# Cement-Matrix Structural Nanocomposites

## D. D. L. Chung*

Composite Materials Research Laboratory, State University of New York
Buffalo, NY 14260-4400, U.S.A.

This paper reviews cement-matrix structural nanocomposites, including those with particulate and fibrous reinforcements. Silica fume is valuable for improving numerous mechanical properties, in addition to enhancing the freeze-thaw durability, the vibration damping capacity, the abrasion resistance, the bond strength with steel rebars, the chemical attack resistance and the corrosion resistance of steel rebars. Furthermore, silica fume decreases the alkali-silica reactivity, the drying shrinkage, permeability, creep rate and thermal expansion. On the other hand, carbon nanofiber is not attractive, as it fails to compete with conventional discontinuous carbon fiber as a reinforcement.

Keywords: composite, cement-matrix, structural, mechanical, silica fume, carbon fiber

## 1. INTRODUCTION

Structural nanocomposites have attracted much scientific interest due to the potentially high reinforcing effectiveness of particles or fibers in nanometer scale. Most attention in this regard has been directed at polymer-matrix composites, due to the importance of these composites for lightweight structures such as aircraft and satellites. However, due to the widespread use of continuous fiber (not nanofiber) reinforcement in polymer-matrix composites and the high effectiveness of the continuous fiber reinforcement, the structural applications of polymer-matrix nanocomposites are limited to components which need to be made by injection molding (a process which is not applicable to continuous fibers) [1] and to continuous fiber (not nanofiber) polymer-matrix composites with discontinuous nanofiber between the laminae for the purpose of vibration damping enhancement [2,3]. Even in these limited structural applications, polymer-matrix nanocomposites face tough competition with conventional composites, such as composites with fibers or particles that are not in nanometer scale and composites with viscoelastic interlayers for damping.

The situation is quite different in the area of cement-matrix composites, which rarely use continuous fibers, because continuous fibers cannot be incorporated in a concrete mix. In addition, the inherent air voids in a cement-matrix com-

posite and the relatively weak bond between cement and reinforcement (weak compared to the bond between, say, epoxy and reinforcement) allow much room for improvement of cement-matrix composites by nanotechnology.

This paper reviews cement-matrix structural nanocomposites, including particulate and fibrous (discontinuous) composites. The nanometer scale reinforcements are chosen by consideration of both cost and performance, as low cost is essential for the practical viability of a concrete. For evaluation of the structural performance, numerous properties are considered, including the mechanical properties, vibration damping capacity, freeze-thaw durability, abrasion resistance, shrinkage, air void content, density, permeability, steel rebar corrosion resistance, bond strength to steel rebar, creep rate, and workability. In addition, the effect of reinforcement surface treatment is considered for the purpose of improving the bond between cement and reinforcement and enhancing the degree of dispersion of the discontinuous reinforcement.

## 2. BACKGROUND ON CEMENT-MATRIX COMPOSITES

Cement-based materials such as concrete have long been used for the civil infrastructure, such as highways, bridges and buildings. However, the deterioration of the civil infrastructure all over the U.S. has led to the realization that

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*Corresponding author: ddlchung@buffalo.edu

cement-based materials must be improved in terms of their properties and durability. The fabrication of cement-based materials involves mixing cement, water, aggregates (such as sand and gravel) and optionally other additives (called admixtures). The use of admixtures is a relatively convenient way of improving cement-based materials. Techniques involving special mixing, casting or curing procedures tend to be less attractive, due to the need for special equipment in the field. An admixture which is particularly effective is silica fume [4-7], although there are other admixtures such as latex and short fibers, which are more expensive.

The property improvements needed for cement-based materials include increases in strength, modulus and ductility (whether under tension, compression, flexure or torsion), decrease in the drying shrinkage (i.e., shrinkage during the curing and simultaneous drying of a cement mix – a phenomenon which can cause cracks to form), decrease in the permeability to liquids and chloride ions (important for the corrosion resistance of the steel reinforcing bars embedded in concrete), and increase in the durability to freeze-thaw temperature cycling (important in cold regions).

## 3. PARTICULATE NANOCOMPOSITES

Silica fume [8-11] is very fine noncrystalline silica produced by electric arc furnaces as a by-product of the production of metallic silicon or ferrosilicon alloys. It is a powder with particles having diameters 100 times smaller than those of anhydrous Portland cement particles, i.e., mean particle size between 0.1 and 0.2 μm. The $SiO_2$ content ranges from 85 to 98 %. Silica fume is pozzolanic.

