

# Interphase Effects in Polymer-Modified Hydraulic Cements

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## Synopsis

Earlier work has indicated the importance of interphase adhesion within these systems. The work here reported shows that, with reactive polymers, substantial chemical modification occurs at the surface of the polymer latex particle. With certain polymer types, such as polyethylene and polystyrene homopolymers, no evidence is found of such reactions; with others, such as poly(vinylidene chloride, vinyl chloride) and poly(ethyl acrylate, methyl methacrylate), substantial reaction occurs. Crosslinking and insolubilization frequently accompany these reactions, and the nature of the polymer is significantly altered.

## INTRODUCTION

As an introduction to a study of polymer-modified cements,<sup>1</sup> several polymer and copolymer species available in latex form were tested for their ability to improve the compressive, tensile, and bond strengths of portland cement mortars. The testing was a survey and was cursory in nature. The customary ASTM tests were used. The mortars consisted of three parts silica sand, one part Type I portland cement, and 0.15 parts latex solids, all by weight. Sufficient water was added to bring the total water:cement ratio to 0.35. Samples were tested after 28 days ambient aging in an air-conditioned laboratory and after 28 such days plus seven days of immersion in water. Two facts emerged: certain species of copolymers produced significantly higher strengths; of these, copolymers of vinylidene chloride were unique in an ability to retain a higher portion of their "dry" strength after the immersion in water. (Samples were tested while still wet.) No allowances were made for any effect of the emulsion stabilizers present in the latexes nor for any change in rate of hydration of the cement which might have been caused by the latexes tested.

Another study<sup>2</sup> of the tensile strengths and moduli of rupture of polymer-modified cements has indicated the importance of interphase adhesion within such systems. It has been found that high tensile strength and modulus of rupture are associated with a high level of adhesion developed at the sand/cement paste and cement paste/polymer interfaces and that this adhesion varies appreciably with the type of polymer latex.

These results suggested further study of the effect of vinylidene chloride levels in copolymers on the strength of modified mortars prior to a detailed study of the mechanism of polymer/cement interaction.

### Latex Polymer Composition

A series of latexes were prepared to study the effect of increasing amounts of vinylidene chloride on the strength of latex-modified mortars. The latexes were batch polymerized in laboratory apparatus using an anionic emulsifier and a water-soluble persulfate initiator. The monomer phase consisted of 10% methyl methacrylate and 90% of a mixture of vinylidene chloride and ethyl acrylate adjusted so that the level of vinylidene chloride in the polymer phase varied from zero to 90%. The polymerizations were carried to greater than 99% conversion.

The resulting latexes were stabilized and mixed into mortars consisting of 3 parts sand, 1 part portland cement, 0.15 parts latex solids, and a total water: cement ratio of 0.35. The mortars were tested by making 2-in. cubes as in ASTM C-109. After 28 days aging in an air-conditioned laboratory they, were tested in compression; the results are shown in Table I. The data suggests that vinylidene chloride plays an important role as a chemical species in the modification of mortars. It should be noted that the physical character of the polymer involved here varies from quite brittle (90% vinylidene chloride) to rather flexible (90% ethyl acrylate).

The data also suggested the possibility of chemical reaction between the polymer phase and the cement; further exploration of this point was made by polymerizing a fixed copolymer ratio (75% vinylidene chloride, 20% vinyl chloride, 5% ethyl acrylate) in systems of varying emulsifier level to obtain latexes of various particle sizes. The particle sizes were measured by light scattering techniques. Examination by electron microscope indicated the latexes were not monodisperse but contained a range of particles such that the larger were about 1.8 times the smaller in diameter. These latexes were used to make mortars as described above. Mortar samples were tested at 28 days in compression and tension. The results are shown in Table II.

