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Mechanical Properties Measurement of Hydrated Cement Paste Using Resonant Ultrasound Spectroscopy

ABSTRACT: The Resonant Ultrasound Spectroscopy (RUS) experimental technique was applied to measure the modulus of elasticity and Poisson's ratio of hydrated cement paste(HCP). RUS is a modern nondestructive acoustic technique which can be used to determine the elastic properties of solids with high-precision but little efforts. By measuring the natural resonance frequencies for a single small cement paste sample with water cement ratio of 0.4, the elastic constants which can be used to compute modulus and Poisson's ratio, were obtained. The RUS measured results E=21.55GPa, ν=0.225 agree with the numerical computation values.

KEYWORDS: RUS, elastic constant, modulus of elasticity, hydrated cement paste

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Introduction

Concrete is one of the most important man-made engineering materials. Properties of concrete is largely dependent on the constituent material: hydrated cement paste. Many experimental techniques as shown in table 1 can be applied to determine the elastic constants of solids, which may be classified as four groups: static and dynamics, ultrasonic method (including pulse-echo and V(z) curve methods), RUS and nanoindentation methods [1-5]. Unfortunately, there is no standard test method for the determination of mechanical properties such as modulus and Poisson's ratio for cement paste. And very few literature on the test method for elastic constants measurement of hydrated cement paste has been reported. On the contrary, several analytical and numerical approaches [6-10] are available though predicting elastic properties of HCP is difficult because of its random and complexity nature.

In most recent years, nanoindentation experimental technique has been widely used in the determination of properties of materials including hydrated cement paste individual constituents[11-13]. Using nanoindentation technique, the properties of hydrated cement paste can only be derived by employing proper microstructural models of HCP along with each individual properties given by nanoindentation test results.

Among all the methods listed in table 1, RUS is a modern nondestructive acoustic technique which can be used to measure the elastic properties of solids directly with high-precision. Migliori [14-15] may be the first to employ RUS to study the elastic constants of single crystals of La_2CuO_4 in 1987. RUS measures the well defined vibrational eigenmodes of parallelepiped, spherical or cylindrical samples to determine the elastic constants of the test solids. The sample size may vary from a few hundred microns, with a mass of less than 100 micrograms, to a dimension of several centimeters and masses of several kilograms[16]. The distinguished advantage of RUS is that only one small sample is needed to have one spectrum, from which the elastic constants of the solid is readily to be determined. Obviously this experimental technique is time saving and cost effective.

There are many applications of RUS such as phase transitions, flaw and crack detection [17], and elastic properties measurement of solids [15]. RUS has been widely used in the studies of solid materials. So et al. [18] measured elastic constants of thin films of colossal magnetoresistance material using thin-film RUS, McCall et al. [19] applied RUS to study the elastic properties of macroscopic rock. Measurement of elastic constants of single crystal chrome-diopside was previously done by Isaak and Ohno [20]. Other interesting applications include the elastic constants measurement of human denti [21] and composite material Ti-6AI-4V/TiB [22].

In this work, RUS was employed to measure the HCP mechanical properties, i.e. modulus of elasticity and Poisson’s ratio. This study serves our first attempt of RUS applications in cement based materials, geomaterials, and possibly nanocomposites.

RUS Measurement of Elastic Constants of HCP

Principles

Solids usually have many vibration modes with peak frequencies that depend on the mechanical properties, geometry and flaws inside [23]. Given the information of sample shape,crystallographic orientation, and density, together with the measured eigenfrequencies (as the RUS spectrum shown in Fig.2), we can calculate all the elastic constants [24], which is so called “the inverse problem”[16].

