

MECHANICAL AND TRIBOLOGICAL CHARACTERIZATION OF HIGH DENSITY POLYETHYLENE (HDPE)/ MULTI WALL CARBON NANOTUBE (MWCNT) NANO COMPOSITE- A REVIEW

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Abstract: Carbon Nano-Tubes (CNTs) have stimulated extreme research into a broad range of applications due to their remarkable structural, mechanical and thermal properties. In the present article, Carbon Nanotube/High Density Polyethylene (CNT/HDPE) composites were manufactured and tested to investigate the effect of incorporation of multiwall carbon nanotubes (MWNTs) on mechanical properties & wear behaviour of nano composites having different wt% of MWNTs. High density polyethylene (HDPE) reinforced with specific volume fraction (up to 5%) of CNTs. Latter the test specimen of tensile dog bone were achieved through the injection moulding at 200°C. It is concluded that both Halpin-Tsai and modified series model can be used to predict Young's modulus of CNT-HDPE composites. Tensile test was carried out Using Universal Testing Machine. To investigate the microstructure & Wear mechanism of warm surface optical microscopic image are used. The HR-TEM microstructure images reveal the homogeneous dispersion of MWNTs in the HDPE polymer matrix. A considerable improvement on mechanical & Wear properties of the material can be observed when the volume fraction of CNT is increased.
Keywords: Polymer matrix composite, MWCNT, DSC-TGA, SEM, Injection moulding machine

I. INTRODUCTION

After the discovery by Iijima (1991), carbon nanotubes have been employed in many diverse areas of applications such as medical, aerospace & defence. CNTs may be categorized as single walled carbon nanotubes (SWNTs), double walled carbon nano-tubes (DWNTs) or multi walled carbon nano-tubes (MWNTs). SWNTs and MWNTs have been considered as unique reinforcements for different polymers. CNT posses high exceptionally mechanical (axial Young modulus 1–5 TPa [1–7], high flexibility [8], bendingfully reversible up to a 110 degree critical angle for SWNT [9]), and physical (metallic or semi-conducting character [10, 11], field emission, high thermal and electrical conductivity, hydrogen adsorption) properties which makes it the suitable candidate for

reinforcing material in nanocomposites and have been the subject of many research works. The best utilization of carbon nanotube in nanocomposites depends on the dispersion quality of CNTs uniformly throughout on the matrix material & adequate interfacial bonding between the CNTs and the matrix. So it is required to perform a chemical treatment of CNTs for better interfacial bonding between CNT and polymer [16]. Gorga and Cohen [20] found that in addition to a good dispersion of CNTs in polymer, their orientation and an interface between CNT and polymer also play a critical role to improve mechanical properties of composites. Carbon fibres reinforcements have high strength, light weight, high-performance and are excellent load bearing reinforcements in composites (Allaouia et.[14]). However, Carbon nanotube, due to their excellent mechanical, thermal and electrical properties, It was generate lot of interest in composite fraternity to use it as an additional reinforcement. The resultant composite will be three phase composite with higher strength and stiffness. Nanotubes will play the role of matrix additives, providing multifunctional properties to the composite (Mukhopadhyay et. [12]). Polymer based composites have been found most suitable for additional reinforcement with CNT (Bal and Samal [15]; Coleman et.[13]). On the other hand, among the most versatile polymer matrices, HDPE is the most widely used thermoplastics in electronic packaging, automobile and other industrial sectors because of its well-balanced physical and mechanical properties and easy process-ability at a relatively low cost that makes them an excellent material (Chrissafis et [22] , Galli et [23]). Enormous studies have been reported on the mechanical and micro-structural properties of this high-performance thermoplastic polymer based composites (Tang et [24], Potschke et [25], Kanagaraj et[26]). Gong et al. [17] reported the role of surfactants as processing aid in CNT-polymer composites and found their enormous influence on mechanical and thermal properties of composites. Ji et al.[18] have discussed the difficulties obtained to get uniform dispersion of CNTs in a polymer matrix. Zou et al.[19] found that HDPE/CNT composites fabricated at higher screw speed give uniform dispersion of