Silica fume used as an admixture in a concrete mix has significant effects on the properties of the resulting material. These effects pertain to the strength, modulus, ductility, vibration damping capacity, sound absorption, abrasion resistance, air void content, shrinkage, bonding strength with reinforcing steel, permeability, chemical attack resistance, alkali-silica reactivity reduction, corrosion resistance of embedded steel reinforcement, freeze-thaw durability, creep rate, coefficient of thermal expansion (CTE), specific heat, thermal conductivity, defect dynamics, dielectric constant, and degree of fiber dispersion in mixes containing short microfibers. In addition, silica fume addition degrades the workability of the mix.

For the sake of consistency, the data given in this review to illustrate the effects of silica fume are all for silica fume from Elkem Materials Inc., Pittsburgh, PA (EMS 965), used in the amount of 15 % by weight of cement. The cement is Portland cement (Type I) from Lafarge Corp. (Southfield, MI). Curing is in air at room temperature and a relative humidity of 100 % for 28 days. The water-reducing agent, if used, is a sodium salt of a condensed naphthalenesulphonic acid from Rohm and Haas Co., Philadelphia, PA (TAMOL SN).

### 3.1. Workability

Silica fume causes workability and consistency losses [8-21], which are barriers against proper utilization of silica fume concrete. However, the consistency of silica fume mortar is greatly enhanced by either using silane treated silica fume, i.e., silica fume which has been coated by a silane coupling agent prior to incorporation in the mix, or using silane as an additional admixture [22,23]. The effectiveness of silane for cement is due to the reactivity of its molecular ends with –OH groups and the presence of –OH groups on the surface of both silica and cement.

Table 1 [22,23] shows that the silane introduction using either coating or admixture methods causes the silica fume mortar mix to increase in workability (slump). With silane (by either method) and no water-reducing agent, the workability of silica fume mortar mix is better than that of the mix with as-received silica fume and water-reducing agent in the amount of 1 % by weight of cement. With silane (by either method) and water-reducing agent in the amount of 0.2 % by weight of cement, the workability is almost as good as the mix with as-received silica fume and water-reducing agent in the amount of 2 % by weight of cement.

The increase in workability due to silane introduction is due to the improved wettability of silica fume by water. The improved wettability is expected from the hydrophylic nature of the silane molecule. Silane treatment involves formation of a silane coating on the surface of the silica fume; it does not cause surface roughening [24].

### 3.2. Mechanical properties

The most well-known effect of silica fume is the increase in strength [20,21,23,25-55], including the compressive strength [20,23,56-84], tensile strength [23,63,66,74,75,85] and flexural strength [62,69,75,86,87]. The strengthening is due to the pozzolanic activity of silica fume causing improved strength of the cement paste [39,82], the increased density of mortar or concrete resulting from the fineness of silica fume and the consequent efficient reaction to form hydration products, which fill the capillaries between cement and aggregate [53], the refined pore structure [58,79] and the

**Table 1.** Workability of mortar mix. The water/cement ratio was 0.35

| Silica fume | Water-reducing agent/cement | Slump (mm) |
|---|---|---|
| Plain | 0 % | * |
| With untreated silica fume | 0 % | 150 |
| With untreated silica fume | 1 % | 186 |
| With untreated silica fume | 2 % | 220 |
| With treated silica fume | 0 % | 194 |
| With treated silica fume | 0.2 % | 215 |
| With silane and untreated silica fume | 0 % | 197 |
| With silane and untreated silica fume | 0.2 % | 218 |

*Too large to be measured.

**Table 2.** Mechanical properties of cement pastes at 28 days of curing

| | Plain | With untreated silica fume[†] | With treated silica fume[†] | With silane[*] and untreated silica fume[†] |
|---|---|---|---|---|
| Tensile strength (MPa) | 0.91 ± 0.02 | 1.53 ± 0.06 | 2.04 ± 0.06 | 2.07 ± 0.05 |
| Tensile modulus (GPa) | 11.2 ± 0.24 | 10.2 ± 0.7 | 11.5 ± 0.6 | 10.9 ± 0.5 |
| Tensile ductility (%) | 0.0041 ± 0.00008 | 0.020 ± 0.0004 | 0.020 ± 0.0004 | 0.021 ± 0.0004 |
| Compressive strength (MPa) | 57.9 ± 1.8 | 65.0 ± 2.6 | 77.3 ± 4.1 | 77.4 ± 3.7 |
| Compressive modulus (GPa) | 2.92 ± 0.07 | 13.6 ± 1.4 | 10.9 ± 1.8 | 15.8 ± 1.6 |
| Compressive ductility (%) | 1.72 ± 0.04 | 0.614 ± 0.023 | 0.503 ± 0.021 | 0.474 ± 0.015 |

[*] 0.2 % by weight of cement
[†] 15 % by weight of cement

microfiller effect of silica fume [79,80]. In addition, the modulus is increased [23,47,51,56,76,88]. These effects are also partly due to the densification of the interfacial zone between paste and aggregate [88].

