YCRETS 2023
YOUNG CONCRETE RESEARCHERS, ENGINEERS & TECHNOLOGISTS
SYMPOSIUM

CEMENT & CONCRETE SA

The effect of nanographene on conventional concrete using a variety of application techniques

Abraham E. van Wyk (1), Carla van Wyk (1) and Riaan Combrinck (1)

(1) Department of Civil Engineering, Stellenbosch University

Abstract

Nanographene was identified by Andre Geim and Konstantin Novoselov in 2004 and was labeled as a "wonder material". Nanographene applied to conventional concrete has shown potential to drastically improve concrete's mechanical performance. Although nanographene added to concrete has exceptional properties the practical application thereof has proven to be difficult. Thus, there is a notion in the concrete industry that this wonder material does not perform so wonderful in concrete. This study aims to address challenges relating to nanographene application in conventional concrete. This is done by treating conventional concrete ingredients with a variety of nanographene application techniques to improve its mechanical performance. This study concluded that nanographene does improve the mechanical performance of conventional concrete, but only for some of the application techniques. These applications techniques are described in detail in this study.

Keywords: Mechanical performance, Nanographene, Concrete, Application techniques

1. INTRODUCTION

Population growth and rapid urbanization have caused pressure on existing urban infrastructure. The pressure exhorted on urban infrastructure let to the demand for building and developments to escalate. These developments need durable, low cost, and accessible materials to implement solutions. Material compositions such as concrete are commonly used in the built environment because of its accessibility and high strength properties with regards to compression. Conventional concrete consists of four constituent materials namely water, sand, aggregate and cement [1]. The need for infrastructure development has brought forth a great demand for these constituent materials.

The demand for these materials brings a variety of benefits but also problems. Unfortunately, some of concrete's age-old problems is still to be resolved. Problems such as the negative effects cement has on the environment and concrete's weak tensile capabilities. For most of the time, steel is incorporated in concrete to improve concretes tensile capability. Both the cement and steel industries are energy hungry during production. These two industries contribute to 16% of the global carbon dioxide emissions released on an annual basis [2, 3]. Carbon dioxide (CO_2) is classified as the main accelerator in the greenhouse effect which drives global warming [3]. This is a tremendous obstacle for the cement and steel industry to overcome as more and more pressure is enforced to comply with Net Zero Emission by 2050. Thus, the need to reduce CO_2 emissions increases by the day.

This study focusses on potential solutions and application techniques that can reduce the CO_2 emissions released by the cement and steel industry. Globally the most cement and steel are used in the built environment [4, 5]. One of the key viable solutions would be to reduce the amount of cement and steel used. The majority of cement and steel used in the built environment is used in concrete structures [4, 5]. By drastically increasing the mechanical performance of concrete, the cement content and steel quantity used in concrete can be reduced. If the desired concrete performance can be achieved with less cement and less steel, the negative environmental impact can be greatly reduced.

Nanomaterials have opened new possibilities for concrete enhancement and alteration. Nanomaterials such as nanographene is a light and extremely strong material that can dramatically affect the mechanical performance of concrete [6]. Only a small amount is needed because of the particle size and large surface area of nanographene [7]. Although nanographene added to concrete has exceptional properties the practical application thereof is difficult. The dispersion of nanographene has proven to be the greatest challenge since the non-sixed graphene flakes flocculates and has hydrophobic tendencies. The dispersion of a nano particles in a cementitious matrix plays an important role to enhance its mechanical performance [8]. Johnson et al. [9] found that ultrasonication is a possible solution to disperse nanographene in a mixture. Sonication is a process in which sound energy is applied to a mixture to agitate the particles in the mixture and cause dispersion. Sonication is costly and not viable on large scale [9]. Thus, a more cost effective, commercially viable dispersion method was developed through high mechanical shearing.

A study by Van Wyk [10] identified which type of dispersion agents allows for the best dispersion of nanographene using mechanical shearing. Furthermore, attention was placed on how the degree of dispersion influenced the performance of concrete. Van Wyk assessed the influence the degree of the dispersion on the fresh properties, mechanical properties, and durability properties of concrete. Experimental analysis showed that a higher the degree of dispersion resulted in a positive enhancement of concrete’s mechanical and durability performance.The combined dispersion action of a polymetric (Polycarboxylate Ether) and a surfactant (Lignosulfonate) admixture resulted in the highest degree of dispersion of nanographene. This led to superior mechanical and durability performance enhancement compared to the other tested admixtures. Unfortunately, van Wyk’s research still did not improve the reference mixture. Thus, nanographene was seen as an expensive and ineffective addition to concrete.

