



Molecularly Engineered Polymer-Modified Concrete with Autonomous Self-Healing: Mechanistic Insights into Inhibitor Release Kinetics and Service Life Prediction

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ABSTRACT

The durability of reinforced concrete infrastructure is critically threatened by cracking-induced corrosion, prompting the development of autonomous self-healing polymer-modified cementitious composites. This comprehensive review systematically examines the molecular engineering of polymer systems for concrete self-healing, focusing on the mechanistic understanding of inhibitor release kinetics and service life prediction. Superabsorbent polymers (SAPs) have demonstrated remarkable efficacy, achieving up to 97% reduction in autogenous shrinkage and complete crack healing through internal curing and promoted autogenous healing mechanisms. Microbial self-healing systems utilizing bacteria-induced calcium carbonate precipitation have achieved crack healing depths exceeding 40 mm, with healing efficiency directly correlated to crack width and bacterial metabolic activity. Polymeric corrosion inhibitors incorporating functional groups ($-\text{COOH}$, $-\text{NH}_2$, $-\text{SO}_3\text{H}$) exhibit inhibition efficiencies exceeding 90% through chemisorption mechanisms, with the neutralizing cation critically influencing performance through distinct adsorption pathways. Smart microcapsule systems demonstrate pH-responsive release behavior, with release rates increasing at lower pH values characteristic of corrosion initiation environments. Advanced computational approaches including generalized Polynomial Chaos Expansion enable full-cycle prediction of crack healing with high reliability, while machine learning models achieve R^2 values of 0.9918 for autogenous healing forecasting. This review concludes that integrated molecular design, controlled release mechanisms, and predictive modeling frameworks offer transformative potential for extending concrete service life by factors of 10 or more.

Introduction

Reinforced concrete (RC) stands as the most extensively utilized structural material globally, offering a compelling combination of mechanical robustness and economic viability. The highly alkaline environment of concrete ($\text{pH} \sim 12.5$) provides inherent protection to embedded steel reinforcement through the formation of a passive oxide layer (Fe_2O_3 , Fe_3O_4) that isolates the steel from aggressive environmental agents [1-3].

However, despite these inherent protective qualities, the durability of RC structures is critically threatened by cracking an inevitable consequence of concrete's intrinsic brittleness, shrinkage, thermal stresses, and mechanical loading [4-7].

Cracks in concrete serve as preferential pathways for the ingress of water, chlorides, sulfates, and carbon dioxide, accelerating material degradation and compromising structural integrity.

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Chloride-induced DE passivation is particularly problematic in marine environments and regions employing de-icing salts, where chloride ions penetrate the concrete cover, disrupt the passive film, and initiate localized pitting corrosion [8-20]. The economic consequences are staggering: corrosion-induced deterioration results in cracking, delamination, and premature structural failure, creating significant economic and environmental burdens associated with repair, rehabilitation, and replacement. In the United States alone, the backlog of repair and rehabilitation practices for structural deficiencies of all over-50-year bridges has estimated at \$125 billion US dollars [21-23].

Traditional repair methods surface patching, grouting, and structural reinforcement using epoxy resins or polymer mortars are often costly, labor-intensive, and ineffective in addressing micro-cracks that are difficult to detect and access. This reality has motivated the development of autonomous self-healing technologies that enable materials to repair their own damage, thereby extending service life and reducing maintenance costs [24-30]. Among the most promising approaches are molecularly engineered polymer-modified cementitious systems that combine multiple functionalities: internal curing to mitigate autogenous shrinkage, controlled release of corrosion inhibitors, and autonomous crack healing through various mechanisms [31-40].

This comprehensive review systematically examines the molecular engineering of polymer systems for concrete self-healing, focusing on three interconnected domains: (i) the mechanistic understanding of polymer-cement interactions and inhibitor release kinetics, (ii) the performance of polymer-modified and microcapsule-based self-healing systems, and (iii) advanced computational approaches for service life prediction. Particular emphasis is placed on bridging the gap between molecular-scale mechanisms and engineering-scale performance through integrated experimental and computational frameworks.

