

HYBRID CNT-GO AS REINFORCING PHASE IN FLY ASH BLENDED CEMENT MORTAR NANOCOMPOSITES AND ITS EFFECT ON COMPRESSIVE STRENGTH

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ABSTRACT: Pozzolanic material such as fly ash is a good partial replacement to cement for economical constructional purposes. Fly ash brick is an appealing and reasonable material for housing construction purposes. Due to its limited strength, it has been mainly used as separation walls inside a building's frame-work and hence, is avoided in practical cases where early age strength is desirable. Main motive of present investigation is to enhance the compressive strength of FA blended cementitious matrix with the aid of hybrid carbon nanomaterials (HCNs). In the present study, functionalized carbon nanotubes (FCNT), graphene oxide (GO) and their Hybrid as reinforcing material in the fly ash blended cement nanocomposites (FCNCs) has been investigated for enhanced mechanical performance. It was observed that addition of 0.02% GO and 0.02% FCNT by weight of cement in FCNCs has shown an improvement in its mechanical strength by 53% and 20% respectively. However, mechanical strength was improved synergistically by 73% for 0.02% HCNs (GO+FCNT in 1:1) after 28 days of curing with respect to the control sample. This remarkable enhancement in mechanical properties of FCNCs can be attributed to the synergistic effect of three dimensional array of hybrid carbon nanomaterials (HCNs) promoting improved dispersion of agglomerated CNTs over GO surface due to π - π interactions. Moreover, HCNs provides one additional dimension for the hydration of cement phases to produce portlandite which further promotes the pozzolanic reactions in the fly ash-cement matrix.

Keywords: Hybrid Carbon Nanomaterials (HCNs); Fly ash-cement nanocomposites (FCNCs); Mechanical strength; Microstructure; Crystallization behavior.

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INTRODUCTION

Cement based materials have been used in construction industry all over the world. Cementitious materials acts as binding agent which glues other materials present in the mortar/ concrete together to a single framework. However, a few drawbacks of these materials such as quasi-brittle behavior and poor tensile strength initiate the crack formation and further crack propagation in the cement matrix at microscopic scale [1-2]. Traditional reinforcing agents such as glass fiber, polymer fiber and carbon fibres etc. were utilized till now to curb these limitations, but incorporation of conventional reinforcements limits the crack upto macroscale only [3-5]. All such factors lead to reduced strength of cementitious matrix ultimately leading to its failure to external loads [6]. In addition to this, production of cement releases a large amount of carbon dioxide gas into the environment, which is considered as a major green house gas [7-8]. So, considerable research should be undertaken on some other alternative replacement to cement for viable development of cement based materials.

On the other hand, fly ash (FA) is an industrial waste generated from thermal power plants and disposal of FA is one of the major issues associated with the thermal power plants [9]. FA is a pozzolanic material which lacks binding properties of its own. However, it contributes to the strength of mortar/concrete through the pozzolanic reaction. In pozzolanic reaction, the calcium hydroxide (C-H) produced during the hydration of silicates (C_2S and C_3S) of OPC reacts with FA particles, which results in the formation of binding gel C-S-H (calcium silicate hydrate) [10]. Cementitious properties such as improved rheological properties, resistance to abrasive environment, corrosion, sulphate attack and freeze-thaw etc. improves with utilization of FA as mineral additive. [11-14]. However, the major drawback of FA incorporation is the slow strength development rate, making its use limited in applications where high early strength is a prerequisite. Previous researchers have tried to control this limitation by various strategies such as mechanical or chemical activation of FA to produce labile FA particles. Mechanical activation of FA via milling devices such as planetary or vibrational mills and chemical activation via alkali activation or sulfate activation [15-18], however, makes the whole process quite expensive.

More recently, in improving the properties of a large number of ceramic matrices including cement matrix, the emergence of nanomaterials has made a huge contribution. The effect of carbon nanomaterials such as 1-D nanotubes and 2-D graphene derivatives have been studied in detail on the cement based materials [19-22]. Carbon based nanomaterials have been broadly utilized to examine their effect on the mechanical , microstructural and crystallization properties of both pure OPC as well as FA based cement matrices [13,14,23]. However, Hybrid carbon nanomaterials (Hybrid of FCNTs and GO) still have their applications limited to the neat OPC based cementitious materials only. Hybrid Carbon Nanomaterials (HCNs) have shown enhanced mechanical performance and durability of cement nanocomposites owing to the synergistic effect between GO and FCNT, which would otherwise have been absent in GO or FCNT based cement nanocomposites. The 3-D hierarchical framework of HCNs provides with both high charge density of graphene oxide and CNTs with high surface area. This leads to better dispersion of HCNs into the cement matrix and hence improved properties [24-26] are obtained.