CNT in HDPE. Edidin and Kurtz [21] showed that toughness of the material is strongly correlated to the wear resistance of polymers. Polymer composites of HDPE reinforced with different percentages of Kevlar and carbon fibre have been developed and using these materials new acetabular cups were prepared by a simple compression moulding technique. The mechanical and tribological characteristics of these materials were studied in standard universal testing machine and pin-on-disc machine [27]. Carbon nanotubes can improve the wear performance of UHMWPE/HDPE composites. The specific wear rate of the composites decreased with increasing CNT content. The nanotubes can be dispersed in the matrix, however, nanotube aggregates also still exist. Further work is needed to improve the homogeneity of the nanotubes in the matrix [28]. By S.E. Franklin Wear experiments have been carried out with a range of filled and unfilled engineering polymers sliding against a hardened steel mating surface under different conditions of sliding speed, mating surface roughness and roughness orientation. The tests were carried out under dry reciprocating sliding conditions that can be compared to the conditions frequently found in the moving parts of various electronic consumer and professional products and equipment. Under dry reciprocating sliding conditions, the abilities of common engineering models to provide wear predictions similar to experimentally determined values vary greatly for different polymers and for different combinations of test conditions [29]. Dispersing nanotubes individually and uniformly into the polymer matrix seems to be fundamental when producing composites with enhanced and reproducible properties. Therefore, for this study, HDPE is chosen due to its known excellent chemical and mechanical properties. To utilize and enhance the properties of HDPE, especially to improve its stiffness, wear resistance and rigidity, CNT-HDPE composites are prepared and the effect of CNT loading on mechanical properties is investigated.

II. EXPERIMENTAL DETAILS

2.1 Materials used by S. Kanagaraj, Fatima R. Varanda etc. from M/s Shenzhen Nanotech Port Co. Ltd. Fig1 shows the SEM image of as-received CNTs. The specifications of MWCNTs are range of diameter 60–100 nm, length of the tubes 5–15 μm , purity >95% & The density is 2.16 g/cm³. The HDPE pellets were obtained from M/s The Dow Chemical Company, Portugal and their grade is HDPE KT 10000 and the density of the HDPE pellets is 0.964 g/cm³. For the Preparation of nanofluids the chemically treated CNTs were added with deionized water and sonicated for 1 h to have a uniform dispersion of CNTs in water. Prepared nanofluid were mixed with the HDPE pellets and heated continuously with magnetically stirred.

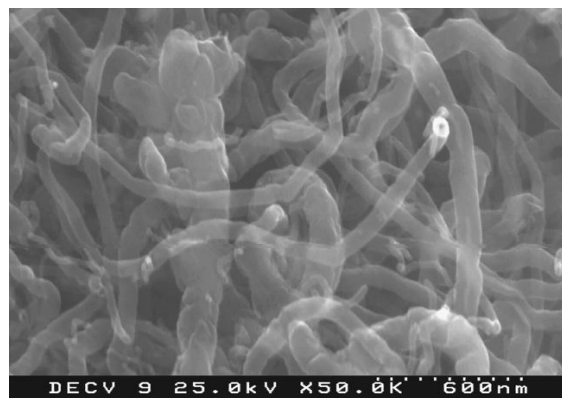


Fig1 SEM image of received CNTs (S. Kanagaraj)

When the fluid was completely evaporated, this HDPE/MWCNT composite was kept on oven for 24H at 110 °C to completely evaporate the moisture present on the composites. For the preparation of tensile specimen injection moulding machine was used. CNT coated HDPE pellets were melted on injection moulding machine at 200°C to induce sufficient softening of polymer to disperse with CNTs and this mixture was injected into a tensile specimen. The test samples were obtained for different volume fraction of CNTs (0.11, 0.22, 0.33 & 0.44%) with HDPE polymer in basic shape of dog bone 100 mm long & centre section 10 mm wide, 2 mm thick and 50 mm long. Tensile test of the composites is carried by universal testing machine respectively. The elastic modulus, ultimate strength, toughness, wear rate linearly increased with increasing with CNT fraction on the composites.

