

Review on the Impact of Polymer-Modified Bonding Agents on the Bond Strength Between New and Old Concrete Layers

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Abstract. This review summarizes the effects of polymer-modified interfacial agents on the bonding performance between new and old concrete layers. It discusses the advantages and disadvantages of various polymers used in interfacial agents from a materials perspective and elucidates the mechanisms by which polymers enhance interfacial bonding. The anchoring effect of fibers and the film-forming action of polymers synergistically improve the bonding strength and toughness of the material. Despite the promising application prospects of polymer-modified materials in concrete repair and strengthening, challenges remain, such as insufficient early strength and variability in bonding performance after modification with different polymers. Therefore, a systematic and standardized investigation into the impact of polymer type and dosage on bonding performance is necessary.

Keywords: Polymer-modified interface agents; Polymers and fibers; Bonding performance; Bonding mechanisms.

1 Introduction

As the construction of global concrete structures increases, many are at risk of aging, making their repair particularly urgent. Examples include the bonding of bridge deck reinforcement layers to old bridge surfaces, the overlaying of new concrete on old concrete pavements, the segmented construction of tunnel corridors, the layer-by-layer pouring of large-volume concrete in excavated tunnels, and the repair and reinforcement of ports and docks ^[1]. During the repair process, the interface is a weak link in the combination of old and new concrete and significantly affects the tensile and shear strength as well as the durability of the overall concrete structure. Therefore, the bond strength between old and new concrete is crucial to the quality of the repaired and retrofitted concrete structures. Due to the restraint of old concrete on new concrete layers, pouring new concrete directly on old concrete can easily lead to cracking issues^[2]. The

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H. Bilgin et al. (eds.), Proceedings of the 2024 6th International Conference on Civil Engineering, Environment Resources and Energy Materials (CCESEM 2024), Advances in Engineering Research 253, https://doi.org/10.2991/978-94-6463-606-2_29

bond strength at the concrete-to-concrete interface mainly depends on factors such as interface adhesion, friction, aggregate interlock, and time-dependent changes^[3]. To enhance the bond between old and new concrete, a popular method currently is to place a new cementitious material layer on the old concrete substrate ^[4]. Materials used in concrete repair come in various forms, including cement-based, modified cement-based, and resin-based, with resin-based and modified cement-based materials becoming increasingly popular^[4]. Polymers, as a common modification material for cement-based materials, are not only used in concrete but also in cement mortars due to their environmental friendliness and cost-effectiveness^[5, 6]. The incorporation of polymers as modifiers in cement mortar is thus gaining more popularity and attention.

This paper critically reviews the testing methods for evaluating the bonding performance between new and old concrete, and also introduces the bonding mechanism between new and old concrete in concrete repair, as well as the interfacial bonding performance of various types of polymer-modified interfacial agents, providing a reference for the selection of suitable polymers. To enhance the toughness and shear resistance of polymer-modified interfacial agents, the paper concludes with an introduction to the impact of incorporating fibers into polymer-modified interfacial agents on their bonding and durability performance.

2 Bonding Mechanism

For cement-based material interface agents, the hydration products of new concrete penetrate into the old concrete, primarily with hydrated calcium silicate infiltrating the old concrete, thereby increasing the mechanical anchoring at the interface, similar to the modification of the Transition Zone (OTZ). The interface agent mainly enhances the bonding performance between the new and old concrete layers through the following points:

Improve the adhesion between the new and old concrete layers, that is, enhance its own bonding performance with concrete.

Have deformation properties similar to those of the new and old concrete, resulting in minimal shrinkage stress between them.

The addition of polymers can enhance the durability and density between the new and old concrete layers, reducing the damage to the structure caused by external erosion.

