Polymer-Impregnated Portland Cement Mortars

S. SACCUBAI,* M. SAROJADEVI and ARAVAMUDAN RAGHAVAN

Department of Polymer Science, University of Madras, Guindy, Madras 600 025, India

SYNOPSIS

Cured precast portland cement mortars were impregnated with the monomer-initiator mixture (mmA or styrene or both and AIBN or benzoyl peroxide), polymerized, and cured and the change in compressive strength, and, in some cases, the change in tensile strength were studied. The effect of impregnation on the compressive strength and environmental stress (freezing and thawing, acid resistance, weathering effect, and sea water resistance) were studied. It was found that the incorporation of polymer into the pores of the already-set cement increased the compressive strength even after freezing and thawing, acid resistance, and sea water resistance and weathering. Among the monomers used, mmA was found to give the best properties to the mortar. Fly ash, when added in small amounts, increased the compressive strength. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Cement concrete is one of the most versatile structural materials today. Low cost, easy moldability to complex forms, and versatility have made cement concrete and other cement-based composites very popular. They are used for a wide range of applications including irrigation and industrial, residential, institutional, transportation, and marine structures. Nevertheless, cement composites suffer from several shortcomings[1] such as low compressive, tensile, and flexural strengths, poor bonding with already-set materials, higher porosity and permeability, poor resistance to acids and other aggressive chemicals, low strength-to-weight ratio, and poor elastic modulus. This results in the deterioration of seaside structures, water seepage in large water-retaining structures, and deterioration of concrete as a result of chemical pollution of the atmosphere due to growing industrial activities.

Efforts have been made to improve the properties of conventional concrete with the use of polymers.[2-4] Over the last 30 years, a new family of composites called polymer concrete composites which are superior to conventional concrete was developed by modifying the cement composites with polymers

which have a high strength-to-weight ratio, impermeability, high tensile, flexural, impact, and compressive strengths, high chemical resistance, low water absorption, rapid strength gain, high bond strength with most of the substrates, and high flexibility.[5]

Depending on the method of polymer modification, three major types of polymer cement composites can be obtained[6]: (i) polymer concrete (PC), (ii) polymer cement concrete (PCC), and (iii) polymer-impregnated concrete (PIC). In PC, the entire binding is polymeric in replacement of cement, and in PCC, either a monomer or a polymer is added to the fresh concrete while mixing and subsequently cured and polymerized, whereas in PIC, hydrated cement concrete is impregnated with a monomer and subsequently polymerized *in situ*. A substantial increase in strength and low permeability can be achieved by the impregnation technique. PIC can be used for the repair and rehabilitation of cracked and deteriorated concrete. It reduces the maintenance costs, offers long-term protection and strengthening, and permits almost uninterrupted use of the structure while restoration takes place.

To fully impregnate the mortar/concrete, it has to be dried, evacuated to remove the air and moisture present in the voids, and then soaked with the monomer at high pressure. Since this is a tedious procedure, and where durability properties are more important, the mortars are impregnated partially[7]

Table I Effect of Impregnation with Different Monomers on Compressive and Tensile Strengths

Sample	Compressive Strength (kg/cm^2)	Tensile Strength (kg/cm^2)
Control	106.5	21.4
Styrene-impregnated	147.0	30.0
mmA-impregnated	318.0	46.0
mmA–styrene-impregnated	326.0	40.7

W/C (g/g) = 0.4; sand = 300 g; monomer = 2 mL; [AIBN] = 1%; polymerization time = 3 h; polymerization temperature = 70°C; water curing = 30 days; air curing = 30 days; air curing after polymerization = 30 days.

(soaking unevacuated samples at atmospheric pressure results in partially saturated specimens and therefore somewhat lower strengths). The quality and strength of polymer concrete depend on the type of polymer or monomer system used. Understanding the nature of polymer concretes is a prerequisite to make the best possible composite and to make the best possible use of it.

