

# Theoretical Predictions of the Elastic Moduli of Polymer-Impregnated Hardened Cement Paste and Mortars

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## Synopsis

Hardened cement pastes with water-to-cement ( $w/c$ ) ratios of 0.4 and 0.6 and hydration times of one, three, seven, and 28 days were oven dried and subsequently impregnated with an epoxy resin formulation which was then polymerized *in situ* at 75°C. Portland cement mortars containing Ottawa sand and asbestos fibers as filler were also subjected to this impregnation process. Dynamic elastic moduli ( $E'$ ) were measured at audio frequencies over a range of temperatures (100–400°K). Experimental values were compared with moduli calculated using various theoretical approaches based on two-phase composite materials theory. Best agreement between experimental and calculated results occurs when Wu's theory for spherical polymer inclusions was applied to a cement-based matrix. In the case of polymer-impregnated mortars, experimental and theoretical results are in closest agreement at low temperatures and at low volume fraction of filler.

## INTRODUCTION

Polymer-impregnated cement paste (PICP) belongs to a class of composite materials where both matrix and filler materials are continuous and interconnected phases. Due to the extreme complexity of the material, an analytical solution for the elastic modulus of the composite is not available. For this reason, various approaches have been taken toward modification of existing theories which deal with discrete two-phase composites. In fact, Krock<sup>1</sup> has shown that, over the same concentration range, dispersed particle and continuous skeleton metallic composites show no significant difference in elastic moduli.

In their studies of polymer-impregnated metallic foams, White and Van Vlack<sup>2</sup> found that the composite moduli roughly followed Kerner's theory.<sup>3</sup> Auskern and Horn<sup>4</sup> have applied a model proposed by Hobbs<sup>5</sup> to describe the elastic properties of PICP. Hasselman et al.<sup>6</sup> have considered stress concentration effects in a modification of Hashin's theory<sup>7</sup> to cover the case of polymer-impregnated ceramics.

Whiting and Kline<sup>8</sup> have shown that a significant amount of the total porosity of hardened cement paste (HCP) remains unfilled by polymer, especially in more mature cements. This, in effect, creates a three-phase composite, the third phase being the unfilled voids. In addition, the effects of filler size and geometry can also affect the elastic modulus. The theory of Wu<sup>9</sup> takes some of these parameters into account and therefore lends itself to the present problem. It is the

aim of the present study to review the major theories in detail and to test them against experimental results on epoxy-impregnated cements and mortars.

## EXPERIMENTAL

### Sample Preparation

All pastes and mortars were prepared using Type 1 portland cement. Pastes were prepared by adding the required amount of water to the cement and hand mixing for 2 min. Specimens with  $w/c = 0.4$  were prepared by troweling the fresh paste into a rectangular PVC mold  $0.635 \text{ cm} \times 0.762 \text{ cm} \times 12.7 \text{ cm}$  in dimensions. Six samples could be prepared at one time. Pastes of  $w/c = 0.6$  were too fluid to be troweled and were therefore poured vertically into the molds, which were then sealed with a PVC lid. The molds were precoated with a mixture of wax and oil to facilitate demolding procedures.

Mortar specimens were formed in a similar manner, except that in this case all specimens were formed by troweling. Mix proportions for the mortars prepared are presented in Table I.

After casting, the pastes and mortars were placed in a fog room (100% R.H.) near  $20^\circ\text{C}$  for 20–24 hr. The castings were then carefully demolded and placed in a saturated limewater solution for the duration of the desired period of hydration. All hydration was carried out at ambient laboratory temperatures ( $18\text{--}25^\circ\text{C}$ ).

After the specimens had reached the desired maturity, they were removed from the limewater, trimmed to a length of 10.2 cm, and placed in a vacuum oven at  $75^\circ\text{C}$ . Samples were continuously evacuated until loss of water equivalent to 1 mg/g of paste per day had been achieved. This process lasted approximately 72 hr. A cold trap contained in a Dewar flask filled with liquid nitrogen ( $\text{bp} = 81^\circ\text{K}$ ) was used to maintain a constant vapor pressure above the samples. At the end of the drying period, the samples were placed in sealed mason jars containing a small quantity of desiccant to prevent any adsorption of water.

