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Short Communication

Carbonation and Electrochemical Corrosion Resistance of Mild Steel Rebar in Concrete Modified by Sodium Polyacrylate as Super Absorbent Polymer exposed to 3.5 wt% NaCl Solution

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In this research, Portland cement (PC) was replaced by sodium polyacrylate (SP) admixture as a super absorbent polymer to consider the carbonation and electrochemical corrosion resistance of mild steel rebar in 3.5wt% NaCl solution. Electrochemical impedance spectroscopy technique, carbonation resistance test and compressive strength were used to assess the mechanical and corrosion resistance of mild steel reinforced concrete. The results indicated that the SP admixtures significantly improved the resistance of chloride penetration and carbonation of concrete. The concrete samples containing 0.5 kg/m^3 SP (SP3) was found as an optimal value of compressive strength. The EIS results show that the highest value of corrosion resistance was obtained for the SP3 sample. The electrochemical result indicates that the addition of SP admixture in concrete structure increase the corrosion resistance and durability of mild steel rebars after being exposed to a corrosive environment by preventing the surface of rebar from reaching the chloride ions. The surface morphologies of the mild steel rebar in PC with SP admixture was more uniform and lower pitting corrosion than the PC mix, which was consistent with electrochemical results.

Keywords: Carbonation resistance; Electrochemical corrosion resistance; Sodium polyacrylate; Modified concrete

1. INTRODUCTION

Today, steel reinforced concrete is used to increase durability of the concrete structure [1, 2]. Though, building materials are usually exposed to corrosive environments such as their coupling effects, carbonization, chloride attack and freeze thaw cycles which commonly cause the corrosion of steel rebars [3, 4]. The building industry has been recognized as one of the industries that absorbs the most materials such as fillers in concrete [5, 6]. If these admixtures have pozzolanic properties, they provide technical benefits to the concrete and allow for greater amounts of cement replacement [7].

Several types of mineral admixtures such as fly ash and slag have been widely utilized to substitute Portland cement (PC) in structure of concretes [8, 9]. However, these admixtures are not easily accessible at all locations and where accessible [10].

Polymers have been used in concrete structure to develop engineering characteristics such as enhancing durable properties of concrete, improving the compressive strength, increasing corrosion resistance and reducing the cracks extension [11, 12]. Hence, superabsorbent polymer (SAPs) can be applied for stated properties. Permeability may be decreased by addition of the polymer fibers [13]. One of the important parameters for making reinforced concrete and increasing the durability of concrete is crack width control [14]. In particular, unexpected cracks formed due to the steel corrosion reduce the service life of reinforced concrete. The previous studies are mostly based on corrosion behavior of cement containing by-product materials and SAPs separately and the performance of such additives along with SAPs has not been well investigated especially, the effect of bagasse ash and SAPs [15, 16]. To this end, sodium polyacrylate (SP) is utilized as SAP in this work since it is obtainable at relatively low-price in China [17]. SP is used widely in the agricultural industries by pervading in the soil of numerous potted plants to assistance them hold moisture. The SPs, also recognized as water lock, have the ability to absorb water up to 250 times its mass.

Since the carbonation depth and electrochemical corrosion resistance of mild steel rebar in concrete modified by SP has not previously reported. Here, the electrochemical corrosion resistance of mild steel rebar in concrete modified by SP was considered. Electrochemical impedance spectroscopy (EIS), carbonation resistance and chloride permeability tests were used to study the corrosion resistance of mild steel rebar.

2. MATERIALS AND METHOD

Portland cement (PC) along with sodium polyacrylate (SP) was utilized as the binder. Table 1 shows the chemical composition of PC. In this work, SP with ratios of 0.0, 0.1, 0.2, 0.5 and 1 kg/m^3 were replaced in the PC.The properties of SP (QINGDAO SOCO NEW MATERIAL CO., LTD. Shandong, China) used as internal curing material are revealed in Table 2. The ratio of concrete mixtures is presented in Table 3.

