

Impregnation of Mortars with Monomers and Their Radiolytic Polymerization

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Synopsis

Mortars were cured for a sufficient period to give sufficient strength and were then dried to remove the free water without dehydrating the compounds formed. Dried specimens were evacuated and impregnated with a mixture of styrene and acrylonitrile monomers which gives high mechanical properties after polymerization. Positive pressure was then applied, and polymerization was done radiolytically. The effect of degree and period of evacuation, the positive pressure and the irradiation dose on monomer loading, tensile and compressive strength were studied, and the optimum operating conditions were established. The achieved strength was correlated with the fraction of open pores impregnated. The composites investigated have the same volume fraction of mortar, and the polymer is added at the expense of the open porosity causing nearly an exponential increase in strength. Only 80% of the open pores were filled with polymers due to the difference in density between the polymer and the monomer, loss of monomer, and the presence of entrapped gas consisting of residual air and residual water vapor and monomer vapor, as well as due to the inability to fill all the micropores with monomer. A compressive strength four times that of plain mortar and a tensile strength eight times that of plain mortar were achieved.

INTRODUCTION

Although concrete is an excellent building material, its use is subject to certain limitations. These include its relatively low tensile strength, a tendency to crack with changes in temperature and moisture, and the deterioration due to permeability absorption, chemical and physical attack under various environmental conditions. Concrete-polymer materials, on the other hand, have outstanding strength and durability and can be used as materials of construction for such applications as reactors, nuclear technology, highways and bridge decks, pipes, desalination plants, marine use, storage bunkers for explosive chemicals and military applications.¹⁻⁵ Extensive work was carried out on composites formed by polymerization of monomers with cement (or concrete) as aggregates (known as polymer-concrete composites, PC) and by adding a monomer to a fresh concrete mixture which is subsequently cured (known as polymer-portland cement concrete, PPCC). While the first type is expensive and its strength decreases with temperature, the second type gives modest strength. On the other hand, incorporating a monomer in the pore structure of preformed cured concretes and *in situ* polymerization is known as polymer-impregnated

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concrete (PIC) and exhibits the highest degree of strength and durability.

Mortars and concretes are particulate composite materials formed from aggregates bound together with a matrix of hydrated cement paste consisting mainly of hydrated calcium silicates. During hardening a continuous intersecting 3-dimensional pore network is formed with a volume fraction depending on the water/cement ratio. These pores are accessible to monomer molecules. On the other hand, gel pores, which are extremely small with average diameter of 2×10^{-7} cm, can be formed by driving off the interlayer water held in cement gel at 105°C, and are not accessible to monomer molecules.

Previous work showed that impregnation of concrete with monomers followed by polymerization gives outstanding strength, low water absorption, high freeze/thaw resistance, and high corrosion resistance. Accordingly, numerous applications have been reported, and many others are still under investigation.¹⁻⁵

Complete hydration of cement to achieve the ultimate strength needs several years; but, after 28 days, cured concrete reaches about 80% of the ultimate strength, and, as stated by Steinberg et al.,⁶ it contains 3.5% by weight hydrated water (chemically combined water) and about 3.5% free water. Reasonable strength is required before impregnation. The strength depends on the water/cement ratio, curing conditions, type of cement, cement/aggregate ratio, type of aggregate, and its particle size distribution. These factors were kept constant during this investigation.

To increase the amount of monomer impregnated, free unreacted water is removed by drying, which should be carried out very carefully to avoid the dehydration of the formed compounds. Kukacka and Romano⁷ reported that a drying temperature of 150°C does not significantly affect the strength. Dikeou et al.⁸ found that drying in the range 150–250°C caused a slight decrease in compressive strength with increasing temperature. Although impregnation is expected to heal most of the damage formed, careful drying is expected to increase the final strength.

Steinberg et al.⁹ reported that evacuation increases sorption. Several authors¹⁰⁻¹² reported also that the rate of penetration could be significantly increased by applying positive pressures of 0.5 N/mm² gauge or more. Vanderhoff et al.¹³ indicated that the monomer will be forced from wide capillaries into narrow ones. The capillary action is opposed by the pressure of entrapped air, residual water vapor, and the vapor pressure developed from the monomer.

A monomer system with low viscosity, high surface tension, low contact angle, and low price, which can be polymerized rapidly in alkaline matrix and forms a bond with hydrated cement is needed. Most of the work was carried out using methyl methacrylate since it was considered to satisfy these requirements. Thermal catalytic and radiolytic polymerizations were carried out after impregnation, and it was found that the higher the initial strength of concrete, the higher the strength of the composites. The relative increase in weaker concretes is greater than the stronger concretes due to the high polymer loading which is achieved in porous weak concretes.¹⁴ Limited work was done on styrene, chlorostyrene, vinyl chloride, or acrylonitrile. Although styrene-acrylonitrile mixtures were tried by Zeldin et al.¹⁵ to prepare polymer-concrete composites, they were not used for im-

pregnating cured concrete and polymerization *in situ*. Bulk radiolytic and thermal catalytic polymerization of these mixtures were recently investigated by Gadalla and El-Derini.¹⁶ They found that the mixture which yields highest strength consists of 60 wt % styrene and 40% acrylonitrile, and, accordingly, this mixture was used in this study.

