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Polymer-based Admixtures

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Abstract

The concept of polymer modification for cement mortar and concrete is not new, since considerable research and development of polymer modification have been performed for the past 70 years or more. As a result, various polymer-based admixtures have been developed, and polymer-modified mortar and concrete using them are currently popular construction materials because of their good cost-performance balance. This article summarizes the classification of polymer-based admixtures, the principles of polymer modification by the use of polymer latexes, redispersible polymer powders, water-soluble polymers and liquid polymers, the properties and applications of polymer-modified mortar and concrete, recent research and development activities, and standardization work. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: polymer-based admixtures, polymer modification, polymer-modified mortar and concrete, polymer–cement ratio, properties, applications, research and development, standards, specifications, guides.

INTRODUCTION

The concept of polymer modification for cement mortar and concrete is not so new, and in 1923 the first patent of the concept 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 polymer modification was published by Lefebure[2] in 1924. Since then, considerable research and development of polymer modification for cement mortar and concrete have been conducted in various countries for 70 years or more. As a result, many effective polymer modification systems for cement mortar and concrete have been developed, and currently are used in various applications in the construction industry.

A polymer-based (or polymeric) admixture, also called a cement modifier, is defined as an admixture which consists of a polymeric compound as a main ingredient effective at modifying or improving the properties such as strength, deformability, adhesion, waterproofness and durability of cement mortar and concrete. Such a polymeric compound is a polymer latex, redispersible polymer powder, water-soluble polymer or liquid polymer. The cement mortar and concrete which are made by mixing with the polymer-based admixtures are called polymer-modified mortar (PMM) and concrete (PMC), respectively. In general, the properties of polymer-modified mortar and concrete depend significantly on the polymer content or polymer–cement ratio (defined as the mass ratio of the amount of polymer solids in a polymer-based admixture to the amount of cement in a polymer-modified mortar or concrete) rather than the water–cement ratio compared with ordinary cement mortar and concrete.

This article summarizes the present knowledge and information necessary for the use of polymer-based admixtures in cement mortar and concrete.

CLASSIFICATION OF POLYMER-BASED ADMIXTURES

Fig. 1 shows the classification of polymer-based or polymeric admixtures. In general, polymer-based admixtures are classified into four main types, i.e., polymer latex (or polymer dispersion), redispersible polymer powder, water-soluble polymer and liquid polymer.

Polymer latexes (or dispersions)

Polymer latexes (or dispersions) which consist of very small (0·05–5 μm in diameter) polymer particles dispersed in water are usually produced by emulsion polymerization. The formulations for emulsion polymerization of typical polymer latexes as polymer-based admixtures are listed in Table 1. 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 solids. The epoxy latex is produced by emulsifying an epoxy resin in water by use of surfactants.

Polymer latexes are generally classified into the following three types by the kind of electrical charges on polymer particles, which is determined by the type of surfactants used in the production of the latexes: cationic (postively charged), anionic (negatively charged) and nonionic (uncharged). In general, the polymer latexes are copolymer systems of two or more different monomers, and their total solids including polymers, emulsifiers, stabilizers, etc. are 40–50% by mass. As seen in Fig. 1, most commercially available polymer latexes as polymer-based admixtures are based on elastomeric and thermoplastic polymers which form continuous polymer films when dried. The polymer latexes which are underlined in Fig. 1 are the main ones that are in general use in the world today. Table 2 gives the chemical structures of the main polymer latexes.

The general requirements for polymer latexes as polymer-based admixtures are as follows:

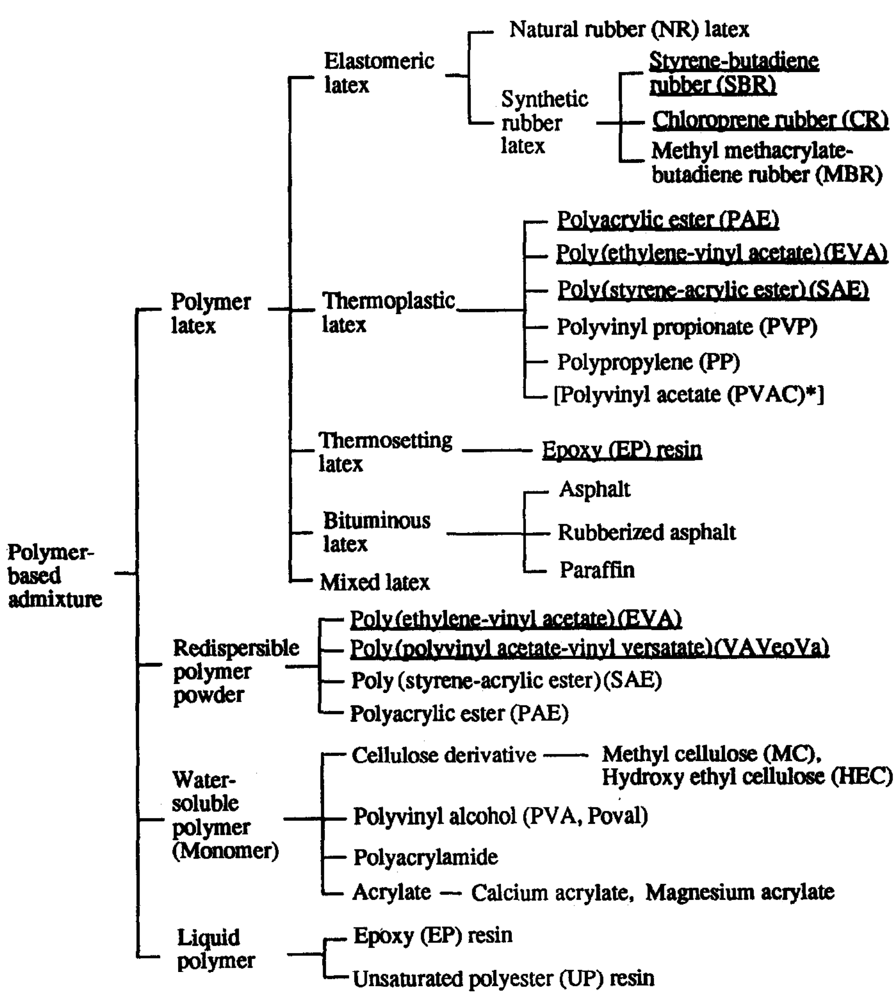


Fig. 1. Classification of polymer-based (or polymeric) admixtures. *At present, PVAC is not used because of its very poor water resistance.

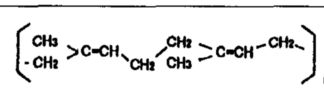
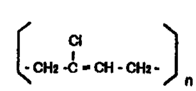
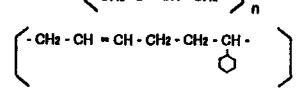
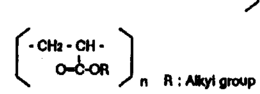
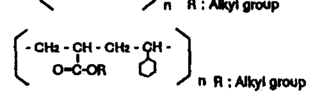
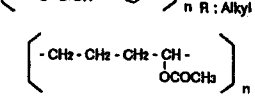
Table 1. Formulations for emulsion polymerization of typical polymer latexes as polymer-based admixtures

Type of latex	*Material*	*Parts by mass*
Vinyl acetate, homo- and copolymer latexes	Vinyl acetate	70.0–100.0
	Comonomer (butyl acrylate, ethylene, vinyl ester of versatic acid)	0.0–30.0
	Partially hydrolyzed polyvinyl alcohol	6.0
	Sodium bicarbonate	0.3
	Hydrogen peroxide (35%)	0.7
	Sodium formaldehyde sulfoxylate	0.5
	Water	80.0
Acrylic copolymer latex	Ethyl acrylate	98.0
	A vinyl carboxylic acid	2.0
	Non-ionic 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–butadiene copolymer latex	Styrene	64.0
	Butadiene	35.0
	A vinyl carboxylic acid	1.0
	Non-ionic surfactant	7.0[a]
	Anionic surfactant	0.1[b]
	Ammonium persulfate	0.2
	Water	105.0

[a]The non-ionic 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.

- Very high chemical stability towards the extremely active cations such as calcium ions (Ca^{2+}) and aluminum ions (Al^{3+}) liberated during cement hydration.
- Very high mechanical stability under severe actions, especially high shear in mortar or concrete mixing and in metering and transfer pumps.
- Low air-entraining action due to the use of suitable antifoaming agents during mortar or concrete mixing.
- No adverse influence on cement hydration.
- 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 continuous polymer films.)

Table 2. Chemical structures of main polymer latexes for polymer-based admixtures

Type of polymer latex	*Abbreviation*	*Chemical structure*
Natural rubber latex	NR	
Chloroprene rubber latex (Neoprene)	CR	
Styrene–butadiene rubber latex	SBR	
Polyacrylic ester latex	PAE	
Poly (styrene-acrylic ester) latex	SAE	
Poly (ethylene-vinyl acetate) latex	EVA or VAE	

- Excellent water resistance, alkali resistance and weatherability of the polymer films formed in mortar or concrete.
- 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 shows the quality requirements for the polymer latexes specified in JIS A 6203 (Polymer Dispersions and Redispersible Polymer Powders for Cement Modifiers).

In particular, the commercial latexes widely used in the world are styrene-butadiene rubber (SBR), chloroprene rubber (CR), polyacrylic ester (PAE) and poly (ethylene-vinyl acetate) (EVA) copolymers. Most commercial polymer latexes for polymer-based admixtures contain proper antifoaming agents, and can be generally used without the addition of the antifoaming agents during mixing.

