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CONCRETE–POLYMER COMPOSITE MATERIALS PRODUCED BY RADIATION POLYMERISATION TECHNIQUES

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* Ready Mixed Concrete Industries Limited

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ABSTRACT

Exploratory studies have been carried out on the production and properties of concrete-polymer composite materials, made by impregnating precast concrete with monomers and polymerising the monomer *in situ* with gamma radiation.

The composites have much greater compressive and tensile strengths, and higher elastic moduli than the original concrete. The main factor influencing the degree of enhancement of these properties is the total polymer loading in the interstices of the concrete, and the ultimate strength attainable in the composites is largely independent of the type of concrete used to make the composite.

(continued)

With polymethyl methacrylate composites, compressive strengths up to 117 MPa, Brazil tensile strengths up to 8.95 MPa and elastic moduli up to 3.75×10^4 MPa were obtained with polymer loadings around 4.7%. Composites made from porous concrete (Besser brick) and polyester resins had compressive strengths around 145 MPa.

Because of the inherently low thermal stability of the polymer component, composites for structural purposes would be restricted to applications where they would not be exposed to fire. Uses envisaged for these new types of material include drain piping in corrosive environments, underwater structures, bridge decking and decorative panelling.

Polymerisation can be accomplished by thermal means as well as by radiation, and the method of choice for a given application will depend largely on relative costs.

Certain types of mineral aggregate are not suitable for concrete which is to be converted to concrete-polymer composites, as their use leads to severe cracking problems. This aspect requires further work.

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CHEMICAL RADIATION EFFECTS; COMPOSITE MATERIALS; COMPRESSION STRENGTH; CONCRETES; DOSE RATES; ELASTICITY; FIRE RESISTANCE; GAMMA RADIATION; IMPREGNATION; PHYSICAL RADIATION EFFECTS; POLYMERIZATION; POLYMERS; RADIATION DOSES; SHRINKAGE; TENSILE PROPERTIES

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1. INTRODUCTION

Concrete is an excellent structural material which can be tailor-made to suit a wide range of applications, but because of its complex structure it has certain limitations.

Strictly speaking, concrete is a multi-phase composite in itself, consisting of the following components: stone (or coarse aggregate), sand (or fine aggregate), cement gel, crystalline products of hydration, unhydrated cement, gel pores, capillary pores, entrapped air voids and pore water. In this report the term 'composite' is used to indicate polymer-impregnated concrete only.

Concrete, throughout its structural life does not remain unchanged; hydration, although progressively slowing down, continues indefinitely. The changes within the material affect the pore structure and it is therefore important to differentiate between the types of air voids present in concrete, the way in which some of them change and the effect of porosity on the properties of concrete itself. As the total amount of gel increases, the volume of interstitial spaces between the gel particles, *i.e.* gel pores, also increases. However, since the products of cement hydration occupy more than twice the volume of the original solid phase alone, the capillary pore system is gradually reduced as hydration progresses.

The volume of capillary pores just after hardening of concrete depends on mix proportions, degree of compaction and, particularly, on the water-cement ratio. The rate of volume change and the pore size distribution of the capillaries is influenced by the curing conditions.

Porosity plays an important role in both the strength and durability of concrete. For a given type of concrete, strength is inversely proportional to the degree of porosity, while durability depends on the pore structure as well as the total amount of porosity. Capillary pores remain relatively permeable to outside moisture. Gases and liquids (the latter often containing salts and acids) can be absorbed into capillaries, causing deterioration and sometimes complete destruction of concrete, if the process is allowed to continue.

Artificially entrained air, in the form of minute bubbles approximately 50 to 100 μm in diameter, prevents the formation of continuous capillaries and hence reduces the permeability of concrete, although total porosity often increases slightly. Accidentally entrapped air bubbles are, on the average, considerably larger in size. These do not reduce permeability of plastic concrete and do not prevent subsequent formation of capillaries, but have a very adverse effect on strength. Hence, reduction in porosity, particularly at the expense of the capillaries and accidentally entrapped bubbles, can be expected to give the hardened concrete better properties.

In 1966, the US Bureau of Reclamation (Department of the Interior) and the US Atomic Energy Commission began to explore the possibility of impregnating precast concrete with monomers, and then using gamma radiation to induce polymerisation of the monomers *in situ*. Early experiments showed great improvements in strength and corrosion resistance, and a formal programme of research and development began in 1967. Seven US Government departments and bureaux, and one industrial organisation (the American Concrete Pipe Association) are participating in this programme (Steinberg *et al.* 1968-1973). Potential applications envisaged for concrete-polymer composites in the USA include: construction of distillation vessels for water desalination plants operating at temperatures around 140°C-180°C; highway bridge decking; light-weight break-away lamp and sign posts; soil and rock stabilisation; structures for use underwater at great depths and pressures; pipes with improved strength and corrosion resistance; light-weight precast wall panels for temporary housing.

Radiation Technology Inc., New Jersey, and Radiation Technology (Canada) Limited, recently began marketing concrete-plastic products (Welt 1970) ranging from building blocks, water and drainage pipes, and rail ties ('RADCRETE') to architectural facade panels and terrazzo-like tiles ('RADSTONE').

In Denmark, the Atomic Energy Commission (RISÖ) and the Concrete Research Laboratory (Karlstrup) recently began a joint programme on radiation cured concrete-polymer materials (Singer *et al.* 1970). A limited amount of work is being done in England on improving the flexural strength of low density concrete, and in reducing the permeability of pipes.

It should be noted that polymerisation of monomers can be produced by thermal catalytic means as well as by gamma radiation, and for some applications the former technique may be preferable. The properties of the final concrete-polymer composite appear to be essentially independent of the method used to induce polymerisation.

Work in the USA indicates that adding liquid monomers to the raw concrete mix does not produce satisfactory results, and work has tended to concentrate on impregnation of hardened concrete.

This report gives results obtained in exploratory work on impregnation of hardened concrete carried out on a cooperative basis by the Australian

Atomic Energy Commission and Ready Mixed Concrete Industries Limited, Sydney. Many varieties of concrete are made, and the properties obtained are controlled by the raw materials and the specific manufacturing techniques used for any given batch. Our work was on a limited scale, the aim being to show trends rather than to establish optimum property values or operating procedures, which would require a much more elaborate research programme.

2. SPECIMEN PREPARATION

Test specimens covering a range of commercial grades of concrete were prepared by the Central Research Laboratory, Ready Mixed Concrete Industries Limited.

2.1 Initial Series

For the pilot trials it was decided to use specimens as small as was practically possible. The specimens selected were cylinders 50 mm diameter by 100 mm high, as per Clause 7.16.3 of ASTM Designation: C595-68. Maximum aggregate size was restricted to 6 mm to obtain concrete samples of reasonable homogeneity. All specimens were moist cured for seven days at 23°C ± 2°C and then air cured at 23°C ± 2°C and 50 ± 4% relative humidity.

Control (unimpregnated) specimens were continuously air stored for just over one month prior to compressive strength evaluation.

Mixes were selected on the basis of 'arbitrary proportions' for comparatively low strength concrete. Compositions of the various grades are set out in Table 1.

2.2 Main Series

The main series of experiments involved specimens of five grades of concrete. Proportions were chosen in accordance with ACI 613-54, 'Standard Recommended Practice for Selecting Proportions for Concrete'. Coarse aggregate, 20 mm and 10 mm nominal size and natural sands were in compliance with Australian Standard (AS) A77-1957, 'Aggregates for Concrete'. Ordinary Portland cement to AS A2-1963 was used in all trials. Laboratory mixes were in accordance with AS A102-1968, and testing was done to AS A100, A101, A103, A108 and A109, using 150 mm diameter by 300 mm cylindrical specimens.

Mix details are given in Table 2.

Laboratory mixed concretes were uniformly consistent at 75 mm slump, but plant mix was considerably more fluid at a consistency of about 125 mm slump. As with the initial series, the specimens were moist cured for seven days at 23°C ± 2°C and then air cured at 23°C ± 2°C and 50 ± 4% relative humidity. AS A113-1970, 'Method for the Determination of Drying Shrinkage of Concrete' was in its draft form at the time of testing and hence shrinkage evaluation was carried out to ASTM Designation: C157-69T.

Shrinkage specimens were 76 x 76 x 286 mm prisms in compliance with ASTM C490.

3. DRYING

USA reports (Steinberg *et al.* 1968) indicated that it is necessary to dry the concrete to get maximum monomer loading. A few preliminary experiments confirmed these reports, so all work was carried out with specimens dried in a forced circulation air oven.

100 x 150 mm diameter specimens: These were dried for a total of 89 h at 110°C, and stored in desiccators until the impregnation step. Weight losses are shown in Table 1.

300 x 150 mm diameter specimens: These were dried for a minimum of 54 h at 150°C. Because the impregnation vessel could handle only one specimen at a time, drying schedules were arranged so that impregnation could be carried out as soon as specimens cooled down after drying. Weight losses for these specimens are shown in Table 2.

