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BIOCHAR AS A BOND ENHANCEMENT IN FIBER-REINFORCED MORTAR

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Abstract
This study focuses on the evaluation of using biochar to enhance the strength performance of cement mortar reinforced with polypropylene (PP) fibers. Biochar was produced with mixed wood sawdust that was discarded from a local sawmill. It was then divided into two groups, with one group being subjected to dosage of carbon dioxide until it reached saturation. Results showed that when reinforcing PP fibers are coated with CO_2-dosed biochar, the cement mortar experienced a 13% and 16% reduction in compressive and flexural strength respectively. However, fibers that were not saturated with CO_2 recorded improvement of about 19% for both compressive and flexural strength respectively over control samples containing PP fibers not coated with biochar. Coating of biochar on the fibers also reduced sorptivity significantly compared to control samples which means that the permeability of mortar would be lower if biochar is used to coat PP fibers. This phenomenon can be explained by the micro-filler effects afforded by the biochar particles, which serves to strengthen the bond between the surface of the PP fibers with the mortar matrix. These results highlight the potential usefulness of biochar as a sustainable carbon sink that can also be used as a bond and strength enhancement for cement mortar.

Keywords:
Polypropylene fibers; Biochar; Sorptivity; Strength

1 INTRODUCTION

Polypropylene fibers (PP) is one of the cost-effective ways to reinforce cement mortar. A number of benefits of using PP fiber in mortar or concrete have been reported including improvement of impact resistance [Badr 2006], spalling behavior [Wu 2002] , fire resistance [Behnood 2009; Rodrigues 2010] and post-cracking behavior [Kurtz 2002] while reducing crack propagation [Richardson 2005] and plastic shrinkage [Sivakumar 2007]. Despite the benefits, several studies have reported loss in strength and increase in permeability due to addition of PP fibers [Richardson 2005; Sadrmomtazi 2010; Ramezanianpour 2013]. It is partly because of weak bonding at PP fiber- cement matrix interface [Yan et al. 1998] because of lack of chemical bond and smooth surface of PP fibers. Moreover, hydrophobic surface of PP fibers introduces a thin film of water at the interface which enhance growth of calcium hydroxide crystals which increase the porosity of the interfacial zone. Therefore, there is scope of improvement of properties of PP fiber reinforced by densifying the transition zone and increasing the adhesion of fiber with the mortar matrix.

Improved fiber bonding with matrix and densification of the interfacial zone may be achieved by coating PP fibers with micro-size biochar particles. Biochar can act as micro-fillers that also contain polar oxygen and nitrogen containing groups on the surface if prepared at low to medium temperature (typically < 400˚C). Small particle size and presence of hydrophilic groups would create improved bonding of coated PP fibers with mortar matrix. Furthermore, using biochar in this way would sequester high volume of carbon in civil infrastructure that would reduce the net amount of carbon emission associated with building material [Gupta 2016; Gupta 2017]. The pores created during conversion of biomass to biochar also act as sites for carbon dioxide adsorption which can capture and store additional carbon besides the fixed carbon inherited from the biomass. Depending on the type of feedstock and preparation conditions employed, biochar has the potential to reduce about 870 kg-equivalent of CO_2 (CO_2-e) per ton dry feedstock, of which 62−66% are realized from carbon capture and storage by the biomass feedstock of the biochar [Roberts et al. 2009]. If biochar is made to adsorb and store carbon dioxide pre-deployment as fiber coating, there can be additional sequestration of up to 300 kg-equivalent of CO_2 (CO_2-e) per ton dry feedstock (corresponding to about 7mmol/g adsorption capacity of biochar). Nevertheless, use of biochar promotes recycling of waste which would reduce the amount of landfill space required for waste disposal.

Over the past few years there have been growing interests in application of biochar as building material in cementitious substances. Khushnood et al. (2016) investigated effect of biochar addition on mechanical

properties of cement paste including modulus of rupture and fracture energy. The biochar was derived from hazelnut shell and peanut shell respectively. Inclusion of biochar was found to result in multiple cracking and caused tortuous crack propagation path that increased the modulus of rupture. Angular biochar particles have been reported to resist crack propagation and lead to increase in fracture energy [Khushnood et al. 2016]. Similar findings have been reported by Restuccia and Ferro (2016) that addition of 0.80% (by cement weight) of hazelnut shell biochar improved post-peak behavior of cement paste and resulted in higher energy absorption before failure. Choi et al. [2012] reported that addition of biochar to cement mortar promotes internal curing at late stage by desorption of absorbed water in biochar during mixing of mortar. Internal curing promotes secondary hydration which increase strength of mortar incorporating biochar.