Redispersible polymer powders

In general, redispersible polymer powders as polymer-based admixtures are manufactured by a two-step process. Firstly, polymer latexes as raw materials are made by emulsion polymerization, and spray-dried to obtain the polymer powders. 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.

The redispersible polymer powders which are underlined in Fig. 1 are the main ones in use worldwide. The redispersible polymer powders are usually free-flowing powders, and have ash contents of 5–15%, 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 1–10 μm. Table 4 shows the quality requirements for the redispersible polymer powders specified in JIS A 6203.

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 re-emulsified. If necessary, powder or liquid antifoaming agents are added to the wet mix.

Water-soluble polymers

Water-soluble polymers as polymer-based admixtures are water-soluble powdered polymer, e.g., cellulose derivatives, polyvinyl alcohol (poval), polyacrylamide, etc., and are added in the form of powders or aqueous solutions to cement mortar or 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. Their main effect is to improve workability. The acrylates, such as calcium acrylate and magnesium acrylate, which are added in monomer form during mixing are included within this category because they are water-soluble.

Liquid polymers

Liquid polymers as polymer-based admixtures are viscous polymeric liquid such as epoxy resin

Table 3. Quality requirements for polymer latexes specified in JIS A 6203 (polymer dispersions and redispersible polymer powders for cement modifiers)

Kind of test	*Test item*	*Requirement*
Latex test	Appearance	Exclusive of coarse particles, foreign substances and coagula
Polymer-modified mortar test	Non-volatile matter	Not less than 35.0%
	Flexural strength	Not less than 5.0 N/mm^{2a} (5.0 MPa)
	Compressive strength	Not less than 15.0 N/mm^{2a} (15.0 MPa)
	Adhesion[c]	Not less than 1.0 N/mm^{2a} (1.0 MPa)
	Water absorption	Not more than 15.0%
	Amount of water permeation	Not more than 20 g[b]
	Length change	0–0·150%

[a]In JIS, N/mm^2 is used in place of MPa.
[b]20 g expresses the amount of water which permeates a speciment under a water pressure of 98 kPa for 1 h.
[c]Adhesion to cement mortar.

Table 4. Quality requirements for redispersible polymer powders specified in JIS A 6203

Kind of test	*Test item*	*Requirement*
Redispersible polymer powder test	Appearance	Exclusive of coarse particles, foreign substances and coagula
	Volatile matter	Not more than 5.0%
Polymer-modified mortar test	Flexural strength	Not less than 5.0 N/mm^{2a} (5.0 MPa)
	Compressive strength	Not less than 15.0 N/mm^{2a} (15.0 MPa)
	Adhesion[c]	Not less than 1.0 N/mm^{2a} (1.0 MPa)
	Water absorption	Not more than 15.0%
	Amount of water permeation	Not more than 20 g[b]
	Length change	0–0·150%

[a]In JIS, N/mm^2 is used in place of MPa.
[b]20 g expresses the amount of water which permeates a specimen under a water pressure of 98 kPa for 1 h.
[c]Adhesion to cement mortar.

and unsaturated polyester resin, and are added with the hardener or catalyst, and accelerator to cement mortar or concrete during mixing. However, the liquid polymers are less widely employed as polymer-based admixtures compared with the other admixtures such as polymer latexes, redispersible polymer powders and water-soluble polymers.

PRINCIPLES OF POLYMER MODIFICATION

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

Modification with polymer latexes

Polymer 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 film formation process by the coalescence of polymer particles in polymer latexes.[3] In due course, a co-matrix phase is formed by both cement hydration and polymer film formation processes. The co-matrix phase is generally formed according to the simplified model shown in Fig. 2.[4–6] Some chemical reactions may take place between the particle surfaces of reactive polymers such as polyacrylic esters (PAE) and calcium ions (Ca^{2+}), $Ca(OH)_2$ solid surfaces, or silicate surfaces over the aggregates, as illustrated in Fig. 3[7]. Such reactions are expected to improve the bond between the cement hydrates and aggregates, and to improve the properties of hardened latex-modified mortar and concrete.

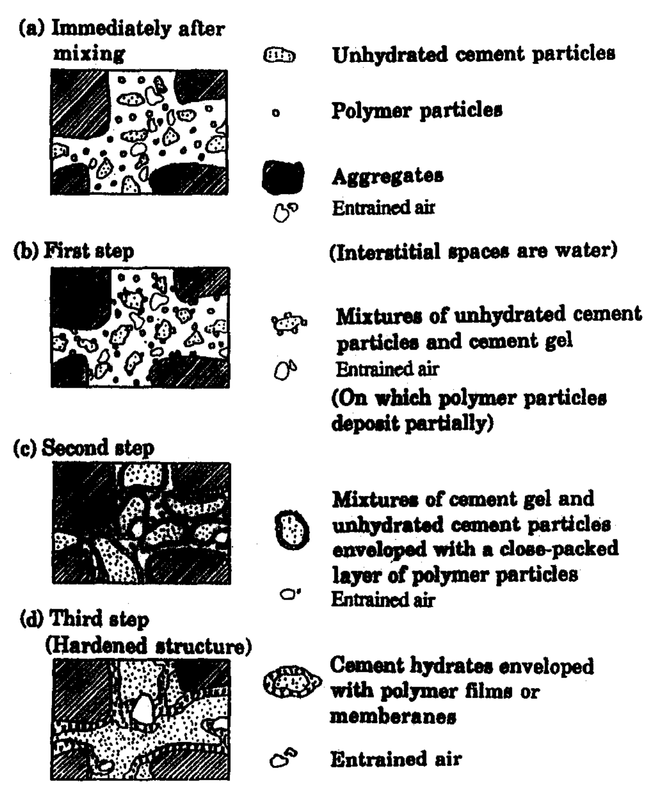


Fig. 2. Simplified model of formation of polymer–cement co-matrix.

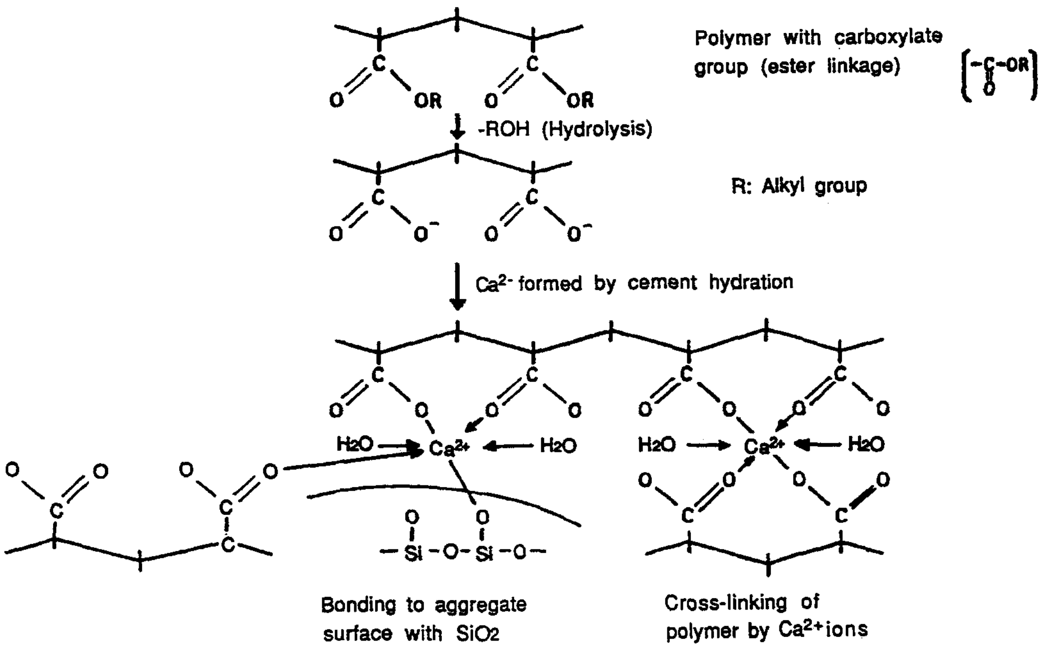


Fig. 3. Schematic illustration of reaction between polymer with carboxylate group (ester linkage), ordinary Portland cement and aggregate.

As explained above, the properties of ordinary cement mortar and concrete are generally improved to a great extent by polymer latex modification. It appears that the microcracks in latex-modified mortar and concrete under stress are bridged by the polymer films or membranes formed, which prevent crack propagation, and that simultaneously a strong cement hydrate–aggregate bond is developed. This aspect is evident in the scanning electron micrographs of cross-sections of SBR-, EVA- and PAE-modified mortars, as shown in Fig. 4. Such effects increase with an increase in the polymer content or polymer–cement ratio, P/C (defined as the mass ratio of the amount of total solids in a polymer latex to the amount of cement in a latex-modified mortar or concrete), and lead to increased tensile strength and fracture toughness. However, excess air entrainment and polymer inclusion cause discontinuities of the formed monolithic network structure whose strength is then reduced, although some chemical reactions proceed effectively, as shown in Fig. 3. The sealing effect due to the polymer films or membranes also provides a considerable increase in waterproofness or watertightness, resistance to moisture or air permeation, chemical resistance and freeze–thaw durability, and is promoted with increasing polymer–cement ratio up to certain limits.