Table 1. Chemical compositions of PC

Composition	Content (wt%)
MgO	1.9
SiO_2	21.8
CaO	62.6
Al_2O_3	4.9
Fe_2O_3	2.1
SO_3	3.7
LoI	1.9

Table 2. The properties of SP

Particle size (μm)	Density (g/cm^3)	Water absorption(g/g)
245	1.22	115

Table 3. Detail of the concrete mixtures

Samples	SP0	SP1	SP2	SP3	SP4
PC (kg/m^3)	500	499.9	499.8	499.5	499
SP (kg/m^3)	0.0	0.1	0.2	0.5	1.0
Aggregate (kg/m^3)	1710	1710	1710	1710	1710
Water (kg/m^3)	225	225	225	225	225
W/C	0.45	0.45	0.45	0.45	0.45

The concrete mixes were poured into a 10×10×10 cm mold, while a mild steel rebar was positioned vertically in the center of the cube. This rebar had 8 mm diameter and 8cm length. Before using, chemical cleaning was done on the mild steel surface. Table 4 indicates the chemical composition of mild steel.

Table 4. The chemical composition of mild steel (wt%)

Si	**S**	**P**	**Mn**	**V**	**C**	**Fe**
0.51	0.03	0.03	1.42	0.03	0.23	Bal.

EIS technique was applied to study the corrosion behavior of mild steel rebars. A triple-electrode system was applied for the measurements which contain the steel bar embedded in concrete as the working electrode, a platinum wire and a saturated calomel electrode as an auxiliary and a reference electrode, respectively. The analysis was performed after immersion to 3.5wt% NaCl solution. The EIS assessments were done at a frequency range from 0.01 Hz to 0.1 MHz after one month immersion time.

Rapid chloride permeability tests were done according to ASTM C1202 [18]. The carbonation resistance assessment was performed consistent with the standard for test technique of long-term durability and performance of ordinary concretes (GB/T50082-2009).The surface morphologies of the steel rebars were considered by scanning electron microscope (SEM, Zeiss Sigma 300 VP).

3. RESULTS AND DISCUSSION

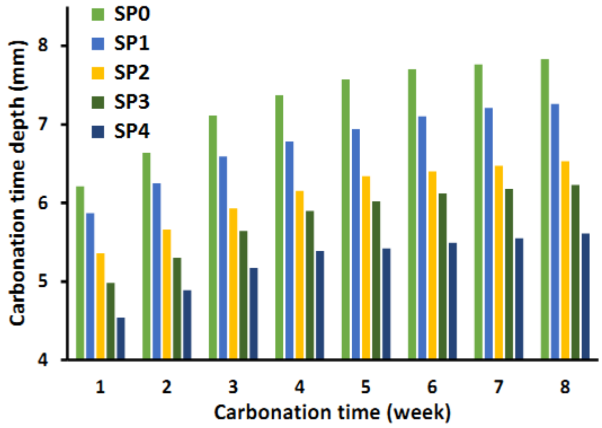

Figure 1. Effect of SP on carbonation depth with various carbonation times in an accelerated carbonation chamber with 20 °C and 70% relative humidity

Figure 1 shows the effect of SP on carbonation depth (CD) with various carbonation times. As shown in Fig. 1, the CD increases constantly by increasing carbonation times. Compared with the PC sample, the CD of concrete including the SP is decreased which indicates that better carbonation resistance in SP samples. The carbonation resistance in concrete structure is associated with the compression of the matrix. SP4 sample revealed lower carbonation depth compared to the other sample in all carbonation times. This indicates that the CD decreases with the reduction of effective water-binder ratio. Furthermore, the SP makes the water-binder ratio variation, therefore influence on the carbonation performance of the concretes and forms a compact concrete matrix. It can be attributed to the free water absorption by SP inside concrete structures. In the concrete hardening process, the water of the SP is diffused into the environment, which causes the further hydration of concrete matrix, hence increasing the concrete compactness.