The principle theory of RUS can be simply expressed as [16,25]:

$$C_{ijkl}\frac{\partial^2 u_k}{\partial x_j \partial x_l} = \rho \frac{\partial^2 u_i}{\partial t^2} \tag{1}$$

where C_{ijkl} are the elastic constants, ρ is the density of the sample, u is the displacement. This expression is a result from the combination of linearized Lagrangian strain tensor, generalized Hook's law and classic Newton's second law, which are listed in Eqs (2)-(5) below, respectively.

$$e_{kl} = \frac{1}{2}\left(\frac{\partial u_k}{\partial x_l} + \frac{\partial u_l}{\partial x_k}\right) \tag{2}$$

$$\sigma_{ij} = C_{ijkl}e_{kl} \tag{3}$$

$$\frac{\partial \sigma_{ij}}{\partial x_j} = \rho \frac{\partial u_i}{\partial^2 t} \tag{4}$$

where e_{kl} is strain tensor, σ_{ij} is stress tensor. Eq. (4) can be understood as net force due to the spatial variation of the stress.

It is not easy to find the exact solution to Eq. 1. In practice, an approximate solution procedure leads Eq. 1 to a generalized eigenvalue problem [25]:

$$\Gamma a = \left(\rho\omega^2\right)\mathrm{E}a \tag{5}$$

where $\lambda = \rho\omega^2$ are eigen values, ω are the resonant frequencies, a are expansion coefficients, Γ and E are matrices in the expression of the Lagrangian for a 3D solid body (details can be referred to [25] page 6009). Eq. (5) can be used to determine the resonance frequencies from the elastic moduli [26].

The procedures to find the elastic constants C_{ijkl} of 3D solids start with a "guessed" set of elastic constants, followed by an iteration procedure to calculate the corresponding spectrum of the solid until the calculated spectrum most closely fit to the measured resonances (frequencies f_n) with an acceptable error[17] .

Experimental

RUS test samples was prepared and cured according to ASTM standard C192. Although the RUS test sample can be different shapes, we used nicely shaped *1.378cm×1.1956cm×0.964cm* parallelepiped as the one shown in Fig. 2. Water: cement ratio for the sample is *w/c*=0.4. We measured much more cement and water than what we actually need for the sample to eliminate the error very small amount materials may cause. After sufficient mixing, the cement paste was poured into a well made wood mould. Then we tapped the sides of the sample until a smooth surface appear. After 24 hours, the sample was removed and transferred to a small water tank for curing. Before testing in 28 days, we used a motor driven polisher to carefully make desired shape and smooth surfaces.

During the test, the sample was supported gently by transducers at diametrically opposite corners as shown in Fig. 1(a). The sample was excited at one point by one of the two transducers, while another transducer collected the resonant response of the sample. When the frequency of the driving transducer matches one of the vibrational eigenmodes of the sample, there will be a large resonant response. The spectrum frequencies are then used as input data for a program which adjusts the initially guessed elastic tensor until the calculated spectrum most closely matches the measured spectrum[17].

Results and Verification

Fig.3 shows the measured spectrum for the cement paste sample. The elastic constants determined from peak fits to these spectra are listed in Table 1. The elastic modulus *E* and Poisson's ratio can be derived from the relationship:

$$E = C_{11} - \frac{2C_{12}^2}{C_{11} + C_{12}} \tag{6}$$

and

$$\nu = \frac{1}{1 + \left({C_{11}}\big/{C_{12}} \right)} \tag{7}$$

the measured spectrum frequencies is 21.27GPa, and the Poisson's ratio *ν* is 0.216.

Numerical and analytical simulation result for modulus of elasticity on the same mixture HCP was given in the author's work [10], which is E= 23.7GPa. In the numerical simulation, a multiscale approach was adopted to model concrete as a hierarchical structural composite material by using tools as molecular dynamics, microporomechanics, and mechanics of composite materials. The RUS measured modulus agrees with the numerical value fairly well.

Conclusions and Discussions`

The elastic constants of hydrated cement paste were determined by RUS with little effort and the yielded results are satisfying. In this work, hydrated cement paste properties were studied by RUS only at room temperature. Stiffness of the concrete and cement paste exposed to fire will be largely reduced [27-28]. Therefore, it is of great importance to study the performance of HCP, concrete and other cement based engineering materials during fire. RUS may measure the elastic constants at very high temperatures and on very small or very large samples[16,26]. Modulus of cement paste or concrete with elevated temperature can be monitored using RUS as shown in Fig. 1 (b).

