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Review
Polymer reinforcement of cement systems
Part 1 *Polymer impregnated concrete*

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In the last couple of decades several cement- and concrete-based composites have come into prominence. Of these, cement–polymer composites, like cement–fibre composites, have been recognised as very promising, and considerable research and development on their properties, fabrication methods and application are in progress. Of the three types of concrete materials which incorporate polymers to form composites, polymer impregnated concrete forms a major development in which hardened concrete is impregnated with a liquid monomer which is subsequently polymerized to form a rigid polymer network in the pores of the parent material. In this first part of the extensive review of the polymer reinforcement of cement systems, the process technology of the various monomer impregnation techniques and the properties of the impregnated composite are assessed critically. It is shown that the high durability and superior performance of polymer impregnated concrete can provide an economic and competitive alternative in *in situ* strengthening, and in other areas where conventional concrete can only at best provide adequate performance.

1. Introduction

Particulate-filled polymeric systems and fibre-reinforced polymer composite materials have been studied on a limited basis for many years; however, it was not until the 1950s that the potential for their use aroused serious interest among researchers all over the world. The addition of polymers to cement systems and their use either as a binding medium to aggregate particles or as a reinforcing agent to the cement matrix also came about at the same time.

In the widest sense concrete can be defined as any material that consists of solid aggregate inclusions bound together with a binding agent. In the case of Portland cement concrete, sand and stone aggregates are bound together with a hydrated calcium silicate matrix. Thus concrete is itself a composite material, the fine and coarse aggregates forming the dispersed phase held together by the continuous matrix phase of hardened cement paste. The aggregate volume in particulate systems like concrete is about 65 to 70%.

The aggregate inclusions dispersed in the cement matrix give the concrete system a measure of pseudo-ductility. The hydrated cement paste structure is also poorly bonded, primarily by Van der Waal's forces – the tensile strength and fracture toughness of the composite are consequently low. The aggregate–matrix bond is thus a very significant, and often critical, factor in all cement-based composites whether they be of plain concrete or reinforced with fibres and/or polymers. Indeed flaws originate at the interfacial bonds during production of the composite and its subsequent volume changes. These flaws thus form the source of much crack development.

The water in the cement matrix–aggregate inclusion system has a dual function. It is responsible for the hydration of the silicates and aluminates contained in the cement; it also imparts to the mix

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a degree of plasticity which is essential for the proper placing of the material. It is thus in the inherent nature of the hydration of Portland cement that excess water must be used to achieve satisfactory workability of the composite system, and the excess water, which is not chemically combined with the cement, gives rise to porous or capillary networks of different kinds. Since sand and stone particles have generally little or no porosity, and occupy some 65 to 70% of the composite volume, the bulk of the porosity of the composite occurs in the remaining cement matrix phase. The volume of these pores depends on the amount of mixing water used and the degree of hydration of the cement.

The pores in the cement matrix are of various sizes and shapes: the gel pores (10 to 100 Å diameter) and capillary pores (100 to 1000 Å diameter) are mainly caused by the evaporation of free water. These pores form interconnected networks; in the open pores and under normal curing conditions, air and water co-exist in a state of equilibrium depending on the ambient temperature and humidity conditions. In addition to these pores, much larger pores ($>$ 1000 Å) are created by entrapped or entrained air and occluded voids during manufacture.

The porosity of the cement matrix and the weakness of the aggregate–matrix interfacial bond are thus the two major factors limiting many of the physical and mechanical properties of cement composites. The pores have a critical role in the action of aggressive agents: they allow deleterious substances to penetrate and attack the matrix, or aggregate or the interfacial bond. Capillary phenomena thus seriously influence the dimensional stability, deformation behaviour, resistance to weathering and chemical attack of the hardened composite material.

2. Cement–polymer composites

Polymer–cement composites are those in which a matrix with a continuous pore system is filled with a second, namely polymeric, material. In the traditional composites, the matrix and the filler are combined before the composite is formed, and the relative volumes of matrix and filler can be varied over wide ranges. In the polymer–cement composites, the volume occupied by the filler phase results from the formation of the matrix, and the pore volume and the pore structure of the matrix determines the extent of the volume and distribution of the filler phase. If the average porosity of the concrete system is considered to be 10 to 20%, and the polymer filling is about 5 to 10%, the polymer addition to concrete, in terms of fibre- and particulate-filled composites, is very small. It is, therefore, more appropriate to talk in terms of cement–polymer materials or composites where the predominant phase is still the Portland cement matrix, rather than polymer–cement materials where, by implication, the polymer is the predominant phase. Cement–polymer composites have thus specific characteristics, from the viewpoint of both quality and cost, and bridge between conventional concrete and metallic and ceramic materials.

The name "polymer concrete", is thus too general and misleading. In the currently accepted terminology, however, three types of concrete materials, which incorporate polymers to form composites, are recognized:

(1) Polymer impregnated concrete or PIC, which is manufactured by impregnating with a liquid monomer, normal hardened concrete – either in precast form or in *in situ* members – which is subsequently polymerized resulting in the incorporation of a relatively small volume of a rigid polymer in the pores of the concrete. In this system, the process of cement hydration (cement curing) the monomer polymerization (polymer curing) are physically separated, and thus any possible undesirable mutual interactions of the polymerization and hydration processes are straightaway eliminated.

(2) Polymer–cement–concrete or PCC, in which a monomer or a polymer in the form of a latex is added during mixing of ordinary concrete with subsequent polymerization or curing initiated after placement of the materials. Polymerization of the added monomer or curing of the polymer may take place immediately after the mixing operation, or alternatively, after the concrete has hardened.

(3) Polymer concrete or PC, in which a monomer or resin is used as a binder, instead of Portland cement and water, for the aggregates. The material is polymerized or cured after placement.

The above classification of concrete–polymer composites does not include the use of modifying additives which are used in amounts so small that they do not significantly change the chemistry of the curing process or the structure of the resulting product.

The development of much of concrete–polymer composites is relatively new. Research on PC and PCC has been in progress since the early 1950s, and much of the early data are contained in the three symposia held by RILEM* and American Concrete Institute between 1965 and 1967 [1–3]. Extensive work on the technology and use of PCC and PC was carried out in Russia during this period and much of the data are well documented by Solomatov [4]† and Moshchanskii and Paturoev [5]†. One distinguishing feature of the Russian research is that there are several documented applications, particularly of PC, as surface coatings of reinforced concrete structures, floors and pipes, as well as in underground mining construction.

Major research on the impregnation of concrete with polymers and epoxies has occurred only since 1965, although a Russian patent is known to have been taken as early as 1960 [6, 7]. The technology of polymer impregnation has, however, been most exhaustively studied in a co-operative research programme at the Brookhaven National Laboratory, and their comprehensive research, documented most systematically in the five Topical reports [8–12], still forms the basis for many subsequent developments in Japan, France, Italy and other parts of the world. Since then, two major International Conferences on polymers in concrete have been held, and both the Concrete Society (UK) and the American Concrete Institute have produced comprehensive state-of-the-art reports [13–16]. Cembureau (The European Cement Association) has produced a bibliography of cement-polymer materials compiled by Idorn and Fördös [17].

3. Polymer impregnated composites

The application of the technique of impregnation arose from the need to protect wood from the dimensional instability caused by moisture interactions with its porous structure. After early unsuccessful attempts at stabilization by surface coatings and impregnants, the pioneering work of Stamm and co-workers on more rigorous impregnation techniques in stabilizing wood [18, 19] led to the application of some of the new techniques of radiation initiation to the grafting and homopolymerization of styrene and other vinyl monomers within the cell wall of the wood [20–22]. Karpov *et al.* [20] first described the preparation of composite materials comprising high polymers dispersed within an initially porous matrix. Polymerization was initiated by gamma radiation from Cobalt 60. The filling of the porous structure of the timber substrate with a tough inert polymer resulted not only in increased strength, hardness and stability but also, due to the polymeric component, in added benefits of good machining properties and resistance to moisture.

The need in desalination plants for a material which would withstand corrosion at high temperatures (290 to 350° F) and resist disintegration when exposed to repeated freezing and thawing led to further developmental work on polymer-wood composites by the US Atomic Energy Commission [23]. The novel properties of reduction in porosity and the increased resistance to corrosive environments endowed by filling the natural pores of the timber substrate with a tough inert polymer also led to similar developments by the UK Atomic Energy Research Establishment [24–27]. The use of irradiation as a technique of polymerization arose probably due to a need to find an outlet for the disposal of stored radiation energy. These techniques of the impregnation process were then extended to the treatment of concrete [8–12, 28–30] and the process has since been applied to a variety of other porous substrates such as soil-cement [31], stone [32], rock [33], glass and other ceramic products [34–37], sand-lime bricks and plaster of paris [38], asbestos cement products [39], brick masonry [40] and building blocks [41]. Polymer impregnation is reported to improve the machinability of porous aluminium compacts [42].

4. Polymer impregnated concrete

4.1. Monomer selection: general comments

Probably the most important consideration in the production of polymer-impregnated composites is the choice of a suitable monomer. The processes of polymerization are divided into two groups known as addition or chain reaction polymerization and condensation or step-reaction polymerization. Monomers which polymerize by condensation reactions are generally unsuitable since they often require high temperatures and acid-type catalysts

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* Réunion Internationale des Laboratoires D'essais et de Recherches sur les Matériaux et les Constructions.

† References [4] and [5] together relate to about 400 original publications: only those relevant to this review are quoted here individually. For a more comprehensive study readers are referred to references [4] and [5].

to initiate the reaction; they also produce contaminants which not only compete with the polymer for the available void space but also might damage the properties of the concrete or the composite. Monomers which polymerize additively such as methyl methacrylate, styrene and acrylonitrile are preferred, because they give no by-products and form polymeric linkages by re-arrangement reactions [43, 44].

The vapour pressures of the monomers at the polymerization temperatures are also important. Solid-type monomers are generally unsuitable for concrete–polymer composites whilst gaseous monomers such as ethylene and vinyl chloride present difficulties in use, as they require pressure chambers for their diffusion through concrete and subsequent polymerization, although they have been used to impregnate precast concrete [9, 10]. Liquid polymers are, in practice, more easily applied [9–11]. The solubility of the polymer in its own monomer is also important.

When the polymer is insoluble, precipitation occurs during the polymerization reaction and such polymers develop little cohesive strength. If the polymer is monomer-soluble, a tough glassy material is produced which gives excellent adhesion to the substrate. Polymers which are soluble in their own monomer are thus most effective. The hardness of the polymer is related to the glass transition temperature, the temperature at which the polymer begins to soften and flow (Table I) [43, 44]. The addition of cross-linking agents can not only increase the softening point but also improves the resistance to organic solvents and chemical attack.

4.2. Monomer types

The selection of a monomer to form a concrete–polymer material depends on the end application of the material, polymerization rate, the process technology and the properties and cost of monomer. For ambient and low-temperature applications below about 100° C, thermoplastic polymers are used. The low-cost monomers used in this category include methyl methacrylate (MMA), styrene, vinyl acetate, 60% styrene–40% acrylonitrile*, chlorostyrene, vinyl chloride, 10% polyester–90% styrene* and 90% MMA and 10% TMPTMA* [8–12]. Of these, MMA has produced generally and consistently the best and more uniform results.

In Russia, ethanol lacquers, perchlorovinyl and carbamide resins and urea formaldehyde resins have been used for impregnation. Murata and Kobayashi [7] successfully impregnated concrete with an uncured epoxy resin to a depth of 10 mm. This treatment was found to inhibit the flow of aqueous media into concrete. Whiting *et al.* [45] also used an epoxy impregnant in concrete. In UK, the atomic energy authority uses a proprietory impregnant containing styrene and acrylonitrile [26, 27].

Thermoplastics can also be introduced into the concrete mix as powders, followed by heating of the hardened concrete to melt the polymer, which then fills the capillaries and micropores in the concrete. Tests have been reported with polyethylene, soft polyvinyl chloride and polystyrene; and although polymer melts have been found in the concrete pores, the improvement in properties has been only marginal [4].

Table I [43, 44] gives strength and other properties of typical monomers used for composite formation. The strength properties of polymers vary widely depending on impurities, polymerization temperature, catalyst concentration and type of catalyst. Styrene and acrylonitrile are cheap compared to MMA; the styrene, however, has a relatively high viscosity compared to others, and is more difficult to polymerize and the acrylonitrile needs careful handling. Although more expensive, MMA is relatively easy to polymerize, and a suitable impregnant in other respects. It is the most widely used monomer system in concrete.

Monomers such as MMA and acrylonitrile are highly volatile and this produces bad surface quality when those monomers are used to impregnate thin sections. The volatilization can be significantly reduced when unsaturated polyester resins are used in mixture with styrene. Such impregnation mixtures have also the advantage of easy gelation with relatively low radiation doses and also require less radiation doses when polymerized at elevated temperatures.

For high temperature applications, such as flash distillation units in water desalination plants, a hard glossy polymer is required to withstand the hot brine and distilled water at temperatures up to 145° C. For such applications, thermosetting monomers are used; if thermoplastic type monomers are used in such conditions, they have to

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* Numbers refer to percentages by weight of the respective components in the mixture.

