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Review
Use of polymers for cement-based structural materials

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Cement-based materials are widely used in the civil infrastructure. Polymers as admixtures can improve the properties, particularly in relation to water absorption reduction, toughness enhancement, vibration damping and increase of the bond strength of cement to reinforcements. Polymeric admixtures include particles, short fibers and organic liquids. Latex in the form of an aqueous particle dispersion is most common. Other than being used as admixtures, polymers are used as partial replacement of fine aggregate, for coating, sealing and repairing concrete and for coating steel reinforcing bars for corrosion protection.

1. Introduction
Cement-based materials are the dominant structural materials for the civil infrastructure. The addition of a minor amount of a polymer to a cement mix can significantly enhance the properties of the resulting material, which is known as a polymer-modified cement-based material. These additives, known as admixtures, can be in the form of polymer particles, short polymer fibers or liquids [1]. Fibers are in general more effective than particles for toughening the cement-based material, but they are more expensive. Any form of polymer is expensive compared to cement. Low cost is critical to the practical viability of a cement-based material.

2. Polymer particles as admixtures
Polymer particles used as admixtures can be in the form of a dry powder or an aqueous dispersion of particles. The latter form is more common. Either form as an admixture results in improved joining of the mix constituents (e.g., sand), due to the presence of interweaving polymer films [2, 3]. The improved joining leads to superior mechanical and durability characteristics. Aqueous dispersions of polymer particles are more effective than dry polymer powder for the development and uniform distribution of polymer films [2]. The most common form of polymer in aqueous dispersions is latex, particularly butadiene-styrene copolymer [3, 4]. The dispersions are stabilized by the use of surfactants.

In polymer-modified cement-based material, polymer particles are partitioned between the inside of hydrates and the surface of anhydrous cement grains [5]. The presence of the polymer results in improved pore structure, thereby decreased porosity [6]. Furthermore, the workability is enhanced and the water absorption is decreased [6, 7]. The enhanced workability allows the use of lower values of the water/cement ratio [7]. The rate of hydration is reduced by the presence of the polymer [5, 8].

The addition of a polymer tends to increase the flexural strength and toughness, but lower the compressive strength, modulus of elasticity and hardness [7–10]. Furthermore, the polymer addition is effective for enhancing the vibration damping capacity [11], the frost resistance [12, 13], and the resistance to biogenic sulfuric acid corrosion (relevant to sewer systems) [14]. In addition, polymer addition imparts stability and thixotropy to grouts [15] and enables control of the rheology and stabilization of the cement slurry against segregation [16].

Dry polymer particles used as an admixture can be water-redispersible polymer particles, such as those obtained by spray drying aqueous dispersions. Examples are acrylic [17] and poly(ethylene-vinyl acetate) [18]. Redispersibility may be attained by the use of functional monomers [17]. The effectiveness of redispersible polymer particles depends on the cement used [19].

A special category of polymer particles is superabsorbent particles (hydrogel), which serve to provide controlled formation of water-filled macropore inclusions (i.e., water entrainment) in the fresh concrete [21]. The consequence is control of self-dessication. Another kind of superabsorbent polymer can hardly absorb alkaline water in fresh/hardened concrete, but can absorb much neutral/acid water and make gel. Thus, when neutral water is poured on concrete after setting, the concrete is coated with the gel and thus can be kept without drying [21].

3. Organic liquids as admixtures
Organic liquid admixtures can be polymer solutions (involving water-soluble polymers such as methylcellulose, polyvinyl alcohol and polyacrylamide [22]) or

resins (such as epoxy [23] and unsaturated polyester resin). The liquid form is attractive in its ease of uniform spatial distribution, and hence effectiveness in even a small proportion. In contrast to polymer solutions, particles (including particle dispersions) tend to require a higher proportion in order to be comparably effective.

Polymer solutions as admixtures can serve to optimize the air void distribution and rheology of the wet mix, thereby improving workability with low air content [24]. They are important for macrodefect-free (MDF) cements, which are attractive in their high flexural strength [22]. However, MDF cements have poor water resistance, due to the water soluble polymers in them [22].

