The Role of Coupling Agents on the Mechanical Properties of Polymer-Impregnated Mortars

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Synopsis

An investigation has been carried out for determining the effect of coupling agents on the mechanical properties of polymer-impregnated mortars. Mortar specimens were impregnated with methyl methacrylate (MMA) monomer and α,α-azobis-isobutyronitrile initiator, and polymerized thermally in water. Three titanate coupling agents, KR-33CS, KR-55, and KR-138S, and one silane coupling agent, the A-174, were used for the investigation. Varying amounts of coupling agent were used in impregnating the mortars *in situ* or in pretreating the mortars with a solvent system. Bulk polymerization of MMA shows no appreciable influence of the coupling agents in the reaction kinetics; however, with the exception of KR-138S, all polymers obtained in the presence of coupling agents came out as insoluble. Similar results were obtained for polymers extracted with acetone from mortars. The mechanical property results show an improvement of properties in mortars containing 5.0 vol % of KR-33CS and A-174 after impregnation *in situ*. A slightly better improvements of mechanical properties were obtained by pretreating the mortar specimens with acetone or toluene/xylene containing coupling agents. Microscopic observation of the fracture surface showed no noticeable difference in the surfaces prepared with and without coupling agents.

INTRODUCTION

Polymers may be combined with other polymers, glasses, ceramics, mortars, or concretes and metals to yield composites which yet possess unique properties of their own. The possibility for improving the durability and mechanical properties obtained with polymer-impregnated concrete (PIC) has attracted a great deal of research interest in recent years.[1] Different technologies are being employed to obtain new types of structural cement–polymer composites, i.e., polymer-impregnated mortars, by impregnating porous materials with monomers for further polymerization.

The normal mortar itself is a cement composite material, consisting of sand, fine aggregates forming the dispersed phase, and the continuous matrix phase of cement paste. The water in the cement matrix-aggregate inclusion system, which is not chemically combined with the cement, gives rise to porous (or capillary) networks that may be filled by liquid monomers, inducing a polymerization process. The polymerization is initiated either by radiation or thermocatalytic means, yielding a relatively small amount of a rigid polymer formed in the porous void volume of the mortar, giving rise to an improvement in its properties over that of normal mortars.

Numerous investigations that deal with an improvement of the mechanical properties of PIC composites have demonstrated that its properties depend on the amount of polymer that remains inside the specimen.[2-5] It is argued that the polymer acts in two ways; First, by filling the voids, it increases the durability

of the composite, and, secondly, due to the anisotropic distribution of the capillary network in the cement paste, by having a higher tensile strength than the cement paste, it forms a continuous network inside the composite and acts as a reinforcement, improving the mechanical properties. In addition, the interaction (or bonding) between the cement matrix and the organic polymer has been identified as another important parameter in obtaining composites with improved physical and mechanical properties.[5]

Experimental studies have shown that the type of bonding that normally occurs between polymer and siliceous aggregates is a physical one.[6] However, microphotographs of the fracture surfaces of polymer-impregnated mortars have revealed that the polymer is not only filling the voids but also serving as a binding agent between the components of the composite.[7]

Coupling agents are molecular bridges between the interface of an inorganic filler and an organic polymer matrix. Organofunctional silane and titanate coupling agents have been used successfully for many years on glass fibers to improve the performance of glass-reinforced polymer composites as well as on mineral-filled composites and mineral-filled elastomers. The coupling mechanism involved with either silanes[8] or titanates[9] for those materials has been widely studied. The coupling agents, R'—X—$(OR)_n$, are characterized by dual functionality, in which R' represents an organo-functional group (such as amino, mercapto, vinyl, epoxy or methacryl), OR represents a hydrolyzable alkoxy group attached to the base atom X, and n is equal to 3 when X is silicon or to 4 when X is titanium.

The protons of the hydroxyl groups on the filler interface are the reaction sites for coupling agents. In use, the alkoxy groups of the coupling agent react with the protons of the filler or proton-bearing species. When a functional group of an organic polymer matrix, such as a methacrylate, is attached to the organic backbone of the coupling agent, the filler becomes chemically bound to the polymer. To be effective in any given system, the coupling agent must be reactive with both the polymer and the filler to some degree. The coupling agent may be applied to the filler in a separate pretreatment step or may be added directly to the resin where it eventually migrates to the filler–resin interface.

Coupling agents may induce chemical bonds between the polymer and mortar components in a way similar to the way they do for filler-reinforced plastics. However, no single research work has been found in the literature concerning the use of coupling agents in polymer-impregnated cement composites. It was the objective of this study to determine the influence of silane and titanate coupling agents on the bonding characteristics between the polymer and mortar components.

EXPERIMENTAL

Mortar Specimens

Portland cement type I was used in all experiments. The mortar specimens were prepared following virtually the ASTM 305–65 with sand/cement ratio of 3.0 and water/cement ratio of 0.5. The mortar specimens were prisms of 4 × 4 × 16 cm. These were demolded 12 h after casting and stored in water for 28 days. After curing, the specimens were dried in an oven at different temperatures for 20 h and kept in a desiccator until impregnation.