TABLE I Properties of typical monomer systems for composite formation

Impregnant	Boiling point (° C)	Glass transition temperature (° C)	Compressive strength (N mm^{-2})	Tensile strength (N mm^{-2})	Radiation dose required (Mrad)	Nature of polymer	Price* (£/tonne)
Vinyl chloride	−14	75	72.5	48.5	1.0–2.0	hard	70
Styrene	145	93	93.5	55.0	2.0–3.0	hard, brittle	77
Vinyl acetate	72	28	–	< 34.5	0.5–0.9	weak	128
Acrylonitrile	77	270	–	–	1.5	hard, powder	130
Vinylidine chloride	37	100	51.5	31.0	0.5–1.0	hard, powder	165
Methyl methacrylate	100	95	100	65.5	1.2–2.0	hard, tough	215
Ethyl acrylate	100	60	–	–	0.5–0.7	soft, rubbery	250
Polyester–styrene	–	≃ 90	160	72.5–112.0	0.8–1.0	hard, tough	340–410
Epoxy–styrene	–	≃ 125	172	70.5	2.0–3.0	hard, tough	350–400

* April 1973 prices [43, 44]. Current prices are approximately double.

be used as a two-monomer system with cross-linking agents. Incorporating a cross-linking agent in a polymer system improves primarily the thermal and chemical resistance properties of the polymer. It also greatly reduces the initiation time required for 100% conversion, but may also increase its shrinkage [46]. Cross-linking agents are polyfunctional compounds capable of taking part in two separate addition reactions simultaneously and form a three-dimensional network. Trimethylolpropane trimethacrylate (TMPTMA) and diallyl adipate are the mostly favoured cross-linking monomers, but several others are available. TMPTMA has also been successfully used for cross-linking in wood composites and is also known to improve the machining properties of polymer-impregnated wood [47].

The mixed monomer system used for high-temperature applications include: 70% MMA–30% TMPTMA, 60% styrene–40% TMPTMA, 90% diallyl phthalate (DAP)–10% MMA, acrylonitrile, diallyl phthalate, polyester–styrene and epoxy–styrene mixtures [8, 9]. 60% styrene–40% TMPTMA, and 90% DAP–10% MMA have been successfully used (Table II). The former has shown best results at working temperatures of 120 to 140° C at which impregnated concrete containing MMA has been known to show partial decomposition after about a year. Riley [48] has used a thermosetting co-polymer of styrene and divinylbenzene and maintained strengths of about 105 N mm^{-2} at temperatures up to 150° C.

Formation of addition polymers usually involves shrinkage. Polymerization shrinkage is an important property to be considered in the selection of monomers. MMA has, for example, a polymerization shrinkage of 20% and if only 80% of the available pores are filled on average, only about 65% of the pores are filled in the final product. Low polymerization shrinkage monomers such as *t*-butyl styrene and chlorostyrene have been used but the results have not been encouraging.

4.3. Viscosity of the monomer

The improved properties of the impregnated concrete depend on the decrease in the porosity achieved and this depends on the depth and uniformity of the penetration of the substrate. The most fundamental property which controls the degree of impregnation is the viscosity of the monomer (which is a function of temperature) which determines its rate of impregnation through

TABLE II Thermal and thermomechanical properties of polymers for elevated temperature applications

Monomer mixtures	Glass transition temperature, T_g (° C)	Softening point (° C)	Onset of decomposition (° C)	Activation energy (kcal mol^{-1})	Coefficient of thermal expansion (× 10^{-5} ° C^{-1})	
					Below T_g	Above T_g
90% diallyl phthalate 10% methyl methacrylate	186	348	200	22	4.7	13.3
60% styrene 40% trimethylolpropane trimethacrylate	214	374	225	17	3.8	12.8

TABLE III Monomer properties

Monomer	Viscosity (cps)	Boiling point (° C)	Freezing point (° C)	Flash point (° C)	Explosive limits, vol % in air
Styrene	0.76	145	−30.6	34.4	1.5–7.0
Methyl methacrylate	0.85	101	−48.0	21.1	2.1–12.5
Trimethylolpropane trimethacrylate (TMPTMA)	50.0	–	−14.0	> 300	–
Polyester–styrene	400–2000	–*	–*	34.4	1.5–7.0

* Values are dependent upon the relative amount and type of polyester base.

the capillary structure (Table III). This is confirmed by the fact that reduction in the polymer shrinkage does not necessarily improve the degree of filling of pores [10].

Experience shows that in addition to viscosity, other properties of the liquid monomer, such as surface tension and vapour pressure are also important. The former controls the capillary attraction while the latter must be comparatively low to enable diffusion through concrete under low pressure. This latter also means less monomer loss if the impregnated concrete is exposed to air for a period before its polymerization.

Monomers with low viscosity are more suitable for total impregnation in order to improve the whole product quality; mixtures with higher viscosity which allow a more regular penetration, are more suitable for surface treatments. In any case, it is possible to vary the vapour pressure and the viscosity of the formed monomer by using varying proportions of prepolymers.

The degree of impregnation depends not only on the viscosity and surface tension of the monomer but also on its molecular size and the size of the capillary pore structure of the hardened cement paste as well as the interaction between the capillary pore walls and the organic molecule [49]. Tests by Mikhail and Selim [50] show that the ability to penetrate into the small pores of the hardened paste system depends largely on the size of the molecule, i.e. the hydrated cement paste matrix acts as a molecular sieve [51].

The significance of the molecular sieve effect is relevant not only to the polymer but also to the catalyst and cross-linking agent added to the monomer. Polymer impregnation of high-density mortars, made from very low water–cement ratios, shows that whereas the monomer (MMA) easily impregnated the mortar, the catalyst such as benzoyl peroxide penetrated only the surface layers – in other words, the hardened paste matrix acted as a true molecular sieve [49]. This absence of the catalyst in the innermost layers of the product impregnated with the monomer prevents a complete and homogeneous polymerization of the monomer. This probably explains why thermocatalytically treated concretes often show lower mechanical strength, especially when benzoyl peroxide is used as a catalyst, compared to radiation-polymerized concrete using the same or styrene monomer [8].

As a class of materials, epoxy resins are of higher molecular weight and hence more viscous than MMA; also, some epoxies are more viscous than others. Their viscous nature prevents deep penetration into the pores of the concrete matrix, and therefore, impregnation with epoxies, while resulting in excellent durability and resistance to water penetration [7, 52] is not as effective in increasing compressive strength as MMA [43, 52, 53]. Reimpregnation of epoxy-impregnated specimens increases their compressive strength to values comparable to MMA-impregnated specimens but would equally increase the cost of strengthening concrete by polymers [52].

For the insulation type of lightweight concrete of low dry density of 400 to 480 kg m^{-3}, a viscous monomer (70 cps, monomer 20% PMMA solution or 50% polyester–50% styrene) has been used in conjunction with vacuum-soak process to produce samples with high polymer loadings, uniform polymer distribution and good surface appearance [54–56]. The molecular sieve effect discussed earlier does not probably apply to open-pore materials such as lightweight concrete.

4.4. Plasticizers

Plasticizers are generally chemically and thermally stable organic materials used to modify the physical properties of polymers. They are widely used to improve the flexibility of polymers and, therefore, processability. Most polymers used for

TABLE IV Resistance characteristics of polymers

Property	Polystyrene	Polymethyl methacrylate	Polyester–styrene
Effect of sunlight	Yellows slightly	None	Yellows slightly
Effect of weak acids	None	None	None
Effect of strong acids	Attacked by oxidizing acids	Attacked only by high concentrations of oxidizing acids	None to slight
Effect of weak alkalis	None	None	None to slight
Effect of strong alkalis	None	Attacked	Attacked
Effect of organic solvents	Soluble in aromatic and chlorinated hydrocarbons	Soluble in aromatic and chlorinated hydrocarbons	Attacked by ketones and chlorinated solvents

concrete–polymer composites are strong and brittle; plasticizers can make them more ductile and capable of absorbing higher impact loads. Some plasticizers, such as dioctyl phthalate, might cause deterioration when subjected to outdoor exposure [46]; compatability and permanence are, therefore, basic requirements for a plasticizer.

Since polymer loadings are very low in impregnated systems, the effects of plasticizers are less pronounced in such materials. However, tests at Lehigh University have shown that concrete can be successfully impregnated with a co-polymer system of MMA and polybutylacrylate, and that if sufficient quantities of polybutylacrylate are combined with MMA, the ductility of the impregnated composite can be substantially increased, although its strength and stiffness are both reduced [57].

4.5. Silane coupling agents

Tests have shown that the type of bonding that normally occurs between polymer and siliceous aggregates is a physical bond [12]. Bond energies resulting from physical bonds, in which the polymer and aggregate are held together by Van der Waals forces, are an order of magnitude weaker than those of chemical bonds ($\simeq 20$ to 150 kcal mol^{-1}). Silane coupling agents can induce chemical bonds between the polymer and aggregate [12]. The simplest method of application, although not the most efficient, is to mix silane with the monomer prior to contact with sand or precast concrete. The effectiveness of silane coupling agents is probably less pronounced for cement–polymer materials in which the cement phase is the binder and most predominant (such as PIC and PCC systems) but more significant in systems where the polymer is the binder (such as PC).

4.6. Chemical stability and flammability

The important requirements of polymers are resistance to acids, alkalis and organic solvents. The significant chemical resistance characteristics of the more common polymer systems used in concrete are shown in Table IV. Since the amount of polymer on the surface of most concrete–polymer composites is small, they are unlikely to suffer deterioration on exposure to sunlight. Cross-linked polymers generally possess high resistance to solvents.

The high boiling points and low freezing points of monomer systems used in concrete systems (Table III) give them great applicability over a wide range of temperatures. Many monomers have, however, low flash points and are, therefore, highly flammable liquids and handling of monomers, particularly in large volumes, requires rigid safety controls. Flame retarders reduce flammability but may also adversely affect the mechanical properties of the polymer.

Most monomers contain an inhibitor to prevent their premature polymerization. Inhibitors are chemical compounds which serve as free-radical scavengers. To be effective they must always be maintained above a minimum concentration or danger level. Ultraviolet light is also effective in initiating polymerization and monomers should be shielded from exposure to sunlight and fluorescent lighting.

4.7. Porosity of cement substrate

Since the ability to penetrate into the pores of the hardened paste systems depends largely on the size of the monomer molecule, the porosity and pore-size distribution of the cement-paste matrix are important factors which determine the various stages of the process technology such as drying and the impregnation time required, which, in turn, determine the amount of possible polymer loading or the amount that could be incorporated in the matrix system.

The permeability of the concrete matrix is, however, mainly related to the capillary pores. The pore structure of the paste matrix depends on the water–cement ratio which determines the amount of capillary pores or channels and the average pore size. The process of hydration or maturity of the paste matrix causes a reduction in capillary porosity, a net filling of large pores, and possibly, a relative change in the shape of the pore [58–60].

If the relationship between applied pressure, P, and the pore diameter, d, developed by Washburn [61] is applied to cylindrical pores, i.e.

$$P = \frac{-4\gamma \cos \theta}{d}, \tag{1}$$

where γ is the surface tension of the liquid and θ is the contact angle between the liquid and solid (which is a function of the state of dryness of the solid), the minimum diameter of micropores that could be impregnated with MMA at a pressure of $0.4\,\mathrm{N\,mm^{-2}}$ is of the order of tenths of a micron or thousandths of an Ångstrom. Since gel pores are much smaller than these, and have an extremely low coefficient of permeability, it is most likely that these pores are not available for monomer penetration particularly in mature pastes of low water–cement ratio [62, 63].

The technology of monomer impregnation is thus very closely related to the water–cement ratio, the maturity of the cement substrate and the properties of the monomer. Tests also show that it is possible, by suitable choice of process technology and careful selection of the impregnant system, to obtain the same degree of loading with a viscous impregnant as with a low viscosity monomer [44, 48, 64]. In other words, the impregnation process has to be adapted to the monomer system and the characteristics of the concrete structure to be impregnated.

The porous structure of the cement paste can also be altered to favour impregnation by increasing the temperature of hydration [10, 65–67]. Autoclave treatment has been suggested to permit the modification of pore distribution favourable to impregnation, without changing the total porosity of the hardened paste system [10, 49]. It has also been suggested that autoclaving transforms the geometric structure of pores, from the "bottleneck" shape characteristic of room-temperature cured products [58] into a cylindrical, more regular shape which is more suitable for impregnation [49].

5. The impregnation process

Because of the interrelationship between the viscosity and the molecular size of the monomer on the one hand, and the pore structure of the hardened cement matrix on the other, many test results show that for a given monomer and concrete system, the properties of the final composite are more dependent on the polymer loading than on the polymer composition [8–12]. Both entrapped air and water have to be removed before the monomer can enter the pores of the system, and therefore the various techniques used in the impregnation process have an important influence in obtaining maximum monomer loading and increasing the efficiency of polymer impregnation.

Theoretical considerations show that pore-impregnation with polymers, even when complete, cannot give the same strength that could be reached by a cement paste without pores [68] which implies that there are pore sizes that cannot be reached by the monomer. The suggestion of the use of very compact concrete of relatively low porosity to maximize the performance of the composite with a low amount of polymer [49] then becomes questionable in relation to the whole concept of polymer impregnation.

6. Process technology: monomer impregnation techniques

Several factors influence the rate and degree of monomer loading in a concrete specimen, and to obtain any desired degree of monomer loading, the various factors, alone or in combination, have to be optimized to give the best preparatory results. Test data show that there is no direct relationship (for concretes of all porosity) between the solid fraction of the cement paste and monomer and the mechanical strength of the impregnated composite [49, 69]. However, for a concrete of given porosity, the strength, elasticity and durability properties increase with the degree of monomer loading [8–12, 62].