### Latex Particle Surface

The work cited above suggests a reinforcement mechanism dependent on the polymer surface presented to the hydrating cement. If the interaction of significance is between these species, a latex particle containing a high percentage

TABLE I  
Data for Plot of Mortar Compressive Strength vs Percent  $\text{VeCl}_2$  in Polymer

% $\text{VeCl}_2$	Compressive strength, psi
90	9083
87	7925
84	8315
80	8175
75	8425
70	8160
60	8140
50	7670
40	7430
30	4330
20	4540
10	4410
0	3640

TABLE II  
Strength of Modified Mortar as a Function of Latex Particle Size

Particle size	Compressive strength, psi	Tensile strength, psi
1630	5400	780
1430	6320	910
1300	6600	1040
1100	7250	1100
1050	7650	1180

of vinylidene chloride at the surface should be as effective as a particle containing an equivalent amount of vinylidene chloride throughout.

To determine this, four latexes were prepared as illustrated schematically in Figure 1. The center portion, or seed, was formed from 5 weight parts styrene plus 5 parts ethyl acrylate, polymerized in 100 parts water containing surfactant and a hydrophilic redox catalyst system. To this seed, 90 parts of a comonomer mix of the composition indicated in Figure 1 was added continuously, the rate of addition being such that all the monomer was added in approximately 12 hr. The fact that comonomer was added continuously permitted a change in comonomer ratio during the polymerization when desired. Heat transfer conditions were such that a 2°–4°C temperature differential existed between the latex (during polymerization) and the surrounding bath. If monomer addition was stopped, the temperature began to equalize within 1 min, indicating no large reservoir of monomer within the latex at any time. Thus, the average copolymer

STRUCTURE OF LATEX PARTICLES

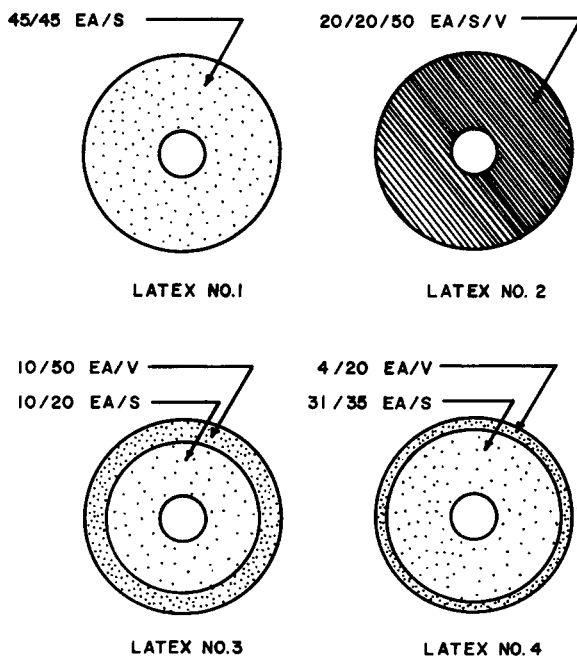


Fig. 1. Variable compositions of latex particle surface layers: (EA) ethyl acrylate; (S) styrene; (V) vinylidene chloride.

composition over any short interval of time was equal to the monomer composition added during that time.

The fact that the particles grew in the manner illustrated is supported by these observations: The latexes were monodisperse; no new particles were formed during polymerization, otherwise the existence of a monodisperse latex would be highly improbable. The fraction of the monomer containing vinylidene chloride is not a solvent for the existing polymer at the time of addition of this monomer. Previous experience with this technique has shown that the radius of the monodisperse latex particle from electron micrographs is always proportional to the cube root of the amount of monomer added at any given time. Any drift in copolymer composition due to relative reactivity of the monomers, minimized by continuous monomer addition, would favor concentration of the vinylidene chloride near the surface of the latex particle.

Comparison of latexes 2, 3, and 4 with 1 (the control) and with a commercially available latex containing 75% vinylidene chloride afforded an opportunity to determine if total vinylidene chloride (the assumed operative species) affected reinforcement or if only that vinylidene chloride at the surface (presumably favorably located for interfacial reaction) determined the effective level of reinforcement.

