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Reducing the drying shrinkage of cement paste by admixture surface treatments

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Abstract

Surface treatment of carbon fibers and/or silica fume by silane prior to using these admixtures in cement paste increases the effectiveness of these admixtures for reducing the drying shrinkage. Silane treatment of fibers is more effective than dichromate treatment or ozone treatment.

Keywords: Shrinkage; Admixture; Cement paste; Fiber reinforcement; Silica fume

1. Introduction

The drying shrinkage of concrete during curing is a source of residual stress and cracks. The problem is particularly severe for a large structure, such as a large concrete floor. Various admixtures such as silica fume [1–3], carbon fibers [1,4–6], and liquid chemicals [7–9] have been used to reduce the drying shrinkage. However, the effect of surface treatment of admixtures on the drying shrinkage has not been previously investigated. In this paper, we report that the surface treatment of an admixture is effective for enhancing the usefulness of the admixture in reducing the drying shrinkage. In earlier papers, we reported that the surface treatment of an admixture improves the mechanical properties [10–12], decreases the air void content [10], improves the workability [12], and increases the specific heat of cement paste [13].

2. Experimental methods

The carbon fibers were isotropic pitch-based, unsized, and of length ~5 mm, as obtained from Ashland Petroleum Co. (Ashland, KY, USA). The fiber properties are shown in Table 1. As-received and three types of surface-treated fibers were used. The fiber content was 0.5% by weight of cement. The surface treatments involved (1) ozone (O_3), (2) an aqueous solution of potassium dichromate ($K_2Cr_2O_7$, 30 wt.%) and sulfuric acid (H_2SO_4, 40 wt.%, which enhances the oxidation ability), and (3) silane. The ozone treatment for surface oxidation involved exposure of the fibers to O_3 gas (0.6 vol.%, in O_2) at 160°C for 5 min. Prior to O_3 exposure, the fibers had been dried at 160°C in air for 30 min. The potassium dichromate treatment for surface oxidation involved immersion in the dichromate solution and heating to 60°C while stirring for 2 h, followed by filtration and washing with water and then drying at 110°C for 6 h. For the silane treatment, the silane coupling agent was a 1:1 (by weight) mixture of Z-6020 ($[H_2NCH_2CH_2NHCH_2CH_2CH_2\text{-}Si(OCH)_3]_3$) and Z-6040 ($[OCH_2CHCH_2OCH_2CH_2CH_2Si\text{-}(OCH)_3]_3$) from Dow Corning Corp. (Midland, MI, USA). The amine group in Z-6020 serves as the catalyst for the curing of epoxy and consequently allows the Z-6020 molecule to attach to the epoxy end of the Z-6040 molecule. The trimethylsiloxy ends of the Z-6020 and Z-6040 molecules then connect to the –OH functional group on the surface of silica fume or carbon fiber. The silane was dissolved in ethylacetate. Surface treatment was performed by immersion in the silane solution, heating to 75°C while stirring, and holding at 75°C for 1 h, followed by filtration, washing with ethylacetate, and drying. After this, heating was conducted in a furnace at 110°C for 12 h.

No aggregate (fine or coarse) was used. The water/cement ratio was 0.35. A water-reducing agent (TAMOL SN, Rohm and Haas Co., Philadelphia, PA, USA; sodium salt of a condensed naphthalenesulphonic acid) was used in the amount of 2% by weight of cement.

The cement used was Portland cement (Type I) from Lafarge Corp. (Southfield, MI, USA). The silica fume (Elkem Materials, Inc., Pittsburgh, PA, USA, EMS 965) was used

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Table 1
Properties of carbon fibers

Filament diameter	15 ± 3 μm
Tensile strength	690 MPa
Tensile modulus	48 GPa
Elongation at break	1.4 %
Electrical resistivity	$3.0 \times 10^{-3}\ \Omega \cdot \mathrm{cm}$
Specific gravity	$1.6\ \mathrm{g\ cm^{-3}}$
Carbon content	98 wt.%

in the amount of 15% by weight of cement. The methylcellulose, used in the amount of 0.4% by weight of cement, was from Dow Chemical, Midland, MI, USA, Methocel A15-LV. The defoamer (Colloids Inc., Marietta, GA, USA, 1010) used whenever methylcellulose was used was in the amount of 0.13 vol.%.

A rotary mixer with a flat beater was used for mixing. Methylcellulose (if applicable) was dissolved in water and then the defoamer was added and stirred by hand for about 2 min. Then this mixture (if applicable), cement, water, water-reducing agent, silica fume, and fibers (if applicable) were mixed in the mixer for 10 min. After pouring into molds, an external vibrator was used to facilitate compaction and decrease the amount of air bubbles. The samples were demolded after 24 h and then cured in air at room temperature and a relative humidity of 100% for 28 days.

