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**STUDIES OF COMPOSITES MADE BY IMPREGNATION OF
POROUS BODIES. 2. POLYMETHYL METHACRYLATE
IN PORTLAND CEMENT SYSTEMS**

ANALYZED

by **R.F. Feldman** and **J.J. Beaudoin**

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STUDIES OF COMPOSITES MADE BY IMPREGNATION OF
POROUS BODIES. 2. POLYMETHYL METHACRYLATE
IN PORTLAND CEMENT SYSTEMS

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ABSTRACT

Porous bodies formed by autoclaving portland cement-silica mixtures and by normally curing portland cement were characterized by measuring Young's modulus, microhardness and porosity. These bodies were impregnated with methyl methacrylate and irradiated, the procedure being carried out twice. The bodies were almost completely impregnated. Increases in mechanical properties were greater for microhardness but less for Young's modulus when compared to sulphur impregnation. It was concluded that polymethyl methacrylate forms a stronger bond with the matrices studied than does sulphur.

Les corps poreux préparés à partir d'un mélange ciment-silice de portland dans un autoclave et du curage habituel du ciment portland ont été caractérisés en déterminant le module de Young, la microdureté et la porosité. Ces corps ont été imprégnés de méthacrylate de méthyle et irradiés. Le procédé a été recommencé deux fois. Les corps ont été presque complètement imprégnés. L'augmentation des propriétés mécaniques a été plus élevée quant à la microdureté, mais moins élevée quant au module de Young en comparant avec l'imprégnation de soufre. En conclusion, le méthacrylate de polyméthyle produit un liant plus fort que le soufre, au moins dans les moules étudiés.

Impregnation of porous bodies can increase the values of their mechanical properties by several hundred per cent and bring about large improvements in their water impermeability (1-3). Several workers (4-6) attempted to explain these large increases using equations based on a mixing rule, but owing to the size of the specimens and problems with homogeneity, consistent results were not obtained.

Hasselman et al (7), in their studies of porous ceramic materials, used expressions derived for composites containing flat or elliptical inclusions, which related the effect of a second phase on elastic behaviour to the stress concentration in the matrix phase. Values calculated from these expressions agreed with large increases in microhardness and Young's modulus observed for a variety of cement-based matrices impregnated with sulphur (8). This paper presents the results for methyl methacrylate impregnation of the cement-based matrices used in the previous study (8). A comparison of the mechanical properties (microhardness and modulus of elasticity) for composites made with the same cement-based matrices and two different impregnants should provide a means of assessing the relative contribution of both impregnants to these composite properties. The use of several matrices having different pore size distributions and surface areas should provide information about the contribution of the matrix and matrix-impregnant interaction to the behaviour of the composite.

Experimental

Specimens used were 3.2 cm diameter discs, 1.3 mm thick to facilitate complete and homogeneous impregnation. Samples used for impregnation were the same type used in previous work (8): silica, portland cement mixtures having 5, 10, 20, 30, 50 and 65% by weight of silica, each series prepared at water to cement ratios of 0.22, 0.26, 0.30, 0.35, 0.40 and 0.45, respectively. Samples of cement paste prepared at water to cement ratios of 0.25, 0.45, 0.70 and 1.1 and hydrated at room temperature for 8 years were also used.

Methods

1. Porosity Determination

Porosity was determined before and after impregnation by measuring solid volume by helium comparison pycnometry; this has been described previously (8). The apparent volume was determined by weighing in methanol, samples saturated with methanol.

2. Mechanical Properties

Young's modulus and microhardness of the samples were determined before and after impregnation. Techniques used for these measurements have been previously described (8). Ten hardness measurements were made on each disc.

3. Impregnation

Five discs, conditioned at 11% R.H., were vacuum-saturated with methyl methacrylate monomer in a vacuum vessel; specimens were contained in a metal basket (9). After saturation the samples were raised above the excess monomer and, in the presence of its vapour, exposed to cobalt radiation, $\approx 2,500$ rad/min for 17 h. After the mechanical properties and porosity were measured, the samples were re-impregnated to reduce residual porosity due to shrinkage during polymerization, and re-exposed to the radiation.

