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Short Communication

The Effect of Polyacrylic Ester on Electrochemical Corrosion Behavior of Low-Alloy Steel in Polymer Modified Concrete Exposed to Marine Environment

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In this work, the effects of bagasse ash (BA) and polyacrylic ester (PE) additives on the durability of polymer modified concrete were investigated. Corrosion behavior of low-alloy steel reinforced concrete mixture modified with BA and PE subjected to the marine environment was studied by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization tests. The PE8 mixture including 8% PE had the best corrosion resistance, according to the EIS findings fitted by a suitable equivalent circuit. In comparison to unmodified concrete, polarization analysis showed that PE-modified concretes had more positive corrosion potential, lowest corrosion current density and high corrosion resistance. PE admixtures significantly increased the compressive strength of concrete. The findings of this study show that the efficiency of PE-modified concrete exposed to corrosive environments was higher than unmodified one. PE-modified concrete contributed to low water absorption and considerable resistance to chemical attack.

Keywords: Polymer modified concrete; Electrochemical corrosion behavior; Polyacrylic ester; Compressive strengths; Water absorption

1. INTRODUCTION

The permeability of concrete, which is the most extensively used construction material, is an important aspect in its long-term durability [1, 2]. Water freezing and thawing in cold conditions causes significant concrete degradation [3]. Water is also the primary carrier of the corrosive medium into the concrete mixes, and the speed at which it does so determines how quickly the concrete deteriorates [4, 5]. As a result, permeability has become the most important criterion for determining the durability of concrete, as it is linked to sulfate attack, frost resistance, chloride ion diffusion, and mechanical properties [6, 7]. So many efforts have been made to determine the impact of mineral additives and polymers on the strength and hardened concrete properties as ordinary Portland cement (OPC) is partially replaced [8]. Because of its superior properties to ordinary concrete, polymer-modified concrete has become a common building material. It is made of polymer in order to boost its durability, drying shrinkage, strength and workability [9].

Acrylate polymers are a kind of polymer produced from acrylate monomers. These polymers have features such as transparency, break resistance, and flexibility [10]. Polyacrylic ester (PE) does have flexible polymer molecular structures that can be used to create flexible film structures in cement-based materials. Every year, thermal power plants in China generate a significant volume of bagasse ash (BA) [11]. As a result, using a sufficient volume of BA in OPC helps both the climate and the economy. The association of various forms of polymer modifiers with BA, on the other hand, needs to be investigated further [12].

Although polymer additives have been shown to improve electrical resistivity and minimize basic surface area and permeability, no previous research on the impact of PEs on the corrosion behavior of low-alloy rebars has been done. As a result, the emphasis of this study was on the corrosion resistance of low-alloy rebars in BA-modified concrete when PEs was present in various concentrations.

2. MATERIALS AND METHOD

In this research, the cementitious substance used was ordinary Portland cement (OPC). The concrete samples were cast using constant content of bagasse ash (BA, 10 wt%) which was prepared by replacement of OPC by BA. The chemical structure of the OPC and BA used is seen in Table 1. Polyacrylic ester (PE) is thought to be useful in enhancing the engineering characteristics of concrete mixes. Table 2 lists the physicochemical properties of PE. In a 0.45 water/cement ratio concrete, the concrete is mixed with polymer modifiers of varying content of 1, 2, 4 and 8% which are shown as PE1, PE2, PE4 and PE8, respectively.

Table 1. Chemical composition of the OPC and BA (wt%)

	OPC	**BA**
SiO_2	19.84	52.76
Al_2O_3	4.88	8.50
Fe_2O_3	3.12	2.75
CaO	63.43	9.72
MgO	2.12	4.46
K_2O	0.57	9.43
Na_2O	0.30	4.52
SO_3	2.53	3.45
LOI	3.21	4.41

A concrete mixer with a speed of 50 revolutions per minute was used to stir the PMC mixture. For 2 minutes, the cement replacement materials and aggregate were combined. The polymer modifier and mixing water were then evenly mixed before being applied to the mixer. After 3 minutes, all of the ingredients had been thoroughly combined. At ambient temperature, the procedure was carried out. Plastic molds with 10×10×15 cm dimensions were filled with the fresh mixture.The samples were dried at room temperature for one day and then demolded.

Table 2. Physicochemical property of PE

pH value	Density	Minimum Film-forming Temperature	Solid content	Viscosity
7	1.07g/cm3	23°	48%	50-500mPa·s

Low-alloy steels with a diameter of 10 mm and a length of 10 cm were stacked vertically in the cube's center. Low-alloy steels with a diameter of 10 mm and a length of 10 cm were placed vertically in the cube's center.The chemical composites of low-alloy steels are seen in Table 3.

