# RELATIONSHIPS BETWEEN ELECTRICAL, MECHANICAL PROPERTIES AND MORPHOLOGY OF PC/CNT COMPOSITES.

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**Keywords:** Carbon nanotube-polymer composites, Electrical conductivity, Fracture, Mechanical properties.

## Abstract

The effect of different toughening strategies on the mechanical properties of multi walled carbon nanotube/polycarbonate composites (MWNT/PC) for electromagnetic interference (EMI) shielding was studied from the mechanical and fracture tests. The effect of processing (injection or compression molding) and manufacturing (annealing) conditions in the mechanical properties was analyzed. The stiffness of MWNT/PC composites grew as function of nanotube quantity. Besides, the impact resistance of PC composites showed the tough-to-brittle transition with a 2 wt.% CNT. The combination of CBT addition and annealing improved the flexural parameters and modified the fracture parameters. Morphology analysis of MWCNT/PC composites was realized and related with their mechanical properties and fracture behavior.

## 1. Introduction

In recent years, carbon nanotubes (CNTs)/polymer composites are attracting much attention due to their excellent electrical conductivity. The incorporation of CNTs, with very high aspect ratio, into the polymer matrix is expected to produce unique physical properties in comparison with those of composites with three-dimensional structured nanoparticles.
In order to obtain new conductive polymer composites, in this work, polycarbonate (PC) and multi walled carbon nanotubes (MWNT) were extruded with different CNT amounts using a twin screw machine. It was demonstrated that the electrical conductivity of CNT/polymer composites strongly depends on matrix characteristics. For this study, polycarbonate (PC) has been selected as matrix for its excellent mechanical properties and its wide range of industrial applications.
Some authors have concluded that MWNT reinforcement is much more effective for ductile matrices, whereas for brittle polymers, the nanotubes do not improve considerably the mechanical properties of the matrix. [1-2]. On the other hand, it is proved that the electrical conductivity of polycarbonate grows with the CNT addition [3-5].
The aim of this study is to improve the mechanical and fracture behavior of multi walled carbon nanotubes (MWNT or CNT) / polycarbonate (PC) nanocomposites with good electrical properties. The conductivity values of new nanocomposites must allow their use for EMI shielding applications. Besides, this work analyzes the influence of filler quantity, the

processing technique used and modifier added (cyclic butylene terephthalate (CBT)) in the structure and physical properties of nanocomposites.

## 2. Materials and testing methods

MWNT /PC nanocomposites were produced by mixing PC granules (Makrolon 2207 by Bayer) with a melt flow index of 38 g/10 min (300º C, 1.2 kg) and ρ=1.19 g/cm$^3$ with a commercial masterbatch (Plasticyl PC1501 supplied by Nanocyl S.A) containing 15 wt.% MWNT produced by extrusion process. The final nanocomposites contain 2 and 5 wt.% MWNTs in the PC matrix. A 5 wt.% low viscosity cyclic butylene terephthalate resin (CBT 100 supplied by Cyclics Corp) with respect to the weight of virgin PC was incorporated as processing aid in the extrusion process.

Prior to mixing, both PC and masterbatch were dried in an oven at 120°C for 5 hours. The dilution was done by melt mixing in a co-rotating twin screw extruder at barrel temperature of 240°C and at a screw rate of 30 rpm. After pelletizing, one part of extruded material was compression-molded into 4 mm plaques at 265°C, under a pressure of 10 bar for 10 min followed by 90 bar for 10 min. Then, these plaques were rapidly cooled by circulating water under a pressure of 90 bar for 30 min. Other specimens were molded by injection (using Batenfeld Plus 350 injection-molding machine). The injection temperature was about 290°C and the mold was kept at 25°C. Lately, some of them were annealed at 150ºC during 5h after injection molding.

Electrical properties were measured using a dielectric analyzer DEA 2971 (TA instruments), on strips (25 mm x 25 mm) cut from compression molded sheets with a thickness of 0.5 mm. The DEA measured the permittivity or dielectric constant (ε') and loss factor (ε'') of composites as function of temperature and frequency. From these parameters, ionic conductivity of the samples was calculated. Isothermal tests were performed at three different temperatures (30, 40 and 80 °C) and in a frequency range from 1,000 to 100,000 Hz.

