



Research Article

Influence of Multi-walled Carbon nanotube on Physical Properties of Epoxy/Cement Nanocomposite

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Abstract

The research effort described in this paper is related to the glycidyl end-capped poly(bisphenol A-co-epichlorohydrin) and white Portland cement nanocomposites. The effect of adding carboxylated multi-walled carbon nanotube (MWCNT) on the properties of polymer/cement composites was considered. The physical parameters considered were morphology, absorptivity, compressive strength, and compressive modulus of the epoxy/cement-based nanocomposites. Two type of significant interaction operated in epoxy/MWCNT composites i.e. • •• interaction and hydrogen bonding. In all nanocomposites, the absorptivity was incessantly increased with time. One of the most striking features of the absorbent polymer-cement composite was viewed by scanning electron microscopic (SEM). The carbon nanotube was evenly distributed in the epoxy/cement matrix and there was the lack of defects such as air bubbles and cracks. The compressive strength and modulus were affected primarily by the nanotube loading and interaction between polymeric phase as well as MWCNT addition. Moreover, the cement addition in epoxy phase was important to increase the mechanical properties of the materials.

Keywords: Poly(bisphenol A-co-epichlorohydrin); cement; nanocomposite; multi-walled carbon nanotube; compressive strength; absorptivity

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1. Introduction

With very different architectures and special multiphysics properties, a major section of nanoscience and nanotechnology research initiatives focuses on the formation of new molecules and submicron systems. One of the most common examples of these nano-materials systems are comprised of carbon nanotube (CNT) which was discovered by Iijima in 1991 [1]. The CNT consists of network of carbon atoms like atomic planes of graphite. The sheet are rolled to form cylindrical tube and about ten thousand times thinner compared to human hair with radius of few nanometers. Where the walls are comprised of single or multiple carbon atoms (MWCNT) based on types of nanotube [2]. Thus the examples about the amalgamation of carbon nanotube into structural materials such as cement and polymers have been found in literature [3]. The CNT addition into composite matrices may lead to considerable changes of some aspects of the material properties. In addition to using carbon nanotube, addition of polymeric phase cement-based composites has been usually synthesized. The use of polymeric matrices in cement was mainly developed in United States, Europe and Japan for the improvement of mechanical and physical properties of cement matrix [4]. In terms of microstructure, the polymeric phase is capable for coating of unhydrated grains of cement which delays the hydration process partially, or completely. In some cases, presence of polymers in cement provides some internal products which prevent crystals formation during the initial hydration [5]. Moreover, polymer matrices in cement lead to reasonable reduction in porosity, with subsequent loss of free paths for crack propagation and enhancement of mechanical strength [6]. Traditionally, cement-based materials have been produced by casting. Thus the porosity of the hardened materials is determined by amount of water used. The excess of water is needed to improve the workability of cement paste and the affinity for cement grains to agglomerate, so resulting in high porosity of hardened cement paste and an extensive range of pore sizes [7]. Subsequently, these are not very strong materials, and they possess serious flaws and an open microstructure. Because most permeable polymers have a general absorption mechanism determined by ion concentration gradient, therefore they display established water absorbency under physical conditions (i.e. temperature and applied load). However various porosity and porous forms have been determined under chemical conditions such as high-valence metal ions and pH of the solvent [8]. The impact of epoxy resin on the mechanical behavior of white Portland cement has been investigated [9]. The polymer/cement composites were mixed with varying weight percentages of resin in absence of water. The results revealed that the presence of the polymeric phase led to an increase in strength and a reduction of the bulk density, compared to pure cement. There was the formation of hydrated cement grains due to the presence of epoxy resin [10]. The effect of adding thermoset and water content into cementitious composites was also investigated [11]. The polymer matrix addition provided not only a decrease in apparent density and porosity, but also an enhancement of compressive strength of the composites. It was also demonstrated that the presence of water contributed to decrease in mechanical strength of cement-based composites. Carbon nanotubes do not only offer an improvement of strength and nanocomposites toughness, but they can also be used as piezoresistive sensors in smart materials. According to the research reports, when a stress field was applied, the electrical resistance of cementitious composites synthesized with CNT was changed thus demonstrating a considerable potential as stress/strain sensors for civil engineering structures [12]. The use of chemical additives provided a uniform dispersion of CNT in cement paste, which can however influence the final properties of the composite [13, 14]. By the addition of epoxy resin in cement paste, one can in principle achieve a material with outstanding mechanical properties from a structural engineering perspective (low density, high toughness and strength). However, for complex heterogeneous materials such as cement-based composites with polymer matrices, the impact of nanophase addition to constituents could be difficult to ascertain with other