2.2 P. Rajeshwari used material HDPE (density of 0.93 g/cm³, average particle size = $21 \pm 3 \mu\text{m}$) supplied by Loba Chemicals (India). MWNTs were obtained from M/S Sky Spring Nano, USA. The MWNTs used in the study were of purity $\geq 98\%$, density 2.16g/cm³ and had an outer diameter of 30-80nm and a length of upto 10 μm . Composites were prepared by melt mixing in a temperature controlled Sigmamixer equipped at the 220°C temperature. When the HDPE polymer was completely melted than required amount of filler material (0.20, 0.40, 0.60 and 0.80 wt. %) are added. After got MWCNT/HDPE composites prepared sample specimen by hot compression moulding at 200°C for 10min. The electron microstructure & nanoscale microstructure of the MWNTs / HDPE composites with different concentrations of MWNTs were characterized by means of the high-resolution transmission electron microscopy (HRTEM: JEM-2100, JEOL, Japan), operating at an accelerating voltage of 200 kV and atomic force microscopy (AFM).

2.3 Yaobang Zou, Yongcheng Feng MWNTs used was supplied by the Chengdu Institute of Organic Chemistry with specification of diameter of 20–40 nm & purity of

94%. And the matrix material HDPE, with a density of 0.947 g/ cm³, from Golden Philips Petroleum Co. Ltd, Shanghai, China. Than for preparation of MWCNTs/HDPE nanocomposites wear prepared by Solution dispersion of MWNTs & Melt dispersion of MWNT by twin-screw extruder for different wt% (0.3, 0.5, 1.0, 2.0 and 3.0) of MWCNTs. Tensile test specimen wear obtained by Injection molding machine at 179°C . The mechanical testing wear performed at 23°C and a humidity of 50%. The tensile & flexure property wear measured on an instron testing machine. Thermal and wear analysis are carried out by thermo gravimetric analysis & scanning electron microscopy of worn surface.

2.4 Yang Xue a, Wei Wu: The sample materials were consisted of 80% UHMWPE and 20% HDPE reinforced by MWCNTs. The purpose of adding HDPE to improve creep Property of UHMWPE because of HDPE has superior creep property & little inferior wear resistance property than UHMWPE. The addition of HDPE to composites reduced the melt viscosity.

III. CHARACTERIZATION & DISCUSSION

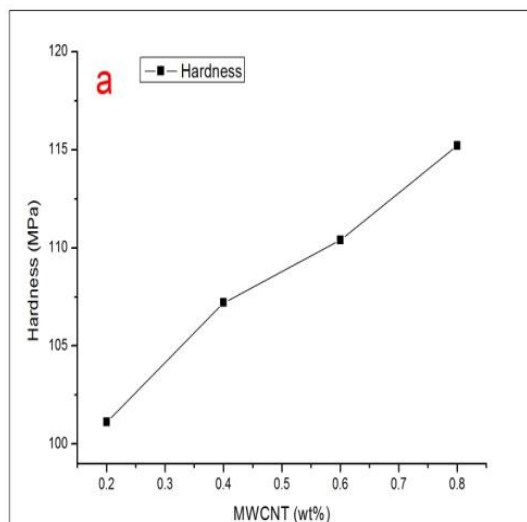
It is observed that by S Kanagrag, Fa'tima R. Varanda etc. The mechanical property of prepared nano composites i.e. young's modulus, toughness; strain at fracture; ultimate strength and wear rate are increased with increment of CNTs wt% in composites. Table 1 shows all these property.