4. IMPREGNATION

4.1 Choice of Monomer

For complete penetration and maximum monomer loadings, it was necessary to use low viscosity monomers such as styrene and methyl methacrylate. These penetrate well, but being volatile, evaporate rapidly from the outer surface so that final surface coverage is poor. Polyester-styrene and epoxystyrene mixtures can be radiation cured, but these are comparatively viscous and give poor penetration. However, with this type of material it is possible to get a thick surface coating of polymer which may be advantageous for corrosion resistance. Styrene is by far the cheapest radiation-curable monomer available, but requires large radiation doses for cure. On balance, methyl methacrylate appears to be the monomer of choice for obtaining maximum strength with minimum dose, so work was concentrated on composites made from this material. Methyl methacrylate, stabilised with hydroquinone (ICIANZ Limited), was used as received. Some experiments were made with a commercially available polyester-styrene mixture ('POLYLITE 8009' - A.C. Hatrick & Co.). This contained approximately 35% styrene.

4.2 Impregnation

A cylindrical aluminium vessel 483 x 178 mm diameter (internal dimensions) was used for impregnations. It was fitted with an O-ring sealed lid which carried vacuum connections and a vacuum tight fitting for attaching a large glass separating funnel holding monomer. The funnel was fitted with a polytetrafluoroethylene stopcock, to avoid contamination of the monomer by stopcock grease. The 300 x 150 mm diameter specimens, weighing around 13.6 kg, were held in a steel frame to facilitate handling.

After loading, the impregnation vessel was evacuated to a pressure of $<$ 66 Pa, which was maintained for 2.50 h. Monomer was then run into the evacuated vessel from the separating funnel, until the specimen was completely immersed. The apparatus was then let down to atmospheric pressure, and left for a minimum of 19 hours, making sure the sample was always covered by monomer. After impregnation, specimens were drained for a short time, then sealed in 0.13 mm polyethylene bags, and taken to the irradiation facility as quickly as possible.

Thorough outgassing of the concrete appears to be the most important factor in getting maximum polymer loading, while drying also has a big effect. This is illustrated in Table 3.

5. RADIATION POLYMERISATION

5.1 Dose Variations in Concrete Specimens

Irradiations were carried out in a water-shielded ^{60}Co gamma facility in which specimens were irradiated from all sides simultaneously. However, attenuation of the gamma ray flux in the concrete leads to significant dose rate variations throughout the specimens. This was estimated using phantoms of varying diameters, made of sand-filled polyethylene cylinders. The minimum dose rate (at the centre of specimens) was measured by means of ferrous sulphate dosimeter tubes embedded along the central axis of the phantoms. The maximum dose rate was measured by dosimeters at the outer surface.

Figure 1 shows the exponential relationship between minimum radiation intensity and specimen diameter. For 50 mm diameter specimens, the uniformity ratio (ratio of maximum to minimum dose) was 1.06. For 150 mm diameter specimens, the uniformity ratio was 1.17. The doses quoted in this report are the estimated minimum doses received by the specimens.

5.2 Effect of Dose Rate on Polymerisation of Various Monomers

For radiation-induced free radical polymerisations, the polymerisation rate is usually proportional to the square root of the dose rate. However, the dose required for complete cure also increases with increasing dose rate. This is shown in Table 4, taken from Steinberg *et al.* (1968).

The completeness of polymerisation was checked by placing irradiated specimens in a drying oven at 105°C and measuring any loss of weight (unpolymerised monomer).

5.3 Polymerisation of Methyl Methacrylate in Besser Brick Concrete

Experiments were carried out with small specimens (approximately 25 mm cubes) of Besser Block concrete. As shown in Table 5, polymerisation was far from complete after doses as high as 7×10^6 rad at a dose rate of 0.61×10^6 rad h^{-1}. Overall losses of monomer due to evaporation, weeping and incomplete polymerisation were also high. The average weight increase was about 7.5%.

5.4 Polymerisation of Methyl Methacrylate in 100 x 50 mm Diameter Concrete Cylinders (Ready Mixed Concrete Type Numbers 1-4)

These specimens were initially given a dose of 1.76×10^6 rad at a dose rate of 0.36×10^6 rad h^{-1}, but as shown in Table 6, at this dose level polymerisation was far from complete. Specimens were given a further impregnation, then sealed in nitrogen filled polyethylene bags, and given an additional dose of 4.44×10^6 rad at a dose rate of 0.54×10^6 rad h^{-1} (equivalent to 3.63×10^6 rad at 0.36×10^6 rad h^{-1}, assuming an inverse square root relationship). At this latter dose level, polymerisation was about 90-95% complete.

5.5 Polymerisation of Methyl Methacrylate in 300 x 150 mm Diameter Concrete Cylinders

These cylinders were irradiated at a dose rate of 0.59×10^6 rad h^{-1}. The results obtained with 100 x 50 mm diameter cylinders indicated that a dose of 4.7×10^6 rad at this dose rate would only give about 90-95% polymerisation (Section 5.4). To ensure complete polymerisation and maximum polymer loadings, these specimens were given doses of 7.8×10^6 rad. Weight loss tests on selected specimens confirmed that there was no unreacted monomer after this dose.

5.6 Dose Required for Complete Polymerisation of Methyl Methacrylate Under Experimental Conditions Used for Concrete Irradiations

One report from the USA (Steinberg *et al.* 1968) suggested that methyl methacrylate in concrete polymerised faster than the monomer alone, and that a dose of 2.2×10^6 rad at 5.4×10^5 rad h^{-1} would be sufficient for complete polymerisation in concrete. This is less than half the dose found necessary in our work, so some comparison experiments were carried out with monomer alone, sealed in polyethylene bags as used for the impregnated concrete specimens. As shown in Table 7 the monomer required about 3.7×10^6 rad for complete polymerisation, compared with about 4.5×10^6 rad for monomer in concrete. Thus there was no evidence of any catalytic effects due to the presence of concrete in our experiments.

5.7 Concrete - Polyester/Styrene Composites

5.7.1 Besser Block Concrete

Small specimens (approximately 25 mm cubes) of Besser Block concrete were impregnated with Polylite 8009. This monomer mixture polymerised far more readily than methyl methacrylate in this type of concrete. Thus, 3 - 3.5 x 10^6 rad at 0.61 x 10^6 rad h^{-1} was sufficient for complete polymerisation, compared with more than 7 x 10^6 rad for methyl methacrylate (Section 5.3).

Weight increases were also higher than in the case of methyl methacrylate, the average being 11.9%, compared with 7.5% for the latter (Section 5.3). This was partially due to the fact that the polyester-styrene, unlike the methyl methacrylate, gave a fairly good surface coating.

5.7.2 Ready Mixed Concrete Grades 1-4 (100 x 50 mm Diameter Cylinders)

Specimens of each of the four grades were impregnated with Polylite 8009 and given doses of 3.5 x 10^6 rad at 0.61 x 10^6 rad h^{-1}. This gave a hard surface coating of polymer but penetration was only about 3 mm. Weight increases ranged from 3.8 to 7.9%,comparable with the methyl methacrylate composites from these concrete grades (Table 6).

6. POLYMER LOADINGS ACHIEVED (POLYMETHYL METHACRYLATE)

The strength of polymer-concrete composites is a strong function of total polymer loading. We used high dose rates in order to complete the polymerisation in the minimum time (see Table 4) hoping thereby to minimise losses of the volatile methyl methacrylate. However, we found that a considerable fraction of the initial monomer was always lost from the concrete during the irradiation period (see for example Table 11). This was mainly due to drainage of liquid monomer from the pores of the concrete, resulting in lumps of solid polymer collecting in the polyethylene bags, or sometimes adhering strongly to ends of the concrete specimens. Workers in the USA have reported similar problems and have suggested that monomer losses can be reduced by irradiating impregnated specimens under water instead of wrapped in plastic or aluminium foil (Steinberg *et al.* 1972).

We experimented with the technique of dipping monomer impregnated specimens in a viscous 40% w/v solution of polymethyl methacrylate (ICIANZ acrylic granules MG101) in methyl methacrylate before sealing in polyethylene and irradiating. 100 x 50 mm diameter specimens 2D, 2E, 3C, 4D, 4E were treated in this way, but no improvement in final polymer loading or compressive strength was obtained.

As shown in Figure 2, polymer loadings achieved were directly related to the water/cement ratio used in making the concrete, and were thus highest in the lower strength concrete grades.

7. STRENGTH PROPERTIES OF CONCRETE-POLYMER COMPOSITES

Strength tests were in accordance with AS A104, 'Method for Determination of the Compressive Strength of Concrete Specimens' and AS A111, 'Method for the Determination of Indirect Tensile Strength of Concrete Cylinders ('Brazil' Test)', except that all specimens were crushed dry. Control specimens were capped with filled sulphur mixtures as per Clauses 4.3.2 and 4.3.3 of AS A104-1969, and the impregnated specimens with Portland cement mortar as per Clause 4.3.4 of the above Standard.

Compressive strengths of impregnated specimens were evaluated at the School of Civil Engineering, University of Sydney.

The mode of failure for impregnated specimens was somewhat different from the controls and resembled that of certain natural stone or very strong mortars. Fracture was sudden, very brittle and mostly only slightly inclined from the vertical axis. This was particularly noticeable with the small specimens.

