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Design, preparation and application of waterborne epoxy-concrete composite repair material

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Abstract

With the extension of service time, the building structure is in urgent need of repair and reinforcement due to its deterioration in safety and durability with the years. Normal cement concrete exposes shortcomings such as high brittleness and low flexural-tensile strength for which fails to meet the requirement of construction repairing. In this paper, a novel waterborne epoxy-concrete composite repair material (WECM) was prepared by using self-synthesized water-based epoxy resin based on the molecular structure-activity relationship. The key flexural and tensile performance parameters of WECM were accurately obtained. The mechanism of WEP and WEP-fiber synergy on the improvement of concrete performance was clarified.

1. INTRODUCTION

Concrete plays a significant role in cement-based materials that serve major engineering construction and building repair. With the extension of the service life, the emergence of diseases, e.g., cracks, peeling off, or even collapse in concrete structures, appears frequently. The deteriorating durability of concrete brings serious threats to building structure safety[1, 2]. Damage (e.g., erosion and cracks) often occurs in stress concentration areas (e.g., steps, joints, corners) and cyclic deformation areas (exposed to a corrosive environment, freeze–thaw roads, bridge piers, wharves, etc.), resulting in hazards and potential harms in concrete structures[3, 4]. Concrete repair and reinforcement are extremely important to extend the service life of the structure. With the slowdown of urban construction and the gradual improvement of infrastructure, the global engineering mode is gradually transforming from new construction to maintenance and reinforcement. Therefore, it is urgent to develop high-performance building repair materials.

At present, the conventional concrete toughening scheme mainly depends on means of incorporating fibers. To improve the "true" ductility of the matrix, there is still much potential in polymer-cement microstructure modification. In addition, the test of concrete tensile properties is limited by difficulty in alignment, stress concentration and specimen size (the small fracture area of the specimen leads to a large influence on the random distribution of coarse aggregates). These limitations lead to the tensile properties of concrete being further studied. In addition, the current ultimate tensile strain of concrete is generally less than 150 μm, which makes it difficult to meet the needs of repair projects[5, 6].

In previous works, we carried out a series of basic studies around the WECM in which a novel WEP was prepared and impregnated[7-10]. The flexibility and toughness of WEP as well as the WECM were further improved[11]. Larger-scale applications such as concrete, however, have yet to be implemented. In this paper, we prepared WEPs by adopting a self-emulsification scheme based on molecular structure design and synthesis for the cement hydration environment. The WECM was prepared by parameter variation, such as the polymer-to-cement ratio (P/C) and basalt fiber composition. With the aid of fine-tuning the loading rate and the microstrain measuring device, the quasistatic mechanical properties of the flexural strength and axial tensile strength of the WECM were accurately measured. The full stress–strain curves of WECMs with various P/Cs were obtained with their mechanical parameters calculated, e.g., elastic modulus, Poisson's ratio, and toughness ratio. Finally, based on molecular dynamics simulation, X-CT scanning data and electron microscopy observations, the microstructures of the fiber-matrix-aggregate interface transition zone and their evolution behavior of the IPN were obtained, and the mechanism of WEP and WEP-fiber synergy on the improvement of concrete performance was further clarified.

2. MATERIALS AND METHODS

2.1 Raw materials

Cement: A commercial Portland cement (52.5 grade) that conforms to Chinese standard GB/T 175-2007 (similar to EN 197-1 and ASTM C150) was used in this study. The chemical composition of the cement is illustrated in Table 1.

Aggregate: Washed river sand was used as fine aggregate. Continuously graded basalt gravel (5~16 mm) was used as the coarse aggregate. The mix proportion of concrete is shown in Table 2.