After impregnation, thermal catalytic and radiolytic polymerization were tried by the present authors. This study presents the results using γ -rays. A principal advantage of using radiation is that the free radical chain reaction can be induced at ambient temperature. This limits vaporization loss and produces polymerization at a uniform rate within thick concrete sections yielding higher strength. Gadalla and El-Derini¹⁶ reported that both crosslinking and degradation take place. Crosslinking increases the strength, while degradation decreases it, and there is an optimum dose for the above styrene-acrylonitrile mixture to get maximum strength.

EXPERIMENTAL

Raw Materials

(a) Pure styrene and pure acrylonitrile were supplied by "Prolabo." While the first was stabilized with 20 ppm of 4-*t*-butylpyrocatechol, the second was stabilized with 100 ppm of hydroquinone monomethyl ether.

(b) Regular Portland cement (Type I-ASTM C-150-74), with ultimate chemical analysis 21.2% SiO₂, 5.4% Al₂O₃, 3.5% Fe₂O₃, 64.3% CaO, 2.3% MgO, 1.8% SO₃, 0.7% ignition loss, and 0.3% insoluble materials, was used.

(c) Siliceous sand, graded as follows, was used:

Sieve	Accumulative % retained
No. 10 (1.65 mm)	none
No. 14 (1.18 mm)	1%
No. 20 (850 μ m)	10%
No. 30 (600 μ m)	35%
No. 40 (425 μ m)	63%
No. 50 (300 μ m)	84%
No. 100 (150 μ m)	99%

Mortar Preparation

The mortar was prepared by thoroughly mixing cement with sand (after washing and drying) in a ratio of 1:3 (by weight). Water required to give water/cement ratio of 0.7 was poured, and mixing was conducted at 23 \pm 1°C for 10 min. The water/cement ratio used in this investigation is relatively high from a technological standpoint, but it was selected to lead a high porosity, which favors impregnation and allows us to study the relative increase in strength due to the higher polymer loading in weaker concretes. Needless to say, lower water/cement ratios will produce higher strengths.

The mixture was poured in specimen molds so that the test specimens conform to the dimensions required by the standard methods for testing compressive strength and tensile strength of hydraulic cement mortars

(ASTM, C-109-73 and C-190-72, respectively). After molding, the molds were covered with moistened cloth and stored for 24 h at $23 \pm 1^\circ\text{C}$. The hardened specimens were immersed under water for the required period before testing or drying and impregnation.

Impregnation

To determine the drying temperature which can be used safely without dehydration of the cement gel, combined thermal analysis was carried out on cured ground mortar. Optimum drying time was determined by following the weight loss in a mortar cube prepared for compression test.

The dried specimens were enclosed with an aluminum foil and kept in a desiccator. Just before impregnation the specimens were weighed and then inserted in an impregnation chamber which could be evacuated to the required pressures. The specimens were left for the desired periods before allowing the monomer to cover the specimens. The specimens were kept for 10 min before applying a positive pressure to increase the loading. The effects of the initial evacuation, final pressure, and duration of impregnation were studied. After impregnation the pressure was released gradually to minimize the loss of monomer due to the sudden decrease in the chamber pressure. The specimens were reweighed to determine the monomer loading and were kept in aluminum foils ready for further steps.

Polymerization

A high intensity Co-60 gamma irradiation unit with activity 3000 curies, which gives a constant intensity of 1.8×10^5 rads/h, was used. The irradiation of impregnated specimens was uniformly conducted from all directions at the atmospheric temperature and pressure for the required time. The impregnated mortars were enveloped in aluminum foils during the irradiation to decrease the monomer loss.

Mechanical Testing

The compressive and tensile strength were conducted using the standard universal hydraulic testing machine "Amsler" with a capacity of 20 tons. All tests and methods of calculations were done according to ASTM C-109 and C-190. For each set of conditions at least five specimens were tested.

Determination of Composite Densities and Porosities

Portions of the produced composites were finely ground to pass a 100-mesh sieve. The powder was dried at 105°C to constant weight. A pycnometer was used to determine the true density (powder density).

Small cubes were cut using a diamond wheel and were dried to constant weight at 105°C . As will be indicated later, this temperature will not cause any dehydration of the cement gel. The dry specimens were immersed in boiling water for 5 h and then allowed to cool in water for 14 h to fill the open pores with water. From the weight of the specimen while soaked in water and its weight when hung in open air, apparent density and bulk density can be determined. These values can be used to calculate the open and closed porosities.