Concrete is strong in compression but weak in tension [1]. One of the reasons for concrete being weak in tension is because of the weak interface bond between the aggregate and mortar [11, 12]. The Interfacial Transition Zone (ITZ) is where tensile failure of concrete occurs. Concrete is described as a heterogeneous material which means it is diverse in character and constituents [1]. Concrete is not uniform in composition due to the difference in stiffness of materials. Cement, water, and sand which is thoroughly blended forms mortar and can be described as a homogenous material [1]. When adding large aggregate or stone to mortar, concrete is formed [1]. Thus, when concrete forms the material transitions from a more homogenous state to a near heterogeneous state due to difference in stiffness between aggregate and mortar. The aggregate and mortar subsequently form a type of cold joint because of the difference in stiffness and composition. A cold joint is described as a difference in consistency between to materials which causes weak adhesion between materials [13]. Therefore, a weak bonding between aggregate and mortar transpires which causes concrete to mostly mechanically fail at the ITZ between the mortar and the stone.

This study aims to develop a variety of nanographene application techniques to improve the mechanical performance of conventional concrete by densifying the mortar matrix as well as the ITZ. Little to no research has been done on the majority of nanographene application techniques developed in this study.

2. EXPERIMENTAL FRAMEWORK

2.1 Nanographene Application Techniques

This study focusses on two mechanisms which can potentially improve the mechanical performance of conventional concrete using nanographene application techniques (NGAT). These two mechanisms are the densification of the mortar matrix and ITZ.

Three NGAT's were implemented to densify the mortar matrix. 1) Nanographene pre-dispersed in a superplasticiser (PCE_LIG_NG) and then added to fresh concrete. 2) Nanographene pre-dispersed in a super absorbent polymer (SAP_NG) and then added to fresh concrete. 3) Nanographene pre-dispersed in a grinding aid (GA) and used to treat cement (TC) with nanographene using a ball mill (TCGA_NG). The pre-dispersion time and intensity of the nanographene was determined by van Wyk's research [10]. A separate reference mixture without nanographene was mixed and tested for each of the three techniques to make results comparable. When nanographene is pre-dispersed in a solution or admixture, it is referred to as a nanographene dispersion agent (NGDA).

There were three NGAT's implemented to densify the ITZ. 1) Wet coating aggregate (WCA) with a NGDA and then use the nanographene coated aggregate to mix in the concrete. 2) Dry coating aggregate (DCA) without pre-dispersing the nanographene and then using the nanographene coated aggregate to mix in the concrete. 3) Wet coating aggregate with a nanographene dispersion agent (Tylose_NG) and then applying a thin material film to the surface of the aggregate. Figure 1-3 illustrates the experimental procedure of the NGAT, WCA_NG.

Figure 1: Pre-dispersion of NGDA (Tylose_NG)

Figure 2: Implementation of pre-dispersed NGDA

Figure 3 : Aggregate coated with pre-dispered NGDA

Three different material film approaches were used. The first approach was to apply a cementitious (WCAC_NG) film to the surface of the aggregate. The second approach was to apply a sand (WCAS_NG) film to the surface of the aggregate. The third approach was to apply a combined cementitious and sand (WCACS_NG) film to the surface of the aggregate.

The multi-particle coated aggregate was then used to mix in the concrete. The amount of material (cement, sand, or combined) that was used to apply the thin film to the surface of the aggregate was deducted from the base mix constituents. A separate reference mixture without nanographene was mixed and tested for the WCA technique to make results comparable.

2.2 Concrete Mix Design

Fifteen different mixtures were prepared in this study as shown in Table 1. Each mixture contained the same amount water, cement, sand, and stone. For the base mix, a water to cement ratio of 0.6, a target strength of 35MPa with a slump of 92.5mm were achieved.

