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**STUDIES OF COMPOSITES MADE BY
IMPREGNATION OF POROUS BODIES. 1. SULPHUR
IMPREGNANT IN PORTLAND CEMENT SYSTEMS.**

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

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STUDIES OF COMPOSITES MADE BY IMPREGNATION OF POROUS
BODIES. 1. SULPHUR IMPREGNANT 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 almost completely with molten sulphur. The bodies were characterized again. It was found that the mechanical properties of the composites could be described by a form of Reuss' mixing law. Equations relating the improvement of the mechanical properties of the composite to the properties of the porous body were derived for both Young's modulus and microhardness.

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 presque complètement de soufre fondu. Les corps ont été caractérisés de nouveau. On a constaté que les propriétés mécaniques de composites obéissaient à une forme de la loi des mélanges de Reuss. Les équations reliant l'amélioration des propriétés mécaniques du composite, aux propriétés des corps poreux ont été établies pour le module de Young aussi bien que pour la microdureté.

New types of composites have been produced by the recently developed technique of impregnating porous materials with polymer. This has been performed on porous ceramic tile (1), cement, and concrete (2,3). Physical properties have been found to increase by several hundred per cent and large improvements in water impermeability and resistance to corrosion have been achieved. These results suggest that polymer-impregnated concrete may have many practical applications and indeed the development of the material has advanced more rapidly than the basic understanding of the system.

Several workers (4,5,6) have tried to apply a mixing rule to the system to explain the results. A high degree of impregnation has been difficult or impossible to achieve, however, owing to the size of the specimens, and thus bodies approximating to non-porous uniformly impregnated specimens were not obtained. Most of this work has involved concrete which is a complex composite. Main conclusions were that the elastic modulus and compressive strength of the impregnated concrete are functions of the residual porosity after impregnation and that the increase of fracture energy of impregnated cement is due entirely to the polymer itself, as opposed to the possible effect of pore filling on the cement or concrete system. It was also concluded that the final strength was independent of the initial strength of the porous body (5).

Hasselman et al (7) noted that large increases in elastic moduli are surprising in the light of present theories of elastic behaviour of composites with fibrous, cylindrical or spherical inclusions. They concluded that the pore geometry must deviate considerably from these models and they theoretically analyzed flat or elliptical inclusions. Expressions were derived relating the effect of a second phase on elastic behaviour to the stress concentration in the matrix phase.

Sulphur impregnation has been shown (8) to improve strength greatly. This paper presents the results for the sulphur impregnation of several porous solids. The theory discussed above is extended in this work to fracture processes; microhardness as well as the elastic properties of the sulphur impregnated composites are correlated with composition by a mixing-rule which accounts for stress concentrations.

Experimental

Specimens used were 3.2-cm diameter discs, only 1.3 mm thick to facilitate complete and homogeneous impregnation. The sulphur was reagent grade containing 3 p.p.m. of H_2S . Samples used for impregnation were the same ones used in previous work (9): silica, portland cement mixtures having 5, 10, 20, 30, 50 and 65% by weight of silica, each series prepared (autoclaved) 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. Discs 0.127 cm thick and 3.2 cm in diameter were cut from each preparation.

Methods

Porosity was determined by measuring the solid volume by helium comparison pycnometry as described previously (9). The apparent volume was determined by weighing samples saturated with methanol in methanol.

The Young's modulus and microhardness of the samples have also been reported (9). These properties were measured again after the samples were impregnated with sulphur. The procedure involved measuring the deflection of the disc specimen when loaded at its centre and supported at three points on the circumference of a circle 2.5 cm in diameter. A Leitz microhardness

testing machine with a Vickers indenter was used for the microhardness measurements. Ten hardness measurements were made on each disc and three discs were tested for each preparation.

Five discs of each preparation were impregnated. Prior to impregnation the samples were maintained at 128°C in vacuum for 24 h. They were then weighed and placed in another vacuum vessel with solid sulphur and evacuated for 1 1/2 h. This vessel was then placed in a 128°C bath for a minimum of 24 h. The sulphur melted and the samples became completely immersed in it. After this the samples were removed and the sulphur allowed to solidify within the pores. A direct weighing after excess sulphur was removed from the surface with kerosene yielded the quantity of sulphur impregnated. Then the residual porosity was measured by determining the new solid and apparent volumes of the specimens by the helium comparison pycnometer.