Polymer Film in SBR-Modified Mortar | Polymer Film in EVA-Modified Mortar | Polymer Film in PAE-Modified Mortar

Fig. 4. Scanning electron micrographs of latex-modified mortars.

Modification with redispersible polymer powders

The principle of modification of cement mortar and concrete with redispersible polymer powders is similar to that of latex modification, except that it also involves the redispersion of the 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 re-emulsified in the modified mortar and concrete, and behave in the same manner as the latexes for polymer-based admixtures.

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 'dry-out' phenomena. 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 films in them. In general, the water-soluble polymers contribute to little improvement in the strength of the modified systems.

Modification with liquid polymers

In the modification with liquid thermosetting resins, considerable amounts of polymerizable 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 is generally 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.

PROPERTIES OF POLYMER-MODIFIED MORTAR AND CONCRETE

It is characteristic of polymer-modified mortar and concrete which are produced by mixing polymer-based admixtures with cement mortar and concrete, to possess co-matrix phases. The properties of the polymer-modified mortar and concrete are characterized by such co-matrix phases, and 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, water–cement ratio, air content and curing conditions. In comparison with conventional cement mortar and concrete, the properties in the fresh and hardened stages of the polymer-modified mortar and concrete using polymer latexes which are most widely employed of many polymer-based admixtures, are described below.

Properties of fresh mortar and concrete

Workability

Generally, latex-modified mortar and concrete provide an improved 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, the entrained air and the dispersing effect of surfactants in the polymer latexes. The water–cement ratio of the latex-modified mortar and concrete at a given consistency (flow or slump) is markedly reduced with an increase in the polymer–cement ratio. This water reduction effect is found to contribute to a strength development and drying shrinkage reduction.

Air entrainment

In most latex-modified mortars and concretes, a large quantity of air is entrained compared with in ordinary cement mortar and concrete because of the action of the surfactants contained as emulsifiers and stabilizers in the polymer latex. Some air entrainment is useful to obtain improved workability. An excessive amount of entrained air causes a reduction in strength, and is controlled by using proper antifoaming agents. Recent commercial polymer latexes as polymer-based admixtures 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 5–20%, and that of most latex-modified concretes is less than 2%, much the same as ordinary cement concrete. The air content also depends on the aggregate size. Proper air entrainment is effective for improvements in the consistency and freeze–thaw durability.

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 the polymer 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. Such excellent water retention of the latex-modified mortar is most helpful and effective for inhibiting dry-out phenomena (the lack of cement hydration due to water loss in the mortar or concrete) on highly water-absorbable substrates such as dried cement mortars and ceramic tiles. The excellent water retention of the latex-modified concrete contributes to an increase in the long-term strength in dry curing.

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 improved flowability. This is due to the hydrophilic colloidal properties of the polymer latexes themselves and the air-entraining and water-reducing effects of the surfactants contained in the latexes. Accordingly, in the latex-modified systems, some disadvantages such as reductions in the strengths and waterproofness caused by bleeding and segregation do not exist.

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. This trend is dependent on the polymer type and polymer–cement ratio.

Properties of hardened mortar and concrete

Strength

In general, latex-modified mortar and concrete show a noticeable increase in tensile or flexural strength but no improvement in compressive strength compared with ordinary cement mortar and concrete. This is interpreted in terms of the contribution of high tensile strength by the polymers themselves and an overall improvement in cement hydrate–aggregate bond. The strength properties of the latex-modified mortar and concrete are influenced by various factors that tend to interact with each other. The main factors are: the nature of materials used such as polymer latexes, cements and aggregates; the controlling factors for mix proportions (e.g., polymer–cement ratio, water–cement ratio, binder–void ratio, air content, etc.); curing methods; and testing methods. The effects of these factors on the strength properties are discussed below.

The effect of monomer ratio (by mass) in SBR, EVA and SAE latexes on the strengths of latex-modified mortars is represented in Fig. 5.[8–10] The monomer ratio in the copolymer latexes affects the strengths to the same extent as the polymer–cement ratio. A general trend, which summarizes the strength–polymer–cement ratio relationships obtained in a number of papers, is presented in Fig. 6.[11–14] Expanding Talbot's void theory on ordinary cement mortar and concrete, Ohama,[15,16] defined a binder–void ratio (α) and a 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:
For latex-modified mortars,

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

For latex-modified concretes,

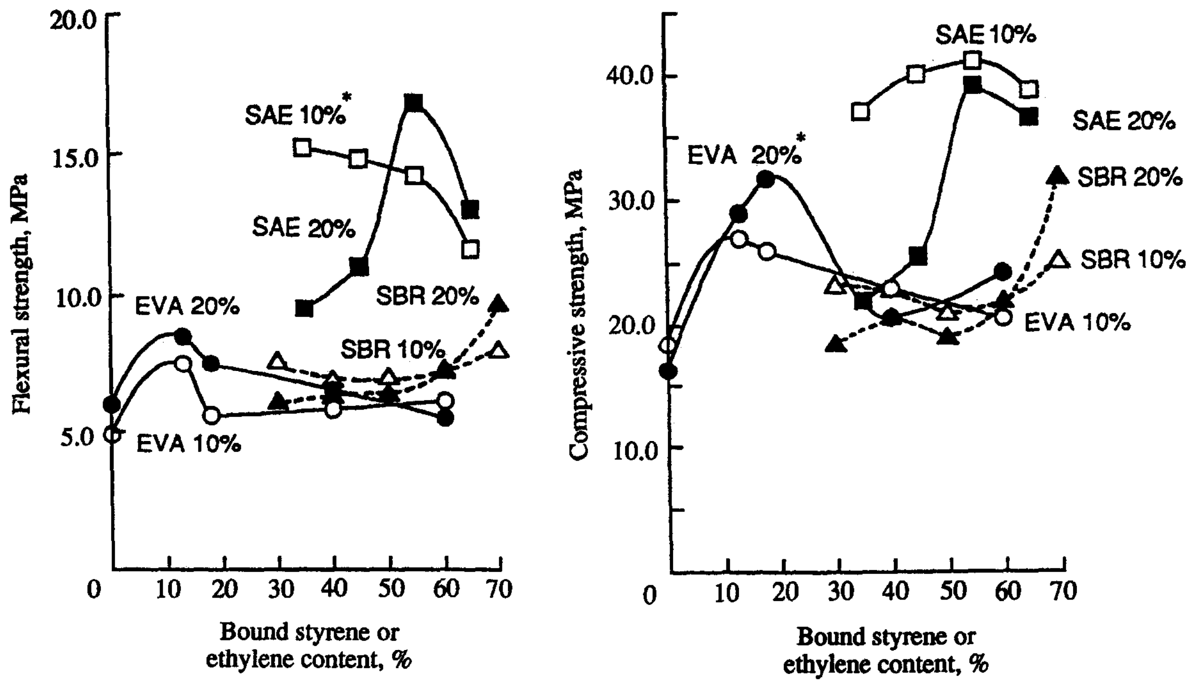


Fig. 5. Effects of monomer ratios in EVA, SBR and SAE latexes on flexural and compressive strengths of latex-modified mortars. *Polymer–cement ratio.

$$\sigma_c = a\alpha + b$$

where σ_c is the compressive strength of the latex-modified mortars and concretes, $\beta = 1/\alpha = (V_a + V_w)/(V_c + V_p)$, V_c, V_p, V_a and V_w 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 indicated in Figs. 7 and 8.[16] The effects of curing conditions on the strength of the latex-modified mortars and concretes are shown in Figs. 9 and 10.[17,18] It is evident from these figures that optimum

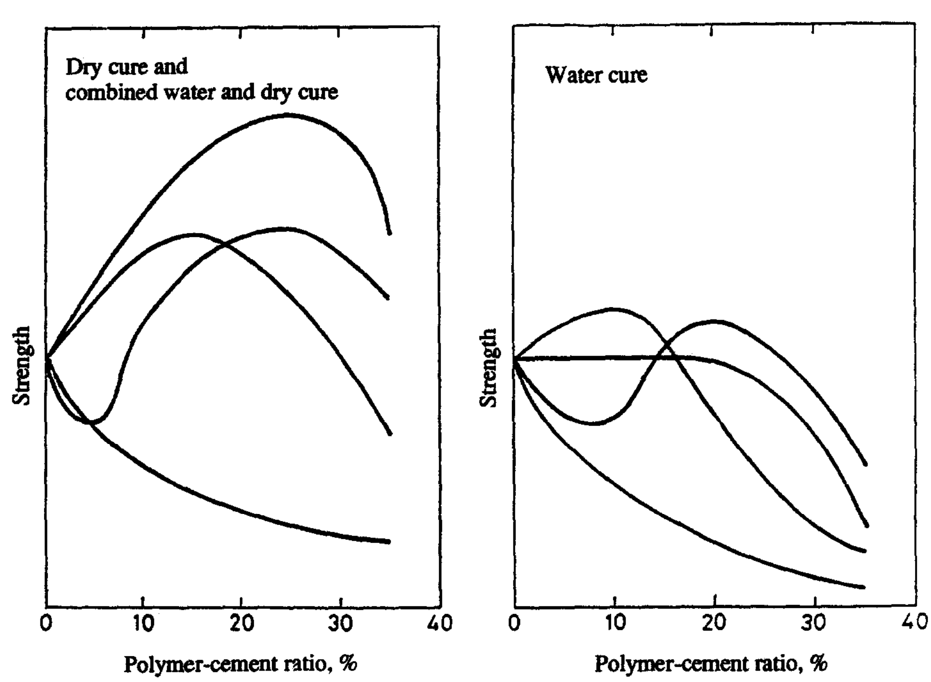


Fig. 6. Typical relationships between strength properties and polymer–cement ratio of latex-modified mortars and concretes.