Results

The volume fraction of polymer and the residual porosity after the two impregnations are presented in Table I together with data for Young's modulus and microhardness. The volume fraction of polymer is derived from the initial

porosity minus the residual porosity. Calculation of the density of the polymer showed some variance between samples indicating that pores had probably formed within the polymerized mass, which could not be reached by the helium during measurement of residual porosity. However, in most cases, a residual porosity of between one and three per cent was observed.

Regression lines of the data for modulus of elasticity versus volume fraction of polymer, and microhardness versus volume of polymer are plotted in Figs. 1 and 2, respectively. The equations for the regression lines are listed in Table II. The results show that the lower the volume fraction of polymer, the higher the values of Young's modulus and microhardness of the composite, as was found for the sulphur impregnated bodies. However, for Young's modulus, the curves for the polymer composites have lower values than the corresponding sulphur composite at the same volume fraction. The data for microhardness shows a different trend; the values at low volume fractions are higher and at high volume fractions similar to those of the sulphur impregnated bodies.

TABLE I

Volume Fraction, Density and Mechanical Property Data for all Samples

SiO ₂ Content %	W/C Ratio	Residual Porosity, %	Polymer		E _c		H _c MPa × 10 ⁻¹ (measured)	E ₀₂ MPa × 10 ⁻³ (calculated)	
			Volume	Density	MPa × 10 ⁻³				
			Fraction	gm/cc	(measured)	(calculated)			
5	0.22	3.16	0.2292	0.921	26.1	13.58	146.0	7.37	
10		3.53	0.2263	1.094	29.1	14.15	161.1	8.69	
20		3.08	0.1841	1.057	30.1	15.50	146.8	10.44	
30		3.70	0.1486	1.145	27.1	16.13	152.9	9.37	
50		1.64	0.1777	1.022	25.5	14.68	135.7	8.84	
65	0.26	1.97	0.2230	1.055	22.5	12.94	124.4	7.79	
5		2.29	0.2896	0.989	25.3	11.17	139.2	9.72	
10		2.77	0.2687	1.039	24.1	12.20	123.1	8.01	
20		0.38	0.2153	-	26.4	13.69	137.6	8.48	
30		2.19	0.1792	0.959	26.2	14.28	126.1	10.23	
50	0.30	2.50	0.1990	0.923	24.4	13.64	123.7	9.01	
65		2.23	0.2790	1.001	23.1	10.93	107.7	10.43	
5		0.82	0.3130	0.988	24.5	10.43	104.6	10.08	
10		1.00	0.3027	1.005	23.5	10.99	102.7	8.70	
20		0.34	0.2662	0.952	23.2	11.60	109.4	8.80	
30	0.35	1.15	0.2368	1.026	24.1	11.81	120.0	10.73	
50		0.97	0.2561	0.954	22.6	11.36	114.2	9.57	
65		0.77	0.3009	0.954	21.3	10.27	98.8	9.26	
5		3.65	0.3581	1.054	20.4	9.33	101.7	8.86	
10		3.54	0.3364	1.097	21.8	10.02	98.5	8.67	
20	0.40	2.40	0.2952	1.082	22.9	10.58	99.8	9.31	
30		3.17	0.2758	1.101	20.5	10.35	108.4	8.93	
50		2.60	0.2981	1.032	19.0	10.21	99.7	8.13	
65		3.29	0.3435	1.040	17.9	9.29	85.8	8.50	
5		3.65	0.3932	1.137	18.9	8.59	103.3	8.77	
10	0.45	3.67	0.3782	1.092	18.0	9.03	102.9	7.72	
20		2.88	0.3249	1.041	20.1	9.91	94.7	9.83	
30		4.04	0.3253	1.135	18.9	9.43	87.2	8.91	
50		2.49	0.3425	1.038	18.0	9.14	83.7	8.46	
65		4.07	0.3578	1.057	16.5	9.00	88.1	7.27	
5	0.45	5.15	0.4146	1.165	17.4	8.21	82.1	8.31	
10		3.47	0.3964	1.113	15.5	8.65	89.1	6.82	
20		2.54	0.3700	1.043	18.5	8.88	101.8	8.58	
30		2.93	0.3611	-	20.0	8.68	79.4	10.39	
50		3.03	0.3707	1.030	16.2	8.59	88.6	7.81	
65	Vycor	3.41	0.3943	1.029	15.3	8.29	82.4	7.21	
ROOM TEMPERATURE PASTE									
		0.25	0.58	0.1437	-	24.7	14.72	142.3	11.84
		0.45	2.11	0.2768	-	21.1	10.03	109.8	11.54
		0.70	2.43	0.4338	-	13.2	7.27	95.5	7.52
	1.10	4.02	0.5653	1.120	9.8	5.95	68.6	6.33	
	Vycor	0.75	0.3087	1.123	18.4	9.27	331.9	7.36	