The quantity of monomer able to penetrate into the concrete during the impregnation phase depends on the quantity of free water and air that can be removed from the sample. In addition, the properties of the monomer system at the temperature of impregnation and the quality of the concrete also influence the degree of monomer loading. All these factors have been extensively investigated

[8–12, 47, 68, 70–74]. The various processes used for monomer impregnation are: (a) drying, (b) evacuation prior to soaking, (c) soaking and (d) application of pressure during soaking.

6.1. Drying

Thermal heating of concrete to temperatures above 100° C removes most of its evaporable water and makes it favourable to monomer impregnation: of all such treatments, thermal drying is most practicable and rapid for water removal. Microwave heating has also been tried with success, but it is certainly uneconomical because of the high energy requirements.

Adequate drying rather than the monomer penetration *per se* is the more important problem in achieving deep impregnations. The monomer will fill only those void spaces that are free, and penetration will proceed until the impregnant reaches the water remaining in these spaces and then stops. Normal weight dried concrete will absorb generally about 4 to 7 wt.% monomer compared with 2 to 3 wt.% absorbed by undried specimens equilibrated under ambient conditions (Fig. 1) [49]. Drying time and treatment temperature both influence the dehydration process and depend on the concrete quality, size of specimen and the degree of dehydration required [8, 10, 12, 46, 71, 75, 76]. The duration of drying also depends on the temperature and curing regime prior to drying [49, 71].

Flame drying at temperatures up to 400° C has been found to be effective in the field impregnation of bridge decks, and although cracking reduces the strength of the concrete, the cracks are healed by impregnation and the strength, compared to that of conventionally dried materials, is restored [77, 78]. Adequate drying does also appear to take longer with salt-contaminated concrete [78].

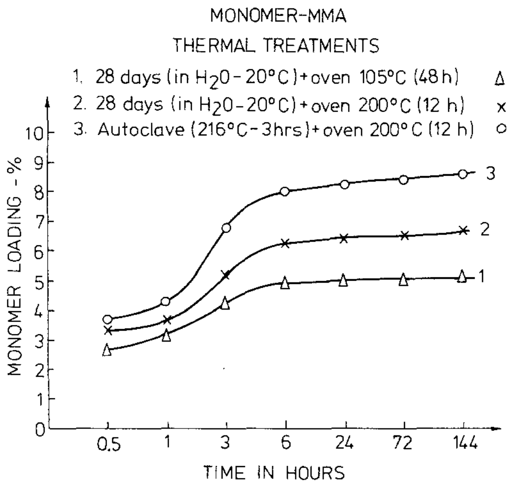


Figure 1 Influence of curing and thermal treatments on monomer loading [49].

Partial drying and incomplete polymerization can have deleterious effects: this may reduce not only strength and stiffness of the composite [46, 62, 75, 79] but there may also be long-term interactions of the unconverted monomer with the alkaline environment of the cement paste and water present in the member [9, 12, 80]. This may have practical implications of cracking and loss of durability in practice when partially dried large specimens are impregnated or in *in situ* polymerization when complete drying is difficult to achieve.

The concept of high temperature thermal drying (Fig. 1) to create a pore-structure most favourable to impregnation without the need for vacuum treatment has also been suggested [49, 81]; however, such treatment may create a metastable concrete and may affect the long-term durability of the impregnated composite.

6.2. Evacuation prior to soaking and soaking time

For concrete dried to constant weight, the polymer loading depends on the duration of soaking in monomer as well as whether or not a vacuum is applied prior to impregnation. Evacuation prior to soaking is generally carried out for full impregnation, to obtain maximum monomer loading, and to increase the effectiveness of impregnation by eliminating entrapment of air towards the centre of the specimen during soaking. Evacuation of specimens after drying to equilibrium also decreases the soaking time required to obtain a given monomer loading. In general, for similar soaking times, the polymer loading is increased by 20 to 30% for evacuated over non-evacuated samples [52, 82, 83]. For a given monomer and drying process, the rate of monomer impregnation, whether without or with vacuum treatment, is influenced by the initial water–cement ratio of the mix [76] (Fig. 2). Maximum monomer loadings are only possible if the specimens are evacuated prior to soaking [52].

6.3. Application of pressure

The application of pressure increases the penetration velocity, and reduces the time required for complete penetration, on average, by one-quarter compared with that required in the absence of

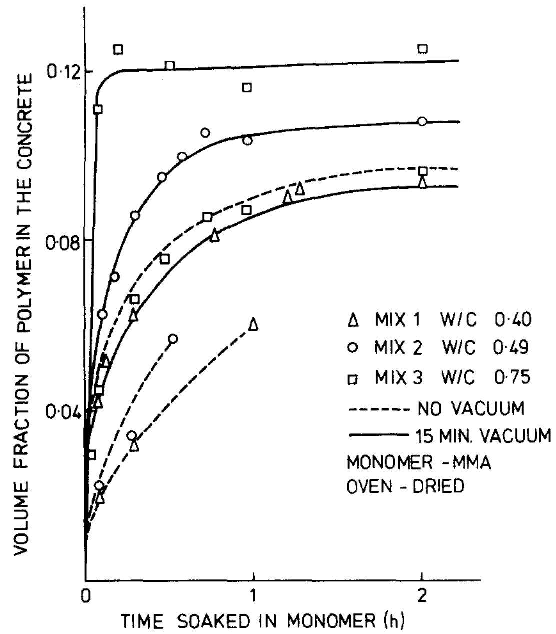


Figure 2 Influence of water–cement ratio and vacuum treatment on polymer (MMA) loading [76].

pressure. For a given applied pressure, the degree of vacuum treatment has a pronounced effect on the saturation time particularly at low impregnation pressures; this also affects the monomer loading and the final strength of the composite (Fig. 3) [12, 68].

The influence of pressure on the impregnation process depends essentially on the viscosity of the monomer. For low viscosity monomers like MMA and styrene, the influence of pressure is less pronounced and low pressures are adequate to increase the velocity of penetration. For higher viscosity monomers such as polyster and styrene mixtures, the use of pressure is important. For non-evacuated specimens, the effect of pressure on monomer loading is generally much less pronounced. For a required polymer loading, the pressure can be adjusted to reduce the evacuation and soaking time to a minimum (Table V) [71, 82, 83].

The combination of evacuation and pressure, together with the water content of the mix, have thus a significant effect on the impregnation rate, impregnation depth and monomer loading of a given dried concrete [46].

6.4. Monomer filling rate

In addition to the impregnating conditions (i.e. drying, vacuum, pressure, etc.), the composition of the concrete and, in particular, the porosity of the cement phase and the viscosity of the monomer also influence the rate of monomer filling into the concrete substrate. For a given monomer and set of process parameters, the presence of high air and water contents in concrete mixes enables

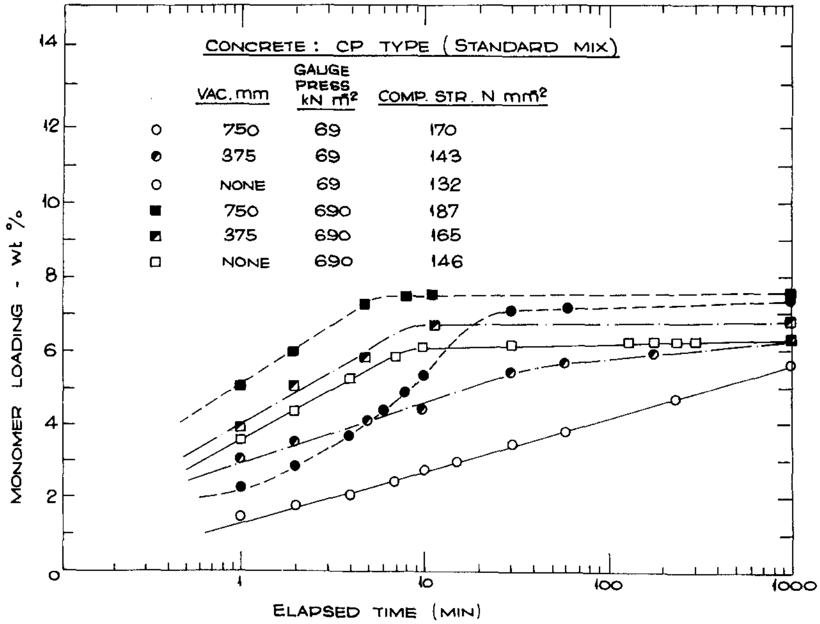


Figure 3 The effect of vacuum and pressure on monomer (MMA) loading of 75 mm × 150 mm cylinders dried at 110° C [68].

TABLE V Influence of evacuation time, soak time and applied pressure on polymer loading

Specimen* no.	Evacuation time (h†)	Soak time in monomer (h‡)	Pressure (N_2), psig (kgf cm^{-2})	Polymer loading, (wt %)
1§	0	3	0	1.89
2	0	3	0	4.61
3	0	1	5(0.4)	3.62
4	0	3	5(0.4)	4.62
5	0	5	5(0.4)	4.81
6	2	1	0	4.54
7	2	3	0	5.44
8	2	5	0	6.32
9	2	1	5(0.4)	6.64
10	2	2	5(0.4)	6.15
11	2	3	5(0.4)	6.43
12	1	1	5(0.4)	6.51

* All specimens are 75 mm × 150 mm cylinders.

† Vacuum pump to ≈ 25 mm Hg.

‡ Methyl-methacrylate monomer.

§ Except for no. 1, all specimens were dried to equilibrium prior to soaking.

saturation to be achieved in much shorter times than for a standard concrete mix (Fig. 4) [68], but the initial filling rate is greatly enhanced for concrete with high air contents than for any other concretes. Long filling times are required for porous aggregates (such as lightweight aggregates) and their monomer loading is likely to be very high [54, 56].

The monomer viscosity also has a significant influence on the filling rate of concrete [12, 68]. However, after polymerization, all the specimens have similar compressive strengths (Fig. 5). All these results show that for a given monomer, the concrete mix and the process conditions can be modified to give a desired monomer loading and strength of composite.

With more viscous monomers and epoxy systems, it is not only necessary to dilute the epoxy resin but the concrete has also to be throughly dried and evacuated prior to impregnation [53]. Higher applied pressures of the order of 1400 kN m^{-2} are also necessary to achieve maximum load-

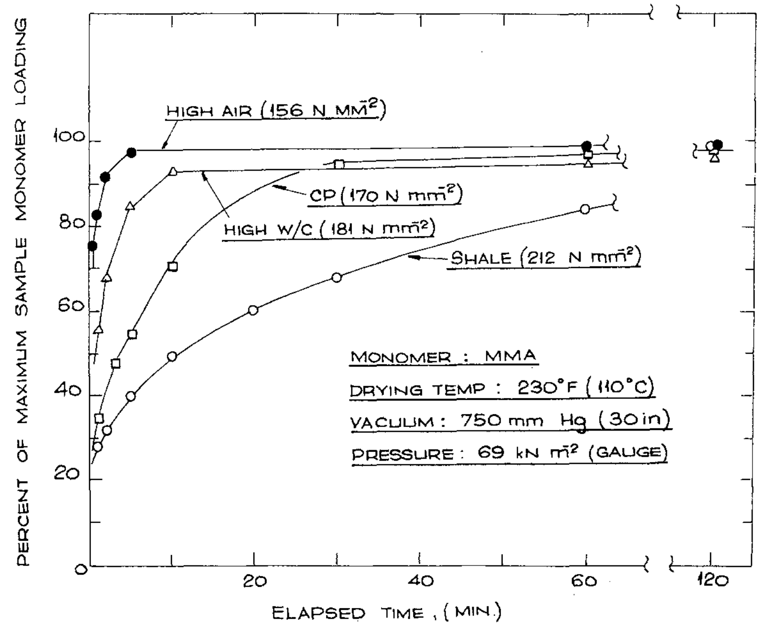


Figure 4 Influence of concrete composition on impregnation rate and compressive strength [68].

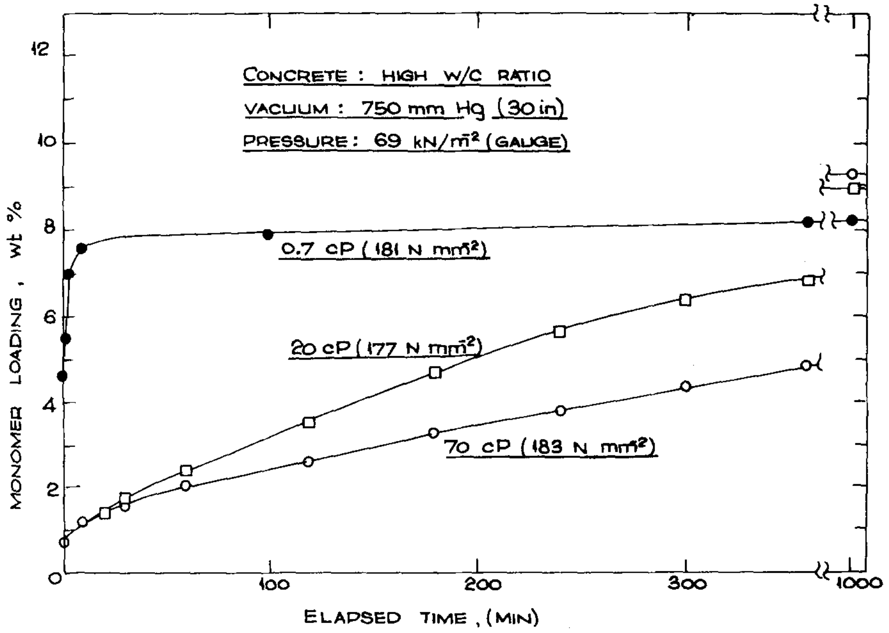


Figure 5 Effect of monomer viscosity on impregnation rate and final compressive strength of composite.

ing in a reasonable time. With very viscous monomers and epoxies, non-uniformity of polymer loading is often observed [8, 53].

