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Mechanical Properties of Alkali-Silica Reaction Gel Measured by Nanoindenter

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Abstract

The mechanical properties, particularly the elastic modulus and hardness of alkali-silica reaction (ASR) gel are measured at the microscopic scale by nanoindentation. The ASR gels are simulated in the laboratory by reacting amorphous silica (i.e., borosilicate glass) with different alkali hydroxide solutions. The measured elastic modulus of gel, formed by reacting borosilicate glass in sodium hydroxide solution was found to have a mean value of 2.96 GPa, while the gel formed from a combination of sodium hydroxide, potassium hydroxide, and calcium hydroxide solution has the mean modulus of 5.17 GPa. The results show that the presence of potassium and calcium alkalis increases the elastic modulus and hardness of the gel. A student's t-test performed on the results confirmed the statistical significance.

Keywords

Alkali-Silica Reaction, Mechanical Property, Nanoindentation

1. Introduction

Alkali-silica reaction (ASR) is the reaction between the hydroxyl ions present in the pore water of concrete and certain forms of silica which are present in some aggregates. The product of this reaction is a highly expandable gel which imbibes water and swells. If sufficient reaction takes place the pressure induced causes micro-cracking and also expansion of the surrounding concrete. The surface of the concrete does not expand to the same extent as the interior of the concrete, because, the surface is subjected to leaching of the alkalis required for the reaction. This causes tensile stresses to be created in the surface which can induce surface macro-cracks. The formation and orientation of both micro and macro-cracks are affected by restraint which also reduces expansion [1]. Thus, ASR in an engineering-scale is a mechanical process with a chemical origin [2].

Numerical models have been investigated to predict ASR damage, and elastic modulus of ASR gel are mainly involved in these models [3]-[9]. However, limited effort has been made to characterize the elastic properties of ASR gels, in relation to their molecular composition and nanostructure. Such information would greatly enhance the overall understanding of the mechanism of ASR damage. The elastic modulus of ASR gel is a fundamental parameter of intrinsic importance to their characterization and this study focuses on the same.

There has been considerable interest in the last two decades in the mechanical characterization of materials using depth-sensing indentation tests. Usually, the principal goal of such testing is to obtain values for elastic modulus and hardness of the specimen material from experimental readings of indenter load and depth of penetration. But other properties such as residual stress, fracture toughness, and viscoelastic behavior may also be measured. The indentation technique can be used on both brittle and ductile materials where conventional testing may result in premature specimen fracture. The forces involved are usually in the millinewton range and measured with a resolution of a few nanonewtons while the depths of penetration are in the order of nanometres, hence the term "Nanoindentation" [10].

In this study, the mechanical properties (i.e., elastic modulus and hardness) of ASR gels are measured using a nanoindenter. The ASR gels are simulated in the laboratory by reacting borosilicate glass slides with different alkali hydroxide solutions. Scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDS) was used to observe the morphology and chemical composition of the ASR gels.

2. Experiment

2.1. Materials and Sample Preparation

ASR gels were simulated in the laboratory by adding highly reactive borosilicate glass slides (a form of amorphous silica with chemical composition SiO_2: 81%, Na_2O: 4%, Al_2O_3: 2%, B_2O_3: 13%) [11]-[13] into beakers containing alkali hydroxide solutions. Two different alkali solutions were chosen to verify the properties of the gel varying with different alkali solutions. The first set of samples (glass slides) was placed in 1N NaOH (NH) solution, and the second set of samples was in 0.5N NH + 0.4N KOH (KH) + $Ca(OH)_2$ (CH) solution. The second set of the solutions was CH saturated in order to simulate the properties that is found in the interior of concrete. The pH value of the two set of solutions was identical around 14. A temperature of 80 degrees centigrade was maintained to enhance the reaction between the glass slides and alkali solutions in a closed system. White gels formation occurred on the surface of glass slides in 4 days and the glass slides were then kept in a desiccator for 24 hours before the nanoindentation testing.