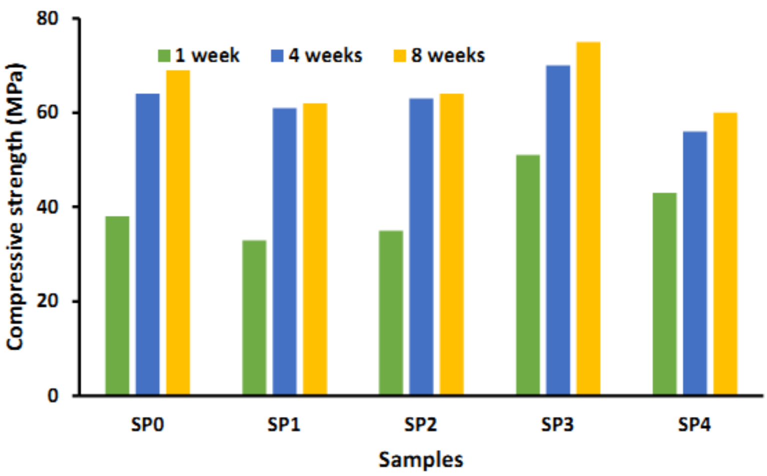

Figure 2. Compressive strength of concrete samples with different concentration of SP at various curing ages

Figure 2 indicates compressive strength of various mixtures. At replacement of the Portland cement with SP, the compressive strength was reduced. As shown, using SP led to an improvement at compressive strength of the concretes for all mixtures and there was an optimum concentration of SP. The strength is enhanced by increasing the SP concentration till 0.5 kg/m^3. After that there is a decrease when 1.0 kg/m^3SP was used. It can be attributed to absorption of CaO using SP from $Ca(OH)_2$ made via hydrating PC which means a lesser amount of CaO in PC to produce material that has cementations properties. It can clarify the higher decrease in our result when 0.5 kg/m^3 content was used in comparison with other research [19]. Furthermore, the improvement of compressive strength can be associated with the SP efficiency in inhibiting the crack growth in the concrete structures which reduces the strength of concrete. The fiber allows the transfer of stress through cracked sections, which allows the concrete to maintain post-cracking strength and to resist deformation much larger than concrete without SP. Based on these findings, replacing a PC with 0.5 kg/m^3SP can be considered optimal.

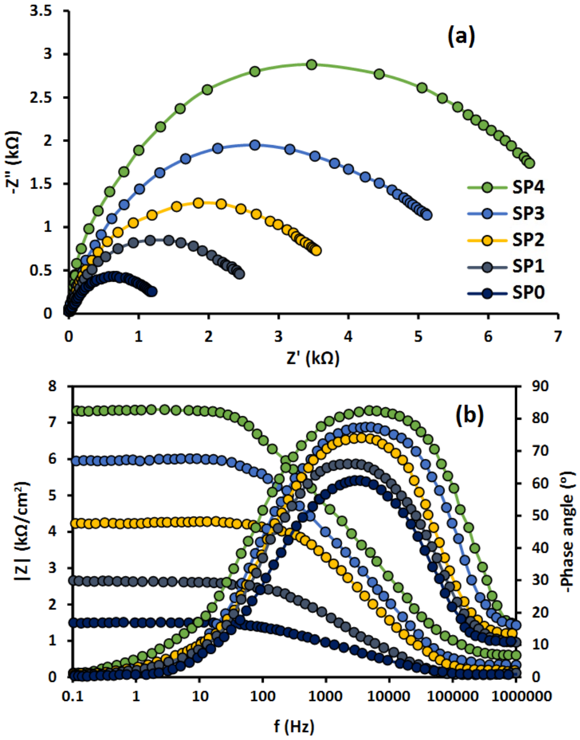

Figure 3. (a) Nyquist plots and (b) bode plots of mild steel reinforced concretes immersed to 3.5wt% NaCl solution at a frequency range from 0.01 Hz to 0.1 MHz after one month immersion time

EIS measurements were done to assess the corrosion resistance of carbon steel reinforced in the various concrete mixtures. Figure 3a reveals the Nyquist diagram of mild steel reinforced concrete in marine environments after 4 weeks. The EIS data were fitted by an equivalent circuit model as indicated in Figure 4. R_s presents the solution resistance, R_f and C_f show resistance and capacitance of coated concrete, respectively. They are used to simulate high-frequency loops. Furthermore, R_{ct} and C_{dl} indicate the charge-transfer resistance and double layer capacitance, respectively [20].