4. Short polymer fibers as admixtures

Short fibers rather than continuous ones are used because they can be incorporated in the cement mix, thereby facilitating processing in the field. Furthermore, short fibers are less expensive than continuous ones. Polypropylene, polyethylene and acrylic fibers are particularly common [25–27], due to the requirements of low cost and resistance to the alkaline environment in cement-based materials.

Compared to carbon, glass and steel fibers, polymer fibers are attractive in their high ductility, which results in high flexural toughness in the cement-based material [27]. Combined use of short polymer fiber and polymer particle dispersion (e.g., latex) results in superior strength (tensile, compressive and flexural) and flexural toughness compared to the use of fiber without polymer particle dispersion [27]. Table I [27] shows the effect of latex addition and of the fiber type on the flexural toughness.

5. Mechanical properties

In the absence of fiber, both flexural toughness and strength increase monotonically with increasing content of polymer particle dispersion (latex). However, in the presence of fiber (e.g., carbon fiber), the flexural toughness decreases monotonically with increasing content of polymer particle dispersion, because the degree of fiber dispersion decreases with increasing content of polymer particle dispersion. In the presence of fiber, the flexural strength attains a maximum at an intermediate content of polymer particle dispersion, because the air void content is minimum at this intermediate content of polymer particle dispersion [27]. Table II [28] shows the effect of competing non-fibrous admixtures on the reinforcing ability of carbon fiber.

TABLE I Flexural toughness of cement mortars [27]

	Flexural toughness (MPa·mm)	
Fiber type (0.35 vol%)	Without latex	With latex[b]
Steel	0.638	1.000
Carbon	0.475	0.856
Polyethylene[a]	1.305	1.318
No fiber	0.223	0.500

[a]High modulus (Spectra 900, Allied Signal, Inc.).
[b]20% by weight of cement.

TABLE II Fractional increase of the tensile strength due to the fibers alone for cement pastes. The increase is relative to the case without fibers but with the corresponding non-fibrous admixture(s) [28]

Fiber volume fraction (%)	With L	With M	With M + SF
0.53	0.040	0.42	1.27
1.06	0.043	0.91	1.45
2.12	0.205	1.23	2.42
3.18	0.096	1.17	2.63
4.24	−0.036	0.93	2.00

Note: L = latex; M = methylcellulose; SF = silica fume.

A comparative study of a latex particle dispersion and a methylcellulose solution, both as admixtures in the presence of carbon fiber, shows that latex gives superior tensile/flexural properties and lower content and size of air voids than methylcellulose, but methylcellulose is superior to latex in giving a high degree of fiber dispersion [27]. Acrylic dispersion is more effective than latex dispersion or methylcellulose solution in enhancing the tensile properties in the presence of carbon fiber [29].

In the absence of fiber, methylcellulose solution as an admixture increases the tensile strength and ductility significantly, such that the effects increase with increasing methylcellulose content [30].

Fig. 1 [28] shows the flexural toughness of cement pastes containing various amounts of latex, with 0 and 0.53 vol% carbon fibers. The flexural toughness increases monotonically with increasing latex/cement ratio when fibers are absent, but decreases monotonically with increasing latex/cement ratio when fibers are present. At any latex/cement ratio, fiber addition greatly increases the toughness.

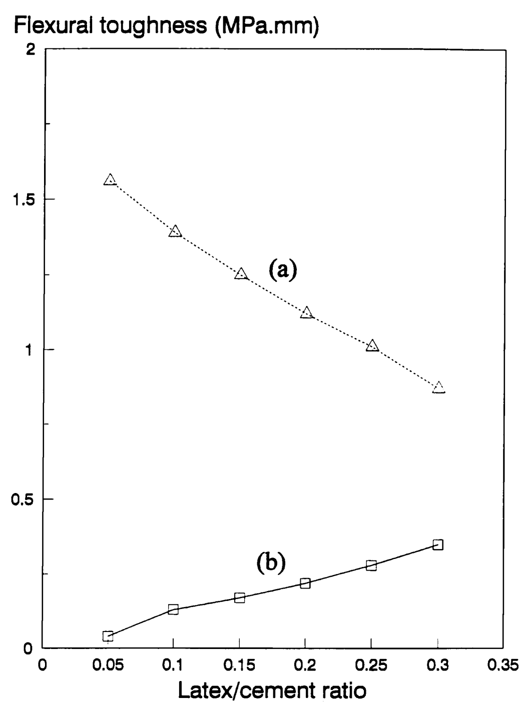

Figure 1 Effect of latex/cement ratio on the flexural toughness when the cement paste contains: (a) 0.53 vol% carbon fibers and (b) no fibers [28].