As shown in Table 2 [23] for cement pastes at 28 days of curing, the tensile strength, tensile ductility, compressive strength and compressive modulus are increased and the compressive ductility is decreased by the addition of silica fume (15 % by weight of cement) which has not been surface treated. The tensile strength and compressive strength are further increased and the compressive ductility is further decreased when silane treated silica fume is used. On the other hand, the tensile modulus is essentially not affected by the silica fume addition. The use of both silane (0.2 % by weight of cement) and untreated silica fume (as two admixtures, last column of Table 2) enhances the tensile strength, compressive strength and compressive modulus, but decreases the compressive ductility, relative to the paste with untreated silica fume and no silane. The effect of using treated silica fume (next to the last column of Table 2) and of using the combination of silane and untreated silica fume are quite similar, except that the compressive modulus is higher and the compressive ductility is lower for the latter due to the network of covalent silane coupling among the silica fume particles in the latter case.

The use of silane as an admixture which is added directly into the cement mix involves slightly more silane material but less processing cost than the use of silane in the form of a coating on silica fume. Both methods of silane introduction result in increases in the tensile and compressive strengths. The network attained by the admixture method of silane introduction does not result from the silane coating method, due to the localization of the silane in the coating, which nevertheless provides chemical coupling between silica fume and cement. The network, which is formed from the hydrolysis and polymerization (condensation) reaction of silane during the hydration of cement, also causes the ductility to decrease.

### 3.3. Vibration damping capacity

Vibration reduction is valuable for hazard mitigation,

structural stability and structural performance improvement. Effective vibration reduction requires both damping capacity and stiffness. Silica fume is effective for enhancing both damping capacity and stiffness (modulus) [23,89-91].

As shown in Table 3 [23], the vibration damping capacity, as expressed by the loss tangent under dynamic 3-point flexural loading at 0.2 Hz, is significantly increased by the addition of silica fume which has not been surface treated. The use of silane treated silica fume increases the loss tangent slightly beyond the value attained with untreated silica fume. The use of silane and untreated silica fume as two admixtures decreases the loss tangent to a value below that attained by using untreated silica fume alone, but still above that for plain cement paste.

The ability of silica fume to enhance the damping capacity is due to the large area of the interface between silica fume particles and the cement matrix and the contribution of interface slippage to energy dissipation. Although the pozzolanic nature of silica fume makes the interface rather diffuse, the interface still contributes to damping. The silane covalent coupling introduced by the silane surface treatment of silica fume can move during vibration, thus providing another mechanism for damping and enhancing the loss tangent. The network introduced by the use of silane and untreated silica fume as two admixtures restricts movement and therefore reduces the damping capacity relative to the case with untreated silica fume alone. Nevertheless, the use of the two admixtures enhances the damping capacity relative to the plain cement paste case, as even less movement is possible in plain cement paste.

The storage modulus (Table 3) is much increased by the addition of untreated silica fume, is further increased by the use of silane treated silica fume, and is still further increased by the use of silane and untreated silica fume as two admixtures. The increase in storage modulus upon addition of untreated silica fume is attributed to the high modulus of silica compared to the cement matrix. The enhancement of the storage modulus by the use of silane treated silica fume is due to the chemical coupling provided by the silane between silica fume and cement. The further enhancement of the stor-

**Table 3.** Dynamic flexural properties of cement pastes at a flexural (3-point bending) loading frequency of 0.2 Hz

|  | Loss tangent (tan δ, ± 0.002) | Storage modulus (GPa, ± 0.03) | Loss modulus (GPa, ± 0.02) |
|---|---|---|---|
| Plain | 0.035 | 1.91 | 0.067 |
| With untreated silica fume[†] | 0.082 | 12.71 | 1.04 |
| With treated silica fume[†] | 0.087 | 16.75 | 1.46 |
| With silane[*] and untreated silica fume[†] | 0.055 | 17.92 | 0.99 |

[*] 0.2 % by weight of cement
[†] 15 % by weight of cement

age modulus by the use of silane and untreated silica fume as two admixtures is due to the network of covalent coupling among the silica fume particles.

