Review

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Advances of graphene- and graphene oxide-modified cementitious materials

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Abstract: Emerging nanomaterials provide an invaluable opportunity for the development of cementitious materials. Many scholars have explored the influence of graphene (GP) and graphene oxide (GO) on the performance of the cementitious materials. This article reviews the previous research on the effect of GP and GO on the properties of cementitious materials. Detailed review of the mechanical properties and durability of cementitious materials containing GP or GO nanofilms is presented, and the mechanism is discussed. The mechanical properties of GO-cementitious materials are significantly enhanced. The optimal improvement of GO-modified compressive, flexural, and tensile strengths is 77.3%, 78.3%, and 78.6%, respectively. The durability of GO- and GP-modified cementitious material is compared with the control group. The incorporation of GP or GO significantly improves the sulfate attack resistance, and the transport properties can be decreased, while the frost resistance of GO- and GP-modified cementitious materials needs further research. This literature review shows that the microstructure of GO- and GP-modified cementitious material is improved in three aspects: accelerating the cement hydration, refining the pore structure, and hindering the crack propagation.

Keywords: cementitious materials, durability properties, graphene, mechanism, mechanical performance

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1 Introduction

Cementitious materials have been generally used in the world and will still be one of the main building materials in the twenty-first century. With the advancement of society and technology, traditional cementitious materials cannot meet the requirements of special engineering under arduous conditions [1]. The development of novel high-performance cementitious materials with low energy consumption and comprehensive cost during infrastructure service life is of great significance for protecting the ecological environment and promoting sustainable development [2,3]. The existence of cracks and pores in the cementitious materials affects the strength and durability. Enhancing toughness and reducing porosity have been research hotspots in this field [4,5]. The addition of mineral admixtures and fibers can be mixed in the cementitious materials to achieve high performance and functionalization [6–9]. At the end of the last century, the emergence of nanomaterials has revolutionized the human traditional understanding of materials [10].

Nanomaterials consisted of ultrafine particles with the size ranging from 1 to 100 nm and can be divided into 0-dimensional nanoparticles, 1-dimensional nanofibers, and 2-dimensional nanofilms [11–13]. Ultrafine particles have a series of excellent physical and chemical properties [14,15]. The addition of nanomaterials into the cementitious materials not only greatly improve the mechanical performance but also lead to better durability and microstructure of the cementitious materials [16,17]. Nanoparticles with most extensive applications in cementitious materials [18–20] and high reactivity can accelerate hydration and can fill microscopic pores in the matrix to increase the compactness of the cementitious materials [21–24]. For example, carbon nanotubes (CNTs) as a microscopic fiber can significantly enhance the strength [25], toughness [26], and durability [27] of cementitious materials and will affect the electrical [28] and thermal [29] conductivity, making cementitious materials multifunctional and smart [30–33].

Graphene (GP) is a type of carbonaceous nanomaterial discovered recently, and it is a significant new material with the lightest, thinnest, highest strength, and the best electrical and thermal conductivity [34]. As a reinforcing material, the

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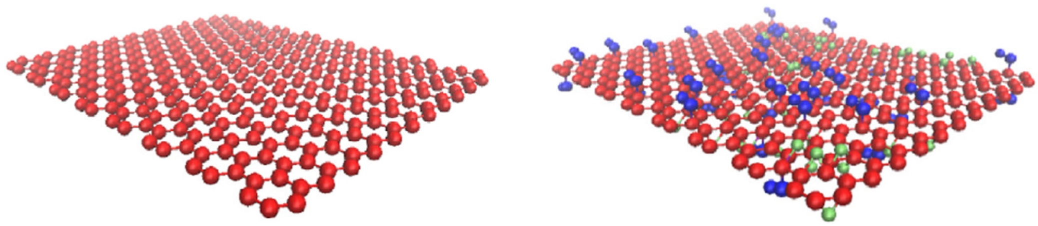

Figure 1: The microstructure of GP and GO [47]: (a) GP and (b) GO.

GP aluminum alloy developed in China can reach 100 times the strength of steel [35]. Graphene oxide (GO) is more reactive than graphene, easy to functionalize, and controllable [36–38]. The atomistic model of GP is shown in Figure 1(a), and the atomistic model of GO is shown in Figure 1(b). In this figure, main functional groups of GO are hydroxyl (C–OH, blue elements) and epoxy (C–O–C, green elements) [39–42]. The results of the previous research have shown that GO can regulate the hydration reaction [43], and GO and GP nanoplatelets can give functions and intelligence to cementitious materials [38,44–46], so the study of the GP- and GO-modified cementitious materials are of great significance and have attracted the attention of scholars.