Effectiveness of the latexes in increasing the strength of modified mortars was assessed by measuring the compressive and tensile strengths at 28 days on mixes composed of 3 parts silica sand, 1 part portland cement, and 0.15 parts latex solids. Water to cement was held at a constant 0.35 parts by weight.

### Effect of Thermal Degradation of Polymer Phase

The exposure of a polyvinylidene chloride copolymer latex-modified mortar to temperature conditions sufficient to severely degrade the polymer (88 hr at 300°F) and to conditions sufficient to burn out the organic phase (600°F for 88 hr) was carried out to note the effect on mortar strength. The data in Table II indicate a loss of strength at the extreme conditions, but the samples retain strength well above the controls.

TABLE III  
Variation of Mortar Strength with Composition of Surface Region of Latex Particle

% VeCl <sub>2</sub> total	% VeCl <sub>2</sub> "skin"	Mortar tensile strength, psi	Mortar compressive strength, psi
0	0	385	3970
50	55	480	6880
50	83	487	6405
20	83	470	6470
75	60±	1070	9200
20	20	465	4540
No polymer	—	220	3280

### Reactivity of Latexes With Cement

In initial experiments the vinylidene chloride–vinyl chloride–ethyl acrylate, 75:20:5, latex was incorporated with sand and cement and then extracted with methyl ethyl ketone at various time intervals up to 24 hr. These showed that somewhat less than half of the polymer was thus extracted, even though the starting polymer was completely soluble in this solvent. Extensive dehydrohalogenation was noted, and significant and progressive changes in the infrared spectra of the polymer relative to the starting material were observed. Solvent extraction and subsequent analyses and IR spectra determinations are complicated, however, by the presence of the cement silicates.

In a similar manner, an ethyl acrylate–methyl methacrylate copolymer latex was found to be completely converted from a methyl ethyl ketone-soluble to an insoluble form. Calcium ion was found to be contained in the polymeric residue to the extent of 0.013 g calcium per 1 g polymer. When the polymeric residue was contacted with 1M HCl for a period of 3 hr, calcium ion was displaced and solubility in methyl ethyl ketone was regained. It appears likely that here the initial reaction, in the alkaline environment, involves saponification of the ethyl acrylate portion of the copolymer and an “ionomer” type bonding of the carboxylate groups thus obtained, this effecting crosslinking of the polymer. It is found further that when this latex is allowed to react with aqueous sodium hydroxide solution, at the pH value of 12.3 characteristic of the cement paste, this insolubilization does not occur.

### Reaction of Other Polymer Types With Aqueous $\text{Ca}(\text{OH})_2$

Four additional latex types were similarly treated, seven days of contact with the  $\text{Ca}(\text{OH})_2$  slurry being provided. A styrene homopolymer latex and an ethylene–vinyl chloride copolymer latex showed no insolubilization; a butadiene–styrene copolymer latex showed partial insolubilization; a Neoprene latex showed nearly complete insolubilization.

### Study of the Interface Between Polymer-Modified Cement Paste and Silica—Examination Utilizing Scanning Electron Microscope

Polymer-modified cement pastes were prepared incorporating the two poly(vinylidene chloride, comonomer) latexes noted above, the acrylic copolymer latex, and a polyethylene latex. Ratio of cement–polymer–water was 100:16:32. Each of these pastes was placed in an approximately 0.01-in.-thick layer between polished and cleaned vitreous silica surfaces, forming “sandwiches,” each silica side measuring 1.2 in. by 0.5 in. by 1.4 in. Following preparation, these specimens were immediately placed for ten days in a desiccator maintained at 75°F and 100% relative humidity. At the end of this period, they were removed and allowed to stand open for four additional days at ambient laboratory conditions. Following this, the specimens were broken in shear and the exposed surface immediately vacuum metallized (gold). Observation and photographing of these matching surfaces was then done, using a Cambridge scanning electron microscope.