A CEM II/A-L 52.5 N cement from Portland Cement (PPC) was used for all the mixes [14]. A coarse natural pit sand, known locally as Malmesbury sand, with a 13mm Greywacke coarse aggregate from Lafarge quarry in Eersterivier were used for all mixes. The relative density (RD) of the Malmesbury sand was 2.63, the fines modulus (FM) was 3.24, and the dust content (<0.075mm) was 4.6%. The nanographene was sourced from First Graphene Ltd. PUREGRAPH®50 and PUREGRAPH®50 AQUA was used for this study [15, 16]. A dosage of 0.07% of the cement weight was used based on recommendation from literature [17]. A dosage of 1% of the cement weight was used for the admixtures, solutions and grinding aids. CHRYSO ADA 25EL grinding aid (GA) was used as a NGDA to treat the cement. Tylose H 6000 YP2 (Hydroxyethyl cellulose) acts as a rheology and viscosity modifier and was used as a NGDA to wet coat the aggregate. The mixes that used an admixture (PCE_LIG) and Super Absorbent Polymer (SAP) was formulated from raw ingredients.

Table 1: Concrete mix constituents and proportions

		NGAT mix names						
Constituents (kg/m^3)	**REF**	**TCGA_NG**	**TC_NG**	**WCA_NG**	**DCA_NGF**	**DCA_NGA**	**PCE_LIG_NG**	**SAP_NG**
Water	209	209	209	209	209	209	209	209
Cement	348	348	348	348	348	348	348	348
Sand	911	911	911	911	911	911	911	911
Aggregate	900	900	900	900	900	900	900	900
Tylose	-	-	-	10,03	-	-	-	-
PCE_LIG	-	-	-	-	-	-	3,48	-
SAP	-	-	-	-	-	-	-	3,48
GA	-	3,48	-	-	-	-	-	-
PG®50	-	0,24	0,24	0,24	0,24	-	0,24	0,24
PG®50_AQUA	-	-	-	-	-	0,82	-	-

2.3 Tests

The slump test was determined in accordance with SANS 5861-1 (2006) and was used to measure the flowability of conventional concrete. At least two slump measurements were conducted, respectively.

The compressive strength of 100mm cubes were determined in accordance with SANS 6253 (2006). Four cubes per concrete mixture were tested after 7 days and on 28 days of curing in the water baths controlled at 23°C temperature. The force (in Newton) applied at the time of failure was then recorded.

The tensile splitting capacity of 100mm cubes were determined in accordance with SANS 5863 (2006). Four cubes per concrete mixture were tested after 28 days of curing in the water baths. A constant stress of 0.03 ±0.01MPa/s was applied up until the point of failure. Equation 1 illustrates the tensile splitting capacity (MPa) calculated using F, force at failure (N), and a, cube width (mm).

$$f_{cu} = \frac{2F}{\pi a^2} \tag{1}$$

3. RESULTS AND DISCUSSION

Table 2 shows the slump measurements after mixing as well as the compressive strength, and tensile splitting capacity of all fifteen mixes at 7 days and 28 days of curing. Each application technique is compared to its respected reference mix as illustrated in Table 2.

The slump results indicated a decrease in flowability when PUREGRAPH®50 (flake) was not pre-dispersed and used in concrete. There was a slight decrease in flowability when the PUREGRAPH®50 AQUA (agglomerate) was used in concrete. The slump results indicate that the flowability remains similar when nanographene was pre-dispersed in an admixture or solution and then added to concrete.

The application techniques, DCA_NGF and DCA_NGA, indicated a 25mm and 5mm decrease in flowability, respectively. DCA_NGF and DCA_NGA increased the compressive strength after 7 days of curing with 2.6% and 3.1% respectively and by 4.3% and 2.8% after 28 days of curing respectively. DCA_NGF indicated a decrease of 9.9% in the tensile splitting capacity while DCA_NGA indicated an increase of 11,4% in the tensile splitting capacity after 28 days of curing. Deflection measurements from the tensile splitting test for DCA_NGF and DCA_NGA was 1,01mm and 0,82mm respectively.