The data for Young's modulus and microhardness, grouped in water/cement ratios, are plotted against the original silica content of the mix (Figs. 3A and 3B). As observed previously for the sulphur (8), the physical and mechanical properties of the matrix material, determined by the silica content and nature of the hydration product, are important in determining the mechanical properties of the composite. Generally, the maximum values are at the low silica end of the curves. These matrices are composed largely of αC₂SH, which has a very high Young's modulus and microhardness, although these properties may not be high for the body itself owing to poor bonding between crystals.

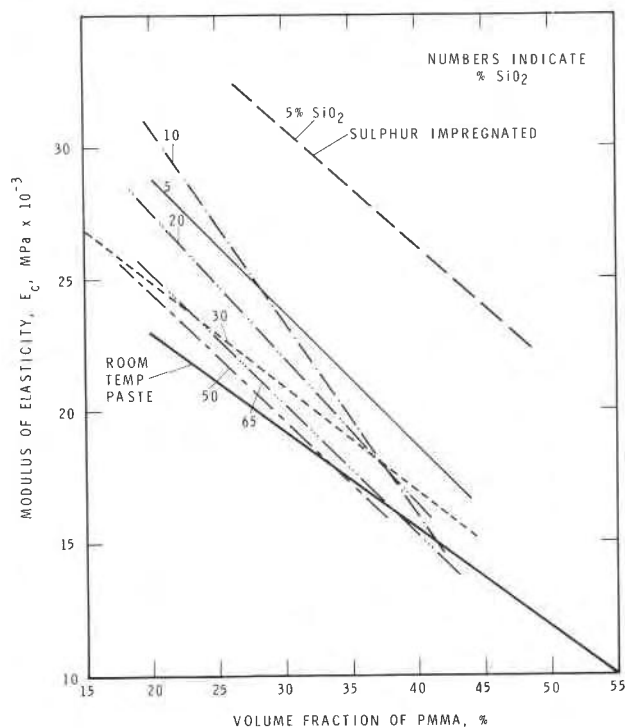
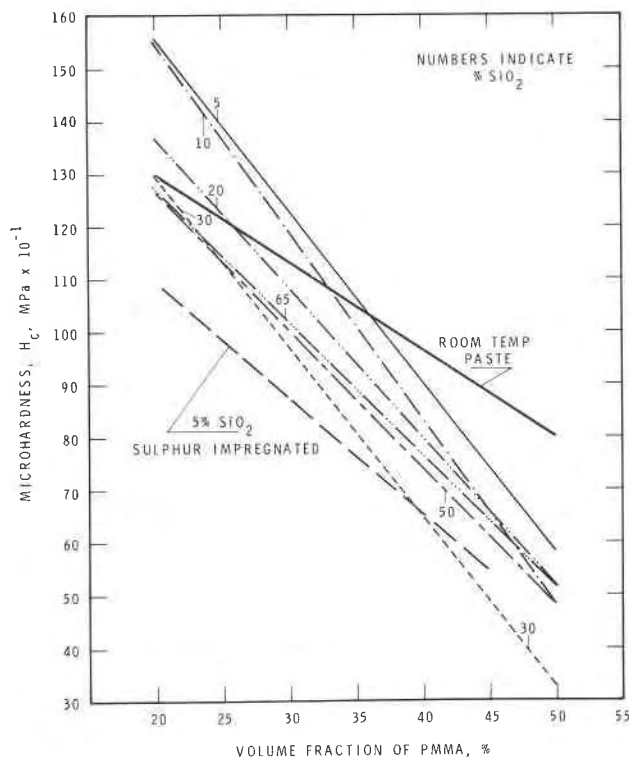


FIG. 1

Young's modulus of composite vs volume fraction of polymethyl methacrylate (PMMA) for preparations with different initial silica contents (linear regression lines)

FIG. 2

Microhardness of composite vs volume fraction of polymethyl methacrylate (PMMA) for preparations with different initial silica contents (linear regression lines)



Discussion

The results from the impregnation of these matrices with sulphur (8) were found to correlate with Reuss's model equation,

$$E_c = 1 / \left(\frac{V_1}{E_{01}} + \frac{V_2}{E_{02}} \right) \quad (1)$$

where E_c , E_{01} , E_{02} are Young's modulus for the composite, zero porosity matrix and zero porosity impregnant, respectively, and V_1 and V_2 are the volume fractions of the matrix and impregnant, respectively. The maximum deviation of the regression lines of the experimental data from the above equations varied between 4 and 18% for the different sulphur impregnated matrices.