environmental factors (water fraction, polymer/cement ratio, manufacturing process). This work describes glycidyl end-capped epoxy i.e. poly(bisphenol A-co-epichlorohydrin) and cement-based composites. The effect of doping polymer/cement composite materials with carbon nanotube has been studied. Prior to reinforcement, MWCNT was acid functionalized. The investigated properties were the morphology, absorptivity, compressive strength and modulus. The interaction effects between the MWCNT and polymer/cement composite and influence on physical properties of the nanocomposites have been evaluated.

2. Experimental

2.1. Materials

Poly(bisphenol A-co-epichlorohydrin), glycidyl end-capped (average $M_n \sim 355$), and CNT, multi-walled (>98% carbon basis, OD×L 6–13 nm ×2.5–20 mm) were purchased from Aldrich. White Portland cement was obtained from local supplier.

2.2. Characterization techniques

IR spectra were taken at room temperature with a resolution of 4 cm^{-1} using Excalibur Series FTIR Spectrometer, Model No. FTSW 300 MX manufactured by BIO-RAD. The compression strength and modulus were measured with a universal electronic tensile machine (Shimadzu, Japan) at a compressive rate of 2 mm/min according to ASTM D 1621-94. The scanning electron microscopic (SEM) images were obtained by Scanning Electron Microscope S-4700 (Japan Hitachi Co. Ltd.).

2.3. MWCNT carboxylation

Raw MWCNT was annealed at 400 °C for 0.5 h to remove the amorphous carbon content. The purified MWCNT were refluxed and sonicated at 70 °C in a mixture of 8 M sulphuric acid:5 M nitric acid (3:1). Then 500 mL of deionized water was added and mixture was filtered and washed several times with deionized water to obtain pH ~ 6 [15, 16].

2.4. Epoxy/cement/MWCNT composite preparation

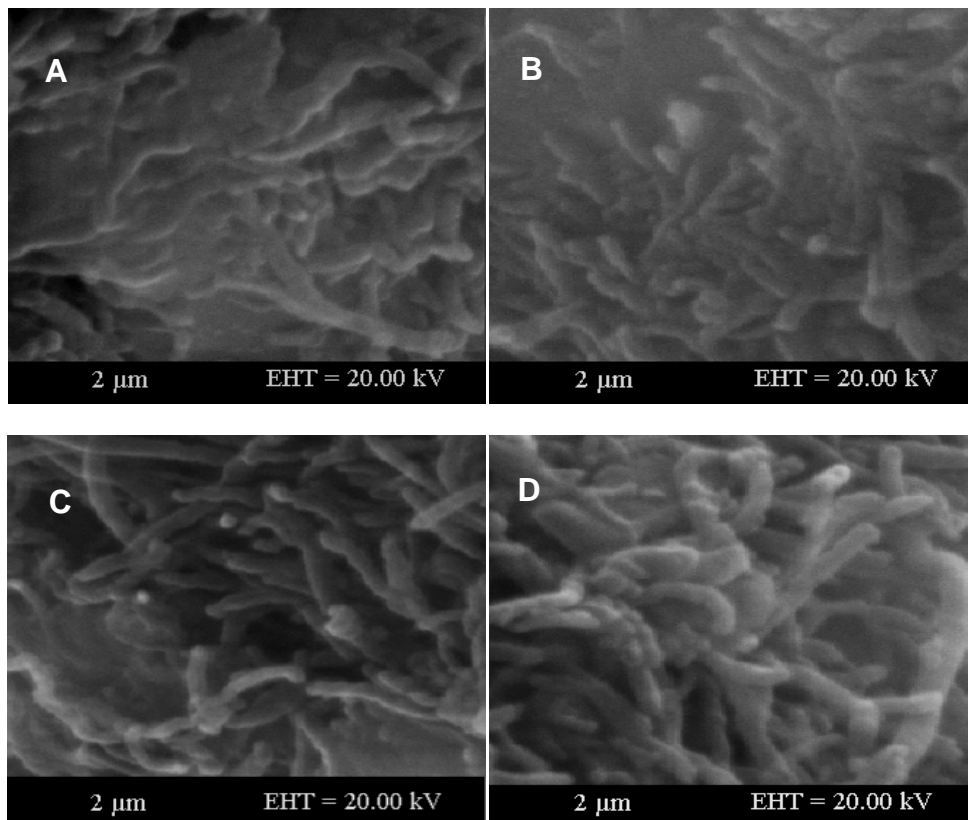
Hobart mixer was used to mix the desired amount of raw materials (epoxy Portland cement, resin, water and MWCNT). The mixture was processed for 7 min. Plastic moulds were used to manufacture the cylindrical samples with the diameter of 20 mm. The setting time for the air sealed samples was 7 days at room temperature [17]. Sample code and composition of Epoxy/cement and Epoxy/cement/MWCNT composites are given in Table 1.