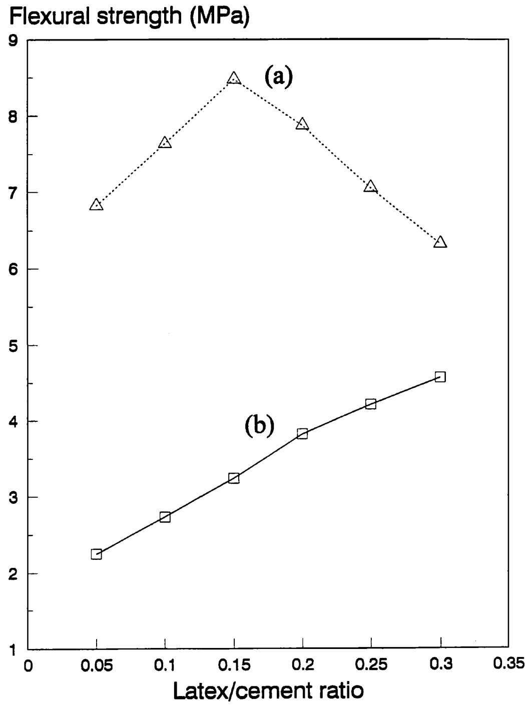

Figure 2 Effect of the latex/cement ratio on the flexural strength when the cement paste contains: (a) 0.53 vol% carbon fibers and (b) no fibers [28].

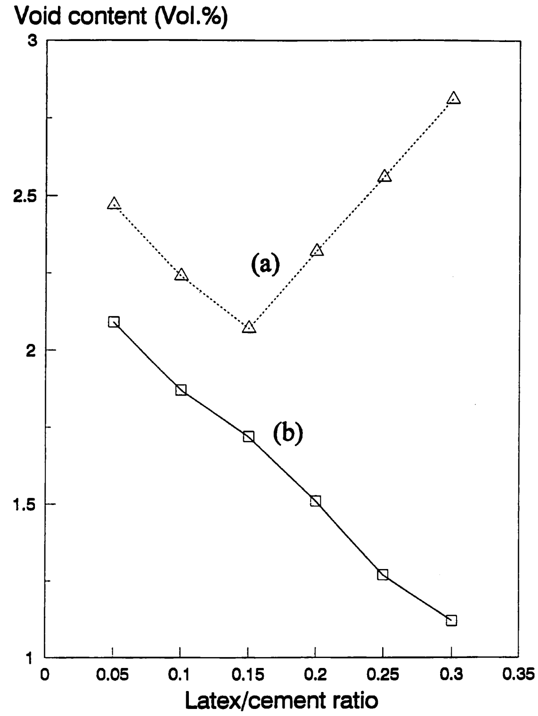

Figure 3 Effect of the latex/cement ratio on the void content when the cement paste contains: (a) 0.53 vol% carbon fibers and (b) no fibers [28].

Fig. 2 [28] shows the flexural strength of cement pastes containing various amounts of latex, with 0 and 0.53 vol% fibers. The flexural strength increases montonically with increasing latex/cement ratio when fibers are absent, but first increases and then decreases with increasing latex/cement ratio (so that the flexural strength is maximum at a latex/cement ratio of 0.15) when fibers are present. At any latex/cement ratio, fiber addition increases the flexural strength.

Fig. 3 [28] shows the void content of cement pastes containing various amounts of latex, with 0 and 0.53 vol% carbon fibers. The void content decreases monotonically with increasing latex/cement ratio when fibers are absent, but first decreases and then increases with increasing latex/cement ratio (so that the void content is minimum at a latex/cement ratio of 0.15) when fibers are present. At any latex/cement ratio, fiber addition increases the void content.

