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**MECHANICAL PROPERTIES OF POLYMER IMPREGNATED
CEMENT SYSTEMS AND THE EFFECT OF MOISTURE
ON THEIR DIMENSIONAL STABILITY**

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

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Des matrices de ciment on été préparées par l'autoclavage de mélanges de ciment Portland et de silice ayant des pourcentages en poids de silice variés et des rapports eau-ciment s'échelonnant entre 0,22 et 0,45. Des échantillons de pâte de ciment témoins ont également été fabriqués à des fins de comparaison. Les échantillons ont été chauffés sous vide à 100°C pendant 24 h avant d'être imprégnés d'un monomère de méthacrylate de méthyle (MMA) qui a ensuite été polymérisé. L'opération était répétée jusqu'à complète imprégnation.

On a procédé ensuite à des mesures du module de Young et de la microdureté en fonction de la fraction en volume de polymère MMA. Les résultats ont été comparés à ceux d'échantillons équivalents ayant été exposés à une humidité relative de 11%.

Des échantillons imprégnés et non imprégnés à l'autoclave et des échantillons de pâte de ciment ayant subi une cure à la température ambiante ont été exposés à un taux d'humidité relative de 100% et leurs variations de longueur mesurées pendant quatre ans.

On a constaté que la perméabilité à la vapeur d'eau des échantillons imprégnés diminuait mais n'était pas complète et que l'imprégnation amplifiait l'expansion pour une exposition de longue durée. L'expansion des échantillons exposés à un taux d'humidité relative de 100% a été plus élevée pour les matrices sèches que pour celles exposées à une humidité relative de 100%. On a constaté que pour celles exposées à une humidité relative de 100% les matrices plus résistantes.

MECHANICAL PROPERTIES OF POLYMER IMPREGNATED CEMENT SYSTEMS
AND THE EFFECT OF MOISTURE ON THEIR DIMENSIONAL STABILITY

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ABSTRACT

Cement matrices were prepared by autoclaving portland cement-silica mixtures having various percentages by weight of silica, with water-to-cement ratios of from 0.22 to 0.45. Normal cement paste samples were also made for comparison. Samples were heated to 100°C in vacuum for 24 h before impregnation with methyl methacrylate monomer (MMA), which was then polymerized; impregnation was repeated for complete impregnation.

Young's modulus and microhardness were measured as a function of volume fraction of PMMA and results compared with those obtained from similar samples conditioned to 11% RH.

Autoclaved impregnated and unimpregnated specimens and room-temperature-cured cement paste specimens at both conditions were exposed to 100% RH and their length changes measured for up to four years.

Permeation to water vapour in the impregnated specimens, although decreased, still occurs and impregnation increased long-term expansion on exposure. Expansion on exposure to 100% RH is much larger for D-dried than for 11% RH-conditioned matrices; the latter produced stronger bodies on impregnation.

Introduction

The mechanical property values of porous cement systems can be increased by several hundred percent by impregnation. Impregnation also results in large decreases in water permeability (1-3). Earlier work with sulphur as an impregnant showed that these large increases can be accounted for using equations based on a Reuss' mixing rule (4). However, exposure of some sulphur-impregnated matrices, especially those with high surface areas, to 100% RH results in dimensional changes, often leading to destruction and extrusion of sulphur (5).

Studies on cement-based matrices impregnated with methyl methacrylate (MMA) have shown that increases in microhardness over the unimpregnated state

are greater than for those with sulphur, for the same volume fraction of impregnant (6). These studies indicated that polymethyl methacrylate (PMMA) in micro-pores forms a better bond with the matrix than sulphur and that the properties of PMMA in the micro-pores of cement paste are different from those for PMMA in large pores. The rate of expansion of MMA-impregnated cement systems exposed to 100% RH might, therefore, be significantly different than the rate of expansion of sulphur-impregnated cement systems. It has been observed that MMA-impregnated porous glass, when exposed to 100% RH, remains stable, although some expansion does occur, and this may be partly due to gradual absorption of water by the polymers (7).

This work is a continuation of the study on MMA-impregnated porous glass. The extent to which water can enter (on long-time exposure) cement systems impregnated with MMA, and the factors controlling their durability, are determined. Autoclaved cement-silica mixtures were selected to obtain matrices having a wide range of properties. For example, varying silica content from 0 to 65% by weight gives hydration products having significantly different pore structure, density, and chemical composition. Properties of D-dried MMA-impregnated cement systems are compared with similar systems conditioned only to 11% RH before impregnation. (At 11% RH many of the interlayer positions in the cement hydrate are occupied by water.) These comparisons are based on the mechanical properties of the composites and the length-change response on exposure to 100% RH.

