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Studying the effects of Polymeric nanomaterial additions in Cement composites

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Abstract

Nanomaterials as studied today are a set of advanced materials which have unique properties and can better the existing behaviors of normal cement concretes. Nanomaterials exist in entangled mass like form which are insoluble in water and therefore are dispersed in new generation polymers prior to mixing. In this paper an attempt is made to study the effects of Nanomaterials like Carbon Nanotubes (CNT) and Nano-Titanium Dioxides (TiO_2) for various proportions ranging from 0.02%, 0.05% and 0.1% of cement weight for CNT & 1% & 2.5% of cement weight for TiO_2. Laboratory tests are carried out using ordinary Portland cement mortar mix in mortar cubes of 70.7 mm dimensions, taking cement: sand=1:3 by weight, keeping the water-cement(w/c) ratio fixed at 0.4.The required water is added as per the standard consistency provided in Indian codal stipulations of IS:4031. The mechanical testing of the cubes is done in laboratory scale under ordinary curing conditions at 7days, 28 days, 90 days, 180 days & 365 days.

Keywords: *Cement, Concrete, Days, Nanomaterials, Test, Water.*

1. Introduction

'Nano' is a Greek word which means 'Dwarf' and it operates in the 10^{-9} m range. From agriculture to food to textiles to electronics to even satellites and every other applications, nanomaterials had made its presence felt or have totally conquered like the Mobile sector. This ultra small has the potential to make enormous changes to our lives due to the fact that material at the nanoscale brings different laws of Physics into play. Also, Nanomaterials have a relatively larger surface area when compared to the same mass of material produced in bulk form. This can make the materials more chemically reactive and affect their strength or electrical properties. The construction industry was the only industry to identify nanotechnology as a promising emerging technology in the UK Delphi Survey in the early 1990s [1] but other industries like tyres, paints, medicines etc have paced ahead. This may be due to the problems of distribution and dispersion, since Carbon Nanotubes & Nano Titanium Di-Oxide naturally exist as entangled mass like form like jute fibers(as shown in Fig.1) having a tendency to agglomerate owing to the intermolecular *Van Der Waals interactions*. Nanomaterials need to get specially surface treated before its application in cement concretes or any other further uses.

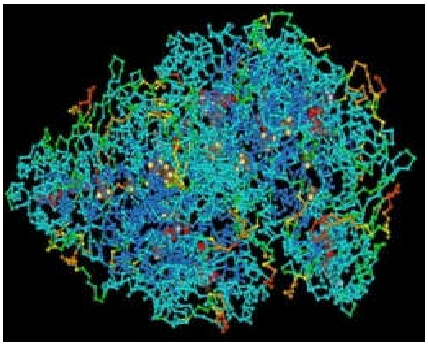

Fig.1: *Nanomaterials as entangled mass like form.*

Fig.2: *Poly Carboxylate Ether (PCE)*

Here we have used new generation polymer (admixture)-Poly carboxylate ether (PCE) as surfactant. Specific properties of PCE are given in Table. 1. Fig. 2 shows the solution of PCE.

Table 1. *Specific properties of Poly Carboxylate Ether (PCE) as per Literature*

Appearance	**Colorless to Light Brown Liquid**
Sp.Gravity	1.11± 0.02
Air entrainment	≤ 1.5% over control mix
pH	≥ 6
Chloride content	NIL, as per BS:5075(Part-I)
Compatibility	OPC,PPC,PSC & SRC

2. Review of existing literatures

Xiaoqing Gao et al [2] has found that, Carbon Nano tubes resist micro crack formation, Multi wall carbon nano tube (MWCNT) gives greater composites with greater strength and stiffness. Excellent thermal conductivity of MWCNT can be achieved when carbon nano tubes are aligned in same direction and optimal carbon nano tube loading are chosen.

Morsy et al [3] has found that, CNT can improve mechanical performance, durability and sustainability of concrete. When OPC was substituted by 6 wt. % of cement by nano metakaolin (NMK) and the carbon nanotube was added by ratios of 0.005, 0.02, 0.05 and 0.1 wt. % of cement. It reduces the amount of cement needed in concrete in order to obtain higher strength. It also reduces the construction periods and produce high-strength concrete with less curing time.