Impregnation and Polymerization Methods

The impregnation of mortar specimens was done by using the impregnation apparatus shown in Figure 1.   Four specimens of mortar were placed simultaneously in the impregnator, a steel tank of 32 × 16 × 16 cm, which was then evacuated to a pressure of 2–3 mm Hg and held at this pressure for 2–3 h. Outgassed monomer with catalyst was then introduced, maintaining the vacuum during this time.   At this stage, coupling agents mixed with the monomer and catalyst were introduced in the impregnator.   This was the method followed in incorporating the coupling agent, so-called *in situ.*   Subsequently, a nitrogen pressure of 1 atm was applied on the monomer solution for 2 h.   Finally, the impregnator was depressurized, and the impregnated specimens were removed and introduced into the polymerization tank.

When the coupling agent was incorporated by the *method of pretreatment,* mortar samples after being evacuated in the impregnator were treated with a solution of the coupling agent in an appropriate solvent, then impregnated with the solution of monomer and catalyst, and pressurized under nitrogen, repeating the aforesaid procedure.

The polymerization reaction was carried out under water at 75 ± 0.1°C for 24 h until the reaction was complete.   Monomer saturated with water was used as the reaction medium in order to avoid monomer evaporation and drainage losses during polymerization.   Unreacted monomer was removed by drying the specimen under vacuum.   The amount of polymer formed was obtained by weighing the specimens before and after polymerization.   In addition, liquid monomer samples were taken from the impregnator and introduced in penicillin ampoules to study the bulk polymerization process at the same conditions.   Continuous recording of the temperature variation during the exothermic reaction of bulk polymerization was done by means of a thermocouple inserted in the penicillin ampoule and connected to a temperature recorder.

The monomer, commercial-grade methyl methacrylate (MMA) from the Aldrich Chemical Co., selected for its polymerization facility and good mechanical
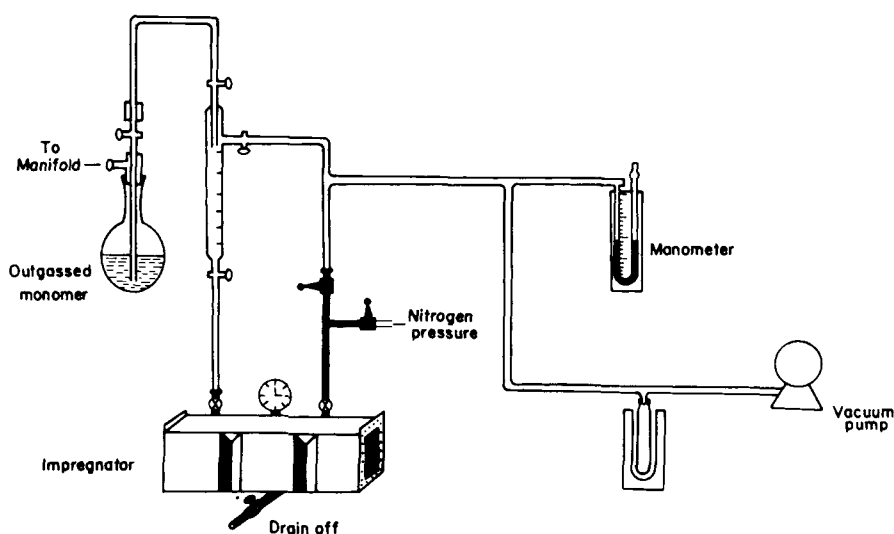

Fig. 1. Impregnation apparatus.

properties shown in PIC,[4] was used as received. α,α'-Aso-isobutyronitrile (AIBN) was selected as catalyst due to its handling facility, room temperature stability, and better mechanical properties for PIC.[10] Three titanate and one silane coupling agents were selected for this study bases on its chemical structure. The structural characteristics of these chemicals are shown in Table I.

All liquid samples were outgassed by the following method: a liquid sample was placed in a reservoir attached to a vacuum manifold. The reservoir was inmersed in liquid nitrogen to freeze the liquid in the bottom of the reservoir. The manifold was opened to the pumps and outgassed. The manifold was then shut off from the pumps, and the liquid melted with the resultant evolution of dissolved gases. The liquid was then refrozen in liquid nitrogen, and the pumping operation repeated. This outgassing step was usually repeated three times since it was shown that further repetitions did not alter polymerization rates.

Polymerization Extraction and Characterization

After the polymerization reaction was completed, mortar specimens were finely ground, and the polymer was extracted in a Soxhlet apparatus by using acetone as a solvent. The polymer obtained in the penicillin ampoule was also dissolved in acetone after the residual monomer was vacuum evacuated. Then polymer solution was added to methanol to precipitate PMMA, filtered, and thoroughly washed with methanol. The polymer samples were dried under vacuum to constant weight at 60°C.

TABLE I

Structural Characteristics of the Coupling Agents Used.

