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Mechanical behaviour assessment of unsaturated polyester polymer mortars filled with nano-sized Al_2O_3 and ZrO_2 particles

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Abstract

There are several ways to change the final properties of composite materials, but the most common one is by adding different types of modifier fillers to the polymeric matrix. Over the last years, nano fillers have brought some interesting properties to composites. Until now, only few works were published concerning the effective impacts of resin binder modification with nano oxides, on mechanical properties of polymer mortars (PM). In this study, unsaturated polyester based PMs with enhanced mechanical performance are developed through polymer modification with nano-sized Al_2O_3 and ZrO_2 particles. Samples without and with nanoparticles (2.5 resin wt.%) were produced, and their mechanical/physical properties assessed by flexural, compressive and Shore D hardness tests. The PM modified with nano zirconia showed better mechanical performance compared to the unmodified PM; more thorough studies are nevertheless required in order to improve mix design formulations towards further enhancement of mechanical behaviour.

Keywords: Polymer mortar; alumina; zirconia; nanoparticles; mechanical characterization.

1. Introduction

Polymer concretes (PC) and polymer mortars (PM) have obtained wide acceptance as materials for many applications in civil construction. PC and PM are made of a resin, mineral aggregates and other fillers. The most commonly used resins have been thermoset ones such as unsaturated polyesters and epoxies [1-3]. There are many ways to change and improve the properties of polymeric composites, but the most common one is adding different types of fillers to the matrix [1-3]. In late years, nano fillers have brought some interesting properties to composites, including improvements in mechanical properties, such as toughness and modulus [4,5]. These improvements are related to the high specific surface area and reduced dimension of nanomaterials (NM) that significantly decrease the mobility of polymer chains and lead to significant changes on volume, surface and functional properties of final nanocomposites (NC). Previous research works (Table 1) have revealed that nano oxides based polyester NCs, with homogeneous NM dispersion, present improved characteristics over unfilled polyester composites and homologous filled polyester microcomposites. Depending on nano oxide nature and content, diverse enhancements were found [6-10].

Despite the large amount of research work carried out on nano oxide modified composite materials, only few works were published concerning the effective impacts of resin binder modification with nano oxides, on final properties of PM or PC [2,11,12].

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Table 1. Some changes made by the nano oxides addition in unsaturated polyester resins.

Nanomaterial			
Type	ϕ^a (nm)	Content (wt.%)	Main conclusions
Al_2O_3	65	0 - 9	↗ Agglomeration above 5 wt.%. ↗ Tensile, flexural, and impact strength. ↗ Thermal stability [6]
	15	0 - 4.5	↘ Mechanical properties of formulations with NP. By adding silane coupling agent, the mechanical behaviour ↗[7]
SiO_2	75	0 - 1.5	↗ Viscosity and the molecular weights. ↗ Glass transition temperatures [8]
	56	0 - 12	↗ Viscosity. The critical silica content was observed at 6-10 wt.% [9]
ZnO	30	0 - 10	↘ UV degradation and ↗ the impact strength [10]

[a] *Average diameter*

The first research works studying the use of nano oxides in PM were presented by M.C.S. Ribeiro *et al.* in 2010 and 2013 [2,3]. Those studies analysed and quantified the effects on fire reaction and mechanical behaviour of an epoxy PMs, induced by polymer binder modification with nano (5 wt.% nanopowders and 10 wt.% nanodispersion, of resin mass) and microsized alumina (5 wt.% micropowders of resin mass). Test results revealed that alumina based fillers, especially with nanoscale size, were effective in improving bending and compressive behaviour of epoxy PM. However, no definite conclusions were obtained regarding the influence of alumina fillers on fire reaction properties of epoxy PM´s.

In 2011, J.M.L. Reis *et al.* published two works examining the mechanical properties of epoxy PMs, with different weight fractions (3%, 5%, 7% and 10%, of resin weight) of nano-Al_2O_3 and nano-Fe_2O_3. Test results showed that flexural and compressive strengths of PMs filled with nanoparticles were lower than those of neat PM, but a considerably stiffness increase was observed for all modified formulations [11,12].