Experimental

Specimens used were thin discs, 32 mm in diameter and 1.3 mm thick, in order to facilitate complete and homogeneous impregnation. Samples used were the same type used in previous work (8): a series of 36 autoclaved (216°C, 2.04 MPa) portland cement-silica mixtures, having 5, 10, 20, 30, 50 and 65% by weight of silica, were prepared with water-to-cement ratios of 0.22, 0.26, 0.30, 0.35, 0.40 and 0.45. Samples of cement paste, prepared at water-to-cement ratios of 0.45, 0.70 and 1.10 and hydrated at room temperature for eight years, were also used. All samples were heated in vacuum for 24 h at 100°C before impregnation.

Methods

Porosity Determination

Porosity was determined before and after impregnation by measuring solid volume by helium comparison pycnometry, as described previously (4). The apparent volume was determined by weighing in methanol, samples saturated with methanol.

Mechanical Properties

Young's modulus and microhardness of the samples were determined before and after impregnation, using techniques described in reference 4. The modulus values given are average values for five discs, and the hardness values are the average of ten measurements made on each of three discs.

Impregnation

Discs conditioned in vacuum at 100°C for 24 h were vacuum-saturated with methyl methacrylate monomer in a vacuum vessel; specimens were contained in a metal basket. After saturation the samples were raised above the excess monomer and, in the presence of its vapour, exposed to cobalt radiation (41.7 rad/s) for 17 h. After the mechanical properties and porosity were measured, the samples were re-impregnated and re-exposed to the radiation (6) to reduce porosity due to shrinkage occurring during polymerization.

Exposure to 100% RH

Thirty by ten millimetre prisms were cut from the discs, both before and

after impregnation, and used for length-change measurements; they were mounted on 25-mm gauge length extensometers with sensitivity of 1×10^{-4} mm/25 mm. These systems were enclosed in vacuum chambers and exposed to 100% RH. Although autoclaved specimens were prepared at several w/s ratios, only those specimens prepared at w/s of 0.45 and the room-temperature-cured paste at w/c of 0.70 were selected for exposure to 100% RH (5). The w/c = 0.70 specimen was used since it has a porosity similar to the autoclaved specimens at w/c of 0.45.

Results

Mechanical Properties

As in the previous paper (samples preconditioned at 11% RH), modulus of elasticity and microhardness of the D-dried samples were plotted against the volume fraction of polymer (6). The regression lines are shown in Figs. 1 and 2. The volume fraction of polymer is derived from the initial porosity minus the residual porosity; most of the residual porosities are less than one percent.

FIG. 1

Modulus of elasticity vs volume fraction of PMMA for autoclaved cement-silica mixtures D-dried prior to impregnation.

FIG. 2

Microhardness vs volume fraction of PMMA for autoclaved cement-silica mixtures D-dried prior to impregnation.

Although the modulus of elasticity, and microhardness vs polymer volume fraction curves for D-dried and 11% RH-conditioned specimens show similar trends, (i.e., the relative position of the curves with respect to each silica content is similar) the values at any volume fraction of polymer for a given

silica content are generally about 20% less for D-dried specimens than for the specimens conditioned at 11% RH. The maximum ratio of modulus of elasticity of impregnated samples to that of unimpregnated, for D-dried specimens, is 2.5 as compared to 3.5 for specimens conditioned at 11% RH; corresponding ratios for microhardness are 5.5 and 7.5.

The data for Young's modulus and microhardness grouped in water/solids ratios are plotted against the original silica content of the mix (Figs. 3A and 3B). As was observed in earlier work with samples conditioned at 11% RH, the maximum values of Young's modulus for D-dried specimens are at the low-silica end of the curves (6). In the case of microhardness there is a maximum at 20% silica content for most ratios.

FIG. 3

Dependence of modulus of elasticity and microhardness on silica content of MMA-impregnated autoclaved cement-silica mixtures D-dried prior to impregnation

Length Change on Exposure to 100% RH

The results for unimpregnated specimens conditioned at 11% RH are presented in Fig. 4. The rate of expansion for most of the unimpregnated specimens decreased considerably after one-day exposure and is lowest for the 5 and 10% silica preparation.

For the impregnated samples conditioned at 11% RH prior to impregnation, (Fig. 5) the rate of expansion is lower than for the unimpregnated bodies for all the specimens up to a maximum of about seven days; after 75 days exposure the impregnated samples have all expanded more than twice the amount of the unimpregnated specimens. The expansion continued in the period measured from 100 to 1450 days without termination. It is greatest for the room-temperature paste. The amount of expansion

FIG. 4

Expansion of unimpregnated autoclaved cement-silica mixtures ($w/s = 0.45$) exposed to 100% RH after equilibration at 11% RH.

approximately conforms to observations made for sulphur-impregnated bodies, where higher surface-area materials had greater expansion (5).

