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Influence of pristine graphene particle sizes on physicochemical, microstructural and mechanical properties of Portland cement mortars

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ABSTRACT

This paper aims to study the effect of the size of pristine graphene (PRG) particles on the compressive and tensile strengths of cement-based mortars and to gain better understandings of the mechanism behind the enhancement of these properties. PRG industrially manufactured by the electrochemical process with a variety of particle sizes including 5µm, 43µm, 56µm, and 73µm was used at the optimal dosage of 0.07% by weight of cement binder. The results indicate that mechanical strengths of cement mortars at 7 and 28 days considerably depend on the size of PRG. The mixes with size 56µm and 73µm show significant influence on both compressive and tensile strengths of cement mortars, which increase approximately 34.3% and 30.1% at 28-day compressive strengths, and 26.9% and 38.6% at 28-day tensile strengths, respectively. On the other hand, the mix with size 43µm of PRG addition exhibits a significant increase only in tensile strength, and there are no significant effects on either compressive strengths or tensile strengths of the mix containing 5µm particles. The observed enhancement in the mechanical properties of cement mortars by large PRG sizes is attributed to the improvement of cement hydration level, the reduction of cement particles' distance in cement gels because of the effect of van der Waals forces between PRG sheets, and the most important from the mechanical adhesion forces between PRG sheets and cement gels. The results from this study indicate that PRG is not only a promising additive in practical application for building materials to improve the current drawbacks of cement composites, but also a feasible option to support the reduction of cement mass used in cement composites, which could reduce the CO_2 footprint and amount of CO_2 emission into the atmosphere.

Keywords: Pristine graphene; Cement mortar; Mechanical properties; Acceleration; Microstructure.

1. Introduction

The most commonly used materials in the construction industry are cementitious composites. Although they are strong in compressive strength, they are weak in tensile and corrosive properties [1]. Researchers have proposed different approaches to improve their properties such as plastic and carbon fibers [2, 3], nanoparticles [4], carbon nanofibers and nanotubes [5, 6]. However, these additives are unable to effectively improve properties of cementitious composites due to limitations in bonding and arresting microcracks [5-7]. Moreover, the core component of cementitious composites, which is Portland cement, is also one of the factors contributing to a major amount of carbon dioxide (CO_2) into the atmosphere that causes greenhouse gases. Global Portland cement production is estimated at 4 billion tons per year which the largest man-made material in the world [8-10]. It was reported that one ton of Portland cement production could release about one ton of carbon dioxide [11, 12], which accounts for about 7% of CO_2 release globally [8, 9, 11, 13]. Therefore, developing approaches and new additives to improve the properties of cement composites and reduce the amount of cement consumption in order to decrease CO2 emission have attracted significant research interests. Improving only 1-2% in the reduction of CO2 release by enhancing properties of cement composites could make a significant contribution to climate change.

To address these problems, several measures were explored by researchers such as improving cement plant efficiency or using supplementary materials [4, 14, 15]. There have been intense studies in using supplementary materials to enhance properties of cement composites and reduce the mass of cement consumption with many publications in recent decades, including using fly ash, ground granulated blast furnace slag, nanoparticles or graphene materials [4, 16-20]. Among them, graphene and its derivatives (i.e. graphene oxide (GO), reduced graphene oxide (rGO) and pristine graphene (PRG), as two-dimensional materials, have shown the great potential for improving properties of cementitious materials owing to their outstanding properties of high mechanical and conductivity properties, large specific surface areas and aspect ratios [16, 18, 21, 22]. These studies showed graphene additives could significantly enhance key properties of cement composites such as compressive and tensile strengths, chloride penetration, and electrical conductivity [16, 18]. However, there is a significant differences in structural, chemical, mechanical and electrical properties of these graphene materials, While difference of GO which is oxidized graphene is well known the differences between rGO and pristine graphene are not well described in papers as both termed as a graphene (nanoplatelets, flakes, sheets etc). The pristine graphene (PGR) made by electrochemical process from graphite preserving its original pristine structure has different properties compared with reduced graphene oxide (rGO) also prepared from graphite but in different way treated by harsh acid and oxidants to make graphene oxide followed by thermal or chemical process. This process is causing a significant level of defects and less crystallinity which are relevant for their application in construction materials.