Although many investigations have been made to study the influence of HCNs on the physico-mechanical properties of cement based materials but negligible studies have been carried out to investigate the effect of HCNs on the mechanical and microstructural behavior of the fly ash based cement matrix. Hence, our present study focuses on the utilization of HCNs as reinforcing agent in

the fly ash based cement matrix with 30% FA replacement to OPC and its comparison to the individual GO-FCNCs and FCNT-FCNCs has further been made.

EXPERIMENTAL

Materials and Chemicals

Graphite powder (GP) with particle size 100 μm and pristine carbon nanotubes of dimensions 10 nm \times 4.5 nm \times 3-6 μm (O.D. \times I.D. \times L) was procured from Sigma Aldrich (India). Other analytical reagent (AR) grades used were potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2), sodium nitrate (NaNO_3), nitric acid (HNO_3) and concentrated sulfuric acid (H_2SO_4) and were purchased from Loba Chemie Pvt. Ltd.

Ordinary Portland Cement (OPC) of Grade 42.5 complying to the IS 8112 (IS 8112, 1989) was purchased from Ambuja Limited (India). Class-F fly ash (FA) which was used as 30% partial replacement to the cement in all mixes was procured from Guru Gobind Singh super thermal power plant situated at Ropar (Punjab), India. The mineralogical composition of OPC and FA as obtained from XRF analysis is given in Table 1. Sand used for the mix fabrication comprising three grades was procured from the local market. Specifications of sand are given in Table 2. A polycarboxylate ether based superplasticizer (SP) (Auramix-300) was purchased from Fosroc Chemicals Pvt. Ltd. SP was utilized to ensure good dispersion of the nanoadditives into the cement matrix.

Table 1 Chemical Composition of Cement and Fly Ash

COMPONENT (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2
OPC	21.99	5.98	4.10	60.78	0.96	2.86	1.18	0.86	0.25
FA	57.6	30.5	3.72	1.10	0.38	0.22	1.35	0.10	1.72

Table 2 Details of Sand Used

GRADE OF SAND	TYPE	PARTICLE SIZE RANGE (mm)	AMOUNT USED IN STUDY (%)
Grade I	Coarse	2 mm to 1mm	33.33%
Grade II	Medium	1 mm to 0.5 mm	33.33%
Grade III	Fine	0.5 mm to 0.09 mm	33.33%

Preparation of Graphene Oxide (GO) from Ball-Milled Graphite Powder (MGP)

Mechanical milling of the GP into fragmented and exfoliated graphite powder (MGP) was done with the help of Planetary ball-mill (Pulverisette 6 (Fritsch)). About 25 grams of GP was taken in planetary jar along with zirconium balls and was milled in wet medium of toluene at 500 rpm for 12 hours. The Zirconia balls were taken in 3:1 to the GP by weight. The milled powder was then collected and labeled as MGP.

GO was prepared by the help of generally used Hummer's Method [27] to obtain the surface functionalized graphite oxide which was then exfoliated in the water with the help of ultrasonication process.

Functionalization of Pristine carbon nanotubes

5 g of pristine multi-walled carbon nanotubes were taken in a round bottom flask and 420 ml of concentrated HNO_3 (69%) was added into it. The RBF was equipped with reflux condenser and the suspension prepared was refluxed for 10-12 hours at 100°C. After cooling, the mixture was added to a beaker containing 1500 ml of water, with constant stirring. This suspension was then centrifuged to remove the acid with repeated de-ionized water washings to get the pH neutral. The obtained functionalized CNT were labeled as FCNT and were stored for further use.

Structural characterizations of GP, MGP, GO, CNT and FCNT

The various materials GP, MGP, GO, CNT and FCNT were characterized using various techniques such as Field-Emission Scanning Electron Microscope (FE-SEM), Energy Dispersive X-Ray Analysis (EDX), and Raman Spectroscopy.

MIX DESIGNS

The tabular form presenting mix designs for different FA based mortars prepared is shown in Table 3. In general, four mixes were fabricated and further tested for various properties. The binder (70% OPC + 30% FA) to sand ratio for all the mortar mixes taken was 1:3 by weight. The water to binder (w/b) ratio for each mix was taken to be 0.43. The first mix was a control mix with 30% FA as partial replacement to the cement, without incorporating any carbon nanomaterial. Other three FA based mixes incorporated FCNT, GO and Hybrid (FCNT+GO in 1:1), respectively by 0.02% (by weight of binder). Before the addition of FCNT, GO and HCNs into the binder-sand mixture, aqueous dispersions of FCNT, GO and HCNs were prepared in distilled water and SP using probe sonicator (VCX 750W). The carbon nanomaterials and SP were weighed by the weight of binder (bwob). The freshly prepared FA based mortar pastes were filled into the cubic moulds of dimension 70.6 mm × 70.6 mm × 70.6 mm. The moulds were then left undisturbed for setting under standard conditions and were demoulded after 24 hours. The cubic specimens were cured in a water tank until curing ages of 7, 14, 28 and 90 days for the evaluation of mechanical strength, microstructural and crystalline behavior.

