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Short Communication

A Partial Replacement of Portland Cement with Bagasse Ash and effect of Polypropylene-fiber reinforcement on Electrochemical Corrosion Behavior of Carbon Steel Rebar in Marine Environment

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This study investigates the effect of incorporating bagasse ash (BA) and also adding polypropylene fibers (PPFs) into concrete on the corrosion behavior of carbon steel rebar. Polypropylene fibers were used at three different fiber volume fractions of 0.15%, 0.3%, and 0.45%. All the fiber-reinforced concrete contained 10% bagasse ash as a cement substitution. Electrochemical impedance spectroscopy (EIS) and polarization measurement analyses in marine environments were used to obtain electrochemical data. Fitting of the EIS data to a suitable equivalent electrical circuit showed that the highest corrosion enhancement was achieved for the PPF0.45BA mixture. Polarization analysis showed that the prepared sample has the lowest corrosion density, highest corrosion potential with highest corrosion protection efficiency. The results of electrochemical measurements and water absorption indicate that the BA and PPFs admixtures enhance the durability of concrete samples exposed to aggressive agents by preventing the surface of carbon steel bars from reaching the aggressive ions.

Keywords: Bagasse ash; Corrosion resistance; Electrochemical impedance spectroscopy; Polarization; Polypropylene fiber

1. INTRODUCTION

Concrete is the most widely construction material due to its well-known properties such as low cost, wide variety applications and high compressive resistance [1]. However, one of the main factors which causes a reduction in durability and properties of reinforced concrete structures is corrosion. This phenomenon affects the service life of concrete and has major economic problems when structures expose to environments including aggressive ions such as chloride or sulfate [2, 3]. Some additives such as silica fume, glass powder, rice husk ash, fly ash, metakaoline, bagasse ash and fibers like polypropylene used for partially replacement of cement have economic and technological benefits [4, 5].

Bagasse ash (BA) is a sugar by-product obtained from the bagasse combustion. Bagasse ash as a pozzolan has reactive silica and can be used in concrete binder [6]. The replacement of Ordinary Portland cement (OPC) with supplementary cementing materials (SCM) is environmentally friendly and cost effective [7, 8]. In a pozzolanic reaction, $Ca(OH)_2$ from the hydration process reacts with SCMs, which leads to decreasing the permeability and porosity of the concrete [9, 10]. An addition of BA between 0% and 30 % as an OPC replacement to the mixture reduces the permeability and diffusion of chloride ions through the concrete [11, 12]. Singh *et al*. in their study reported that the presence of 10 percent of Bagasse ash into Portland cement improves the compressive strength compared to OPC and reduce the permeability of mortars [13, 14].

Polymers and fibers have been used in concrete mixtures in order to improve the engineering properties such as improving durable characteristics of concrete, increasing the compressive strength, corrosion resistance and reducing the cracks extension. Hence, polypropylene fibers (PPFs) can be used for mentioned properties [15, 16]. Combination of PPFs with other fibers, for instance glass/PPF or carbon/PPF and also steel/PPF reinforced concrete in order to evaluate the mechanical properties have been studied [17, 18]. Permeability can be reduced by adding the polymer fibers and also encasement of concrete in a polymer resin or polymer composite [19]. An important parameter for manufacturing reinforced concretes and enhancing the concrete durability is the control of the crack width [20, 21]. In particular, unexpected cracks created because of the steel corrosion reduce the service life of reinforced concrete [22]. Therefore, shrinkage cracking can be reduced by using polypropylene fibers in mortar mixtures or concretes. Peliiser et al. studied different fibers in concrete which reduced the crack opening [20, 23]. In another study, Ramezanianpour et al. found out that the inclusion of PPFs in concrete caused the higher resistance against the penetration of chloride ions. Therefore, probability of steel rebar corrosion decreases because of a reduction in the inner conductivity of pores [16]. Toutanji reported that the improvement of fiber dispersion results in reduction of the chloride penetration remarkably by introducing SF along with PPFs in concrete [24]. The previous studies are mostly based on corrosion behavior of cement containing by-product materials and PPFs separately and the performance of such additives along with PPFs has not been well investigated especially, the effect of bagasse ash and PPFs.

In this study different mixtures were manufactured to investigate the effect of bagasse ash and polypropylene fibers in the concrete on the corrosion protection of embedded steel rebar. A reinforced concrete made with OPC was used as a control sample. The corrosion behavior of samples was studied in marine environments using open circuit potential, electrochemical impedance spectroscopy and polarization methods for 6 weeks. Morphology of samples was investigated using scanning electron microscopy and water affinity of them.

