Research Article

An Effective Method for Hybrid CNT/GNP Dispersion and Its Effects on the Mechanical, Microstructural, Thermal, and Electrical Properties of Multifunctional Cementitious Composites

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This paper reports a study undertaken to achieve a compatible and affordable technique for the high-quality dispersion of carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) in an aqueous suspension to be used in multifunctional cementitious composites. In this research work, two noncovalent surfactants with different dispersion mechanisms (Pluronic F-127 (nonionic) and sodium dodecylbenzene sulfonate (SDBS) (ionic)) were used. We evaluated the influences of various factors on the dispersion quality, such as the surfactant concentration, sonication time, and temperature using UV-visible spectroscopy, optical microscopic image analysis, zeta potentials, and particle size measurement. The effect of tributyl phosphate (TBP) used as an antifoam agent was also evaluated. The optimum suspensions of each surfactant were used to produce cementitious composites, and their mechanical, microstructural, electrical, and thermal behaviors were assessed and analyzed. The best dispersed CNT+GNP aqueous suspensions using Pluronic and SDBS were obtained for concentrations of 10% and 5%, respectively, with 3 hours of sonication, at 40°C, with TBP used for both surfactants. The results also demonstrate that cementitious composites reinforced with CNT+GNP/Pluronic showed better mechanical performance and microstructural characteristics due to the higher quality of the dispersion and the increasing hydration rate. Composites prepared with an SDBS suspension demonstrated lower electrical and thermal conductivities compared to those of the Pluronic suspension due to changes in the intrinsic properties of CNTs and GNPs by the SDBS dispersion mechanism.

1. Introduction

Various types of multifunctional cementitious composites employing carbon fillers have attracted widespread attention due to their potential applications, including monitoring, thermal management, and transportation [1–4]. Among carbon fillers, carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) are the most widely used fillers to improve the mechanical, microstructural, electrical, and thermal behavior of composites due to their unique properties, including their small size, low density, high stiffness, high strength, and excellent electronic and thermal conductivity [5]. CNTs and GNPs can act as a nucleation agent and raise the hydration rate in cementitious composites [6]. Graphene is a 2D monolayer of sp²-hybridized carbon atoms arranged in a hexagonal packed lattice structure, and CNTs are 1D nanoscale tubes with an empty inner cavity that consists of single or multiple graphite atomic layers that are curved back on themselves [5, 7].

The high aspect ratio and large specific surface area of GNPs lead to a high contact area between composites and nanofillers and cause a maximized transferred stress and phonon transference from the matrix to the nanofillers. Hence, GNP-reinforced composites can be expected to
exhibit better mechanical, thermal, and electrical behavior even in comparison to CNTs [8]. However, in many cases, the potential applications of GNPs and CNTs are limited due to their high aspect ratio and large specific surface, which leads to large van der Waals forces and strong π-π interactions originating entanglement and agglomeration [9]. This is particularly important in multifunctional cementitious composites that normally use high concentrations of nanofillers to obtain higher electrical or thermal efficiency [10] (causing agglomerate formation and reducing their mechanical and microstructural performance [11]), since the physical properties are of significant importance in multifunctional cementitious composites [12].

Recently, several studies have been conducted to measure the CNT+GNP hybrid effects on multifunctional polymeric composites. The results show an improvement in the mechanical, microstructural, electrical, and thermal performance in comparison to their individual usage. Hence, the synergic effects of CNT+GNP combinations can decrease the required concentration of carbon nanomaterials (CNMs) by reducing the percolation threshold and subsequently significantly alleviating concerns regarding the costs and formation of porosities [8, 9, 13, 14]. Although no study has been found on the development of multifunctional cementitious composites of CNT+GNP combinations, we expect similar assumptions for this type of matrix. The combination of 1D (CNT) and 2D (GNP) nanoparticles with a high aspect ratio can increase the electron quantum tunneling effect as well as the percolation mechanism. CNT+GNP combinations can increase the hydration rate more than each would individually, due to the larger specific surface area that acts as a nucleation agent [6, 15]. They can also fill a wider range of micro- and nanopores, which leads to denser microstructures and bridges the hydration products of cement. However, a compatible and effective technique is required for the dispersion of CNT+GNP combinations in cementitious matrices, due to their agglomerate potential.

Therefore, our present study proposes a compatible and affordable method for the high-quality dispersion of CNT+GNP in multifunctional cementitious composites. Various chemical, biological, and physical techniques, such as high shear mixing, ultrasonication, ball milling, plasma, calendaring and irradiation methods, and noncovalent and covalent functionalization, have been extensively studied to modify and improve GNP and CNT dispersion in various matrices [16–25]. Although they often have an adverse effect on nanoparticles and/or composite features, preparing dispersed CNT and GNP suspensions through the noncovalent functionalization method does not alter the inherent optical, electrical, or mechanical properties of these nanoparticles. CNTs and GNPs are commonly dispersed along this route using different surfactants, aromatic small molecules, polymers, the endohedral method, and biomacromolecules [10, 24–42].

Currently, Pluronic F-127 (PF-127) is receiving increased attention among the different surfactants due to its lower toxicity and higher biocompatibility compared to other surfactants [43–47]. Pluronic F-127 (PF-127) is a nonionic triblock copolymer consisting of a core hydrophobic chain of polyoxypropylene (PPO) flanked by two polyoxyethyl-
Aldrich (Portugal) [59]. Their chemical structures are presented in Figure 3 [59, 60].

Ordinary Portland cement type I and CEN Standard sand (EN 196-1 and ISO 679:2009) from the SNL company were used to prepare cementitious composites (mortar). The particle size distribution of the sand and chemical composition of the ordinary Portland cement (OPC) are shown in Tables 2 and 3 [61].

