EFFECT OF NANO-CLAY AND WASTE GLASS POWDER ON THE PROPERTIES OF FLAX FIBRE REINFORCED MORTAR

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ABSTRACT

The main concern for natural fibres reinforced cement composites (NFRC) is the durability of the fibres. The alkalinity of the cement matrix is the main causes of the loss of resistance of NFRC. The aim of this work was to determine the effect of partial replacement of Ordinary Portland cement (OPC) by finely ground waste glass powder (WG) and nano clay particles (NC) on the mechanical performance and durability of flax fibre reinforced cement composites (FRC). Tests were designed to study the alkali-silica reaction (ASR), X-ray diffraction analysis (XRD), differential thermal analysis (DTA) and the mechanical performance of the composites. Additionally, the durability of the composites aged under wetting and drying cycles are presented. The results show that incorporation of WG has a positive effect on the mechanical properties and durability of FRC especially when NC is presented. In addition, the DTA results and XRD analysis show a reduction in the calcium hydroxide (CH) content in mortars with both WG and a hybrid combination of WG and NC. This confirms the improvement of mechanical properties and the occurrence of the pozzolanic reaction after 28 days of hydration.

Keywords: fibre reinforced composites, glass powder, cement matrix, nano-clay, mechanical properties.

1. INTRODUCTION

Fibre-reinforced composites have been used for millennia. The first to be used were naturally occurring composites, such as wood and bamboo, but man also found that there were great benefits from using artificial mixtures of materials with one component fibrous, such as straw in clay (for bricks) or horse hair in lime plaster (for ceilings) [1]. The addition of fibres (either natural or synthetic) significantly enhances many of the engineering properties of the cement matrix, especially impact strength and toughness. This enhanced performance in the fibre reinforced cement matrix compared to the unreinforced matrix comes from its great capacity to absorb energy during fracture. The chief contribution of fibres to the cement matrix can mainly be observed after matrix cracking. While an unreinforced matrix fails in a quasi-brittle behaviour after cracking, the randomly distributed, short fibres in the matrix arrest microcracks, bridge these cracks, undergo a pull-out process and limit crack propagation in the reinforced matrix. Hence, debonding and pulling out the fibres require more energy, which leads to a significant improvement in toughness, and a resistance to cyclic and dynamic loading occurs, which helps maintain structural integrity and cohesion in the matrix [2, 3].

Natural fibres offer many advantages which make them attractive for cement reinforcement. For example natural fibres are abundant, relatively cheap, low in density, environmentally friendly and less abrasive than glass fibres [4]. However, the chief drawback of using natural fibres in cement composites is their degradation in the alkaline cement matrix [5]. The decomposition of natural fibres in cement-based composites occurs due to the alkaline pore water dissolves the lignin and hemicelluloses existing in the middle lamellae of the fibres, thus weakening the link between the individual fibre cells [5, 6]. Currently, two approaches have been explored for the reduction of alkaline attack to fibres in NFRC. This involves the modification of cement matrix by using pozzolanic materials to reduce or remove the alkaline compounds, or the modification the surface of the fibres with chemical or physical treatments to increase their stability in the cementitious matrix [6].

Reduction of cement matrix alkalinity by using pozzolanic materials, such as silica fume [5], fine powdered metakaolin and calcined waste crushed clay brick [7] is one of the most successful techniques for improving the durability of natural fibre cement composites Silva et al., [8]. In this technique, cement is partially replaced by pozzolanic materials such as silica fume, rice husk ash, pumice and diatomite, metakaolin and calcined waste crushed clay brick. Silva et al., have recorded a marked improvement in durability by replacing 50% of the cement by calcined clays [8]. In addition, Tolêdo Filho et al., found an improvement in the durability of sisal cement composites through replacing 10% of the cement by undensified silica fume [5].