2. MATERIALS AND METHODS

The chemical compositions of carbon steel are listed in Table 1.

Table 1. Chemical compositions of carbon steel rebar used in this work.

Element	C	Si	Mn	Cr	Ni	Al	Cu	Fe
(wt.%)	0.1	1.5	0.83	0.06	0.1	0.01	0.34	Bal.

The chemical compositions of Ordinary Portland cement and bagasse ash are described in Table 2. Also the properties of polypropylene fibers are given in Table 3. Bagasse ash was added as a cement replacement for 10% by weight of cement. Moreover, different mixtures containing BA and various volume fractions of PPFs (0.15, 0.3, 0.45) were produced. For concrete casting, the mixing ratio of OPC with water was 0.3. The mixture design is demonstrated in Table 4. To fabricate uniform fiber-reinforced concretes, the blend cements were mixed by a high-speed mixer. For each measurement, three samples were produced and the average value as the final result was shown.

Table 2. Chemical composition of Ordinary Portland cement and Bagasse ash (% by mass)

Composition	Materials	
	Ordinary Portland cement	Bagasse ash
SiO_2	19.99	51.71
Fe_2O_3	3.01	2.68
Al_2O_3	4.78	9.56
CaO	63.49	9.78
MgO	2.01	4.33
K_2O	0.68	9.56
Na_2O	0.30	4.42
SO_3	2.65	3.42
L.O.I	3.09	4.54

The concrete samples were poured into the PVC pipe cylindrical molds with a diameter of 10 cm and a height of 30 cm for 24 h at 95% relative humidity and room temperature to complete the hydration reaction.

Table 3. Properties of polypropylene fibers

Property	Value
Density (g/cm^3)	0.91
Water absorption	0
Torsion resistibility (MPa)	300-400
Melting point (ºC)	170
Diameter (µm)	22

EIS was done using a potentiostat with reference to OCP with a voltage amplitude of 10 mV and in the frequency range of 100 KHz to 0.01 Hz. A triple-electrode system was applied for the measurements which contains 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 EIS data were fitted using ZView software by appropriate equivalent electric circuits. The potentiodynamic polarization measurement was carried out with a rate of 1 mV s^{-1}. The corrosion current density (i_{corr}) and the corrosion potential (E_{corr}) were obtained from the Tafel extrapolation of polarization curves (50-100 mV away from E_{corr}). All measurements were carried out in 3.5 wt% NaCl solution as a marine environment. According to ASTM C642 water absorption value was determined by drying a sample with a constant mass, and then immersing it in water and measuring the mass of standard surface dry. Water absorption was the proportion of the difference between the two values measured to the dry mass. The surface morphologies of specimens were studied by Zeiss Sigma 300 VP scanning electron microscope.

Table 4. Compositions of prepared mixtures

Mixture ID	Cement (kg/m^3)	Water (kg/m^3)	Bagasse ash (kg/m^3)	Fine aggregates (kg/m^3)	Coarse aggregates (kg/m^3)	Fiber Volume fraction (%)
OPC	520	156	---	862	888	---
BA	468	156	52	853	879	---
PPF0.15 BA	468	156	52	851	877	0.15
PPF0.3BA	468	156	52	849	875	0.3
PPF0.45BA	468	156	52	847	873	0.45

3. RESULTS AND DISCUSSION

The open circuit potential (OCP) test is a well-known technique to measure the corrosion behavior by the half-cell potential technique. Figure 1 represents the results of open circuit potential values of the steel rebar embedded in different concrete mixtures exposed to the marine environment for 6 weeks. In this method, the difference in potential between rebar embedded into concrete and a reference electrode is measured in accordance with ASTM C-876 [25-27]. The cement specimen can be considered as an insulator because the high internal moisture may not be. With exposing one of the surfaces of the samples to the electrolyte solution, it can permeate to the samples. Therefore, the electrode inside the sample is in contact with the electrolyte. Due to the different free energy between two phases of the solution and the electrode, the surface of the electrode is dissolved by the electrolyte and also free ions are adsorbed by the electrolyte. As a result, potential changes at the electrode surface. In fact, the change of OCP potential reflects the unstable to stable process of potential between the two electrodes [28].