2.2. Method

The surface morphology and chemical composition of the ASR gels were studied with a field emission scanning electron microscope (SEM, FEI Quanta 600) with energy dispersive X-ray spectroscopy (EDS). The experiments at the microscopic scale by nanoindentation were performed using a Triboindenter Nanoindenter. This instrument continuously monitors the displacement of the indenter by a capacitance gauge as load is applied. The load and displacements resolutions of the apparatus are 1 nN and 0.04 nm respectively. The measurements of elastic reduced modulus and hardness were obtained using a Berkovich indenter, i.e., three-sided pyramid diamond, with the same nominal area to depth relationships as the standard Vickers pyramid [14].

A load of 400 µN was applied to three different samples from two different alkali solutions. The load-displacement graph was plotted which is then used for determining the reduced elastic modulus of the gel. To find the actual elastic modulus of the gel, the equation from contact mechanics is used as mentioned in Eq. (1).

$$\frac{1}{E_r} = \frac{1-\upsilon_i^2}{E_i} + \frac{1-\upsilon_s^2}{E_s} \qquad (1)$$

Where υ is the Poisson's ratio. The subscript i refers to the indenter and s refers to the sample. For a diamond indenter tip, the elastic modulus (E_i) is 1140 GPa and Poisson's ratio (υ_i) is 0.07. The Poisson's ratio of sample (υ_s) is generally between 0 and 0.5 for most materials and the appropriate selection of υ_s is a crucial decision in order to determine its elastic modulus.

It has been found that the Poisson's ratio of various ASR gels ranges from 0.16 to 0.25, and the calculated elastic modulus will only be impacted by a couple percent [15], [16]. In addition, the Poisson's ratio of a material does not depend only on its composition but also the structure of the material. For example, both of graphite and diamond are made up of carbon yet their properties are very different from each other due to the difference in their structural arrangement of carbon. To be sure of the Poisson's ratio of the ASR gel, more experiment needs to be carried out but this is outside of the scope of this study. Thus, a Poisson's ratio of 0.2 was assumed throughout the experiment.

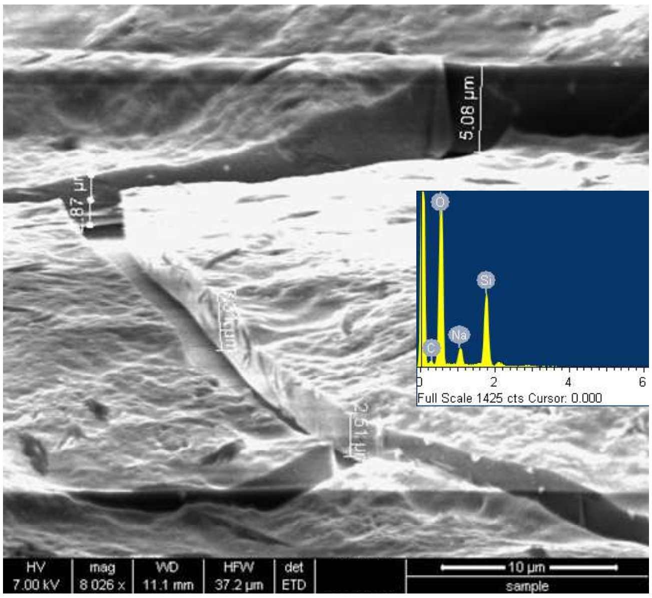

Fig. 1. *Appearance of ASR gels under SEM and EDS.*

3. Results and Discussion

3.1. SEM-EDS

SEM with EDS was conducted to ensure (i) the formation of ASR gels on the surface of borosilicate glass, (ii) the chemical composition of the gels, and (iii) thickness of the gels in order to prevent the subtract effects on the nanoindentation measurements.

Figure 1 shows the appearance of gels at 1N NH under SEM with chemical composition by EDS as an example. The thin layer of gels was found to have a thickness of 2-5 µm. The chemical composition of ASR gels was found to have a Na/Si molar ratio of 0.2 which falls into the typically range of ASR gel composition (i.e., 0.05-0.6 [17], [18]). This indicates that the gels formed throughout the glass surfaces due to ASR.

3.2. Nanoindentation

ASR gels are generally considered to be isotropic and homogenous, with material properties independent of direction [19]. The elastic modulus and hardness of the gel were measured by nanoindentation at penetration depths between 400 and 600 nm (shown in Figure 2) depicts the load-displacement curve for an applied force of 400 µN on samples 1 and 2.