As reported by Shao et al., [9], a typical pozzolanic material should satisfy three characteristics: contain high silica content, be amorphous in nature and have a large surface area. Compared to silica fume, glass contains relatively large quantities of silica (54-81% by weight) and is amorphous in nature. Therefore, in theory glass is pozzolanic or even cementitious in nature and might satisfy the basic requirements for a pozzolan if it was finely ground to mitigate the alkali silica reaction (ASR) and to activate the pozzolanic behaviour. Hence, it
can be used as a cement replacement in Portland cement composites [10].

The use of finely ground glass as a pozzolanic material is relatively recent, and has been encouraged as a result of continual accumulation of waste glass and its environmental issues. According to the requirements of ASTM C 618 [11], glass has the potential to acceptably function as a cement replacement; however, one of the limiting factors in the use of finely ground waste glass powder in concrete is the lower reactivity of the materials when compared to cement powder. Overcoming this limitation requires practical methods for increasing the reactivity of waste glass powder [12]. Recent studies have shown that nano-sized particles such as nano-clay particles (NC) have a high surface area to volume ratio that has the potential for tremendous chemical reactivity [13]. As the previous works show, addition of a small amount NC accelerates pozzolanic activity, improves workability, increases the level of control of ASR, and increases the strength and durability of concrete [13-14]. Therefore, using NC to increase the pozzolanic activity of WG would be a promising approach to improving the performance of NFRC. The literature review has shown that studies on this subject are very limited. This study focused on the use of WG and NC as a partial weight replacement for cement in order to improve the durability of the FRC.

In this study, flax fibres were used to reinforce the cement matrix. In addition, WG and NC were used as a partial replacement for cement. In order to characterise these developed composites, a series of tests were conducted consisting of a study of the alkali-silica reaction (ASR), X-ray diffraction analysis (XRD), differential thermal analysis (DTA) and the mechanical performance of the composites. Furthermore, the durability of the composite when exposed and aged under alternating wetting and drying cycles is presented.

2. MATERIALS AND METHODS

Ordinary Portland cement was used in this study and supplied by Irish Cement Ltd. The cement was grade 42.5 with a specific gravity of 3.15 g/cm³. Sand with a particle size up to 1.18 mm and a specific gravity of 2.65 g/cm³ was obtained from a local supplier in Ireland. The clay used in this study, Closite® 30B, is commercially available from Southern Clay Products Inc, USA. This is an organically modified montmorillonite (OMM) with quaternary ammonium salt which has an initial d-space of 18.5 Å. The SEM micrograph of Closite® 30B particles is shown in Figure-1. It can be seen that the particles consist mainly of fine ball-milled particles with an irregular microstructure and an average particle size of 6 µm.

Waste glass used in this study was obtained from recycled green alcohol bottles. In order to satisfy the physical requirement for fineness, the glass has to be ground fine enough to pass through a 75 µm sieve. This is accomplished by crushing and grinding the glass in a ball mill in the laboratory and by sieving the ground glass to the desired particle size.

Figure-1. SEM micrograph of Closite® 30B.

SEM examinations indicate that the ground waste glass powders consist mainly of fine angular particles with a narrow particle size range, as shown in Figure-2.

Figure-2. SEM photographs of ground green waste glass powder.

The crystallinity of the green glass powder was examined using X-ray diffraction. The X-ray spectrum of the glass is shown in Figure-3. It is evident that green glass powder is a typical amorphous material. Raw flax fibres used in this work were obtained from Egypt and came in straight long fibre form. Sodium hydroxide pellets were purchased from Aldrich Company.

Organically modified montmorillonite particles (OMM) have a relatively higher surface area per unit volume and are difficult to mix at the same time with water, cement, fibres and sand. Hence, the microstructure and mechanical properties of cement mortars reinforced with OMM are considerably influenced by the mixing procedure of their constituent materials. Kuo et al., [14] have successfully used the high-shear mixing technique to incorporate OMM into the cement matrix. Therefore, this technique has been chosen to prepare cement-NC composites. Accordingly, mixing was performed as
follows. The OMM were mixed with total mixing water and stirred vigorously by a high speed shear mixer for 24
hours at room temperature to form a well dispersed suspension solution. To prepare the cement composite, the
PC, flax fibres, WG (if applicable) and sand were stirred at high speed for about 3 minutes. Afterwards, the total
suspension solution was added slowly into the mixture and stirred for 3 minutes. Then, the well mixed composite was
poured into moulds. After moulding, the specimens were kept in sealed conditions at a constant temperature of 20
°C until curing age was achieved (28 days). For all specimens an equal ratio of binder and sand was used for all mixes. The water/binder ratios were tested to reach a flow of 110 ± 5 to permit a medium workability to be used for mixing the specimens. A range of composites were prepared based on variations of the composition as shown:

a) **Control:** OPC mortar reinforced with randomly distributed sort flax fibre (30 mm, 1% volume fraction);
b) **FRCG:** reinforced mortar with a cement replacement by 20 % WG;
c) **FRCN:** OPC reinforced mortar with 2.5% NC;
d) **FRCGN:** reinforced mortar with a cement replacement by 20 % WG and 2.5% NC.

The durability of the composite was obtained from the fracture energy, bending and impact behaviour of the composite. In order to study the aging mechanism, the composite was subjected to 50 controlled wetting and drying cycles. In these cycles, the composites were soaked in water at 20°C for 1 day and left to dry for 6 days in the laboratory room.

**3. EXPERIMENTAL TECHNIQUES**

**Testing of composites**

A study of the ASR was performed in accordance with ASTM C1260 [15]. Mortar bars 25 x 25 x 100 mm in size were caste. Then, the moulds were covered carefully with plastic sheets and placed in the lab at 22 °C for 24 hours. After that, the bars were placed in water at 80°C for another 24 hours to gain a reference length. They were then transferred to a solution of 1N of NaOH at 80°C. Readings were then taken every day for 14 days.

The thermal behaviour of the composites was analysed using thermal gravimetric analysis (Stanton Redcroft DTA/TGA, UK). The weight of specimens used for analysis ranged from 19 to 24 mg. These specimens were analysed in a Platinum pan in which the analyser heated the furnace from room temperature to 1000°C at 10°C/min. Dry Nitrogen gas was circulated within the test cell at a flow rate of 60 cc/min.

For the three point flexure test, specimens of 40 x 40 x 160 mm size were prepared in accordance with ASTM C348 [16]. Flexure strength was obtained using the Zwick machine. This machine is equipped with a 50 kN load cell and attached to a PC interface with Test Xpert 2 version 2.1 software for data acquisition. Three point bending tests on notched beams were performed to evaluate the fracture energy in accordance with RILEM 50-FMC [17]. All specimens were tested at room temperature with a cross head speed of 1 mm/min. Flexure values were obtained by averaging the measurements of at least three samples. The notched Charpy impact strengths of the specimens (20 x 20 x 55 mm) were measured using a MAT21 universal pendulum impact tester at a room temperature of 20°C. The impact strength was reported in J/m², and the results are the average of four specimens.

In order to study microstructure, a scanning electron microscopy (SEM) machine model Hitachi S-3000N VP was used. The fibres examined were extracted from the failed bending test specimens. Fibres which had been pulled out from one fractured surface were coated with a gold layer using an Edwards sputter coater, model Pirani 50 L. X-ray diffraction (Bruker AXS D8 Advance, USA) analysis with Cu-Kα radiation and a graphite monochromator with a current of 40 mA and a voltage of 40 mV was used with a diffraction intensity in the range of 6 to 60° (20-angle range).

**4. RESULTS AND DISCUSSIONS**

**Alkali silica reaction (ASR)**

ASR tests were carried out on control, FRCG, FRCN and FRCGN specimens. The percentage expansions in the composites are shown in Figure-4. Evidently, FRCGN had less expansion compared to the control specimen, followed by FRCG then FRCN. It is clear that all specimens had expansions of less than 0.2% and, therefore, according to ASTM C1260, the expansion was within accepted limits. The expansion tests showed that the addition of glass powder assisted in hindering the expansion compared to the control specimen, which confirms the results obtained by Shao et al., [9]. Moreover, the hybrid incorporation of glass powder and NC greatly reduced the possible ASR. The role of NC in reducing ASR expansion is therefore in decreasing the amount of CH, which is confirmed by DTA analysis and

![Figure-3. X-ray spectrum of ground green waste glass powder.](image-url)
XRD results, and hence preventing formation of a swelling gel [18].

