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Short Communication

Effect of Partial Replacement of Hydroxypropyl Methylcellulose Nanofibers of Portland Cement on the Corrosion Behavior of Reinforced Concrete Structures

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Nowadays, steel reinforced concretes have been widely used as a building material. However, building materials are usually exposed to corrosive environments which frequently leads to the corrosion of steel rebar. In this work, the effect of hydroxypropyl methylcellulose nanofibers (HMFs) as a partial replacement in Portland cement on corrosion behavior of mild steel rebar were studied in 3.5 wt% NaCl solution. Electrochemical impedance spectroscopy analysis, polarization measurement and permeability test were used to investigate the corrosion behavior of mild steel rebar. The lower permeability of the concrete was directly related to the increase in HMFs concentration which had led to the production of denser concrete. The electrochemical results revealed that the sample with 2 kg/m^3 HMFs had higher corrosion potential and resistance than all the others. Moreover, the resistance of passive layer increased in the reinforced concrete sample with 2 kg/m^3 HMFs, which revealed that the protective property of the passive layer developed was strong. These findings revealed that partial replacement of HMFs in Portland cement caused a reduction of corrosion rate and increased corrosion resistance of mild steel rebar because of the decrease of chloride ion and water permeability.

Keywords: Hydroxypropyl methylcellulose nanofibers;Partial replacement;Corrosion behavior;Reinforced concrete; Electrochemical analysis

1. INTRODUCTION

Steel reinforced concretes have been widely used as a building material for a long time [1]. However, building materials are usually exposed to corrosive environments like chloride attack, freeze thaw cycles, their coupling effects, and carbonization which frequently lead to the corrosion of steel rebars[2-4]. Premature destruction and failure of concrete occurred often to the building structures because of the corrosion of steel rebars[5, 6]. These changes typically lead to a huge economic losses and pose a threat to contemporary society. Therefore, the corrosion problem of steel rebars in concrete structures must be solved immediately. Cathodic protection, concrete coating, electro-chemical chlorine removal, concrete re-alkalization, and the concrete density improvement have been assumed to prevent the corroding of steel bars [7-9]. However, it is difficult to protect all steel rebars in concrete with these methods. Some studies indicated that the use of supplementary cementing materials (SCMs) in concrete are the most effective and simple technique to reduce both cost of construction and environmental pollution and improve the concrete durability [10]. The concrete properties are enhanced by the addition of SCMs as cement replacement. Moreover, it can reduce the emission of CO_2 and further decrease the density of concrete.

Many studies had been carried out to expand concrete reinforced by different kind of fibers, which had led to the improvement of its mechanical properties and chemical resistance [11, 12]. These properties are the key variables that can cooperate the concrete application in the construction sector. Furthermore, nanofiber mixture is a significant strategy that can be adopted to decrease physical and mechanical limitations of reinforced concrete structures and develop their range of applications [13].

Although methylcellulose nanofibers (HMFs) have been proven able to enhance the electrical resistivity and reduce the specific surface area and permeability, the effect of HMFs on the corrosion resistance of steel rebars had not been previously reported. Hence, this work focused on the effect of HMFs in various concentrations in concrete on the corrosion resistance and electrical resistivity of steel rebars.

2. MATERIALS AND METHOD

Portland cement (PC) was utilized for the cementitious material. Table 1 indicates the chemical composition of the PC used. In this research, methylcellulose nanofibers (HMFs) with ratios of 0.0, 0.5, 1.0, 1.5 and 2 kg/m^3 was replaced in PC. The concrete mixture ratios are shown in Table 2. A 0.13 wt% dry powdered defoamer was used to decrease foaming and minimized air entrainment in concrete mixes. HMFs was dissolved in water. After that the defoamer was added to the solution and stirred for 5 min. Then, cement, water and the prepared mixture were blended in the rotating mixer for 10 min. The water/cement ratio was 0.48. After pouring the mixture into molds, the vibrator was used to reduce the air bubbles. The samples were demolded after one day and then cured for one month at room temperature.

