IOP Conf. Series: Materials Science and Engineering **346** (2018) 012004 doi:10.1088/1757-899X/346/1/012004

A study on mechanical properties of PBT nano-composites reinforced with microwave functionalized MWCNTs

Revati Deshpande[1], Garima Naik[1], Swamini Chopra[1], Kavita A. Deshmukh[1], Abhay D. Deshmukh[2] and D. R. Peshwe[1]
[1] Dept. of Metallurgical and Materials Engineering, Visvesvaraya National institute of Technology, Nagpur – 440010, India
[2]Energy Materials and Devices Laboratory, Dept. of Physics, RTM Nagpur University, Nagpur – 440010, India

Abstract. Polybutylene Terephthalate (PBT) is a synthetic thermoplastic polymer with fast crystallization rate; and is extensively used in many automobile applications where it is prone to continuous wear. Carbon Nanotubes (CNTs) as reinforcements are most ideal and promising reinforcement in enhancing mechanical properties of polymers. Owing to strong van der Waals' interaction between the nanotubes; they tend to aggregate. To overcome this behavior, CNTs are generally functionalized in acid solutions to help stabilize the dispersion and allow interaction with polymer matrix. Thus, the present study focuses on the effect of reinforcing microwave-functionalized CNTs on the mechanical and tribological properties of PBT polymer matrix. The homogenous dispersion of CNTs in PBT matrix was successfully achieved by functionalizing the CNTs. DSC and XRD analysis confirms better crystallization and reduced crystallite size due to improved nucleation. Apart; an increase in the hardness and MFI value was also noted, which again hinted towards improved dispersion. However, the reduction in tensile strength and % elongation indicated embrittlement of the PBT matrix after addition of functionalized CNTs. Furthermore, the peeling and scuffing phenomenon observed for virgin PBT, during sliding wear, was suppressed after CNT addition.
Keywords: *Functionalization; MWCNTs; PBT; Tensile; Wear*

1. INTRODUCTION

Carbon nanotube reinforced composites have gained rapid importance amongst engineers, scientists and product designers as they are light-weight and show excellent mechanical properties. Thus, they are exceedingly being used in automobiles and other performance enhancing applications [1]. CNTs have remarkable electronic, chemical, and mechanical properties that make them leading materials for a variety of potential applications, especially as reinforcements in composites. The outer walls of CNTs are nearly chemically inert and the strong van der Waals' interaction between the nanotubes causes aggregation. These aggregates act as stress concentration points in the composites, thereby decreasing the actual strength that can be achieved from these composites. This difficulty can be overcome by functionalizing the outer wall of the CNT. Functionalization works by creating similar polar bonds, thus repelling each other and preventing agglomeration. Chen and Mitra [2] have demonstrated that microwave assisted functionalization of MWNTs is a rapid, cost-effective and environmentally friendly method. Wang et. al. [3] reported that rapid functionalization of SWCNTs occurs by microwave treatment in a 1:1 mixture of HNO_3 and H_2SO_4 for addition of –COOH bonds on the walls. The microwave exposure for 3 minutes was found to be most favorable to obtain better degree of functionalization.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

Polybutylene terephthalate (PBT) is a thermoplastic engineering polymer that is used as an insulator in electrical and electronic industries. It is a semi-crystalline thermoplastic polymer and a type of polyester. PBT is resistant to solvents, shrinks very little during forming, mechanically strong and heat-resistant up to 150°C [4]. The previous literature indicates that the effect of using functionalized CNT as reinforcement on the physical, mechanical and tribological properties of PBT polymer matrix has gained little attention, as best to our knowledge. Moreover, reinforcement of microwave functionalized MWCNTs in PBT has not been explored anywhere. PBT composites are extensively used in many automobile applications [4,5]. But extreme loading conditions subject the parts to continuous wear and tear, which gives rise to problems related to the strength of materials, performance of the components, safety and life of the part. The increasing use of these composites in aerospace and automobile applications, demands for more understanding about their structure and the mechanisms involved in their enhanced properties. Hence, PBT was an excellent choice for investigating the effect of reinforcing microwave functionalized MWCNTs on the enhancement of mechanical properties.