2.2. CNT+GNP Dispersion. We dispersed 1% of CNT+GNP (wt of water) in aqueous solution by 5%, 10%, and 15% of each surfactant. The surfactant was first added to the water and mixed for 1 hour using a magnetic stirring mixer with a speed of 800 rpm/min. CNT+GNP was then added to the solution and stirred for one additional hour. The samples were then placed in a sonicator bath (Crest Ultrasonicator, CP 230T) for 1, 2, and 3 h, at 45 kHz frequency and 80 W power, at different temperatures.

A digital temperature regulator (NESLAB RTE-111 MP) was used to adjust the temperature during the ultrasonication process with a circulation system through a radiator and sensors. The TBP was completely dissolved in water before the addition of the surfactant.

2.3. Cementitious Composite Fabrication. Plain and CNT+GNP-reinforced specimens were prepared by mixing optimized CNT+GNP aqueous suspensions with ordinary Portland cement and standardized sand, using a laboratory mixer, following the EN 196-1:1994 standard. In all samples, a cement-to-water ratio of 0.5 was used. At first, the required amount of cement (450 g) was poured in the mixer’s stainless steel bowl in order to prepare the mortar mixtures. Then, the prepared CNT+GNP suspension with 125 g of water was added to the cement and the required amount of sand (1350 g), and the remaining 100 g of water was poured into the mixing machine’s hopper. The mixer was then run for 1.5 min, with a stainless steel blade rotational speed of 140 m/min, followed by a 30 s timeout, and then run at 285 m/min for another 2.5 min. The mixture was placed into 160 mm × 40mm × 40mm (for the capillarity test) prismatic molds and placed on a jolting machine for 1 min for vibrating compaction. The molds were placed in a humid atmosphere (90%) for 24 h, and then, the samples were demolded and kept under water for 28 days. Two copper meshes of 40mm × 50 mm were embedded in the cementitious composite as electrodes, at 5 cm from the middle of the specimen, to measure the electrical behavior.

2.4. Characterization of CNT+GNP Aqueous Suspensions. Different techniques were used for characterizing various parameters of the prepared CNT+GNP suspensions.

2.4.1. UV-Visible Spectroscopy. Due to the additional absorption caused by 1D van Hove singularities, the dispersed carbon nanotubes and graphene nanoplatelets in aqueous suspensions are active in the region of UV-Vis [28, 62, 63]. Hence, we used UV-Vis spectroscopy (Shimadzu, UV 2401 PC) to evaluate the dispersed CNT+GNP concentrations in different aqueous suspensions. The mixture was placed into 160 mm × 40mm × 40mm and 40mm × 40mm × 40mm (for the capillarity test) prismatic molds and placed on a jolting machine for 1 min for vibrating compaction. The molds were placed in a humid atmosphere (90%) for 24 h, and then, the samples were demolded and kept under water for 28 days. Two copper meshes of 40mm × 50 mm were embedded in the cementitious composite as electrodes, at 5 cm from the middle of the specimen, to measure the electrical behavior.

2.4.2. Zeta Potential and Particle Size Measurement. The zeta potential and bundle size of the carbon nanomaterials (CNMs) are extremely active in the wavelength region between 200 and 1200 nm due to the quenching of photoluminescence, which results in a weak and wide signal [49]. A solution with the same concentration of the surfactant agent was used as the blank sample to eliminate the peaks provided by the surfactant.
bundle size of CNM in aqueous suspensions; however, this technique is more accurate for perfectly spherical particles [49, 64, 65]. The results of CNM particle size determinations may highly be affected by their orientation toward the laser source and the combined morphology due to their high aspect ratio. Therefore, the analysis of the CNM particle size results was performed while considering these factors. The zeta potential ($\zeta$) was determined using Equation (1) and the Smoluchowski approximation from electrophoretic mobility ($\mu$).

$$\mu = \frac{\zeta \varepsilon_m V}{4\pi \eta D},$$

Table 2: Particle size distribution of the sand [61].

| Mesh size (mm) | 0.08 | 0.16 | 0.5 | 1   | 1.6 | 2   |
|---------------|------|------|-----|-----|-----|-----|
| Cumulative retained (%) | 99 ± 1 | 87 ± 5 | 67 ± 5 | 33 ± 5 | 7 ± 5 | 0   |

Figure 2: Morphology of (a) the CNT and GNP dry mix, (b) CNTs, and (c) GNPs.

Figure 3: The chemical structures of (a) Pluronic F-127, (b) sodium dodecylbenzene sulfonate (SDBS), and (c) tributyl phosphate (TBP).
where \( \eta \) is the viscosity of the solution, \( V \) is the applied voltage, \( D \) is the electrode separation, and \( \epsilon_{m} \) is the dielectric constant of the medium.

### 2.4.3. Optical Microscopy and Image Analysis

In order to monitor the carbon nanotubes and graphene nanoplatelet agglomeration presence in the aqueous suspensions and quantify the area of agglomeration, we used optical microscopy. For this purpose, a water suspension drop was analyzed through deposition on a glass plate and covered with a coverslip. Visual inspection was performed with 10x, 20x, and 50x magnifications, while for quantification analysis of the agglomeration area, 10x magnification was used. In this route, three drops were taken as samples from each aqueous suspension; the photos were prepared accurately by microscope software to completely cover the drop area. The samples’ optical micrographs were investigated with ImageJ software. The total area of agglomeration was computed by the summation of the total agglomerate area measured for a sample, divided by the total analyzed image area for each drop. The final amount of the agglomeration area was obtained from the average of three drops and expressed as a percentage with standard deviation.