However, there is lack of study that explores and extends application of biochar to fiber reinforced mortar. Therefore, this study explores the effect of biochar coated PP fiber on properties of mortar. The biochar is added in two different forms – unsaturated form meaning the pores are not saturated with adsorbed CO_2 , and saturated form where the pores contain adsorbed CO_2 molecules.

2 MATERIALS AND METHODS

2.1 Fiber, cement and sand used

Monofilament polypropylene (PP) fibers have been used in the study. The length of the PP fibers is 19 mm and thickness 18 µ. The elastic modulus is 3.45 GPa. Locally available natural sand with maximum size of 2.75 mm was used. The specific gravity and fineness modulus of sand used are 2.55 and 2.58 respectively. Ordinary Portland cement CEM I 52.5N is used for all the mixes.

2.2 Preparation and properties of biochar

The biochar used in the study is prepared by pyrolysis of mixed wood saw dust at 300 ˚C with heating rate of 10 ˚C/min. The prepared char is grinded before mixing into mortar. Bulk of the particle is in the particle size range of 300-600µm while about 20% of the particles are less than 75µm. Particles below 300µm were sieved and used in the preparation of the coating. Elemental composition and physical properties of biochar used is presented in Tab 1.

2.3 Saturation of biochar with carbon dioxide and preparation of fiber coating

Biochar was saturated by passing pure CO_2 over a three-day period. A part of prepared biochar to be used for coating was kept in a sealed glass tank and pure CO_2 was injected into the tank. The reduction in CO_2 concentration due to adsorption by biochar was recorded every 4 hours during the monitoring period. The saturation point was reached when no more reduction in CO_2 concentration could be observed over a period of 6 hours. The amount of CO_2 adsorbed was calculated to be 1.67mmol/g of biochar by means of thermogravimetry analysis.

Both types of biochar- fresh biochar (without adsorbed CO_2) and CO_2 saturated biochar were used to prepare the coating on PP fibers. A paste for the coating was prepared by mixing biochar (fresh and saturated) with cement and water. The ratio by weight of PP fiber, biochar and cement and water followed is 1:3:2:2.5. Individual strands of PP fiber were separated and then coated with the paste till the entire surface of fiber was uniformly coated. The coated fibers were allowed to cure for 7 days before mixing into the mortar.

Tab. 1: Elemental composition and physical properties of biochar

	Composition (% by weight)
Carbon	62.25
Hydrogen	7.17
Oxygen	25.60
Calcium	0.20
Magnesium	0.26
Potassium	0.42
Silica	0.40
O/C ratio	0.47
H/C ratio	0.11
pH	11.85
Bulk density(g/cc)	1.55
Specific surface area (BET (m^2/g)	0.53
Average pore diameter(nm)	0.80
Total volume in pores (x10^{-3} cm^3/g)	
<2.02 nm	41.97
<400.30 nm	80.75
Water uptake capacity (g/g of biochar)	2.50±0.20

2.4 Mix proportions, mixing process and tests conducted

Tab. 2 presents the different mixes and mix proportions used in this study. Sand to cement ratio of 2.75 and water-cement ratio of 0.40 were followed for all the mixes.

Compressive strength was carried out following the preparation and loading conditions stated in BS EN 12390-3. Flexural strength was performed using prisms of dimension 40x40x60 mm loaded at displacement rate of 0.1mm/minute. Sorptivity test was carried out as per ASTM C1585-13 to study the effect of biochar coating on permeability of mortar. Samples for sorptivity test were cut from cylinder samples using a highspeed concrete cutter. The samples were conditioned following the standard and the test was carried out at 25±1 ˚C.

For each of these tests, at least 4 samples were tested. Scanning electron microscopy was conducted to study the morphology of samples including the bonding of fibers (coated or uncoated) with the mortar paste.