2. EXPERIMENTAL DETAILS

2.1 Materials and Sample preparation

MWCNTs with purity >98% were procured from AdNano Technologies Pvt. Ltd. with mean outer diameter 20-30 nm, mean inner diameter 10-20 nm and mean length of 20-30 μm. The chemicals; nitric acid (purity~69%) and sulphuric acid (purity~98%), were obtained from Loba Chemie. The as-received CNTs were added to 1:1 solution of HNO_3:H_2SO_4 and were subjected to microwave exposure (at 50% capacity of 700W) in a PTFE beaker for 3 minutes. The said duration of microwave exposure was attained by incorporating alternate 15 seconds ON and 30 seconds OFF cycle in order to minimize the damage to CNTs by over-exposure. The MWCNTs were then washed with DI water until neutral pH was obtained and later dried at 80°C for 2 hours. PBT in the form of granules (grade: PBT-R1-D0035, density: 1.31 g/cm^3) was procured from Sipchem and the melt-compounding technique was used to mix CNT powder into the PBT polymer matrix.

2.2 Characterization of PBT and PBT/CNT composites

The IR spectra of the samples were generated using the Perkin Elmer FTIR (Spectrum One) device. The samples were scanned against Zinc selenide reference for wave number range of 450 cm^{-1} to 4000 cm^{-1}. The XRD patterns of the samples were generated by using PAN-analytical XRD machine (X'Pert Pro) for 2 theta angle range of 10° to 100°. The hardness of the polymer and composites were measured using a Shore hardness tester (Make: STECH Engineers) according to ASTM standard D2240 at test load of 4.5 kgs. An extrusion plastometer (Make: KAYENESS) was used to determine the MFI value of virgin PBT and PBT/CNT composites. The thermal changes on incorporation of CNTs in PBT matrix are examined using a differential scanning calorimeter (DSC) (Make: Mettler Toledo, Model: DSC 821). The sample of approx. 6 mg weight was subjected to four step cycle as: heating up to 250°C at the rate of 10°C/min, holding at 250°C for 5 min, cooling till room temperature at the rate of 10°C/min and holding at room temperature for 5 min.

The tensile properties of the samples were determined according to ASTM Standard D638 using a universal testing machine (Make: INSTRON, Model: 4467) at a crosshead speed of 5 mm/min. The wear performance of both the virgin PBT and the PBT/ CNT nanocomposites was evaluated on a Wear and Friction monitor (Make: DUCOM, Model: TR-20LEMI) under different load conditions from 20 N to 100 N. The worn out surfaces of the samples were investigated by scanning electron microscope (Make: SEM-JEOL, Model: 6380A) at different magnifications. Prior to this study, the surfaces of polymer and its composites were sputter-coated with a thin palladium layer using auto fine coater (Make: JEOL, Model: JFC-1600) to make the surface conducting for obtaining images.

3. RESULTS AND DISCUSSIONS

3.1 Structural characterization of PBT and PBT/CNT composites by FTIR and XRD

The FTIR spectra of virgin PBT, PBT-CNT and PBT-fCNT are compared in **Fig. 1(a)**. The typical IR bands of virgin PBT appear at 777cm^{-1} (Aromatic C-H bending), 1092cm^{-1} (Aromatic ring), 1115cm^{-1} (O-CH_2 bond), 1280cm^{-1} (CO-O stretch in esters), 1387cm^{-1} (Aromatic ring), 1704cm^{-1} (C=O stretch), 2738cm^{-1} and 2917cm^{-1} (both CH_2 stretching), 3861cm^{-1} and 3920cm^{-1} (O-H stretch of moisture), respectively [6]. These bands are slightly shifted in case of PBT-CNT nanocomposite at 723cm^{-1}, 1016cm^{-1}, 1114cm^{-1}, 1252cm^{-1}, 1394cm^{-1}, 1699cm^{-1}, 2850cm^{-1}, 2919cm^{-1}, 3867cm^{-1} and 3908cm^{-1}, respectively. Whereas, for PBT-fCNT nanocomposite these peaks appear at 718cm^{-1}, 1015cm^{-1}, 1170cm^{-1}, 1245cm^{-1}, 1394cm^{-1}, 1699cm^{-1}, 2850cm^{-1}, 2919cm^{-1}, 3794cm^{-1} and 3834cm^{-1}, respectively. It can be clearly seen from **Fig. 1** that the intensity of the O-CH_2 bond increases after CNT addition. This intensity is more for non-functionalized CNTs which point out the fact that the CNTs bond with the PBT matrix via hydrogen OH bonding. The reduced intensity after functionalization attributes that the bonding becomes poor as the CNT surfaces are functionalized because of interference of –COOH species on the CNT surfaces. This may affect the interfacial adhesion between CNT and PBT matrix when the material is subjected to loading.