2.5. Epoxy/cement composite preparation

An epoxy/cement composite was also prepared using the similar procedure mentioned in Section 2.4. The ratio of the epoxy/cement was kept same as the other samples prepared. The difference was that the composite was not reinforced with the modified carbon nanotube.

Table 1 Sample code and composition of Epoxy/cement and Epoxy/cement/MWCNT composites.

Sample	Epoxy (wt.%)	Cement (wt.%)	MWCNT (wt.%)	Water/cement ratio
Epoxy/cement	90	10	0	0.5
Epoxy/cement/MWCNT 10	90	10	10	0.5
Epoxy/cement/MWCNT 20	90	10	20	0.5
Epoxy/cement/MWCNT 30	90	10	30	0.5
Epoxy/cement/MWCNT 40	90	10	40	0.5
Epoxy/cement/MWCNT 50	90	10	50	0.5

**Fig. 1** FESEM images of (A) Epoxy/cement/MWCNT 10 (2 μm); (B) Epoxy/cement/MWCNT 20 (2 μm); (C) Epoxy/cement/MWCNT 30 (2 μm); and (D) Epoxy/cement/MWCNT 50 (2μm).

3. Results and Discussion

3.1. Microscopic studies

Fig. 1 shows the images of Epoxy/cement/MWCNT 10, Epoxy/cement/MWCNT 20, Epoxy/cement/MWCNT 30 and Epoxy/cement/MWCNT 50 composites. In Fig. 1A & B, it is possible to observe a clustering of carbon nanotube spread and embedded in the samples. The carbon nanotube tends to cluster due to van der Waals forces, leading to changes in the distribution of the matrix. However, at optimum concentration there was proper dispersion of nanotube in polymer-cement matrix in order to obtain superior properties. Fig. 2 shows the interfacial interaction between the carbon nanotube and epoxy phase, exhibiting a good interface condition without any micropores. Both the π - π interaction and hydrogen bonding played important role in developing well dispersed nanotube composite with improved mechanical properties. The hydrogen bonding was present between the acid carbonyl of functional nanotube and hydroxyl group of poly(bisphenol A-co-epichlorohydrin). However, relatively weak interaction (benzene ring stacking) existed between nanotube and epoxy. Fig. 1C & D show Epoxy/cement/MWCNT composites with higher nanotube content. At higher loading, more nanotubes were observed in the matrix. The carbon nanotube was coated with the matrix comprised of polymer/cement. However, the nanotube structure was not destroyed at the fractured surface.