COMMERCIAL NAME	DESCRIPTIVE NOMENCLATURE AND FORMULA	MANUFACTURE
A - 174 (Silane)	Gamma - Methacryloxy - Propyltrimethoxy-Silane $CH_2\text{=}C\text{-}C\text{-}O\text{-}(CH_2)_3\text{-}Si\text{-}(O\text{-}CH_3)_3$	UNION CARBIDE
KR-33CS (Titanate)	Trimethacryl Isopropyl Titanate $CH_3\text{-}CH\text{-}O\text{-}Ti\text{-}(\text{-}O\text{-} C\text{-}C\text{=}CH_2)_3$	Kenrich-Petro Chemicals, INC.
KR-55 (Titanate)	Tetra (2,2 - Diallyloxymethyl-1-Butenoxy Titanium di(di-Tridecyl) phosphite	Kenrich-Petro-Chemicals INC.
KR-1385 (Titanate)	Titaniun di-(dioctylpyrophosphate)Oxy-acetate	Kenrich-Petro-Chemicals INC.

In order to obtain the rest of polymer remaining in the ground mortar after solvent extraction, the ground mortar was treated with concentrated hydrofluoric acid (HF) to dissolve the inorganic matrix. After this, polymer was separated by filtration, washed, and dissolved in acetone to purify it.

Molecular weights of the polymer inside the mortar specimens and in bulk were determined indirectly by measuring the intrinsic viscosity at 30°C in acetone and using the following equation[11]:

$$|\eta| = 5.2 \times 10^{-2} \times \overline{M}_v{}^{0.76}$$

Mechanical Properties and Fracture Analysis

Untreated mortar and polymer-impregnated mortar properties were obtained by flexural test of the prisms with center point loading and compressive test of the broken parts in accordance with CCCA standardized tests.[12] Scanning electron micrographs (SEM) of the fracture surface of mortars were taken by using a P-SEM 500 Philips instrument. Substrates were carefully dried, vacuum coated with carbon and gold, mounted on microscope and analyzed.

RESULTS AND DISCUSSION

Bulk Polymerization of MMA

In a previous study[13] the effect of catalyst concentration on monomer conversion was reported. In Table II the effect of AIBN concentration on reaction time, reaction temperature, monomer conversion, and molecular weight of polymer are presented for the bulk polymerization of MMA. As can be seen, the higher the initiator concentration, the shorter the reaction time, the higher the maximum reaction temperature, and the lower the molecular weight. Those results are in agreement with the free radical bulk polymerization theory.[14] The differences in conversion after 24 h are mainly due to monomer losses during the polymerization. Since the penicillin ampoules, in which polymerization reactions were carried out, were provided with a rubber cap for the monomer to be degassed, conversions up to 100% were obtained when the specimens were introduced in sealed flasks to avoid any evaporation. In this study, an AIBN concentration of 0.0279 mol/L monomer was chosen based on the results shown in Table II.

The level of coupling agent to be used is based on available protons provided by the inorganic and organic in the polymer matrix system.[15] More coupling agent is not better since it will leave unreacted alkoxy groups. The proper

TABLE II
Bulk Polymerization of MMA with AIBN at 75°C.

AIBN Concentration mols l^{-1} monomer	Reaction time • (min)	Maximum Temperature (°C)	Conversion after 24 hr (%)	Molecular Weight $\overline{M}_v$
0.0400	23	136	96.6	130.000
0.0279	32	130	98.1	220.000
0.0061	68	120	90.9	1.200.000
0.0040	80	118	91.9	1.500.000

* Time to reach the maximum reaction temperature of the exotherm.

amount of coupling agent in a polymer-impregnated mortar should depend on the type and brand of the cement, the characteristics of the sand, and the characteristics and monomer loading. Studies on concrete–polymer using polyester–trimethylolpropane trimethacrylate (TMPTMA) (60%–40%)[6] have reported significant improvement on the mechanical properties of composites when 1% of a silane coupling agent was added. Because of the unknown quantities to use, the quantities chosen in this study were 0.5–5.0 vol % in monomer. Higher concentrations than 5.0 vol % in monomer are not economically justified.

Table III shows the effect of the type and concentration of coupling agents on the bulk polymerization of MMA in AIBN. As can be seen, due to the shorter reaction times, there seems to exist an acceleration of the polymerization rate produced by the addition of 0.5 vol % of coupling agents. However, this catalytic effect is diminished at a higher concentration of coupling agents, that is, at 2.0 vol % of coupling agents.

Table III also shows that the molecular weight of PMMA is affected by the presence of coupling agents in the polymerization reaction. With the concentration of 0.5 vol % of coupling agent, the molecular weight of all polymers obtained in presence of coupling agent, except for the KR-138S, were higher than the concentration of 2.0 vol % of coupling agent the effect was more pronounced because in some cases the polymers obtained were insoluble. For the concentration of 5.0 vol % of coupling agent, all the polymers obtained were insoluble with the exception of the polymer obtained in the presence of KR-138S. This effect might be due to the multifunctional unsaturation in KR-33CS and KR-55, and the potential for hydrolysis and siloxane condensation for A-174, while KR-138S has no unsaturation to incorporate into PMMA. Summarizing, there is no significant effect of the coupling agent in the kinetics of the polymerization reaction; however, the coupling agents, apparently, produce a certain crosslinking effect among the polymer molecules, which increases with the concentration of the coupling agents.