Epon 828, a diglycidal ether of bisphenol A, was chosen as the monomer in this

TABLE I  
Mix Proportions for Mortars

Ottawa Sand Mortars (Variable $v_f$ )				
	$v_f = 0.1$ $w/c = 0.4$	$v_f = 0.2$ $w/c = 0.4$	$v_f = 0.4$ $w/c = 0.4$	$v_f = 0.6$ $w/c = 0.6$
Cement, g	100	100	100	100
Sand, g	20.6	46.3	123	355
Water, g	40	40	40	60
Asbestos Fiber Mortars (Variable $v_f$ )				
	$v_f = 0.052$ $w/c = 0.6$	$v_f = 0.094$ $w/c = 0.67$	$v_f = 0.139$ $w/c = 1.10$	$v_f = 0.189$ $w/c = 2.30$
Cement, g	100	75	50	30
Asbestos, g	15	22.9	34.4	54.9
Water, g	60	50	55	68.9

TABLE II  
Porosity of Hardened Cement Pastes

<i>w/c</i>	Maturity, days	Total porosity, %
0.4	1	47.5
	3	44.5
	7	40.3
	28	37.0
0.6	1	54.4
	3	51.5
	7	50.5
	28	48.2

case, owing to its low shrinkage on cure and relatively low vapor pressure. Formulation of the epoxy resin system is discussed in the Appendix.

A detailed description of the impregnation apparatus is given by Whiting.<sup>10</sup> Samples are placed in the impregnation chamber and evacuated to a pressure of 100 microns. Monomer is then introduced into the chamber and allowed to completely cover the samples. The system is then brought up to 200 psig pressure with compressed nitrogen. Specimens were kept under pressure for 8 hr. At the end of this period, samples were removed from the chamber, weighed, and subjected to the appropriate polymerization procedure.

Epoxy-impregnated specimens were given time to gel at ambient temperature (24 hr). They were then placed in a laboratory oven at 75°C for an additional 24 hr, and subsequently removed from the oven and allowed to cool slowly to room temperature. Samples were stored in sealed test tubes prior to testing.

For determination of the modulus of the bulk epoxy resin, the resin was cast into 1/4-in. glass tubes, sealed, and cured under the conditions described above.

### Porosity Measurements

Porosities of the cement paste specimens were determined by the method of Copeland and Hayes.<sup>11</sup> Total porosity ( $\epsilon_T$ ) data on representative specimens are presented in Table II.

Porosity of the mortars was determined simply from the water removed from the samples during oven drying at 75°C for 72 hr. Porosity (%) in this case is expressed as

$$\text{porosity (\%)} = \frac{\text{water removed (g)} \times 100}{\text{bulk volume of specimen (cm}^3\text{)}} \quad (1)$$

TABLE III  
Porosity of Mortars

Filler	<i>w/c</i>	Maturity, days	Volume fraction filler	Porosity, %
Ottawa sand	0.4	7	0.1	36.9
	0.4	7	0.2	33.6
	0.4	7	0.4	25.4
	0.6	7	0.6	20.4
Asbestos	0.6	7	0.052	49.9
	0.67	7	0.094	49.9
	1.10	7	0.139	59.5
	2.30	7	0.189	63.5

TABLE IV  
Loading of Hardened Cement Paste

$w/c$	Maturity, days	Volume loading, %
0.4	1	39.4
	3	33.4
	7	22.9
	28	15.3
0.6	1	47.1
	3	41.2
	7	32.7
	28	24.1

Porosity of all mortar specimens is presented in Table III.

Volume loading of the specimens, in percent, is expressed as

$$\text{volume loading (\%)} = \frac{\text{weight loaded (g)} \times 100}{\rho \times V_b} \quad (2)$$

where  $\rho$  is the density of the polymer (1.16 g/cm<sup>3</sup>) and  $V_b$  (cm<sup>3</sup>) is the bulk volume of the specimen. Volume loading of all HCP specimens is presented in Table IV. Volume loading of all mortar specimens is presented in Table V.