Typically, in any given area the paste layer remains attached predominantly to one side, so that for convenience is reference here, such an area is designated

TABLE IV  
Effect of Thermal Degradation of Polymer Phase<sup>a</sup>

Compressive strength, psi			Tensile strength, psi		
28 days, room temp.	300°F	600°F	28 days, room temp.	300°F	600°F
Control					
4125	4275	4550	430	390	350
4438		4550	450	420	325
4325			370		
			340		
15% Polymer					
8825	7875	5665	905	830	525
8390	7025	5540	955	750	
8640		5540	990		
5465			885		
			480		

<sup>a</sup> After 88 hr at specified temperatures.

as a "paste" surface, while the matching area is referred to as a "clean" surface. Six magnifications were used in each case, ranging from about 20X to about 20,000X. Figures 2 and 3 relate respectively to a representative clean and matching paste area of the 85% poly(vinylidene chloride) latex described earlier. Scale is shown on each photograph, and the area "zoomed in" on going stepwise from low to high magnification is also framed by markings on the photographs.

In the photographs, a clean area shows up darker than its matching paste area; for example, in the two matching photos marked with the 0.5-mm scale, the two white circular areas located roughly in the center of the photograph correspond to paste pulled from the two black circular areas located slightly above the center in Figure 3.

Note the latex particles which can be most clearly seen in the 5000-Å scaled photo of Figure 2 in the vertical profile of this paste layer. Of more significance in this same photograph is the particulate matter adhering to the clean area of the silica surface and forming a continuous layer over the left side and lower half of this photograph. This is noted invariably also with other clean areas and with the other three latexes. Such a layer is not found on control silica surfaces that have never been contacted with cement paste. From enlargement "blowups" of such photographs, the diameter of these closely packed particles is estimated at about 350–750 Å.

## SUMMARY AND DISCUSSION

In the pH range of 12.3–11.7, at ambient temperatures, vinylidene chloride homopolymers and copolymers in latex form undergo substantial dehydrohalogenation. Where such polymers exhibit solubility in organic solvents prior to such reaction, a large weight fraction (typically 25%–65%) becomes insoluble after reaction. This insolubilization occurs not only where Ca<sup>2+</sup> is present but also where only Na<sup>2+</sup> is available.