Zaki et al [4] have found that, the well-known performance of concrete without nanoparticles was compared with that after the addition of nano-particles for both fresh and hardened states. Nano-Silica concrete requires additional amount of water or super plasticizer to maintain the same workability level. Nano carbon tubes can improve the properties of concrete. Nano-Silica addition results in significant increase in concrete compressive strength after 28-days up to one year and the optimum amount of nano silica is 0.5% by weight of cementitious material.

Ashwani et al [5] has found that, the article examines the potential areas where nanotechnology can benefit construction engineering. The data and information collected is from current literature. The purpose is to point out clear cut direction among the nanotechnology development areas where the construction process would immediately harness nanotechnology, by specifying clear recommendations. The information would be beneficial to both construction engineering education and research. In this paper a broad overview of the potential application of various nanotechnology developments in the construction engineering field is discussed, and the potential for further basic research that may lead to improved systems is evaluated. Nanotechnology has been concerned with developments in the fields of microelectronics, medicine and materials sciences. The potential for application of many of the developments in the nanotechnology field in the area of construction engineering is growing.

Pacheco-Torgal et al [6] have found that, the paper reviews current knowledge about nanotechnology and nano materials used by the construction industry. It covers the nanoscale analysis of Portland cement hydration products, the use of nanoparticles to increase the strength and durability of cementations composites, the photo catalytic capacity of nanomaterials and also nanotoxicity risks. Nanotechnology seems to hold the key that allows construction and building materials to replicate the features of natural systems improved until perfection during millions of years.

Tiago Martins et al [7] have concluded that 1% nano-TiO_2 content seems to be an optimal percentage for compressive strength. The increase in the nano-TiO_2 content leads to a decrease in the compressive strength. Also the mixture with 1% nano-TiO_2 content seems to have the best performance concerning resistance to acid attack.

Jayapalan et al [8] have discussed that throwed light on the effect of nano-sized titanium dioxide on early age hydration of Portland cement. He said that the addition of TiO_2 to cement modifies the hydration rate primarily due to dilution, modification of particle size distribution & heterogeneous nucleation. But when the dosage is increased, cement dilution is resulted with an increase in w/c ratio.

Lucas et al [9] have concluded that photo catalytic activity of TiO_2 increases with increase in dosage but its mechanical strength decreases for addition of more than 1% wt. of TiO_2.

Madhavi et al [10] have found an increase in compressive and split-tensile strengths of samples with increasing MWCNT.0.045% of MWCNT has improved the 28 days compressive strength by 27% while the split tensile strength increased by 45%. Crack propagation was reduced and water absorption decreased by 17% at 28 days curing.

Kumar et al [11] have discussed the effect of Multiwalled Carbon Nanotubes (MWCNT) on strength characteristics of hydrated Portland cement paste by mixing various proportions of MWCNT and found an increase in compressive and tensile strength of 15% and 36% at 28 days.

Guillermo Bastos have et al [12] have described the findings reported in the last decade on the improvement of these materials regarding, on the one hand, their mechanical performance and, on the other hand, the new properties they provide.

3. Materials and Methods

3.1. Carbon Nanotubes

Carbon nanotubes are large molecules of pure carbon that are long and thin and shaped like tubes, about 1-3 nanometers (1 nm = 10^{-9} m in diameter, and hundreds to thousands of nanometers long. As individual molecules, nanotubes are 100 times stronger-than-steel and one-sixth its weight. Nanotubes have been constructed with length-to-diameter ratio of up to 132,000,000 and are categorized as Single-Walled Nanotubes (SWNTs) and Multi-Walled Nanotubes (MWNTs) [12]. The following Table 2 shows the specific properties of Carbon Nanotubes (as shown in Fig. 3).

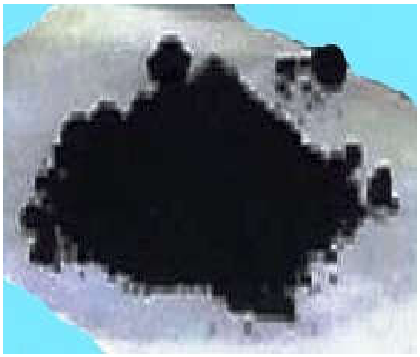

Fig. 3. *Industrial Grade Multiwalled Carbon Nanotubes as used in the Laboratory.*

Table 2: *Specific properties of multi-walled industrial grade carbon nanotubes used as per Literature*