Results

(i) Volume fraction of sulphur

The porosity, pore and bulk volume data for all the samples are presented in Table I; also included is the residual pore volume after impregnation.

The initial porosity minus the residual porosity, A-C, is taken as the volume fraction of solid sulphur. Calculations for volume of sulphur impregnated, based on an assumed bulk density showed, however, that pores were probably formed within the solidified mass that could not be reached by the helium in the measurement of residual porosity. The amount of sulphur taken up and the use of the bulk density for liquid sulphur indicated that all but the samples of water-cement ratio 0.22 and 0.26, were almost completely impregnated. Using A-C as the volume fraction of solid sulphur, the average density of the solid sulphur is 1.872 gm/cc, but omitting water-cement ratios 0.22 and 0.26, the density is 1.937 gm/cc which is about 5% lower than the bulk value of 2.066 gm/cc. The shrinkage of the sulphur on solidification is probably responsible for this difference. Thus there are two types of porosity present in the samples; one that is inaccessible and one that is accessible to helium. If the density of the sulphur in the pores is equal to that of bulk solid then the volume fraction may be calculated from the weight as shown in Table I column D. This differs from A-C by an average of about 2% pore volume. It is concluded that the inaccessible porosity was trapped in the solidified sulphur. This occurred to a relatively greater extent for the low volume fractions of sulphur; the accessible porosity occurred mainly for the higher volume fractions.

Least square fits were made to observe dependence of Young's modulus of the composite on the volume fraction of sulphur determined by the two foregoing methods. This analysis showed that the dependence was about the same for both, indicating that the shape and orientation of the pores within the solidified sulphur was such that their effect on Young's modulus was minor compared with the effect of accessible pores of the original matrix. Assuming this, however, can be a source of error. Young's modulus, for the different silica contents, is plotted against volume fraction of sulphur (A-C), in Fig. 1.

(ii) Mechanical properties of impregnated samples

The results presented in Table I and Figs. 1 and 2 show that the larger the sulphur volume fraction, the smaller the Young's modulus and microhardness, respectively, for each composition; also that the volume fraction of sulphur does not uniquely define the mechanical properties.

TABLE I - Volume Fraction and Residual Porosity Data for All Samples

Si Content %	W/C Ratio	Porosity %	Pore Volume cc	Bulk Volume cc	Residual Porosity %	A-C %	Volume Fraction of Sulphur Using Solid Bulk Density
		A	B		C		D
5	0.22	28.0	1.376	4.92	0.02	27.98	21.77
10		26.3	1.207	4.60	0.11	26.10	22.63
20		21.5	1.092	5.10	0.32	21.18	17.55
30		19.0	0.912	4.85	0.40	18.60	15.11
50		20.8	1.050	5.12	0	20.80	15.82
65		24.6	1.213	5.01	0	24.60	19.80
5	0.26	32.46	1.568	4.83	2.82	29.64	26.96
10		29.90	1.94	2.42	2.78	27.48	
20		20.80	1.011	4.86	1.54	19.26	16.44
30		18.69	0.929	4.97	0.78	17.91	15.45
50		20.41	1.086	5.32	1.67	18.74	16.64
65		27.25	1.455	5.34	1.59	25.66	21.84
5	0.30	32.36	1.612	4.98	1.47	30.89	28.74
10		31.31	1.575	5.03	1.33	29.98	27.56
20		23.63	1.172	4.96	0.73	22.90	20.85
30		23.05	1.164	5.05	1.43	21.62	19.39
50		25.45	1.257	4.94	0.63	24.82	20.93
65		27.94	1.433	5.13	1.42	26.52	25.54
5	0.35	39.30	1.910	4.86	2.35	36.95	35.82
10		36.47	1.707	4.68	2.65	33.82	33.44
20		30.29	1.439	4.75	2.29	28.00	26.42
30							
50		32.81	1.575	4.80	2.90	29.91	27.25
65		36.57	1.719	4.70	2.64	33.93	31.70
5	0.40	42.15	1.981	4.70	4.36	37.79	37.46
10		40.34	1.916	4.75	3.87	36.47	36.21
20		34.93	1.722	4.93	3.10	31.83	30.18
30		35.34	1.735	4.91	3.36	31.98	30.31
50		35.64	1.739	4.88	2.48	33.16	31.23
65		38.96	2.026	5.20	3.23	35.73	34.15
5	0.45	46.17	2.193	4.75	4.21	41.96	39.73
10		44.63	2.196	4.92	3.76	40.87	37.95
20		40.55	2.056	5.07	3.75	36.80	34.44
30		40.46	1.999	4.94	3.74	36.72	34.74
50		41.52	1.993	4.80	1.98	39.54	35.40
65		44.01	2.157	4.90	3.16	40.85	37.18
ROOM TEMPERATURE PASTE							
	0.45	32.20	1.506	4.67	1.99	30.21	28.10
	0.70	49.57	2.345	4.73	5.08	44.49	43.21
	1.1	62.54	2.905	4.65	4.59	57.95	54.58
	0.25	12.10	0.575	4.75	1.49	10.61	10.55

