

Studies on Polymer Impregnated Plaster of Paris

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ABSTRACT: Studies on the changes in compressive strength, split tensile strength, acid resistance, and percentage water absorption are reported for systems of plaster of paris and plaster of paris blends upon impregnation with monomer (MMA) followed by polymerization (*in situ*), as well as for systems of plaster of paris-epoxy resins with subsequent monomer impregnation. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1243–1249, 1997

INTRODUCTION

Plaster of paris (PP) has been used for the construction of slabs, molds, partition blocks, sheets, tiles, insulation boards, etc. Although its physical properties and relatively low cost make it a widely used construction material, conventional PP has a number of limitations¹ such as low flexural strength, low tensile strength, low compressive strength, low resistance to chemicals, and high water permeability. In certain situations these problems can be solved by using materials that contain a polymer or resin (commercial polymer) instead of or in conjunction with PP. These relatively new materials offer the advantages² of higher strength, improved durability, good resistance to corrosion, and reduced water permeability.

Since their commercial introduction in the early 1950s, epoxy resins have been increasingly in demand, particularly due to their manifold importance in the field of building and construction.^{3,4} The resins, depending on the ratio of the components used (*viz.*, bisphenol A and epichlorohydrin), can result in a range from low viscosity, low molecular weight products to high molecular weight solids; and, in combination with suitable hardeners (polyamines, polyamides, etc.) they can

form room temperature curing compositions that are very useful in the construction industry. The properties that have lent this distinguished role to the epoxy resins are: excellent adhesion to almost all materials; low shrinkage during and after cure; exceptional dimensional stability; good weatherability; good thermosetting nature; excellent compressive, flexural, tensile, and impact strengths; good chemical resistance; and ease of curing under most conditions at room temperature.

A survey of the existing literature shows that considerable work has been done^{5,6} on polymer-impregnated cement concrete and polymer cement concrete, which have also been put to practical use. However, very few studies have been attempted on polymer impregnated and polymer-PP specimens.^{7,8} In this article the results of a study on this subject are presented.

EXPERIMENTAL

Materials

Commercially available PP (calcium sulfate hemihydrate), epoxy resin (SIP Resin Ltd.) of equivalent weight, EPG 180, and diethylene triamine (Fluka) were used as received. Methylmethacrylate (MMA; S.D. Fine Chemicals) was vacuum distilled before use. Azobisisobutyroni-

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Table I Formulations of Plaster of Paris Specimens

Specimen	Plaster of Paris (g)	Water (mL)	Sand (g)	Portland Cement (g)	MMA (mL)	AIBN (g)
P1	100	20	—	—	2.0	0.040
P2	100	30	—	—	2.0	0.040
P3	100	40	—	—	2.0	0.040
P4	100	50	—	—	2.0	0.040
P5	100	60	—	—	2.0	0.040
PM1	100	40	—	—	0.5	0.016
PM2	100	40	—	—	1.0	0.024
PM3	100	40	—	—	1.5	0.032
PM4	100	40	—	—	2.0	0.040
PM5	100	40	—	—	2.5	0.048
PS1	90	40	10	—	2.0	0.040
PS2	80	40	20	—	2.0	0.040
PS3	70	40	30	—	2.0	0.040
PS4	60	40	40	—	2.0	0.040
PS5	50	40	50	—	2.0	0.040
PC1	90	40	—	10	2.0	0.040
PC2	80	40	—	20	2.0	0.040
PC3	70	40	—	30	2.0	0.040
PC4	60	40	—	40	2.0	0.040
PC5	50	40	—	50	2.0	0.040

trile (AIBN; BDH) was used after recrystallization. Fly ash was from Neyveli Lignite Corporation, India. Sand was used as received. The coarse sand was sieved through 20–45 mesh before use. The other materials were sulfuric acid (E. Merck) and portland cement.

