Mechanical Characterization of Cement Composites Reinforced with Fiberglass, Carbon Nanotubes or Glass Reinforced Plastic (GRP) at High Strain Rates

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Abstract. Advanced researches on concrete are directed toward investigating the behavior of reinforced concrete structures in severe conditions such as those promoted by impact loads. Some particular structures (protective shelters, nuclear reactor containment, offshore structures, military structures, chemical or Energy production plant) may be subjected to loading at very high rate of stress or strain caused by impact of missiles or flying objects, also by vehicle collisions or impulses due to explosions and earthquakes. Resistance to impact loads is guaranteed by using cementitious materials having both high strength and ductility. In order to improve ductility cementitious mortars with Glass Reinforced Plastics (GRP) replacing partially the natural sand were manufactured. Moreover, glass fiber (GF) reinforced mortars were produced to enhance toughness. For this scope two types of glass fibers were used different in length and diameter. Since the use of GRP and GF don't produce any increase in strength of the cementitious composite. Flexural, compressive and Hopkinson bar tests were carried out to evaluate the role of the different materials used.

Replacing partially the natural sand with Glass Reinforced Plastics (GRP), compressive and flexural strength decrease (about 20%) with respect those of the reference mortar both on static and dynamic condition as a consequence of an anomalous air entrapment. Adding glass fibers (GF), GRP or/and Carbon Nanotubes (CNTs) no substantial improvement in terms of mechanical properties under static condition was occurred. The Dynamic Increase Factor of the reference mortar was higher than that of the reinforced mixtures, but fracture energy was lower. In particular, combined addition of carbon nanotubes and GRP determines an increase in the energy fracture. The higher the carbon nanotubes content, the higher both fracture energy and tensile strength because nanoparticles oppose to wave and crack propagation, increasing the high strain rate strength. GRP and CNTs reinforced mortars need more fracture energy to failure at 150 s⁻¹ strain rate.

Introduction

Modern research on concrete is directed toward investigating the behaviour of concrete in severe conditions. Often, concrete structures are subjected to exceptional loads or exposed to very severe environmental aggression not taken into account by international codes. Therefore, structural designs haven't relevant tools both to choose correctly construction materials and to design reinforced concrete structures. Use of high-performance concretes should lead to new design concepts, with attention focused on durability and maintenance of concrete structures, including repairs and retrofitting. Impact loads are rather uncommon events but they might occur in the lifetime of the concrete structures. Aircraft crashes as well as explosions near or in the structure are examples of this rare loading case to have to consider in design of defensive structures, nuclear reactor, military structures, chemical or energy production plant. The behaviour of structures when loaded dynamically differs from that under static loading. Study of concrete (plain and composite)



behaviour over a large range of strain rates has been the aim of this research. State of art in this field points out that constitutive laws of plain concrete at high strain rate depends on the specimen size, on its water content and on the strain-rate level, but this particular concrete behavior is not completely known [1]. In the past only a few experimental researches investigated tensile and compressive strength of concrete under impact loads. In this research, results of rheological, mechanical and dynamic properties of reinforced mortars are presented. Glass Reinforced Plastic (GRP), Glass Fibers (GF) and Carbon Nanotubes (CNT) are used to reinforce the cement matrix. Flexural and compressive strength tests were carried out at University of Bergamo Laboratory. High strain rate tests were carried out by means of a JRC-Split Hopkinson Tensile Bar located at the DynaMat Laboratory of the University of Applied Sciences of Southern Switzerland - Lugano. The principal aim of this research was to optimize the reinforced cementitious mixture to sustain high strain-rate loads.

Experimental procedure: Materials, Mixing Procedure and test

The experimental program was carried out on mortars reinforced with different materials. Rheological, static and dynamic properties of the cementitious mixtures were evaluated. Details of the experimental research are listed below.

Portland cement (CE I, 52.5 R according to EN 197-1) and standard sand, as prescribed by the UNI EN 196-1, were used. A GRP powder coming directly from a shipyard as an industrial by-product was added to the mixtures. Glass fibers 6mm (HD) and 12 mm (HP) in length and Multi-Wall CNTs (provided by Shenzhen NANO Tech. Port. Co. Ltd., China) with average diameters about 10–30 nm (Table 1.) were mixed in the cement matrix. In order to attain highly workable mixtures, without changing the w/c, a superplasticizer was used (Table 2). To disperse efficiently CNTs in cement matrices, a non-covalent surface modification (Sodium Linear Alkylbenzene Sulfonate: LAS) was used. Finally a defoamer, tributyl phosphate, was added to the mixture to eliminate the entrapped air.