Tab. 2: Mixes and mix proportions explored in this study

Mortar mix	Mix description	Cement(g)	Sand(g)	Water(g)	PP fiber (g)	Biochar(g) (as coating on PP fiber)
Control 1	Mortar with PP fiber without coating	10000	27500	4000		_
Control 2	Plain mortar (without fiber)	10000	27500	4000		
Fib-FreshBC	Mortar with fresh biochar coating on PP fibers	10000	27500	4000	60	150
Fib-SatBC	Mortar with CO_2 saturated biochar coating on PP fibers	10000	27500	4000	60	150

3 RESULTS AND DISCUSSIONS

3.1 Effect on biochar coating on compressive and flexural strength

Fig. 1 shows that addition of PP fibers coated with fresh biochar (Fib-FreshBC) resulted in significantly higher 7 day and 28-day compressive strength compared to control mixes. Introduction of biochar results in reduction of capillary pores by evaporation of free water because biochar absorbs part of mixing water. It reduces the effective local water-cement ratio around the biochar particles in mortar paste resulting in densification of the mix. The physically bound water in biochar is later released to promote hydration by internal curing at later age [Choi et al. 2012].

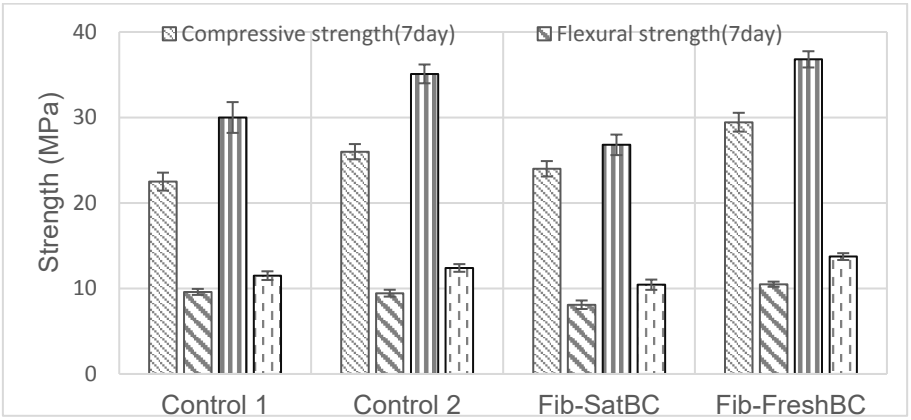

Fig. 1: Compressive and flexural strength of plain mortar, mortar with only PP fiber and PP fiber coated by saturated and unsaturated biochar

Hydrophobic surface coating on PP fiber makes it unstable in water resulting in localized agglomeration of fibers in mortar paste. It is responsible for reduction in strength due to fiber balling. Hydrophilic biochar coating on fibers means that the fibers are better dispersed which reduced fiber balling in the mortar mix. Nevertheless, the friction between the PP fiber and the surrounding mortar paste is improved because of the biochar coating. While PP fiber surface is smooth and therefore weakly bonded with the mortar paste, biochar mixed with little cement makes the surface much rougher which increases the bonding and anchorage of coated fibers. Fig 2 and Fig. 3 presents the SEM image of PP fiber surface before addition to mortar and after mixed in mortar paste respectively. It can be observed that even after addition of PP fiber in mortar mix, the surface of fiber is smooth and clean which suggest absence of strong adhesion to mortar paste. However, when the surface of PP fiber is coated with biochar, it becomes rougher (Fig.4) which ensures stronger friction with the surrounding paste. Growth of crystals can be observed on the surface of coated fiber that matches with morphology of calcium hydroxide. It may be the result of hydration of little quantity of cement that was used for adhesion of biochar particles to the fiber surface.

However, one can observe from Fig.1 that addition of coating using saturated biochar (Fib-SatBC) affected compressive strength at both 7 day and 28-day age of mortar. Although 7-day strength is slightly higher than Control 1, it is lower than Control 2 while 28-day strength of Fib-SatBC is reduced by about 13% and 25% compared to Control 1 and Control 2 respectively. Reduction in strength can be attributed to carbonation induced by adsorbed carbon dioxide in the pores of saturated biochar. Carbon dioxide at surface pores can

dissolve in the pore solution which can then react with calcium hydroxide and calcium silicate hydrate formed by hydration of cement either in the coating of PP fiber or mortar paste (equation 1 -4).