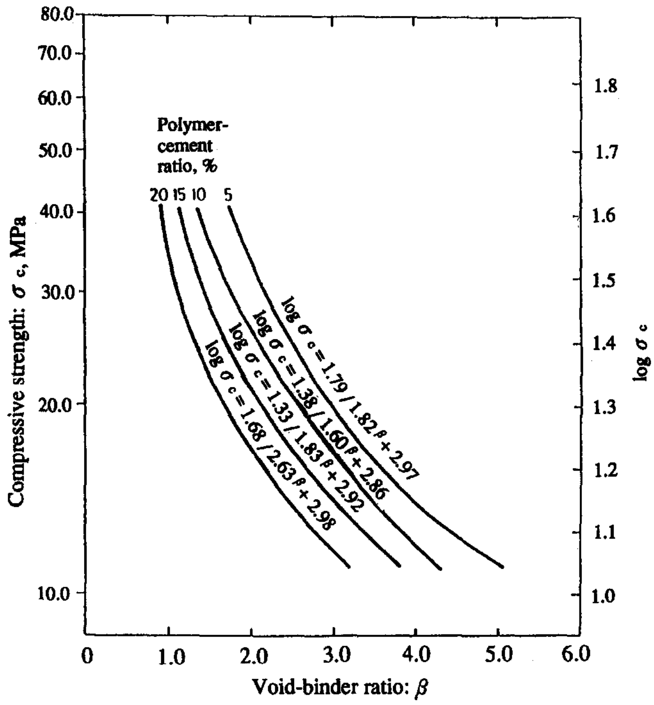


Fig. 7. Relation between void–binder ratio and compressive strength of latex-modified mortars (except PVAC-modified mortar) with sand–cement ratio of 3.

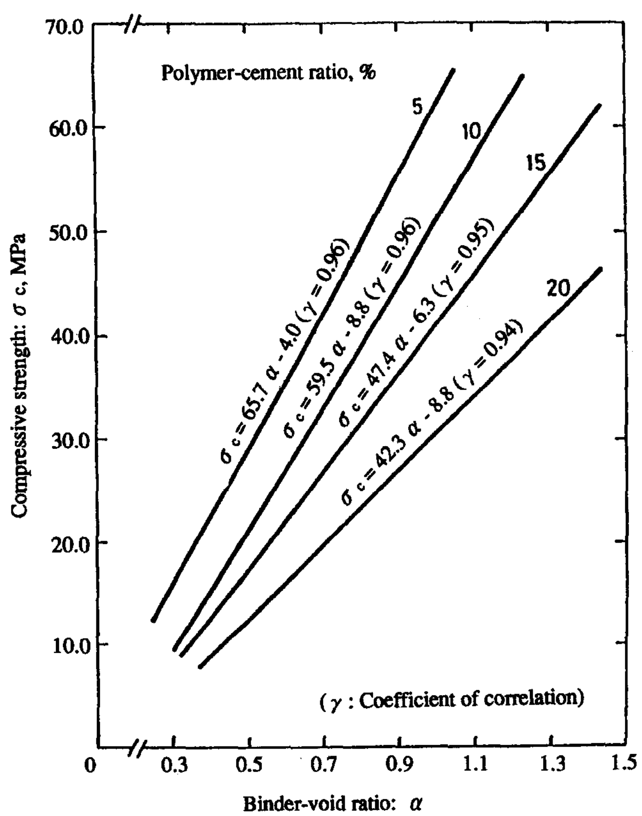


Fig. 8. Relation between binder–void ratio and compressive strength of latex-modified concretes.

strength in most latex-modified mortars and concretes is obtained by achieving a reasonable degree of cement hydration under wet conditions at eary ages, followed by dry conditions to promote a polymer film formation due to the coalescence of the polymer particles. In other words, such curing conditions are most suitable or ideal for most latex-modified mortars and concretes. As seen in Fig. 11,[19] the development of the compressive strength of the latex-modified concretes is remarkable even during a considerably long dry curing period. The main reason for this is that the hydration of cement in latex-modified concretes progresses through such a long dry curing period because of their excellent water retention capacity due to polymer film formation. Such a high strength development is found to be one of the advantages of the latex-modified concretes over conventional cement concrete.

Deformability, elastic modulus and Poisson's ratio

Latex-modified mortar and concrete contain polymers (elastic modulus, 0.001–10 GPa) with considerably smaller elastic modulus compared to cement hydrates (elastic modulus, 10–30 GPa). Consequently, their deformation behavior or deformability can differ to a great extent from those of ordinary cement mortar and concrete. Most latex-modified mortars and concretes provide a higher deformability and elasticity than ordinary cement mortar and concrete, their magnitude depending on the polymer type and polymer–cement ratio. In general, the deformability and elastic modulus of the latex-modified mortars and concretes tend to increase and decrease, respectively, with an increase in the polymer–cement ratio. However, their Poisson's ratio is hardly affected by the polymer–cement ratio.

Drying shrinkage, creep and thermal expansion

The drying shrinkage of latex-modified mortar and concrete may be either larger or smaller than that of ordinary cement mortar and concrete, and is dependent on the polymer type and polymer–cement ratio. The drying shrinkage increases with additional dry curing period, and becomes nearly constant at a dry curing period of 28 days, regardless of the polymer type and polymer–cement ratio. Generally, the

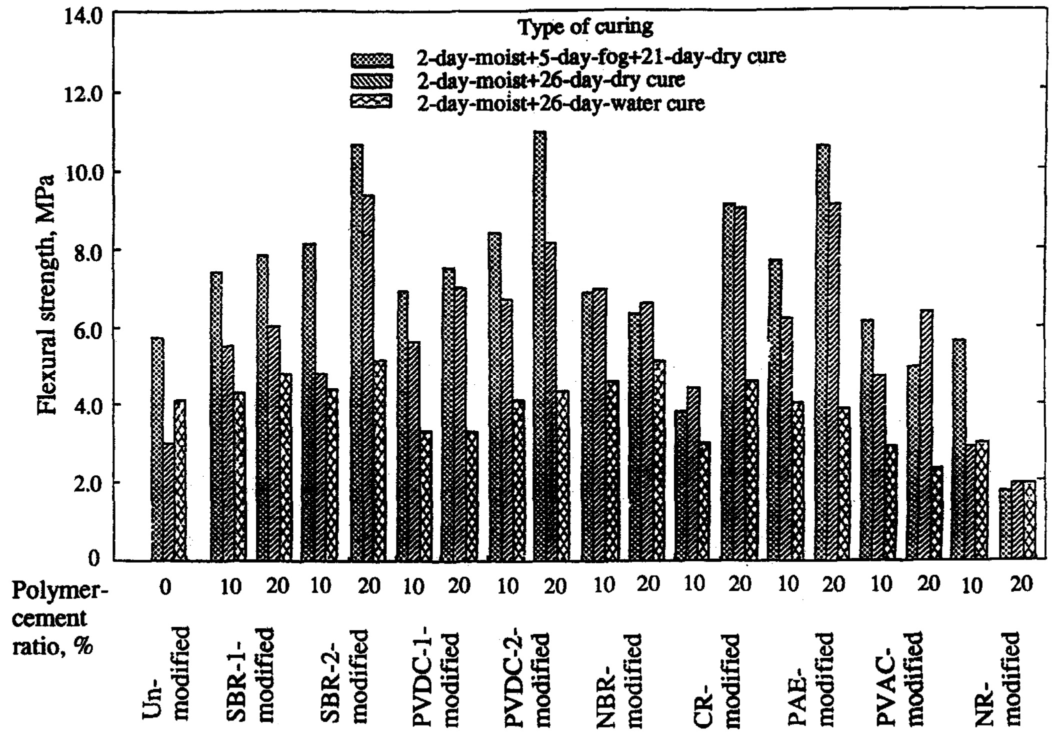


Fig. 9. Effects of curing conditions on flexural strength of latex-modified mortars.

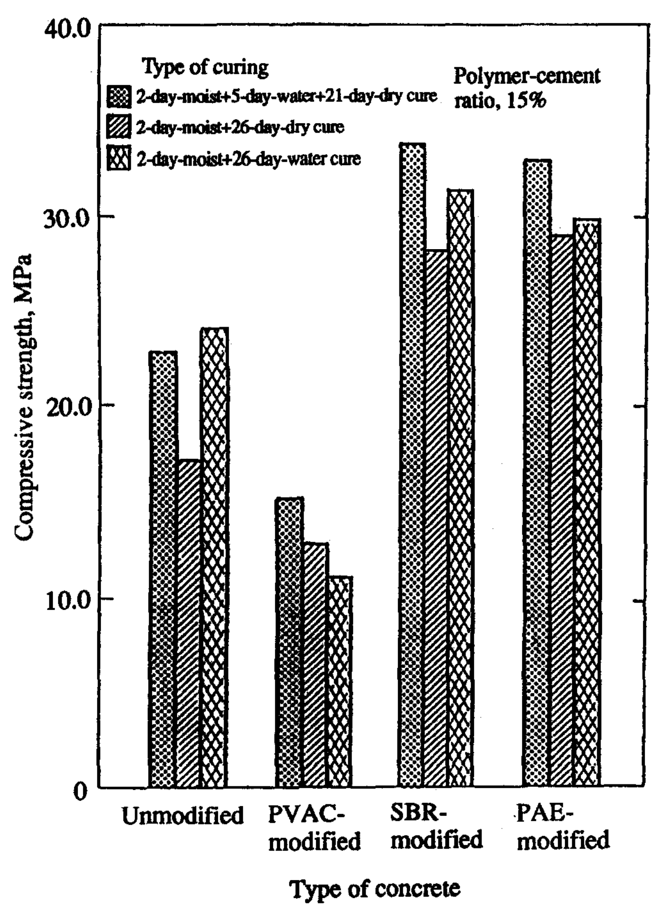


Fig. 10. Effects of curing conditions on compressive strength of latex-modified concretes.