The capacity of using small (single-crystals) and larger size sample make it possible to study a wide range of engineering materials such as cement paste, aggregate, even sand. Or it may be possible to study the properties of hydrated cement paste products mineral crystals such as CH, jennite and tobermorite 14Å, the last two are structurally related to Calcium-Silicate-Hydrate (C-S-H): the main hydrated cement product and strength contributor of cement based materials. Moreover, RUS may have a potential usage in the determination of elastic properties for nanocomposites.

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References

[1] Hearmon, R.F.S., “The elastic constants of anisotropic materials.” Review of modern physics, Vol. 18(3), 1946, pp. 409-440.

[2] Constantinides, G. and Ulm, F-J., “On the use of nanoindentation for cementitious materials,” Mater Struct., Vol. 36(257), 2003, pp.191-196.

[3] Schwarz, R.B. and Vuorinen, J. F., “Resont ultrasound spectroscopy: applications,current status and limitations,” Journal of Alloys and Compounds, Vol. 310, 2000, pp.243-250.

[4] Kim, N., Kim, H-J., Oh, S-W., Hozumi, N., Lee, C-K. and Hong, M., “Ultrasonic measurement of elastic properties of nanostructured alumina,” Key Engineering Materal, Vol. 321-323, 2006, pp.1711-1714.

[5] Kim, D.K. (n.d.). Nanoindentation lecture 1: basic principle. Department of materials science and engineering, KAIST, Daejeon, South Korea.

[6] Bernard, O., Ulm, F.-J. and Lemarchand, E., “A multiscale micromechanics-hydration model for the early-age elastic properties of cement-based materials,” Cem. Conc. Res., Vol. 33, 2003, pp. 1293-1309.

[7] Haecker., C.-J., Garboczi, E.J., Bullard, J.W., Bohn, R.B., Sun, Z., Shah, S.P.and Voigt, T., “Modeling the linear elastic properties of Portland cement paste, Cement and Concrete Research, Vol. 35(10), 2005, pp.1948-1960

[8] Smilauer, Vit, Bittnar, Zdenek, “Microstructure-based micromechanical prediction of elastic properties in hydrating cement paste,” Cement and Concrete Research, Vol. 36 (9), 2006, pp. 1708-1718.

[9] Sun, Z., Ye, G., SHAH Surendra P. “Microstructure and early-age properties of portland cement paste-effects of connectivity of solid phases,” ACI Materials Journal, Vol. 102(2), 2005, pp. 122-129.

[10] Wu, W., Al-Ostaz, A., Alexander, H.-D. Cheng and Song, C.R., “ Concrete as a hierarchical structural composite material,” Unpublished work.

[11] Constantinides, G. and Ulm, F-J., “On the use of nanoindentation for cementitious materials,” Mater Struct. Vol. 36(257), 2003, pp.191-196.

[12] Hughes, J. J. ; Trtik, P., “Micro-mechanical properties of cement paste measured by depth-sensing nanoindentation: a preliminary correlation of physical properties with phase type,” Materials characterization , Vol. 53(2-4), 2004, pp. 223-231.

[13] Mondal, P. , Shah, S. P. and Marks L. D., “Nanoscale Characterization of Cementitious Materials,” ACI materials journal , Vol. 105(2), 2008, pp. 174-179.

[14] Migliori, A., Visscher, W.M., Brown, S.E., Fisk, Z., Cheong, S.-W., Alten, B., Ahrens, E.T., Kubat-Martin, K.A., Maynard, J.D., Huang,Y., Kirk, D.R., Gillis, K.A., Kim, H.K., and Chan, M.H.W., “Elastic constants and specific-heat measurements on single crystals of La_2CuO_4,” Physical Review *B*., Vol. 41(4), 1990, pp. 2098-2102.

