Dispersion of Graphene Oxide in Saturated Ca(OH)₂ Solution by Using Different Water-reducing Agents

Yanan Wang¹, Xiangyu Li*, Ya Chen², Zhuopeng Liu³

¹College of Civil Engineering, Taiyuan University of Technology, Taiyuan, Shanxi 030024, China
²*Corresponding author’s E-mail: lixiangyu@tyut.edu.cn

Abstract: As a two-dimensional nano-material, graphene oxide (GO) has been found to be promising on improving properties of cement based materials. However, GO is prone to be agglomerated in the cement matrix. In this study, three different water reducing agents, including two polycarboxylate-based superplasticizers (PC1, PC2) and calcium lignosulfonate (CS), were used to study their effects on dispersion of GO in saturated Ca(OH)₂ solution by conducting UV-vis analysis. The results showed the dispersion of GO can be largely improved when the mass ratio between PC1, PC2, CS and GO was 4:1, 4:1, 6:1, respectively. The UV absorptions increased with increase of the ultrasonication duration. When the ultrasonication was 10 minutes, CS showed better performance on the dispersion of GO. The dispersion of GO modified with PC1 can be improved by increasing the ultrasonication amplitude; while the amplitude showed little effect on the dispersion of GO modified by PC2 and CS.

1. Introduction

Concrete is the second most used material on earth[1]. However, concrete is prone to crack formation due to its brittleness and relatively lower tensile strength, which has caused significant economic losses to the society.

In recent years, nanomaterials have attracted increasing attentions as additive materials to improve properties of cement based materials, owing to their special physical and chemical characteristics. These nanomaterials include zero-dimensional nanoparticles such as nano CaCO₃ and nano silica, one-dimensional carbon nanotubes (CNTs), and two-dimensional nanomaterials such as Graphene and Graphene Oxide (GO).

GO has oxygen-containing functional groups (hydroxyl, carboxyl and epoxy groups)[2] on its surface, which makes it easier to disperse in water. The large specific surface area of GO makes interactions between it and cement hydration products more efficiently. In addition, GO has excellent mechanical properties, such as a tensile strength of 130 GPa and a Young's modulus of 0.5 TPa[3]. Recently, many studies have shown that the addition of GO helps to enhance the mechanical properties of cement-based materials. Lu et al.[4] proved that the addition of 0.05% GO by weight of cement can increase the compressive strength and flexural strength of cement paste by 11.1% and 16.2%, respectively. Lv et al.[5] also found small amount of GO can significantly increase mechanical properties of cement composites. However, GO was also found to be prone to form large agglomerates in cement paste due to chelations of calcium cations[6]. The formation of GO agglomerates can significantly affect its effect on improving properties of cement-based materials.

Therefore, it is imperative to improve GO dispersion in cement based materials. In this study, we investigated effects of different water reducing agents on dispersion of GO in saturated Ca(OH)₂ solution,
which was used as simulated pore solution. Three different water reducing agents, including two polycarboxylate-based superplasticizers and calcium lignosulfonate, were used. The influences of ultrasonication, including its amplitude and duration, were also studied.

2. Materials

2.1. GO solution

GO solution sourced from Graphenea (Spain) has a concentration of 4 mg/ml. The elemental compositions of GO is shown in Table 1.

| Element | C  | H  | N  | S  | O   |
|---------|----|----|----|----|-----|
| %       | 49-56 | 0-1 | 0-1 | 0-2 | 41-50 |

2.2. Saturated Ca(OH)₂ solution

At room temperature, a saturated Ca(OH)₂ solution was prepared according to the solubility of Ca(OH)₂ (0.16g) to simulate the pore solution in Portland cement based materials.

2.3. Water reducing agents

Two polycarboxylate-based superplasticizers are PC1 (Melflux 5581 from BASF) in solid form and commercial available PC2 in liquid form with solid content of 20%. Calcium lignosulfonate with purity of 99% was sourced from Sigma-Aldrich.

3. Experimental

3.1. UV-vis analysis

The UV-vis analysis was conducted by using a Shimadzu UV-1800 ultraviolet spectrophotometer. According to Lambert-Beer law, the absorbance value is proportional to the concentration of the solution. In addition, GO has two characteristic peaks located at 230 nm and 300 nm, corresponding to the transitions of π-π bonds in C=C bonds and n-π bonds in C=O bonds, respectively. Therefore, the UV absorbance of GO-Ca(OH)₂ solution can be used to characterize the GO dispersion. The higher the absorbance values, the better the dispersion of GO in the solution.

3.2. Ultrasonication schemes

The ultrasonication was conducted by using a Scientz-750F (Ningbo Xinzhi Biotechnology Co., Ltd). The ultrasonication schemes are shown in Table 2.

| Ultrasonic time (min) | Ultrasonic amplitude (%) | Ultrasonic energy (J/ml) |
|----------------------|--------------------------|--------------------------|
| 10                   | 20                       | 900                      |
| 30                   | 20                       | 2700                     |
| 60                   | 20                       | 5400                     |
| 10                   | 30                       | 1350                     |
| 10                   | 40                       | 1800                     |
| 10                   | 50                       | 2250                     |

3.3. Sample preparations and tests

(1) The samples (GO-Ca(OH)₂ solutions) were prepared by adding correct amounts of water reducing agents modified GO solution to the saturated Ca(OH)₂ solution according to Table 3. If water-reducing agents were used, they are added to GO solution first.

(2) The sample solutions were sonicated to ensure uniformity. Use an ice bath during ultrasonication to prevent excessive heat from affecting the GO dispersion.
(3) Dilute the GO-Ca(OH)₂ solution to appropriate concentration before conducting UV-vis analysis. The UV-vis spectra were then obtained with the wavelength range of 200 nm -1000 nm. Three sets of spectra are measured for each group of solution, and the average is taken as the final result.