6.5. Mechanism of monomer penetration

The rate of penetration and equilibrium sorption of monomer into concrete depends on the porosity of the substrate (i.e. on its prevous curing regime and preparation prior to impregnation), the monomer structure and properties (i.e. its interfacial energy and viscosity), and the experimental conditions of impregnation.

The rate at which a liquid penetrates a small capillary pore of radius r follows Poisseuille's law and has been investigated by Washburn [84] and Rideal [85]. It is given by

$$h^2 = \frac{\gamma}{\eta}\frac{\cos\theta}{2}rt, \qquad (2)$$

where h is the height of capillary rise in time t, θ is the contact angle, γ and η, the surface tension and viscosity of the fluid, respectively. For a given contact angle and pore size, h should, therefore, vary directly with the term $(\gamma t/\eta)^{1/2}$. The penetration of a fluid into a porous substrate should proceed according to Equation 2 until it is counterbalanced by evaporation from the surface or stopped by entrapped air or water. Since the rate of penetration is a function of both time and applied pressure [12, 46, 68, 86] the rate of penetration under a pressure gradient Δp may be represented as [86].

$$h = Kt^{1/2}\Delta p(\gamma/\eta)^{1/2}, \qquad (3)$$

where K is a function of pore radius and contact angle of the monomer on the concrete substrate. The time required to reach a given depth is, therefore proportional to $(\Delta p)^2$. The penetration behaviour in the field can thus be predicted from laboratory specimens.

Vanderhoff *et al.* [87] have shown that, for a given porosity, the equilibrium sorption is the same for a wide variety of liquids, although their rates of penetration were different. The presence of salt in the pore system results in a decrease in the rate of penetration due to a reduction in porosity and a decrease in equilibrium sorption [87]. The salt clogs the capillary pores and restricts the movements of water and monomer. This, therefore, has practical implications in the impregnation of bridge decks contaminated with de-icing salts.

Godard *et al.* [88] have studied the kinetics of penetration of low molecular weight monomers into asbestos–cements. They showed that the parabolic law of impregnation is only valid for degrees of impregnation not greater than 55% and that the flow of liquids in pores less than 300 Å diameter cannot be considered as "Poisseuillian". The second model based on Fick's second law of diffusion was found to express the overall kinetics of impregnation quite satisfactorily despite the fact that the phenomenon is very different from a molecular diffusion. They found their experimental results to be in excellent agreement with the theory up to a degree of impregnation of 80%.

It is obvious that in the present state of our knowledge of the kinetics of impregnation of monomeric liquids into the pores of the cement–concrete system, numerical values relating to individual impregnation treatments should not be generalized, because of the wide range of variables that influence the degree of impregnation.

6.6. Monomer losses

Extrusion of the monomer from the concrete occurs because of the presence of residual air and also its expansion due to the exothermic reaction. It is, therefore, important to take steps to minimize monomer evaporation and drainage losses prior to and during the polymerization reaction. Such losses became appreciable when low-density concrete is impregnated or when high vapour pressure monomers such as MMA are used; the losses also depend on the time required for polymerization. Specimens fully impregnated without surface protection show monomer loss from the surface and are likely to have a more permeable skin [89].

Several methods of reducing these losses have been studied [9, 55, 68, 70, 75, 90, 91], such as wrapping the specimens in polyethylene sheets or aluminium foil, which are not suitable for industrial production. An alternative method is to provide, following impregnation, a surface coating by means of a concentrated solution of the polymer in its own monomer to prevent the outward migration of the monomer and its evaporation. This method requires the specimen to be rotated during polymerization which becomes impractical when large sections are involved [55].

The use of a liquid medium in which neither the monomer nor the polymer is soluble, such as water, enables the operations of protection and polymerization to be carried out simultaneously and is suitable for industrial and field applications. Such a system reduces polymer losses, gives better appearance and prevents polymerization that occurs, with other methods, outside the treated specimens. With high-porosity concretes such as those using lightweight aggregates and lean mixes used for roads which have higher drainage losses, encapsulation of the concrete in tight-fitting forms has been found to be more effective than underwater polymerization [55].

7. Polymerization techniques

After impregnating concrete with liquid monomer, polymerization of the monomer has to be carried out to fill and seal the pores of the concrete with the solid polymer. Addition polymerization is initiated by free radicals, which can be formed by heat, generally in the presence of catalysts. Alternatively, high-energy radiation emitted by radioactive materials can be used, and gamma radiation from Cobalt-60 has special advantages in composite formation [92, 93].

7.1. Radiation-induced polymerization

The use of nuclear radiation to produce new polymeric materials of improved strength and thermal stability was first carried out in Russia [20] and has been the subject of much research [25, 92–95]. Reaction in this technique is initiated by the direct interaction of radiation and the monomer, and no catalyst is used which allows essentially unlimited storage and re-use of monomer. The technique has been performed in air and under water [8–10, 12, 44, 79, 96, 97].

The principal advantage of this method is that polymerization can be initiated at ambient temperatures which limits vaporization losses especially for high vapour pressure monomers. Gamma radiation has characteristics similar to X-rays and permits controlled and uniform polymerization reaction to be carried out at low temperatures even when the concrete sections are relatively thick. Absorption of radiant energy does not cause a significant rise in temperature of the irradiated medium and in the absence of the chemical initiator the rate of reaction is controlled by the intensity of the applied radiation. Such methods, therefore, allow the use of more volatile

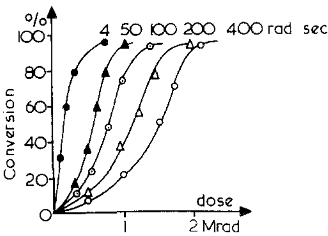


Figure 6 Conversion rate of methyl methacrylate in wood in the presence of esters of methylphosporic acid [98].

monomers which are, in general, relatively cheap compared with monomers of high boiling point.

There is some evidence that radiation polymerization imparts greater benefit to concrete properties probably through a better concrete–polymer bond and decreased vaporization losses. Radiation polymerization, on the other hand, involves high cost of radiation sources and requires massive biological shielding; and larger members require higher intensity radiation and longer processing times. There is, however, no residual radioactivity in the polymerized concrete.

Much of the knowledge on the kinetics of polymerization of methyl methacrylate is derived from the radiation chemical modification of wood by polymer. Experiments with wood show that as the dose rate decreases the monomer conversion increases per unit of total dosage (Fig. 6) [98]. Irradiating at elevated temperatures can be used to reduce substantially the radiation dose required for curing the impregnation, and this is particularly true when mixtures of unsaturated polyester resins with a high styrene content are used.

Research on radiation polymerization of methyl methacrylate and styrene shows that the addition of suitable compounds or cross-linking agents can cause acceleration of polymerization as well as reduction of irradiation dose [99]. In the case of styrene, for example, the addition of dimethyl phosphite causes acceleration of polymerization. The presence of tri-(2-ethyl chloride)-phosphite, on the other hand, reduces the irradiation dose. In the work at BNL the cross-linking agent TMPTMA is used to improve the thermal and solvent-resistant properties of polystyrene and MMA; the addition of small percentages (3 to 4%) is enough to reduce the amount of radiation energy required for the polymerization of these monomers.

The amount of energy needed for 100% conversion of monomer depends on the radiation intensity. A lower radiation intensity requires generally lower total dosage and results in lower polymerization rates and longer processing times for complete conversion (Table VI) [8, 100, 101]. Extensive test results [8–12] show that the polymerization rate is higher for the monomer when impregnated in concrete than when in bulk – in heterogeneous systems energy transfer effects at interfaces can take place in a radiation field resulting in higher rates of polymerization.

The amount of energy required for polymerization also depends on the activation energy of the monomer, and the rate of polymerization, for constant radiation intensity and temperature, is different for the various monomers.

Sunlight and microwave radiation have also been used as sources of energy [102]. The possibility of anionic polymerization using the "living polymer technique" [43], where chain termination mechanisms are not present, has also been suggested [102].

TABLE VI Effect of radiation intensity on processing requirements for various monomers

Monomer	Radiation intensity ($\times 10^5$ rad h^{-1})	Overall rate of polymerization	Radiation time for 100% conversion (h)	Total dose ($\times 10^6$ rad)
Methyl methacrylate	5.3	11.00	9.1	4.8
	1.0	4.80	21.0	2.1
Styrene	5.3	1.06	94.3	50.0
	1.0	0.50	217.0	21.7
Acrylonitrile	5.3	33.00	3.0	1.6
	1.0	14.50	6.9	0.7
Styrene–acrylonitrile	5.3	10.40	9.6	5.1
	1.0	4.50	22.0	2.2
Vinyl acetate	5.3	10.40	9.6	5.1
	1.0	4.50	22.0	2.2
Isobornyl methacrylate	5.3	44.00	2.3	1.2
	1.0	18.90	5.3	0.5
Trimethylolpropane trimethacrylate	5.3	58.80	1.7	0.9
	1.0	25.60	3.9	0.4
Diallyl phthalate	5.3	0.91	105.6	58.0
	1.0	0.40	243.0	24.3

7.2. Thermal-catalytic polymerization

In the thermal-catalytic process, polymerization is initiated by chemical means and heat, by the action of a free radical on a monomer molecule: the free radical is formed by the thermal decomposition of a relatively unstable material called initiator or catalyst. The catalyst concentration is important: generally, it is used in concentrations of 1 to 5% by weight to initiate the free-radical chain reaction at temperatures of 70 to 75° C [77, 103]. Among the catalysts mostly used are benzoyl peroxide, methyl ethyl ketone peroxide and azobisisobutyronitrile which have good chemical stability and permit storage and re-use under appropriate safety conditions.

The principal advantage of the thermal-catalytic process is the rapid polymerization rate and the consequent shorter processing time. Relatively simple heat sources can be used, such as simple ovens, water or even raw steam and the polymerization can be carried out in air or water, and is complete in about 2h [12, 55, 71, 75, 90, 91]. The chemical initiator has, however, to be dissolved in the monomer prior to impregnation; this creates potential hazards of flammability and explosion and rigorous safety codes are necessary to reduce hazards to a minimum [11, 12].

All catalysts have a decomposition temperature below which no effective polymerization takes place, and while heat is applied to reach this temperature monomer losses by evaporation occurs. The losses can be minimized by choosing catalysts with lower decomposition temperature but care should be taken to ensure the chemical stability of the initiators. As with the radiation method, the addition of small amounts (3 to 4%) of the cross-linking agent TMPTMA also decreases the polymerization temperature in the thermo-catalystic treatment of MMA and styrene.

In practice, the effects of the catalyst concentration and polymerization temperature are interdependent and affect the properties of the polymer in the concrete [60, 104]. Combinations of heat, radiation and catalyst have also been experimented with to reduce radiation and catalyst requirements and increase the rate of polymerization [8, 9].

7.3. Promoter-catalyst polymerization

Promoters or accelerators are used to reduce the temperature at which the catalyst normally decomposes and to effect polymerization at ambient temperatures. It has been found that benzoyl peroxide will initiate polymerization of MMA at room temperature when cobalt naphthenate is added to the monomer used for impregnation [8, 9]. Dimethyl aniline (DMA) and dimethyl toluidene have also been used as promoters. The combination of monomer–catalyst–promoter system has distinct advantages in field applications and shows good promise [12, 52, 68, 90, 105]. It is possible to add the catalyst to the concrete mix prior to curing and to add the promoter to the monomer used for impregnation. The different concentrations of catalyst and promoter influence both the polymerization time and temperature [52]. The optimum concentrations of initiator or initiator and promoter both with regard to processing time and polymer properties can generally be determined only by tests.

7.4. Shrinkage during polymerization

Shrinkage in polymer impregnated concrete occurs through two stages: during drying in the specimen preparation stage, and later, during polymerization. Shrinkage during polymerization is peculiar to polymer-impregnated cement composites and tests show that this could be of the order of 500×10^{-6} to 1000×10^{-6}, several times greater than the normal drying shrinkage (Fig. 7) [46, 76]. Examination of cut surfaces of impregnated cement composites lead to the conclusion that the polymer most likely shrinks towards the monomer-concrete interface [76]. The magnitude of the final shrinkage depends on the type of matrix and the type of monomer, and increases linearly with monomer loading. Certain cross-linking agents tend to increase shrinkage [46].

The effect of partial drying prior to impregnation can sometimes cause swelling during polymerization [76]. It appears that the internal stresses developed in the polymer and concrete phases due to shrinkage during polymerization might adversely influence the strength properties of the composite. It has been suggested that annealing or the addition of a good quality plasticizer (such as dioctyl phthalate) might reduce these internal stresses [46].