Residual porosity ( $\epsilon_R$ ) is expressed as

$$\epsilon_R = \frac{\epsilon_T - \text{volume loading (\%)}}{100} \quad (3)$$

### Dynamic Mechanical Testing

All specimens were tested in an apparatus developed by Kline.<sup>12</sup> The specimen is suspended by two cotton threads located just outside the nodes of the fundamental free-free flexural mode, approximately  $\frac{1}{2}$  in. from the ends of the specimen. The specimen is excited in the audio frequency range by a magnetostrictive transducer. The output signal is detected by a piezoelectric crystal pickup, amplified, filtered, and displayed both on a level recorder and an oscilloscope. The dynamic modulus is calculated from the following expression:

$$E' = \frac{6.10617\rho L^4 f_1^2}{h^2} \quad (4)$$

TABLE V  
Loading of Epoxy-Impregnated Mortars

Mortars	$w/c$	$\nu_f$	Volume loading, %
Ottawa sand mortars	0.4	0.1	22.7
	0.4	0.2	20.5
	0.4	0.4	17.0
	0.6	0.6	22.4
Asbestos fiber mortars	0.60	0.052	39.7
	0.67	0.094	41.1
	1.10	0.139	52.9
	2.30	0.189	60.9

in the case of rectangular specimens, and from the expression

$$E' = \frac{0.6323(L/d)^4 w f_1^2}{L} \quad (5)$$

for the case of cylindrical specimens where  $L$  is the length of the specimen (in.),  $\rho$  is the density of the specimen ( $\text{g}/\text{cm}^3$ ),  $h$  is the height (in.),  $d$  is the width (in.),  $w$  is the weight (g), and  $f_1$  is the fundamental frequency of vibration.

For low-temperature measurements, specimens were cooled in a chamber surrounded by a Dewar flask containing liquid nitrogen (bp =  $81^\circ\text{K}$ ). Testing was conducted at a rate of  $1^\circ\text{K}$  per min.

## RESULTS AND DISCUSSION

The modulus of HCP is a strong function of its porosity. This has been studied by Helmuth and Turk,<sup>13</sup> Lawrence et al.,<sup>14</sup> Sereda et al.,<sup>15</sup> and others. Helmuth and Turk<sup>13</sup> made a study of the moduli of HCP with porosities ranging from  $\epsilon_T = 0.25$  to  $\epsilon_T = 0.67$ , where  $\epsilon_T$  is the total porosity. By plotting the measured dynamic modulus  $E'$  versus  $(1 - \epsilon_T)^3$ , they extrapolated to obtain a value of  $74.4 \times 10^{10}$  dynes/cm<sup>2</sup> at  $(1 - \epsilon_T)^3 = 1$  (solid phase, no porosity). Also, Lawrence et al.<sup>14</sup> found values of  $60.7 \times 10^{10}$  dynes/cm<sup>2</sup>. In the Powers equation,<sup>16</sup> then,

$$E_c = E_m(1 - \epsilon_T)^3 \quad (6)$$

where  $E_c$  is the modulus of the HCP and  $E_m$  is the modulus of the nonporous solids. Helmuth and Turk suggest justification of this equation with a simple model.<sup>13</sup>

Using a value of  $E_m$  (such as  $74.4 \times 10^{10}$  dynes/cm<sup>2</sup> shown above) for nonporous cement paste, one can combine constants of the filler (polymer) with the matrix (cement) to estimate the composite modulus  $E_c$  for PICP and other systems using the theories available. The estimate can then be compared to other values. When applicable, a correction, based on either Powers' equation, eq. (6), or on one of the theories previously discussed, can also be made to correct for the residual porosity due to unfilled regions of the system. Table VI lists the values used for the elastic constants of polymer, cement, fillers, and voids in making the calculations.