Under this framework, the present study is an effort to develop a new unsaturated polyester based PM with improved mechanical properties, through matrix modification with nano oxides (alumina and zirconia). First, the effect of nanoparticles addition to unsaturated polyester resin was investigated, and then, the behaviour of the PM formulations using those modified matrixes as binders were analysed. Mechanical properties were analysed and quantified by flexural, compressive and Shore D tests. Scanning electron microscopy analyses were also used to assess the occurrence of filler agglomeration and resulting morphologies.

2. Materials and Methods

2.1. Raw materials and manufacturing procedures

A commercially available unsaturated polyester resin, with trade name Aropol® FS3992 (Ashland Chemical Hispania S.L., Spain) was used as matrix. Physical and mechanical properties of the cured resin, as supplied by the manufacturer, are displayed in Table 2.

Table 2. Physical and mechanical properties of cured resin.

Property	Method	Values
Heat distortion temperature (ºC)	ASTM D 648	90-100
Water absorption (%)	ASTM D 570	0.2
Tensile strength (MPa)	ASTM D 638	50-70
Ultimate tensile elongation (%)	ASTM D 638	3
Flexural strength (MPa)	ASTM D 790	90-110
Barcol hardness	ASTM D 2583	45

Polymerization process of the resin system was induced by a cobalt octoate accelerator solution, and a 50% methyl ethyl ketone peroxide solution, as initiator. The zirconia nanoparticles (ZrO_2, 20 nm average size and 25.0 m^2/g specific surface area) were provided by Innovnano (Portugal) and the alumina nanoparticles (NanoDur® Al_2O_3, 45 nm average size and a 36.0 m^2/g specific surface area) were purchased from Cymit Quimica S.L. (Spain). The chosen foundry sand for PM production is a high-grade silica (>99.0%) sand with fine uniform grain size (245 µm) from Fundipor (Portugal).

Three different resin formulations were prepared: control, 2.5 wt.% nano-Al_2O_3 and 2.5 wt.% nano-ZrO_2.

Prior to the manufacturing process, foundry sand and nanomaterials were dried in an oven until constant weight, in order to prevent possible inhibition of polymerization due to moisture.

For the modified formulations, a well determined quantity of filler (2.5 wt.% of resin) was manually pre-mixed with the unsaturated polyester resin for a few minutes (~5 min) at room temperature. The mixing process was then complemented by ultrasonication (pulsing mode: 0.5 s on/0.5 s off) for 60 min, for an effective sonication time of 30 min in a container surrounded by an ice bath. The pulsing mode and the ice bath were used to prevent heat build-up of the mixtures during ultrasonication. Then, the promoter (0.5 wt.% of resin) and the initiator (1 wt.% and 2 wt.% of resin, for polymeric NC and PM,

respectively) were added separately to the mixture and mixed thoroughly, to initiate and promote the polymerization process at room temperature.

The neat resin and NC mixtures were poured into moulds and allowed to cure during 6h at 55ºC. After de-moulding, they were subjected to an additional thermal treatment (10h/80ºC), before being used to cut standard specimens for flexural properties tests.

Neat resin and nano oxide modified unsaturated polyester mixtures were also prepared to be used as binders for PM manufacturing. PM compositions were prepared by mixing the different NC formulations with the foundry sand aggregates in an automatic mixer. For all PM formulations, the polyester resin system to sand weight ratio was maintained equal to 1:4. A total of 5 prismatic standard specimens were casted for bending and compression testing. The curing process followed the same procedure used for NC.

2.2. Tests procedures

Flexural mechanical properties of the NCs were obtained according to the test procedure described in standard ISO 178 [13]. Five beam specimens (100×10×5 mm) of unfilled and nano oxide modified polyester composites were tested in three-point bending at a constant loading rate of 2.0 mm/min, over a 74.0 mm span (Fig. 1). For each specimen, a load-deflection curve was obtained, from which the flexural strength and elastic modulus were obtained.

PM specimens (160×40×40 mm) were tested in three-point bending up to failure at the loading rate of 1.0 mm/min, over a span length of 100 mm, according to RILEM CPT PCM-8 standard test method [14]. For each specimen, a load-deflection curve was also obtained which allowed the determination of both flexural strength and flexural elasticity modulus. One of the two leftover parts of each broken specimen in bending were then tested in compression at the loading rate of 1.25 mm/min, following the procedure described in UNE 1015-11 standard [15].