Table 3 Composition of cement mortars

MIX	FA (% BY WEIGHT OF CEMENT)	DOSAGE	w/b RATIO	SUPER PLASTICIZER	ULTRASONICATION TIME (MIN)
Control	30	0	0.43	0.15	20
FCNT-FCNC	30	0.02	0.43	0.20	20
GO-FCNC	30	0.02	0.43	0.20	20
⁽¹⁾ HCN-FCNC	30	0.02	0.43	0.20	20

⁽¹⁾ HCN was incorporated in 1:1 of GO to FCNTs

⁽²⁾ Dosage of carbon nanomaterial and superplasticizer were taken by weight% of OPC-FA blend.

TEST METHODS

Compressive Strength

Universal Testing Machine of capacity 2000 was utilized to test the compressive strength of mortars as per IS-516. Three cubic specimens from each mix were taken for the testing at curing ages of 7, 14, 28 and 90 days. The average of readings as shown by digital meter was taken as representative strength for each mix.

Microstructural and crystalline phase analysis

The microstructure and hydration products formed in the mortar samples were examined with the help of Nova Nano FE-SEM 450. The broken mortar sample during compressive strength testing was taken from each mix design and was sputtered with layer of gold before analyzing under FE-SEM.

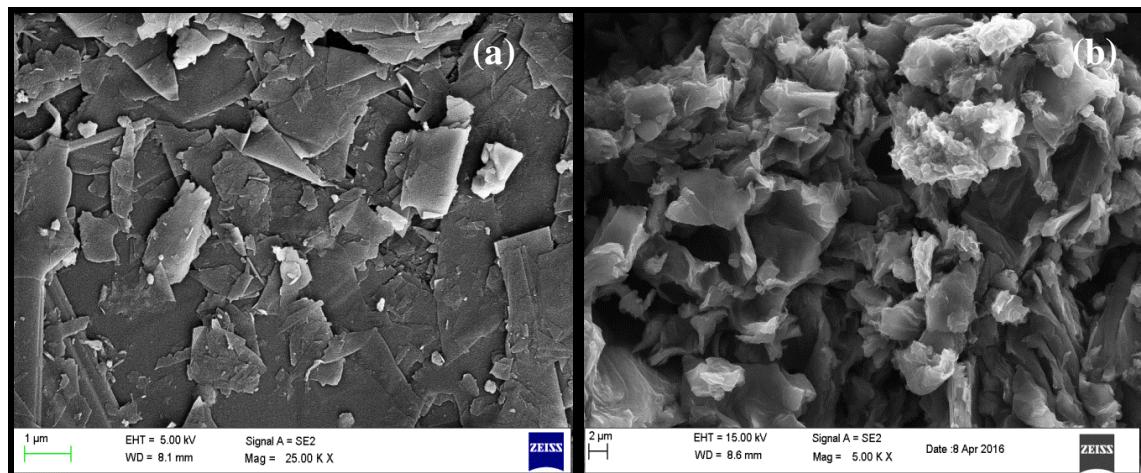
X-Ray diffraction patterns were obtained with the help of PANalytical XPERT-Pro Diffractometer operated at 45 kV and 40 mA using CuK α radiation. The fractured mortar samples during compressive strength testing were taken and were powdered using pestle and mortar. The powder was sieved prior the XRD investigation to remove the coarse aggregates.

RESULTS AND DISCUSSIONS

Structural characterizations of carbon nanomaterials

Field Emission Scanning Electron Microscopy (FE-SEM) and Energy Dispersive X-Ray (EDX) results

The morphology as well as elemental composition analysis of pristine and functionalized materials was carried out with the help of NOVA Nanosem 450 Field Emission Scanning Electron Microscope coupled with Electron Dispersive Spectroscopic (EDS).