RESULTS AND DISCUSSION

Optimum Conditions for Curing and Drying the Mortar

The compressive strength was found to increase with the curing period and the rate of increase in strength decreases with time. Accordingly, mortars were prepared and cured for 15 days to achieve high strength then they were dried and impregnated immediately thereafter.

Using a heating rate of 10 K/min for cured mortar (after grinding), combined DTA, TG, and DTG curves were obtained. They are similar to those published by Stebnicka-Kalické¹⁷ and show that the maximum rate of drying occurs at 150°C. Thick specimens need much longer drying periods and/or higher temperatures. To determine the optimum drying period, a cured cube was heated gradually to 200°C using a rate of 10 K/min and the weight change was followed as a function of drying period at 200°C. After a nearly constant-rate period, for 0.5 h, the rate of drying decreases with time, and, after 4 h, only a slight decrease in weight occurred. On drying the mortar at 200°C for 4 h and repeating the thermal analysis, the peak corresponding to moisture content disappeared and all other dehydration peaks were preserved. Moreover, no deterioration of strength was detected when drying was carried out, gradually followed by maintaining the specimens at 200°C for 4 h. The compressive and tensile strengths after drying were found to be 9.4 and 1.4 N/mm², respectively, with a total porosity of about 30% (by volume). The open porosity (apparent) was about 25% while the closed porosity, which is not accessible, was found to be about 5%. The low values obtained for strength are due to the high initial water/cement ratio used in preparation to induce high porosities accessible for the monomer mixture as explained above.

Effect of Degree of Evacuation of Monomer Loading and Strength

Dried specimens were kept at absolute pressures of 600, 450, 300, 150, and 40 mm Hg for 3 h before inserting the monomer. A constant positive pressure of 0.5 N/mm² was then applied for 15 h. This pressure was selected in view of results reported by Whiting et al.¹⁰ To study the effect of degree of evacuation and other operating conditions on monomer loading and strength, polymerization was carried out using a constant dose of 7×10^6 rads. This dose was found later to be close to the optimum value for this system (see Effect of Irradiation Dose, below). For each specimen the monomer loading, the loss in monomer after polymerization, compressive strength, and tensile strength were determined. Figures 1 and 2 show the results obtained and indicate that the monomer loading and strength increase with lowering the pressure. The apparent porosity was also determined and the percentage open pores filled with polymer were found to be 33, 43, 50, and 77 at pressures of 760, 450, 300, and 40 mm Hg, respectively.

It is also evident that the loss in monomer from the thick specimens (prepared for compression) is less than the loss observed in thin specimens (prepared for tension). This conclusion is expected since the thin specimens offer less resistance to the escape of monomer. By comparing the loadings before and after polymerization, it could be concluded that the higher the degree of evacuation (deeper penetration), the lower is the monomer loss

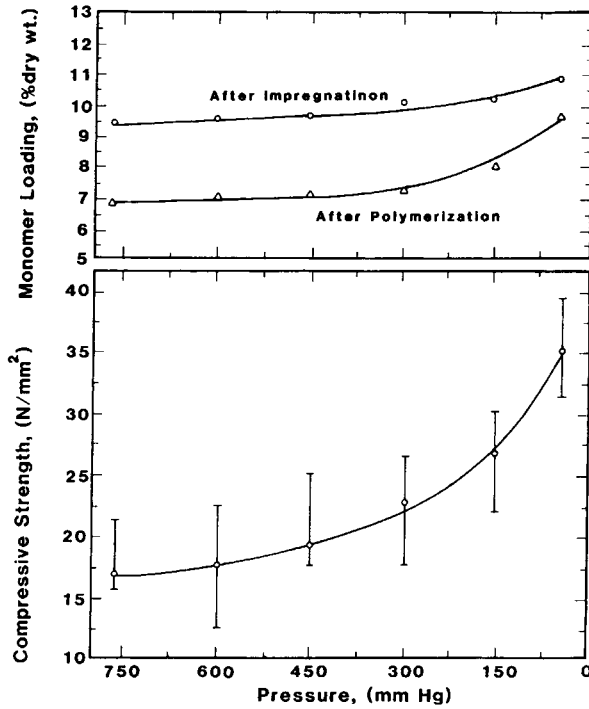


Fig. 1. Effect of evacuation pressure on monomer loading and compressive strength of PIM.

