DISPERSION OF CARBON FIBERS IN CEMENT

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Introduction

Short fibers are used as admixtures in cement-based materials for the purpose of decreasing the drying shrinkage, increasing the flexural toughness and, in some cases, for increasing the flexural strength as well [1-5]. In the case that the fibers are electrically conductive, the fibers may also provide non-structural functions, such as self-sensing (for sensing the strain, damage or temperature), self-heating (for deicing) and electromagnetic reflection (for electromagnetic interference shielding, i.e., EMI shielding) [6].

Although continuous fibers are more effective than short fibers as a reinforcement [7], they are not amenable to incorporation in a concrete mix and they are relatively expensive. Low cost is critical to the practical viability of cement-based materials. Thus, this paper is focused on short fibers in cement-based materials.

Although macroscopic steel fibers of diameter around 1 mm are used, the most effective fibers are usually microfibers of diameter ranging from 5 to 100 μm. For example, carbon fibers are typically around 10 μm in diameters [8]. Nanofibers of diameter typically around 0.1 μm are less effective than microfibers as a reinforcement, although they are more effective than microfibers for providing EMI shielding (due to the small diameter and the skin effect) [9]. In general, the smaller the fiber diameter (which relates to a higher aspect ratio), the more difficult is the fiber dispersion. Similarly, the smaller the fiber length (which relates to a lower aspect ratio), the easier is the fiber dispersion. This is due to the tendency for fibers of a small diameter or a long length to cling to one another.

The effectiveness of a fiber admixture for improving the structural or functional properties of cement-based materials is greatly affected by the degree of fiber dispersion. The attainment of a high degree of fiber dispersion is particularly critical when the fiber volume fraction is low. A low fiber volume fraction is usually preferred, as the material cost increases, the workability decreases, the air void content increases and the compressive strength decreases as the fiber content increases [10].

The fiber dispersion is enhanced by improving the hydrophylicity of the fibers, as the cement mix is water-based. The hydrophylicity can be controlled by surface treatment of the fibers prior to incorporation of the fibers in the cement mix [11,12]. Furthermore, the fiber dispersion is affected by the admixtures that may be used along with the fibers. These other admixtures may be fine particles (such as silica fume [13], which has a

typical particle size around 0.1 μm), the presence of which helps the fibers break loose from one another as mixing occurs [2,14]. Other admixtures may be polymers such as latex particle dispersions, which help the fiber-cement bond as well as the fiber dispersion [2,15-17].

This paper provides a review of the dispersion of short fibers in cement-based materials. The methods for enhancing fiber dispersion, the factors that affect fiber dispersion, and the relationship of fiber dispersion with the properties of the cement-based materials are all considered. The use of special mixers to improve fiber dispersion is not considered in this review, because it increases the processing cost and limits the field applicability (due to the limited availability of special mixers in the field).

The use of microscopy to assess the degree of fiber dispersion is ineffective, as it can tell if fiber clumps are present, but it is insensitive to small differences in the degree of fiber dispersion.

Although the mechanical properties are more important to concrete applications than the electrical conductivity, the electrical conductivity can reflect the degree of fiber dispersion better than the mechanical properties. In case that the fiber volume fraction is below the percolation threshold, the greater is the degree of fiber dispersion, the higher is the conductivity of the composite. This is because of the relatively long length of conduction path within the matrix in case of poor fiber dispersion [18]. The mechanical properties depend on the fiber-matrix bonding and the amount of air voids, in addition to depending on the degree of fiber dispersion. However, for fibers that are much more conductive than the matrix and are at volume fractions below the percolation threshold, the electrical conductivity of the cement-based material depends mostly on the degree of fiber dispersion. Therefore, this paper uses volume electrical conductivity measurement to assess the degree of fiber dispersion on a relative scale. For this reason, the paper is focused on carbon fibers, which are electrically conductive.

Effect of admixtures used along with the fibers

Admixtures used along with the short fibers in the cement mix can cause increase or decrease of the degree of fiber dispersion. Admixtures include silica fume, polymer particles water-based dispersions, polymer water-based solutions and silane.

<u>Effect of silica fume</u>

Silica fume 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 Portland cement, 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 [13]. 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, and thermal conductivity. In addition, silica fume improves the degree of fiber dispersion in mixes containing short microfibers [2,19,20].

At a carbon fiber (15 μm diameter, ~5 mm length) content of 0.35% (below the percolation threshold [14]), cement mortar exhibits an electrical resistivity of 1.59 x 10^6 Ω.cm ($\pm$ 4.5%) in the absence of silica fume [21]. In the presence of silica fume (15% by mass of cement), the resistivity is reduced to 1.13 x 10^6 Ω.cm ($\pm$3.9%) [21]. Consistent with the reduction in electrical resistivity is the increase in tensile strength from 1.04 $\pm$ 0.11 to 1.45 $\pm$ 0.11 MPa [21]. The reduction in resistivity is an indication of an improvement in the degree of fiber dispersion.