Hence, in this article, we have presented the results of impregnating partially the dried conventional portland cement mortar with mmA and/or styrene and studied the effect of varying the monomer concentration, polymerization time, monomer and initiator concentrations, and environmental stress on the mechanical and the durability properties.

EXPERIMENTAL

Materials

Different brands of portland cement available in the market were used. River sand (sieved through 20–45 mesh) and, in some cases, blue metal (coarse [granules] and fine [powder]) were used as aggregates. Methyl methacrylate (Fluka) and styrene (S.D. Fine Chemicals) were used after removing the inhibitor by washing with 5% NaOH and vacuum distillation.[8] Fly ash obtained from Neyveli Lignite Corp. India, was used as such after drying at 120°C. The initiators azobisisobutyronitrile and benzoyl peroxide (BDH) were recrystallized twice from chloroform. Epoxy resin (SIP Resins Ltd.) of an equivalent weight, EPG 180, and the hardener diethylene triamine (Fluka) and sulfuric acid (S.D. Fine Chemicals) were used as such. Single distilled water was used for making up the cement slurry.

Table II Effect of Monomer Concentration on Compressive Strength

Volume of mmA (mL)	Compressive Strength[a] (kg/cm^2)	Compressive Strength[b,c] (kg/cm^2)
0.0	207.5	207.5
1.0	233.5	—
1.6	331.6	—
2.2	270.6	—
2.4	292.0	—
3.0	267.0	288.0
12.0	—	243.7
18.0	—	222.7

[a] Initiator = AIBN (1%).
[b] Initiator = persulfate–sodium malonate (0.5 g/0.125 g in 82 mL of water).
[c] Unpublished results from the MSc project work of D. Vasu.

Mortar Preparation

The cement and sand previously sieved and dried in an air oven were weighed out in proper proportions and mixed thoroughly with calculated quantities of admixtures[9] (if any, like epoxy resin, fly ash, or blue metal) and water to a workable slump. This was then made into specimens through molds. The molds used for all the tests (except tensile
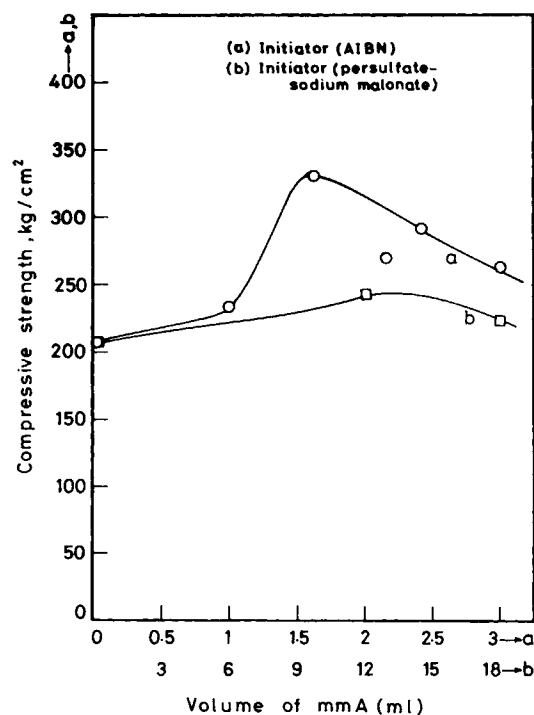

Figure 1 Plot of compressive strength vs. volume of mmA.