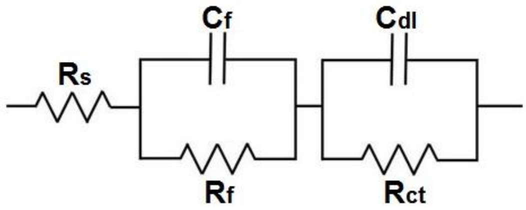

Figure 4. An equivalent circuit model used in this work

Obtained data exhibited in Table 5 show that by introducing SP into the concrete structures, R_c and R_{ct} increase and C_{dl} and C_f reduce which can be associated to the passive layer stability on carbon steel rebar improving the corrosion resistance. This enhancement in corrosion resistance of mild steel corresponds to the creation of extra calcium silicate hydrate in the hydration process of SP into the concrete structure so that large penetrable pores can be transformed into slight resistant pores. Studies have shown that a smaller amount of porosity in the concrete structure causes lower permeability and therefore it protects the steel rebar in concrete against the aggressive environment [21]. Furthermore, as shown in Table 5 concrete samples containing SP reveal the higher corrosion resistance than PC samples. Especially, the concrete sample containing 0.5 kg/m^3 SPs show higher value of corrosion resistance than the other samples. In fact, by increasing the content of SPs, concrete structure becomes denser resulting in less permeability and enhancement of corrosion resistance.

Table 5. Achieved EIS parameters from the Nyquist diagrams fitted by an equivalent circuit

Mixtures	R_s(Ω)	R_f(kΩ)	C_f (μFcm^{-2})	R_{ct}(kΩ)	C_{dl}(μFcm^{-2})
PS0	37	0.84	62.6	1.33	15.1
PS1	45	1.97	54.2	2.85	9.7
PS2	42	3.21	23.3	4.17	8.5
PS3	41	5.87	9.4	7.66	2.4
PS4	36	4.12	16.7	6.14	4.2

Figure 3b shows the Bode plots corresponding to the Nyquist plot, which shows that at lower frequencies, the absolute impedance increases with the SP concentration. This is because the larger the SP concentration, more molecules are adsorbed on the mild steel surface.

Figure 5indicates the influence of SP on the diffusion coefficient of Cl ion at 4 weeks. The variation of Cl ion diffusion coefficient was similar to that of CD with different content of SP. As shown in Fig.5, the incorporation of SP into concrete structure has a great effect on the diffusion coefficient of Cl ions in concretes. Compared with the SP0 sample as reference mixture, the Cl ion diffusion coefficient of SP3 concrete with 0.5 kg/m^3 SPs decreased, which reveals that the internal curing concretes mixed with SP significantly enhanced the resistance to Cl ion corrosion into reinforced concrete. It can be attributed to the incorporation of SP improves the environment of cement hydration, and helps another hydration reaction among hydration products into the cement. More hydration yields form the more compact concrete. The structure of the pores tends to change, and the connection between the capillary pores is severed, which efficiently restricts the diffusion of Cl ions and improves the resistance to Cl ion penetration.

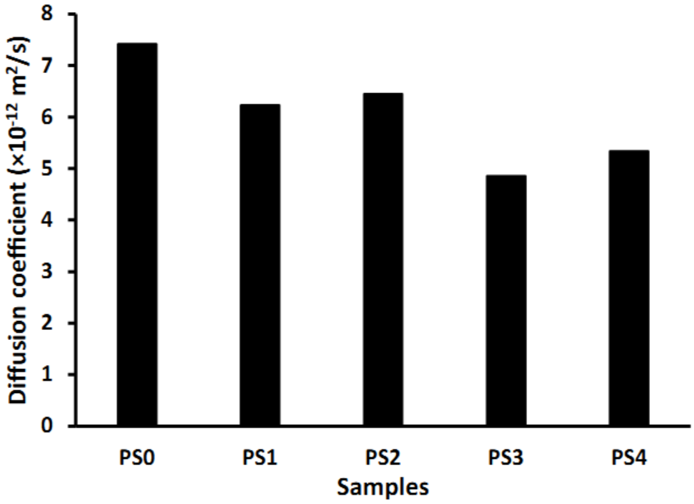

Figure 5. The influence of SP concentration on diffusion coefficient of chloride ions at 4 weeks at room temperatures

