HANDBOOK OF POLYMER-MODIFIED CONCRETE AND MORTARS

Properties and Process Technology

by

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Preface

Polymer-modified or polymer cement mortar (PCM) and concrete (PCC) are a category of concrete-polymer composites which are made by partially replacing the cement hydrate binders of conventional cement mortar or concrete with polymers, i.e., polymeric admixtures or cement modifiers, thereby strengthening the binders with the polymers. Polymermodified or polymer cement paste, which is prepared without any aggregate, is sometimes used.

For the past seventy years or more, active research and development of polymer-modified mortar and concrete has been conducted around the world, resulting in products which are currently used as popular, important construction materials. To match the technical innovations in the construction industry in recent years, useful polymeric admixtures or polymermodified mortar and concrete have been developed in advanced countries. There is currently great interest in using polymer-modified mortar and concrete as repair materials for deteriorated reinforced concrete structures. Polymer-modified concrete and mortar are promising construction materials for the future because of the good balance between their performance and cost compared to other concrete-polymer composites.

In spite of the popularity of polymer-modified mortar and concrete as important construction materials, until now no book has been published which deals comprehensively with their concepts, theories, and practical applications. That is my reason for writing this book. I have actively worked in the research and development of polymer-modified mortar and concrete for thirty-five years or more. This book is a concise crystallization of information from my long experience which I believe will be useful.

I prepared this book at the suggestion of Dr. V. S. Ramachandran, National Research Council of Canada, and Mr. G. Narita of Noyes Publications. I am very grateful to them for their encouragement.

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Introduction

1

Mortar and concrete made with portland cement has been a popular construction material in the world for the past 170 years or more. However, cement mortar and concrete have some disadvantages such as delayed hardening, low tensile strength, large drying shrinkage, and low chemical resistance. To reduce these disadvantages, many attempts to use polymers have been made. One such attempt is polymer-modified (or polymercement) mortar or concrete, which is made by the modifying ordinary cement mortar or concrete with polymer additives such as latexes, redispersible polymer powders, water-soluble polymers, liquid resins, and monomers. Polymer-modified mortars and concretes have a monolithic co-matrix in which the organic polymer matrix and the cement gel matrix are homogenized. The properties of polymer-modified mortar and concrete are characterized by such a co-matrix. In the systems modified with the latexes, redispersible polymer powders, and water-soluble polymers, the drainage of water from the systems along with the cement hydration leads to film or membrane formation. In the systems modified with the liquid resins and monomers, the addition of water induces the hydration of the cement and the polymerization of the liquid resins or monomers.

1.0 HISTORICAL BACKGROUND

The concept of a polymer-hydraulic cement system is not new, and in 1923 the first patent of the system had already been issued to Cresson.^[1]

This patent refers to paving materials with natural rubber latexes, and in the patent, cement was used as a filler. The first patent with the present concept of the polymer latex-modified systems was published by Lefebure^[2] in 1924. He appears to be the first worker who intended to produce a latex-modified mortar and concrete using natural rubber latexes by a mix-proportioning method. This patent is important from a historical point of view. A similar idea was patented by Kirkpatrick^[3] in 1925. Throughout the 1920s and 1930s, polymer-modified mortars and concretes using natural rubber latexes were developed. A patent to Bond,^[4] which for the first time suggested the use of synthetic rubber latexes for the polymer-modified systems, was issued in 1932, and Rodwell's patent,^[5] which first claimed to apply synthetic resin latexes including polyvinyl acetate latexes to the modified systems, was issued in 1933. In other words, the 1930s were a turning point in the use of latexes as cement modifiers (from the natural rubber latexes to the synthetic rubber or resin latexes).

In the 1940s, some patents on the polymer-modified systems with synthetic latexes such as chloroprene rubber (Neoprene) latexes^[6] and polyacrylic ester latexes^[7] were published. Also, polyvinyl-acetate-modified mortar and concrete were actively developed for practical applications. Since the late 1940s, polymer-modified mortar and concrete have been used in various applications such as deck coverings for ships and bridges, paving, floorings, anticorrosives, and adhesives. In the U.K., feasibility studies on the applications of the natural-rubber-modified systems were conducted by Griffiths^[8] and Stevens.^[9] Meanwhile, a strong interest focused on the use of the synthetic latexes in polymer-modified systems. In 1953, Geist et al.^[10] reported a detailed fundamental study on the polyvinyl-acetate-modified mortar, and provided a number of valuable suggestions for the later research and development of the polymer-modified systems.

In the 1960s, styrene-butadiene rubber-,^[11] polyacrylic ester-,^[12] and poly(vinylidene chloride-vinyl chloride)-^[13] modified mortars and concretes became increasingly used in practical applications. Since the 1960s, the practical research and development of polymer-modified mortar and concrete have been considerably advanced in various countries, particularly U.S.A., U.S.S.R., West Germany, Japan, and U.K. Consequently, a considerable number of publications including patents, books, papers, and reports have appeared. Of these, the main and important studies are as follows:

- Patents by E. I. du Pont de Nemours and Co.,^[14] The Master Mechanics Co.,^[15] American Cyanamid Co.,^[16] Dow Chemical Co. ^[17] and Onoda Cement Co.^[18]
- 2. Books written by Cherkinskii,^[19] Namiki and Ohama,^[20] Solomatov,^[21] Satalkin et al.,^[22] Paturoev,^[23] Wilson and

Crisp,^[24] ACI Committee 548,^[25] Ohama,^[26] Schorn,^[27] and Ramakrishnan.^[28]

- 3. Papers written by Wagner,^{[29]-[32]} Petri,^[33] Mori, Kawano, Ohama et al.,^[34] and Ohama.^{[35]-[38]}
- 4. Papers presented at main congresses and conferences on polymers in concrete listed in Table 1.1.

Year	Venue	Congress or Symposium Name
1967	Paris, France	RILEM Symposium, Synthetic Resins in Building Construction
1973	Tyne, U.K.	Symposium, Resins and Concrete
1975	London, U.K.	First International Congress on Polymers in Concrete
1978	Austin, Texas, U.S.A.	Second International Congress on Polymers in Concrete
1981	Koriyama, Japan	Third International Congress on Polymers in Concrete
1981	Prague, Czechoslovakia	ICP/RILEM/IBK International Symposium, Plastics in Material and Structural Engineering
1984	Liege, Belgium	International Symposium, Future for Plastics in Building and in Civil Engineering
1984	Darmstadt, West Germany	Fourth International Congress on Polymers in Concrete
1986	Prague, Czechoslovakia	International Symposium, Mechanics of Polymer Composites
1986	Aix-en-Provence, France	RILEM International Symposium, Adhesion between Polymers and Concrete
1 987	Brighton, U.K.	Fifth International Congress on Polymers in Concrete
1990	Shanghai, China	Sixth International Congress on Polymers in Concrete
1991	Bochum, Germany	International Symposium on Concrete-Polymer Composites
1991	San Francisco, California, U.S.A.	ACI-ICPIC North American Workshop on Polymers in Concrete
1992	Johannesburg, South Africa	Second South African Conference on Polymers in Concrete
1992	Moscow, Russia	Seventh International Congress on Polymers in Concrete
1993	Salvador, Brazil	ICPIC / IBRACON Workshop on Polymers in Concrete

 Table 1.1
 Major International Congresses and Symposiums on Polymers in Concrete.

Nutt^{[39][40]} developed a system modified with an unsaturated polyester resin in the late 1960s. The system is called "Estercrete" (brand name), and now is commercially available. In 1971, Dikeou, Steinberg, et al.^[41] also studied other systems. Donnelly^[42] and Duff^[43] patented systems based on epoxy resins in 1965 and 1973 respectively. In 1959, a system modified with urethane prepolymer was patented.^[44]

Methyl cellulose is very popular as a water-soluble polymer used as a cement modifier, and has been widely used in the field of adhesive polymermodified mortars for ceramic tiles since the early 1960s.^[45] In this case, the polymer content (to the cement used) is 1% or less. Shibazaki^[46] showed that other polymers, such as hydroxyethyl cellulose and polyvinyl alcohol (poval) are effective for the water-soluble polymer-modified mortars.

In 1974, a summarized review of the polymer-modified systems was written by Riley and Razl.^[47]

Considerable research and development of polymer-modified mortar and concrete were conducted in the world in the 1970s. In the 1980s, the polymer-modified mortar and concrete became the dominant materials in the construction industry. At present, they are used as popular construction materials in the advanced countries.

2.0 STANDARDS, STANDARD SPECIFICATIONS, AND GUIDES

In recent years, polymer-modified mortars and concretes using various polymer latexes, redispersible polymer powders, water-soluble resins, epoxy resins, etc. have been widely used in the world. Among the advanced countries using the polymer-modified mortars and concretes, standardization work on test methods and quality requirements has been in progress in U.S.A., Japan, U.K., and Germany. Tables 1.2 and 1.3 give JISs (Japanese Industrial Standards) and BSs (British Standards) on polymer-modified mortars which have been published up to the present time. Table 1.4 lists the JCI (Japan Concrete Institute) Standards for Test Methods for Polymer-Modified Mortars in Japan. In addition, Table 1.5 shows the standard specifications and guides for polymer-modified mortars and concretes which are prevalent in U.S.A., Germany, Japan, and RILEM.

JIS A 1171	Method of making test sample of polymer-modified mortar in the laboratory	
JIS A 1172	Method of test for strength of polymer-modified mortar	
JIS A 1173	Method of test for slump of polymer-modified mortar	
JIS A 1174	Method of test for unit weight and air content (gravimetric) of fresh polymer-modified mortar	
JIS A 6203	Polymer dispersions for cement modifiers	
JIS A 6906	Wall coatings for thin textured finishes	
JIS A 6910	Multi-layer wall coatings for glossy textured finishes	
JIS A 6915	Wall coatings for thick textured finishes	
JIS A 6916	Cement filling compounds for surface preparation	
JIS A 6917	Lightweight aggregate coating materials	

Table 1.2JISs for Polymer-Modified Mortars.

 Table 1.3
 BSs for Concrete-Polymer Composites (including Polymer-Modified Mortars).

BS 6319	Testing of resin compositions for use in construction
BS 6319 ; Part 1 : 1983	Method for preparation of test specimens
BS 6319 ; Part 2 : 1983	Method for measurement of compressive strength
BS 6319 ; Part 3 : 1983	Method for measurement of flexural strength
BS 6319 ; Part 4 : 1984	Method for measurement of bond strength (slant shear method)
BS 6319 ; Part 5 : 1984	Method for determination of density of hardened resin compositions
BS 6319 ; Part 6 : 1984	Method for determination of modulus of elasticity in compression
BS 6319 ; Part 7 : 1985	Method for measurement of tensile strength
BS 6319 ; Part 8 : 1984	Method for the assessment of resistance to liquids
BS 6319 ; Part 9 : 1987	Method for measurement and classification of peak exotherm temperature
BS 6319 ; Part 10 : 1987	Method for measurement of temperature of deflection under a bending stress
BS 6319 ; Part 11 : 1993	Methods for determination of creep in compression and in tension
BS 6319 ; Part 12 : 1992	Methods for measurement of unrestrained linear shrinkage and coefficient of thermal expansion

Table 1.4 JCI Standards for Test Methods for Polymer-Modified Mortars.

- (1) Method of test for setting time of polymer-modified mortar
- (2) Method of test for tensile strength of polymer-modified mortar

(3) Method of test for shear strength of polymer-modified mortar

(4) Method of test for flexural strength and flexural toughness of polymer-modified mortar

- (5) Method of test for adhesion of polymer-modified mortar
- (6) Method of test for adhesion durability of polymer-modified mortar after warm-cool cycling
- (7) Method of test for impact resistance of polymer-modified mortar
- (8) Method of test for abrasion resistance of polymer-modified mortar
- (9) Method of test for resistance of polymer-modified mortar to rapid freezing and thawing
- (10) Method of test for incombustibility of polymer-modified mortar

(11) Method of test for resistance of polymer-modified mortar to accelerated carbonation

(12) Method of test for chloride ion penetration depth of polymer-modified mortar

(13) Method of test for compressive strength and modulus of elasticity of polymer-modified mortar

(14) Method of test for thermal expansion of polymer-modified mortar

(15) Method of test for bond of polymer-modified mortar to reinforcing bar

(16) Method of test for chemical resistance of polymer-modified mortar

(17) Method of test for corrosion-inhibiting property of polymer-modified mortar

Table 1.5 Standard Specifications and Guides for Polymer-Modified Mortars and Concretes in U. S., Germany, Japan, and RILEM.

Institution or Organization	Standard Specification or Guide	
American Concrete Institute (ACI)	ACI 548.IR-92 Guide for the Use of Polymers in Concrete (1992) ACI 548.4 Standard Specification for Latex-Modified Concrete (LMC) Overlays(1992) ACI 546.1R Guide for Repair of Concrete Bridge Superstructures (1980) ACI 503.5R Guide for the Selection of Polymer Adhesives with Concrete (1992)	
The Federal Minister for Transport, The Federal Länder Technical Committee,Bridge and Structural Engineering (West Germany)	 ZTV-SIB Supplementary Technical Regulations and Guidelines for the Protection and Maintenance of Concrete Components (1987) TP BE-PCC Technical Test Regulations for Concrete Replacement Systems Using Cement Mortar/Concrete with Plastics Additive (PCC) (1987) TL BE-PCC Technical Delivery Conditions for Concrete Replacement Systems Using Cement Mortar/Concrete with Plastics Additive (PCC) (1987) 	
Architectural Institute of Japan (AIJ)	Guide for the Use of Concrete-Polymer Composites (1987) JASSs (Japanese Architectural Standard Specifications) Including the Polymer-Modified Mortars JASS 8 (Waterproofing and Sealing) (1993) JASS 15 (Plastering Work) (1989) JASS 18 (Paint Work) (1989) JASS 23 (Spray Finishing) (1989)	
International Union of Testing and Research Laboratories for Materials and Structures (RILEM)	Recommended Tests to Measure the Adhesion Properties between Resin Based Materials and Concrete (1986)	

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Principles of Polymer Modification for Cement Composites

1.0 INTRODUCTION

Polymer-modified mortar and concrete are prepared by mixing either a polymer or monomer in a dispersed, powdery, or liquid form with fresh cement mortar and concrete mixtures, and subsequently curing, and if necessary, the monomer contained in the mortar or concrete is polymerized in situ. The polymers and monomers used as cement modifiers are shown in Fig. 2.1.

Several types of polymer-modified mortars and concretes, i.e., latex-redispersible polymer powder-, water-soluble polymer-, liquid resin-, and monomer-modified mortars and concretes, are produced by using the polymers and monomers shown in Fig. 2.1. Of these, the latex-modified mortar and concrete are by far the most widely used cement modifiers.

Although polymers and monomers in any form such as latexes, water-soluble polymers, liquid resins, and monomers are used in cement composites such as mortar and concrete, it is very important that both cement hydration and polymer phase formation (coalescence of polymer particles and the polymerization of monomers) proceed well to yield a monolithic matrix phase with a network structure in which the hydrated cement phase and polymer phase interpenetrate. In the polymer-modified mortar and concrete structures, aggregates are bound by such a co-matrix phase, resulting in the superior properties of polymer-modified mortar and concrete compared to conventional.



Figure 2.1 Polymers and monomers for cement modifiers.

2.0 PRINCIPLES OF LATEX MODIFICATION

Latex modification of cement mortar and concrete is governed by both cement hydration and polymer film formation processes in their binder phase. The cement hydration process generally precedes the polymer formation process.^[1] In due course, a co-matrix phase is formed by both cement hydration and polymer film formation processes. It is important to understand the mechanism of the co-matrix phase formation.

2.1 Mechanism of Polymer-Cement Co-matrix Formation

It is believed that a co-matrix phase which consists of cement gel and polymer films is generally formed as a binder according to a three-step simplified model shown in Fig. 2.2.^{[2]-[4]} Grosskurth proposed a similar model indicating the formation of the polymer-cement co-matrix.^[5] Sugita, et al.^[6] have recently investigated the microstructures and composite mechanism of latex-modified pastes and mortars, and found the interfacial layer of cement hydrates with a large amount of polymer particles on the aggregates and cement particles. As a result, both the particle dispersion of the polymer and the formation of polymer films are necessary for explaining the composite mechanism of the latex-modified systems.





The process of the polymer film formation on the cement hydrates is represented in Fig. 2.3.^[2]

First Step. When polymer latexes are mixed with fresh cement mortar or concrete, the polymer particles are uniformly dispersed in the cement paste phase. In this polymer-cement paste, the cement gel is gradually formed by the cement hydration and the water phase is saturated with calcium hydroxide formed during the hydration, whereas the polymer particles deposit partially on the surfaces of the cement-gel–unhydrated-cement particle mixtures. It is likely that the calcium hydroxide in the water phase reacts with a silica surface of the aggregates to form a calcium silicate layer.^[7] It is confirmed that the formation of the calcium hydroxide and ettringite in the contact zone between the cement hydrates and aggregates is attributed to the bond between them.^{[8][9]}



Figure 2.3 Simplified model of process of polymer film formation on cement hydrates.

Su, Bijen and Larbi^{[10][11]} found from studies on the interaction between latex-modified pastes and aggregates that calcium hydroxide [Ca(OH)₂] crystals are formed at the contact zone or interfacial zone between the cement hydrates and limestone or granite in the presence of the polymer latexes and oriented with their c-axes perpendicular to the interface. Afridi et al.^{[12][13]} pointed out that the behavior and morphology of calcium hydroxide crystals formed in latex-modified mortars affect their properties.

Second Step. With drainage due to the development of the cement gel structure, the polymer particles are gradually confined in the capillary pores. As the cement hydration proceeds further and the capillary water is reduced, the polymer particles flocculate to form a continuous close-packed layer of polymer particles on the surfaces of the cement-gel-unhydratedcement particle mixtures and simultaneously adhere to the mixtures and the silicate layer over the aggregate surfaces. In this case, the larger pores in the mixtures are found to be filled by the adhesive and autohesive polymer particles. This may be explained by considering that the size of the pores in the cement paste ranges from a few hundred picometers to several hundred nanometers, whereas that of the polymer particles in a typical latex ranges from 50 to 500 nanometers.^[14] Some chemical reactions may take place between the particle surfaces of reactive polymers such as polyacrylic esters (PAE), poly(styrene-acrylic ester) (SAE), poly(vinylidene chloride-vinyl chloride) (PVDC) and chloroprene rubber (CR) latexes and calcium ions (Ca²⁺), calcium hydroxide [Ca(OH)₂] crystal surfaces, or silicate surfaces over the aggregates.^{[15]-[18]} Based on some studies cited, Ohama proposed the mechanism of these reactions as shown in Fig. 2.4.^[19] Such reactions are expected to improve the polymer-cement co-matrixes themselves and the bond between the cement hydrates and aggregates, and to improve the properties of hardened latex-modified mortars and concretes. However, the effects of the chemical bonds on the properties of the latex-modified mortars and concretes appear to be governed by their volume fraction in the latex-modified mortars and concretes, and the chemical bonds do not necessarily act effectively to improve the properties. The effects of the chemical bonds are apt to be offset by increasing entraining air as discussed later.

Third Step. Ultimately, with water withdrawal by cement hydration, the close-packed polymer particles on the cement hydrates coalesce into continuous films or membranes, and the films or membranes bind the cement hydrates together to form a monolithic network in which the polymer phase interpenetrates throughout the cement hydrate phase. Such a structure acts as a matrix phase for latex-modified mortar and concrete, and the aggregates are bound by the matrix phase to the hardened mortar and concrete.



Figure 2.4 Schematic illustration of reaction between polymer with carboxylate group (ester linkage), ordinary portland cement and aggregate.

2.2 Influence of Latex Modification on Physical and Mechanical Properties

As explained by a model showing the mechanism of polymercement co-matrix formation as represented in Fig. 2.2, the properties of ordinary cement mortar and concrete are generally improved to a great extent by latex modification. It is generally considered that hardened cement paste mainly has an agglomerated structure of calcium silicate hydrates and calcium hydroxide bound together by the weaker van der Waals forces, and therefore, microcracks occur easily in the paste under stress. This leads to poor tensile strength and fracture toughness of ordinary cement mortar and concrete. By contrast, in the latex-modified mortar and concrete, it appears that the microcracks are bridged by the polymer films or membranes which prevent crack propagation, and simultaneously, a strong cement hydrate-aggregate bond is developed. This aspect is evident in the scanning micrographs of cross-sections of SBR-and PAE-modified mortars, as shown in Fig. 2.5.

This effect increases with an increase in the polymer content or polymer-cement ratio (defined as the weight ratio of the amount of total solids in a polymer latex to the amount of cement in a latex-modified mortar or concrete), and leads to increase tensile strength and fracture toughness. However, excess air entrainment and polymer inclusion cause discontinuities of the formed monolithic network structure whose strength is reduced although some chemical reactions proceed effectively, as shown in Fig. 2.4. The sealing effect due to the polymer films or membranes formed in the structure also provides a considerable increase in waterproofness or watertightness, resistance to chloride ion penetration, moisture transmission, carbonation and oxygen diffusion, chemical resistance and freeze-thaw durability. Such an effect is promoted with increasing polymer-cement ratio.

The cement gel which is formed as the hydration product of portland cement has a high specific surface, including the so-called gel pores within its structure. Generally, the specific surface area which can ultimately be reached is about one-thousand times as large as that of the unhydrated cement powder. Accordingly, the development of the surface area can be used as a measure of the degree of hydration. Wagner studied the influence of polymer modification on the rate of the specific surface area development of latex-modified pastes.^[20] According to his results, the rate of cement hydration can be accelerated or retarded by the addition of the latexes at the initial stage, depending on their chemical nature. However, the specific surface area of all the pastes after a 28-day cure is comparable. It appears from this fact that the polymer modification does not finally affect the cement hydration under Wagner's test conditions.