7.5. Underwater polymerization

Polymerization in an aqueous solution has many attractions in being not only simple by eliminating some of the stages in the conventional process technology but also in being most practical for large scale applications. Underwater polymerization

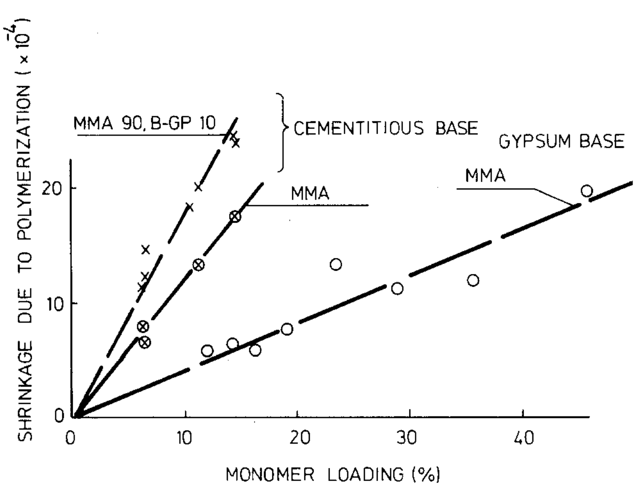


Figure 7 Shrinkage due to monomer loading [46]. (B-GP refers to a mixture of glycerine trimethacrylate, glycerine dimethacrylate and chlorohydrin methacrylate.)

has been successfully used in conjunction with radiation or thermal catalytic processes [12]. Apart from reducing losses, hot-water polymerization permits uniform and easy control of temperature during polymerization. For asbestos cement products, a heating bath containing a strongly concentrated solution of sodium chloride has proved suitable [39]. Temperatures of 70 to 80° C have been found adequate for polymerization with MMA [54, 55, 57, 71–73, 75, 76] and 70 to 100° C for styrene [106, 107]. Some reduction in polymer loading has been observed with hot-water polymerization of MMA [108].

7.6. Partial or surface impregnation

Total impregnation of full-scale concrete units is not only expensive but also often difficult to achieve in large members and thick sections [109, 110]. In many practical applications, the prime requirement is a good surface resistance against abrasion, absorption or chemical agents, or in general, good impermeability; and in all these cases it is sufficient to carry out partial impregnation [11, 111].

The partial impregnation process does not require vacuum or pressure soaking and the concrete is impregnated to controlled depths of penetration. Such a material is designed to cater more to the needs of good durability than of high strength [10].

It is important then, that the monomers should effectively seal the surface and penetrate to an adequate depth to prevent separation of the impregnated layer and cause premature failure. Viscous monomers are generally preferred for surface impregnation to obtain uniform and regular penetration and to control depth of penetration; the monomer losses due to evaporation are also then lower.

Techniques for partial impregnation have been established [10, 11, 54, 75, 111]. Polyester–styrene epoxy–styrene and MMA prepolymer solutions have generally been used for such processes.

Surface treatments of concrete structures and bridge decks have also been successfully achieved [90, 112]; for deeper penetration, a combination of rigorous drying and either ponding or pressurization of monomer has been developed [78, 86, 113]. Polyisobutylmethacrylate has been found successful in field tests.

8. Properties of polymer-impregnated concrete

Polymer-impregnated concrete looks very much like conventional concrete and usually contains about 6 to 7% polymer by weight. The polymer is distributed throughout the concrete in the pores and flaws of the system, and to some extent, in the cement paste and aggregate particles, although occasionally the presence of the polymer can be detected in the surface voids of the material.

Typical mechanical and physical properties of unimpregnated and MMA-impregnated concrete polymerized by radiation and thermal-catalytic means are shown in Table VII [8, 12, 91]. The results show little variation when the specimens are subjected to a given set of process conditions, although changes in the treatment process or the concrete mix will be reflected in the degree of void filling and polymer loading, and consequently, on the properties of the composite. Table VII shows major improvements in strength and elastic

TABLE VII Typical mechanical and physical properties of PIC for normal temperature applications

Property		Unimpregnated concrete	MMA - impregnated	
			Radiation Poly.	Thermal–Catalytic
Compressive strength	(N mm^{-2})	36.5	140	126
Modulus of elasticity	(kN mm^{-2})	24.5	44.1	43.4
Direct tensile strength	(N mm^{-2})	2.9	11.0	10.3
Modoulus of Rupture	(N mm^{-2})	5.1	18.0	15.9
Flexural el. modulus	(kN mm^{-2})	30.1	43.4	49.1
Hardness, "L" - type Hammer		32	55	52
Abrasion loss	(mm)	1.25	0.40	0.38
Abrasion loss	(g)	14	4	4
Cavitation 2 hrs.	(mm)	8	1.6	0.5
Water absorption	(%)	6.40	1.08	0.34
Water permeability 3×10^6 mm y^{-1}		5.3	0.8	1.4
Thermal conductivity	(kg cal m h^{-1} m^{-2} °C^{-1})	1.985	1.941	1.881
Diffusivity, 23° C	(cm^2 sec^{-1})	0.0099	0.0106	0.0094
Coefficient of expansion	(10^{-6} m m^{-1} °C^{-1})	7.24	9.65	9.45
Specific heat	(J g^{-1} °C^{-1})	1.0	0.895	0.921
Specific gravity		2.317	2.319	2.386

Polymer loadings 4.5 to 6.7% by weight.

Size of test specimens:
compressive strength : 75 mm × 150 mm cylinders
tensile strength : 75 mm × 150 mm cylinders
flexural strength : 75 mm × 75 mm × 400 mm prisms.

properties, and resistance to abrasion, cavitation, water absorption and permeability. The thermal properties are the same as normal concrete, although the coefficient of expansion is about 30% higher. The differences between radiation and thermal-catalytically polymerized specimens are minor, although generally, radiation produces marginally improved properties.

8.1. Strength characteristics of PIC

The effect of polymer impregnation on strength properties has been investigated extensively [8–12, 38, 49, 52, 53, 71, 78, 82, 96, 104]. The strength of PIC often exceeds the strength of the aggregate from which it is made, and therefore failure in PIC often occurs through the aggregate [60].

For a given concrete, curing and process methods, the polymer loading is generally much more critical than the type of polymer (Fig. 8) [52]. Concrete impregnated with epoxy systems tends to give lower polymer loadings, and generally lower strengths than MMA, for example, for the same polymer loading [52, 53]. Vinyl acetates on the other hand, appear to undergo hydrolysis in the alkaline medium of the matrix [38].

Plasticizers such as dioctyl phthalate (DOP) when added to MMA increase flexural and compressive strengths, but there is an optimum concentration beyond which strength is reduced. Flexural strength with DOP is also substantially reduced when the composite is exposed to the outside atmosphere [46].

Monomer loading, catalyst concentration, promoter concentration and temperature during polymerization are obvious variables in the strength obtained in *in situ* polymerization, and affect the properties of the polymer and the degree of polymer loading [52]. The degree of polymerization is also important since the unreacted MMA also acts as an untrapped solvent, softening the polymeric material that is formed.

8.2. Influence of concrete composition and curing on composite strength

Test results show that strong PIC can be made with almost any type of concrete, and that, within some wide limits, variations in cement content, type of cement, water–cement ratio, entrained air, and type of aggregate (normal and lightweight) have relatively small effects on the strength of the final composite (Table VIII) [11, 38, 104]. Concretes with large air contents, and low and high initial strengths and those made with porous lightweight aggregates, all apparently produce high-strength, durable composites [52, 55, 56].

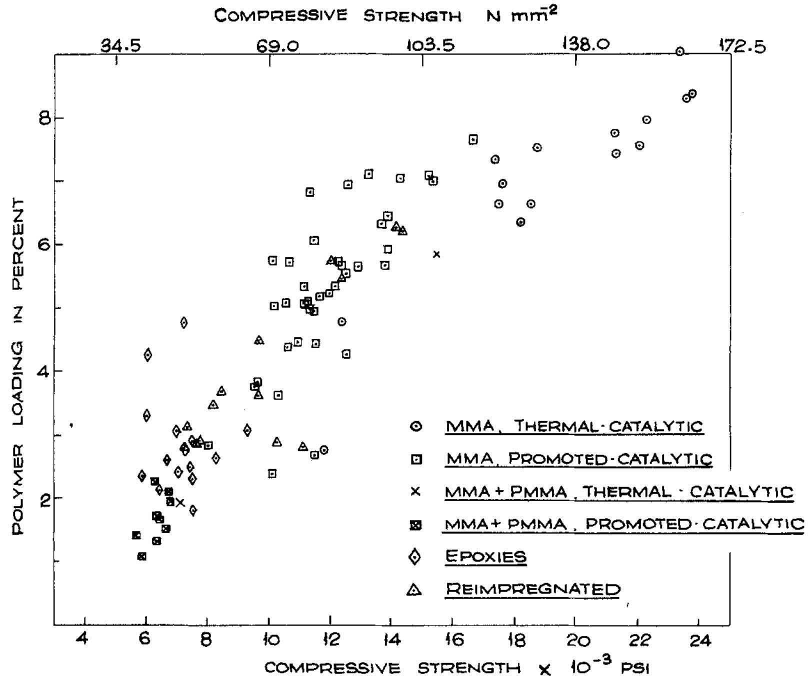


Figure 8 Influence of polymer loading on compressive strength of the composite [52] (PMMA-polymethyl methacrylate).

The method and duration of curing affects the pore structure of the matrix, and hence, produces varied effects on polymer loading and composite strength [10, 11, 75]. However, prolonged curing is not necessary to produce good quality, durable polymer-impregnated composites: rapidly cured (steam) or partially cured concrete is just as effective in producing high quality composites (Table VIII) [10, 11, 48, 75, 91]. Partial drying and the presence of moisture prior to impregnation is, nevertheless, critical to polymer loading and also affects the strength properties [46, 80].

All the strength results show two significant effects of polymer impregnation. First is the remarkable increase in flexural and tensile strengths and second, is the significant improvements in strength characteristics imparted to low-strength porous materials. Thus impregnating low-quality (waste) materials may be more efficient and bring about far greater improvements in the properties

TABLE VIII Influence of matrix composition on composite strength

Concrete mix	Air content (%)	Unimpregnated comp. st. (N mm^{-2})	MMA-impregnated	
			Comp. st. (N mm^{-2})	Poly. loading (%)
Standard*	6.5	35.8	153.0	8.0
Low W/C	3.6	62.0	176.0	6.1
High W/C*	6.5	29.0	140.0	7.9
Low entrained air	1.6	56.5	170.0	5.9
High entrained air	11.2	12.4	167.0	9.9
Low-porosity limestone aggregate	5.0	43.5	155.0	6.9
High-porosity limestone aggregate	7.2	17.2	118.0	18.0
Expanded shale aggregate	10.2	53.8	165.0	25.9
Concrete with 25%* fly ash replacement	6.3	31.8	107.0	7.0

75 mm × 150 mm cylinder specimens fog-cured for 28 days.

* Radiation-induced polymerization; all others polymerized under water.

of the impregnated composite than impregnating high-strength dense materials [49].

In literature, undue emphasis appears to have been given to the large increases in compressive strength that could be obtained by polymer impregnation. In practice, it is unlikely that compressive strengths higher than 100 to 120 N mm^{-2} can be utilized in design, except in special circumstances, without creating problems of large deformations, instability and destructive failures. In economic terms, it is far more important to utilize a higher proportion of this strength than a smaller proportion of much higher strengths. Also, the need is not so much for high strength, as for early development of strength [114].

It would then appear that the use of polymer impregnation to achieve high strength is not economically justifiable. The unique and distinguishing feature of polymer impregnation, however, is its ability to impart high strength to existing *in situ* concrete and particularly to deteriorated concrete, which no other technique can achieve.

8.3. Deformation characteristics of PIC

One of the effects of polymer impregnation is to transform conventional concrete, with its large inelastic behaviour, to an essentially elastic material in both tension and compression. Compared to plain concrete, the polymer impregnation has several significant effects [57, 76, 78, 115] (Fig. 9):

(i) to increase the strength of the composite;

(ii) to increase the linear part of the load–deformation curve – to about 70 to 80% of the ultimate strength from about 30 to 40% for unimpregnated concrete;

(iii) to increase the elastic modulus of the composite;

(iv) to increase the strain at maximum load;

(v) to increase the energy absorption capabilities of the material.

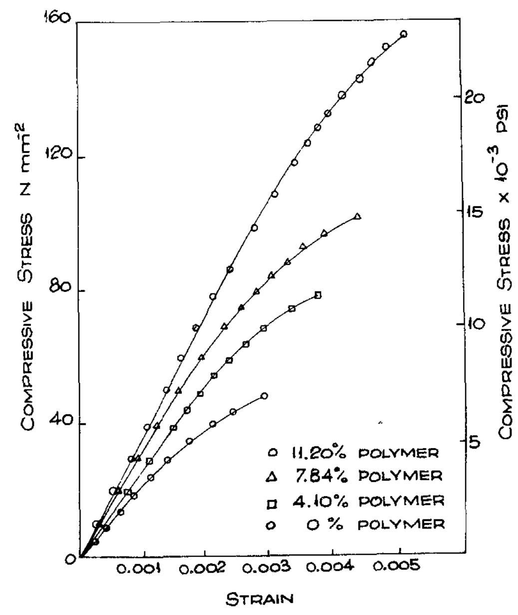


Figure 9 Stress–strain behaviour of PIC in compression [76].

The pseudo-ductility observed in conventional concrete arises from the porosity of the material and the presence of flaws and microcracking at the aggregate–matrix interfaces [116, 117]. The transformation into an elastic material implies that filling the pores and the microcracks at the bond interface removes this pseudo-ductility. The improved linearity results in a sudden brittle-type failure of the material – fracture surfaces of PIC appear smoother because of saturation of gel with polymer [118] and invariably pass through the aggregate particles. The aggregate–matrix bond strength is thus very much strengthened by impregnation and is generally greater than the strength of the aggregate itself. However, brittle fracture of the composite does not necessarily mean lack of ductility for the structural component [119, 120].