The Increment of young's modulus are starts from 6.7% to 22.2% at 0.11 to 0.44 wt% of CNTs. And its increment is reached 100% at the wt% of about 2% of CNTs. When compare with the pure HDPE/ 0% of CNTs composites the increment of ultimate strength is within 4%. And the strain in fracture is 863.4 for pure HDPE and linearly increased with CNTs wt% increasing 948.5, 978.5, 1020.4 & 1096 respectively for 0.11, 0.22, 0.33 & 0.44 of CNTs. The percentage increment of strain is 24% up to 0.44% of CNTs contains. As the CNTs percents are increase the stiffness of the composites increased and CNTs tends to have more surface area per unit volume it increase the load transfer property of nanocomposites.

Table1 : Mechanical properties of CNT/HDPE composites.

Volume fraction of CNTs (%)	Young's modulus (E) (GPa)	% increment of E	Ultimate stress (MPa)	Strain (ε) at fracture (%)	% increment of ε	Toughness (J)	% increment of toughness
0.00	1.095	0.00	105.8	863.4	0.00	634.53	0.00
0.11	1.169	6.67	105.5	948.5	9.86	743.35	17.15
0.22	1.228	12.13	106.67	978.5	13.34	756.24	19.18
0.33	1.287	17.56	106.38	1020.4	18.19	776.25	22.34
0.44	1.338	22.23	109.86	1069	23.82	842.47	32.77

By p maheshwari to calculate the mechanical property hardness and the modulus of elasticity of prepared MWCNT/HDPE composites oliver and pharr method was used. The calculated mechanical property of nanocomposites Hardness H, and Elastic modulus E are plotted against MWCNT volume % in fig1 a & b. It is observed from fig2 (a) the hardness is increased from 101.11 to 115.21 MPa for MWCNT volume 0.2% to 0.8%. For 0.2% of MWCNT composite hardness is 101.1MPa and elastic modulus value 3.21GPa respectively. The increment of hardness is 6.27% for 0.4% MWCNT/HDPE composites. This increase for composite 0.6% MWCNT was observed 9.11% and for 0.8% MWCNT was 13.33%. the elastic modulus was also increased by adding of MWCNT filler material on HDPE polymeras shown in fig 2 (b). For nanocomposites having MWCNTs 0.4 wt %, 0.6 wt% and 0.8 wt% the elastic modulus is observed 3.77,



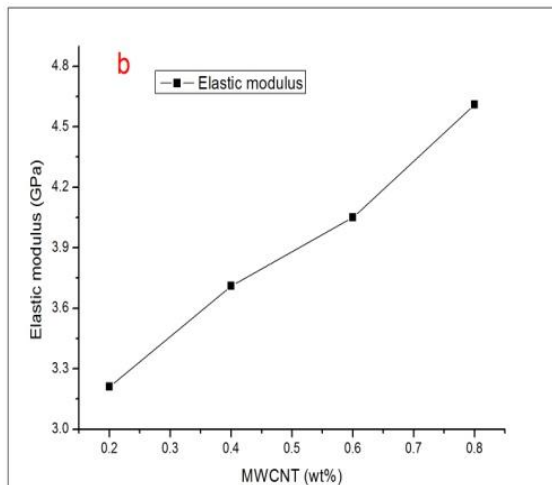


Fig 2 (a) Hardness & (b) Elastic modulus as a function of MWCNT wt%

4.05, and 4.61GPa. Showing a maximum increment of elastic modulus was found that 43.33% for 0.8 wt% of MWCNT/HDPE nanocomposites.