Drying shrinkage measurement was conducted as a function of curing age on samples of size 280 × 25.4 × 25.4 mm. A stainless steel contact point was positioned at each end along the length of each sample, such that the exterior tips of the two contact points were outside the sample and the interior tips of the two contact points were inside the sample and were separated by a distance of 250 mm, which was the gage length for drying shrinkage measurement. The measurement was conducted in accordance with ASTM Method C490-93a.

Table 2
Drying shrinkage strain (10^{-4}, ±0.015) at different curing ages

	With as-received silica fume				With silane-treated silica fume			
Formulation	1 day	4 days	8 days	28 days	1 day	4 days	8 days	28 days
B	1.13	3.02	3.72	4.41	1.01	2.88	3.62	4.18
BF	0.83	2.42	3.05	3.51	0.78	2.25	2.81	3.19
BO	0.83	2.36	3.02	3.48	0.76	2.24	2.79	3.09
BK	0.82	2.32	3.02	3.48	0.76	2.23	2.79	3.09
BS	0.81	2.32	2.98	3.31	0.75	2.12	2.72	2.99

B, cement + water + water reducing agent + silica fume + methylcellulose + defoamer; BF, B + as-received fibers; BO, B + O_3-treated fibers; BK, B + dichromate-treated fibers; BS, B + silane-treated fibers.

Ten compositions, as listed in Table 2, were studied. Five of them had as-received silica fume; the other five had silane-treated silica fume.

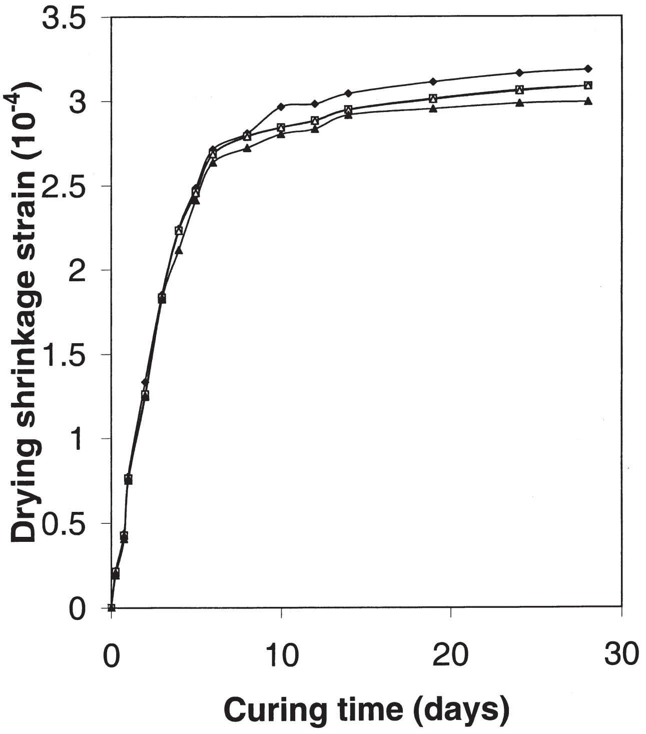

Fig. 1. Drying shrindage strain vs. curing time for cement paste with as-received silica fume and as-received fibers (◆), ozone-treated fibers (□), dichromate-treated fibers (△), and silane-treated fibers (▲).

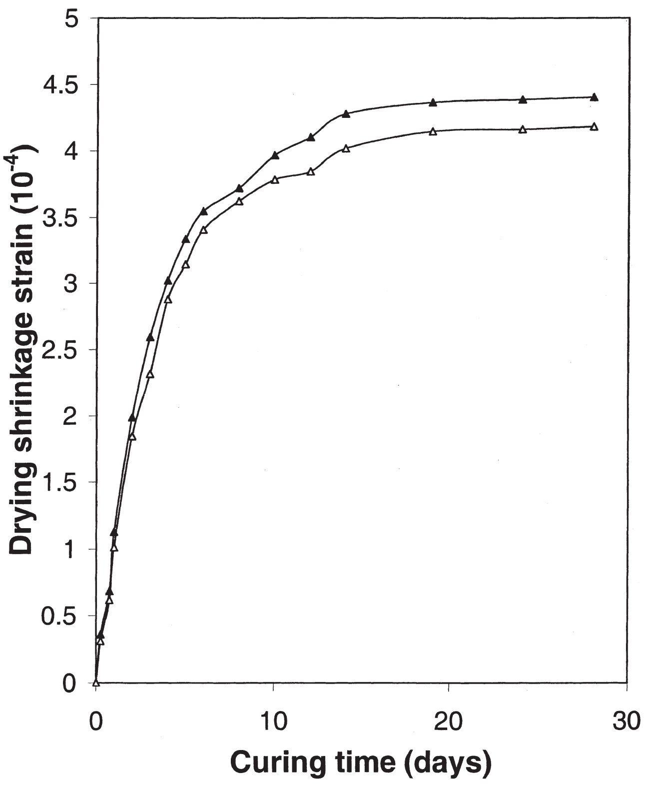

Fig. 2. Drying shrinkage strain vs. curing time for cement paste with as-received silica fume (no fiber) (▲) and for cement paste with silane-treated silica fume (no fiber) (△).