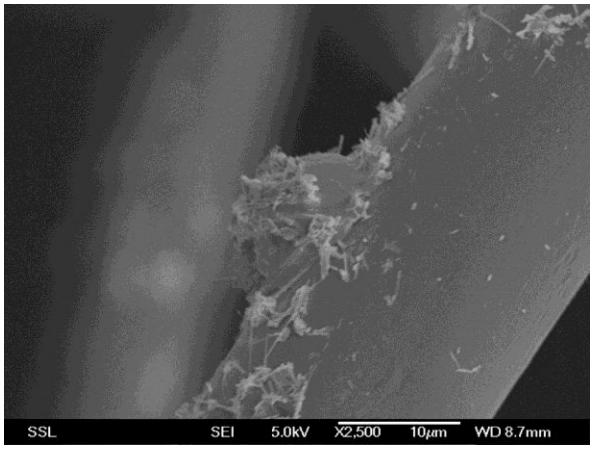

Fig.2: Smooth surface of polypropylene fibers before addition to mortar

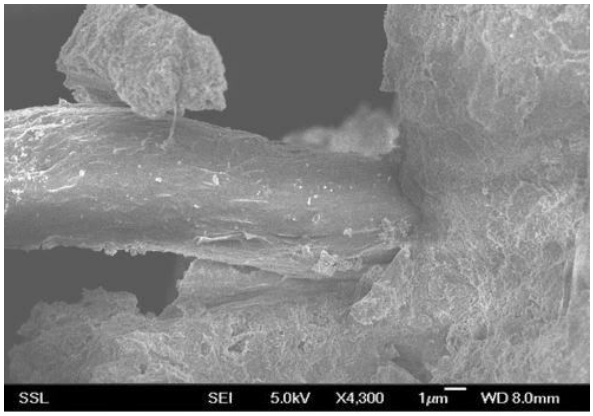

Fig.3: Surface of uncoated polypropylene fibers in mortar (Control 1). Clean surface shows no apparent chemical interaction

This phenomenon would compromise the bonding ability of fibers.

$$CO_2(\text{ from biochar pores}) + H_2O \rightarrow H_2CO_3 \quad (1)$$

$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O \quad (2)$$

$$3CaO.2SiO_2.3H_2O + 3H_2CO_3 \rightarrow 3CaCO_3 + SiO_2.3H_2O \quad (3)$$

$$3CaO.SiO_2 + 3H_2CO_3 \rightarrow 3CaCO_3 + SiO_2.3H_2O \quad (4)$$

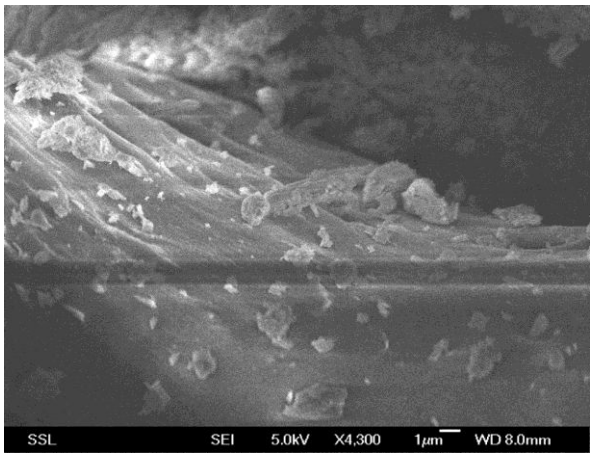

Fig. 4: Increased surface roughness of biochar coated polypropylene fibers. Some crystal growths also observed on the fiber surface

Phenolpthalein test showed the indication of carbonation in hardened Fib-SatBC mortar at 28 day while there was a strong change of color to purple in case of Fib-FreshBC mortar suggesting no such effect.

The poor bonding of fibers with the mortar paste is caused due to carbonation taking place around the fiber locations. Although it was not clear whether carbonation lead to microcracking at the interface of fibers, it was observed that part of mortar attached to PP fibers with saturated biochar was separated as lumps from the rest of the hardened paste (Fig. 5) during failure under compressive loading.

