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Experimental Investigation to study the Effect of Multi Walled Carbon Nanotubes in Polymer/Cement- Based Matrix for Structural Applications

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***Abstract*.**
The present paper investigates the behaviour of polymer/cement beams reinforced with multi-walled carbon nanotubes (MWCNTs). The addition of MWCNTs was varied at 0.25, 0.5, 0.75 and 1 per cent by weight of polymer/cement matrix. Dispersion of MWCNTs was carried out using ultrasonic energy. Composite beams were tested under flexure in order to evaluate their mechanical property such as load–deflection criteria. These results were then compared with those from plain polymer/cement beams. The present work also investigates the optimum percentage of MWCNTs that gives the best results in terms of both enhanced properties and economy. Scanning electron microscopy was conducted to examine the bond between the MWCNTs and the polymer/cement matrix.

Keywords: *Multi-walled carbon nanotubes; Polymer composites; Cement composites; Three-point loading; Scanning electron microscopy*

1. Introduction

Carbon nanotubes (CNTs) have been considered as an ideal filler for polymer composites owing to their outstanding mechanical properties as well as high aspect ratio [1,2]. However, their performance in reinforcing a polymer matrix so far has been inadequate, which was attributed by many researchers to two main issues: (1) the difficulty of dispersing CNTs in polymer matrix (2) insufficient bonding at the nanotube/polymer interface. It has been recognized for some time that the mechanical properties of polymeric materials can be engineered by fabricating composites that are comprised of different volume fractions of one or more reinforcing phases. A number of techniques have been considered to improve the mechanical properties of structural adhesives. As time has progressed, practical realization of composites has begun to shift from micro-scale composites to nanocomposites, taking advantage of the unique combination of mechanical and physical properties of nanofillers – fillers with a characteristic dimension below 100 nm. There are a number of advantages associated with dispersing nanofillers in polymeric materials. While some credit can be attributed to the intrinsic properties of the fillers, most of these advantages stem from the extreme reduction in filler size combined with the large enhancement in the specific surface area and interfacial area they present to the matrix phase. In addition, whereas traditional composites use over 40 wt% of there in reinforcing phase, the dispersion of just a few weight percentages of nanofillers into polymeric matrices could lead to dramatic changes in their mechanical properties with added functionalities. In this work, we propose to reinforce the adhesive layer through the homogeneous dispersion of only a small fraction of carbon nanotubes (CNTs). CNTs are regarded as one of the most promising reinforcement materials for the next generation of high-performance structural and multifunctional composites [3]. These molecular scale tubes of graphitic carbon have outstanding mechanical, thermal and electrical properties. In fact, some CNTs are stronger than steel, lighter than aluminum and more conductive than copper [4]. Theoretical and experimental studies have shown that CNTs exhibit extremely high tensile modulus (1 TPa) and strength (150 GPa). In addition, CNTs exhibit high flexibility, low density (1.3–1.4 g/cm^3) and large aspect ratios (1000s). Due to this unique combination of physical and mechanical properties, CNTs have emerged as excellent candidates for use as tailoring agents in polymeric materials to yield the next generation nanocomposites. Recent work in this area shows that the scientific community is adopting a variety of different methods to develop these nano-reinforced composites with varying

levels of success. The number of factors that include the CNT synthesis and purification process, the geometrical and structural properties of the CNTs, their alignment in the matrix, the dispersion process, and the fabrication process.
Perhaps the most remarkable improvement in the tensile modulus and yield strength of a polymer through the dispersion of CNTs was observed by Liu et al. [5]. By dispersing only 2 wt% of multi-walled carbon nanotubes (MWCNTs) in a nylon-6 matrix Liu et al. observed an increase of approximately 214% in the tensile modulus and 162% in the yield strength. They attributed these impressive improvements in the stiffness and strength to a uniform and fine dispersion of the CNTs and good interfacial adhesion between the nanotubes and matrix which were assessed using SEM.
In the present work the mechanical performance of polymer beam reinforced with MWCNTs is compared with mechanical performance of cement beams reinforced with MWCNTs for load vs deflection based on the performance we can conclude that polymer reinforced beam yielded best results as compared to cement reinforced beams. This could be due to the mechanical joggling of the nanotubes at the fiber/polymer interface.

2. Experimental Programme

The properties of the MWCNTs used in the present study are given in Table 1; the MWCNTs were of industrial grade with a purity of greater than 95 percent. The specimen characteristics have been mentioned in Table 2 .Uniform dispersion of MWCNTs against their agglomeration due to Vander Waals bonding is the first step in the processing of nano composites. Dispersion is a critical issue while mixing CNTs in either water or organic solvents. Moreover, the method of sonication duration of sonication and method of casting the specimens were maintained uniformly throughout. Different amounts of MWCNTs were added to polymer/cement as shown in Table 3 and the whole mixture was kept in an ultrasonication for 90 min to achieve homogeneous dispersion.
At the first stage of this study, small-scale experimental testing was conducted to investigate the efficacy of using uniformly dispersed, randomly oriented CNTs as reinforcement for epoxy composites. Three-point bending tests on 20 mm x 20 mm x 80 mm beams were carried out to compare the load v/s deflection responses of plain epoxy beams and CNT reinforced epoxy/cement composite beams.