Table 1. Oxide compositions (%) of cement

CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3	SO_3	K_2O	Na_2O	LOI
64.38	21.60	4.38	3.43	3.42	2.23	-	0.11	7.01

Table 2. Mix proportion of concrete

	P/C	W/C	Cement (kg/m3)	Fine aggregate (kg/m3)	Coarse aggregate (kg/m3)	NEP-EP (kg/m3)	NEP-HD (kg/m3)	Fiber (vol.%)
C	0		480			0	-	-
CF								2
E2C	0.2	0.35	450	590	1260	48	48	-
E2CF								2
E4C	0.4		420			96	96	-
E4CF								2

Fiber: F- concrete with chopped basalt fiber of a length of 12 mm was used as the fiber component, and the main performance indicators are shown in Table 3.

Table 3. Main performance indicators of basalt fiber

Properties	performance indicators
Single wire diameter (μm)	11
Density (g/cm3)	2.8
Coefficient of linear expansion (×10/k)	5.5
Tensile strength (MPa)	3297
Modulus of Elasticity (GPa)	95.3
Elongation at failure (%)	1.008
Water absorption rate (%)	0.04

2.2 Preparation of WEP

The WEP was prepared using a self-emulsifying scheme (refer to previous works [7, 9]) in which the bisphenol-A-Type epoxy resin (the E-51 type epoxy resin) was used as part A of WEP (NEP-EP). In the case of part B (NEP-HD), the self-emulsifying hardener constituted by a self-emulsifying curing agent (hardener-S, LHD) and a modified Mannich curing agent (hardener-M, SBP) was used. LHD facilitates the water solubility of WEP based on the 'like dissolves like' rule [12], while SBP promotes the cross-linking reaction efficiency between NEP-EP and NEP-HD. All the synthetic methods are shown in the supporting information, wherein the properties of WEP are shown in Figure 1 and Table 4.

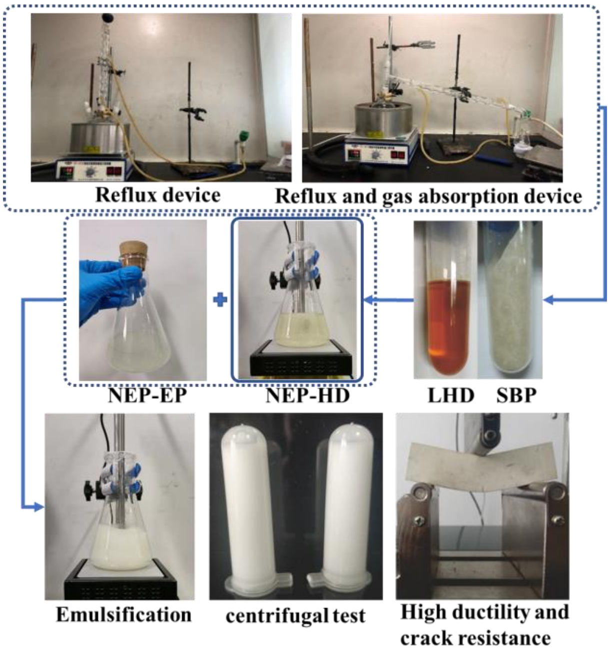


Figure 1. preparation process of WEP

Table 4. Properties of WEP

	Active Substance Equivalent	Viscosity at 30oC (mPa·s)	Volume Shrinkage of Consolidated matrix (vol.%)	Water Absorption (wt.%)	Curing Time
NEP-EP (part A)	Epoxide value 0.45~0.53 (mol/100 g)	~4000	3~6	5~10	Operation window period: ~3 h Curing time: ~9 h
NEP-HD (part B)	Amine value 200~230 (mg KOH/g)	~500			