Microstructure Analysis:

Fig .3(a and b) shows a high resolution TEM microstructure image of 0.60 wt. % MWNTs in HDPE nano composites at lower and higher magnifications. Fig .3(a and b) also shows that the MWNTs loosely entangled together within the HDPE polymer matrix. For all compositions of MWNTs in nanocomposites, homogenous dispersion of MWNTs is achieved throughout the HDPE matrix. Liu et al. (2004) reported a homogeneous and fine distribution of functionalized MWNTs in polyamide 6 (PA6) / MWNTs composites. The author reported that after melt-mixing CNTs / PA6 composites, the random dispersion of individual CNTs had been observed without preferred orientation or alignment

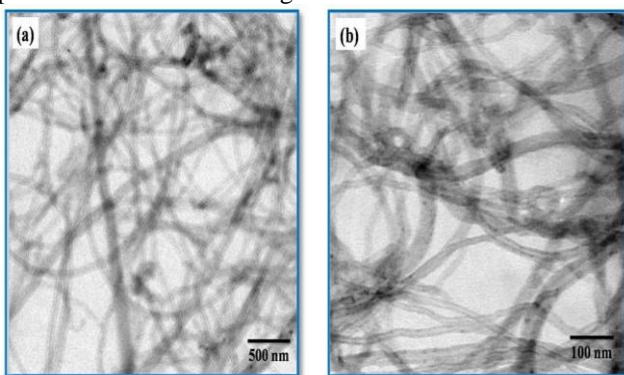


Fig.3. HR-TEM images for 0.60 wt. % MWNTs / HDPE composite showing well distributed MWNTs: (a) low magnification and (b) high magnification (P. Rajeshwari)

Furthermore, it is also observed that the majority of CNTs remain interwoven or curved in the composites, demonstrating significant flexibility of CNTs. Interestingly, in our investigation typical homogenous distribution phenomenon of multi walled carbon nanotubes over the entire polymer matrix might indicate a strong interfacial adhesion between MWNTs and HDPE polymer matrix.

A small punch test is carried out by Brian B. Johnson, Michael H. Santare etc to calculate the some mechanical property stiffness, maximum load & work to failure of newly prepared nanocomposites. The sample specimens were 0.5mm thick and 6.35 mm in diameter. Test was carried out by a hemispherical indenter apparatus on a material testing machine. Punch test were done for different wt% of CNT and it is found that the material property stiffness, maximum load and work to failure increase with the increment of CNT wt% in nanocomposites as shown in fig 3.

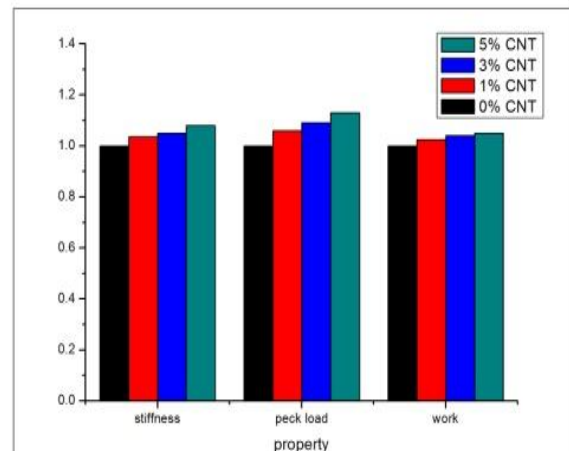


Fig 4 Comparison of material property of HDPE with nanocomposites

Wear testing: block on ring wear & friction tester was used for wear testing. The testing condition provided on the basis of hip joint loading A 45 kg (100 lb) load, applied to the contoured wear test specimen was chosen as a convenient loading for the wear test setup. De-ionized water was used in the chamber for lubrication And to maintain temperatures at around 40°C. The tester ran at a rate of 200 rpm and data were recorded every minute, over a period encompassing 500,000 cycles, which is approximately equivalent to 6 months of walking for an average person. From the test it is found that the wear rate decreasing with CNTs contents increasing. The test data confirmed the hypothesis that the addition of nanotubes to HDPE decreases the wear rate of the material. Table 2 shows average wear rates and the decrease in wear rates for increased CNT by weight content.