**Figure-4.** ASR test results of target specimens.

**Deferential thermal analyses**

Deferential thermal analyses (DTA) were carried out on selective specimens of control, FRCG and FRCGN. DTA thermo grams of these specimens are presented in Figure-5. The DTA curves show 4 different endothermic peaks. The first peak is located between 65-90°C while the second peak is observed at ≈ 90-110°C, these are mainly due to the decomposition of ettringite and calcium silicate hydrates (CSH) respectiv ely [19-22]. The third endothermic peak detected  between 470-475°C, is attributed to the decomposition of calcium hydroxide (CH). The fourth endothermic peak located between 777-790°C, represents decomposition of calcium carbonate (CaCO₃) [19, 20].

**Figure-5.** DTA curves of control, FRCG and FRCGN specimens.

No peak related to the decomposition of the flax fibre was detected, probably due to its low content (less than 2% of the total weight). Evidently, the addition of ground glass powder decreases the formation of CH in the hydration product. On the other hand, it causes a significant increase in the formation of CSH especially when NC is loaded (FRCGC). This behaviour could be attributed to the dilution effect and to the consumption of CH by pozzolanic reaction, which is supported by the XRD results in the next section and also confirms the results obtained by Morsy et al., [21] and Li et al., [22]. This result agrees with the improvement in the mechanical properties of mix FRCGN with cement replacement by 20% ground glass powder and 2.5% NC.

**Mineralogical composition**

XRD analyses were conducted to investigate the mineralogical composition of selective specimens of the control, FRCG and FRCGN after 28 days of hydration. For comparison, the peak of CH at 18º (2θ) and the peak of CSH at 28.6º (2θ) have been selected [23, 24]. As shown in Figure-6, a sharp peak in CH is observed in the control specimen representing the pure hydration product (CH), which is released from the hydration of cement. Evidently, the intensity of the CH peak is decreased in FRCG and significantly reduced in mix FRCGN, which reflects the consumption of CH by pozzolanic reaction. On the other hand, the intensity of the CSH peak significantly increased in FRCGN compared to the control specimen, which agrees with the DTA results in the previous section. Consequently, the XRD results confirm the improvement in the mechanical properties of specimens FRCG and FRCGN compared to the control specimen.

**Scanning electron microscopy (SEM)**

SEM was carried out in order to study the influence of WG and NC particles on the microstructure of the cement matrix. Additions of WG and NC particles were found to influence the manner of hydration and resulted in differences in the microstructure of hardened cement systems. Figure-7 shows the microstructure of selective specimens of the PC control, FRCG and FRCGN. Figure-7(a) presents the typical composition of hydrated mortar in the control mix. The microstructure of the control specimen displayed the existence of CSH surrounded by and connected with many needle-hydrates. When a part of cement was replaced by WG, the CSH became relatively dense and fine, as shown in Figure-7(b). As expected, FRCGN Figure-7(c) showed a perfectly dense and compact formation of hydration products. The densest mortar structure was observed for the specimen with a hybrid combination of 20% glass and 2.5% NC particles, followed by the mix with 20% glass powder (FRCG). This suggests that the densification of mortar increased by adding NC particles. These improvements could be attributed to the packing effect of NC particles (due to their great surface area) fills the interstitial spaces inside the skeleton of cement mortar, which leads to increases in toughness and strength [25].
Figure-6. X-ray spectrum of control, FRFG and FRCGN specimens (a) CH peaks and (b) CSH peaks.
Mechanical properties

The results of fracture energy, flexure strength and impact strength of flax fibre cement composites are shown in Figures 8 to 10. Basically, the replacement of OPC by 20 % WG improves the fracture energy, flexure strength and impact strength of cement composites at 28 days of hydration compared to the control specimen, which agrees with the results obtained by Chen et al., [26]. Moreover, specimen FCRGN, which contained 20 wt. % WG and 2.5 wt. % NC, revealed the highest mechanical properties, where it also recorded increases in fracture energy, flexure strength and impact strength by 180%, 38% and 31% respectively compared to the control specimen at 28 days of hydration. It should also be noted that the mechanical properties of the FRCN are in between those of the FRCG and FRCGN specimens. These increases indicate that the hybrid combination of NC and WG greatly improves the mechanical performance of the FRC.