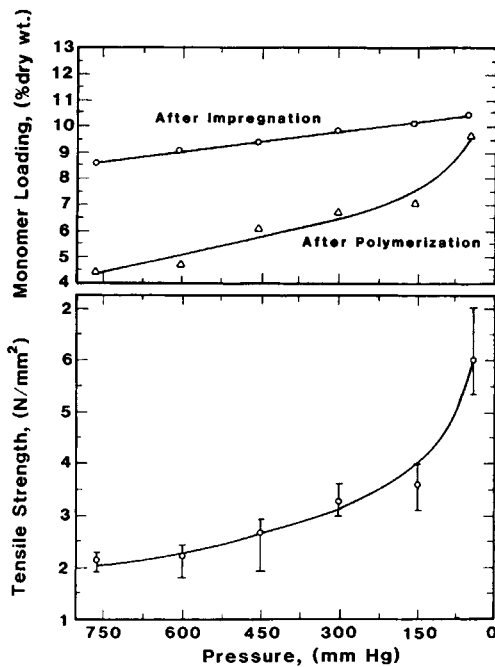


Fig. 2. Effect of evacuation pressure on monomer loading and tensile strength of composite.

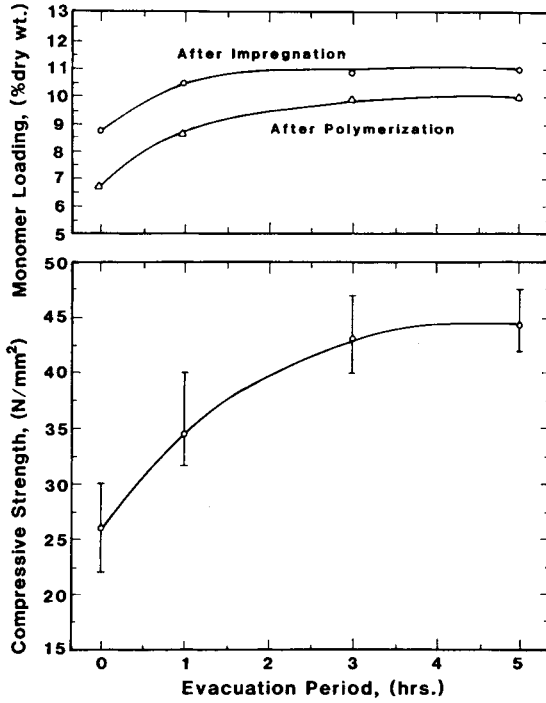


Fig. 3. Effect of evacuation period on monomer loading and compressive strength of PIM.

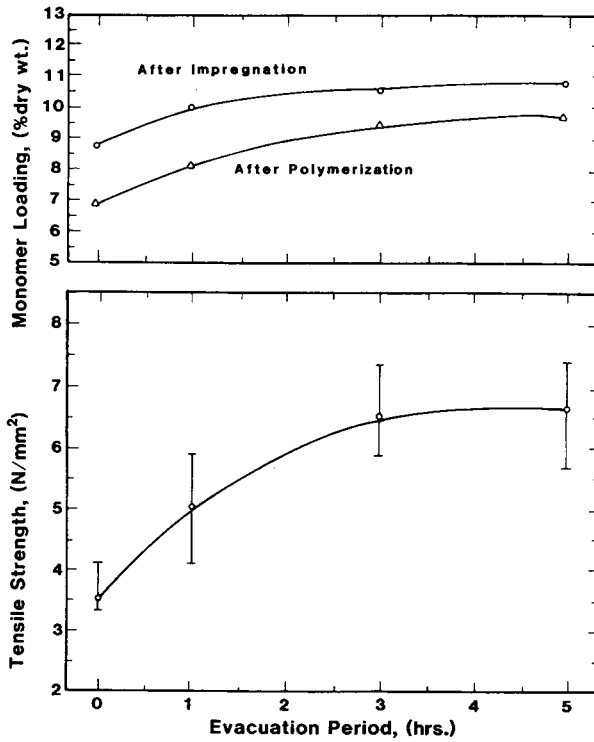


Fig. 4. Effect of evacuation period on monomer loading and tensile strength of PIM.

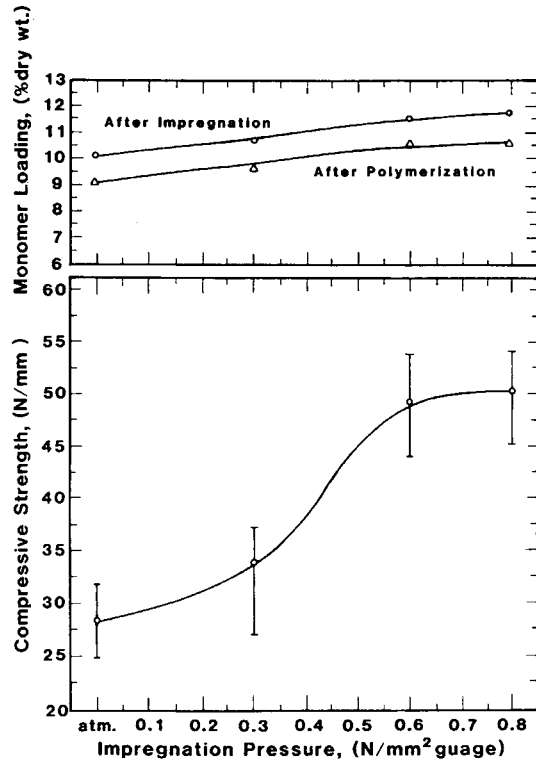


Fig. 5. Effect of impregnation pressure on monomer loading and compressive strength of PIM.