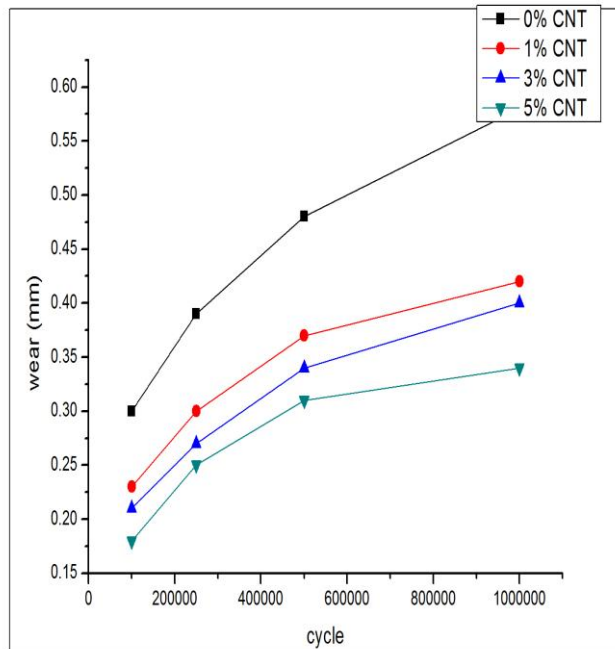


Fig 5 Comparison of wear for varying CNT% content by weight.

Table 2: Wear rates for varying CNT% content.

Material	Average wear rates (mm/106 cycle)	% Decrease of wear rates compared to 0% CNT (Logarithmic wear (%))	% Decrease of wear rates compared to 0% CNT (Linear wear (%))
0% CNT	0.1546	0	0
1% CNT	0.0840	25.8	45.7
3% CNT	0.0798	29.7	48.4
5% CNT	0.0637	38.10	58.8

In order to study the wear mechanisms responsible for the observed variations in the wear, the worn surfaces studied using an optical microscope. Load and property of the material are the important factor for the depth and length of wear. Fig 6 shows that some wear mechanism of the pin worn surface. It is observed from the microscopic image some wear mechanism i.e. micro cutting, wear debris, crater wear, abrasion wear, layer separation & plastic flow are higher in the HDPE polymer and reduces on the nano composites. Fig 6 of, a, d & f represent wear mechanism for pure HDPE polymer and b, c, e & g, represent wear mechanism for nanocomposites.

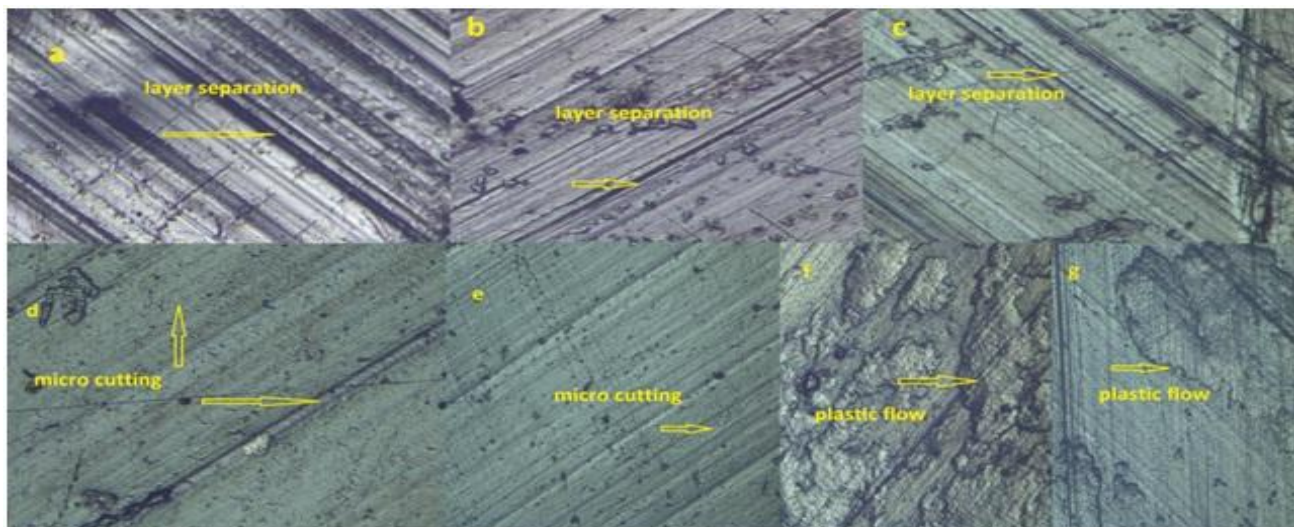


Fig 6:-microscopic image of wear mechanism here a, d & f pure HDPE and b, c, e, & g for composites.