Table 3. Chemical composition of low-alloy steel (wt%)

C	Si	S	Mn	P	Cr	Ni	Fe
0.18	0.32	0.11	1.33	0.25	0.31	0.30	Bal.

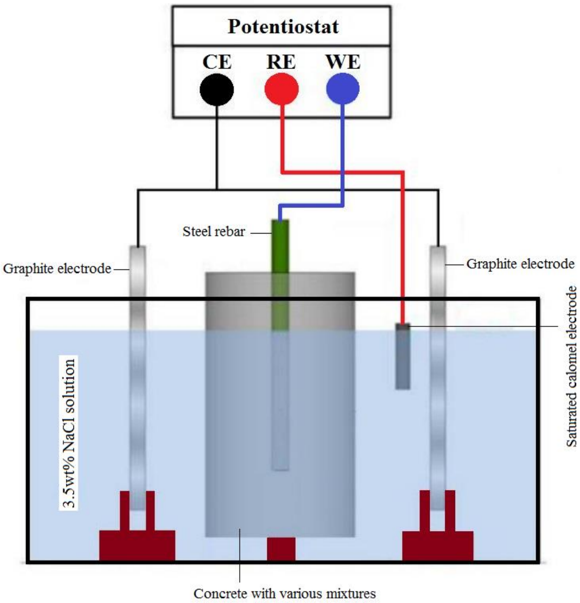

Figure 1. Schematic diagram of EIS test

EIS and polarization were used to evaluate corrosion behavior of low-alloy steels. The schematic diagram of the EIS test is indicated in Figure 1. Steel rebar, saturated calomel, and graphite electrodes were used as working, reference, and counter electrodes in an electrochemical process. After being subject to a corrosive environment of 3.5wt% NaCl solution, the findings were collected. Corr Test Instruments Corp conducted the EIS experiments at a frequency ranging from 0.01Hz to 0.1 MHz. The polarization analysis was done at a scan rate of 1mV/s. Compressive strength was performed in accordance to BS-1881 technique on 15×15×15 cm cube samples for all concrete mixes on 1, 2, 4 and 8 weeks of curing. Water absorption of mixtures was done according to ASTM C642. The specimens were exposed to 3.5 wt% NaCl solution. The water absorption of specimens was recorded after immersing to 3.5 wt% NaCl solutions with 1, 2, 4 and 8 weeks exposure time, which was the average value of three samples. The samples' morphologies were examined using a Zeiss Sigma 300 VP scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

The water absorption of the concrete with the aggregates examined was commonly very high (over 10%) [13], but this problem can be overcome by using mineral admixtures and a super-plasticizer. Unmodified OPC with BA and super-plasticizer has water absorption of 5.5% on average in this study (Figure 2). The addition of polymer to unmodified OPC, on the other hand, resulted in a significant reduction in water absorption. As shown in figure 1, a reduction in the water absorption of PE-modified OPCs was observed which can be attributed mostly to a decrease in permeability due to thew/creduction. Such a reduction in w/c influences the gel–space ratio and reduces the system's capillary porosity, allowing the pore optima of the porosity range to change the pore of the smaller porosity.

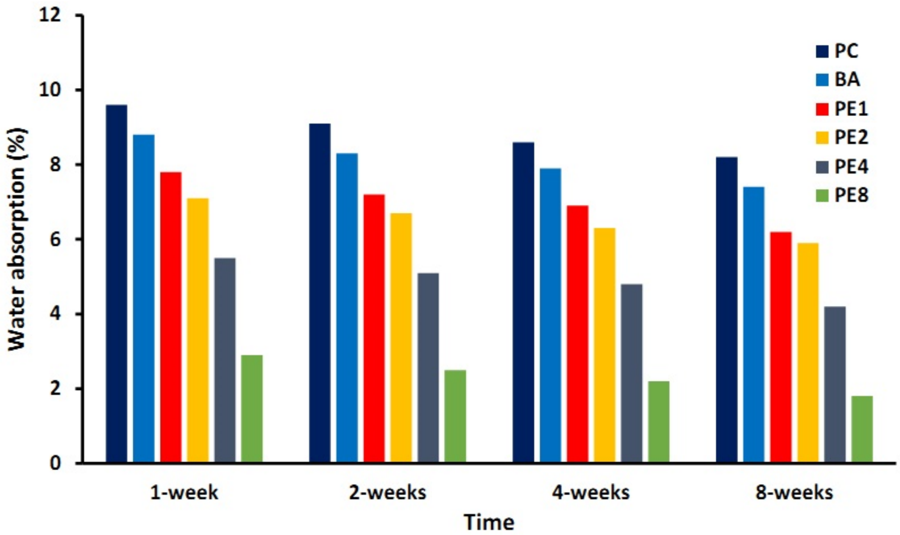

Figure 2. Water absorption of various concrete mixtures after 1, 2, 4 and 8 weeks of exposure time in a 3.5 wt% NaCl solution at room temperature