Polymer Film in SBR-Modified Mortar





x1000

Polymer Film in EVA-Modified Mortar

Polymer Film in PAE-Modified Mortar

Figure 2.5 Electron micrographs of latex-modified mortars.

The pore structure of latex-modified systems is influenced by the type of polymer in the latexes used and polymer-cement ratio as discussed in detail later. The total porosity or pore volume generally tends to decrease with an increase in the polymer-cement ratio. This contributes to improvements in the impermeability, resistance to carbonation, and freeze-thaw durability.

3.0 MODIFICATION WITH REDISPERSIBLE POLYMER POWDERS

The principle of modification of cement mortar and concrete with redispersible polymer powders is almost the same as that of latex modification except that it involves the addition of redispersible polymer powders. Mostly the redispersible polymer powders are used by dry mixing with the cement and aggregate premixtures, followed by wet mixing them with water. During the wet mixing, the redispersible polymer powders are reemulsified in the modified mortar and concrete, and behave in the same manner as the latexes for cement modifiers.

4.0 MODIFICATION WITH WATER-SOLUBLE POLYMERS

In the modification with water-soluble polymers such as cellulose derivatives and polyvinyl alcohol, small amounts of the polymers are added as powders or aqueous solutions to cement mortar and concrete during mixing. Such a modification mainly improves their workability because of the surface activity of the water-soluble polymers, and prevents the "dryout" phenomena (explained in Ch. 4, Sec. 3.1, Water Retention). The prevention of the "dry-out" is interpreted in terms of an increase in the viscosity of the water phase in the modified cement mortar and concrete and a sealing effect due to the formation of very thin and water-impervious film in them. In general, the water-soluble polymers hardly contribute to an improvement in the strength of the modified systems.

5.0 MODIFICATION WITH LIQUID RESINS

In the modification with liquid thermosetting resins, considerable amounts of polymerisable low-molecular weight polymers or prepolymers are added in a liquid form to cement mortar and concrete during mixing. The polymer content of the modified mortar and concrete generally is higher than that of latex-modified systems. In this modification, polymerization is initiated in the presence of water to form a polymer phase, and simultaneously the cement hydration occurs. As a result, a co-matrix phase is formed with a network structure of interpenetrating polymer and cement hydrate phases, and this binds aggregates strongly. Consequently, the strength and other properties of the modified mortar and concrete are improved in much the same way as those of the latex-modified systems.

6.0 MODIFICATION WITH MONOMERS

The principle of modification of cement composites with monomers is about the same as that of liquid resin modification except that it involves the addition of monomers instead of the liquid resins. In such a modification, considerable quantities of the monomers are mixed with the cement mortar and concrete, and both polymerization and cement hydration occur at the same time, during or after curing, to make a monolithic matrix which binds aggregates. Generally, such a modification has not been successful because of the poor properties of the modified systems. The reasons for this are the interference with the cement hydration, the degradation of the monomers by the alkalis from the cement and the difficulty in uniformly dispersing the monomers and other components during mixing.

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Process Technology of Latex-Modified Systems

The process technology of latex-modified mortar and concrete is almost the same as that of conventional cement mortar and concrete. Most polymers such as latexes are in a dispersed form, and are added to the cement mortar or concrete during mixing. The polymers are used in very large amounts in comparison with air-entraining agents or water-reducing agents which are normally employed in ordinary cement mortar and concrete. The latex-modified mortar and concrete with proper mix proportions are mixed and placed like the ordinary cement mortar and concrete, and then cured under optimum conditions.

1.0 MATERIALS

The materials used in latex-modified mortar and concrete are the same as those employed in ordinary cement mortar and concrete.

1.1 Cements

Ordinary portland cement is widely used for latex-modified mortar and concrete. According to their applications, other portland cements such as high-early-strength portland cement, ultrahigh-early-strength portland cement, sulfate-resisting portland cement, moderate-heat portland cement and white portland cement, blended cement, high alumina cement and ultrarapid-hardening cement are also employed. Air-entraining cement should not be used because air entrainment occurs due to latex addition.

1.2 Polymer Latexes

Polymer latexes which consist of very small (0.05–5 μ m in diameter) polymer particles dispersed in water as shown in Fig. 3.1 are usually produced by emulsion polymerization.



SBR Latex x30000 (Courtesy of the Japan Synthetic Rubber Co., Ltd.)



EVA Latex x10000 (Courtesy of the Hoechst Gosei Co., Ltd.)

Figure 3.1 SBR and EVA latexes for cement modifiers.

A typical recipe of the materials used for emulsion polymerization is given in Table 3.1.^[1] These materials are charged in a reactor under agitation, and heated to a desired temperature. The initiator generates a free radical, and the free radical causes the chain polymerization of the monomers to form a polymer latex. After polymerization, unreacted monomers in the resultant latex are removed by a stripping process. The latex is concentrated or diluted, and small amounts of preservatives, stabilizers or antifoaming agents are added to the latex. However, natural rubber latex and epoxy latex are not produced by such emulsion polymerization. The natural rubber latex is tapped from the rubber trees, Hevea brasiliensis, etc., and then concentrated to have the proper total solid content. The epoxy latex is produced by emulsifying an epoxy resin in water by use of surfactants.

Table 3.1	Typical Recipe of Materials for Emulsion Polymerization. (©
	1991, American Concrete Institute, Reprinted with permission.)

Material	Parts by Weight	
Monomers	100.0	
Surfactant	1.0-10.0	
Initiator	0.1-2.0	
Water	80.0-150.0	
Other Ingredients	0-10.0	

Polymer latexes are generally classified into the following three types by the kind of electrical charges on the polymer particles, which is determined by the type of surfactants used in the production of the latexes: cationic (or positively charged), anionic (or negatively charged) and nonionic (not charged). The formulations for emulsion polymerization of typical polymer latexes as cement modifiers are listed in Table 3.2.^[1]

In general, polymer latexes are copolymer systems of two or more different monomers, and their total solid content including polymers, emulsifiers, stabilizers, etc. are 40 to 50 % by weight. As seen in Fig. 3.2, most commercially available polymer latexes for cement modifiers are based on elastomeric and thermoplastic polymers which form continuous polymer films when dried. The polymer latexes that are underlined in Fig. 3.2 are the main ones that are in general use today in the world. Table 3.3 gives the chemical structures of the main polymer latexes. Of these polymer latexes, polyvinyl acetate latex and poly(vinylidene chloride-vinyl chloride) latex are generally not recommended as cement modifiers because of the very poor water resistance and chloride ion liberation respectively as mentioned later. Both latexes are not currently used as cement modifiers in Japan. Table 3.4 provides the typical properties of the polymer latexes.

Type of Latex	Material	Parts by Weight
Vinyl Acetate,	Vinyl Acetate	70.0-100.0
Homo- and Copolymer	Comonomer (butyl acrylate, ethylene, vinyl ester of versatic acid)	0.0-30.0
Latexes	Partially Hydrolyzed Polyvinyl Alcohol	6.0
	Sodium Bicarbonate	0.3
	Hydrogen Peroxide (35%)	0.7
	Sodium Formaldehyde Sulfoxylate	0.5
	Water	80.0
Acrylic	Ethyl Acrylate	98.0
Copolymer	A Vinyl Carboxylic Acid	2.0
Latex	Nonionic Surfactant	6.0 ^a
	Anionic Surfactant	0.3 ^b
	Sodium Formaldehyde Sulfoxylate	0.1
	Caustic Soda	0.2
	Peroxide	0.1
	Water	100.0
Styrene-	Styrene	64.0
Butadiene	Butadiene	35.0
Copolymer	A Vinyl Carboxylic Acid	1.0
Latex	Nonionic Surfactant	7.0 ^a
	Anionic Surfactant	0.1 ^b
	Ammonium Persulfate	0.2
	Water	105.0

Table 3.2Formulations for Emulsion Polymerization of Typical Polymer
Latexes as Cement Modifiers. (© 1991, American Concrete
Institute, Reprinted with permission.)

^a The nonionic surfactants may be nonyl phenols reacted with 20-40 molecules of ethylene oxide.

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



Figure 3.2 Commercially available polymer latexes for cement modifiers.

 Table 3.3
 Chemical Structures of Main Polymer Latexes for Cement Modifiers.

Type of Polymer Latex	Abbreviation	Chemical Structure							
Natural Rubber Latex	NR	$ \begin{pmatrix} CH_3 \\ -CH_2 \end{pmatrix} C = CH_{CH_2} \begin{pmatrix} CH_2 \\ CH_2 \end{pmatrix} C = CH^{-CH_2} \\ n \end{pmatrix}_n $							
Chioroprene Rubber Latex (Neoprene)	CR	$ \begin{pmatrix} CI \\ I \\ -CH_2 - C = CH - CH_2 - \end{pmatrix}_n $							
Styrene-Butadiene Rubber Latex	SBR	$\left(\begin{array}{c} -CH_2 - CH = CH - CH_2 - CH_2 - CH - \\ 0 \\ n \end{array}\right)_n$							
Polyacrylic Ester Latex	PAE	(- CH ₂ - CH - O=C-OR n R : Alkyl group							
Poly (Styrene -Vinyl Acrylic Ester) Latex	SAE	(- CH ₂ - CH - CH ₂ - CH - O=C-OR O n R : Alkyl group							
Poly (Ethylene-Vinyl Acetate) Latex	EVA or VAE	(- CH ₂ - CH ₂ - CH ₂ - CH - OCOCH ₃)							
Polyvinyl Acetate Latex	PVAC	(- CH ₂ - CH - ococH ₃) n							
Type of Polymer	Brand Name	Stabilizer Type	Appearance	Particle Size (ηm)	Total Solids (%)	Specific Gravity (20°C)	рН (20°С)	Viscosity (20°C, cP)	Surface Tension (20°C, dyn/cm)
--------------------	---	--------------------	-------------	-----------------------	------------------------	-------------------------------	--------------	-------------------------	---
SBR	Asahi Chemical Industry Latex DL-460	Nonion	Milky-White	200	46.5-49.5	1.010	10.0-11.0	10-12	32
	JSR Tommaku Super	Anion	Milky-White	219	44.0-46.0	1.016	7.06	53	31
PAE	Primal M-30	Nonion	Milky-White	500	44.5-45.5	1.054	8.6-10.2	29	45
	Rhoplex MC- 450	Nonion	Milky-White	500	44.0-46.0	1.054	9.4-10.0	1328	45
CR	Neoprene 950	Cation	Milky-White	120	50.0	1.100	9.0	16	35
	Denka Chloroprene LK-50	Cation	Milky-White	700	50.0	1.100	6.0	10	30
EVA	NS Hiflex 1000	Nonion	Milky-White	700	52.8	1.050	6.0	1100-1600	75
	Movinyl 101E	Nonion	White	400	55.0	1.060	4.5-6.5	3000-7000	40-45

300

50.0

1.127

5.0-7.0

5000

40

Table 3.4 Typical Properties of Commercially Available Polymer Latexes.

Milky-White

Anion

Moviton

M310

28

The general requirements for polymer latexes as cement modifiers are as follows:

- a. Very high chemical stability towards the extremely active cations such as Ca²⁺ and Al³⁺ liberated during cement hydration.
- b. Very high mechanical stability under severe actions, especially high shear in mortar or concrete mixing and in metering and transfer pumps.
- c. Low air-entraining action due to the use of suitable antifoaming agents during mortar or concrete mixing.
- d. No bad influence on cement hydration.
- e. Formation of continuous polymer films in mortar or concrete due to a lower minimum film-forming temperature than the application temperature, and the high adhesion of the polymer films to cement hydrates and aggregates. (The minimum film-forming temperature is defined as the lowest temperature at which the polymer particles of a latex have sufficient mobility and flexibility to coalesce into a continuous polymer films.)
- f. Excellent water resistance, alkali resistance and weatherability of the polymer films formed in mortar or concrete.
- g. Thermal stability for wide variations in temperature during transportation and storage (e.g., freeze-thaw stability in cold climate areas or in winter, or high temperature storage stability in hot climate areas or summer).

Table 3.5 shows the quality requirements for the polymer latexes specified in JIS A 6203 (Polymer Dispersions for Cement Modifiers).

In particular, the commercial latexes widely used in the world are styrene-butadiene rubber (SBR), polychloroprene rubber (CR), polyacrylic ester (PAE) and poly(ethylene-vinyl acetate) (EVA) copolymers. Most commercial polymer latexes for cement modifiers contain proper antifoaming agents, and can be generally used without the addition of the antifoaming agents during mixing. Table 3.5Quality Requirements for Latexes Specified in JIS A 6203
(Polymer Dispersions for Cement Modifiers). (© 1980,
Japanese Standards Association. Reprinted with permission.)

Kind of Test	Test Item	Requirement		
Latex Test	Арреагалсе	Exclusive of coarse particles, foreign substances and coagula		
	Total solids	Not less than 35.0% and within ±1.0% of the value marked by the manufacturer		
		Not less than		
	Flexural strength	40kgf/cm ² (3.9MPa)		
		Not less than		
Polymer-Modified Mortar Test	Compressive strength	100kgf/cm ² (9.8MPa)		
		Not less than		
	Adhesion	10kgf/cm ² (0.98MPa)		
	Water absorption	Not more than 15.0%		
	Amount of water permeation	Not more than 30g		
	Length change	0 to 0.150%		

1.3 Aggregates

Fine and coarse aggregates such as river sands and gravels, crushed sands and stones, silica sands, and artificial lightweight aggregates recommended for ordinary cement mortar and concrete, are used for latexmodified mortar and concrete. For the purpose of corrosion resistance, silica sands and siliceous crushed stones may also be used. The use of aggregate with excessive water content should be avoided because the required polymer-cement ratio is not achieved. The aggregates should be clean, sound, and have a proper grading. Like ordinary cement mortar or concrete, the selection of the aggregates generally depends on the thickness of the application, cover in reinforced concrete, and the type and density of reinforcement.

1.4 Other Materials

When the coloring of latex-modified mortar and concrete is required, alkali-resistant, weatherproof pigments are used. Furthermore, it is important that the pigments do not obstruct the stability of polymer latexes and the hydration of cements. Alkali-resistant glass, steel, polyamide, polypropylene, polyvinyl alcohol (poval), aramid and carbon fibers are employed as mixable reinforcements. Reinforcing bars for ordinary cement concrete are also used for the reinforcement of the latex-modified concrete.

2.0 MIX PROPORTIONING

The mix design of latex-modified mortar and concrete is usually carried out in much the same way as that of ordinary cement mortar and concrete, depending on the workability, strength, extensibility, adhesion, waterproofness (or watertightness) and chemical resistance requirements.

Latex-modified mortar and concrete mix design should recognize its improved properties such as tensile and flexural strengths, extensibility, adhesion, and durability over conventional mortar and concrete. These properties are controlled by the polymer-cement ratio rather than the watercement ratio. Therefore, the polymer-cement ratio should be determined to meet desirable requirements. The polymer-cement ratio is defined as the weight ratio of the amount of total solids in a polymer latex to the amount of cement in a latex-modified mortar or concrete mixture.

The mix proportions of mostlatex-modified mortars are in the range of the cement-fine aggregate ratio = 1:2 to 1:3 (by weight), the polymercement ratio of 5 to 20% and the water-cement ratio of 30 to 60%, depending on the required workability. The standard mix proportions for the latexmodified mortars for various applications are shown in Table 3.6.^[2]

The mix proportions of most latex-modified concretes cannot be easily determined in the same manner as those of latex-modified mortars because of many factors considered in the mix design. Normally, the polymer-cement ratio of the latex-modified concrete ranges from 5 to 15%, and the water-cement ratio from 30 to 50%. A rational mix design system developed for the latex-modified concrete by Ohama is described below.

		Stand	Thickness of			
Application	Location of Work		Cement	Sand	Latex	Troweling or
			(by weight)			- Coating (mm)
Paving Materials	Floors for general houses, warehouse, of shops, toilet floors, etc.	fice and	1	3	0.2-0.3	5-10
Floorings	Passages, stairs, chemical plants, railway platforms, roads, garages, etc.			3	0.3-0.5	10-15
Waterproofing Materials	Concrete roof-decks, mortar and concrete walls, water tank, swimming pools, septic silos, etc.	1	2-3	0.3-0.5	5-20	
	Adhesives when flooring materials, wallir materials, heat insulting materials etc. are concrete floors and walls.	ig bonded to	1	0-3	0.2-0.5	-
Adhesives	Jointing new concrete to old concrete and mortar to old mortar.	l new	1	0-1	over 0.2	-
	Repair cracks		1	0-3	over 0.2	-
Anticorrosive Linings	Effluent drains, chemical factory floors, grouting for acid-proof tiles, septic tanks, foundations for machinery plants, floors for chemical laboratories, pharmaceutical warehouses, etc.		1	2-3	0.4-0.6	10-15
	Internal and external ship decks, bridge decks,	Undercoat	1	2-3	0.9-1.0	1-2
Deck Coverings	train or car floors,	Midcoat	1	3	0.4-0.6	5-6
	foot bridge decks, etc.	Topcoat	1	3	0.5-0.6	3-4

Table 3.6 Typical Applications and Standard Mix Design of Latex-Modified Mortars.

2.1 Notation

The following symbols are used in this mix design system:

- oc: Compressive strength of latex-modified concrete (kgf/cm²)
- Sl: Slump (cm)
- $\alpha: \quad \text{Binder-void ratio (by volume)} = (Vc + Vp)/(Va + Vw)$
- φ : Slump control factor (by volume) = Vp + Vw (l/m^3)
- Vc, Vp, Va, Vw, Vs, Vg: Volumes of cement, polymer, air, water, sand, and gravel per unit volume of latexmodified concrete, respectively (*l*/m³)
- C, P, W, S, G: Weight of cement, polymer,* water,** sand,*** and gravel*** per unit volume of latexmodified concrete, respectively (kg/m³), i.e., unit cement content, unit polymer content, unit water content, unit sand content, and unit gravel content
 - P/C: Polymer-cement ratio (by weight)
- W/C: Water-cement ratio (by weight)
 - A: Air content (by volume)
- S/a: Sand-aggregate ratio or sand percentage (by volume)
- a: Unit aggregate content (by volume) = Vs + Vg

Notes: * Calculated as the total solids in the polymer latex.

- ** Calculated as a total weight of the mixing water and the water in the polymer latex, exclusive of any previously absorbed by the aggregates.
- *** Calculated in a saturated surface-dry condition.

2.2 Equations for Slump Predictions

The slump (Sl) of latex-modified concrete can be predicted with every polymer type and at each sand-aggregate ratio by using slump control factor (ϕ) as follows:

$$Sl = j\varphi - k(1-s/a)$$

where j and k are empirical constants. This relationship is described in detail in Ch. 4, Sec. 1.1.

2.3 Equations for Strength Predictions

Regardless of polymer type, the compressive strength (σ c) of latexmodified concrete can be predicted at polymer-cement ratios of 5, 10, 15 and 20% by using the binder-void ratio (α) as follows :

> Polymer-Cement Ratio, 5%: $\sigma c = 657 \alpha - 40$ 10%: $\sigma c = 595 \alpha - 88$ 15%: $\sigma c = 474 \alpha - 63$ 20%: $\sigma c = 423 \alpha - 88$

These relationships are presented in detail in Ch. 4, Sec. 2.1.

2.4 Preparation of Nomographs

The water-cement ratio (W/C) and unit cement content (C) of latexmodified concrete can be generally expressed as a function of the bindervoid ratio (α) with every polymer type at each polymer-cement ratio by the following equations:

$$W/C = -m\alpha + n$$
$$C = q\alpha + r$$

where m, n, q, and r are empirical constants. The examples of nomographs for estimations of W/C and C, which are drawn using the above relationships, are illustrated in Fig. $3.3.^{[3]}$ These figures are obtained for a type of SBR-modified concrete.

2.5 Proposed Mix Design System

By using the above-mentioned equations for slump and compressive strength predictions and nomographs for water-cement ratio and unit cement content estimations, an appropriate mix design system is proposed as represented in Fig. 3.4.^[4]

The limits of validity of these equations and nomographs are as follows: Types of Materials Used:

> Type of cement : ordinary portland cement (ASTM-Type I) Type of aggregate: river sand (size, 2.5 mm or finer) and river gravel (size, 5–20 mm) ; saturated, surface-dry

> Type of polymer latex for cement modifier: commercial polymer latexes, irrespective of polymer types (containing antifoamers)



Figure 3.3 Nomographs for water-cement ratio and unit cement content of SBRmodified concretes.



Figure 3.4 Chart showing mix design procedure for latex-modified concretes.

Range of Proportions in Practical Use:

Unit cement content (C): from 250 to 400 kg/m³ Polymer-cement ratio (P/C): from 0.05 to 0.20 (5 to 20 wt% of polymer with respect to cement)

Water-cement ratio (W/C): from 0.30 to 0.50 (30 to 50 wt% of water with respect to cement)

Sand-aggregate ratio (S/a): from 40 to 50 vol%

Slump (Sl): from 1 to 21 cm

Compressive strength (cc): from 200 to 600 kgf/cm²

According to Fig. 3.4, the procedure for determining the mix proportions of latex-modified concrete is carried out according to the following steps:

- The required workability of fresh latex-modified concrete and the required primary and secondary performance of hardened latex-modified concrete are determined corresponding to its applications. Then the required slump (Sl), compressive strength (oc), and secondary properties such as flexural and tensile strengths, waterproofness, adhesion, chemical resistance, and abrasion resistance of the concrete are determined. The required slump is measured according to JIS (Japanese Industrial Standard) A 1101 (Method of Test for Slump of Concrete). The compressive strength is determined in accordance with JIS A 1108 (Method of Test for Compressive strength of Concrete).
- 2. The polymer-cement ratio (P/C) to give the required secondary properties is determined on the basis of information shown in catalogs and technical data by the manufacturers of polymer latexes for cement modifiers. Simultaneously, the binder-void ratio (α) to satisfy the required σc and P/C is determined by using an equation for compressive strength prediction.
- 3. The water-cement ratio (W/C) and the unit cement content (C) are estimated by introducing the determined α into the nomographs.
- 4. The unit polymer content (P) and the unit water content(W) are calculated by applying the estimated C to the

determined P/C and W/C respectively. Then the slump control factor (ϕ) is obtained as the sum of the Vp and Vw derived from the P and W and the specific gravities of polymer and water. The sand-aggregate ratio (S/a) to satisfy the required S*l* and the estimated ϕ is determined by using the equation for slump prediction.