Specimen Preparation

The PP and the materials used as admixtures in the preparation of the specimens were dried in an air oven and were weighed out according to the formulations (Tables I, II). Calculated quantities of water were added and they were mixed thoroughly to a workable slump. This was then made into specimens (cylindrical, dimensions 25 × 25 mm) through molds made out of rigid polyvinylchloride pipes. These specimens were air cured for 7 days at room temperature before impregnation.

Process of Modification and Impregnation

Epoxy resin modified PP specimens were prepared by adding epoxy resin and the required quantity of diethylene triamine (11.4%) directly to the PP (with or without fly ash). It was mixed thoroughly and molded.

An MMA-AIBN (monomer-initiator) mixture for impregnation was prepared by dissolving 2%

of the initiator by weight in the MMA. This monomer-initiator system was transferred onto the specimens through a syringe and was allowed to percolate slowly into the specimens. The specimens were covered with aluminum foil to prevent

Table II Formulations of Plaster of Paris Specimens

Specimen	Plaster of Paris (g)	Epoxy Resin (g)	Fly Ash (g)
PF1	90	—	10
PF2	80	—	20
PF3	70	—	30
PF4	60	—	40
PF5	50	—	50
PE1	98	2	—
PE2	96	4	—
PE3	94	6	—
PE4	92	8	—
PE5	90	10	—
PEF1	86	4	10
PEF2	76	4	20
PEF3	66	4	30
PEF4	56	4	40
PEF5	46	4	50

40 mL H₂O, 2 mL MMA, and 0.04 g AIBN were used.

the evaporation of the monomer. After standing overnight for successful percolation into the pores, polymerization was carried out at 80°C for 4 h by immersing the specimens in hot water kept in an air oven. Tests were carried out after letting the specimens stand for a further period of 2 days at room temperature.

The compressive strength⁹ (CS) and split tensile strength¹⁰ were measured using a Universal testing machine (model FUT-10) with a capacity of 10 tons. The flexural test¹¹ was also conducted on the Universal testing machine. Water absorption was determined by immersing the molding in water for 3 days at room temperature. The surface water was wiped off and weight of the pat was taken. It was then dried in an air oven and its weight recorded.

$$\% \text{ absorption} = \frac{\text{wet wt} - \text{dry wt}}{\text{dry wt}} \times 100,$$

$$\% \text{ porosity} = \frac{\text{wet wt} - \text{dry wt}}{\text{vol of mortar}} \times 100.$$

Acid resistance was tested by immersing the weighed mortar samples in 5% sulfuric acid for 3 days. The samples were then removed from the acid solution, thoroughly washed with water, dried in an air oven, and their weights noted.

$$\text{acid resistance} = \frac{\text{initial wt} - \text{final wt}}{\text{initial wt}} \times 100.$$

Thermogravimetric traces were recorded for the specimens before and after impregnation.

RESULTS AND DISCUSSION

Percentage of Water and Workability

A preliminary experiment was conducted to ascertain the water requirement for the best mixing conditions (Table III) by following the variation in compressive and split tensile strengths for PP as a function of the percentage of water added. Cohesiveness suffered at $\leq 20\%$ water (too dry) as well as at $\geq 60\%$ (too fluidic) for molding purposes. The highest values for the strengths were obtained at 40% water addition. Hence, this was maintained constant in all the subsequent experiments as the optimum water requirement.

Concentration of MMA in Impregnation

Upon impregnation with MMA, PP specimens showed an increase in compressive and tensile strengths (Table III). This general observation lends credit to the assumption that the impregnation leads to the monomer being polymerized in the pores of the PP specimen, contributing thereby to an increase in strength.

A variation in the quantity of monomer added from 0.5 to 2.5 mL resulted in the strength values reaching a maximum for 2.0 mL addition, registering no increase for further addition of monomer [Fig. 1(A)]. Thus, for the chosen specimen size and the condition of the mold, a saturation effect was reached with a 2 mL addition of the monomer, which may be taken as an expression of the degree of porosity of the specimens.