3. RESULTS AND DISCUSSION

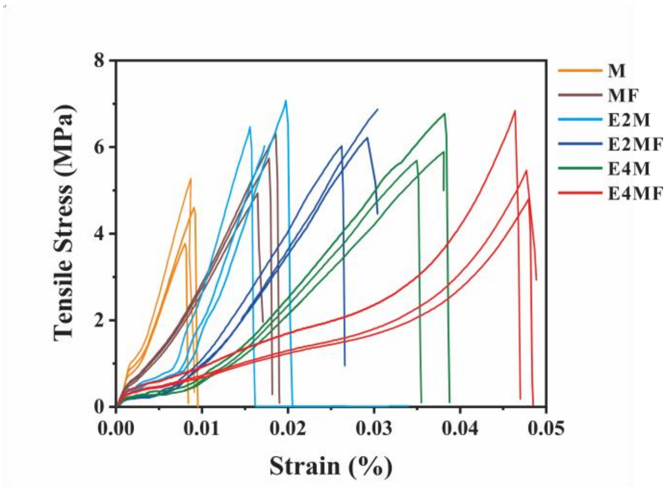
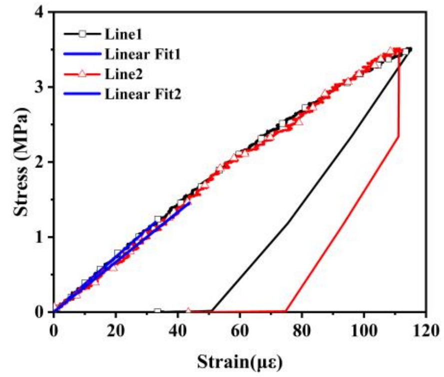


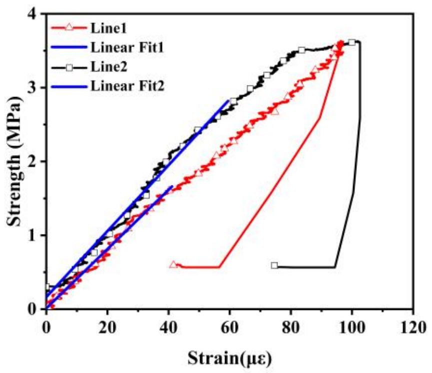
Figure 2. Tensile stress-deflection curves of the mortar specimens with different P/C ratios

Plain concrete is a typical brittle natural material with a low tensile strength of 150 με to 250 με, which limits its application in the field of concrete structure repair [13, 14]. The main purpose of using WEP to modify concrete was to improve its tensile strength while increasing the elongation before failure, i.e., flexibility and ductility. The synergy of WEP at various P/Cs (0, 0.2, 0.4) with fiber components on the flexural strength of mortar and concrete was experimentally studied. The tensile stress–strain curves of each mortar (Figure 2) show that there was an upward trend in the tensile strength of the mortar with increasing WEP content, while the ultimate tensile strain increased remarkably. The tensile strength of the control cement mortar (specimen-M) was approximately 4.4 MPa, and the ultimate tensile strain was approximately 90 με; the E2 M increased to 5.5 MPa and 155 με; and the E4 M increased to 5.6 MPa and 350 με. When the P/C of the mortar was 0.2 and 0.4, the ultimate tensile strain of the control group was increased by 72% and 280%, respectively. The toughening properties of the fiber became more obvious with increasing WEP content, presumably because the polymer increased the gripping force of the matrix to the fiber. WEP weakened the cutting effect of CH and other crystals generated by cement hydration on fiber as well as the corrosive effect of the alkaline solution. Nevertheless, ductile failure at the yield stage when the WECM reached the peak stress was not very obvious, which manifested as an instant drop in the force curve. The tensile stress–strain curve of the WECM specimen generated no obvious descending section (ductile cracking). The enhancement of the tensile performance of cement mortar by WEP was mainly manifested in the elastic stage. When the substrate was under tensile load, the WEP film not only withstood the tensile stress but also increased the tensile strength. Meanwhile, the ductility of the substrate radically surged by WEP, making the substrate less prone to stress concentration or brittle fracture [15, 16].