Both flexural and compressive testing set-ups are presented in Fig. 1.

The Shore D hardness of NC and PM formulations was measured according to ISO 868 [16], using a commercial CEAST® (Turin, Italy) durometer (Fig. 2). The specimens' thickness was at least 4 mm and the measuring points were at least 9 mm from any edge and 6 mm apart.

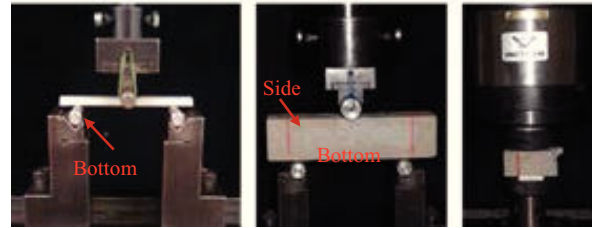All specimens were conditioned at 23°C/50% RH for 48 hours before testing.

Fig. 1. Set-up used for flexural and compression tests of NC and PM formulations.
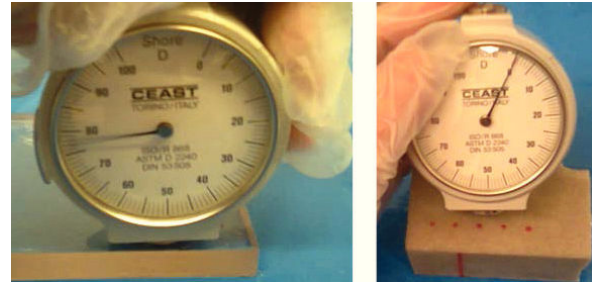

Fig. 2. Set-up used for shore D test.

Both NC and PM fracture surfaces were analysed by scanning electron microscopy (SEM) using a FEI Quanta 400 FEG ESEM machine (CEMUP - Materials Centre of the University of Porto) to assess the homogeneity of nanofillers distribution within resin matrix.

3. Experimental Results and Discussion

The test results for NC and PM formulations are summarized in Tables 3 and 4, respectively. Flexural strength (σ_f), apparent flexural elasticity modulus (E_f), and Shore D hardness are presented for both NCs and PMs. In the case of PMs, compressive strength (σ_c) was also evaluated. Average values and corresponding standard deviations are for five replicates.

Table 3. Mechanical tests results of nanocomposites.

Formulation	Flexural		Shore hardness
	σ_f (MPa)	E_f (GPa)	D scale
Control	94.6 ± 9.3	3.2 ± 0.4	89.6 ± 0.6
2.5% Al_2O_3	57.9 ± 6.5	2.9 ± 0.1	89.8 ± 0.5
2.5 % ZrO_2	99.0 ± 6.8	3.8 ± 0.1	82.2 ± 2.5

From SEM images (Figs. 3 and 4), it can be observed a high fillers concentrations for NC and PM formulations.

Table 4. Mechanical tests results of polymer mortars.

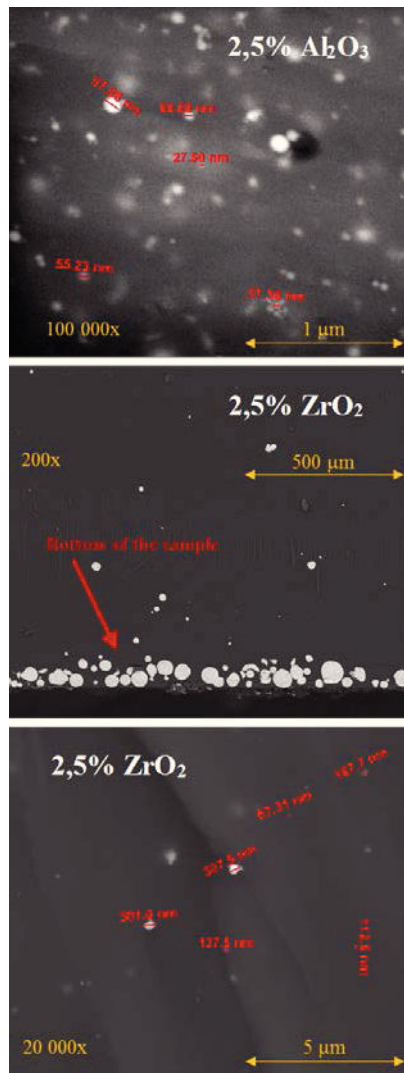| Formulation	Flexural		Compression	Shore hardness
	σ_f (MPa)	E_f (GPa)	σ_c (MPa)	D scale
Control	28.0 ± 1.3	4.1 ± 0.4	79.2 ± 3.1	79.2 ± 3.1
2.5% Al_2O_3	26.8 ± 0.9	4.0 ± 0.5	78.4 ± 3.9	78.4 ± 3.9
2.5 % ZrO_2	28.8 ± 1.2	4.0 ± 0.3	783 ± 1.0	78.3 ± 1.0