3. Preparation of specimens

The CNTs employed in this work were industrial grade MWCNTs with a purity of 95 wt% and a concentration of 0.25%, 0.50%, 0.75% and 1% by the total weight of the epoxy/cement matrix. The final product was placed in 20mm x 20mm x 80 mm wooden molds in layers, which were compacted by using a tamping rod. The specimens were then cured in a room for 24 hrs before being removed from the molds.

Specifications	**Dimensions**
Diameter	10–30 (nm)
Length	1–2 (mm)
Purity	0.95 (%)
Surface area	350 (m^2/g)
Bulk density	0.05–0.17 (g/cm^3)
Carbon fibers (as supplied by Fosroc-Chemicals, Bangalore)	
Density	1.8 (g/cm^3)
Tensile strength	3500 (N/mm^2)
Length of fiber	5 (mm)
Fiber thickness	0.3 (mm)

Table 1: Properties of the MWCNTs used in the present work, supplied by Intelligent Private Limited

Size	20(mm) x 20(mm) x 80(mm)
Amount of MWCNTs	0.25, 0.5, 0.75, and 1 per cent by Weight of epoxy
Epoxy resin	L-12

Table 2: Specimen characteristics utilized for experimental work

Sample no.	Specimen reference	Constituents	Percentage of MWCNTs by weight
1	PE	Plain epoxy	Nil
2	A1	Plain epoxy + MWCNTs	0.25
3	A2	Plain epoxy + MWCNTs	0.50
4	A3	Plain epoxy + MWCNTs	0.75
5	A4	Plain epoxy + MWCNTs	1.00
6	PC	Plain cement	Nil
7	B1	Plain cement + MWCNTs	0.25
8	B2	Plain cement + MWCNTs	0.50
9	B3	Plain cement + MWCNTs	0.75
10	B4	Plain cement + MWCNTs	1.00

Table 3: Details of the test specimens

4. Three point load test on beams

The mechanical performance of the hybrid nano-composite material reinforced with MWCNTs in polymer/cement based matrix was evaluated by fracture mechanic test. Beam specimen of size 20mm x 20mm x 80mm were tested by three–point loading test as shown in Fig.1. Three replications were made for each nano-composite tested. A hydraulic closed loop testing machine was used. For experimental accuracy, ASTM D-7264M-07 was followed to determine the average values of the flexural strength for polymer beams. ASTM C348 was followed to determine the average values of flexural strength (ASTM C 348 determines the flexural strength of hydraulic-cement mortars).The equipment used for the three-point load test is shown in Fig.2. The specimen size and type of test conducted is shown in Table 4.


Figure 1: Sample placements for three point load set-up
Figure 2: Equipment used for three- point load set-up

Sl. No.	Type of test conducted	Size of specimen
01	Flexural test (Beam) a) Three point load	80(mm) x 20(mm) x 20 (mm)

Table 4: Specimen size used for the structural scale tests

5. Results and Discussions

Evaluation of optimum percentage of MWCNTs required reinforcing in plain epoxy/cement composite beams based on three point loading test

We evaluate the optimum percentage of MWCNTs by wt % of epoxy/cement required to reinforce the plain epoxy/cement beams, which gives highest structural efficiency in terms of load carrying capacity. Hence the flexural behavior of multiwall carbon nano-tubes reinforced in epoxy/cement composite is investigated. Composite beams were tested under flexure (Three point loading) to evaluate their mechanical properties such as strength, deflection criteria etc. The results obtained were compared with the results of the tests using control beams. The designation of the test specimen used is shown in Table 5.

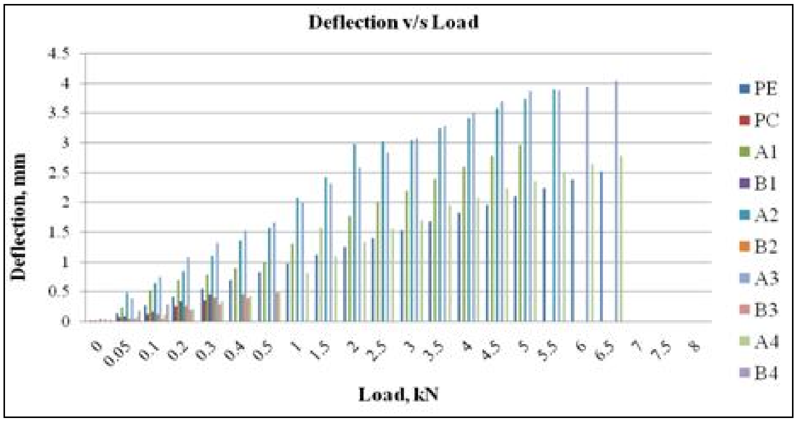

Figure 3: Load-Deflection curves for different proportions for MWCNTs reinforced epoxy/cement composite beams subjected to three point loading test