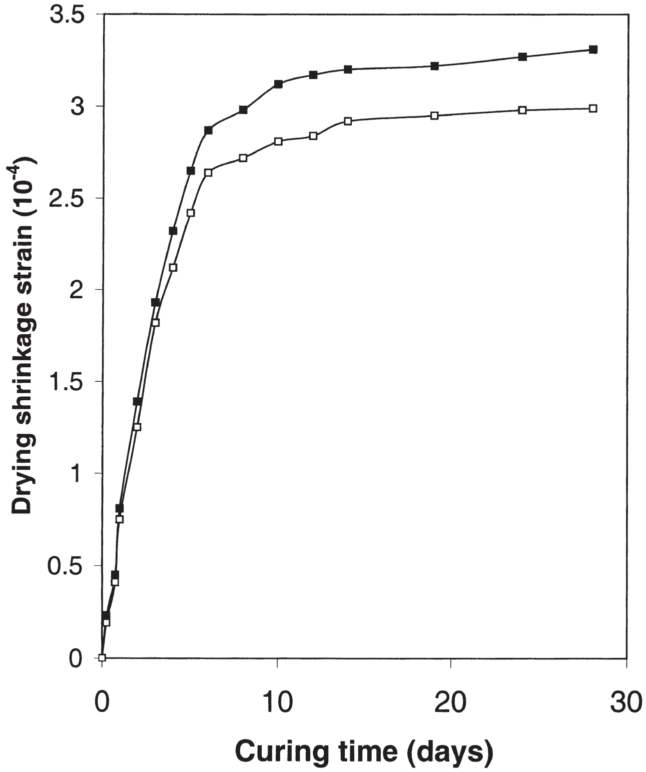

Fig. 3. Drying shrinkage strain vs. curing time for cement paste with as-received silica fume and silane-treated fibers (■) and for cement paste with silane-treated silica fume and silane-treated fibers (□).

The surface composition of carbon fiber and silica fume, with and without treatment, was measured by electron spectroscopy for chemical analysis (ESCA).

3. Results

Table 2 gives the drying shrinkage strains of the 10 types of cement paste as a function of curing age. The drying shrinkage is decreased by the addition of carbon fibers; it decreases in the order: as-received fibers, ozone-treated fibers, dichromate-treated fibers, and silane-treated fibers (Table 2 and Fig. 1). This trend applies for any curing age, whether the silica fume is as-received or silane-treated. The drying shrinkage is decreased by the use of silane-treated silica fume in place of as-received silica fume, whether fibers are present or not (Table 2, Figs. 2 and 3). The drying shrinkage strain at 28 days is decreased by 5% when fibers are absent and silane-treated silica fume is used in place of as-received silica fume. When silane-treated fibers are present, it is decreased by 10% when silane-treated silica fume is used in place of as-received silica fume. The drying shrinkage strain at 28 days is decreased by 15% when both silane-treated silica fume and silane-treated carbon fibers are used in place of as-received silica fume and as-received carbon fibers. Compared to the cement paste without fibers but with as-received silica fume, the drying shrinkage strain is decreased by 25% when silane-treated fibers are added. Compared to the cement paste without fibers but with silane-treated silica fume, the drying shrinkage strain is decreased by 28% when silane-treated fibers are added. Compared to the cement paste without fibers but with as-received silica fume, the drying shrinkage strain is decreased by 32% when silane-treated fibers are added and silane-treated silica fume is used in place of as-received silica fume.

ESCA results are shown in Tables 3, 4, 5, and 6 for carbon fibers. The surface carbon concentration is decreased and the surface oxygen concentration is increased by any of the three surface treatments (Table 3). In the case of the O_3 and dichromate treatments, this is due to the oxidation of the fiber surface and the introduction of hydrophylic functional groups such as –OH and –COOH to the surface. The charge-corrected binding energies (C_{ls} and O_{ls}) of both O_3- and dichromate-treated carbon fiber surfaces (Tables 4 and 5) confirm the existence of these functional groups. In the case of the silane treatment, the oxygen, nitrogen, and silicon concentrations on the surface increase and the carbon concentration on the surface decrease after the treatment, due to the composition of the silane coating of the surface (Table 3). That the surface chloride concentration is not zero after silane treatment is a result that is not understood.