Fig. 3. Scanning electron microscopy of NC (fracture surface).

Different trends were found from the incorporation of NMs in the resin matrix and resulting NCs and PMs. ZrO_2 incorporation leads to small improvements in the flexural strengths of both resin matrix and PM, in the flexural elasticity modulus of resin matrix. Slight decreases were observed for the other analysed properties (i.e., resin matrix hardness, and compressive strength of PM) and the flexural elastic modulus were not affected.
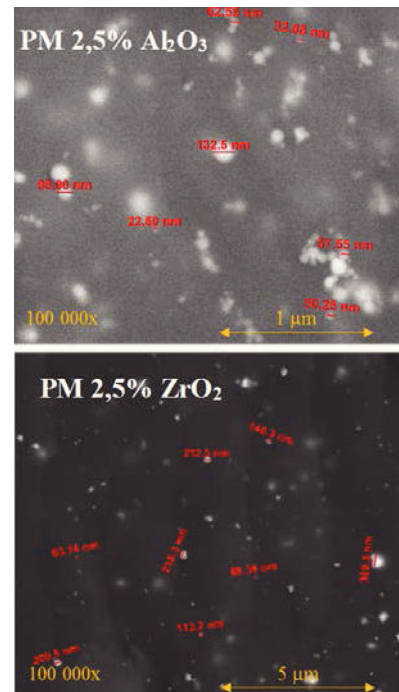

Fig. 4. Scanning electron microscopy of PM (fracture surface).

The formulations with nano alumina had significant decreases relatively to the flexural strength of the resins and negligible declines on the mechanical properties of resulting PM, but Shore D hardness remained similar to that of the control formulation.

The NM agglomerations, observed in the SEM images, result in weaker nanofiller/polyester interfacial interactions. The formulation showing better dispersion is the NC with nano alumina, with average nanoparticle agglomerates lower than 100 nm in size; although there was greater homogenization of nano alumina within the resin matrix, this did not have the expected outcome on mechanical test results.

4. Conclusions

Based on test results, the following conclusions can be drawn from the investigation:

– The introduction of nano alumina leads to quite considerable decreases in flexural strength (-39%) in the resins and does not have significant impact in the other analysed mechanical properties of resin matrix and resultant PM. The observed decline in flexural properties of NC may be associated to a weak filler-matrix interface and/or a non-homogeneous filler dispersion aggravated by NM agglomeration during polymerisation process (SEM analyses showed nano alumina agglomerations higher than 100 nm and it was

also observed, at naked eye, that filler dispersion was not fully achieved in the NC formulations). This feature is not so evident within resin binder matrix of correspondent PM, possibly due to a slower polymerization process in the presence of sand aggregates;

– The incorporation of nano zirconia has, in general, a slight improvement effect on the overall mechanical properties of resin matrix and PM, with the exception of the resin flexural elasticity modulus, in which a significant improvement was observed (18%). In the NC formulations, it was observed an accumulation of the NM on the bottom of the produced specimens that could be seen at naked eye. In the PM formulations, this effect was not observed, probably as a result of the greater mix viscosity, and a better dispersion is confirmed by SEM images.

The nano-filler content value and its dispersion level within the resin matrix are fundamental factors regarding nanocomposite final properties. Additional studies are thus foreseen in order to explore the effect of using a silane-coupling agent on the homogeneity of the matrix, so that products with better mechanical performance and with other enhanced properties can be obtained.

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