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Informal Report

**FRACTURE ENERGY AND STRENGTH OF
POLYMER IMPREGNATED CEMENT**

A. Auskern and W. Horn

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FRACTURE ENERGY AND STRENGTH OF POLYMER IMPREGNATED CEMENT

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ABSTRACT

The fracture energy, or effective surface energy of hardened cement paste and polymer-impregnated hardened cement paste, was measured by an analytical method. The fracture energy of polymer impregnated hardened cement paste is considerably higher than the unimpregnated paste (7.5×10^4 to 0.91×10^4 ergs/cm²). The increase appears to be entirely due to the polymer contribution. The results predict a factor of 5 improvement in the fracture strength of hardened cement paste upon polymer impregnation.

Introduction

It has been known for some time that the impregnation of concrete by a liquid monomer followed by in situ polymerization of the monomer results in a material with vastly improved mechanical, elastic, and durability properties (1,2,3,4). For a typical fog or water cured portland cement concrete of compressive strength $\sim 350 \text{ Kgm/cm}^2$ ($\sim 5000 \text{ psi}$) the compressive and tensile strengths, upon polymer impregnation, increase by factors of 4-5 and Young's modulus increases by 2-3 times. A relatively small volume of polymer is responsible for this increase; typically 10-15 volume %. Since the cement phase of concrete is porous, it is in this phase that the polymer is concentrated. The concentration of polymer in the cement phase can be between ~ 30 -40 volume %, depending upon the cement content, water-cement ratio, and air content. Earlier work concludes that the effect of polymer impregnation is to increase the strength and modulus of the cement phase, and to improve the bonding between the cement and aggregate phases (2,5). It was also demonstrated that Young's modulus of polymer impregnated cement and mortar could be predicted from composite theory (5). That work indicated an improvement in modulus by a factor of about 3 upon impregnation of hardened cement paste with methyl methacrylate polymer.

The fracture energy (or effective surface energy) is

generally defined as the work required to create a unit area of new fracture surface. It is the surface energy value used in the Griffith equation, and thus is of fundamental importance in elucidating the mechanical properties of brittle materials (6). By comparing the fracture energy of polymer impregnated hardened cement paste with that of unimpregnated hardened cement paste, it should be possible, through the Griffith equation, to rationalize the observed strength improvements of polymer impregnated hardened cement and polymer impregnated concrete.

Only a few measurements of the effective surface energy of hardened cement paste have been reported (7,8,9). No measurements of the effective surface energy of polymer impregnated cement have been found. In general the effective surface energy of hardened cement paste is around that of glass, $5-10 \times 10^3$ ergs/cm² (6). It appears to increase slightly with duration of cure, and is about the same for mortar. It is about 50% greater for concrete (7).

In the present work measurements are made of the fracture energy of a hardened cement paste and a polymer impregnated hardened cement paste. An attempt is then made to rationalize the improvement in strength upon polymer impregnation using the Griffith equation. This has been used by Tazawa and Kobayashi (10). Their observations will be discussed in the appropriate section.

Experimental

Rectangular cement bars, 1.27 cm x 1.27 cm x 7.62 cm, water to cement ratio of 0.5, were cast from a type II A portland cement. The bars were demolded after one day, and were cured under water at room temperature for 13 additional days. The specimens were allowed to dry at room temperature for a week, and then were slowly heated (3 days) to 100°C for an additional week.

After drying, half the group was impregnated with methyl methacrylate monomer which was then polymerized. Impregnation was done by first evacuating the samples with a fore-pump, adding the monomer (which contained 0.5% AIBN^{*} catalyst), and soaking for 0.5 hr. with an overpressure of 25 psi argon. The monomer filled bars were then individually wrapped in aluminum foil, sealed in a polyethylene bag, and immersed in a water bath at 80°C overnight. The impregnated samples had an average weight loading of $27.9 \pm 0.2\%$ ^{**} which is equivalent to a volume concentration of $35.8 \pm 0.3\%$.

Young's modulus was measured for all the specimens by loading the bars in 3 point bending to a load estimated to be 25% of the fracture load.