Wang^[7]pointed out that the old concrete is linked by physical forces such as mechanical interlocking, van der Waals forces, and surface tension. Among these, the mechanical interlocking at the macro level is provided by the roughness of the old concrete surface. The mechanical interlocking at the micro level is composed of the following three parts^[8]:

Mechanical anchoring is produced by the growth of hydration products in the pores of the old concrete as the hydration reaction of the new concrete or interface agent continues. The spikes on the surface of the hydrated calcium silicate and the radiating needleshaped ettringite of the new concrete penetrate into the capillary pores of the old concrete, connecting the new and old concrete into a single entity. c. Unhydrated or partially hydrated substances in the existing concrete undergo hydration in the new concrete.

The van der Waals forces between the new and old concrete layers are generated by the interaction between crystal molecules in the cement stone at the interface.

Even if chemical reactions can occur at the interface of the new and old concrete. such reactions are extremely weak and can be neglected in terms of their impact on the bonding between the new and old concrete layers. The bonding mechanism of polymers with the interface mainly proceeds through the following steps: First, polymer particles are evenly distributed in the cement paste, forming polymer-modified mortar. Secondly, the polymer-modified mortar penetrates into the pores and capillaries of the substrate and forms a polymer film within the pores and capillaries. Then, with further hydration, the polymer film generates a bridging effect by anchoring and self-tension at the interface between the polymer-modified mortar and the tile, causing the polymer film to firmly adhere to the interface. Finally, the polymer forms a sub-adhesive composite, distributed in the form of bridging and porous polymer films to absorb and transfer energy, coagulate together, and form a continuous polymer network microstructure, connecting the cementitious substrate and hydration products together to form a tight bond^[9]. The film formation of the polymer not only increases its interface bonding strength but also contributes to improving the impermeability of the interface. Peng et al.^[10]found through SEM that after mixing with cement mortar, the polymer film can adsorb onto the surface of the aggregate and may partially fill the pores in the Interface Transition Zone (ITZ), preventing partial water invasion. The above analysis is from the perspective of polymer film formation. Li^[11]analyzed from the perspective of polymer modification of the mortar's pore structure and found that the addition of polymers optimizes the internal structure of the mortar, making the microstructure more compact. The polymers diffuse and connect with each other, forming a polymer film network structure within the mortar, tightly connecting the hydration products and thereby enhancing the interface bonding strength. The addition of polymers, while reducing the pore size, also increases the porosity of the mortar. The reason may be the air-entraining effect of the polymer ^[10].

3 Influence of Polymer Types in Interface Agents on the Bonding Performance between New and Old Concrete Layers

To mitigate the adverse effects of the weak interface between new and old concrete layers on the performance of repaired structures, the use of interface agents can enhance the bonding performance between these layers in practical engineering applications. Interface agents are primarily categorized into three types: cementitious, epoxy^[12], and polymer-based. This paper focuses mainly on polymer-based interface agents. Compared to conventional cement-based materials, polymer-modified cementitious materials exhibit superior deformability, and the incorporation of polymers can improve the

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distribution of pores^[13], increasing the number of smaller pores and reducing the number of larger ones. The microstructure is denser, and the macroscopic toughness and durability are enhanced^[14-16]. Owing to these advantages, polymer-modified cementitious materials have been widely applied in bonding areas such as road surfaces, bridge decks, facades, and concrete repair, making them an important alternative material for the repair and reinforcement of concrete structures.

3.1 Classification of Polymers in Interface Agents

Polymers in interface agents can be categorized into polymer dispersions and watersoluble polymers (monomers or powdered polymers). Polymer-modified cementitious interface agents are prepared by modifying cement paste and cement mortar with emulsion or dry powder forms of high molecular weight polymers. The types of polymers commonly used in engineering for adhesive polymer-modified cementitious materials are presented in Table 1^[17, 18].