For instance, in GO studies, Li et al. [23] showed that incorporating of 0.04% GO into cement paste produced a 14% improvement in its compressive strength at 28 days, and there was no positive effect on its compressive strengths when the incorporation of GO below 0.03%. Another study performed by Wang et al. [24] reported that cement paste and cement mortar with 0.05% GO additive showed the highest enhancement rates in their compressive and flexural strengths, which could increase by 40.4% & 90.5% and 24.4% & 70.5% in compressive & flexural strengths of cement paste and cement mortar at 28 days, respectively. Although a significant process has been made in studying the effects of GO additives on properties of cement composites, the mechanism between GO and cement composites in the strength improvement has not been studied in-depth [18]. Few studies have recently explored the influence of oxygen functional groups from GO on the mechanism of the intermolecular interaction between GO sheets and the cementitious matrix, resulting in the improvement in the properties of cement composites [16, 25, 26]. Besides, the effects of different GO dosages and sizes on microstructures of cement mortars were also revealed in the study performed by Sharma and Kothiyal [27]. They showed that the mix with a smaller GO size (i.e. 100nm) improved compressive strength by 86% at 1% GO concentration. This improvement was more than that of using the larger GO size (i.e. 900 nm) at the same dosage, which was improved by 63% only. This enhancement was explained by the effects of a larger level of oxygen-functional groups (e.g. carboxyl, hydroxyl) of GO with the smaller size compared to those with the larger size, resulting in stronger chemical adhesion forces between them and cement gels in the cement matrix [16, 28].

In the case of PRG additives, recent studies on a combination of PRG and cement composites have shown great potential in strength improvement in PRG-cement composites [16, 18]. These studies were mainly focused on the effects of dosages with limited numbers of studies revealing the influence of other parameters such as the sizes, number of layers, functional groups and the mechanism of the strength improvement of cement composites. In the study performed by Wang et al. [29], which only compared compressive strengths of cement mortars between the control and the mix with 0.05% PRG, compressive and flexural strengths at 7 days of the mortar with 0.05% PRG was respectively improved by 8% and 24%. Another study with four different PRG concentrations (i.e. 0%, 2.5%, 5.0%, and 7.5%) performed by Du and Dai Pang [30] showed that the incorporation of PRG into cement mortars could considerably decrease water penetration depth whereas there were insignificant effects of PRG on compressive and flexural strengths of cement mortars, which was due to the agglomeration of PRG coming from the high PRG dosages rate used. In 2019, Tao et al.

[31] combined cement mortars with five different PRG dosages (i.e. 0%, 0.05%, 0.1%, 0.5%, and 1%) and revealed that 0.05% PRG additive was the optimal dosage and could respectively improve compressive and flexural strengths of the mortar at 28 days by 8.3% and 15.6%, however, the strengths started decreasing when PRG dosages over 0.05% owing to the agglomeration of PRG.

Even though these studies show a strong dependence of the properties of cement composites on PRG dosages, the mechanisms of this dosage dependence have not been clearly explained. Additionally, unlike GO, rGO and PRG sheets (PRGs) have very few oxygen-functional groups that indicate a different mechanism to enhance the cement matrix, which is likely based on friction adhesion forces between PRGs and cementitious gels [32]. Also, all the studies on PRG-cement composites from the literature have used PRGs with the average size varying from 5µm to 25µm [16, 18, 29, 31], with no study has been exploring how an ultra-large size influences on strength improvement in PRG-cement composites, together with revealing its enhancement mechanism. Our previous study [32] was the first study investigating the effects of dosages using the ultra-large PRG size (56um) on mechanical, microstructural and physicochemical properties of cement-based mortars. The study showed that at the optimal concentration (0.07% PRG), compressive and tensile strengths at 28 days of the mortar mix with PRG size 56um could enhance 34.3% and 26.9%, respectively. The study also revealed that the strengthening mechanism of cement mortars with the ultra-large PRG size was mostly due to friction adhesion forces between PRGs and cementitious gels. Compared with GO materials that have high levels of defects, high costs and environmental impact in production, and weaker mechanical properties [33, 34], PRG materials have low levels of defects, stronger crystalline and mechanical properties and can be produced by an environmentally sustainable process in high quality at industrial scales with much lower costs.

