

Report on Polymer-Modified Concrete

Reported by ACI Committee 548



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Report on Polymer-Modified Concrete

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Report on Polymer-Modified Concrete

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This report addresses concrete made with organic polymers combined with hydraulic cement and discusses the polymer systems used to produce polymer-modified concrete, including their composition and physical properties. It explains the principle of polymer modification and reviews the factors involved in selecting appropriate polymer systems. The report also discusses mixture proportioning and construction techniques for different polymer systems and summarizes the properties of fresh and hardened polymer-modified concrete and common applications.

Keywords: abrasion; acrylic resins; admixtures; bridge deck; construction; corrosion; curing; durability; epoxy resins; latex; mixture proportioning; mortar; pavements (concrete); plastic; polymer; polymer-cement concrete; repair; resin; resistance to chemical attack; resistance to freezing and thawing; test.

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PREFACE

Polymer-modified concrete (PMC) is developed by mixing a polymer material to portland-cement concrete with the interest of enhancing the concrete durability and bond strength. PMC, also known as polymer portland-cement concrete (PPCC) or latex-modified concrete (LMC), was originally developed during the 1950 and 1960s. The material quickly found its way to awaiting industry to make use of its unique properties and became a common material in bridge deck slab overlays, industrial floors and as repair material with enhanced tensile and bond strength. Extensive research and numerous publications on the behavior of PMC were produced from the late 1970s up to the early 1990s. These publications constitute most of our current knowledge on PMC and polymer-modified mortars (PMM). While the development of PMC has significantly slowed down in the last decade, this document is designed to provide a major source of collective information for the public about PMC. The intent is to provide insight on most up-to-date standards, current practices, and the state of the art on research developments on PMC.

The International Congress on Polymers in Concrete (ICPIC) served during the last four decades as the international forum for research and development (R&D) on all types of polymer concrete including PMC. Proceedings of the ICPIC reflected the state of R&D on PMC and the issues of current interest for both academia and industry. The first ICPIC was held in London (UK) in 1975, and the most recent ICPIC was held in Chuncheon (South Korea) in 2007. For the last three decades, the ICPIC forum has served to connect interested specialists in PMC while providing insight on new technologies and future development trends.

Research on PMC continues to date with little addition to the main body of knowledge that was generated in the last 20 years of the twentieth century. Research developments in the 1980s and 1990s explained the principles of polymer modification of cement hydration (Ohama 1987) and provided the basis for selecting the suitable polymer type for PMC. Today, styrene butadiene rubber (SBR) and styrene-acrylic (S-A) copolymer represent the most usable polymers in PMC. It is therefore evident that PMC production and use has reached a high level of maturity and most research investigations in the last two decades were applications directed to further establish the procedures and standards for the material's use in the field.

Within the past few years, the most interesting developments in PMC are the development of new very-early-strength LMC (Sprinkel 2005) and the use of chopped glass and carbon fibers as additives to reduce LMC plastic shrinkage cracking (Issa et al. 2007). Both developments have found their way to bridge deck slab overlays for their ability to provide fast construction and reduce plastic shrinkage cracking. The recent work by Ohama and Demura (2001) and Ohama (2007a) on self-repair epoxy-modified mortars is definitely worth noting.

CHAPTER 1—INTRODUCTION AND SCOPE

1.1—Introduction

Polymer-modified cementitious mixtures (PMCs), also called polymer portland-cement concrete (PPCC) and latex-modified concrete (LMC), are defined as hydraulic cement combined at the time of mixing with organic polymers that are dispersed or redispersed in water, with or without aggregates. An organic polymer is a substance composed of thousands of simple molecules combined into large molecules. The simple molecules are known as monomers, and the reaction that combines them is called polymerization. The polymer may be a homopolymer if it is made by the polymerization of one monomer, or a copolymer when two or more monomers are polymerized. The organic polymer is supplied in three forms: as a dispersion in water that is called latex; as a redispersible powder; or as a liquid that is dispersible or soluble in water. Dispersions of polymers in water and redispersible polymer powders have been in use for many years as admixtures to hydraulic-cement mixtures. These admixtures are called polymer modifiers. The dispersions of these polymer modifiers are called latexes, sometimes incorrectly referred to as emulsions.

In this report, the use of the general term “polymer-modified cementitious mixture” includes polymer-modified cementitious slurry, mortar, and concrete. Where specific slurry, mortar, or concrete mixtures are referenced, specific terms are used, such as LMC and latex-modified mortar (LMM). Several other terms used in this report are defined in ACI 548.1R.

The improvements from adding polymer modifiers to concrete include increased bond strength, flexural and tensile strengths, split strength, and reduced elastic modulus. These lead to improved physical resistance such as impact resistance and abrasion resistance (Shaker et al. 1997; Wong et al. 2003; Colak 2005). A reduced elastic modulus might be particularly helpful when LMC is applied as a bridge deck overlay or repair surface. The reduced elastic modulus results in a reduction of the stresses developed due to differential shrinkage and thermal strains that would reduce the tendency of the material to crack. PMC can also improve corrosion resistance, resistance to chemical attack and severe environment (such as sulfuric acid attack, penetration by water and dissolved salts, and freezing-and-thawing resistance), and it reduces need for sustained moist curing. These improvements are largely due to reduced water permeability in PMC (Shaker et al. 1997; Ohama 1995b). The improvements are measurably reduced when PMC is tested in the wet state (Popovics 1987; Soroushian et al. 1993). The specific property

improvement to the modified cementitious mixture varies with the type of polymer modifier used.

The proportioning of ingredients and mixing procedures are similar to those for unmodified mixtures. Curing of modified mixtures, however, differs in that only 1 to 2 days of moist curing are required, followed by air curing. Applications of these materials include tile adhesive and grout, floor leveling concrete, water tanks, swimming pools, roof deck, concrete patches, bridge deck overlays, and ship decks (Su et al. 1991; Kardon 1997; Pinelle 1995; Cabrera and Al-Hasen 1997; Gerharz 1999; Hare 1999; Jingang et al. 2005).