Table 1. Chemical composition of the PC

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

Table 2. Details of the concrete mixes

Samples	0 kg/m^3 HMFs	0.5 kg/m^3 HMFs	1 kg/m^3 HMFs	1.5 kg/m^3 HMFs	2 kg/m^3 HMFs
PC (kg/m^3)	400	39.5	399	398.5	398
HMF (kg/m^3)	0.0	0.5	1.0	1.5	2.0
Aggregate (kg/m^3)	1750	1750	1750	1750	1750
Water (kg/m^3)	190	190	190	190	190
W/C	0.48	0.48	0.48	0.48	0.48

The concrete mixture was poured into a 15 x 15 x 15 cm mold, while a steel rebar was placed vertically at the center of the cube. The mild steel rebar had 10 mm diameter and 150 mm length. Prior to use, chemical cleaning was performed on the steel surface. Table 3 shows the chemical composites of mild steel rebar.

Table 3. The chemical compositions of mild steel rebar (wt%)

Si	**S**	**Mn**	**P**	**V**	**C**	**Fe**
0.52	0.03	1.43	0.03	0.03	0.21	Bal.

Open circuit potential (OCP) were performed by a high-impedance voltmeter for the different systems with an input resistance. Linear polarization resistance and electrochemical impedance spectroscopy (EIS) as nondestructive monitoring methods were applied to consider the corrosion behavior of steel rebars. An electrochemical process was used with the steel rebar, graphite and saturated calomel electrode as a working, counter and reference electrodes, respectively. The analysis were recorded after exposure to 3.5 wt% NaCl solution as a corrosive environment. The EIS tests were done by CorrTest Instruments Corp at a frequency range of 0.01Hz to 0.1 MHz. The permeability measurements were done by a TORENT permeability set. The morphologies of the specimens were studied by Zeiss Sigma 300 VP scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

The polarization curves of reinforced concrete samples exposed to 3.5 wt% NaCl solution for 4 months are shown in Figure 1 to evaluate the effect of HMFs concentration on corrosion behavior of steel rebars. The values of the corrosion current density and the corrosion potential are indicated in table 4 which are achieved from the polarization diagrams in Figure 1. The concrete sample without nanofibers had the minimum corrosion potential compared to the other concrete specimens. This sample was very susceptible to corrosion. The reinforced concrete sample with 0.5 kg/m^3 of HMFs was in a passive state and had a lower trend toward corrosion. As shown in figure 1, increasing HMFs content leads to a significant increase in corrosion potential (E_{corr}). Thus, the potential had shifted to more positive values. Furthermore, corrosion current density (I_{corr}) shifted toward the left side which indicated that there was lower corrosion current on the surface of rebar [14]. The level of corrosion can be defined in four levels provided by the Durar Network Specification [15]. However, the corrosion current density of 2.0 kg/m^3 HMFs sample in 3.5wt% NaCl environment was lower than that of the other samples (Table 4). Thus, except the 0.0 kg/m^3 HMFssample, all steel reinforced concretes stayed in the passive state during the experiment process which revealed their excellent corrosion resistance of steel rebar in the marine environment [16].

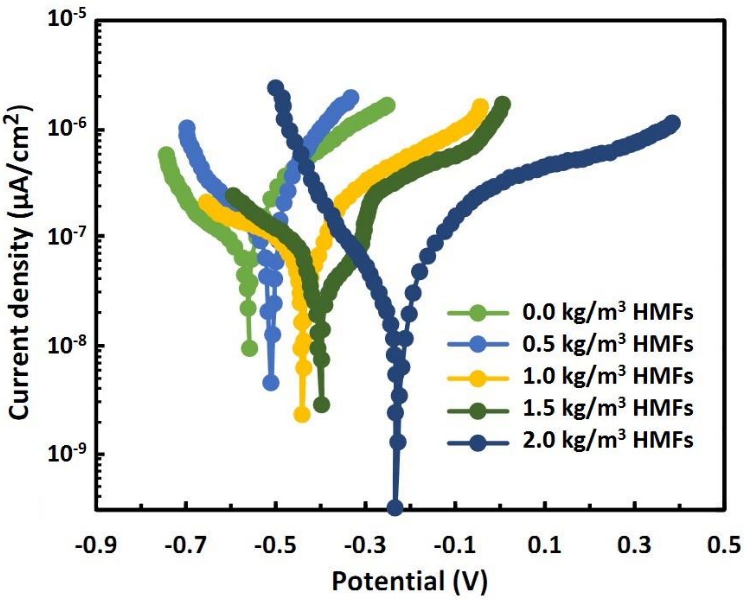

Figure 1. Polarization curves of steel reinforced concrete samples with different HMFs contents exposed to 3.5 wt% NaCl solution for 4 months

