Effects of chemical and mechanical funtionalization of carbon nanotubes on the behavior of a CNT/Phenolic nanocomposite

M.J. Hadianfard, M. Alizadeh and M. Moradzaman

Deptment of Materials Science and Engineering, School of Engineering, Shiraz University, Shiraz, Iran
**Corresponding Author: hadianfa@shirazu.ac.ir*

Abstract

Carbon nanotubes and their treatments play an important role in fabrication and properties of the nanocomposites. In this study effects of acid functionalization and mechanical treatment of CNTs by ball milling on the chemical structure, weight loss and mechanical strength of a 1 weight % CNTs reinforced phenolic polymer has been investigated by using FTIR, XRD, TGA, electron microscopy and tensile tests. Results show that both chemical and mechanical treatment has considerable effects on properties of the composite. Maximum strength was obtained by chemical treatment followed by 2 hours of mechanical treatment, further milling treatment caused to decrease the strength of the composite.

Keywords: Carbon nanotubes, Nanocomposites, Functionalization, Ball milling, Mechanical properties

Introduction

Carbon nanotubes are widely used for fabrication of nanocomposites [1-4]. Multiwall carbon nanotubes present greater mechanical properties compared to the other carbon materials, in addition, they offer excellent specific strength and stiffness together with low weight and high specific area [2, 5]. Major difficulties in the use of carbon nanotubes in different areas are their hydrophobicity, surface chemistry, a tendency to clustering and building aggregate [6-8]. Functionalization methods are providing techniques for overcoming these barriers and increasing compatibility of carbon nanotubes with other materials. [9,10]. Properties of a composite reinforced with certain amount of CNTs is dependent on several factors such as degree of dispersion of the CNTs in the matrix [8,11], sort and density of the functional groups on the surface of the CNTs, which are controlling type and strength of the CNT/matrix interfaces [12,13] and aspect ratio of the CNTs [14]. Chemical and mechanical functionalization are methods which can manage the degree of dispersion and CNT/matrix interface properties [15] while chemical functionalization methods are studied widely, less attention has been paid to the effects of mechanical functionalization on the properties of a composite reinforced with CNTs. Therefore the main aim of this study is to investigate effects of mechanical treatment with and without chemical functionalization on the mechanical behavior of a composite reinforced with CNTs.

Experimental Procedures

For reinforcement phase multiwall carbon nanotubes (MWCNT) with an average diameter of 15 nm, the diameter range of 9-21 nm and an average length of 20 µm with 95% purity were purchased.

A thermoset novolac phenolic resin with a particle size of 60 µm with the hardener of hexamethylenetetramine ($C_6H_{12}N_4$) was used as a matrix of the composite.

For chemical functionalization, the raw CNTs were poured into ethanol alcohol and sonicated for 4 hours. Then 5 gr of the CNTs were added to 250 ml of 0.65 molar nitric acid and heated to 80 Cº stirred for 1.5 hours, then the mixture cooled to the room temperature. Next residual nitric acid was removed from the mixture and the CNTs were washed with distilled water for several times until their pH reached 7. After filtration, The CNTs were dried at 70 Cº in a vacuum oven for 24 hours and FCNTs were formed.

Mechanical functionalization was performed by mixing the raw CNTs or FCNTs with resin powders and milled with the ball mill for different duration of time ranging from 0 to 6 hours. For this propose a planetary ball mill with powder to ball ratio of 1 to 10, the speed of 50 rpm and ball diameter of 5 mm was used.

Nanocomposite specimens were fabricated by adding 1 wt % raw CNTs or FCNTs to the phenolic resin powders and milled for a designated time to obtain a uniform mixture of the CNTs into the resin. After separation balls, the mixture was poured into a metallic die and cured under pressure of 80 bar and temperature of 180 Cº for two hours.

For evaluation effects of chemical and mechanical functionalization, 5 specimens were fabricated from each FCNTs/phenolic and raw CNTs/phenolic with 0, 1, 2, 4 and 6 hours of ball milling.