| Polymer state | Polymer type | Polymer type Polymer name | | | |
|--|----------------------|--|--|--|--|
| | Rubber emul- | Rubber emul- Polymerized Styrene Butadiene Rubber(SBR), Butadiene Rub- | | | |
| | sion, ber (BR), etc. | | | | |
| | | Thermosetting emulsion: Epoxy Resin Emulsion, Bituminous | | | |
| | Resin emulsion | Emulsion, Bitumen Rubber. | | | |
| Emulsion | | Thermoplastic emulsion: Polyvinyl Acetate (PVAc), Polyacry- | | | |
| | | late Emulsion (PAE), etc. | | | |
| | Blended emul- | | | | |
| | sion | Blended Latex, etc. | | | |
| Liquid | | Epoxy resin, etc. | | | |
| Water-soluble poly- mers and monomers | | Polyvinyl alcohol (PVA), Cellulose Ether (CE), Magnesium Polyacrylate, etc. | | | |
| Redispersible powders | Hermoplastic | Vinyl Acetate-Vinyl Carbonate (VAc/VC), Ethylene-Vinyl Ac- | | | |
| | powders | etate (EVA), Ethylene-Acrylic Acid (EAA), etc. | | | |
| | Elastic powders | Styrene-Butadiene etc. | | | |

| Table 1. Polymers Commonly Used in Engineering for Adhesive Polymer-Modified Cementi- |
|---|
| tious Materials ^[17, 18] |

Currently, some scholars also use epoxy polymers for the modification of interface agents. Epoxy possesses several advantages such as low shrinkage during curing, high adhesion to many substrates, chemical resistance and moisture-proofing, low cost, good mechanical strength, dimensional stability, flame retardancy and corrosion resistance, and being non-volatile organic compounds ^[19, 20]. However, the performance of epoxy-based adhesives deteriorates significantly at high temperatures. Some thermosetting polymer structures in epoxy make it more brittle and less capable of resisting crack

initiation and growth^[21], Additionally, epoxy-based interface agents are also susceptible to the effects of curing temperature, and freeze-thaw cycles can lead to a reduction in their interfacial shear strength^[22]. Epoxy is also sensitive to the external environment: epoxy resins are particularly sensitive to ultraviolet light, which can lead to the oxidation of ether and amine groups, causing surface scaling and cracking^[23]. Abdwais^[24]found through research that the mechanical properties of epoxy-based polymer matrices rapidly deteriorate at high temperatures, and toxic fumes can be produced when the temperature exceeds its glass transition temperature, which is detrimental to individuals within structures filled with such materials. Therefore, many scholars have turned to cement-based adhesives as an alternative to epoxy-based adhesives, which is crucial for improving the high-temperature performance and durability of the adhesive, reducing material costs, minimizing toxic hazards to humans, and reducing the environmental impact of volatile organic compound emissions. Lim^[25]conducted research on crack propagation in interface failure and found that engineered cementitious composites (ECC) are more effective in capturing interface cracks, with tortuous cracks becoming trapped or lodged within the ECC material. Consequently, the role of cement-based polymer-modified interface agents in repair materials has once again gained attention.

3.2 The Impact of Polymer Type on the Bonding Performance between New and Old Concrete Layers in Interface Agents

Incorporating polymers into cementitious grout interface agents can significantly enhance the interfacial bonding performance between new and old concrete layers. $Xu^{[26]}$ and others have found through experiments that polymer-modified cement grout interface agents can improve the transverse and axial pull-off performance between new and old concrete layers. The interface pull-off strength increased by 114% and 96% after 7 days and 28 days, respectively, after incorporating styrene-butadiene latex. $Xu^{[26]}$ compared the influence of different styrene-butadiene latex proportions on the pull-off bonding performance between new and old concrete layers through pull-off tests. It was found that when the polymer-to-cement ratio was 1:3, the styrene-butadiene modified interface agent provided the optimal enhancement of bonding performance between new and old concrete layers, with an improvement of 18.7%.