Therefore, PRG materials are expected to be more acceptable to be applied for building and infrastructure materials. This is a strong motivation to have more studies on the effects of other parameters of PRGs on properties of cementitious composites.

To address the above-mentioned research gaps, this study aims to explore the effects of different PRG sizes, which was industrially manufactured by an electrochemical process, on compressive and tensile strengths of cement mortars. The objectives of the study not only consider a range of PRG sizes including 5 µm, 43 µm, 56 µm, and 73 µm on these properties, but also evaluate their effects on physicochemical and microstructural properties of the mortars. The outcomes of this study will provide better understandings of the strengthening mechanism of compressive and tensile strengths of cement mortars, which is still lacking in the case of research of PRG-cement composites. The results of this study will contribute to future studies on using PRGs as additives in cement composites to enhance the performance of construction materials. The reduced mass of Portland cement in the binder of cement composites as a result of strength improvement due to the addition of PRGs will result in a reduction of the environmental impact of Portland cement products thanks to reduced CO_2 emission.

2. Experimental programs

2.1. Materials

The physical properties of four different PRG sizes provided by First Graphene Ltd in Perth, Australia are shown in Table 1. From the table, it is important to note that although they are different in sizes, the other properties are similar. General purpose cement provided by Adelaide Brighton Cement LTD and complied with Australian Standard AS 3972-2010 [35] was used as the binder of mortar mixes and its typical chemical properties are shown in Table 2. Natural sand with 2.36-mm maximum particle sizes was used as fine-aggregate of mortar mixes. MasterGlenium SKY 8100 complied with Australian Standard AS 1478.1-2000 [36] was used as the superplasticizer to improve the dispersion of PRGs in water.

2.2. Specimens

In this study, we designed the mixes with different PRG sizes at the optimal dosage (0.07% PRG), which is based on our previous study [32] on the effects of PRG concentrations on mechanical properties of cement mortars, to investigate the effects of different PRG sizes on mechanical, physicochemical, and microstructural properties of cement mortars. The details of the designed mixes of cementitious composites are shown in Table 3. As shown in the table, the four different PRG sizes considered in this study are a small size 5µm, a large size 46µm, and two ultra-large sizes 56µm and 73µm. Prior to the mixing of the mortars, the aqueous solutions including water, superplasticizer and PRG were sonicated for 30 minutes by using Ultrasonication UIP1000hdT. Then, these solutions were gradually added for 5 minutes to natural sand and binder, which were mixed for four minutes. All samples were vibrated for one minute after mounting to mitigate entrapped air during the mounting process. After that, they were covered with wet fabrics and plastic sheets to prevent moisture loss and were demounted after 24 hours cured at room temperature. After that, all the samples continued to be cured in a fog room until testing days.

2.3. Test methods

Compressive and tensile strengths were tested at 7 and 28 days to investigate the influence of different PRG sizes on cement mortars. For compression, 50×50×50 mm^3 cubes complied with ASTM C109/C109M-07 [37] were used. Dog-bone shaped samples, according to ASTM C307-03 [38], were used for tensile tests. The values of each designed mix at testing days were calculated by averaging values obtained from three nominal identical samples of each mix. Scanning electron microscopy (SEM) were obtained by using the FEI Quanta 450 to analyze PRG sizes and surface morphologies of the mortars. X-ray diffraction (XRD) was performed by using the Rigaku MiniFlex 600 X-Ray diffractometer to find the mineralogical characteristics of cement hydration products of the mortars and PRGs. Fourier transform infrared spectroscopy (FTIR) was conducted using the Nicolet 6700 to determine specific functional groups of PRG-cement based mortars. Raman spectra and particle size distribution (PSD) were respectively performed by using the HORIBA LabRAM HR Evolution and Mastersizer 2000 - Malvern to test the number of layers and particle sizes of PRGs. Analysis of variance (ANOVA) method was also used to evaluate how significant effects of different PRG sizes on compressive and tensile strengths of PRG-cement based mortars.