TABLE III

Bulk Polymerization of MMA with AIBN in Presence of Coupling Agents at 75°C (AIBN Concentration = 0.0279 mol $\times$ l^{-1} Monomer).

| Coupling Agent Concentration (Vol. %)	Type of Coupling Agent	Reaction Time (min)	Maximum Reaction Temperature (°C)	Conversion (%)	Molecular Weight $\bar{M}_v$
-	-	32	130	98.13	220,000
0.5	A-174	26	130	96.98	Partially soluble
0.5	KR-33CS	24	134	99.39	240,000
0.5	KR-55	26	130	96.64	Partially soluble
0.5	KR-138S	26	129	97.31	200,000
2.0	A-174	29	132	97.0	Partially soluble
2.0	KR-33CS	27	128	98.9	Insoluble
2.0	KR-55	29	132	97.4	Insoluble
2.0	KR-138S	28	129	95.7	220,000
5.0	A-174	30	130	97.5	Insoluble
5.0	KR-33CS	29	131	96.8	Insoluble
5.0	KR-55	30	130	96.6	Insoluble
5.0	KR-138S	29	129	95.8	180,000
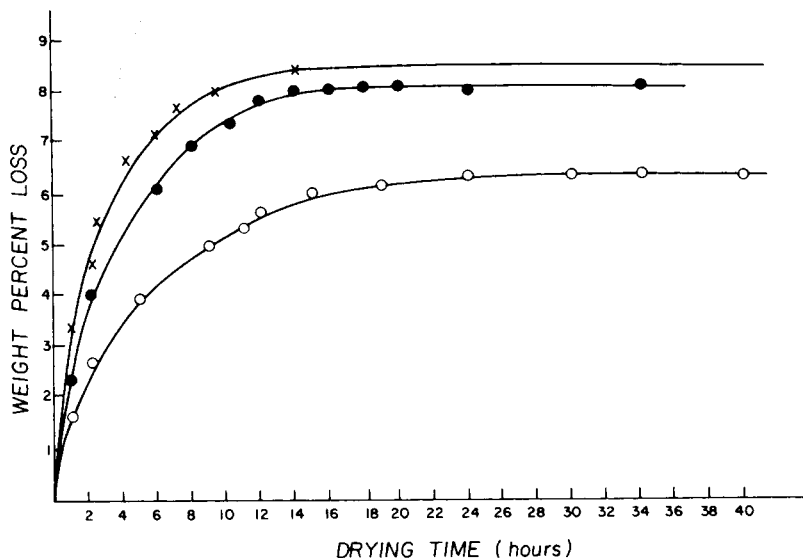
Fig. 2.   Drying curves for mortar specimens at various temperatures: (O) 80°C; (●) 110°C; (X) 125°C.

Specimen Impregnation

The degree of monomer loading is mainly determined by the free water and air that can be removed from the mortar specimens.   The monomer will fill only those cavities that are free to penetration since it has been shown that a suitable drying is even more important than the monomer penetration per se in reaching a maximum monomer loading.[16]   Special care was placed on selecting the drying conditions.   Figure 2 shows that wt % loss as a function of drying time for different drying temperatures.   Although the data indicates that 20 h are sufficient to reach the equilibrium point in removing the unreacted water at a given temperature, specimens were dried for 30 h at 125°C in order to ensure a uniform monomer loading during impregnation.

Table IV gives the monomer loading and the loading of coupling agent in monomer for an impregnation time of 2 h and at the nitrogen pressure of 1 atm for the mortar specimens impregnated *in situ*.   As can be seen, the monomer loading obtained for the mortar (6.74 ± 0.30%) was of the same magnitude as that reported in a previous study[13] by one of the authors for the same kind of mortar. The results show an adequate drying of the mortars specimens.

TABLE IV
Monomer Loading and Conversion to Polymer for MMA Containing Different Concentrations of Coupling Agents for Mortars Impregnated *in situ*.

	TYPE OF COUPLING AGENT																
	NONE	A – 174				KR 33 CS				KR 55				KRI 385			
COUPLING-AGENT LOADING IN MONOMER (Vol %)	———	0.5	1.0	2.0	5.0	0.5	1.0	2.0	5.0	0.5	1.0	2.0	5.0	0.5	1.0	2.0	5.0
MMA-LOADING (W%)	6.74±0.30	6.79	7.51	6.93	6.93	6.96	7.01	7.07	7.17	5.30	6.82	6.41	6.49	6.70	6.83	6.74	6.70
PMMA-LOADING (W%)	6.02±0.38	5.74	6.48	5.94	5.93	6.72	6.00	6.41	6.10	5.14	6.04	5.81	5.84	5.86	5.57	6.07	5.71
CONVERSION (W%)	89.29±2.94	84.57	86.26	89.61	85.02	96.57	85.55	90.67	85.08	96.63	88.57	90.6	90.0	87.61	81.59	89.99	85.0

