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Mechanism behind the improvement of coupling agent in interface bonding performance between organic transparent resin and inorganic cement matrix

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HIGHLIGHTS

- We adopt the tapping mode AFM to study surface morphology structure.
- The micro morphology is studied in detail by ESEM.
- We study the interfacial chemical reaction by FTIR spectra analysis.
- The interface performance is systematic studied from the perspective of micro and meso.
- The coupling agent could significantly improve interface bonding properties of RLCCM.

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ABSTRACT

Resin light conductive cementitious materials (RLCCM) is a kind of advanced composite materials with good prospects for development, but there is the most vulnerable area on the interface of RLCCM. To find out the effect of coupling agent on interface bonding mechanism of organic-inorganic composite, the micro-hardness, micro-topography, surface morphology structure and chemical reaction of organic transparent resin and inorganic cement matrix interface were evaluated by the micro-hardness tester, environmental scanning electron microscopy (ESEM), atomic force microscope (AFM) and Fourier transform infrared spectroscopy (FTIR) tests. The results show that the silane coupling agent A-151 and aluminate coupling agent not only reduced the transparent resin performance weakened region thickness up to 100 μm and the micro-hardness in the transition region was increased by 19.6% and 39.9%, respectively, but also improved the micro-hardness of the surface of the cement matrix in the range of 30 μm, 20 μm to 22.2 and 21.9 MPa, respectively. The interface treated with silane coupling agent A-151, the interfacial micro cracks caused by the sampling process have narrowed and discontinuous in the direction of length. The interface treated with aluminate coupling agent, although the boundary between transparent resin and cement matrix still exists, but the micro cracks caused by the sampling process is almost disappeared, and two substances are closely combined together to present a natural transition state. Silane coupling agent A-151 and cement hydration products formed flat spherical particle diameter of about 78 nm, and these particles mosaiced and fused in the surface of hydrate as a whole, therefore the surface become more denser and smoother. Hydrolyzing silane coupling agent A-151 to produce silanol (–SiOH), which could react with hydroxy (–OH) function groups of CSH to form Si–O–Si bond. Hydrophilic inorganic groups of aluminate coupling agent reacted with hydroxyl (–OH) function groups of CSH to form Al–O–Si bond, and hydrophilic organic groups and resin make crosslinking, twisting reaction happened.

1. Introduction

Resin light conductive cementitious materials prepared from organic transparent resin and inorganic cement matrix is a kind of advanced building materials, and the organic-inorganic interface of this composite material is the weakest area [1–3]. Generally, coupling agents are applied to improve the adhesion between inorganic fillers and polymers, and the performance of composite materials. Coupling agents possess two different chemical reactive groups in their molecular structures. One end can react with the hydroxyl groups on the surface of fillers to form strong chemical

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bonds and the other end links with the polymer molecules through physical entanglement or chemical action. The coupling agent has significant modification on the interface of organic inorganic composite materials [4–6].

Feresenbet study that the effects of silane coupling agent on the surface morphology, chemical reaction and microstructure of the fiber/fiber matrix interface by FTIR, SEM and other test methods. The results show that the bonding mechanism of the interface has changed significantly and the bond strength is obviously enhanced [7]. Chieh used titanate coupling agent to modify the interface of PA/rGO composite, and used SEM, TEM, AFM and other test methods to observe and study the interface of composite materials. The results showed that the coupling agent improved the binding mode of the interface between the two materials, and the graphene was better integrated into the PA matrix material [8].Yoshihara used synthesis of silane containing adhesive by silane coupling agent to improve the interface of CAD/CAM composite, and then interface bonding mechanism of composite materials were evaluated by FTIR and ^{13}C NMR tests. The results showed that the interface bond strength was obviously enhanced [9]. Li study that the interaction mechanism of coupling agent in HAC/PVA based MDF (no macroscopic defects) material by XPS and IR. The study showed that the M–O–Si (Al, M=Ca) bond was formed by the crosslinking reaction the interface between silane coupling agent and $CaAl_2O_4$, and enhance the bond strength the interface of the $CaAl_2O_4$/PVA composite, whereas improve the mechanical properties and water resistance of MDF materials [10,11]. Redondo, Yoshida, Oromiehie, Nakatani and Eun-Beom study that the effect of coupling agent on interfacial bonding mechanism of composite materials by FTIR, SEM, XPS, XRD, AFM and other test methods. The results showed that the coupling agent promoted the interaction of various components in the composite so that the interface transition zone was no longer the weakest part [12–16].