The loss modulus (Table 3) is the product of the loss tangent and the storage modulus. As vibration reduction requires both damping and stiffness, both loss tangent and storage modulus should be high for effective vibration reduction. Hence, the loss modulus serves as an overall figure of merit for the vibration reduction ability. The loss modulus is much increased by the addition of untreated silica fume and is further increased by the use of silane treated silica fume. However, the use of silane and untreated silica fume as two admixtures decreases the loss modulus to a value below the paste with untreated silica fume alone, due to the decrease in the loss tangent. As a result, the use of silane treated silica fume gives the highest value of the loss modulus.

### 3.4. Sound absorption

Sound or noise absorption is useful for numerous structures, such as pavement overlays and noise barriers. The addition of silica fume to concrete improves the sound absorption ability [91]. The effect is related to the increase in vibration damping capacity (last section).

### 3.5. Freeze-thaw durability

Freeze-thaw durability refers to the ability to withstand changes between temperatures above 0 °C and those below 0 °C. Due to the presence of water, which undergoes freezing and thawing (which in turn cause changes in volume), concrete tends to degrade upon such temperature cycling. Air voids (called air entrainment) are used as cushions to accommodate the changes in volume, thereby enhancing the freeze-thaw durability.

The addition of silica fume to mortar improves the freeze-thaw durability [60, 92-94], in spite of the poor air-void system [60]. However, the use of air entrainment is still recommended [95-99]. The addition of silica fume also reduces scaling [100].

### 3.6. Abrasion resistance

The addition of untreated silica fume to mortar increases the abrasion (both solid and hydraulic) resistance [51,100, 101], as shown by the depth of wear decreasing from 1.07 to

0.145 mm (as tested using ASTM C944-90a, Rotating-Cutter Method) [101]. The abrasion resistance is further improved by using acid treated silica fume [102].

### 3.7. Shrinkage

The hydration reaction that occurs during the curing of cement causes shrinkage, called autogenous shrinkage, which is accompanied by a decrease in the relative humidity within the pores. In case that the curing is conducted in an open atmosphere, as is usually the case, additional shrinkage occurs due to the movement of water through the pores to the surface and the loss of water on the surface by evaporation. The overall shrinkage that occurs in this case is known as the drying shrinkage, which is the shrinkage that is practically important.

Drying shrinkage can cause cracking and prestressing loss [103]. The addition of untreated silica fume to cement paste decreases the drying shrinkage [23,37,103-107] (Table 4). This desirable effect is partly due to the reduction of the pore size and connectivity of the voids and partly due to the prestressing effect of silica fume, which restrains the shrinkage. The use of silane treated silica fume in place of untreated silica fume further decreases the drying shrinkage, due to the hydrophylic character of the silane treated silica fume and the formation of chemical bonds between silica fume particles and cement [23]. The use of silane and untreated silica fume as two admixtures also decreases the drying shrinkage, but not as significantly as the use of silane treated silica fume [23].

### 3.8. Air void content and density

The air void content of cement paste (Table 5) is increased by the addition of untreated silica fume [23,108]. Along with this effect is a decrease in density (Table 6). Both effects are related to the reduction in drying shrinkage. The introduction of silane by either coating or admixture method decreases

**Table 4.** Drying shrinkage strain ($10^{-4}$, ± 0.015) of cement pastes at 28 days

| Plain | 4.98 |
|---|---|
| With untreated silica fume | 4.41 |
| With treated silica fume | 4.18 |
| With silane and untreated silica fume | 4.32 |

**Table 5.** Air void content (%, ± 0.02) of cement pastes

| | |
|---|---|
| Plain | 2.32 |
| With untreated silica fume | 3.73 |
| With treated silica fume | 3.26 |
| With silane and untreated silica fume | 3.19 |

the air void content, but the value is still higher than that of plain cement paste. The use of the admixture method of silane introduction increases the density to a value almost as high as that of plain cement paste, due to the network of covalent coupling among the silica fume particles [23]. On the other hand, the air void content of concrete is decreased by silica fume addition [11,20], probably due to the densification of the paste-aggregate interface [88].

### 3.9. Permeability

The permeability of chloride ions in concrete is decreased by the addition of untreated silica fume [8,11,20,25,28,33-35,49, 50,53,60,62,81,105,109-132]. Related to this effect is the decrease in the water absorptivity. Both effects are due to the microscopic pore structure resulting from the calcium silicate hydrate (CSH) formed upon the pozzolanic reaction of silica fume with free lime during the hydration of concrete [133-157].

### 3.10. Steel rebar corrosion resistance

The addition of untreated silica fume to steel reinforced concrete enhances the corrosion resistance of the reinforcing steel [157-171]. This is related to the decrease in the permeability (last section).

