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Investigation of the Electrical Properties of Graphene-Reinforced Geopolymer Composites †

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Abstract: Geopolymer composites provide an environmentally friendly alternative to cement-based composites in the construction industry. Due to their distinctive material composition, geopolymers also exhibit electrically conductive properties, which permit their application as a functional material. The current work aims to study the distinctive electrical properties of fly-ash-based geopolymer composites. Varying dosages of graphene oxide (i.e., 0, 0.1, 0.2, 0.3, 0.4% (by wt. of binder)) were introduced into the geopolymer matrix to enhance electrical conductivity. While GO (graphene oxide) is typically less conductive, the interaction of GO sheets with the alkaline solution during geopolymerisation reduced the functional groups and produced cross-linked rGO (reduced graphene oxide) sheets with increased mechanical and electrical conductivity properties. Solid-state impedance spectroscopy was used to characterize the electrical properties of geopolymer composites in terms of several parameters, such as impedance, electrical conductivity and dielectric properties, within the frequency ranging from 10^1 to 10^5 Hz. The relationship between the electrical properties and graphene oxide reinforcement can effectively establish geopolymer composite development as smart materials with desirable functionality. The results suggest an effective enhancement in electrical conductivity of up to 7.72 × 10^{-13} Ω·mm^{-1} and the dielectric response performance of graphene-reinforced fly-ash-based geopolymer composites.

Keywords: geopolymer composite; graphene; electrical conductivity; electrical property; microstructure

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1. Introduction

Geopolymers—at the micro-level—are primarily composed of amorphous materials of the long matrix, cross-linked polymer chains of tetrahedral AlO_4 and SiO_4 units [1,2]. Geopolymers are usually dielectric materials due to the silica content and alkali metal ions, which could work as ionic conductors via an applied electric field [3,4]. Although pure geopolymers are electrically conductive due to the availability of water molecules and hydroxide in their composition, the open pore networks in the matrix produce conductivity [5,6]. Therefore, the introduction of filler materials becomes predominately necessary to improve electrical conductivity [7,8]. The most common additives preferred for the

fabrication of conductive geopolymer composites include carbon and metallic fillers, such as carbon fibres [5,9], nanotubes [10,11], graphite [8], graphene derivatives [7,8], steel fibres, etc.

Several research projects have been carried out to study and comprehend the influence of conductive fillers in the geopolymer matrix system. In one such examination, Payakaniti et al. optimized the inclusion of carbon fibre and stated that 0.5 wt.% provided superior electrical conductivity as well as mechanical properties [12,13]. Similar examinations were also carried out with carbon nanotubes [11,14]. The incorporation of 1 wt.% carbon nanotube in the geopolymer matrix enhanced the electrical conductivity performance by almost three times. Carbon nanotubes also reduce the electric resistance and impedance of associated composites [11,15]. Thus, it can be argued that the physical characteristics and the synthesis mechanisms of the conductive fillers play a vital role in the enhancement of geopolymer properties.

Research on the electrical properties of geopolymer composites is still a novel, diverse and challenging area, resulting in a lack of a universal approach and indicating the high complexity of the underlying problem [16]. Presently, one of the most promising multi-functional composites seems to be geopolymers incorporating graphene derivatives. The current study is therefore focused on the investigation of different effects of GO dosages (0, 0.1, 0.2, 0.3 and 0.4 wt.%) on the electrical properties and the dielectric response of fly-ash-based GRGC (graphene-reinforced geopolymer composite) specimens.

2. Experimental Procedure

2.1. Materials

Fly ash was procured from NTPC, Kaniha, in Odisha. The chemical composition of the FA (fly ash) mostly contained SiO_2 and Al_2O_3 with 60.34 and 30.83 wt.%, respectively. The particle size of FA was 19.18804 µm (median) and 36.73520 µm (mean). Low-cost GO synthesized via mechanical exfoliation with a layer thickness (>10 stacking layers) was given by CSIR-IMMT, Odisha. The particle size of the GO varied from 3 to 200 nm. NaOH flakes were of 99.6% purity, and the Na_2SiO_3 solution consisted of Na_2O (15.85 wt.%), SiO_2 (32.15 wt.%), and H_2O (52 wt.%).