### 2.5. Characterization of the CNT+GNP Cementitious Composites

Flexural and compressive testing was carried out according to the BS EN 196-1:1995 standard. The apparent porosity, dry bulk density, and capillary water absorption of the samples were measured as stated by ASTM C20, BS EN 1015-3:1995, and BS EN 1015-18 standards. For evaluating the consistency of fresh cementitious composites, the diameters of the paste were measured by using a scanning electron microscopy (SEM-FEG, Nano SEM NOVA 200, FEI) using an accelerated voltage of 10 kV and the secondary mode of the electron after coating with an Au-Pd thin film (30 nm), in a high-resolution sputter coater (Cressington 208HR), to investigate the microstructure.

We used a thermogravimetric analyzer (TGA, PerkinElmer) in a nitrogen atmosphere (100 mL/min), at a heating rate of 10°C/min up to 1000°C and energy dispersive X-ray analysis (EDX) with 1.8 nm at 3 kV (Helix detector) of vacuum resolution. The EDX tests were carried out from the cement hydration product accumulation. The graphs were obtained by means of at least five different points of analysis for each specimen. The nondestructive ultrasonic test was performed for microstructural evaluation according to the BS EN 12504-4 standard from Pundit Lab, using the ultrasonic test device H-2984 through two probes along the longitudinal transverse axis. The electrical resistance of the specimens was measured with an Agilent 34461A multimeter, after drying at 34°C for 72 hours. A portable thermal camera, model FLIR 60BX, with a resolution of 320 × 240 pixels and thermal sensitivity < 0.045°C with a temperature range from -20°C to +650°C was used to evaluate the thermal conductivity of the specimens. Photographs were taken after heating the samples at 70°C for 72 hours. In this route, surface calibration was done before infrared thermography by measuring the emissivity and reflected temperature (ISO 18434-1:2008).

## 3. Results and Discussion

### 3.1. Aqueous Suspension Characterization

#### 3.1.1. UV-Visible Spectroscopy

The UV-Vis absorption spectra diagrams for the CNT+GNP suspensions prepared with Pluronic F-127 and SDBS surfactants are displayed in Figures 4 and 5. The dispersion rate of CNT+GNP in liquid suspensions was directly related to the amount of energy absorbance; i.e., a higher energy absorbance indicated a more homogeneous dispersion of CNT+GNP particles within the liquid. Molecules containing bonding and nonbonding electrons \((n\text{-electrons})\) can absorb energy in the form of UV to excite these electrons to higher antibonding molecular orbitals [66]. The more easily the electrons are excited (i.e., a lower energy gap), the longer the wavelength of UV light that is absorbed. The maximum energy absorbances of SDBS and Pluronic suspensions occurred at 275 and 260 nm, respectively. This is likely due to the stronger bonding between Pluronic and CNT+GNP particles, which can guarantee the long-term stability of the liquid suspension.

Parveen et al. [49] also reported similar results for CNT/SDBS and CNT/Pluronic aqueous suspensions through long-term storage stability evaluation. The results also indicate that the increase in the sonication time for both types of surfactants and all concentrations improved the dispersion of the nanoparticles, but at different efficiency levels. The amount of energy absorbed in the SDBS aqueous suspension increased by an average of 17% for each hour of increased sonication time, while for Pluronic, the average was 9%. The sonication time was not increased by more than 3 hours in order to prevent adverse effects on the CNM structural quality, such as edge-type defects, reduction in the aspect ratio, and sp2 domain crystallinity (La), which can cause deleterious influences on the mechanical, electrical, and thermal properties. However, the optimum sonication energy for CNM dispersion can be higher than the 80 W power for 3 hours that was used in this study [67, 68].

Bath sonication dispersing techniques exfoliate GNFs or debundle nanotubes into individual plates or tubes and/or thinner bundles, which consequently are stabilized through electrostatic repulsions and/or the steric force of surfactants. During sonication, mechanical vibrations overcome the van der Waals interactions between the GNP or bundles of

### Table 3: Chemical composition and properties of ordinary Portland cement.

| Component | Value |
|-----------|-------|
| SiO₂      | 19.94 |
| Al₂O₃     | 4.76  |
| Fe₂O₃     | 3.38  |
| MgO       | 1.31  |
| CaO       | 63.93 |
| Na₂O      | 0.17  |
| TiO₂      | 0.24  |
| K₂O       | 0.44  |
| MnO       | 0.075 |
| P₂O₅      | 0.063 |
| SO₃       | 2.54  |
| LOI       | 2.97  |
| Fineness (m²/kg) | 360  |
| Specific gravity | 3.15 |
CNTs and provide high positional shear, particularly to the end of the GNP sheets or nanotube bundles. Once gaps or spaces at the bundle ends are formed, molecules of the surfactant are absorbed onto the surface of the nanoparticles instantly leading to their exfoliation. According to the unzipping mechanism [69], surfactant molecules have to settle among the small spaces into the bundle to exfoliate the tubes and sheets and to prevent them from reagglomeration. Hence, short-time ultrasonication in surfactant molecules with bulky hydrophobic groups (Pluronic) showed lower debundling efficiency due to being hindered in their penetration into the intertube or sheet regions. In the case of nonionic surfactants, these bulky hydrophilic groups demonstrated advantages for CNT and/or GNP dispersions likely due to the enhanced steric stabilization caused by longer polymeric groups. The results also demonstrate that an increase in temperature to a certain range (40°C) improved the dispersion of nanoparticles for both suspensions prepared by Pluronic and SDBS, likely by increasing the solvability of the surfactant molecules and the mobility of electrons. However, excessive temperature rises (more than 45°C) caused bond breakage as well as a change in the critical micelle concentration and led to temporary reagglomeration.