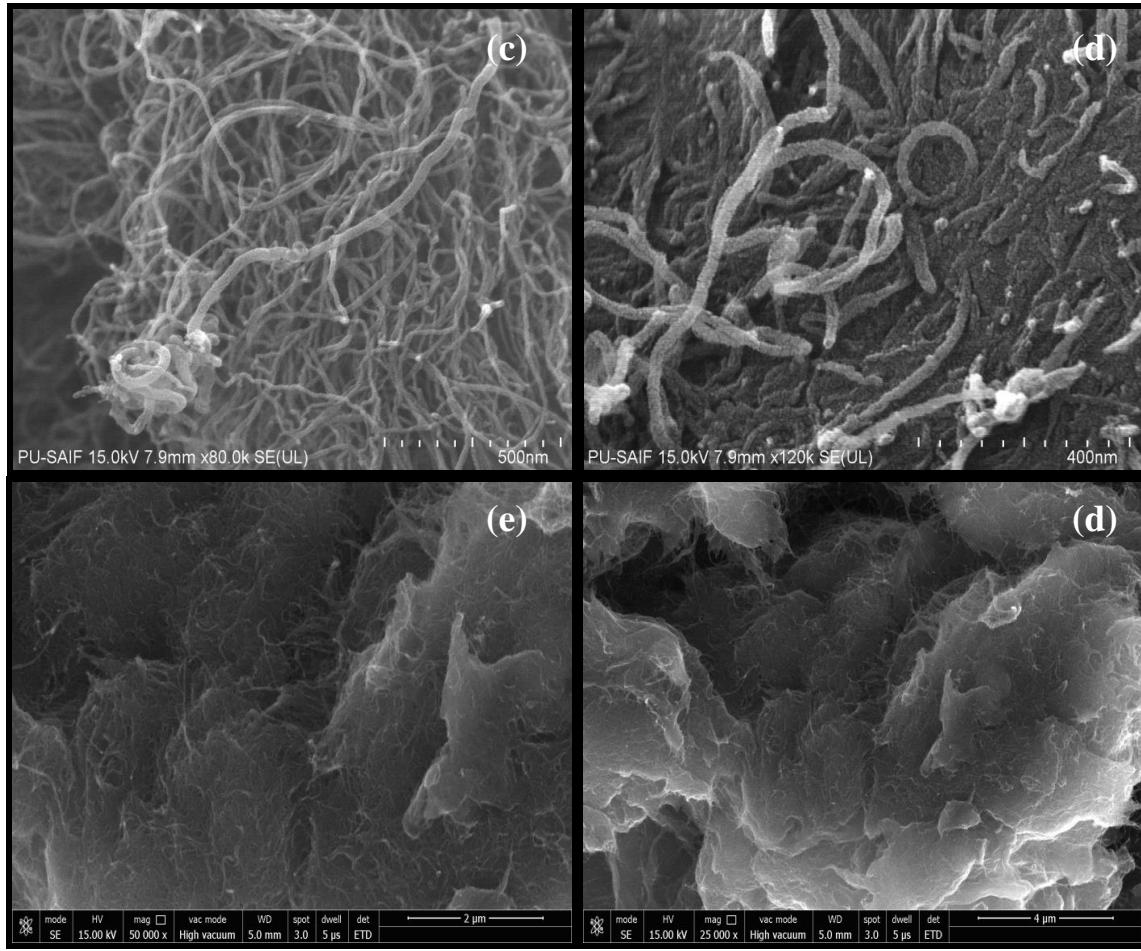


Figure 1 FE-SEM images of (a) MGP (b) GO (c) CNT (d) FCNT and (e,f) HCNs

Fig. 1(a) MGP shows flaky morphology while in case of GO (Fig. 1(b)) well exfoliated corrugated sheets can be observed after functionalization. In Fig. 1(c) agglomerated bundles of CNTs can be seen due to high surface energy and after functionalization (Fig. 1(d)) SEM image depicts the defect generation onto the CNT walls which has also been represented by Raman spectroscopy. Fig. 1(e-f) shows the morphology of FCNT-GO hybrid. It is evident that the FCNTs are dispersed properly onto the surface of GO's graphene sheets through π - π interactions. Table 4 presents the elemental compositions of MGP, GO, CNTs and FCNTs.

Table 4 Elemental composition of MGP, GO, CNT and FCNT

MATERIAL	PERCENTAGE OF ELEMENTS (%)		
	C	O	Si
MGP	100	0.00	0.00
GO	62.68	37.32	0.00
CNT	100	0.00	0.00
FCNT	86.01	13.47	0.52

Raman spectroscopy results

Raman spectroscopy was carried out using STR 500 Confocal Micro Raman spectrometer to examine the defect intensity of raw and functionalized materials as shown in Fig.2. In case of MGP, a feeble D-band at 1350 cm^{-1} and a strong G-Band was observed at 1585 cm^{-1} signifying the defect free nature of graphite sample. However, I_D/I_G ratio for GO increased from 0.37 (MGP) to 0.95 due to structural imperfections generated after functionalization of graphene sheets. In a similar way, I_D/I_G ratio for FCNT increased from 1.1 to 1.5 due to structural distortions onto the CNT framework. However, HCNs showed a slight different I_D/I_G ratio (i.e. 1.5) owing to the interactions between FCNT and GO hydrophobic aromatic regions. [28-29].