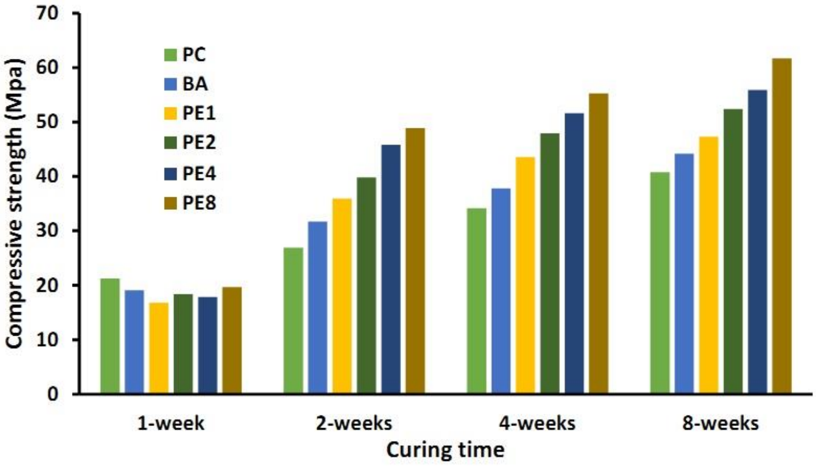

Figure 3. The compressive strength of BA-modified OPCs with different concentration of PE after 1, 2, 4 and 8 weeks of exposure time in a 3.5 wt% NaCl solution at room temperature

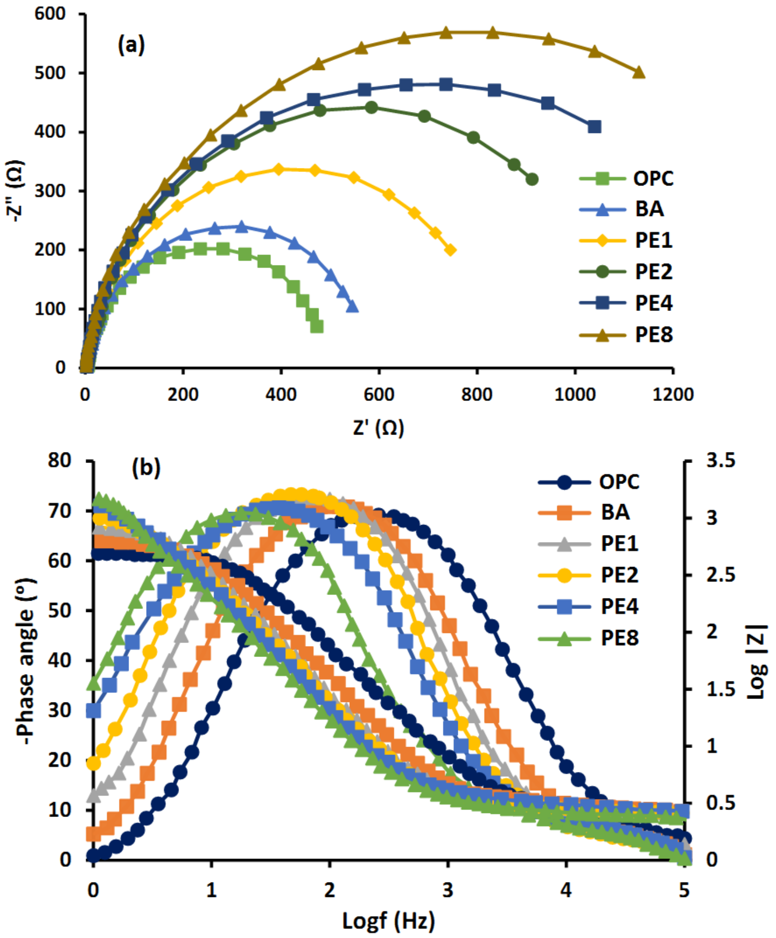

Figure 4. (a) The Nyquist and (b) Bode plots of low-alloy steel reinforced concrete with various additives in a 3.5wt% NaCl solution after two weeks exposure time at room temperature