The mechanical characterization was realized according to ISO 527 for tensile tests. [6] Each composition was tested at room temperature using an Instron 5566 universal testing machine (Instron, MA). The tests were performed at a crosshead speed of 1 mm min$^{-1}$. From stress–strain curves obtained, Young's modulus, tensile strength and ultimate strain were determined. To measure the elongation at break in PC samples, some tests were achieved at a rate of 50 mm min$^{-1}$. To measure Charpy impact properties, an instrumented impact pendulum Instron-Wolper PW5 of nominal energy of 7.5 J and a speed of 3.85 m s$^{-1}$ was employed according to ISO 179. [7]. At least 7 unnotched samples were tested for each composition.

The fracture toughness tests were carried out according to ASTM D5045 [8] in a Instron 5566 universal testing machine using single edge-notched three point bend (SENB) specimens (dimensions: 80 mm x10 mm x 4 mm). Each specimen was prenotched, 5.0 ± 0.5 mm deep, with a Ceast Spa notching machine and a sharp notch was produced using a fresh razor blade to obtain a final sharp crack. The pre-cracked specimens were tested at room temperature in a three-point bend apparatus with a support span of 40 mm and a crosshead speed of 1 mm min$^{-1}$. The load was measured as a function of displacement. Critical stress intensity factor ($K_{IQ}$) values at initiation were obtained following ASTM D-5045 standard recommendations. The $K_{IQ}$ can be considered, in a completely elastic material, equivalent to $K_{IC}$. When the ASTM rules are not satisfied, the fracture parameters are calculated for comparative purposes only.

For morphology study, some specimens were cryo-fractured using liquid nitrogen. Then, their fracture surfaces and those of specimens broken in fracture tests were examined using a JEOL JSM-6400 scanning electron microscope (SEM) at an accelerating voltage of 20 kV. Previously, the samples were sputter-coated with a thin layer of gold. The failure mechanisms of composites were determined by direct observation of the fracture surface topography in fracture toughness specimens. The macrodispersion of CNT in the matrix was studied using a light transmission microscope (Leica DM2500 microscope) combined with a DFC295 camera). Previously, thin sections (about 5 µm) of samples were cut with a Microm HM 355 microtome (Thermo Fisher Scientific GmbH , Dreieich, Germany).

## 3. Discussions

### 3.1. Electrical properties

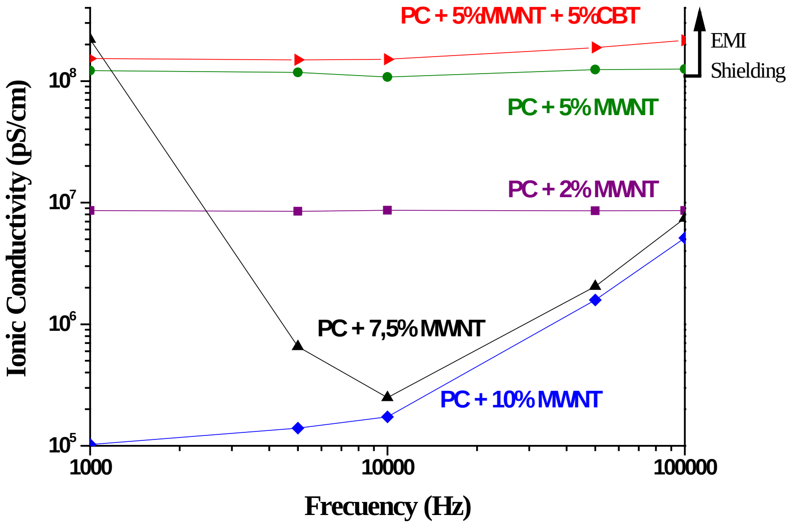


**Figure 1:** Ionic conductivity at 30°C.

The ionic conductivity of nanocomposites grows proportionally to CNT amount up to 5 wt.%. Even it is slightly higher when a 5 wt.% CBT is added in this formulation. Above 5 wt.% CNT, the conductivity values of CNT/PC composites are lower or not constant throughout the frequency range studied. As Figure 1 shows, only nanocomposites with 5 wt.% MWNT present conductivity values in the range of EMI shielding applications. The electrical properties are in accordance with the fact that there is a limit concentration of nanotubes above which the material conductivity does not increase. This limit concentration is different for each polymer matrix [3-5]. From these data, we chose the PC composites with 2 wt.% and 5 wt.% MWNT (with and without 5 wt.% CBT) for mechanical characterization because they presented the best electrical properties.