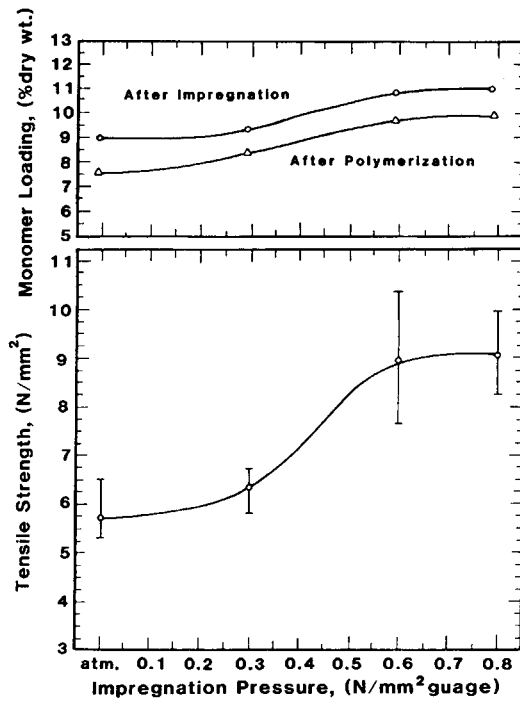


Fig. 6. Effect of impregnation pressure on monomer loading and tensile strength of PIM.

during the polymerization process. This implies that higher evacuation produces low pressure for the entrapped gases in the core and higher hydraulic heads, thus decreasing the driving force for escape.

Effect of Evacuation Period on Monomer Loading and Strength

In view of the above results the lowest pressure (40 mm Hg) was selected and evacuation was carried out for periods of 1, 3, and 5 h. All other parameters were kept constant and the results are shown in Figures 3 and 4.

It is evident that increasing the evacuation period up to 3 h increases both the monomer loading and strength but with a decreasing rate. Above 3 h, only a slight increase in loading, compressive, and tensile strength was observed. Accordingly, the optimum evacuation period was taken for the remaining part of this work as 3 h.

Effect of Positive Pressure on Monomer Loading and Strength

Dry mortars were evacuated at 40 mm Hg for 3 h; then the monomer mixture was inserted, and impregnation was carried out using compressed air to achieve gauge pressures of 0.3, 0.6, and 0.8 N/mm², which were applied for 15 h. Polymerization was carried out using the same dose and the results are shown in Figures 5 and 6. The apparent porosity was determined and 70%, 78%, and 78% of the open porosity were found to be filled with polymer at atmospheric pressure and for 0.6 and 0.8 N/mm² gauge, respectively.

Both compressive and tensile strength increase with pressure up to 0.6 N/mm² due to the increase in monomer loading. Above 0.6 N/mm² the change in loading or strength was not significant.

Effect of Pressurized Impregnation Period on Monomer Loading and Strength

Dry mortars were evacuated at 40 mm Hg for 3 h then the monomer mixture was inserted, and impregnation was conducted at the optimum pressure determined earlier (0.6 N/mm² gauge) for periods of 1, 4, 8, 14, and 20 h. Polymerization was carried out using a dose of 7×10^6 rads, and the results are shown in Figures 7 and 8, indicating that as the impregnation period increases the monomer loading and strength increase.

Effect of Irradiation Dose

Mortar specimens prepared and impregnated using the optimum conditions established above were polymerized using a constant intensity of 1.8×10^5 rads/h for various periods. The results obtained are shown in Figures 9 and 10. Increasing the irradiation dose up to about $(8.5 \pm 0.5) \times 10^6$ rads increases both the compressive and tensile strength. Higher doses were found to decrease the strength. The same trend was observed by Gadalla and El-Derini¹⁶ for bulk polymerization of the monomers using a lower intensity of 1.1×10^5 rads/h. The initial increase in strength with dose may be attributed to the increase in the percentage conversion of the mon-