2.2. GRGC Fabrication

A NaOH solution of 12M was prepared by mixing 480 g of NaOH flakes and 1000 mL of tap water, resulting in an exothermic reaction. GRGC specimens were prepared in 5 different batches with varying GO additions (0, 0.1, 0.2, 0.3 and 0.4) wt.% of FA, as shown in Table 1. The alkali activator solution was mixed via a magnetic stirrer at low rpm. GO was consequently introduced to the solution carefully to achieve maximum dispersion and to avoid the agglomeration phenomenon. Later, the solution was ultrasonicated for 30 min and mixed with FA for 10-15 min. The geopolymer slurry was poured into custom molds (10 × 3) mm^3 and cured at 25 °C (±3 °C) for 24 hr. The GRGC specimens were de-molded and cured in ambient conditions for 28 days. Figure 1a illustrates the cured GRGC specimens prior to SSIS (solid state impedance spectroscopy) characterization studies. The specimens were polished with emery paper at different grift sizes to obtain the necessary dimensions for the experimental setup, as shown in Figure 1a,b, for precise results.

Table 1. GRGC mixture composition.

Mixture	FA (g)	NaOH Soln. (g)	Na_2SiO_3 Soln. (g)	NaOH/Na_2SiO_3	Liquid/Binder	GO (wt.%)
GRGC0	100	16.66	33.33	0.5	0.5	0
GRGC1	100	16.66	33.33	0.5	0.5	0.1
GRGC2	100	16.66	33.33	0.5	0.5	0.2
GRGC3	100	16.66	33.33	0.5	0.5	0.3
GRGC4	100	16.66	33.33	0.5	0.5	0.4

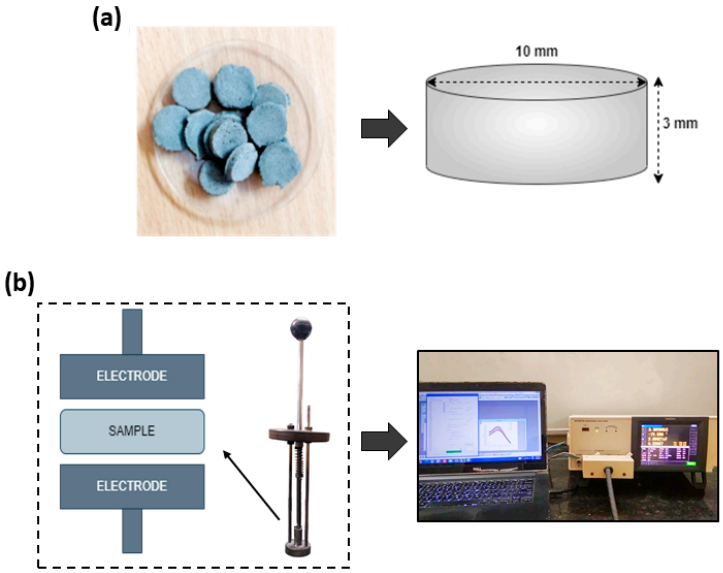

Figure 1. GRGC characterization process: (**a**) specimen specifications and (**b**) SSIS measurement methodology.

2.3. Testing Methods

Solid State Impedance Spectroscopy

The SSIS results were obtained from HIOKI IMPEDANCE ANALYZER IM3570 (AC) using LCR sample application software. The GRGC specimens were investigated using the two-probe method with electrodes, as depicted in Figure 1b, in a dry state under ambient laboratory conditions. The values for different parameters, such as impedance, capacitance and tan delta over a frequency range of 10^1 to 10^5 Hz, were obtained from the instrument. The values of the dielectric constant, dielectric loss and conductivity were calculated from Equations (1) to (4) [17–19]:

$$\varepsilon_r = \frac{C_P t}{\varepsilon_0 A} \quad (1)$$

$$\mathrm{D} = \frac{\varepsilon_r''}{\varepsilon_r} \quad (2)$$

$$\omega = 2\pi f \quad (3)$$

$$\sigma = \varepsilon_0 \varepsilon_r'' \omega \quad (4)$$

where

C_p = capacitance of the specimen;
t = thickness of the specimen;
ε_0 = permittivity of free space constant (8.854×10^{-12} F/m);
ε_r = dielectric constant
ε_r'' = dielectric loss
A = area of the electrode (113.09 mm^2);
f = frequency;
ω = angular frequency;
σ = *conductivity*.