1.2—History

The use of polymers as an additive to construction material is not new. In Babylonia in 4000 B.C. and in Indus Valley in 3000 B.C., clay brick walls were produced by using natural polymers such as albumen and rice paste (Chandra and Ohama 1994; Kardon 1997). More recently, in 1923, the first patent of a polymer-hydraulic-cement system, issued to Cresson (1923), refers to paving materials with natural rubber latexes where cement was used as filler. The first patent of the modern concept of a polymer-modified system was granted to Lefebure in 1924 (Lefebure 1924). Lefebure appears to be the first worker who intended to produce a PMC using natural rubber latexes by proportioning latex on the basis of cement content; Cresson, in contrast, based his mixture on the polymer content. In 1925, Kirkpatrick patented a similar idea (Kirkpatrick 1925). Throughout the 1920s and 1930s, LMM and concrete using natural rubber latexes were developed. Bond's patent in 1932 (Bond 1932) suggested the use of synthetic rubber latexes, and Rodwell's patent in 1939 (Rodwell 1939) first claimed to use synthetic resin latexes, including polyvinyl acetate latexes, to produce polymer-modified systems.

In the 1940s, patents on polymer-modified systems with synthetic latexes, such as polychloroprene rubber latexes (Neoprene) (Cooke 1941) and polyacrylic ester latexes (Jaenicke et al. 1943) were published. Also, polyvinyl acetate-modified mortar and concrete were actively developed for practical applications. Since the late 1940s, polymer-modified mixtures have been used in various applications such as deck coverings for ships and bridges, paving, floorings, anticorrosives, and adhesives. In the United Kingdom, feasibility studies on the applications of natural rubber-modified systems were conducted by Stevens (1948) and Griffiths (1951). Also, a strong interest was focused on the use of synthetic latexes in the polymer-modified systems. Geist et al. (1953) reported a detailed fundamental study on polyvinyl acetate-modified mortar and provided a number of valuable suggestions for later research and development of polymer-modified systems. The first use of epoxy resins to modify hydraulic cement was reported by Lezy and Paillere (1967).

Research efforts in the 1970s, 80s, and 90s were focused on examining the properties of LMC and selecting the most suitable polymer latex for modifying cement in polymer-modified mortar (PMM) and PMC (Popovics and Tamas 1978; Lavelle 1988; Ohama 1995b; Okba et al. 1997). A major milestone during that time period was revealing the

principles of latex modification of the cement hydration and identifying the mechanism of polymer-cement co-matrix formation (Ohama 1987; Su et al. 1991, 1996; Puterman and Malorny 1998; Jenni et al. 2006). Later efforts examined the long-term behavior of PMC with focus on durability and deterioration resistance aspects as a main characteristic of PMC (Ohama et al. 1985; Shaker et al. 1997; Mirza et al. 2002) and on controlling the rheological properties of LMC (Barluenga and Hernández-Olivares 2004).

Recently, researchers developed and examined very-early-strength LMC using rapid hardening cement (Sprinkel 1999, 2005). The use of the new very-early-strength LMC proved efficient for replacing bridge deck overlays. Moreover, the use of fiber-reinforced LMC has been recently promoted (Cao and Chung 2001; Issa et al. 2007). The use of glass and carbon fiber-reinforced LMC provides a watertight micro-structure of LMC with very low permeability and the ability of the chopped fibers to limit plastic shrinkage cracking. Such combined benefits make fiber-reinforced LMC an excellent alternative for bridge deck slabs (Issa et al. 2007). Finally, a bibliography developed and updated by Ohama (2007b) represents an excellent source of information on historical and recent developments of PMC.

1.3—Scope

This report reflects the current state of knowledge of PMC and intends to provide the reader with a credible source of knowledge on PMC reflecting the maturity of that technology and highlighting R&D efforts taking place in the last few years. It is not the intention of this document to cover all research efforts on PMC but rather to highlight the significant efforts that helped shape the current state of knowledge of that material.

CHAPTER 2—ACRONYMS AND DEFINITIONS

2.1—Acronyms

ASTM	—ASTM International
FHWA	—Federal Highway Administration
ICPIC	—International Congress on Polymers in Concrete
ICRI	—International Concrete Repair Institute
LMC	—latex-modified concrete
LMM	—latex-modified mortar
MFFT	—minimum film-forming temperature
PAE	—acrylic polymer and copolymer
PMC	—polymer-modified cementitious mixture
PMM	—polymer-modified mortar
PPCC	—polymer portland-cement concrete
PVA	—polyvinyl acetate homopolymer
R&D	—Research & Development
RH	—relative humidity
S-A	—styrene-acrylic copolymer
S-B	—styrene-butadiene copolymer
SBR	—styrene-butadiene rubber
VAC	—vinyl acetate copolymer
VAE	—vinyl acetate ethylene copolymer
VA-VEOVA	—vinyl acetate-vinyl ester of versatic acid copolymer
VEOVA	—vinyl acetate-vinyl ester of versatic acid copolymer
UV	—ultraviolet

2.2—Definitions

coagulum—polymer in the form of particles that are larger than intended due to such actions as particle agglomeration or skin formation.

comonomer—a monomer that is mixed with one or more other monomers to react and form a copolymer.

emulsion—a two-phase liquid system in which small droplets of one liquid (the internal phase) are immiscible in, and dispersed uniformly throughout, a second continuous liquid phase (the external phase).

glass transition temperature—the midpoint of the temperature range over which an amorphous material (such as glass or a high polymer) changes from (or to) a brittle, vitreous state to (or from) a plastic state.

latex—a water emulsion of a high-molecular-weight polymer, used especially in coatings, adhesives, leveling compounds, and patching compounds.

minimum film-forming temperature—the minimum temperature at which a synthetic latex or emulsion will coalesce when laid on a substrate as a thin film.

monomer—an organic molecule of relatively low molecular weight that creates a solid polymer by reacting with itself or other compounds of low molecular weight, or both.

nonvolatile content—the portion of a material that remains after volatile matter has been evaporated under specified ambient or accelerated conditions.

plastic-shrinkage crack—surface crack that occurs in concrete prior to initial set.

polymer—the product of polymerization; more commonly a rubber or resin consisting of large molecules formed by polymerization.

polymerization—the reaction in which two or more molecules of the same substance combine to form a compound containing the same elements and in the same proportions but of higher molecular weight.

resin—polymeric material that is rigid or semi-rigid at room temperature, usually with a melting point or glass transition temperature above room temperature.

setting time—the length of time required to set or harden resin or adhesive under heat or pressure.

stability—a measure of resistance to coagulation when a latex is subjected to mechanical action, chemicals, or temperature variations.

surface tension—an internal molecular force that exists in the surface film of all liquids and tends to prevent the liquid from flowing.

surfactant—a substance that markedly affects the interfacial or surface tension of solutions when present, even in low concentrations.

van der Waals forces—the attractive or repulsive forces between molecules (or between parts of the same molecule) other than those due to covalent bonds or to the electrostatic interaction of ions with one another or with neutral molecules.

viscosity—a measure of the resistance of a fluid to deform under shear stress.