Table III Effect of Variation of Water/Cement Ratio on Compressive Strength

| W/C (g/g) | Compressive Strength (kg/cm²) | |
	Control Sample	Impregnated Sample
0.300	211.1	323.3
0.325	209.0	349.0
0.350	219.0	350.1
0.375	222.5	370.3
0.400	299.0	420.5
0.425	247.0	350.1

Conditions as in Table I.

strength) were cylinders (25 × 25 mm), prepared by cutting out rigid PVC pipes. The moldings were removed easily from the mold by the use of thin polythene sheets. The moldings after being released from the molds were water-cured for 30 days and then air-cured for 30 days before being impregnated. After polymerization, the specimens were also air-cured for 30 days. The mold used for tensile strength was of a briquet model:
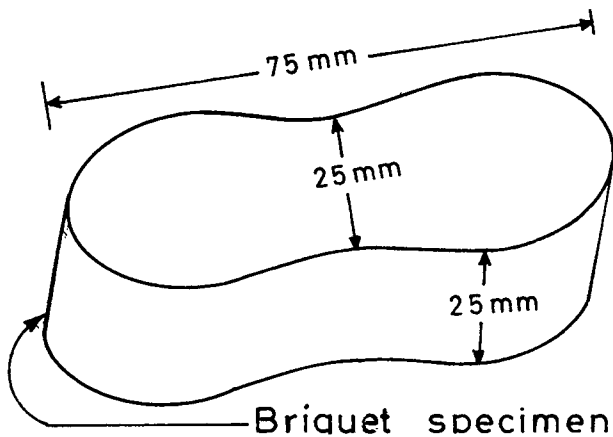
Impregnation Method

The cured precast mortar specimens were dried overnight at 120°C and then cooled to room temperature.[10] To the dried cylinders, specified amounts of the monomer–initiator mixture were added in drops and then placed in beakers containing hot water and kept in a thermostat maintained at 70°C for polymerization (by a thermal catalytic method).[11] After the specified polymerization time, the specimens were washed with water to remove the unreacted monomer as well as the precipitated polymer adhering to it. They were air-cured at room temperature and the following tests were carried out:
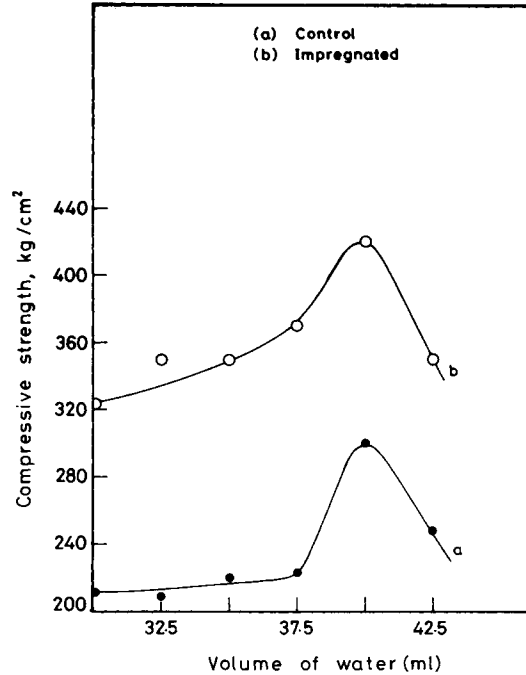

Figure 2 Plot of compressive strength vs. volume of water.

1. Compressive strength[12] (Universal testing machine model [FUT-10]);
2. Tensile strength[13] (Hounsfield tensometer);
3. Freeze–thaw effect (the impregnated mortar was subjected to freezing and thawing by placing it at 0°C in a refrigerator at night and at room temperature in the daytime and the compressive strengths were measured);
4. Resistance to sea water and 5% H_2SO_4 (the impregnated mortar was kept immersed in sea water or 5% H_2SO_4 for 30 days and dried

Table IV Effect of Variation of Polymerization Time on Compressive Strength

| Polymerization Time (h) | Compressive Strength (kg/cm²) | | |
	Sand = 300 g	Blue Metal (Coarse) = 300 g	Blue Metal (Fine) = 300 g
0.0	207.5	119.0	168.2
1.0	238.0	—	—
1.5	—	162.0	306.1
2.0	317.0	—	—
3.0	381.0	200.0	395.6
4.0	362.0	235.0	—
5.0	271.5	267.7	421.6

Conditions as in Table I.