The first research of GO-modified cementitious materials was carried out by Peyvandi et al. [48] in 2013, and it was found that GP at a low dosage of 0.05% can significantly improve the acid attack resistance of concrete and significantly reduced water permeability. Parallelly, in China, Lv et al. [44,49] studied the mechanism of GO-modified cementitious materials and proposed that GO can regulate cement hydration. In addition, for the application of new cementitious materials, cost is an important factor affecting its popularization, and the development of the GP manufacturing process has promoted the reduction of GP production costs. For example, in 2015, it is reported that the cost of GP can be reduced by 100 times [50], and thus, industrialization of GP- or GO-modified cementitious materials is feasible.

This article reviews recent studies on GP- and GO-modified cementitious materials, focuses on the mechanical and durability properties of GP- and GO-modified cementitious materials, and discusses the related mechanism.

2 Mechanical performance of GP- and GO-modified cementitious materials

Most studies indicate that the mechanical performance of GP- and GO-modified cementitious materials are improved. The improvement effects of GO and GP in strength are different corresponding to compressive, flexural, and tensile strength, and these three strengths are discussed. In this article, the effects of nanoplatelets on the cementitious material strengths have been analyzed by calculating the relative strength ratio. The relative strength ratio refers to the strength ratio between GO- or GP-modified and unmodified in the research literature, and when calculating the ratio, the mix ratio of the modified and the unmodified group in the literature must be consistent, and the dosage in this paper is the percentage of cement mass.

2.1 Compressive strength

Based on the research results, the effects of the compressive strength in the literature are normalized and presented in Table 1, and GO significantly improves the cementitious material's compressive strength, and the most effective increase is the relative strength rate of 177.3% obtained at 1% GO in the study by Lv et al. [51]. Sharma et al. [52] observed that the mortar compression strength was enhanced to 151.08% with the addition of 0.02% GO. The effect of GO on improving the ultra-high strength concrete (UHSC) is poor, the compressive strength of UHSC containing 0.01–0.03% GO was increased to 104.59–107.82% [53], and this is the lowest compressive strength improvement effect.

The compressive strength of GP-modified cementitious materials in the literature is normalized and presented in Table 2. The compressive strength of GP-modified cementitious materials is not significantly improved, and the most effective improvement is 122.86% relative strength rate obtained at 0.1% GP in the examination by Sharma and Arora [58]. In the study by Bai et al. [59], adding 0.1–2% GP to the cement paste results in the reduced compressive strength. The improvement effect in the studies is mostly within 15%.

Table 1: Compressive strength of GO-modified cementitious materials

Scholar	Dosage (%)	Relative strength ratio (%)	Cementitious materials
Lv et al. [49]	0.05	147.90	Mortar
	0.04	142.20	
	0.03	138.90	
Sharma et al. [52]	1	177.30	Mortar
	0.5	165.30	
	0.2	140.60	
	0.1	123.00	
Liu et al. [54]	0.03	115.80	Cement paste
Lu and Dong [53]	0.01	107.82	UHSC
	0.03	104.59	
Lv et al. [51]	0.02	151.08	Mortar
Long et al. [55]	0.2	119.20	Mortar (recycled fine aggregates)
Lu et al. [56]	0.05	111.05	Cement paste
Zhu et al. [57]	0.05	133.00	Cement paste

Table 2: Compressive strength of GP-modified cementitious materials

Scholar	Dosage (%)	Relative strength ratio (%)	Cementitious materials
Tragazikis et al. [60]	0.2	110.45	Mortar
	0.4	113.43	
Sharma and Arora [58]	0.05	108.00	Mortar
	0.1	122.86	
Bai et al. [59]	0.1	93.00	Cement paste
	2	69.00	
Wang et al. [61]	0.05	103.00	Cement paste
Jiang and Wang [62]	0.05	107.50	Cement paste

In summary, GO is superior to GP in improving the compressive strength. According to the modification mechanism, the functional groups on the GO surface play an important role, which is not available in the GP-modified cementitious materials. However, Liu et al. [63] found that the concrete compression strength was enhanced by 36.8% with the addition of 0.8% GP and enhanced by 40.1% with the addition of 1.6% GO, and GP modification may also have better impact.

The influence of GO and GP dosage on cementitious material's compressive strength is significant for the application of modified cementitious materials. The dosages and the compressive strength effect in the literatures are shown in Figure 2. As the GO dosage increases, the effect of the increasing compressive strength increases [49,52]. The GO dosage of 1% significantly improved the compressive strength. It can be known from the previous mechanism that GP does not show high reactivity, and this is reflected in the compressive test results. Insufficient dispersion of GP in cement materials may be the cause of the decrease in the strength when the content is 2% [59].