In accordance with ASTM C876, the potential values which are less than -350 mV are in high risk region, the ones between -200 mV and -350 mV are in intermediate corrosion risk region and also the values are more than -200 mV in the low risk region. As it can be seen in Figure 1, the potential values of mixtures shift to more positive values of E_{corr} with introducing BA and also increasing the volume fraction of PPFs which show less corrosion probability. Also the mixture includes 0.45% PPF (PPF0.45BA mix) shows the most positive potential values among all polypropylene fiber-reinforced bagasse ash concretes. The protection provided against corrosion may be attributed to remarkable influence on the enhancement of the concrete durability because of the reduction in calcium hydroxide and change in pore solution [29, 30]. On the other hand, less permeability and therefore lower penetration of aggressive ions can cause the higher durability which postpones corrosion [16].

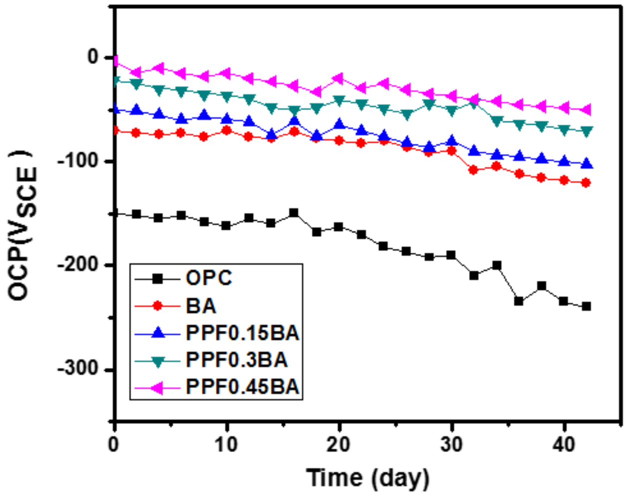

Figure 1. Open circuit potential values of the steel rebar embedded in different concrete mixtures containing BA and various volume fractions of PPFs exposed to the marine environment for 6 weeks

Electrochemical impedance spectroscopy **(**EIS) measurements were carried out to evaluate the corrosion behavior of carbon steel rebar embedded into the different concrete mixtures. Figure 2 presents the Nyquist and Bode plots of impedance spectra for carbon steel rebar in the reinforced concrete in marine environments after 6 weeks.

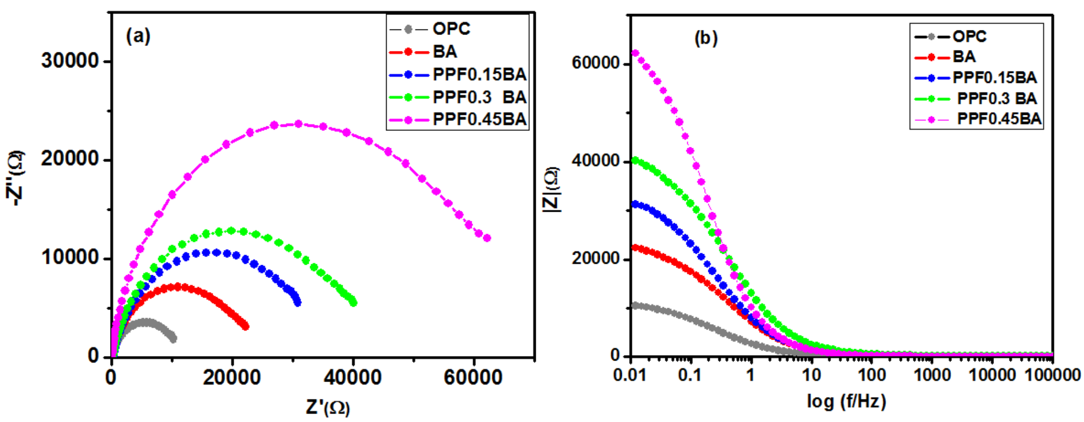

Figure 2. a) Nyquist and b) Bode diagrams for carbon steel rebar in different reinforced concrete mixtures containing BA and various volume fractions of PPFs exposed to the marine environment after 6 weeks