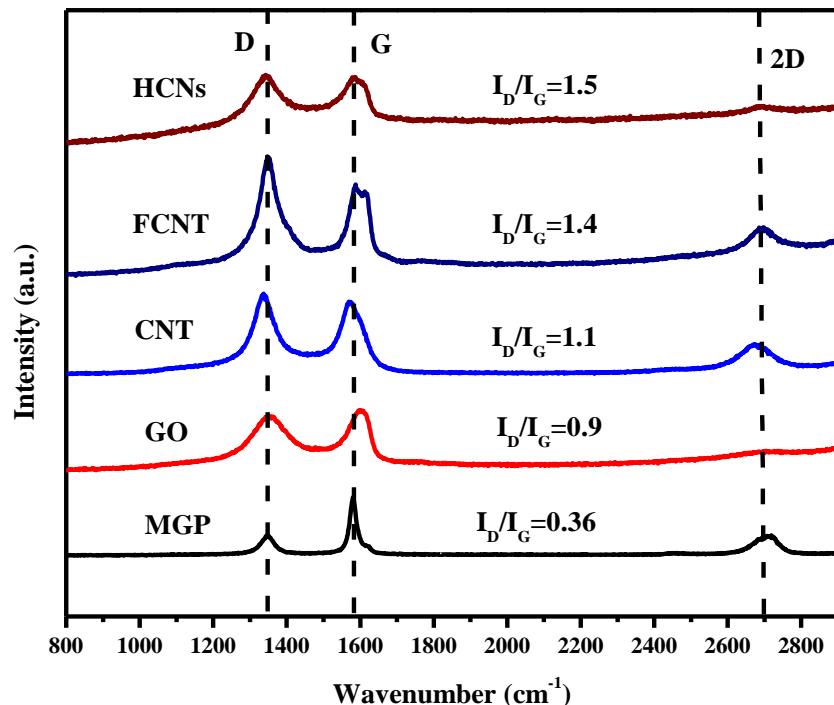


Figure 2 Raman Spectra of MGP, GO, CNT, FCNT and HCNs

Physico-mechanical results of CN & HCN reinforced Fly Ash Based Cement nanocomposites (FCNCs)

Graphical representation of compressive strength results for Control, FCNT-FCNC, GO-FCNC and HCN-FCNC as a function of increasing curing age is shown in Fig. 3. It is clearly noticeable that compressive strength values have been improved for each mix as compared to control sample. Moreover, as curing age increases (i.e. from 7 to 90 days), a gradual increase in the compressive strength values was observed for all the mixes. The maximum increase in compressive strength has been obtained for HCN-FCNC of 46.7% in comparison to control, at 90 days of curing. The improvement in compressive strength for FCNT-FCNC, GO-FCNC and HCN-FCNC were found to be 24.5%, 35.6% and 46.7% at 90 days of curing, respectively.