Sl. No.	Specimen Reference	Ultimate load in (kN)	Maximum deflection in (mm)
1	Plain epoxy (PE)	6.5	2.52
2	PE + 0.25 wt. % of MWCNTs* (A1)	5.0	2.97
3	PE + 0.50 wt. % of MWCNTs* (A2)	5.5	3.89
4	PE + 0.75 wt. % of MWCNTs* (A3)	6.5	4.04
5	PE + 1.0 wt. % of MWCNTs* (A4)	6.5	2.78

Table 5: Test results for MWCNTs reinforced in epoxy composite beam subjected to three point loading test: Ultimate load
**Note-wt. % w.r.t. to epoxy*

Sl. No.	Specimen Reference	Ultimate load in kN	Maximum deflection in (mm)
1	Plain cement (PC)	0.3	0.36
2	PC + 0.25 wt. % of MWCNTs* (B1)	0.3	0.464
3	PC + 0.50 wt. % of MWCNTs* (B2)	0.4	0.46
4	PC + 0.75 wt. % of MWCNTs* (B3)	0.5	0.49
5	PC + 1.0 wt. % of MWCNTs* (B4)	0.1	0.29

Table 6: Test results for MWCNTs reinforced in cement composite beams subjected to three point loading test:
**Note- wt. % w.r.t to cement*

The aim here is to determine the optimum percentage of MWCNT dosage and its effect on the ultimate load-carrying capacity of the epoxy/cement composite beam under three-point loading. Fig.3 shows the load–deflection curves for composites with different percentages of MWCNTs in the epoxy/cement matrix. The variation of ultimate load was studied keeping the PC and PE beams as reference. The ultimate load followed an increasing trend up to 0.75 wt. % of MWCNTs (A3, B3) showed a maximum ultimate load, Since the composite at greater MWCNTs contents has a tendency to undergo large deflections, the MWCNTs provide additional toughness to the composite. Deflections observed showed that it is maximum in (A3, B3) case and that the ultimate load of the material is also high.

For higher MWCNTs contents the composite has a tendency to undergo large deflections and the fibers provide additional toughness to the composite. By this the energy absorbing capacity of the composite generally increases because greater amount of load has been carried as the MWCNTs resists the crack propagation. Therefore **(**A3, B3) is considered to be optimum from both deflection and strength criteria. This suggests that the energy-absorbing capacity of the composite generally increases, because a greater amount of load is carried as the CNTs resist the crack propagation. Fig 3.0 shows variation of load with deflection for various control beams considered .From fig it follows that plain polymer shows higher resistance for deflection when compared to cement. This could be due to load transferring ability of the fibers was found to be improved due to the mechanical joggling of the nanotubes at the fiber/polymer interface. As the % of CNTs increased in both cement/polymer based matrix the strength further increased , this is observed till 0.75% by weight of CNTs this could be due to the high surface area of nano-particles attracts the polymer molecule which reduces the mobility of polymeric chains and hence causes increase of viscosity in the polymer matrix. For 1% CNTs by weight in polymer/cement based matrix the strength decreased drastically this could be due to increase in the nanotube waviness may be an additional mechanism limiting the modulus enhancement of nanotube-reinforced polymer/cement beams. It has been observed that even slight nanotubes waviness significantly reduces the effective reinforcement when compared to straight nanotubes.

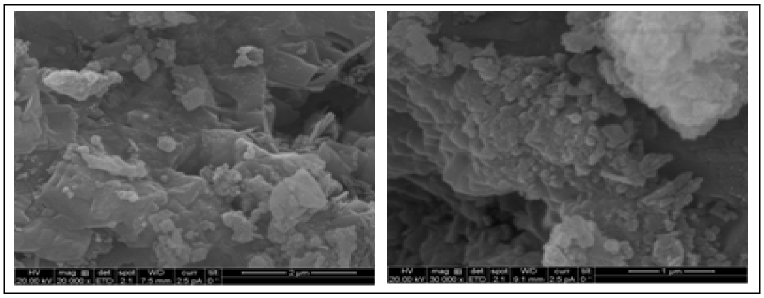

Figure 7: (a) SEM micrograph of the MWCNT/epoxy composite with 0.25wt% CNTs.
(b) SEM micrograph of the MWCNT/cement composite with 0.25wt% CNTs

Figure 7 shows a SEM micrograph of the CNT/epoxy composite/cement composite with 0.25 vol% CNTs, from which it follows that CNTs act as bridges across pores and cracks. They are tightly wrapped by C-S-H. This indicates that high bonding strength between the CNTs and epoxy matrix is achieved. This is consistent with other results published in the literature [6, 7]. Experimental observations revealed that the MWCNT-reinforced epoxy composite beams showed increased strength compared with plain epoxy/cement beams. The nano-level reinforcement significantly improved the flexural strength of the beams [7, 8]. The results showed an increase in the load carrying capacity of the composite beams compared with the reference beams.

6. Conclusion

From the above experiment we can conclude that polymer beams reinforced with MWCNTs show optimum results for mechanical properties as compared to cement beams this could be due to the mechanical joggling of nanotubes at the fiber/polymer interface, the high surface area of nanoparticles attracts the polymer molecule which reduces the mobility of polymeric chains and hence causes increase of viscosity in the polymer matrix.

7. References

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