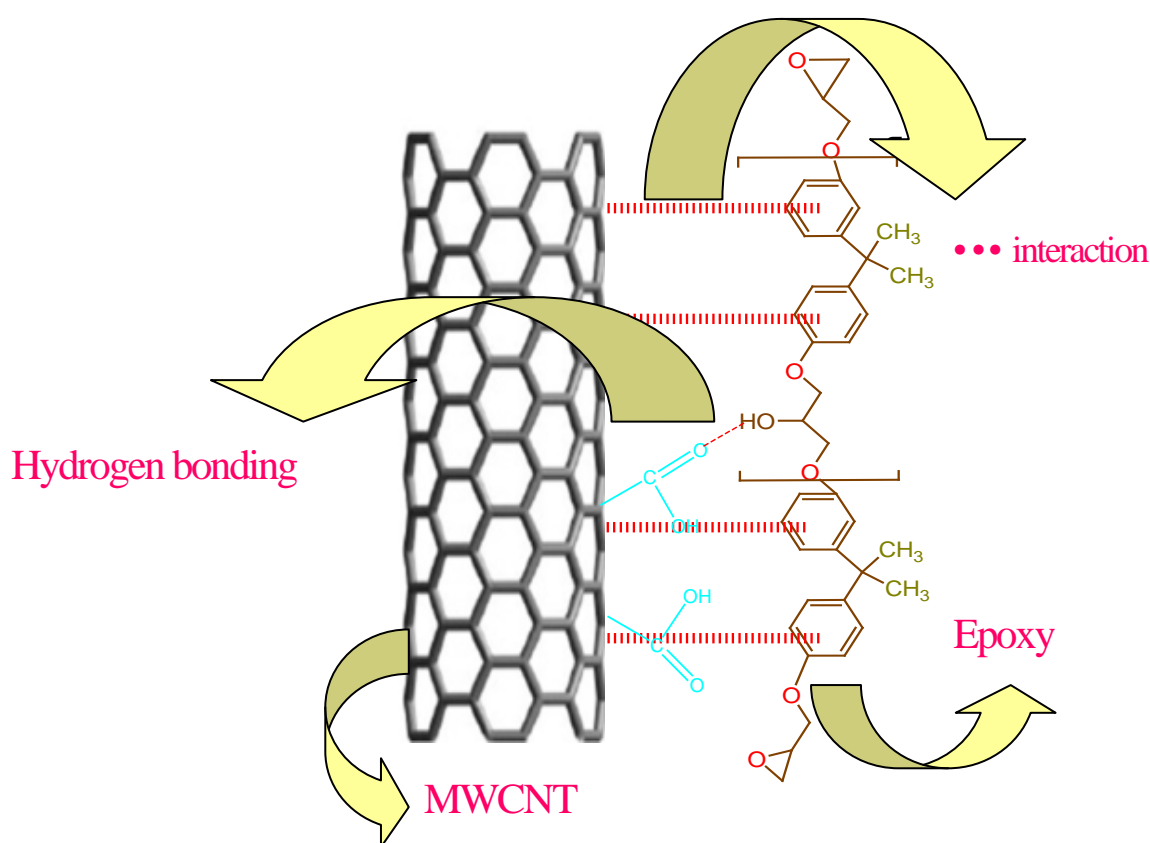


Fig. 2 Interaction between epoxy and carbon nanotube.

3.2. Absorptivity of Epoxy/cement/MWCNT composites

We also scrutinized the absorption power of three composites i.e. Epoxy/cement/MWCNT 10, Epoxy/cement/MWCNT 30 and Epoxy/cement/MWCNT 50 using 1% NaCl solution with time. Fig. 3 shows the absorbency of absorbent materials. The absorbency of Epoxy/cement/MWCNT 10 composite was higher in NaCl solution. Epoxy/cement/MWCNT 30 showed a reduction of absorbency relative to Epoxy/cement/MWCNT 10. While increasing the nanotube content up to 50 % in Epoxy/cement/MWCNT 50 showed a large reduction of absorbency. Because in 10 wt. % epoxy/cement composite, the nanotubes were aggregated, the ionic electrolyte did not incorporate well into the network of polymer main chains. Whereas, in Epoxy/cement/MWCNT 50 composite, NaCl solution incorporated well in the polymer/nanotube network occupied by cement. However, in all the composites the absorptivity was continuously increased with time [18].