FIG. 1

Young's modulus of composite vs volume fraction of sulphur for preparations with different initial silica contents

The physical and mechanical properties of the matrix material, determined by the silica content and nature of hydration product, are important in determining the mechanical properties of the composite and a closer examination of this is necessary. The dependence of the modulus of elasticity and microhardness on silica content for the impregnated specimens is presented on Figs. 3A and 3B respectively. Figure 3A shows that for a given water to cement ratio the modulus decreases with increasing silica content. At the higher water-cement ratios the effect is not so great. This is in contrast to the modulus of elasticity of the unimpregnated bodies, for which there is a sharp maximum at 20 to 30% silica content (4). In Fig. 3B it is shown that the hardness data for impregnated samples has a maximum at 20 to 30% silica content similar to the data for unimpregnated samples; however a similar change between the impregnated and unimpregnated samples was observed as with the modulus data in that values of microhardness of the low silica content materials increased with respect to the others.

Figures 1, 2 and 3 (A and B) show that both the characteristics of the matrix and the volume fraction of the impregnant influence the properties of the composite. The regression lines for modulus of elasticity and microhardness vs volume fraction of sulphur and the correlation coefficients are included in Table II and are mostly in the 95% range. The room-temperature hydrated paste has the lowest modulus values and is not very different from the 20, 30 and 50% silica composites. The

FIG. 2

Microhardness of composite vs volume fraction of sulphur for preparations with different initially added silica contents

increasing sulphur content) shown in Fig. 1. When the porosity of the unimpregnated material is increased, the modulus of elasticity decreases, but the potential for an increase on impregnation becomes greater. E_C/E_U is greatest for the 5 and 10% silica composition. This emphasizes that relatively high moduli were obtained for these bodies despite their low initial values.

Observations on the dependence of H_C/H_U , microhardness of the impregnated to that of the unimpregnated samples, on volume fraction of sulphur are plotted on Fig. 5A along with regression lines. The behaviour is very similar to that for the modulus of elasticity, with the 5 and 10% silica compositions showing the greatest increase. The points for the room temperature paste are again close to the lines for 20 and 30% silica compositions.

FIG. 3

Young's modulus (A) and microhardness (B) vs initially added silica for composites with different water-cement ratios

microhardness measurements show similar but not as well-defined trends as the modulus results.

(iii) Improvement of mechanical properties by impregnation

In Fig. 4A regression lines are drawn through each set of points for given silica contents. The points for the room temperature paste are again close to the 20 and 30% silica composition lines. E_C/E_U increases with volume fraction of sulphur; this is not inconsistent with the results for modulus versus volume fraction of sulphur, (decreasing modulus with

TABLE II - Equations and Correlation Coefficients from Linear Regression Analysis of Data