3. Results and Discussion

3.1. Solid-State Impedance Spectroscopy

3.1.1. Capacitance and Impedance/Resistance

The degree of (C_p) and (Z) of the GRGC specimens can be perceived in Figure 2a,b. At a lower frequency (10^1 Hz), higher capacitance values ranging from 9.26×10^{-10} to

4.5×10^{-9} were obtained, but the (C_p) values tend to drop and become constant (almost zero) at higher frequencies (i.e., specifically after 10^3 Hz). The incorporation of GO in the geopolymer composites results in higher (C_p) values, whereas in an opposite trend, lower (Z) was observed with a higher dosage of GO (4.36×10^5 Ω). The impedance of all geopolymer composites became almost constant at higher frequencies, but higher impedance values were observed at lower frequencies for GRGC0 specimens with no addition of GO (5.32×10^6 Ω). This could suggest that GRGC4 specimens offer minimal resistance and accelerate the movement of ions in the GRGC matrix in contrast with the GRGC0 specimen. This could also be signified by the acceleration effect of GO on the polycondensation reaction of the geopolymer composites [7]. The reduction in functional groups from GO may have enhanced the electrical conductivity properties of reduced GO (i.e., rGO), as similarly noted in the study by Saffi et al. [20].

3.1.2. Dielectric Constant, Dielectric Loss and Tangent Loss/Tan Delta

Figure 2c,d show the resulting values of dielectric constant (ε_r) and dielectric loss (ε_r'') for different GRGC specimens when measured at different frequencies. The incorporation of GO in the geopolymer mix leads to higher (ε_r) and (ε_r'') values of (10^{-5}–10^{-4}) and (10^{-4}–10^{-3}) at low frequencies, respectively. Both (ε_r) and (ε_r'') show a significant decrease with the increase in frequency initially. However, the decrease rate of (ε_r) and (ε_r'') was reduced at a higher frequency range and reached an approximately constant value. This phenomenon of the dielectric properties of GRGC specimens can be attributed to the polarization relaxation of molecules in the GRGC matrix. Initially, at lower frequencies, the molecules in the matrix have sufficient time and start orienting in the direction of the applied current. Consequently, at higher frequencies, the re-orientation is limited due to which the values of both (ε_r) and (ε_r'') are reduced drastically [21]. The polarization of the molecules can be firmly influenced by different aspects of the geopolymer mix, i.e., alumino-silicate gel, unreacted particles, impurities available in the composite mix, etc. A study by Hanjitsuwan et al. observed a similar phenomenon and described the rationale as electrode/specimen interfacial polarization and double-layer polarization [17,18]. Alternative polarization mechanisms include ionic, dipolar or molecular, electronic and atomic mechanisms [22].

The (D) curves for the GRGC specimens are exhibited in Figure 2e. The (D) curve peaks ranged between 3.06 and 12.7 and ought to be related to the trend of the dielectric properties. However, GRGC3 obtained the highest (D) value: 10^1 Hz. The (D) values decreased with an increase in frequency, and the curves became almost constant at higher frequencies for all GRGC specimens. This exception can be closely related to the compactness of the specimens and the function of GO in enhancing the strength of the composites primarily via their pore-filling characteristics. Earlier investigations also indicated the limit of GO (0.1–0.3 wt.%) in improving the strength of geopolymer composites, as higher dosages tend to decrease the compactness due to the consequence of agglomeration [16,23–26].

3.1.3. Conductivity

Figure 2f illustrates the conductivity (σ) results of the GRGC specimens. The conductivity values increase with the increase in GO dosage and range between 6.05×10^{-14} and 7.72×10^{-13} Ω·mm^{-1} for GRGC0 and GRGC4 at low frequencies of (10^1) Hz, respectively. The in situ reduction of GO improved electrical conductivity properties and contributed to enhancing GRGC conductive properties. At higher frequencies (i.e., 10^5 Hz), (σ) increased for all GRGC specimens, and the corresponding values include 1.18×10^{-12}–2.27×10^{-12} Ω·mm^{-1}. At lower frequencies, the (σ) of the GRGC specimens remained approximately constant. However, the increment in conductivity is significantly higher when the frequency is more than 10^4 Hz. This occurrence could be associated with the geopolymerisation reaction. The study by Hanjitsuwan et al. detected the same trend of increased conductivity for the geopolymer pastes with increased frequencies [17,18]. The molecular structure of geopolymeric gel is attributed to the increment of electrical conductivity at higher frequencies, mostly