Calculations for polymethyl methacrylate impregnated bodies have been made. When E_c is computed using Reuss's equation and 3.63×10^3 MPa as the value for E_{02} (the value measured for polymethyl methacrylate formed in the bulk phase, i.e., outside the pores), one observes that the measured E_c is 1.7 to 2.3 times this calculated value. The two values of E_c are compared in Table I.

TABLE II

Equations and Correlation Coefficients from Linear Regression Analysis of Data for Mechanical Properties and their Ratios E_c/E_u and H_c/H_u vs Volume Fraction of Polymethyl Methacrylate

% SiO_2	H_c		H_c/H_u	r (%)
	MPa $\times 10^{-1}$	r (%)		
5	220.92 - 324.7 V_p^*	91.45	-3.78 + 27.3 V_p	96.9
10	226.6 - 356.7 V_p	87.66	-2.30 + 20.7 V_p	86.5
20	193.3 - 283.8 V_p	89.98	-0.03 + 9.5 V_p	84.1
30	194.3 - 323.0 V_p	97.7	1.16 + 5.1 V_p	92.7
50	178.3 - 257.8 V_p	97.5	0.64 + 8.3 V_p	86.4
65	178.3 - 254.0 V_p	97.5	-0.77 + 12.7 V_p	84.0
Room Temp.				
Paste	162.7 - 165.6 V_p	98.5	-5.64 + 37.9 V_p	92.3

% SiO_2	E_c		E_c/E_u	r (%)
	MPa $\times 10^{-3}$	r (%)		
5	39.06 - 50.93 V_p	96.18	-0.890 + 9.4 V_p	98.5
10	45.36 - 73.31 V_p	97.86	0.423 + 4.3 V_p	82.5
20	38.75 - 55.66 V_p	98.75	0.697 + 2.6 V_p	89.0
30	32.95 - 39.9 V_p	94.98	0.705 + 2.9 V_p	96.4
50	34.12 - 48.07 V_p	99.00	0.654 + 3.7 V_p	99.6
65	35.15 - 49.6 V_p	92.53	0.623 + 3.8 V_p	87.3
Room Temp.				
Paste	30.45 - 37.4 V_p	99.17	1.25 + 1.97 V_p	68.9

* Volume fraction of polymer

The discrepancy between the calculated and measured values for E_c may be due to one of three factors: Reuss's model is not applicable, the properties of the polymer in the pores are dissimilar to those of the bulk phase, or the polymer acts in a different way in reinforcing the composite. If Reuss's equation is used to calculate E_{02} , using the measured value of E_c , the values vary from 6.3 to 11.8×10^3 MPa (Table I). This is approximately two to over three times the value of the polymer formed in bulk. However, these moduli values for the polymer are still lower than the value for sulphur (13.9×10^3 MPa).

* Any relation between the calculated E_{02} and pore size in the autoclaved samples is not clear but on the other hand there is not a very sharp distinction between the pore size distributions of these samples. The room-temperature hydrated paste samples, however, cover a wide range of porosities and the 0.7 and 1.1 water/cement ratios would contain a large proportion of large pores. The calculated