A majority of theories developed to predict the elastic moduli of two-phase

TABLE VI  
Elastic Constants of Materials Used

Material	Elastic modulus, (dynes/cm <sup>2</sup> ) $\times 10^{-10}$	Poisson's ratio
Epoxy resin	3.31 <sup>a</sup>	0.334 <sup>17</sup>
Cement solids	74.4 <sup>13</sup>	0.27 <sup>13</sup>
Ottawa sand	75.8 <sup>14</sup>	0.22 <sup>14</sup>
Asbestos	175 <sup>17</sup>	0.22 <sup>b</sup>
PICP	calculated	0.27 <sup>b</sup>
Voids	0	0.5 <sup>c</sup>

<sup>a</sup> Experimental value at  $300^\circ\text{K}$  ( $E'$ ).

<sup>b</sup> Assumed value. No experimental data available.

<sup>c</sup> Assume void filled with an incompressible fluid.

composite materials consider particulate or fiber-filled systems. The rule of mixtures relationship based on elementary isostrain conditions is the simplest of these and applies primarily to fibrous fillers oriented in a specific fashion. For instance, for fibers oriented along the principal stress axis,  $E'$  often follows the rule of mixtures relationship.<sup>17</sup>

In particulate composites, the elastic modulus is often a more complex function of  $v_f$  than a rule of mixtures relationship. In a direct approach to particulate filled systems, Hashin<sup>7</sup> used isostress and isostrain estimates in the fillers and matrix with strain energy calculations to establish rigorous bounds for composite moduli. The gap between these bounds is rather large when the moduli of the matrix and filler differ considerably.

Hasselman et al.<sup>6</sup> have applied a modification of Hashin's theory<sup>7</sup> to the problem of polymer-impregnated ceramics. Preliminary results for ceramic materials<sup>6</sup> indicate fair agreement with the experimental data. Hasselman's expression for the elastic modulus of a polymer-impregnated porous material is given by

$$E_c = E_m \left( \frac{1 + \alpha_G v_f}{1 + \gamma v_f} \right) \quad (7)$$

where  $E_m$  is the modulus of the nonporous solids and  $v_f$  is the volume fraction of filler polymer.

A stress concentration factor  $\alpha_G$  is given by the following expression:

$$\alpha_G = \frac{(K - 1)(p + 1)}{\left( \frac{(1 - K)(R - 1)^2}{(R + 1)^2 - (Kp + 1)} \right)} \quad (8)$$

where  $K = E_f/E_m$ ;  $p = 3 - 4\nu_m$ ;  $R = R_1/R_2$ ;  $E_f$  is the modulus of the filler;  $E_m$  is the modulus of the matrix;  $\nu_m$  is Poisson's ratio of the matrix; and  $R_1$  and  $R_2$  are the major and minor axes, respectively, of the ellipsoidal inclusion. The correction factor  $\gamma$  is introduced to satisfy boundary conditions and is given by

$$\gamma = \frac{\alpha_G - K + 1}{K - 1} \quad (9)$$

For spherical phase geometry, the following expression is applicable:

$$\alpha_G = \frac{4(K - 1)(1 - \nu_m)}{(3 - 4\nu_m)(K + 1)} \quad (10)$$

However, application of this treatment to the present experimental results indicated that there was poor agreement between calculated and observed moduli.

Goodier<sup>18</sup> has derived the exact solution to the problem of a single spherical inclusion in a block of matrix material subjected to a uniform stress. By St. Venant's principle, the perturbation in the stress field is effectively smoothed out in a relatively short distance. Thus, when particulate fillers do not approach each other too closely, the composite can be visualized as an array of blocks with spheres (filler) inside, and the modulus estimate would be that of Goodier. Kerner<sup>3</sup> followed this model assuming no filler-matrix slippage, to estimate moduli for high  $v_f$  values. His model was a sphere (filler) in a shell of matrix material surrounded by a third medium with composite properties. This approach leads to a conservative (too low) estimate for the composite modulus.