Table 4. Corrosion current density and corrosion potential of the carbon steel rebars

Concrete	Corrosion current density	Corrosion potential
0.0 kg/m^3 HMFs	0.134 μA/cm^2	-548 mV
0.5 kg/m^3 HMFs	0.097 μA/cm^2	-506 mV
1.0 kg/m^3 HMFs	0.056 μA/cm^2	-429 mV
1.5 kg/m^3 HMFs	0.045 μA/cm^2	-384 mV
2.0 kg/m^3 HMFs	0.022 μA/cm^2	-238 mV

The permeability of concrete is directly related to the increase in HMFs concentration. On the other hand, lower permeability leads to the production of denser concrete [17]. This means that fewer ions were allowed to enter the concrete samples. Therefore, the I_{corr} will be less and the E_{corr} will be more positive. Corrosion of steel rebar in the concrete specimen with 2 kg/m^3 HMFs was intensely decreased after 4 months exposure in 3.5 wt% NaCl solution which was more resistant to corrosion than the other concrete samples. It can be attributed to the amount of HMFs which had a direct effect on the performance of the reinforced concrete.

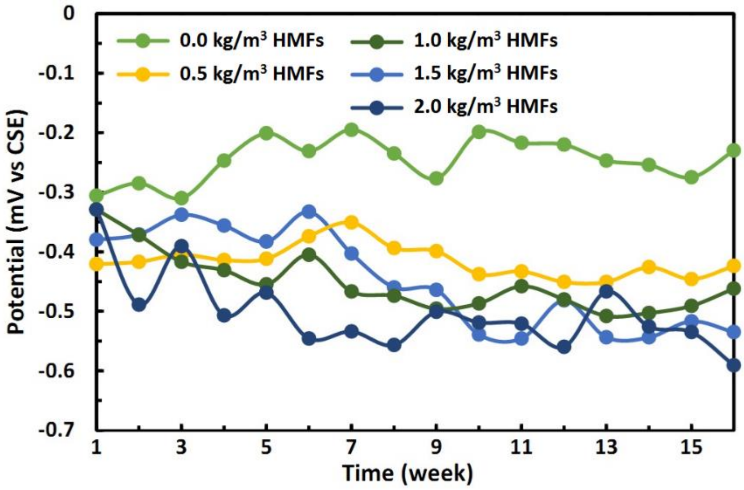

Figure 2. OCP of reinforced concrete samples with different HMFs contents exposed to 3.5 wt% NaCl solution

One of the well-known techniques for evaluation of steel corrosion in concrete samples is the OCP method. The potential difference between reinforcement steel into concrete sample and a copper/copper sulphate electrode as a reference electrode was determined and was in agreement with ASTM C-876. Figure 2 reveals the result of the OCP for four months. With increasing NFs concentration to 2 kg/m^3, the potential values were considerably shifted to more positive. The corrosion rate of reinforced concretes with different HMFs content are shown in figure 3. The concrete prepared with nanofibers were indicating a lower corrosion rate in comparison with the samples without nanofibers after one month exposure to salty solution. The sample with 2 kg/m^3 HMFs has the smallest corrosion rate. It can be attributed to the physical and chemical properties of HMFs that delayed the initial corrosion process and decreased the permeability, contraction and volumetric expansion. Furthermore, it had also shown the ability of nanofibers to reduce the formation and propagation of cracks [18].