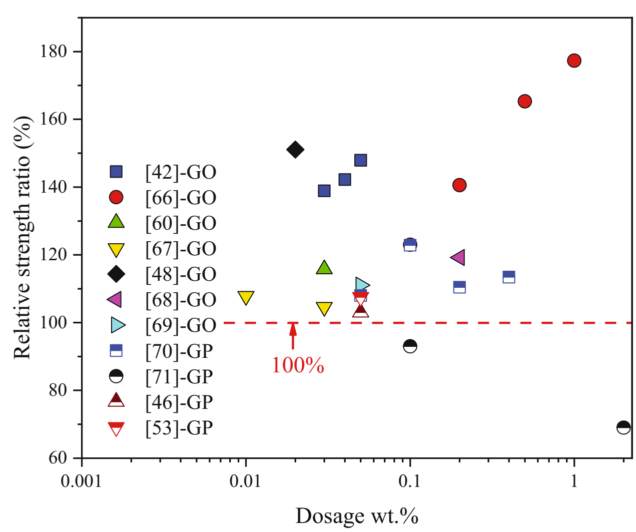

Figure 2: The dosages and the compressive strength effect.

2.2 Flexural strength

The flexural strength of GO-modified cementitious materials in the literature is shown in Table 3. In the existing research, 0.02% GO increases the flexural

Table 3: Flexural strength of GO-modified cementitious materials

Scholar	Dosage (%)	Relative strength ratio (%)	Cementitious materials
Jiang et al. [64]	0.08	131.62	UHSC
Qian et al. [65]	0.01	109.30	Cement pastes
	0.03	109.30	
	0.04	104.65	
Li et al. [66]	0.02	133.33	Cement paste
	0.04	178.33	
Long et al. [67]	0.05	115.90	Mortar (recycled fine aggregates)
	0.1	127.00	
	0.2	141.30	
Lv et al. [49]	0.01	151.70	Mortar
	0.02	132.90	
	0.03	160.70	
	0.04	130.50	
	0.05	130.20	
Murugan et al. [68]	0.02	123.00	Cement paste
Li et al. [69]	0.022	122.55	Cement paste
Chuah et al. [70]	0.03	126.55	Cement paste
Zhu et al. [57]	0.05	159.00	Cement paste
Lu et al. [56]	0.05	116.20	Cement paste
Long et al. [55]	0.2	147.50	Mortar (recycled fine aggregates)
Lv et al. [51]	0.02	185.11	Mortar
Lu and Dong [53]	0.01	111.88	Ultra-high strength concrete
	0.03	106.95	
Liu et al. [54]	0.03	135.50	Cement paste
Long et al. [71]	0.06	119.00	Mortar (recycled fine aggregates)

strength by 85.11%, which shows the best effect of GO-modified cementitious materials [51]. The improvement of GO-modified cementitious material's flexural resistance is mostly above 30%, and the improvement effect is significant. The improvement of the flexural strength shows significance to the toughness of cementitious materials.

As presented in Table 4, the effect of GP on improving the flexural strength is lower than GO modified. The flexural strength of the GP-modified mortar is significantly reduced in the study by Tragazikis et al. [60]. For the GP-modified cement paste, Wang et al. [61] and Jiang and Wang [62] used the same dosage of 0.05%, and the obtained flexural strength improvement effect was the same, with a relative compressive strength of 121.2–123.5%. In the researches by Long et al. [55,67,71], GO-modified recycled fine aggregate mortar was studied, and the mortar strength is significantly improved.

The effect of GO and GP dosage on cementitious materials flexural strength is shown in Figure 3. As the GO dosage increases, the GO-modified cementitious material's flexural strength increases first and then decreases. When the GO dosage is 0.02–0.04%, the

Table 4: Flexural strength of GP-modified cementitious materials

Scholar	Dosage (%)	Relative strength ratio (%)	Cementitious materials
Tragazikis et al. [60]	0.2	66.1	Mortar
	0.4	78.6	
Sharma and Arora [58]	0.05	113.0	Mortar
	0.1	115.0	
Bai et al. [59]	0.1	103.0	Cement paste
	2	77.0	
Wang et al. [61]	0.05	123.5	Cement paste
Jiang and Wang [62]	0.05	121.2	Cement paste

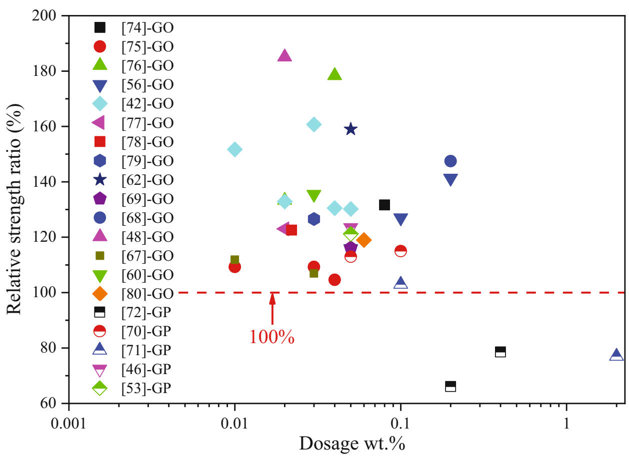

Figure 3: The effect of dosages and the flexural strength.