The volume electrical resistivity of cement pastes increases monotonically with increasing latex/cement ratio, whether with 0 or 0.53 vol% carbon fibers. At any latex/cement ratio, fiber addition greatly decreases the resistivity. Fig. 4 [28] gives the ratio of the measured conductivity (reciprocal of the measured resistivity) to the calculated conductivity (obtained from the Rule of Mixtures by assuming, for the sake of computational simplicity, that the fibers were unidirectional and continuous along the direction of resistivity measurement). In using the Rule of Mixtures, the matrix conductivity is taken as the conductivity of the cement paste without fibers, but with the corresponding latex/cement ratio. Fig. 4 shows that the degree of fiber dispersion decreases with increasing latex/cement ratio.

Figs 1 and 4 point to the conclusion that the degree of fiber dispersion decreases with increasing latex/cement

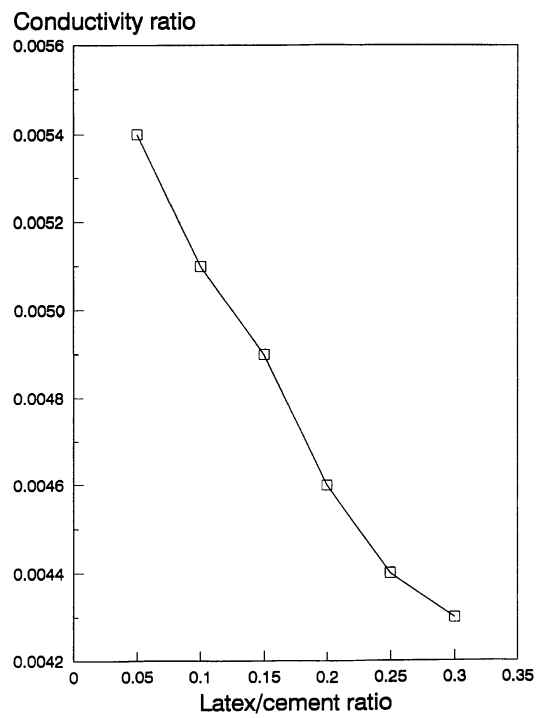

Figure 4 Effect of the latex/cement ratio on the measured/calculated conductivity ratio when the cement paste contains 0.53 vol% carbon fibers [28].

ratio. In other words, the decrease in the flexural toughness with increasing latex/cement ratio when fibers are present is due to the decrease in the degree of fiber dispersion.

Figs 2 and 3 point to the conclusion that the flexural strength is governed by the void content, so that it increases when the void content decreases and decreases when the void content increases. The void content decreases with increasing latex/cement ratio from 0.05

TABLE III Loss tangent (tan δ, ± 0.002) of cement pastes at 0.2 Hz [32]

Plain	0.035
+L (20%)	0.122
+L (25%)	0.135
+L (30%)	0.142
+M (0.4%)	0.073
+SF (15%)	0.107
+M (0.4%) +SF (15%)	0.105

Note: L = latex; M = methylcellulose; SF = silica fume. Percentages are by weight of cement.

to 0.15 when fibers are present, because of the matrix, as indicated by the similar decrease when the fibers are absent (Fig. 3). The void content increases with increasing latex/cement ratio from 0.15 to 0.30 when fibers are present, because of the fibers (rather than the matrix, the void content of which decreases with increasing latex/cement ratio from 0.15 to 0.30), even though the fiber volume fraction is only 0.53%.

Latex addition is effective for enhancing the abrasion resistance. However, it is less effective than silica fume, which is a fine ceramic particulate admixture [31].

6. Vibration damping capacity

The vibration damping capacity, as expressed by the loss tangent, is enhanced by the use of latex particle dispersion or methylcellulose solution. The effect increases with increasing latex content. This is due to the viscoelastic behavior of the polymers. Methylcellulose solution (in a relatively small proportion) in combination with silica fume is also effective, due mainly to the contribution to damping by the interface (though diffuse) between silica fume and cement [32]. Table III [32] shows the loss tangent at 0.2 Hz, as measured under dynamic flexure.