### 3.2. Mechanical properties

The tensile behaviour of PC is clearly different to PC/MWNT composites.Whereas stress-strain curves of PC showed a ductile behavior, all nanocomposites exhibited brittle behavior. Their failure occurred with a precipitous drop of load at the maximum stress. No necking occurred before fracture in the tensile tests. Table 2 shows mechanical parameters for PC/MWNT composites. CNT addition increases the polycarbonate stiffness at the expense of tensile strength and deformation at break. So, $\sigma_{max}$ and $\varepsilon_B$ fell up to 15 MPa and a 1.1%, respectively, in composite with 5 wt.% CNT. Besides, when the CBT was incorporated to formulation, the Young`s modulus improved and the tensile strength and material ductility grew slightly.

The worsening of tensile properties with the nanotube content might be attributed to the presence of CNT aggregates which act as stress concentrators. The larger agglomerates tend to initiate voids acting as crack nuclei and, as a consequence, they encourage the brittle behaviour through rapid crack propagation. Other authors have yet reported an improvement in stiffness and tensile toughness of other polymers with MWNT, only adding extremely low contents of carbon nanotubes. The ductile-brittle transition was detected around 2 wt.% of MWNT [9-10]. However, it is necessary a high amount of CNT to obtain electrical properties in EMI range.
In spite of this, specimens with CBT and 5 wt.% CNT show a slightly improvement, with tensile strength values similar than composites with 2 wt.% CNT.

| | | **PC** | **PC +2%MWNT** | **PC +5% MWNT** | **PC +5% MWNT +5%CBT** |
|---|---|---|---|---|---|
| **Tensile Tests** | **E(MPa)** | 1343 ± 24 | 1448 ± 35 | 1591 ± 23 | 1888 ± 33 |
| | **$\sigma_{max}$ (MPa)** | 57.4 ± 0.3 | 30.9 ± 4.3 | 15.2 ± 4.6 | 28.0 ± 5.1 |
| | **$\varepsilon_B$ (%)** | 50 ± 11* | 2.6 ± 0.5 | 1.1 ± 0.3 | 1.7 ± 0.4 |
| **Charpy Impact Energy** | **(kJ/m2)** | 168 ± 1 | 31 ± 4 | 22 ± 6 | 23 ± 6 |

**Table 1.** Mechanical parameters obtained from tensile and impact tests.

Impact properties of the unnotched samples are shown in Table 1. Increasing filler amount, impact resistance of nanocomposites decreases. The more pronounced decrease in nanocomposite with 2 wt.% filler is due to the presence of some nanotube agglomerations in the PC matrix, which provides points of stress concentrations, thus providing sites for crack initiation. At higher filler content (5 wt. %), any significant differences were found in impact strength [11].

| | Formulations | Flexural Modulus (MPa) | Flexural Strength (MPa) | Flexural Strain at flexural strength (%) |
|---|---|---|---|---|
| Injection molding | **PC** | 2502 ± 16 | 87.7 ± 0.8 | 6.21 ± 0.03 |
| | **PC+2% MWNT** | 2185 ± 28 | 38.6 ± 9.4 | 1.83 ± 0.52 |
| | **PC+5% MWNT** | 2373 ± 49 | 24.2 ± 4.3 | 1.03 ± 0.18 |
| | **PC+5% MWNT+5%CBT** | 2606 ± 61 | 29.5 ± 4.1 | 1.15 ± 0.16 |
| Annealing after injection molding | **PC** | 2535 ± 144 | 101.8 ± 4.9 | 6.99 ± 0.17 |
| | **PC+2% MWNT** | 2632 ± 76 | 43.1 ± 4.5 | 1.69 ± 0.20 |
| | **PC+5% MWNT** | 2886 ± 30 | 26.3 ± 3.6 | 0.92 ± 0.13 |
| | **PC+5% MWNT+5%CBT** | 3230 ± 74 | 36.4 ± 3.8 | 1.15 ± 0.12 |
| Compression molding | **PC** | 2302 ± 108 | 91.0 ± 2.1 | 6.52 ± 0.4 |
| | **PC+2% MWNT** | 2837 ± 78 | 29.1 ± 10.0 | 1.07 ± 0.38 |
| | **PC+5% MWNT** | 3119 ± 133 | 15.2 ± 4.4 | 0.44 ± 0.08 |
| | **PC+5% MWNT+5%CBT** | 2902 ± 89 | 11.4 ± 1.5 | 0.39 ± 0.05 |