The application techniques, TCGA_NG, WCA_NG and WCACS_NG, indicated a 15mm, 17,5mm and 50mm increase in flowability, respectively. TCGA_NG, WCA_NG and WCACS_NG decreased the compressive strength after 7 days of curing with 8.5%, 15.8% and 16.2% respectively and by 5.5%, 4.2% and 9.1% respectively after 28 days of curing. TCGA_NG decreased the tensile splitting capacity by 22.0% while WCA_NG and WCACS_NG indicated an increase of 2,9% and 4.8% respectively after 28 days of curing. Deflection measurements from the tensile splitting for TCGA_NG, WCA_NG and WCACS_NG was 0,74mm, 0,82mm and 0,79mm respectively.

The application techniques, WCAC_NG and WCAS_NG, indicated a 27.5mm and 15mm decrease in flowability, respectively. WCAC_NG and WCAS_NG increased the compressive strength after 7 days of curing with 6.5% and 2.8% respectively and by 4.0% and 5.4% respectively after 28 days of curing. WCAC_NG and WCAS_NG increased the tensile splitting capacity after 28 days of curing with 15,0% and 13,1% respectively. Deflection measurements from the tensile splitting test for WCAC_NG and WCAS_NG was 0,78mm and 0,84mm respectively.

The application techniques, PCE_LIG_NG and SAP_NG, indicated a 5mm increase and 5mm decrease in flowability, respectively. PCE_LIG_NG and SAP_NG decreased the compressive strength after 7 days of curing with 3,3% and 4,2% respectively, but increased the compressive strength after 28 days of curing with 8,2% and 3,4% respectively. Both PCE_LIG_NG and SAP_NG indicated a decrease of 0,7% in the tensile splitting capacity after 28 days of curing. Deflection measurements from the tensile splitting test for PCE_LIG_NG and SAP_NG was 0,81mm and 0,91mm respectively.

Table 2: Flowability, compression, and tensile results

	Flowability	Compression				Tensile		
Mix	**Slump (mm)**	**7-Days (kN)**	**%>OR<**	**28-Days (kN)**	**%>OR<**	**28-Days (kN)**	**Deflect (mm)**	**%>OR<**
REF_MIX	92,5	300,90	Ref	352,70	Ref	2,63	0,81	Ref
DCA_NGF	67,5	308,80	2,6%	368,50	4,3%	2,37	1,01	-9,90%
DCA_NGA	87,5	310,10	3,1%	362,60	2,8%	2,93	0,82	11,40%
TC_NGF	65	311,20	3,4%	374,50	6,2%	2,68	0,82	1,90%
TCGA_REF	107,5	341,70	Ref	370,60	Ref	2,73	0,73	Ref
TCGA_NG	122,5	312,50	-8,5%	350,10	-5,5%	2,13	0,74	-22,00%
WCA_REF	87,5	294,50	Ref	332,80	Ref	2,38	0,82	Ref
WCA_NG	105,0	248,10	-15,8%	318,90	-4,2%	2,45	0,75	2,90%
WCACS_NG	137,5	246,70	-16,2%	302,40	-9,1%	2,50	0,79	4,80%
WCAC_NG	115,0	313,70	6,5%	346,10	4,0%	2,74	0,78	15,00%
WCAS_NG	72,5	302,80	2,8%	350,80	5,4%	2,69	0,84	13,10%
PCE_LIG_REF	165,0	342,60	Ref	399,00	Ref	2,86	0,74	Ref
PCE_LIG_NG	170,0	331,40	-3,3%	366,40	-8,2%	2,88	0,81	0,70%
SAP_REF	85,0	367,30	Ref	417,00	Ref	2,61	0,81	Ref
SAP Ref_NG	80,0	382,60	4,2%	431,20	3,4%	2,63	0,91	0,70%

The application techniques, TC_NGF and DCA_NGA, prove to facilitate the best overall improvement in mechanical performance of conventional concrete. This improvement is visible in the 28 day compressive strength and tensile splitting capacity results. The application technique where cement was treated with nanographene in flake form (TC_NGF) showed the best improvement in compressive strength with an increase of 6,2%. It is known that finer materials (<0,075mm) such as ground limestone, slag and fly ash fill pours and voids in concrete, resulting in increased strength [1]. Thus, nanographene flake is believed to have had the same effect and facilitated the densification of the mortar matrix which enhanced the compression performance of the concrete.