Effect of Sand

The variations reflected in the strength values of specimens marked PS1, PS2, PS3, PS4, and PS5 (Table III) testify to the general dilution effect that observed with an increase in the quantity of filler material. Up to the composition PS3, the compressive strengths for the impregnated and unimpregnated samples registered a strength increase (the maximum at PS1); at PS3 the strength values for P3 and PS3 were practically the same, showing no onset of damage to the cohesiveness. However, at PS4 the sharp fall in the CS (MMA impregnated, for example) to a value of 77 (which also corresponds to the P4 value with a higher quantity of water than the optimum 40%) clearly demonstrated the break down in the cohesiveness as purely a dilution effect. This observation was also true of the unimpregnated case (PS4 24 and P4 26).

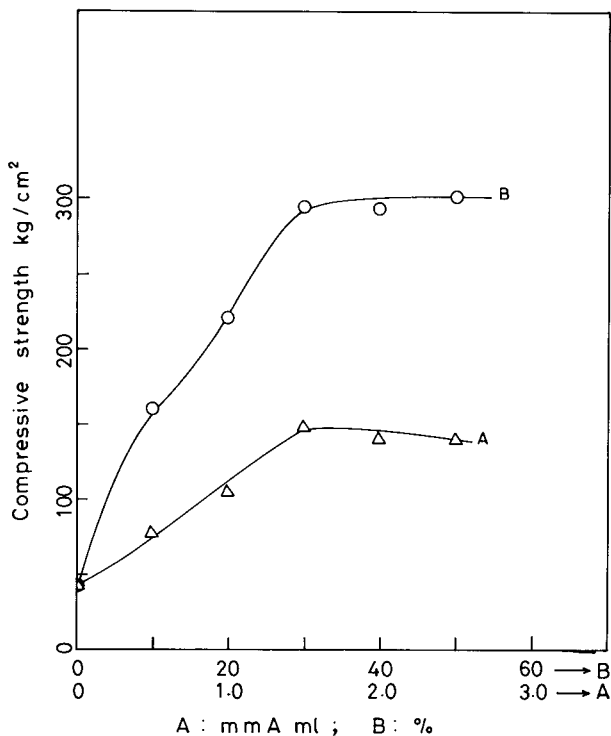
The trend in the corresponding split tensile strength values should be viewed in terms of the nature of the test. While CS involves a compression of the sample and its ability to withstand this compression, the split tensile strength involves a different type of resistance by the sample to the splitting, where the added sand intercedes with the PP matrix in such a way as to facilitate a collapse under the split.

Effect of Cement Addition

The addition of cement to the PP (samples PC1, PC2, PC3, PC4, and PC5 with 10–50% cement addition in that order) presented some interesting

Table III Properties of Unimpregnated and Impregnated Plaster of Paris Specimens

Specimen	Compressive Strength (kg/cm ²)		Split Tensile Strength (kg/cm ²)	
	Unimpregnated	MMA Impregnated	Unimpregnated	MMA Impregnated
P1	21	50	12	22
P2	33	99	14	28
P3	43	147	20	44
P4	26	77	17	34
P5	21	57	15	28
PM1	43	77	20	32
PM2	43	104	20	37
PM3	43	147	20	44
PM4	43	139	20	44
PM5	43	140	20	45
PS1	57	166	21	37
PS2	56	152	18	36
PS3	47	144	12	26
PS4	24	77	10	22
PS5	20	63	7	16
PC1	47	160	22	36
PC2	74	221	24	46
PC3	96	296	29	66
PC4	117	292	32	67
PC5	144	302	37	70

**Figure 1** Effect of (A) monomer concentration and (B) cement content on the compressive strength of the mortars.

results in terms of an increase in the strength values [Table III, Fig. 1(B)]. For the unimpregnated values, there was an increase on the order of ~ 20–25 units from PC1 to PC5, whereas the impregnated samples showed a limiting value at about 290–300 from PC3 onward. The addition of cement obviously contributed to a firming up of the matrix, leading at the same time to a decrease in porosity (as evidenced by the oozing out of monomer for PC3, PC4, and PC5). While the decrease in porosity should have led to poorer monomer impregnation and a fall in strength, the firming up of the matrix by the increased cement percentage provided a compensatory effect, resulting in a limiting value. The increase in PC1 to PC5 for unimpregnated samples (reaching no limiting value) confirms the firming up supposition and a pore-minimization effect.