28-day drying shrinkage tends to decrease with increasing polymer–cement ratio.

In general, the creep stain and creep coefficient of latex-modified mortar and concrete are considerably smaller than those of ordinary cement mortar and concrete. Fig. 12 represents the creep behavior of SBR- and PAE-modified concretes.[20] The reason for such a small creep may be related to the lower polymer content of approximately 3 vol%, the strengthening of their binders with the polymers, and the long-term strength development with improved water retention.

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, being equal to or slightly larger than that of ordinary cement mortar and concrete. Consequently, the coefficient of thermal expansion is about $9\text{–}10 \times 10^{-6}$/°C.

Waterproofness, water resistance, chloride ion penetration resistance and carbonation resistance

Latex-modified mortar and concrete have a structure in which the larger pores can be filled with polymers or sealed with continuous poly-

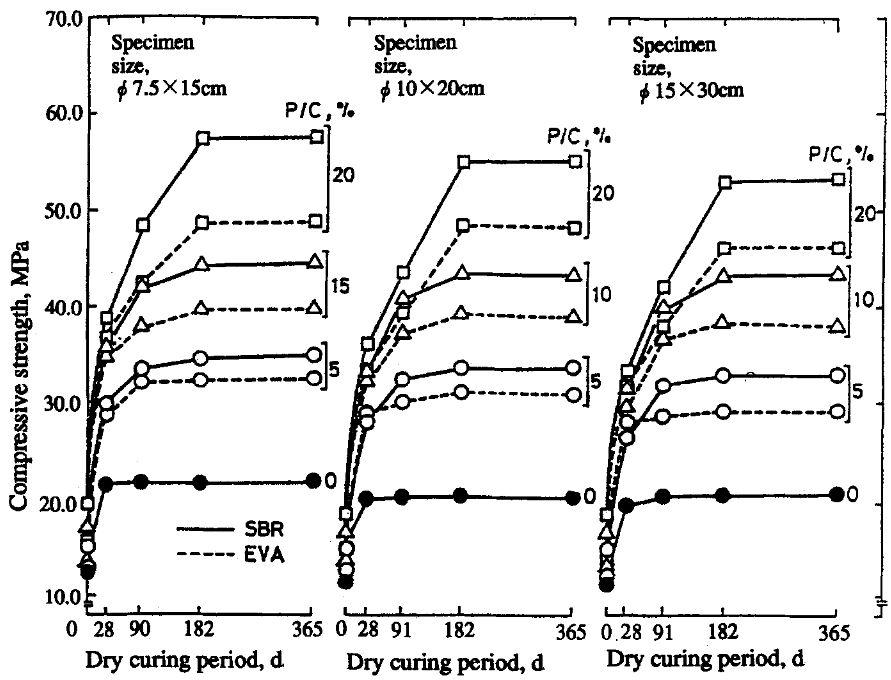


Fig. 11. Dry curing period vs. compressive strength of latex-modified concretes.

mer films. In general, the effect of polymer filling or sealing increases with a raise in the 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 cement mortar and concrete. Fig. 13 illustrates the water absorption and permeation of latex-modified mortars.[21] Generally, the water absorption and permeation are considerably reduced with an increase in the polymer–cement ratio. In contrast to the increased strengths of ordinary cement mortar and concrete, most latex-modified mortars and concretes tend to lose some strength with water immersion, and this trend is more significant for the flexural strength. However, most latex-

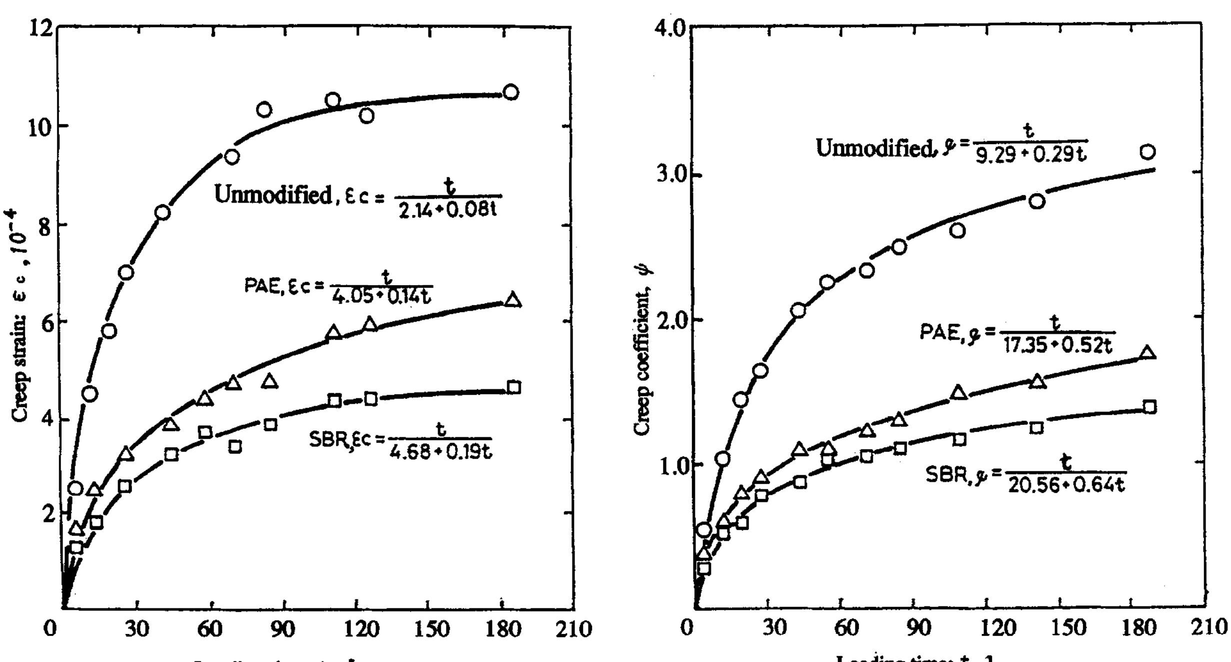


Fig. 12. Loading time vs. creep strain and creep coefficient of latex-modified concretes. (Polymer–cement ratio, 10%.)

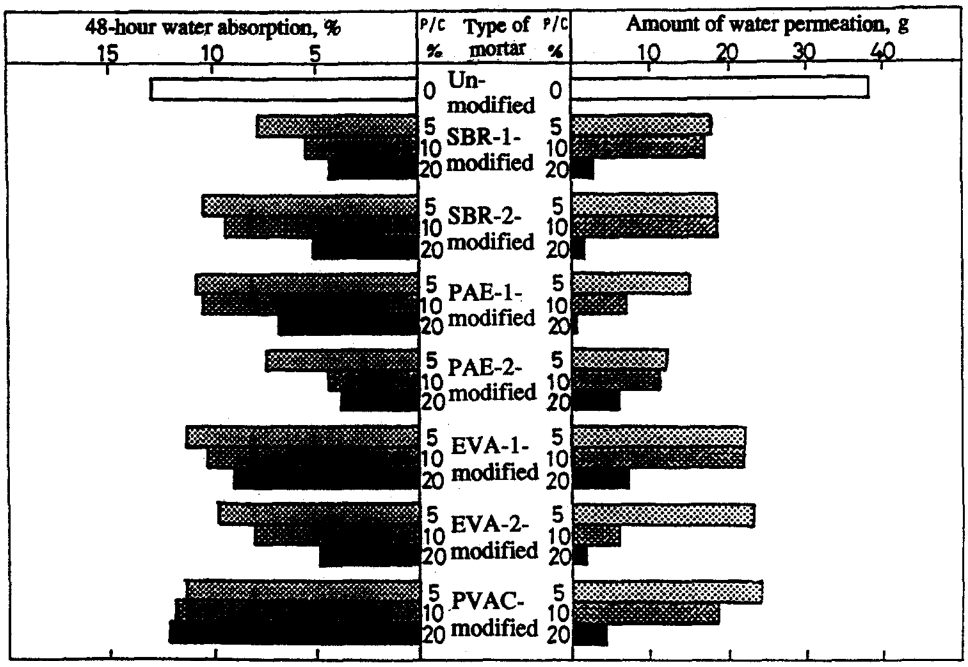
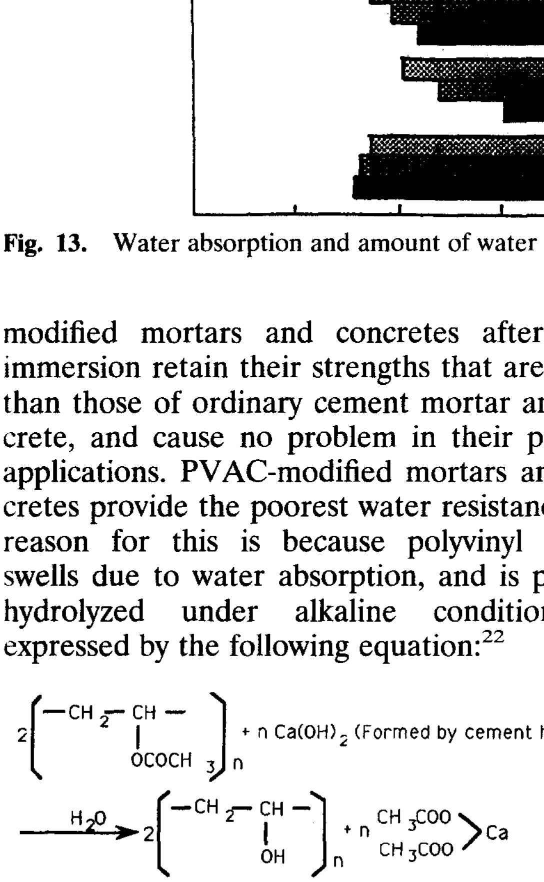