Table 3 Different mass ratios of different water-reducing agents

| Water reducing agents | Mass ratio (GO: Water reducing agent) |
|-----------------------|-------------------------------------|
| PC1                   | 1:0       1:1       1:2       1:3       1:4       1:5       |
| PC2                   | 1:0       1:1       1:2       1:3       1:4       1:5       |
| CS                    | 1:0       1:2       1:3       1:4       1:5       1:6       1:7       |

4. Experimental results and discussions

4.1. Effects of water reducing agents

Figure 1 and Figure 2 show the UV spectra of GO-Ca(OH)₂ solutions modified by PC1 and PC2 with different proportions.

Figure 1: UV-vis spectra of GO-Ca(OH)₂ solution modified by PC1 of different ratios

Figure 2: UV-vis spectra of GO-Ca(OH)₂ solution modified by PC2 of different ratios

It can be seen from Figure 1 and Figure 2 that the GO dispersion in the aqueous solution is better than that in the saturated Ca(OH)₂ solution. This is due to the oxygen-containing functional groups on the surface of GO make it disperse better in water, however, these negatively charged oxygen-containing functional groups readily chelate with the Ca²⁺ cations in the Ca(OH)₂ solution to form agglomeration which can not absorb UV. After adding PC1 and PC2, the absorbances at 230 nm of the GO-Ca(OH)₂ solution were much higher than that of aqueous GO solution and the GO-Ca(OH)₂ solution without PC1 and PC2. It is possible that polycarboxylate-base superplasticizer PC1 and PC2 can absorb onto surface of GO and prevent it from chelating with calcium cations due to the steric hindrance effect. Thus the GO dispersion can be improved without forming agglomerates.

However, when the mass ratio of PC1 (or PC2) to GO exceeds 4:1, the absorbance at 230 nm became lower. There were an optimum ratio between PCs and GO to ensure the dispersion. In this study, the optimum ratios for PC1 and PC2 were found to be around 4:1.
Figure 3: Absorption spectra of GO in saturated Ca (OH)₂ solution modified with different proportions of wood calcium.

Figure 3 shows the spectra of GO-Ca(OH)₂ solution modified with different dosage of CS. It can be seen from Figure 3 that the absorbance at 230 nm increased with increase of CS content until the ratio reached 6:1. When the mass ratio of CS and GO is 7:1, the absorbance decreased. Therefore, the optimum ratio between CS and GO is 6:1, although the absorbance when CS to GO ratio is 7:1 was much higher than that of aqueous and saturated Ca(OH)₂ solution. However, future study is needed to explain the larger amount of CS is needed to achieve better GO dispersion, compared to PC1 and PC2.

4.2. Influences of ultrasonication schemes

The GO-Ca(OH)₂ solutions modified with optimum amounts of PC1, PC2 and CS were prepared, respectively. Then the influences of ultrasonication on GO dispersion are investigated.

As shown in Figure 4, when ultrasonic amplitude of 20% was kept constant, GO dispersion was slightly improved with increase of ultrasonication duration[8]. For CS, GO dispersion was found, however, to be negatively influenced when increase the ultrasonication duration. There was an optimum ultrasonication energy for GO dispersion when using CS, which was 10 mins in current study.
5. Conclusions

(1) The dispersion of GO in saturated Ca(OH)₂ solution can be improved by using PC1, PC2, and CS. In current study, there were optimum ratios between PC1, PC2, and CS and GO, which were 4:1, 4:1, and 6:1, respectively.

(2) For polycarboxylate-based PC1 and PC2, increase of ultrasonication energy barely improved the GO dispersion. However, it was found increase of ultrasonication energy negatively influenced the GO dispersion in Ca(OH)₂ solution. The optimum ultrasonication duration for CS was 10 mins in current study.

Acknowledgments

The authors are grateful for the financial support of the Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering (Shenzhen University) in conducting this study. The corresponding author is Xiangyu Li.

References

[1] Shang Y, Zhang D, Yang C, et al. Effect of graphene oxide on the rheological properties of cement pastes[J]. Construction & Building Materials. 2015, 96: 20-28.

[2] Stankovich S, Dikin D A, Dommett G H, et al. Graphene-based composite materials[J]. Nature. 2006, 442(7100): 282-286.

[3] Lu Z, Li X, Hanif A, et al. Early-age interaction mechanism between the graphene oxide and cement hydrates[J]. Construction & Building Materials. 2017, 152(oct.15): 232-239.

[4] Lu Z, Hou D, Meng L, et al. Mechanism of cement paste reinforced by graphene oxide/carbon nanotubes composites with enhanced mechanical properties[J]. Rsc Advances. 2015, 5(5): 100598-100605.

[5] Lv S, Ma Y, Qiu C, et al. Effect of graphene oxide nanosheets of microstructure and mechanical properties of cement composites[J]. Construction & Building Materials. 2013, 49(dec.): 121-127.
[6] Li X, Liu Y M, Li W G, et al. Effects of graphene oxide agglomerates on workability, hydration, microstructure and compressive strength of cement paste[J]. Construction and Building Materials. 2017, 145: 402-410.

[7] Li X, Korayem A H, Li C, et al. Incorporation of graphene oxide and silica fume into cement paste: A study of dispersion and compressive strength[J]. Construction and Building Materials. 2016, 123: 327-335.

[8] Kawashima S, Seo J T, Corr D, et al. Dispersion of CaCO3 nanoparticles by sonication and surfactant treatment for application in fly ash–cement systems[J]. Materials and Structures. 2013, 47(6): 1011-1023.