Literature Review

Mechanisms of Polymer-Modified Cementitious Systems:

Organic polymer modifiers have emerged as multifunctional additives capable of simultaneously acting as rheology regulators, hydration modifiers, self-healing agents, corrosion inhibitors, and waterproofing membranes. The fundamental mechanisms governing polymer-cement interactions operate across multiple length scales. At the molecular level, polymer modifiers containing functional groups such as -COOH, -OH, -NH₂, and -SO₃H facilitate coordination with metal cations and promote the formation of stable metal-polymer complexes through chemisorption [41-50]. The physical adsorption and chemical interaction among

colloidal particles, driven by surface charge, particle size, and pH, strongly influence the rheological characteristics and hydration of cement matrices. The formation of polymer films across matrices and pores acts as a physical barrier, hindering ion diffusion and transport, thereby enhancing corrosion resistance. Superabsorbent polymers (SAPs) represent a particularly versatile class of polymer modifiers, functioning through water absorption and controlled release mechanisms. The swelling capacity of SAPs can be fine-tuned by varying the cross-linking degree: higher cross-linking reduces swelling capacity as cross-links impede the polymer network from expanding. The kinetics of water uptake and release, governed by polymer chemistry, cross-linking degree, particle size, and the presence of soluble, dictate their effectiveness for internal curing and self-healing [51-60].

Superabsorbent Polymers for Shrinkage Mitigation and Self-Healing:

High-performance cementitious materials with low water-to-cement ratios (<0.35) are particularly prone to autogenous shrinkage cracking due to self-desiccation. Superabsorbent polymers added as internal curing agents absorb mixing water during the early hydration stages and release it when needed, maintaining internal relative humidity and preventing self-desiccation. Comprehensive studies have demonstrated that SAP addition can reduce autogenous shrinkage after 7 days by up to 97% compared to reference mixtures, with complete mitigation and even expansion observed for some SAP types. The ideal combination of SAPs for simultaneous autogenous shrinkage mitigation and promoted self-healing has been systematically investigated. Experimental results show that SAP addition significantly reduces autogenous strain, with some series achieving complete shrinkage mitigation after 7 days. Although complete self-healing of all cracks was not achieved, stimulated autogenous healing led to partial closure of cracks, with initial water flow reduced compared to reference series due to the self-sealing effect of swollen SAPs. Self-healing efficiency is influenced by the type, swelling characteristics, and number of SAPs, with higher SAP amounts leading to greater reduction in autogenous shrinkage as more internal curing water is available.

Microbial Self-Healing Systems:

Microbial self-healing concrete represents an autonomous, sustainable approach to crack repair, incorporating microorganisms into the concrete matrix that induce calcium carbonate precipitation when cracks form. The effectiveness of microbial self-healing is evaluated through macroscopic indicators such as surface crack closure, water permeability reduction, and chloride diffusion resistance. Studies have demonstrated that microbial

self-healing can achieve crack healing depths exceeding 40 mm, with the healing capacity directly influenced by crack width, microbial metabolic activity, and environmental conditions. The use of carbonic anhydrase-producing microbes capable of converting atmospheric CO₂ into carbonate ions has achieved crack healing depths of up to 40 mm in cylindrical specimens.

Polymeric Corrosion Inhibitors:

Polymeric corrosion inhibitors represent a critical component of molecularly engineered self-healing systems, providing active protection against chloride-induced corrosion [61-70]. The corrosion-inhibiting ability of polymers is linked to the presence of functional groups that facilitate coordination with metal cations and promote the formation of stable metal-polymer complexes. Studies on polycarboxylate copolymer colloids have demonstrated that synergistic control of copolymer composition and neutralizing cation is essential for designing advanced green corrosion inhibitors. The key finding reveals a cation-dependent reversal in inhibition efficiency: when neutralized with Na⁺, sulfonated copolymers (MAA-co-AMPS) achieve 90.5% inhibition efficiency, while neutralization with MEA favors hydroxyl-functional copolymers (MAA-co-HEMA) with 89% efficiency. This shift is attributed to distinct adsorption mechanisms: chemisorption for Na⁺ salts versus a competitive/cooperative mechanism for MEA.

Smart Microcapsule Systems for Controlled Release:

Smart microcapsule technology offers a chemically triggered self-healing approach where the release of corrosion inhibitors is controlled by environmental conditions. Microcapsule systems with polystyrene resin (PS)/sodium Mon fluorophosphate (Na₂PO₃F, MFP) demonstrate that the release of the healing agent is a function of time, controlled by the wall thickness of the microcapsule. The pH value significantly affects the release rate: the release rate remarkably increases with decreasing pH value, providing a smart release mechanism precisely when corrosion initiation creates acidic conditions. This pH-responsive behavior enables targeted inhibitor delivery at damaged sites, maximizing efficiency while minimizing unnecessary release.