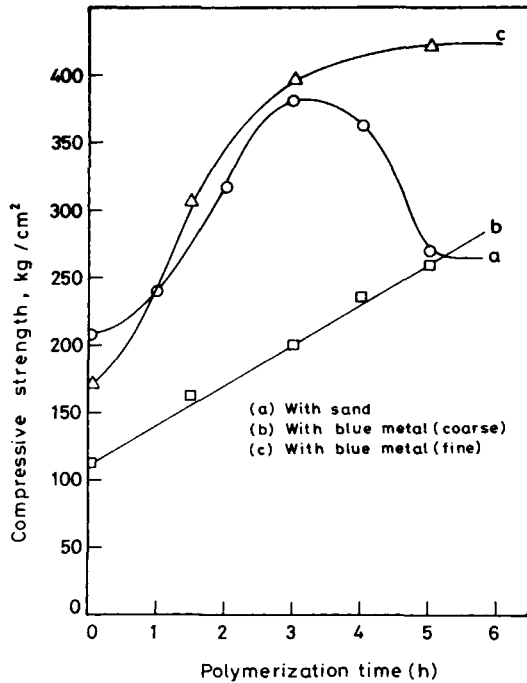**Figure 3** Plot of compressive strength vs. polymerization time.

Figure 4 Plot of compressive strength vs. initiator concentration.

and then the compressive strengths were measured); and

5. Weathering effect (the impregnated mortars were left on the open terrace for one month and the strength measured).

The effects of impregnating the epoxy-modified mortars with methyl methacrylate and/or styrene

Table V Effect of Variation of Initiator Concentration on Compressive Strength

[Initiator] × 10^2 (m/L)	Compressive Strength (kg/cm²)	
	AIBN	Bz_2O_2
0.00	207.5	207.5
2.75	—	349.5
4.00	323.1	—
4.13	—	333.0
5.51	—	397.6
6.00	375.3	—
6.88	—	309.6
8.10	411.2	—
8.26	—	376.2
10.20	453.2	—
12.50	485.0	—

Conditions as in Table I.

and that of replacing a part of the aggregate with blue metal in the polymer-impregnated mortar on the compressive strength were studied. Also, the effect of replacing a part of the cement with fly ash in the case of epoxy-modified, polymer-impregnated mortar on the compressive strength was studied.

RESULTS AND DISCUSSION

Polymer-impregnated concrete possesses strength of the order of 102 kg/cm², is very impermeable, is durable against freeze–thaw and sea water attack, and is highly abrasion-resistant.

In the present study, among mmA, styrene, and an mmA–styrene mixture, the mixture was found to give the highest compressive strength and mmA was

Table VI Effect of the Variation of Temperature

Temperature (°C)	Compressive Strength (kg/cm²)
60	279.0
70	286.4
80	293.0
90	311.6

Conditions as in Table I.

Table VII   Effect of Butyl Acrylate on Compressive Strength

Sample	Volume of mmA (mL)	Volume of Butyl Acrylate, (mL)	Compressive Strength (kg/cm^2)
Control	0	0	134.0
A	2	1	330.0
B	1	2	192.5

Conditions as in Table I.

found to give the maximum tensile strength (Table I). It was also found that increase in the concentration of the monomer generally increased the compressive strength. (The compressive strength of the mortar increased significantly when the monomer is polymerized in the pores of these materials, as observed by other authors[12] [Table II].)

The polymer in the matrix makes a significant and discrete contribution to the matrix. The increase in the compressive strength with the monomer concentration was due to increase in the rate of polymerization up to about 1.6 mL [Fig. 1(a)]. After that, the strength was found to decline. At very high monomer concentrations, e.g., when the mortar samples were immersed in larger quantities of monomer or when the precast concrete was allowed to be impregnated for longer times (in both cases, the volume of polymer accumulated in the concrete pores increased very much and exerted a lateral force or pressure on the concrete particles, thereby decreasing the strength of concrete), the strength decreased to such an extent that the specimen when taken in hand broke into a number of pieces (crumbled). A similar result was also noticed with an aqueous persulfate–sodium malonate system [Table II; Fig. 1(b)].