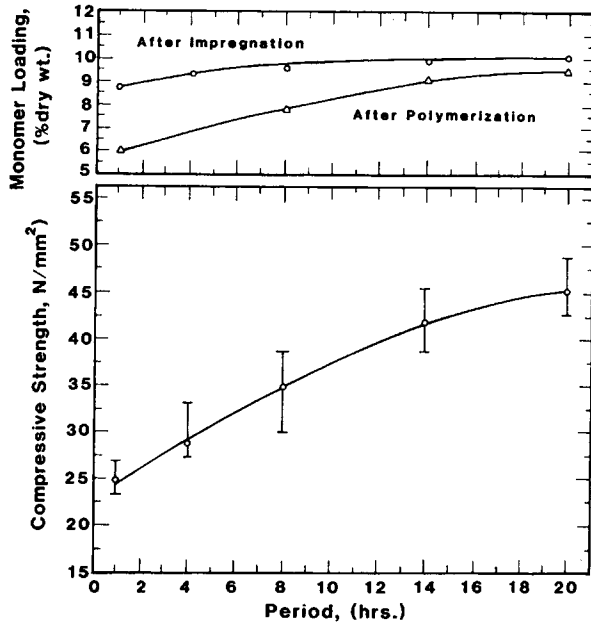


Fig. 7. Effect of pressurized impregnation period on monomer loading and compressive strength of PIM.

omer to the copolymer and crosslinking. The final decrease in strength with high doses may be due to degradation reactions.

Effect of Polymer Fraction on Strength

For all composites prepared using a constant dose of 7×10^6 rads, the

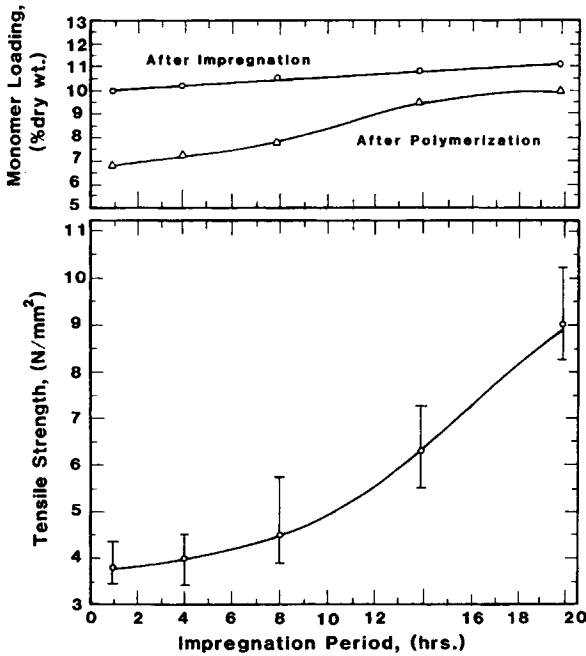


Fig. 8. Effect of pressurized impregnation period on monomer loading and tensile strength of PIM.

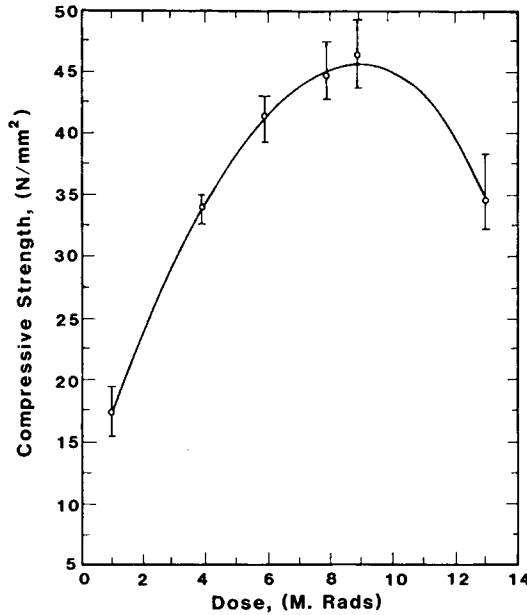


Fig. 9. Effect of irradiation dose on composite compressive strength.

porosities (open and closed) were calculated. Irrespective of the degree of evacuation, period of evacuation, the value of positive pressure and its duration, the composition of each product was expressed as volume fraction mortar, polymer, and pores and is plotted on the ternary diagram shown in Figure 11. It is clear that all compositions lie on a straight line parallel to the edge representing the binary "polymer-pores." This implies that they have a constant volume fraction of mortar (as expected) of 67% and that addition of polymer occurred at the expense of the total porosity.