Table 1 summarized the reduced elastic modulus and hardness of the gel for different alkali solutions along with the calculated actual elastic modulus when a Poisson's ratio of 0.2 was assumed. The values shown in the table are an average of 10 readings on each sample. Table 2 provides the Student's t-test calculated results for the tested samples.

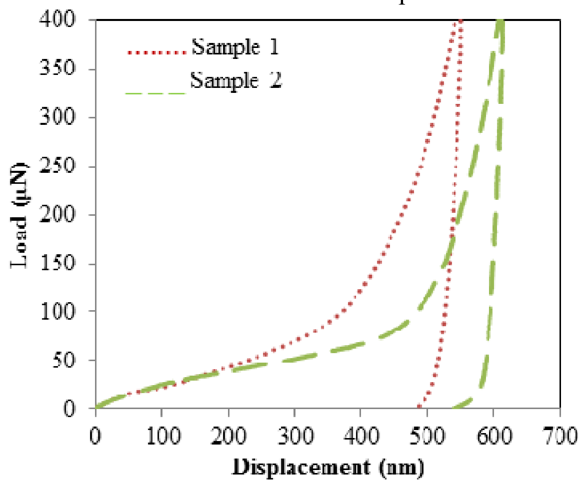

Fig. 2. *Typical load-displacement curve for samples 1 and 2.*

Table 1. *Elastic modulus and hardness of the ASR gel.*

Sample	Solution	E_r, GPa	Poisson's Ratio	E_s, GPa	Coefficient of Variation, %	Hardness, GPa
1	1N NH	3.08	0.2	2.96	28.7	0.0346
2	0.5N NH + 0.4N KH + CH	5.39	0.2	5.17	33.7	0.0398

Table 2. *Student's t-test results.*

P-value	Confidence Level	Statistical Significance
0.0027	99.73	Significant

The results in Table 1 show that sample 2 has a higher elastic modulus and hardness than sample 1. This might be attributed to the fact that the presence of both K and Ca in the solution forms denser gels and increases the elastic modulus and hardness. Based on the Student's t-test, the confidence level of 99.73% proves that the results of sample 2 are statistically different from that of sample 1. The addition of different alkali has an effect on the mechanical properties of the gel as expected.

Phair et al. [20] have found the Bulk elastic modulus of the gel using Brillouin scattering experiment. The bulk moduli were found to be 4 GPa for the gel formed from 0.08M CH and 10 GPa for the gel formed from 0.8M CH. Converting this value to elastic modulus using the Poisson's ratio of 0.2, the elastic modulus was found to be 7.2 GPa for 0.08M CH and 18 GPa for 0.8M CH. These results are different from the one obtained using Nanoindenter. This could be due to the following possible reasons:

- The gel conditions (e.g., undried) before indentation might increase the Bulk modulus of the sample due to the presence of water.
- The reliability of model using the measured sound velocities of the material (i.e., the compressional velocity and shear velocity) to determine the moduli may need verifications.
- Studies have shown that varying the ASR gel composition affects the swelling behavior of the gels [18], [21]. Therefore, it is expected that the mechanical properties of the gel will vary with compositions.

4. Conclusion

While it is accepted that ASR results in the formation of gels that cause damage through swelling, the physiochemical nature of these gels and their precise expansive mechanism remain poorly understood. In particular, limited effort has been made to characterize the mechanical properties of ASR gels, in relation to their molecular composition and nanostructure. Such information would greatly enhance the overall understanding of the mechanism of ASR damage. This study focusses on finding the mechanical properties (i.e., elastic modulus and hardness) of the gel using Nanoindenter. ASR gels simulated from different sources of alkalis were used to find how the mechanical properties change with the composition of alkali solutions. It was found that the elastic modulus of ASR gels ranges between 3 to 5 GPa for different alkali solutions. It was also found that the presence of potassium and calcium alkalis increases the elastic modulus and hardness of the ASR gel.

5. Future Work

An attempt will be made to verify the findings of the present study by testing more number of samples. This can be accomplished by testing with varying concentration of alkalis to match with the pore solution concentrations reported in literatures.

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