3. Results and Discussion

3.1. Characteristics of PRGs

Fig. 1 shows typical SEM images and related PSD graphs of four PRG samples used for this study. As shown in the figure, their average particle sizes determined from SEM and PSD data are 5±2μm (Fig. 1(a)), 43±8μm (Fig. 1(b)), 56±12μm (Fig. 1(c)) and 73±13μm (Fig. 1(d)), and the PRG structures show wrinkled and irregular shapes with few layer thicknesses. Their XRD patterns presented in Fig. 2(a) show the typical peaks of these PRGs at the position 26.64°, resulting in their d-spacing between layers is 0.334nm that can contribute to a few layers of PRGs [28, 39]. Fig. 2(b) shows the Raman spectra of different PRG sizes. As shown in the figure, the relative intensity ratios of $I_D/I_{D'}$ and I_{2D}/I_G of all the PRG samples are respectively below 3.5 and 1. These mean that these PRG samples don't have basal plane defects [40] and contain mostly several layers (from four layers) [41], showing the high quality of PRGs used in this study and being consistent with their average thickness and other properties provided by the provider.

3.2. Mechanical properties of PRG-cement based mortars

Compressive strengths and their enhancement rates at 7 and 28 days of the mortars with different PRG sizes are shown in Fig. 3. As shown in Fig. 3(a) and (b), the addition of PRGs has a positive effect on compressive strengths of the mortars at 7 and 28 days regardless of PRG sizes. The mix with size 56µm shows the highest compressive strength at 7 days and 28 days (49.96 MPa and 56.33 MPa respectively), which increase approximately 36.8% and 34.3%, respectively, in comparison with the control mix that is 36.53 MPa and 41.96 MPa. A similar trend is observed in size 73µm, which rises approximately 24.3% and 30.1% at 7 days and 28 days, respectively. However, the mixes with size 5µm and 43µm present low enhancement rates in compressive strengths of cement based mortars at both testing days, which are respectively approximately 0.5% and 4.5% for size 5µm, and 7% and 7.7% for size 43µm. Therefore, it is concluded that the ultra-large sizes (56µm and 73µm) have a stronger influence on compressive strengths of cementitious composites than those of the small size and large size (5µm and 43µm), which will be discussed in Section 3.3.

Fig. 4 presents tensile strengths and their enhancement rates at 7 days and 28 days of the mortars with different PRG sizes. Fig. 4(a), (b) shows that tensile strengths of the PRG-cement mortars of different PRG sizes at both testing days increase with the addition of PRG, and their enhancement strength rates depend on the sizes of PRGs. The size 73µm mix shows the highest values in direct tensile strengths at 7 days (4.14 MPa) and 28 days (5.05 MPa), which enhance approximately 33.5% and 38.6%, respectively, compared to the control mix (3.1 MPa at 7 days and 3.67 MPa at 28 days). The size 43µm and 56µm mixes show similar enhancement rates in tensile strengths of the mortar mixes at 7 and 28 days, which respectively increase approximately 25% and 26.3% for size 43µm, and 25.3% and 26.9% for size 56µm. In contrast, the mix with size 5µm presents the lowest enhancement in tensile strengths at both testing days, which are approximately 10.1% at 7 days and 3.1% at 28 days. In summary, it is evident from the results that the large size (43µm) and ultra-large sizes (56µm and 73µm) shows significant enhancement on tensile strengths of the cement mortars whereas the small size (5µm) presents less enhancement on tensile strengths of cementitious composites, which will be further discussed in Section 3.3.