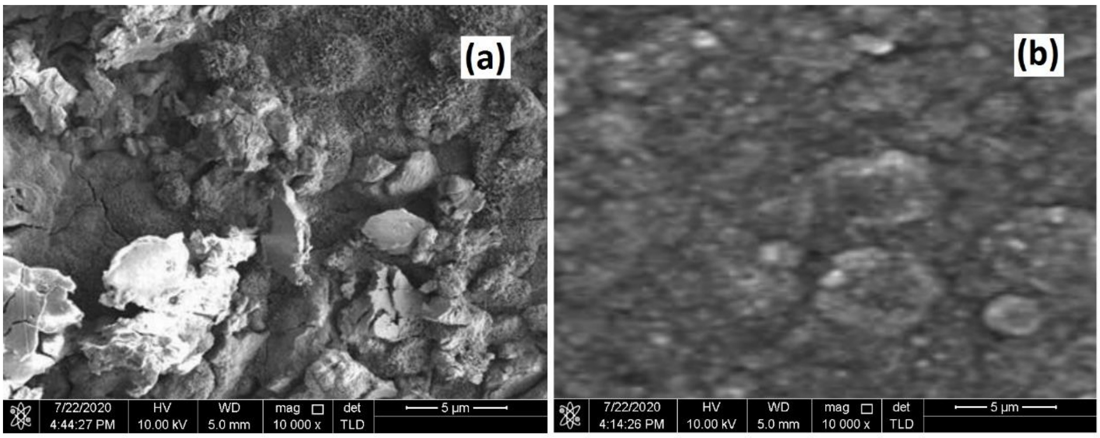

Figure 6. Surface morphologies of mild steel in various concretes (a) PC mixture, (b) SP mixture exposed to the 3.5wt% NaCl solution for 4 weeks.

Furthermore, the diffusion coefficients of Cl ions reduce with the reduction in the water ratio of binder. In addition, the SP with the fraction of internal water cured from mixing water can decrease the total volume of pores and porosity of concrete, improving concrete compactness. Previous studies confirm that diffusion coefficients of Cl ions is reduced when superabsorbent polymer added in concrete structures [22].

Figure 6 reveals the surface morphologies of the mild steel rebar in PC without SP (SP0) andSP3 mixture exposed to 3.5wt% NaCl solution after 4 weeks. Fig. 6b exhibited that the sample with

SP is more uniform and smooth than the PC mix which agrees with previous reports. SPs create the bridging effect which can improve the flexural and tensile strength. Moreover, the SPs include C-S-H gels and aggregates as binders can have the pore blocking effects leading to less permeability. In fact, by reducing the internal conductivity of the pores, it reveals less capillary porosity [23].

4. CONCLUSION

Recent studies indicate that corrosion resistivity of steel reinforced concrete may be enhanced by changing the concrete structure, particularly cement replacement by SAP additives. In this research, PC was replaced by SP admixture as a super absorbent polymer to consider the carbonation depth and electrochemical corrosion resistance of mild steel rebar in 3.5wt% NaCl solution. EIS, carbonation resistance test and compressive strength were used to assess the mechanical and corrosion resistance of mild steel reinforced concrete. The results indicated that the SP admixtures significantly improved the resistance of chloride penetration and carbonation of concrete. The concrete samples containing 0.5 kg/m3 SP (SP3) was found as an optimal value of compressive strength. The EIS results show that the highest value of corrosion resistances was obtained for the SP3 sample. The electrochemical result indicates that the addition of SP admixture in concrete structure increase the corrosion resistance and durability of mild steel rebars after being exposed to a corrosive environment by preventing the surface of rebar from reaching the chloride ions.

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