[15] Migliori, A., Sarrao, J.L., Visscher, W.M., Bell, T.M., Lei, M., Fisk, Z. and Leisure, R.G., Resonant ultrasound spectroscopic techniques for measurement of the elastic moduli of solids,” Physica B., Vol. 183, 1993, pp. 1-24.

[16] Maynard, J., “ Resonant ultrasound spectroscopy,” Physics Today, Vol. 49, 1996, pp. 26-31.

[17] Gladden, J. "Thin film resonant ultrasound spectroscopy," Retrieved May 1, 2008, from http://www.phy.olemiss.edu/~jgladden/rus/index.html, 2006.

[18] So,J., Gladden, J. R., Hu, Y., Maynard, J. D., and Q. Li, "Measurements of Elastic Constants in Thin Films of Colossal Magnetoresistance Material ," Physical Review Letters, Vol. 90(3), 2003, pp. 036103.

[19] McCall, K.R., Ulrich, T.J., Johnson, P.A., Darling, T.W. and Migliori, A., "Application of Resonant ultrasound spectroscopy to determine the elastic properties of macroscopic rock samples," Proceedings of the resonancxe meeting, Vol. 1, 2001, pp. 66-76.

[20] Saak, D.G. and Ohno, I., "Elastic constants of chrome-diopside: application of resonant ultrasound spectroscopy to monoclinic single-crystals," Physics and Chemistry of Minerals, Vol. 30(7), 2003, pp. 430-439

[21] Kinney, J.H., Gladden, J.R., Marshall, G.W., Marshall, S.J., So, J.H., and Maynard, J.D., "Resonant ultrasound spectroscopy measurements of the elastic constants of human dentin," Journal of Biomechanics.,Vol. 37(4), 2004, pp.437-441.

[22] Gorsses, S. and Micracle, D.B., "Mechanical properties of Ti-6AI-4V/TiB composites with randomly oriented and aligned TiB reinforcements," Acta Materialia, Vol. 51(9), 2003, pp. 2427-2442.

[23] Andrews, D.R., "Ultrasonic resonance spectroscopy for quality assurance testing of concrete, aerospace and other industrial components," Retrieved May 1, 2008, from http://www.cambridge-en.com/Reports/BriteEuRam%20BE-5029.html, 1996.

[24] Migliori, A. and Sarrao, J.L., *Resonant Ultrasound Spectroscopy.* John Wiley & Sons Inc., New York, 1997, p.53.

[25] Leisure, R.G., and Willis, F.A., "Resonant ultrasound spectroscopy," J. Phys.: Condens. Matter, Vol. 9, 1997, pp. 6001-6029.

[26] Migliori , A. and Maynard, J. D., "Implementation of a modern resonant ultrasound spectroscopy system for the measurement of the elastic moduli of small solid specimens," Review of Scientific Instruments, Vol. 76(12), 2005, pp. 121301.1-121301.7.

[27] Li, M., Qian, C. and Sun, W., "Mechanical properties of high-strength concrete after fire," Cement and Concrete Research, Vol. 34, 2007, pp. 516-522.

[28] Arioz, O., "Retained properties of concrete exposed to high temperatures: Size effect," Fire and Materials, DOI 10.1002/fam.996, 2009