**Table 2.** Flexural properties of PC/MWNT composites

The flexural parameters of PC/MWNT composites are displayed in Table 2. The addition of carbon nanotubes reduces slightly flexural modulus in injection molded composites. A 5 wt.% CNT causes about 8-10% increase in modulus over the 2 wt.% CNT composites. On the other hand, there is a decrease in flexural strength and deformation at maximum, caused by the carbon nanotubes presence. It may probably due to the fact that the nanotubes form clusters or agglomerates among themselves, resulting in a filler–filler interaction and lower interfacial properties promoting an internal shear delamination in accordance with others CNT/polymer composites [12].

Processing effect on flexural properties reveals compression molding conditions caused even higher stiffness but lower flexural toughness. On the other hand, the thermal annealing let to enhance flexural modulus and flexural strength of composites and polymer matrix.
CBT addition improves the flexural properties for injection molded specimens with or without annealing, whereas for compression molded ones, CBT does not practically change the mechanical values.
The annealing and CBT adding, significantly improve the flexural modulus up to 30%. The flexural modulus is closely related to the macrodispersion of MWNT in the composites. Varela-Rizo et al. [13] found that CNT/PMMA based composites were more likely to entangle and to form agglomerates. The presence of these bundles in nanocomposites reduced the flexural modulus with respect to neat matrix. In order to increase flexural modulus with nanotubes, the absence of large agglomerates and a good dispersion are needed. On the other hand, some authors [14] have suggested the brittle fracture of PC nanocomposites may be induced by annealing. In our case, deformation at maximum of composites was practically the same after annealing. Flexural properties of composites with 5 wt.% CBT and annealing were close than the values of injection molded specimens with only 2 wt.% CNT. With 5 wt.% MWNT, the use of CBT or annealing is insufficient to counteract the brittleness increase and flexural toughness decrease, whereas a combination of both strategies let to optimize these parameters.

### 3.3. Fracture tests

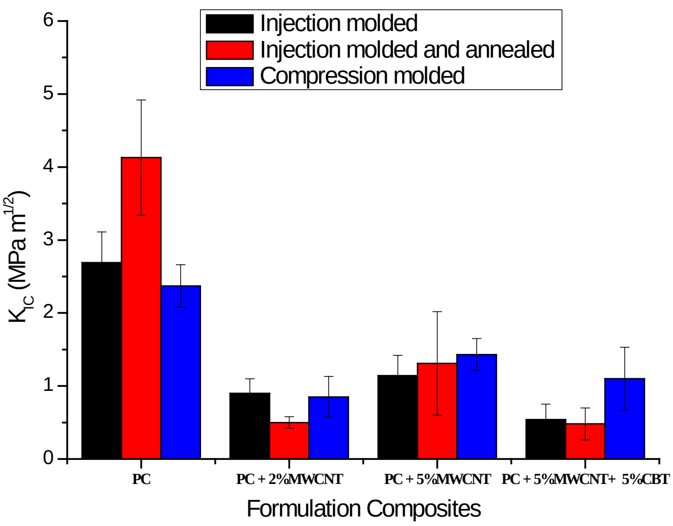


**Figure 3.** Fracture parameters of PC/MWNT composites.

Figure 3 shows the critical stress intensity factor ($K_{IQ}$) for nanocomposites. It is well known than for polycarbonate specimens with a sharp notch, $K_{IC}$ is typically 2.24 MPa m$^{1/2}$and $\sigma$ = 64 MPa [15]. At 10 mm min$^{-1}$, de Melo et al. found a $K_{app}$ value of 3.72 MPa m$^{1/2}$ in polycarbonate using LEFM with specimens with similar dimensions [16]. The calculation for the necessary specimen dimensions indicates that PC specimens with thickness > 3 mm would fracture under plane strain conditions. However, for polycarbonate samples that meet this condition, extensive plastic deformation is still visible. The $K_{IQ}$ parameters for the PC/MWNT composites, decreases dramatically respect the matrix values [17]. In this study, fracture behavior changes to more brittle with carbon nanotubes. Previously, Sathapathy et al. found that fracture toughness of PC/MWNT composites in films, for plane-stress conditions, decreases from 2 wt.% CNT [18]. In this study, however when increasing the MWNT content to 5 wt.%, the critical stress intensity factor, $K_{IQ}$, increases in all specimens, regardless of the processing technique employed.