### 3.11. Alkali-silica reactivity reduction

The alkali-silica reactivity refers to the reactivity of silica (present in most aggregates) and alkaline ions (present in cement). It is detrimental due to the expansion caused by the reaction product. This reactivity is reduced by the addition of silica fume [123, 172-187], because of the effectiveness of silica fume to remove alkali from the pore solution [178, 179,184], to reduce the alkali ion ($Na^+$, $K^+$, $OH^-$) concentrations in the pore solution [186,187], and to retard the transportation of alkalis to reaction sites (due to the refinement and segmentation of the pore structure) [184]. However, silica fume with coarse particles or undispersed agglomerates can induce distress related to alkali-silica reactivity [174].

### 3.12. Chemical attack resistance

The addition of untreated silica fume to concrete enhances the chemical attack resistance [188-204], whether the chemical is acid, sulfate, chloride, etc. This effect is related to the decrease in permeability.

### 3.13. Bond strength to steel rebar

The addition of untreated silica fume to concrete increases the shear bond strength between concrete and steel rebar [205-211]. This effect is mainly due to the reduced porosity and thickness of the transition zone adjacent to the steel, thereby improving the adhesion-type bond at small slip levels [208-211]. The combined use of silica fume and methylcellulose (0.4 % by weight of cement) gives even higher bond strength, due to the surfactant role of methylcellulose [209,212].

### 3.14. Creep rate

The addition of untreated silica fume to cement paste decreases the compressive creep rate at 200 °C from $1.3 \times 10^{-5}$ to $2.4 \times 10^{-6}$ $min^{-1}$ [108]. The creep resistance is consistent with the high storage modulus (Table 3), which remains much higher than that of plain cement paste up to at least 150 °C [108]. However, silica fume increases the early age tensile creep, which provides a mechanism to relieve some of the restraining stress that develops due to autogenous shrinkage [213].

### 3.15. Coefficient of thermal expansion

The CTE is reduced by the addition of untreated silica fume [108]. This is consistent with the high modulus and creep resistance.

### 3.16. Specific heat

A high value of the specific heat is valuable for improving the temperature stability of a structure and to retain heat in a building. The specific heat ($C_p$, Table 7) is increased by the addition of untreated silica fume [108]. The use of silane treated silica fume in place of untreated silica fume further increases the specific heat, though only slightly [214]. The effect of untreated silica fume is due to the slippage at the interface between silica fume and cement. The effect of the silane treatment is due to the contribution of the movement of the covalent coupling between silica fume particles and cement. The use of silane and untreated silica fume as two admixtures greatly increases the specific heat, due to the network of covalent coupling among the silica fume particles contributing to phonons [23].

**Table 6.** Density (g/cm³, ± 0.02) of cement pastes

| | |
|---|---|
| Plain | 2.01 |
| With untreated silica fume | 1.72 |
| With treated silica fume | 1.73 |
| With silane and untreated silica fume | 1.97 |

**Table 7.** Specific heat (J/g.K, ± 0.001) of cement pastes

| | |
|---|---|
| Plain | 0.736 |
| With untreated silica fume | 0.782 |
| With treated silica fume | 0.788 |
| With silane and untreated silica fume | 0.980 |

## 3.17. Thermal conductivity

Concrete of low thermal conductivity is useful for the thermal insulation of buildings. On the other hand, concrete of high thermal conductivity is useful for reducing temperature gradients in structures. The thermal stresses that result from temperature gradients may cause mechanical property degradation and even warpage in the structure. Bridges are among structures that tend to encounter temperature differentials between their top and bottom surfaces. In contrast to buildings, which also encounter temperature differentials, bridges do not need thermal insulation. Therefore, concrete of high thermal conductivity is desirable for bridges and related structures.

The thermal conductivity (Table 8) is decreased by the addition of untreated or silane treated silica fume [23,108, 214], due to the interface between silica fume particles and cement acting as a barrier against heat conduction. However, the thermal conductivity is increased by the use of silane and untreated silica fume as two admixtures [23], due to the network of covalent coupling enhancing heat conduction through phonons.

## 3.18. Fiber dispersion

Short fibers (not nanofibers), such as carbon, glass, polypropylene, steel and other fibers, are used as an admixture in concrete to enhance the tensile and flexural properties and decrease the drying shrinkage. Effective use of the fibers, which are used in very small quantities (such as 0.5 % by weight of cement in the case of carbon fibers), requires good dispersion of the fibers. The addition of untreated silica fume to microfiber reinforced cement increases the degree of fiber dispersion, due to the fine silica fume particles helping the mixing of the microfibers [135, 215-259]. In addition, silica fume improves the structure of the fiber-matrix interface, reduces the weakness of the interfacial zone and decreases the number and size of cracks [135].