In Table IV it can also be seen that the monomer loading of mortars impregnated with A-174 and KR-33CS is slightly higher than the monomer loadings of mortars impregnated with KR-55 and KR-138S, but there is no appreciable difference compared with the monomer loading of the reference or the mortar specimen without coupling agent. Some authors[17] have pointed out that the coupling agents can induce changes in the surface energy of the substrate, allowing more wetting of the mortar matrix by the impregnating monomer. This phenomenon may explain the observed slight differences in monomer loading produced by the different coupling agents. However, the differences found in monomer loading are not really considerable and might be due to small variations in the characteristics of the mortars specimens. The percentage of monomer conversion, shown in Table IV, is in most cases lower for the monomer containing coupling agents than for the pure monomer. Such behavior has been found to be typical of mortars with high monomer loading,[18] and this has been explained by the fact that mortars containing higher monomer loading have higher evaporation losses; it is argued that when the mortar cavities have been filled up completely by the monomer, there will not be enough free volume to accommodate the expansion of monomer created by the increase in temperature during the reaction, in such a way that the monomer will have a greater tendency to escape. The differences betwen the polymer conversion obtained in the bulk polymerization of MMA (see Table III) and the polymerization occurring inside the mortars (see Table IV) may be attributed also to differences in monomer evaporation. Obviously, during the polymerization reaction the monomer may escape more easily from the mortar than from the penicillin ampoule. Note that the penicillin ampoule was filled only to half of its volume, and therefore there was a free space for monomer expansion. The encapsulation techniques, though preventing the monomer from evaporating, are not advisable since, in many cases, the monomer may accumulate in the surface, causing irregularities in the mechanical properties of polymer-impregnated mortars.

Table V gives the results obtained for the impregnation of mortar specimens with the monomer containing 5.0 vol % of coupling agents, by using the pretreatment method. For the pretreatment step, two types of solvent systems were used: (1) acetone and (2) a mixture of toluene and xylene having a volumetric ratio of 1:1. The reason that only a concentration of coupling agent is shown

TABLE V
Monomer Loading and Conversion to Polymer for MMA Containing 5.0 Vol % of Coupling Agents in Monomer for Mortar Impregnated by Pretreatment Con Solvent

| | SOLVENT SYSTEM | | | |
| | Acetone | | Toluene_ Xylene | |
COUPLING AGENT	A-174	KR33CS	A-174	KR33CS
MMA loading (W-%)	6.75 ± 0.11	7.13 ± 0.19	6.26 ± 0.21	6.30 ± 0.05
PMMA loading (W-%)	5.97 ± 0.12	6.15 ± 0.16	5.24 ± 0.17	5.29 ± 0.15
Conversion (W-%)	88.40 ± 0.87	86.31 ± 0.43	84.00 ± 1.74	87.15 ± 1.79

for the pretreatment step is based on the fact that significant improvement in mechanical properties was obtained at that concentration by the impregnation *in situ*, as discussed later.   As can be seen, the monomer loading is affected by the volatility of the solvent system used.   In the case of the acetone used as the solvent system, the monomer loading obtained were similar to those reported in Table IV for the method of impregnation *in situ*.   However, the monomer loading obtained for the mortars, pretreated with toluene–xylene solutions of coupling agents, is considerably low.   It is worth mentioning here that, in spite of the fact that the toluene–xylene system was a better solvent for any of the coupling agents used than the acetone, it was not possible to recuperate the original weight of the mortars pretreated with the toluene–xylene solutions, although the specimens were vacuum dried at 125°C; however, with acetone, the original weight was recuperated by vacuum dry at 60°C.   It is also important to mention there that, in all the impregnations where the KR-33CS was used, the monomer loading was higher, indicating that such a chemical favors the absorption of monomer by the mortar.

Polymer Extraction and Characterization

It has been found in previous works[13,19] that when polymer impregnated concrete samples are finely ground and treated with solvent for the polymer removal, the amount of polymer extracted is smaller than the polymer contents calculated from the polymer loading, suggesting that there is a chemical or mechanical bonding between cement hydrate or aggregate and the polymer.   Table VI gives the percentages of polymer extracted with acetone from the mortar impregnated with the monomer containing coupling agents.   Although Table VI does not contain the complete data for the monomer containing 5.0 vol % of coupling agents, it shows very interesting results.   In all cases, with the exception of the KR-138S, the amount of polymer extracted with acetone is lower in presence of the coupling agent compared with the polymer without coupling agent.   This may be attributed to two combined effects.   One is that crosslinking of the polymer produced by the presence of the coupling agent reduces the solubility of the polymer.   Note that this effect is not found with the KR-138S, because there was found no appreciable effect on the molecular weight of polymers obtained where it was present (see Table III).   Another effect is that a better

TABLE VI
Percentages and Molecular Weights of Polymer Extracted from Mortars Impregnated with MMA Containing Coupling Agents

Type of Coupling Agent	Coupling Agent Concentration (Vol%)	Extracted With Acetone (w-%)	Extracted With HF (w-%)	Total Polymer Extracted (w-%)	Molecular weight $\bar{M}_v$
-	-	40	33	73	420,000
A-174	2.0	27	4	31	Insoluble*
KR-33CS	2.0	30	23	53	Insoluble*
KR-55	2.0	26	22	48	Insoluble*
KR-138S	2.0	55	26	81	Insoluble*
A-174	5.0	9			Insoluble*
KR-33CS	5.0	25	-	-	Insoluble*
KR-55	5.0	30.5	-	-	Insoluble*
KR-138S	5.0	43.3	-	-	398,000

TABLE VII
Mechanical Properties of MMA-Impregnated Mortars
(Polymer Loading: 6.02 ± 0.36)

Property	Mortar without impregnation A	MMA-Impregnated Mortars B	% Improvement
Flexural Strength Kg /cm^2	79 ± 7	260 ± 14	228
Compressive Strength Kg /cm^2	479 ± 15	1314 ± 58	175

attachment of the polymer to the mortar aggregate is achieved by the coupling agent. If this is the primary effect, the mechanical properties of the composite should be improved, as will be discussed in the next section.