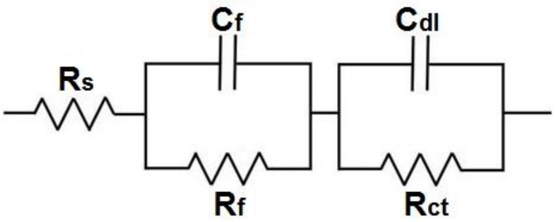

Figure 5. Proposed circuit model

Figure 3 reveals the compressive strength of BA-modified OPCs with different concentrations of PE. The compressive strength of BA-modified concrete begins to decline as PE increases in OPC concrete. It can be related to the aggregate of polymer particles on the surface of the cement particles, forming films of various thicknesses and delaying the hydration process [14]. Besides, calcium ions in the pore solution are bound by the polymer. In the meantime, the development of gels (CH and C-S-H) has slowed. And, as the PE content rises, this retardation degree increase. The compressive strength of PE-modified concretes increases as the curing time and polymer content increases. The pores in the cement would be filled with polymers sufficient to increase the compressive strength of the PE-modified concretes. The sufficient amount of polymer may fill the pores to minimize the overall porosity of the cement pastes, which is close to previous studies [15]. However, because the polymer modifier contains hydrophobic units, air is added to the cement pastes, and the polymer modifier can reduce the compressive strength of the concrete [16]. The use of polymer modifiers aids the production of concrete strength. Furthermore, the BA acts as an activator in a pozzolanic reaction, resulting in denser structures and faster hydration, increasing compression strength [17].

The corrosion activity of low-alloy steel reinforced concrete with various additives in a 3.5wt% NaCl solution was evaluated using the EIS process. The Nyquist plots achieved by the EIS analysis are shown in Figure 4. Figure 5 shows an equivalent circuit that was used to match the EIS result. Where R_s denotes the solution's resistance. The capacitance and resistance of coated concrete are shown by C_f and R_f, respectively [18]. The double-layer capacitance and charge-transfer resistance of a low-alloy steel rebar are represented by R_{ct} and C_{dl}, respectively. Table 4 summarizes the information gathered.

Table 4. Attained EIS parameters from low-alloy steel reinforced concrete with various additives in a 3.5wt% NaCl solution after two weeks exposure time at room temperature

Mixture	**R_s (Ω)**	**C_f(µF cm^{-2})**	**R_f (Ω)**	**C_{dl}(µF cm^{-2})**	**R_{ct} (Ω)**
OPC	27	24.16	263	28.49	487
BA	32	22.82	316	27.38	593
PE1	29	17.62	549	23.73	865
PE2	31	14.71	7253	19.98	1134
PE4	26	12.67	9591	18.45	1362
PE8	28	9.83	1240	16.74	1530

These results indicate that by replacing PEs and BA in the OPC, R_f rises and C_f decreases, resulting in an improvement in the passive layer's stability and corrosion resistance of low-alloy steel rebar. BA's high surface area allows it to form a strong bond with hydrated cement, which assists to prevent $Ca(OH)_2$ from growing [19]. The admixtures cover capillary pores and minor cracks in the cement system, shrinking it and improving steel bar corrosion resistance in corrosive environments. Furthermore, when C_{dl} and C_f were compared in all concrete samples, C_f was found to be lower than C_{dl}, indicating that the formation of double and passive layers in the interface has great capacitive performance.

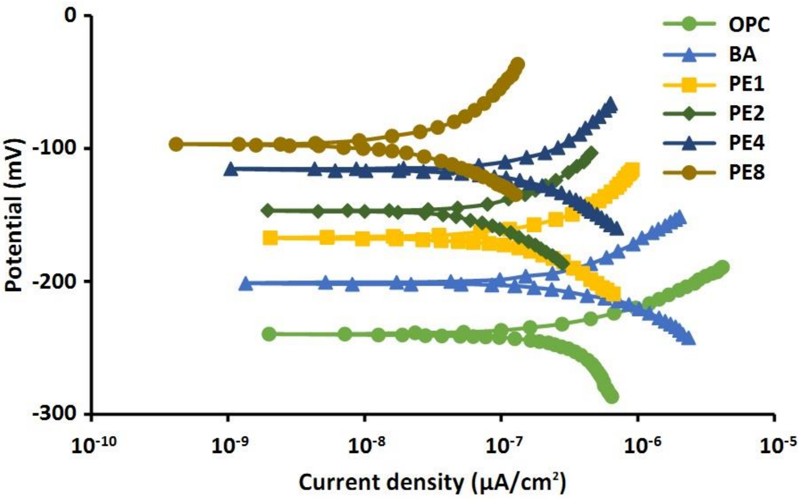

Figure 6. Potentiodynamic polarization curves of low-alloy steel reinforced concrete samples in 3.5wt% NaCl solution after two weeks at room temperature