In a previous study conducted by Yan et al. [48], a stable and homogeneous aqueous suspension of 0.5% graphene was obtained at a low temperature (25°C) under ultrasonic irradiation with Pluronic F-127. Chen et al. [70] also found that a competent dispersion of graphene (0.56 mg mL⁻¹) could even...
be achieved at 165°C in a mixture of N,N-dimethylacetamide and water, via microwave. The results also indicate that the dispersion of CNT+GNP particles was strongly dependent on the surfactant concentration, and the best dispersion occurred with 10% of Pluronic and 5% of SDBS. SDBS is an ionic surfactant while Pluronic is a nonionic surfactant, and their interaction mechanisms with nanocarbon particles are different. In previous studies, Parveen et al. [49] observed that the use of 1% Pluronic for a 0.1% CNT concentration, 5% for 0.2% and 0.3% CNT, and 0.8% SDBS for 0.2% CNT resulted in highly homogeneous CNT dispersions. Yan et al. [48] also achieved a competent aqueous suspension with a 1% Pluronic concentration for 0.5% graphene.

By comparing these results with the present studies, the amount of the required surfactant for dispersing CNT and GNP particles in the hybrid combination appears much greater than the individual cases, in both types of ionic and nonionic surfactants. This is likely due to the combinations of carbon nanoparticles with different geometries (1D and 2D), which leads to an increase in the aspect ratio, as well as the specific surface area. Therefore, in this case, the contact surface between the CNMs was larger than that in the observed CNMs individually, which causes stronger van der Waals attractions and hinders the dispersive efficiency of the surfactant at low concentrations.

The effects of the CNM aspect ratio on the dispersion quality were also demonstrated by Goodman et al. [71] through the investigation of prepared aqueous suspensions with 1 wt% CNTs with a similar length and different diameter, dispersed by alkali lignin (AL), SDS, and CTAB. They observed that the amount of absorbance in the UV-Vis decreased more in the AL suspension when the CNT diameters were decreased from 50 to 8 (nm). These observations revealed that the aspect ratio demonstrated a more prominent effect on the CNT suspensions when AL was used as a surfactant. This reflects the differences in how these molecules adsorb onto the surface of CNMs.

In nonionic surfactants, such as AL and Pluronic, in contrast to ionic surfactants, such as SDS, ASBS, and CTAB, the \( \pi-\pi \) interactions are responsible for the surfactant molecule adsorption on the CNM surface. The lower aspect ratio of CNMs exhibited a lower surface curvature, which led to a stronger affinity to the -COOH and -OH groups due to a higher overlap between the \( \pi \) electrons. As a result, a higher amount of nonionic surfactant molecules is required for CNM individualization with a high aspect ratio. The interaction type and the nature of the surfactant and, consequently, the concentration are known to play a crucial role in the colloid phase behavior [72] as well as for the nanoparticles [73]. A stabilization mechanism of colloidal type particles is described in the theory of Derjaguin–Landau–Verwey–Overbeek, and this mechanism typically relies on a surface load presence that can be induced by surface group deprotonation or through ion adsorption from the solvent to the colloidal particle surface. A diffuse layer of counterions was attracted by the surface charge from the solvent and formed an electric double layer with a diffuse nature due to the Brownian motion. This can lead to an effective surface charge due to Coulomb repulsion among charged colloidal particles [11].

This mechanism can be applied to GNP and CNT by introducing a removable and temporary surface load through permitting the molecules of the surfactant to adsorb via the hydrophobic tails on the nanoparticle surface. An ion normally dissociates itself from the head of hydrophilic groups and serves as a counterion. Then, the adsorbed molecular ions have interactions with water [74]. The active charge signs and magnitude, through the zeta potential, are correlated with the double surface. This is an electrostatic potential of the bound tail group layer edge [11]. For dispersing carbon nanotubes, the concentration of the surfactant has to generally exceed the critical concentration of micelles [75, 76]. The concentration of the surfactant must be higher than the concentration of nanotubes. [11].

Regarding graphene dispersion, the latter condition is not always justified as some surfactants have better performance at concentrations below the critical micelle level while not exceeding the concentration of graphene [76]. The critical micelle concentration in the case of SDBS surfactants may also depend on the nanoparticle concentration [77, 78].

The quality of the dispersion and the individualization/exfoliation degree of GNP and CNT are normally measured by the zeta potential. In contrast to carbon nanotubes, this occurs for graphene nanoplatelets within two separate ionic surfactant groups: sulfides, such as SDBS, and other ionic surfactants. Since the zeta potential reflects the electrostatic potential at the edge of the bound ion layers, we assume that maximizing the surface charge in this layer can lead to the zeta potential increase [79]. Hence, the ionic surfactant SDBS with a low molecular weight can pack tightly on the GNP and CNT surface and disperse them with a low concentration.

In Pluronic, as a nonionic surfactant, the lack of Coulomb repulsion for preventing GNP and CNT aggregation is compensated for by steric effects. Therefore, the main factor determining the dispersibility of CNTs and GNP in aqueous suspension is the presence of branched and long polar (PEO) chains. This leads to efficiency enhancement by increasing the molecular weight of the surfactant [80]. This occurs due to the surfactant’s affinity of \( \pi \)-electrons to the benzene rings of the GNP and CNT, which can remain to an extent even after water elimination, in contrast to SDBS (Figure 6).

However, in dry mixes of CNT and GNP without the presence of surfactants, they are arranged in the form of individual spheres without interactions due to the van der Waals attraction forces between the CNTs and repulsion electrostatic forces between the GNP and CNT (Figure 2). This is important in the context of carbon nanoparticle refinement and purification from suspensions and can be considered one of the disadvantages of using Pluronic in comparison to SDBS.

3.1.2. Optical Micrograph Analysis. For the evaluation of the agglomerate total area, we analyzed CNT+GNP aqueous suspension optical micrographs and expressed the results as percentages (Table 4). Similar to the previous section, we observed that the dispersion quality was increased by increasing the surfactant concentration up to a certain
Beyond this level, a further increase in concentration led to a reduction in the dispersion quality and, consequently, to an increase in the agglomeration area. Hence, the optimum surfactant concentrations were 15% and 5% for Pluronic and SDBS, respectively, which provided the lower agglomeration area. However, these concentrations were higher than their critical micelle concentrations [49]. Further increases in Pluronic and SDBS concentrations above these optimal values not only represented a surfactant waste but also induced undesired effects. This is consistent with other studies reporting CNT or GNP aqueous dispersions with various types of surfactants [28, 71, 81].