CHAPTER 3—GENERAL INFORMATION ON POLYMER MODIFIERS

3.1—Polymer modifiers and their properties

Table 3.1 lists the various polymers that have been used to modify hydraulic cements. The materials in italics are the ones that are in general use today, and those marked with an asterisk are available in a redispersible powder form.

Mixed latexes are blends of different types of latex, such as an elastomeric latex with a thermoplastic latex. Although these blends are occasionally used for modifying cement, the practice is limited.

Each type of polymer latex imparts different properties when used as an additive (or a modifier) to hydraulic-cement mixtures. Moreover, variations within each type of latex, particularly copolymer latexes, yield different properties of hardened mortar and concrete.

With few exceptions, a process known as emulsion polymerization produces the latexes used with hydraulic cements. The basic process involves mixing the monomers with water, a surface-active agent (refer to Section 3.1.1.3 for a description of surfactants), and an initiator. The initiator generates a free radical that causes the monomers to polymerize by chain addition. Examples of chain addition polymerization are presented in Fig. 3.1. A typical formulation for emulsion polymerization is given in Table 3.2.

One method of polymerization is to charge the reactor with the water, surfactants, other ingredients, and part of the monomer or monomers under agitation. When the temperature is raised to a desired point, the initiator system is fed to the reactor, followed by the remainder of the monomer. By temperature control and possibly by other chemical additions, 90 to more than 99% conversion of the reaction normally occurs. Unreacted monomer is reduced to acceptable levels by a process known as stripping. The resultant latex may be concentrated or diluted, and small amounts of materials, such as preservatives and surfactants, may be added.

Other ingredients are often used in the polymerization process and are incorporated for many reasons, such as controlling pH, particle size, and molecular weight.

Redispersible powders are manufactured by using two separate processes. The latex polymer is made by emulsion polymerization, and is then spray-dried to obtain the powder (Walters 1992a).

Many latexes and redispersible polymer powders are available on the market, but only about 5% of them are suitable for use with hydraulic cements. The other 95% lack the required stability, and they coagulate when mixed with cement.

Latexes can be divided into three classes according to the type of electrical charge on the particles, which is determined by the type of surfactants used to disperse them. The three classes are cationic (positively charged), anionic (negatively charged), and nonionic (no charge). In general, latexes that are cationic or anionic are not suitable for use with hydraulic cements because they lack the necessary stability. Most of the latexes used with portland cement are stabilized with surfactants that are nonionic.

Typical formulations for the three types of latex used with portland cement are given in Table 3.3.

Table 3.1—Polymers used to modify hydraulic cementitious mixtures

Elastomeric	Natural rubber latex
	Synthetic latexes
	<i>Styrene-butadiene, polychloroprene (Neoprene), acrylonitrile-butadiene</i>
Thermoplastic	<i>Polyacrylic ester,* styrene-acrylic,* polyvinyl acetate,* vinyl acetate copolymers,* polyvinyl propionate, vinylidene chloride copolymers, polypropylene</i>
Thermosetting	<i>Epoxy resin</i>
Bituminous	Asphalt, rubberized asphalt, coal-tar, paraffin
Mixed latexes	

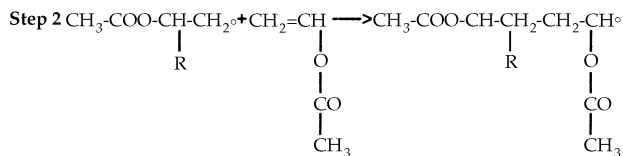
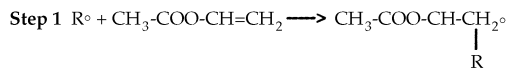
*Available in a redispersible powder form.

Note: Italics = in general use today.

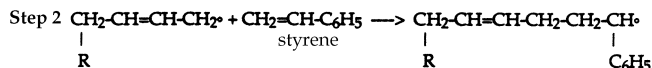
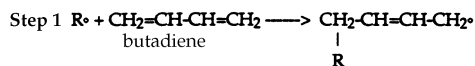
Table 3.2—Typical formations for emulsion polymerization

Item	Parts by mass
Monomers	100.0
Surfactant	1.0 to 10.0
Initiator	0.1 to 2.0
Water	80.0 to 150.0
Other ingredients	0 to 10.0

Homopolymerization of Vinyl Acetate



Copolymerization of Butadiene and Styrene



• = reactive valence
R° = free radical

Fig. 3.1—Typical chain addition polymerization.

Preservatives added to latex after polymerization provide protection against bacterial contamination and give improved aging resistance. Sometimes, additional surfactants are added to provide required stability. Antifoaming agents may be added to reduce air entrainment when the latex is mixed with the cement and aggregates.

Not all latexes are made by emulsion polymerization. For these other products, the polymer is made by another polymerization process, and the resultant polymer is then dispersed in water by the dosage of surfactants.

Table 3.3—Typical formulation for latexes used with portland cement

Vinyl acetate, homo- and copolymer latexes	
Item	Parts by mass
Vinyl acetate	70.0 to 100.0
Comonomer (butyl acrylate, ethylene, vinyl ester of versatic acid)	0.0 to 30.0
Partially hydrolyzed polyvinyl alcohol	6.0
Sodium bicarbonate	0.3
Hydrogen peroxide (35%)	0.7
Sodium formaldehyde sulfoxylate	0.5
Water	80.0
Acrylic copolymer latex	
Ethyl acrylate	98
A vinyl carboxylic acid	2
Nonionic surfactant	6*
Anionic surfactant	0.3†
Sodium formaldehyde sulfoxylate	0.1
Caustic soda	0.2
Peroxide	0.1
Water	100.0
Styrene-butadiene copolymer latex	
Styrene	64
Butadiene	35
A vinyl carboxylic acid	1
Nonionic surfactant	7*
Anionic surfactant	0.1†
Ammonium persulfate	0.2
Water	105

*The nonionic surfactants may be nonyl phenols reacted with 20 to 40 molecules of ethylene oxide.

†The low levels of anionic surfactant are used to control the rate of polymerization.

Polymer modifiers in a powder form are redispersed either in water or during mixing of the cementitious mixture. The use of polymer powders allows for the supply of one-part, prepackaged mixtures, requiring only the addition of water at the construction site. Where latex is used, the proportioning of the latex (and water) to the dry cementitious material is performed at the construction site.

3.1.1 Influence of polymer composition—The composition of the polymer modifier has marked effects on the properties of PMC mixtures, both in the wet and hardened states (Ohama 1995a; Walters 1990, 1992b).