7. Bond strength to reinforcements

Latex particle dispersion and methylcellulose solution as admixtures enhance the bond strength with steel rebar, steel fiber or carbon fiber, such that latex (20% by weight of cement) is as effective as methylcellulose (0.4–0.8% by weight of cement). The combined use of methylcellulose (0.4% by weight of cement) and silica fume (15% by weight of cement) as admixtures is more effective than either methylcellulose or silica fume in increasing the bond strength. Latex in combination with silica fume does not work, due to low workability [33].

Figs 2 and 6 [33] show the effects of latex, methylcellulose and silica fume as admixtures in concrete and of ozone treatment of steel rebar on the bond strength of concrete to steel rebar. The bond strength is correlated with the contact electrical resistivity of the steel-concrete interface, as found by measuring both quantities for each interface specimen. Polymer admixtures (curves (b) and (c) of Fig. 5) are slightly less effective than ozone treatment of rebar (curve (d) of Fig. 5) for increasing the bond strength between rebar and concrete (as well as that between carbon fiber and cement paste [33]). Between the two polymer admixtures, latex

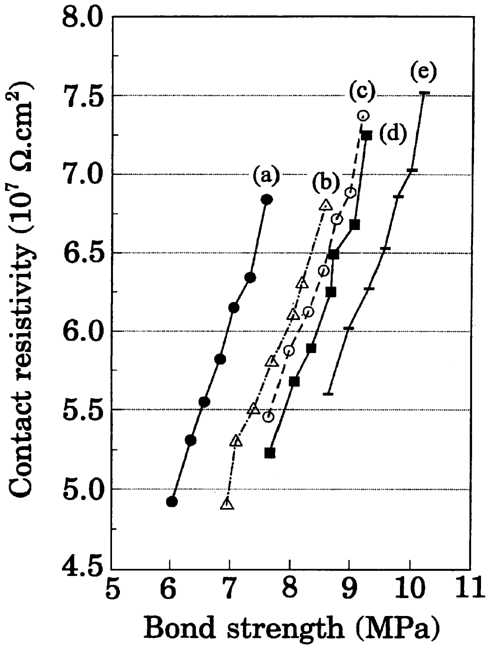

Figure 5 Variation on the contact electrical resistivity with bond strength between steel rebar and concrete: (a) plain concrete and untreated rebar, (b) concrete with methylcellulose addition and untreated rebar, (c) concrete with latex addition and untreated rebar, (d) plain concrete and ozone treated rebar and (e) concrete with latex addition and ozone treated rebar [33].

(curve (c) of Fig. 5) increases the bond strength slightly more significantly than methylcellulose (curve (b) of Fig. 5), at least partly due to the large amount of latex compared to the amount of methylcellulose. The combined use of latex and ozone treatment (curve (e) of Fig. 5) gives significantly higher bond strength than ozone treatment alone (curve (d) of Fig. 5). Relative to the combination of plain concrete and untreated rebar, the combined use of latex and ozone treatment results in a 39% increase in the bond strength. Ozone treatment, latex addition and combined ozone treatment and latex addition cause similarly small increases in the contact resistivity.

The contact resistivity increase after latex addition is presumably due to the high volume resistivity of the latex present at the rebar-concrete interface. The bond strength increase after latex or methylcellulose addition is attributed to the adhesion provided by the polymer at the interface.

The combined use of silica fume and methylcellulose as two admixtures further enhances the bond strength between rebar and concrete beyond the values attained by the use of silica fume as the sole admixture or the use of methylcellulose as the sole admixture, as shown in Fig. 6.

In spite of the fact that the mechanical interlocking between rebar and concrete due to the surface deformations on the rebar contributes much to the bond strength between rebar and concrete (as shown by the much higher bond strength between rebar and concrete than that between steel fiber and cement paste [33]), the ozone treatment of the rebar and the polymer admixtures to the concrete give significant increases to the bond strength between rebar and conrete. In the case of