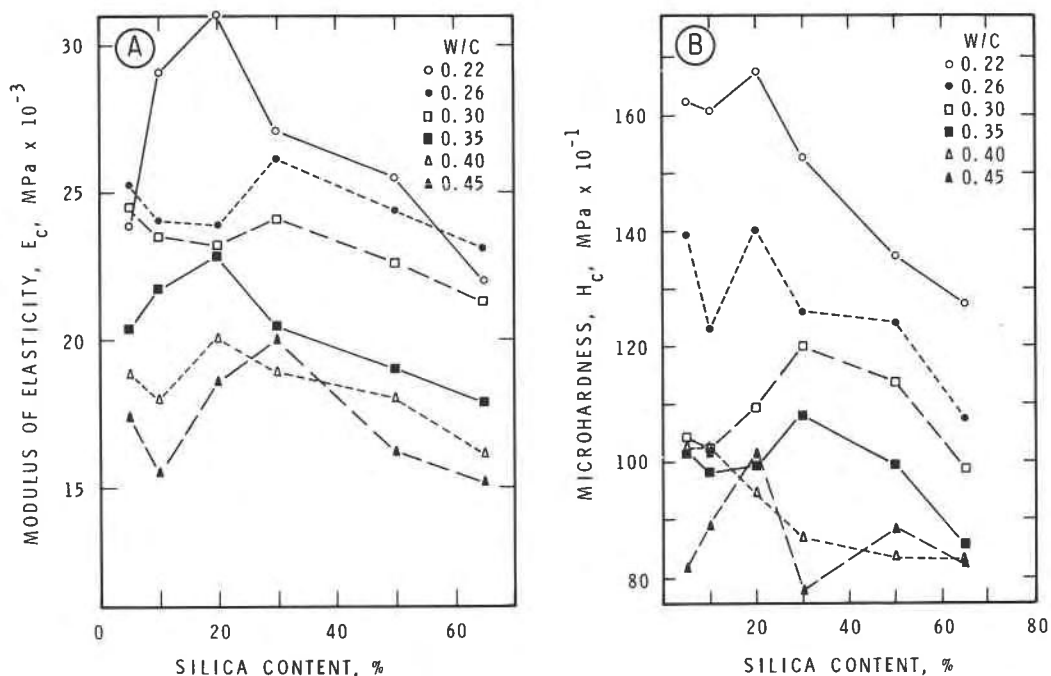


FIG. 3

Initial silica content vs (A) Young's modulus and (B) microhardness

values for E_{02} for the water/cement ratios of 0.25, 0.45, 0.7 and 1.1 are 11.84, 11.54, 7.52 and 6.33×10^3 MPa, respectively (Table I). The Young's modulus of the bulk polymer is largely determined by van der Waal's force between the long chains. However, when these long chains are formed in pores having diameters of the same size as the length of the chains, they may bond on both sides of the pore or crack; as a result, the properties of the polymer as it affects the composite may depend on the covalent bonds within the chain, resulting in a higher Young's modulus. As the proportion of large pores in which bonding across surfaces cannot occur, increases, one should expect the mean Young's modulus to decrease. This effect may be illustrated in the results for the room-temperature cured paste (Table I). Manson (2) has reported changes in the glass transition temperature of about 50°C for the polymethyl methacrylate in the pores; this may be due to the effects discussed above.

The ratios E_c/E_u (modulus of elasticity of impregnated sample to that of unimpregnated sample) vs volume fraction of polymer and the corresponding H_c/H_u ratios are plotted in Figs. 4A and 4B, respectively. The equations for the regression lines are listed in Table II. The fact that Young's modulus values are lower for polymer impregnated bodies than sulphur impregnated bodies at the same volume fraction is clearly shown, the maximum values being 2.8 for the polymer and 3.9 for the sulphur; this is consistent with Reuss's model. However, the converse is shown for microhardness where the maximum value is 7.4 for the polymer and 5.7 for the sulphur. The results for polymer show, as did sulphur, that the 5 and 10% silica contents yield the maximum ratio.