In order to obtain the polymer that could not be dissolved from the ground mortar by normal solvents, the inorganic matrix was destroyed by treatment with concentrated HF. As can be seen in Table VI, the amount of polymer extracted with HF is lower for the polymer extracted from mortars impregnated with the monomers containing coupling agents. Adding the amounts of two extracted polymers, it is found that, with the exception of the KR-138S, the coupling agents reduce the amount of the polymer extracted from the inorganic matrix, indicating that those agents may effectively introduce an inorganic–polymer coupling.

The molecular weight of the polymer extracted with acetone from the mortar, impregnated with MMA without the coupling agent, was determined as 420,000, while the molecular weight of the polymer, obtained in the bulk polymerization of the MMA, was determined as 220,000. This seems to indicate that the inorganic material has a catalytic effect on the polymer formation. Similar results were found in previous works[13,20,21] in which higher polymerization rates were detected. This result is in disagreement with some earlier studies on PIC,[22,23] which report that the molecular weight of the polymer prepared outside the concrete is higher than that of the polymer prepared within the concrete, pro-

TABLE VIII
Normalized Mechanical Properties of Mortars Impregnated *In Situ* with MMA Containing
Different Concentrations of Coupling Agents

Coupling Agent	Test Method (kg/cm^2)	MECHANICAL STRENGTH (kg/cm^2)				
		Without Coupling Agent	0.5 %[*] Coupling Agent	1.0 %[*] Coupling Agent	2.0%[*] Coupling Agent	5.0%[*] Coupling Agent
A-174	Compressive	1314	1408 (7.1)	1387 (5.5)	1431 (8.9)	1603 (22.0)
	flexural	260	278 (6.9)	254 (2.3)	258 (-0.8)	278 (6.9)
KR-33CS	compressive	1314	-	1392 (5.9)	1370 (4.3)	1497 (13.9)
	flexural	260	-	251 (-3.5)	259 (-0.4)	298 (14.6)
KR-55	compressive	1314	1366 (4.0)	1302 (-0.9)	1391 (5.9)	1247 (-5.1)
	flexural	260	264 (1.5)	262 (0.8)	252 (3.0)	245 (-5.8)
KR-138S	compressive	1314	1410 (7.8)	1418 (7.9)	1303 (0.8)	1397 (6.3)
	flexural	260	269 (3.5)	247 (-5.0)	251 (-3.5)	268 (3.0)

TABLE IX
Normalized Mechanical Properties of Mortars Impregnated by Pretreatment of Solvent with MMA Containing Different Concentrations of Coupling Agents.

Solvent System	Coupling Agent	Mechanical Strength (Kg/cm²)	COUPLING AGENT CONCENTRATION IN MONOMER (v %)		
			0	2.0 (% *)	5.0 (% *)
Acetone	A-174	compressive	1314	1527 (16.2)	1728 (31.5)
		flexural	260	304 (16.9)	287 (10.4)
	KR-33CS	compressive	1314	1418 (7.9)	1540 (17.2)
		flexural	260	285 (9.6)	268 (3.0)
Toluene/Xylene	A-174	compressive	1314	1452 (10.5)	1675 (27.5)
		flexural	260	273 (5.0)	302 (16.2)
	KR-33CS	compressive	1314	1382 (5.2)	1423 (8.30)
		flexural	260	268 (3.1)	295 (13.5)

posing that the presence of the ingredients of the inorganic material accelerates the inhibitor decomposition, producing a larger concentration of free radicals that yields a lower molecular weight polymer. Such a disagreement indicates that a systematic research is required to elucidate the mechanism through which the inorganic ingredients affect the polymerization rate and the molecular weight of the polymer formed inside the mortar.

(a)

(b)

(c)