Effect of Added Fly Ash

This aspect was looked into as a means of waste elimination of heaps of fly ash from industrial and power plants through use in the construction industry. In this system the quantity of fly ash was varied and blended with the PP. As the quantity of fly ash increased, the strength of the specimens

Table IV Properties of Mortars with Fly Ash and/or Epoxy

Specimen	Compressive Strength (kg/cm ²)		Split Tensile Strength (kg/cm ²)	
	Unimpregnated	MMA Impregnated	Unimpregnated	MMA Impregnated
P3	43	147	20	44
PF1	60	179	20	38
PF2	74	213	17	37
PF3	45	128	15	34
PF4	43	122	11	21
PF5	24	45	5	13
PE1	48	143	22	30
PE2	98	315	26	49
PE3	80	168	27	48
PE4	39	47	27	43
PE5	25	28	24	32
PEF1	59	188	24	42
PEF2	63	158	20	34
PEF3	50	94	19	33
PEF4	60	108	16	25
PEF5	45	122	11	20

increased (below 30%)¹² [Table IV, Fig. 2(A)]. But higher percentages of fly ash caused a decrease in the strengths. As expected the impreg-

nated specimens showed higher compressive and split tensile strengths than the unimpregnated specimens. This system showed the same trend as the PP-sand system but with much better results.

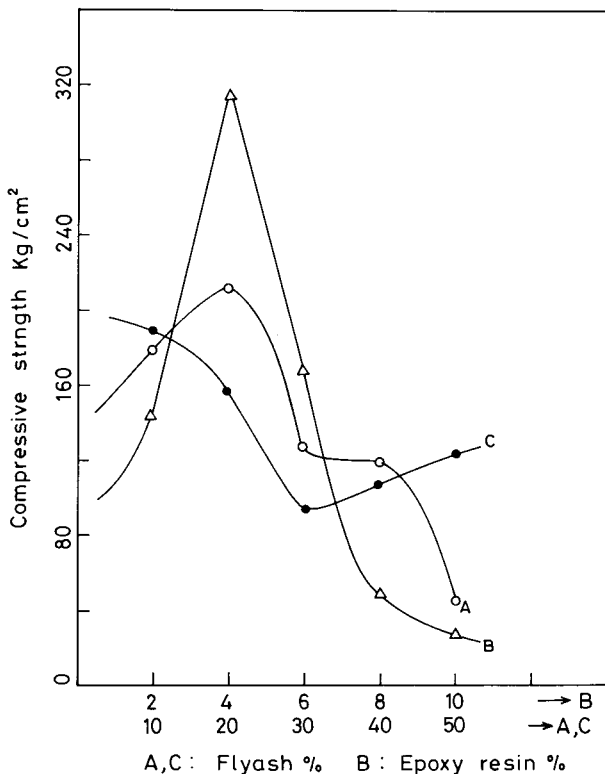


Figure 2 Effect of the variation of (A) fly ash, (B) epoxy, and (C) fly ash in the presence of 4% epoxy on the compressive strength of the mortars.

PP-Epoxy Formulations

PE1 to PE5 have epoxy addition from 2 to 10 wt %. The values for CS and split tensile strength registered a maximum for PE2, with a 4% by weight incorporation of the epoxy resin. A further increase in the epoxy component obviously led to a weakening of the gypsum matrix with correspondingly lower strength values [Table IV, Fig. 2(B)]. In the case of specimens with fly ash added, the combination PEF1 (with MMA impregnation) registered the highest strength value, which was, however, lower than that for PF2 and far lower than that for PE2 [Table IV, Fig. 2(C)]. The important conclusion from this set of results is that there is no synergistic effect for a combination of PP-epoxy resin-fly ash. As in the case of fillers like sand and fly ash, the split tensile strength values do not show a matching improvement to the CS.