3.3. Physicochemical, microstructural and ANOVA analyses of PRG-cement mortars with different sizes of PRGs

3.3.1 XRD, FTIR and SEM characterizations

The XRD patterns of the mortars with different sizes of PRGs at 28 days are shown in Fig. 5(a). It is important to note that these XRD spectra were standardized to the equal intensity at the major peak of natural sand of 26.7° for making the equal percentage of existing sand in all the samples [32, 42]. Also, only main crystalline phases that relate to the cement hydration process were marked in XRD patterns to avoid a distraction from the analysis (most of the remaining peaks, such as 21.2°, 36.7°, or 77.9°, indicate crystalline phases of quartz [32]). As shown in Fig. 5(a), all the samples have similar spectrum patterns, showing similar main crystalline phases confirmed including cement hydration products (i.e. Portlandite and Ettringite) and un-hydrated cement (i.e. Alite). This means the addition of PRGs into cementitious composites does not create any new crystalline phases in the cement matrix. Moreover, the main cement hydration product in cementitious composites is calcium silicate hydrate (CSH) gels could not recognize in these spectra because CSH gels often exist at amorphous phases in a cement matrix and it is thus hard to identify with XRD test [29, 43]. However, CSH contents can be inferred from the contents of portlandite and alite phases [32, 42]. It can also be seen from the figure that the portlandite phases in the mixes with size 43µm, 56µm and 73µm show higher intensities than the others. This observation, together with the fewer contents of alite in these mixes (size 43µm, 56µm and 73µm) compared with those in the other mixes (control and size 5µm), can result in higher degrees of the hydration of cement pastes in these mixes than the control and size 5µm mixes [32, 42]. This could account for the better enhancement in compressive and tensile strengths of the large size and ultra-large sizes than the others due to higher CSH gels created, as discussed above in Section 3.2. Moreover, it can also be seen in Fig.5(a) that although the mix with size 5µm has the higher peak intensity of un-hydrated alite phases than the control, it still has a higher peak intensity of portlandite than the control. This could be because the mix with size 5µm had a higher amount of belite hydrated in the cement hydration process than the control (i.e. (alite, belite) + H_2O → portlandite + CSH [28, 32]), contributing to a higher peak intensity of portlandite of this mix at the short-term mechanical strengths.

Fig. 5(b) shows the FTIR patterns of the mixes with different PRG sizes at 28 days. As shown in the figure, all the samples have similar spectra with some functional groups determined in the range of the band from 400 cm^{-1} to 4000 cm^{-1}, showing that there are no new distinguishing groups observed in all the samples, which are consistent with the results of XRD discussed above and the previous research [44]. From the figure, some functional groups are observed in these samples including Si-O bonds in CSH gels, which are in the ranges of 400-550 cm^{-1} and 800-1200 cm^{-1} [45, 46], and O-H bond in CSH gels and portlandite, which are in the range of 2800-3600 cm^{-1} [46, 47] and 3600-3650 cm^{-1} [45, 48]. C-O bond in $(CO_3)^{2-}$ groups are observed in a range of 1350-1550 cm^{-1} [46, 47], which indicates the appearance of $CaCO_3$ in these samples due to the chemical reaction between cement products and carbon dioxide during the curing and testing period. Although all the spectra show the same functional groups, it is evident from the figure that the intensities of functional groups belonging to CSH gels in the mixes with PRGs are higher than the control.

This could be attributed to higher hydration degrees of cement binder in the mortars with PRGs additive, resulting in the improvement in compressive and tensile strengths of these mixes as discussed above in Section 3.2.

SEM images of microstructures of the mortars with different sizes of PRGs at 28 days are shown in Fig. 6. It is evident from the figure that although these samples show similar components in their SEM images, they are different from how these components are distributed and compacted. In particular, the control mix and size 5µm mix not only show less compact in the microstructure, which is large sizes in microcracks and less dense in the interfacial transition zones (ITZ) (Fig. 6(a) and (c)), but also present smaller sizes of crystal components and larger contents of pores distributed in the cement matrix (Fig. 6(b) and (d)) than the others (Fig. 6(e)-(j)). It can also be seen from the figure that the mixes with size 56µm (Fig. 6(g), (h)) and 73µm (Fig. 6(i), (j)) show the most compact in the cement matrix of the mortars, followed by the size 43µm mix (Fig. 6(e), (f)). This is attributed to the higher cement hydration degree and a stronger connection between PRGs and cement gels in the cement matrix of these mixes than the others, resulting in their stronger enhancement rates in compression and tension [29, 32, 49] as discussed in Section 3.2.