Thermogravimetric analysis of the specimens was completed in the atmospheric environment by an STA-1500, Rheometric Scientific, USA. For chemical analysis, a Fourier transform infrared spectroscopy (FTIR) was performed by using Nicolet Magna-IR760 FTIR spectrometer. A strength of the specimens was measured by flexural tests according to ASTM D-790 test method on specimens with 2.8×11.2 mm cross-section. Structure of the specimens was evaluated by X-ray diffraction method and electron microscopy.

Results

Figure 1 displays a TEM micrograph obtained from the raw CNTs this figure shows that the CNTs have a large aspect ratio and made bundles with each other. FTIR spectrum of the raw and chemical functionalized multiwall carbon nanotubes are shown in Figure 2. The broad absorption peak at 3433 cm-1 is due to O-H stretching vibration bond [16], this peak can be generated by absorption hydroxyl (O=C-H and C-OH) groups due to reaction of acid with surface of the CNTs during chemical treatment in functionalization process, it may also be produced due to water absorption by the raw CNTs from environment. Higher absorption of FCNTs at 3433 cm-1 wavenumber compared to the raw CNTs is observed in Fig. 2 and exhibits formation of a hydroxyl group on the surface of the FCNTs.

The peaks at 1635 cm-1 are formed by vibrational stretching of C=C bond and peaks at 1367 cm-1 is due to C-C stretch [17, 18]. Both peaks showing higher absorption in the raw CNTs compared to the FCNTs these differences can be resulted from oxidation of carbon by acid during chemical functionalization process. It seems that introducing functionalities leads to partly distraction of the graphitic surface layer.

Another difference between FTIR spectrum of the raw CNTs and FCNTs appears at 2360 cm-1 which is showing higher absorption in the case of FCNTs, This peak formed by vibrational absorption of C-O-C bonds and confirming the success of the functionalization process.

Small peaks around 1736 cm-1 which are only observed for FCNTs are due to carboxyl (COOH) groups. These peaks confirm attachment of carboxyl group to the surface of the CNTs. Peaks between 1150 to 1050 cm-1which are observing stronger in the spectra of FCNTs are representing a stretch of C-O bond in the hydroxyl group

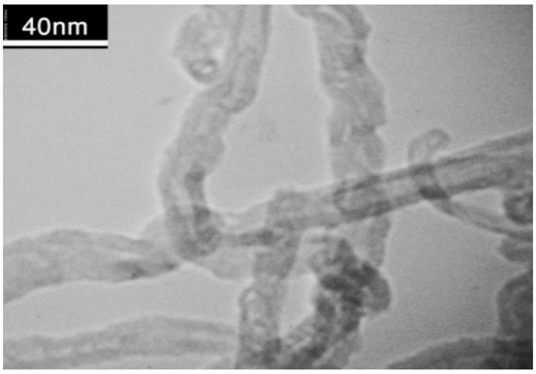

Figure 1. TEM micrograph obtained from raw CNTs.