External diameter [nm]	$10 \div 30$	Ash [%]	< 0.2
Length [µm]	5 ÷ 15	Specific surface area [m ² /g]	$70 \div 90$
Purity [%]	> 95.0	Density [ml/g]	$4 \div 6$
Amorphous carbon [%]	< 2.0	Electric Conductivity [S/cm]	$100 \div 0.0001$

Table 1. Properties of multi-walled carbon nanotubes (CNTs)

TYPE	DRY POLIMER CONTENT [%]	DENSITY
Polycarboxylate Superplasticizer	23 ÷ 25	$1.03 \div 1.12$

Table 2. Chemical and physical properties of the admixture

Mixing procedure and experimental tests

Cement, sand, water and fibers (GRP, GF or CNTs), if scheduled, were mixed according to UNI EN 196–1:2005. In cement mortars containing nanotubes, the surfactant was firstly mixed with water using a magnetism stirred for 10min. Then, CNTs were added into aqueous solution and sonicated with an ultrasonicator for 2 hours to make a uniformly dispersed suspension. A mortar mixer was used to mix this suspension, cement and sand for 3 minutes. Finally a defoamer in the amount of 0.5% by cement volume was added into the bowl and mixed for another 3 minutes [2]. Seven cement mortars (w/c = 0.50; sand–cement ratio: s/c = 2) were prepared (Table 3). Spread and specific mass of the fresh paste were determined. Immediately after the mortar was introduced into the steel mould to manufacture prismatic specimens (40x40x160mm). The specimens were surface-smoothed and covered by a polyethylene film to avoid water evaporation during the first hours and then cured at 20°C and 95% R.H. Flexural strength was evaluated by three-point bending test and

then compressive strength tests were carried out on the two prism halves obtained from the bending test according to UNI EN 196-1:2005 at 1, 7 and 28 days. Direct tension was measured at 28 days. After the same curing period, prismatic specimens were cored to obtain cylindrical specimens (h/d=1; d=20mm) in order to carry out dynamic test by means of a Modified Hopkinson Bar (DynaMat Laboratory - University of Applied Sciences of Southern Switzerland) [3].

A test with the JRC-SHTB is performed as follows:

- (a). First, a hydraulic actuator, of maximum loading capacity of 600 kN, is pulling the pretension high strength steel bar; the pretension stored in this bar is resisted by the blocking device.
- (b). Second, operation is the rupture of the fragile bolt in the blocking device which gives rise to a tensile mechanical pulse of 2.4 ms duration with linear loading rate during the rise time, propagating along the input and output bars bringing to fracture the specimen.

MIXTURES		RM	GRP	GF	GF- GRP	GF-GRP- CN0.1%	GRP CN0.1%	GRP- CN1.0%
INGREDIENTS								
Cement (kg/m ³)		635	635	617	617	616	628	625
Water (kg/m ³)		317	317	309	308	305	314	313
Sand (kg/m ³)		1270	1140	1234	1110	1118	1130	1125
Superplasticer	(% vs c.m.)	0.3	0.5	0.5	0.5	0.5	0.5	0.5
	(kg/m^3)	2.0	3.0	3.0	3.0	3.0	3.0	3.0
GRP - Glass Reinforced Plastic	% sand volume substitute	-	10	-	10	10	10	10
	(kg/m ³)	-	63	-	60	60	63	63
HD (short glass fiber)	(% vs c.m.)	-	-	1.0	1.0	1.0	-	-
	(kg/m^3)	-	-	6.0	5.0	5.0	-	-
HP (long glass fiber)	(% vs c.m.)	-	-	3.0	3.0	3.0	-	-
	(kg/m^3)	-	-	19	18	18	-	-
CNTs	(% vs c.m.)	-	-	-	-	0.1	0.1	1.0
	(kg/m^3)	-	-	-	-	1.0	1.0	6.0
Surfactant (LAS)					-	5.0	5.0	5.0
Defoamer					1.0	1.0	2.0	2.0
RHEOLOGICAL PROPERTIES								
Spread (mm)		230	240	210	200	190	270	180
Specific mass (kg/m ³)		2100	1920	2060	2095	2050	2080	2132

Table 3. Composition and rheological properties of the mortars

Results and discussion

In Figure 1 specific mass values of fresh and hardened mortars are shown. In particular on the right percentage variation of specific mass with respect the reference mortar is presented. Mortar containing Glass Reinforced Plastic (GRP) presents a specific mass lower than the reference mixture as a consequence of an anomalous air entrapment. Therefore, to avoid entrapped air in excess a defoamer was used when GRP was added to the mixture. As a consequence of this addition all the mortars present specific mass values in fresh and hardened state very similar to that of the Reference Mixture [4].