**Figure 6:** Morphology of dry CNT+GNP extracted agglomerate from an aqueous suspension: (a) prepared by Pluronic F-127 and (b) prepared by SDBS.

**Table 4:** Agglomerate total area of various CNT+GNP aqueous suspensions.

| SDBS                  | Total area of agglomerates ± SD (%) | Pluronic F-127  | Total area of agglomerates (%) |
|-----------------------|-------------------------------------|-----------------|---------------------------------|
| 1%CG-1H-05%S          | 16.5 ± 0.95                         | 1%CG-1H-5%P     | 29.6 ± 1.27                     |
| 1%CG-2H-05%S          | 11.3 ± 0.61                         | 1%CG-2H-5%P     | 22.4 ± 0.93                     |
| 1%CG-3H-05%S          | 9.1 ± 0.48                          | 1%CG-3H-5%P     | 18.3 ± 0.81                     |
| 1%CG-1H-10%S          | 20.1 ± 1.08                         | 1%CG-1H-10%P    | 12.3 ± 0.77                     |
| 1%CG-2H-10%S          | 16.8 ± 1.1                          | 1%CG-2H-10%P    | 8.1 ± 0.96                      |
| 1%CG-3H-10%S          | 13.3 ± 0.72                         | 1%CG-3H-10%P    | 3.5 ± 0.62                      |
| 1%CG-1H-15%S          | 38.1 ± 1.36                         | 1%CG-1H-15%P    | 17.4 ± 0.87                     |
| 1%CG-2H-15%S          | 32.7 ± 1.09                         | 1%CG-2H-15%P    | 13.8 ± 0.95                     |
| 1%CG-3H-15%S          | 28.3 ± 1.22                         | 1%CG-3H-15%P    | 10.6 ± 1.14                     |
| 1%GC-05%S-1H+TBP      | 12.4 ± 0.84                         | 1%CG-1H-10%P+TBP | 10.1 ± 1.03                     |
| 1%GC-05%S-2H+TBP      | 9 ± 0.73                            | 1%CG-2H-10%P+TBP | 6.3 ± 0.79                      |
| 1%GC-05%S-3H+TBP      | 8.4 ± 0.66                          | 1%CG-3H-10%P+TBP | 2.9 ± 0.52                      |
| 1%GC-05%S-3H+TBP+45°C | 6.4 ± 0.71                          | 1%CG-3H-10%P+TBP+45°C | 2.1 ± 0.84                     |
| 1%GC-05%S-3H+TBP+40°C | 5.6 ± 0.5                           | 1%CG-3H-10%P+TBP+40°C | 1.2 ± 0.71                     |
| 1%GC-05%S-3H+TBP+25°C | 9.1 ± 0.94                          | 1%CG-3H-10%P+TBP+25°C | 5.7 ± 0.59                     |

Aqueous suspension without a surfactant

|                | Total area of agglomerates ± SD (%) | Pluronic F-127 | Total area of agglomerates (%) |
|----------------|-------------------------------------|----------------|--------------------------------|
| 0.5%CG-1H      | 88.3 ± 2.37                         |                |                                |
| 0.5%CG-2H      | 79.1 ± 1.61                         |                |                                |
| 0.5%CG-3H      | 67.6 ± 1.89                         |                |                                |

CG: CNT+GNP (%); S: SDBS (%); P: Pluronic F-127 (%); H: time of sonication (h); ±SD: standard deviation.
stable aqueous suspensions, a balance is reached between single CNMs and their bundles, which varies with the surfactant concentration. At low concentrations, the surfactant adsorption is limited and does not efficiently counterbalance the van der Waals-induced aggregation of GNP and CNT. When the surfactant amounts in the aqueous suspension are above a certain value, large micelles are formed around the bundles of CNMs and they exert an osmotic pressure creating a depletion-induced attraction [82]. Excessively increasing surfactant dosages at higher concentration levels than the critical micelle concentration can lead to nanoparticle reagglomeration due to changing the micelle geometry and even changing the viscosity of the aqueous suspension system. As mentioned before, in similar conditions for sonication, concentration, and temperature, the difference of the dispersion efficiency for different surfactants is closely related to their interactions with CNMs, which depends on the presence of benzene rings, the length of their alkyl chain, and the head group types. At the optimal concentrations, the individualized CNM degree in aqueous suspension is comparable among the various dispersions, with a significant increase on the order of Pluronic > SDBS, as indicated by their respective agglomerate areas.

Interestingly, the presence of TBP enhanced the dispersion of nanoparticles, likely due to the TBP molecular structure that contains three methyl branches. A methyl group is a hydrophobic alkyl functional group derived from methane (CH₄) by removing one hydrogen atom (CH₃-), and methyl groups are extremely reactive and capable of bonding covalently with other carbon atoms due to the free capacity of eight radical electrons [83]. However, TBP was added to the suspension as an antifoam agent for removing the bubbles that form on cementitious composites by Pluronic [49].

The optical micrograph analysis also showed the effect of temperature and the increasing sonication time on the nanoparticle dispersion improvement, which was obtained from the UV-visible spectroscopy. The aqueous suspension of 1% CNT+GNP with 10% Pluronic and 3-hour sonication time, at 40°C, with TBP, and the suspension of 5% SDBS with the same amount of TBP, temperature, and sonication time exhibited very low agglomerate areas (only 5.6% and 1.2%, respectively) indicating very competent dispersion qualities (Figure 7). Hence, these suspension systems can be considered to be the optimized suspensions prepared using SDBS and Pluronic. However, compared to the optimized Pluronic suspensions, the suspensions prepared using the optimized percentage of SDBS showed a higher agglomerate area.