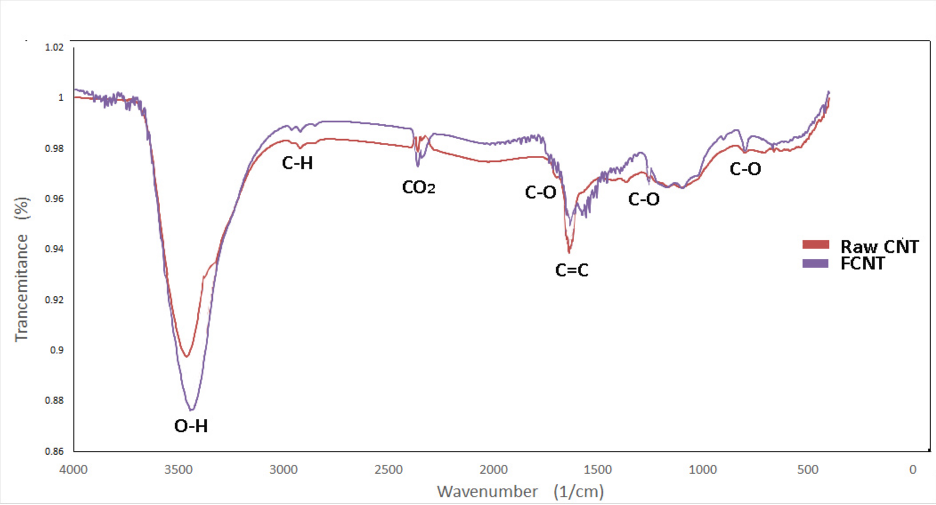

Figure 2. FTIR spectrum from the raw and chemical functionalized CNTs.

FTIR spectra of the unreinforced (pure) phenolic resin presented in Figure3. Various oxygen arrangements in the structure of this resin including the vibration mode of epoxide (C-O-C) at 1235 cm-1, ester (C=O) at1600 cm-1, carboxyl (COOH) at 1729 cm-1, and hydroxyl vibrations at 3385 and 1051 cm-1 [19, 20] are observed. Oxygen-containing groups provide suitable bases for chemical bonding between CNTs and the polymer. FCNTs which are holding higher oxygen groups offer better situation for chemical bonding between the CNTs and polymer matrix.

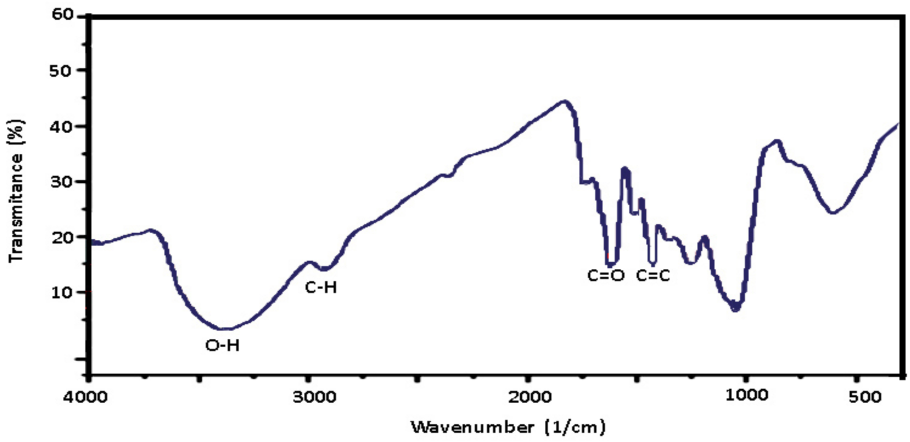

Figure 3. FTIR spectra of unreinforced phenolic resin which is used as a matrix of the nanocomposite.

Figure 4 shows the result of FTIR analysis of the composites containing carbon nanotubes; chemical functionalized or raw, and phenolic resin both after 2 hours milling. Although the addition of CNTs to the polymer matrix and also mechanical milling have caused some changes in the spectrum of the resin, FCNTs and raw CNTs are demonstrating a similar spectrum. Few small differences are observed between spectra of FCNTs/phenolic and raw CNTs/phenolic including higher absorption of FCNTs/phenolic at 3400 and 1093 cm-1 wavenumbers (corresponding to O-H bounds) and also at 2923 cm-1(corresponding to C-H bonds) and higher absorption of raw CNTs/phenolic at 1639 cm-1 (corresponding to C=C bonds). These results show that more oxidation has happened in the case of FCNT/phenolic composite, therefore more oxygen-containing groups are present in this nano-composite.