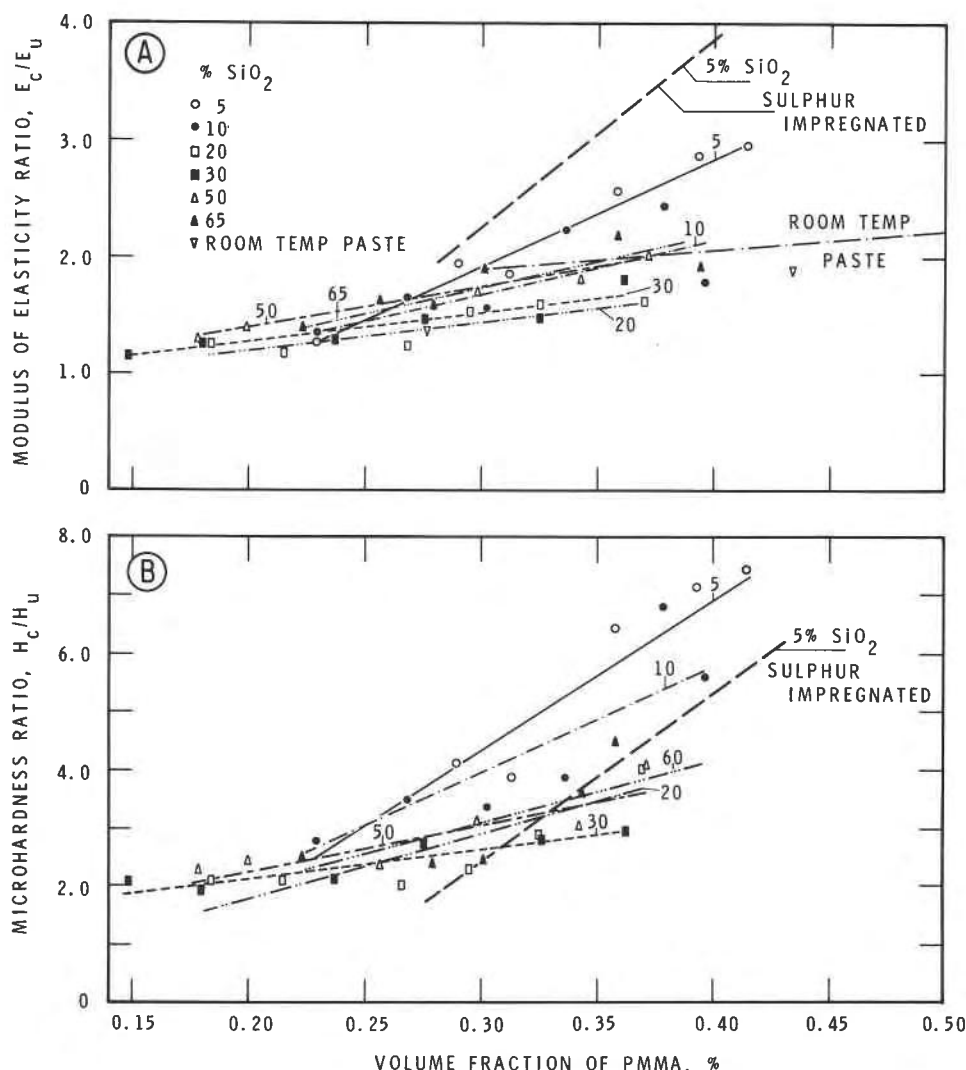


FIG. 4

Volume fraction of polymethyl methacrylate (PMMA) of composite vs (A) ratios E_c/E_u (modulus of elasticity of impregnated sample to that of unimpregnated sample) and (B) ratios H_c/H_u (microhardness of impregnated sample to that of unimpregnated sample). (Linear regression lines)

The microhardness of bulk polymethyl methacrylate was measured to be 290 MPa, while H_0 for sulphur (microhardness at zero porosity) had a minimum value of 716 MPa. Calculations of microhardness of the composite, using expressions employed by Hasselman (7) (assuming the bulk value for microhardness of the polymer in the pores), gave values that were lower than the measured values, contrary to the results for sulphur impregnated composites. The difference between the calculated and measured microhardness values of the

polymer impregnated composites decreases dramatically as the porosity of the unimpregnated porous body increases.

These results suggest that either the H_0 for the polymer in the pores is much higher than for the bulk polymer (and for the sulphur) or the polymer has a much greater facility for bonding with the surface of the hydrated portland cement or modifying regions of stress concentration in the composite. It is also possible that these mechanisms occur simultaneously.

In the previous study (8), all the sulphur composite samples expanded when exposed to 100% R.H. They disintegrated within ten days, with the exception of the 5 and 10% original silica content samples which remained intact. This disintegration did not occur with the polymer composite indicating that the polymer-matrix bond is superior to the sulphur-matrix bond. Further work on this aspect of the problem is continuing and will be reported subsequently.

Conclusions

1. Large increases in Young's modulus and microhardness of portland cement-based porous bodies can be achieved by impregnation with methyl methacrylate.
2. Increases in microhardness due to impregnation are greater with methyl methacrylate than sulphur at the same volume fraction; increases in Young's modulus are less with methyl methacrylate.
3. Reuss's model mixing rule cannot be applied directly to results for methyl methacrylate by assuming bulk properties of the impregnant.

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