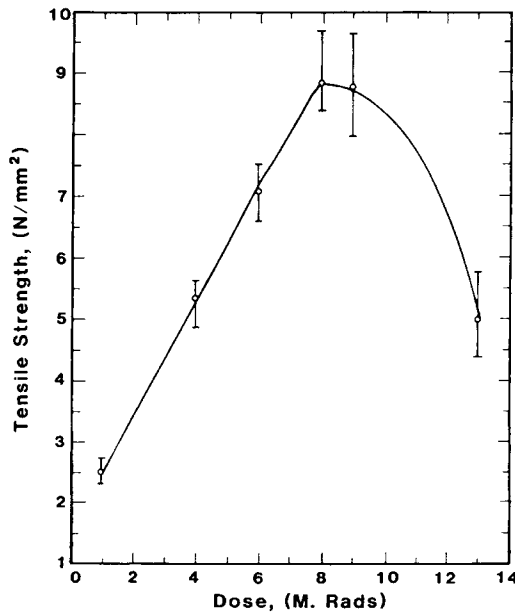


Fig. 10. Effect of irradiation dose on composite tensile strength.

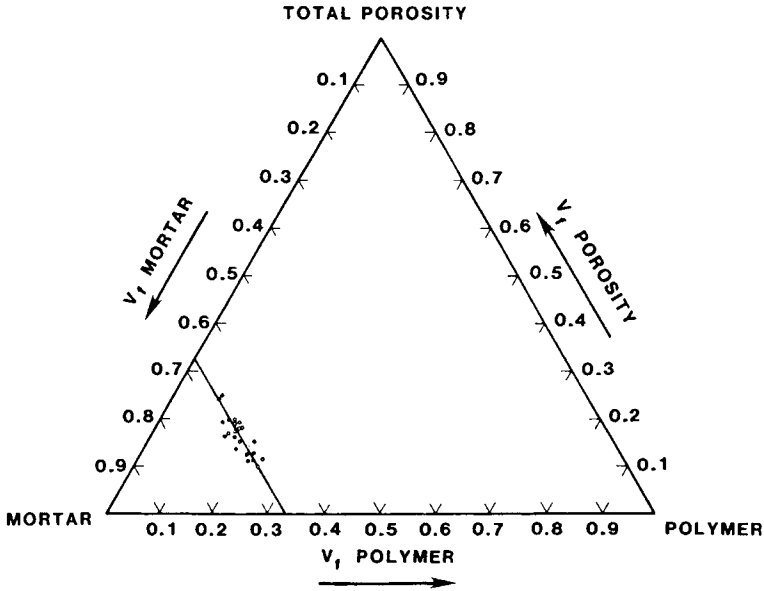


Fig. 11. Compositions (in volume fractions) of the irradiated composites.

Accordingly, Figure 12 was constructed to show the variation of tensile strength as a function of percentage open pores filled with polymer (since closed pores are not accessible to the monomer). The results showed that the tensile strength increases tremendously on filling the pores. On plotting the results on a semilogarithmic plot a straight line was obtained, indicating that

$$\sigma_T = 1.4 + 0.0568e^{0.063x} \quad \text{N/mm}^2$$

where σ_T is the tensile strength and x is the percentage of open pores filled with polymer. The variation of compressive strength with porosity was determined by Auskern and Horn⁴ for cements and concretes impregnated with methyl methacrylate. Their proposed model was based on both the mixture rule for the constituents of concrete and polymer (for the pore free material) and on using a strength-porosity relation developed for sintered ceramics $\sigma_s = C(1 - P)^6$, where C is a constant depending on the constituents and P is the porosity. It should be noted that exponential functions similar to the present one were also reported for some nonglassy ceramic systems⁴ and for impregnated mortars.¹⁸

It is also evident that during this investigation only 80% of the available porosity (open porosity) was filled with polymers. This limiting value may be due to evaporation losses, the difficulty of filling all micropores, entrapping a gaseous phase which consists of residual air, residual water vapor and monomer vapor, and the fact that the polymer is generally more dense than the monomer. Using methyl methacrylate, Auskern and Horn⁴ were able to fill 80% of the total porosity and mentioned that a maximum filling of about 64% of available porosity was possible in their composites. In spite of this difficulty, a compressive strength four times that of plain mortar and a tensile strength eight times that of plain mortar were achieved.

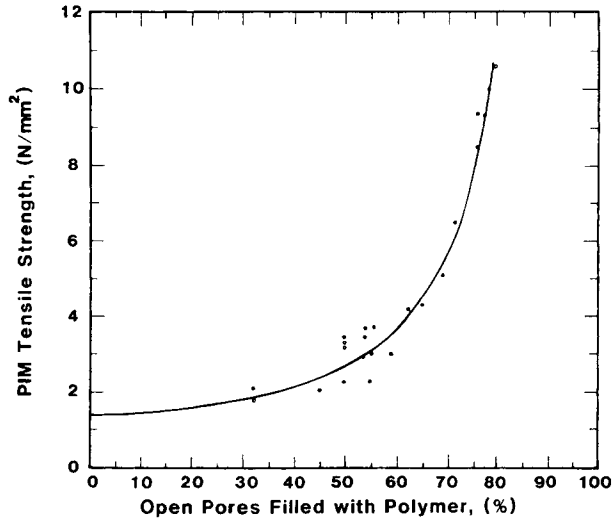


Fig. 12. Variation of tensile strength with the percentage open porosity filled with polymer.

