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IMPROVING THE BOND STRENGTH BETWEEN CARBON FIBER AND CEMENT BY FIBER SURFACE TREATMENT AND POLYMER ADDITION TO CEMENT MIX

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ABSTRACT

The bond strength between carbon fiber and cement was enhanced by oxidizing chemical treatments, with ozone treatment giving the greatest effect. The effect was accompanied by an increase in the electrical contact resistivity of the interface. These effects are mainly attributed to oxygen-containing functional groups on the fibers due to the treatments. The bond strength and contact resistivity were also increased by polymer (latex, methylcellulose) admixtures in the cement mix, but the effects were less than those of ozone treatment.

Introduction

Concrete reinforced with short fibers (e.g., steel, carbon, polymer) is attractive due to its high flexural toughness and low drying shrinkage, and, in some cases, high tensile and flexural strength as well [1-5]. The bond between fiber and cement matrix is critical to the effectiveness of the fibers, particularly in relation to drying shrinkage and strength. In the case of steel rebars, the bond between rebar and cement is significantly enhanced by the surface deformations on the rebar, as the deformations result in mechanical interlocking between rebar and cement. However, microfibers, such as carbon fibers (typically 10 μm in diameter), do not have surface deformations, so the use of fiber surface treatment and admixtures to the cement mix to improve the bond between fiber and cement matrix is particularly important. It has been reported that treatment of steel by water (to form rust) [6,7] or by either acetone [6,8] or NaOH [6] (to degrease) improves the bond between steel and cement. It has also been reported that the addition of polymer admixtures to the cement mix improves the bond between steel and cement [9] and that between carbon fiber and cement [10] and that the addition of silica fume to the cement mix improves the bond between carbon fiber and the cement matrix [11]. In this work, we investigated the use of fiber surface treatments (using acetic acid, nitric acid, NaOH, H_2O_2 and O_3) and of polymer admixtures (latex and methylcellulose) on the bond between carbon fiber and cement. The highest bond strength was attained in this work by the use of O_3 treated fibers. The focus on carbon fibers is due to the high tensile and flexural strength [5,12-19] and strain sensing ability [20-25] of cement with short carbon fibers. No previous work has been reported on the effects of carbon fiber surface treatment on the fiber-cement bond strength. The use of a polymer admixture in the mix should be distinguished from the use of a polymer coating on the steel. The latter is known to be harmful to the steel-cement bond [26,27].

Experimental Methods

The carbon fibers were isotropic pitch based and unsized, as obtained from Ashland Petroleum Co. (Ashland, Kentucky). The fiber properties are shown in Table 1. As-received and five types of surface treated fibers were used. The surface treatments included immersion (with stirring) of the fibers at room temperature for 24 h in acetic acid (99.9% reagent, 2 N), H_2O_2 (31.2% reagent, 2 N), NaOH solution (98.4% reagent, 1.5 N) or nitric acid (60% reagent, 1.5 N) (followed by water washing at room temperature and air drying at 110°C) and exposure of the fibers to O_3 gas (0.3 vol.%, in air) for 10 min at 160°C. Prior to O_3 exposure, the fibers had been dried at 110°C in air for 1 h.

Cement paste made from Portland cement (Type 1) from Lafarge Corp. (Southfield, MI) was used for the cementitious material. Three types of pastes were used, namely (i) plain cement paste (with only cement and water, such that the water/cement ratio is 0.45), (ii) cement paste with methylcellulose in the amount of 0.4% by weight of cement (together with water reducing agent in the amount of 1% by weight of cement, and with water-cement ratio = 0.32), and (iii) cement paste with latex in the amount of 20% by weight of cement (water-cement ratio = 0.23, without water reducing agent). The water reducing agent used in cement paste (ii) was TAMOL SN (Rohm and Haas Co., Philadelphia, PA), which contained 93-96% sodium salt of a condensed naphthalenesulfonic acid. Methylcellulose (Dow Chemical, Midland, MI, Methocel A15-LV) in the amount of 0.4% of the cement weight was used in paste (ii). The defoamer (Colloids Inc., Marietta, GA, 1010) used whenever methylcellulose was used was in the amount of 0.13 vol.%. The latex (Dow Chemical, Midland, MI, 460NA used in cement paste (iii) was a styrene-butadiene polymer; it was used in the amount of 20% of the weight of the cement. The antifoam (Dow Corning, Midland, MI, 2410) used whenever latex was used was in the amount of 0.5% of the weight of the latex.