From the above observations and analyses, it can be concluded that physicochemical, microstructural and mechanical properties of cement-based mortars are strongly dependent on the sizes of PRGs additives. The benefits of PRG additives in the cement matrix could come from the combination of the following reasons: (1) a part of the enhancement in the cement hydration process due to the better spreading water of PRGs in a cement matrix, and the reduction of distances between cement particles in cement gels because of the effect of van der Waals forces between PRGs [18, 32, 49]; (2) most of the mechanical adhesion forces created from the friction forces between surfaces of PRGs and cement gels [32], suggesting that PRGs with larger sizes will have stronger friction adhesion forces due to having larger surface areas to connect with cement gels (e.g. 5µm×5µm (25µm^2), 73µm×73µm (5329µm^2)), resulting in their better enhancement rates in mechanical strengths of cement composites as discussed in Section 3.2. This type of friction forces between PRGs and cement gels was also identified by previous research in simulation studies using molecular dynamics simulation methods [50, 51]. Therefore, PRGs can reinforce cement gels in cementitious composites, integrating PRGs into cement gels to create PRG-cementitious gels in the cement matrix, resulting in the improvement of microstructures of the PRG-cement mortars and contributing to a better capacity in stress-distribution and propagation of cracks of these PRG-cement mixes.

3.3.2 ANOVA analysis to evaluate the benefit of different sizes of PRGs on compressive and tensile strengths of cement mortars

The ANOVA analysis by applying the Dunnett method is used to determine whether the enhancement of different sizes of PRGs on compressive and tensile strengths of cement mortars is statistically significant or not. This analysis method is based on the null hypothesis theory with a significant level of 0.05 to assess how significant differences between the mortar mixes, which is detailed in previous studies [52, 53]. The results of the ANOVA analyses for compressive strengths at 7 days and 28 days of the different mixes are shown in Table 4. As can be seen from the table, only the ultra-large sizes mixes (size 56µm and 73µm) are significant improvements in compressive strengths at both testing days compared to the others (their P-values < 0.05). Moreover, while the size 56µm mix shows the most benefit at the 7 days test because it shows significant difference even with the size 73µm (i.e. P-value=0.009), there is no significant difference between them at 28 days (i.e. P-value=0.186).

Table 5 presents the results of the ANOVA tests at 7 days and 28 days for tensile strengths of the different mortars. It is evident from the table that the mixes with size 43µm, 56µm and 73µm show significant benefit in tensile strengths at both testing days compared with the control. In addition, the size 73µm mix presents the strongest effect at the age of 7 days compared to size 43µm (i.e. P-value=0.026) and size 56µm (i.e. P-value=0.03), whereas there are no significant differences between these PRG sizes on tensile strengths at 28-day.

In summary, it is evident from all the above analyses that compressive and tensile strengths of cement based mortars at 7 days and 28 days strongly depend on the sizes of PRG additives. While the small size (5µm) does not show any significant influence on compressive and tensile strengths of the cement mortars at both testing days, the large size (43µm) only shows a significant influence on tensile strengths at both testing days. In contrast, the ultra-large sizes (56µm and 73µm) show a significant influence on both compression and tension at all the testing days. This confirms the strong benefit of the ultra-large sizes on the mechanical properties of cementitious composites.

3.3.3 Prediction the benefit of PRG additive to reduce the amount of Portland cement used in building materials

As mentioned in the Introduction Section, the use of Portland cement accounts for about 7% of CO_2 emission into the atmosphere globally, causing greenhouse gases. Thus, it is important to find methods to reduce the amount of cement used in building materials without impacting on requirements of their designed strengths. In this case, PRG appears as a promising additive for building materials to reduce the amount of Portland cement used globally. From the previous sections, it can be concluded that the addition of PRGs to cement mortars can enhance their mechanical strengths. The ultra-large sizes (56µm and 73µm) show the significant improvement in both compressive and tensile strengths at all the testing days.