### 3.1.3. Zeta Potential

As mentioned before, the stability of colloidal suspensions is frequently determined by their zeta potential, which indicates the magnitude of the electrostatic interactions between colloidal particles. Particles with a zeta potential higher than +15 mV or less than -15 mV are expected to be stable due to electrostatic considerations. However, colloidal suspensions with zeta potentials between +15 and -15 mV can also be stable if they are stabilized uninterruptedly [64].

The zeta potentials of the CNT+GNP suspensions are listed in Table 5.

The dispersions of 1% CNT+GNP in 5%, 10%, and 15% SDBS with 3-hour sonication showed zeta potentials of -48.6, -17.7, and -29 (mV), respectively. However, these amounts for Pluronic suspensions were approximately -2.9, -9.3, and -5.7 (mV), respectively. The addition of 5% of TBP over SDBS, with 3-hour sonication, obtained a -56.4 (mV) zeta potential, which supports the positive effect of TBP to improve CNT and GNP dispersion. Increasing the temperature to 40°C led to increasing the zeta potential to -71.9 (mV), which shows more colloidal particle stability for this suspension. However, the excessive increase in temperature decreased the quality of the CNM dispersion. Similarly, increasing the temperature up to 40°C for the 10% Pluronic prepared through 3-hour sonication with TBP led to the formation of more stable colloidal particles with a -23.1 (mV) zeta potential.

The high negative zeta potential for SDBS suspensions is due to the high negative surface charges of this surfactant. Consequently, due to the nonionic chemical structure of Pluronic, the CNT+GNP suspensions prepared by this surfactant presented lower negative zeta potential. Owing to nonelectrostatic and steric interactions, the Pluronic suspensions could also be stable. The polyoxyethylene (PEO) hydrophilic groups extend into the water while hydrophobic chains of polyoxypropylene (PPO) interact with the surfaces of the GNP and CNT. The exfoliation and stabilization of separated GNP and CNT happen as a result of steric hindrances that were induced by the long PEO chain.

The functionalized CNM zeta potential was relatively higher due to -COOH functional groups, which leads to the surface negative charge on GNP and CNTs.

### 3.1.4. The Average CNT+GNP Bundle Size

The average size of the CNM bundles and the polydispersity index (PDI) of the CNT+GNP suspensions, determined through DLS by measuring the hydrodynamic diameter, are presented in Table 6. The PDI is used as a scale to indicate the extent of the particle size distribution range, and the larger PDI demonstrates the wider molecular size spectrum. The results indicate that the particle sizes of CNT+GNP suspensions dispersed in 5%, 10%, and 15% Pluronic and SDBS were around 512, 328, and 389 nm and 491, 671, and 588 nm, respectively, which shows an optimum concentration around 10% for Pluronic and 5% for SDBS, as discussed before.

The small average size of CNM bundles in Pluronic suspensions, in comparison with SDBS ones, indicates the efficiency of the -COOH functional groups on the unbundling process. A lower particle size (219 nm) and lower PDI (0.315) were obtained for 10% of Pluronic, with 3-hour sonication with TBP at 40°C, showing low agglomeration and high quality of the dispersion. The average particle size and the amount of PDI in the SDBS-dispersed suspensions, at optimum conditions, were around 393 nm and 0.462, respectively.

### 3.2. Cementitious Composite Characterization

#### 3.2.1. Mechanical Microstructural Behavior

After obtaining the best dispersed mixed design for hybrid CNT+GNP
aqueous suspensions with each surfactant, the mechanical and microstructural properties of the reinforced cementitious composites were evaluated to determine their effects. The mechanical and microstructural parameters of the cementitious composites in different cases are shown in Figure 8 and Table 7. The results were obtained as the means of at least three specimens for each test performed. Reinforcing the cementitious composites with CNT+GNP/Pluronic suspensions led to a higher bulk density compared to CNT+GNP/SDBS. Consequently, the time required for an ultrasonic wave to pass and the apparent porosity values of the CNT+GNP/Pluronic-reinforced specimens were lower than those of the CNT+GNP/SDBS specimens.

The general trend of the results showed an improvement in the flexural and compressive strength of CNT+GNP/Pluronic-incorporated cementitious mortars. These results demonstrate more homogeneous and denser microstructures for the CNT+GNP/Pluronic-reinforced cementitious composites. The positive effects of the CNTs and GNP s on the improvement of the cementitious composite microstructures and their mechanical behaviors, including their flexural and compressive strength, have been reported in many previous studies [84–86]. The unique features of these 1D and 2D nanomaterials with high aspect ratios enhance the microstructural and the mechanical properties of the cementitious composites, generally, by reducing the microporosities, accelerating the hydration process, and bridging the cement hydration product mechanism, which is highly controlled by the CNM aspect ratio and dispersion technique [6, 87, 88].

Therefore, we concluded that the differences between the cementitious composite mechanical and microstructure parameters in the cases of CNT+GNP/Pluronic and CNT+GNP/SDBS were due to the dispersion quality and the secondary effects of the surfactant on the hydration process and/or on the nanoparticle features and/or structures. However, considering the mechanical and microstructural results for the nonreinforced composites prepared with only Pluronic and SDBS (without CNMs), the presence of these two surfactants did not demonstrate adverse effects on the cementitious composite features, at least after 28 days of hydration and for the tested concentrations.
Large agglomerations of CNTs and GNPs, due to lower quality dispersions in CNT+GNP/SDBS-reinforced cementitious composites, led to the formation of microporosities. The CNM agglomerated between the growing units of C-S-H to create large gaps among them, which prevented their physical connection (Figure 9(a)). This is especially important for the GNPs, which are larger in size. As can be seen in Figure 10, the CNTs showed a higher reinforcement capacity to improve the bridging behavior for the pull-out strength with a better dispersion. The presence of large GNP agglomerates between the hydration products produced a nanoscale discontinuity when applying stress, which may facilitate the formation of microcracks.