cementitious material's flexural strength can be significantly improved. When the GP dosage is 0.05%, the relative strength ratio is 113–123.5%; when the GP dosage is 0.1%, the relative strength ratio is 103–115%; and when the GP dosage is 0.2–2%, the relative strength ratio is 66.1–78.6%.

Table 5: Tensile strength of GO-modified cementitious materials

Scholar	Dosage (%)	Relative strength ratio (%)	Cementitious materials
Lv et al. [49]	0.01	147.0	Mortar
	0.02	159.5	
	0.03	178.6	
	0.04	136.6	
	0.05	135.8	
Li et al. [73]	0.01	109.5	Cement paste
	0.02	140.5	
	0.03	159.5	
	0.04	161.9	
Sharma et al. [52]	0.1	132.5	Cement paste
	0.2	137.5	
	0.5	120.0	
	1	115.0	
Li et al. [74]	0.02	115.1	Mortar
	0.04	116.6	
	0.02	114.8	Cement paste
	0.04	115.0	
Babak et al. [72]	0.1	102.2	Mortar
	0.3	112.6	
	0.5	127.0	
	1	138.9	
	1.5	147.8	
	2	83.7	

2.3 Tensile strength

Currently, there are few studies on the tensile strength of GO-modified cementitious materials, while the research on GP-modified cementitious materials tensile test was not found. The influence of GO on improving the tensile strength is presented in Table 5. GO-modified cementitious materials have shown excellent tensile properties in the study by Lv et al. [43], where 0.03% of GO increases the tensile strength by 78.6%. Babak et al. [72] found that 2% GO decreases the tensile strength, and the excessive addition of GO-modified cementitious materials is disadvantageous. Li et al. [73] compared the tensile strength of GO-mortar and GO-cement paste, and the influences of GO on mortar and cement paste are consistent.

The influence of GO dosage on cementitious material's tensile strength is shown in Figure 4. When the GO dosage is 0.02–0.05%, the cementitious materials tensile strength can be significantly improved. Statistical results on the literature indicate that as the GO dosage increases, the tensile strength of GO-modified cementitious materials increases first and then decreases.

In the research literature, the maximum relative compressive strength ratio is 177.3% [62]; the maximum relative flexural strength ratio is 178.3% [73]; the maximum relative tensile strength ratio is 178.6% [38]; and the optimal improvement of GO on compressive, flexura, and tensile strengths is 77.3%, 78.3%, and 78.6%, respectively. It can be concluded that GO has greatly improved the mechanical performance of cementitious materials.

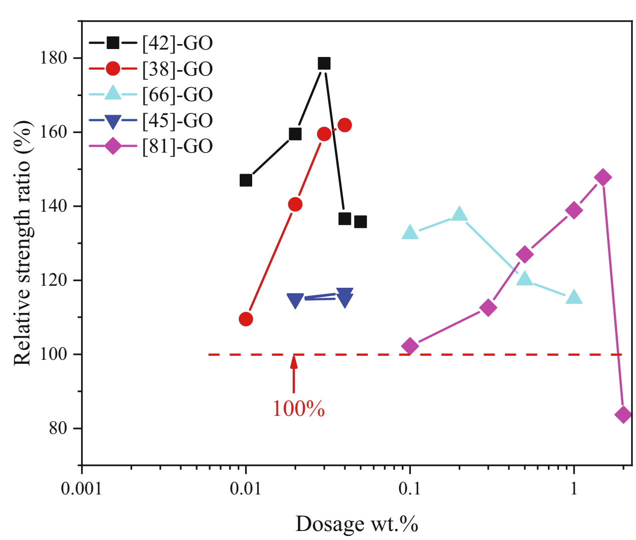

Figure 4: The GO dosages and the tensile strength effect.

3 Durability properties of GP- and GO-modified cementitious materials

The current research on the cementitious material's durability of GO- or GP-modified is insufficient. Scholars' research on the durability modified by GO and GP has mainly focused on three aspects: frost resistance, acid attack, and transport properties.