3.1.1.1 Major components of polymer—The major components of a polymer modifier are the monomers that form the polymer's bulk, and are generally present in levels of greater than 10% by mass of the polymer modifier. Such monomers include, but are not limited to: acrylic esters (such as butyl acrylate, ethyl acrylate, and methyl methacrylate), acrylonitrile, butadiene, ethylene, styrene, vinyl acetate, vinyl ester of versatic acid (VEOVA), and vinylidene chloride.

These components have major effects on the hardness of the polymer modifier and its resistance to hydrolysis and ultraviolet light. The latter characteristics have significant effects on resistance to water penetration and color stability, respectively, of the PMC. The hardness of the polymer modifier is related to its glass-transition temperature, T_g .

Table 3.4—Glass transition temperatures T_g of various homopolymers

Monomer of homopolymer	T_g , °F (°C)
Ethylene	< -184 (< -120)
Butadiene	-110 (-79)
N-butyl acrylate	-65 (-54)
Ethyl acrylate	-7 (-22)
Vinylidene chloride	0.0 (-18)
Vinyl acetate	86 (30)
Acrylonitrile	208 (98)
Styrene	212 (100)
Methyl methacrylate	221 (105)

Table 3.4 gives typical T_g values for homopolymers of the listed monomers. In general, the higher the T_g , the harder the polymer and the higher the compressive strength of the PMC; the lower the T_g , the lower the permeability of the PMC.

Where resistance to discoloration by exposure to ultraviolet light is required, the desired polymer modifiers are acrylic copolymers (Lavelle 1988) and, possibly, vinyl acetate-ethylene copolymers (Walters 1990). Butadiene copolymers should not be used in such applications because they exhibit marked discoloration.

Where resistance to penetration of water and dissolved salts is of prime importance, hydrolysis resistance of the polymer modifier is necessary. The highly alkaline environment of hardened wet portland cement mixtures causes severe degradation of some polymer modifiers, such as vinyl acetate homopolymers. The hydrolysis of these homopolymers results in the formation of polyvinyl alcohol and metallic acetates. Both of which are water-soluble and can leach out of the concrete. Such degradation results in a PMC with higher permeability than unmodified mixtures. Hydrolysis resistance of vinyl acetate can be improved by copolymerizing with ethylene, VEOVA, or acrylic esters. These comonomers not only retard the rate of hydrolysis of the vinyl acetate, but even when hydrolysis occurs, the result is formation of a copolymer of vinyl alcohol with the comonomer. Such copolymers are usually not water-soluble and remain in the cementitious mixture with a marginal increase in permeability. Styrene-butadiene copolymers show no tendency to hydrolyze in alkaline environments. The majority of acrylic copolymers hydrolyze slowly, if at all. Consequently, styrene-butadiene or acrylic polymer modifiers should be used where resistance to water penetration is paramount.

Polymer modifiers made from monomers containing chloride groups should not be used in steel-reinforced concrete or mortar. In the alkaline environment of portland cement, some of the chloride groups are liberated in the ionic form and assist in corroding any reinforcing steel or steel surfaces. The primary monomer in this category is vinylidene chloride.

3.1.1.2 Minor components of polymer—The minor components are monomers incorporated into the polymer modifier for their reactivity or some other special property. They are usually present at levels of less than 5% by mass, more often in the 1 to 2% range. Such materials include carboxylic acids, such as acrylic or methacrylic, and N-methylol

acrylamide. These monomers, which form part of the polymer, have side groupings that can combine chemically with other substances in the cementitious mixture. Ohama (1995a) suggests that such reactions improve the bond between the cement and aggregates. Incorporation of carboxylic acids in the polymer modifier may lower the permeability of the resultant PMC (Walters 1992b). Reactive groups, such as acrylic acid and N-methylol acrylamide, have the potential of retarding the hydration of the cement.

3.1.1.3 Colloidal system of the polymer—The colloidal system consists of surfactants used to emulsify the monomers during polymerization and surfactants added later to modify the stability of the system. The colloidal system has effects on the properties of the polymer modifier (Walters 1987), which in turn has effects on the resultant PMC, particularly in the unhardened state. In general, the colloidal system of the majority of polymer modifiers for hydraulic cements is nonionic. Such systems give the latex sufficient stability to the multivalent ions of the cement and stability to freezing and thawing.

Antifoam agents, such as silicone emulsions, are often incorporated to reduce the tendency of the system to entrap air during mixing with the cement and aggregates. Surfactants (also referred to as stabilizers, soaps, and protective colloids) are chemical compounds added during manufacture of the latex that attach themselves to the surface of the latex particles. By doing so, they affect the interactions of the particles themselves as well as the interactions of the particles with the materials to which the latex is added. This is particularly true of portland cement. The surfactant's main effect is probably on the workability of the mixture as it allows for a reduction in the water-cementitious material ratio (w/cm) without reducing the slump of the modified mixture. If excess quantities are used, however, it can also reduce water resistance and adhesion of the hardened concrete.

3.1.2 Influence of compounding ingredients—Compounding ingredients are the materials added after polymerization is complete. They improve the properties of the product, such as resistance to chemical or physical attack. The most common compounding ingredients are bactericides that protect the polymer and surfactants against attack by bacteria and fungi. Antioxidants and ultraviolet protectors are added to provide protection against aging and sunlight attack. The levels of these added materials are relatively low, ranging from parts per million for bactericides to a few percent for surfactants. Other ingredients that may be added are defoaming or antifoaming agents. If the latex does not contain such a material, one of these agents should be added before use to avoid high air content in the hydraulic cement mortar or concrete.

3.2—Test procedures for polymer modifiers

Certain test procedures for measuring colloidal and polymeric properties of polymer modifiers are frequently used for quality-control purposes to ensure a supply of a consistent product. The tests can also be used to assess the suitability of polymer modifiers for specific uses.

3.2.1 Nonvolatile or total solids content—Nonvolatile content is important in that it is the major factor in determining the cost of the product. It is determined by weighing a small representative sample of the latex, drying it under certain conditions, and weighing the residue. The residue is expressed as a percentage of the original mass. Although there are several acceptable published methods, different values may be obtained by different test methods. Table 3.5 shows three different nonvolatile contents of the same latex using three different test temperatures and times of drying. The main difference is in the temperature and time used to dry the latex. If there is a dispute, the generally accepted method is ASTM D1076.