(d)
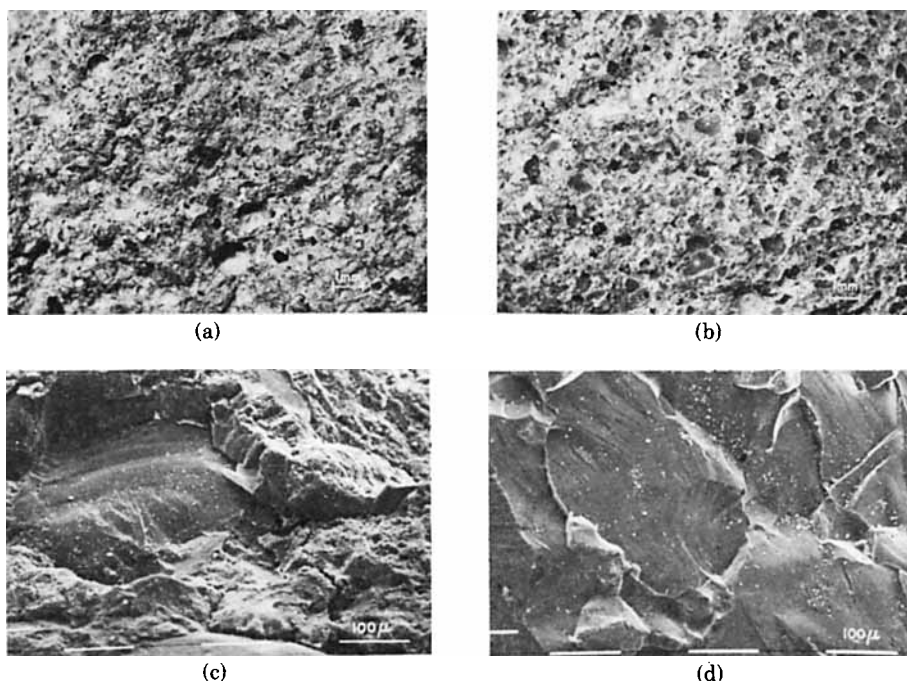
Fig. 3. Micrographs of the fracture surface of mortars: (a) normal mortar; (b) PMMA-impregnated mortar; (c) normal mortar; (d) PMMA-impregnated mortar.
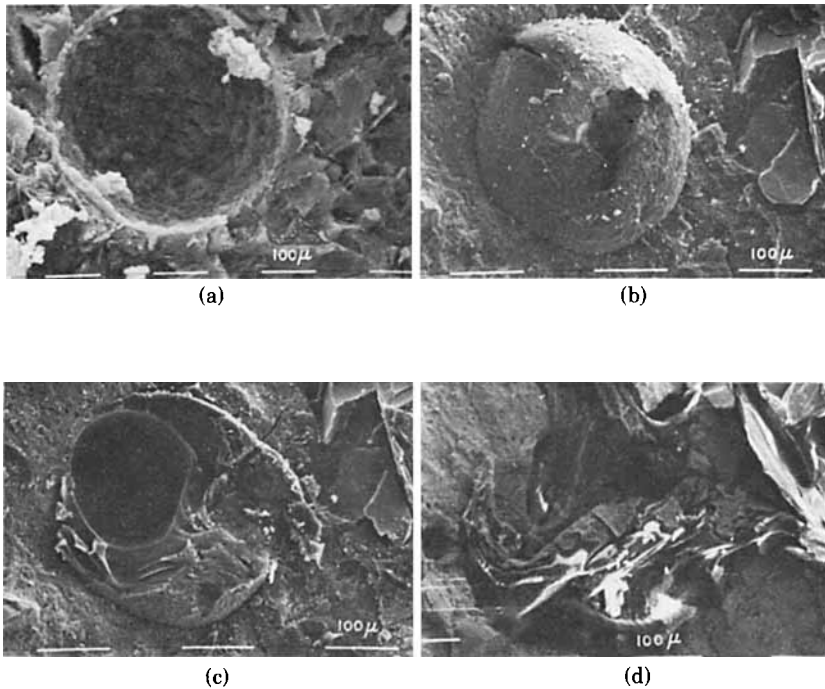
Fig. 4. Micrographs of the fracture surface of PMMA-impregnated mortars: (a) an air void surrounded by polymer ring; (b) an air void completely filled by impregnated resin; (c) the sample in (b) showing the polymer inside the sphere; (d) the sample in (c) after 12 h in acetone extraction.

It is worth mentioning the fact that the polymer, extracted either with acetone or with HF, cannot be the true molecular weight because, unexpectedly, the polymer after being filtered and dried, turned out to be insoluble by normal solvents.

Mechanical Properties and Fracture Behavior

Several researchers[6,9,23,24] have shown 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. Also, it has been shown[7] that, in order to develop a true composite, a minimum amount of polymer inside the specimen is required, depending on the characteristics of the polymer. Table VII gives the flexural and compressive strength of the mortar without impregnation and the MMA-impregnated mortars containing a polymer loading of 6.02 ± 0.36. For each measurement five mortar specimens were taken, having a standard deviation less than 5% of the average value. The percent of improvement given in Table VII demonstrates that the polymer loading is above the critical value required for having a true composite.

The reasons for an improvement in strength properties are not fully clear and are still the subject of considerable research. Apparently, the polymer is distributed throughout the pores of the mortar, acting as a filler of the microcracks, which tend to eliminate fracture-propagating behavior, resulting in a decrease

in stress concentration.   However, the improvement in strength properties cannot be predicted by the pore-filling concept alone.   It has to be related to the improvement in interfacial bonding as well.[5]   As can be seen in Table VII, the percent improvement in strength properties subjected to the flexural loads is higher than that subjected to the compressive loads, indicating that the sensitivity of the material to the microcracks is greater when it supports flexural loads.