3.1 Frost resistance

Scholars have discussed the frost resistance of GO-modified cementitious materials, and the test results are very different. Zhou [75] observed the effect of GP and GO on the frost resistance of cementitious materials, and it was found that the weight loss of the GO-modified mortar is lower than the GP-modified mortar and control mortar. The length change percentage of it is the smallest among all the groups, and the results show that GO is effective to improve the frost resistance. After 540 freeze–thaw cycles, the weight loss of the modified cement paste with 0.06% and GO dosage was 0.25%, which is far lower than those of 0.8% in the unmodified cement paste [76]. Bin et al. [77] studied the improvement of GO on the durability of recycled concrete, when the GO dosages is within 0.02%. With the increase of the GO dosages, the frost resistance gradually decreases, and when the GO content is between 0.02% and 0.06%, the frost resistance of the recycled concrete gradually increases. Teng et al. [47] comparatively studied the effects of GP and GO on the frost resistance of cementitious composites, and the addition of GO will slightly reduce the frost resistance of mortar specimens and the reduction is approximately 0.2%. There is no unified result on the influence of GO on the frost resistance. Researches on the effects of GP on frost resistance have not been identified. Therefore, whether GO and GP are effective in improving the frost resistance remains to be studied.

3.2 Sulfate attack

The service area of concrete or mortar for water pipelines and dam is typical saline-alkali environment, containing a lot of corrosive attack such as sulfuric acid. The nanosheet-modified cement material provides a new method to solve this problem. Sharma and Arora [58] studied the sulfate attack resistance of GP-cement mortar, and 0.05% GP modified mortar can achieve excellent resistance to sulfate attack. The relationship between the sulfate exposure time and the percentage decrease of the compressive strength is shown in Figure 5. The microstructure analysis indicates that well-aligned hydrates is a key to improving resistance to the sulfuric acid attack.

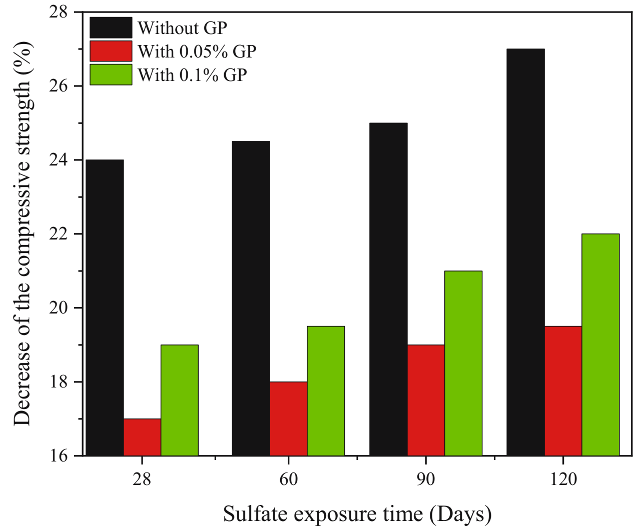

Figure 5: GP-modified mortar resistance to sulfate attack [58].

The improvement of GO-modified cementitious materials resistance to the sulfate attack has also attracted scholars' attention. In the study by Muthu and Santhanam [78], the GO-modified and nanoalumina-modified cement pastes were soaked in the acidic solution, and when compared with the unmodified sample, the porosity of the cement pastes was reduced by 46% and 51%, respectively. The study by Jiang et al. [64] showed that under the condition of sulfate corrosion for 135 days, the compressive strength improvement rate of GO to cementitious materials is 12.3%. The results of the research on the sulfate attack by GO-modified cementitious materials are basically consistent, and scholars have proven the effectiveness of GO to enhance the resistance of cementitious materials to the sulfate attack. GO refined the pore structure of the cementitious materials, and this is the reason for the improvement of sulfate attack resistance [78].

3.3 Transport properties

Transport properties of cementitious materials are an important aspect affecting the durability. GO was

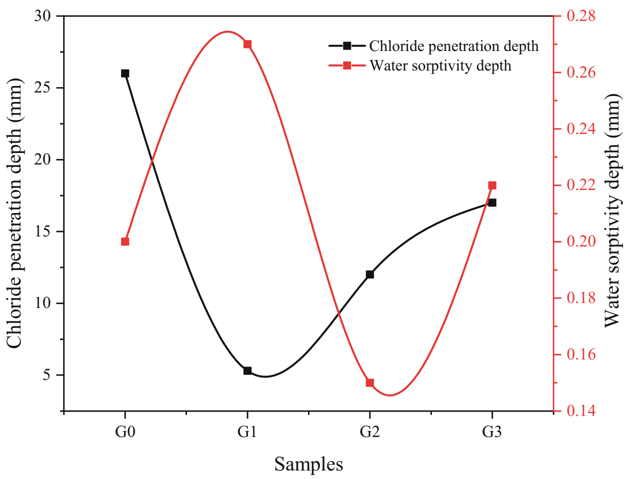

Figure 6: Chloride penetration depth and water sorptivity depth of the GO-modified mortar: G0 without GO, G1 with 0.01% GO, G2 with 0.03% GO, and G3 with 0.06% GO [79].