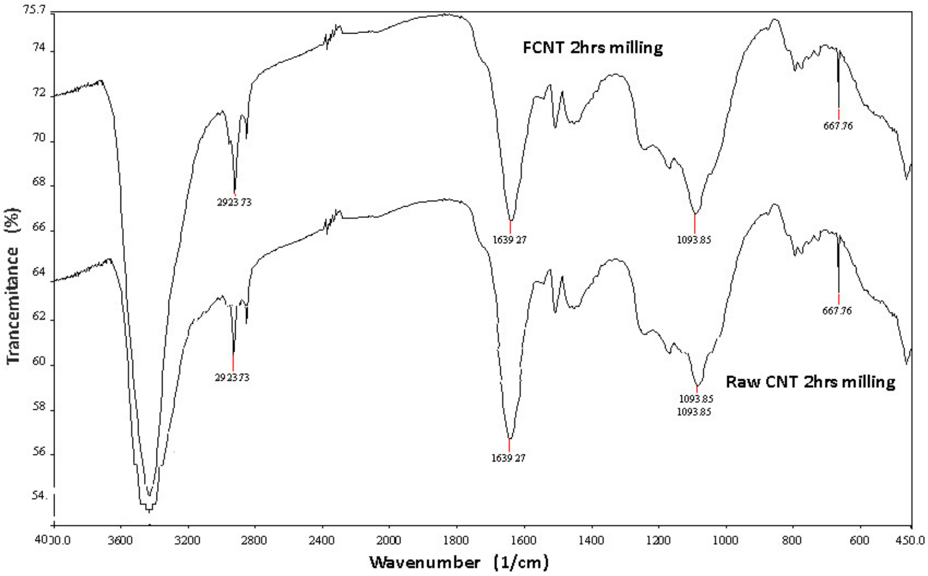

Figure 4. FTIR spectra of FCNTs/phenolic and raw CNT/phenolic composites after 2 hours milling.

FTIR spectrum of FCNTs/phenolic after 2 and 6 hours milling is presented in the Figure5. Both composite show almost the same spectra, it appears that continuing ball milling of the composite more than 2 hours has no noticeable effect on the chemical structure of the composite. The same result has been obtained for raw CNTs/phenolic composite.

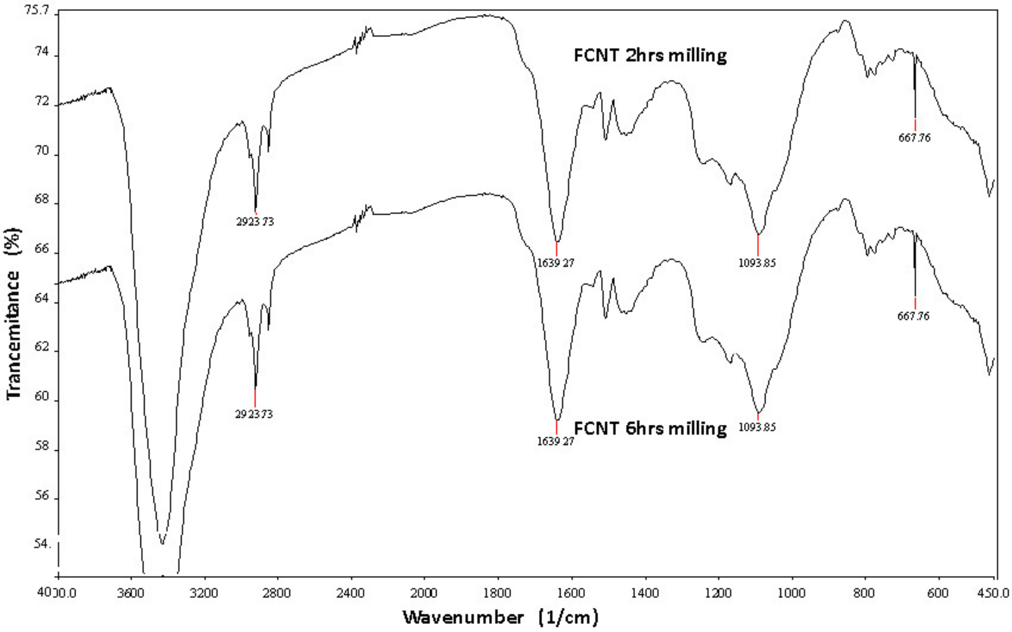

Figure 5. FTIR spectra of FCNTs/phenolic composite after 2 and 6 hours milling.