Most of studies are based on the interfacial chemical reaction and tensile bond strength as so to illuminate the coupling agent mechanism and to evaluate the effect of coupling agent, the lack of systematic study on the interaction between the coupling agent and interface from meso and micro multi-scale. Based on the above situation, transparent resin and cement matrix are used as carriers, the influence of coupling agent on the micro-hardness, micro morphology, chemical reaction and modification of resin-cement interface were systematically studied from the meso and micro multi-scale. The micro-hardness of interface is characterized by hardness value on the mesoscopic scale. The micro morphology and chemical reaction are characterized by ESEM, AFM and FTIR on the microscopic scale.

2. Materials and methods

2.1. Materials

Cement (ordinary portland cement, OPC. Compressive strength = 42.5 MPa) was purchased from Nanchang Yadong Cement Co., Ltd. (Nanchang, China). The aggregate was obtained from Ganjiang River (size = 0.15 mm ~ 1.18 mm, the aggregate pass through Hammer type standard sieve machine), (Nanchang, China). The polycarboxylic acid high performance water reducer, with a solid content of 20% (water reducing rate ≥25%), was supplied from Nanchang Kechuang building materials Co., Ltd (Nanchang, China). The cement matrix is made of cement, high-performance water-reducing agent and water (mass ratio = 750.0 g: 5.0 g: 300.0 g). The m-phthalate unsaturated polyester resins (transparent liquid, hereafter referred to as transparent resin, viscosity = 0.3 ~ 0.5 Pa·s, solid content = 59% ~ 67%, the bending strength = 112 MPa, Gelation time = 8 ~ 16 min, destroy the elongation = 3.7%) were purchased from Nantong glass fiber reinforced plastic composite materials plant, (Wuxi, China). Promoter (a blue uniform) and curing agent (no particle impurities and stimulating odour colorless transparent liquid), used in this study were purchased from Nantong glass fiber reinforced plastic composite materials plant, (Wuxi, China). The silane coupling agent A-151 (CH_2=CHSi—$(OC_2H_5)_3$, molecular weight = 190.31; colorless transparent liquid, purity ≥98%, density = 0.911 g/cm^3, refractive index = 1.396) and liquid aluminum coupling agent ((C_3H_7O)xAL(OR_1)–(OR_2)n, pale yellow viscous liquid, viscosity range ≥98.0%, thermal decomposition temperature = 300) were supplied by Nanjing Daoning Co., Ltd. (Nanjing, China). The anhydrous ethanol (purity ≥99.7%, density = 0.789–0.791 g/ml) was purchased from Tianjin Hengxing chemical manufacturing Co., Ltd. (Tianjin, China). The deionized water (colorless clear liquid, no irritant smell, pH = 6.5–7, resistivity ≥1 MΩ·cm, Cu ≤ 2 μg/L, Zn ≤ 5 μg/L, Na ≤ 5 μg/L, K ≤ 5 μg/L, Si ≤ 50 μg/L) was supplied from Henan Xinyuan technology Co., Ltd. (Henan, China). The acetic acid (CH_3COOH, concentrations = 99.9%).

2.2. Sample preparation

2.2.1. Preparation of specimens for micro-hardness

Cylinder type plastic dies (diameter = 45 mm, height = 80 mm) were machined to prepare Micro-morphology blocks. First of all, cement matrix was poured in the lower half of the mold to form cement matrix blocks, which were cured 3 d under standard curing condition after 24 h. After surface of cement matrix specimen were polished process by sandpaper, then the coupling agent was coated on surface. The samples were replaced inside the mold after 24 h to dry at room temperature. Subsequently transparent resin was poured in the upper half of the mold to form cement matrix blocks, which were cured 14 d under standard curing condition after 24 h. Finally the samples were cut into sheet (40 mm × 40 mm × 5 mm) through cutting laser machine. Then the surface of sheets were polished by metallographic polishing machine with 1000, 2000, 3000, 5000, 7000 purpose sandpaper, and keep the sheet's upper and lower parallel.

2.2.2. Preparation of specimens for ESEM

ESEM specimens and micro-hardness specimens of the preparation steps are the same, but their sizes and thicknesses are relatively small.

2.2.3. Preparation of specimens for AFM

The smooth and flat plastic plate dies (2 mm × 10 mm × 10 mm) were machined to prepare cement and resin blocks, which were cured 14 d at room temperature. The blocks were polished process by sandpaper, then the coupling agent was coated on their surface, respectively. The blocks were directly used as sample for the observation of AFM.

2.2.4. Preparation of specimens for FTIR

Making small samples with cement matrix and under standard curing condition maintain 28 d, then the small samples are ground into a powder. While making small samples with transparent resin and at room temperature maintain 3 d, then the small samples are ground into a powder. Finally, the cement matrix powder and transparent resin powder are all divided into three equal parts,