5. The air content (A) is estimated by introducing the estimated C, P, W and the specific gravities of cement, polymer and water into the equation

$$\alpha = (Vc + Vp)/(Va + Vw)$$

Therefore,

$$A = 0.1 VA = (Vc + Vp - \alpha Vw)/10\alpha$$

Also, from the balance of the quantities of the materials which constitute the concrete, the unit aggregate content (a) is calculated by the following equation:

$$a = Vs + Vg = 1000 - (Vw + Vc + Vp + Va)$$

The unit sand content (S) and the unit gravel content (G) are estimated by applying the determined S/a, a, and the specific gravities of sand and gravel.

2.6 Mix Example

A procedure is described by means of the following example:

Calculate the quantities of the different materials required to design a mix for a latex-modified concrete for an anticorrosive floor.

Cement: ordinary portland cement (specific gravity, 3.17)

Aggregate: river sand (size, 2.5 mm or finer; specific gravity, 2.62) and river gravel (size, 5–20 mm; specific gravity, 2.55); saturated, surface-dry

Cement modifier: SBR latex (total solids, 47.8%; specific gravity of the total solids, i.e., polymer, 1.01)

Required slump (Sl): 15 cm

Required compressive strength (oc): 400 kgf/cm²

Polymer-cement ratio (P/C) corresponding to the required chemical resistance: 15% (based on the chemical resistance data given in the catalog)

Substituting $\sigma c = 400 \text{ kgf/cm}^2$ and P/C =15% for an appropriate compressive strength prediction equation

$$\sigma c = 474 \alpha - 63$$

 $\alpha = (400 + 63)/474 = 0.98$

is estimated. From Fig. 3.3, W/C = 42% and C = 317 kg/m³ corresponding to P/C = 15% and α = 0.98. By introducing C = 317 kg/m³ into P/C and W/C, P and W are estimated to be 48 kg/m³ and 133 kg/m³ respectively. As the specific gravities of the polymer and water are 1.01 and 1.00 respectively,

$$\varphi = (48/1.01) + (133/1.00) = 181 \ l/m^3$$

Substituting Sl = 15 cm and $\phi = 181 \ l/m^3$ for an appropriate slump prediction equation

$$Sl = 0.26\varphi - 18.5/(1 - S/a)$$

hence

is obtained. Substituting $\alpha = 0.98$, C = 317 kg/m³, P = 48 kg/m³, W = 133 kg/m³, and the specific gravities of the cement, polymer, and water for

$$A = 0.1Va = (Vc + Vp - \alpha Vw)/10\alpha$$

hence

Also, from the balance of the quantities of the materials,

$$a = 1000 - (317/3.17 + 48/1.01 + 133/1.00 + 18)$$
$$= 701 \ l/m^3$$

is found. Since S/a = 42.3% and the specific gravities of sand and gravel are 2.62 and 2.55 respectively, S and G are calculated as follows:

S = 701 x 0.423 x 2.62 = 777 kg/m³ G = 701 x (1 - 0.423) x 2.55 = 1031 kg/m³

Since the total solids of the SBR latex are 47.8%, the required amount of latex is $48/0.478 = 100 \text{ kg/m}^3$. The required amount of mixing water is also calculated by subtracting the amount of water in the SBR latex from W = 133 kg/m^3 as follows:

$$133 - 100(1 - 0.478) = 81 \text{ kg/m}^3$$

Therefore, the required mix proportions by weight of the SBR-modified concrete for trial mixing in this example would be as follows :

Ordinary portland cement: 317 kg/m³ SBR latex: 100 kg/m³ Water: 81 kg/m³ River sand: 777 kg/m³ River gravel: 1031 kg/m³

2.7 ACI Guidelines

Tables 3.7 and 3.8 give the ACI (American Concrete Institute) suggested guidelines for the mix proportions of latex-modified concretes for bridge deck applications and patching work respectively.^[5] Also, Standard Specification ACI 548.4.^[6] provides a guideline for the mix proportions of SBR-modified concrete overlays, for new construction as well as repair and rehabilitation, of highway bridge decks as shown in Table 3.9.

Table 3.7ACI Suggested Guidelines for Mix Proportions of Latex-
Modified Concrete for Bridge Deck Applications. (© 1992,
American Concrete Institute, Reprinted with permission.)

Unit Cement Content (kg/m ³)	700
Sand-Aggregate Ratio (%)	55:45 to 65:35
Polymer-Cement Ratio (%)	15
Water-Cement Ratio (%)	25 to 40
Air Content (%)	Less than 6

Table 3.8ACI Suggested Guidelines for Mix Proportions of Latex-
Modified Concrete for Patching Applications. (© 1992, American
Concrete Institute, Reprinted with permission.)

Material		Weight (kg)	
Portland Cement		94	
Aggregate	(blend of coarse and fine)	300	
Polymør –	Dry (total solids) Basisª	14 to 19	
	Wet (liquid with 50% total solids) Basis ^b	29 to 38	
Total Water (includes that in polymer and aggregate)		4 to 25	

^a For patching conventional concrete where there may not be a need for improved chemical resistane and a lower modulus, the polymer-cement ratio can be lowered to 7 to 12 %.

^b The latex polymer should be formulated with an antifoamer prior to adding it to the mix.

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Table 3.9ACI Guidelines for Mix Proportions of SBR-Modified Concrete
Overlays. (© 1992, American Concrete Institute, Reprinted with
permission.)

Unit Cement Content, Minimum	390 kg/m ³
Unit SBR Latex Content, Minimum	121 kg/m ³
Unit Water Content, Maximum	94 kg/m ³
Air Content, Maximum (ASTM C 231)	6.5 %
Slump, Range	7.5 - 20.5 cm
Overlay Thickness, Minimum	2.5 cm
Coarse Aggregate Size, Maximum	No. 8
Fine Aggregate - Aggregate Ratio	55-70 wt%
Cement : Fine Aggregate : Coarse Aggregate (aggregates assumed saturated, surface dry)	1.0 : 2.8 : 1.7 (weight ratio)

3.0 MIXING

Latex-modified mortar and concrete are easily prepared by using all conventional mixing equipment and tools such as mortar or concrete batch mixers and ready-mix trucks, as well as by hand-mixing in mortar boxes or concrete mixing vessels. Before actual mixing, trial mixing should be performed to determine the mix proportions. Polymer latexes are initially mixed with mixing water, and directly added to the cement and aggregate mixes. The speed and time of mixing should be properly selected to avoid unnecessary entrapment of air even though antifoaming agents are used. Air-entraining agents cannot be used because the polymer latexes entrain air.

4.0 PLACING AND CURING

After mixing, latex-modified mortar and concrete are placed and finished in almost the same manner as ordinary cement mortar and concrete. The latex-modified mortar and concrete have a shorter working time than the cement mortar and concrete. Although the working time depends on the ambient temperature, the latex-modified mortar and concrete should be placed and finished within about one hour after mixing.

Because they have an excellent adhesion to various materials, even to metals, all the equipment and tools such as mixers, trowels, and vibrators should be washed down or cleaned immediately after use. It also is advisable to use the most effective mold-release agents, e.g., silicone wax or grease.

For resurfacing, flooring, and patching applications, all loose and nondurable materials including laitance and mud on the substrates must be removed by sandblast, wire-brushing and blowing with compressed air. Oils, greases, and other chemicals should be removed with a detergent or solvent. The surfaces cleaned by the above operations should be thoroughly wetted immediately prior to the placement of the modified systems. After wetting, the substrates should be wiped off with rags or blown with compressed air to remove any standing water.

The choice of a latex-modified mortar or concrete depends on the thickness of the overlay or coating to be applied. Generally, the modified mortar can be recommended for thicknesses of 30 mm or less, and the modified concrete for the thickness exceeding 30 mm.

Latex-modified mortar and concrete are usually somewhat difficult to finish the surfaces by troweling compared to conventional cement mortar and concrete because of wet drag. The modified systems set, forming a surface skin which will easily tear. It is advisable to finish the surfaces by troweling two to three times. The over-troweling is not advisable for the modified systems. Because thin polymer films are formed on the trowel surfaces during troweling, the trowels should be frequently cleaned to remove such films. Retroweling after initial set is not recommended. Excessive vibration for compaction must be avoided to prevent water with polymers bleeding to the finished surfaces. In application to large areas, it is advisable to provide joints with a width of about 15 mm at intervals of 3 to 4 m.

Latex-modified mortar and concrete should never be placed at temperatures lower than 5°C or higher than 30°C. Adequate care should be taken to prevent floating the polymer solids to the finished surfaces due to wetting by water or rainfall immediately after placing. It is desirable that the surfaces are promptly covered with wet burlap or polyethylene sheets. In applications in cold climate areas or winter, the use of high-early-strength cement, ultrarapid-hardening cement and high alumina cement can be recommended.

The curing under wet conditions such as water immersion or moist curing applicable to ordinary cement mortar and concrete is detrimental to latex-modified mortar and concrete. Normally, the latex-modified mortar and concrete require a different curing method because of the incorporation of polymer latexes. Almost optimum properties of the modified systems are achieved by a combined wet and dry cure, i.e., moist cure for 1 to 3 days, followed by dry cure at ambient temperature. The curing of the modified systems can be accelerated by moderate heating; however, steam curing is not recommended. The effects of curing conditions on the strength of the latex-modified mortar and concrete are described in Ch. 4, Sec. 2.1.

Generally, polymer latexes used as cement modifiers are not toxic, and are safe materials to handle. Consequently, they require no special precautions.

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Properties of Latex-Modified Systems

Latex-modified mortar and concrete are made by using a composite binder of inorganic cements and organic polymer latexes, and have a network structure which consists of cement gels and microfilms of polymers. Consequently, the properties of the latex-modified mortar and concrete are markedly improved over conventional cement mortar and concrete. The properties of the fresh and hardened mortar and concrete are affected by a multiplicity of factors such as polymer type, polymer-cement ratio, watercement ratio, air content, and curing conditions.

1.0 PROPERTIES OF FRESH MORTAR AND CONCRETE

1.1 Workability

Generally, latex-modified mortar and concrete provide a good workability over conventional cement mortar and concrete. This is mainly interpreted in terms of improved consistency due to the ball bearing action of polymer particles and entrained air and the dispersing effect of surfactants in the latexes. Tateyashiki, et al.^[1] proved by zeta-potential determination and cryo-scanning electron microscopy that the improved consistency or fluidity is due to the ball bearing action of the polymer particles among cement particles.

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Figures 4.1 and 4.2^{[2][3]} represent the effect of unit water content (or water-cement ratio) and polymer-cement ratio on the consistency of latexmodified mortars and concretes, respectively. The flow of the latexmodified mortars increases with increasing water-cement ratio and polymercement ratio. The slump of the latex-modified concretes tends to increase with rising unit water content (or water-cement ratio) and polymer-cement ratio, and at each unit water content, a rise in the polymer-cement ratio causes an increase in the slump. This tendency is more significant at smaller sand-aggregate ratios and at large unit cement content. Considering these factors, Ohama, et al.^[3] have expanded Lyse's rule of constant water content on ordinary cement concrete,^[4] and defined *slump control factor* as follows:

$$\varphi = \mathbf{V}\mathbf{p} + \mathbf{V}\mathbf{w}$$

where φ is the slump control factor of the latex-modified concretes, and Vp and Vw are the volumes of polymer and water per unit volume of the latexmodified concretes respectively. A typical example of slump control factorslump relationship obtained at different sand-aggregate ratios is presented in Fig. 4.3.^[5] As shown in Fig. 4.3, there is a high correlation between the slump control factor and slump in the slump range of 1 to 21 cm, and the slump of the latex-modified concretes may be generally expressed as a function of the slump control factor by the following equation:

$$Sl = K\varphi - l/(1 - s/a)$$

where Sl is the slump of the latex-modified concretes, φ is the slump control factor, s/a is the sand-aggregate ratio or sand percentage, and k and l are empirical constants. Predictions of the slumps are possible by applying this equation.

As seen in the Fig. 4.4,^[6] the water-cement ratio of latex-modified concrete at a given slump is markedly reduced with an increase in the polymer-cement ratio. This water reduction effect is found to contribute to strength development and a drying shrinkage reduction.



Figure 4.1 Effects of water-cement ratio and polymer-cement ratio on flow of latex-modified mortars.



Figure 4.2 Effects of unit water content (water-cement ratio) and polymer-cement ratio on slump of SBR-modified concrete.



Figure 4.3 Prediction of slump of SBR-modified concretes.



Figure 4.4 Relation between polymer-cement ratio and water-cement ratio of SBR-modified concretes.

1.2 Air Entrainment

In most latex-modified mortars and concretes, a large quantity of air is entrained compared to that in ordinary cement mortar and concrete because of an action of the surfactants contained as emulsifiers and stabilizers in polymer latexes. Some air entrainment is useful to obtain improved workability as mentioned in Sec. 1.1. An excessive amount of entrained air causes a reduction in strength and must be controlled by using proper antifoaming agents. Recent commercial latexes for cement modifiers usually contain proper antifoaming agents, and the air entrainment is considerably decreased. Consequently, the air content of most latex-modified mortars is in the range of 5 to 20%, and that of most latex-modified concretes is less than 2%, much the same as ordinary cement concrete. Such decreased air content of the latex-modified concretes over the latex-modified mortars is probably explained by the fact that air is hard to entrain in the concretes because of the larger size of aggregates used. This tendency is evident from Figs. 4.5^[7] and 4.6.^[8] In Fig. 4.5, the air content decreases as the polymercement ratio is increased at a constant flow or water-cement ratio. Variation of the air content in the latex-modified mortars is larger than that in the latexmodified concretes with an increase in the polymer-cement ratio. The effects of antifoaming agents on the air content and strength of the latex-modified systems are discussed in Sec. 2.1.

1.3 Water Retention

Latex-modified mortar and concrete have a markedly improved water retention over ordinary cement mortar and concrete. The water retention is dependent on the polymer-cement ratio. The reasons for this can probably be explained in terms of the hydrophilic colloidal properties of latexes themselves and the inhibited water evaporation due to the filling and sealing effects of impermeable polymer films formed. Accordingly, a sufficient amount of water required for cement hydration is held in the mortar and concrete and, for most latex-modified systems, dry cure is preferable to wet or water cure. This is also examined in Sec. 2.1.

Figure 4.7^[9] gives the polymer-cement ratio vs. water retention of latex-modified mortars, measured according to JIS A 6908 (Finish Coatings and Wall Coverings for Decorative Use) and ASTM C 91 (Standard Specification for Masonry Cement). The water retention generally increases with rising polymer-cement ratio, and becomes nearly constant at a polymer-cement ratio of 5 to 10%. Such excellent water retention of the latex-modified mortars is most helpful or effective to inhibit *dry-out* phenomena (the lack of cement hydration due to water loss in the mortar or concrete) in thin layer linings or coatings on highly water-absorbable substrates such as dried cement mortars and ceramic tiles.



Figure 4.5 Polymer-cement ratio vs. air content of latex-modified mortars.



Figure 4.6 Polymer-cement ratio vs. air content of latex-modified concretes.



Figure 4.7 Polymer-cement ratio vs. water retention of latex-modified mortars.

1.4 Bleeding and Segregation

In contrast to ordinary cement mortar and concrete, which are apt to cause bleeding and segregation, the resistance of latex-modified mortar and concrete to bleeding and segregation is excellent in spite of their larger flowability characteristics. This is due to the hydrophilic colloidal properties of latexes themselves and the air-entraining and water-reducing effects of the surfactants contained in the latexes. Accordingly, in the latexmodified systems, some disadvantages such as reductions in strengths and waterproofness caused by bleeding and segregation do not exist.

1.5 Setting Behavior

In general, the setting of latex-modified mortar and concrete is delayed to some extent in comparison with ordinary cement mortar and concrete, and this trend is dependent on the polymer type and polymercement ratio.

Figures 4.8^[10] and 4.9^[8] show the setting behavior of the latexmodified mortars and concretes respectively. The setting is delayed with an increase in the polymer-cement ratio. The slower setting does not cause inconvenience in practical applications. NR-modified mortar causes the most delay in setting. Usually, the reasons for the setting delay are that the surfactants such as alkylbenzene sulfonates and caseinates contained in latexes inhibit the hydration of cement.^[11] Rheological studies on PVACmodified concrete by Zivica^[12] revealed that the hydration of cement is inhibited by the adsorption of the surfactants on the binder surface.

2.0 PROPERTIES OF HARDENED MORTAR AND CONCRETE

2.1 Strength (Factors Affecting Strength)

In general, latex-modified mortar and concrete show a noticeable increase in the tensile and flexural strengths but no improvement in the compressive strength as compared to ordinary cement mortar and concrete. This is interpreted in terms of the contribution of high tensile strength by the polymer itself and an overall improvement in cement-aggregate bond. The strength properties of the latex-modified mortar and concrete are influenced by various factors which tend to interact with each other. The main factors



Figure 4.8 Elapsed time vs. degree of setting of latex-modified mortars.



Figure 4.9 Elapsed time vs. penetration resistance of SBR-modified concrete.

are: the nature of materials used such as latexes, cements, and aggregates; the controlling factors for mix proportions (e.g., polymer-cement ratio, water-cement ratio, binder-voids ratio, etc.); curing methods; and testing methods.

Effect of the Nature of Materials. The nature of polymers in latexes mainly depends on monomer ratio in copolymers and the type and amount of plasticizers. The properties of latexes such as mechanical and chemical stabilities, bubbling, and coalescence on drying are dependent on the type and amount of surfactants and antifoamers and the size of dispersed polymer particles.

Ohama^{[13][14]} studied the effect of monomer ratio in EVA, SBR, and poly(styrene-butyl acrylate, SAE) latexes on the strengths of latex-modified mortars (Fig. 4.10). The monomer ratio affects the strengths of the latexmodified mortars to the same extent as the polymer-cement ratio. The maximum strengths of EVA- and poly(styrene-butyl acrylate)-modified mortars are obtained at a bound ethylene content of 13% and a bound styrene content of 55% respectively. The strengths of SBR-modified mortar increase with a rise in the bound styrene content. These results are similar to those obtained by Cherkinskii, et al.^[15] The tensile strength of the dry films made from SBR latexes increases sharply when the bound styrene content is raised, and there is a positive correlation between the strength of the films and the flexural strength of SBR-modified mortars with polymer-cement ratios above 10% as shown in Fig. 4.11.^[13]

The effect of plasticizer (i.e., dibutyl phthalate) content in PVAC latexes on the strengths of PVAC-modified mortars is represented in Fig. 4.12.^[16] Like SBR-modified mortars, the strengths are governed by the nature of polyvinyl acetate (with variation of the plasticizer content), and is reduced with an increase in the plasticizer content.

Figure 4.13 shows the effect of the glass transition temperature (Tg) of polymers on the flexural and compressive strengths of latex-modified mortars with a polymer-cement ratio of 15%, plotted by using Walter's and Ohama's data.^{[17][18]} According to this data, the flexural and compressive strengths of the latex-modified mortars appear to reach a maximum value at a glass transition temperature depending on a change in the minimum film-forming temperature of the latexes with rising glass transition temperature.

Generally, the mechanical and chemical stabilities of latexes are improved with an increase in the content of the surfactants selected as stabilizers, and the stabilized latexes can disperse effectively without coagulation in latex-modified mortar and concrete. On the other hand, an excess amount of surfactant may have an adverse effect on the strength of the latexmodified mortar and concrete because of the reduced latex film strength, the



Figure 4.10 Effects of monomer ratio in EVA, SBR and poly(styrene-butyl acrylate, SAE) latexes on flexural and compressive strengths of latex-modified mortars.



Figure 4.11 Relationship between tensile strength of SBR latex films and flexural strength of SBR-modified mortars.



Figure 4.12 Effect of plasticizer content in PVAC latexes on flexural and compressive strengths of PVAC-modified mortars.



Figure 4.13 Effect of glass transition temperature (Tg) of polymers on flexural and compressive strengths of latex-modified mortars with polymer-cement ratio of 15%. (© 1993, ASTM, reprinted with permission.)

delayed cement hydration and excess air entrainment. Consequently, the latexes used as cement modifiers should have an optimum surfactant content to provide the high strength of the latex-modified mortar and concrete. Optimum surfactant contents ranging from 5 to 30% of the weight of the total solids can be found in Fig. 4.14,^[19] which illustrates the relation between the surfactant content of the latexes and the flexural strength of the latex-modified mortars.

Suitable antifoamers are usually added to the latexes to prevent excess air entrainment. Figure $4.15^{[20]}$ shows the effect of silicone emulsion-type antifoamer on the air content and compressive strength of the latexmodified mortars. Increased antifoamer content causes a pronounced decrease in the air content and an increase in the compressive strength.



Figure 4.14 Relation between surfactant content of latexes and flexural strength of latex-modified mortars.


Figure 4.15 Effect of silicone emulsion-type antifoamer on air content and compressive strength of latex-modified mortars.

As demonstrated in Table 4.1,^[21] it is most important that the antifoamers and the surfactants selected as stabilizers or emulsifiers should produce no adverse effect on cement hydration. Polyoxyethylene nonyl phenol ether and silicone emulsion are a good surfactant and antifoamer respectively, but a large amount of sodium alkyl benzene sulfonate which is a popular emulsifier causes the delayed hydration of cement, and extends the setting times.