A Hobart mixer with a flat beater was used for mixing. For the case of cement paste containing latex, the latex and antifoam first were mixed by hand for about 1 min. Then this mixture, cement, water and the water reducing agent were mixed in the mixer for 5 min. For the case of cement paste containing methylcellulose, methylcellulose was dissolved in water and then the defoamer was added and stirred by hand for about 2 min. Then this mixture, cement, water and water reducing agent were mixed in the mixer for 5 min.

TABLE 1
Properties of Carbon Fibers

Filament diameter	10 μm
Tensile strength	690 MPa
Tensile modulus	48 GPa
Elongation at break	1.4%
Electrical resistivity	3.0×10^{-3} Ω cm
Specific gravity	1.6 g cm^{-3}
Carbon content	98 wt.%

The contact electrical resistivity between the fiber and the cement paste was measured at 28 days of curing using the four-probe method and silver paint as electrical contacts, as illustrated in Fig. 1 of Ref. 28. One current contact and one voltage contact were on the fiber, while the other voltage and current contacts were on the cement paste embedding the fiber to a distance ranging from 0.51 to 1.20 mm, as measured for each specimen. The cement paste thickness was 1 mm on each side sandwiching the fiber. The fiber length was 1 cm. The current was 0.5-2.0 A; the voltage was 3-4 V. The resistance between the two voltage probes was measured; it corresponds to the sum of the fiber volume resistance, the interface contact resistance and the cement paste volume resistance. The measured resistance turned out to be dominated by the contact resistance, to the extent that the two volume resistance terms can be neglected. The contact resistivity (in $\Omega.cm^2$) is given by the product of the contact resistance (in Ω) and the contact (interface) area (in cm^2), such that the contact area depends on the embedment length of the particular specimen.

Single fiber pull-out testing was conducted on the same interface samples and at the same time as the contact resistivity was measured. For pull-out testing, one end of the fiber was embedded in cement paste, as in Fig. 1 of Ref. 28. A Sintech 2/D screw-action mechanical testing system was used. The contact resistivity was taken as the value prior to pull-out testing. The bond strength was taken as the maximum shear stress during pull-out testing. Refer to Fig. 2 of Ref. 28 for typical plots of shear stress vs. displacement and of contact resistivity vs. displacement simultaneously obtained during pull-out testing.

Results and Discussion

Fig. 1 shows the correlation of the contact resistivity and the bond strength for plain cement paste in contact with six different types of fibers (as-received and five types of treated fibers). Among the samples in each case, a high bond strength is associated with a low contact resistivity, because a high bond strength is associated with a low content of interfacial voids, which are electrically insulating. This trend within each case is consistent with that in Ref. 28. Comparison among the curves in Fig. 1 shows that all treatments increased both bond strength and contact resistivity, such that the magnitude of either effect increased in the order: acetic acid, H_2O_2, NaOH, nitric acid and O_3. Both effects are mainly attributed to the formation of an interfacial layer of high volume resistivity due to the treatment. This interfacial layer enhances the bonding and increases the contact resistivity. For the oxidizing chemicals, such as acetic acid, H_2O_2, nitric acid and O_3, the interfacial layer is believed to be oxygen-containing functional groups [29], which help the wettability of the fibers by the cement. Among the chemical used, ozone (O_3) is the most oxidizing chemical and nitric acid is the second most oxidizing chemical, so O_3 gave the largest effects while nitric acid gave the second largest effects. The NaOH treatment probably resulted in OH functional groups, which also help wettability of the fibers by the cement. Other than increasing the oxygen-containing functional groups, the oxidizing treatments are also believed to increase the active specific surface area [29], the number of bonding sites on the fiber surface [30] and the surface roughness [30]. These effects of the treatments also cause bond strength increases, but may not cause contact resistivity increases.

Fig. 2 shows the effect of polymer admixtures (methylcellulose and latex) on the bond between as-received fibers and cement. Either admixture increased both bond strength and contact resistivity. The latter is because the polymers are less conducting than cement. The former is because the polymers improve the adhesion between fiber and cement. Latex gave