As mentioned previously, a very limited number of specimens were tested and there was considerable scatter in the results, which show trends and not necessarily the optimum values obtainable.

7.1 100 x 50 and 300 x 150 mm Cylinders

Strength properties of these specimens are summarised in Tables 8 and 9.

7.1.1 Compressive Strength

Perhaps the most striking feature is that the maximum compressive strength obtained was largely independent of the initial strength of the concrete used to make the composite. Thus the maximum observed compressive strengths of methyl methacrylate composites ranged from 83.5 to 117 MPa, with an average value of 105 MPa, for nine different grades of concrete with initial compressive strengths ranging from 8 to 66 MPa. The maximum compressive strength was obtained with lower polymer loadings in the case of the higher initial strength concrete specimens. Indeed, the major factor affecting the compressive strength of composites made from a given grade of concrete was the total polymer loading. This is clearly shown in Figures 3 and 4.

On a percentage increase basis, the initially weaker concrete grades showed the greater improvements in compressive strength. The maximum increase observed was 1,165% (for 8 MPa concrete) and the minimum increase was 67% (for 66 MPa concrete).

The need to have deep penetration of monomer into the pores of the concrete in order to get maximum strength is shown by comparing the results of the polyester/styrene and methyl methacrylate impregnated specimens (Table 8). The polyester polymer, although present in amounts comparable with those of the polymethyl methacrylate, was confined to the outer layers of the specimens and the compressive strengths of these composites were very much lower than those obtained with the deeply penetrating methyl methacrylate.

7.1.2 Tensile Strength

Despite the limited amount of data (Table 9) trends can be seen similar to those found in the case of compressive strength. The maximum tensile strength of the composites was largely independent of the initial strength of the concrete; thus the weakest concrete (1.60 MPa) and the strongest concrete (5.60 MPa) gave composites with tensile strengths of 9.15 and 8.95 MPa respectively. However, as shown in Figure 5, the stronger concrete grades reached their maximum tensile strength with polymer loadings lower than those of the weaker concrete.

The results for the 180 grade concrete show that the tensile strength of composites made from a given grade of concrete is a strong function of polymer loading. On a percentage increase basis, the weaker concrete grades show the greater improvements in tensile strength. The maximum increase observed was 471% (for 180 grade) and the minimum increase was of the order of 45-60% (for the 420-540 grades).

7.1.3 Elastic Modulus

The stress-strain relationship for concrete is curvilinear and the term 'Young's Modulus of Elasticity' can strictly be applied only to the tangent to the curve at the origin. This is the initial tangent modulus, but it is of little practical importance. ASTM Designation: C469-65 covers the procedure for determining chord modulus of elasticity between the points corresponding to stress at 50×10^{-6} microstrain (longitudinal) and stress at 40 per cent of ultimate load bearing capacity of concrete. The above stress-strain relationship is well within the working range of structural concrete, and all elastic moduli in these series were evaluated in accordance with ASTM C469.

In the case of elastic modulus we do not find the clear trends observed with compressive and tensile strengths. Improvements in elastic modulus as a result of polymer impregnation were much smaller than in the latter cases and the moduli of the composites made from the weaker grades of concrete do not reach those of composites made from the stronger concretes.

Further, as shown in Figure 6, there is little correlation between polymer loading and elastic modulus for composites made from a given grade of concrete.

7.2 Besser Brick-Polymer Composites

A few experiments carried out with samples of Besser Brick concrete show that compressive strengths around 145 MPa can be attained in composites.

With Besser Brick concrete, it was found that much higher polymer loadings were obtained with polyester/styrene than with methyl methacrylate (*e.g.* up to 12.9% compared with about 7.5% with the latter).

This led to big increases in compressive strength, as shown in Table 10, where results are compared for composites made from Besser Brick and from Ready Mixed Concrete of approximately the same initial strength. The dominating effect of total polymer loading on compressive strength can be seen in the table.

8. SHRINKAGE TEST

By far the largest proportion of volume change in concrete is contributed by the water loss, *i.e.* 'drying shrinkage', and the specimens used in this test (as per ASTM C490, with stainless steel gauge studs of AISI Type) were virtually 'pre-shrunk' when dried in a forced circulation air oven prior to impregnation. After impregnation they were given a dose of 5.9×10^6 rad at 0.6×10^6 rad h^{-1}. The polymer loadings achieved, and monomer losses due to drainage and evaporation from impregnated specimens are shown in Table 11.

Possibly partly due to 'pre-shrinking' and partly to impregnation *per se*, no volume change in polymerised specimens was observed when tested in accordance with ASTM C157-69T.

9. RESISTANCE TO CHEMICAL ATTACK

Extensive laboratory and field studies in the USA (Steinberg *et al.* 1972) indicate that complete impregnation of concrete with polymers leads to remarkable improvements in resistance to chemical attack, and in durability under cyclic freeze-thaw conditions. This is related directly to the low water absorption and permeability of the concrete-polymer composites.

We have not studied this aspect in detail, although preliminary tests indicate marked improvements in resistance of our compositesto acid solutions which caused rapid deterioration of unimpregnated control specimens.

However, we have made an important observation which indicates the need for careful screening of local raw materials. Thus we have found that certain types of low grade aggregates are not suitable for concrete which is to be impregnated with polymethyl methacrylate. Composite specimens containing these aggregates showed remarkable deterioration when immersed in weakly alkaline solutions such as limewater. Cracks developed spontaneously and specimens began to disintegrate into fragments after as little as 24 h immersion in some cases.

There were indications that omitting the drying process before impregnation may reduce the susceptibility of polymethyl methacrylate concrete composites to attack by limewater.

In one experiment, an untreated shrinkage specimen (No. 1976) was cut into four pieces each about 76 x 76 x 6 mm, so that on at least one face of each specimen, aggregate was exposed. These were treated as follows:

Specimen No.	Drying (88 h at 150°C)	Impregnation and Irradiation (5.9×10^6 rad at 0.34×10^6 rad h^{-1})	PMMA Loading % w/w
A (control)	No	No	Nil
B	No	Yes	3.63
C (control)	Yes	No	Nil
D	Yes	Yes	4.35

After 27 h immersion in saturated limewater at ambient temperature, control specimens A and C showed no change; specimen B had one small crack; specimen D showed two cracks.

After 93 h immersion, control specimens A and C were unchanged; specimen B showed one medium and one fine crack; specimen D had five major cracks and fragments were spalling off.

In specimen D, a large proportion of the exposed aggregate pieces were severely cracked, and some pieces were reduced to a weak, friable mass in which polymer was dispersed. By contrast, in specimen B only a few of the exposed aggregate pieces were observed to be cracked.

Figures 7 and 8 show the general appearance of these specimens after 93 h in limewater. An interesting observation was the presence of small plastic bubbles in a few isolated spots on the surface of specimens B and D (Figures 9 and 10). These suggest evolution of gas produced either by irradiation decomposition of the polymer or by subsequent reaction of irradiated polymer with the limewater.

Further work is required to clarify this cracking phenomenon.

10. FIRE RESISTANCE TESTS

Concrete-polymer composites have possible applications as building materials for both structural and decorative purposes. For the former, composites made from materials of low thermal stability, such as polymethyl methacrylate which softens markedly around 100°C, would have to be restricted to applications where they were not exposed to high temperatures. In the latter type of application, there is another problem, the evolution of smoke or toxic fumes due to decomposition of the organic polymer by high temperatures, in the case of fire. In recent years increasing attention is being paid to this aspect of building materials (Martin 1971). Because polymer-composite materials are so new, there are as yet no standard tests specifically designed for them, but it was thought desirable to examine the behaviour of concrete-polymethyl methacrylate composites when exposed to flames. Accordingly, specimens were tested by the general test methods set out in AS A30, Sections 3 and 4.

This test requires specimens 600 x 455 mm, and as it was not possible to impregnate a panel this size, four panels each 455 x 150 x 45 mm were impregnated and irradiated separately, then bolted together to form the test panel. The radiation dose was 6×10^6 rad at 3.83×10^5 rad h^{-1}. Polymer loadings were as follows:

(455 x 150 mm) Specimen Number	% Polymer (w/w)
1	4.0
4	3.7
5	3.5
9	4.1

Tests were carried out at the CSR Building Materials Research Laboratories, Sydney. In the Early Fire Hazard test, panels were exposed to an intense heat source for 20 seconds, while smoke/fume evolution was monitored. The concrete-polymer panel met the requirements of this test.

In the Fire Resistance test, the specimen was subjected to an intense heat source for 2 hours and at the conclusion of the test, liquid polymer was running out of the specimens.

Drill core specimens were cut from the fire-tested panel, and used for compressive strength measurements. Results are shown in Table 12. The compressive strength of untreated concrete was essentially unaffected by both fire tests. In the case of the concrete-polymethyl methacrylate composite, there was no change in compressive strength after the Early Fire Hazard test, but after the Fire Resistance test, in which the temperature was sufficient to melt the polymer, the composite structure was severely damaged, and the compressive strength was greatly reduced, in some cases to that of the original concrete.