The size of dispersed polymer particles in the latexes can affect the strength of latex-modified mortar and concrete to a certain extent. Geist, et al.^[22] and Brocard^[23] found that PVAC-modified mortar developed a maximum strength as the particle size ranges from 1 to 5 μ m or 2 to 5 μ m. Wagner, et al. found increases in the compressive and tensile strengths of PVDC-modified mortar with decreasing particle size, as shown in Table 4.2.^[24] Walters investigated the effect of latex particle size on the chloride ion permeability of SBR-modified mortars with a polymer-cement ratio of 15% as seen in Table 4.3.^[17] The chloride ion permeability was tested by ASTM C 1202 (Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration). SBR latexes with smaller particle size appear to initially provide lower chloride ion permeability to the mortars using the latexes, but a difference in the permeability between the smaller and larger particle sizes eventually becomes insignificant with additional curing period. Such an initial decrease in the permeability is attributed to the fact that the latexes with smaller particle size coalesce faster than the ones with larger particle size, as indicated in the paint field.^[25]

It appears that the molecular weight of the latex polymers does not have an effect on the strength of latex-modified mortar and concrete.^[23]

The strength of latex-modified systems is affected to a lesser extent by the type of cement, except when high-alumina cement is used as shown in Fig. 4.16.^[26]

The latex-modified mortars using high-alumina cement exhibit a strength 1.5 to 2 times higher than that of the mortars using other cements. This is due to a difference in the structure formation at the initial stage of setting.

The effects of blended cements containing various mineral admixtures on the flexural strength of dry-cured EVA-modified mortars are illustrated in Fig. 4.17.^[27] The flexural strength of EVA-modified mortars with the blended cements increases with an increase in the polymer-cement ratio, and is similar to that of unmodified mortar except in a few cases.

Surfactant	Content	Setting time (h-min)			
and Antifoamer	(% of cement)	Initial Set	Final Set		
No Addition	0	2-40	3-30		
Polyoxyethylene	0.05	2-45	3-45		
Nonyl Phenol	0.1	2-40	3-40		
Ester	0.4	2-10	3-45		
	0.7	2-45	3-30		
	1.0	2-25	3-30		
Sodium Alkyl	0.05	2-20	3-25		
Benzene	0.1	2-45	4-00		
Sulfonate	0.4	3-25	5-45		
	0.7	11-00	14-00		
	1.0	16-15	18-35		
Silicone Emulsion-	0.1	2-40	3-45		
Type Antifoamer	0.5	2-45	4-15		
	1.0	2-30	3-35		

 Table 4.1
 Effects of Surfactants and Antifoamer on Setting Behavior of Cement.

Table 4.2Strength of PVDC-Modified Mortar as a Function of Latex
Particle Size.

Particle Size (η m)	Compressive Strength (kgf/cm ²)	Tensile Strength (kgf/cm ²)	
163	380	55	
143	444	64	
130	464	73	
110	510	77	
105	538	83	

Table 4.3Effect of Latex Particle Size on Chloride Ion Permeability of
SBR-Modified Mortars with a Polymer-Cement Ratio of 15%
by ASTM C 1202.

Curing Period -	Chloride Ion Permeability (coulombs) Average Particle Size (nm)		
14	1150	2100	
28	960	1420	
56	810	800	







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Figure 4.17 Effects of blended cements on flexural strength of dry-cured EVA-modified mortars. (© 1993, Advances in Cement Research, Thomas Telford Services Ltd., reprinted with permission.)

Figure 4.18^[28] indicates the effect of the fineness modulus of sand on the strength of latex-modified mortars. The flexural and compressive strengths tend to increase with rising fineness modulus, that is, with increasing particle size of the sand, like unmodified mortar.

Effects of Control Factors for Mix Proportions. The binder of latex-modified mortar and concrete consists of polymer latex and inorganic cement, and their strength is developed as a result of an interaction between them. The polymer-cement ratio has a more pronounced effect on the strength properties than the water-cement ratio. However, this effect depends on polymer type, air content, curing conditions, etc. The relation between the strength properties and polymer-cement ratio has been discussed in a number of papers.^{[29]-[32]} A general trend which summarizes the results obtained in these papers is presented in Fig. 4.19.

Table 4.4^[33] shows the strength properties of typical latex-modified concretes at various polymer-cement ratios and a constant slump of 18±1 cm, which were given a 2-day-20°C-moist plus 5-day-20°C-water plus 21-day-20°C-50% R.H. dry cure. The development of tensile and flexural strengths is more remarkable than that of the compressive and shearing strengths except those of PVAC-modified concrete. Most latex-modified mortars and concretes show a maximum strength at polymer-cement ratios of 10 to 20% and 20 to 30% in the dry cure and the combined water and dry cure, and at polymer-cement ratios of 5 to 15% and 15 to 25% in the water cure. Some latex-modified systems show a minimum strength at a polymercement ratio of 5 to 10% irrespective of the curing conditions. A few systems provide a sharp decrease in strength with rising polymer-cement ratios regardless of the curing conditions. Generally speaking, most latexmodified mortars and concretes cured under favorable conditions have effective strength properties at polymer-cement ratios up to 20 to 30%, and the strength may be reduced at polymer-cement ratios exceeding 20 to 30%. Up to these ratios, the polymer acts to strengthen the mortar or concrete microstructure, but a further increase in the polymer-cement ratio leads to discontinuities in the microstructure which reduce the strength. Low polymer-cement ratios of 5% or less also are not effective because of little improvement in the strength. Consequently, the polymer- cement ratio range of 5 to 20% is used in practice.

As seen in Table 4.4, at a given consistency, a considerable reduction in the water-cement ratio due to increased polymer-cement ratio contributes largely to an increase in the strength of most latex-modified systems.

Entrainment of air exerts a marked influence on the strength of most latex-modified systems as indicated in Fig. 4.15.



Figure 4.18 Effects of fineness modulus of sand on flexural and compressive strengths of latex-modified mortars.



Figure 4.19 Relation between strength properties and polymer-cement ratio of latex-modified mortars and concretes.

	Relative Strength				Strength Ratio					
Type of Concrete	Polymer- Cement Ratio (%)	Water- Cement Ratio (%)	Com- pressive	Flexural	Direct Tensile	Shearing	σc ^a ∕σf ^b	σc∕σt ^c	Tf/Tt	σs ^d ∕σc
Unmodified	0	60.0	100	100	100	100	6.88	12.80	1.86	0.174
	5	53.3	123	118	126	131	7.13	13.84	1.94	0.185
SBR-	10	48.3	134	129	154	144	7.13	12.40	1.74	0.184
Modified	15	44.3	150	153	212	146	6.75	10.05	1.49	0.168
	20	40.3	146	178	236	149	5.64	8.78	1.56	0.178
	5	43.0	159	127	150	111	8.64	15.17	1.77	0.120
PAE-1-	10	33.6	179	146	158	116	8.44	16.23	1.96	0.111
Modified	15	31.3	157	143	192	126	7.58	11.65	1.55	0.139
	20	30.0	140	192	184	139	5.03	10.88	2.19	0.170
	5	59.0	111	106	128	103	7.23	12.92	1.81	0.161
PAE-2-	10	52.4	112	116	139	116	6.65	11.40	1.71	0.178
Modified	15	43.0	137	167	219	118	5.64	9.06	1.62	0.148
	20	37.4	138	214	238	169	4.45	8.32	1.88	0.210
	5	51.8	98	95	112	102	7.13	12.53	1.78	0.178
PVAC-	10	44.9	82	105	120	106	5.37	9.76	1.81	0.221
Modified	15	42.0	55	80	90	88	4.69	8.39	1.81	0.274
	20	36.8	37	62	91	60	4.10	5.76	1.38	0.275

^aCompressive strength,

^bFlexural strength, ^cDirect tensile strength,

^dShearing strength.

Wagner^[34] expanded Powers and Brownyard's theory for ordinary cement paste,^[35] and developed a general expression to predict the compressive strength of latex-modified mortars, using the water-cement ratio and the content of entrained air:

$$Fc = C_1 + C_2 / Wo + C_3 A$$

where Fc is the compressive strength of the latex-modified mortars, Wo is the water-cement ratio, A is the volume percentage of entrained air, and C_1 , C_2 and C_3 are constants. However, this expression was obtained under a special condition of complete exclusion of water loss during curing. It appears that the practical application of this equation is somewhat difficult.

For the purpose of developing the equations for the compressive strength prediction for latex-modified mortars and concretes, all-inclusive consideration of various factors such as polymer-cement ratio, water-cement ratio, and air content is required. Expanding Talbot's void theory^[36] on ordinary cement mortar and concrete, Ohama^{[37]-[39]} defined *binder-void ratio* (α) or *void-binder ratio* (β), and empirically proposed the equations using α and β to predict the compressive strength of the latex-modified mortars and concretes as follows:

Latex-modified mortars:

$$\log \sigma c = (A/B^{\beta}) + C \text{ or } \sigma c = (A/B^{\beta}) + C$$

Latex-modified concretes:

$$\sigma c = a\alpha + b$$

where oc is the compressive strength of the latex-modified mortars and concretes, $\beta = 1/\alpha = (Va + Vw)/(Vc + Vp)$, Vc, Vp, Va and Vw are the volumes of cement, polymer, air, and water per unit volume of the latex-modified mortars and concretes respectively, and A, B, C, a and b are empirical constants. Examples of these relationships are presented in Figs. 4.20 and 4.21.^{[38][39]}

Effect of Sand-Cement Ratio. When the sand-cement ratio increases, the flexural and compressive strengths of latex-modified mortars are remarkably reduced, and the effect of the polymer-cement ratio on the strengths gradually becomes smaller.

As seen in Fig. 4.22,^[40] the addition of steel fibers into latexmodified systems has a positive effect on the strength with increasing polymer-cement ratio and steel fiber content. In general, the flexural and compressive strengths can be predicted by the following equations:^[39]



Figure 4.20 Relation between void-binder ratio and compressive strength of latex-modified mortars (expect PVAC-modified mortar) with sand-cement ratio of 3.



Figure 4.21 Relation between binder-void ratio and compressive strength of latex-modified concretes.



Figure 4.22 Steel fiber content and polymer-cement ratio vs. flexural strength of latex-modified concretes.

Flexural Strength:

$$\sigma f = A \sigma fo(1 + P/C) (1 - W/C) + B/(1 + Vf)$$

Compressive Strength:

$$\sigma c = a\sigma fo(1 + P/C)(1 + Vf) + b/(1 - W/C)$$

where of and oc are the flexural and compressive strengths of steel fiber reinforced latex-modified mortars respectively, of and oco are the flexural and compressive strengths of steel fiber reinforced unmodified mortars with a constant volume fraction of steel fibers respectively, P/C is the polymercement ratio, W/C is the water-cement ratio, Vf is the volume fraction of steel fibers, and A, B, a and b are empirical constants. Such relationships are illustrated in Fig. 4.23.^{[40][41]}

Effects of Curing Conditions. Favorable curing condition requirements for latex-modified mortar and concrete differ from those for ordinary cement mortar and concrete, because their binder consists of two phases of latex and hydraulic cement with different properties. Optimum strength in the cement phase is developed under wet conditions such as water immersion and high humidities, where strength development in the latex phase is attained under dry conditions. Figures 4.24 and 4.25^{[42][43]} show the effect of the curing conditions on the strength of the latex-modified mortars and concretes respectively.

It is evident from these figures that optimum strength in most latexmodified mortars and concretes is obtained by achieving the reasonable extent of cement hydration under wet conditions at early ages, followed by dry conditions to promote a polymer film formation due to the coalescence of polymer particles in the latexes. In other words, such curing conditions are most suitable or ideal for most latex-modified mortars and concretes. This is confirmed by Wagner's study.^[29] It appears from these figures that the curing conditions are more sensitive for the mortars than for the concretes because of a difference in the water retention due to their specimen sizes.

The water resistance of latex-modified systems evaluated by a strength change after water immersion is discussed in Sec. 2.4, including the lower water resistance of PVAC-modified systems. Water immersion subsequent to dry cure causes a sharp reduction in the strength of all the latex-modified systems. Such an influence on strength appears reversible because of the recovery of the strength by drying storage subsequent to water immersion as ascertained by Ohama,^[44] and Frondistou-Yannas and Shah.^[45]



Figure 4.23 Prediction of flexural and compressive strengths of steel fiber reinforced latex-modified mortars.



Figure 4.24 Effects of curing conditions on flexural strength of latex-modified mortars.



Figure 4.25 Effects of curing conditions on compressive strength of latexmodified concretes.

The dry curing period after a 2-day-moist and 5-day-water cure vs. compressive strength, as well as the surface area-volume ratio, polymercement ratio vs. compressive strength of latex-modified concretes are illustrated in Figs. 4.26 and 4.27 respectively.^[46] In general, the compressive strength of SBR-modified concretes does not change markedly with additional dry curing period, and becomes nearly constant at an age of 182 days regardless of specimen size. The compressive strength at this age increases sharply with a rise in the polymer-cement ratio, and reaches 2 to 3 times the value before dry cure, i.e., after 7-day wet cure. The main reason for this is the hydration of cement in the latex-modified concretes progresses through a considerably long dry curing period because of their excellent water retention capacity due to polymer film formation. Such a large strength development is found to be one of the advantages of the latex-modified concretes over ordinary cement concrete. The compressive strength tends to increase with increasing surface area-volume ratio, i.e., with decreasing specimen size irrespective of the polymer-cement ratio. The trend is almost the same as for unmodified concrete.^{[47][48]}

The probability of formation of cracks and flaws in a specimen will increase with an increase in its volume, i.e., with an increase in its size.^[49]

A method of developing high strength by the heat treatment of latexmodified systems using thermoplastic copolymers with special thermal properties has been devised.^[50] The copolymers were made from two monomers which form homopolymers with different second-order transition points above and below ambient temperatures. Superior flexural and compressive strengths obtained by this method are represented in Fig. 4.28.^[50] Optimum strength properties by this special curing are attained in the temperature range of 70 to 120°C. The mechanism of such high strength development seems to be explained in terms of the promotion of continuous polymer film formation and pore filling effect.

Relation Between Surface Hardness and Compressive Strength. The surface hardness of latex-modified systems is generally improved to some extent over ordinary cement systems, depending on the polymer type and the polymer-cement ratio. A definite correlation between the surface hardness and compressive strength of most latex-modified systems is recognized as shown in Fig. 4.29.^[51]



Figure 4.26 Dry curing period vs. compressive strength of latex-modified concretes.



Figure 4.27 Surface area-volume ratio and polymer-cement ratio vs. compressive strength of latex-modified concretes.



Figure 4.28 Relationship between heating temperature and flexural and compressive strengths of latex-modified mortars.



Figure 4.29 Polymer-cement ratio vs. brinell hardness and compressive strength of latex-modified mortars.

2.2 Stress-Strain Relationship, Modulus of Elasticity and Ductility

Latex-modified mortar and concrete contain polymers (modulus of elasticity, $0.001-10 \times 10^4 \text{ kgf/cm}^2$) with considerably smaller modulus of elasticity compared to cement hydrates (modulus of elasticity, $10 \sim 30 \times 10^4 \text{ kgf/cm}^2$). Consequently, their deformation behavior and ductility (or extensibility) can differ to a great extent from those of ordinary cement mortar and concrete. Most latex-modified mortars and concretes provide a higher deformation, ductility (or extensibility), and elasticity than ordinary cement mortar and polymer-cement ratio.

Figure 4.30^[52] shows the compressive stress-strain curves for latexmodified mortars. Generally, the maximum compressive strain at failure increases with rising polymer-cement ratio, even though there is no pronounced change in the modulus of elasticity in compression. The maximum compressive strain at a polymer-cement ratio of 20% increases to 2 to 3 times that of unmodified mortar.

Figures 4.31 and 4.32^[53] represent the tensile stress-strain curves and the polymer-cement ratio-elongation (i.e., maximum tensile strain at failure) relationships of SBR-modified concretes respectively. As seen in these figures, as the polymer-cement ratio is raised, the modulus of elasticity in tension decreases, and the elongation increases and is 2 to 3 times greater than that of unmodified concrete. This is explained by considering that the polymer films formed in the concrete may effectively halt propagating microcracks through their high tensile strength and elongation.

The modulus of elasticity in compression and Poisson's ratio of latex-modified concretes are listed in Table 4.5.^[54] The modulus of elasticity generally tends to decrease with a rise in the polymer-cement ratio. The Poisson's ratio of PAE- and SBR-modified concretes is nearly equal to that of unmodified concrete regardless of the polymer-cement ratio, but that of PVAC-modified concretes increases with rising polymer-cement ratio.

Figure 4.33^[55] illustrates the flexural load-deflection curves for steel fiber reinforced SBR- and EVA- modified mortars. It seems that after reaching the maximum flexural load, steel fibers in the mortars can resist the rupture due to work needed to pull them out of the matrix. Accordingly, the toughness is remarkably improved with increasing steel fiber content and polymer-cement ratio. The effect of the steel fiber content on the toughness is much more significant than that of the polymer-cement ratio. Soroushian^[56] showed the improved flexural toughness due to SBR latex modification of pitch-based carbon fiber reinforced mortars.



Figure 4.30 Compressive stress-strain curves for latex-modified mortars.

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Figure 4.31 Tensile stress-strain curves for SBR-modified concretes.



Figure 4.32 Relation between polymer-cement ratio and elongation of SBRmodified concretes.

Type of Concrete	Polymer- Cement Ratio (%)	Modulus of Elasticity in Compression (x10 ⁵ kgf/cm ²)	Poisson's Ratio
Unmodified	0	2.11	0.17
	5	2.27	0.16
PAE-	10	2.36	0.17
Modified	15	2.30	0.17
	20	2.24	0.17
	5	2.28	0.16
SBR-	10	2.43	0.18
Modified	15	2.42	0.18
	20	2.02	0.18
• <u>•••</u> ••••••••••••••••••••••••••••••••	5	1.90	0.16
PVAC-	10	1.79	0.19
Modified	15	1.35	0.24
	20	1.00	0.29



Figure 4.33 Flexural load-deflection curves for steel fiber reinforced SBR- and EVA-modified mortars.

2.3 Shrinkage, Creep, and Thermal Expansion

The drying shrinkage of latex-modified mortar and concrete may be either larger or smaller than that of unmodified mortar and concrete, and is dependent on polymer type and polymer-cement ratio. Data on the shrinkage measurement are somewhat variable for different testing methods or investigations. The drying shrinkage of latex-modified mortars is shown in Figs. 4.34 and 4.35.^[57] The drying shrinkage increases with additional dry curing period, and becomes nearly constant at a dry curing period of 28 days regardless of polymer type and polymer-cement ratio. Generally, the 28-day drying shrinkage tends to decrease with increasing polymer-cement ratio. PVAC-, NR- and CR-modified mortars have a larger shrinkage compared to that of unmodified mortar. The largest shrinkage of PVAC-modified mortars is probably caused by the evaporation of a larger amount of water absorbed in the polymer phase due to the low water resistance of the polyvinyl acetate itself. Ohama^[58] found that such an excessive shrinkage could be reduced by as much as 50% of that of unmodified mortar by the introduction of ethylene into the polymer formulations as seen in Fig. 4.36. In this study, the optimum effect was obtained at bound ethylene contents of 17 to 40% and at polymer-cement ratios of 15 to 20%. NBR-modified mortars have the smallest shrinkage of all the mortars tested. This may be because the surfactant content of the NBR latex is several times higher than that of other latexes, and hence causes noticeable improvements in water retention and water reduction effects.

Figure 4.37^[46] shows the relationship amongst the volume-surface area ratio (specimen size change), polymer-cement ratio, and drying shrinkage of EVA-modified concretes. The drying shrinkage is reduced with increasing specimen size and polymer-cement ratio because of improved water retention.

Kawano^[59] found that, compared to ordinary cement mortar, a reduction in the drying shrinkage of latex-modified mortars is mainly due to the effects of the surfactants and antifoamers contained in the latexes.

The use of expansive additives such as calcium sulfoaluminate (CSA)- and calcium oxide (lime)-based compositions causes an effective reduction in the drying shrinkage of latex-modified mortars. Figure 4.38^[60] represents the length change of the latex-modified mortars with CSA- and lime-based expansive additives. In general, the drying shrinkage of the latex-modified mortars with the expansive additives is reduced with an increase in the expansive additive content, and transformed into expansion at higher expansive additives tend to be marked at higher polymer-cement ratio. From these data, the adequate consideration of the type of polymer and expansive

additive, expansive additive content, polymer-cement ratio, and curing conditions is required in the mix design of the latex-modified mortars with the expansive additives.



Figure 4.34 Twenty-eight-day drying shrinkage of latex-modified mortars.



Figure 4.35 Dry curing period vs. drying shrinkage of latex-modified mortars with polymer-cement ratio of 20%.



Figure 4.36 Effect of bound ethylene content on 28-day drying shrinkage of EVA-modified mortars.



Figure 4.37 Volume-surface area ratio and polymer-cement ratio vs. drying shrinkage of EVA-modified concretes.



Figure 4.38 Fifty-six-day length change of latex-modified mortars with expansive additives.

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Figure 4.39^[61] illustrates the steel fiber content and polymer-cement ratio vs. 84-day drying shrinkage of steel fiber reinforced latex-modified mortars. The reinforcement of the latex-modified mortars with steel fibers provides a marked decrease in the drying shrinkage with increasing polymer-cement ratio and steel fiber content and, at a polymer-cement ratio of 20% and a steel fiber content of 2.0 vol%, can cause a reduction of about 35% in the drying shrinkage. The drying shrinkage may generally be predicted by the equation:

$$Sf = ASo (1-P/C) (1-Vf) + B(P/C)$$

where Sf and So are the drying shrinkages of the steel fiber reinforced latexmodified mortar and steel fiber reinforced unmodified mortar respectively, P/C is the polymer-cement ratio, Vf is the volume fraction of steel fibers, and A and B are empirical constants.