However, well-dispersed GNPs were more able to anchor the neighboring C-S-H clusters and bridge the voids between them. The large specific surface area of GNPs led to a high contact area with the hydration products and maximized the stress transferring, delaying the microcrack and macrocrack propagation. In contrast to SDBS, the CNT +GNP/Pluronic-reinforced cementitious composites contained lower porosities due to the better dispersion of the nanoparticles.

The results of the capillary water absorption shown in Figure 11 also emphasize this. According to the slope of the capillarity result graphs, the rates of capillarity water absorption in the GNP+CNT/Pluronic-reinforced specimens were significantly lower than those in the GNP+CNT/SDBS specimens.

However, the rates of capillary water absorption for CNT +GNP-reinforced composites prepared by both Pluronic and SDBS were lower than those for the plain composite.

The presence of both surfactants increased the flowability of the plain mortar. According to Table 7, the flow values of the specimen with 10% individual Pluronic increased by 9% and 5%, respectively, compared to those of the SDBS and the plain cases. The chemical structure of Pluronic F-127 contains hydrophilic PEO (polypropylene oxide) side chains similar to commonly used superplasticizers of polycarboxylate, as mentioned before. Polypolyethylene oxide side chains were reported to be the main chemical components of these
superplasticizers that are responsible for the cement particle
dispersion and the improvement of the flowability [89].

It is generally accepted that the cement paste fluidity is
directly pertinent for the performance of hardened cement
(such as the pore structure and strength) [90]. However,
the presence of CNT and GNP reduced the flowability of
cementitious composites [49, 50]. Due to the large surface
area of GNPs and CNTs, they can absorb water molecules;
hence, a significant reduction occurred in the free water con-
tent needed for lubrication, and this led to a reduction in the fluidity. For this reason, the flowability of CNT+GNP-rein-
samples prepared with Pluronic and SDBS decreased by 27% and 36% compared to that of the plain cementitious
composite, respectively.

Generally, cement hydration products have a strong ten-
dency to form on the surface of CNTs and GNPs due to the
large specific surface area accompanied by a high amount
of oxygen functional groups, which serve as nucleation sites
[15, 91]. Although the hydration CaS and Ca2S produce C-S-H
gel and C-H crystals, any deficiency in the water content
surrounding these silicates can slow down the hydration
reactions [91]. This is especially true around agglomerates
caused by the lower quality of dispersion (Figure 9(a)).

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caused by the lower quality of dispersion (Figure 9(a)).

High-magnification SEM images (Figure 9(b)) of the
reinforced cementitious composite with CNT+GNP/Pluronic
investigated by EDX tests indicate that CNTs and GNPs
were embedded appropriately within the hydration products,
in contrast to the CNT+GNP/SDBS-reinforced specimens. This
is due to the higher quality of the dispersion and the
presence of the PEO side chains, which are preferentially
adsorbed on the surfaces of the C-S-H gel as well as along
the CNT lengths and GNP surfaces [91]. In the early periods
of hydration, this causes a slight discoloration of the gra-
phene and increases the CNT diameters due to the extremely
cementitious composite carbonation, which was observed ascribed to calcium carbonate coming from the clinker and attributed to the dehydroxylation of CH. Fourth, the last decay was observed between 105 and 400 °C.

The results of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for different cementitious cases are shown in Figure 12. From the TGA curve, the first decay is observed up to 105°C, which can be attributed to the removal of the moisture and free water of the cementitious composite samples. The second decay was observed between 105 and 400°C, due to the dehydration of the chemically bonded water existing in the hydrates, i.e., ettringite, carboaluminates, and C-S-H. The next major decay was found between 400 and 550°C, which can be attributed to the dehydroxylation of CH. Fourth, the last decay was ascribed to calcium carbonate coming from the clinker and cementitious composite carbonation, which was observed between 600 and 800°C [92, 93].

The results indicate that the amounts of hydration products in the CNT+GNP/Pluronic-reinforced specimens were more than those in the CNT+GNP/SDBS specimens; however, the hydration product amounts in both cases were more than those in the plain sample.

In the case of the reinforced cementitious composites with MWNTs, Konsta-Gdoutos et al. [94, 95] reported similar findings. They observed, by nanoindentation tests, that multiwall carbon nanotubes could increase the formation of a larger amount of high-stiffness calcium silicate hydrate gel and decrease the nanoscale porosity owing to the gap filling between gels of C-S-H through CNTs. Therefore, based on the results of the previous research [88] and from the present study, one of the major effects of nanoparticles in the cementitious composite is to increase the hydration rate. The energy-dispersive X-ray spectroscopy (EDX) results for cementitious composites are shown in Figure 13. These results were obtained from the mean of five different points of cement hydration product accumulation for each case.

Despite higher carbon concentration in the place of cement hydration product accumulation for CNT+GNP/SDBS-reinforced specimens compared to CNT+GNP/Pluronic specimens, lower amounts of hydration products were observed. The reason for this is likely the changing nanoparticle features and/or structures due to the SDBS dispersion mechanism. This statement could be verified by evaluating the electrical behavior.

3.2.2. Electrical Resistance. The electrical resistances of specimens after 28 days of hydration were measured using a digital multimeter (Table 8). Since humidity, as an electrically conductive factor, has a relatively significant effect on the cementitious specimen electrical resistance changes [96, 97], the electrical resistance was measured after drying the specimens at 34°C for 72 hours. The electrical resistances of individual CNT- and GNP-reinforced specimens were also measured using a similar method in order to compare with that of hybrid CNT+GNP.