Fig. 13. Water absorption and amount of water permeation of latex-modified mortars.

modified mortars and concretes after water immersion retain their strengths that are higher than those of ordinary cement mortar and concrete, and cause no problem in their practical applications. PVAC-modified mortars and concretes provide the poorest water resistance. The reason for this is because polyvinyl acetate swells due to water absorption, and is partially hydrolyzed under alkaline conditions, as expressed by the following equation:[22]



Because of such very poor water resistance, PVAC-modified mortars and concretes are hardly used at present. In recent years, the very poor water resistance of the polyvinyl acetate has been overcome by copolymerization with ethylene, and EVA-modified mortars and concretes have widely been used.

Latex-modified mortar and concrete have an excellent water impermeability, as described above. 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 5[23] gives the apparent chloride ion diffusion coefficient of latex-modified mortars and concretes, which were estimated as a result of the examination of the chloride ion penetration kinetics in artificial seawater (NaCl content, 2.4%). The resistance to the chloride ion penetration of the

Table 5. Apparent chloride ion diffusion coefficient of latex-modified mortars and concretes

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)*
Unmodified	0	6.4×10^{-8}	Unmodified	0	2.2×10^{-8}
SBR-modified	10	6.4×10^{-8}	SBR-modified	10	1.9×10^{-8}
	20	3.9×10^{-8}		20	0.93×10^{-8}
EVA-modified	10	4.4×10^{-8}	EVA-modified	10	0.79×10^{-8}
	20	2.4×10^{-8}		20	1.0×10^{-8}
PAE-modified	10	3.8×10^{-8}	PAE-modified	10	0.62×10^{-8}
	20	4.4×10^{-8}		20	0.58×10^{-8}

latex-modified mortars and concretes tends to be improved with increasing polymer–cement ratio.

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 the polymer–cement ratio, depending on the type of polymers and carbon dioxide exposure conditions. The carbonation resistance is also an important factor in the corrosion of reinforcing bars, as well as the resistance to chloride ion pentration. Fig. 14[24] shows the carbonation depth of latex-modified mortars after 10-year outdoor and indoor exposures.

Adhesion or bond strength

A very useful aspect of latex-modified mortar and concrte is their improved adhesion or bond strength to various substrates compared with conventional mortar and concrete. The development of the adhesion is ascribed to the high adhesion of the polymers. The adhesion is usually affected by the polymer–cement ratio and the properties of substrates used. The data on the adhesion often show a considerable scatter, and may vary depending on the test methods, service conditions, or porosity of substrates. Fig. 15[25] exhibits the adhesion of latex-modified mortars to ordinary cement mortar as a substrate, measured by two types of test method. In general, the adhesions in tension and flexure of the latex-modified mortars to ordinary cement mortar increase with a rise in the polymer–cement ratio, irrespective of the polymer type and test method.

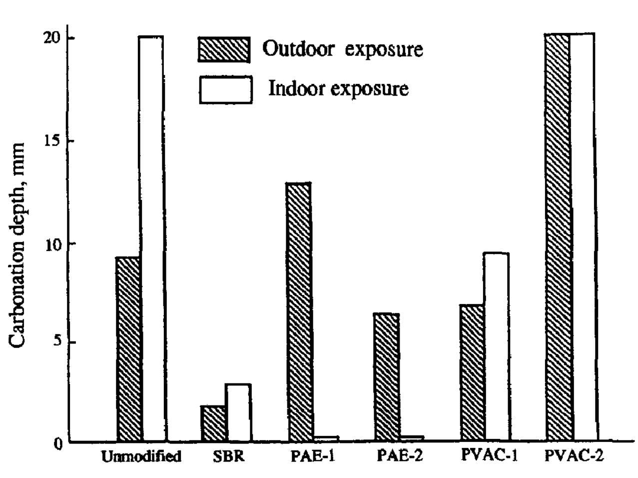


Fig. 14. Carbonation depth of latex-modified mortars after 10-year outdoor and indoor exposures. (Polymer–cement ratio, 20%.)

Most latex-modified mortars and concretes have an excellent adhesion to ceramic tiles, brick, steel, wood and stone.

Impact resistance

Latex-modified mortar and concrete have an excellent impact resistance in comparison with conventional mortar and concrete. This is because polymers themselves have a high impact resistance. The impact resistance generally increases with raising polymer–cement ratio. The data of the impact resistance vary markedly between different testing methods. The impact resistance of elastomer latex-modified mortars tends to be superior to that of plastomer latex-modified mortars.

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 the polymer–cement ratio.

Chemical resistance

The chemical resistance of latex-modified mortar and concrete is dependent on the nature of polymers added, the 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 cement hydrates which are 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.

Temperature effect, thermal resistance and incombustibility

The strength of latex-modified mortar and concrete is dependent on temperature because of the temperature dependence of the polymers themselves (especially thermoplastic polymers). The latex-modified mortar and concrete generally show a rapid reduction in the strength or deflection with increased temperature. This trend is substantial at temperatures higher than the glass transition temperatures of the polymers and at higher polymer–cement ratio.[26] Most thermoplastic polymers in latex have glass transition temperatures of 80–100°C.

The thermal resistance of latex-modified mortar and concrete is governed by the nature of the polymers used, especially their glass transition temperature, polymer–cement ratio and heating conditions, and ultimately by the thermal degradation of the polymers.

From the viewpoints of the temperature dependence and thermal resistance of latex-modified mortar and concrete, the maximum

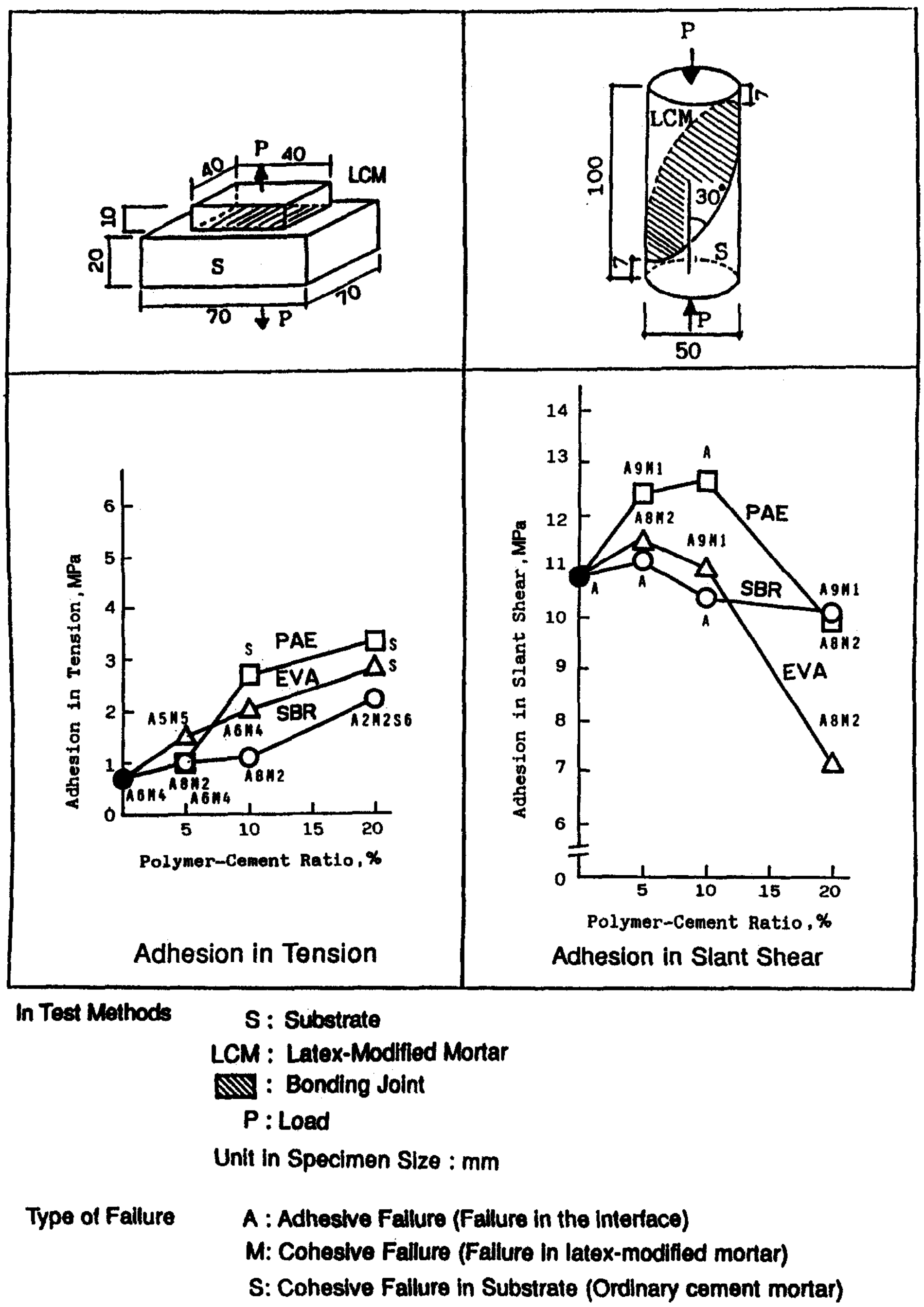


Fig. 15. Adhesion of latex-modified mortars to ordinary cement mortar, measured by two types of test methods.