Figure 6 shows XRD pattern of carbon nanotubes under three different conditions; raw CNTs, FCNTs (0 hours milling) and FCNTs after 2 hours milling together with phenolic powder, all tested specimens exhibited a similar pattern including (002), (100), (004) and (110) planes of the CNTs. Increased intensity of (002) peak in the FCNT pattern due to the purification of the CNTs during chemical functionalization and peak broadening in the case of FCNT 2 hrs milling due to mechanical functionalization are major differences between XRD pattern of the specimens.

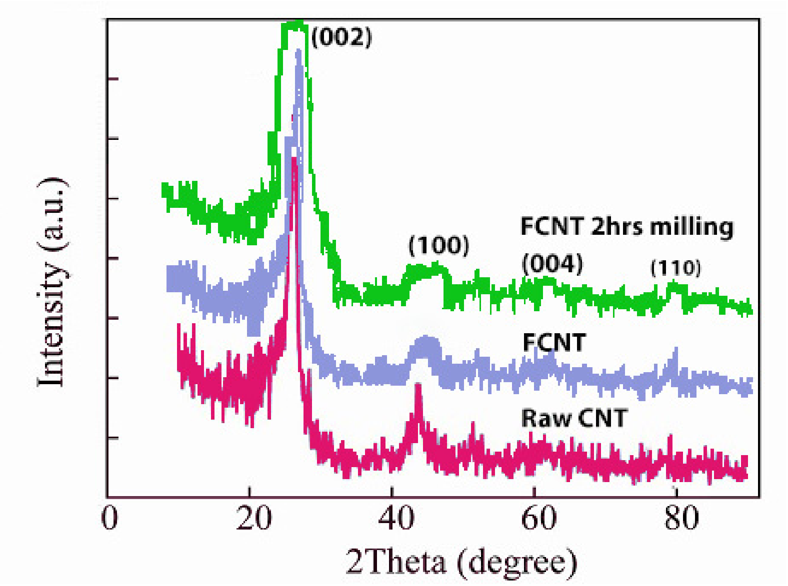

Figure 6. XRD pattern of carbon nanotubes under three conditions; raw CNTs, FCNTs 0 hours milling, and FCNTs after 2 hours milling.

TG curve of the composites and the unreinforced polymer is displayed in Figure 7. This graph shows three distinct areas in the behavior of the tested specimens, in the primary area which is between room temperature to 450 Cº specimens lose less than 10 % of their weight and all of them exhibit same behavior in losing weight , this action is assigned to losing water, in the second area which is between 450 Cº and 680 Cº the specimens lose weight with a similar trend, in this area FCNTs/phenolic with 2 hours milling shows more residual weight and smaller slop in the weight loss, at the same condition FCNT/phenolic with 6 hours milling and unreinforced polymer shows less residual weight and greater slope in the weight loss this action is related to decomposition of the polymer.

In the tertiary area from 680 Cº up to 800 Cº while the composite specimens continuing their behavior from the previous area, unreinforced polymer shows higher residual weight and lower slope of weight loss this behavior is due to decomposition of the polymer and oxidation of the CNTs. Since the unreinforced polymer is free of the CNTs it is losing weight only by polymer decomposition, therefore, it loses less weight compared to composite materials. It may be concluded that among the composites FCNTs/phenolic with 2 hours milling shows more stable behavior and FCNT/phenolic with 6 hours milling performs less stability, the stability of FCNT/phenolic with 1 hours milling is between those two specimens.