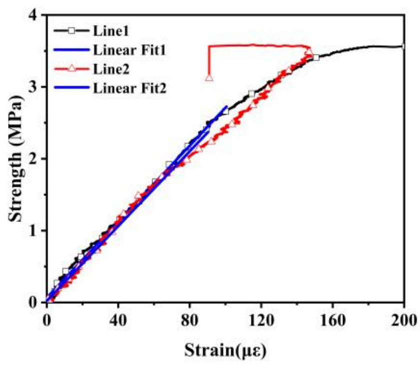
The concrete tensile parameters, e.g., strength, ultimate tensile strain, elastic modulus, axial tensile toughness ratio, and Poisson's ratio, were further accurately obtained. Figure 3 shows the tensile stress–strain curves of the 28-day concrete specimens. The average tensile strength, tensile strain, and elastic modulus of ordinary concrete were 3.47 MPa, 100.32 με, and 22.3 GPa, respectively. The average tensile strength of the WECM increased to 3.65 MPa (increased by ~5% compared to the control value, P/C=0.2) and 5.14 MPa (increased by ~48%, P/C=0.4). The average ultimate tensile strain increased to 147.13 με (increased by ~47%, P/C=0.2) and 372.87 με (increased by ~271%, P/C=0.4). The average elasticity modulus, however, dropped to 21.7 GPa (down ~3%, P/C=0.2) and 13.1 GPa (down ~42%, P/C=0.4). Combining the flexural and tensile test results, two obvious regular patterns could be drawn: WEP radically promoted the ductility of concrete in the elastic stage, where a P/C of 0.2 was the turning point for WEP to effectively enhance the flexural and tensile strength of concrete. Therefore, P/C>0.2 was the appropriate dosage of WEP to be incorporated into concrete. With increasing P/C, the axial tensile toughness ratio of C, E2C, and E4C increased gradually from 0.917 to 1.224 and 4.825 (5 times that of the control), with the flexibility increasing greatly. The WEP spiraled the fiber’s extension effect in the tensile performance, which was manifested in the improvement of tensile strength, axial tensile toughness ratio, and ultimate tensile strain.



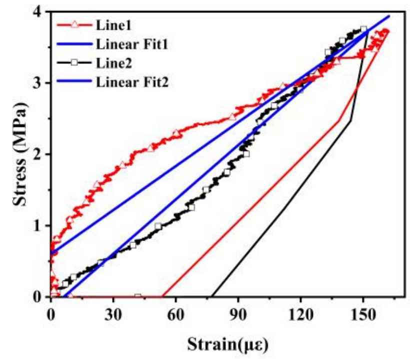
（a）C,P/C=0



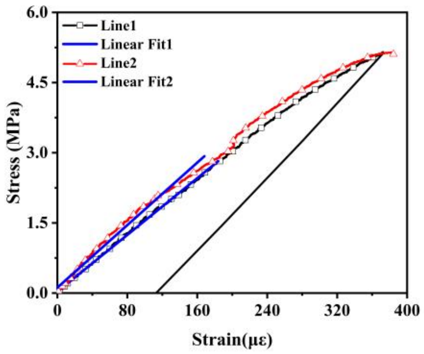
（b）CF, P/C=0



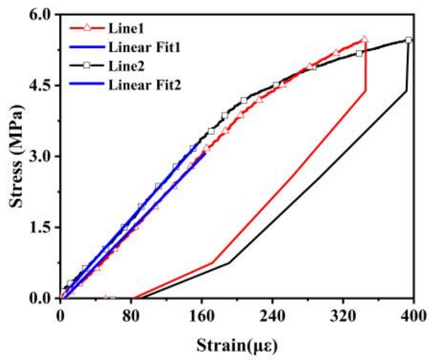
（c）E2C, P/C=0.2



（d）E2CF, P/C=0.2



（e）E4C, P/C=0.4



（f）E4CF, P/C=0.4

Figure 3. Tensile stress–strain curves of the concrete specimens with different P/C ratios

The mechanical performance parameters of the concrete specimens in terms of axial tensile strength, axial tensile toughness ratio, ultimate tensile strain, average elastic modulus, and Poisson's ratio are shown in Figure 14. E4C and E4CF exhibited considerable increases in strength and strain, which resulted in a surge in the axial tensile toughness ratio from ~1 to ~5 (up ~400% compared with the control value). The toughness ratio was the ratio of the tensile work to the total fracture energy. A higher toughness ratio signified that the WECM consumed more strain energy in the elastic deformation stage before fracture, i.e., a higher resistance to impact, fatigue, and ultrahigh loads than normal concrete. Even though the WECM matrix showed a softening trend with increasing P/C (the elastic modulus decreased from ~20 GPa to ~10 GPa), its Poisson's ratio did not increase significantly. This result indicated that WEP mainly filled pores in the concrete and presented a compressible state.