It can be seen from Table III that the compressive strength increased with the water/cement (W/C)

ratio up to 0.4, after which it decreased in the case of the control as well as in the impregnated samples [Fig. 2(a) and (b)]. This may be because at higher ratios excess water is present which is higher than that utilized for the hydration of cement. This excess water evaporates on curing, leaving behind voids or pores. Thus, during the initial increase, more hydration and, hence, higher strength was achieved, whereas at very high ratios (>0.4), the pores created decreased the strength.

The compressive strengths for the impregnated samples which were polymerized for different times are given in Table IV. The compressive strength was found to reach a maximum in the case of sand (at 3 h and decrease thereafter), whereas in the case of blue metal as an aggregate (both fine and coarse), the strength increased even after 3 h up to 5 h [Fig. 3(a)–(c)]. As the polymerization time increased, more and more of the impregnated monomer might have come out (diffused) and become polymerized in the water present outside the mortar, or water might have slowly entered the mortar to replace more of the monomer. This leaching out or diffusion process may be easy in a cement–sand mixture as the sand particles have a more polished surface than the rough surface of the blue metal. Also, the pores may be large enough in the former case to leave the monomer out into the surrounding water.

An increase in the initiator concentration increased the rate of polymerization and, hence, the strength of the impregnated samples (Table V). An approximately threefold increase of the AIBN concentration increased the compressive strength by 2.34 times [Fig. 4(a)]. In the case of benzoyl peroxide, although a regular increase in the compressive strength was not noticed with the (fourfold) increase of the initiator concentration, yet a definite (1.5–2.9 times) increase in the strength was observed [Fig. 4(b)]. There was no pronounced effect of the polymerization temperature on the strength of the im-

Table VIII   Effect of Variation of Epoxy With and Without Impregnation on Compressive Strength

Amount of Epoxy (%)	Compressive Strength (kg/cm^2)					
	Without Impregnation	Volume of Styrene (mL)		Volume of mmA (mL)		
		2	6	2	4	6
5	209	325.0	395.0	241.0	260.5	372.5
10	277	318.0	321.5	323.5	355.5	334.0
15	283	209.5	283.0	380.5	291.5	269.0

Hardener = diethylene triamine (11.4% of the epoxy). Conditions as in Table I.

Table IX Effect of Environmental Stress on Compressive and Tensile Strength

Sample		Compressive Strength (kg/cm^2)	Tensile Strength (kg/cm^2)
(i)	Control (C)	187.0	28.9
	Styrene-impregnated (S)	194.0	29.8
	mmA-impregnated (M)	335.0	55.0
	(mmA–styrene)-impregnated (M–S)	256.0	39.4
(ii)	C	148.0	24.1
	S	191.0	33.7
	M	322.0	49.5
	M–S	290.0	44.6
(iii)	C	183.0	24.1
	S	184.0	33.7
	M	328.0	49.5
	M–S	339.0	44.6
(iv)	C	218.0	36.6
	S	189.0	27.0
	M	311.0	44.6
	M–S	309.0	53.6

(i) Freeze–thaw cycle; (ii) effect of sea water; (iii) weathering effect; (iv) effect of 5% H_2SO_4. Conditions as in Table I.

pregnated sample. The strengths improved definitely after polymerization, but the effect of temperature was only negligible (Table VI). This may be due to the balancing effects of increasing % conversion by the increase in the production of initiator radicals at higher temperature and the easy diffusion of the polymerization mixture (monomer–initiator) from the mortar to the hot water surrounding the samples. Hence, the strength remained almost constant.