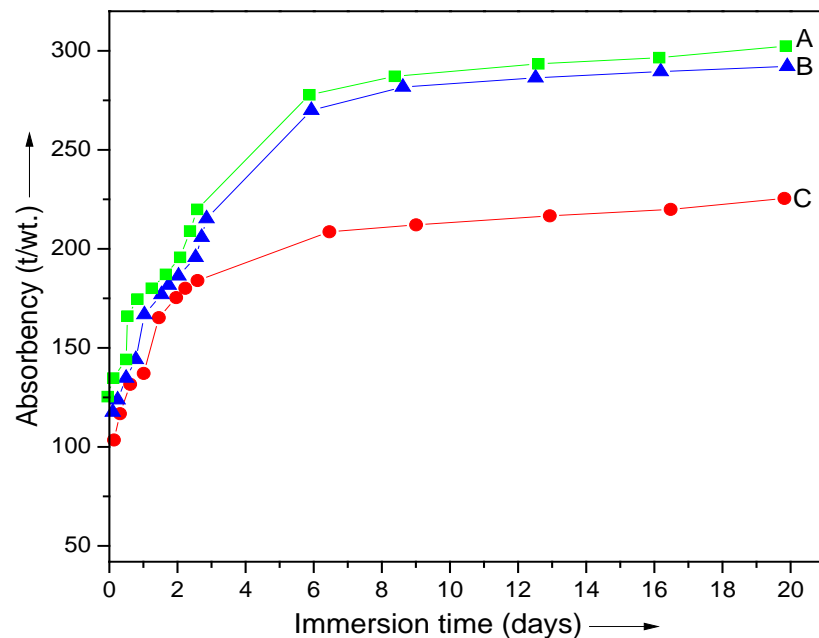


Fig. 3 Absorbency of composites (A) Epoxy/cement/MWCNT 10; (B) Epoxy/cement/MWCNT 30; and (C) Epoxy/cement/MWCNT 50 with time.

3.3. Compressive strength and modulus

Fig. 4 shows the compression strength of Epoxy/cement/MWCNT composites, while compression modulus is given in Fig. 5. Epoxy/cement possesses compression strength of 25.5 MPa and compression modulus of 4.43GPa. Table 2 depicts that the compressive strength and modulus of the composites increased progressively with the increase in nanotube content from 10 to 50 wt. % [19]. Results demonstrated that Epoxy/cement/MWCNT 10 had compressive strength and modulus of 26.3 MPa and 6.88 GPa respectively. In Epoxy/cement/MWCNT 20 composites the values increased to 41.9 MPa and 12.1 GPa respectively. The compressive strength and modulus of the Epoxy/cement/MWCNT 30 composite further increased to 44.8 MPa and 14.8 GPa and to 56.7 MPa and 19.2

GPa respectively in Epoxy/cement/MWCNT 40. Highest values for the compressive strength and modulus were obtained for the Epoxy/cement/MWCNT 50 material (71.2 MPa and 22.3 GPa respectively). Since the compatibility of poly(Bisphenol A-co-epichlorohydrin) and carbon nanotube increased with loading due to the presence of cement.

Table 2 Mechanical properties of Epoxy/cement and Epoxy/cement/MWCNT composites.

Sample	Compression strength (MPa)	Compression modulus (GPa)
Epoxy/cement	25.5	4.43
Epoxy/cement/MWCNT 10	26.3	6.88
Epoxy/cement/MWCNT 20	41.9	12.1
Epoxy/cement/MWCNT 30	44.8	14.8
Epoxy/cement/MWCNT 40	56.7	19.2
Epoxy/cement/MWCNT 50	71.2	22.3