It should be noted that compressive strength measurements are not part of the requirement of AS A30. Very low height to diameter ratio of the cores, possible formation of invisible (to a naked eye) incipient cracks due to drilling, 'popping' of aggregate which is cut by a drill kerf, difficulty in capping etc., make the absolute values of strength doubtful and the scatter of readings much larger than with the cast specimens. Therefore, only the trends should be taken into consideration.

11. COLOURED COMPOSITES

It is possible to produce coloured composites by dissolving dyes in the monomer used to impregnate the concrete. Generally speaking, dyestuffs tend to inhibit free radical polymerisations of the type considered here. Some experiments were carried out with a number of dyes dissolved in methyl methacrylate. The solutions were sealed in polyethylene bags and irradiated to various dose levels. After irradiation, samples were dried to remove unpolymerised monomer, and weighed. Comparison with control samples of monomer showed, as expected, that the dyes had an inhibiting effect on the polymerisation. Thus, for dyed composites, extra radiation dose would be required, depending on the dye and dye concentration chosen.

Typical results are shown in Table 13.

12. RECOMMENDATIONS FOR DESIGNING CONCRETE MIXES FOR POLYMER COMPOSITES

For a particular concrete, the strength after impregnation and polymerisation is a strong function of the extent to which saturation with polymer is achieved. Therefore when designing concrete mixes for polymerisation, it is essential to aim at the lowest possible porosity so that complete impregnation involves a minimum of the relatively expensive monomer.

At the same time, since the strength of the unimpregnated concrete has little effect on the strength characteristics of the final concrete-polymer composite, the cement content of a mix should be just sufficient to produce the desired porosity.

The criterion of 'minimum cement content at a minimum porosity' implies the importance of careful attention to compacting and the workability of the concrete mixture. The most efficient compacting methods should therefore be used in order to economise on polymer.

On the other hand, and contrary to conventional concrete practice, permeability of unimpregnated concrete is a desirable characteristic, as long as it is associated with low porosity, and steps (such as special curing techniques) should be taken to ensure permeable concrete, which is relatively simple to impregnate effectively.

It is appreciated that some of the requirements stipulated may be to some degree in conflict, and optimum design must involve proper balancing of these factors.

The optimum mix proportions will also depend on the relative costs of monomer and cement used.

13. SUMMARY AND CONCLUSIONS

Exploratory studies have been made of the production and properties of concrete-polymer composite materials, made by impregnating precast concrete with monomers, and polymerising the monomer *in situ* with gamma radiation.

The composites have much greater compressive and tensile strengths, and higher elastic moduli than the original concrete. The main factor influencing the degree of enhancement of these properties is the total polymer loading in the interstices of the concrete. Concretes of low initial strength take up larger amounts of monomer than high strength concretes, so that the ultimate strength attainable in concrete-polymer composites is largely independent of the type of concrete used to make the composites.

Maximum polymer loadings can only be achieved by thoroughly drying the concrete before impregnation, and it is necessary to minimise losses of monomer during the irradiation process by wrapping specimens or possibly irradiating specimens under water.

With polymethyl methacrylate-concrete composites, compressive strengths up to 117 MPa, Brazil tensile strengths up to 8.95 MPa, and elastic moduli up to 3.75×10^4 MPa were obtained with polymer loadings around 4.7%.

Radiation doses of the order of 5×10^6 rad at a dose rate of 0.6×10^6 rad h^{-1} were required for complete polymerisation of this monomer in the concrete.

For conventional precast concrete, viscous monomers such as polyester/styrene mixtures are not suitable, as they do not penetrate into the pores. Compressive strengths approaching 145 MPa were obtained with Besser Brick concrete composites containing around 13% polyester/styrene resin. For this monomer, a radiation dosage of about $3.0 - 3.5 \times 10^6$ rad at 0.6×10^6 rad h^{-1} was sufficient for complete polymerisation.

Concrete-polymer composites made from precast concrete are necessarily more expensive than conventional concrete, but there are many potential specialised applications where composites may be preferred to concrete because of their greatly superior strength. Overseas work indicates that composites have greatly superior durability and resistance to chemical attack, but the present work indicates that this may not always be true; clarification of this aspect requires further work.

14. ACKNOWLEDGEMENTS

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Mr. T.M. Benson (AAEC) was responsible for the greater part of the experimental impregnation and irradiation work and Mr. G. Smorchevsky (RMCI Limited) for the experimental concrete work; their enthusiastic and skilful assistance is gratefully acknowledged.

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TABLE 1

DETAILS OF 100 x 50 mm DIAMETER SPECIMENS

(Initial Series)

	Concrete Type Number			
	1	2	3	4
Material, Parts by Weight				
5 mm aggregate	4	3	6	6
Sand	2	2	4	4
Cement	1	1	1	1.5
Water/Cement Ratio	0.7	0.75	0.9	0.7
Free Water (Weight loss at 110°C - % of as-received weight)	3.7-4.0	4.0-4.1	4.2-4.7	5.4-6.3
Compressive Strength of Control Specimens (MPa)	19.0	12.8	7.9	19.3

TABLE 2

DETAILS OF 300 x 150 mm DIAMETER SPECIMENS

(Main Series)

Mix Type	Mix Proportion, Parts by Weight				
	180	240	420	540	Plant
Coarse Aggregate	6.8	3.9	2.7	2.1	4.0
Sand	4.5	2.5	1.6	1.0	2.8
Cement	1.0	1.0	1.0	1.0	1.0
Water/Cement Ratio	1.26	0.68	0.45	0.36	0.64
Air % (fresh concrete)	1.6	1.8	1.7	1.7	5.6*
Free Water (% Weight Loss at 150°C after air curing)	4.4	5.4	5.4	5.5	5.1

* *Air entraining agent was used in the plant mix.*

TABLE 3

EFFECTS OF DRYING AND EVACUATION ON POLYMER LOADING

Sample Number (38 mm cubes of Besser Brick Concrete)	Pre-Treatment		Polymer Loading Achieved (% w/w) - Polymethylmethacrylate
	Oven-drying	Evacuation	
1	Yes	Yes	5.3
4	No	Yes	4.0
5	No	No	0.2

TABLE 4

EFFECT OF DOSE RATE REQUIREMENTS AND POLYMERISATION TIME

Monomer	Dose Rate (10^5 rad h^{-1})	Polymerisation Rate (% Conversion h^{-1})	Time for Complete Polymerisation (h)	Total Dose Required (10^6 rad)
Methyl Methacrylate	5.3	11.0 *(a)*	9.1 *(a)*	4.8 *(a)*
	1.0	4.8 *(b)*	21.0 *(b)*	2.1 *(b)*
Styrene	5.3	1.06 *(a)*	94.3 *(a)*	50.0 *(a)*
	1.0	0.5 *(b)*	217.0 *(b)*	21.7 *(b)*
Polyester-Styrene (Hetron-197)	5.3	44.0 *(a)*	2.3 *(a)*	1.2 *(a)*
	1.0	18.9 *(b)*	5.3 *(b)*	0.5 *(b)*

(a) *Experimentally determined.*

(b) *Calculated, assuming square-root rate dependence.*

TABLE 5

POLYMERISATION OF METHYL METHACRYLATE IN BESSER BLOCK CONCRETE

(Dose Rate 0.61 x 10^6 rad h^{-1})

Specimen Number	Dose (10^6 rad)	Initial Uptake of Monomer (% of Dry Weight)	Final Polymer Loading (% of Dry Weight)	Unpolymerised Monomer (% of Monomer and Polymer Loading at end of Irradiation Period)	Overall loss of Monomer Due to Weeping, Evaporation, and Incomplete Polymerisation (% of Initial Monomer Uptake)
29	2.5	12.2	7.1	35.7	41.7
31	3.5	11.4	5.1	21.9	32.6
14	4.5	11.1	7.4	20.6	33.6
16	5.5	10.7	8.1	9.2	24.1
18	6.5	11.0	8.3	5.9	24.3
19	7.0	10.5	7.1	13.2	32.4

TABLE 6

POLYMERISATION OF METHYL METHACRYLATE IN 100 x 50 mm DIAMETER CONCRETE CYLINDERS (READY MIXED CONCRETE TYPE NUMBERS 1-4)

Specimen Number	Dose (10^6 rad)	Dose Rate (10^6 rad h^{-1})	Unpolymerised Monomer (% of Initial Monomer Uptake)	Polymer Loading (% of Dry Weight)	
				After First Treatment	After Second Treatment
1A	1.76	0.36	39.7	5.3	
	4.44*	0.54	5.9		6.4
1B	1.76	0.36	31.7	5.9	
	4.44*	0.54	6.9		6.7
2A	1.76	0.36	36.1	5.8	
	4.44*	0.54	3.2		6.7
2B	1.76	0.36	23.0	6.0	
	4.44*	0.54	7.1		5.9
3A	1.76	0.36	35.3	7.5	
	4.44*	0.54	11.1		8.0
3B	1.76	0.36	23.4	7.5	
	4.44*	0.54	6.9		8.9
4A	1.76	0.36	28.9	6.5	
	4.44*	0.54	11.1		7.0
4B	1.76	0.36	22.7	6.8	
	4.44*	0.54	9.1		7.3