The EIS spectra were fitted with an equivalent circuit as shown in Figure 3, in which R_s stands the resistance of the solution, R_c and CPE_c elements in the parallel circuit are related to the resistance and constant phase element of coated concrete, respectively which are applied to simulate high-frequency loop. Moreover, R_{ct} and CPE_{dl} refer to the charge transfer resistance of the constant phase element of the double layer, respectively [31]. The ideal capacitor is replaced with the constant phase element (CPE) that CPE impedance is given by the following equation [32]:

$$Z_{CPE} = \frac{1}{(CPE)(j\omega)^n} \quad (1)$$

Where, CPE and n are adjustable parameters. Some factors such as surface roughness and layer porosity lead to a change in the value of n between 0 and 1 [33]. Obtained data presented in Table 5 indicate that by introducing BA into the concrete, R_{ct} and R_c increase and also CPE_{dl} and CPE_c reduce. It can be related to the stability of the passive film on the carbon steel rebar which improves corrosion resistance.

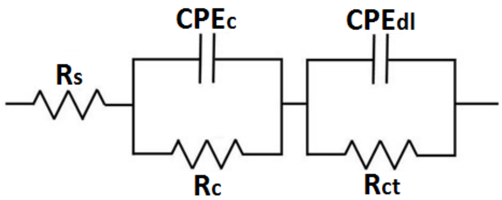

Figure 3. Used electrical equivalent circuit to fit the EIS data

This improvement in corrosion resistance of steel corresponds to the formation of additional calcium silicate hydrate (C-S-H gel) during the process of hydration of bagasse ash in concrete so that large permeable pores may be transformed into small impermeable pores. Studies showed that less porosity in the concrete results in lower permeability and thus it protects the reinforced concrete from the aggressive environment [6]. It can be seen in Table 5 concrete mixtures containing PPFs indicate the higher corrosion resistance compared to OPC, in particular in the case in which the sample with BA 10% and highest amount of volume fraction of PPFs with 0.45 % (PPF0.45BA mixture). In fact, with increasing the amount of fibers, concrete structures become denser with less permeability and enhance corrosion resistance.

Table 5. Obtained electrochemical parameters of fitting the Nyquist diagrams with an equivalent cuircuit

Mixtures	R_s(Ω)	R_c(Ω)	CPE_c (μFcm^{-2})	n_c	R_{ct} (Ω)	CPE_{dl}(μFcm^{-2})	n_{dl}
OPC	49	1980	70.4	0.61	9040	16.1	0.78
BA	52	3000	59.1	0.65	19900	10.7	0.82
PPF0.15 BA	51	5600	28.2	0.72	28000	9.5	0.85
PPF0.3BA	50	6200	19.3	0.76	35500	8.9	0.88
PPF0.45BA	49	22661	9.7	0.84	39838	3.4	0.9

Polarization curves for studying the effect of substitution of bagasse ash and also polypropylene fibers on corrosion behavior of concrete mixtures with various volume fractions of PPFs (0.15%, 0.30%, 0.45%) exposed to marine environment for 6 weeks are shown in Figure 4. In Table 6, the values of corrosion potential, corrosion current density, anodic and cathodic Tafel slopes obtained from polarization curves are given. It can be observed that the corrosion potential of steel rebar in different reinforced concrete specimens indicates a positive shift relative to OPC sample which means a higher corrosion resistance. It can be concluded that the anodic metal dissolution was retarded by varying the concrete content. Introducing bagasse ash into concrete reduces water absorptivity and porosity which will be explained in the next section. Thus, the corrosion resistance of samples can be enhanced. The concrete containing 0.15% PPF (PPF0.15BA mix) shows the lowest value of corrosion potential compared to the other samples containing polypropylene fiber. Therefore, this sample has a higher tendency towards corrosion.

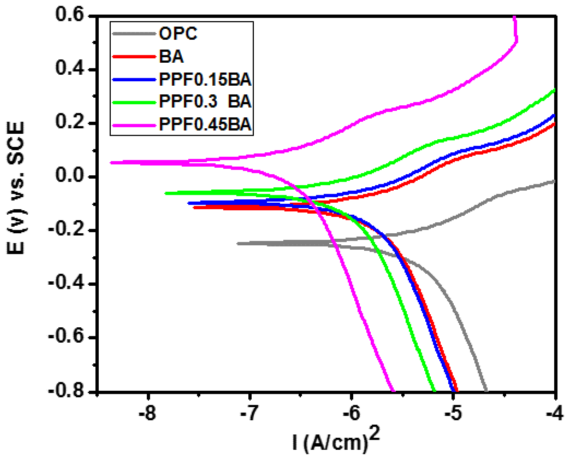

Figure 4. Polarization curves of carbon steel embedded in different concrete mixtures containing BA and various volume fractions of PPFs exposed to the marine environment for 6 weeks