% Si	H_{01} MPa $\times 10^{-2}$	H_c MPa $\times 10^{-1}$	$r(\%)$	H_c/H_u	$r(\%)$
5	30.27	$152.7 - 230.4 V_s$	88.8	$-5.71 + 27.1 V_s$	98.8
10	33.96	$183.2 - 329.4 V_s$	87.8	$-2.28 + 15.96 V_s$	92.8
20	32.89	$167.7 - 280.2 V_s$	97.3	$+0.550 + 5.50 V_s$	93.9
30	18.16	$149.1 - 231.7 V_s$	97.2	$+0.614 + 5.32 V_s$	98.6
50	21.83	$120.3 - 154.1 V_s$	90.0	$+0.644 + 5.00 V_s$	93.8
65	39.45	$108.5 - 146.1 V_s$	87.5	$-0.943 + 9.985 V_s$	96.5
Rm. temp. Paste	14.5				
Sulphur	7.2				

% Si	E_{01} MPa $\times 10^{-2}$	E_c (MPa $\times 10^{-3}$)	$r(\%)$	E_c/E_u	$r(\%)$
5	704.7	$59.4 - 88.29 V_s$	98.9	$-2.35 + 15.5 V_s$	96.0
10	887.2	$53.8 - 74.6 V_s$	95.7	$-0.51 + 9.24 V_s$	91.5
20	568.9	$41.9 - 51.7 V_s$	89.7	$0.61 + 4.10 V_s$	98.0
30	387.3	$37.9 - 40.7 V_s$	92.5	$0.59 + 4.37 V_s$	98.6
50	419.8	$35.7 - 36.4 V_s$	94.8	$0.42 + 5.95 V_s$	97.7
65	477.5	$39.9 - 49.2 V_s$	94.5	$0.76 + 5.01 V_s$	81.7
Rm. temp. Paste	300.0	20.69			
Sulphur	139.0	19.3			

The ratios E_c/E_u and H_c/H_u for modulus of elasticity and microhardness are plotted against each other in Fig. 6. The regression line is $H_c/H_u = -0.4576 + 1.323 E_c/E_u$ with a correlation coefficient of 89.1%. An H_c/H_u value of 3.0 for hardness was found to be equivalent to an E_c/E_u value of 2.6 for the modulus of elasticity.

(iv) Factors contributing to the properties of the composite

These results show that the volume fraction of the impregnant is an important factor controlling the mechanical properties of the composite and one would expect that the mechanical properties of the impregnant are

also important. It was shown that some characteristics of the matrix are also important. This last factor can be considered as composed of the bulk material and the interfacial interactions between the bulk material and the second component, be it a pore or impregnant. For the purpose of this analysis, E_{01} and H_{01} , the values of E_u and H_u of the solid constituent obtained by extrapolation of the logarithm of the mechanical property vs porosity plot to zero porosity (9), are listed in Table II. The quantities $-\partial E_c/\partial V_s$ and also $\partial(E_c/E_u)/\partial V_s$ are plotted against E_{01} in Fig. 7; a significant correlation is evident.

Linear regression analysis gave correlation coefficients of 0.85 and 0.63 respectively. This shows that the rate of change of modulus of the composite with volume fraction of sulphur is dependent on E_{01} of the matrix material; this is true to a lesser extent for the E_c/E_u ratio. Analysis of the microhardness relationship of $\partial H_c/\partial V_s$ and $\partial(H_c/H_u)/\partial V_s$ vs H_{01} showed no significant correlation, but when these terms were plotted against E_{01} , linear regression analysis gave correlation coefficients of 0.74 and 0.69 respectively.

This last correlation may be surprising but previous work (9) showed that there was a linear correlation between Young's modulus and microhardness for a variety of preparations including samples for all the silica contents except 65% and including all the porosities studied. If this correlation is assumed valid also for zero porosity then values of E_{01}/H_{01} in Table II should be constant within the accuracy of the analysis. The better correlations obtained with E_{01} as well as the fact that the hardness data correlates significantly with E_{01} and not at all with H_{01} leads one to suspect that some of the H_{01} extrapolations presented in the previous paper (9) were inaccurate. This will be discussed later.

(v) Models and equations to predict properties of impregnated bodies.

(1) Moduli of elasticity

FIG. 4

Ratios E_C/E_u (modulus of elasticity of impregnated sample to that of unimpregnated sample) vs volume fraction of sulphur of composite.

(A - Experimental; B - Theoretical)

FIG. 5

Ratios H_C/H_u (microhardness of impregnated sample to that of unimpregnated sample) vs volume fraction of sulphur of composite.