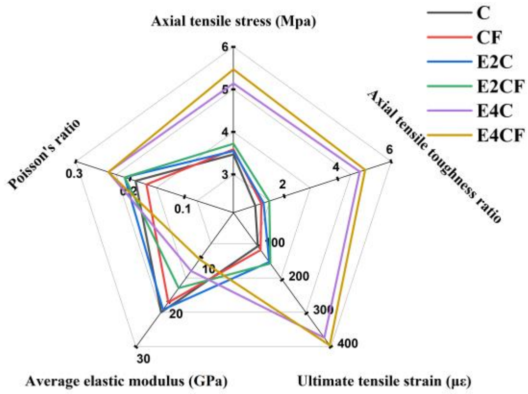


Figure 4. Mechanical performance parameters of the concrete specimens with different P/C ratios

Then, the volumetric modulus (bulk modulus or K value) of the material is defined as the ratio of the infinitesimal pressure increase to the resulting relative decrease in the volume. This reflected the resistance of the concrete to uniform compression of the outside under the elastic system. The shear modulus (G value) described the response to shear stress.
The volumetric and shear stiffness of concrete were calculated from Equation (1) [17, 18]

$$K_{con} = \frac{E_{con}}{3(1-2v_{con})}, G_{con} = \frac{E_{con}}{2(1+v_{con})} \qquad (1)$$

where Kcon and Gcon are the volumetric stiffness and shear stiffness of concrete, respectively, and vcon is the Poisson's ratio of each concrete.

The volumetric modulus describes the elasticity of homogeneous isotropic solids, i.e., incompressibility, which is one of the important parameters for the repair of load-bearing structures. The shear modulus characterized the ability of a material to resist shear strain. A large modulus indicated a strong rigidity of the material. From the perspective of the concrete microstructure, in the elastic deformation stage, the first deformed area should be the macroscopic defects (cracks, pores, interface transition zone), and then the cement microstructure (capillaries, gel, and interlayer) would be affected. However, the shear deformation bears more tensile stress on the microstructure than the compression deformation. The volumetric and shear stiffnesses of concrete specimens with different P/C ratios are shown in Figure 4. When the P/C reached up to 0.2, the bulk modulus of the WECM showed slight changes from that of normal concrete. The shear modulus of elasticity dropped significantly, indicating that WEP filled the macroscopic defects of concrete at first and then gradually merged into a continuous structure.

4. SUMMARY AND CONCLUSION

In this study, we designed a WEP that matches the concrete system based on the molecular structure-activity relationship and synthesized WEPs by introducing amine groups and polyether groups. into epoxy resin molecules through chemical grafting and copolymerization. Furthermore, WEP was compounded with cement mortar and concrete to prepare a novel WECM. Second, the key mechanical parameters of the WECM and the performance development law related to P/C were accurately obtained by several reasonable flexural and tensile testing methods. Finally, by means of molecular dynamics simulation and X-CT, the toughening effect of WEP and the mechanism of WEP fiber synergistic improvement of concrete performance were clarified.