In addition to incorporating styrene-butadiene latex, other scholars have also studied the impact of other polymers on interfacial bonding performance. Nong^[27, 28]compared the bonding performance of acrylic, styrene-acrylic, and chlorobutyl polymer emulsion-modified interface agents under different curing methods. It was discovered that polymer-modified interface agents generally enhance the bonding performance between new and old concrete layers compared to conventional interface agents, with the acrylic-modified interface agent showing the highest improvement in bonding performance with old concrete. Moreover, polymer-modified interface agents each have their own suitable bonding curing methods. He^[29]also studied the bonding performance of acrylic, pure acrylic, and chlorobutyl polymer-modified interface agents through eightshaped bond strength and core drilling pull-off tests, indicating that the acrylic-modified interface agent has excellent bonding performance, while the other two polymers perform relatively poorly. $Xu^{[26]}$ used pull-off and splitting tests to investigate the impact of styrene-butadiene, styrene-acrylate, acrylic, and vinyl acetate-ethylene cement grout interface agents on interfacial bonding performance. The results showed that the styrene-butadiene polymer-modified cement grout interface agent had the best pull-off bonding performance, with the interface bonding strength first increasing and then decreasing as the polymer-to-cement ratio increased. Concurrently, the splitting strength of horizontally cast interface agents was higher than that of laterally cast ones.

The incorporation of polymers not only enhances interfacial bonding performance. but numerous scholars have also conducted research on toughness and durability. Liu et al. ^[30]modified cement grout interface agents with ethylene-vinyl acetate (EVA) emulsion polymers and found that the addition of polymers could reduce the shrinkage rate of the interface agent, with improved permeability resistance, carbonation resistance, and frost resistance all increasing with the increase in polymer content. Ma et al.^[31]modified interface agents by incorporating polypropylene ester (PA) and polyurethane (PU/PA) polymers. The tests revealed that the addition of polymers would decrease the compressive strength and modulus of elasticity of the interface agent, but would not affect the relationship between modulus of elasticity and compressive strength, yet it would improve its flexural strength and toughness, with PU/PA showing greater improvement in strength and toughness compared to PA. EVAE latex powdermodified interface agents exhibit higher interfacial bond strength than SBR-modified interface agents, and EVA latex powder-modified interface agents possess excellent carbonation resistance, erosion resistance, water reduction, and permeability resistance^[32]. Among the four polymers of styrene-acrylic, styrene-butadiene, EVA, and acrylic, styrene-butadiene has the highest water reduction rate and permeability resistance, styrene-acrylic has the strongest retarding effect, and the addition of polymers generally increases the basic toughness of the interface agent [33]. Ma et al.[31]modified interface agents by incorporating polypropylene ester (PA) and polyurethane (PU/PA) polymers. The tests found that the addition of polymers would decrease the compressive strength and modulus of elasticity of the interface agent, but would not affect the relationship between modulus of elasticity and compressive strength, yet it would improve its flexural strength and toughness, with PU/PA showing greater improvement in strength and toughness compared to PA.

Polymers enhance interfacial bonding performance and durability, and some scholars have conducted microscopic research and explanations. At the microscopic level, the interfacial transition zone (ITZ) with incorporated polymers is denser than the internal structure without polymers^[9], with fewer obvious defects, improving the compactness of the ITZ and thus enhancing interfacial bonding performance^[34]. In addition, the addition of polymers can form polymer bridges between new and old concrete, increasing the bonding effect between them^[12]. Mansur et al. ^[35]studied the bonding performance of PVA-modified cement interface agents using SEM and found that after incorporating PVA into the interface agent, almost no pores were visible at the interface, and the transition zone was minimal, indicating that the addition of PVA reduced the thickness of the ITZ. Macroscopically, the addition of PVA changed the failure mode from adhesive failure to cohesive failure, further confirming that the addition of polymers indeed improves the interfacial bonding performance of polymer-modified interface agents.

The enhancement of interfacial bonding performance and durability by polymers is influenced by factors such as the type of polymer^[36], curing conditions^[11], and the amount of polymer incorporated^[37]. Ramli et al. ^[38]modified interface agents with SBR, PAE, and EVAE polymers and studied their mechanical and durability performance under different curing conditions. The study found that the early water curing effect of polymer-modified interface agents was more beneficial than air curing, with SBR developing strength more rapidly than other types of interface agents. In terms of shrinkage, the addition of polymers would reduce the shrinkage of the interface agent but was also affected by the amount of polymer incorporated; a lower amount of SBR incorporation could cause greater shrinkage. Therefore, this paper summarizes the impact of different polymers on the flexural strength of interface agents in Table 2 below, and the impact of polymer type on the tensile bond strength after the incorporation of polymers, and positive numbers indicate an increase in strength.