3.2.2 pH value—ASTM D1417 gives the method for testing the pH of latexes. The pH range of latex varies significantly, depending on the type of latex. For styrene-butadiene copolymer latexes used with hydraulic cement, it is usually 10 to 11; for acrylic copolymer latexes, it is usually 7 to 9; and for vinyl acetate homopolymer and copolymer latexes, it is usually 4 to 6. Walters (1992b) showed that with styrene-butadiene copolymer latexes, no significant change in flow, wet and dry density, and permeability properties of the PMC occurred when the pH value was varied from 4 to 10.

3.2.3 Coagulum—The sieve sizes used to measure the coagulum in ASTM D1076 are 150, 75, or 45 μm (formerly No. 100, 200, or 325 mesh). The test measures the quantity of polymer that has particles larger than intended, usually formed by particle agglomeration or skin formation. Typical coagulum values are less than 0.1% by mass.

3.2.4 Viscosity—Viscosity can be determined in many ways and the viscosity of a fluid can vary depending on the test method.

A method used with latex uses a viscometer manufactured by Brookfield (ASTM D1417), but its several speeds of rotation can give different values. Also, the temperature at which the test is run can have a significant effect. A combination of these effects can be dramatic, as illustrated in Table 3.6, which presents the viscosity indications obtained from one latex sample using different methods. When reporting Brookfield viscosity values, the model number, spindle number, speed of rotation, and temperature used in the test should be reported.

The styrene-butadiene and acrylic latexes used with hydraulic cements are very fluid, having viscosities of less than 14,280 psi (100 MPa) when measured at standard conditions (ASTM D445, ASTM D1417). As a reference, the viscosity of milk is approximately 14,280 psi (100 MPa).

3.2.5 Stability—Stability is a measure of resistance to coagulation when latex is subjected to mechanical action, chemicals, or temperature variations:

- Mechanical stability is determined by subjecting the latex to mechanical action, usually high-speed agitation for a specific time, and then measuring the amount of coagulum that is formed, as described in ASTM D1417;
- Chemical stability may be assessed by determining the amount of a chemical required to cause complete coagulation or by adding a quantity of the chemical and measuring the amount of coagulum. A method is described in ASTM D1076; and

Table 3.5—Effect of test method on nonvolatile content of a latex

Test temperature	158 °F (70 °C)	221 °F (105 °C)	257 °F (125 °C)
Time of drying, hours	16.0	0.75	0.50
Nonvolatile content, %	62.7	61.3	58.3

Table 3.6—Effect of test method on viscosity of a latex

Brookfield model	Speed, rpm	Temperature, °F (°C)	Viscosity, cps (Pa·s)
LVF	1.5	60 (16)	8000 (8.00)
RVF	20	75 (24)	1150 (1.15)
LVF	60	90 (32)	480 (0.48)

- Thermal stability is determined by subjecting the latex to specified temperatures for a specific period and determining thermal effects on other properties. An FHWA report (Clear and Chollar 1978) describes a freezing-and-thawing stability test in which the amount of coagulated latex after two cycles of freezing and thawing is determined. Freezing-thawing cycles are performed at a rate of one half-cycle/day. The test indicates the ability of the latex emulsion to resist freezing-thawing cycles prior to use in concrete.

These stability properties are important for latexes used with hydraulic-cement mixtures. Mechanical stability is required because the latexes are frequently subjected to high shear in metering and transfer pumps. Chemical stability is required because of the reactivity of hydraulic cements. Thermal stability is required because the latex may be subjected to wide variations in temperature. The surfactants used in the latex have a major influence on its stability.

3.2.6 Density—Similar to solids or nonvolatile content, density indicates the polymer content of the latex. The density of styrene-butadiene latex is approximately 1.01 kg/L (0.6 lb/gal.), whereas that of an acrylic is typically 1.07 kg/L (0.63 lb/gal.). If both latexes have solids of 47% by mass, the styrene-butadiene latex contains approximately 0.475 kg of polymer per liter (0.28 lb/gal.), whereas a liter of acrylic latex contains 0.503 kg (0.31 lb/gal.).

3.2.7 Particle size—Particle size is a measure of the size of the polymer dispersed in the water. It will vary from 50 to 5000 nm. Particle size can be determined using equipment such as electron microscopes, centrifuges, and photospectrometers. Particle size is dependent, to a large degree, on the levels and types of surfactants.

3.2.8 Surface tension—The FHWA report (Clear and Chollar 1978) describes a procedure that is accepted by most State Departments of Transportation. The lower the value of surface tension, the better the wetting ability of the latex. This property affects the workability or finishability of a latex-modified mixture. The surface tension is dependent, to a large degree, on the levels and types of surfactants. A typical value for a styrene-butadiene copolymer latex is about 40 dynes/cm (2.28×10^{-4} lbf/in.), while that of water is about 75 dynes/cm (4.28×10^{-4} lbf/in.).

3.2.9 Minimum film-forming temperature (MFFT)—Minimum film-forming temperature (MFFT) is defined as

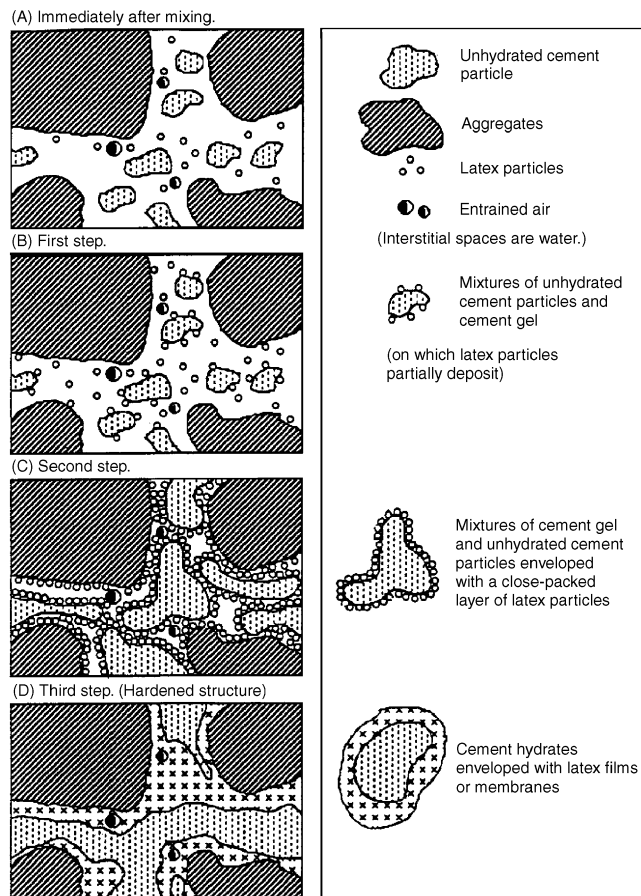


Fig. 3.2—Simplified model of formation of latex-cement comatrix (Ohama 1987).