* *Irradiated in nitrogen filled polyethylene bags.*

TABLE 7

POLYMERISATION OF METHYL METHACRYLATE IN 0.13 mm POLYETHYLENE BAGS

(^{60}Co γ radiation at 0.61 x 10^6 rad h^{-1})

Dose Actually Given (10^6 rad)	Calculated Equivalent Dose at 0.54 x 10^6 rad h^{-1} (10^6 rad)	% of Monomer Polymerised
1.0	0.94	10.0
1.25	1.18	10.5
1.5	1.41	14.6
1.75	1.65	30.6
2.0	1.88	21.5
2.5	2.35	40.8
3.0	2.82	98.6
3.25	3.06	98.7
4.0	3.76	100.0

TABLE 8

100 x 50 mm DIAMETER CONCRETE POLYMER COMPOSITES

STRENGTH PROPERTIES

Concrete Grade	Specimen Number	Polymer* Loading % w/w	Compressive Strength (MPa)		
			Untreated	Treated	% Increase
1		0.0	19.0		
		MMA			
	1A	6.4		98.5**	420
	1B	6.7		107	466
		Polyester			
	1C	4.6		37	96
	1D	4.9		36	91
	1E	4.3		33	75
2		0.0	12.8		
		MMA			
	2A	6.7		107.5	743
	2B	5.9		93.5**	632
	2D †	5.3		64	400
	2E †	4.8		54	324
		Polyester			
	2C	7.9		72.5	468
3		0.0	7.9		
		MMA			
	3A	8.0		100.5	1,165
	3B	8.9		67**	743
	3C †	3.9		87.5	1,004
		Polyester			
	3D	7.9		35	339
4		0.0	19.3		
		MMA			
	4A	7.0		100	420
	4B	7.3		112	480
	4D †	5.6		69.5	261
	4E †	6.4		93	382
		Polyester			
	4C	3.8		25	29

* *MMA: Methyl methacrylate; Polyester: Polylite 8009*

** *Cap failure.*

† *Dipped in 40% poly MMA solution.*

TABLE 9

STRENGTH PROPERTIES OF 300 x 150 mm DIAMETER CONCRETE-METHYL METHACRYLATE COMPOSITES

Treated Specimen Number	Concrete Grade	Polymer Loading % w/w	Compressive Strength (MPa)			Brazil Tensile Strength (MPa)			Elastic Modulus (10^4 MPa)			Ratio of Average Compressive Strength to Average Tensile Strength	
			Untreated	Treated	% Increase	Untreated	Treated	% Increase	Untreated	Treated	% Increase	Untreated	Treated
1967	180	6.1	11	80.5 (a)	628 (a)	1.60	7.25	348	1.39	2.58	86	6.9	9.3
1968	180	6.5	-	83.5	656								
1971	180	5.8 (b)		67.5	512								
1972	180	7.0					9.15	471		2.55	84		
1979	240	4.8 (b)	30	76	153							7.9	11.3
1980	240	5.7		114	279								
1983	240	5.3				3.80	8.40	122	2.48	3.24	31		
1991	420	4.7	53	117	121							12.3	16.9 (d)
1992	420	4.3 (b)		95	79								
1995	420	4.5				4.30	6.25 (c)	45	3.19	3.75	17		
2003	540	4.2	66	109.5 (c)	67							11.8	12.2 (e)
2004	540	4.5				5.60	8.95	60	3.36	3.36	0		
1956	Plant Mix	6.3	24	103.5	329							9.2	18.0
1957	Plant Mix	6.1 (b)		98.5	309								
1958	Plant Mix	6.6				2.60	5.60	114	2.32	2.94	37		

(a) *Rough test on fragment from Brazil tensile specimen.*

(b) *Not wrapped during irradiation.*

(c) *Unusual failure.*

(d) *Affected by unusual failure in tensile specimen.*

(e) *Affected by unusual failure in compressive specimen.*

TABLE 10

COMPARISON OF COMPRESSIVE STRENGTHS OF COMPOSITES MADE FROM BESSER BRICK AND RMC PLANT MIX CONCRETES

Concrete Type	Original Compressive Strength (MPa)	Polymer Loading (% w/w)	Polymer Type	Compressive Strength of Composites (MPa)	Increase in Compressive Strength (%)
Besser Brick	25.2	11.4	Polyester	119.3	374
		12.6	Polyester	140.0	448
		12.9	Polyester	145.1	477
RMC Plant Mix	24.1	6.1	Methyl Methacrylate	98.6	309
		6.3		103.4	329

TABLE 11

CONCRETE SHRINKAGE SPECIMENS POLYMETHYL METHACRYLATE LOADINGS AND MONOMER LOSSES

Specimen Number	Concrete Grade	Initial Monomer Uptake (% w/w)	Polymer Loading	
			% w/w	% of Initial Monomer Uptake
1975	180	13.9	11.5	82.7
1987	240	12.1	9.7	80.2
1999	420	4.3	3.6	83.7
2011	540	6.0	3.8	63.3
1961	Plant Mix	6.3	4.7	74.6

TABLE 12

EFFECT OF FIRE EXPOSURE TESTS ON COMPRESSIVE STRENGTH OF CONCRETE AND CONCRETE-POLYMETHYL METHACRYLATE COMPOSITES

Core Specimen Numbers	Material	Fire Test	Average Compressive Strength (MPa)
17,18,19,20	Concrete	Nil	38 ± 4.0
21,22	Concrete	Early Fire Hazard	34 ± 6.5
9,10,13,14 15,16	Concrete	Early Fire Hazard and Fire Resistance	40 ± 3.0
23,24	Composite	Early Fire Hazard	64 ± 4.5
3,4	Composite	Fire Resistance	37 ± 1.0
1,2,5,6,7,8	Composite	Early Fire Hazard and Fire Resistance	51 ± 4.5

TABLE 13

EFFECT OF DYES ON RADIATION POLYMERISATION OF METHYL METHACRYLATE

(Dose Rate 0.6 x 10^6 rad h^{-1})

Dye	Dye Concentration in Monomer (% w/v)	Dose (10^6 rad) required for	
		50% Polymerisation	95% Polymerisation
Nil	Nil	2.7	2.9
Sudan IV Scarlet R	1.0	3.4	4.4
Waxoline Purple	1.0	3.8	4.0
Waxoline Blue	1.0	4.2	6.2
Waxoline Red	1.0	4.6	5.2