Despite of annealing improves significantly the fracture toughness of polycarbonate; it does not seem to be effective when nanotubes are added. Respect to the processing technique, compression-molded specimens reached higher level of stress intensity factor ($K_{IQ}$) than injection-molded specimens. The differences may be related with the microscopic structure of materials, as will be commented in the morphologic analysis section.

CBT has a positive effect only in compression molded specimens, where fracture toughness grew further obtaining similar values than those of composite with 2 wt.% MWNT.

### 3.4. Morphological analysis

Using light microscopy, a large amount of self-organized MWNTs bundles or agglomerates were observed in all samples. (See in figure 4)

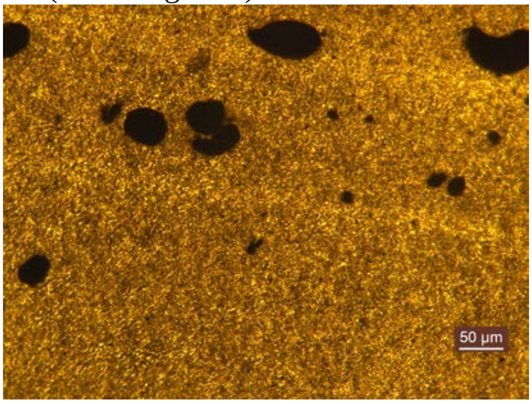


**Figure 4.** LM images of polycarbonate with 5 wt.% MWNT at 200x.

SEM micrographs of Figure 5 present cryo-fracture surfaces of the different injection molded specimens. Nanotubes seem well dispersed on polycarbonate matrix, including when CBT is used as processing aid [19]. It is clear that both mechanical and electrical properties depend on the balance between CNT agglomerates and dispersed nanotubes in matrix. Morphology with the best CNT dispersion does not guarantee the best conductivity.

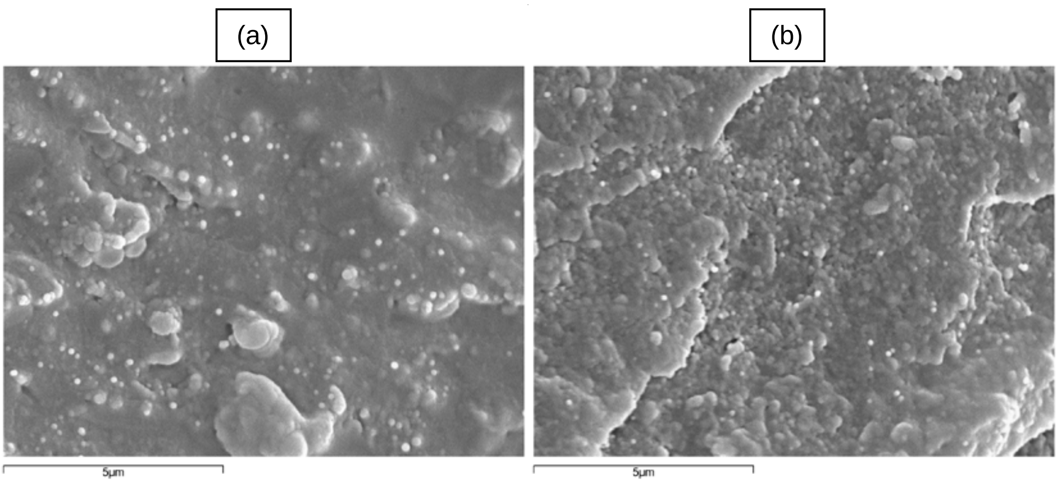


**Figure 4.** SEM images from cryogenic surfaces of polycarbonate with 5%MWNT (a) and 5%MWNT + 5%CBT (b) at 10000x.

## 4. Conclusions

The influence of processing methods on the morphological and mechanical properties of MWNT/PC composites with EMI shielding properties was investigated. Further, the changes induced by annealing and by CBT were analyzed too. From the experimental data, the following conclusions can be drawing:

- The ionic conductivity of nanocomposites grows proportionally to CNT amount up to 5 wt.%, into EMI shielding range. Above 5 wt.% CNT, the conductivity values are lower or not constant throughout the frequency range studied.
- CBT addition has a positive effect on tensile behavior of nanocomposites with 5 wt.% CNT. The combination of CBT addition and annealing also enhances the flexural parameters with an increase in flexural modulus of 30%.
- Fracture toughness decreases with MWNT. But, annealing after injection molding improves fracture toughness in MWNT composites and compression molding seems to be most appropriate processing for the nanocomposites with CBT.
- Morphology analysis shows a better dispersion of CNT in injection molded specimens although there are still agglomerates.