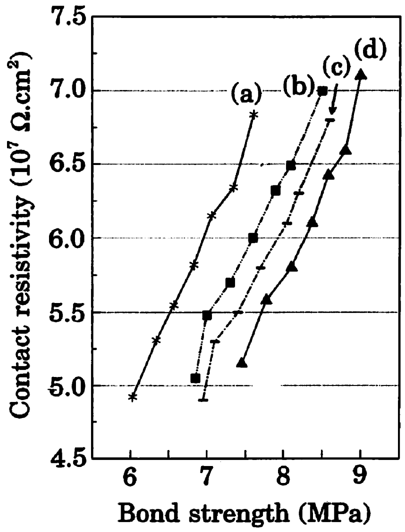

Figure 6 Variation of contact electrical resistivity with bond strength between steel rebar and concrete: (a) plain concrete, (b) concrete with silica fume, (c) concrete with methylcellulose and (d) concrete with silica fume and methylcellulose [33].

the bond between stainless steel fiber and cement paste, the polymer admixtures (latex or methylcellulose) in the cement paste cause the bond strength to increase by 90% [33]. If the surface deformations on the steel rebar were absent, the effects of ozone treatment of rebar and of polymer admixtures in concrete would have been much larger than those described above.

8. Thermal properties

The thermal properties are relevant to the thermal insulation of buildings. A low thermal conductivity and a high specific heat are desired [34, 35]. The thermal conductivity and creep rate are decreased and the specific heat is increased by latex particle dispersion or methylcellulose solution. As shown in Table IV [34], methylcellulose (0.6–0.8% by weight of cement) is as effective as latex (20–25% by weight of cement) for decreasing the thermal conductivity, and methylcellulose (0.6–0.8% by weight of cement) is more effective than latex (20–30% by weight of cement) for increasing the specific heat. Methylcellulose (0.4% by weight of cement) gives higher flexural storage modulus than latex (20–30% by weight of cement) [34].

TABLE IV Thermal conductivity and specific heat of cement pastes at room temperature [34]

Cement paste	Thermal conductivity (W/m·K) (±0.03)	Specific heat (J/g·K) (±0.001)
Plain	0.52	0.703
+ L (20%)[a]	0.38	0.712
+ L (25%)[a]	0.32	0.723
+ M (0.4%)[a]	0.28	0.736
+ M (0.6%)[a]	0.38	0.737
+ M (0.8%)[a]	0.32	0.742
+ SF (15%)[a]	0.36	0.765
+ SF (15%)[a] + M (0.4%)[a]	0.33	0.771

Note: L = latex; M = methylcellulose; SF = silica fume.
[a]Percentage by weight of cement.

Cement pastes with methylcellulose or latex contract upon compression and heating, mainly due to softening upon heating, though creep also contributes to the contraction. Plain cement paste expands upon heating due to thermal expansion up to 113°C, beyond which contraction occurs due to softening and creep.

9. Applications

In addition to conventional structural applications, polymer-modified cement-based materials are used for floor finishing (self-leveling mortars [36]), heavy metal immobilization [37], repair [38, 39], permeable porous concretes (for drainage and noise absorption) [40], masonry mortars [41], and well cementing [42].

10. Recycled polymers

Due to their low cost, recycled polymers are attractive. Recycled plastics and tire rubber are used as partial replacement of fine aggregate for providing soft inclusions [43, 44]. The bond between crumb rubbers and cement can be enhanced by the addition of latex [44]. Recycled waste latex paint is also used as an admixture [45].

11. Polymers not as admixtures

Polymers (rather than polymer-modified cement-based materials) are used for coatings on concrete for protection and decoration [46]. Examples are epoxy [47, 48], polyurethane [47], silane [49] and siloxane [49]. Epoxy is also used to fill gaps [50, 51], concrete repair [52, 53], structural connection [54], and the coating of steel reinforcing bars (rebars) for corrosion protection [55–57]. Furthermore, epoxy and high-molecular-weight methacrylate are used for sealing [58, 59], latex and polyvinyl chloride solution are used for coating concrete [60].

12. Conclusion

Polymers in the form of aqueous particle dispersions, dry powder, solutions or resins are used as admixtures to improve the properties of cement-based materials. The improvement pertains to increase of the workability, flexural strength, toughness, vibration damping capacity, frost resistance, resistance to biogenic sulfuric acid corrosion, and bond strength of cement to reinforcements, in addition to decrease of the water absorption and thermal conductivity. Recycled polymers are also used as partial replacement of fine aggregate. Moreover, polymers are used for coating, sealing, gap filling, repair, structural connection and corrosion protection of steel rebars.

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