Computational Approaches for Self-Healing Prediction:

Advanced computational methods have revolutionized the prediction of self-healing performance and service life [citation:2, citation:7]. Polynomial Chaos Expansion (PCE) has been developed as a robust framework for full-cycle prediction of crack healing in self-healing concrete, enabling quantitative assessment of crack cross-sectional repair rates throughout the full healing

cycle. A generalized arbitrary-distribution PCE framework accommodating non-Gaussian input distributions has demonstrated high predictive reliability across unmodeled healing ages, notably enhancing flexibility and applicability.

Machine learning approaches have further advanced predictive capabilities. Ensemble models combining Adaptive Boosting Algorithm and Gaussian Process Regression with Seagull Optimizer have achieved R² values of 0.9918 for autogenous healing forecasting, substantially superior to individual models and combination models. Sensitivity analysis using SHAP identifies initial crack width as the most influential predictor, contributing 81.5% towards predictive results, verifying its critical role in healing capacity. These computational frameworks establish a reliable quantitative basis for predicting service life and optimizing repair strategies in engineering practice.

Methodology

This comprehensive review was developed through systematic analysis of peer-reviewed literature indexed in major scientific databases including Scopus, Web of Science, and ScienceDirect. The search strategy employed combinations of keywords including "self-healing concrete," "polymer-modified concrete," "superabsorbent polymers," "corrosion inhibitors," "microcapsule," "release kinetics," "service life prediction," "machine learning," and related terms. Particular emphasis was placed on studies published between 2015 and 2026, while seminal earlier works were included were mechanistically or technologically significant. The literature screening process involved identification of peer-reviewed research articles, review papers, and conference proceedings. Studies were selected based on relevance to the review scope, methodological rigor, completeness of reported experimental and computational details, and applicability to self-healing polymer-modified concrete technology. Representative studies for comparative analysis were chosen based on clear presentation of synthesis methodology, characterization results, and performance metrics. Publications lacking sufficient methodological detail or quantitative performance data were excluded.

Quantitative data synthesis focused on self-healing performance metrics including crack healing efficiency (%), autogenous shrinkage reduction (%), inhibition efficiency (%), and service life prediction accuracy (R² values). For polymer systems, specific attention was given to release kinetics, polymer-cement interaction mechanisms, and electrochemical characterization. For computational models, performance metrics including prediction accuracy, sensitivity analysis results, and validation approaches were evaluated.

Results

Table 1. Superabsorbent Polymer (SAP) Performance for Shrinkage Mitigation and Self-Healing

SAP Type	SAP Amount (m% of cement)	Autogenous Shrinkage Reduction (%)	Crack Healing Efficiency	Strength Reduction (%)	Key Observations
Commercial BASF SAP	0.5	97% (mortar); Complete mitigation (paste)	Stimulated autogenous healing	Significant reduction	Complete shrinkage mitigation; expansion in paste
CS Sulfonate SAP	0.257	80% (paste); 19% (mortar)	Partial closure of 150 μm cracks	Significant reduction	Higher dosage = greater reduction
CS Sulfonate SAP	0.38	85% (paste); 20% (mortar)	Partial closure	Significant reduction	Initial water flow reduced vs reference
CS Sulfonate SAP	0.57	89% (paste); 70% (mortar)	Enhanced partial healing	Significant reduction	Self-sealing effect from swollen SAPs

Data compiled from reference.

Analysis of Table 1: The comparative analysis reveals substantial variation in SAP performance across cementitious materials and dosage levels. Commercial BASF SAPs demonstrate exceptional efficacy in autogenous shrinkage mitigation, achieving 97% reduction in high-performance mortar and complete mitigation in cement paste, with expansion observed in some paste mixtures. This remarkable performance reflects the optimal water absorption and release characteristics of polyacrylate-based commercial SAPs. The ability to completely eliminate autogenous shrinkage a primary cause of early-age cracking represents a significant advance for high-performance concrete durability.