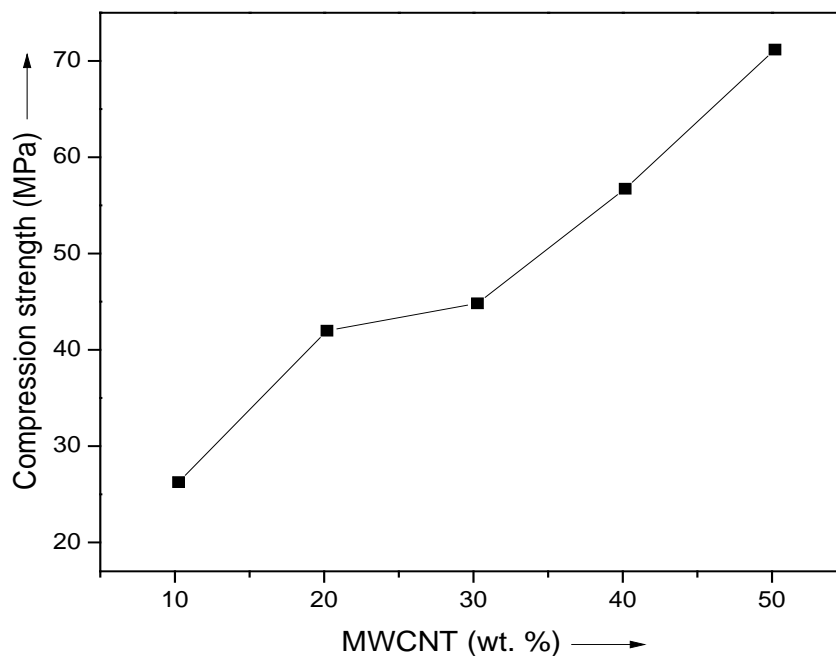


Fig 4 Compression strength of Epoxy/cement/MWCNT composites.

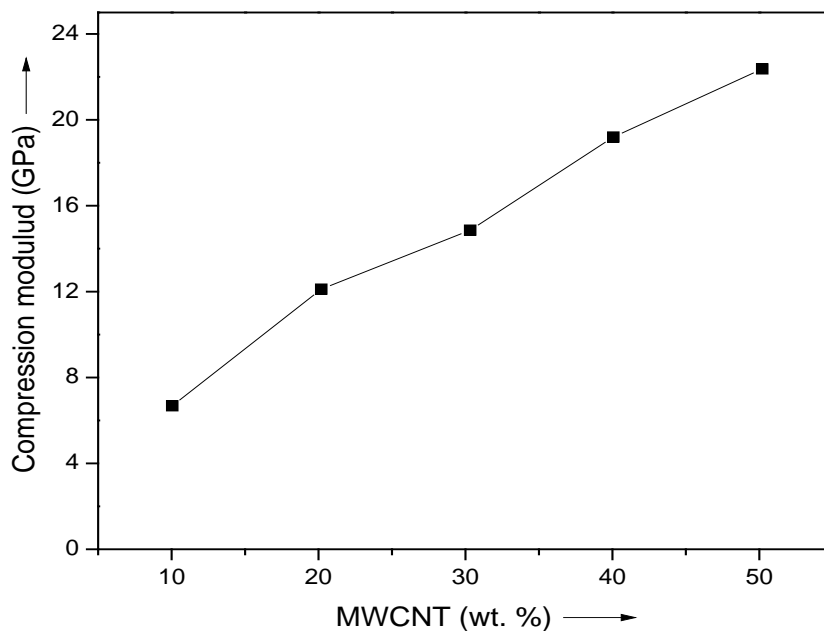


Fig. 5 Compression modulus of Epoxy/cement/MWCNT composites.

4. Conclusions

This research attempt is concerned with the influence of carbon nanotube inclusions on the mechanical and other physical properties of glycidyl end-capped poly(bisphenol A-co-epichlorohydrin) and white Portland cement composites. The epoxy resin was the matrix phase in these composites, whereas the ceramic phase was Portland cement. Both the cement and MWCNT acted as filler, however only the nanotube content was varied to study the effect on composite properties. The addition of carbon nanotube contributed to increase the compression strength and modulus. The addition of MWCNT in polymeric phase provided lower bulk density and absorptivity by filling the pores formed by the cementitious phase. The microstructural analysis revealed good interface interaction between the MWCNT cluster and thermoset phase. The composite manufactured with 50 wt. % of MWCNT phase (10 wt.% of cementitious phase) exhibited superior compressive strength. The inclusion of carbon nanotube into cementitious materials is potentially important for civil structures monitoring.