Effective surface energy measurements were made by the analytical method described by Davidge and Tappin (6). Cracks

* azobis isobutyronitrile

** Average deviation from the mean.

were cut in the samples with a 0.03 cm thick diamond wheel. The crack depth to sample depth was 0.3. The expression used is

$$\gamma = \frac{9(1-v^2)P^2 l^2 f(c/d)}{8Eb^2(d-c)^3} \quad (1)$$

where γ is the effective surface energy; v is Poisson's ratio; P is the load at fracture; l is the span; $f(c/d)$ is a dimensionless parameter equal to 0.41 for $c/d = 0.3$; E is Young's modulus, b is the breadth; d is the depth; and c is the machined crack depth. Poisson's ratio for hardened cement paste was taken as 0.25 (11). For the polymer impregnated paste, Poisson's ratio of 0.31 was used to reflect an approximate 25% increase in Poisson's ratio when concrete is polymer impregnated (12).

The specimens were fractured in 3 point loading in an Instron testing machine at a crosshead speed of 0.0051 cm per minute. Typical load-deflection curves are shown in Fig. 1. Failure in the unimpregnated specimens was in a controlled manner.

Results and Discussion

The fact that the specimens were dried resulted in the presence of some unavoidable cracks. The drying was done in order to permit full polymer impregnation and to simulate more closely the conditions under which polymer impregnated concrete and control concrete have been evaluated. The presence of these drying cracks did not appear to influence P , the failure load

FIG. 1

Typical load-deflection curves for fracture specimens.

or c, the machined crack depth in equation 1. With two impregnated samples after most of the load had fallen off, an arresting effect was noted which might have been due to a crack perpendicular to the propagating crack. This can be seen in Fig. 1.

The machined crack had a rather square bottom, and the failure crack always propagated from a corner of the machined crack.

The effective surface energies for the unimpregnated and impregnated samples were calculated using equation 1 with the measured Young's modulus for each sample. These results are tabulated below.

TABLE I**Modulus and Fracture Energy**

<u>Loading</u>		<u>Young's Modulus</u> [*] (Kg/cm ²)	<u>Fracture Energy</u> [*] (erg/cm ²)
Unimpregnated	-	$1.3 \pm 0.1 \times 10^4$	$0.91 \pm 0.04 \times 10^4$
Impregnated	35.8 vol. %	$4.3 \pm 0.4 \times 10^4$	$7.5 \pm 0.9 \times 10^4$

* Average of 5; $\pm$ average deviation from the mean.

The work most directly comparable to that here is the work of Cooper and Figg and of Moavenzadeh and Kuguel. Cooper and Figg (8) measured, by the work of fracture method, the effective surface energy of wet and dried (at room temperature) hardened cement pastes. They used a water/cement ratio of 0.5, and their samples were cured for 40 days. They measured a surface energy of 1.2×10^4 erg/cm² for the wet samples and 1.5×10^4 erg/cm² for dry samples. These values are similar to, but somewhat greater than, the results here for unimpregnated samples. Moavenzadeh and Kuguel (7) report effective surface energies calculated from work of fracture, critical strain energy release, and critical stress intensity factor experiments. For a hardened cement paste of w/c = 0.5 cured for 14 days the range of effective surface energies is from 0.23×10^4 to $.42 \times 10^4$ erg/cm², which is about a quarter to a half the values measured here.

Brown (9) measured the fracture toughness of wet hardened

cement pastes ($w/c = .35$, 84 days cure) in a manner that accounted for slow crack growth prior to failure. His results can be compared with the critical stress intensity factors of Moavenzadeh and Kuguel (7), but only indirectly to the fracture energy. He observed a critical stress intensity factor of $390 \text{ lb/in}^{3/2}$ compared to $150 \text{ lb/in}^{3/2}$ by Moavenzadeh and Kuguel. This suggests that the effective surface energy of Brown's sample is ~ 6 times that of Moavenzadeh and Kuguel (7), or in the range $1.5 - 2.8 \times 10^4 \text{ erg/cm}^2$. This is somewhat higher than that of Cooper and Figg (8) and the present work.