The size of the ester side-chain group affects the properties of the polymer. As the side chain becomes longer, the strength of the polymer is decreased and elongation increases.[4] It can be seen from Table VII that the compressive strength decreased with increase in the concentration of butyl acrylate, as expected.

Table X Effect of Fly Ash

Fly Ash (Wt %)	Compressive Strength (kg/cm^2)
0	267.0
10	347.0
20	240.5
30	172.8
40	96.3
50	65.4

Epoxy = 6%. Conditions as in Table I.

It may be inferred from the above results that the addition of polymer to unmodified mortar mixes altered the properties with respect to their microstructure and this influenced the stress
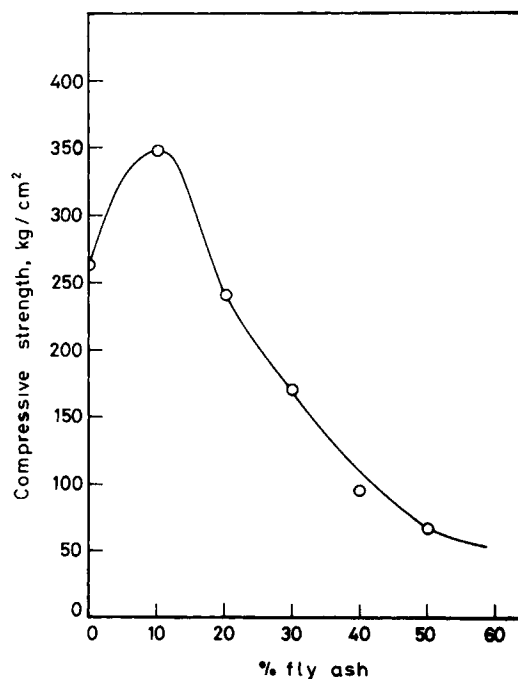

Figure 5 Plot of compressive strength vs. percentage of fly ash.

Table XI   Effect of Cure Time

	Compressive Strength (kg/cm²)	
Wet Curing (h)	Control	Impregnated
54	106.0	244.0
248	116.0	288.0

Conditions as in Table I.

transmission—characteristics within the heterogeneous material under mechanical load. The hardening of the polymer-modified cementitious system involved withdrawal of water by cement hydration followed by the coalescence of the polymer particles to form a continuous matrix phase with an interpenetrated network structure. In a nutshell, it may be interpreted that portland cement hydration can be referred to as the primary binding media, and the polymer coalescing, as the secondary binding media.[13]

Epoxy resin, a thermosetting plastic material, is characterized by unsurpassable adhesion and high mechanical strength. Hence, the effect of modifying the mortar (without impregnation) with epoxy on the compressive strength was studied. Addition of epoxy as an admixture increased the strength in the case of unimpregnated mortar (Table VIII). The effect of modifying the mortar with epoxy and further impregnation on the strength was also studied (Table VIII). The modification increased the strength, and with increasing quantities of epoxy added, the strength increased. But, as the volume of monomer used for impregnation increased, increasing epoxy content decreased the strength.

The effect of environmental stress on the control and impregnated samples was studied. It was found that (Table IX) after 30 freeze/thaw cycles the compressive strength of impregnated mortars was higher than that of the control mortars. Among styrene and methyl methacrylate, the latter was found to give higher compressive and tensile strength to the mortar. The methyl methacrylate–styrene mixture gave a mortar with lower compressive and tensile strengths. Similar observations were made with the weathering effect also. After soaking the impregnated and control mortars in sea water, the compressive and tensile strengths were measured. When impregnated on the mortar, the mmA–styrene mixture gave the highest compressive strength, whereas mmA gave the highest tensile strength.