(A - Experimental; B - Theoretical)

Modulus of elasticity of unimpregnated portland cement paste has been shown to be dependent on porosity. Hasselman (7,10) demonstrated that for porous ceramic bodies having flat pore geometry, major changes in elastic moduli resulting from polymer impregnation can be explained even when the elastic modulus of the impregnant is considerably less than that of the matrix.

When porous bodies of this type are filled with sulphur it is probable that stress concentrations arising from low area bonds between crystallites are modified, their modification being dependent on the ratio E_{01}/E_{02} . Those small pores which may not have become filled with sulphur probably do not significantly affect the value obtained for modulus of elasticity if the stress required for crack propagation is not reached.

Hasselman applied an expression that relates the relative effect of the impregnant on the elastic behaviour of the composite to the stress concentration factor in the matrix phase. The shear modulus of the composite is

FIG. 6

Ratio E_c/E_u for Young's modulus vs ratio H_c/H_u for microhardness

FIG. 7

Plot of $-\partial E_c/\partial V_s$ and $\partial(E_c/E_u)/\partial V_s$ respectively for the various systems vs E_{01}

expressed as follows:

$$G_c = G_{01} [1 + \{\alpha V_s / (1 + \gamma V_s)\}] \quad (1)$$

where G_c is the shear modulus of the composite, G_{01} is the shear modulus of the bulk material of the matrix and V_s is the volume fraction of the second phase. The constant ' α ' is given by

$$\alpha = [(\eta - 1)/\eta]\beta \quad (2)$$

where $\eta = G_{02}/G_{01}$ and G_{02} is the shear modulus of the second phase; β is a stress concentration factor. The effect of an elliptical discontinuity in an infinite plate under shearing edge forces was studied by Donnell (11). Donnell derived the following equation for stress concentration factor β :

$$\beta = \frac{K(P + 1)}{[(1 - K) \{(R - 1)^2 / (R + 1)^2\}] - (KP + 1)} \quad (3)$$

where $K = E_{02}/E_{01}$, $P = (3 - \nu)/(1 + \nu)$ for plane stress and R is the major to minor axis ratio of the elliptical inclusion. Substitution in Eq. (2) results in:

$$\alpha = \frac{(K - 1)(P + 1)}{[(1 - K)(R - 1)^2 / (R + 1)^2] - (KP + 1)} \quad (4)$$

The Poisson's ratio, ν , of the two phases are assumed equal. The term $\gamma = (\alpha - K + 1)/(K - 1)$. For flat pore geometry ($R \rightarrow \infty$) and Eq. (4) becomes

$$\alpha = (K - 1)/K \quad (5)$$

As $R \rightarrow \infty$, $\beta \rightarrow 1$ and the effect of stress concentration is removed. When R varies from 10 to 100, β increases from 0.71 to 0.997, demonstrating that β can be approximately equal to unity for a value of $R > 100$. For an isotropic elastic material

$$G = E/2(1 + \nu) \quad (6)$$

and assuming the Poisson's ratio, ν , of the two phases are equal, Eq. (1) can be written as follows:

$$E_c = E_{01} [1 + \{\alpha V_s / (1 + \gamma V_s)\}] \quad (7)$$

When $\beta \rightarrow 1$, Eq. (7) reduces to:

$$E_c = 1 / \left(\frac{V_1}{E_{01}} + \frac{V_2}{E_{02}} \right) \quad (7A)$$

Equation (7A) is the same as the equation derived from Reuss' model (10). There is closer agreement between Eq. (7) and experimental values of composite modulus of elasticity as $\beta \rightarrow 1$. This observation suggests that if flaws are present they do not significantly influence the modulus of elasticity of the composite for the cementitious systems studied. Equation (7A) is plotted in Fig. 1 using values for E_{01} and E_{02} obtained by extrapolation of plots of $\log E$ versus porosity to zero porosity for each phase (9,12). The maximum deviations from Eq. (7A) of the regression lines of the experimental data for preparations containing 5, 10, 20, 30, 50 and 65% silica are 7.2, 18.8, 17.9, 4.0, 9.4 and 18.8% respectively. It is clear that at higher volume fractions of sulphur, the actual moduli values decrease at a greater rate than predicted by Eq. (7). Possible reasons for this aside from assumptions made in the derivation of theory, are:

(a) There is a residual porosity as shown in Table 1. This becomes larger at higher volume fractions of sulphur and the shape of these residual pores might change with volume fraction.