The presence of polymer in the cement results in an eight-fold increase in fracture energy. Since polymer fills the continuous pore structure of the hardened cement, during fracture that polymer along the advancing crack path is fractured. The fracture energy of polymethyl methacrylate is $6 \times 10^5 \text{ erg/cm}$ (6), which is around 50 times that of unimpregnated cement. If it is assumed that one-third of the polymer is effectively perpendicular to the fracture surface, then the energy to fracture this much polymer is $1/3 (0.358) (6 \times 10^5) \text{ erg/cm}^2$ or $7.2 \times 10^4 \text{ erg/cm}^2$. This is essentially the fracture energy of polymer impregnated cement. So the fracture energy of polymer impregnated cement is due almost entirely to the fracture of the polymer; the fracture of hardened cement makes a negligible contribution.

Tazawa and Kobayshi (10) assumed for polymer impregnated mortar and concrete that all the polymer is in the form of

spheres, filling the air voids of the matrix. They then computed by an additive law the effective fracture energy of polymer impregnated mortar and concrete, using the fracture energy values from reference (7). They reach a similar conclusion, that the fracture energy of the impregnated materials is dominated by the fracture energy of the polymer. Their model, however, appears to be over simplified. First, most of the polymer resides in capillary pores, not air voids (5). Second, microscopic observation of fracture surfaces of polymer impregnated cements and mortars shows that fracture surfaces rarely pass through polymer filled voids. They generally pass around these voids. It has been observed that these voids are usually lined with a thin layer of polymer (13). Figs. 2 and 3 are scanning electron micrographs of fracture surfaces observed in this study. These areas were selected because they contain small spherical voids. Fig. 2 is of the unimpregnated sample, and the fracture surface passes right through the void. Fig. 3 is from the polymer filled sample. The impinging crack passes around the polymer filled (or partially filled) void. So the high concentration of polymer in this void did not contribute to the measured fracture energy. Note the background features in these figures. Fig. 3 appears to have a somewhat less rough texture, but it is difficult to positively identify the polymer phase.

With a knowledge of the effective surface energies, the strength improvement to be expected upon polymer filling may be

FIG. 2

Fracture surface of unimpregnated sample showing an air void of about 25 microns diameter.

FIG. 3

Fracture surface of impregnated sample showing an air void containing polymer.

predicted using Griffith's equation. This equation is

$$\sigma = A \left(\frac{E\gamma}{C} \right)^{1/2} \quad (2)$$

where σ is the fracture stress, A is a constant depending on the sample geometry, and C is the intrinsic crack or flaw length.

Using the subscript i for impregnated and u for unimpregnated,

$$\frac{\sigma_i}{\sigma_u} = \left(\frac{E_i}{E_u} \right)^{1/2} \left(\frac{\gamma_i}{\gamma_u} \right)^{1/2} \left(\frac{C_u}{C_i} \right)^{1/2} \quad (3)$$

The moduli and the surface energies are known. Tazawa and Kobayashi (10) in their analysis assumed the intrinsic flaws are the spherical voids, and that they are reduced in size upon polymer filling by an amount equal to the polymerization and thermal shrinkages - about 30%. It is assumed here that the presence of polymer does not affect the flaw length. Equation 3 can then be evaluated:

$$\sigma_i/\sigma_u = (3.31)^{1/2} (8.24)^{1/2} (1)^{1/2} = 5.2$$

These results predict a factor of ~ 5 improvement in the strength of hardened cement paste upon polymer impregnation. This seems a not unreasonable prediction, in view of the widely published results for polymer impregnated mortars and concretes (1-4, 12) and some compressive strength results for cement pastes (2). The predicted strength improvement will probably

be less for lower water/cement ratio pastes because γ_i will be lower due to the lower polymer content. This would be consistent with the observation that weaker pastes, mortars, and concretes show a greater relative strength improvement than stronger ones upon polymer impregnation (3,4,12,13).

Conclusions

The fracture energy, or effective surface energy of polymer impregnated cement is considerably higher than the unimpregnated cement and appears to be essentially all contributed by the polymer phase.

The Griffith equation predicts a not unreasonable increase in fracture strength of about 5 times for the materials tested here. The increase would be less for less porous cement pastes. The increase in fracture strength is due largely to the fracture energy increase, but there is also a significant contribution from the increase in Young's modulus.

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FIG. 1

Typical load-deflection curves for fracture specimens.

FIG. 2

Fracture surface of unimpregnated sample showing an air void of about 25 microns diameter. Taken at 1000 X.

FIG. 3

Fracture surface of impregnated sample showing an air void containing polymer. Taken at 1000 X.