Lewis and Nielsen,<sup>19</sup> Jenness and Kline,<sup>17</sup> and others found Kerner's prediction too low and note that the estimate is equivalent to the lower bound of Hashin's theory.<sup>7</sup>

Kerner's theory<sup>3</sup> can also be applied to PICP. Kerner's expression for shear modulus  $G_c$  of a particulate composite with spherical filler particles is given by

$$G_c = G_m \left[ \frac{\frac{v_f G_f}{(7 - 5\nu_m)G_m + (8 - 10\nu_m)G_f} + \frac{1 - v_f}{15(1 - \nu_m)}}{\frac{v_f G_m}{(7 - 5\nu_m)G_m + (8 - 10\nu_m)G_f} + \frac{1 - v_f}{15(1 - \nu_m)}} \right] \quad (11)$$

where  $G_c$  = shear modulus of composite;  $G_m$  = shear modulus of matrix;  $G_f$  = shear modulus of filler;  $\nu_m$  = Poisson's ratio of matrix; and  $v_f$  = volume fraction of filler. Unfortunately, agreement between experimental and observed results is poor in this case as well.

Wu<sup>9</sup> has developed a comprehensive theory for fillers of various shapes (spheres, needles, and disks). Wu's equations have been experimentally investigated by Jenness,<sup>17</sup> and, for a reasonably well-defined geometry of filler, the results were quite encouraging.

Wu based his theory on Eshelby's<sup>20</sup> treatment of the strain field resulting from an ellipsoidal inclusion in a homogeneous isotropic matrix. For no slippage, the inclusion has uniform stress when the matrix has uniform stress at relatively large distances from the filler. To determine the effective composite modulus, the stress at intermediate points need not be known. Wu generalized results for closely spaced ellipsoidal fillers, averaging over all orientations. He obtained relatively complicated expressions for composites with randomly oriented filler particles.

Wu's relationship between the filler volume fraction  $v_f$  and the elastic modulus  $E_c$  of a particulate composite with spherical filler particles is given by

$$v_f = \frac{\left[ \frac{E_c(1 + \nu_m)}{E_m(1 + \nu_c)} - 1 \right]}{\left[ \frac{E_f(1 + \nu_m)}{E_m(1 + \nu_f)} - 1 \right]} \left\{ 1 + \frac{2(4 - 5\nu_c)}{15(1 - \nu_c)} \left[ \frac{E_f(1 + \nu_c)}{E_c(1 + \nu_f)} - 1 \right] \right\} \quad (12)$$

where  $E_m$  = elastic modulus of matrix;  $E_f$  = elastic modulus of filler;  $\nu_m$  = Poisson's ratio of matrix;  $\nu_f$  = Poisson's ratio of filler; and  $\nu_c$  = Poisson's ratio of composite.

Results are presented in Table VII. In this table,  $E_c$  represents the value of the composite modulus calculated on the basis of the two-phase model, eq. (12), assuming all porosity to be filled by polymer. A correction for residual porosity using eq. (12) with  $E_f = 0$  gives the values in the column headed  $E_{c1}$ . A correction for residual porosity using Powers' equation, eq. (6), gives the values in the column headed  $E_{c2}$ . Experimental values are designated by  $E'$ . Comparison with experimental results indicates fairly good agreement.

The agreement between experimental and calculated results is quite surprising in view of the limitations inherent in Wu's derivations. He assumed that there is no contiguity between the filler particles, that they are perfect spheres, and that perfect adhesion exists between the filler and the matrix. Tests of this