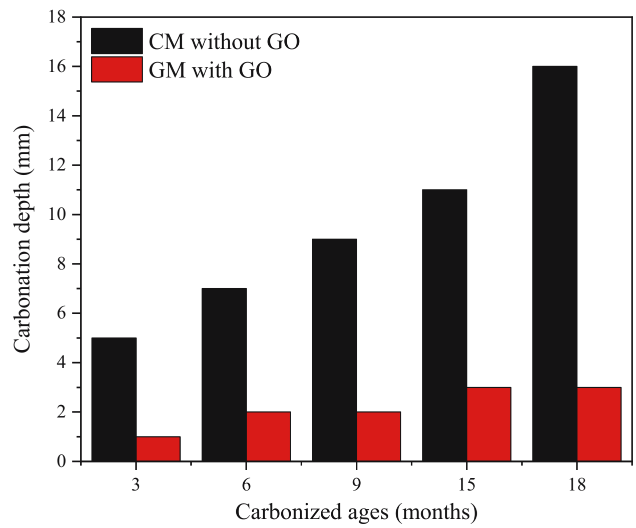

Figure 7: Carbonation depth of the GO-modified mortars [83].

dispersed in cement mortar, and the chloride penetration of the mortar was tested [79]. The results show that 0.01% GO can effectively prevent the entry of chloride, and 0.03% GO can effectively reduce water absorption. The chloride penetration depth and water sorptivity depth of the mortar are significantly reduced as shown in Figure 6. GO is effective in improving the transport properties. Jiang et al. [64] showed that the chloride migration coefficient of GO-modified cementitious materials at day 28 was reduced from 7.3 to $4.3 \times 10^{-12}\ m^2/s$. Du and Pang [80,81] studied the transport properties of GP-modified cement mortar, and when the GP dosage is 1.5%, water penetration depth, chloride diffusion, and migration coefficients were reduced by 80%, 50%, and 37%; when the GP dosage is 2.5%, these three data were reduced by 64%, 70%, and 31%, respectively. The pore structure analysis shows a 30% reduction in the pore size, which is believed to be the mechanism that improves transport properties. The study by Wang et al. [82] confirmed that the GP modification can improve the pore structure and reduce the chloride migration coefficient.

GO-modified cementitious materials also has better resistance to the carbon dioxide attack. In the study by Mohammed et al. [83,84], tests for monitoring carbonation progress showed the low carbonation depth for the GO-modified mortars, as shown in Figure 7. The carbonization depth of the GO-modified mortars is only 3 mm after carbonation for 18 months, which is 18% of the control group.

Most of the studies have reported that the beneficial effects of GP and GO improved the durability in cementitious materials as the references cited earlier. However, researches on the effects of GP on frost resistance have no definite conclusion. While GO-modified cementitious material has improved the sulfate attack resistance, transport properties has been reduced by the GO and GP nanofilms.

4 Mechanism of GP- and GO-modified cementitious materials

With the inclusion of GP or GO, the microstructure of cement hydration products can be affected by the template effect to accelerate cement hydration [49,85], refine pore structure [74], and hinder cracks propagation [61]. The following sections review the mechanism from the effect on hydration, pore structure, and crack propagation.

4.1 Effect on hydration of cementitious materials

The hydration reaction is accelerated in the GO-cement composite [85], and the hydration products can form ordered microstructures [51]. The hydration effect mechanism is mainly divided into two stages: GO adsorbed on cement particles and ordered hydration product formation. Wang et al. [86] studied the adsorption phenomenon and morphological distribution, considered that the adsorption ability of GO on the cement is strong, and calculated that the thickness of the adsorption layer is about 10.16 nm. Compared with GP,