In Figure 4, it can be seen that the value of corrosion potential increases significantly with increasing the volume fraction of PPFs. In addition, corrosion current densities of steel rebar in different mixtures containing BA and also BA and PPF are lower than that in concrete without additional materials. This parameter is the lowest value for the PPF0.45BA mix among samples containing PPF. As mentioned before, increasing the volume fraction of fibers creates denser structures with lower permeability. Therefore, lower corrosive ions can enter the concrete samples. Clearly, corrosion potential and current density will be higher and lower, respectively [34]. The protection efficiency η (%) of samples is calculated by Equation 2 [35] where $i_{corr-abs}$ and $i_{corr-pres}$ are the corrosion current density of steel rebar in concrete without and with additive materials, respectively.

$$\eta(\%) = \frac{i_{corr-abs} - i_{corr-pres}}{i_{corr-abs}} \times 100 \quad (2)$$

Resulting values of η listed in Table 6 indicate that steel rebar is protected against corrosion by introducing the BA and PPFs into concrete. When carbon steel reinforced concrete was produced with replacement of OPC by 10% BA, the value of protection efficiency is η =62%. Adding the higher amount of PPF in concrete results in more corrosion prevention so that the highest value belongs to the

PPF0.45BA sample (η =94%). These results are consistent with the EIS results. The variation of Tafel slopes values may correspond to anodic or cathodic protection mechanism for carbon steel rebar, the concentration of electrolyte, the composition of working electrodes [36].

Table 6. Corrosion parameters of steel rebar obtained from polarization curves

Mixtures	E_{Corr} (V vs. SCE)	i_{Corr}($\mu A/cm^2$)	β_a (mV/dec)	-β_c (mV/dec)	η(%)
OPC	-0.250	0.561	176	399	---
BA	-0.115	0.210	173	395	62
PPF0.15BA	-0.098	0.185	174	393	67
PPF0.3BA	-0.062	0.110	172	394	80
PPF0.45BA	-0.050	0.032	174	394	94

In order to study the permeability of samples, a water absorption test was performed. Figure 5 shows the water absorption of the produced samples exposed to the marine environment after 6 weeks. The average value of three measurements for each sample are given. It shows the partial substitution of OPC with BA and specially adding PPFs along with BA has noticeable effect on less water absorption of samples, which varies between 8.3% and 5.9%. The hydration heat arising from the water-cement reaction decreases due to the presence of high concentration of SiO_2 and Al_2O_3 in bagasse ash [37]. Moreover, bagasse ash as a filler, reduces the permeability of concrete and enhances the durability. Also it prevents the corrosive ions from reaching the steel rebar surface. Also in samples containing PPFs, the reduction in absorption water may be related to less capillary porosity which can correspond to pore blocking effect. PPF0.45BA mix indicates the lowest value of water absorption percentage.

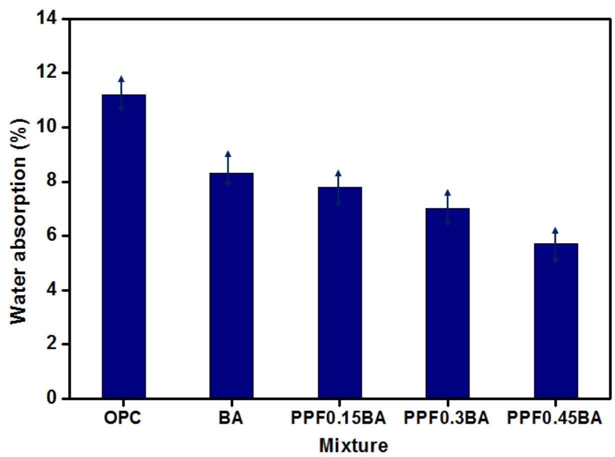

Figure 5. Water absorption of the samples containing BA and various volume fractions of PPFs exposed to the marine environment after 6 weeks.

Figure 6 shows the surface morphology of carbon steel rebar in OPC without additional materials, BA mix and PPF0.45BA mix exposed to marine environment after 6 weeks. When BA is added, the irregularity and separation of structures are seen. Figure 6(b) demonstrates that the sample with 10% BA is more uniform than the OPC mixture which agrees with previous studies [11]. Figure 6(c) indicates less pitting corrosion on the surface of carbon steel. PPF creates the bridging effect which may improve the tensile and flexural strength. Also we can see that fibers are encompassed with C-S-H gel and aggregates as binders may have the pore blocking effect which leads to less permeability. In fact, it shows less capillary porosity by decreasing inner conductivity of pores [16, 38].