“the lowest temperature at which the polymer particles of the latex have sufficient mobility and flexibility to coalesce into a continuous film” (Concrete Society 1987). The type and level of monomer(s) used to make the polymer control the MFFT. This temperature might be reduced by the addition of plasticizers. A plasticizer is a chemical added to brittle polymers to increase flexibility.

Generally, for successful application of latex-modified hydraulic-cement mixtures, the MFFT should be lower than the application temperature. In some cases, however, satisfactory performance has been obtained with the application temperature below the MFFT of the latex because the cement reduces the effective MFFT of the latex. ASTM D2354 describes a method for measuring MFFT.

3.3—Principle of polymer modification

Polymer modification of hydraulic cementitious mixtures is governed by two processes: cement hydration and polymer coalescence.

Generally, cement hydration occurs first. As the cement particles hydrate and the mixture sets and hardens, the polymer particles become concentrated in the void spaces. Figures 3.2 and 3.3 indicate the type of change that occurs during polymer modification (Ohama 1973, 1995b; Wagner and Grenley 1978; Lavelle 1988; Puterman and Malorny 1998). With continuous water removal by cement hydration,

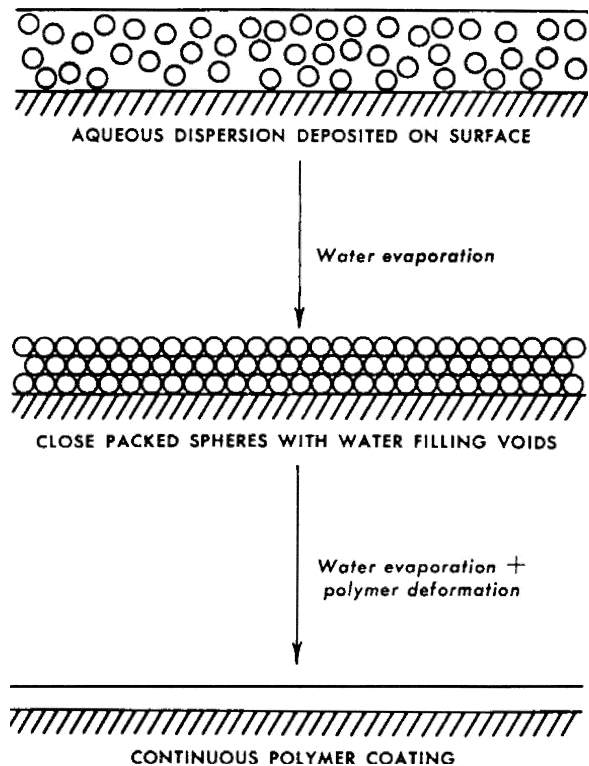


Fig. 3.3—Simplified model of formation of polymer film on cement hydration (Lavelle 1988).

evaporation, or both, the polymer particles coalesce into a polymer film that is interwoven in the hydrated cement, resulting in a mixture or comatrix that coats the aggregate particles and lines the interstitial voids (Fessenden and Fessenden 1998; Afridi et al. 2003).

Unlike conventional cementitious mixtures, PMC does not produce bleed water and, during its fresh state, polymer-modified mixtures are more sensitive to plastic-shrinkage cracking than unmodified mortar or concrete because of the water-reducing influence of the polymer's surfactant system (De Puy 1996; Beeldens et al. 2001). This phenomenon (plastic-shrinkage cracking) is caused by water evaporation at the surface. Two things can happen, both of which contribute to the problem: 1) the polymer particles may start to coalesce before the cement hydration is complete; and 2) the cement paste may shrink before sufficient tensile strength develops to restrain crack formation. Recognizing that PMC does not produce bleed water, particular care should be taken to restrict surface evaporation by use of various cover systems.

Because latex particles are typically greater than 100 nm in diameter, they cannot penetrate the small capillaries in the cement paste that may be as small as 1 nm. Therefore, it is in the larger capillaries and voids that the latex can be most effective.

Some of the polymers used in portland cement mixtures contain reactive groups that may react with calcium and other metallic ions in the cement, and with the silicate and other chemical radicals at the surface of the aggregates (Wagner 1965). Such reactions would improve the polymer-cement bond and, hence, the strength of the mixture.

Hardened portland cement paste is predominantly an agglomerated structure of calcium silicates, aluminates, and hydroxides bound together by relatively weak van der Waals forces. Consequently, microcracks are induced in the paste by stresses such as those caused by evaporation of excess mixing water (drying shrinkage). Polymer modification helps in two ways. Not only do the polymer particles reduce the rate and extent of moisture movement by blocking the passages, but when microcracks form, the polymer film bridges the cracks and restricts propagation. Figure 3.4 shows electron micrographs of polymer-modified and unmodified concrete; the micrograph of the PMC shows latex strands bridging a microcrack while such strands are absent in the unmodified concrete. This results in increased tensile strength and flexural strength. The moisture-movement-blocking property naturally works both ways and also restricts the ingress of most fluids (Ohama 1995a), thus reducing permeability and increasing resistance to both chemicals and freezing-and-thawing resistance. PMC does not require additional air entrainment because of its typically high air content of approximately 6%. There is little or no free water in PMC and the polymer restricts ingress and movement of water. The resistance to freezing and thawing of PMC has been shown to be superior to that of unmodified concrete due to the ability of the polymer latex to block water transport in concrete and the air entrained by the polymer latex in the concrete (Maultzsch 1989; Ohama and Shiroishida 1984).

Kim et al. (1999) experimentally investigated the fracture surface of PMC. They observed that the fracture surface of PMC was propagated through the aggregate instead of around the aggregate, and that debonding of the aggregate was rarely observed compared with unmodified concrete. This observation was not reported by other researchers examining fracture of PMC. However, PMC and polymer-modified mortar (PMM) were reported to have relatively higher fracture toughness compared with normal concrete and mortar (Chou et al. 1990; Bureau et al. 2001; Xu et al. 2004).

The optimum degree of polymer modification is usually achieved between 7.5 and 20% dry polymer solids by mass of cement in the mixture. Optimal polymer content is related to enhancing watertightness, durability, cracking strength, and fracture toughness of concrete while maintaining an acceptable compressive strength and workability. The use of excess polymer is not economical, can cause excessive air entrainment, and can cause the mixture to behave like a polymer filled with aggregates and cement. Levels of polymer lower than the recommended optimal content cannot achieve the level of modification necessary for producing the unique characteristics of PMC previously described.