The application technique where the surface of the aggregate was dry coated with nanographene in aqua form (DCA_NGA), showed the best improvement in tensile splitting capacity with an increase of 11,4%. It is believed that the increase is due to a high coating efficiency the agglomerated nanographene had on the surface of the aggregate. This high coating efficiency is facilitated by a smearing action caused by the agglomerated nanographene. It is believed that this smearing action also enhances the ability of the nanographene to remain on the surface of the aggregate when introduced into a robust mixing environment. This allows for the nanographene to densify the ITZ and not be diluted into the mortar paste. Therefore, the nanographene is focussed at the ITZ and enhances the tensile splitting capacity of conventional concrete.

Several application techniques as shown in Table 2 drastically decreased the mechanical performance of conventional concrete. The results indicate that a major decrease in mechanical performance occurred when nanographene was pre-dispersed (TCGA_NG, WCA_NG and WCACS_NG) in a dispersion agent. It is believed that the viscosity and the chemical composition of the dispersion agent does influence the degree of dispersion. The degree of dispersion relates to how long nano particles remain in suspension after separation through dispersion methods. The goal is to separate the nanographene from each other and keep the particles in suspension before adding to concrete. Van Wyk proved that the higher the degree of dispersion, the higher the higher the mechanical performance of conventional concrete [10]. Therefore, more research needs to be done on the factors that influences the application of nanographene pre-dispersed in a dispersion agent.

Only a few application techniques improved the mechanical performance beyond the performance of the base mix (REF_MIX). Figure 1 shows the percentage improvement in mechanical performance when NGAT's implemented are compared to the base mix (Ref mix). The results indicate that a specific application technique, DCA_NGA, showed a small improvement in the compression performance and a significant improvement tensile performance of conventional concrete. Therefore, DCA_NGA can be used specifically to densify the ITZ and improve the tensile performance of conventional concrete.

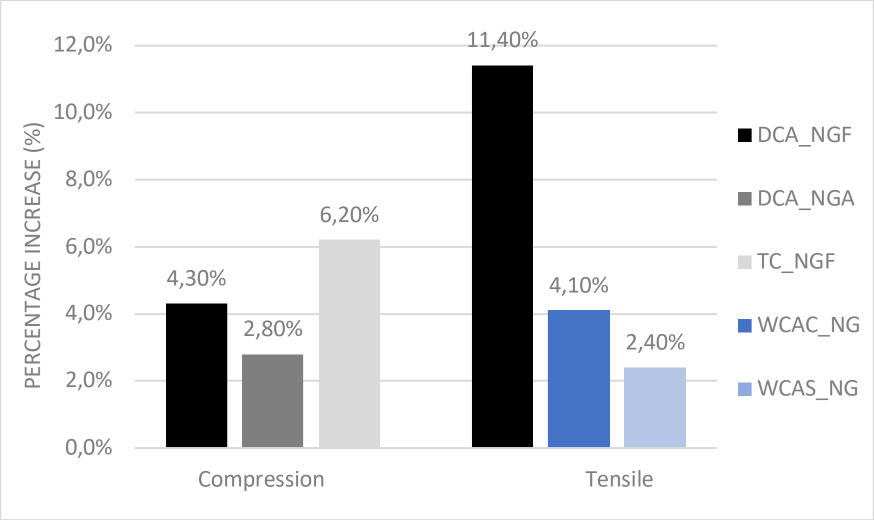

Figure 1: Percentage Increase in mechanical performance compared to the base mix (REF_MIX)

4. CONCLUSIONS

The main conclusions from this study are as follows:

- There are indications that when nanographene is not pre-dispersed in a dispersion agent, the flowability of the concrete decreases. Rheology testing needs to be done to confirm this phenomenon.
- Conventional admixtures and solutions increase the compression performance of conventional concrete far greater than nanographene. Although it should be kept in mind that the admixtures were added at dosages more than 100 times that of the nanographene.
- There is more research to be done on the factors that have an impact on the application of nanographene pre-dispersed in a dispersion agent. This includes the dosage of nanographene used.
- Nanographene improved the tensile performance of almost every concrete mix compared to its respected reference mix.
- The nanographene application technique (NGAT), DCA_NGA, slightly improved the compression performance of conventional concrete. It outperformed all other concrete mixes with respect to tensile performance. Thus, this NGAT is seen as a viable option to improve the mechanical performance of conventional concrete, especially in tension.