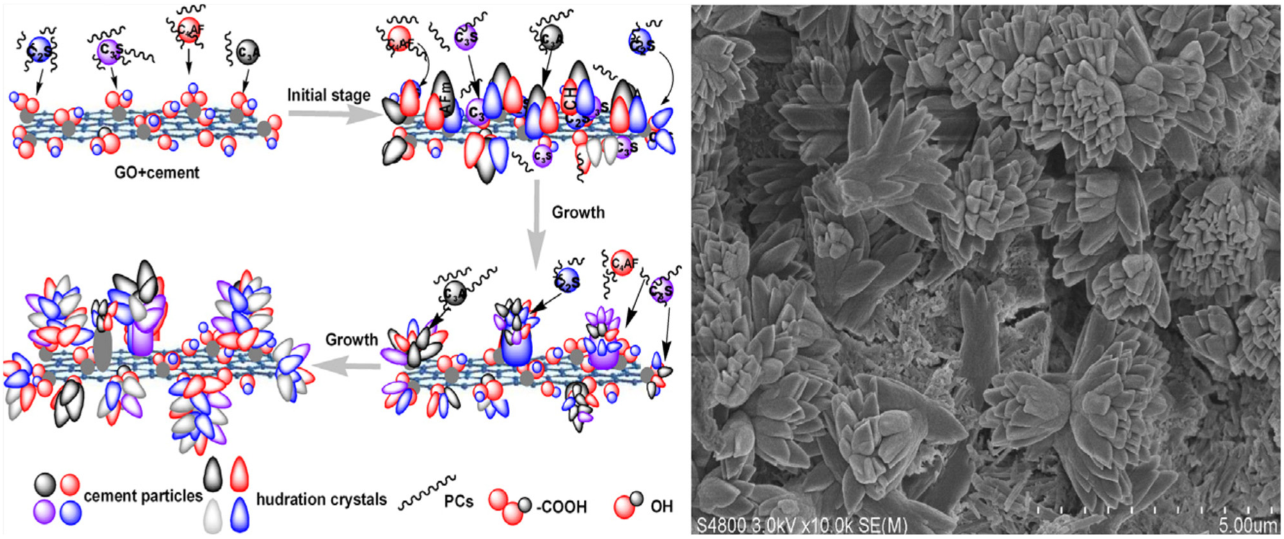

Figure 8: Template effect of GO and flower-like crystals [49].

the interface adhesion between GO and cement is stronger [87]. Lin et al. [85] considered that the adsorption phenomenon can accelerate the hydration reaction and the believed that this is a catalytic behavior.

GO exhibited the template effect and contributed to the formation of ordered hydration product. Lv et al. [49,51,88] observed that the GO regulate the cement hydration products forming polyhedron crystals and “flower-like crystals,” resulting in a large-scale ordered structure as shown in Figure 8. The composition of the hydration product crystals was tested by XRD [89], and the results show that GO modification cement hydration products still contain C–S–H, CH, and AFt as main components, indicating that GO only changed the shape of cement hydration products. Scholars call this a “template effect,” which is conducive to the formation of ordered microstructures [43,90,91]. The ordered structure is found only in the GO-modified cement and does not appear in the GP-modified cement [62]. Kudzma’s [92] study found that the strength of hydration products with the GO-modified cement increased. Lu et al. [93] wrapped GO on the carbon fiber surface, and the high reactivity of GO promoted the hydration of the cement between the fiber and the mortar matrix. Currently, most scholars believe that the crystal is formed by hydration products, while in the article by Cui et al. [94], they consider that the flower-like crystals are calcium carbonate crystals.

From the aforementioned research, we can conclude that GO has the effect of promoting the hydration reaction of cement, while GP does not have. This mainly depends on the oxygen functional group of GO, which adsorbs on cement and affects hydration.

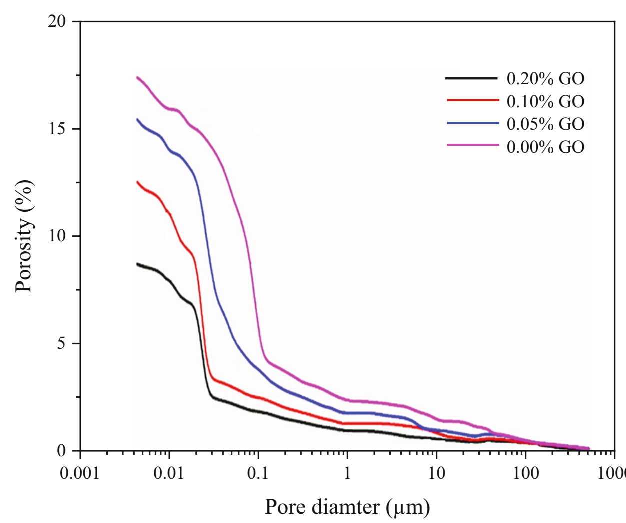

Figure 9: Mercury intrusion porosimetry test results of GO-modified cementitious materials [67].