IV. CONCLUSIONS

In this work a nanocomposites were prepared and tribological testing, mechanical testing are carried out and also studied microscopic image of worn surface for nanocomposites. Following conclusion are drawn from the above study when compare with the pure HDPE polymer.

- Wear is examined for pure polymer & nano composites and concluded that wear resistance is

increased with increase in % wt of CNTs.

- The coefficient of friction of HDPE polymer is increased significantly by adding CNTs contents.
- It is also found that the intensity of wear mechanisms such as plastic flow, micro cutting, and craters are less on the prepared hybrid composites compared to pure HDPE polymer.
- The Increment of young's modulus are starts from

6.7% to 22.2% at 0.11 to 0.44 wt% of CNTs. And its increment is reached 100% at the wt% of about 2% of CNTs. When compare with the pure HDPE/ 0% of CNTs composites.

- It was also found that mechanical property i.e. toughness, ultimate strength and strain at fracture are linearly increased with increment of CNT contents in the nanocomposites.

REFERENCES

- [1] Robertson DH, Brenner DW, Mintmire JW. 1992 "Energetics of nanoscale graphitic tubules." *Phys Rev B* 1992; 45:12592–5.
- [2] Yakobson BI, Brabec CJ, Bernholc J. 1996 "Nanomechanics of carbon tubes: instabilities beyond linear response." *Phys Rev Lett* 1996;76: 2511–4.
- [3] Lu JP. 1997 "Elastic properties of carbon nanotubes and nanoropes." *Phys Rev Lett* 1997;79:1297–300.
- [4] Wong EW, Sheehan PE, Lieber CM. 1997 "Nanobeam mechanics: elasticity, strength, and toughness of nanorods and nanotubes". *Science* 1997;277:1971–5.
- [5] Cornwell CF, Wille LT. 1997 "Elastic properties of single-walled carbon nanotubes in compression." *Solid State Commun* 1997;101:555–8.
- [6] Ajayan PM, Stephan O, Colliex C, Trauth D. 1994 "Aligned carbon nanotube arrays formed by cutting a polymer resin-nanotube composite." *Science* 1994;265:1212–4.
- [7] Treacy MMJ, Ebbesen TW, Gibson JM. 1996 "Exceptionally high Young's modulus observed for individual carbon nanotubes." *Nature* 1996;381:678–80.
- [8] Despres JF, Daguerre E, Lafdi K. 1995 "Flexibility of graphene layers in carbon nanotubes." *Carbon* 1995;33:87–9.
- [9] Iijima S, Brabec Ch, Maiti A, Bernholc J. 1996 "Structural flexibility of carbon nanotubes." *J Phys Chem* 1996;104:2089–92.
- [10] Dai H, Wong EW, Lieber CM. 1996 "Probing electrical transport in nanomaterials: conductivity of individual carbon nanotubes." *Science* 1996;272:523–6.
- [11] Ebbesen TW, Lezec HJ, Hiura H, Bennett JW, Ghaemi HF, Thio T. 1996 "Electrical conductivity of individual carbon nanotubes." *Nature* 1996;382:54–5.
- [12] Mukhopadhyay, K., Ram, K., Bhasker Rao, K.U., 2008. "Carbon Nanotubes and Related Structures." *Defence Science Journal* 58, 437-450.
- [13] Coleman, J. N., Khan, U., Blau, J. W., Gun'ko, Y. K., 2006. "Small but strong: A review of the mechanical properties of carbon nanotube-polymer composites." *Carbon* 44, 1624–1652.