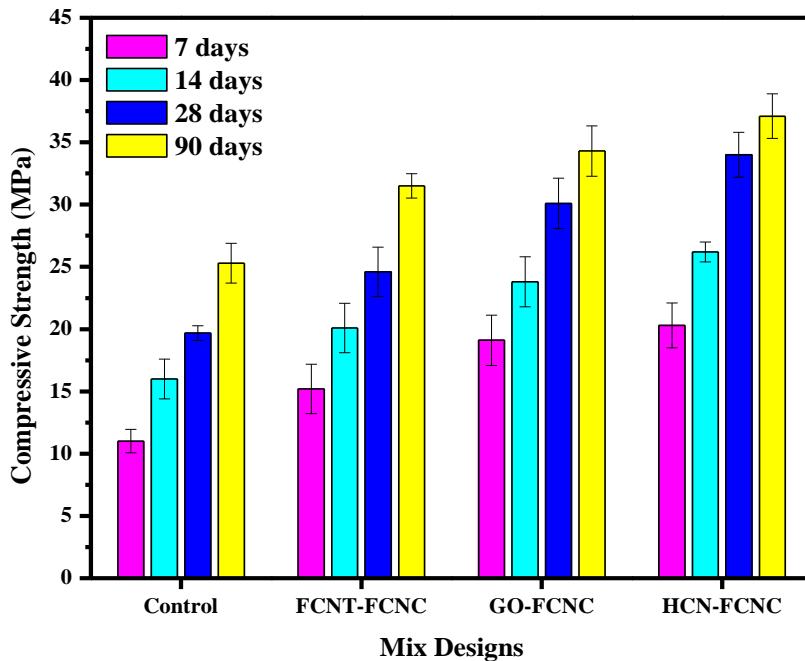


Figure 3 Compressive strength values of control and CN/HCN-FCNC

It is quite obvious that three dimensional framework of FCNT-GO provided more nucleation sites for growth of hydration products such as calcium silicate hydrate and calcium hydroxide (C-S-H and C-H), which profuse further into the cracks and voids of cement matrix to improve the overall strength. Moreover, HCNs acted as better reinforcing agents as compared to GO and FCNTs, owing to better dispersion of FCNT-GO Hybrid into the cement-FA matrix, which in turn improved the mechanical strength of FA based mortar. The hydration by-product calcium hydroxide (C-H) undergoes pozzolanic reaction with FA producing further C-S-H, which provides firmness to the structure on the whole [33].

Table 5 Percentage increase in compressive strength (%) with respect to control mix

MIX DESIGN	CHANGE IN COMPRESSIVE STRENGTH (%)			
	7 DAYS	14 DAYS	28 DAYS	90 DAYS
Control	--	--	--	--
FCNT-FCNC	38.1	25.7	20.1	24.5
GO-FCNC	73.6	48.8	53.0	35.6
HCN-FCNC	84.5	63.7	72.9	46.7

Microstructural investigations of FCNCs

FE-SEM investigations were carried out at different curing ages of 7, 14, 28 and 90 days to inspect the effect of HCNs on the microstructure and hydration products of FA based cement mortars. The FE-SEM micrographs for control have been shown in Fig. 4. In Fig. 4(a) unhydrated FA particles freely adhered over the hydrated cement products can be seen.

However, with increase in the curing age, these FA particles begin to be consumed up as shown in Fig. 4(b). At 28 days of curing age (Fig. 4(c)), a rigid, however spongy mass of C-S-H was produced, where adhesion further improved till 90 days as shown in Fig. 4(d).

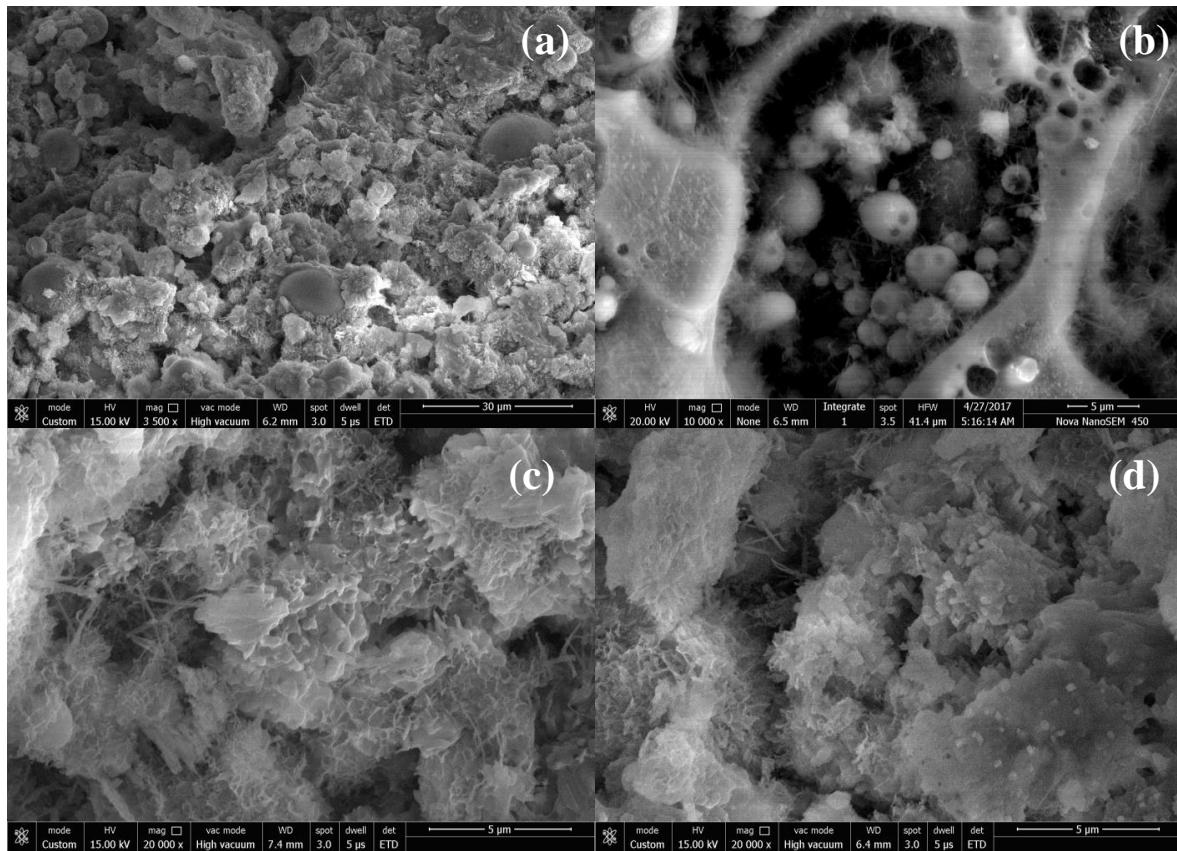
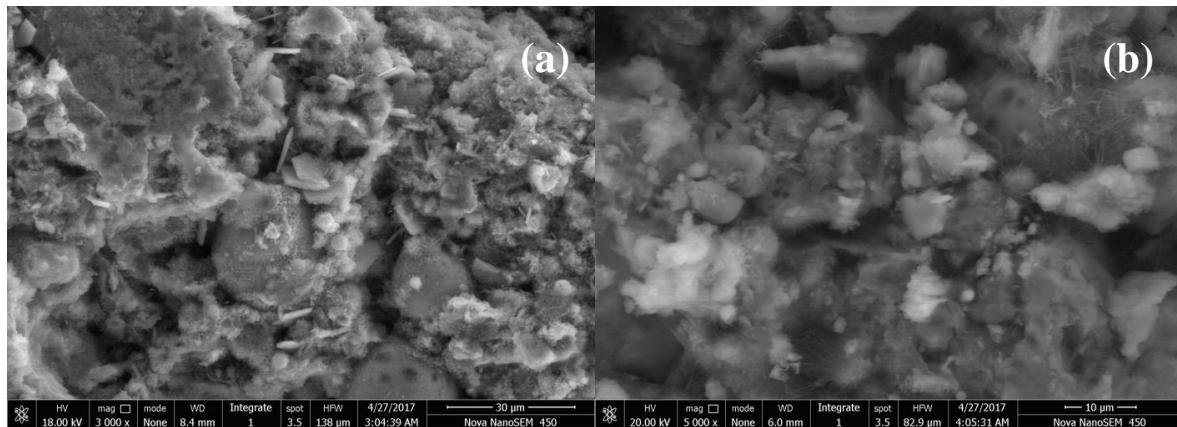