Wagner (1965) studied the influence of latex modification on the rate of surface area development of polymer-modified pastes. This work indicated that although polymer modification can either accelerate or retard the initial setting time, it has little or no effect on the final setting of cement. Zhihong et al. (2003) showed the possible control of the initial setting time by changing the polymer content.

The type of latex used and the latex-cement ratio influence the pore structure of latex-modified systems. According to



Latex-modified concrete



Portland cement concrete

Fig. 3.4—Electron micrograph of latex-modified and portland-cement concrete (magnification = 12,000 $\times$) (Dow Chemical Co. 1985).

Kasai et al. (1982), Ohama and Shiroishida (1983), and Tantawi (1997), the porosity and pore volume of the PMM differs from unmodified mortar in that the former has a lower number of pores with a radius of 200 nm, but significantly more with a smaller radius of 25 nm or less. The total porosity or pore volume tends to decrease with increasing polymer-cement ratios. This can contribute to improvements in impermeability to liquids, resistance to carbonation, and resistance to freezing and thawing. Similar observations were reported by Shaker et al. (1997).

Walters (1992b) showed that the polymer modification of concrete using styrene-butadiene rubber (SBR) improved flexural strength, permeability resistance, and ductility as the polymer-cement ratio increased at a constant water-cement ratio (w/c). Tubbesing (1993) and Schulze and Killermann (2001) studied the microstructural characteristics of wet-stored PMM. In the study, it was shown that PMM does not show significant damage over 10 years of outdoor exposure. In Su et al. (1991), Cook and Hover (1999), and Silva et al. (2001), the effect of water content on the pore size distributions was investigated. De Belie et al. (1998) and Monteny et al. (1999) performed immersion tests in which the concrete tests showed that the PMC resistance to chemical attack was

significantly improved due to the beneficial effect of interpenetrating network of polymer film (Monteny et al. 2001).

The curing regime used with PMC requires initial moist curing to prevent plastic-shrinkage cracking, followed by air curing. The air curing should be considered drying rather than curing, although there is much data showing the properties of PMC enhance with time, as is the case with unmodified mixtures. After initial moist curing, the latex particles at the surface coalesce into a film, preventing further moisture loss. The entrapped moisture hydrates the cement particles, and as free water is consumed, latex particles in the interior of the mixture form films. As these films develop, reactive groups in the polymer are able to crosslink. Both cement hydration and polymer crosslinking are considered to be components of curing.

3.4—Selection of polymer modifier

The major polymers used for modification of cementitious mixtures are acrylic polymers and copolymers (PAE), styrene-acrylic copolymers (S-A), styrene-butadiene copolymers (S-B), vinyl acetate copolymers (VAC), and vinyl acetate homopolymers (PVA). The major vinyl acetate copolymers are vinyl acetate-ethylene (VAE) and vinyl acetate-vinyl ester of versatic acid (VA-VEOVA). Vinyl acetate-acrylic copolymers are also sometimes used. The selection of a particular polymer for a PMC depends on the specific properties required for the application. The significance of discoloration of concretes incorporating specific types of polymers shall be considered especially when concretes are used for architectural features.

For applications where permeability resistance and high bond strength are required but colorfastness is not important, SBR latex (Clear and Chollar 1978) might be the polymer of choice, based on performance. For applications where colorfastness, permeability resistance, and bond strength are required, PAE or S-A latexes might be used. For applications where some colorfastness, permeability resistance, and bond strength are required, vinyl acetate copolymers might be used. Where only bond strength is required and the product would not be exposed to moisture, vinyl acetate homopolymers can be used (Walters 1990). PVA is known to deteriorate with water exposure due to partial hydrolysis (Ohama 1995b). The significance of water exposure on PMC shall be carefully examined before selecting the appropriate polymer to be used.

Redispersible powders are invariably more expensive than their equivalent latex because the powders are made typically by spray-drying the latex. Consequently, the powders are used where cost is not as critical and convenience is more important, such as in do-it-yourself applications or jobs where smaller quantities are required. Currently, the only polymers available as redispersible powders are PAE, S-A, VAE, VA-VEOVA, and PVA. Another reason for using redispersible powders is that the mixture proportioning is better controlled, with batching of dry ingredients usually occurring in manufacturers' plants and not at the job site, as when latexes are used. Refer to Section 4.4 for more information on redispersible polymer powders.

3.5—Specification and test methods for PMC

In 1999, ASTM issued ASTM C1438, a specification for latex and polymer modifiers for hydraulic-cement mixtures. At the same time, test method ASTM C1439 for polymer-modified mixtures was issued. In the latter, PMC specimens are cured by being covered with plastic sheeting for 24 hours followed by air curing at 23 °C (73 °F) and 50% relative humidity (RH) until the time of the test. These standards do not apply to epoxy-modified hydraulic cementitious mixtures.

CHAPTER 4—POLYMER MODIFIERS FOR LATEX-MODIFIED CONCRETE

4.1—Styrene-butadiene latex

4.1.1 Background—The development of synthetic SBR latex as an admixture to portland-cement mortar began in the U.S. in the mid-1950s. Initial applications were in mortar for patching kits, stucco, ship-deck coatings, floor-leveling compounds, and tile adhesives. In 1956, application to bridge decks as a protective mortar overlay began. The increased use of deicing salts and the recognition of their destructive effects paralleled the evolution of modified mortar mixtures into concrete, and styrene-butadiene LMC became a common protection system used for bridge decks in the U.S. (Clear and Chollar 1978). In 1991, Walters (1991) estimated that over 10,000 bridges were protected with this system. Because parking garages suffer from the same deicing salt deterioration problems as bridge decks, LMC is also used as a protective overlay on the decks of parking garages. Since the mid-1990s, the use of this system has been reduced due to replacement by less expensive systems.

Styrene-butadiene latex-modified mortars and concrete are useful for a variety of applications by means of a variety of improved material characteristics. For most of these applications, bond to substrate and low permeability are most beneficial properties. In outdoor applications, resistance to freezing and thawing is important. These and other primary properties are discussed in the following sections.

4.1.2 Mixture proportioning—The inclusion of styrene-butadiene latex in portland-cement mortar and concrete results in less water being required for a given consistency. Components in the latex function as dispersants for the portland cement and, thus, increase flow and workability of the mixture without additional water. Therefore, the selection of the amount of latex will affect the physical properties of the hardened system in two ways: by the amount of latex included, and by the amount of water excluded.

The effects of the amount of latex on the properties of the mortar and concrete are discussed in detail in the next section.