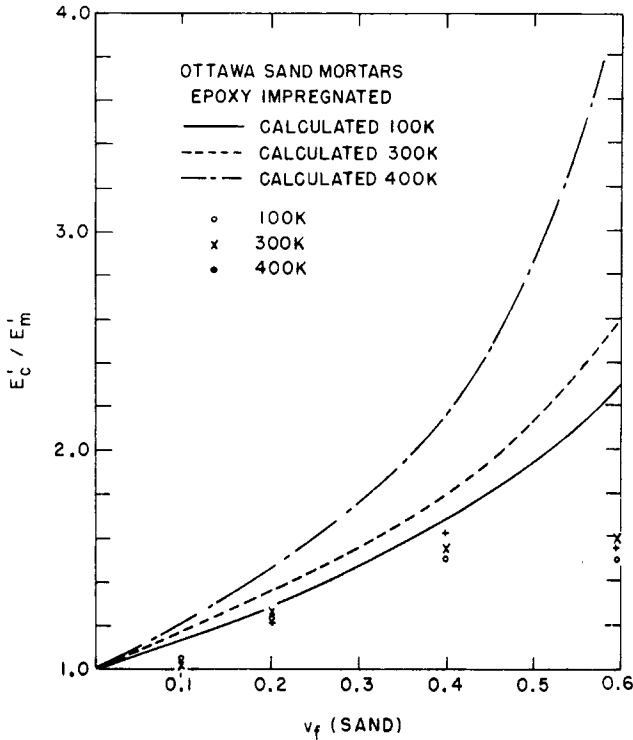


Fig. 1. Ratio of composite moduli ( $E'_c$ ) to matrix moduli ( $E'_m$ ) for OSM of varying  $v_f$ .

theory versus experimental results on other PICP systems are necessary before its general validity can be established.

Wu's theory also can be applied to the prediction of the elastic moduli of PIM. In this case, the PICP is considered as the matrix and Ottawa sand or asbestos (Table VI) as the filler.

TABLE VII  
Theoretical Predictions of Elastic Moduli: Wu's Theory

$w/c$	Maturity, days	Volume fraction filler $v_f$	Residual porosity $\epsilon_R$	Elastic modulus, (dynes/cm <sup>2</sup> ) $\times 10^{-10}$			
				$E_c^a$	$E_{c1}^b$	$E_{c2}^c$	$E'^d$
Spherical Inclusions							
0.4	1	0.394	0.081	24.9	17.9	19.3	18.2
	3	0.334	0.111	31.2	20.9	21.9	20.0
	7	0.229	0.174	43.1	24.4	24.3	22.0
	28	0.153	0.217	52.3	25.9	25.1	23.4
0.6	1	0.471	0.072	18.0	13.2	14.4	14.5
	3	0.412	0.103	23.3	15.8	16.7	17.2
	7	0.327	0.178	31.9	17.9	17.7	18.6
	28	0.241	0.241	41.7	19.0	18.2	19.8

<sup>a</sup> Calculated from two-phase model (Wu's equation).

<sup>b</sup> Calculated from Wu's equation, eq. (12), with  $E_f = 0$  and  $E_m = E_c$ .

<sup>c</sup> Calculated from Powers' equation, eq. (6), with  $\epsilon_R = \epsilon_t$  and  $E_m = E_c$ .

<sup>d</sup> Experimental data.



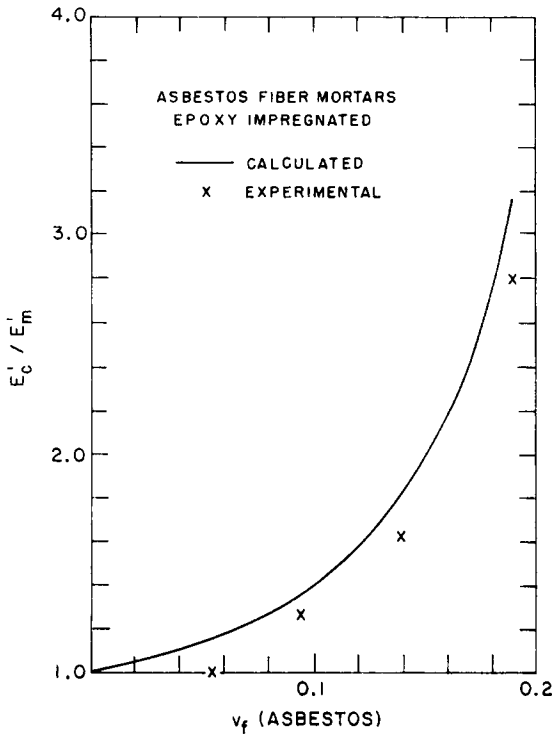


Fig. 2. Ratio of composite moduli ( $E'_c$ ) to matrix moduli ( $E'_m$ ) for AFM of varying  $v_f$ .