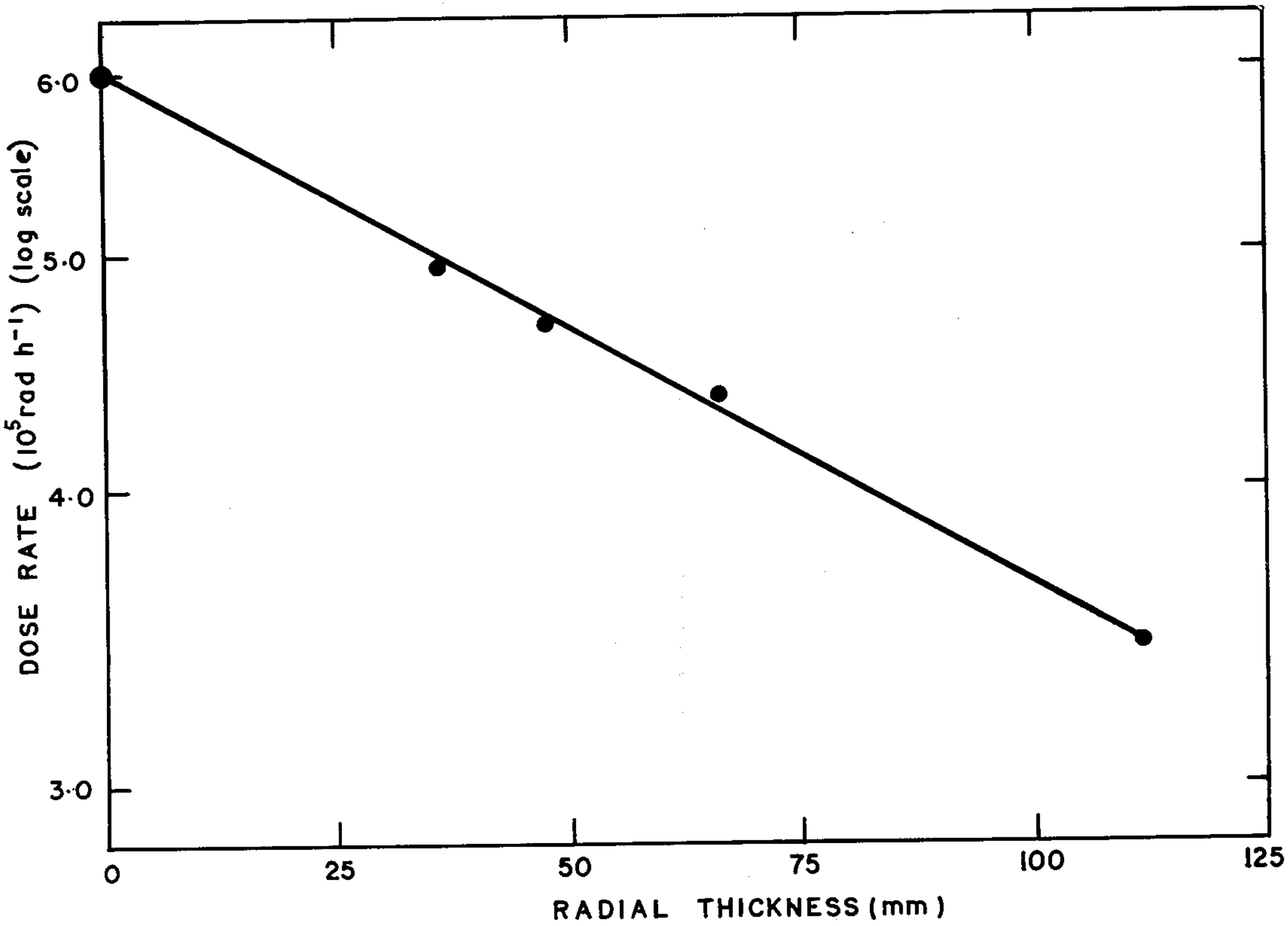

FIGURE 1. MINIMUM DOSE RATE IN CONCRETE CYLINDERS AS A FUNCTION OF RADIAL THICKNESS

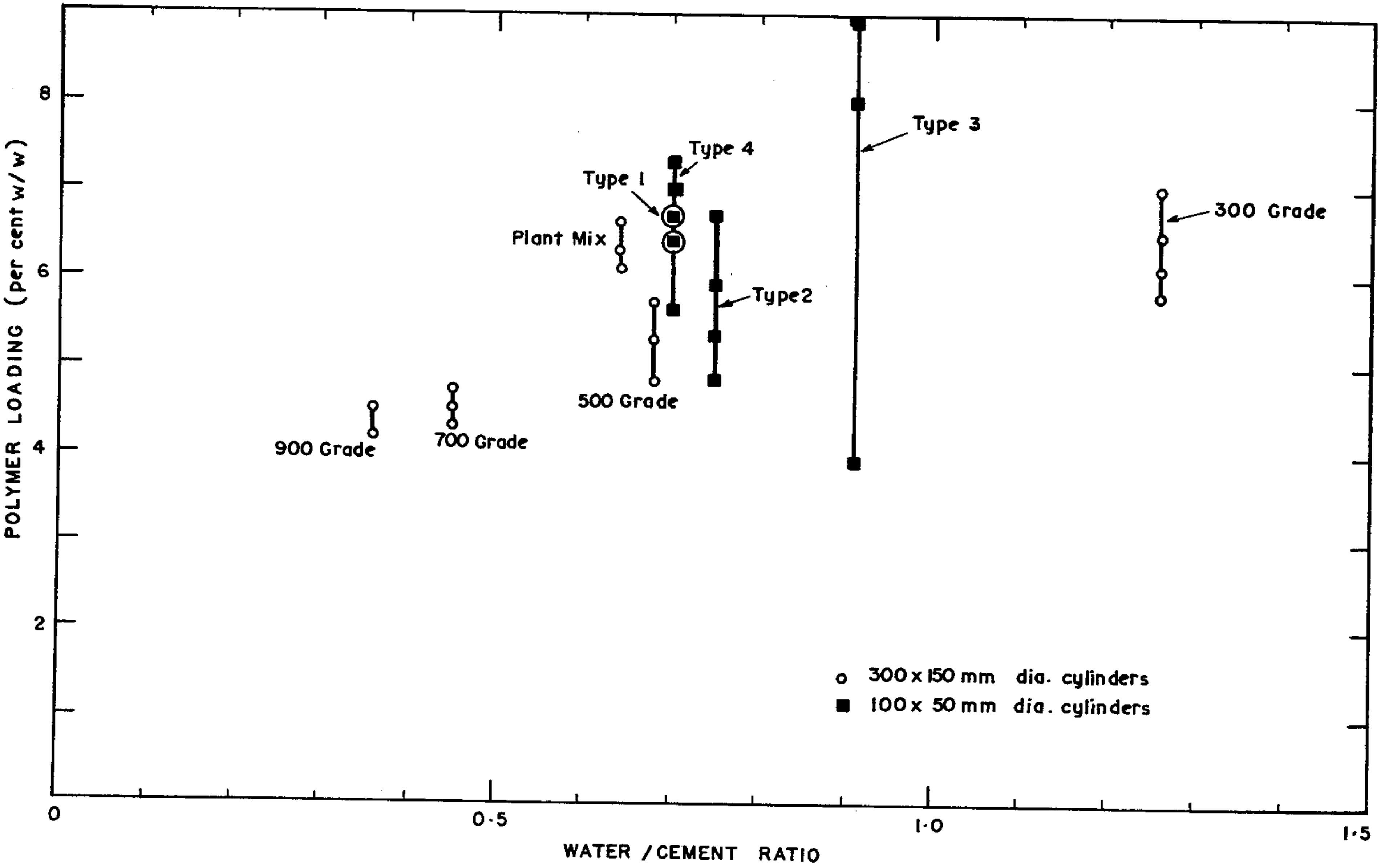

FIGURE 2. POLYMER (PMMA) LOADING AS A FUNCTION OF H_2O/CEMENT RATIO IN CONCRETE

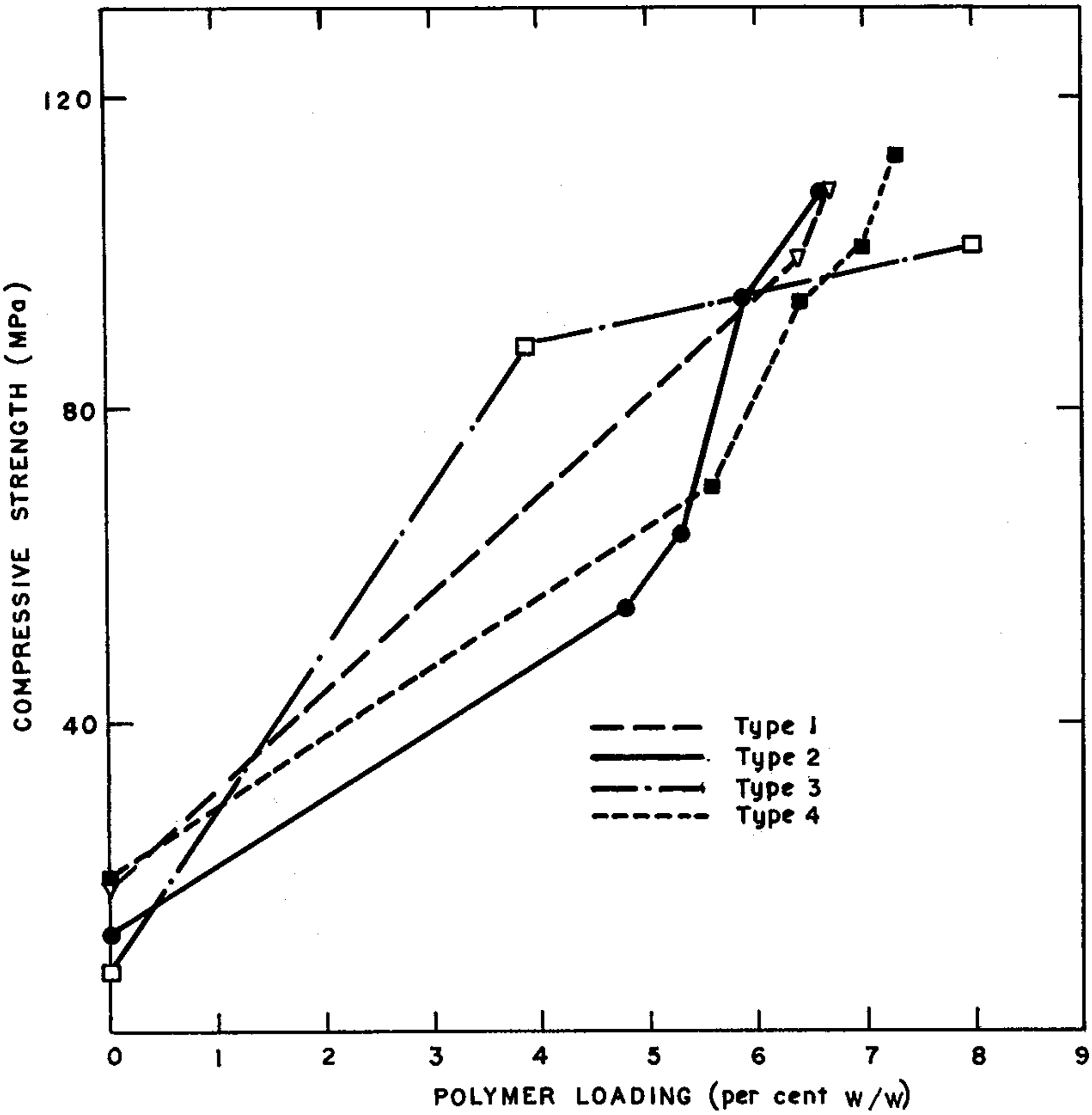

FIGURE 3. CONCRETE-PMMA COMPOSITES, 100 × 50mm DIA. CYLINDERS. COMPRESSIVE STRENGTH AS A FUNCTION OF POLYMER LOADING

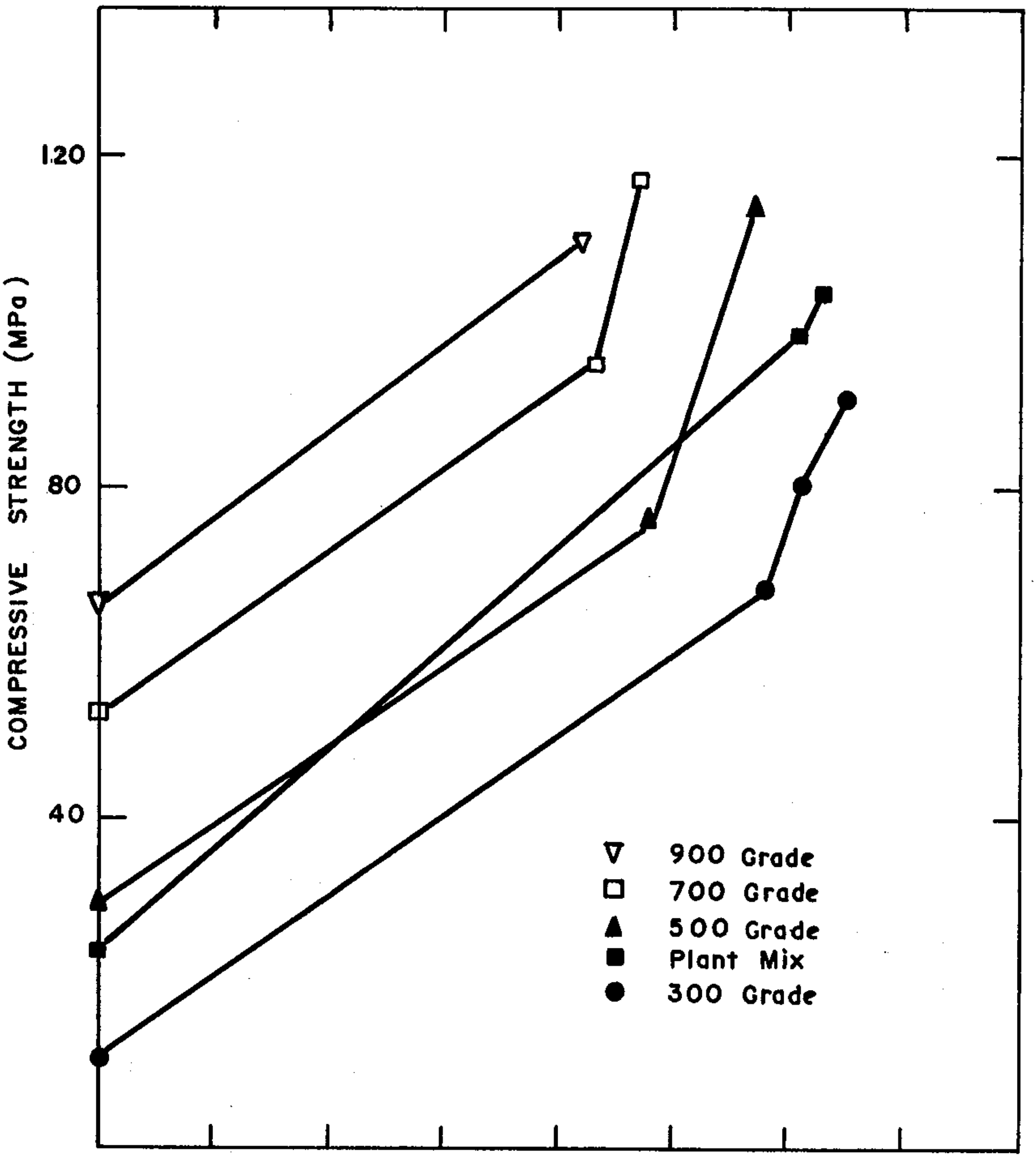

