The effect of nanosilica and titanium dioxide on the mechanical and self-cleaning properties of waste-glass cement mortar

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Abstract

The recycling of waste glass is a major problem for municipalities worldwide due to high disposal costs and environmental concerns. Recycling glass from the municipal solid waste stream in order to manufacture new glass products is limited due to high costs, impurities, and mixed color. Although colorless waste glass has been recycled effectively, colored waste glass with its low recycling rate, has mostly been dumped into landfills. Due to its high level of impurity, colored glass cannot be processed easily. A new use was found for it, instead of creating waste: an additive in building materials.

In this study, the self-cleaning properties and strength development characteristics of mortar containing waste glass and nanomaterials (nanosilica – nSiO\textsubscript{2} and titanium dioxide – TiO\textsubscript{2}) are analyzed in terms of waste glass content and the effectiveness of commercially available nanomaterials. Quartz sand is replaced with brown waste glass at ratios of 25%, 50% and 100% by weight. The photodegradation of the rhodamine B test has been conducted to analyze the effect of titanium dioxide, nanosilica and waste glass presence in the cement mortar for its potential application in self-cleaning façades.

Studies have shown that waste glass can act as a successful replacement for sand, especially when mixed partially with sand. Additionally, a positive influence of nanomaterials on the self-cleaning and mechanical properties was noted.

Keywords: nanosilica; titanium dioxide; nanomaterials; waste glass; cement mortar

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1. Introduction

Concerns related with disposal of generated wastes have increased tremendously in the last two decades. Awareness of the environment and solid waste management gathered major concern throughout the world. Material that especially aroused the interest of many researchers, due to low recycle rate and high disposal costs, is waste glass. The construction industry (especially the cement and concrete industry) found a useful solution for the environmental impact of waste glass. The physical properties of glass and its chemical composition, similar to that of sand and cement, make this material very appealing. It is able to provide an environmentally friendly solution for the glass and cement industries. Theoretically, glass can be recycled completely and infinitely without losing any of its chemical and physical properties – Jani and Hogland [1]. However, broken, mixed colored and diverse origin of waste glass, make the recycling process impractical and highly expensive. Different chemical compositions, impurities and contaminants of recycled glass can highly affect the properties of the produced new glass. Therefore, there is a need to develop markets for mixed waste glass.

The use of glass as cement concrete aggregates in last few decades has again come under investigation. Application of waste glass used as an aggregate or glass powder seems to be a very interesting approach to create ecological composites but there are still some obstacles that need to be resolved. First of all, studies held by Bhandari and Tajne [2], Degirmenci et al. [3] and Terro [4] have shown that use of waste glass as an aggregate can contribute to decrease the mechanical strength of composites when it is replaced with more than 10% - 30% of sand. Also, the experimental studies showed that similar or higher flexural and tensile strength can be obtained in samples containing up to 25% and 20% of sand replacement respectively. In the case of utilization of waste glass powder as a cement additive, studies have shown that the proposed optimum percentage of waste glass that can be used as a partial replacement to cement (to produce concrete) are varied from 10% by Schwarz et al. [5], 20% by Nassar and Soroushian [6] or even up to 40% by Aly et al. [7] while supplementary cementing materials are used.

Moreover, due to presence of waste glass in cementitious composite, the possibility of expansion and cracking exists and detailed analysis of the problem is presented comprehensively by Shi and Zeng [8]. However, this phenomenon is still discussed. Aly et al. [7] and Ling and Poon [9] have shown that the expansion of composites is within the accepted limits. The materials often used to reduce or eliminate the alkali–aggregate reactions are supplementary cementing materials such as ground blast furnace slag, fly ash, silica fume, and metakaolin. Despite some inconveniences with application of waste glass, there are also few positive aspects of utilization the waste glass in the cement-based materials. Ling and Poon [9] and Terro [4] show that due to impermeable and smooth surface of the glass cullets, the use of waste glasses as an aggregate can improve the fluidity of the fresh mortar. Moreover, Shi and Zheng [8] reported that finer grounded glass particles exhibit very good pozzolanic reactivity. Materials that can help to reduce the negative effect of waste glass presence and contribute to novel ecological sustainable materials are nanomaterials such as nanosilica (nSiO2) and titanium dioxide (TiO2).

