the result of the continuous change of the microstructure with the progress of the hydration process. The physical properties of concrete can be detected by, for example the speed of an ultrasonic pulse propagating through the concrete [1-6]. Researchers have shown that the ultrasonic pulse velocity is controlled by the volume and the connectivity of the solid phase [7]. In a previous study [8], a micromechanical model based on the percolation theory was presented. The mechanical parameters, such as elastic modulus and shear modulus were shown to be a function of the percolation threshold of solid phase, the total volume of solid phase and the ultrasonic pulse velocity. With the use of the numerical microstructural model it was demonstrated how the evolution of the elastic modulus could be formulated as a function of the microstructural parameters, which could be monitored with ultrasonic pulse velocity measurements. The preliminary simulation result was compared with experiments as shown in Figure 1. It was found that the discrepancy of elastic modulus...
between simulated and experimental values is big. It can be assumed that this is caused by the overestimation of the structure parameter \( k \) in Eq. 1. This shows that an accurate determination of this structure parameter is important for the application of the model.

![Figure 1 Simulated elastic modulus of different cement](image)

According to Bergman and Kantor [9] the stiffness of a porous material can be expressed as a function of the volume fraction of the solid phase, \( p \), and the volume fraction of the solid phase at which the solid starts to become interconnected, \( p_c \), known as the percolation threshold. For example, the shear modulus \( G \) can be expressed as:

\[
G = k (p - p_c)^\tau
\]

where \( k \) (GPa) is the structure parameter to be determined from experiments and \( \tau \) is a constant. For a three dimensional matrix the exponent \( \tau \) has been found to vary between 1.53~1.75 [15]. In the absence of experiments, the structure parameter \( k \) was taken as 100 GPa. This is the main reason that causes the big discrepancy between simulated and experimental values of the elastic modulus in Figure 1[7].

The aim of this study is to experimentally determine the structure parameter \( k \) in Eq. 1. In order to do so, cement paste with a water/cement ratio of 0.50 and 0.60 were used. The dynamic shear modulus and elastic modulus were measured by the resonant frequency method according to ASTM-Standard C215. The degree of hydration was measured by thermogravimetric analysis (TGA). The microstructural parameters, such as percolation threshold of solid phase and total solid volume fraction were simulated by a cement hydration model, HYMOSTRUC3D. The experimental data are evaluated and the structure parameter is obtained. In order to validate \( k \), the longitudinal ultrasonic pulse
velocities were measured on the same samples. The micromechanical model for predicting the modulus of elasticity is applied. The predicted elasticity moduli are compared with experiments.

2 Theoretical Background

2.1 Microstructural simulation model
The development of the microstructure during cement hydration can be simulated by the numerical simulation model HYMOSTRUC3D [10]. In the HYMOSTRUC model [10, 11], the cement hydration is simulated on the basis of a “growth mechanism” with the particle size distribution, the chemical composition of cement, the water/cement ratio and the reaction temperature as important model parameters. The simulation starts from unhydrated cement particles distributed in a 3D representative volume. With the progress of the hydration process, cement particles and hydration products form a porous structure. By applying a serial section method associated with an overlap criterion, the total volume and the percolation threshold of the solid and pore phase can be determined explicitly [10]. Figure 2 shows the development of the solid phase and the percolation phenomena during cement hydration simulated by HYMOSTRUC3D model.

![Figure 2 The development of the microstructure and the percolation phenomena during cement hydration simulated by HYMOSTRUC3D model [8]](image)

2.2 Micromechanical model
As presented in a previous study [7], the evolution of the elastic modulus $E_{\text{pave}}$ (Eq. 2) can be modeled as a function of the ultrasonic pulse velocity measurement, the volume fraction and the percolation threshold of the solid phase.
In Eq. 2 the parameters $p$ and $p_c$, represent the volume fraction and the percolation threshold of the solid phase and can be calculated directly by the simulation model HYMOSTRUC3D. The density of the cement paste $\rho_{\text{paste}}$ can be measured experimentally. The parameter $\tau$ is a constant with the value of 1.35. The longitudinal ultrasonic pulse velocity $V_L$ can be calculated from:

$$ V_L = \sqrt{\frac{E_{\text{paste}}(1-\nu)}{\rho_{\text{paste}}(1+\nu)(1-2\nu)}} $$

where, $\nu$ is the Poisson’s ratio. As mentioned, in a sealed curing condition, a minor change of density of cement paste may occur because of a hydration-induced autogenous volume change. Compared to the changes in the modulus of elasticity with progress of the hydration process, the effect of hydration-induced changes in the density can be neglected. Derived from experiments, a density value of 1.792 g/cm$^3$ for the sample with w/c = 0.50 and 1.732 g/cm$^3$ for the sample with w/c = 0.60 will be used in the calculation.