Infrared spectra obtained on the polymer fractions resulting from these re-

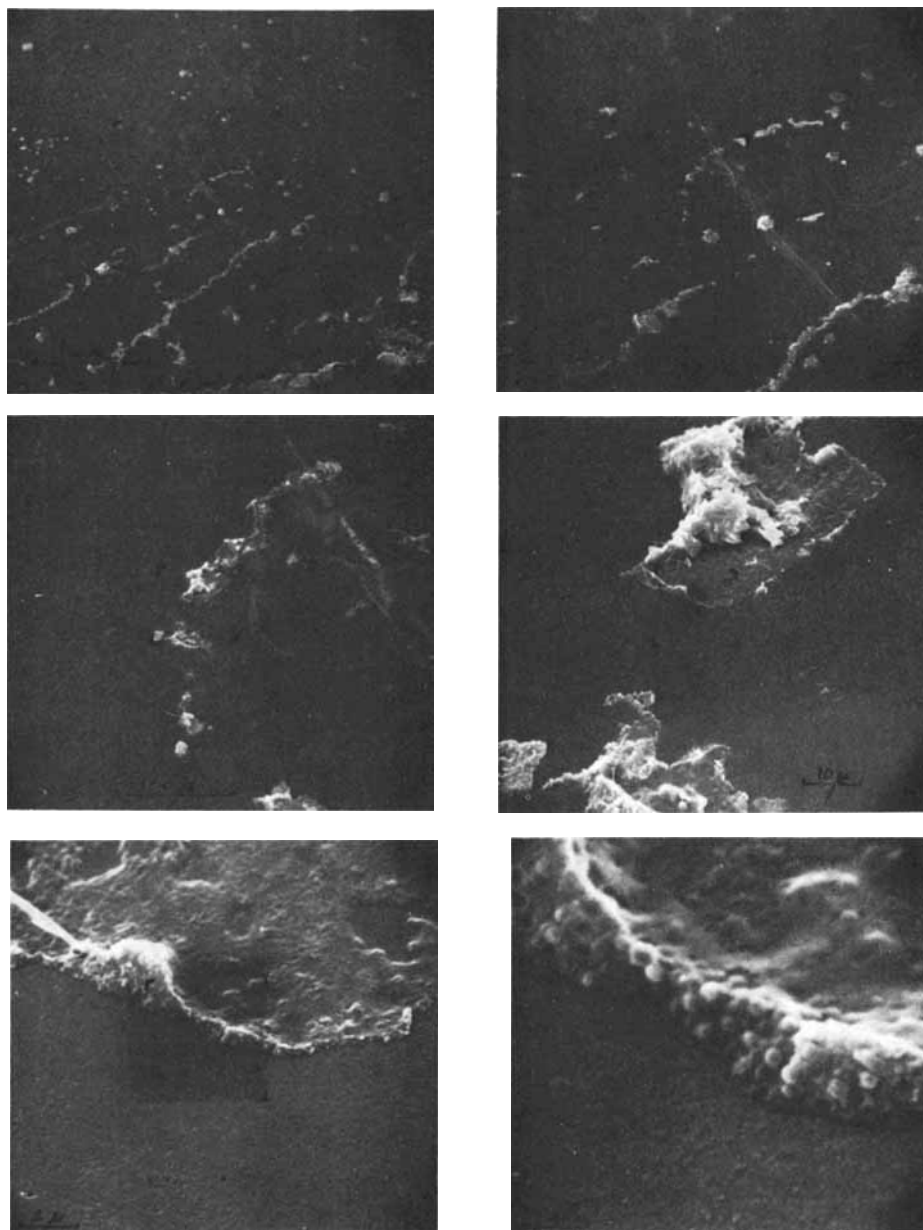


Fig. 2. "Clean" paste area; magnification 20X to 20,000X.

actions show that significant production of carbonyl groups has occurred. The development of new chromophoric groups as reaction progressed was evident, this being almost entirely associated with the insoluble polymer fraction. This latter effect can probably be explained on the basis of development of conjugated double bonds.

With the ethyl acrylate-methyl methacrylate copolymer latex, the insolubilization in the presence of  $\text{Ca}^{2+}$  is believed to result from hydrolysis of the ethyl acrylate mer, followed by crosslinking of the carboxylate ions by  $\text{Ca}^{2+}$ . No insolubilization is effected here by  $\text{Na}^+$ . In the initial reaction between these latex