Flexural strength of biochar coated fiber samples also follow similar trend as compressive strength results. Fib-FreshBC show increase in 28-day flexural strength by 11% and 19% compared to control 1 and control 2 respectively. However, addition of saturated biochar coating resulted in reduction of flexural strength by about 9% and 16% compared to control 1 and control 2 respectively at 28 day.

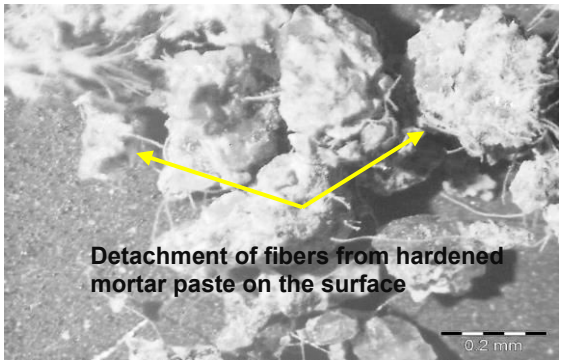

Fig. 5: Detachment of fiber coated with saturated biochar on the (a) surface of hardened mortar paste

Fig. 6 shows load-deflection behavior of control samples and samples with fresh and saturated biochar coated fibers. The coated fiber mixes show slightly higher residual strength at failure compared to control 1. Furthermore, it can be observed that Fib-FreshBC maintains steady residual load level over a large deflection range compared to Fib-SatBC. It suggests that crack bridging action is more efficient when PP fibers are coated with fresh biochar. It may relate to strong anchorage and bonding of fibers at fiber-mortar interface that offer improved post-cracking ductility to Fib-FreshBC.

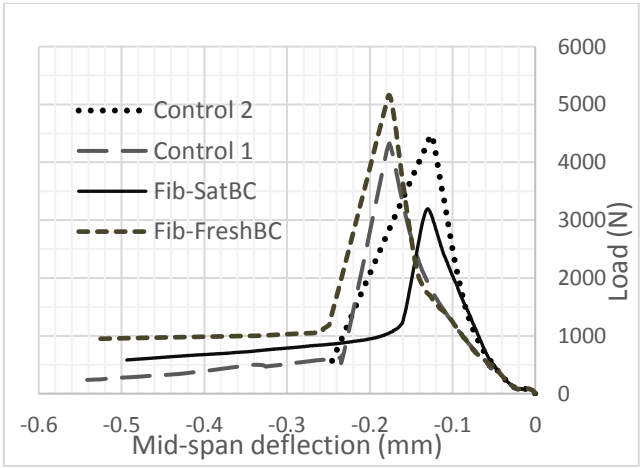

Fig.6: Load-deflection plots for control samples and samples with PP fiber coated with fresh biochar and saturated biochar

3.2 Effect of biochar coating on sorptivity

Fig. 7 shows that addition of saturated biochar coating and fresh biochar coating on PP fiber reduce sorptivity compared to control samples. Especially, initially sorptivity is significantly reduced because of both types of biochar coating which suggest reduction of continuous porous network responsible for faster initial absorption of mortar. Secondary sorptivity which is mainly attributed to filling of bigger air voids is also significantly lowered due to addition of fresh biochar coating on fibers. However, in case of Fib-SatBC

although the initial part of secondary sorptivity is lower than control 1 and control 2, it is similar as control samples at the end of 8-day period. It is because the rate or coefficient of sorptivity has increased due to introduction of saturated biochar coated PP fibers, which can be observed from Fig. 8. Carbonation around saturated biochar particles resulted in localized poor bonding of saturated biochar coated fibers with the mortar paste. Poor attachment of fibers with mortar paste would leave air voids around the interfacial zones of fiber and mortar paste. Although capillary channels are blocked by fine biochar particles, large number of air- voids would accelerate the absorption of water once the capillary pores are saturated. One can observe from Fig.7 and Fig. 8 that although the amount of water absorbed by Fib-FreshBC is significantly lower than control 1 and control 2, the coefficient sorptivity is similar. It means that although the absorption of moisture is reduced by coating fibers with biochar, rate of absorption is not significantly affected. It may be attributed to hydrophilic nature of biochar which contribute to sorptivity especially when some particles are situated at the water absorbing face of test samples.