Table 3
Surface elemental composition (in atomic %) of carbon fiber

Element	As-received	O_3-treated	Dichromate-treated	Silane-treated
O	13	20.2	20.6	21.8
N	–	–	–	9.3
C	85.4	79.8	79.4	54.3
Cl	–	–	–	4.0
Si	1.7	–	–	10.6

Table 4
Charge-corrected binding energies (eV) and possible assignment for O_3-treated carbon

Energy level	Binding energy (eV)	Assignment
C_{ls}	285.0	$(CH_2)_n$
	286.7	C–O
	288.6	C=O
O_{ls}	531.8	C=O
	533.6	C–O

Table 5
Charge-corrected binding energies (eV) and possible assignment for dichromate-treated carbon fiber

Energy level	Binding energy (eV)	Assignment
C_{ls}	285.0	$(CH_2)_n$
	286.7	C–O
	288.6	C=O
O_{ls}	531.8	C=O
	533.6	C–O

Table 6
Charge-corrected binding energies (eV) and possible assignment for silane-treated carbon fiber

Energy level	Binding energy (eV)	Assignment
C_{ls}	285.0	$(CH_2)_n$
O_{ls}	531.9	Si–O
Si_{2p}	102.2	Organic silicone
N_{ls}	399.0	C–N
	401.1	N–O

The charge-corrected binding energies of the silane-treated fiber surface (Table 6) confirm the presence of silane.

Tables 7 and 8 show the ESCA results of silica fume particles with and without treatment. Compared to as-received silica fume, the silane-treated silica fume particle surface has more carbon, less oxygen, and less silicon. This is consistent with the fact that the surface is partly covered by the silane coating and that Z-6020 contains C, Si, and O atoms. That the nitrogen atoms in Z-6040 are not observed on the surface of the silica fume particles suggests that only Z-6020 adheres to the silica fume particle surface while Z-6040 merely serves as a catalyst, as expected from the epoxy group in Z-6020. Table 8 shows the charge-corrected binding energies of silane-treated silica fume particles, confirming the presence of silane on the surface.

4. Discussion

Carbon fiber addition is effective for decreasing the drying shrinkage, as previously reported [1,4–6,14]. The effectiveness is further enhanced by surface treatment of the fibers, although the effect of the fiber surface treatment is small compared to the effect of the fiber addition. The drying shrinkage strain at 28 days is decreased by 6% when silane-treated fibers are used in place of as-received fibers, in the presence of as-received silica fume. The drying shrinkage strain at 28 days is decreased by 10% when silane-treated silica fume is used in place of as-received silica fume, in the presence of silane-treated carbon fibers. The drying shrinkage strain at 28 days is decreased by 15% when both silane-treated silica fume and silane-treated carbon fibers are used in place of as-received silica fume and as-received carbon fibers. The greater effectiveness of silane treatment compared to the other fiber surface treatments for drying shrinkage reduction is consistent with its greater effectiveness for improving the mechanical properties [10,11], decreasing the air void content [10], and increasing the specific heat [13].

Table 7
Surface elemental composition (in atomic %) of silica fume

Element	As-received	Silane-treated
O	56.7	50.0
C	10.5	19.3
Si	32.8	30.7
N	–	–

Table 8
Charge-corrected binding energies (eV) and possible assignment for silane-treated silica fume

Energy level	Binding energy (eV)	Assignment
C_{ls}	285.0	$(CH_2)_n$
O_{ls}	532.5	Si–O
Si_{2p}	103.4	Organic silicone

The ESCA results show that both carbon fiber and silica fume particle surfaces are partly coated by or bonded to silane molecules. Due to the hydrophylic nature of silane, the treated fibers and treated silica fume are expected to be more uniformly distributed in the cement. More importantly, the formation of chemical bonds at which silane serves as bridges between the surface of fiber or silica fume and the cement matrix is expected to make the composite denser and stronger, as shown in the case of silica fume [12]. Therefore, the drying shrinkage strain is decreased by silane treatment of fibers and/or silica fume.

Previous work on both mortar and concrete shows that the drying shrinkage strain of concrete is much smaller than that of mortar, but the fractional reduction of drying shrinkage strain caused by the addition of silica fume to concrete (33%) is much larger than that for mortar (6%) [14]. When carbon fibers are present, the addition of silica fume causes over 50% reduction of the drying shrinkage strain in concrete, but only a small effect on the drying shrinkage strain in mortar [14]. This suggests that the observed effect of silica fume surface treatment on the drying shrinkage of cement paste probably corresponds to an even larger effect in concrete.

5. Conclusions

Silane treatment of silica fume and/or carbon fiber is highly effective for decreasing the drying shrinkage of cement paste. The increase of the hydrophylic character of fibers and particles after the treatment and the formation of chemical bonds between fibers/particles and cement are believed to be the main reasons for the observed decrease of the drying shrinkage. By adding silane-treated carbon fibers and replacing as-received silica fume by silane-treated silica fume, the shrinkage at 28 days is decreased by 32%.

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