Figure 4 FE-SEM Images of Fly Ash Based Control Cement Mortar at (a) 7 days (b) 14 days (c) 28 days (d) 90 days

Fig. 5 shows the microstructural behavior of HCNs incorporated FCNCs at different curing ages. In Fig. 5(a), C-H crystals along with unhydrated FA particles can be observed. However, until 14 days (Fig. 5 (b)) a large amount of FA particles have disappeared owing to the huge production of hexagonal C-H crystal which initiates pozzolanic reaction [33].



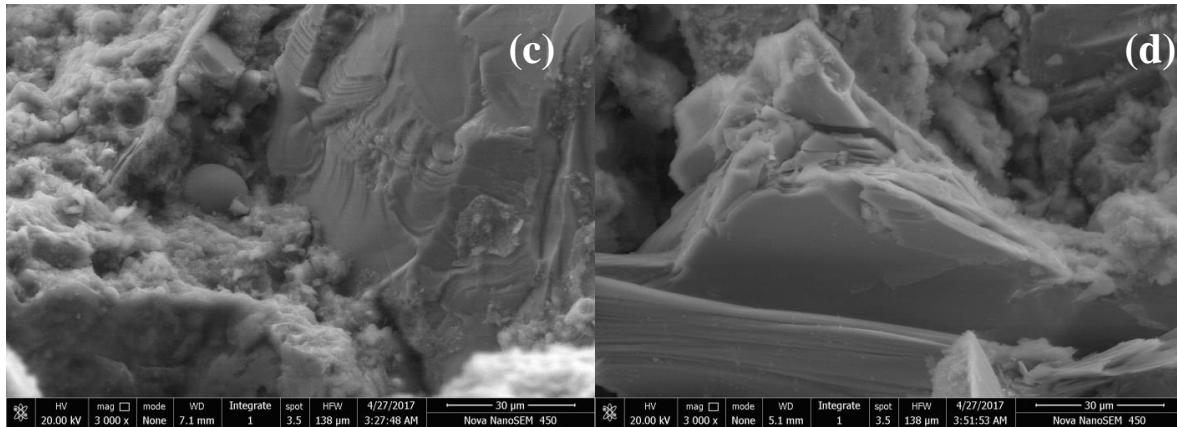


Figure 5 FE-SEM images of HCN-FCNCs mortars at (a) 7 days (b) 14 days (c) 28 days (d) 90 days

Sufficient precipitation of C-H can be attributed to the superior nucleation caused by 3-D hierarchy of FCNT-GO (HCNs) as compared to individual GO or FCNTs. Fig. 5(c) shows regularly oriented C-S-H sheets stacked over each other with only a handful of FA particles present in the pockets of hydrated cement matrix which further gets consumed until 90 days of curing (Fig. 5(d)) giving a well oriented and rigid C-S-H gel structures.