Values for epoxy PICP of  $w/c = 0.4$  and seven-days maturity were used for the matrix values for PIM with  $v_f = 0.1, 0.2,$  and  $0.4$ . Values of  $E'_m$  in these cases are 26.3, 22.0, and 13.8 (dynes/cm<sup>2</sup>)  $\times 10^{10}$  at 100°K, 300°K, and 400°K, respectively. Values for epoxy PICP of  $w/c = 0.6$  and seven-day maturity were used for PIM with  $v_f = 0.6$ . Values of  $E'_m$  are 23.4, 18.6, and 9.5 (dynes/cm<sup>2</sup>)  $\times 10^{10}$  at 100°K, 300°K, and 400°K in this case. Filler values are given in Table VI.

Results using eq. (12) for spherical filler particles are presented in Figure 1. The ratio of the measured composite modulus  $E'_c$  to the measured modulus of the matrix  $E'_m$  has been calculated for the various volume fractions of filler used. Results for  $T = 100^\circ\text{K}, 300^\circ\text{K},$  and  $400^\circ\text{K}$  are presented. It is evident that agreement is best at low temperatures (100°K) and at low volume fractions of filler ( $\leq 0.4$ ). At high temperatures, considerable slippage between matrix and filler can occur; and at high  $v_f$ , agglomeration of filler particles can occur, both of which violate assumptions of Wu's theory.

Results calculated using Wu's relationship, eq. (13), for needle-shaped fillers imbedded in a PICP matrix are presented in Figure 2. Asbestos fibers were used as the filler (see Table VI). In this case, no PICP was available with appropriate  $w/c$  ratios. PICP matrix moduli  $E'_m$ , therefore, were calculated from eq. (12). This was accomplished by calculating the PICP composite modulus  $E_c$  based on known values for the cement solids and polymer. This PICP composite modulus is then used as  $E'_m$  in the next calculation, eq. (13), where PICP serves as the matrix and asbestos as the filler:

$$\begin{aligned}
\frac{1}{\nu_f} = \frac{1}{5} & \left[ \frac{E_f(1 + \nu_m)}{E_m(1 + \nu_f)} - 1 \right] \left\{ \frac{4}{\frac{(1 + \nu_c)E_f}{(1 + \nu_f)E_c} + 1} + \frac{2}{2 + \left[ 1 + \frac{1 - 2\nu_c}{2(1 - \nu_c)} \right] \left[ \frac{(1 + \nu_c)E_f}{(1 + \nu_f)E_c} - 1 \right]} \right. \\
& + \frac{\left[ 1 - \frac{2(1 - 2\nu_c)}{3(1 - \nu_c)} \right] \left[ \frac{(1 + \nu_c)E_f}{(1 + \nu_f)E_c} - 1 + \frac{3(\nu_f - \nu_c)E_f}{(1 - 2\nu_f)(1 + \nu_f)E_c} \right]}{1 + \left[ 1 - \frac{1 - 2\nu_c}{2(1 - \nu_c)} \right] \left[ \frac{(1 + \nu_c)E_f}{(1 + \nu_f)E_c} - 1 \right] + \left[ 3 - \frac{2(1 - 2\nu_c)}{1 - \nu_c} \right] \left[ \frac{(\nu_f - \nu_c)E_f}{(1 - 2\nu_f)(1 + \nu_f)E_c} \right]} \\
& + \frac{2 \left[ 1 + \left( 3 - \frac{1 - 2\nu_c}{2(1 - \nu_c)} \right) \left( \frac{(1 + \nu_c)E_f}{4(1 + \nu_2)E_c} - \frac{1}{4} \right) + \left( 3 - \frac{2(1 - 2\nu_c)}{1 - \nu_c} \right) \left( \frac{(\nu_f - \nu_c)E_f}{(1 - 2\nu_f)(1 + \nu_f)2E_c} \right) \right]}{\left[ 1 + \left( \frac{1}{2} + \frac{1 - 2\nu_c}{4(1 - \nu_c)} \right) \left( \frac{(1 + \nu_c)E_f}{(1 + \nu_f)E_c} - 1 \right) \right] \left[ 1 + \left( 1 - \frac{1 - 2\nu_c}{2(1 - \nu_c)} \right) \left( \frac{(1 + \nu_c)E_f}{(1 + \nu_f)E_c} - 1 \right) \right]} \\
& \left. + \left( 3 - \frac{2(1 - 2\nu_c)}{1 - \nu_c} \right) \left( \frac{(\nu_f - \nu_c)E_f}{(1 - 2\nu_f)(1 + \nu_f)E_c} \right) \right\} \quad (13)
\end{aligned}$$