Figure 4.39 Steel fiber content and polymer-cement ratio vs. 84-day drying shrinkage of steel fiber reinforced latex-modified mortars.

Conflicting data exist on the creep behavior of latex-modified mortar and concrete. The creep characteristics of SBR- and PAE-modified concretes reported by Ohama^[62] are represented in Fig. 4.40. Like ordinary cement concrete, the relationships between loading time (t) and creep strain (ϵ c) or creep coefficient (ϕ) (i.e., creep strain/elastic strain ratio) of the latex-modified concretes fit approximately the expression :

$$\varepsilon c \text{ or } \phi = t/(A + Bt)$$

where A and B are constants. Both creep strain and creep coefficient of SBR- and PAE-modified concretes are considerably lower than those of unmodified concrete. This tendency is similar to the creep data^[63] on latex-modified mortars. The latex-modified mortars and concretes generally exhibit small creep in spite of the inclusion of flexible polymers with low glass transition temperatures. This may be related to the lower polymer content of about 3 vol%, the strengthening of binder with polymers, and the long-term strength development with improved water retention.

By contrast, Solomatov^[64] found that the creep deformation in flexure of poly(vinyl acetate-dibutyl maleate)-modified mortar was several times larger than that of unmodified concrete at 20°C, and its catastrophic deformation occurred at 50°C since the polymer developed a high plasticity above its glass transition temperature.

In general, the coefficient of thermal expansion of latex-modified mortar and concrete is directly influenced by that of the aggregates used, as in ordinary cement mortar and concrete. Latex-modified mortar and concrete usually have coefficients of thermal expansion equal to or slightly larger than that of ordinary mortar and concrete. Table 4.6^[65] gives the coefficient of linear thermal expansion of SBR- and PVDC-modified mortars with variation of polymer-cement ratio.

2.4 Waterproofness and Water Resistance

Latex-modified mortar and concrete have a structure in which the larger pores can be filled with polymers or sealed with continuous polymer films. In general, the effect of polymer filling or sealing increases with a rise in polymer content or polymer-cement ratio. These features are reflected in reduced water absorption, water permeability, and water vapor transmission. As a result, the latex-modified mortar and concrete have an improved waterproofness over ordinary mortar and concrete. On the other hand, they have poorer water resistance so that their strength is decreased when exposed to water or high humidities.


Figure 4.40 Loading time vs. creep strain and creep coefficient of latex-modified concretes.

Type of Mortar	Polymer- Cement Ratio (%)	Coefficient of Linear Thermal Expansion (10 ⁻⁶ /°C, -18 to 38°C)
Unmodified	0	7.9 8.5
SBR- Modified	10 15 20	7.99.28.69.67.710.1
PVDC- Modified	10 15 20	7.4 7.9 9.0 10.3 8.8 9.9

 Table 4.6
 Coefficient of Linear Thermal Expansion of Latex-Modified Mortars.

Figure 4.41^[66] illustrates the water immersion period and polymercement ratio vs. water absorption of latex-modified mortars. The water absorption increases with additional water immersion period, and at lower polymer-cement ratios becomes nearly constant at 48 hours regardless of polymer type. Figures 4.42^[66] shows the 48-hour water absorption and the amount of water permeation (under a water pressure of 1 kgf/cm²) of the latex-modified mortars. Generally, the water absorption and the amount of water permeation are considerably reduced with an increase in polymercement ratio. In all cases, except PVAC-modified mortar, as the resistance to water absorption increases, the resistance to water permeation also increases. The waterproofness of PVAC-modified mortar is low. Polyvinyl acetate swells due to water absorption, and is partially hydrolyzed under alkaline conditions as expressed by the following equation:^{[67]-[69]}

$$2 \begin{pmatrix} -CH_2 - CH - \\ | \\ OCOCH_3 \end{pmatrix} + n Ca(OH)_2 (Formed by cement hydration)$$
$$-\frac{H_2O}{2} 2 \begin{pmatrix} -CH_2 - CH - \\ | \\ OH \end{pmatrix} + n \frac{CH_3COO}{CH_3COO} Ca$$



Figure 4.41 Water immersion period and polymer-cement ratio vs. water absorption of latex-modified mortars.



Figure 4.42 Water absorption and amount of water permeation of latex-modified mortars.

At the initial stage of water permeation through PVAC-modified mortar, the swelling can have a self-sealing effect on the pores, and the mortar may show a smaller amount of water permeation. The water permeation data of NBR-modified concretes which were tested by using hollow cylindrical specimens filled with water are indicated in Fig. 4.43.^[70] The resistance to water permeation is markedly improved with rising polymer-cement ratio.

Figure 4.44^[27] shows the water permeability as measured parameter, time (s), by Figg's method^[71] of dry-cured EVA-modified mortars with blended cements containing various mineral admixtures. According to this method, the measured parameter is the time taken for a standard volume of water to be permeated into the specimen through a 10 mm diameter x 40 mm deep hole.^[27] An increase in the measured parameter of EVA-modified mortars with the blended cements indicates a decrease in the water permeability, and increasing polymer-cement ratio decreases the water permeability by a factor of 10 or more.

Figure 4.45^[72] represents the water vapor transmission of latexmodified mortars. Like the water absorption and water permeation, the water vapor transmission decreases remarkably with increasing polymercement ratio.

Figures 4.46 and $4.47^{[73]}$ show the effect of water absorption on the flexural and compressive strengths of latex-modified mortars with a polymer-cement ratio of 20%. In Figs. 4.46 and 4.47, dry means 14-day dry cure, and wet refers to 14-day water immersion after the dry cure. In contrast to the increased strengths of unmodified mortar, most of latexmodified mortars tend to lose their strength to some extent after water immersion, and this trend is more significant for the flexural strength. However, most latex-modified mortars after water immersion retain their strengths that are higher than those of unmodified mortar, and cause no problem in their practical applications. The poor water resistance is most probably caused by a partial re-emulsification (or redispersion) of the polymer phase in the latex-modified mortars. Re-drying will usually allow the strengths to be recovered if irreversible chemical change in the polymer phase has not taken place. PVAC-modified mortars provide the poorest water resistance. The reasons for this are already discussed. Many attempts have been made to improve the poor water resistance of PVAC-modified mortars and concretes.^{[67][69][74]} This problem has been overcome by the use of copolymer modifiers, for example, poly(ethylene-vinyl acetate) (EVA) latex, and vinyl acetate-type copolymer latexes for high water-resistant latex-modified mortars and concretes that are commercially available. In particular, EVA latex has been widely used. The relation between bound ethylene content and flexural and compressive strengths of EVA-modified mortars is demonstrated in Fig. 4.48.^[75] The water resistance of EVA-modified mortars is improved at an optimum bound ethylene content of about 20%.



Figure 4.43 Relation between water permeating period and amount of water permeation of NBR-modified concretes.



Figure 4.44 Water permeability (by Figg's method) of dry-cured EVA-modified mortars using blended cements. (© 1993, Advances in Cement Research, *Thomas Telford Services Ltd., reprinted with permission.*)



Figure 4.45 Effect of polymer-cement ratio on water vapor transmission of SBRmodified mortars.



Figure 4.46 Effect of water absorption on flexural strength of latex-modified mortars.



Figure 4.47 Effect of water absorption on compressive strength of latex-modified mortars.



Figure 4.48 Relation between bound ethylene content and flexural and compressive strengths of EVA-modified mortars.

2.5 Adhesion or Bond Strength

A very useful aspect of latex-modified mortars and concretes is their improved adhesion or bond strength to various substrates compared to conventional mortar and concrete. The development of adhesion is attributed to the high adhesion of polymers. The adhesion is usually affected by polymer-cement ratio and the properties of substrates used. The data on adhesion often show considerable scatter, and may vary depending on the testing methods, service conditions or porosity of substrates.

Figure 4.49^[76] indicates the adhesion in flexure of latex-modified mortars to ordinary cement mortar as a substrate, measured by patched beam method. The adhesion of most latex-modified mortars tends to increase with rising polymer-cement ratio, although for a few types there are optimum polymer-cement ratios. The adhesion is also influenced by the mix proportions, namely, the strength of mortar substrate. In 1:2 mix substrate, failure in flexure occurs mostly through the interface but in 1:3 mix substrate through the substrate rather than through the interface. However, it appears that the adhesion is lower than the flexural strength. Similar improvements in adhesion are also achieved in shear compression.^[77]

Figure $4.50^{[78]}$ indicates the adhesion of latex-modified mortars to ordinary cement mortar as a substrate, measured by four types of test methods. Generally, the adhesions in tension, flexure, and direct compressive shear of the latex-modified mortars to ordinary cement mortar increase with a rise in the polymer-cement ratio regardless of the type of polymer and test method. The adhesion in slant (indirect) compressive shear of the latex-modified mortars at a polymer-cement ratio of 5 or 10%, and is extremely large compared to the adhesions determined by other test methods irrespective of the polymer type and polymer-cement ratio. The reasons for this may be due to the effects of the combined shear and compressive stresses and their relaxation by the polymer films formed on the bonding joints. Considering the above adhesion data, it is most important to select the best test methods to successfully reproduce service conditions in the applications of the latex-modified mortars.

Kuhlmann^[79] developed a test method that accurately measures the bond strength of latex-modified mortar or concrete to conventional concrete under direct tension, using the specimens prepared by casting the latexmodified mortar or concrete on the concrete substrates in 76-mm (diameter) steel pipe nipples as molds. The bond test by this method demonstrated a coefficient of variation of less than 10%.



Figure 4.49 Polymer-cement ratio vs. flexural adhesion of latex-modified mortars to ordinary cement mortar.



Type of Failure, A : Adhesive Failure (Failure in the interface) M: Cohesive Failure (Failure in latex-modified mortar) S: Cohesive Failure in Substrate (Ordinary cement mortar)

The respective approximate rates of A, M and S areas in the total area of 10 on the failed crosssections are expressed as suffixes for A, M and S.

Figure 4.50 Adhesion of latex-modified mortars to ordinary cement mortar, measured by four types of test methods. (Cont'd next page)



The respective approximate rates of A, M and S areas in the total area of 10 on the failed crosssections are expressed as suffixes for A, M and S.

The use of latex-modified pastes as bonding agents for ordinary cement mortar to mortar or concrete substrates is a widespread practice for troweling work. Figure 4.51^[80] exhibits the effect of the polymer-cement ratio of the latex-modified pastes on the adhesion in tension of bonded ordinary cement mortar to latex-modified paste-coated mortar substrates. The adhesion in tension of the bonded mortar to the latex-modified pastecoated mortar substrates increases with increasing polymer-cement ratio of the latex-modified pastes, and reaches a maximum at polymer-cement ratios of about 5 to 10%. The failure modes in adhesion tests are almost cohesive in the bonded mortar. Figure 4.52^[80] shows the microstructures of the interfaces between the bonded mortar and latex-modified paste-coated mortar substrates. The presence of the latex-modified paste layers in the diffused edges facing the bonded mortar is distinctly seen. The diffusion of the latex-modified pastes in the bonded mortar signifies the formation of a monolithic bond between the bonded mortar and latex-modified pastes. Moreover, the very workable latex-modified pastes fill the nonuniform mortar substrates, and develop a good bond by micromechanical interlocking mechanisms.

Ohama^[13] found a nearly ten-fold increase in adhesion to ordinary cement mortar of SBR-modified mortar with a polymer-cement ratio of 20%, compared to unmodified mortar. In this case, the monomer ratio of the copolymer was important, and the high adhesion was attained at a bound styrene content of 70%.

One disadvantage of latex-modified mortar and concrete is that under wet service conditions, adhesion is reduced as seen in Fig. 4.53.^[81] The adhesion strength of most latex-modified mortars after water immersion is, however, larger than that of unmodified mortar. Accordingly, this does not deter the practical use of most latex-modified mortars.

Table 4.7^[82] gives the adhesion of latex-modified mortars to ceramic tiles, measured by shear compression test. The adhesion between ceramic tiles and that between the tiles and ordinary cement mortar tend to increase with rising polymer-cement ratio.

The adhesion of latex-modified mortars to various substrates is also listed in Table 4.8. Most latex-modified mortars have an excellent ability to bond to steel, wood, brick, and stone.

The adhesion or bond of latex-modified mortars to reinforcing bars is found to be very important for their use in repair work for damaged reinforced concrete structures. Figure $4.54^{[83]}$ illustrates the bond strength of the latex-modified mortars to the reinforcing bars, determined under direct tension by pull-out method. In general, the bond strength of the latex-



Figure 4.51 Effect of polymer-cement ratio on adhesion in tension of bonded ordinary cement mortar to latex-modified paste-coated mortar substrates.

Type of Latex-Modified Paste SBR



PAE



x 500

Figure 4.52 Microstructures of interfaces between bonded ordinary cement mortar and latex-modified paste-coated mortar substrates.





Type of	Polymer-	Shear Adhesion (kgf/cm ²)				
Mortar	Cement Ratio (%)	Tile-Tile	Tile-Cement Mortar			
Unmodified	0	1.6	5.0			
CDD	5	5.3	5.5			
Modified	10	8.1	8.5			
Monued	20	8.9	9.0			
NDD	1	7.5	6.7			
Modified	3	8.0	12.9			
Moumeu	5	10.0	9.6			
PVAC-	5	6.1	12.9			
Modified	10	8.4	12.5			
Polyvinyl Alcohol-	0.8	3.5	4.2			
Modified	1.3	4.0	6.5			
Methyl Cellulose-	0.2	6.4	7.3			
Modified	0.5	6.6	7.5			

 Table 4.7
 Shear Adhesion of Latex-Modified Mortars to Ceramic Tiles.

 Table 4.8
 Adhesion of Latex-Modified Mortars to Various Substrates.

Type of Mortar	Substrate	Testing Method	Polymer-Cement Ratio (%)	Adhesion (kgf/cm ²)
NR-Modified (121) ^b	Steel	Shear tension	20	8.0
	Wood	Shear tension	20	8.5
CP Modified (191)	Steel	Shear tension	25	34.8
CR-Modified (121)	Wood	Shear tension	25	2.8
	Brick	Tension	0 ^a	3.8
SBR-Modified (122)	Brick	Tension	10 ^a	20.4
	Brick	Tension	20 ^a	41.5
•	Brick	Tension	0 ^a	5.9
	Brick	Tension	5 ^a	7.4
PAE-Modified (123)	Brick	Tension	10 ^a	14.1
	Brick	Tension	20 ^a	22.1
	Brick	Tension	25 ^a	17.6
PVAC-Modified (124)	Stone	Tension	15	23.0

^a The values were read on the graphs.

^bReference No.



Figure 4.54 Polymer-cement ratio vs. bond strength of latex-modified mortars to reinforcing bars.

modified mortars to the reinforcing bars increases with an increase in the polymer-cement ratio, and reaches a maximum at polymer-cement ratios of about 10 to 15%. Cationic latex-modified mortars develop a much higher bond strength than unmodified, anionic and nonionic latex-modified mortars. Such good adhesion or bond between the latex-modified mortars and reinforcing bars is the result of the presence of electrochemically active polymer-cement co-matrixes at the interfaces which helps to relax stresses during loading and retards the friction-controlled slip of the reinforcing bars. Nakayama, et al.^[84] investigated the bond strength development between latex-modified pastes and steel at early ages by use of an overhanging beam method, and found that the bond strength depends on nonevaporable water content, heat of hydration, and calcium hydroxide content.

2.6 Impact Resistance

Latex-modified mortar or concrete has an excellent impact resistance in comparison with conventional mortar and concrete. This is because polymers themselves have high impact resistance. The impact resistance generally increases with rising polymer-cement ratio. The data of the impact resistance vary markedly between the testing methods reported by workers. Figure 4.55^[85] shows the impact resistance of the latex-modified mortars, measured as the falling height of steel ball at failure. The impact resistance of the latex-modified mortars with elastomers is superior to the mortars with thermoplastic resins. The impact resistance of NR- and SBR-modified mortars with a polymer-cement ratio of 20% is about 10 times greater than that of unmodified mortar. Ohama^[86] obtained excellent impact resistance of typical latex-modified mortars (evaluated by flexural-impact test of beam specimens). Another set of data^[13] of SBR-modified mortar indicated that its impact resistance was lowered significantly by increasing the bound styrene content.

As shown in Fig. 4.56,^[87] the reinforcement of latex-modified concretes with steel fibers causes a pronounced improvement in the impact strength with increased polymer-cement ratio and steel fiber content.

2.7 Abrasion Resistance

The abrasion resistance of latex-modified mortar and concrete depends on the type of polymers added, polymer-cement ratio, and abrasion or wear conditions. In general, the abrasion resistance is considerably improved with an increase in polymer-cement ratio. Figure 4.57^[88] illustrates the abrasion resistance of typical latex-modified mortars, which was tested according to JIS A 1453 [Method of Abrasion Test for Building Materials and Part of Building Concrete (Abrasion-Paper Method)] using a testing machine similar to Taber's abraser. The abrasion resistance at a polymer-cement ratio of 20% increases up to 20 to 50 times that of unmodified mortar. Similar results are also obtained by Bright, et al. Teichmann^[89] found that PAE-modified mortar with a polymer-cement ratio of 20% had an abrasion resistance 200 times higher than conventional mortar. Gierloff^[90] developed a traffic simulator for abrasion test, and showed that various PAE-modified concretes with a high polymer-cement ratio and a low water-cement ratio resisted traffic abrasion very well. Ohama's study^[13] of SBR-modified mortar reveals that its abrasion resistance is increased by a rise in bound styrene content.



Figure 4.55 Impact resistance of latex-modified mortars.







Figure 4.57 Abrasion resistance of typical latex-modified mortars.

2.8 Chemical Resistance

The chemical resistance of latex-modified mortar and concrete is dependent on the nature of polymers added, polymer-cement ratio and the nature of the chemicals. Most latex-modified mortars and concretes are attacked by inorganic or organic acids and sulfates since they contain hydrated cement that is non-resistant to these chemical agents, but resist alkalis and various salts except the sulfates. Their chemical resistance is generally rated as good to fats and oils, but poor to organic solvents.

Tables 4.9^[91] and 4.10^[92] give the chemical resistance data of mortars using elastomeric and thermoplastic latexes respectively at a polymer-cement ratio of 20%. In particular, NBR-modified mortar shows excellent resistance to organic solvents and oils, but NR-modified mortar does not resist these agents. Although ordinary cement mortar completely fails on contact with rapeseed oil, most elastomeric and thermoplastic latex-modified mortars are hardly attacked. In general, PVAC-modified mortar hardly resists acids and alkalis, but is stable to a great extent toward organic solvents such as mineral oils.^[93]

2.9 Temperature Effect, Thermal Resistance, and Incombustibility

The strength of latex-modified mortar and concrete is dependent on temperature because of the temperature dependence of polymers themselves (especially thermoplastic polymers). The latex-modified mortars generally show a rapid reduction in strength and deflection with increased temperature. This trend is substantial at temperatures higher than the glass transition temperature of the polymers and at higher polymer-cement ratios.^[94] Most thermoplastic polymers in latex have a glass transition temperature of 80 to 100°C. Test temperature vs. flexural strength of SBR-, PAE-, and EVA-modified mortars is plotted in Fig. 4.58.^[94] At 100 to 150°C, a difference in their strength at different polymer-cement ratios becomes smaller, and the strength of the modified mortars is equal to or larger than that of unmodified mortar. Most latex-modified mortars lose 50% or more of their strength at temperatures exceeding 50°C. On the other hand, their strength at less than 0°C is higher than that at 20°C.^[95]

The thermal resistance of latex-modified mortar and concrete is governed by the nature, especially glass transition temperature of polymers used, polymer-cement ratio, and heating conditions, and ultimately by the thermal degradation of the polymers. Figure 4.59^[96] indicates the thermal resistance of SBR-, PAE-, and EVA-modified mortars at 100 to 200°C. The flexural strength of most latex-modified mortars at 100°C tends to initially

			Weight Change (%)					Volume Change (%)				
Type of	Concentration	Type of Mortar				Type of Mortar						
Chemicals	(%)	Un- Modified	SBR- Modified	EVA- Modified	PAE- Modified	PVDC- Modified	Un- Modified	SBR- Modified	EVA- Modified	PAE- Modified	PVDC- Modified	
Sulfuric Acid	1	-8.8	-6.1	-2.2	-19.1	3.5	-17.0	-9.9	-6.6	-23.8	-2.1	
Hydrochloric Acid	1	-50.0	-50.9	-48.4	-46.4	-47.9	-54.2	-52.5	-48.0	-48.2	-50.9	
Nitric Acid	1	-38.6	-37.6	-34.0	-38.2	-38.6	-43.6	-40.0	-37.0	-41.1	-41.8	
Acetic Acid	1	-21.1	-20.4	-21.6	-20.3	-22.7	-28.4	-23.5	-24.7	-24.1	-27.4	
Lactic Acid	1	-9.3	-13.7	-13.6	-11.5	-10.1	-18.2	-17.5	-17.0	-16.4	-16.2	
Sodium Hydroxide	45	6.2	-5.0	-4.7	-10.7	-1.1	-6.3	-5.5	-6.7	-9.4	-5.0	
Sodium Sulfate	Sat.	12.1	4.5	3.7	4.6	7.7	-0.2	0.7	0.4	-0.3	0.1	
Sodium Chloride	Sat.	10.2	-0.4	2.4	3.4	6.1	-0.5	-4.1	-1.2	-0.9	-0.9	
Calcium Chloride	10	11.4	3.6	5.8	5.0	8.5	-0.4	-0.7	1.2	0.4	1.9	
Ammonium Nitrate	10	1.5	-6.4	-6.7	-4.9	-8.3	-5.6	-6.7	-8.6	-8.1	-11.5	
Sodium Carbonate	10	6.7	3.6	4.4	3.6	7.9	-3.1	-1.6	-0.9	-1.4	0.0	
Methyl Ethyl Ketone	100	5.7	5.0	7.4	7.7	8.2	-5.8	-0.6	0.1	0.2	2.5	
Xylene	100	5.3	2.3	5.5	3,1	9.8	-1.7	-2.8	-1.2	-0.5	-0.2	
Rapeseed Oil	-	-100.0	2.7	6.1	5.3	7.4	-100.0	-1.2	1.0	-0.1	-0.3	
Gasoline	-	3.6	0.8	0.9	1.9	0.7	-2.8	-1.5	-0.9	-0.7	-0.1	
Heavy Oil	-	8.3	2.5	4.9	4.5	8.4	-2.1	-2.0	-1.4	-1.0	-0.9	
Cane Sugar	Sat.	5.8	0.1	1.1	0.3	2.9	-3.4	-1.8	-1.4	-2.0	-1.8	
Tap Water	-	6.9	5.1	7.4	7.8	7.1	-1.6	-0.5	-0.1	-0.3	0.1	

Table 4.9	Chemical Resistance of Thermoplastic Latex-Modified Mortars with Polymer-Cement Ratio of 20%.
Table 4.9	Chemical Resistance of Thermoplastic Latex-Modified Mortars with Polymer-Cement Ratio of 20%.