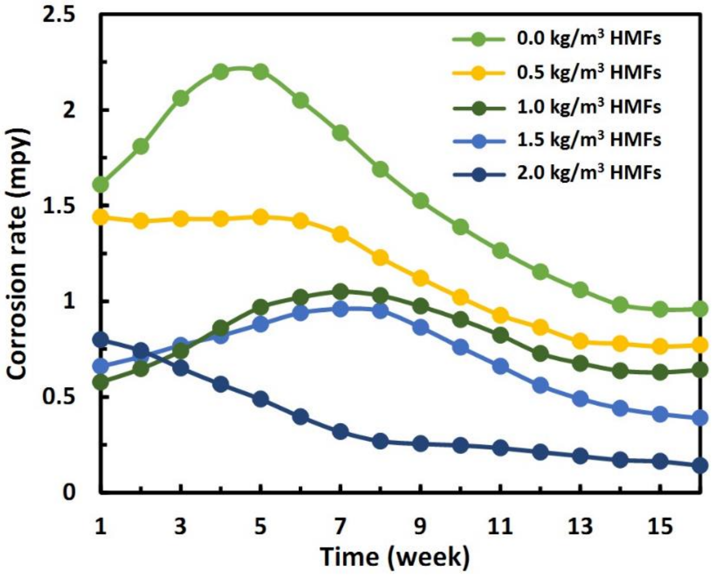

Figure 3. Corrosion rate of reinforced concretes with different HMFs content

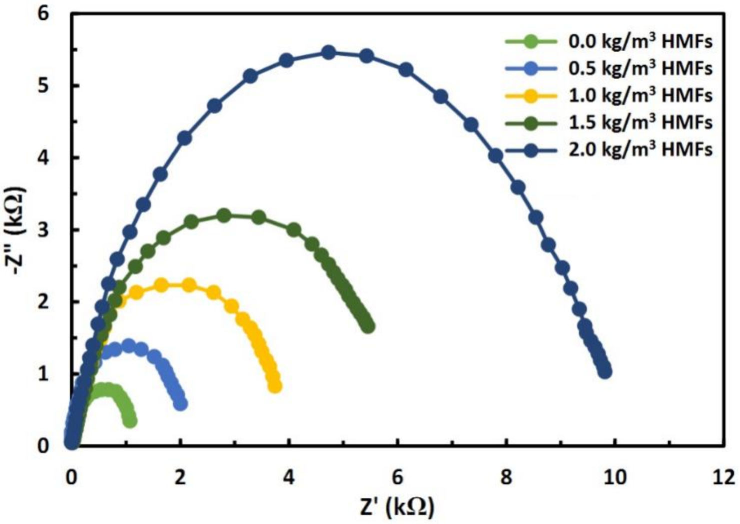

Figure 4. Nyquist plots of carbon steel rebar in various concrete specimens after four months exposed to 3.5 wt% NaCl solution

Electrochemical method has been broadly used in the passive layer analysis because of its capability to consider redox reactions of reinforcement steels in a seawater environment [19]. EIS was employed to evaluate the corrosion resistance of carbon steel rebar in various concrete specimens after four months exposure to 3.5 wt% NaCl solution. Fig. 4 shows Nyquist diagrams of the specimens. The changes in HMFs content caused a difference in the capacitive loop radius which shows an improvement of the corrosion behavior for carbon steel rebar. Figure 5 shows an equivalent circuit utilized for the impedance spectra. R_{ct} and R_f are the resistances of charge-transfer and passive layer, respectively[20]. CPE_{dl} and CPE_f are the capacitances of double-layer and passive film/solution interface. R_s is the resistance of solution [21].