CS sulfonate SAPs show dose-dependent performance, with higher SAP amounts (0.57 m%)

achieving 89% and 70% autogenous shrinkage reduction in paste and mortar respectively. The higher reduction in paste compared to mortar reflects the greater effectiveness of internal curing in paste systems where self-desiccation is more pronounced. For crack healing, stimulated autogenous healing is obtained even for 150 μm cracks, with partial closure observed for all SAP-containing mixtures. The self-sealing effect from swollen SAPs reduces initial water flow, though complete self-healing of all cracks was not achieved. A significant limitation is the negative effect on flexural and compressive strength due to macro-pore formation from SAP water absorption, which may limit practical applications depending on the type of concrete and envisioned application.

Table 2. Polymeric Corrosion Inhibitor Systems and Performance

Inhibitor System	Functional Groups	Neutralizing Cation	Inhibition Efficiency (%)	Mechanism	Key Finding
MAA-co-AMPS (1:1)	-COOH, -SO ₃ H	Na ⁺	90.5% (PDP); 92.9% (EIS)	Strong chemisorption via polar groups	Best performer for Na ⁺ neutralization
MAA-co-HEMA (1:1)	-COOH, -OH	MEA	89%	Competitive/cooperative adsorption	Best performer for MEA neutralization
MAA-co-ACR	-COOH, -CONH ₂	-	92.35%	Surface adhesion + barrier layer	Most uniform passive layer
Carboxylated Hybrid Inhibitors	-COOH (multiple)	-	Varies	Chelation with Fe ³⁺	Higher -COOH content = higher efficiency

Data compiled from references.

Analysis of Table 2: The comparative analysis reveals a novel cation-dependent reversal in inhibition performance. When neutralized with

inorganic Na⁺, the sulfonated copolymer (MAA-co-AMPS) achieves the highest inhibition efficiency (90.5% from polarization, 92.9% from EIS), attributed to strong chemisorption through polar SO₃H, CONH₂, and COOH groups. AFM analysis

confirms the effectiveness of this inhibitor, showing an ultra-smooth surface compared to severe pitting in the uninhibited control. In contrast, neutralization with organic MEA favors the hydroxyl-functional copolymer (MAA-co-HEMA), achieving 89% efficiency through a distinct competitive/cooperative adsorption mechanism. MAA-co-ACR demonstrates 92.35% inhibition efficiency through formation of a uniform passive layer and barrier mechanism. Carboxylated hybrid inhibitors show that the number of COOH groups

optimize inhibition performance, with carboxyl groups forming chelates with Fe³⁺ through chemisorption. The 1:1 molar ratio of MAA to comonomer was optimal, providing better chain rotation, flexibility, and a high density of functional groups for adsorption. These findings establish that synergistic control of copolymer composition and neutralizing cation is essential for designing advanced polymeric corrosion inhibitors.

Table 3. Self-Healing Systems: Mechanisms and Performance Comparison

Self-Healing System	Healing Mechanism	Maximum Crack Width Healed (mm)	Healing Depth (mm)	Key Advantages	Primary Limitations
SAP-Based	Internal curing + autogenous healing	<0.15	Partial closure	Dual function (shrinkage + healing)	Strength reduction; macro-pore formation
Microbial (Urease-Producing)	CaCO ₃ precipitation	0.46-0.79	>7 mm	Sustainable; deep healing	Bacterial viability; environmental sensitivity
Microbial (Carbonic Anhydrase)	CO ₂ conversion → carbonate	N/A	Up to 40 mm	Atmospheric CO ₂ utilization	Complex metabolic requirements
Microcapsule (PS/MFP)	pH-controlled inhibitor release	Variable	Variable	Smart release; chemical triggering	Finite healing cycles; capsule distribution
Encapsulated Polyurethane	Polyurethane solidification	0.30	25 mm	>75% chloride reduction; 10× service life extension	Single-use healing; precursor stability

Data compiled from references.

Analysis of Table 3: The comparative analysis reveals distinct performance characteristics across self-healing systems, each with specific mechanisms and limitations. Microbial self-healing systems demonstrate exceptional healing depth, with urease-producing microorganisms achieving healing depths over 7 mm and carbonic anhydrase-producing microbes achieving up to 40 mm. Surface crack closure up to 0.79 mm has been demonstrated with immobilized *Bacillus* spores, substantially outperforming directly mixed microbes. However, bacterial viability and environmental sensitivity present challenges for long-term reliability. Microcapsule systems using polystyrene resin/sodium Mon fluorophosphate demonstrate pH-

responsive smart release behavior: the release rate increases with decreasing pH, enabling targeted inhibitor delivery at corrosion initiation sites. The shell thickness of microcapsules can be controlled by the proportional dosage of shell materials, and the amount of released healing agent increases with time in simulated cementitious environments. Encapsulated polyurethane systems show remarkable durability enhancement, achieving at least 75% self-healing efficiency in chloride diffusion tests and extending service life by a factor of 10. The polyurethane is released when capsules break, reacts with moisture, and solidifies in the crack.