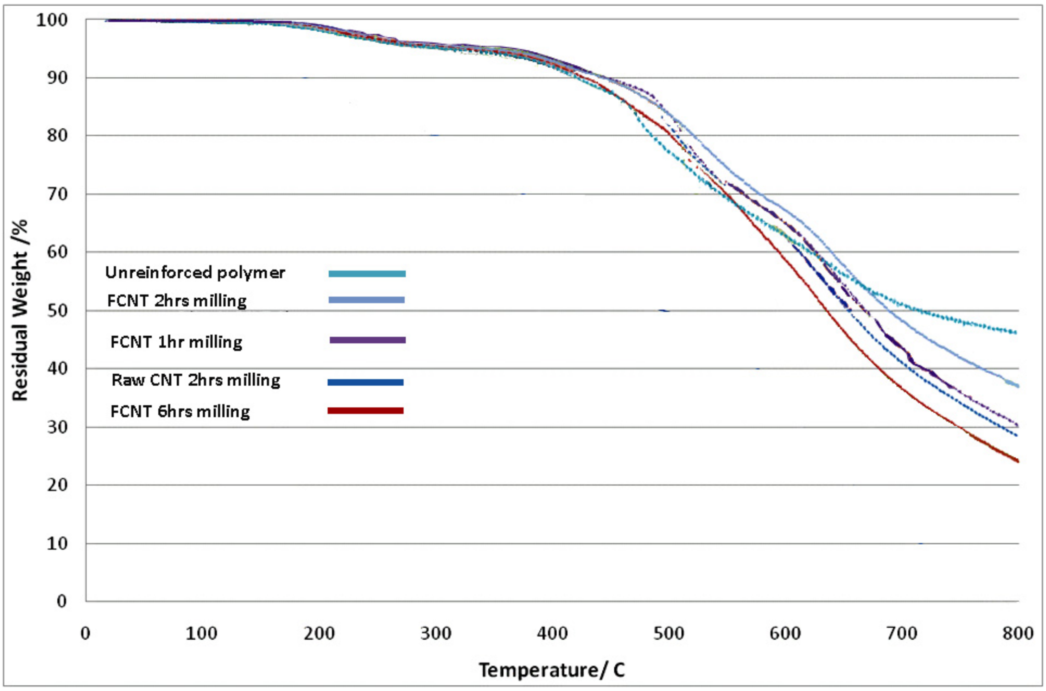

Figure 7. TG curve of the composites and unreinforced specimens.

Figure 8 shows the flexural strength of the FCNTs/phenolic and raw CNTs/phenolic composites. These results show that strength of the specimens which are made from chemical functionalized CNTs are higher than the strength of the composites made from raw CNTs regardless of the milling time. This behavior may be attributed to improvement in CNT/matrix interface of the composites by chemical functionalization. On the other hand, both groups of the composites show an increase in strength with increasing milling time up to 2 hours, a small decrease in strength is observed with further milling.

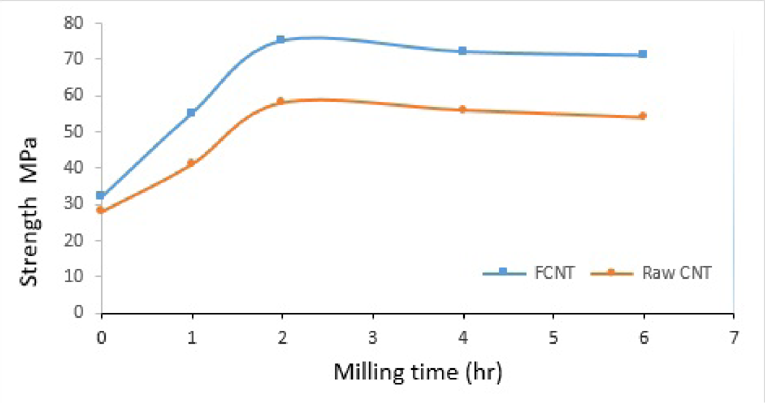

Figure 8. The flexural strength of the FCNTs/phenolic and raw CNTs/phenolic composites as a function of milling time.