			Weij	ght Chang	ge (%)	<u></u>		Volu	me Chan	ge (%)	
Type of	Concentration	Type of Mortar				Type of Mortar					
Chemicals	(%)	Un- Modified	SBR- Modified	CR- Modified	NBR- Modified	NR- Modified	Un- Modified	SBR- Modified	CR- Modified	NBR- Modified	NR- Modified
Sulfuric Acid	5	-38.8	-44.4	-80.9	-62.6	-86.1	-43.8	-46.9	-70.3	-64.1	-87.3
Hydrochloric Acid	5	-87.7	-77.8	-87.9	-76.7	-82.9	-89.1	-78.1	-89.1	-76.6	-84.4
Chromic Acid	5	-59.5	-52.8	-46.4	-48.4	-55.8	-75.0	-53.1	-48.4	-39.1	-57.8
Hydrofluoric Acid	5	-33.3	-27.6	-37.9	-27.0	-57.0	-37.5	-28.1	-40.6	-31.3	-57.8
Sulfurous Acid	6	-61.0	-25.4	-58.9	-60.5	-59.4	-60.9	-26.6	-57.8	-60.9	-59.4
Acetic Acid	5	-66.7	-42.1	-56.1	-	-44.3	-56.6	-43.8	-54.7	-	-43.8
Butyric Acid	5	-	-4.8	-	-	-	-	-6.3	-	-	-
	10	-52.5	-	-46.7	-42.5	-55.2	-68.8	-	-18.4	-57.8	-62.5
Lactic Acid	5	•	-23.8	-	-	-	-	-25.0	-	-	-
	20	-77.6	-	-63.7	-59.2	-72.7	-79.7	-	-65.6	-60.3	-73.4
Sodium Hydroxide	45	-13.0	-	0.0	0.0	-32.0	-21.8	-	0.0	0.0	-34.4
Sodium Sulfate	10	10.9	-	2.4	1.6	6.9	0.0	-	0.0	0.0	0.0
Magnesium Sulfate	Sat.	7.5	-	3.3	1.6	2.8	0.0	-	0.0	0.0	0.0
Ammonium Nitrate	50	2.4	0.0	-1.6	-1.6	4.5	0.0	0.0	0.0	0.0	0.0
Sodium Hydrogencarbonate	e 10	11.0	-	5.6	3.1	8.9	0.0	-	0.0	0.0	0.0
Sodium Chloride	Sat.	11.9	1.6	3.2	0.8	5.0	0.0	0.0	0.0	0.0	0.0
Benzene	100	7.4	- ·	0.8	2.4	48.5	0.0	-	0.0	0.0	68.8
Trichloroethylene	100	11.5	-	-100.0	3.9	101.8	0.0	-	-100.0	0.0	95.3
Rapeseed Oil	-	-100.0	0.0	0.0	0.8	3.9	-100.0	1.6	0.0	0.0	0.0
Gasoline	-	8.3	2.4	2.5	1.6	24.3	0.0	1.6	0.0	0.0	28.3
Kerosene	-	7.5	0.8	1.6	1.6	16.5	0.0	-3.1	0.0	0.0	15.6
Heavy Oil -	-	7.3	-	0.8	1.6	1.9	0.0	-	0.0	0.0	0.0
Cane Sugar	50	8.1	-	1.6	0.8	0.9	0.0	-	0.0	0.0	0.0

Table 4.10 Chemical Resistance of Elastomeric Latex-Modified Mortars with Polymer-Cement Ratio of 20%.



Figure 4.58 Effect of temperature on flexural strength of latex-modified mortars.



Figure 4.59 Thermal resistance of latex-modified mortars.

reach a maximum value because of the strengthening of polymer films with drying, and the strength reduction is hardly recognizable at heating periods of 7 days or more. However, the strength of the mortars heated at 150 and 200°C sharply decreases within a short heating period owing to the thermal degradation of the polymers, and then becomes nearly constant with additional heating period. Even after a 28-day heating at 200°C, most latex-modified mortars with different polymer-cement ratios have strength higher than that of unmodified mortar.

From the above data of the temperature dependence and thermal resistance of latex-modified mortars, the maximum temperature limit for retaining useful strength properties is found to be about 150°C.

Generally, the incombustibility of latex-modified mortar and concrete depends on the chemical compositions of polymers used and polymercement ratio or polymer content (by volume). In Japan, the incombustibility of building materials is evaluated as "Grade 1 (incombustible material), 2 (semi-incombustible material), 3 (quasi-incombustible material) and below Grade 3 (not accepted)" by JIS A 1321 (Test Method for Incombustibility of Internal Finish Material and Procedure of Buildings). The incombustibility of the latex-modified mortars by JIS A 1321 is presented in Table 4.11.^[97] The incombustibility ranges from "Grades 1 to 3" except CR-modified mortar with a polymer-cement ratio of 20%. The mortars modified with chlorinecontaining polymers, i.e., CR and PVDC, and PVAC give excellent incombustibility values. The incombustibility of PVAC-modified mortars is due to the action of a large quantity of acetic acid, formed by the thermal decomposition of the polymer.^[98] The incombustibility of most latex-modified mortars tends to become poorer with increasing polymer-cement ratio. All the mortars with a polymer-cement ratio of 5% show "Grade 1" rating.

2.10 Pore Size Distribution, Resistance to Chloride Ion Penetration, Carbonation, and Oxygen Diffusion

The pore structures of latex-modified mortar and concrete are influenced by the type of polymers in the latexes used and the polymercement ratio. Examples of their pore size distribution are illustrated in Fig. 4.60.^[99] Generally, the porosity or pore volume of the latex-modified mortar and concrete reduces in the large radii of 0.2 μ m or more, and increases greatly in the smaller radii of 75 nm or less compared to unmodified mortar and concrete. The total porosity or pore volume tends to decrease with an increase in the polymer-cement ratio. This contributes to improvements in the impermeability and durability of the latex-modified mortar and concrete.

Type of Mortar	Polymer- Cement Ratio, P/C (%)	Polymer ^a Content (vol %)	Time until Smoking (s)	Time until Flaming (s)	Time to ^b Reach 810°C (s)	Class of Incombustibility
Unmodified	0	0	Not smoked	Not flamed	-	Grade 1
	5	1.50	Not smoked	Not flamed	-	Grade 1
CR-	10	3.01	245	242	-	Grade 1
Modified	15	4.70	190	185	-	Grade 1
	20	6.58	100	122	190	Under grade 3
<u></u>	5	2.10	155	89	-	Grade 1
SBR-	10	4.22	62	49	290	Grade 2
Modified	15	6.27	52	45	304	Grade 2
	20	8.40	26	26	329	Grade 3
	5	1.71	Not smoked	Not flamed	-	Grade 1
PAE-	10	3.33	128	82	256	Grade 2
Modified	15	4.94	60	35	144	Grade 2
	20	6.45	35	35	80	Grade 3
	5	1.37	Not smoked	Not flamed	•	Grade 1
PVDC-	10	2.80	Not smoked	Not flamed	-	Grade 1
Modified	15	4.19	Not smoked	Not flamed	-	Grade 1
	20	5.58	Not smoked	Not flamed	-	Grade 1
	5	1.76	Not smoked	Not flamed	•	Grade 1
PVAC-	10	3.56	Not smoked	390	-	Grade 1
Modified	15	5.43	Not smoked	303	-	Grade 1
	20	6.58	Not smoked	60	-	Grade 1
	5	1.77	Not smoked	Not flamed	-	Grade 1
EVA-	10	3.65	99	90	-	Grade 1
Modified	15	5.73	51	44	102	Grade 2
	20	7.51	41	41	220	Grade 2

Table 4.11 Incombustibility	of Latex-Modified Mortars b	y JIS A 1321.
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^a Calculated from unit weight of polymer-modified mortars.

^bAccording to this JIS, the furnace inside temperature should not exceed 810°C within 20 minutes.



Figure 4.60 Pore size distribution of latex-modified concretes.

Latex-modified mortar and concrete have an excellent water impermeability as described in Sec. 2.4. Such good water impermeability also provides the high resistance of the latex-modified mortar and concrete to chloride ion (Cl⁻) penetration, which is one of the most important factors affecting the corrosion of reinforcing bars in reinforced concrete structures. Table $4.12^{[100]}$ gives the apparent chloride ion diffusion coefficient of latexmodified mortars and concretes, which were estimated as a result of the chloride ion penetration kinetics examination in substitute seawater (NaCl content, 2.4%). The resistance to the chloride ion penetration of the latexmodified mortars and concretes tends to be improved with increasing polymer-cement ratio.

For a quicker determination of the chloride ion penetration or permeability, a rapid test method was developed by Whiting,^[101] and has widely been used in the United States and Canada. According to this test method,^[101] the chloride ion permeability of latex-modified concretes is checked by the total charge passed through the specimens, and evaluated by the required chloride ion permeability ratings. The test method has recently been published as ASTM C 1202 (Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration). Figure 4.61^[102] represents the chloride ion permeability of five types of latexmodified mortars with a polymer-cement ratio of 15%, evaluated by the same method. Except for PVAC-modified mortar, the other four types of latex-modified mortars provide chloride ion permeability values in the moderate to low ranges. PVAC-modified mortar gives a high chloride ion permeability because of the hydrolysis of polyvinyl acetate. Table 4.13^[103] shows the chloride ion permeability of field-placed SBR-modified concrete overlays, whose samples were taken in several locations throughout the United States. The chloride ion permeability of SBR-modified concretes is very low regardless of the sampling locations, and significantly decreases with age.

Marusin^[104] determined the penetrated chloride ion content of acrylic and SBR-modified concretes by the potentiometric titration of chloride ions in the drilled powder from their specimens, and showed that both latexmodified concretes have similar performance in minimizing the penetration of chloride ions into them.

The effects of filling and sealing with polymers in latex-modified mortar and concrete are reflected in the reduced transmission of such gases as air, carbon dioxide (CO_2), oxygen (O_2), and water vapor, as well as increased water impermeability. The carbonation resistance of the latex-modified mortar and concrete is remarkably improved with an increase in

Type of Mortar	Polymer- Cement Ratio (%)	Apparent Chloride Ion Diffusion Coefficient (cm ² /s)	Type of Concrete	Polymer- Cement Ratio (%)	Apparent Chloride Ion Diffusion Coefficient (cm ² /s)
Un- Modified	0	6.4x10 ⁻⁸	Un- Modified	0	2.2x10 ⁻⁸
SBR-	10	6.4x10 ⁻⁸	SBR-	10	1.9x10 ⁻⁸
Modified	20	3.9x10 ⁻⁸	Modified	20	9.3x10 ⁻⁹
EVA-	10	4.4x10 ⁻⁸	EVA-	10	7.9x10 ⁻⁹
Modified	20	2.4x10 ⁻⁸	Modified	20	1.0x10 ⁻⁸
PAE-	10	3.8x10 ⁻⁸	PAE-	10	6.2x10 ⁻⁹
Modified	20	4.4x10 ⁻⁸	Modified	20	5.8x10 ⁻⁹



Figure 4.61 Chloride ion permeability of latex-modified mortars with polymer-cement ratio of 15%. (© 1990, American Concrete Institute, reprinted with permission.)
Three of		Overlay	Ago at	Chloride
Project	Location	Thickness ^a	Age at	Permeability
Floject		(mm)	Iest	(coulombs) ^b
Bridge	Indiana	35.0	5 months	524
		44.5		302
		47.6		346
		35.0		257
		38.0		214
		31.7		323
		38.0		285
		44.5		274
		38.0		419
		38.0		310
Bridge	Pennsylvania	47.6	6 years	243
		47.6		215
		44.5		366
		41.3		160
		47.6		249
		50.8		104
		47.6		269
Parking	Pennsylvania	50.8	4 months	619
Garage		50.8	4 months	538
Bridge	Washington	50.8	5 months	260
		50.8	5 months	260
Bridge	Illinois	50.8	4 years	287
		50.8	4 years	277
Bridge	Illinois	50.8	3 years	433
		50.8	3 years	441
Stadium	Illinois	50.8	3 years	48
		50.8	-	65
		50.8		43
		50.8		65
		50.8		26
Parking	North	50.8	2 years	397
Garage	Dakota	50.8	2 years	379

Table 4.13 Chloride Ion Permeability of Field-Placed SBR Latex-Modified Concrete Overlays. (© 1993, ASTM, reprinted with permission.)

^aAll samples were 50.8mm thick when tested; therefore some samples contained conventional deck concrete.

^bChloride permeability ratings are as follows:

Chloride	Total Charge Passed
Permeability	(Coulombs)
High	4000
Moderate	2000 - 4000
Low	1000 - 2000
Very Low	100 - 1000
Negligible	Below 100

polymer-cement ratio, depending on the type of polymers and carbon dioxide exposure conditions. The carbonation resistance is also the most important factor in the corrosion of reinforcing bars as well as the resistance to chloride ion penetration. Figs. 4.62 and $4.63^{[105][106]}$ illustrate the carbonation depths of latex-modified mortars under accelerated carbonation at 30°C, 50% R.H., and a CO₂ gas concentration of 5.0% and after 10-year outdoor and indoor exposures, respectively. Ohama and Demura^[105] found that the carbonation depth of the latex-modified mortars through outdoor exposure can be predicted by the following equation as for ordinary cement mortar and concrete:

$$C = a\sqrt{t} + b$$

where C is the carbonation depth of the latex-modified mortars, t is outdoor exposure period, a is carbonation rate coefficient, and b is an empirical constant.

Latex-modified mortar and concrete also have an excellent oxygen diffusion resistance, since they have an impermeable structure as stated above. Figure $4.64^{[107]}$ represents the effect of the polymer-cement ratio on the oxygen diffusion coefficient of latex-modified mortars. Such excellent oxygen diffusion resistance is found to contribute to the prevention of the rust formation in the corrosion of reinforcing bars in reinforced concrete structures.

In recent years, various latex-modified mortars or pastes have widely been used as repair materials for reinforced concrete structures because of their superior resistance to chloride ion penetration, carbonation, and oxygen diffusion as mentioned above. Rust-inhibitors such as calcium nitrite [Ca(NO₂)₂] and lithium nitrite (LiNO₂) are often added to the latexmodified mortars or pastes to improve their corrosion-inhibiting property. Figure 4.65^[108] represents the effects of polymer-cement ratio and calcium nitrite content on the corrosion rate of reinforcing bars embedded in the latex-modified mortar with calcium nitrite as repair mortars. The corrosion-inhibiting property of the latex-modified mortars as repair mortars for reinforced concrete structures is considerably improved with rising polymer-cement ratio and calcium nitrite content. The corrosion-inhibiting property at low polymer-cement ratio is remarkably improved by the addition of calcium nitrite without increasing polymer-cement ratio. Ohama,^[108] et al. reported that a difference in the corrosion-inhibiting property between the calcium nitrite and lithium nitrite as rust-inhibitors is hardly recognized.



Figure 4.62 Exposure period vs. carbonation depth of latex-modified mortars under accelerated carbonation.



Figure 4.63 Carbonation depth of latex-modified mortars after 10-year outdoor and indoor exposures.



Figure 4.64 Effect of polymer-cement ratio on oxygen diffusion coefficient of latex-modified mortars.



Ca(NO2)2 Content , wt% of Cement

Figure 4.65 Effects of polymer-cement ratio and calcium nitrite content on corrosion rate of reinforcing bars embedded in latex-modified mortars containing calcium nitrite.

2.11 Frost Resistance and Weatherability

Latex-modified mortar and concrete have improved resistance to freezing and thawing, i.e., frost attack, over conventional mortar and concrete. This is due to the reduction of porosity as a result of decreased water-cement ratio and filling of pores by polymers, and the air entrainment introduced by polymers and surfactants. Figures 4.66 and 4.67 represent the freeze-thaw durability in water (-18 to 4°C) of combined water and dry-cured SBR-, PAE-, and EVA-modified mortars.^[109] The frost resistance of SBR-, PAE-, and EVA-modified mortars is improved markedly at polymer-cement ratios of 5% or more. As the degree of expansion by frost (calculated



Figure 4.66 Number of cycles of freezing and thawing vs. relative dynamic modulus of elasticity of latex-modified mortars.



Figure 4.67 Number of cycles of freezing and thawing vs. degree of expansion due to frost of latex-modified mortars.

from the residual expansion of specimens after thawing) is increased, the relative dynamic modulus of elasticity of SBR-, PAE-, and EVA-modified mortars is reduced. Increasing polymer-cement ratio of the latex-modified mortars does not necessarily cause an improvement in the frost resistance. Accordingly, good frost resistance should be obtained by the composite effects of polymer modification and air entrainment.

According to the data of Solomatov^[110] on latex-modified concrete using a copolymer of vinyl acetate and didutyl maleate, the wet-cured concrete is more liable to be affected by freeze-thaw cycles than the drycured concrete.

A few studies on the frost resistance of latex-modified mortar and concrete have been conducted in chloride^[111] and sulfate^[110] solutions.

Figure 4.68^[102] illustrates the weatherability of five types of latexmodified mortars with a polymer-cement ratio of 15%, assessed by measuring a flexural strength retention after 336 accelerated weathering (4hour-60°C-ultraviolet light plus 4-hour-50°C-100% R.H. exposure) cycles.



Figure 4.68 Weatherability of latex-modified mortars with polymer-cement ratio of 15%. (© 1990, American Concrete Institute, reprinted with permission.)

Generally, the latex-modified mortars provide the high retention of flexural strength. SBR-and PAE-modified mortars have a higher weatherability than the other latex-modified mortars.

In the early 1980s, the corrosion of structural steel supports due to chloride ions liberated from PVDC-modified mortar which had been used to repair an old brick building, led to a civil suit in the United States;^[112] therefore, PVDC latex is not currently used as a cement modifier in the United States and other countries. In a laboratory study, the liberation of chloride ions is observed in such a chloride-containing polymer, and a possibility of the corrosion of the reinforcing bars which is induced by the chloride ions in reinforced concrete structures is suggested.^[113][^{114]} The use of PVDC-modified mortars with polymer-cement ratios of 5% or more causes the liberation of sufficient chloride ions to exceed the tolerable corrosion limits for the reinforcing bars in reinforced concrete structure.

Under long-term outdoor exposure, involving frost action and carbonation, latex-modified mortar shows increased resistance to weathering in comparison with conventional mortar and concrete. The weatherability of the latex-modified mortars is shown in Fig. 4.69.^[106] The exposure test was done at the Building Research Institute Outdoor Exposure Site in Ibaraki Prefecture, Japan. Except for PVAC-modified mortars, the flexural and compressive strengths of most latex-modified mortars under outdoor exposure conditions tend to become nearly constant at one year or more, and a weatherability factor is greater or similar to that of unmodified mortar.

Durability of latex-modified mortars in terms of the adhesion (to ordinary cement mortar) after 10-year outdoor exposure in Tokyo is shown in Fig. 4.70.^[115] In contrast to unmodified mortar-bonded specimens which failed within one year of outdoor exposure, most latex-modified mortar-bonded specimens had a satisfactory adhesion for practical use after the 10-year exposure.

In the United States, SBR-modified concrete has been used as an overlay for highway bridge decks over the past 20 years since its first application to a bridge deck in Virginia^[116] in 1969. Sprinkel^[117] investigated the performance of 14 bridge decks with SBR-modified concrete overlays ranging in age 2 to 20 years, and reported that SBR-modified concrete overlays are performing satisfactorily compared to ordinary cement concrete overlays. In particular, SBR-modified concrete overlays placed on decks with chloride ion contents of less than 1.2 kg/m³ at the reinforcing bars can be expected to have a service life exceeding 20 years.



Figure 4.69 Weatherability of latex-modified mortars.



Figure 4.70 Adhesion durability of latex-modified mortars.

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Fabrication and Properties of Redispersible Polymer Powder-Modified Systems

1.0 FABRICATION

1.1 Manufacture of Redispersible Polymer Powders

In general, redispersible polymer powders as cement modifiers are manufactured by a two-step process. Firstly, polymer latexes as raw materials are made by emulsion polymerization, and then are spray-dried, using the system as illustrated in Fig. 5.1,^[1] to get the polymer powders. An example of the recipe for the emulsion polymerization of typical poly(ethylene-vinyl acetate) (EVA) latex as the raw material is given in Table 5.1.^[1] Before spray drying, the latexes are formulated further with some ingredients such as bactericides, spray drying aids and antifoaming agents. Anti-blocking aids such as clay, silica, and calcium carbonate are added to the polymer powders during or after spray drying to prevent "caking" of the powders during storage.