FIGURE 4. CONCRETE-PMMA COMPOSITES, 300 × 150mm DIA. CYLINDERS. COMPRESSIVE STRENGTH AS A FUNCTION OF POLYMER LOADING

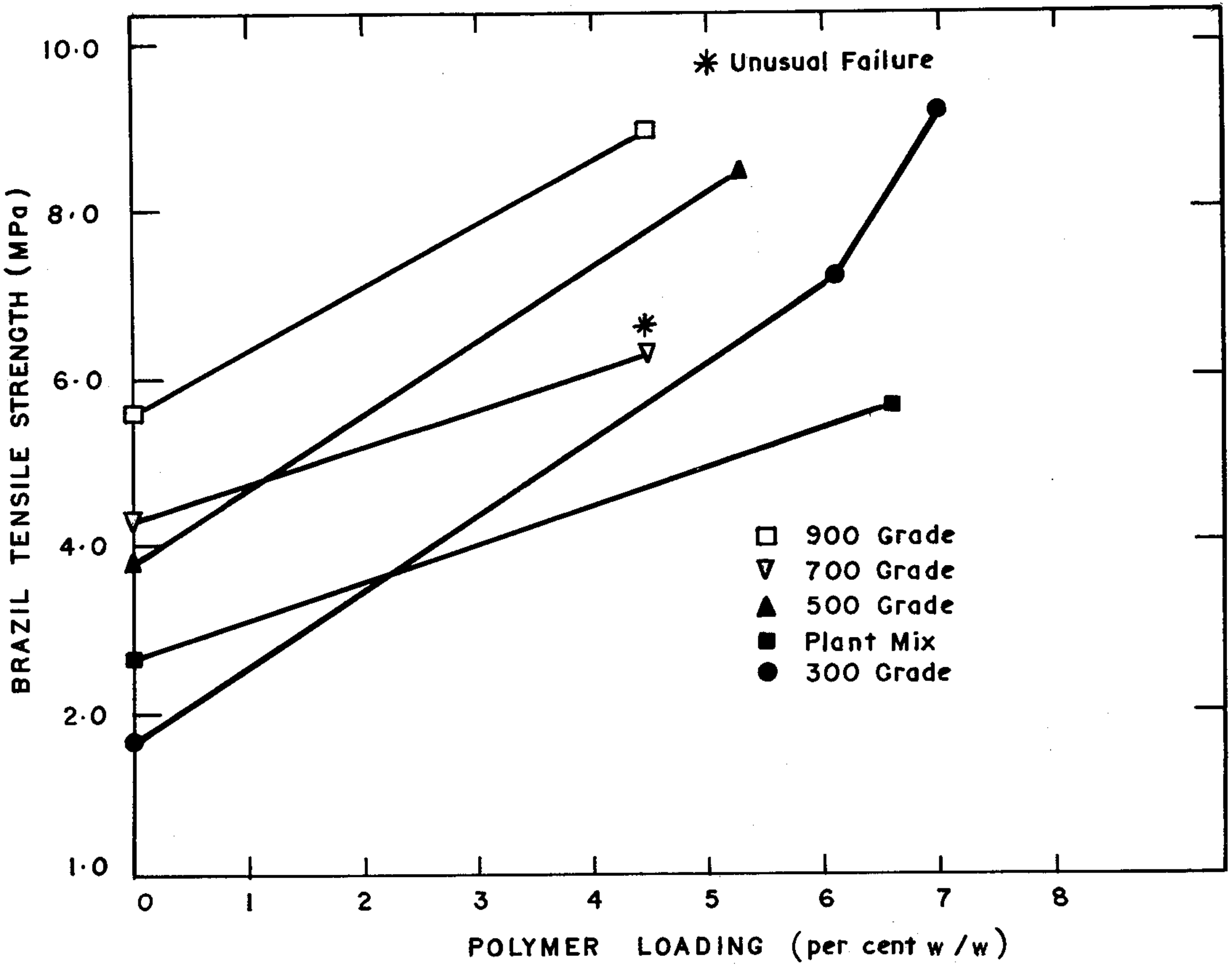

FIGURE 5. CONCRETE-PMMA COMPOSITES, 300 × 150mm DIA. CYLINDERS. BRAZIL TENSILE STRENGTH AS A FUNCTION OF POLYMER LOADING

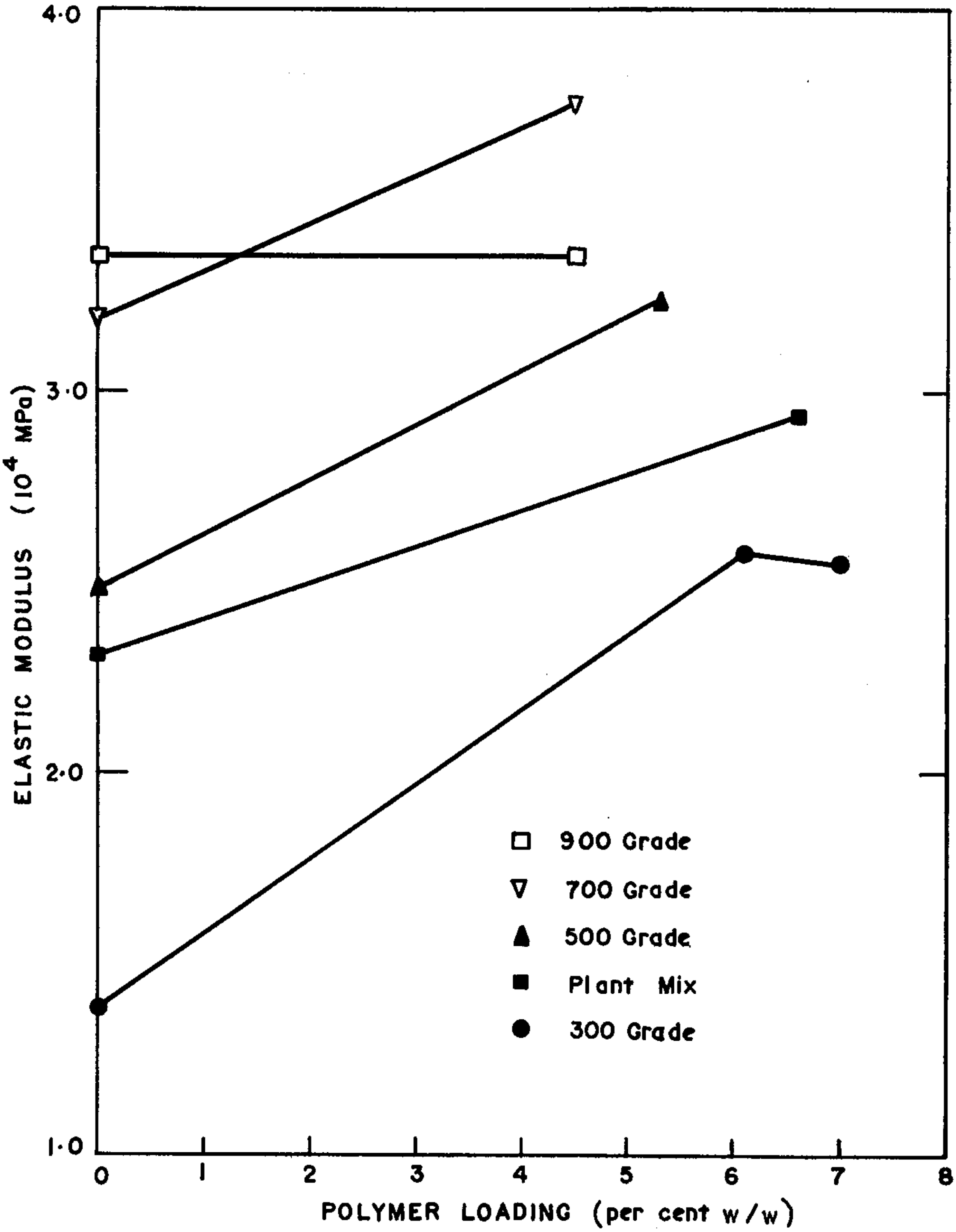

FIGURE 6. CONCRETE-PMMA COMPOSITES, 300 × 150mm DIA. CYLINDERS. ELASTIC MODULUS AS A FUNCTION OF POLYMER LOADING

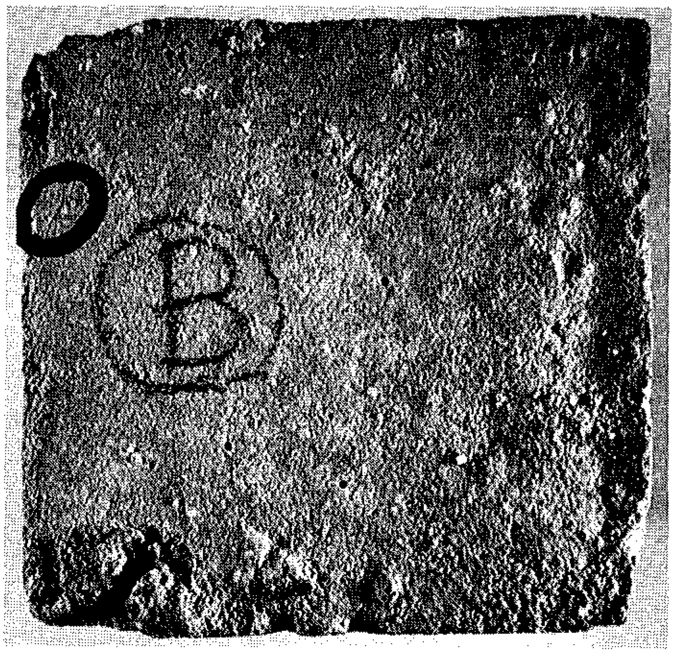