A common value for latex addition is a latex solids-cement mass ratio of 0.15. Using this ratio, the mixture proportions shown in Table 4.1 are typical of what is used. ASTM C150 Types I, II, and III portland cements are used in styrene-butadiene LMC and mortar. Typically, Type I cement has been used, but Sprinkel (1988a, 1993, 2003) reported the use of Type III cement to achieve early strength where the overlay is to accept service loads within 24 hours. Minimum and maximum cement contents have not been established for either mortar or concrete mixtures containing latex. The

Table 4.1—Typical proportions for LMC and mortar mixtures

Mortar	
Ingredient	Amount
Cement	100 lb (45.4 kg)
Sand	290 lb (131.5 kg)
Latex*	3.7 gal. (14.1 L)
Water	2.6 gal. (10.0 L)
Yields approximately 3 ft ³ (0.1 m ³).	
Concrete	
Ingredient	Amount
Cement	658 lb (299 kg)
Sand	1710 lb (776 kg)
Coarse aggregate	1140 lb (517 kg)
Latex*	24.5 gal. (92.7 L)
Water	19.0 gal. (71.9 L)
Yields approximately 1 yd ³ (0.765 m ³).	

* Assumed 48% solids, 52% water by mass.

particular cement content used has been based on the application of the modified mixtures. For LMC, the most common cement content has been approximately 230 kg/m³ (15 lb/ft³). For mortar applications, cement content varies with the end use. Most of the reported data included in this report are based on a sand-cement ratio of 3.

The fine-coarse aggregate ratio will vary with the specific aggregate used, but with the aforementioned proportions, a workable concrete having a slump of 100 to 200 mm (4 to 8 in.) and a maximum w/cm of 0.40 should be possible. It is noted that the w/cm of latex-modified mixtures is used in this report, and it includes the water in the latex, the free water in the aggregates, and the added water.

4.1.3 Properties

4.1.3.1 Film properties—To help understand what effect the environment of freshly mixed portland cement might have on the latex addition, films of styrene-butadiene latex were immersed in saturated lime solutions and tested for tensile strength (Shah and Frondistou-Yannas 1972). Figure 4.1 shows that the film is not weakened by exposure to the lime solution, but, in fact, gains in tensile strength after immersion. Figure 4.2 indicates that during this immersion period, the film increased in mass by about 5% during the first 2 days, but gained no additional mass thereafter. The pH of the lime solution remained nearly constant during this immersion period.

4.1.3.2 Properties of fresh mortar and concrete

4.1.3.2.1 Air content—Because of the surfactants used in the manufacture of latex, excessive amounts of air can be entrained when latex is mixed into a portland cement system, unless an antifoam agent is incorporated in the latex. For styrene-butadiene latexes, these are usually silicone products, and are often added by the latex supplier. Figure 4.3 shows an example of the relationship between the antifoam agent (expressed as a percentage of the latex) and the air content of the mortar (Ohama 1973). Okba et al. (1997) reported the ability of defoaming agents to control the air content of LMC incorporating SBR latex.

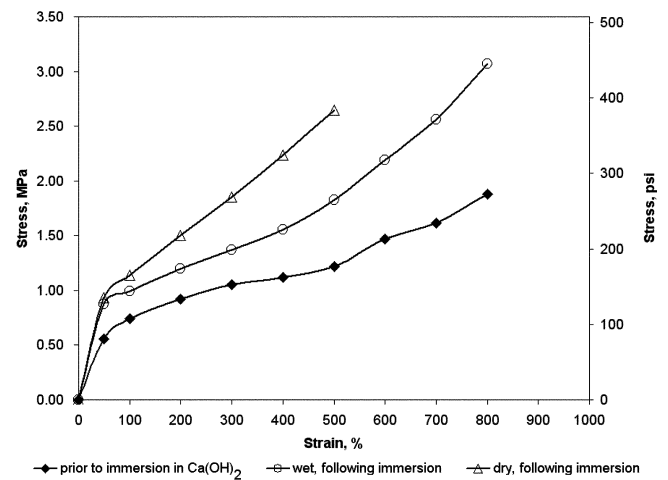


Fig. 4.1—Tensile stress-strain curves of styrene-butadiene films. (Data from work by Shah and Frondistou-Yannas [1972].)

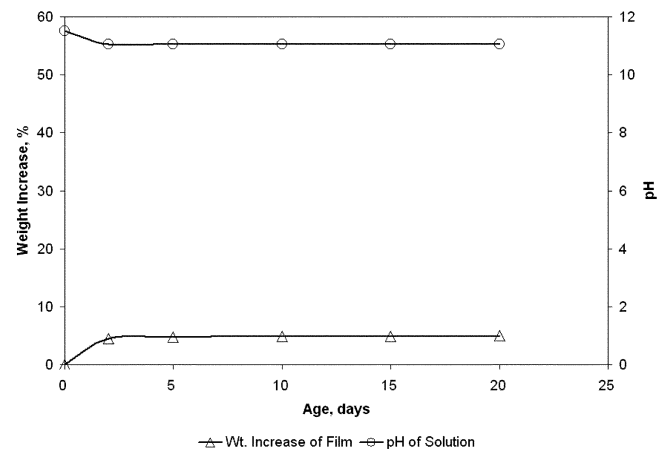


Fig. 4.2—Effects of immersion in lime solution on styrene-butadiene films. (Data from work by Shah and Frondistou-Yannas [1972].)

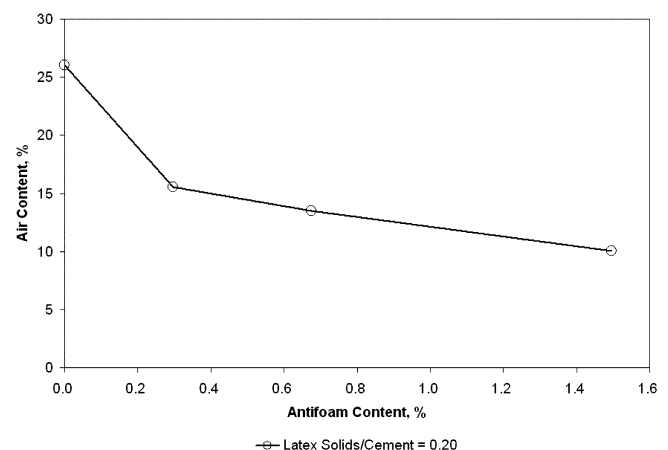


Fig. 4.3—Antifoam content versus mortar air content. (Data from work by Ohama [1973].)