193



Figure 1 – Specific mass of fresh mixtures and hardened specimens (on the right the percentage variation with respect the reference mortar).

Figure 2 summarizes flexural strength results. The GRP-mortar flexural strength decreases both for 1 and 28-day cured specimens as a consequence of the anomalous air entrapment (Figure 1). Flexural strength of GF reinforced mortar is higher than that of the plain mortar. For the other mixtures, no substantial differences of flexural strength with respect that of reference mortar was detected.

Figure 3 shows compressive strength of cement composites after 1, 7 and 28 days curing. Likewise flexural strength data, compressive strength is similar for all mortars with the exception of GRP-mixture where the higher porosity caused by the air entrapment is responsible for the lower compressive strength. The compressive strength values of the other mixtures are similar to that of the RM because entrapped air was eliminated by using the defoamer. As expected, the addition of both glass fiber and carbon nanotubes doesn't produce any significant increase in compressive strength since fibers act only when the matrix is cracked.

Figure 4 shows direct tensile strength at 28 days. Tensile strength of GRP reinforced mortar is similar to that of reference mortar. Data seem to indicate that extra-air entrapped doesn't influence the tensile strength. Addition of GF determines a decrease of tensile strength. Probably compaction of the fresh mortar favours the alignment of the fibers perpendicular to the drilling and, hence, tensile stress direction. As a consequence of this fibers are not effective to improve tensile capacity of the mortars. Adding GRP and CNTs, tensile strength values increase. In particular, the higher CNTs percentage the higher tensile strength. Probably, carbon nanotubes are capable to bridge the micro-crack present in the specimens, improving the tensile strength.

Figure 4 shows the comparison between tensile strength values obtained on static and dynamic conditions. In general dynamic tensile strength is about three times higher than the corresponding static value. The better results were obtained for GRP and 1% CNTs reinforced mortar as a consequence of the combined effect of drying-shrinkage reduction by GRP [4] and the continuous network guaranteed by CNTs.

The Dynamic Factor Increase (DIF) is shown in Figure 5. As previously pointed out, dynamic tensile strength is higher than static. In static condition, cracks propagation is restricted in the transition zone (aggregates and cement matrix interface). Otherwise, on dynamic condition, waves and fractures cross aggregates grain and inside the specimens a map-cracking arises, increasing mechanical property of cementitious materials [5].

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194 Performance, Protection and Strengthening of Structures under Extreme Loading

Finally, fracture energy was calculated (Figure 6) integrating stress/COD curve from the peak to failure. GRP addition doesn't change the energy fracture with respect to the reference mixture. Otherwise, fiber glass reinforcement reduces energy fracture, as well as dynamic tensile strength and DIF. This behaviour, as previously mentioned, should be ascribed to the alignment of glass fibers perpendicular to the direction of load responsible for a more rapid propagation of waves and cracks. The fracture energy of Carbon nanotubes (CNTs) and GRP reinforced mortars was higher, about 20%, than that of the reference mortar. The higher the CNTs percentage, the higher the fracture energy, similarly as tensile strength. This behaviour can be related to the carbon nanotubes capacity to slacken crack and wave propagation during dynamic test.



Figure 2 – Flexural strength vs. Time.

Figure 3 – Compressive strength vs. Time.



Figure 4 – Tensile strength on static and dynamic condition.





Conclusion

Replacing partially the natural sand with Glass Reinforced Plastics (GRP), compressive and flexural strength decrease (about 20%) with respect those of the reference mortar both on static and dynamic condition as a consequence of an anomalous air entrapment. Adding glass fibers (GF), GRP or/and Carbon Nanotubes (CNTs), no substantial improvement in terms of mechanical properties under static condition was occurred. The Dynamic Increase Factor of the reference mortar was higher than that of the reinforced mixtures, but fracture energy was lower. In particular, adding carbon nanotubes and GRP together to cement composites, fracture energy increases. Increasing carbon nanotubes content, fracture energy and tensile strength increase. A good CNTs dispersion inside cement composites guarantees an increase of tensile strength and a dynamic behavior improvement. Nanoparticles oppose to wave and crack propagation, increasing the high strain rate strength. GRP and CNTs reinforced mortars need more fracture energy to failure at 150s⁻¹ strain rate.

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