Item	Description
Diameter	20-40nm
Length	25-45nm(Tubes occur in bundles; individual length not taken)
Purity	80-85 Vol% (a/c Raman Spectrometer & SEM analysis) for Industrial Grade
Amorphous Carbon	5-8%
Residue(Calcination In Air)	5-6% by Wt.
Average Interlayer Distance	0.34nm
Specific Surface Area	90-220 m^2/g
Bulk Density	0.07-0.32 gm/cc
Real Density	1-8 gm/cc
Volume Resistivity	0.1-0.15 ohm.cm (measured at pressure in powder)
Other Specification	Contains no residual catalyst impurities

3.2. Nano Titanium Di-Oxides

Though most widely used in applications from paint to sunscreen to mirror to food coloring it has also been tested in construction-Jubilee Church, Rome. Titanium dioxide has the ability to absorb ultraviolet light from sunlight, becoming more powerfully reactive thus breaking down pollutants that come in contact with its surface- it has been aptly called self cleansing agent [12]. The following Table 3 shows the specific properties of Nano Titanium Di-Oxides (as shown in Fig. 4.)

Fig. 4. *Nano Titanium dioxide as used in the Laboratory.*

Table 3. *Specific properties of Nano Titanium dioxide as per Literature.*

Nano Titanium dioxide %	97
Rutile content %	98
pH	7
Average particle size (TEM)	30-40 nm
Treatment	Nil
Moisture %	1.75-2
Bulk Density	0.31gm/cc
Water Solubility	In-soluble
Melting Point Range	1830°C

3.3 X-ray diffraction studies

Here nanomaterials were tested for XRD results as shown in Fig. 5 and Fig. 6. X-ray diffraction techniques are widely used for determining the identity and structure of crystalline materials. Graph is drawn between 2θ and counts. Thus the quantitative and qualitative measures of the sample have done by using this test. The X-Ray Diffraction (XRD) technique is used to measure atomic spacing between lattice layers in a crystal. This can be calculated from the X-Ray Diffraction test results using the Braggs Law equation, is as follows: $n\lambda = 2d \sin\theta$, where, λ = wavelength of the incidental X-Ray beam; d = the atomic spacing between the layers; θ = angle of incidents; n is taken as unity.