| Refer- | Mechanical per- formance | Polymer Type | Dos- age | Flexural Strength Improvement at Different Ages | |
|--------|--|--|-------------|--|--------|
| ences | | | | 7d | 28d |
| | [29] [33] [39] | Pure Acrylic Emulsion | 20% | -45.2% | 31.9% |
| [29] | | Chlorobutyl Rubber Emul- sion (CR) | 15% | -43.8% | -31.9% |
| [33] | | Vinyl Acetate-Ethylene Emulsion (VAE) | 20% | 29.2% | 11.9% |
| | | Acrylic Emulsion (BXS) | 20% | -50.5% | -41.0% |
| [39] | | Styrene-Acrylate Emulsion (SAE) | 8% | 1.7% | 5.6% |
| | | SBR | 8% | -1.1% | 8.5% |

Table 2. The Impact of Polymers on the Flexural Strength of Interface Agents

| Table 3. | The Impact o | of Polymer | Type on the | Tensile Bondi | ng Performance | e of Interface A | Agents |
|----------|--------------|------------|-------------|---------------|----------------|------------------|--------|
|----------|--------------|------------|-------------|---------------|----------------|------------------|--------|

| References | Bonding Per- formance | Polymer Type | Dosage | Bond Strength Improvement at Different Ages | |
|--------------|--------------------------|--|--------|--|-------|
| | | | | 7d | 28d |
| [29] | Shear Strength | Polymerized Styrene Butadi- ene Rubbe (SBR) | 12% | 84.6% | 90.8% |
| [32, 33, 36] | Pull-off Strength | Butadiene Rubbe (SBR) | 67% | 144% | 96% |
| | | | 25% | -13% | -6% |
| | | | 21% | -37% | -11% |
| | | | 40% | 3% | 189% |
| [33] | | Acrylic Emulsion (BXS) | 67% | - | 24% |
| [32] | | Emulsion (CR) | 30% | -33% | -9% |
| [36] | | Ethylene-Vinyl Acetate (EVA) | 40% | 147% | 369% |

The aforementioned studies indicate that although the incorporation of polymers may slightly reduce the compressive strength of polymer-modified interface agents in the early stages, their flexural and compressive properties can be enhanced with extended curing time. Moreover, the addition of polymers can form a polymer film within the bonding layer, enhancing its toughness and improving the pore structure of the bond between new and old concrete, thereby improving the bonding and durability performance between new and old concrete.

3.3 The Impact of Fiber Incorporation in Interface Agents on the Bonding Performance between New and Old Concrete Layers

Since the shrinkage of repair materials affects the interfacial bonding performance within a certain extent ^[40], many scholars currently incorporate fibers into polymermodified interface agents to improve the shrinkage properties of the interface agents. The method of reinforcing cement and repair materials with fibers is considered a very effective way to enhance the mechanical and durability performance of repair interface agents. The incorporation of fibers can suppress the shrinkage cracking of repair materials^[41], reduce stress concentration phenomena at the interface, and enhance the fracture toughness at the interface. It can also improve the compactness of the interface, which contributes to the durability of the structure. As the fiber content increases, the cohesive force gradually increases; on the other hand, fibers also increase the toughness of the ITZ (Interface Transition Zone), and this increase in cohesive force and toughness is attributed to the crack deflection and crack pinning caused by micro-cracks in the presence of fibers ^[20]. Secondly, the addition of fibers leads to a redistribution of stress around the main crack, resulting in crack blunting and the ability to form chemical bonds with the cementitious matrix ^[20]. Larger depressions in rough interfaces can cause steel fibers to align perpendicular to the shear plane, creating a dowel effect that helps improve shear bond strength^[42].