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REFERENCES

1. Hou B, Li X, Ma X, Du C, Zhang D, Zheng M, Xu W, Lu D, Ma F. The cost of corrosion in China [J]. npj Materials Degradation, 2017, 1(1): 1-10.
2. Hou D, Zhang W, Sun M, Wang P, Li Z. Modified Lucas-Washburn function of capillary transport in the calcium silicate hydrate gel pore: A coarse-grained molecular dynamics study [J]. Cement & Concrete Research, 2020, 136: 106166.
3. Vejmelková E, Koňáková D, Kulovaná T, Keppert M, Žumár J, Rovnaníková P, Keršner Z, Sedlmajer M, Černý R. Engineering properties of concrete containing natural zeolite as supplementary cementitious material: Strength, toughness, durability, and hygrothermal performance [J]. Cement and Concrete Composites, 2015, 55(0): 259-267.
4. Celik K, Meral C, Petek Gursel A, Mehta P K, Horvath A, Monteiro P J M. Mechanical properties, durability, and life-cycle assessment of self-consolidating concrete mixtures made with blended portland cements containing fly ash and limestone powder [J]. Cement and Concrete Composites, 2015, 56: 59-72.
5. Wee T, Lu H, Swaddiwudhipong S. Tensile strain capacity of concrete under various states of stress [J]. Magazine of Concrete Research, 2000, 52(3): 185-193.
6. Swaddiwudhipong S, Lu H-R, Wee T-H. Direct tension test and tensile strain capacity of concrete at early age [J]. Cement and Concrete Research, 2003, 33(12): 2077-2084.

7. Pang B, Jia Y T, Pang S D, Zhang Y S, Du H J, Geng G Q, Ni H M, Qian J J, Qiao H X, Liu G J. The interpenetration polymer network in a cement paste-waterborne epoxy system [J]. Cement and Concrete Research, 2021, 139: 106236.
8. Pang B, Zhang Y, Liu G, She W. Interface Properties of Nanosilica-Modified Waterborne Epoxy Cement Repairing System [J]. Acs Appl Mater Interfaces, 2018, 10(25): 21696-21711.
9. Pang B, Zhang Y S, Liu G J. Study on the effect of waterborne epoxy resins on the performance and microstructure of cement paste [J]. Construction and Building Materials, 2018, 167: 831-845.
10. Pang B, Jia Y T, Zhang Y S, Ni H M, Liu G J, She W, Yang L, Qian R S. Effect of the combined treatment with inorganic and organic agents on the surface hardening and adhesion properties of cement-based materials [J]. Materials & Design, 2019, 169: 107673.
11. Pang B, Jia Y, Pang S D, Zhang Y, Du H, Geng G, Ni H, Qian J, Qiao H, Yang L, Liu G, Yang Y. Research on the toughening mechanism of modified nano-silica and silane molecular cages in the multi-scale microfracture of cement-epoxy composite [J]. Cement and Concrete Composites, 2021, 119: 104027.
12. Montes I, Lai C, Sanabria D. Like Dissolves Like: A Classroom Demonstration and a Guided-Inquiry Experiment for Organic Chemistry [J]. Journal of Chemical Education, 2003, 80(4).
13. García V J, Márquez C O, Zúñiga-Suárez A R, Zúñiga-Torres B C, Ríos-Gónzalez P J. Mechanical and electrical properties of MWCNTs-high early strength cement-mortars composite: Dispersion of CNTs and effect of chemical admixtures [J]. Anais da Academia Brasileira de Ciências, 2021, 93.
14. Geng G, Myers R J, Li J, Maboudian R, Carraro C, Shapiro D A, Monteiro P J. Aluminum-induced dreierketten chain cross-links increase the mechanical properties of nanocrystalline calcium aluminosilicate hydrate [J]. Scientific reports, 2017, 7(1): 1-10.
15. Huang W, Hu G, Miao X, Fan Z. Seismic performance analysis of a novel demountable precast concrete beam-column connection with multi-slit devices [J]. Journal of Building Engineering, 2021, 44: 102663.
16. Zhou J, Yu B, Gao Y, Yang W, Cheng B. Effect of epoxy emulsion on properties of ultra-high toughness cementitious composites; proceedings of the Journal of Physics: Conference Series, F, 2021 [C]. IOP Publishing.
17. Landau L D, Lifshitz E M. Course of theoretical physics [M]. Elsevier, 2013.
18. Maekawa K. Multi-scale modeling of structural concrete [M]. Crc Press, 2008.