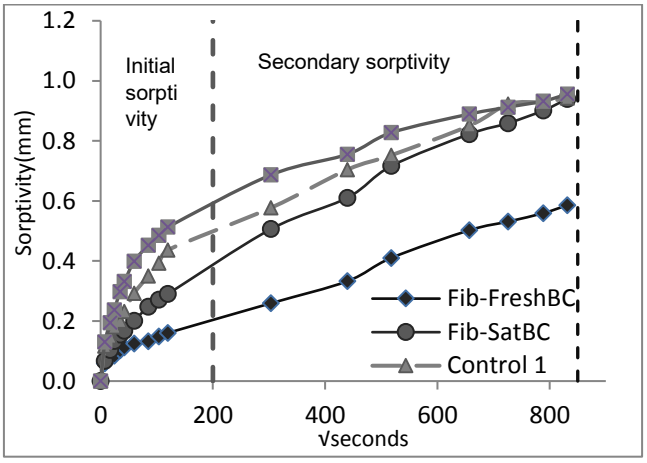

Fig.7 : Sorptivity in case of control mixes and mixes with fresh and saturated biochar coating on PP fiber

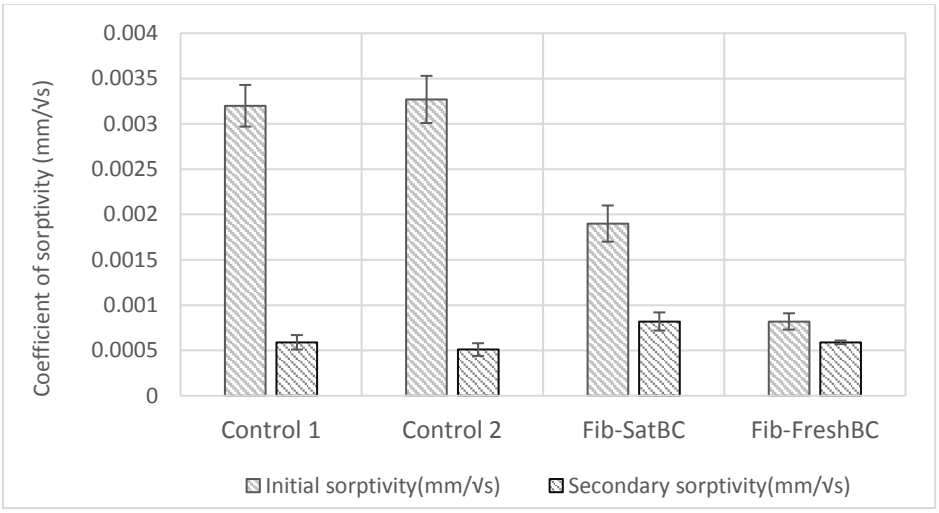

Fig.8: Coefficient of sorptivity for control mixes and mixes with fresh and saturated biochar coating on PP fiber

4 SUMMARY

The key findings from this study can be summarized as follows

a) Coating of fresh (or unsaturated) biochar on polypropylene fiber significantly improve compressive and flexural strength and post-cracking ductility of fiber reinforced samples.

b) Introduction of CO_2 saturated biochar as coating demonstrate poorer bonding because of possible carbonation reaction around the biochar particles. It results carbonation reaction around the biochar particles. It results in reduction of peak strength.

c) Both saturated biochar and fresh biochar coating reduced initial sorptivity while fresh biochar also reduced secondary sorptivity unlike saturated biochar. It can be concluded that use of unsaturated biochar coating on PP fiber can significantly reduce permeability of PP fiber reinforced mortar. However, rate of sorptivity is not significantly affected due to addition of biochar coating.

Biochar as additive is not only sustainable but also a cost-effective solution to improve mortar properties, because it is derived from bio-waste and production and mixing of biochar in mortar does not require any special technique or sophisticated set-up which many developing countries may not be willing to invest. Further research may be conducted to test the impact of other factors including feedstock and preparation impact on reduction of carbon footprint associated with the construction industry temperature on carbon sequestration potential of biochar in mortar and concrete and assess its life cycle.

5 ACKNOWLEDGEMENT

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