CONCLUSIONS

Mortars which were prepared using cement/sand ratio of 1:3 (by weight) and water/cement ratio of 0.7 followed by curing for 15 days under water developed enough strength of 9.4 N/mm^2 for further processing. High water/cement ratio was used to induce high porosity which favors impregnation. Gradual drying up to 200°C and maintaining the temperature constant for 4 h does not cause any dehydration of the hydration products of cement and does not affect the strength. This drying technique was adopted in this study to increase impregnation. The degree of evacuation, the period of evacuation, the value of positive pressure, and its duration were thoroughly studied after radiolytic polymerization using a dose of 7×10^6 rads. The monomer loading before and after polymerization as well as compressive and tensile strength were determined.

It was found that the monomer loading before and after polymerization as well as tensile and compressive strength increase with the degree of evacuation and period of applying negative pressures. Evacuation to 40 mm Hg for 3 h was used before inserting the monomer.

Applying a positive pressure on the monomer increases the monomer loading before and after polymerization as well as the composite strength. A pressure of 0.6 N/mm^2 was selected since higher pressures caused insignificant increase in strength. Applying this pressure for 1 h is equivalent to soaking under normal pressure for 120 h. Increasing the impregnation period increases the strength and produces minimum losses.

The strength of the polymer-impregnated mortars was found to increase with dose up to 8.5×10^6 rads due to increase of conversion and crosslinking. Above this dose the strength was found to decrease due to degradation.

The composites investigated have the same volume fraction of mortar, and the polymer is added at the expense of the open porosity causing nearly an exponential increase in strength. Only 80% of the open pores were filled with polymers due to contraction on polymerization, loss of monomer and

entrapped gas consisting of residual air, residual water vapor, and monomer vapor as well as due to inability of filling all the micropores with monomer. A compressive strength four times that of plain mortar and a tensile strength eight times that of plain mortar were achieved.

References

1. E. Kirlikovali, *Polym. Eng. Sci.*, **21**(8), 507 (1981).
2. J. A. Manson, "Applications of Polymer Concrete," Pub. SP-69, pp. 1, Amer. Concrete Inst., Detroit, 1981, p. 1.
3. M. Steinberg, "Polymers in Concrete," Pub. SP-40, Amer. Concrete Inst., Detroit, 1973.
4. A. Auskern and W. Horn, *J. Am. Ceram. Soc.*, **54**(6), 282 (1971); also, "Polymers in Concrete," Ref. 3, pp. 223.
5. M. Steinberg, J. Dikeou, L. Kukacka, P. Backstrom, and P. Columbo, First Topical Report, BNL 50134 (T-509), Upton, N. Y., 1968.
6. M. Steinberg, L. Kukacka, P. Columbo, and B. Manowitz, *J. Nucl. News*, **48** (1970). See also: *Adv. Chem. Ser., Am. Chem. Soc.*, **99**, 547 (1971).
7. L. Kukacka and A. Romano, "Polymers in Concrete," Ref. 3, pp. 15-31.
8. J. Dikeou, M. Steinberg, L. Kukacka, and A. Auskern, Third Topical Report, BNL 50275 (T-602), Upton, N. Y., 1971.
9. M. Steinberg, J. Dikeou, W. Cowan, and A. Auskern, Fourth Topical Report, BNL 50328, 1972.
10. D. Whiting, D. Kline, and P. Blankenhorn, *Cement Concrete Res.*, **4**, 467 (1974).
11. D. Fowler and D. Paul, Research Report, Univ. Texas, Cent. Highway Res., Austin, 1974.
12. H. Mehta, W. Chin, J. Manson, and J. Vanderhoff, "Polymers in Concrete," SP-58-9, Am. Concrete Inst., Detroit, 1977.
13. J. Vanderhoff, J. Hoffman, and J. Manson, *Polym. Prep.*, **14**(2), 1136 (1973).
14. D. Manning, and B. Hope, "Polymers in Concrete," Ref. 3, p. 191.
15. A. Zeldin, L. E. Kukacka, and N. Carciello, *J. Appl. Polym. Sci.*, **23**, 3179 (1979).
16. A. M. Gadalla and M. E. El-Derini, *J. Appl. Polym. Sci.*, **28**, 3695 (1983).
17. I. Stebnicke-Kalicka, Thermal Analysis, ICTA 80, Berkhauer-Verlag, Basel, Boston, Stuttgart, 1980, p. 369.
18. Y. N. Liu, J. A. Manson, W. F. Chen, and J. W. Vanderhoff, *Polym. Eng. Sci.*, **17**(5), 325 (1977).

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