Figure 5.1 Spray drying system for redispersible polymer powders. (© 1990, American Concrete Institute, reprinted with permission.)

Table 5.1Recipe for Emulsion Polymerization of Typical EVA Latex for
Redispersible EVA Powder. (© 1990, American Concrete
Institute, reprinted with permission.)

Raw Material	Parts by Weight
Vinyl Acetate	80-90
Ethylene	20-10
Polyvinyl Alcohol	4-10
Catalyst System	<2
Water	80-100

1.2 Process Technology

The fabrication technique of redispersible polymer powder-modified mortar and concrete is about the same as that for latex-modified mortar and concrete. The materials and mix proportions used in this modified mortar and concrete are the same as those used in the latex-modified systems except that the addition of the redispersible polymer powders is involved. At present, commercially available redispersible polymer powders as cement modifiers are classified in Fig. 5.2. Table 5.2 gives the properties of typical redispersible polymer powders. The redispersible polymer powders are usually free-flowing powders, and have ash contents of 5 to 15%, which primarily come from the anti-blocking aids. When the polymer powders are placed in water under agitation, they redisperse or re-emulsify easily, and provide the polymer latexes with polymer particle sizes of 1 to 10 μ m.

Generally, redispersible polymer powders are dry blended with cement and aggregate mixtures, followed by wet mixing with water. During the wet mixing, the redispersible polymer powders are redispersed or reemulsified. If necessary, powder or liquid antifoaming agents are added to the wet mix. Tables 5.3 to $5.5^{[1]}$ give the typical mix proportions of self-leveling floor overlay, ceramic tile adhesive, and patching mortar using redispersible EVA powders, respectively. The curing of the modified systems is similar to that of latex-modified systems.

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Figure 5.2 Commercially available redispersible polymer powders for cement modifiers.

	Type of Redispersible Polymer Powder			
	VA/VeoVa	EVA	PAE	SBR
Appearance	White Powder	White Powder	White Powder	White Powder
Average Particle Size (µm)	10 - 250	70	45 - 75	5 - 50
Bulk Density (g/cm ³)	0.54 - 0.64	0.40	0.31 - 0.51	0.40
pH (redispersed, 50 % solids)	4	5 - 6	10 - 12	7 - 8

 Table 5.3
 Self-Leveling Floor Overlay Using Redispersible EVA Powder.

 (© 1990, American Concrete Institute, reprinted with permission.)

Raw Material	Parts by Weight	
Portland Cement	70.0	
Alumina Cement	25.0	
Gypsum	5.0	
Fine Silica Sand	70.0	
Calcium Carbonate	20.0	
Superplasticizer (Powder)	1.0	
Rheology Modifier	0.1	
Redispersible EVA Powder	10.0	
Water	≈50.0	

Table 5.4Ceramic Tile Adhesive Using Redispersible EVA Powder. (©
1990, American Concrete Institute, reprinted with permission.)

Raw Material	Parts by Weight	
Portland Cement	100.0	
Fine Silica Sand	100.0	
Cellulosic Thickener	0.2	
Redispersible EVA Powder	10.0	
Water	≈45.0	

 Table 5.5
 Patching Mortar Using Redispersible EVA Powder. (© 1990, American Concrete Institute, reprinted with permission.)

Raw Material	Parts by Weight	
Portland Cement	100.0	
Graded Silica Sand	250.0	
(ASTM C 33)		
Redispersible EVA Powder	10.0	
Water	≈38.0	

2.0 **PROPERTIES**

Similar to latex-modified systems, the properties of redispersible polymer powder-modified systems are improved in comparison with ordinary cement mortar and concrete, and these depend on the nature of polymer and polymer-cement ratio. Figs. 5.3 to 5.5^[1] represent the strengths, adhesion to cement mortar, water resistance, and water absorption of the redispersible polymer powder-modified mortars. The properties are improved with an increase in the polymer-cement ratio. This tendency is very similar to that of the latex-modified systems. In general, the redispersible polymer powder-modified mortars are inferior to SBR-modified mortar (control) in certain properties. VA/VeoVa powder-modified mortars show better properties than EVA powder-modified mortars as seen in Fig. 5.5. The film formation characteristics of recent redispersible polymer powders for cement modifiers are improved, and continuous polymer films can be found in the redispersible polymer powder-modified systems as seen in Fig. 5.6. This contributes greatly to improvements in their properties.



Figure 5.3 Polymer-cement ratio vs. flexural and compressive strengths of redispersible polymer powder-modified mortars.



Figure 5.4 Water resistance of redispersible polymer powder-modified mortars, evaluated by adhesion change with water immersion.



Figure 5.5 Polymer-cement ratio vs. water absorption of redispersible polymer powder-modified mortars.



x400

Figure 5.6 Electron micrograph of polymer films formed in redispersible EVA powder-modified mortar.

According to a recent study, Bright, et al.^[3] compared the physical properties of various latex-modified mortars and redispersible EVA powder-modified mortars, and showed that the properties of EVA powdermodified mortars are at least equal to those of the latex-modified mortars as seen in Figs. 5.7 to 5.9^[3] Figure 5.10 exhibits the strength properties of patching mortars using redispersible polymer powders.^[4]

Lambe, et al.^{[5][6]} reported that repair mortars using redispersible polymer powders for concrete structures show high resistance to the diffusion of chloride ions, oxygen and carbon dioxide, and also low shrinkage.

Afridi, et al.^[7] found that redispersible polymer powder-modified mortars provide a freeze-thaw durability similar to that of latex-modified mortars. Fig. 5.11 shows the polymer-cement ratio vs. freeze-thaw durability of redispersible polymer powder- and latex-modified mortars.^[7] Figure 5.12 shows the weatherability of patching mortars using redispersible polymer powders.^[4]



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Polymer-Modified Concrete and Mortars

Type of Mortar

Figure 5.7 Comparison of tensile strength of latex- and redispersible EVA powder-modified mortars. (© 1993, ASTM, reprinted with permission.)



Figure 5.8 Comparison of adhesion of latex- and redispersible EVA powder-modified mortars. (© 1993, ASTM, reprinted with permission.)





Figure 5.9 Comparison of abrasion resistance of latex- and redispersible EVA powder-modified mortars. (© 1993, ASTM, reprinted with permission.)



Type of Mortar

Figure 5.10 Strength properties of patching mortars using redispersible polymer powders with polymer-cement ratio of 10%. (© 1993, ASTM, reprinted with permission.)


Figure 5.11 Polymer-cement ratio vs. freeze-thaw durability of redispersible polymer powder-and latex-modified mortars.



Figure 5.12 Weatherability of patching materials using redispersible polymer powders with polymer-cement ratio of 10%. (© 1993, ASTM, reprinted with permission.)

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Schneider, et al.^[8] examined the effect of glass transition temperature (Tg) on the adhesion (to plywood) and flexibility of redispersible EVA powder-modified mortars for plywood substrates, and found that EVA powder with a glass transition temperature of -10° C is more effective than one with a glass transition temperature of 10° C.

Redispersible polymer powders are widely used to produce prepackaged-type products such as decorative wall coatings, ceramic tile adhesives, self-leveling floor overlays, and patching mortars for concrete structures.

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Fabrication and Properties of Water-Soluble Polymer-Modified Systems

1.0 FABRICATION

In the fabrication of water-soluble polymer-modified mortar and concrete, the materials and their mix proportions conform to the procedures for ordinary cement mortar and concrete. Small amounts of the polymers are added in the form of powders or aqueous solutions to cement mortar and concrete during mixing. When added in the powder form, it is advisable to dry-blend the polymers with the cement-aggregate mixtures, and then to mix them with water. The water-soluble polymers are normally used at polymer-cement ratios less than 3%, and their main effect is to improve workability. The water-soluble polymers employed as cement modifiers are cellulose derivatives including methyl cellulose (MC), carboxymethyl cellulose (CMC) and hydroxyethyl cellulose (HEC), polyvinyl alcohol (PVA, poval), polyethylene oxide, polyacrylamide, etc. The water-soluble polymer-modified mortar and concrete are easily handled during mixing, troweling, or placing, as ordinary cement mortar and concrete. No special curing is required for the modified systems.

2.0 **PROPERTIES**

Water-soluble polymer-modified systems are generally used at very low polymer-cement ratios for improved workability. The consistency of the water-soluble polymer-modified systems is markedly improved at lower water-cement ratios over that of ordinary cement mortar and concrete, because of the plasticizing and air-entraining effects of the polymers. As seen in Fig. $6.1^{[1]}$ and Table 6.1,^[2] the modified systems show a remarkably higher water retention than the ordinary cement systems, and the water retention is raised with increasing polymer-cement ratio. This may contribute greatly to an improvement in workability and the prevention of *dry-out*, and also leads to superior adhesion to porous substrates such as ceramic tiles, mortars, and concretes. This trend can be recognized in Table 6.1. The adhesion to tiles is increased with a rise in the polymer-cement ratio. Usually, the setting of the modified systems is delayed to a certain extent compared to the ordinary cement systems, depending on the polymer type and polymer-cement ratio.^{[3][4]}

The strength properties of water-soluble polymer-modified mortars are shown in Tables 6.1 and 6.2.^[4] The tensile, flexural, and compressive strengths normally tend to decrease with the addition of the polymers. Such strength reduction is opposite to the results obtained in latex- or liquid resimmodified systems.

As shown in Table 6.1, the water absorption of methyl cellulosemodified systems increases with rising polymer-cement ratio. By contrast, the water permeation decreases with an increase in the polymer-cement ratio, as represented in Fig. 6.2.^[1] Methyl cellulose causes a considerable swelling due to water absorption, and seals capillary cavities in the modified systems, and hence decreases permeability.

The drying shrinkage of water-soluble polymer-modified systems is generally larger than that of unmodified systems.^[4] However, methyl cellulose-modified systems exhibit a smaller drying shrinkage than the unmodified systems as shown in Fig. 6.3.^[5] The drying shrinkage is reduced with an increase in the polymer-cement ratio.



FOR MASONRY CEMENT)

Figure 6.1 Suction time vs. water retention of methyl cellulose-modified mortars.

		Polymer- Cement Ratio (%)	Water- Cement Ratio (%)	Water Retention (%)	Tensile Strength (kgf/cm ²)	Adhesion to Tile (kgf/cm ²)	Water Absorption (%)
		0.0	56.0	84.2	25.4	2.5	8.2
		0.1	30.9	92.5	32.8	16.2	4.6
Paste		0.2	31.2	96.4	32.1	20.1	4.8
		0.5	33.5	97.5	38.4	32.2	4.8
		1.0	38.0	99.1	35.1	23.1	6.1
.	Cement · Sand	0.0	56.0	84.2	25.4	2.5	8.2
		0.2	76.2	96.3	21.2	6.5	12.1
Mortar	=1.2	1.0	74.2	99.9	18.1	8.3	14.5
		0.0	85.0	73.2	14.3	1.6	10.9
	Cement : Sand	0.2	79.8	82.5	12.5	6.4	13.2
	=1:3	0.5	80.8	93.1	11.2	6.6	12.8
		1.0	90.3	97.4	11.3	8.3	14.3

	Polymer-	Flexu	ral Strength (k	gf/cm ²)	Compre	ssive Strength	(kgf/cm ²)
Type of Mortar	Cement [–] Ratio (%)	3 Days	7 Days	28 Days	3 Days	7 Days	28 Days
Unmodified	0.00	26.9	43.8	69.6	112	223	408
Hydroxy Ethyl Cellulose- Modified	0.39	13.7	32.3	50.9	42	129	252
Poval-Modified (A)	0.39	23.0	33.4	48.5	78	128	223
Poval-Modified (B)	1.12	17.1	27.9	39.6	51	99	185
Polyacrylamide- Modified	0.46	22.3	36.8	62.3	80	170	320
Polyethylene Oxide-Modified	0.06	27.5	42.6	62.8	103	189	320

 Table 6.2
 Flexural and Compressive Strengths of Water-Soluble Polymer-Modified Mortars.

Cement : Standard Sand = 1:2 (by Weight)

Water-Cement Ratio = 65.0%

1-Day-20°C-Moist plus 27-Day-20°C-Water Cure



Figure 6.2 Polymer-cement ratio vs. relative water permeation of methyl cellulosemodified mortars.



Figure 6.3 Relationship between dry curing period and drying shrinkage of methyl cellulose- modified mortars.

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Fabrication and Properties of Liquid Resin and Monomer-Modified Systems

1.0 EPOXY-MODIFIED SYSTEMS

1.1 Epoxy Modifiers

7

Most liquid epoxy resins for cement-modifiers are synthesized by the reaction of one molecule of bisphenol with two molecules of epichlorohydrin, and contain two functional groups, i.e., epoxide and hydroxyl groups. Figure 7.1 illustrates the chemical structure of a typical bisphenol A-type epoxy resin, diglycidyl ether of bisphenol A (DGEBA). The epoxy resins react with hardeners or curing agents such as amines and polyamides, and harden to form the thermosetting polymers with network structures. In general, epoxy resin systems as cement modifiers are supplied as two-part systems which consist of epoxy resin parts and hardener or curing agent parts, and contain surfactants to effectively disperse the epoxy resins throughout the mortars or concretes and antifoaming agents to prevent excessive air entrainment.



Figure 7.1 Chemical structure of typical epoxy resin.

1.2 Process Technology

The first patent of an epoxy-modified system was taken by Donnelly in 1965.^[1] According to this patent, in the preparation of the epoxymodified system, bisphenol A-type epoxy-curing agent mixture is first emulsified with water, and then mixed with the cement-aggregate-water premixture. The polymer-cement ratio varies widely in the system. Like Estercrete, polymerization and cement hydration occur at the same time in this system. Valenta^[2] carried out a detailed study on various emulsifiers. The mixing procedures for the epoxy-modified systems was fairly complicated in the early stage of their development. Recently, however, the procedures have been improved to a considerable extent. The incorporation of the epoxy modifiers into mortars and concretes does not require significant changes in the process technology compared to other cement modifiers. The mix proportioning of the epoxy-modified systems is similar to that of latexmodified systems. In some past investigations, the optimum polymer-cement ratios for the epoxy-modified systems were recommended as follows:

Raff and Austin ^[3]	30% or more
Sun, et al. ^[4]	50% or more
Nawy, et al. ^[5]	30 to 45%
McClain ^[6]	20%

Recently, the useful polymer-cement ratios appear to be 15 to 20% as shown in Table 7.1.^[7] The unit cement content of the epoxy-modified systems is generally in the range of 356 to 415 kg/m³, and their water-cement ratio is about 30%.^[7] In the recommended mixing procedure for epoxy-modified systems, the cement, aggregates, and half of the mixing water are mixed first, and then the epoxy resin-hardener premixture and the remainder of the mixing water are thoroughly mixed with the cement-aggregate-water mixture. Also, the epoxy resin-hardener premixture can be added to the ready-mixed concrete in the agitating trucks at the job site.

Table 7.1Typical Mix Proportions of Epoxy-Modified Concrete. (©
1987, American Concrete Institute, reprinted with permission.)

Material	Parts by Weight
Ordinary Portland Cement	317
Fine Aggregate	873
Coarse Aggregate (Pea gravel, maximum size, 10mm)	657
Epoxy Resin-Hardener Mixture	57
Water	83

1.3 Properties

Epoxy-modified systems harden by the simultaneous progress of cement hydration and epoxy polymerization. The hardened or cured epoxy resins form irregular thin epoxy layers on the cement hydrates, and the epoxy layers bind the cement hydrates together to form a network structure in which the epoxy phase interweaves throughout the cement hydrate phase.^[8]-^[10] This network structure acts as a matrix phase for the epoxy-modified systems, and the aggregates are bound by the matrix as seen in Fig. 7.2. The internal structure is similar to that of latex-modified systems which means that they develop high strength and adhesion, low permeability, good water resistance, and chemical resistance like latex-modified systems. Table 7.2^[6] compares the properties of the typical epoxy-modified concrete (using a water-reducible epoxy resin) with those of an unmodified concrete. A major advantage of these systems is their ability to be cured under moist or wet conditions.



x 700

Figure 7.2 Electron micrograph of epoxy-modified mortar.

	Туре о	f Concrete	
Property	Epoxy-Modified Concrete	28-Day Water-Cured Unmodified Concrete	
Tensile Strength (kgf/cm ²)	57.6 (51.3) ^a	30.9 (32.3) ^a	
Flexural Strength (kgf/cm ²)	115 (114) ^a	59.8 (60.5) ^a	
Compressive Strength (kgf/cm ²)	527 (492) ^a	387 (429) ^a	
Modulus of Elasticity (kgf/cm ²)	19.0 x 10 ⁴	21.8 x 10 ⁴	
Shear Strength (kgf/cm ²)	45.0	7.03	
Setting Shrinkage (%)	0.03		
Coefficient of Linear Thermal Expansion (cm/cm/°C)	1.4 x 10 ⁻⁵	1.1 x 10 ⁻⁵	
Resistance to Freezing and Thawing	No effect at 50 cycles	Pronounced scaling at 20 cycles	
Wear Resistance (steel wheel passes necessary for 1cm wear)	7700	2400	
Chemical (water, 5% NaOH, Resistance (bleach, or detergent)	Very gradual penetration	Rapid penetration	
(15% hydrochloric acid, 10% citric acid, or 25% acetic acid	Slow effervescence	Rapid disintegration	

Table 7.2	Properties of a Typical Epoxy-Modified Concrete in Comparison
	with Those of an Unmodified Concrete.

^a Strength after 28-day water immersion.

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Popovics et al.^[11] showed that the incorporation of epoxy resin into portland cement pastes and mortars produces a decrease in the degree of hydration of the cement, probably because covering the cement particles with the epoxy resin reduces the contact between the cement and water. As a result, the addition of the epoxy resin retards the setting or hardening of the pastes and mortars. Furthermore, he detected by a silylation method that there is no chemical reaction between the epoxy resin and calcium silicates in the cement. Popovics^[12] suggested the use of accelerators in epoxymodified systems, and found that their strength reduction can be counterbalanced by a suitable accelerator. The addition of concrete admixtures such as fly ash, silica fume, and superplasticizers to epoxy-modified systems were reported by him to improve their strength.^{[13][14]} Figure 7.3 illustrates the effect of fly ash on the compressive strength of the epoxy-modified concrete.^[4]

In recent years, there have been some interesting developments in epoxy-modified mortar and concrete in Germany. The developments include a one-component epoxy resin system for the cement modifier^[15] and a dry mortar using epoxy resin.^[16] The former does not need any hardeners added at the construction site. The latter is produced as a dry mixture of an epoxy resin with a hardener, cement, and aggregates, and can be applied by adding only water in the field.

In the process technology of conventional polymer-modified mortars using epoxy resin, the use of a hardener or curing agent has been considered indispensable for the hardening of the epoxy resin. Recently, Ohama et al. noticed that the hardening of epoxy resin occurs in the presence of alkalis in cement mortar as shown in Fig. 7.4,^{[17][18]} and conducted a unique study on epoxy-modified mortars.^[19] According to the results of the study, the epoxy-modified mortars using the epoxy resin without any hardener are successfully made, and have some superior properties compared to conventional epoxy-modified mortars, as represented in Figs. 7.5 to 7.8.^[19] It is concluded that polymer-cement ratios of 5 to 10% are considered optimum for the preparation of such epoxy-modified mortars.



Figure 7.3 Compressive strength of epoxy-modified concretes.



Figure 7.4 Hardening reaction of epoxy resin in presence of alkali from cement hydration.



Figure 7.5 Polymer-cement ratio vs. flexural strength of epoxy-modified mortars without and with hardener.



Figure 7.6 Polymer-cement ratio vs. adhesion in tension to ordinary cement mortar of epoxy-modified mortars without and with hardener.



Figure 7.7 Polymer-cement ratio vs. 28-day drying shrinkage of epoxy-modified mortars without and with hardener.



______0 70 80

Figure 7.8 Polymer-cement ratio vs. chloride ion penetration depth and carbonation depth of epoxy-modified mortars without and with hardener.

2.0 POLYESTER-MODIFIED SYSTEMS

In the late 1960s, Nutt developed an unsaturated polyester-modified system^{[20][21]} called "Estercrete." In the preparation of this system, unsaturated polyester resin dissolved in styrene is mixed with portland cement at a polymer-cement ratio higher than 30%, together with a water-soluble redox catalyst. Table $7.3^{[20]}$ gives the typical formulations of Estercrete.

Material	Parts by Weight
Polvester Resin	50-70
Unsaturated Monomer (styrene)	25-65
Powdered Ammonium Persulfate	3-5
Powdered Sodium Bisulfite	1-3
Portland Cement (with stearic acid)	80-150

 Table 7.3
 Typical Formulations of Estercrete for Mortar Coating.

The resin can be produced using a wide range of polycarboxylic acids and polyhydric alcohol by polycondensation. Immediately before use, it is mixed with aggregates and water. When the catalyst is activated by the addition of the water, polymerization and cement hydration occur simultaneously. The optimum water-cement ratio is about 22%. The aggregate content can be selected depending on the application.

Estercrete has many advantages such as rapid setting and high strength development, high bond strength to concrete and good durability including water resistance, chemical resistance, abrasion resistance, and thermal resistance, in comparison with those of latex-modified systems. The strength properties of Estercrete with typical mix proportions are given in Table 7.4.^[22]

Similar systems have also been examined by Dikeou, Steinberg, et al.,^[23] Samy Abdel Monem El-Garf,^[24] Birkimer and Lindeman,^[25] and Ye and Wu.^[26] Figure 7.9 represents the effects of curing conditions on the strength development of polyester-modified mortars.