Effect of polymer solution

Due to the need for water in a cement mix, polymer solutions based on water are more suitable than those based on other solvents. Methylcellulose is a polymer that is soluble in water.

At a carbon fiber (15 μm diameter, ~5 mm length) content of 0.35% (below the percolation threshold [14]), in the absence of silica fume, the electrical resistivity of cement mortar is reduced from 1.59 x 10^6 Ω.cm ($\pm$ 4.5%) to 0.68 x 10^6 Ω.cm ($\pm$2.8%) upon addition of methylcellulose (0.4% by mass of cement) [21]. Consistent with the reduction in resistivity is the increase in tensile strength from 1.04 $\pm$ 0.11 to 2.26 $\pm$ 0.08 MPa [21].

The reduction in resistivity is an indication of an improvement in the degree of fiber dispersion. The presumed presence of methylcellulose, which is not conductive, at the fiber-matrix interface is expected to increase the resistivity of the mortar. In spite of this, the resistivity of the fiber mortar is decreased by the methylcellulose addition. The increase in tensile strength upon methylcellulose addition is consistent with the increase in fiber-matrix shear bond strength upon methylcellulose addition [22].

Effect of polymer particle dispersions

Due to the need for water in a cement mix, polymer particle dispersions based on water are more suitable than those based on other liquids. The polymers used in the dispersions are not soluble in the liquids used. As most polymers are not soluble in water, the choice of polymers for dispersions is wide compared to that of polymers for solutions.

At a carbon fiber (15 μm diameter, ~5 mm length) content of 0.35%, in the absence of silica fume, the electrical resistivity of cement mortar is reduced from 1.59 x 10^6 Ω.cm ($\pm$ 4.5%) to 0.58 x 10^6 Ω.cm ($\pm$ 6.0%) upon addition of acrylic water-based dispersion (20%

by mass of cement) [21]. Latex and styrene acrylic water-based dispersions (also 20% by mass of cement) are less effective than the acrylic dispersion, as they reduce the resistivity to 0.89 x 10^6 Ω.cm ($\pm$ 7.7%) and 0.83 x 10^6 Ω.cm ($\pm$ 5.1%) respectively. As polymer particle dispersions are used in much larger amounts than methylcellulose, the cost of using the dispersions is relatively high.

The presumed presence of polymer at the fiber-matrix interface is supported by the increase in the fiber-matrix shear bond strength upon latex addition [22]. In spite of this, the polymer dispersion addition causes the resistivity of the fiber mortar to be decreased by the addition of the polymer dispersion. This means that the addition of the polymer dispersion improves the degree of fiber dispersion.

In the absence of fiber, both flexural toughness and strength increase monotonically with increasing content of polymer particle dispersion (latex) [2]. However, in the presence of fiber (e.g., carbon fiber), the flexural toughness decreases monotonically with increasing content of polymer particle dispersion, because the degree of fiber dispersion decreases with increasing content of polymer particle dispersion [2].

Upon increase of the amount of acrylic dispersion from 10 to 20% by mass of cement, the electrical resistivity of carbon fiber mortar is decreased from 0.67 x 10^6 Ω.cm ($\pm$ 6.9%) to 0.58 x 10^6 Ω.cm ($\pm$ 6.0%) [21]. However, for the case of latex in place of acrylic, the resistivity is increased 0.66 x 10^6 Ω.cm ($\pm$ 5.8%) to 0.89 x 10^6 Ω.cm ($\pm$ 7.7%). In the absence of fiber, an increase in the polymer content causes the resistivity to increase, as shown at least for the case of the polymer being latex [23]. Therefore, the decrease of the resistivity of carbon fiber mortar as the acrylic dispersion content is increased from 10% to 20% by mass of cement is attributed to an increase in the degree of fiber dispersion. However, the dependence of the resistivity of carbon fiber mortar with latex content is opposite in trend and the flexural toughness results point to a decrease in the degree of fiber dispersion with increasing latex content. Hence, the combination of electrical and mechanical results indicate that the degree of fiber dispersion increases with increasing acrylic dispersion content, but decreases with increasing latex dispersion content. Nevertheless, the use of a polymer particle dispersion (whether acrylic or latex) gives a higher degree of fiber dispersion than the use of no dispersion, at least for the range of dispersion content from 10% to 20% by mass of cement.