(b) The determination of the zero porosity modulus, obtained by extrapolation is subject to error.

(c) E_{02} , assumed constant, may not be independent of pore size in the matrix. If E_{02} is not correct error in E_c will be magnified as volume of sulphur increases.

(2) Microhardness

Experimental values of microhardness for the sulphur impregnated preparations showed a similar dependence to that for modulus of elasticity on volume fraction of sulphur. The ratio H_c/H_u also showed a dependence on volume fraction of sulphur similar to that in the E_c/E_u ratio.

Consequently one would expect a similar form of mixing rule equation relating microhardness of the composite to volume fraction of sulphur, thus:

$$H_c = H_{01} \left[1 + \left(\alpha V_s / (1 + \gamma V_s) \right) \right] \quad (8)$$

where α , γ and V_s are as previously defined and H_c and H_{01} are the microhardness values of the composite and the matrix material respectively.

Unlike the modulus of elasticity property, microhardness measurements involve failure processes; any sharp-angled crevices present in the preparations would represent sites of potential crack propagation and failure. If stress concentration factors are not included, i.e., $\beta \rightarrow 1$ the agreement of Eq. (8) with experiment is extremely poor. To try to account for this poor agreement, stress concentration factors in the matrix due to the presence of a solid discontinuity were considered.

Donnell (11) studied the effect of an elliptical discontinuity in an infinite plate subjected to uniaxial tension. He derived the following expression for stress concentration in the matrix:

$$\beta = \frac{(8 + 2K - K^2) R^2 + (4 + 13K + K^2) R + 9K}{9K(R^2 + 1) + 2(2 - K + 8K^2) R} \quad (9)$$

Here, the terms are the same as for modulus, as in Eq. (3) but in the expressions for α and γ , the normal K is replaced by κ (defined as H_{02}/H_{01}).

As $R \rightarrow \infty$ the following values are obtained for β :

%Si	5	10	20	30	50	65	Room Temp. Hydrated
β	4.66	5.71	4.19	2.64	2.85	3.34	2.10

Equation (8) is plotted in Fig. 3 (with $R \rightarrow \infty$) together with the regression lines for the experimental data. It is clear that there is greater deviation between theory and experiment for microhardness than there is for the modulus of elasticity. However, except for the 65% silica composition, the microhardness at the low volume fraction of sulphur is within 15% of the equation, but the experimental values decrease at a much greater rate with volume fraction. This may be due again to the increase in volume of residual pores as discussed for modulus of elasticity and due to the shortcomings of the simple theoretical approach; this will be discussed later.

Ratios E_c/E_u and H_c/H_u

The ratios E_c/E_u and H_c/H_u can be calculated by dividing Eqs. (7) and (8) by $E_u = E_{01} \exp(-b_E P)$ and $H_u = H_{01} \exp(-b_H P)$ (9). This means that the terms E_{01} and H_{01} in Eqs. (7) and (8) outside the main bracket will be eliminated. The calculated elastic modulus ratios are plotted on Fig. 4b; it can be seen that there is fair agreement with the experimental values in Fig. 4a. The curve for the room temperature paste is close to the 20% silica content in both sets of curves. The experimentally determined microhardness ratios are plotted on Fig. 5a, and range at 40% volume fraction of sulphur from 2.7 to 5.1. The ratios calculated for microhardness are plotted on Fig. 5b and range from 3.1 to 4.4 at 40% volume fraction. At 20% volume fraction of sulphur, both sets of data are clustered around the microhardness ratio of 1.5. In the case of the ratios of H_c/H_u for the 65% silica composition, the agreement between observed and calculated curves at the high volume fraction of sulphur is considerably improved over the microhardness, H_c , predictions. This suggests that the extrapolation for H_{01} for the 65% composition is too high, and accounts for the large discrepancy between the experimental and calculated microhardness shown on Fig. 2.