The results for exposure of the D-dried specimens to 100% RH are presented in Fig. 6 (unimpregnated) and Fig. 7 (impregnated). The unimpregnated samples were all still expanding at 1450 days, even though the rate of expansion decreased with time throughout. The expansion was greatest for the 0.70 w/c paste and least for the 5 and 10% SiO₂ preparations; the expansion for most of the preparations is about four times that of the specimens conditioned to 11% RH.

The D-dried impregnated specimens show similar characteristics to those conditioned at 11% RH in that they exceeded the expansion of the unimpregnated specimens at 3-11 days exposure. After 920 days of exposure they all exceeded the values of the unimpregnated specimens by about 40 to 100% and the rate of expansion at the termination of measurement was considerably in excess of those for the unimpregnated bodies. It was also slightly greater than the rate for the impregnated specimens conditioned at 11% RH in the period between 200 and 1000 days of exposure.

FIG. 5

Expansion of MMA-impregnated autoclaved cement-silica mixtures ($w/s = 0.45$) exposed to 100% RH after equilibration at 11% RH.

FIG. 6

Expansion of unimpregnated autoclaved cement-silica mixtures ($w/s = 0.45$) exposed to 100% RH after D-drying.

All the autoclaved cement-silica specimens conformed approximately to the observation that the greater the specific surface area of the matrix material, the greater the expansion on exposure to water vapour.

A comparison of length-change results on exposure to 100% RH for the 0.70 w/c paste specimens with four different treatments is presented in Fig. 8. The increased length change due to D-drying, as opposed to conditioning at 11% RH, is evident. Expansion of impregnated samples is greater than that of unimpregnated samples after 20 days.

Discussion

D-dried portland cement systems containing polymerized MMA have greatly-increased mechanical properties. These increases, however, are not as high as those for systems pre-dried to only 11% RH prior to impregnation; in that case, they are probably partly due to the presence of interlayer water. This factor may not be as important with regard to durability as the increased shrinkage of D-dried bodies during drying over the 11% RH condition or as the

FIG. 7

Expansion of MMA-impregnated autoclaved cement-silica mixtures ($w/s = 0.45$) exposed to 100% RH after D-drying.

FIG. 8

Expansion of room temperature hydrated MMA-impregnated cement paste ($w/c = 0.70$) exposed to 100% RH.

resultant larger expansion of D-dried bodies that may occur when the impregnated body is exposed to high humidities. It is clear that impregnation does not completely seal the pores from water vapour; not only does the water vapour re-enter the pores and adsorb on some of the cement matrix interface, as was shown previously for porous glass (7), but it also re-enters the vacated interlayer spaces of the D-dried specimen. This is apparent from the magnitude of the expansion. However, the expansion is somewhat retarded by the presence of polymerized MMA in the pores. This result also suggests that little MMA enters the interlayer spaces in the time available before polymerization.

The expansion of the impregnated D-dried and 11% RH-conditioned specimens is considerably greater than of similar specimens not impregnated. The rate of expansion after 100 days exposure is of the same order as a normal creep rate for cement paste. Beyond ten days exposure, some of the expansion may be due to creep of the matrix brought on by pressure created within the pores by swelling of polymerized MMA due to absorption of water. This explanation is supported by the observation that in this region the expansion increases with surface area of the matrix, which generally increases with silica content (5).

The difference between sulphur-impregnated and MMA-impregnated cement systems (where the sulphur-impregnated matrices of larger surface areas are totally destroyed on exposure to water vapour) is in the interaction between the impregnant and the matrix. In the case of the MMA as impregnant, an interaction seems to occur with the matrix at the interface, although it is not clear whether it is chemical or purely physical (9); PMMA acts as a good stress modifier and reinforces the matrix, despite the fact that it provides the forces which cause the matrix to creep.

The above phenomena will undoubtedly take place in impregnated concrete, although slowly. The specimens used in this study were thin (about 1 mm) and measurements were carried out over a period of four years. In sulphur-impregnated systems, paste was destroyed in 24 hours and concrete in a few years (5). The present study would indicate that polymer-impregnated concrete will probably not be destroyed even over long periods of exposure. However, it would be beneficial to avoid the extreme D-drying that normally is done prior to impregnation.

Conclusions

1. PMMA-impregnated cement matrices have improved mechanical properties over unimpregnated material.
2. Permeability to water vapour is decreased by impregnation but water can

- still permeate the body at a slower rate.
3. Water vapour enters both the pores and the layered structure of the C-S-H material after impregnation.
 4. Expansion on exposure to 100% RH is larger for D-dried matrices than for matrices conditioned at 11% RH before impregnation.
 5. Expansion on exposure to 100% RH is increased by impregnation for both D-dried and 11% RH-conditioned material.
 6. Stresses in the pores of impregnated material are caused by absorption of water in PMMA in the pores. This appears to cause long-term creep expansion.
 7. Concrete conditioned to 11% RH can be successfully impregnated and is more stable to water exposure than the D-dried material.

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