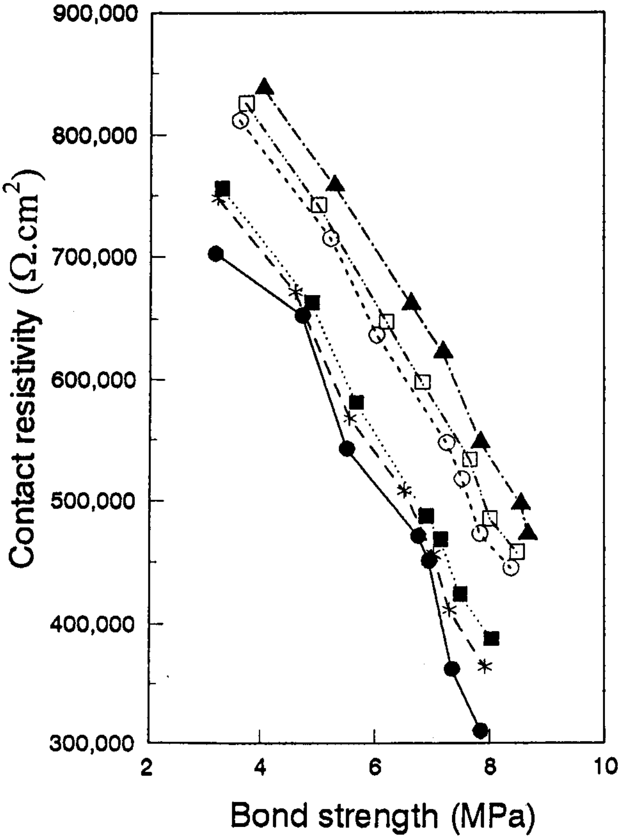

FIG. 1.
Variation of contact electrical resistivity with bond strength for plain cement in contact with as-received (●) and five types of treated carbon fibers: acetic acid (*), H_2O_2 (■), NaOH (○), nitric acid (□) and O_3 (Δ).

larger effects than methylcellulose, at least partly because latex was present in a much larger quantity than methylcellulose. Also shown in Fig. 2 are the data (also in Fig. 1) for plain cement in contact with O_3 treated fibers. The O_3 treatment of the fibers was even more effective than the use of polymer admixtures for enhancing the bond strength.

Conclusion

The bond strength between carbon fiber and cement was enhanced by oxidizing treatments, such as ozone and nitric acid treatments, mainly due to the resulting oxygen-containing functional groups on the fibers helping the wettability of the fibers by the cement. The highest bond strength was attained by ozone treatment. The increase in bond strength was associated with an increase in the fiber-cement contact resistivity due to the high resistivity of the oxygen-containing functional groups. The bond strength and contact resistivity were also enhanced by polymer admixtures in the cement mix. Latex gave larger effects than methylcellulose, but less effect than ozone treatment of the fibers.

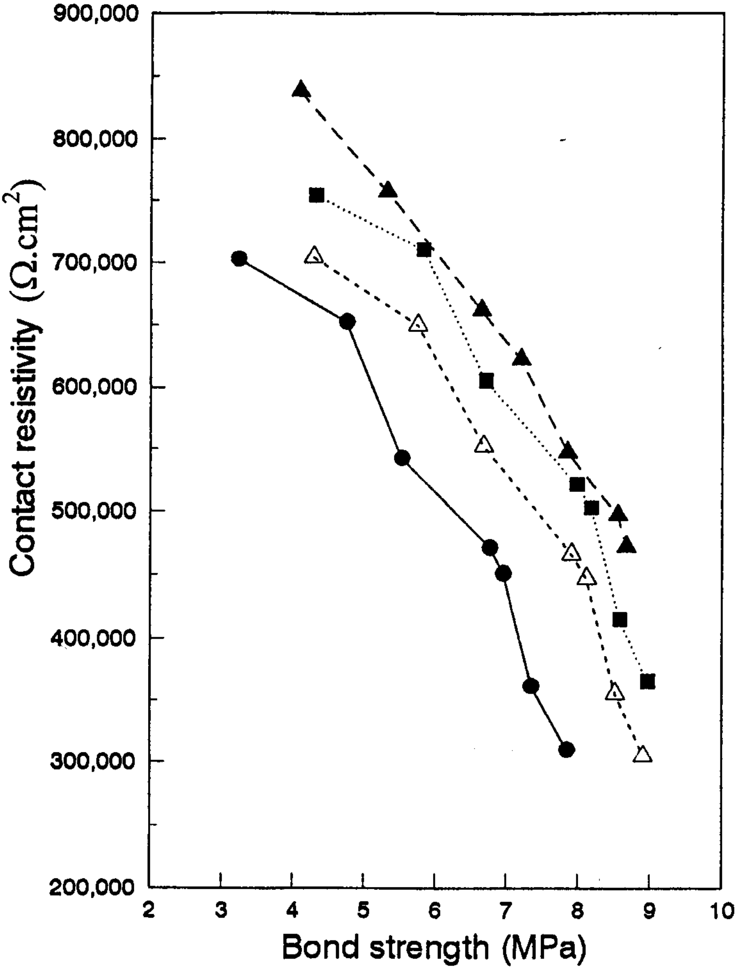

FIG. 2.

Variation of contact electrical resistivity with bond strength for as-received carbon fibers in contact with plain cement (●), cement with methylcellulose (▵) and cement with latex (▪). Also shown is that for O_3 treated fiber in contact with plain cement (▲).

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