Dissection

For the raw CNTs with a low concentration of oxygen-containing groups is difficult to react properly with the polymer matrix and produce strong CNT/matrix interface. During loading the material weak interfaces lead to create microvoids and crack at the CNT/matrix interfaces and reduces load caring capacity and strength of the composite [21, 22]. Chemical functionalization changes the chemical structure of the surface of the CNTs and improves CNT/matrix interface by facilitation chemical reaction between CNTs and polymer matrix. The result of the thermogravimetric test shows higher residual weight of FCNT 2 hours milling composites compare to raw CNT 2 hours milling composites and provides further evidence for improving bonding of CNTs to the polymer matrix

On the other hand, due to high surface areas CNTs tend to create clusters, these clustering affects the mechanical property of the composites [8] another role of chemical functionalization is assisting better dispersion of the CNTs into the matrix [2].

The higher strength of a composite is obtained by a homogeneous distribution of a reinforcement into a matrix [2,5], mechanical functionalization through ball milling enhance distribution of the CNTs into the polymer matrix and increases contact between CNTs and polymer matrix lead to rising chemical bonding between them. Increase in milling period up to certain time improves mixing of the CNTs with the matrix, in the same time milling treatment, introduces damages into the CNTs and breaks them into the smaller parts. Increasing milling time increases damages and decreases aspect ratio of the CNTs and causes decrease in the strength of the composite [14]. A decrease in the crystallite size of CNTS by milling leads to peak broadening in XRD analysis which is observing in figure 6, in addition, damaged and broken CNTs tend to faster and easier oxidation and show lower stability in the thermogravimetric test. Figure 7 shows lower residual weight for FCNT/phenolic 6 hours milling than FCNT/phenolic 2 hours milling. Results show that in the first stage, mechanical treatment improves CNTs/matrix interfaces and CNTs distribution as a result strength of the composite increases, in contrast, effect of long milling time (more than 2 hours) on the CNTs/matrix interfaces and CNT distribution is small, but its effect on damages and reducing aspect ratio of the CNTs is high and causes decrease in the strength of the composite.

Conclusions

Acid chemical functionalization introduces chemical changes into the surface structure of the CNTs and increases the concentration of the oxygen-containing groups. These chemical changes improve CNTs/matrix interface and raise the composite's strength.

Mechanical functionalization by ball milling improves CNTs distribution into the matrix and presents some changes in the surface structure of the CNTs and modifies the strength of the composite.

Mechanical milling creates damages on the CNTs and reduces the aspect ratio of the CNTs, therefore prolonging milling time decrease strength of the composite.

In the tested composite highest strength is obtained by chemical functionalization followed by 2 hours mechanical milling.

References

[1]M. Tarfaoui, K. Lafdi, A. El Moumen, Mechanical properties of carbon nanotubes based polymer composites, Composites Part B 103 (2016) 113-121Tsu-Wei Chou, Limin Gao, Erik

[2] T. Thostenson, Zuoguang Zhang, Joon-Hyung Byun,An assessment of the science and technology of carbon nanotube-based fibers and composites, Composites Science and Technology 70 (2010) 1–19

[3] Yeh MK, Tai N-H, Liu J-H. Mechanical behavior of phenolic-based composites reinforced with multi-walled carbon nanotubes. Carbon 44 (2006), 1–9

[4] R. Taheriana, M. J. Hadianfard, A. Nozad Golikandc, Manufacture of a polymer-based carbon nanocomposite as bipolar plate of proton exchange membrane fuel cells, , Materials & Design,Volume 49 (2013), 242–251

[5] S. Kumar Swain, Itishree Jean, Polymer/Carbon Nanotube Nanocomposites: A Novel Material, Asian Journal of Chemistry, 22, No. 1, (2010), 1-15

[6] C. N. R. Rao, Achim Müller, Anthony K. Cheetham, The chemistry of nanomaterials: synthesis, properties and application, Wiley-VCH; (2004), 208-239