via the Na^+ ion hopping mechanism between the cation sites. A higher dosage of graphene in geopolymer composites leads to higher conductivity. Still, a significant increase in conductivity was observed at higher frequencies, which could be explained via the combination of Na^+ ion hopping and the electronic conductivity of in situ reduced GO, leading to the shortening of conduction distance. Thus, GO could be considered an effective agent for improving the (σ) of geopolymer composites for different applications [12]. The relationship between the (Z) and (σ) curves demonstrates the homogenous dispersion of GO in the geopolymer matrix since the agglomeration of GO could lead to improper conductivity in the GRGC specimens. The results also suggest that there might be a percolation threshold between 0.1 and 0.2 wt.% GO addition in the GRGC matrix. The manifestation is evident via the slight difference in the behaviour of curves in Figure 2b,f. Therefore, it can be considered that conductive fillers such as GO largely facilitate conductivity in geopolymer composites and can be tailored for appropriate piezoresistive responses according to the required applications.

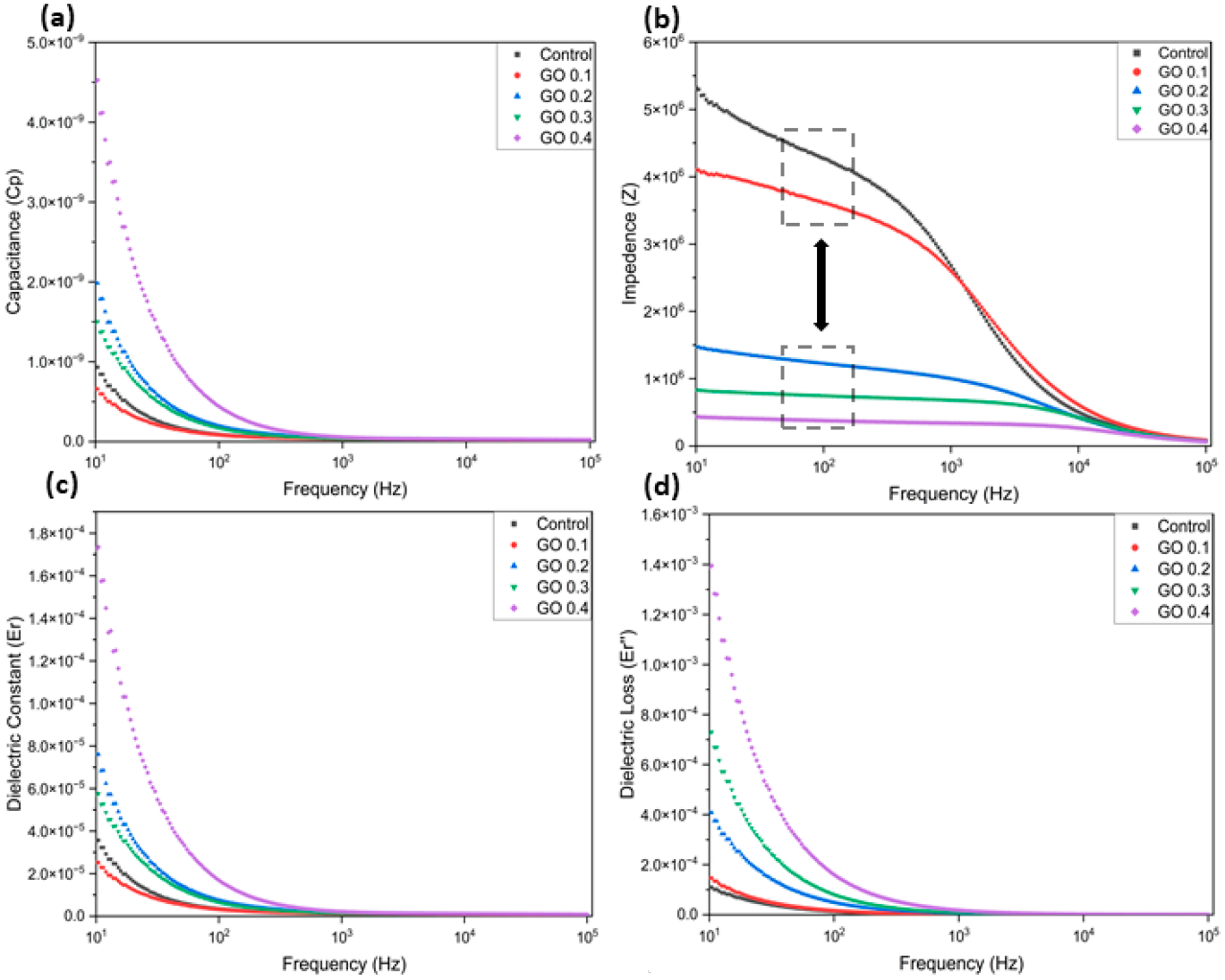

Figure 2. *Cont.*

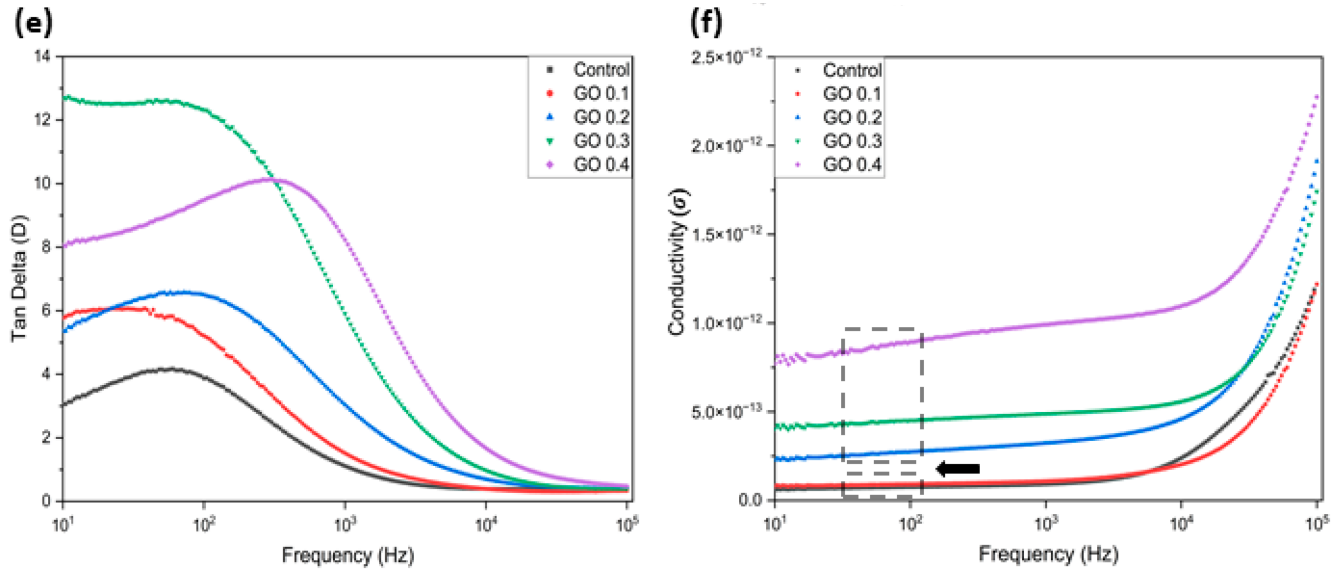

Figure 2. Influence of GO on different electrical parameters of geopolymer composites: (**a**) capacitance, (**b**) impedance, (**c**) dielectric constant, (**d**) dielectric loss, (**e**) tan delta and (**f**) conductivity.

4. Conclusions

In this study, different dosages of low-cost GO were incorporated in geopolymer composites to fabricate sustainable GRGC specimens for various smart applications. SSIS investigations were conducted at room temperature to characterize and assess the significant dielectric properties of GRGC specimens, which are concluded as follows.

The interaction of the GO sheets with the alkaline activator in geopolymeric reactions produced highly reduced and cross-linked GO sheets, enhancing the electrical conductivity properties of the composites.

At 10^1 Hz, GRGC specimens with 0.4 wt.% GO obtained a maximum ionic/electrical conductivity of 7.72×10^{-13} $\Omega \cdot mm^{-1}$ and a minimum impedance of 4.36×10^5 Ω, suggesting desirable low-frequency-based applications.

A percolation threshold was observed between 0.1 and 0.2 wt.% of GO introduction in the geopolymer matrix.

Increasing the GO dosage up to 0.4 wt.% aided in reducing the electrical impedance of GRGC specimens up to 91.81%.

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