The Effect of Compatibility and Dimensionality of Carbon Nanofillers on Cement Composites

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INTRODUCTION

Cement is by far the most important and widespread building material in the industrialized world, with 4.2 billion tons of cement being produced in 2017. Cement production is, nonetheless, ecologically harmful, as a result of the CO_2 produced both by clinker and cement kilns. One possible solution lies in reducing the amount of clinker in the cement composites. This demand could be met by enhancing the mechanical properties of cement-based composites, for example, by loading them with nanofillers (NFs) that improve the resistance to crack propagation in the cement-based composites.

When using NFs to improve the properties of cement matrixes, the optimal reinforcing effect is achieved when the NFs are individually dispersed in the host matrix. Poor dispersion resulting in agglomeration of the nanofiller leads, in turn, to the formation of stress concentration, from which a crack can start developing. Most carbon-based nanofillers, such as carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs), are *hydrophobic*, which poses a challenge for dispersing them in the *hydrophilic* cement matrix. This problem is usually addressed by sonicating an aqueous medium containing the carbon-based nanofiller in the presence of a surfactant prior to its mixing with the cement powder. However, the nanofiller will dramatically increase the viscosity of the cementitious composite, thereby reducing its workability. This problem is commonly dealt by the addition of a superplasticizer (SP).

In the present work, we investigated four NF systems namely: CNTs, GNPs, and their hydrophilic versions graphene oxide (GO) and functionalized CNTs (f-CNT). This systematically study would isolate the effects of the NF *dimensionality* [namely, 1D (CNT or f-CNT) vs 2D (GNP or GO)] and *compatibility* (oxidized, non-oxidized) on the mechanical properties of the cement nanocomposites. In addition, we optimized the NF loading for maximal enhancement in the mechanical strength for each type of NF. The mechanical properties enhance with the increased NF loading up to a certain limit called optimal NF concentration (ONC) and beyond this, the properties deteriorate gradually.

RESULTS AND DISCUSSION

1.1 Mechanical properties

The influence of incorporating NFs at various concentrations on the compressive and flexural strengths of the nanocomposites is shown in Figure 1. Both compressive and flexural strengths increased up to the ONC and then deteriorate with further increase in the NF concentration. This behavior is typical of NFs in cementitious matrixes. The decrease in the compressive and flexural strengths beyond the ONC is due to agglomeration of the nanoparticles, leading to the formation of weak points in the hardened matrix. Under loading, these weak points can become focal points of failure [1].

The enhancement in compressive strength of the composites relative to the plain cement paste without NFs (PC) is presented in Figure 1a. An enhancement of ~30% in the compressive strength was obtained for all the NFs, and for most of them at an ONC loading of 0.1 wt% (Figure 1a), which was independent of the NF type. GO showed the same compressive strength enhancement at a lower loading of 0.05 wt%. While all NFs showed similar enhancement of the compressive strength measurements, a wide spectrum of ONC values characterized the enhancement in flexural strength measurements (Figure 1b). For the flexural strength, GO demonstrated the best reinforcement, with 62% enhancement at a very low ONC value of 0.025 wt% (Figure 1b), while the CNT- and GNP-based composites showed enhancements of 49% (ONC = 0.05 wt%) and 44% (ONC = 0.1 wt%), respectively. The f-CNT showed an enhancement of as little as 35% at an ONC value of 0.05 wt%.

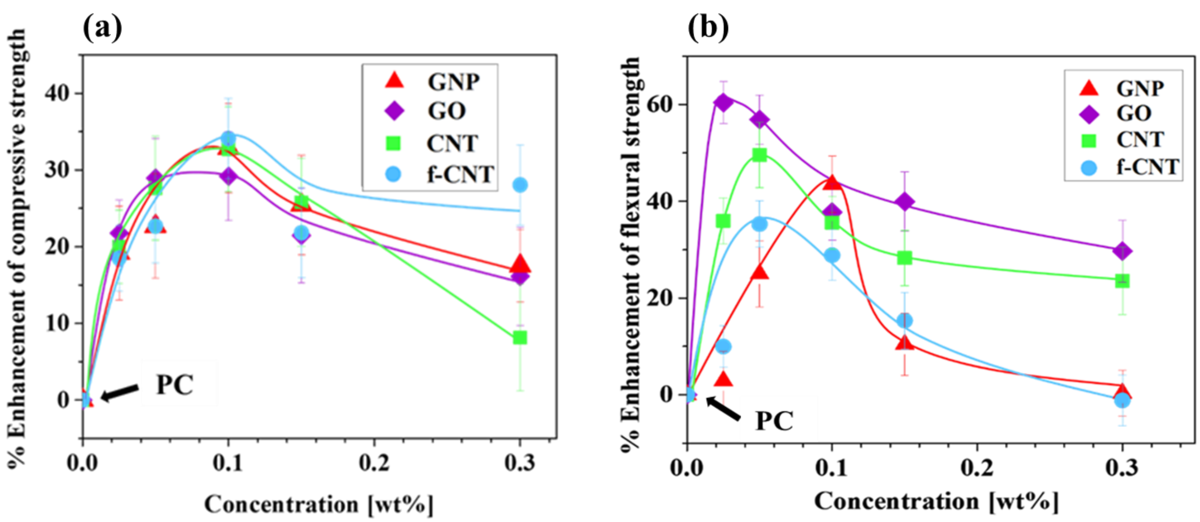

Figure 1. *Enhancement of (a) compressive strength and (b) flexural strength of hardened composites as a function of NF concentration relative to plain cement paste. The lines are drawn as a guide for the eye. [SP] = 0.2 wt% for all examined systems. The systems were examined at age for 14 days. The compressive strength (cubes:15×15×15 mm^2) of the PC was 44 MPa and flexural strength (prisms:8×8×60 mm^2) 7 MPa.*