In this study, the self-cleaning properties and the strength characteristics of mortar containing waste glass and nanomaterials (nanosilica and titanium dioxide) are analyzed in terms of waste glass content and the effectiveness of commercially available nanomaterials. Quartz sand is replaced with brown soda-lime waste glass at ratios of 25%, 50% and 100% by weight. The influence of nanosilica on the fluidity and strength development has been tested, in order to determine the impact of nanosilica and waste glass on the properties of cement mortar. In addition, the photodegradation of the rhodamine B test has been conducted to analyze the effect of titanium dioxide, nanosilica and waste glass presence in the cement mortar for its potential application in self-cleaning façades.
2. Materials and methods

2.1. Materials

Cement used in the mortar mixture was CEM II/A-S 42.5 R (according to EN 197-1 standard) containing nano-crystalline titanium dioxide. Commercially available amorphous nanosilica (NS) containing 20 wt% of solid material was used. Quartz fine aggregate conforming EN 196-1 was used for this study. Brown soda-lime waste glass (WG), widely used for bottles, was obtained from a local recycling company and applied as quartz sand replacement (figure 1). Waste glass was washed with water in order to remove organic contaminants, dried, and crushed in the mill to five different sizes. The grading of WG is presented in Table 1.

![Fig. 1. Photograph of obtained waste glass (left) and after milling process (right) with particles size less than 2 mm.](image)

Cement mortar components were mixed according to EN 196-1 procedure. In the case of NS application (3 wt%), the suspension was stirred with the mixing water at high speed for one minute in order to obtain uniform dispersion of nanomaterial. Next, the fresh mortar, was poured into oiled molds to form samples with a size of 40 mm x 40 mm x 160 mm in accordance with the requirements of PN-EN 196-1. The samples were demolded after 24 hours and then cured for 28 days in a standard water bath at a temperature of 20°C ± 2°C. After 28 days of curing, the samples were examined. Proportions of all mixture components were given in Table 2.

A range of composites were prepared based on variations of the composition as follows:

- R: reference sample
- RNS: reference sample containing nanosilica (NS)
- G25, G50, G70, G100: samples containing waste glass (number indicates percentage of glass content)
- G25NS, G50NS, G70NS, G100NS samples containing waste glass and NS 3 wt% (number indicates percentage of glass content)

| Table 1. Grading of sand and waste glass (WG) aggregates. |
|-----------------------------------------------------------|
| **Sieve size (mm)** | **Mass (%)** |
|---------------------|--------------|
| Passing             | Retained     |
| 2.00                | 1.60         | 7±5         |
| 1.60                | 1.00         | 33±5        |
| 1.00                | 0.50         | 67±5        |
| 0.50                | 0.16         | 87±5        |
| 0.16                | 0.08         | 99±1        |
The photocatalytic efficiency was evaluated by monitoring the discoloration of rhodamine B (Tetraethylrhodamine chloride) applied to the surface of the materials that were then exposed to artificial sun light. Rhodamine B is very soluble in water and can therefore be spread uniformly on a given surface. Also, rhodamine B is little sensitive to the alkalinity of cementitious materials. For testing procedure three cylindrical samples of each tested mortar in diameter of 35 mm and 20 mm of thickness were prepared. Aqueous solution of rhodamine B (0.5 g/dm³) has been poured on each sample and afterwards samples were illuminated at light level of 1925 lux (UV lamp) up to 120 minutes.

| Sample designation | Cement [kg/m³] | Water [kg/m³] | Nanosilica | Sand [kg/m³] | Waste glass content [%] |
|--------------------|----------------|--------------|------------|--------------|------------------------|
| R                  | 519            | 257          | -          | 1546.0       | 0                      |
| RNS                | 519            | 257          | -          | 1546.0       | 0                      |
| G25                | 519            | 257          | -          | 1159.5       | 25                     |
| G50                | 519            | 257          | -          | 773.0        | 50                     |
| G75                | 519            | 257          | -          | 386.5        | 75                     |
| G100               | 519            | 257          | -          | -            | 100                    |
| G25NS              | 519            | 195          | 78         | 1159.5       | 25                     |
| G50NS              | 519            | 195          | 78         | 773.0        | 50                     |
| G75NS              | 519            | 195          | 78         | 386.5        | 75                     |
| G100NS             | 519            | 195          | 78         | -            | 100                    |