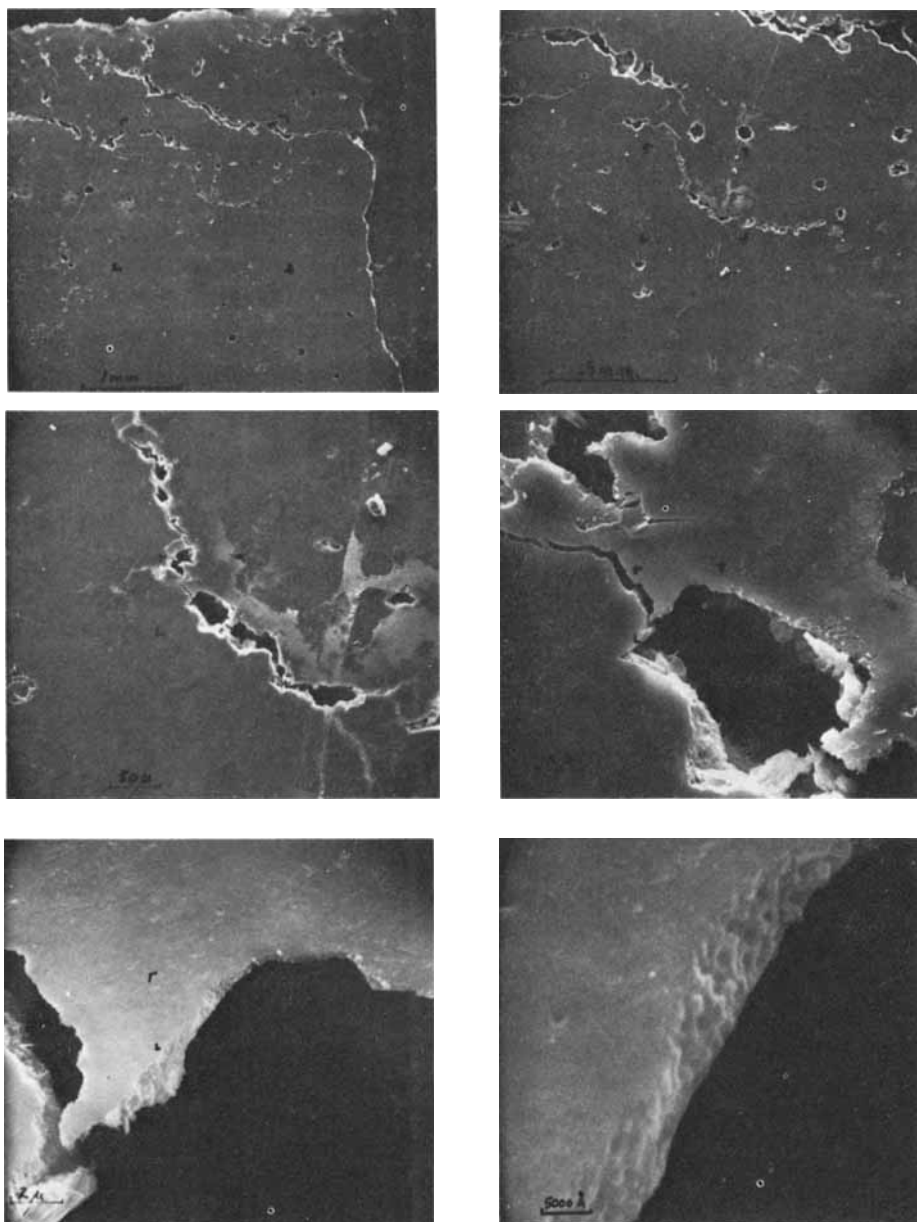


Fig. 3. Matching paste area; magnification 20 $\times$  to 20,000 $\times$ .

particles and the aqueous phase, there is no evidence of reaction of any species other than  $\text{OH}^-$  from the aqueous phase nor of separation of any ion other than  $\text{Cl}^-$  from the polymer phase. Reaction can progress into the interior of the latex particles only by intrusion of  $\text{OH}^-$  ions, this being by release of  $\text{Cl}^-$  ions. If representative values found for quantity of reacted  $\text{Cl}$  in the  $\text{Ca}(\text{OH})_2$  slurry reactions are taken and if the reaction is assumed to be concentrated in the "outermost" regions of the polymer latex particles, it is calculated that a 1500- $\text{\AA}$ -diameter latex particle need be "penetrated" to a depth of about 45–50



Å. This figure is based on an average removal of only one Cl atom from each  $\text{VeCl}_2$  mer unit. If both Cl atoms are removed from all  $\text{CaCl}_2$  units, this distance would be reduced to about 25 Å. Conversely, if appreciable crystallinity exists in the polymer structure and these regions are inaccessible to reaction, this distance would be correspondingly increased.

Perhaps a more realistic picture of this process is not penetration by the  $\text{OH}^-$  ion but sufficient polymer segment mobility in amorphous regions near the particle surface so that access to Cl atoms on these is offered to  $\text{OH}^-$  ions. As formation of carbonyl—and perhaps also hydroxyl—groups progresses at these sites, the hydrophilic character of these polymer segments would be increased and this process facilitated. It is also possible that disruption of crystalline regions of the polymer structure might accompany reaction and thus a gradual “unraveling” of the initial polymer structure be brought about.