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 polymer–cement ratio or polymer content (by volume). The mortars and concretes modified with chlorine-containing polymers, i.e., CR and PVAC give an excellent incombustibility. The incombustibility of PVAC-modified mortars and concretes is due to the action of a large quantity of acetic acid, formed by the thermal decomposition of the polymer.[27] The incombustibility of most latex-modified mortars and concretes tends to become poorer with increasing polymer–cement ratio.

Freeze–thaw durability 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. Fig. 16 represents the freeze–thaw durability in water (−18 to 4°C) of combined water and dry-cured SBR-, PAE- and EVA-modified mortars.[28] The frost resistance of SBR-, PAE- and EVA-modified mortars is markedly improved at polymer–cement ratios of 5% or more. Increasing the polymer–cement ratio does not necessarily cause a further improvement in the freeze–thaw durability.

Under long-term outdoor exposure, involving frost action and carbonation, latex-modified mortar and concrete show improved resistance to weathering in comparison with conventional mortar and concrete. The weatherability of the latex-modified mortars is shown in Fig. 17.[24] 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 1 year or more, and their weatherability is greater than 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. 18.[29] In contrast to unmodified mortar-bonded specimens which failed within 1 year of outdoor exposure, most latex-modified

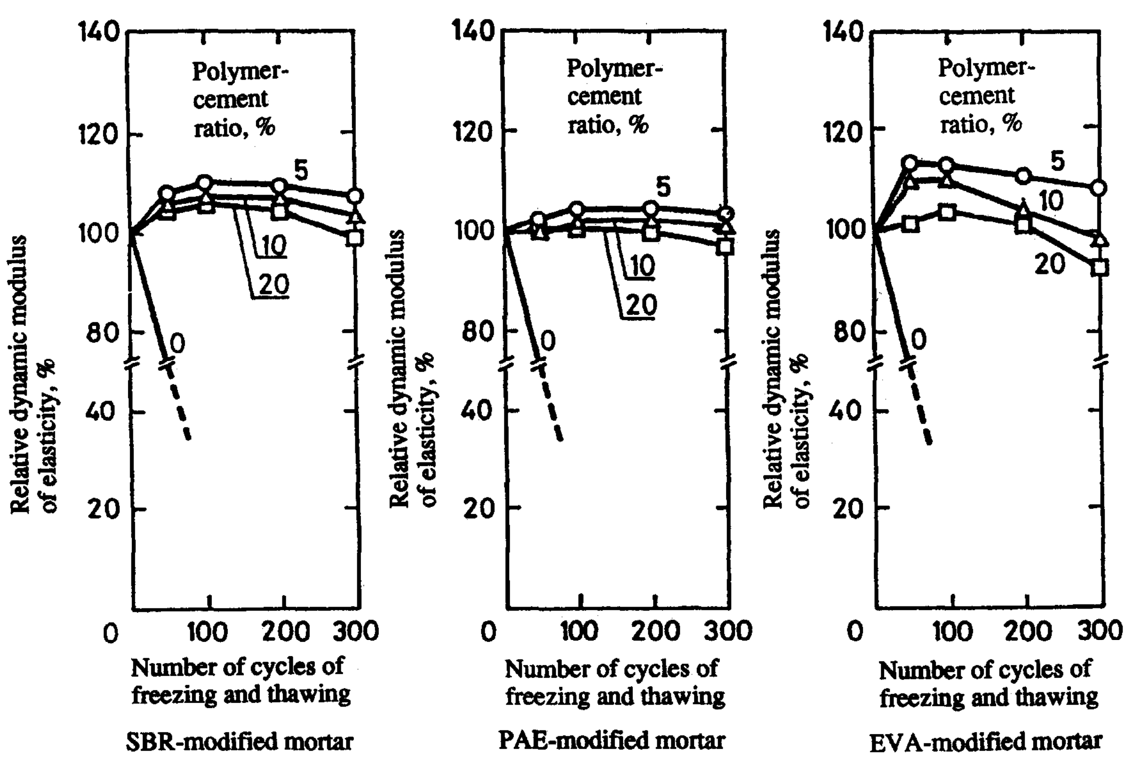


Fig. 16. Number of cycles of freezing and thawing vs. relative dynamic modulus of elasticity of latex-modified mortars.

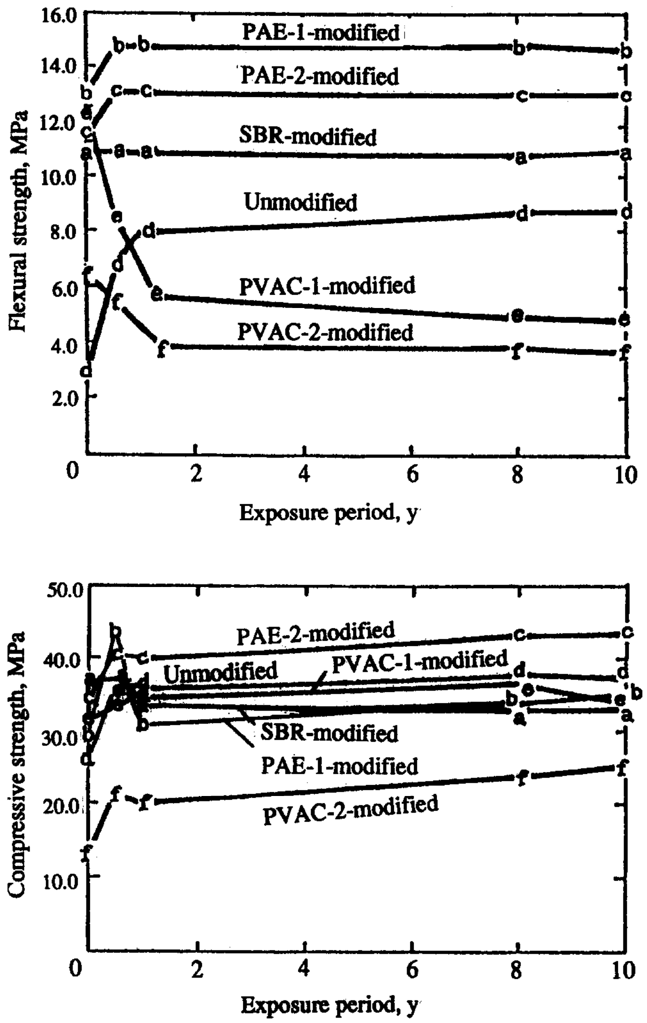


Fig. 17. Weatherability of latex-modified mortars. (Polymer–cement ratio, 20%.)

mortar-bonded specimens had a satisfactory adhesion for practical use after the 10-year exposure.

APPLICATIONS OF POLYMER-MODIFIED MORTAR AND CONCRETE

Of various polymer-modified mortars and concretes, 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 with 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 until 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. The typical applications of the latex-modified mortar and concrete are listed in Table 6.

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

Although more expensive compared with latex-modified mortar and concrete, liquid polymer-modified mortar and concrete appear to be gaining increasing acceptance in the construction industry. This may be because they give more rapid hardening, higher thermal stability

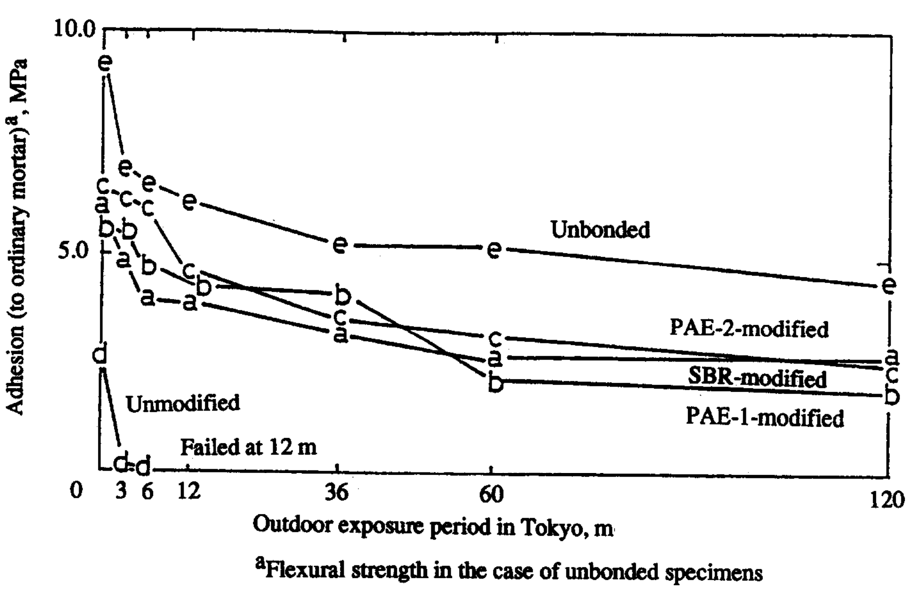


Fig. 18. Adhesion durability of latex-modified mortars. (M, months.)