Effect of silica fume in combination with polymer solution

Both silica fume and methylcellulose solution, when used separately, help the fiber dispersion. The combined use of these two admixtures is even more helpful. The combined use of silica fume (15% by mass of cement) and methylcellulose (0.4% by mass of cement) causes the resistivity to decrease from 1.59 x 10^6 Ω.cm ($\pm$ 4.5%) to 0.31 x 10^6 Ω.cm [21]. This decrease is more than that attained by using silica fume alone (decreased to 1.13 x 10^6 Ω.cm ($\pm$ 3.9%)) or that attained by methylcellulose alone (decreased to 0.68 x 10^6 Ω.cm ($\pm$ 2.8%)). On the other hand, silica fume in combination with latex dispersion does not work, due to low workability [22].

<u>Effect of Silane</u>

Silane is molecular, but is not a polymer. Due to its hydrophylic nature, silane is effective as an admixture for improving the degree of fiber dispersion, as shown for steel fibers (60 μm diameter, 5 mm length). The electrical resistivity of steel fiber (0.05 vol.%, much below the percolation threshold) mortar is decreased from 2.03×10^6 Ω.cm ($\pm$ 5.3%) to 1.65×10^6 Ω.cm ($\pm$ 3.9%) upon addition of silane (aqueous amino vinyl silane, chosen due to its stability in aqueous systems) [21]. In the absence of fiber, silane addition has negligible effect on the resistivity of mortar [21]. Thus, the decrease in resistivity of steel fiber mortar upon silane addition is attributed to increase in the degree of fiber dispersion.

Effect of fiber surface treatments

<u>Ozone treatment</u>

Fiber surface treatments that improve the wettability of the fiber by water are useful for improving the fiber dispersion in cement, in addition to improving the fiber-matrix bond [11]. At a carbon fiber content of 0.24 vol.% (below the percolation threshold), the electrical resistivity of cement mortar is decreased from 3.62×10^3 to 3.27×10^3 Ω.cm upon surface treatment of the carbon fibers by ozone prior to incorporation of the fibers in the cement mix [11]. Even though ozone treatment increases the contact resistivity between fiber and cement [11], the volume resistivity of the fiber mortar is decreased by the ozone treatment. Thus, the decrease in volume resistivity indicates an increase in the degree of fiber dispersion.

Ozone treatment involves exposure to an O_2-O_3 mixtures with 0.6 vol.% O_3 at 160°C for 5 min [11,24]. It results in oxygen-containing surface functional groups and is effective for improving the wettability of carbon and steel fibers [24]. A contact angle of 0° is attained by ozone treatment of carbon fibers [24].

Ozone treatment is effective for increasing the tensile strength, modulus and ductility, as well as the compressive strength, modulus and ductility, of both carbon fiber (15 μm diameter, 0.5 vol.%) cement paste and carbon nanofiber (0.1 μm diameter, 0.5 vol.%) cement paste [9,25]. The nanofiber paste is inferior to the fiber paste in terms of these properties. The strain-sensing ability of carbon fiber cement is also improved by ozone treatment of the fibers [26].

Treatments with acetone, hydrochloric acid and sodium hydroxide

Acetone treatment involves immersion in acetone for 1 h. It is effective for improving the wettability of steel and polyethylene fibers [24]. For polyethylene fibers, hydrochloric acid treatment (immersion in 1.0 N HCl solution for 24 h) and sodium hydroxide treatment (immersion in 1.0 N NaOH solution for 24 h) are more effective than acetone treatment [24].

Silane treatment

Instead of using silane as an admixture (Sec. 2.5), silane can be used to coat fibers prior to incorporation of the fibers in the cement mix. However, the use of silane to coat steel fibers (60 μm diameter, 5 mm length) is less effective than the use of silane as an admixture for improving the degree of fiber dispersion [21].

Silane coating has been applied to carbon fibers for the purpose of improving the tensile strength [12]. However, the effect of the silane coating on the degree of carbon fiber dispersion has not been assessed.

Conclusion

Short fibers are used as admixtures in cement-based materials for structural and functional reasons. Dispersion of the fibers is important and is particularly challenging for microfibers at a small volume fraction. Assessment of the degree of fiber dispersion by microscopy is ineffective. In this paper, the degree of dispersion of short microfibers (such as carbon and steel fibers) in cement mortar or cement paste is assessed by measurement of the volume electrical resistivity when the fibers are electrically conductive and are at volume fraction below the percolation threshold. This degree is improved by the use of admixtures such as silica fume, polymer particle dispersions, methylcellulose solution, and silane.   The combined use of silica fume and methylcellulose is most effective. Acrylic particle dispersion is more effective than latex particle dispersion. The degree of fiber dispersion is also improved by the use of fiber surface treatment such as ozone treatment, which improves the wettability by water.

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