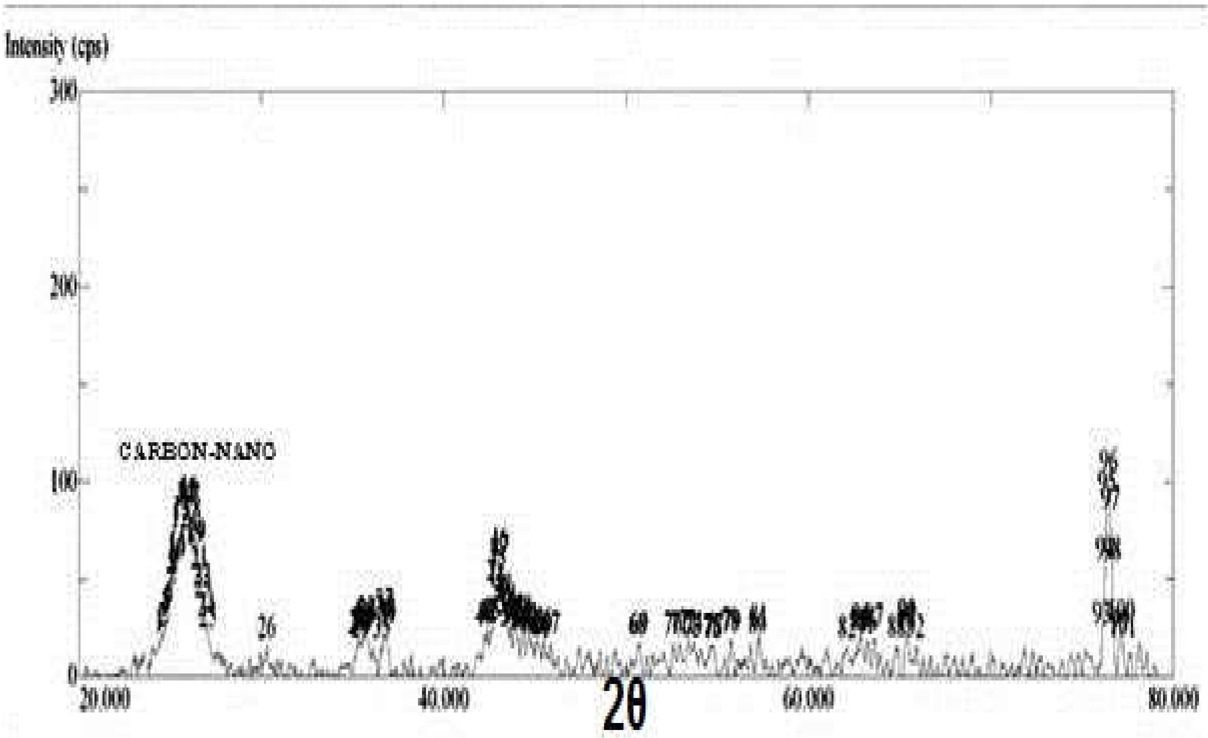

Fig. 5. *XRD image of CNTs*

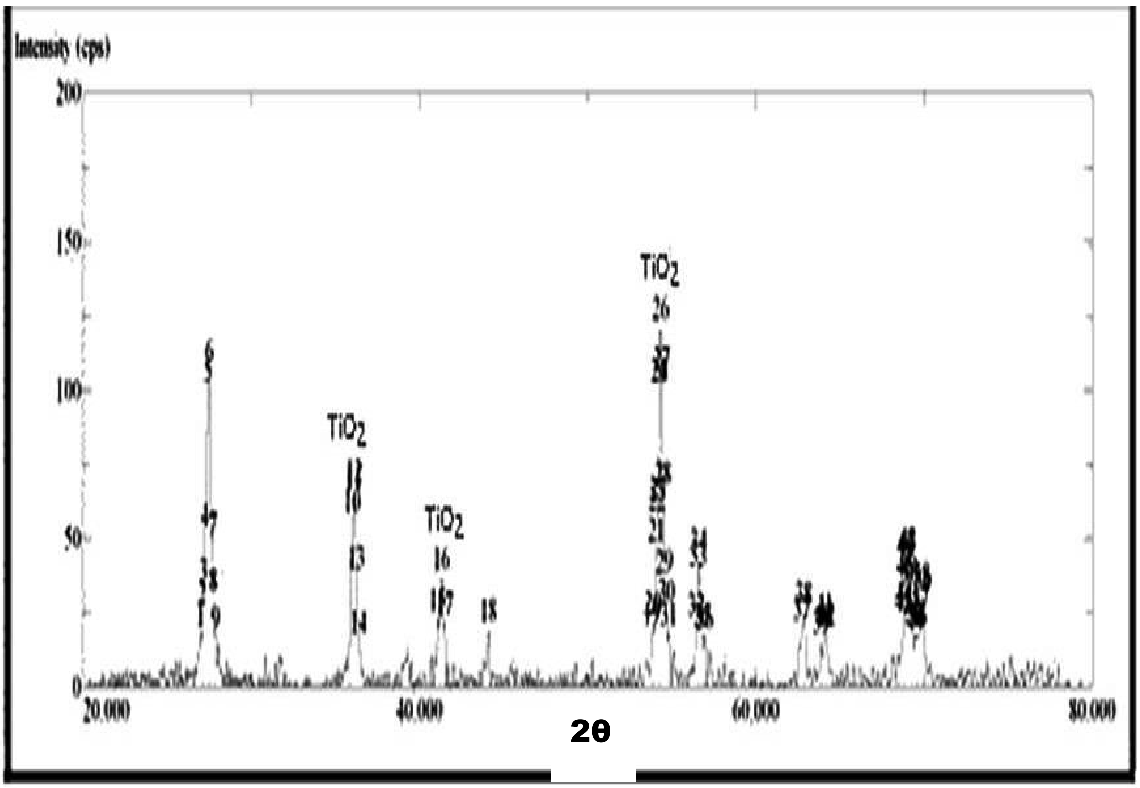

Fig.6. *XRD images of Nano Titanium dioxide.*

Table 4. *Strength (MPa) of OPC Mortar & its Composites (% increase w.r.t. ordinary cubes)*