4.2 Effect on pore structure of cementitious materials

The microstructure analysis shows that the GO-modified cement matrix has a dense structure and the GO in the cement matrix can optimize the pore structure and reduce the porosity. The mercury intrusion porosimetry (MIP) test results are shown in Figure 9 [67], and with the increase of the GO content, the porosity decreased significantly. Due to the nanosize of GO and GP nanosheets, these nanomaterials can fill micron or nanoscale pores in the porous materials [95]. This refinement of the microstructure by the GP and GO was validated by the MIP results [80]. The study by Chu et al. [96]

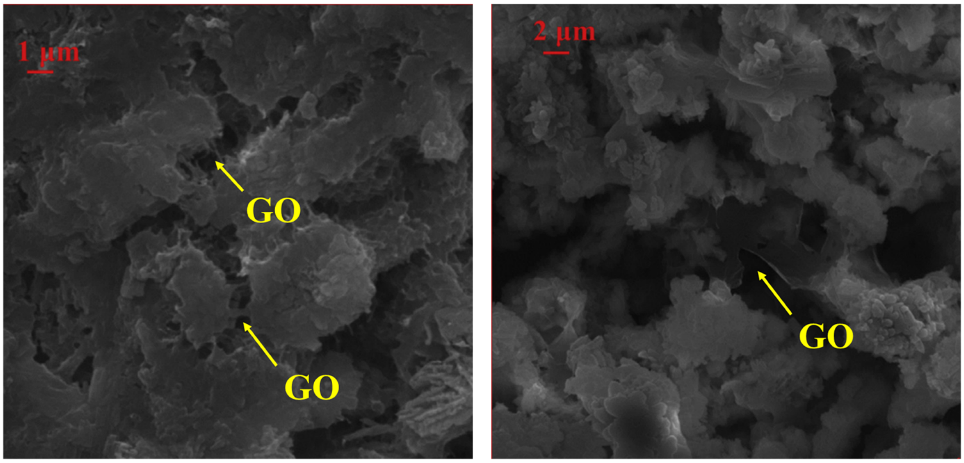

Figure 10: SEM images of GO nanosheet-modified cement.

showed that the incorporation of GP sulfonate nanosheets reduces the porosity of concrete by 2–6%. Liu et al. [54] considered that the template effect of GO promotes cements the hydration products tightly and improving the pore structure of the cement matrix. The addition of 0.02% GP in cement will reduce the number of transitional pores (size ranges from 10 to 100 nm) [97].

4.3 Effect on crack propagation of cementitious materials

The introduction of GP and GO nanosheets hinders the propagation of cracks in cementitious materials and reduces the density of microcracks. The scanning electron microscopic (SEM) image shows fine cracks and few branches in GO-modified cementitious materials, indicating that the 2D nanosheet structure of GO may be a hindrance to crack propagation [57]. Min et al. believed that GO monomers can be connected to each other through chemical reactions to form a 3D network structure in matrix. Moreover, the adsorption between GO and hydration products makes the GO-3D network structure tightly connected to the hydration products [98,99], as shown in Figure 10.

This 3D network structure can prevent crack propagation. The microstructure of this GP-reinforced cement matrix was also observed [61] and believed that the plicate morphology and the tortuous behavior of GP hindered the development of cracks. Yanturina et al. [100] found that the nanoadditive of GP contributes to the formation of a dense structure of the cement stone. Horszczaruk et al. [101] found that GO interacts well with the hydration products of cement.

The impact of the microstructure in the form of GP and GO on cementitious materials has been reviewed. When GO is added to cementitious materials, the hydration reaction of cement is accelerated and the hydration products can form ordered microstructures and reduce pores and cracks in the cement matrix. The 3D network structure is formed by nanosheets and cement matrix to hinder the propagation of cracks.

5 Conclusions

The mechanical properties, durability, and mechanism of GO- and GP-modified cementitious materials was reviewed through the literature. Based on the literature research, the main conclusions are as follows:

(1) The strength of GO-modified cementitious materials is significantly improved, and GP is less than GO in improving the strength of cementitious materials. The optimal improvement of the GO-modified compressive, flexural, and tensile strengths are 77.3%, 78.3%, and 78.6%, respectively. The effect on the strength is affected by the dosages of GO and GP.
(2) GO- and GP-modified research on the durability of cementitious materials focuses on three aspects, frost resistance, acid attack, and transport properties. Whether GO and GP can be used to improve the frost resistance remains to be studied, and GO-modified cementitious material has improved the sulfate attack resistance, and transport properties can be decreased by the addition of GO and GP nanofilms.
(3) When GO is added to cementitious materials, the hydration reaction of cement is accelerated and the

hydration products can form ordered microstructures and reduce pores and cracks in the cement matrix. The 3D network structure formed by GO and GP nanosheets and cement matrix plays an important role in hindering the propagation of cracks.

In summary, there are multiple other themes that need further exploration, such as the micromechanical properties of GO-modified cementitious materials. In terms of durability of GO-modified cementitious materials, the study on frost resistance have not been identified, and the effects of temperature, load, and dry–wet cycle on early cracking inhibitor of GO-modified concrete have not been covered. In addition, the study of the functional characteristics of GO- and GP-modified cementitious composites is not systematic and need more research.

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