**Table 8.** Thermal conductivity (W/m.K, ± 0.07) of cement pastes

| | |
|---|---|
| Plain | 0.53 |
| With untreated silica fume | 0.35 |
| With treated silica fume | 0.33 |
| With silane and untreated silica fume | 0.61 |

**Table 9.** Tensile properties and electrical resistivity of mortars that contain carbon fibers and methylcellulose (0.4 % by mass of cement). The water/cement ratio is 0.350

| | Without silica fume | With silica fume[*] |
|---|---|---|
| Electrical resistivity ($10^6$ Ωcm) | 0.68 (± 2.8 %) | 0.31 (± 3.1 %) |
| Tensile strength (MPa) | 2.26 ± 0.08 | 2.36 ± 0.06 |
| Tensile modulus (GPa) | 12.5 ± 0.3 | 13.5 ± 0.9 |
| Tensile ductility (%) | 0.0150 ± 0.0009 | 0.0168 ± 0.0009 |

[*]Without treatment.

Table 9 shows that silica fume (without treatment) decreases the resistivity of carbon fiber mortar and increases the tensile strength, modulus and ductility [260]. The lower resistivity indicates better fiber dispersion.

## 3.19. Defect dynamics during elastic deformation

Defects in a solid respond to applied stresses. When the applied stress is dynamic, the response of the defects is also dynamic. The response encompasses the generation, healing and aggravation of defects. Defect generation refers to the formation of defects which usually occurs during loading. Defect healing refers to the diminution of defects. Healing can occur during compressive loading of a brittle materials, such as a cement-based material. Defect aggravation refers to the propagation or enlargement of defects; it can occur during removal of a compressive stress from a brittle material.

Figs. 1 and 2 show the variation of the fractional change in longitudinal resistivity with Cycle No. during initial cyclic compression of plain mortar and silica-fume (without treatment) mortar respectively in the elastic regime [261]. The stress amplitude used increased cycle by cycle. For both mortars, the resistivity increased abruptly during the first loading (due to defect generation) and increased further during the first unloading (due to defect aggravation). Moreover, the resistivity decreased during subsequent loading (due to defect healing) and increased during subsequent unloading (due to defect aggravation); the effect associated with defect healing was much larger for silica-fume mortar than for plain mortar. In addition, this effect intensified as stress cycling at increasing stress amplitudes progressed for both mortars, probably due to the increase in the extent of minor damage. The increase in damage extent was also indicated by the resistivity baseline increasing gradually cycleby
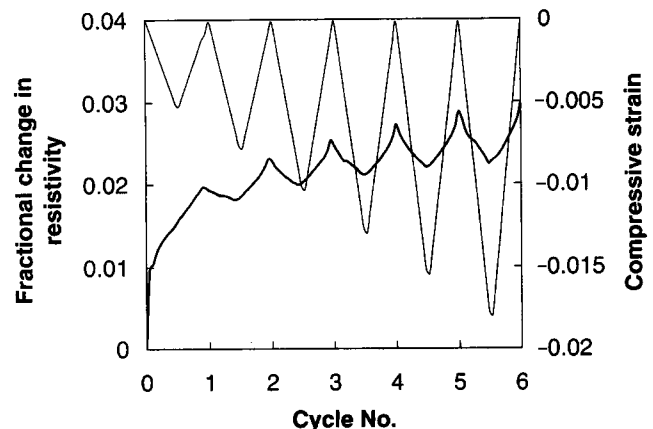


**Fig. 1.** Variation of the fractional change in resistivity with Cycle No. (thick curve) and of the compressive strain with Cycle No. (thin curve) during repeated compressive loading at increasing stress amplitudes within the elastic regime for plain mortar (without silica fume).
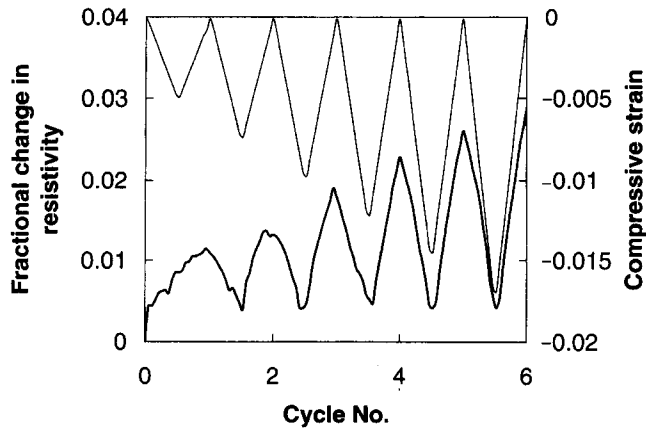
**Fig. 2.** Variation of the fractional change in resistivity with Cycle No. (thick curve) and of the compressive strain with Cycle No. (thin curve) during repeated compressive loading at increasing stress amplitudes within the elastic regime for silica fume mortar.

cycle. In spite of the increase in stress amplitude cycle by cycle, defect healing dominated over defect generation during loading in all cycles other than the first cycle.