Incorporating fibers into the interface agent can also effectively improve the basic mechanical properties of the interface agent and enhance the strength of interface shear and tensile bonding ^[43]. Wang et al.^[44]studied the deformation and failure patterns of cement interface agents with different ages of polypropylene fiber content. Through uniaxial compression tests, they found that the compressive strength of the interface agent first increased and then decreased with the increase of polypropylene fiber content. By analyzing the SEM images of the fracture surface, they found that the incorporation of fibers can reduce the number of micro-pores inside the specimen and increase the compactness of the specimen. An appropriate amount of polypropylene fibers can form a stable spatial framework within the structure, while an excessive amount of fibers can lead to more weak layers in the specimen, disrupting the optimal structure and resulting in lower compressive strength.

Chen et al.^[45]found that the surface of polypropylene fibers at the fracture was smooth, and there was a clear gap at the interface with the cement matrix. After modi-fying the polypropylene fibers to create grafting points on their surface, the polypro-

pylene surface was covered more tightly by the cement hydration products. The roughness of the modified fiber surface increased, enhancing the mechanical interlocking force between the fiber and the cement matrix.

Tran et al.^[46]studied the changes in the microstructure of three types of fibers—PP (polypropylene), PE (polyethylene), and PVA (polyvinyl alcohol)—under high and low temperature conditions. The study showed that the addition of fibers increases the porosity of cement-based materials. Hydrophilic fibers and ultra-fine fibers can create more refined pores. Hydrophobic fibers, when introduced with reactive functional groups, can also enhance the interaction between the fibers and the matrix, thus enhancing the interface performance with the cement paste. At high temperatures, due to the melting of fibers, micro-cracks and voids are formed, exhibiting good resistance to spalling.

The incorporation of fibers can improve the micro-pore structure of polymer-modified interface agents, blunt cracks, reduce the shrinkage of repair materials, and enhance the toughness of repair materials, among other effects. However, comparative studies on the improvement of interfacial bonding performance with various fibers incorporated into polymer-modified interface agents are not yet comprehensive. The impact of various fibers on the microstructure is not deeply understood, and there is no standardized guideline for the range of fiber content. In the future, modifying the fiber surface to enhance the coverage by cement hydration products will be a cutting-edge direction.

4 Conclusions

This study comprehensively introduces various testing methods for interfacial bonding performance, analyzes the influence of polymer types and fiber types on the interfacial bonding performance of interface agents, outlines the bonding mechanism between new and old concrete layers, organizes and analyzes existing domestic and international research results, and summarizes the following recommendations for future research and development of interface agents.

The strength and bonding performance of polymer-modified interface agents are significantly affected by the type and amount of polymers. Polymers such as styrene-butadiene and VAE (Vinyl Acetate-Ethylene) exhibit good bonding performance.

Polymer-modified interface agents possess excellent interfacial bonding properties, have similar shrinkage to concrete, and the formation of a polymer film within the interface agent can effectively improve the system's pore structure and toughness. Incorporating fibers into polymer-modified interface agents can further enhance the toughness and durability of the bonding material, thereby improving the durability of interfacial bonding. Although the incorporation of polymers can improve the basic mechanical properties of the interface agent in the long term, it may still reduce its compressive strength in the short term. Further research is needed on how to modify polymers to improve the short-term strength of polymer-modified interface agents.

Currently, there is considerable research on the impact of polymer types on the bonding strength of modified interface agents, but the studies are relatively fragmented. Conducting bonding performance studies of modified interface agents with a variety of polymers in the same experiment would aid in the selection of polymer types and amounts.

Since different interfacial bonding testing methods often yield inconsistent results, studying the correlations between various testing methods and establishing a unified interfacial bonding testing method will advance the research on polymer-modified interface agents.

Despite the many drawbacks of epoxy, current research is focused on improving its mechanical and thermal properties, and enhancing its interfacial bonding with concrete, by adding nanomaterials such as carbon nanotubes and nano-silica to epoxy adhesives. The addition of nanomaterials can enhance the performance of epoxy-based adhesives, but it can still lead to low dispersion and weak interfacial interactions^[47]. The toxicity of epoxy adhesives modified with nanomaterials remains to be investigated.

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