3. Results and discussion

3.1. Consistency

Consistency test results determined by flow table method are depicted in Figure 2. An increase of waste glass replacement improves the fluidity of fresh mortar. In the case of plain cement mortars, the impact is not as significant, but the effect of waste glass presence is significant when nanosilica is applied. Application of nanosilica by 3 wt% (RNS) reduced the fluidity of samples by 13% when compared to the reference sample R. Specimens containing 100% of waste glass and nanosilica (G100NS) had the same fluidity as reference sample containing quartz sand (R). Most of the nanomaterials, due to their high surface area to volume ratio, exhibit high water demand which leads to significant reduction of fluidity and creating local agglomerates of nondispersed, nanomaterial which was reported by Horszczaruk et al. [10]. This can cause a problem with uniform dispersion of nanomaterial in the cement matrix, reduce the content of free water for hydration process, and cause problems with achieving desired workability – Horszczaruk et al. [11]. Waste glass due to its lower specific surface and smooth impermeable surfaces usually reduces the water demand. Therefore, nanosilica can be successfully applied to the waste glass cement mortars without problems associated with its application.
3.2. Rhodamine B discoloration test

Discolouration of rhodamine B under UV light has been conducted up to 120 minutes of irradiation. Every 20 minutes samples were visually observed in order to determine degradation of rhodamine B on the surface of cement mortar. Figure 3 presents one of the tested set consisting of 10 different cement mortars. For all tested samples, regardless of glass content, nanosilica presence, and time of exposure created no noticeable differences between discolorations of rhodamine B on the surface of cement mortars. It can be noticed that commercially available cement containing nano-cristalline titanium dioxide can effectively degrade rhodamine B and its performance is related to the time of irradiation.

3.3. Flexural and compressive strength

Flexural strength development is presented in Figure 4. Studies have shown that after two days of curing samples containing nanosilica already exhibited slightly improved flexural strength and can be attributed to properties of nanosilica. After seven and 28 days of curing, there is noticeable decrease of flexural strength reported while the content of waste glass aggregate is more than 25%. In general, nanosilica improved the flexural strength of specimens but the affect after 28 days was unnoticeable.
The presence of waste glass and nanosilica is more noticeable in the compressive strength development of cement mortar. Results of compressive strength determination are depicted in figure 5. From the first days of curing it can be seen that with the increased glass content samples have tendency to decrease their strength. Only in the case of a sample containing 25% of waste glass (G25) compressive strength was higher by 10% than the reference sample (R). The compressive strength of samples R-G100 and RNS-G100NS decreased by 8% and 12% respectively while compared to reference samples R and RNS. It can be noticed that application of nSiO₂ significantly improved compressive strength of cement mortars by 10% to 20% when compared to reference samples without nSiO₂ addition. Moreover, it was reported that sample containing nanosilica and 100% of waste glass (G100NS) exhibited higher compressive strength than the reference sample containing 100% of quartz sand (R). In general, all tested samples containing waste glass and nSiO₂ had higher compressive strength than the reference sample. Therefore, application of nanosilica can overcome the negative impact of poorer cohesion between the glass aggregates and cement paste which is an effect of smooth impermeable surfaces of WG aggregate. Nanosilica due to its properties improves the pozzolanic reaction, hydration rate, improves the interfacial transition zone and compacts the microstructure of cement matrix leading to improve the mechanical and physical properties of cementitious composites.
3.4. Microstructure analysis

Figure 6 presents microstructure of cement mortars containing 0%, 50% and 100% of waste glass. It can be noted that the sample containing quartz sand (R) presents uniform structure of cement mortar and spherical aggregate. In samples G50 and G100 there is noticeable difference between fine aggregate particles shape. Milled waste glass aggregate is flat, needle-shaped and elongated. Therefore, high content of WG aggregate can lead to high stress concentrations and hence a reduction in strength.

![Figure 6. Microstructure of cement mortars containing different waste glass content (0%, 50% and 100%).](image)

4. Conclusions

An experimental investigation of the influence of the nanomaterials on the self-cleaning and mechanical properties of waste glass cement mortars was presented. Based on the results presented in the report, the following conclusions can be drawn:

- Visual observation of rhodamine B discoloration on the surfaces of cement mortars showed that presence of waste glass did not affect the self-cleaning properties of commercially available cement containing titanium dioxide.
- Due to smooth impermeable surfaces and lower absorption rate for water the fluidity value of fresh cement mortars increase with higher percentages of waste glass. Therefore, application of waste glass as an aggregate can neutralize negative effect of nanosilica’s high water demand. Hence, nSiO₂ can be successfully incorporated into the cementitious composites without help of any additional dispersing agents.
- Application of nanosilica due to its properties improves the cohesion between the glass aggregates and cement paste resulting in compacting the structure of cement mortars.
- Use of 3 wt% of nanosilica enables to obtain noticeable increase (while compared to reference sample containing quartz sand) of flexural and compressive strength of samples containing waste glass aggregate and reduce the negative impact of WG presence.

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