The electrical resistances of the reinforced specimens with CNT+GNP/SDBS, CNT/SDBS, and GNP/SDBS were improved by 71.73%, 66%, and 53.2%, respectively, in comparison to that of the plain mortar, while the results are 60.94%, 70.3%, and 64.3%, respectively, for the Pluronic-reinforced specimens. According to the previous section’s discussion, CNT+GNP/SDBS-reinforced specimens contained more and larger CNM agglomerations compared to CNT+GNP/Pluronic specimens due to the lower dispersion quality. Although the existence of a certain agglomeration quantity can act as a key factor in raising the conductivity significantly and reducing the percolation threshold value [11], the cementitious composite reinforced with CNT+GNP/Pluronic showed higher electrical conductivity.

Therefore, the decreasing electrical conductivity of the CNT+GNP/SDBS-reinforced composites is likely due to the nanoparticle features and/or structure changes provided by the SDBS dispersion mechanism.

In previous studies, significant deterioration in the electrical properties was also reported due to disturbances of the graphene/CNT surface π-electron delocalization.

The synergic effects of hybrid CNT+GNP specimens decreased the electrical resistance of the cementitious composites more than what was observed for individual CNT or GNP utilization, as was expected.

A comparison of the CNT+GNP effects on the electrical conductivity of cementitious composites with previous studies that used individual CNT, graphene, or other carbon-based particles (Table 9) clearly indicated that the hybrid combination of CNTs and GNPs was more efficient to create a conductive path among the cementitious composites as was expected. This combination can reduce the percolation threshold and enhance the quantum tunneling effect due to the 1D and 2D geometrical shapes.

3.2.3. Thermal Photography. In this study, for the first time, thermal photography was used for the evaluation of CNT+GNP dispersion in hardened specimens through the difference between the thermal diffusion coefficient and the thermal conductivity. Thermal photography of cementitious
composite specimens of the same size (160 mm × 40 mm × 40 mm) in different periods of cooling time is shown in Figure 14, after heating to 70°C, for 72 hours. As expected, reinforced CNT+GNP cementitious composite samples absorbed more heat due to the high thermal conductivity [98]. They also lost heat more rapidly over time due to the high thermal transfer coefficient compared to the plain composites. As shown in Figures 14(a) and 14(b), the CNT+GNP/Pluronic-reinforced specimens lost heat more rapidly in comparison to the CNT+GNP/SDBS specimens. This was likely due to disturbances in the delocalization of π-electrons on the nanoparticle surfaces, which were caused by the SDBS dispersion mechanism. This verifies the previous results.

Nonhomogeneous heat distribution caused by considerable large agglomerations on CNMs for CNT+GNP/SDBS composites indicated the inappropriate dispersion of nanoparticles in the hardened sample, as discussed before.

4. Conclusion

In this work, we conducted an extensive experimental research study on hybrid CNT+GNP dispersion techniques using a high concentration of noncovalent surfactants and aqueous suspensions. For this purpose, a nonionic Pluronic F-127 and ionic SDBS surfactants were studied in 1 wt% of CNT+GNP (0.5% CNT and 0.5% GNP) dispersions,
to analyze the effect of factors, including the surfactant concentration, sonication time, temperature, and the use of an antifoam agent (TBP).

We evaluated the effects of optimized CNT+GNP suspensions prepared by SDBS and Pluronic on the mechanical, electrical, and thermal properties of cementitious composites by various tests. UV-spectroscopy and optical microscopy image analysis indicated that high-quality CNT+GNP dispersions with a low agglomeration area (less than 1.2%) were achieved with 10% Pluronic (wt% of nanoparticles), with 3-hour
sonication, at 40°C, with the presence of tributyl phosphate (50 wt% of the surfactant as an antifoam agent). The optimum percentage of SDBS (5 wt%) led to a lower dispersion quality and a higher agglomeration area (5.6%).

Increasing the temperature up to 40°C, as mentioned before, played a positive role in the dispersion of suspensions prepared with Pluronic or SDBS; however, higher temperatures led to the reagglomeration of CNT+GNP. The presence of TBP significantly reduced the agglomeration area. Increasing the sonication time improved the dispersion in both CNT+GNP/Pluronic and CNT+GNP/SDBS aqueous suspensions, which was also confirmed by the zeta potential and particle size measurements. SEM photographs showed that CNTs and GNPs in prepared aqueous suspensions using Pluronic presented better interactions between each other, even after water elimination, when compared to CNT+GNP/SDBS suspensions.

Cementitious composites reinforced with hybrid CNT+GNP showed enhanced mechanical, microstructural, electrical, and thermal properties, for both the Pluronic and SDBS dispersion cases. However, the general result trends demonstrate higher efficiency for CNT+GNP/Pluronic due to the compatible mechanism and the dispersion quality.

The results obtained for the dry bulk density, water content, ultrasonic nondestructive test, and capillarity water absorption also indicate denser microstructures for the CNT+GNP/Pluronic-reinforced composites due to the lower agglomeration caused by the high-quality dispersion. The TGA, DSC, and EDX results show that dispersed CNT+GNP/Pluronic increased the hydration rate due to the nucleation agent effects of CNTs and GNPs and the oxygen functional groups of graphene, which acted as growing points for hydration products. SEM image analysis showed that CNMs were completely embedded in the hydration products, bridging them. However, this is not observed for CNT+GNP/SDBS due to the lower quality dispersion and also to the changing CNM features and structures caused by the SDBS dispersion mechanism. For the same reason, CNT+GNP/SDBS-reinforced specimens also presented lower electrical and thermal conductivities compared to those reinforced with CNT+GNP/Pluronic.

**Data Availability**

Requests for all types of data used to support the findings of this study, after the publication of this article, will be
considered by the corresponding author, subject to obtaining permission from the owners.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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