Although all polymers produce essentially the same behaviour of the impregnated composite in tension and compression, there are some notable differences on the effect of the type of polymer on strength, elastic modulus and strain capacity [62, 77]. The brittle behaviour of MMA impregnated concrete can be transformed into ductile behaviour by using a co-polymer of MMA and butyl acrylate (BA) [57, 77] (Fig. 10) or by the addition of fibre reinforcement [121–123]; the increase in ductility obtained with co-polymers, however, is accompanied by substantial reductions in strength and stiffness (Table IX) [57].

The addition of 10% of the cross-linking agent TMPTMA appears to have a complex effect on the load–deformation characteristics, generally reducing slightly strength, strain and ductility [77]. The presence of salt also tends to reduce strength, but in practice this could be overcome by additional drying. The degree of drying prior to impregnation has also an influence on the stress–strain behaviour in compression [80, 86].

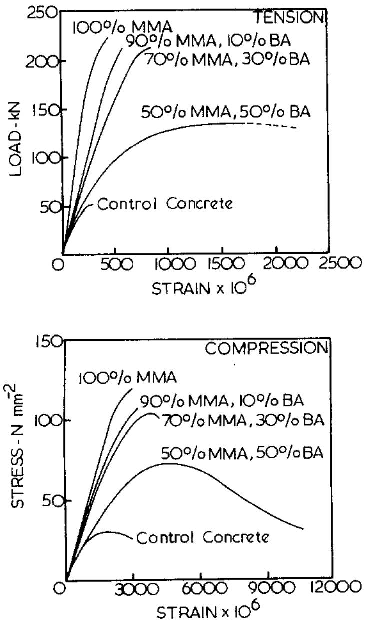


Figure 10 Influence of co-polymer on the stress–strain behaviour of PIC in tension and compression [57].

8.4. Creep deformation in PIC

Concrete is subjected to time-dependent deformations due to shrinkage and creep. There are two basic requirements for normal concrete to undergo creep. One is the presence of free or mobile water, and second, the water must have somewhere to go or escape to. In polymer-impregnated concrete there are two processes involved which affect these two requirements and thereby reduce creep. During the impregnation process, drying removes much of the free water, and such concrete will only show very little creep. The polymerization process also seals off most of the pores of the concrete so that any remaining water in the system has no means of escaping. Polymer impregnation therefore reduces creep substantially (Table X) [12]. All the available test results [8–12, 104] show that up to a stress–strength ratio of 0.3, specific creep of PIC is less than 20% of that of the unimpregnated concrete. Comparing MAA and chlorostyrene impregnated specimens with unimpregnated specimens under the same load, at a stress of 48.3 N mm^{-2}, polymer impregnation produces about 10 times less creep deformation per unit stress than unimpregnated concrete [12, 124].

At very low stresses, polymer-impregnated concrete shows negative creep, i.e. expansion under compressive loading (Fig. 11) [8, 71, 125]; the real reason for this phenomenon is not clear. In PIC creep is relatively low at stress levels up to 70 to 75% of the ultimate. At higher stresses, creep occurs very rapidly and early failure occurs. Failure at these stress levels within 34 h of loading has been reported [126].

If the polymer loading is high as in impregnated lightweight concrete (35 to 65%) substantial creep deformation will occur but even then the specific creep of polymer-impregnated lightweight concrete is less than that of the unimpregnated specimen [127]. At such high polymer contents, the composite becomes almost a three-phase material, and not only is part of the applied load carried by the polymer phase but also the stress intensity in the polymer phase is likely to be higher than that in the cement matrix phase. The resultant creep deformation is then much higher than that observed in PIC with polymer loadings of 6 to 8% [128].

8.5. Fracture toughness of PIC

The fracture toughness or the fracture energy of polymer-impregnated cement and mortar has been studied both experimentally and analytically [46, 48, 60, 129–132]. Susceptibility to microcracking is substantially retarded by polymer impregnation. These studies appear to show that the increases in fracture energy found in PIC composites are entirely due to the polymer phase

TABLE IX Influence of MMA-BA co-polymer on strength and elasticity of PIC composite

Specimen	Tensile strength (N mm^{-2})	Compressive strength (N mm^{-2})	Young's modulus* (kN mm^{-2})
100% MMA	11.79	118.6	46.19
90% MMA, 10% BA	11.17	107.6	37.23
70% MMA, 30% BA	11.03	104.8	34.47
50% MMA, 50% BA	7.38	72.4	24.13*
Control concrete (oven-dried)	2.96	30.3	26.20*

* Young's modulus for the control and 50% MMA + 50% BA specimens is the "secant modulus" measured at 0.5 times ultimate strength. The "tangent modulus" is given for the other specimens.

TABLE X Long-term creep deformation of plain and polymer concrete

Type of concrete	Compressive strength ($N mm^{-2}$)	Sustained stress ($N mm^{-2}$)	Creep stress/ strength	Creep coefficient	Specific creep $\mu m m^{-1}$ per $N mm^{-2}$	Age (days)
Plain, 0.51 W/C	36	5.5	0.15	0.98	38.0	1500
Plain, 0.51 W/C oven-dried	36	5.5	0.15	0.27	13.6	1500
Plain, 0.51 W/C oven dried	36	16.0	0.45	3.65	62.0	836
Polymer impregnated	74–149	5.5	0.037–0.074	0.30–0.60	7.0–21.0	1500
Polymer impregnated	138	16.0	0.116	1.0	8.7	836
Polymer impregnated	138	48.3	0.35	3.45	7.1	836
Plain, 0.55 W/C	40	14.3	0.36	3.00	94.5	1000
Plain, 0.28 W/C	100	28.6	0.29	1.70	44.5	1000
Plain, 0.33 W/C	86	34.4	0.40	2.07	48.6	650

and that the fracture energy of the impregnated materials is dominated by the fracture energy of the polymer. Failure still occurs in a brittle fashion with little or no post-cracking ductility.

8.6. Effect of temperature on properties of PIC

Most monomers used in practice have low glass transition temperatures of 100° C or less (Table I). The Young's modulus of a polymer decreases greatly near the glass transition temperature at which the polymer changes from a glass-like substance to a rubbery one. Polymer composites and polymer-impregnated concretes [8–12] and ceramics [35] therefore lose strength progressively at higher temperatures. The addition of cross-linking agents increases the thermal stability of the composite [8–12, 46] and special monomer systems have been developed for applications at higher temperatures of 180 to 200° C (Table II). Most monomers retain their properties for ambient temperature applications, while high-temperature polymers retain their properties to about 175° C. Thermal conductivity and coefficient of thermal expansion of PIC are, on average, of the order of 15 to 20% greater than those of unimpregnated concrete.

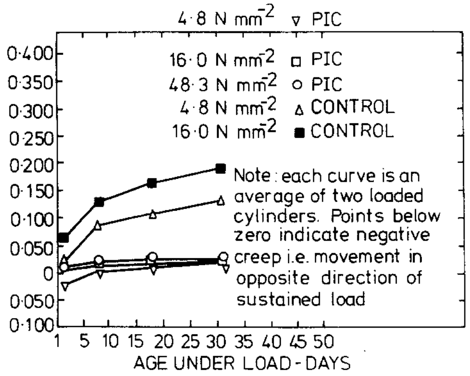


Figure 11 Creep characteristics of plain and polymer-impregnated concrete.

The typical effects of temperature on the structure (Fig. 14) [141] and photomicrographs of pregnated with cross-linked monomer systems are shown in Table XI and Fig. 12 [12, 64, 82, 103, 118, 133, 134]. The effects of loading temperature on flexural strength for different monomer systems have also been studied.

Tests appear to show that so far as thermal stability is concerned, radiation polymerization has no particular advantage over thermal-catalytic process [118]. It has been suggested that the effects on strength of the differences in expansion of the polymer and concrete phases can be reduced by annealing or using a plasticizer such as dioctyl phthalate [46].

The effect of temperature on creep at different stress levels is shown in Fig. 13 and Table XII. At temperatures up to 143° C, the effect on creep deformation is much less on PIC than on untreated concrete.

9. Durability of PIC

Deterioration of normal concrete occurs primarily because of its porosity. Sealing all the pores and voids in the concrete by an impermeable interpenetrating network of solid polymer appears to be the most effective method of ensuring the long-term resistance to external and internal deterioration.

Unlike strength characteristics, durability properties of PIC are less dependent on the method of polymerization [8, 89, 118], although some

TABLE XI (a) Temperature effects on polymer-impregnated concrete in compression

Type of concrete	Test temperature (° C)	Compressive strength (N mm^{-2})	Mod. of elasticity (kN mm^{-2})	Elastic limit (N mm^{-2})	Ultimate strain (μm m^{-1})	Poisson's ratio
Unimpregnated	21	34.5	24.5	8.3	2320	0.16
Unimpregnated	177	34.5	20.3	7.9	2630	0.14
Styrene-TMPTMA 5.7% loading	21	117.0	44.8	72.5	2920	0.21
Styrene-TMPTMA 5.6% loading	177	100.0	37.1	68.3	2950	0.18
MMA-TMPTMA 6.4% loading	21	122.0	41.3	94.0	3280	0.19
MMA-TMPTMA 6.0% loading	143	86.0	32.9	61.5	29.70	0.17

TABLE XI (b) Temperature effects on polymer-impregnated concrete in tension

Type of concrete	Test temperature (° C)	Tensile strength (N mm^{-2})			Ultimate strain† (μm m^{-1})
		Direct tension	Tensile splitting	Flexure	
Unimpregnated	21	2.1	2.3	4.9	136
Unimpregnated	177	–	2.3	4.5*	–
Styrene-TMPTMA, 5.5% loading	21	7.5	6.1	10.2	172
Styrene-TMPTMA, 6.1% loading	177	–	5.5	8.6*	–
MMP-TMPTMA, 6.0% loading	21	–	7.1	11.7	–
MMP-TMPTMA, 6.5% loading	143	–	5.9	7.9*	–

* At 143° C.

† In direct tension.

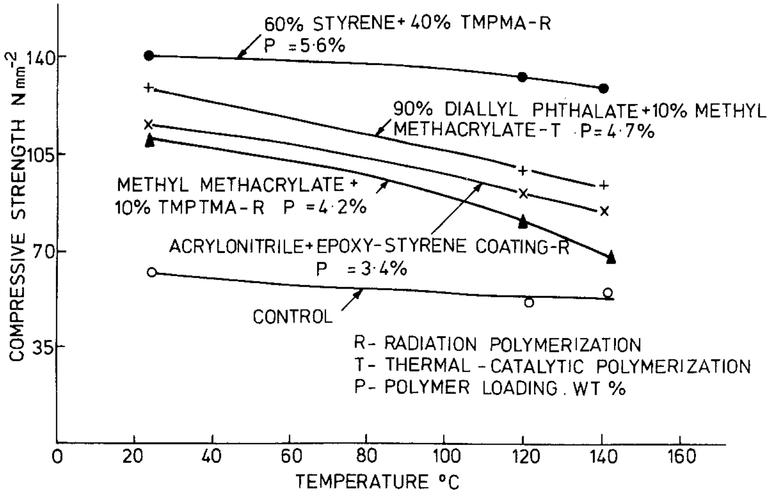


Figure 12 Effect of temperature on compressive strength of polymer-impregnated concrete [133].

TABLE XII Temperature effects on polymer-impregnated concrete: specific creep μm m^{-1} per N mm^{-2} at 400 days

Type of concrete	121° C			143° C		
	Sustained stress (N mm^{-2})	Stress / strength	Specific creep	Sustained stress (N mm^{-2})	Stress / strength	Specific creep
Unimpregnated	5.5	0.15	53.5	5.5	0.15	90.0
Unimpregnated	16.0	0.45	38.0	16.0	0.45	68.0
Styrene-TMPTMA	16.0	0.14	15.2	16.0	0.15	25.1
Styrene-TMPTMA	48.3	0.42	14.5	48.3	0.46	25.1
MMP-TMPTMA	16.0	0.17	25.1	16.0	0.20	27.8
MMP-TMPTMA	48.3	0.50	20.0	48.3	0.59	23.5

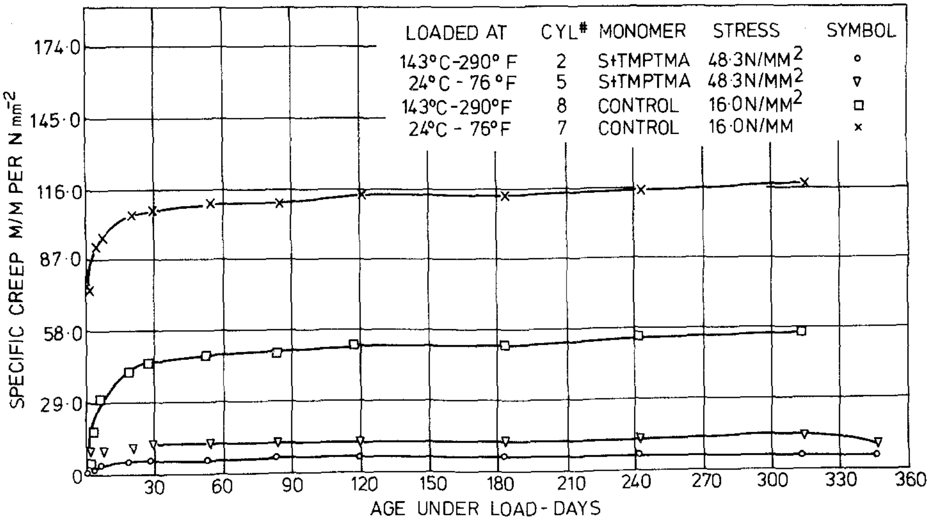


Figure 13 Temperature effect on the specific creep characteristics of polymer-impregnated concrete.

tests seem to indicate greater freeze–thaw resistance for thermal-catalytically polymerized samples than for those polymerized by radiation [82, 135]. The effective sealing of the pores in the concrete by impregnation and the degree of polymer loading are the most important factors that determine the reduction of absorption and permeability of the concrete which, in turn, determine its durability. Complete impregnation would appear to be necessary if extreme exposure conditions are to be encountered. The effectiveness of partial or surface impregnation depends on the continuity of the surface layer and the success with which the controlled depth of penetration is achieved. Defective or inadequate sealing will produce erratic results and some deterioration in time: in general, MMA impregnation appears to give the best durability results and acrylonitrile the least [8, 89]. Typical durability test results on fully and partially impregnated concrete (Table XIII) show excellent resistance to freeze–thaw, sulphate, and acid attack [8–12, 136, 137].