Discussion

1. A porous body, having randomly distributed pores, has regions of stress concentration when loaded externally. The impregnation of the body by some material should modify these stress concentrations. The extent of modification will depend on how well the impregnant has penetrated the smaller pores and sharp angle contact points between crystallites, if they exist, and its bonding to the surface.

The application of Eqs. (7) and (8) assumes implicitly that the bond at the interface between the two phases is enough to allow transfer of stress at any point along the interface. It is possible to conceive of the situation where little or no stress is transferred due to poor or zero bond, and the mixing rule equations could not be expected to apply. When many areas of stress concentration exist in unimpregnated bodies, values of their mechanical properties may be low even though values of mechanical properties of the individual crystallites are high. The improvement in mechanical properties when these bodies are impregnated with sulphur is due to a modification of these stress concentrations and increased content of solid in the porous body.

The analysis of the results for the moduli of all the composites by Eq. (7A), indicates that, when under shear load and assuming the flat plate model, there are no stress concentrations in the fully impregnated two-phase composite. However in the unimpregnated porous body shear stress transfer takes

place only at points of contact between crystals which gives rise to stress concentrations in the matrix in the region of the contact points. Impregnation apparently modifies the material in such a way that stress concentrations in the matrix are eliminated when the two-phase composite is subjected to shear. This conclusion is contrary to that of Auskern (5) who, in determining fracture energies of impregnated paste, assumed that the increase in fracture energy of the composite "is considerably higher than the unimpregnated cement and appears to be all contributed by the polymer phase".

Analysis of the results of microhardness by Eq. (8) shows that for all compositions application of uniaxial stress on the composite still produces stress concentrations in the body, but relatively high ratios H_c/H_u compared with the ratios E_c/E_u would indicate that stress concentrations have been modified. This conclusion explains the relatively high increase in modulus and microhardness of the 5 and 10% silica composition. Despite their relatively high E_{01} , H_{01} and density (9) both these compositions had relatively low values of E_u and H_u . Very high stress concentrations at points of low contact area and poor bonding between strong crystallites can result in a weak matrix; these concentrations appear to have been modified by the impregnant and the bonding of the crystallites improved.

2. The difference for all compositions between the experimental data and the curves calculated from Eqs. (7) and (8), is much greater for microhardness than for Young's modulus (Figs. 1 & 2). The residual porosity which becomes greater at high volume fractions of sulphur is one of the reasons for the discrepancy of both sets of data. Errors in values of E_{02} and H_{02} as well as imperfect matrix/sulphur bond might also be reasons for the discrepancy. Microhardness determinations involve stresses up to crack initiation levels and the results might thus be more susceptible to error due to residual porosity than the moduli results.

The derivation of Eq. (8) cannot be considered as rigorous. It was derived essentially for a crack propagating from a single source rather than the more complicated case of a distribution of stress concentrations forming several small cracks which join to form a catastrophic crack. The validity of applying mixture laws to the fracture process must also be questioned. It depends on how the individual phases perform during the fracture process.

The results of this study are for cement-silica systems which were maintained dry. It is not known what effect water vapour will have on these systems because some water may enter them due to inadequate sealing of the pores.

Conclusions

1. Increase in hardness of nearly 500%, and in elastic modulus of nearly 300% has been obtained through impregnation with sulphur. Impregnation of the 5 and 10% silica preparations, initially the weakest bodies, resulted in the strongest bodies, presumably due to the presence of large quantities of potentially strong but poorly bonded crystallites.

2. Young's modulus and microhardness of a completely impregnated composite may be described by an equation similar to that derived from Reuss' model.

(a) For modulus of elasticity the volume fraction of each component and its elastic modulus at the zero porosity state are the main variables. For the modulus data it is found that the behaviour of the composite is described assuming elliptical flat pore geometry.

(b) The increase in microhardness depended on volume fractions of each component and the microhardness at zero porosity of each component, H_{01} and H_{02} . Reuss' model was modified to describe microhardness behaviour. This

conclusion appears valid for all the compositions studied including room-temperature cured paste.

3. The increase in elastic modulus and microhardness can be predicted from the derived equations.

4. Mechanical properties data for sulphur-impregnated room-temperature hydrated paste is similar to that for impregnated and autoclaved 20 and 30% silica content systems. This suggests the similarity of these matrices in the impregnated and unimpregnated states.

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