According to elastic theory, the relation between shear modulus and elastic modulus is:

$$ \nu = \frac{E_{\text{paste}} - 1}{2G} . $$

By inserting Eq. 4 and Eq. 3 to Eq. 2, the elastic modulus can be calculated as function of ultrasonic pulse velocity and the change of the microstructure during cement hydration.

### 3 Materials and experimental method

#### 3.1 Materials

The dynamic moduli and the ultrasonic pulse velocity test series were performed for cement pastes with water/cement-ratios of 0.5 and 0.6 at an isothermal curing temperature of 25°C. Ordinary Type I Portland cement provided by Lafarge was used. The chemical compositions and constituents are listed in Table 1. The Blaine surface area is 365m$^2$/kg.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>C$_3$S</th>
<th>C$_2$S</th>
<th>C$_3$A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lafarge</td>
<td>20.4</td>
<td>65.3</td>
<td>4.8</td>
<td>2.8</td>
<td>68</td>
<td>-</td>
<td>8</td>
</tr>
</tbody>
</table>

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3.2 Experimental method

In this study, the degree of hydration was determined by thermogravimetric analysis (TGA). The calculation of the degree of hydration based on TGA measurements is described in detail in this proceeding [14]. The dynamic moduli measurements conducted by the resonant frequency method and ultrasonic pulse velocity measurements are described in the following sections.

3.2.1 Dynamic moduli measurements

The resonant frequency method was adopted to determine the dynamic moduli of the cement pastes. Samples of the size 50×75×230 mm were used. During the tests, one end of the sample was brought in contact with a contact type vibration generator and the other end was connected to a contact pick-up. Both the driver and the pick-up were connected to the E-meter, which in turn was connected to an oscilloscope (Figure 3). By changing the frequency of the driver force, the reaction of the specimen was recorded. The frequency of the driver force at which the specimen has the maximum reaction is defined as resonance frequency. By changing the location of the driver and pick-up, the resonance frequencies at longitudinal and torsional vibration modes can be determined. According to ASTM-Standard C215, dynamic Young’s and shear moduli can be calculated from Eq. 5 - 6 by measuring the resonance frequencies of the test specimens when vibrating in longitudinal and torsional modes, respectively.

\[
E = B \cdot W \cdot (n')^2 \tag{5}
\]

\[
G = D \cdot W \cdot (n'')^2 \tag{6}
\]

In these equations \( E \) and \( G \) are dynamic Young’s and shear moduli, \( B \) and \( D \) are factors accounting for the shape and the size of the specimen, \( W \) is the weight of the specimen, and \( n' \) and \( n'' \) are the measured longitudinal and torsional resonance frequencies, respectively.

![Figure 3 Experimental setup for dynamic moduli measurements](image-url)
3.2.2 Ultrasonic pulse velocity measurements
Details of the ultrasonic measurements are illustrated in Figure 4. The ultrasonic pulse velocity measurement is conducted using a C-4902 plus equipment produced by James Instruments Inc. The frequency of the transducer is 150 kHz. The accuracy in time is ±0.1us. The ultrasonic transducers are integrated in a 70×56×76 mm mold made of polymethyl methacrylate. The transducers are fixed by strong glue and coupled directly through a piece of plastic membrane stuck on the inner wall of the mold. The plastic mold was inserted into a water bath where the temperature was controlled by a cooling system with an accuracy of ΔT=±0.1°C. The ultrasonic pulse velocity was recorded manually every 10 minutes in the first 8 hours and 30 minute in the later stage.

Figure 4 Experimental testing system for monitoring UPV in cementitious materials

4 Results and discussions

4.1 Evolution of the dynamic moduli
The tests of the dynamic moduli were performed on three specimens and the mean values of the three readings were calculated. Computations of the dynamic E-modulus and G-modulus based on Eq. 5 and Eq. 6 are shown in Figure 5. Both dynamic stiffnesses (elastic modulus and shear modulus) show that for the samples with lower water/cement ratio, the evolution of the stiffness in the cement paste is much faster than in the sample with a higher water/cement ratio. Moreover, the final stiffness values of the samples with the low water/cement ratios are much higher than the samples with high water/cement ratios. This is in good agreement with the observation by Nagy [13] on dynamic E-modulus of young concrete determined by the same method.
The microstructural parameters including the total and the connected solid volume fraction and the percolation threshold of the solid phase are computed by the HYMOSTRUC3D model. In the simulation, the degree of hydration was calibrated by thermogravimetric measurements in order to guarantee the reliability of the simulation results. The hydration process and the microstructural development of a $100 \times 100 \times 100 \mu m^3$ cubic sample of cement paste was simulated with w/c-ratio 0.50 and 0.60 cured at 25°C. The minimum cement particle size of 1 $\mu m$ was used in the simulations. A 3D simulated structure with 0.25 $\mu m$ spacing and 400 serial sections was employed in the calculations.