Desalination plants have gained some importance recently in view of the increasing water shortage in many parts of the world. Short- and long-term exposure tests of PIC (with MMA and styrene) to concentrated sea-water brine at 120° C and de-ionized water at 100° C show some corrosion and loss of strength [81, 118].

Tests show that impregnation by brushing monomer on or soaking alone does not lead to adequate resistance to water absorption [52]. Drying, evacuating and adequate soaking are all necessary to achieve a high degree of impermeability. Impregnation with epoxies appear to result in much better resistance to water absorption than impregnation with MMA or MMA + PMMA; where exceptional impermeability is required re-impregnation can be most effective [52]. In field applications, impregnation from one surface can also result in excellent durability characteristics and good corrosion resistance in the presence of salts [86] and also reduce the penetration of salt by an order of magnitude [77].

10. The role of the polymer in PIC

The role of the polymer and the mechanism of strength improvement in polymer-impregnated cement systems is still the subject of considerable research and is not entirely clear. Since polymeric solids have a low elastic modulus and normal concrete–polymer composites contain low volumes of polymer, the observed strengthening cannot be expected to result from mechanical reinforcement as happens in fibre-reinforced plastics and fibre–cement composites [121]. However, when substantial volumes (20 to 30%) of the polymer are incorporated, as in polymer-impregnated ceramics, mechanical reinforcement appears to play a major role [34, 37]. The strengthening of such porous, brittle ceramics by polymer impregnation has been attributed to the major decreases in stress concen-

TABLE XIII Durability of fully impregnated and partially impregnated concrete

Property	Unimpregnated concrete	MMA-impregnated		Partially impregnated	
		R	T	P–S, R	PMMA, R
Freeze-thaw					
No. of cycles	740*	8110	3650†	2310	1900
% wt loss	25	8	2	10	0
% improvement		> 996	> 393	> 212	> 157
Sulfate attack					
Test cycle days	480*	1436	1436	908	300
% expansion	0.467	0.032	0.017	0.077	0.015
% improvement		> 199	> 199	> 89	–
Acid, 15% HCl					
Exposure, days	105*	1395	1395	940	–
% wt loss	27	13	10	8	–
% improvement		> 1229	> 1229	> 795	–
Acid, 15% H_2SO_4					
Exposure, days	49*	126*	119*	–	–
% wt loss	35	29	26	–	–
% improvement		157	143	–	–
Acid, 5% H_2SO_4					
Exposure, days	210*	210	–	252	252
% wt loss	33	14	–	21	18
% improvement		–	–	20	20

MMA = methyl methacrylate.
R = radiation polymerization.
T = thermal-catalytic polymerization.
Results are for tests still in progress, except as noted:
* = test completed; failure criteria is 25% weight loss for acid immersion and freeze–thaw test and 0.5% expansion for sulphate attack test.
† = test discontinued; specimen removed for examination.

tration in the matrix and the load-bearing ability of the polymer [138].

Several factors influence the amount and the microstructure of the polymer incorporated in the matrix phase. It has already been shown that not all pores and voids in the cement matrix are available to the monomer for filling [139, 140]. The rate of polymerization is also different – with radiation, the rate is higher for the monomer when impregnated in concrete than when in bulk [101], whereas the rate of thermal polymerization of MMA in cement appears to be slower than that in bulk by a factor of 8 to 10 [139]. Further, the monomer appears first to reach the polymerization temperature at the concrete–monomer interface and shrink towards the interface.

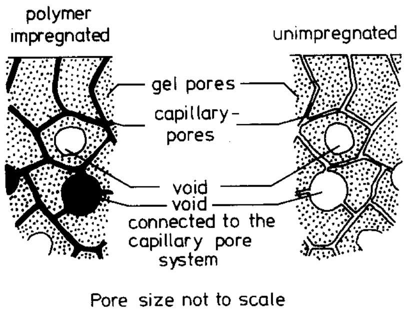


Figure 14 Schematic representation of pore filling in hardened cement paste.

The pore structure in the cement system is essentially three dimensional; the solid polymer also, therefore, forms a continuous three-dimensional structure (Fig. 14) [141] and photomicrographs of the polymer extracted from polymer-impregnated hardened cement paste confirm this [9]. It is likely, then, that most of the polymer in the impregnated composite resides in the capillary pores; voids may be partly or completely filled. Tests by Hastrup *et al.* [140] show that from pore-structure analysis, the polymer appears to be partly absorbed on the internal surface and partly condensed in capillary pores.

The real interaction between the hardened cement phase and the polymer is not known. Some possible chemical reaction between calcium hydroxide and acrylic monomer or polymer is indicated by thermal analysis results of MMA-impregnated cement pastes, although no such reaction has been observed with styrene-impregnated cement pastes [118]. Tests by Auskern and Horn [129, 139] on polymer-impregnated pastes and mortars show that the hydrated cement paste is possibly saturated with polymer which is mainly responsible for the improvement in structural properties and corrosion resistance of the composite (Fig. 15).

The pore structure of the matrix determines how the polymer is held within the matrix. Electron microscope studies show that when no pressure is applied, a large pore of 1 mm diameter is only lined with the polymer (Fig. 16) and the latter would then appear in the form of a hollow spheroid adhering to the lining of the void. A pore of 80 μm, on the other hand, is completely filled (Fig. 17) [60, 111]. Not all the incorporated polymer is, however, in the form of spheres filling air voids in the matrix as is sometimes assumed [46]. There is some evidence to suggest that the polymer is increasing the constrictions, i.e. decreasing the pore openings and not completely filling the pores. Porosity measurements of impregnated pastes and mortars also appear to suggest that a number of pores are sealed off by a film of the polymer [68] which can be either deformed or penetrated so that results of porosity studies depend on the type of technique used to study them.

Electron microscope studies and examination of fractured surfaces all suggest that the fracture surface in PIC passes through sand grains and aggregates implying a much improved interfacial bond than that found in unimpregnated specimens [118, 142]. The presence of the polymer could not, however, always be recognized at the sand–cement paste interface [60].

The reinforcing effect of the polymer in the impregnated concrete is better understood by determining the molecular weight of the extracted polymer from the hardened paste. Tests show that the amount of extract depends upon (1) the type of solvent used, (2) the polymerization temperature, and (3) the impregnation depth from which the polymer is extracted [46, 104, 140, 143]. The amount of extract decreases with impregnation depth and increases with polymerization temperature [144]. The fact that not all the polymer impregnated in the cement system can be extracted suggests some form of chemical interaction or mechanical bonding or some other interaction between the hardened cement paste, aggregate and polymer [11, 46, 104, 118, 145].

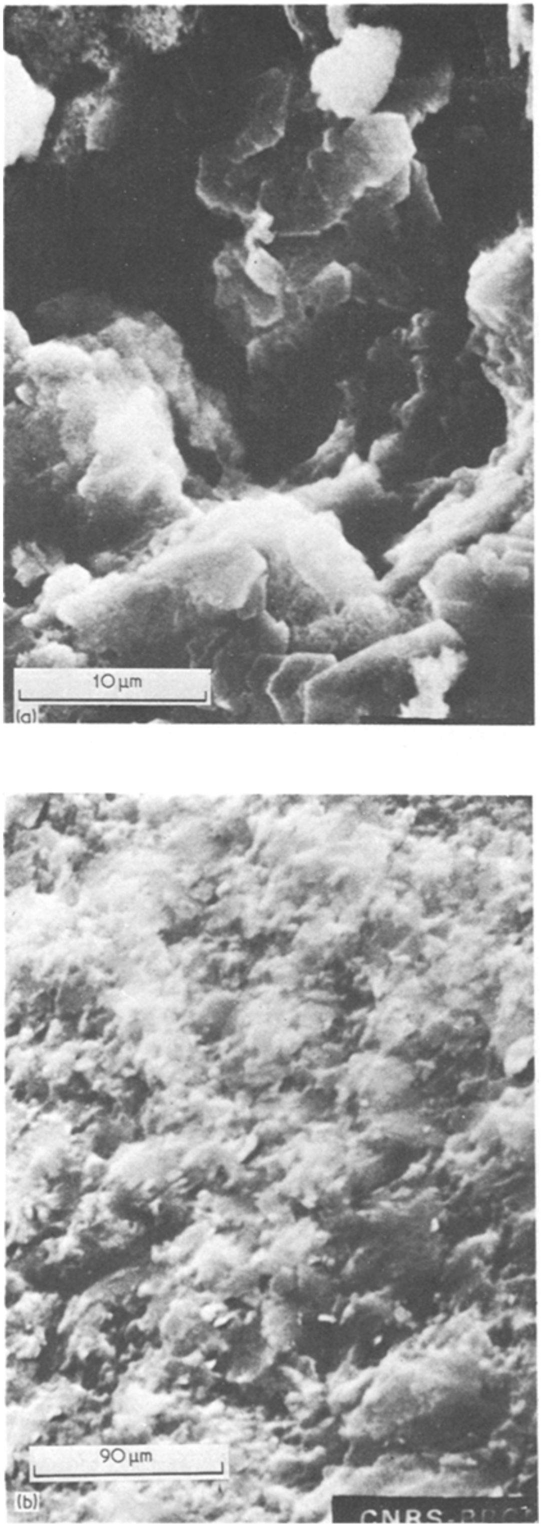


Figure 15 Microstructure of (a) hardened cement paste in unimpregnated concrete, (b) impregnated hardened cement paste.

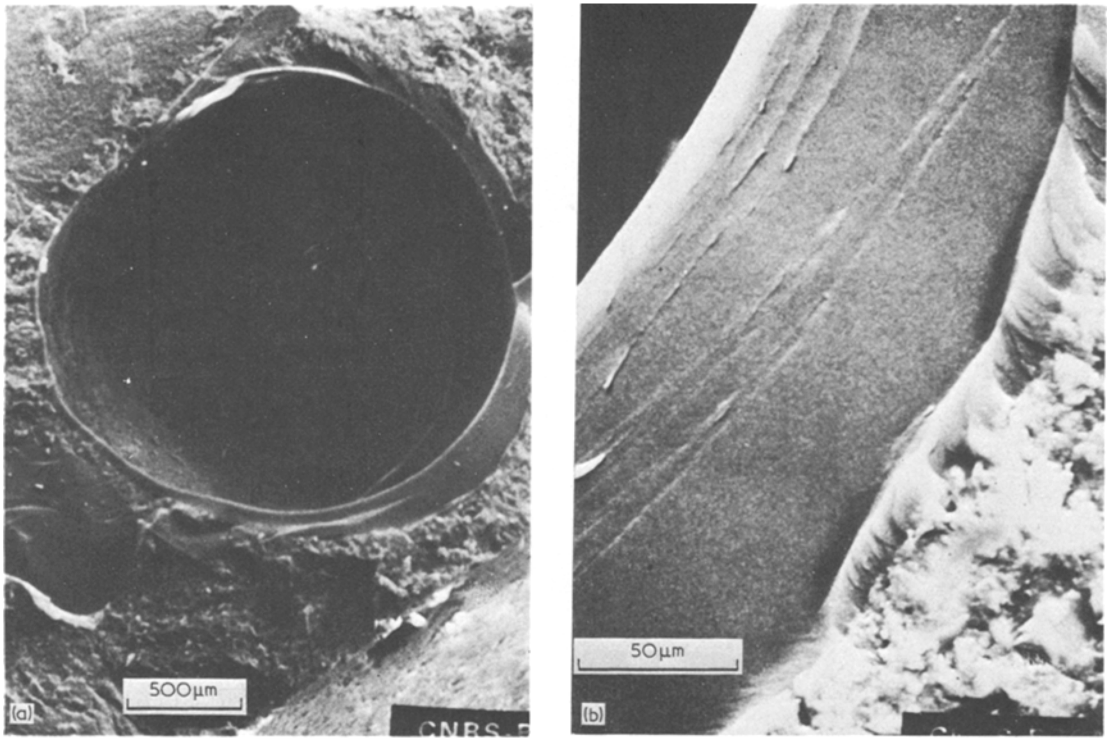


Figure 16 (a) View of a large 1 mm diameter pore lined with polymer. (b) Detail of (a) showing the bonding of the polymer on the surface of the concrete matrix.