With 5% H_2SO_4 also, the impregnated mortars gave higher compressive and tensile strengths. This improvement in the strength of impregnated mortars even after environmental stress was due to the formation of the interpenetrated network structure (involving cement hydration and polymer coalescing)[13] as cited earlier. In the case of control mortars, the pores contain water vapor which on freezing increases in volume (on solidification) and exerts lateral pressure on the adjacent mortar particles, thereby decreasing the strength, whereas in the case of impregnated mortars, the pores are filled with polymer and, hence, on freezing, no lateral pressure is exerted on the adjacent mortar particles and, thus, the higher strength. Similarly, the impregnated mortars on treatment with sea water (or acid) did not absorb it because the pores were filled with polymer, whereas with control mortars, the pores, being empty, took up the sea water (or the acid), which, in turn, decreased the strength of the mortar because of deterioration by aggressive chemicals.

Fly ash plays the dual role of a fine aggregate and binding component when added to concrete.[14] (It is a byproduct of the burning of pulverized coal in power plants.[15]) Hence, the effect of replacing a part of the cement with fly ash on the strengths of epoxy-modified and mmA-impregnated mortars was studied (Table X). Fly ash, when added in small quantities (e.g., 10%) in the place of cement, acted as a filler (fine particles), occupied the pores in the mortar, and increased the strength. It is generally known that for large amounts of replacement of cement by fly ash, the latter being a filler, the binding effect is decreased between the aggregates, because hydrated cement acts as a binding agent for the aggregates. This synergestic effect was observed also in the present studies (Table X; Fig. 5). Increase in cure time (wet) increased the strength of both the control and the impregnated mortar (Table XI).

CONCLUSIONS

1. The impregnated cement mortars were found to possess better strength and durability properties.
2. Even with impregnated mortars, an optimum water/cement ratio had to be maintained to get the best strength properties.
3. MmA was found to give a mortar with the highest compressive and tensile strength when compared to styrene and the styrene–mmA mixture, after subjecting the mortars to environmental stress, except in a few cases.
4. Addition of epoxy as an admixture increased the strength of the mortars.

5. Very high monomer concentration, longer duration of polymerization, and extended impregnation time led to lower strength of mortars.

6. Addition of small amounts of fly ash increased the compressive strength.

REFERENCES

1. S. Seshadri and S. V. Ramana Kumar, *Indian Concr. J.*, **66**, 33 (1992).
2. V. S. Ramachandran, Ed., *Concrete Admixtures Handbook*, Noyer, NJ, 1984, p. 5.
3. D. G. Walters, *ACI Mater. J.*, **87**, 371 (1990).
4. J. A. Lavelle, *ACI Mater. J.*, **85**, 41 (1988).
5. N. M. Bikales, H. F. Mark, and N. G. Gaylord Eds., *Encyclopedia of Polymer Science and Technology*, Vol. 7, Wiley-Interscience, New York, 1965.
6. L. Czarnecki, *Concr. Int.*, **7**, 47 (1985).
7. M. S. Shetty, Ed., *Concrete Technology—Theory and Practice*, S. Chand, New Delhi, India, 1992, p. 543.
8. S. S. Dixit, A. B. Deshpande, L. C. Anand, and S. L. Kapur, *J. Polym. Sci. Polym. Chem. Ed. A1*, **7**, 1973 (1969).
9. M. Neelamegam, in *Proceedings of Advanced Course on Recent Developments in New Concrete Composites*, Madras, India, 1994, p. 259.
10. S. Vaithyanathan, *Chem. Eng. World*, **22**, 57 (1987).
11. N. M. Bikales, H. F. Mark, and N. G. Gaylord, Eds., *Encyclopedia of Polymer Science and Technology*, Vol. 8, Wiley-Interscience, New York, 1965.
12. D. Manning and B. Hope, *Cem. Concr. Res.*, **1**, 631 (1971).
13. R. G. Limaye and M. K. Kamat, *Indian Concr. J.*, **66**, 153 (1992).
14. E. E. Berry and V. M. Malhotra, *ACI J.*, **77**, 59 (1980).
15. R. O. Lane and J. F. Best, *Concr. Int.*, **4**, 81 (1982).