TABLE 1— *Methods commonly used for measuring elastic properties of solids*

Methods		Equation for elastic constant	Notes
Static Methods	Static tension or compression	$\frac{pl}{A\Delta l}$	*p*-applied tensile or compressive load
	Static uniform bending	$\frac{CR}{J}$	*C*-Applied bending moment *R*- Radius of curvature *J*-Moment of inertia
	Static non-uniform bending	$\frac{P_0 l^3}{3Jx_0}$	cantilever
Dynamics methods	Dynamic longitudinal vibration	$\frac{4l^2\nu^2\rho}{n^2}$	Specimen clamped at middle point and free at both ends
	Dynamic flexural vibration	$\frac{4\pi^2 A l^4 \nu^2 \rho}{J\alpha}$	Specimen clamped at one end and loaded with mass M at the other.
Ultrasonic methods	Pulse-echo		Use time-of-flight of plane bulk wave propagating in the material
	V(z) curve		Use surface acoustic wave traveling on the surface
RUS	RUS	$C_{ijkl}\frac{\partial^2 u_k}{\partial x_j \partial x_l} = \rho\frac{\partial^2 u_i}{\partial t^2}$	High precision, small and big sample size, single measurement for all elastic constants
Indentation	Micro-indentation		Mechanical properties measurement in micro-scale
	Nano-indentation	$\frac{1}{E^*} = \frac{1-\nu^2}{E} + \frac{1-\nu_{indenter}}{E_{indenter}}$	Measure hardness and elastic modulus of localized material, a smaller scale

TABLE 2— *The fitting of the measured resonances and calculated resonances*

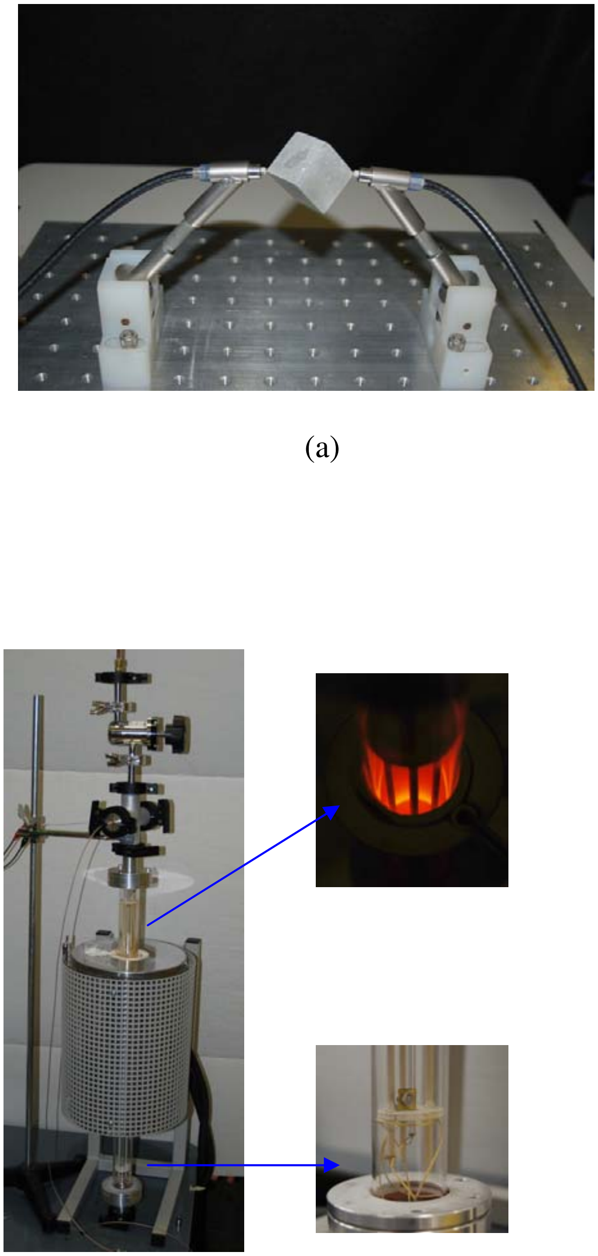
Peak	Measured freq (MHZ)	Calculated freq (MHZ)	Error (%)	Included/Excluded
1	0.067361	0.067118	0.362	INC
2	0.088249	0.089107	-0.963	INC
3	0.095751	0.096265	-0.534	INC
4	0.100099	0.099825	0.274	INC
5	0.103022	0.103084	-0.06	INC
6	0.111741	0.111261	0.431	INC
7	0.114769	0.114553	0.188	INC
8	0.115898	0.115421	0.413	INC
9	0	0.11636	0	--
10	0.119356	0.11901	0.291	INC
11	0.124559	0.124982	-0.338	INC
12	0.125949	0.126052	-0.082	INC
13	0.128436	0.128334	0.08	INC
14	0	0.136486	0	--
15	0.143455	0.143776	-0.223	INC
16	0.147126	0.149897	-1.849	EXC
17	0	0.15416	0	--
18	0	0.155213	0	--
19	0	0.157388	0	--
20	0.158854	0.158771	0.052	INC