Comparison of Figs. 1 and 2 showed that silica fume contributed significantly to the defect dynamics during elastic deformation. The associated defects were presumably at the interface between silica fume and cement, even though this interface was diffuse due to the pozzolanic nature of silica fume. The defects at this interface were smaller than those at the sand-cement interface, but this interface was large in total area due to the small particle size of silica fume compared to sand.

### 3.20. Dielectric constant

Due to the presence of ionic bonding and moisture in cement, electric dipoles are present and the dielectric constant has been measured for the purpose of fundamental understanding of cement-based materials [262]. The relative dielectric constant of cement paste at 10 kHz 1 MHz is decreased by silica fume (without treatment) addition (from 29 to 21 at 10 kHz) [263], due to the volume occupied by silica fume in place of cement.

## 4. FIBROUS NANOCOMPOSITES

### 4.1. Carbon nanofibers

Carbon nanofibers are mainly those that are grown catalytically from carbonaceous gases 500-700 °C [264,265], although they include those that are grown by the electric arc discharge method. Their diameter is typically 2000 Å or below. The yield in production is higher for carbon nanofibers of diameter above 100 Å than those of diameter below 100 Å, so the former is more abundant than the latter and applications involving the former are more well developed than those involving the latter. Carbon nanofibers are to be distin-

guished from carbon nanotubes [266] in that they are typically more than 50 Å in diameter, whereas nanotubes are less than 50 Å in diameter. They are also to be distinguished from conventional carbon fibers, which are typically of diameter 5-20 μm and are made by pyrolysis of pitch or polymer [267-269]. Moreover, they are to be distinguished from vapor grown carbon fibers (VGCF), which can have diameter as high as 10 μm and are prepared by pyrolysis of carbonaceous gases to non-catalytically deposit carbon on catalytically grown carbon nanofibers at 950-1100 °C [270-277]. Both carbon nanofibers and VGCF are not continuous, though the latter can be longer than the former. In contrast, conventional carbon fibers can be continuous. In spite of the discontinuous nature of carbon nanofibers, the aspect ratio can be quite high, due to the small diameter. Carbon nanofibers tend to be not straight, especially for those that are relatively long. Each nanofiber has an axial hollow channel in the middle, due to the catalyst particle used in the filament growth. The hollow channel is akin to that in a carbon nanotube.

Carbon nanofibers are commercially available, though not in large volumes. As the amount of usage increases, the price of carbon nanofibers will fall. According to Applied Sciences Inc. (Cedarville, Ohio), which manufactures catalytically grown carbon nanofibers, the price will fall to U.S. $ 2-3 per pound. This price is even lower than that of short isotropic pitch based carbon fibers.

Unless noted otherwise, the results described in this section for the sake of illustration involve the use of 1600 Å diameter carbon nanofibers grown from methane, using an iron containing catlyst, as provided by Applied Sciences Inc. (Cedarville, Ohio, U.S.A.). The specific surface area of these nanofibers is 12.5 m²/g. The density is 2 g/cm³. The aspect ratio is 50-200. There is no sizing, although a surface treatment that yields nitrogen-containing functional groups on the surface of the nanofibers has been applied. The nanofibers are intertwined and have a morphology that resembles cotton wool (Fig. 3). Moreover, they are disordered crystallographically, unless it has been mentioned that they have been graphitized by heat treatment. However, even a disordered nanofiber exhibits a fishbone morphology for the carbon layers (Fig. 4). The fishbone (also called herringbone) morphology is like a stack of cones; it is to be distinguished from the concentric cylinders of carbon layers in the case of multiwalled carbon nanotubes [266].