References

1. Iijima S. Helical microtubules of graphitic carbon. *Nature*. 1991, 354: 56-58
2. Kausar A and Ashraf R. Electrospun, non-woven, nanofibrous membranes prepared from nanodiamond and multi-walled carbon nanotube filled poly(azo-pyridine) and epoxy composites reinforced with these membranes. *J Plast Film Sheet*. 2014, 30: 369-387
3. Kausar A. Formation of aramid-silica-grafted-multi-walled carbon nanotube-based nanofiber via sol-gel route: Thermal and mechanical profile of hybrids with poly(methyl methacrylate). *e-polymers*. 2014, 14: 177-185

4. Ashraf R, Kausar A and Siddiq M. Preparation and properties of new layered carbon nanotube/polyazopyridine/nanodiamond composites. *J Plast Film Sheet*. 2014, 30: 412-434
5. Van Gemert D, Czarniecki L, Maultzsch M, Schorn H, Beeldens A and Łukowski P et al. Cement concrete and concrete-polymer composites: two merging worlds. *Cem Concr Res*. 2005, 27: 926-933
6. Silva D A and Monteiro P J M. The influence of polymers on the hydration of portland cement phases analyzed by soft x-ray transmission microscopy. *Cem Concr Res*. 2006, 36: 1501-1507
7. Jenni A, Zurbriggen R, Holzer L and Herwegh M. Changes in microstructures and physical properties of polymer-modified mortars during wet storage. *Cem Concr Res*. 2006, 36: 79-90.
8. Taylor R, Richardson I G and Brydson R M D. Composition and microstructure of 20-year-old ordinary Portland cement-ground granulated blast-furnace slag blends containing 0 to 100% slag. *Cem Concr Res*. 2010, 40: 971-983.
9. Rengguang L I U and Peiyu YA N. Hydration characteristics of slag in cement-slag complex binder. *J Chin Ceram Soc*. 2012, 40: 1112-1118
10. de Paiva Cota F, Panzera T H, Schiavon M A, Christoforo A L, Borges P H R, Bowen C and Scarpa F. Full factorial design analysis of carbon nanotube polymer-cement composites. *Mat Res*. 2012, 15: 573-580
11. Panzera T H, Sabariz A L R, Strecker K, Borges P H R, Vasconcelos D C L and Vasconcelos W L. Propriedades mecânicas de materiais compósitos à base de cimento portland e resina epóxi. *Cerâmica*. 2010, 56: 77-82
12. Madke R R, Chakraborty S and Chowdhury R. Multiscale approach for the nonlinear behavior of cementitious composite. *Computat Mater Sci*. 2014, 93: 29-35
13. Yu X and Kwon E. A carbon nanotube /cement composite with piezoresistive properties. *Smart Mater Struct*. 2009, 18: 1-5
14. Parveena S, Rana S, Fangueiro R and Paiva M C. Microstructure and mechanical properties of carbon nanotube reinforced cementitious composites developed using a novel dispersion technique. *Cem Concr Res*. 2015, 73: 215-227
15. Hussain S T, Abbas F, Kausar A, Khan M R. New polyaniline/polypyrrole/polythiophene and functionalized multi-walled carbon nano-tubes based nanocomposites: Layer by layer *in-situ* polymerization. *High Perform Polym*. 2012, 25: 70-78
16. Kausar A. Proton exchange fuel cell membranes of poly(benzimidazole-amide)/sulfonated polystyrene/titania nanoparticles-grafted-multi-walled carbon nanotubes. *J Plast Film Sheet*. 2015, 31: 27-44
17. Madke R R, Chakraborty S and Chowdhury R. Multiscale approach for the nonlinear behavior of cementitious composite. *Computat Mater Sci*. 2014, 93: 29-35
18. Xiao L, Jin Y and Gu L. Preparation and properties of a new composite of epoxy emulsion (EEM) modified cement. *J Wuhan Univ Technol-Mater Sci Ed*. 2009, 24: 843-845
19. Rha C Y, Kim C E, Lee C S, Kim K I, Lee S K. Preparation and characterization of absorbent polymer-cement composites. *Cem Concr Res*. 1999, 29: 231-236