Water Absorption and Acid Resistance

As expected, the polymer impregnated specimens had a lower degree of water absorption compared to unimpregnated specimens because the pores had been taken up by polymer formation. The

Table V Effect of Impregnation on Properties of Plaster of Paris Specimens

Specimen	Acid Resistivity (%)		Water Absorption (%)		Apparent Porosity (%)	
	U	MMA	U	MMA	U	MMA
P3	82	92	29	18	37	20
PS5	87	94	21	11	31	18
PC5	91	95	16	8	24	13
PF5	86	92	30	16	39	23
PE5	95	98	11	6	18	9

U, unimpregnated; MMA, MMA impregnated.

same was valid for acid resistance too, with the impregnated specimens showing better acid resistance. The extent of influence of the various fillers on the porosity of the PP specimen is reflected in the values of the apparent porosity (Table V); in the unimpregnated samples, PC5 and PE5 registered the lowest percentages, indicating the high binding ability of cement and the epoxy versus the poor binding ability of fly ash, with PF5 registering the highest value. This trend remained unaltered, even after MMA impregnation.

The thermograms in Figure 3, however, indicate the highest weight loss and hence the lowest thermal stability in the PP-epoxy resin with MMA impregnation. The polymers suffering thermal degradation⁹ at lower temperatures contributed to this phenomenon.

In conclusion, it may be stated that modifying PP through filler additions like sand, cement, fly

ash, epoxy, etc. followed by impregnation of monomer and subsequent polymerization leads to a perceptible improvement in the CS of the specimens, the strength actually doubling from P3 (MMA impregnated) to PC3 (MMA impregnated) as well as P3 to PE2. The usefulness of fly ash as an additive comes to the fore as the next best case, with P3 to PF2 registering a change from 147 to 213. Sand addition also produced a positive change in CS, but the porosity factor seemed to counter it. This level of improvement in CS was hardly matched by the results with regard to the split tensile strength. Even here, however, the addition of cement bolstered the split tensile strength value to a considerable extent (e.g., P3 44 to PC3 67).

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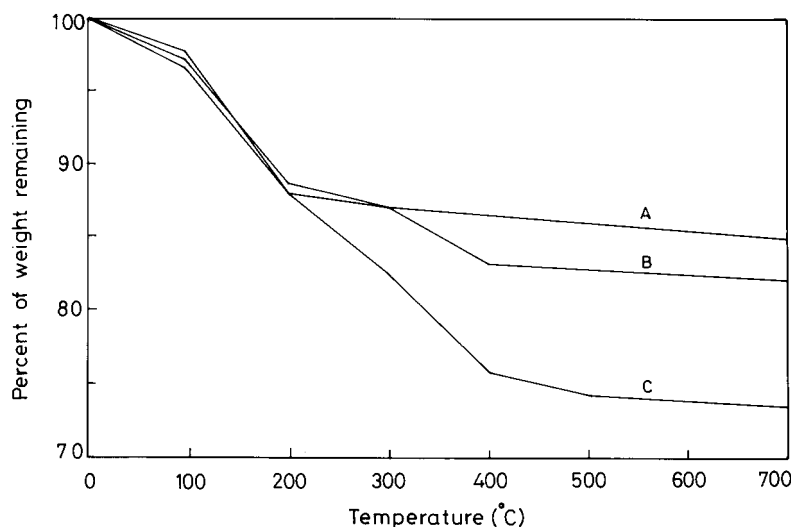


Figure 3 Thermogravimetric curves: (A) plaster of paris, (B) MMA impregnated plaster of paris, and (C) epoxy resin modified and MMA impregnated plaster of paris mortar.

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