Figure 6 shows the polarization plots of low-alloy steel reinforced concrete samples subjected to 3.5wt% NaCl media after two weeks to determine the impact of PEs content on low-allay rebar corrosion activity. Table 5 shows the values of corrosion parameters obtained from the polarization cures in Figure 5. As shown in table 5, the corrosion potential of the concrete sample without additives was the lowest of all the concrete specimens. The steel reinforced concrete sample of 8% PEs was in a passive condition and exhibited less corrosion tendencies. As seen in Figure 6, raising the PEs content increases the corrosion potential (E_{corr}) significantly. As a result, the potential had shifted to a more positive value. Furthermore, the corrosion-current density (I_{corr}) moved to the left, indicating that the low-alloy rebar surface has less corrosion current. The Durar-Network Specification divides the corrosion standard into four categories [20]. However, the I_{corr} of the PE8 sample in saltwater was lower when compared to the other samples. As a result, with the exception of the OPC sample, all low-alloy rebars remained in a passive state throughout the electrochemical process, indicating their high corrosion resistance in a saltwater environment.

Table 5. Corrosion parameters obtained from the polarization cures in Figure 6

Admixture	I_{corr} (μA/cm^2)	E_{corr} (V)
OPC	0.68	-0.244
BA	0.56	-0.200
PE1	0.39	-0.178
PE2	0.23	-0.143
PE4	0.12	-0.118
PE8	0.08	-0.097

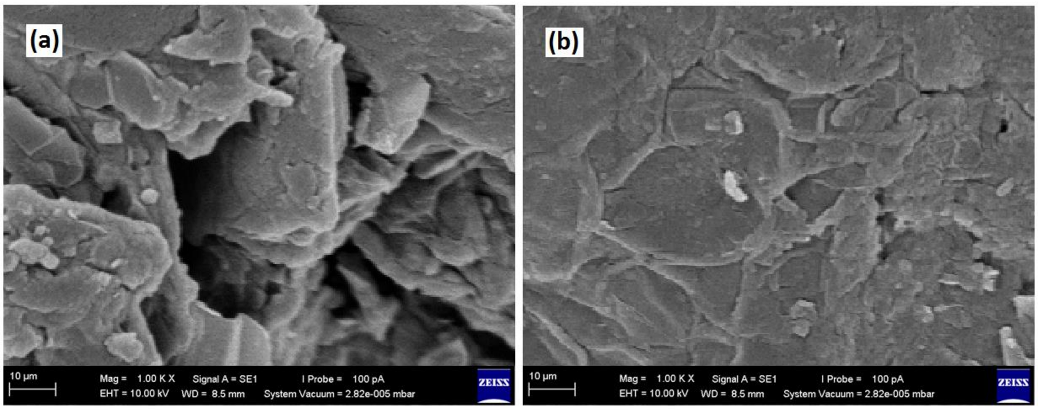

Figure 7. SEM images of low-alloy steel surfaces after 8 weeks of exposure in a 3.5wt% NaCl environment for (a) OPC and (b) FE8 samples

Figure 7 displays SEM images of low-alloy steel surfaces after 8 weeks of exposure in a 3.5wt% NaCl environment for OPC and FE8 samples. The surface of steel embedded in PE-modified concrete shows low pits and corrosion materials, indicating moderate pitting corrosion on the surface of low-alloy rebar, which is consistent with electrochemical experiment findings. It's connected to a reduction in concrete's water permeability and chloride ion permeability. PE's reaction with calcium hydroxide can result in hydration products that significantly reduce concrete porosity. Furthermore, the composition of concrete may be influenced by the addition of BAs to the mix.

4. CONCLUSIONS

Here, the influence of BA and PE admixtures on the durability of polymer-modified concrete was investigated. Corrosion behavior of low-alloy steel reinforced concrete modified with BA and PE was studied by EIS and potentiodynamic polarization assessments. The PE8 mixture including 8% PE had the best corrosion resistance, according to the EIS findings fitted by a suitable equivalent circuit. Polarization study revealed that PE-modified concretes had a higher positive corrosion potential, lower corrosion current density, and higher corrosion resistance than unmodified concrete. The findings of this study show that the efficiency of PE-modified concrete exposed to corrosive environments was higher than unmodified one. PE-modified concrete contributed to low water absorption and considerable resistance to chemical attack. The low-alloy rebar in OPC with PE admixture had more smooth surface morphologies and less pitting corrosion than the unmodified OPC mixture, which met the electrochemical findings.

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