**Acknowledgements**
Authors acknowledge the financial support to MICINN-FEDER (research project IPT-420000-2010-004) and Xunta de Galicia-FEDER (Program of Consolidation and structuring competitive research units (CN2011/008)).

## References

[1] Spitalsky Z., Tasis D., Papagelis K., Galiotis C. Carbon nanotube–polymer composites: Chemistry, processing, mechanical and electrical properties. *Progress in Polymer Science,* **35,** 357–401(2010).
[2] Satapathy B.K., Weidisch R., Potschke P., Janke A. Tough-to-brittle transition in multiwalled carbon nanotube (MWNT)/polycarbonate nanocomposites, *Composites Science and Technology*, **67**, 867–879 (2007).
[3] Poschke P, Dudkin SM, Alig I. Dielectric spectroscopy on melt processed polycarbonate–multiwalled carbon nanotube composites. *Polymer,* **44,** 5023–5030(2003).
[4] Potschke P, Bhattacharyya AR, Janke A, Goering H. Melt mixing of polycarbonate/multi-wall carbon nanotube composites. *Compos Interf*aces, **10,** 389–404 (2003).
[5] Poschke P, Abdel-Goada M, Alig I, Dudkin S, Lellinger D. Rheological and dielectrical characterization of melt mixed polycarbonate–multiwalled carbon nanotube composites. *Polymer,* **45** , 8863–70(2004).
[6] ISO 527 *Determination of tensile properties*. (2012)
[7] ISO 179 *Determination of Charpy impact properties* (2010)
[8] ASTM D5045-93 *Standard test methods for plane-strain fracture toughness and energy release rate determination of plastics materials* (1993)
[9] Kausch HH and Michler GH. Effect of nanoparticle size and size-distribution on mechanical behavior of filled amorphous thermoplastic polymers. J App Polym Sci 2007; 105: 2577–2587
[10] Famá LM, Pettarin V, Goyanes SN, Bernal CR. Starch/multi-walled carbon nanotubes composites with improved mechanical properties, Carbohyd Polym 2011; 83(3):1226-1231.

[11] Zhang H, Zhang Z. Impact behavior of polypropylene filled with multi-walled carbon nanotubes, Eur Polym J 2007; 43 (8): 3197-3207
[12] Prashantha K, Soulestin J, Lacrampe MF, Krawczak P, Dupin G, Claes M Masterbatch-based multi-walled carbon nanotube filled polypropylene nanocomposites: Assessment of rheological and mechanical properties Compos Sci Technol 2009;69: 1756–1763.
[13] Varela-Rizo H, Weisenberger M, Bortz DR, Martin-Gullon I. Fracture toughness and creep performance of PMMA composites containing micro and nanosized carbon filaments. Compos Sci Technol 2010; 70(7): 1189-1195
[14] Chandra A, Turng L-S, Li K, Huang H-X. Fracture behavior and optical properties of melt compounded semi-transparent polycarbonate (PC)/alumina nanocomposites, Comps Part A-Appl S 2011; 42(12) 1903-1909.
[15] Williams J.G., Fracture Mechanics of Polymers, John Wiley and Sons, NY, 1987.
[16] de Melo NH, Weber RP, Miguez Suarez JC. Toughness behavior of gamma-irradiated polycarbonate. Polym Test 2007;26(3) 315-322.
[17] Kuronuma Y, Shindo Y, Takeda T, Narita F. Fracture behavior of cracked carbon nanotube-based polymer composites: Experiments and finite element simulations. Fatigue Fract Eng M 2010;33: 87–93.
[18] Satapathy BK, Weidisch R, Pötschke P, Janke A. Crack Toughness Behavior of Multiwalled Carbon Nanotube (MWNT)/Polycarbonate Nanocomposites. Macromol Rapid Commun 2005; 26:1246–1252.
[19] Kushwaha S, Kamal KK, Krishnan PSG, Sharma SK. Preparation and characterization of nickel coated carbon fiber reinforced polycarbonate composites J Reinf Plast Comp 2011;30:1185-1196.