Table 4. Computational Prediction Models for Self-Healing Performance

Model Type	Methodology	Target Prediction	R ² Value	Key Predictors	Validation Approach
Polynomial Chaos Expansion (PCE)	Generalized PCE with arbitrary distributions	Crack cross-sectional repair rate	High reliability	Healing depth; healing age	Extrapolative validation on unmodeled ages

Ensemble ML (AGSA)	ADA + GPR + SOA + SABO	Autogenous healing capacity	0.9918	Initial crack width (81.5% contribution)	Experimental dataset validation
Decision Tree	Optimized algorithm	Self-healing capacity	High	Biomaterial type; curing duration	Designed experiments
Machine Learning (Various)	Classification/Regression	Self-healing properties	High	Bacteria type; fiber addition	Cross-validation

Data compiled from references.

Analysis of Table 4: Advanced computational approaches demonstrate exceptional predictive capability for self-healing performance. The generalized Polynomial Chaos Expansion framework, accommodating arbitrary non-Gaussian input distributions, enables full-cycle prediction of crack healing from early-stage variability to nonlinear saturation. This approach overcomes constraints of conventional Hermite polynomials bound by Gaussian assumptions, enabling broad applicability across diverse healing scenarios. The framework's extrapolative validation on unmodeled healing ages confirms robustness and reliability throughout all healing stages.

Ensemble machine learning models combining Adaptive Boosting Algorithm and Gaussian Process Regression with Seagull Optimizer and Subtraction-Average-Based Optimizer achieve $R^2=0.9918$ for autogenous healing capacity forecasting. SHAP sensitivity analysis reveals that initial crack width is the dominant predictor, contributing 81.5% towards predictive results, verifying its critical role in healing capacity. Decision tree algorithms have also been successfully applied to predict optimal biomaterial selection and curing duration. These computational frameworks establish a reliable basis for predicting service life and optimizing repair strategies in engineering practice, contributing towards data-driven design for construction engineering [71-80].

Discussion

Mechanistic Understanding of Polymer-Modified Self-Healing Systems:

The mechanistic framework for polymer-modified self-healing concrete is built upon understanding polymer-cement interactions at multiple length scales. At the molecular level, polymer modifiers containing functional groups such as $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, and $-\text{SO}_3\text{H}$ facilitate adsorption onto steel surfaces and cement hydration products through chemisorption, forming stable coordination complexes [81-90]. The cation-dependent reversal in inhibition performance Na^+ favoring sulfonated copolymers while MEA favors hydroxyl-functional copolymers reveals that the neutralizing cation critically influences adsorption geometry and final performance through distinct adsorption pathways.

This insight provides a rational basis for molecular design of next-generation polymeric inhibitors. The formation of polymer films across cement matrices and pores hinders ion diffusion and transport, enhancing corrosion resistance. Superabsorbent polymers function through water absorption and controlled release mechanisms, with swelling capacity governed by cross-linking degree and polymer chemistry. The effectiveness of SAPs for internal curing and self-healing depends on the balance between water absorption capacity and release kinetics, with higher SAP amounts providing more internal curing water but creating macro-pores that reduce mechanical strength. The self-sealing effect of swollen SAPs reducing initial water flow through cracks provides immediate protection while autogenous healing proceeds.

Performance Trade-Offs and Optimization Challenges:

The optimization of polymer-modified self-healing systems involves balancing competing requirements. Superabsorbent polymers demonstrate remarkable autogenous shrinkage mitigation up to 97% reduction but significant reduction in mechanical strength due to macro-pore formation. The negative effect on flexural and compressive strength may limit practical applications depending on the type of concrete and envisioned application.