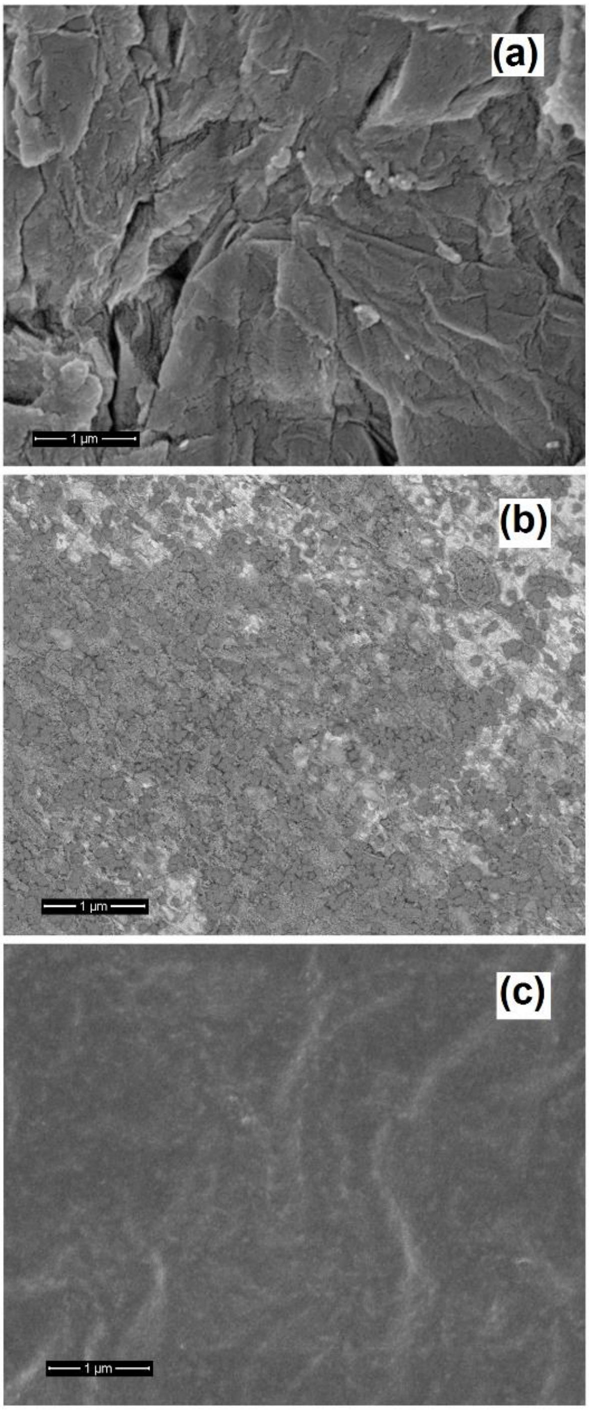

Figure 6. SEM images of carbon steel surface in different concretes (a) OPC mixture, (b) BA mixture and (c) PPF0.45BA mixture exposed to the marine environment after 6 weeks.

4. CONCLUSION

The effect of introducing bagasse ash (BA) and also adding polypropylene fibers (PPFs) into concrete on the corrosion behavior of carbon steel rebar was studied. Some mixtures were produced with polypropylene fibers at different fiber volume fractions of 0.15%, 0.3%, and 0.45%. All the fiber-reinforced concretes contained 10% bagasse ash as a cement replacement. EIS analysis and polarization measurement in marine environments were used to obtain electrochemical data. Fitting of the EIS data to a suitable equivalent electrical circuit showed that the highest corrosion enhancement was achieved for the PPF0.45BA mixture. Polarization measurements also showed that this sample has the lowest corrosion density, highest corrosion potential with corrosion protection efficiency of 94%. Consistent results of electrochemical measurements and water absorption indicate that the BA and PPFs enhance the durability of concrete exposed to aggressive agents by preventing the surface of steel rebar from reaching the aggressive ions. Bagasse ash as a filler, reduces the permeability of concrete and enhances the durability. Also adding the PPFs reduces inner conductivity of pores and capillary porosity.

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