On the basis of the above picture, it is interesting to attempt to correlate this with the relative amounts of soluble and insoluble polymer fractions observed. In principle, a given polymer molecule should be found in the soluble fraction only if no mer units contained in it have crosslinked to some other molecule, the latter being incorporated in the soluble fraction. If 60 wt-% is taken as a typical value across a number of these experiments for the fraction of polymer remaining soluble, then the diameter of this soluble polymer “core” should be about 1270 Å, where the initial, total particle diameter is 1500 Å. Thus, such an uncrosslinked molecule should have no component segment closer to the particle than about 115 Å. This suggested, then, that while  $\text{OH}^-$  “penetration,” with accompanying dehydrohalogenation and crosslinking, may only extend 25–50 Å beneath the particle surface, attached but unreacted polymer segments may extend into the next 50- to 60-Å-deep zone, so as to bring this fraction of the polymer also into the insoluble fraction.

Turning now to the results obtained with the scanning electron microscope, it is believed that the particle matter detected over the silica surface, after contact with cement paste, is significant. Kolthoff and Stenger<sup>3</sup> have shown that aqueous calcium hydroxide reacts with a silica surface, calcium ion being absorbed and calcium silicate being produced. The extent of this adsorption as determined by Kolthoff and Stenger, and results we have obtained following this adsorption with methyl red, appears to correspond to little more than a monolayer of the silicate. The silicate formed here is considered to be the disilicate since, utilizing the silicate ion equilibrium constants of Roller and Ervin,<sup>4</sup> the disilicate form predominates in the pH range of saturated  $\text{Ca}(\text{OH})_2$  solution. Our observations of the silica surface after contact with the cement paste, however, indicate a surface layer much thicker than that produced in the presence of a  $\text{Ca}(\text{OH})_2$  alone.

On the basis of the foregoing and earlier reported observations, the following is our present picture of the sequence of events occurring during hardening of polymer latex-modified cements and leading to polymer reinforcement of these compositions:

(1) During the initial period following mixing of cement powder, sand, and latex, several processes occur simultaneously, these being (a) formation of the “cement gel” at the cement grain surfaces and within the water phase; (b) development of an adherent layer of calcium silicate over the sand particle surfaces; and (c) with reactive polymers, substantial modification of the chemical nature

at and within the polymer latex particle surfaces. With certain polymer types studied, such as polyethylene and polystyrene, no evidence has been found of the latter reaction, and from chemical considerations, none would be expected. With others, such as poly(vinylidene chloride, vinyl chloride), Neoprene, and poly(ethyl acrylate, methyl methacrylate) substantial extents of reaction occur. Crosslinking and insolubilization frequently accompany these reactions, and the nature of the polymer is substantially altered.

(2) During the next period, attachment of latex particles to the cement gel particulate matter and to the silicate layer at the sand surface interface occurs. With the reactive polymers, this may involve chemical reaction and bonding between the now-modified polymer particle surfaces and the silicate surfaces. The nature of these reactions seems specific to the particular polymer latex.

(3) During the final period, namely, during withdrawal of water by cement hydration, coalescence of the polymer latex particles occurs. It is during this last period that the polymer "network" structure is developed. Polymers that are not "film forming" initially and that undergo no modification in the cement environment show no coalescence; however, even polymers that are initially not film forming may nevertheless exhibit coalescence after such chemical alteration.

In compressive strength reinforcement, latex-modified systems lead to a densification of the gel phase because of lower water requirements to meet rheological needs. This densification is sufficient to account for the increased strength of the hydrated cement. In terms of other strengths, the development of strong adhesive bonding at phase interfaces is the important effect. Those polymer latexes which, in the alkaline cement environment, develop strong bonding at the sand-paste interface and at the cement gel-polymer interface produce correspondingly increased tensile strengths, moduli of rupture, and shear strengths in mortar compositions.<sup>5</sup>

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