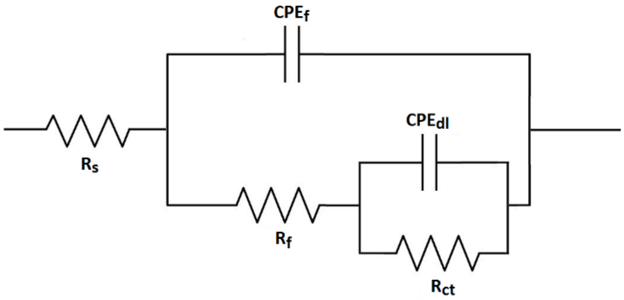

Figure 5. Equivalent circuit utilized for the impedance spectra

Given that the higher polarization resistance (R_p; $R_p= R_{ct}+R_f$) value shows higher corrosion resistance, concrete sample with 2 kg/m^3 HMFs indicate a significantly increase of R_p value exhibiting a greater corrosion resistance in marine environment. As shown in table 5, the CPE_{dl} value reduced for sample with 2 kg/m^3 HMFs, which shows that an enhancement in the thickness of passive layer and causing an enhancement of the protective capacity once the concrete content was added with nanofibers. The HMFs nanofibers filled the tiny cracks and capillary pores and finally condensed the cement structure. Compared to CPE_{dl} and CPE_f values, it was observed that CPE_{dl} was higher than CPE_f in all specimens which approved that the thin passive layer and the double layer formation at the interfaces indicated a high capacitive behavior [22].

Table 5. Electrochemical parameters obtained from the equivalent circuit (Fig. 5) for carbon steel reinforced in various concrete specimens after four months exposed to 3.5 wt% NaCl solution

Concrete	R_s (Ω cm^2)	R_f (kΩ cm^2)	CPE_f (μF cm^{-2})	R_{ct} (kΩ cm^2)	CPE_{dl}(μF cm^{-2})
0.0 kg/m^3 HMFs	64.2	0.73	9.2	1.23	11.8
0.5 kg/m^3 HMFs	53.8	1.46	7.1	2.28	9.3
1.0 kg/m^3 HMFs	51.7	2.34	4.3	4.05	5.6
1.5 kg/m^3 HMFs	61.6	3.69	2.8	6.48	3.2
2.0 kg/m^3 HMFs	59.4	7.45	0.7	11.23	0.9

Table 6. Permeability of various concrete specimens after four months exposed to 3.5 wt% NaCl solution

K_T (×10^{-16} m^2)					
Time (week)	**Concrete**				
	0 kg/m^3HMFs	**0.5 kg/m^3HMFs**	**1.0 kg/m^3HMFs**	**1.5 kg/m^3HMFs**	**2.0 kg/m^3HMFs**
1	9.635	4.621	1.163	0.842	0.654
4	6.567	2.438	0.658	0.687	0.531
8	2.143	0.753	0.324	0.458	0.387
12	1.149	0.872	0.098	0.132	0.084
16	1.036	0.096	0.079	0.062	0.028

The compared permeability results of different samples are listed in Table 6. High level of permeability in the first month can be related to the incorrect operation of the samples when the specimens were removed from the mold [23]. However, it was observed that samples with nanofibers had lower permeability compared to those without nanofibers. It was associated to the formation of Connection Bridge by HMFs which prevent the growth of concrete cracks. According to Table 4, it is clear that the concrete sample with the HMFs content of 2 kg/m^3 has more suitable KT than the others. Therefore, this sample indicated lower permeability of chloride ion in the reinforced concrete which introduced an alternative admixture for the enchantment of durability and corrosion resistance of steel reinforcement concerts.