Table 7.4	Strength of	Estercrete	Mortar.
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Age (days)	Compressive Strength (kgf/cm ²)	Tensile Strength (kgf/cm ²)
1	175	28
7	262	38
14	280	40
28	350	44



C, 1-day-20°C-moist (in molds) plus 1-day-60°C- hot water plus 12-day-20°C-water cure
 20°C-dry cure to desired age

Figure 7.9 Effects of curing conditions on strength development of polyestermodified mortars. (© 1990, International Academic Publishers, reprinted with permission.)

3.0 POLYURETHANE-MODIFIED SYSTEMS

The first patent of a polyurethane-modified system was taken by Szukiewicz^[27] in 1959. Another system modified with a polyurethane resin was patented by Shearing^[28] in 1970. In 1969, Ohama reported the results of a wide-ranging study of a polyurethane-modified mortar system,^[29] and this product now is commercially available in Japan. The product consists of three components, i.e., promoter, polyol, and polyisocyanate. The modified system is prepared by the following procedure: cement and sand are dry-blended, the promoter component is added to the cement-sand mixture, and then the polyol component is blended with the mixture. Finally, the polyisocyanate component is mixed with the cement-sand-promoter-polyol mixture until a uniform mortar is obtained.

The main advantage of polyurethane-modified mortar is an improvement in the strength development at low temperatures or under wet conditions, good adhesion to wet substrates, waterproofness, and abrasion resistance. The properties of the polyurethane-modified mortar are shown in Table 7.5.^[29]

	Type of N	fortar	
Property	Polyurethane-Modified Mortar	Unmodified Mortar	
Flexural Strength (kgf/cm ²)	174 (205) ^a	44 (47) ^a	
Compressive Strength (kgf/cm ²)	381 (412) ^a	157 (247) ^a	
Tensile Strength (kgf/cm ²)	76	19	
Modulus of Elasticity (kgf/cm ²)	5.25 x 10 ⁴	32.8 x 10 ⁴	
91-Day Drying Shrinkage	8.92 x 10 ⁻⁴	12.5 x 10 ⁻⁴	
Relative Water Absorption	0.03	1.00	
Relative Water Permeation	0.01	1.00	
Adhesion in Flexure (kgf/cm ²)	53	28	

Table 7.5Properties of a Typical Epoxy-Modified Concrete in Comparisonwith Those of an Unmodified Mortar.

a Water cure.

4.0 OTHER RESIN-MODIFIED SYSTEMS

Systems modified with thermosetting resins such as phenol formaldehyde and urea-formaldehyde (carbamide) resins have been developed by Russian workers,^[30] but they have not yet been commercialized.

5.0 MONOMER-MODIFIED SYSTEMS

The fabrication procedure of monomer-modified systems is similar to that of liquid resin-modified systems, except monomers are used instead of liquid resins. These systems are prepared by directly mixing the monomers with cement, aggregate, and water, followed by thermal-catalytic or radiation polymerization process. The polymerization occurs during and/or after the setting or hardening of the cement systems. Finally, the polymerization process converts the monomer-modified systems to polymer-modified systems.

The compressive strength of the polymer-modified systems using monomers, obtained by some investigators,^{[31]-[34]} is summarized in Table 7.6. As demonstrated in this table, it appears that improvements in strength properties are generally small, and are related to the interference effects of monomers on the cement hydration. Accordingly, such monomer-modified systems are not commercialized at present. In U.S.S.R., Leirikh^[34] reports a study in which the concrete modified with furfuryl alcohol and aniline hydrochloride provides pronounced improvements in the tensile and flexural strengths, bond to reinforcing bars, watertightness, chemical resistance, and freeze-thaw durability. The strength properties of the furfuryl alcohol-modified concrete cured under various conditions are shown in Table 7.7.^[34] In other investigations, it is reported that the use of furfuryl alcohol in concrete contributes to the strength properties only to a small extent.^{[35][36]}

			Com	pressive	Streng	th (kgf/c	cm²)	
Curing Method		Rª	R	Τp	R	Т	R	т
Polymer-Cement Ratio (%)		25-30	20	20	5	5	10	10
Type of Monomer- Modified Concrete	Unmodified (Control)	269	550	550	372	280	496	509
	Methyl methacrylate- Modified	С	360	291	399	294	433	380
	Styrene- modified	300	756	707	328	311	499	401
	Acrylonitrile- modified	462	-	-	374	263	-	-
	Vinyl acetate- modified	-	-	-	287	207	-	-
	Polyester-styrene- modified	-	-	-	140	76	-	-
Reference	Reference No.		(32)	(32)	(33)	(33)	(34)	(34)

Table 7.6 Compressive Strength of Polymer-Modified Concretes Using Monomers.

^aRadiation.

^b Thermal-catalytic.

^c No test due to premature failure.

Curing Condition	Compressive Strength (kgf/cm ²)			Tensile Strength (kgf/cm ²)			Flexural Strength (kgf/cm ²)		
<u> </u>	1 day	28 days	1 year	1 day	28 days	1 year	1 day	28 days	1 year
Moist Medium	-	247	330	-	18	27	-	37	55
Fast Steaming	140	267	364	10	17	27	20	34	54
Steaming	140	224	300	6	14	27	13	28	54
Moist Medium	-	227	380	-	18	32	-	36	65
Fast Steaming	190	278	383	16	20	33	32	40	66
Steaming	200	267	387	15	18	30	30	36	60

Table 7.7 Strength Properties of Furfuryl Alcohol-Modified Concrete.

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Special Polymer-Modified Systems

1.0 HYDRATED-TYPE FLEXIBLE WATERPROOFING MATERIALS

Hydrated-type flexible waterproofing materials are polymer-modified pastes or slurries with very high polymer-cement ratios of 50% or more, sometimes 100% or more, and have been widely used as liquid-applied membrane waterproofing materials, repair materials, etc. for apartment houses, silos, underground tanks, etc. in Japan and Germany.^{[1]-[4]} The flexible waterproofing materials consist of portland cement or alumina cement, silica sand, polymer latexes such as SBR, PAE, EVA, SAE, epoxy and asphalt latexes, water and various additives. They form flexible waterproofing membranes with thicknesses of 2 to 4 mm and, generally, they are manufactured as prepackaged-type products. In Japan, more than 2 million m² of reinforced concrete substrates are applied as flexible waterproofing materials each year, and the demand for the materials reaches 7000 tons or more per year.^[2] Their performance advantages are as follows :

- a. Safe application due to no organic solvent systems.
- b. Application and good adhesion without considering the moisture conditions of the substrates.
- c. Excellent elongation, flexibility, and crack resistance.
- d. Good waterproofness, resistance to chloride ion penetration, and carbonation resistance.

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Figure 8.1 represents the elongation of hydrated-type flexible waterproofing materials.^[1] PAE-modified waterproofing materials appear to have excellent elongation and water resistance. The crack-bridging capacity of flexible waterproofing materials, which is most important, is being successfully tested in Germany.^[5] Flexible waterproofing materials with the properties shown in Fig. 8.2 are currently used for inhibiting alkali-aggregate reaction in reinforced concrete structures in Japan.^[6]

In Japan, an interesting flexible waterproofing material which solidifies in water has recently been developed by Moriyoshi, et al.,^[7] and has potential as a shock-absorbing, waterproof backfill material for tunnels and dams. The material is composed of an asphalt emulsion, a superabsorbent polymer emulsion, and cement.



Figure 8.1 Elongation of hydrated-type flexible waterproofing materials.



Figure 8.2 Polymer-cement ratio vs. elongation, adhesion and water permeability of hydrated-type flexible waterproofing materials. (\bigcirc 1993, ASTM, reprinted with permission.)
2.0 ULTRARAPID-HARDENING POLYMER-MODIFIED CONCRETES

Ultrarapid-hardening polymer-modified concretes have been developed for the past several years in Japan, and are classified into two types; a shotcrete system using an ambient-temperature–polymerizable monomer which reacts with ordinary portland cement, and a concrete system using ultrarapid-hardening cement. The former is prepared by mixing cement concrete with a magnesium acrylate monomer, and its setting time can be controlled within a few seconds or less. Figure 8.3 represents the schematic diagram of this shotcrete system.^[8] The shotcrete system is employed as repair and protective material for concrete structures with leaking and flowing water. The latter system is produced by modifying ultrarapidhardening cement concrete with SBR latex, and is often used for urgent construction works such as repairs or overlays of roads.^[9] Figure 8.4 shows the relation between polymer-cement ratio and tensile and flexural strengths of the ultrarapid-hardening SBR-modified concrete.^[9]

3.0 POLYMER-FERROCEMENTS

Ferrocements are composite materials consisting of cement mortar and reinforcement in the form of multiple layers. The ferrocements have been used for housing units, water tanks, roofings, and grain silos because of their excellent toughness, crack control, and impact resistance, but they easily form cracks under small load because cement mortar with low tensile strength has conventionally been used as a matrix. For the purpose of improving the flexural behavior and durability of the conventional ferrocements, polymer-ferrocements have been developed using latex-modified mortars instead of the ordinary cement mortar as matrixes. In particular, the use of SBR- and EVA-modified mortars as the matrixes is very effective in improving their flexural behavior,^[10] impact resistance,^[11] drying shrinkage,^[12] and durability.^[13] Incorporation of short fibers such as steel and carbon fibers into the latex-modified mortars is also effective for further improving the flexural behavior. Figure 8.5 illustrates the comparison of the flexural behavior of the polymer-ferrocements using SBRmodified mortar, steel fiber reinforced SBR-modified mortar, and carbon fiber reinforced cement as their matrixes.^[14]



^b SPS, Sodium persulfate

Figure 8.3 Schematic diagram of ultrarapid-hardening polymer-modified shotcrete system.



Figure 8.4 Relation between polymer-cement ratio and tensile and flexural strengths of ultrarapid-hardening SBR-modified concretes. (© 1989, Materials Research Society, reprinted with permission.)



^f CFRC. Carbon fiber reinforced cement

Figure 8.5 First crack stress and flexural strength of polymer-ferrocements.

4.0 MDF CEMENTS

An interesting current topic relating to the applications of watersoluble polymers is the development of MDF (macrodefect-free) cements, whose technical origin is traced back to a study by J. D. Birchall, et al. in 1981.^[15] MDF cements are composed of hydraulic cements (e.g., ordinary portland cement, alumina cement, etc.), water-soluble polymers (e.g., PVA, polyacrylamide, etc.) and proper admixtures, and processed as highly filled polymers with the cements, utilizing very low water-cement ratios of 10 to 20%. The materials have very high flexural strengths of 1000 kgf/cm² or more but very poor water resistance. For the purpose of improving the poor water resistance, some attempts such as latex modification,^[16] coupling agent addition,^[17] polymer impregnation,^[18] crosslinkage by an isocyanate,^[19] and silica fume addition,^[20] have been examined, but it seems that they have not yet succeeded. Consequently, MDF cement products have been used in very few applications. The polymer modification of DSP (densified system containing homogeneously arranged ultrafine particles) materials has also been tried to improve their mechanical properties.^[21]

Recently, it has been found that the use of alumina cement and autoclave cure after moist and heat cure are most effective for improving the water resistance of MDF cements.^[22] Figure 8.6^[22] shows the flexural strength of heat plus autoclave cured MDF cements using the alumina cement before and after 48-hour water immersion.

As MDF cements generally have very high flexural strength, it is expected that ideal composite materials can be made by reinforcing them with fibers. An example of the development of high flexural strength by the fiber reinforcement of MDF cements is demonstrated in Table 8.1.^[19]

5.0 ANTIWASHOUT UNDERWATER CONCRETES

In recent years, as concrete structures in harbor, bridge, and marine construction have become larger in the scale, the need for antiwashout underwater concretes to assure correct underwater placement has been increasing. The major requirements for the antiwashout underwater concretes are antiwashout or segregation resistance, flowability, self-leveling ability, and bleeding control. The antiwashout underwater concretes are produced by the addition of polymeric admixtures, namely antiwashout admixtures at polymer-cement ratios of 0.2 to 2.0% during the mixing of

ordinary cement concrete. The antiwashout admixtures are water-soluble polymers, and classified into two types, cellulose-type polymers such as MC and HEC, and polyacrylamide-type polymers such as polyacrylamide and polyacrylamide-sodium acrylate. Figure 8.7 illustrates the mechanism by which a water-soluble polymer acts as an antiwashout admixture in antiwashout underwater concrete.^[24] The water-soluble polymer bonds to a part of mixing water by hydrogen bonds in the concrete, and disperses in a molecule form in the mixing water. As a result, the mixing water is confined in the network structure of the dispersed polymer, and becomes very viscous. The very viscous water envelops cement and aggregate particles to impart an antiwashout character to the concrete. Table 8.2 shows the properties of the antiwashout underwater concretes using typical antiwashout admixtures.^[24]



Figure 8.6 Moist curing period vs. flexural strength of heat plus autoclave cured MDF cements using alumina cement before and after 48-hour water immersion.

 Table 8.1
 Comparison of Physical Properties of Fiber Reinforced MDF Cement and Aluminum. (© 1991, Materials Research Society, reprinted with permission.)

Property	Fiber Reinforced MDF Cement	Aluminum
Flexural Strength (MPa)	150-250	150
Elastic Modulus (GPa)	45-55	70
Fracture Energy (J/m ²)	10 ⁵	10 ⁶
Specific Gravity	2.4	2.8
Specific Strength ^a (MPa)	63-104	54
Relative Energy Cost	1	30

^a Specific Strength=(Flexural Strength) / (Specific Gravity).



Figure 8.7 Mechanism of antiwashoutability development by water-soluble polymer in antiwashout underwater concrete. (© 1991, JSCE, reprinted with permission.)

Table 8.2Properties of Antiwashout Underwater Concretes Using Typical Antiwashout Admixtures. (©
1991, JSCE, reprinted with permission.)

Property		Type of Antiwashout Admixture	Cellulose Type (MC)	Hydroxyethyl Cellulose Type (HEC)	Polyacrylamide Type
Slump-Flow (cm)	In Air	After Mixing	48.5	51.0	50.0
		30 min after Mixing	48.0	52.0	47.5
	Underwater	After Mixing	47.5	52.0	46.5
Air Content (%)			3.0	2.6	2.1
Ostrins Times (h		Initial Set	13:20	16:40	12:46
Setting time (n : r	nin)	Final Set	15:58	19:58	15:09
Contraction	pН		10.9	11.0	11.7
Segregation Su	Suspensoid Conte	nt (mg/l)	22	31	211
Compressive Strength (kgf/cm ²)	Age : 7 Days	Underwater	227	219	211
		In Air	249	252	250
		Control	254	252	268
	Age : 28 Days	Underwater	336	322	298
		In Air	368	361	374
		Control	372	360	384
Compressive Strength Ratio	Age 7 Days	Underwater / In Air	0.91	0.87	0.85
		Underwater / Control	0.90	0.87	0.79
	Age : 28 Days	Underwater / In Air	0.91	0.89	0.80
		Underwater / Control	0.91	0.90	0.78

6.0 ARTIFICIAL WOOD

In Japan, calcium silicate-SBR latex-glass fiber-based composites^[25] or portland cement-fly ash-SBR latex-carbon fiber-based composites^[26] have recently received much attention as new artificial wood. Table 8.3 gives the comparison of the properties of the calcium silicate-SBR latexglass fiber-based artificial wood with natural wood.^[25]

7.0 COMPOSITE CEMENT MODIFIERS

As a recent trend, there have been a few attempts to use polymer latexes with chemical admixtures such as superplasticizers,^[27] alkyl alkoxy silane,^[28] and amino alcohol derivative^[29] at low polymer-cement ratios of 5.0% or less. A trial to inhibit alkali-aggregate reaction with chemical admixtures and SBR latex has also been done.^[30] When such attempts are completed, new polymeric chemical admixtures for ordinary cement concrete may successfully be developed in the near future.

 Table 8.3
 Comparison of Properties of Calcium Silicate-SBR Latex-Glass Fiber-Based Artificial Wood with Natural Wood. (© 1986, Cement and Concrete, reprinted with permission.)

Type of Wood	Specific Gravity (20°C)	Flexural Strength (kgf/cm ²)	Modulus of Elasticity (kgf/cm ²)	Compressive Strength (kgf/cm ²)	Length Change (%)
Artificial Wood	0.50	102	26x10 ³	105	0.04
Hemlo	ck 0.47	710	105x10 ³	437	0.15
Natural Wood Ceda Red La	uan 0.54	541 818	79x10 ³ 116x10 ³	353 418	0.15

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Applications

9

Of various polymer-modified mortar and concrete, latex-modified mortar and concrete have superior properties, such as high tensile and flexural strengths, excellent adhesion, high waterproofness, high abrasion resistance, and good chemical resistance, compared to ordinary cement mortar and concrete. Accordingly, they are widely used in many specialized applications in which the ordinary cement mortar and concrete have been employed to a lesser extent till now. In these applications, the latex-modified mortar is widely used rather than the latex-modified concrete from the viewpoint of a balance between their performance and cost. Typical applications of the latex-modified mortar and concrete are listed in Table 9.1.

Recently, redispersible polymer powder-modified mortar has been increasingly used in much the same applications as ordinary mortar and concrete.

Although more expensive compared to latex-modified mortar and concrete, liquid resin-modified mortars and concretes appear to be getting increased acceptance in the construction industry. This may be because they give more rapid hardening, higher thermal stability, and better water resistance over the latex-modified systems. Of them, epoxy-modified systems have begun to gain popularity recently, and for the other liquid resinmodified mortars and concretes, further testing in laboratories and more onsite experience are required.

Application	Location of Work
Floorings and Pavements	Floors for houses, warehouses, schools, hospitals, offices, shops, toilets, gymnasiums and factories, passages, stairs, garages, railway platforms, roads, airport runways, monorails, etc.
Integral Waterproofings and Liquid-Applied Membrane Waterproofings	Concrete roofdecks, mortar walls, concrete block walls, water tanks, swimming pools, septic tanks, silos, etc.
Adhesives	Tile adhesives, adhesives for floorings, walling materials and heat-insulating materials, adhesives for joining new cement concrete or mortar to old cement concrete or mortar, etc.
Decorative Coatings (including surface-preparing materials)	Wall coatings, lightweight aggregate coating materials, cement filling compounds and self-levelling cements for surface preparations, etc.
Repair Materials	Grouts for repairing cracks and delaminations of concrete structures, patching materials for damaged concrete structures, rustproof coatings for corroded reinforcing bars, etc.
Anticorrosive Linings	Effluent drains, chemical or machinery plant floors, grouts for acid-proof tiles, floors for chemical laboratories and pharmaceuticals warehouses, septic tanks, hot spring baths, rustproof coatings for steel roof decks and soils, etc.
Deck Coverings	Internal and external ship-decks, bridge decks, footbridge decks, train floors, etc.

Table 9.1 Typical Applications of Latex-Modified Mortar.

Modification of cement mortar and concrete by small amounts of water-soluble polymers such as cellulose derivatives and polyvinyl alcohol is used popularly for improving workability. In this case, the water-soluble polymers are mixed with the mortar and concrete as powders or aqueous solutions, and act as plasticizers because of their surface activity.

In Japan, polymer-modified mortar is most widely used as a construction material for finishing and repair work, but polymer-modified concrete is seldom employed because of a poor cost-performance balance. However, the polymer-modified concrete is widely used for bridge deck overlays and patching work in U.S. In particular, it is estimated that each year over 1.2 million m² of bridge decks are overlaid with the polymermodified concrete.^[1] In recent years, about 60,300 m³ of the polymermodified concrete has been placed each year on both new and existing deteriorated concrete structures in U.S.^[2] Table 9.2 lists the main projects that have used SBR-modified concretes as overlays on bridge decks in U.S. for the past 20 years.^[3] Because the rapid deterioration of reinforced concrete structures has become a serious problem in Japan, a strong interest is focused on polymer-modified mortar and paste as repair materials, and there is a growing demand for them. This trend is similar to that in other advanced countries. As stated above, about 60,300 m³ per year of polymermodified concrete is employed for the repair work for damaged concrete structures in U.S. In U.K., about £500 million are spent each year on the repair of the concrete structures.^[4] Thus the polymer-modified mortars and concretes are currently becoming low-cost, promising materials for preventing chloride-induced corrosion and repairing damaged reinforced concrete In their practical applications, the potential importance of structures. property mismatch between repair materials and the reinforced concrete substrates has been highlighted.^{[4][5]}

Year Overlay Installed	Project	Location
1973	Rip Van Winkle Bridge over Hudson River	Catskill, N.Y.
1972	University Ave. Bridge, I-676 over Schuylkill River	Philadelphia, Pa.
1981-1985	Chicago Skyway	Chicago, Ill.
1975	Floating Bridge, Hwy. 520 over Lake Washington	Seattle, Wash.
1980	I-480 over Rock River1500 ft long	Cleveland, Ohio
1980	Mile Long-Bensonville Street Bridge	Chicago, III.
1979	Clark's Summit BridgePennsylvania Turnpike	Pennsylvania
1978	New River Gorge Bridge	West Virginia
1982-1988	Delaware Memorial Bridge I-295 over Delaware River	Wilmington, Del.
1984	Newburgh-Beacon Bridge I-84 over the Hudson River	New York
1985	Reedy Point Bridge over Chesapeake- Delaware Canal	Delaware
1982	Columbia River Bridge	Portland, Ore.
1983	Marquham Street Bridge	Portland, Ore.
1983	Wicasset Bridge	Wicasset, Me.
1980	Denny Creek Bridge	Snoqualmie Falls, Wash.
1980	Sandusky Bay Bridge	Sandusky, Ohio
1978	O'Hare Departure Ramp	Chicago, Ill.
1987	Chesapeake Bay Bridge	Maryland

Table 9.2Bridge Deck Overlay Projects Using SBR-Modified Concretes
in U.S.

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