Crystalline phase investigation of FCNCs

The quantitative and qualitative aspects of various crystalline phases of CNs and HCNs incorporated mortars were carried out with the help of XRD at the curing age of 90 days.

In Fig. 6, the peaks corresponding to unhydrated silicates of OPC (i.e. C₂S and C₃S) appears at (2θ = 32.7°) and (2θ = 29.5°, 32.2°), respectively.

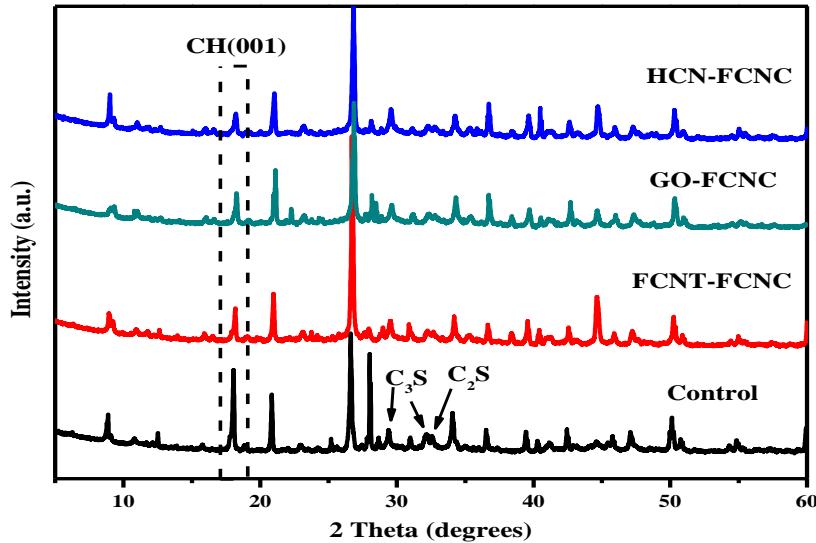


Figure 6 Diffraction Patterns of Control and CN/HCN-FCNCs after 90 days curing

The peaks representing these silicates have been found to be lower in CNs/HCNs incorporated samples as compared to the control, signifying consumption of cement components, hence accelerating the hydration mechanism. The main crystalline hydration product of cement is calcium hydroxide (C-H) and peaks corresponding to it appear at 18.3°, 34.2°, 47.1° and 50.1°. The pozzolanic reactions are often characterized by the peak at 18.3° [33-36]. It was found that intensity for the peak at 18.3° decreases for the nanocomposites as compared to control sample, showing that pozzolanic reaction has taken place in a better way in carbon nanomaterial incorporated cement matrices. FCNT, GO and HCNs resulted in the production of hydration products such as C-S-H and C-H at an elevated rate than control sample of mortar. Moreover, uniform production of C-H takes place in case of HCN-FCNCs throughout the cement matrix due to uniform dispersion of HCNs as compared to control and individual GO and FCNTs. The consistently produced C-H further reacts with FA particles in the cement matrix producing C-S-H gel and hence densifying the gel network. The decrease in the C-H amount further reduces the peak intensity at 18.3°. This reduction was observed to be maximum in case of HCN-FCNCs, indicating the maximum C-H consumption leading to a greatest rate of pozzolanic reaction.

CONCLUSIONS

From the results, it can be concluded that HCNs improved the compressive and tensile strength to a greater extent than that of individual FCNT or GO in the FA based cement matrix. This was also in agreement with the result drawn from microscopic observations and crystalline phase interpretation studies. The hexagonal C-H crystallites which act as precursor for the pozzolanic reaction initiation was produced uniformly in case of HCNs. Consumption of C-H by FA further produced C-S-H gel uniformly throughout the matrix increasing the overall strength of complete framework. In addition to this, very few unreacted particles of FA are observed in FE-SEM images during early hydration stages of HCN-FCNCs. On the other hand, in case of 1-D FCNT and 2-D GO, the pozzolanic reaction was not competent to that of HCN-FCNCs. Thus, this research would pave a new way to bring fly ash blended bricks into practical applications where strength equivalent to that of neat OPC based mortars is needed.

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