[7] C.A. Dyke, M.J. Tour, Overcoming the insolubility of carbon nanotubes through high degrees of sidewall functionalization Chemistry - A European Journal, 10(4), (2004), 812-817

[8] Sung-Hwan Jang, S. Kawashima, H. Yin, Influence of carbon nanotube clustering on mechanical and electrical properties of cement pastes, Materials (Basel), 9(4), (2016), 220-236

[9] M.E. Lipin´ ska, S.L.H. Rebelo, M.F.R. Pereira b, J.A.N.F. Gomes, C. Freire, J.L. Figueiredo, New insights into the functionalization of multi-walled carbon nanotubes with aniline derivatives, Carbon, 50 (2012) 3280 –3204

[10] O-K. Park, H-S Chae, G. Y. Park, N-H You, S. Lee, Y. H. Bang, D. Hui, B-C Ku, J. H. Lee, Effects of functional group of carbon nanotubes on mechanical properties of carbon fibers, Composites Part B 76 (2015) 159-166

[11] J. Amiran, V. Nicolosi, SD Bergin, U Khan, PE Lyons, JN Coleman, High quality dispersions of functionalized single walled nanotubes at high concentration. J. Phys. Chem C, 112(10), (2008), 3519–3524.

[12] O-K Park, S Lee, H-I Joh, J K Kim, P-H Kang, J H Lee, B-C Ku, Effect of functional groups of carbon nanotubes on the cyclization mechanism of polyacrylonitrile (PAN), Polymer 53, (2012), 2168-2174

[13] M. Moniruzzaman, J. Chattopadhyay, W. Edward Billups, K.I. Winey, Tuning the Mechanical Properties of SWNT/Nylon 6, 10 Composites with Flexible Spacers at the Interface**,** Nano Lett. 7(5), (2007), 1178-1185

[14] D. Molina, Polymer nanocomposites based on carbon nanotubes, thesis, Politecnico di Milano, (2012)

[15] B. Ribeiro1, E. C. Botelho, M. L.Costa1, C. F. Bandeira, Carbon nanotube buckypaper reinforced polymer composites: a review, Polímeros, 27(3), (2017), 247-255,

[16] D. S. Ahmeda, A. J. Haider, M. R. Mohammad, Comparesion of Functionalization of multi walled carbon nanotubes treated by oil olive and nitric acid, Energy Procedia, 36, (2013), 1111–1118

[17] M. Vesali Naseh, A. A. Khodadadi, Y. Mortazavi, O. Alizadeh Sahraei, F. Pourfayaz, S. Mosadegh Sedghi, Functionalization of carbon nanotubes using nitric acid oxidation and DBD plasma, World Academy of Science, Engineering and Technology, 27, (2009), 567-569

[18] Sudesh, N Kumar, S Das, C Bernhard, G D Varma, Effect of graphene oxide doping on superconducting properties of bulk MgB2, Supercond. Sci. Technol. 26 (2013) 095008, 1-8

[19] N. A. Abd Ghani, N. Izzati Zakaria, D. Samsudin, N. M. Abdul Wahab, N. Aishatun Majid, R. Daik and M. A. Mohd Ishak, New method for novolac type liquefied coconut coir Husk Lignin/ Phenol/ Formaldehyde resin, Journal of Applied Science and Agriculture, 10(5) Special (2015), 47-51

[20] A. Bobrowski, B. Grabowska, FTIR method in studies of the resol-type phenol resin structure in the air atmosphere over certain time intervals, Metallurgy and Foundry Engineering ,41 (3), (2015), 107–113

[21] M.J. Hadianfard, J. Healy and Y-W. Mai, Fracture Characteristics of a Particulate reinforced Metal Matrix Composite, J. Mat. Sci. 29 (1994), 2321-2327

[22] K. Alasvand Zarasvand, H. Golestanian, Effects of Nanotube/Matrix Interface on Multi-Walled Carbon Nanotube Reinforced Polymer Mechanical Properties, Mechanics of Advanced Composite Structures, 4, (2017), 211-223