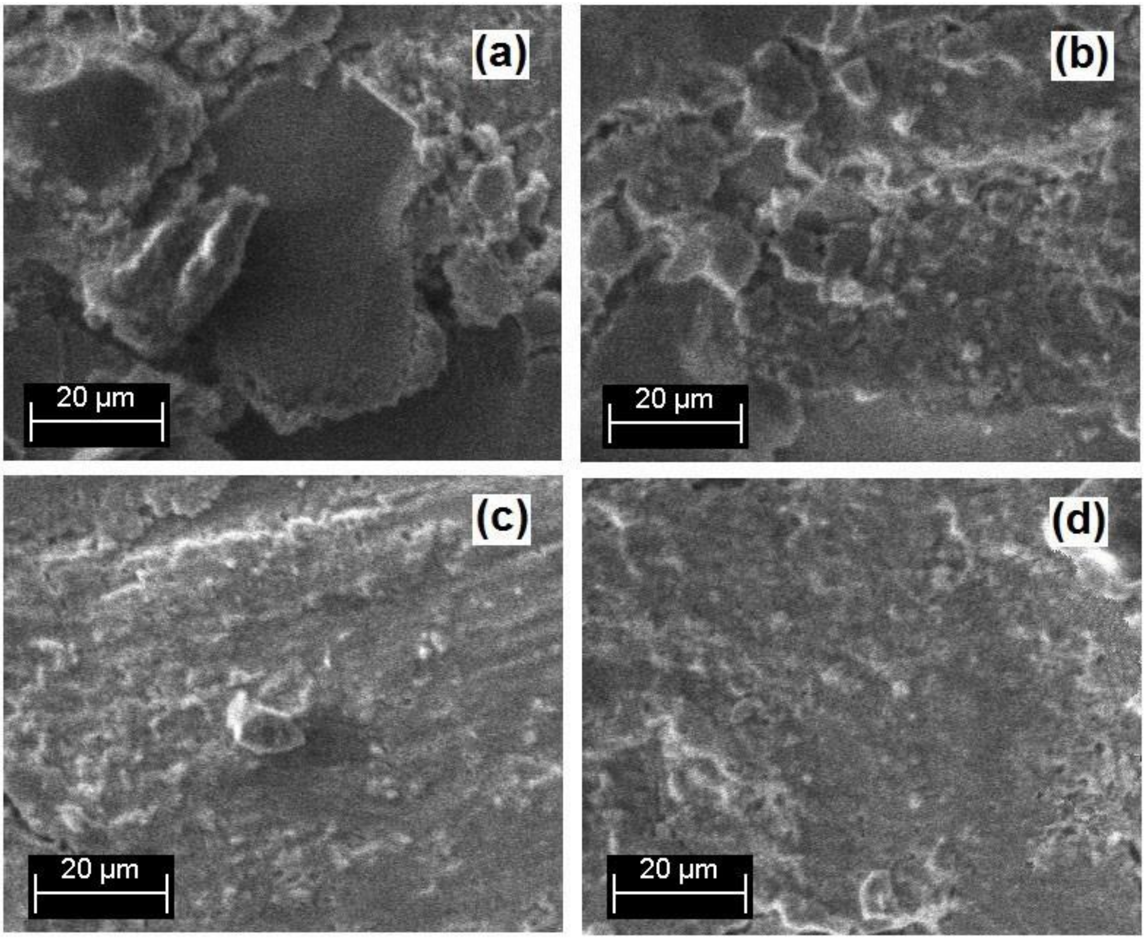

Figure 6. FESEM images of various concrete specimens (a) 0 kg/m^{3}HMFs, (b) 0.5 kg/m^{3}HMFs, (c) 1.0 kg/m^{3}HMFs and (d) 2.0 kg/m^{3}HMFs after four months exposed to 3.5 wt% NaCl solution

Figure 6 shows the FESEM images of various concrete specimens after four months exposure to 3.5 wt% NaCl solution. The surface of sample with 2 kg/m^3 HMFs content indicates minimum pits and low corrosion products, revealing the mild pitting corrosion formed on the surface of carbon steel rebar, which is in accordance to the results obtained from electrochemical analysis. It can be related to the decrease of chloride ion and water permeability in reinforced concrete specimen. The large pores can be changed to smaller pores by adding HMFs, resulting in a change in the structure of the cement paste. These findings revealed that partial replacement of HMFs in Portland cement had caused a reduction of corrosion rate and increased the corrosion resistance of carbon steel rebar because of the decrease of chloride ion and water permeability.

4. CONCLUSIONS

In this work, the effect of HMFs as a partial replacement in PC on corrosion behavior of mild steel rebar were studied in 3.5 wt% NaCl solution. The lower permeability of the concrete was directly related to the increase in HMFs concentration which led to the production denser concrete. The electrochemical results revealed that the sample with 2 kg/m^3 HMFs had higher corrosion potential and resistance than all the others. Moreover, the resistance of passive layer increased in the reinforced concrete sample with 2 kg/m^3 HMFs, which revealed that the protective property of the passive layer developed was strong. These findings revealed that partial replacement of HMFs in Portland cement had caused a reduction of corrosion rate and increased the corrosion resistance of mild steel rebar because of the decrease of chloride ion and water permeability. The surface of sample with 2 kg/m^3 HMFs content indicated minimum pits and low corrosion products, revealing the mild pitting corrosion formed on the surface of carbon steel rebar

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