Sl. No	Nano additions (%) in cement (OPC/PPC)	Avg. 7 day cube strength (% increase)	Avg. 28 day cube strength (% increase)	Avg. 90 day cube strength (% increase)	Avg. 180 day cube strength (% increase)	Avg. 365 day cube strength (% increase)
1.	OPC (0%/CNT)	21.08	31.89	31.20	30.01	30.01
2.	OPC (0.02% CNT)(Opt.)	17.69 (-10.4%)	43.75 (38.7%)	35.59 (15.48%)	30.89 (10%)	28.53 (-4.93%)
3.	OPC (0.05% CNT)	27.19 (-16.1%)	34.88 (37.2%)	31.85 (14.07%)	38.55 (3.0%)	41.69 (38.92%)
4.	OPC (0.1% CNT)	21.69 (28.9%)	24.83 (9.37%)	31.5 (2.08%)	30.16 (23.55%)	50.78 (69.21%)
5.	OPC (1% TiO_2) (Opt.)	25.24 (19.7%)	36.71 (12.6%)	35.92 (15.1%)	33.42 (11.4%)	41.16 (37.2%)
6.	OPC (2.5% TiO2)	20.34 (-3.5%)	34.97 (9.6%)	37.80 (21.2%)	40.95 (36.5%)	28.16 (-6.2%)

The XRD pattern (Fig. 5) of CNTs shows a peaking pattern thus suggesting that CNTs used were of crystalline nature rather being amorphous black powders. The XRD pattern (Fig. 6) of TiO_2 shows a multi peaking pattern thus suggesting that TiO_2 used were of crystalline nature rather being amorphous white powders.

4. Experimental programme

4.1 Tests on Cement Mortar Composites:

Mortar Cubes of 70.7mm x 70.7mm x 70.7mm size were casted with cement: sand = 1:3 ratio, as per the Indian Standards. Carbon Nanotubes added in proportions as per literature review i.e., 0.02%, 0.05% & 0.1% w.r.t. cement weight and Nano Titanium Di-Oxides in the ratio 1% & 2.5% by cement weight after proper dissolutions(as shown in Fig. 7) in a suitable Superplastcizer (Poly Carboxylate Ether) after ultrasonication for about 30 minutes in an external ultrasonicator bath(250W Piezo-U-Sonic Ultrasonic Cleaner), keeping the w/c ratio fixed at 0.4.

Fig .7. *Dispersed CNTs in PCE.*

Water added as shown in Fig.8, according to the standard formula P'=(P/4 +3)(1 part Cement+3parts Sand).Here P'=Quantity of water & P=Consistency of Cement used.i.e. amount of water used to make 300gms cement paste to support a penetration of 5-7mm in a standard Vicat mould with a Vicat needle.

Fig. 8. *Mortar mixing being done in Laboratory.*

Fig. 9*. Cement Mortar cubes being tested under Compression Testing Machine.*

Now we would be testing the Compressive Strength of both composite & ordinary Cement Mortar after 7 days, 28 days, 90 days, 180 days, 365 days ordinary cure in a compression cube Crushing/Testing Machine as shown in Fig. 9.

Table 4 shows the Test Results. The Test Results shows that:-

1. The mortar compressive strength determined as per IS: 4031 for CNTs shows a gain in strength of 38.7% at 28 days but falling to 15.48% at 90 days & 10% at 180 days as depicted in Table 4 & Fig. 10. For long term for CNTs it is observed that slight increased dosages from the previous optimized @ 28 days gave increased strength.

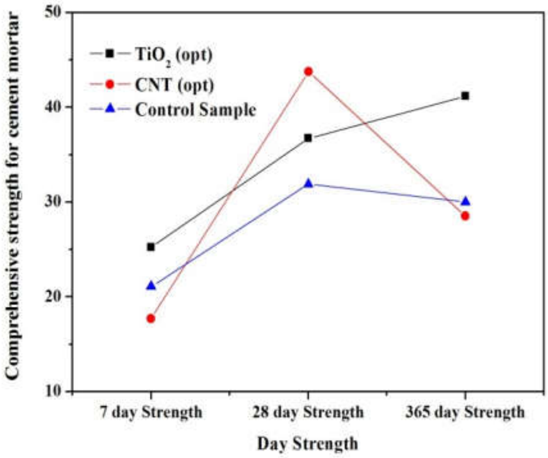

Fig.10. *Effect of Nanomaterials on Compressive Strength of Cement Mortar at 7,28 & 365 days.*

2. The 28day strength for optimized Nano Titanium dioxide never varied with increased addition of TiO_2 in the long term. That is 1% optimized TiO_2 as found by others [7] holds good for both short & long terms respectively.

5. Conclusions

The results showed that the optimizations for Carbon nanotubes, CNT=0.02% & Nano-Titanium Oxide,n-TiO_2=1.0% by weight of cement for gain in strength in OPC mortar up to 28 days. For long term strength the trend is not clear. Further research on micro structural studies is necessary for characterization of nano materials in concrete.

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