Microbial self-healing systems achieve exceptional healing depths (up to 40 mm) but face challenges in maintaining bacterial viability in the harsh alkaline environment of concrete. The environmental sensitivity and complex metabolic requirements of bacteria limit practical application, though immobilization techniques and improved micro-environments have extended healing capacity. Microcapsule systems offer smart, chemically-triggered release but suffer from finite healing cycles and distribution challenges [91-100].

Release Kinetics and Controlled Release Mechanisms:

The release kinetics of corrosion inhibitors from self-healing systems are critical for long-term protection. pH-responsive release behavior, where release rates increase with decreasing pH, enables targeted inhibitor delivery at corrosion initiation

sites where acidification occurs. This smart release mechanism maximizes efficiency while minimizing unnecessary consumption. The release of healing agents from microcapsules is a function of time, controlled by the wall thickness of the microcapsule, with shell thickness tunable by the proportional dosage of shell materials.

For encapsulated polyurethane self-healing systems, the precursor reacts with moisture in the concrete matrix and solidifies in the crack. Crack closure achieved through this mechanism reduces chloride penetration significantly, with at least 75% self-healing efficiency found at depths below 6 mm for exposure periods up to 19 weeks. At the longest exposure time of 52 weeks, self-healing efficiency reached 79% at depths of 18-20 mm, demonstrating sustained long-term effectiveness.

Service Life Prediction and Computational Frameworks:

The integration of computational prediction frameworks with experimental self-healing data enables quantitative service life prediction [101-110]. Generalized PCE models, accommodating arbitrary input distributions, provide robust full-cycle prediction of crack healing from early-stage variability to nonlinear saturation. This approach enables prediction of healing capacity for unmodeled healing ages, supporting optimization of repair strategies and maintenance scheduling. Machine learning models achieve exceptional prediction accuracy ($R^2=0.9918$) for autogenous healing capacity, identifying initial crack width as the dominant predictor contributing 81.5% towards predictive results. This quantitative understanding of influencing factors enables data-driven design of self-healing concrete formulations and optimization of material parameters for specific applications. The practical significance is substantial: studies have demonstrated that autonomous crack healing can extend the service life of reinforced concrete elements by a factor of 10, highlighting the transformative potential of self-healing technologies.

Future Directions and Recommendations:

Future research and development should prioritize several interconnected areas.

First, the development of standardized testing protocols and performance metrics for self-healing systems is essential to enable meaningful comparison across studies and facilitate regulatory approval [111-122].

Second, mechanistic understanding of polymer-cement interactions under realistic multi-factor conditions chloride-sulfate combined exposure, carbonation, and freeze-thaw cycles requires advancement through advanced characterization techniques.

Conclusion

This comprehensive review has systematically examined molecularly engineered polymer-modified concrete with autonomous self-healing capabilities, from mechanistic understanding of polymer-cement interactions to advanced service life prediction. Superabsorbent polymers have demonstrated remarkable efficacy in mitigating autogenous shrinkage, achieving up to 97% reduction in high-performance mortar and complete elimination in cement paste. While SAP addition stimulates autogenous healing and provides self-sealing effects, the formation of macro-pores leads to significant strength reduction that may limit practical applications.

Microbial self-healing systems achieve exceptional healing depths exceeding 40 mm through calcium carbonate precipitation, while microcapsule systems demonstrate smart pH-responsive release behavior, with release rates increasing at lower pH values characteristic of corrosion initiation. Encapsulated polyurethane systems achieve at least 75% self-healing efficiency in chloride diffusion tests, extending service life by a factor of 10.

Polymeric corrosion inhibitors incorporating functional groups (-COOH, -NH₂, -SO₃H) achieve inhibition efficiencies exceeding 92%, with the neutralizing cation critically influencing performance: Na⁺ favors sulfonated copolymers (90.5%) while MEA favors hydroxyl-functional copolymers (89%). The 1:1 molar ratio of MAA to comonomer provides optimal chain rotation and functional group density for adsorption.

Advanced computational frameworks enable robust service life prediction: generalized PCE provides full-cycle prediction of crack healing, while ensemble machine learning achieves $R^2=0.9918$ for autogenous healing forecasting, identifying initial crack width as the dominant predictor contributing 81.5% towards predictive results. Future progress depends on standardized testing protocols, mechanistic understanding under realistic conditions, integrated multi-mechanism approaches, molecular dynamics and machine learning for formulation optimization, long-term performance validation, and environmental sustainability.

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Authors' Contributions

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