Average error magnitude of included peaks= 0.306 %
Density used in the calculation is 1.940 g/cm^3.

TABLE 3— RUS results for hydrated cement paste with w/c=0.4

Symmetry	C_{11}	C_{33}	C_{12}	C_{13}	C_{44}	ν	E	G
Isotropic/Cubic	24.23		6.69		8.77	0.216	21.55	8.8

Units are GPa with the exception of the Poisson's ratio (ν),which is dimensionless. E is the Young's modulus and G is the shear modulus.



(a)

(b)

FIG.1— *(a) A room temperature RUS system (b) A high temperature RUS system*

FIG.2— *A 1.378cm×1.1956cm×0.964cm parallelepipedal shape cement paste sample*

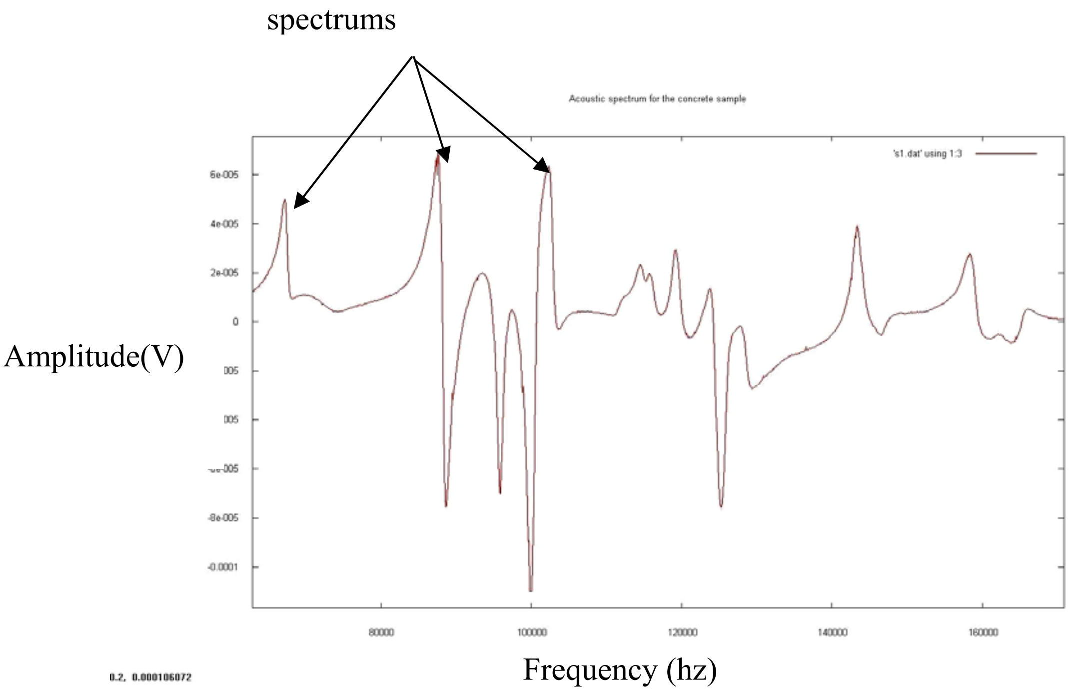


FIG.3— *The spectrum for a 1.378cm×1.196cm×0.964cm parallelepipedal shape cement paste sample.*