The evolution of the total solid volume fraction and the connected solid volume fraction as a function of time and as a function of degree of hydration is shown in Figure 6a and Figure 6b. As it can be seen from Figure 6, the percolation threshold $p_c$ of the solid phase for cement pastes with a w/c-ratio of 0.50 and 0.60 are 0.38 and 0.41, respectively. This implies that at this solid volume fraction, for example when the solid volume reaches 0.38 for the sample with w/c = 0.50, there exists a path, which connects the solid phase from one side to another. The physical meaning of the percolation threshold of the solid phase in Figure 6 corresponds to the initiation of the setting process of the cement paste. This has been described in detail in [8] and is mentioned in this proceeding [14].
The structure parameter $k$ can be determined from Eq. 1. Regarding to the input in the formula $\tau$ is a constant; a value of 1.35 was used in the calculations. The microstructural parameters, i.e. volume fraction of the solid phase and the percolation threshold of solid phase calculated from the HYMOSTRUC3D model, were taken from Figure 6. The dynamic shear modulus $G$ of two different cement pastes obtained from experiments was shown in Figure 5.

Thus, $k$ can be calculated directly by inserting $G$ to Eq.1 (Figure 7a). It is observed from Figure 7a that the $k$ value is almost constant after 40 hours curing. The average $k$ value is 26.72 after 40 hours. This value is independent of the water/cement ratio and curing age. Moreover, the unique relationship between the total solid volume and $(p-p_c)^2$ is found as shown in Figure 7b. This also proves that the stiffness of cementitious materials is determined mainly by their volume of solid phase and its spatial arrangement of the materials.
4.4 Prediction of modulus of elasticity

In order to validate the structure parameter $k$, the elastic modulus was calculated from Eq. 2 and compared with experiments. In Eq. 2, the ultrasonic pulse velocity $V_l$ was examined for the same cement pastes with water/cement ratio of 0.5 and 0.60. The results, shown in Figure 5a, reveal a similar shape and trend for the two pastes. It is evident that at the same curing condition, mixtures with a higher water/cement ratio show lower values of the pulse velocity. This phenomenon can be explained by the difference in the amount of solid phase in the pastes with different water/cement ratio [7].

With the help of the total solid volume presented in Figure 6a, the percolation threshold of the solid phase presented in Figure 6b, the $k$ value presented in Figure 7a and the ultrasonic pulse velocity $V_l$ shown in Figure 8a, it is possible to predicted the modulus of elasticity with Eq. (2) as a function of the curing time. The latter representation allows comparison with the experimental results of dynamic elastic modulus as shown in Figure 8b. An excellent agreement can be found from the comparison between the experiments and the simulation by the micromechanical model. From the finding it can be inferred that the micromechanical model is sufficiently accurate for using it in the calculation procedure for predicting the modulus of elasticity in combination with the microstructural simulation and ultrasonic pulse velocity measurements.
Figure 8 Elastic modulus of different cement paste versus the degree of hydration (Eq. 5)

5 Conclusions

Through the combination of a non-destructive technique, i.e. ultrasonic pulse velocity measurement and numerical simulation, this paper has shown that the evolution of material properties i.e. elastic modulus could be related directly to the evolution of fundamental microstructural parameters. The coefficient $k$ was determined by experiments of shear modulus with the resonant frequency method, coupled with percolation theory. It was found that the coefficient $k$ is independent of water/cement ratio and curing age, especially in the later stage. It is shown that the evolution of the stiffness in the materials is determined mainly by the solid volume and the connectivity of the solids in the material. The micromechanical model using a corrected structure parameter $k$ is sufficiently accurate for predicting the modulus of elasticity.

6 References

3. Keating, J., Comparison of shear modulus and pulse velocity techniques to measure the build-up of structure in fresh cement pastes used in oil well cementing, Cement Concrete Research 19 (1989) 554-566.