Table 6. Typical applications of latex-modified mortar and concrete

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 thermal-insulating materials, adhesives for joining new cement concrete or mortar to old cement concrete or mortar, etc.
Decorative coatings (including surface preparation materials)	Wall coatings, coating materials for textured finishes of buildings, surface preparation materials for coatings, 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 or coatings	Effluent drains, chemical or machinery plant floors, grouts for acid-proof tiles, floors for chemical laboratories and pharmaceutical 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.

and better water resistance over the latex-modified system. Of them, epoxy-modified system has begun to gain popularity recently, but for the other liquid polymer-modified mortar and concrete, further testing in laboratories and more on-site experience are required.

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 works, 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 the US. Because the rapid deterioration of reinforced concrete structures has become a serious problem in Japan in recent years, 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. Thus, the polymer-modified mortar and concrete are currently becoming low-cost, promising materials for preventing chloride-induced corrosion and repairing damaged reinforced concrete structures. In their practical applications, the potential importance of property mismatch between repair materials and the reinforced concrete substrates has been highlighted.[30,31]

RECENT RESEARCH AND DEVELOPMENT ACTIVITIES

Tables 7 and 8 list recent research and development activities in polymer-based admixtures, polymer-modified mortars and concretes over the past several years. Some comments on such recent research and development activities are made below.

In recent years, the quality of the redispersible polymer powders has markedly been improved, in particular, in their film formation characteristics, and the properties of polymer-modified mortars and concretes using the redispersible polymer powders have become similar to those of polymer-modified mortars and concretes using polymer latexes. It is suggested from this fact that the polymer latexes will be replaced by the redispersible polymer powders in the production of the polymer-modified mortars and concretes in the near future.

When the combined use of polymer latexes and chemical admixtures advances further, new multifunctional chemical admixtures for cement concrete will successfully be developed in the future. Polymer-modified mortars and concretes using an epoxy resin without any hardener at polymer–cement ratios of 5–20% are the epoxy-hydraulic cement systems of new concept, and will develop the new applications of epoxy-modified mortars and concretes.

For the purpose of improving the workability, drying shrinkage and durability of fiber-reinforced cements and concretes, or increasing the flexural strength, toughness and impact resistance of polymer-modified mortars and concretes, fiber-reinforced polymer-modified cements and concretes are produced using steel, glass, polymer and carbon fibers. In particular, the polymer modification of glass fiber-reinforced cements is very effective in improving their durability. Recently, a strong interest has been oriented toward the polymer modification of carbon fiber-reinforced cements.

There are not commercially available MDF (macro-defect-free) cement products in the world at present because of their very poor water resistance. MDF cements using an anhydrous phenol resin precursor, which were newly developed by Maeda *et al.*,[55,56] have similar high flexural strength and very high water resistance compared with conventional MDF cement. Such superior water resistance may lead to the development of commercially available MDF cement products.

Because the rapid deterioration of reinforced concrete structures has become a serious problem in Japan, an intense interest is focused on polymer-modified mortars and pastes as repair materials, and there is a growing demand for them. As mentioned above, this trend is similar to that in other advanced countries. In connection with such a trend, the carbonation, chloride ion penetration and oxygen diffusion of the polymer-modified mortars and concretes have been most actively investigated in various countries. As a result, it is found that they have a marked resistance to carbonation, chloride ion penetration or oxygen diffusion. They can be recommended as a low-cost, promising repair materials for reinforced concrete structures.

Topics 10, 11, 12 and 13 in Table 8 are mainly concerned with environment-conscious developments in the field of polymer-modified mortar and concrete. In comparison with conventional membrane waterproofing systems

Table 7. Recent developments in polymer-modified mortar and concrete (Part 1)

Topic	*Outline*
1. High-grade redispersible polymer powders	Marked quality improvement of redispersible polymer powders (EVA, VAVeoVa, SAE and PAE) for PMM, and the development of prepackaged-type products such as decorative wall coatings, tile adhesives and filling compounds for surface preparation, using the redispersible polymer powders[32,33]
2. Combined use of polymer latexes and chemical admixtures	(1) Development of polymeric admixtures consisting of polymer latexes and chemical admixtures such as alkyl alkoxy silanes,[34] calcium nitrite as a corrosion inhibitor[35] and amino alcohol derivative[34] for highly durable concrete (2) Combined use of polymer latexes and superplasticizers[36,37] (3) Combined use of polymer latexes and an EP resin[38]
3. Combined use of polymer latexes and mineral admixtures	Combined use of polymer latexes and fly ash[39] or silica fume[40]
4. Unique polymer modification systems	(1) New epoxy modification systems[41,42] (2) UP-modified systems[43,44] (3) Vegetable oil-modified mortars[45]
5. Unique applications of superabsorbent polymers	(1) Development of waterproof backfilling material composed of asphalt emulsion, superabsorbent polymer and cement for underground structures[46] (2) Use of cooled superabsorbent polymer in precooling placement system for cement concrete[47] (3) Development of precast products manufactured by using superabsorbent polymers such as polyacrylates and applying compression or extrusion molding process[48]
6. Polymer modification for fiber reinforced mortars and concretes, and ferrocements	(1) Polymer modification of fiber-reinforced cement mortars and concretes using steel, glass, polymer and carbon fibers[49–52] (2) Polymer modification of ferrocements[53,54]
7. MDF cements	(1) Development of new MDF cements using an anhydrous phenol resin precursor, which has flexural strengths of 120–220 MPa and very high water resistance[55,56] (2) Improvements in the water resistance of MDF cements[57,58] (3) Fiber reinforcement of MDF cements[59]

Table 8. Recent developments in polymer-modified mortar and concrete (Part 2)

Topic	*Outline*
8. Very rapid-hardening PMM and PMC	(1) Development of shotcreting systems using magnesium acrylate, having a setting time of 1 s or less[60] (2) Development of SBR-modified ultrarapid-hardening PMM and PMC using ultrarapid-hardening cement for repair materials and overlays[61]
9. Durability of PCM	(1) Examination on carbonation[62,63], chloride ions (Cl^-)[63] or oxygen (O_2)[64] diffusion behavior of PMM (2) Long-term durability of polymer-modified concrete[65]
10. Repairing systems using PMM for reinforced concrete structures[66]	(1) Development of repairing systems using PMM and corrosion inhibitors[67] (2) Development of repairing systems using PMM and alkalinity-imparting agents (3) Development of PMM permanent forms using PAE emulsion with polyethylene nets or SAE emulsion with alkali-resistant glass fiber nets[68] (4) Development of repairing systems using PMM and carbon fiber reinforcement (carbon fiber-epoxy resin prepreg sheets)[69,70]
11. PMM waterproofing systems	(1) Development of PMM for liquid-applied membrane waterproof systems[71,72] (2) Development of siliceous coatings with EVA and PAE emulsions[73] (3) Development of waterproofing shotcrete system using rubberized asphalt-modified plates[74]
12. Artificial wood	Development of calcium silicate–SBR latex–glass fibers mixtures[75]
13. New paving materials	(1) Development of cold-mixed asphalt concrete using cement and asphalt emulsions[76–79] (2) Development of polymer-modified permeable concrete using SBR latex, PAE and EVA emulsions[80,81]

such as asphalt membrane waterproofing and liquid-applied membrane waterproofing systems with organic solvents, liquid-applied membrane waterproofing systems using polymer-modified mortars or slurries are free from hazardous and toxic organic solvents or gases with disagreeable odors, and do not pollute the atmosphere. In Japan, it is very difficult to execute hot-applied asphalt membrane waterproofing systems in built-up or urban areas at present, and the polymer-modified mortar liquid-applied membrane waterproofing systems are promising for deck roof waterproofing. The developments of artificial wood and permanent forms as replacements for plywood forms are most important from the viewpoint of the preservation of forest resources, especially tropical rain forests.

Table 9. JISs for polymer-modified mortars

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 and redispersible polymer powders for cement modifiers
JIS A 6909	Coating materials for textured finishes of buildings
JIS A 6916	Surface preparation materials for coatings

STANDARDS, STANDARD SPECIFICATIONS AND GUIDES

In recent years, polymer-modified mortars and concretes using various polymer-based admixtures such as polymer latexes, redispersible polymer powders, water-soluble polymers, 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 USA, Japan, UK and Germany. Tables 9 and 10 give JISs (Japanese Industrial Standards) and BSs (British Standards) on polymer-based admixtures and polymer-modified mortars, which have been published up to the present time. Table 11 lists the JCI (Japan Concrete Institute) Standards for Test Methods for

Table 10. 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: 1990	Method for measurement of modulus of elasticity in flexure and 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 11. 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 12. Standard specifications and guides for Polymer-modified mortars and concretes in USA, Germany 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) ICI 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 Ministry for Transport, The Federal Länder Technical Committee, Bridge and Structural Engineering (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) (1998) JASS 18 (Paint Work) (1998) JASS 23 (Spray Finishing) (1998)
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)

Polymer-Modified Mortars in Japan. In addition, Table 12 shows the standard specifications and guides for polymer-modified mortars and concretes, which are prevalent in USA, Germany, Japan and RILEM.

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