FIGURE 7. PMMA-CONCRETE COMPOSITE AFTER 93 h IMMERSION IN SATURATED LIMEWATER. SPECIMEN NOT DRIED BEFORE IMPREGNATION

FIGURE 8. PMMA-CONCRETE COMPOSITE AFTER 93 h IMMERSION IN SATURATED LIMEWATER. SPECIMEN DRIED BEFORE IMPREGNATION

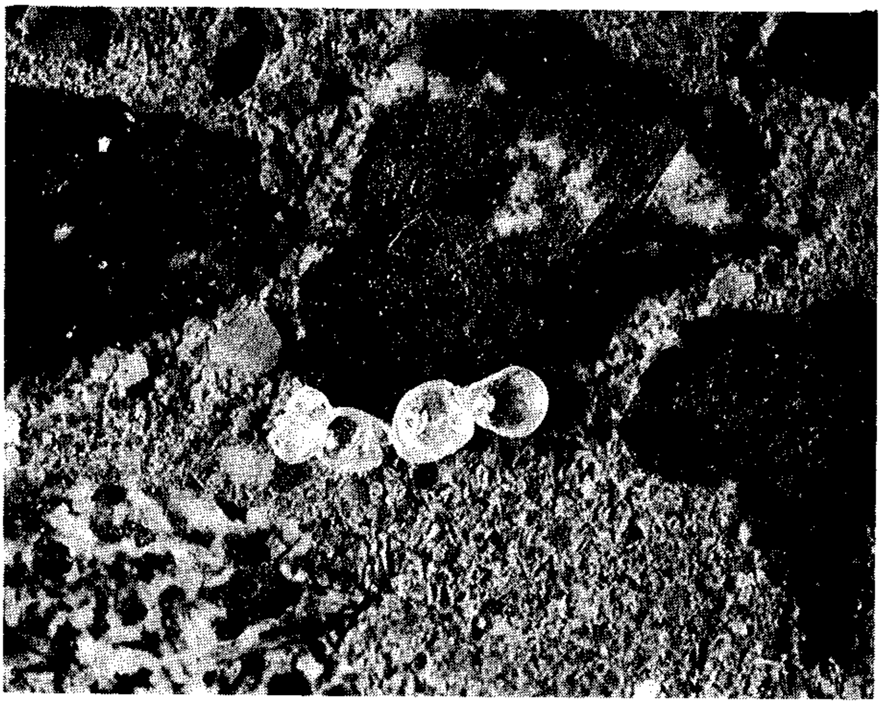

FIGURE 9. SPECIMEN B, SHOWING PLASTIC BUBBLES (×5.75)

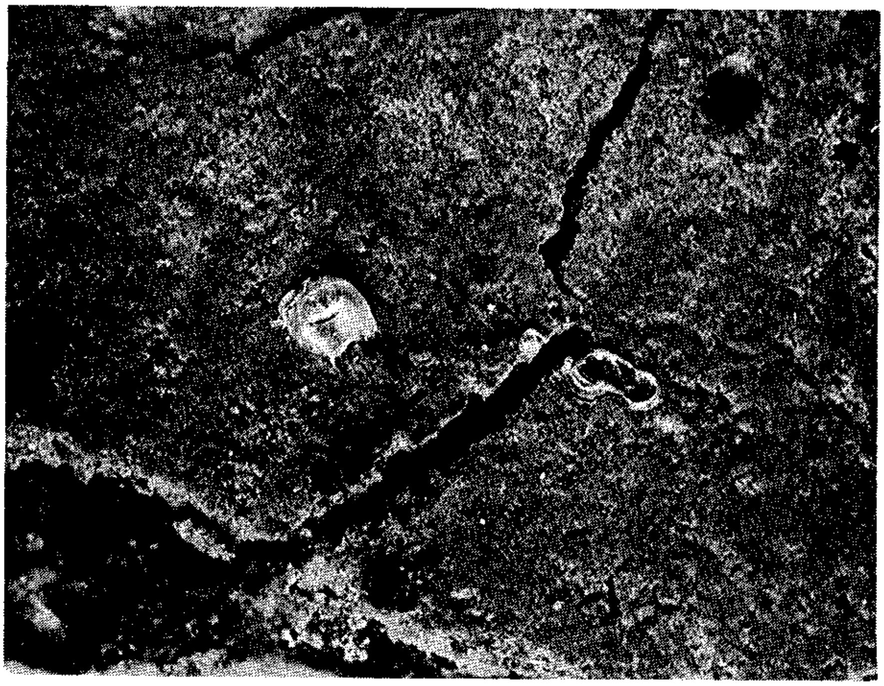

FIGURE 10. SPECIMEN D, SHOWING PLASTIC BUBBLES (AREA MARKED IN FIG. 8, ENLARGED ×5.75)