The molecular weight of the extracted polymer has been computed by various investigators [104, 140, 143, 144] who have shown that the molecular weight of the polymer found in the small pores of the cement system was much smaller than that in bulk. The molecular weight of the extracted polymer also depends on the amount of initiator used [46, 104, 143]; and polymers with a range of molecular weight (300 to 1) have been extracted [145].

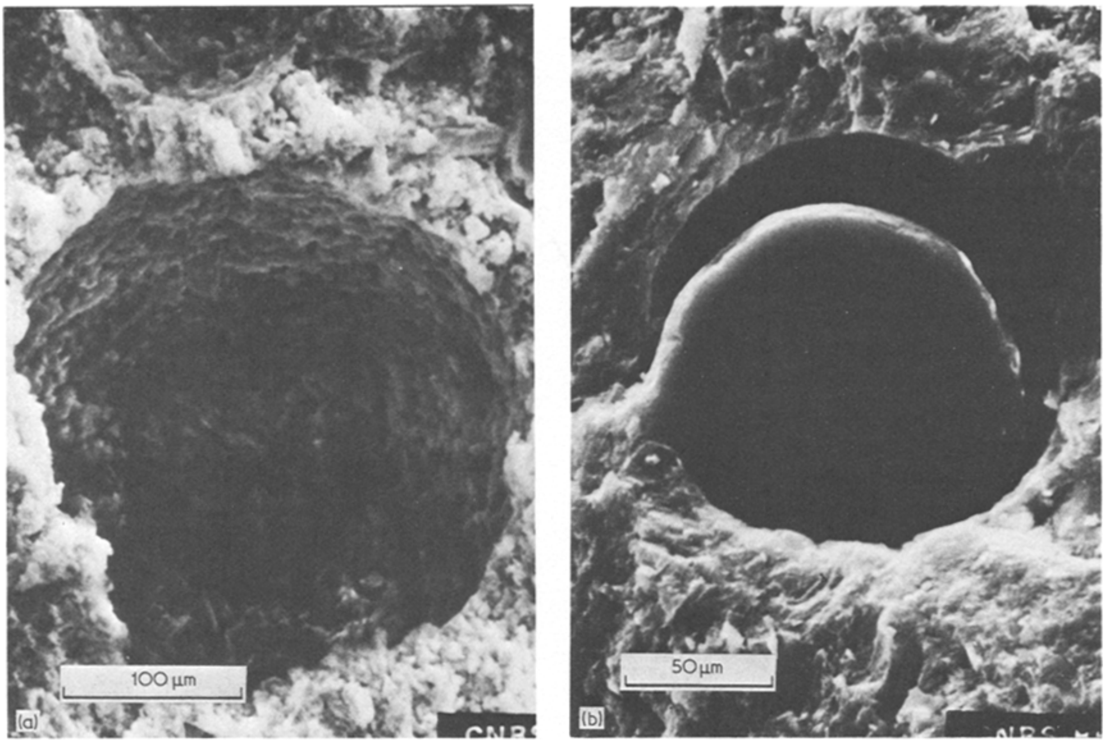
It is thus clear that the properties of the polymer in polymer-impregnated cement systems is influenced by a host of parameters. Much of the difference in strength due to different polymers and the differences in tensile and compressive strength can be explained by the differences in the structure and properties of the polymer in bulk and of the polymer in the pores of the matrix.

In an ideal polymerization, chain propagation continues until all of the growing polymer chains reach an optimum length, at which point polymerization terminates because all of the monomer has been consumed. Under such conditions, the polymer can be expected to reach those molecular sizes that result in optimum physical properties. In practice, chain propagation is a statistically controlled process and chain growth can be terminated by random events or the presence of certain chemical substances. Such premature chain termination may prevent the optimum lengths of polymer chains from being attained.

Even when the reactants and the reaction conditions are favourable to polymerization to produce polymers of optimum properties, as in porous materials, where the size of the pores is two or three magnitudes larger, the properties are not obtained readily. Hastrup *et al.* [140] found that the molecular weight of the extracted polymer from the cement paste was higher than that extracted from porous glass. Thus, although more polymer could be filled into the pores of glass, it is of inferior quality; thus the reduced filling in cement paste is to some extent compensated by the rigidity of the polymer.

From all microstructural studies and tests on the mechanical behaviour of polymer-impregnated cement composites, the positive influence of the polymer appears to be two-fold:

(i) increased strength, reduced porosity and permeability of the matrix phase (Fig. 15);



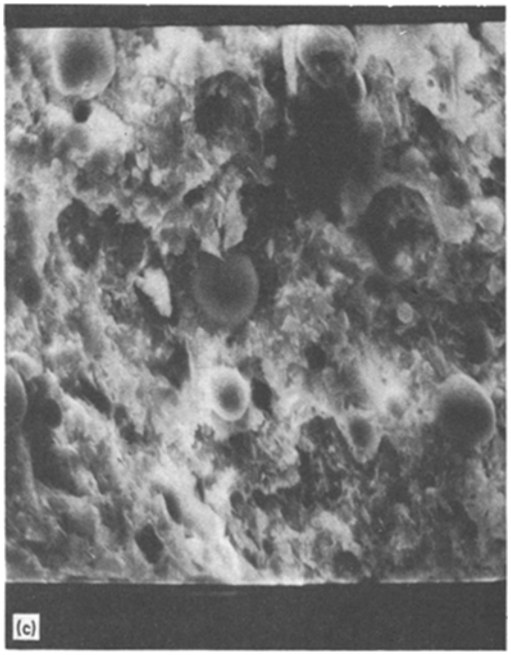


Figure 17 (a) View of a void in unimpregnated concrete. (b) View of 80 μm void filled with polymer (15% shrinkage). (c) Polymer–cement interface in polymer-impregnated lightweight concrete (35% polymer loading).

(ii) improvement of interfacial bonding in the gel matrix and between the matrix and aggregate phases.

This sealing of the pores and interfacial flaws improves not only the strength and elastic properties of the composite but also increases its resistance to crack propagation.

10.1. The filling and bonding effects

The two major mechanisms of polymer reinforcement thus arise from the filling or sealing of the pores and the bonding of the constituents. The simple filling effect is more significant in compression than in tension and is a function of the stiffness of the polymer. The filling effect reduces porosity and reduces the effect of pores and microcracks as stress raisers. Porosity is most critical in compression and strength and elasticity are both direct functions of porosity for plain and polymer-impregnated concrete (Fig. 18) [76, 122, 146–151]. However, there is no single compressive strength–porosity relationship for plain concrete [152] and polymer-impregnated concrete [46, 76, 102] and the same applies to flexural strength [46, 102, 122] and elasticity [153].

Further analysis of all the available PIC strength data shows that the improvement in strength shown by PIC cannot be predicted by the pore-filling concept alone. All these data point to the fact that the strength improvement has to be related to the improvement in interfacial bonding as well.

The role of the polymer in bonding the aggregate and matrix phases is more important in tension and in the load-deformation behaviour in compression (Fig. 10). The flexural strength of cement systems depends on the physical bonding forces – the Van der Waal's forces – and increases in flexural strength such as those obtained in PIC can only be achieved by increased aggregate–matrix bonding and not by modifying conventional concrete by, for example, water–cement ratio.

10.2. Strength and stiffness models for PIC

Attemps to predict the strength and elasticity properties of normal concrete and impregnated cement composites have only been partially successful. Most of the theoretical predictions for normal concrete are based either on a composite mechanics approach or Griffith's criterion [154, 155]. Although composite theories and composite models are well developed for fibre-reinforced materials, for particulate systems such as concrete, many energy dissipation systems other than crack extension occur in its fracture process and a purely crack-opening criterion can only tell part of the fracture story of concrete composites [156]. Polymer-impregnated cement systems behave more like composite materials than normal unimpregnated concrete, and naturally the concepts of composite mechanics and Griffith's energy criterion have been applied to predict the strength and stiffness characteristics of PIC systems.

Porosity is probably the most significant single dominant phase in all ceramic and cement systems, whether plain or impregnated [76, 122, 146–148] and it is only natural that the strength and stiffness predictions of such systems are related to the porosity of the continuous phase [149, 150, 152, 157–159]. Several semi-empirical composite models have been proposed to predict strength and stiffness of impregnated cement systems as a function of porosity and filler content, taking into account the improvements in interfacial bonding [53, 69, 76, 139, 160–163]. Although quantitative agreement between theory and experiment is often not exact, these models show the significance of the role of the polymer phase in improving interfacial bonding. The composite model approach has also been applied to explain the elastic behavior of polymer-impregnated ceramic systems [37].

Griffith's energy criterion has also been applied to predict strength [46] and fracture toughness of PIC composites [129, 130]. Many of the experimental results show that they violate the basic mixture's law and that the role of the polymer in PIC is not confined to a simple matter of the addition of phases. Filling the pores and repairing the flaws and micropores at the interfaces goes far beyond the simple concept of the addition of

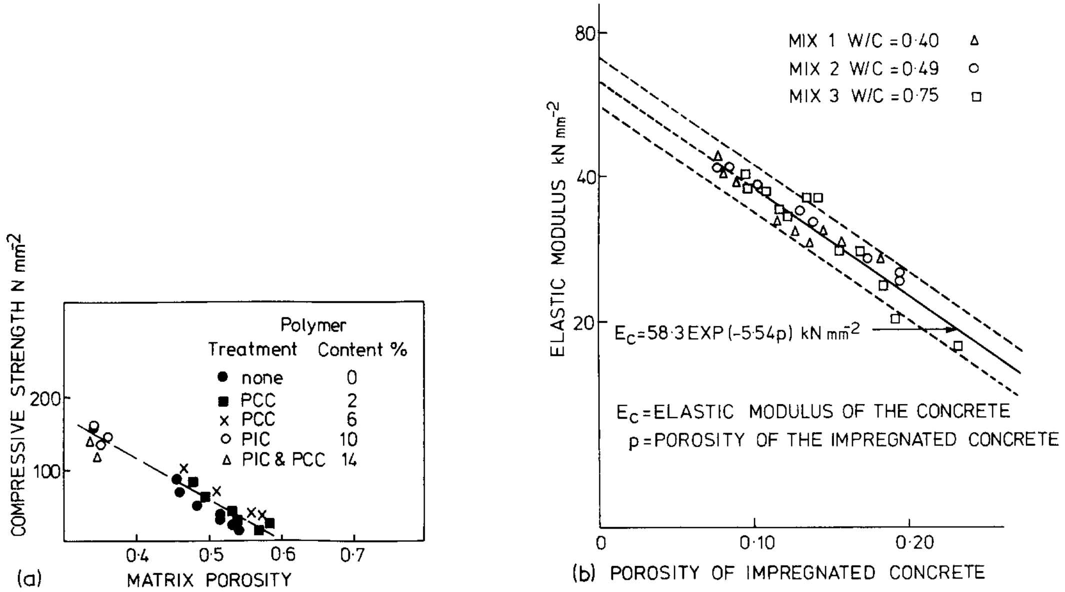


Figure 18 Influence of matrix porosity on (a) compressive strength [122], and (b) elastic modulus of cement–polymer composites [76].

phases. Therefore, it is not surprising that although the models predict general trends of strength and stiffness, quantative agreement is limited and often diverse.

Two further aspects of the role of the polymer in PIC systems are worth emphasizing. Unlike normal concrete which behaves more like a particulate system impregnated composites behave more like true composites. Further, unlike that in the untreated concrete, the matrix of the impregnated system consists of two interpenetrating continuous phases – the cement phase and the polymer phase. It would appear, then, that it is much more realistic to look upon PIC as a new material rather than as an extension or modification of conventional concrete [164].

10.3. Practical applications

Recent experiences show that improved methods of construction and better economics could be achieved not so much from refinements of theoretical analysis, important as they undoubtedly are, but by improving existing materials, and by the development of new materials. Of the many new composite materials, concrete–polymer materials are in a class by themselves, and the use of polymer impregnation is probably the most potentially useful technique in engineering applications.

Apart from high stiffness, ductility and negligible creep deformation, the most notable property of PIC is its combination of high durability with high strength. Polymer impregnation thus provides several new areas of utilization – in providing long-term protection to existing deteriorated concrete when continuous maintenance or the provision of new structures will be prohibitive in cost, in *in situ* strengthening, and in its ability to transform porous low-density waste products into high-strength, durable construction materials.

Although monomers and epoxies are expensive compared to concrete constituents (Table I), preliminary costings indicate that a polymer-impregnated precast prestressed bridge deck, for example, will cost no more than about twice that of a conventional prestressed bridge deck. Nevertheless, it is unrealistic to base economics on the cost of materials and fabrication alone; if performance and maintenance costs are also considered, PIC can then provide an economic and competitive alternative particularly in those areas where conventional concrete can only provide inadequate performance.

It appears likely that full impregnation will be used only in very aggresive environments and that partial or surface impregnation will find wider applications in civil engineering. Although practical applications of PIC are limited, several applications have been reported, and numerous others are in the development stage in the laboratory or in the field. The notable applications of PIC have been in bridge decks, surface impregnation of dams, tunnel support and lining systems, highway pavements, acid- and alkali-resistant floors, desalination plants, concrete pipes, underground mine support systems, sea-floor structures and ships [16]. Because of the reduced weight-to-strength ratio, PIC is also likely to find extensive use in prefabricated and prestressed building elements, lightweight aggregate products, building blocks and foundations.

Acknowledgements

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