As the above results show then, the NC/WG combination showed the best results in terms of fracture energy, flexure and impact strength. It seems that NC behaves not only as a filler to refine microstructure, but also as an activator to accelerate the pozzolanic reaction; this is due to the large and highly reactive surface of nano particles [14, 23]. These results are confirmed by SEM micrographs, XRD patterns and DTA analysis of the cement composites after 28 days of hydration. In fact, the improvements in the properties of hardened cement composites due to the addition of NC particles can be explained by two mechanisms. The first is the chemical effect, which works on two levels [25]:

- Accelerating the dissolution of $C_3S$ and rapid formation of the CSH phase in the cement paste; and
- The pozzolanic reaction of silica with CH generates additional CSH gel in the final stages.

The second mechanism is the physical effect; NC can fill the remaining voids in young and partially
hydrated cement paste, which leads to a denser and more compact structure.

Comparing the mechanical properties of specimens under ageing, it can be seen that FRCGN showed a smaller reduction in mechanical properties followed by FRCN, as presented in Figures 8-10. Referring to Figures 8-10, FRCGN retained, respectively 75%, 77% and 90% of the fracture energy, flexure strength and impact strength values compared to those recorded prior to the ageing process. While for the control specimen, retention was respectively 40%, 50% and 40% of fracture energy, flexure strength and impact strength values at 28 days. Figure-11 presented the changes in the fibre surface after 50 wet/dry cycles. As is clear from these micrographs, the surface of fibres extracted from specimen FRCGN does not present signs of significant damage. On the other hand, the surface of fibres extracted from the control Specimen does reveal signs of degradation, most likely due to mineralisation of the fibres. As is clear, these results demonstrate that the replacement of cement by 20% WG and 2.5% NC introduces an effective method to improve the durability with time. Hence, the mechanism by which the NC and WG could enhance the microstructure and strength of cement matrix can be explained by the following paragraph:

When exfoliated clay and glass powder are uniformly dispersed in the cement matrix, the high pozzolanic activity that combines silicon and alumina elements in WG and NC with the lime elements of calcium oxide and hydroxide in cement, leads to reduce the alkalinity of the cement matrix and mitigate fibre-cement composite degradation.

![Figure-8. Fracture energy of target specimens.](image-url)
Figure-9. Flexure strength of target specimens.

Figure-10. Impact strength of target specimens.
5. CONCLUSIONS

The following conclusions may be drawn from the obtained experimental results:

- Based on the ASR test results, no damaging effect can be detected at a macroscopic level due to the reaction between glass powder and cement paste with particle size up to 75 µm;
- The addition of NC particles has great potential to accelerate the pozzolanic reaction. It seems that their nano size allows them to react more readily with the CH, thereby increasing CSH conversion at 28 days of hydration. The hybrid combination of NC and WG was found to be a very effective way to use ground waste glass as a cement replacement and to achieve good performance at reasonable cost; and
- Replacement of OPC by 20% ground glass powder and 2.5% NC in flax fibre cement mortars increases fracture, bending and impact properties after 28 days of hydration. Moreover, it improves the durability of flax fibre cement mortar due to wet/dry cycles. The improvements in fracture energy, bending, impact and compressive properties were 68%, 45%, 23% and 18% higher than the reinforced OPC containing only 2.5% NC.

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Figure-11. SEM photographs of flax fibre surfaces before and after ageing: (a) before ageing, (b) fibre extracted from control specimen after aging and (c) fibre extracted from FRCGN specimen after aging.