The application of nanographene in concrete remains challenging and more research needs to be done before it can be applied to the construction industry. Several application techniques in this study shows promise. More research on especially the impact these nanographene application techniques has on the rheology and durability of the concrete is needed.

ACKNOWLEDGEMENTS

The following people are acknowledge for their support during this study. Barry Jollife, for introducing the world of Nanographene and supplying the nanographene and raw chemicals. Concrete and admixture specialists, Darius Herbs and Alexander Smith from Nanoproof. Paul Botha from Fine Bubble Technologies (Pty).

REFERENCES

[1] Alexander, K.M., Wardlow, J. and Gilbert, D., "*Fulton's concrete technology TENTH EDITION", 2021*. Cement & Concrete SA.

[2] McKinsey & Company, 2020. *Decarbonization challenge for steel Hydrogen as a solution in Europe*.

[3] Badel, A. et al., "Concrete needs to lose its colossal carbon footprint. *Nature", 2021.* Volume 597, pp. 593-594

[4] IEA, *Cement*, 2022. http://www.Cement – Analysis - IEA/ [Accessed 07 April 2023].

[5] WSA, 2023. *Steel in building and Infrustructure*. http://www.Buildings and infrastructure - worldsteel.org/ [Accessed 07 April 2023].

[6] T. S. Qureshi and D. K. Panesar, "Nano reinforced cement paste composite with functionalized graphene and pristine graphene nanoplatelets," *Compos B Eng*, vol. 197, Sep. 2020, doi: 10.1016/j.compositesb.2020.108063.

[7] P. Demo, A. Sveshnikov, Š. Hošková, D. Ladman, and P. Tichá, "Physical and Chemical Aspects of the Nucleation of Cement-Based Materials," 2012.

[8] A. H. Korayem, N. Tourani, M. Zakertabrizi, A. M. Sabziparvar, and W. H. Duan, "A review of dispersion of nanoparticles in cementitious matrices: Nanoparticle geometry perspective," *Construction and Building Materials*, vol. 153. Elsevier Ltd, pp. 346–357, Oct. 30, 2017. doi: 10.1016/j.conbuildmat.2017.06.164.

[9] D. W. Johnson, B. P. Dobson, and K. S. Coleman, "A manufacturing perspective on graphene dispersions," *Current Opinion in Colloid and Interface Science*, vol. 20, no. 5–6. Elsevier Ltd, pp. 367–382, Oct. 01, 2015. doi: 10.1016/j.cocis.2015.11.004.

[10] C. Van Wyk, "Nanographane dispersed in admixtures to enhance concrete performance" Final year project, Stellenbosch University, 2022.

[11] R. Liu, H. Xiao, J. Liu, S. Guo, and Y. Pei, "Improving the microstructure of ITZ and reducing the permeability of concrete with various water/cement ratios using nano-silica," *J Mater Sci*, vol. 54, no. 1, pp. 444–456, Jan. 2019, doi: 10.1007/s10853-018-2872-5.

[12] V. Nežerka, P. Bílý, V. Hrbek, and J. Fládr, "Impact of silica fume, fly ash, and metakaolin on the thickness and strength of the ITZ in concrete," *Cem Concr Compos*, vol. 103, pp. 252–262, Oct. 2019, doi: 10.1016/j.cemconcomp.2019.05.012.

[13] İ. Bekem Kara, "Experimental Investigation of the Effect of Cold Joint on Strength and Durability of Concrete," *Arab J Sci Eng*, vol. 46, no. 11, pp. 10397–10408, Nov. 2021, doi: 10.1007/s13369-021-05400-5.

[14] PPC Limited, "PPC Limited," *PPC Limited*, 2023. https://www.ppc.africa/ [Accessed 09 Feb 2023].

[15] First Graphene Ltd, *PureGRAPH-datasheet_v1-02, 2021*. http://www.PureGRAPH-datasheet_v1-02.pdf (firstgraphene.net)/[Accessed 07 April 2023].

[16] V. D. Ho, T. G. Tg, T. Ozbakkaloglu, A. Goodwin, C. McGurkin, R. U. Karunagaran, D. Losic., "Investigating the reinforcing mechanism and optimized dosage of pristine graphene for enhancing mechanical strengths of cementitious composites," *RSC Adv*, vol. 10, no. 70, pp. 42777–42789, Nov. 2020, doi: 10.1039/d0ra07639b.