The effect of the NF compatibility (hydrophobic-hydrophilic) with the hydrophilic cement matrix was examined while keeping the dimensionality (1D or 2D) constant. The compatibility of the oxidized NFs, f-CNT and GO, with the aqueous cement matrix was superior to that of the non-oxidized nanocarbons, CNT and GNP. For the 1D nanofillers, it was expected that the functionalization of CNT would substantially enhance the interaction of the NF with the cement matrix, leading to better mechanical performance. Nevertheless, f-CNT conferred only a relatively low enhancement of 35% in the flexural strength as compared to the 49% enhancement conferred by CNT (Figure 1b). A possible reason for this finding could be the introduction of defects into f-CNT during the functionalization procedure. The induced defects also made the f-CNT more prone to breakage under mechanical agitation (ultrasonication and mixing) [2]. For the 2D NFs, GO gave far better enhancement (62%) and at a lower ONC (0.025 wt%) than GNP. GO showed better compatibility with the cement matrix due to the presence of oxygen functional groups in higher amount (40.1 vs. 3.6%).

Evaluating the effect of NFs dimensionality at a given degree of oxidation gave the following findings. For the hydrophobic nanofillers CNT and GNP, the 1D CNT exhibited better flexural reinforcement compared to the 2D GNP, due to the cylindrical shape and the higher aspect ratio of the particles, which contribute to bridging nano-cracks [3]. For the hydrophilic NFs GO and f-CNT, the 2D GO exhibited higher flexural enhancement compared to the 1D f-CNT (62% vs 35%). It was expected that functional groups in the f-CNT would make it more compatible with the cement matrix, thereby providing greater enhancement in mechanical properties, but f-CNT was found, in fact, to be less effective. Again, a possible explanation is that the functional groups of f-CNT weaken the nanotubes, which become prone to shortening upon sonication and mixing. The suggested effect of functionalization in GO and f-CNT is depicted schematically in figure 2. For GO, the oxygen functional groups contribute to reducing the number of layers in the material (leading to a high aspect ratio and therefore more efficient reinforcement). In contrast, for f-CNT, the functionalization becomes counterproductive, as the nanotubes tend to break due to the introduced defects; the shorter f-CNTs so formed are less effective in enhancing the mechanical properties of the composites.

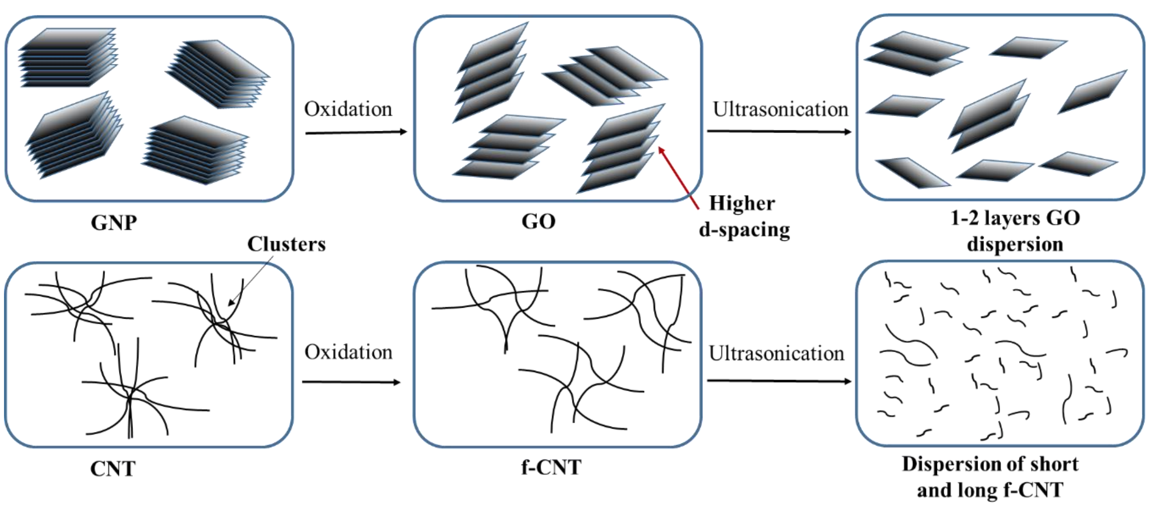

Figure 2. *Schematic representation of stages of functionalization and dispersion of GNP (top) and CNT (bottom).*

SUMMARY AND CONCLUSIONS

- The effect of the nanofillers on the mechanical properties of the hardened composites was evident in both the compressive strength and the flexural strength. All the nanofillers conferred the same enhancement in compressive strength at the same ONC, with the exception of GO, which gave the same enhancement at half the loading.

- In contrast, the flexural strength of the cement-based composites was strongly influenced by both the dimensionality and compatibility of the nanofillers. GO – giving 62% enhancement of the flexural strength – was found to be the best reinforcing agent among the four nanofiller materials due to its compatibility with the cementitious paste and its high aspect ratio.

- GO was followed by the 1D CNT, with 49% enhancement, and then by GNP, with 44% enhancement. f-CNT was found to be less effective than CNT, as the functionalization weakened the nanotubes, causing them to break during mechanical agitation.

In summary, –graphene oxide (2D-GO) provided the highest efficiency combined with the lowest ONC, making it an ideal filler for cementitious systems. GO is, however, much more expensive, making Graphene nanoplatelets (2D-GNP) the most cost effective alternative, as it provides 75% of the GO enhancement.

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