- [14] Allaouia, A., Baiab, S., Chengb, H.M., Baia, J.B., 2002. "Mechanical and electrical properties of a MWNT/epoxy composite." *Composites Science and Technology* 62, 1993–1998.
- [15] Bal, S., Samal, S. S., 2007. "Carbon nanotube reinforced polymer composites—A state of the art." *Indian Academy of Science* 30 (4), 379-386.
- [16] V. Datsyuk, M. Kalyva, K. Papagelis etc. 2008 "Chemical oxidation of multiwalled carbon nanotubes" *C A R B O N* 4 6 (2 0 0 8) 8 3 3 – 8 4 0
- [17] Gong X, Liu J, Baskaran S, Voise RD, Young JS. 2000 "Surfactant-assisted processing of carbon nanotube/polymer composites." *Chem Mater* 2000;12(4):1049–52.
- [18] Ji XL, Jing JK, Jiang W, Jiang BZ. 2002 "Tensile modulus of polymer nanocomposites." *Polym Eng Sci* 2002;42(5):983–93.
- [19] Zou Y, Feng Y, Wang L, Liu X. 2004 "Processing and properties of MWNT/HDPE composites." *Carbon* 2004;42:271–7.
- [20] Gorga RE, Cohen RE. 2004 "Toughness enhancements in poly (methyl methacrylate) by addition of oriented multiwall carbon nanotubes." *J Polym Sci, Part B: Polym Phys* 2004;42:2690–702.
- [21] Edidin AA, Kurtz SM. 2001 "Development of validation of the small punch test for UHMWPE used in total joint replacements." *Funct Biomater* 2001;198:1–40.
- [22] K. Chrissafis, K. M. Paraskevopoulos, I. Tsiaoussis, D. Bikiaris. *J App. Polym. Sci.* 114 (2009) 1606–1618.
- [23] P. Galli, G. Vecellio, *J App. Polym. Sci.: Part A: Polym. Chem.* 42 (2004) 396–415.
- [24] W. Tang, M.H. Santare, S.G. Advani, *Carbon* 41 (2003) 2779–2785.
- [25] P. Potschke, A. R. Bhattacharyya et al. "Fullerenes, Nanotubes, and Carbon Nanostructures", 13 (2005) 211–224.
- [26] S. Kanagaraj, F. R. Varanda, T. V. Zhiltsova, M.S.A. Oliveira, J.A.O. Simoes. 2007 "Mechanical property of HDPE/CNT composites". *Sci. Technol.* 67 (2007) 3071–3077
- [27] S.K. Roy Chowdhury, A. Mishra, B. Pradhan, D. Saha in 2003 "Wear characteristic and biocompatibility of some polymer composite acetabular cups." Elsevier B.V. All rights reserved.
- [28] By Yang Xue a, Wei Wu a, Olaf Jacobs b, Birgit Scha'del 2005 "Tribological behaviour of UHMWPE/HDPE blends reinforced with multi-wall carbon nanotubes". Elsevier Ltd
- [29] S.E. Franklin in 2001 "Wear experiments with selected engineering polymers and polymer composites under dry reciprocating sliding

- conditions.” Elsevier Ltd.
- [30] Wenzhong Tang, Michael H. Santare, Suresh G. Advani 2003 “M elt processing and mechanical property characterization of multi-walled carbon nanotube/ high density polyethylene (MWNT/HDPE) composite films” *Carbon* 41 (2003) 2779–2785
- [31] P. Rajeshwari 2015 “Microstructure and Mechanical properties of Multiwall carbon nanotubes reinforced Polymer Composites” *Materials Today: Proceedings* 2 (2015) 3598 – 3604
- [32] Brian B. Johnson, Michael H. Santare , John E. Novotny 2009 “Wear behavior of Carbon Nanotube/High Density Polyethylene composites” *Mechanics of Materials* 41 (2009) 1108–1115