$E_m$  = elastic modulus of matrix;  $E_f$  = elastic modulus of filler;  $\nu_m$  = Poisson's ratio of matrix;  $\nu_f$  = Poisson's ratio of filler; and  $\nu_c$  = Poisson's ratio of composite. This equation represents Wu's relationship between the filler volume fraction  $\nu_f$  and the elastic modulus  $E_c$  of a particulate composite with needle-shaped filler particles.

Using this procedure, values of  $E_m = 16.1 \times 10^{10}$ ,  $13.8 \times 10^{10}$ ,  $7.3 \times 10^{10}$ , and  $4.1 \times 10^{10}$  dynes/cm<sup>2</sup> for  $w/c = 0.60, 0.67, 1.10,$  and  $2.30$ , respectively, were calculated. Results indicate good agreement between experimental and calculated values. This may be expected in view of the low ( $<0.2$ )  $\nu_f$  employed.

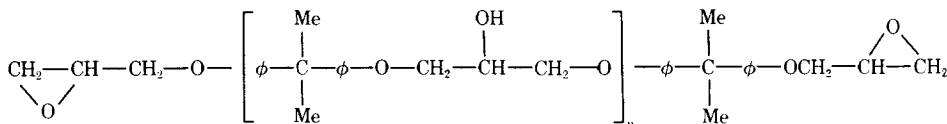
## CONCLUSIONS

This study has shown that the elastic moduli of polymer-impregnated portland cement pastes having a wide variety of maturities and  $w/c$  ratios can be rather accurately predicted using presently available composite materials theory, provided that a low volume fraction of filler is employed and that temperatures remain at or below ambient. Wu's theory applied for spherical polymer inclusions in a rigid matrix, in particular, yields results which agree rather well with experimental data at ambient temperatures. Elastic moduli of polymer-impregnated mortars can also be calculated, in this case using either experimental or calculated values for the matrix constants. Due to the significant amount of residual porosity remaining in polymer-impregnated cement pastes, it is suggested that a correction must be made to the calculated value of the moduli, either by use of Wu's formula or by a semiempirical porosity function. Although this approach should work well with other polymer-impregnated systems, its general validity remains to be established.

## Appendix

### Structure and Proportioning of the Epoxy Resin System

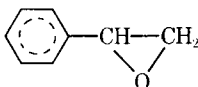
The basic component of the epoxy resin system used in the present research was Epon 828, a diglycidial ether of bisphenol A with the following structure:



where  $\phi$  represents the phenyl group.

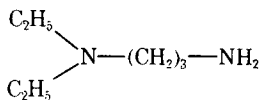
The average molecular weight of the resin is 370–384,<sup>21</sup> yielding a weight per epoxide (WPE) of 185–192. An average WPE of 186 was chosen for calculational purposes.

Since Epon 828 has a viscosity of 10,000 to 15,000 cps at 25°C, a monofunctional diluent, styrene oxide, was introduced at a concentration of 25 parts per hundred of resin (phr) in order to reduce the viscosity of the mix. Styrene oxide has the following structure:



with a WPE of 120.

Since a long pot life is needed to allow sufficient time for the epoxy resin system to penetrate into the cement, DEAPA (diethylaminopropylamine) was chosen as the curing agent. It has the following structure:



Previous research<sup>22</sup> has shown that mechanical strength and crosslinking are optimized when the concentration of DEAPA is at 25% of the stoichiometric amount (SA).

On these bases, then, the system Epon 828/DEAPA (25% SA)/styrene oxide (25 phr) was chosen in the present work as the basic mix for use in impregnation of HCP and mortars.

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