As discussed in Section 3.2, the size 56µm mix can enhance the 28-day compressive and tensile strengths of the mortar up to 56.33 MPa (↑34.3%) and 4.62 MPa (↑26.9%) compared to the control mix 41.96 MPa and 3.67 MPa, respectively. In practice, we often use the compressive strength at 28 days as the most important parameter to design for new constructions. As shown in Table 3, the mass of Portland cement in 1 m^3 of cement mortars for the current design mixes is 527 kg, and the compressive strength at 28 days of the control mix is 41.96 MPa. Based on compressive strengths of cement pastes and water/cement ratio of mortars, we can predict compressive strengths of cement mortars and one of the precise design-oriented models for predicting was proposed by Kargari et al. [54], which considers different formulas for different cement paste classes. In this study, we used the cement paste with 45 MPa at 28-day compressive strength. According to Kargari et al. [54], the formula used to predict compressive strengths of cement mortars with cement paste class 42.5 MPa is shown below:

$$f'_{c28} = 25.32(1/(W/C)-0.443); \quad (1)$$

where W/C means water and cement ratios. The water and cement ratio we used in this study is 0.485. According to the formula above, the compressive strength of the cement mortar is 40.1 MPa, which is only a 2.31% error compared to the experimental result (41.96 MPa). If we simply assume that the required compressive strength for designing building construction is 56.33 MPa. From Equation (1), the requirement of water and cement ratio for the cement mortar calculated is 0.375. Thus, the mass of Portland cement for the practical design mix with the above water and cement ratio (0.375) is 610 kg. This means if we use 369 gram PRG size 56µm as the additive for 1 m^3 cement mortar with 0.485 water/cement ratio, we can reduce about 83 kg (↓15.75%) Portland cement for the required compressive strength at 0.375

water/cement ratio. As reported in Refs. [8-10], it takes approximately 4 billion tons of cement production in the world yearly, and thus, PRG additive can support to reduce the mass of cement production down to 3.37 billion tons, which can decrease approximately 1.1% of the CO_2 emission caused by cement production every year. This will be a significant contribution to mitigate greenhouse gases, which accounts for the global warming gases and climate change. The PGR is produced by electrochemical process which is recognized as one of the greenest and most environmentally sustainable graphene manufacturing process with minor CO^2 and environmental (water/waste) footprint compared with other conventional processes involving acid oxidation and reduction (rGO) with enormous environmental footprint [55]

4. Conclusions

The effects of different sizes of PRGs on physicochemical, microstructural and mechanical properties of cement-based mortars have been presented and evaluated in this study. Based on the results and discussion above, the following conclusions have been drawn:

- The addition of PRGs additive to cement-based mortars enhances their compressive and tensile strengths at 7 days and 28 days. The enhancement accounts for the improvement of compactness of mortars, which is due to the increase in cement hydration degrees, the reduction of distances between cement particles, and the most important part from mechanical adhesion forces between PRGs and cement gels.
- Compressive and tensile strengths of the cement mortars considerably depend on the sizes of PRGs additive. While the small size (5µm) presents no significant effect on both mechanical tests, the large size (43µm) only shows a significant influence on tensile strengths. The ultra-large sizes (56µm and 73µm) have shown the most prominent benefit to compressive and tensile strengths at both testing days.

- The results from XRD, FTIR, and SEM analyses show that compressive and tensile strengths PRG-cement mortars have a close relationship with their physicochemical and microstructure properties. The higher mechanical strengths they are, the better microstructures they have.
- The use of PRGs in cement composites as an additive can support to reduce the mass of cement production, and thus decrease the amount of the CO_2 emission into the atmosphere caused by cement production, contributing to mitigating the global warming gases and climate change yearly.

The results from the study confirm the prominent benefit of the ultra-large sizes on mechanical properties of cementitious composites. This provides the potential to apply ultra-large PRG sizes to cementitious composites as additives to not only enhance both compressive and tensile strengths but also contribute to alleviating the global warming gases. The study also contributes to providing a fast track in studying PRG and cement composites to investigate the influence of PRGs on other properties of cementitious composites, such as permeability, toughness, shrinkage, or corrosion; therefore, the application of this promising additive in practice for building materials could complete soon.

Declaration of Competing Interest

The authors declare that they have no known competing for financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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