### 4.2. Carbon nanofiber composites

Structural applications are most important for conventional continuous carbon fibers. Due to the discontinuous nature, carbon nanofibers are far less effective than continuous carbo fibers as a reinforcement in composites. Due to their small diameter and the consequent large area of the interface between nanofibers and matrix in a composite, and due to their texture with the carbon layers at an angle from
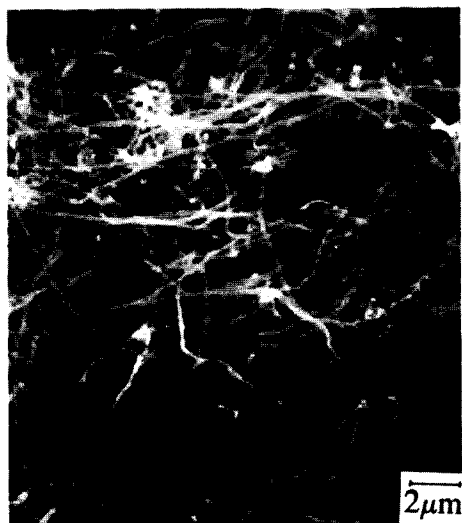
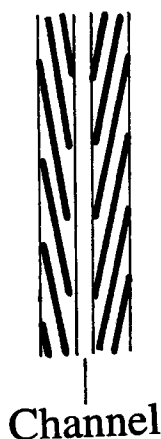**Fig. 3.** Scanning electron micrograph of carbon nanofibers.



# Channel

**Fig. 4.** Schematic illustration of a carbon nanofiber, showing the fishbone morphology of the carbon layers and the hollow channel along the axis of the nanofiber.

the nanofiber axis, carbon nanofibers are not as effective as short carbon fibers (even those based on isotropic pitch) at the same volume fraction as a reinforcement, as shown for both thermoplastic [278,279] and cement matrices [280]. For example, in a thermoplastic matrix, carbon nanofibers at 19 vol.% give a tensile strength of 27 MPa [279], whereas carbon fibers (isotropic pitch based, 3000 μm long) at 20 vol.% give a tensile strength of 64 MPa [278]; in a cement paste matrix, carbon nanofibers at 0.51 vol.% give a tensile strength of 1.2 MPa, whereas carbon fibers (isotropic pitch based, 5 mm long) give a tensile strength of 1.7 MPa [280]. Although the nanofibers do not reinforce as well as the fibers, they still reinforce under tension. In a cement matrix, the tensile strength, modulus and ductility and the compressive modulus are all increased by the nanofibers (0.51 vol.%), but the compressive strength and ductility are decreased by the nanofibers [280]. Neither the carbon nanofi-

bers nor the carbon fibers have much effect on the damping capacity or the thermal conductivity of cement [281,282].

The bond between carbon and a cement matrix is weak compared to that between carbon and a polymer matrix. Therefore, surface treatment of carbon for improving the bond with cement is particularly important. The treatment of carbon nanofibers with ozone gas (0.3 vol.% in air, 160 °C, 10 min) increases the tensile strength, modulus and ductility, and the compressive strength, modulus and ductility of cement pastes, relative to the values for pastes with the same volume fraction of untreated nanofibers [283]. Similar effects apply to the ozone treatment of carbon fibers [284], for which it has been shown that the ozone treatment improves the wetting by water, the degree of fiber dispersion in cement, and bond strength with cement, in addition to increasing the surface oxygen concentration [285,286].

# 5. CONCLUSION

Cement-matrix nanocomposites involving silica fume are attractive for structural applications. However, nanocomposites involving carbon nanofibers are not attractive, due to their inferiority compared to composites with conventional discontinuous carbon fibers.

The use of silica fume as an admixture in cement-based materials increases the tensile strength, compressive strength, compressive modulus, flexural modulus and the tensile ductility, but decreases the compressive ductility. In addition, it enhances the freeze-thaw durability, the vibration damping capacity, the abrasion resistance, the bond strength with steel rebars, the chemical attack resistance and the corrosion resistance of reinforcing steel. Furthermore, it decreases the alkali-silica reactivity, the drying shrinkage, permeability, creep rate, coefficient of thermal expansion and dielectric constant. Moreover, it increases the specific heat and decreases the thermal conductivity, though the thermal conductivity is increased if silica fume is used with silane, another admixture. Silica fume addition also increases the air void content, decreases the density, enhances the dispersion of fibers, and decreases the workability. In addition, the defects associated with the interface between silica fume and cement contribute to the defect dynamics during elastic deformation.

The use of silane treated silica fume in place of untreated silica fume increases the consistency, tensile strength and compressive strength, but decreases the compressive ductility. Furthermore, the silane treatment increases the damping capacity and specific heat, and decreases the drying shrinkage and air void content.

The use of silane and untreated silica fume as two admixtures, relative to the use of silane treated silica fume, increases the compressive modulus, but decreases the compressive ductility and damping capacity. It also decreases the

air void content and increases the density, specific heat and thermal conductivity.

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