Table VIII gives the normalized mechanical properties of mortars impregnated with MMA *in situ* containing 0.5, 1.0, 2.0, and 5.0 vol % of A-174, KR-33CS, KR-55, and KR-138S, respectively, in MMA.   Since the polymer loading affects the final properties of the composite, in order to compare the mechanical properties of the mortars impregnated with and without coupling agents and different polymer loading, it was necessary to normalize the mechanical properties results, by taking the average polymer loading of mortars without coupling agent as a basis, 6.02 (see Table VII).   In normalizing the results it was assumed, as has been shown in the previous paper,[13] that above the critical polymer loading there exists a linear relationship between the mechanical properties and the polymer loading which can be expressed as:

$$MP_N = F_N \times MP_0$$

where MP_N is the normalized mechanical property, F_N is the normalization factor which is the ratio of the polymer loading without coupling agent and the polymer loading with coupling agent, and MP_0 is the mechanical property determined by experiment.

As can be seen in Table VIII, the KR-55 and KR-138S, even at the concentration of 5.0 vol % in monomer, produced no appreciable improvement in the mechanical properties of mortars.   It should be pointed out here that KR-55 also has unsaturation, but that it is in the form of the allyl radical which is not as likely to copolymerize with MMA.   For the other two coupling agents, the A-174 and the KR-33CS, the percent improvement becomes appreciable only at the concentration of 5.0 vol %.   A-174 produced 22% improvement in compressive strength and 6.9% in flexural strength, while the KR-33CS produced 13.9% improvement in compressive strength and 14.6% in flexural strength.   These results show that A-174 and KR-33CS apparently produce a bonding effect between the inorganic matrix and the polymer.   The differences in percent improvement of mechanical properties of mortar, impregnated with MMA in presence of A-174 and KR-33CS, and the KR-55 and KR-138S, these last two coupling agents producing little improvement, can be attributed to the following effects: (1) the formation of a true chemical bond, as mentioned before, favored by the unsaturation of the organic part of the A-174 and KR-33CS (see Table I) and (2) the modification of the characteristics of the polymer produced in the presence of the coupling agent (see Table VI).

Due to the fact that the improvement in mechanical properties was obtained only at 5.0 vol % of A-174 and KR-33CS in monomer by impregnation of the mortars *in situ*, a different method of mortar impregnation, the so-called pretreatment method, was followed.   Table IX gives the mechanical properties of mortars impregnated with MMA by pretreatment of acetone and toluene/xylene containing 2.0 and 5.0 vol % of A-174 and KR-33CS.   As can be seen, both coupling agents apparently improve the mechanical properties of PMMA-impreg-

nated mortars.   Again, Table IX shows that the improvement becomes appreciable only with the concentration of 5.0 vol % of coupling agent.   However, when Tables VIII and IX are compared, it can be established that the pretreatment of mortars by solvents containing coupling agents contributes to the enhancement of the mechanical properties of polymer-impregnated mortars.   By and large, with *in situ* impregnation as well as with pretreatment impregnation, A-174 produced a better improvement in mechanical properties than KR-33CS.   This fact can be due to a greater compatibility of this silane coupling agent to the inorganic paste mortar (or due to its greater miscibility with either the monomer or the solvent system), since in all cases A-174 exhibited higher solubility than KR-33CS.   It should be noted that there was no way to detect whether the coupling agent had penetrated completely or just partially into the mortar since the hydrated cement paste matrix may act as a molecular sieve[25] for the coupling agent molecules.   If the molecular sieve effect could be the controlling factor for the penetration of coupling agents into the capillary pore structure of the mortar, the best way of introducing these chemicals of large molecules, especially the titanates, would be to add them as water-soluble compounds at the time of preparing the mortar premix.

In the past the fracture of normal concrete and mortar have been studied in detail by many researchers.[26,27]   The fracture behavior of polymer-impregnated mortar is significantly different from that of the normal mortar.   Figures 3(a) and 3(b) show micrographs of the fracture surface of the normal and the polymer-impregnated mortar, respectively.   The normal mortar presents a large number of microcracks and air voids while the polymer-impregnated mortar shows that the microcracks are relatively absent; the discontinuous and rather big voids are either completely filled with the impregnated resin or partially filled by air surrounded by a polymer ring.   A close look at these surfaces shows in detail the microcracks exhibited by the fracture surface of the normal mortar [Fig. 3(c)], in which the microcracks are located at the interface betwen the cement and aggregate.   However, in the polymer-impregnated mortar [Fig. 3(d)], the microcracks are virtually eliminated, and in some cases the aggregate particles are broken, indicating that the cement-aggregate bond is considerably improved by polymer impregnation.

After the mortar is impregnated by the polymer, the voids, as pointed out above, are partially filled by air surrounded by a polymer ring, as shown in Figure 4(a), or completely filled by the impregnated resin, giving the appearance of cement spheres in the fracture surface, as shown in Figure 4(b).   Whenever a concretelike sphere was found, it was perforated by a pin, as shown in Figure 4(c), to verify that they were effectively polymer-formed spheres.   Figure 4(d) shows the surface of that given in Figure 4(c) after 12-h extraction in acetone, indicating the polymer fills not only the voids but passes through sand grains or aggregate, introducing a better interfacial bond.

Visual comparison of many micrographs of the fracture surface of polymer-impregnated mortars, containing different concentrations of coupling agents in monomer, did not allow us to establish a quantitative difference among surfaces.

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