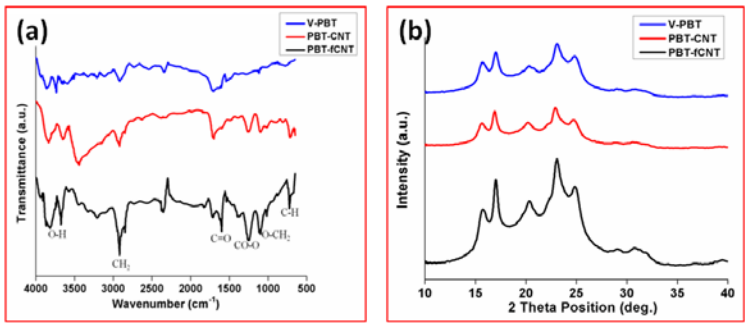


Fig. 1(a) FTIR spectra; **(b)** XRD diffractograms of PBT and PBT/CNT composites

Fig. 1(b) shows the XRD diffractograms of virgin PBT and both PBT/CNT nanocomposites.

For virgin PBT, strong diffraction peaks are observed at 2θ positions of 15.61°, 16.97°, corresponding to the β-crystallite form of PBT and at 20.30°, 23.15° and 24.94°, corresponding to the α-crystallite form of PBT, both with a triclinic configuration. These peaks are the reflections from (011), (010), (110), (100) and (111) planes, respectively [7,8]. These characteristic peaks were also observed in PBT-CNT and PBT-fCNT composites and their positions remained almost unchanged with the incorporation of both types of CNTs. This indicates that the addition of CNTs (functionalized or non-functionalized) into the PBT matrix does not change the crystal structure of PBT.

3.2 Hardness, Melt Flow Index (MFI) and Crystallite size of PBT and PBT/CNT composites

It can be seen from **Fig. 2(a)** that the shore D hardness of PBT has increased upon addition of pristine as well as functionalized CNT's. The hardness of V-PBT is 80.6, while that of PBT-CNT composite is 82.3. There was no significant rise in hardness of the composite and this can be attributed to the presence of numerous CNT agglomerates throughout the PBT matrix. After functionalization, the hardness of the composite increased significantly to 87.9. This indicates uniform dispersion of CNTs within the matrix for PBT-fCNT composite, but there are also chances of inducing brittleness at such high values of hardness.

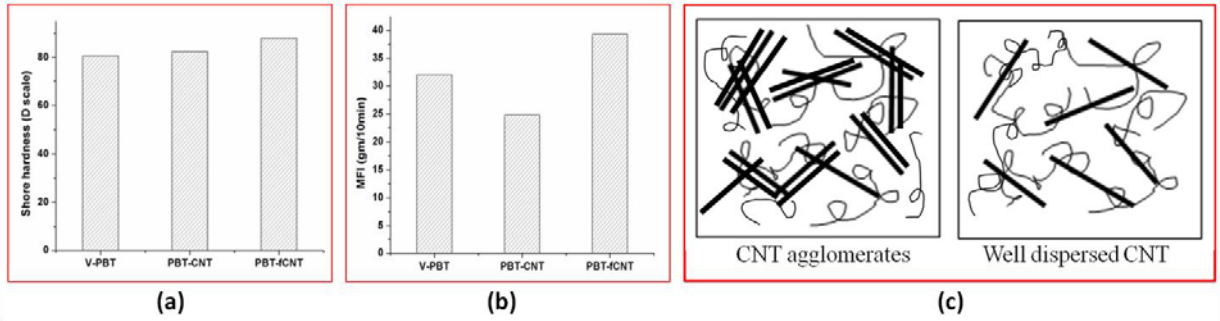


Fig. 2(a) Shore Hardness values of PBT and PBT/CNT composite; **(b)** MFI of PBT and PBT/CNT composites; **(c)** Schematic showing interconnected network of CNTs and PBT chains

The dispersion quality of MWCNTs was verified from the Melt Flow Index (MFI) of virgin PBT and PBT/CNT composites, shown in **Fig. 2(b)**. It is clear that the MFI value has reduced for PBT composite with non-functionalized CNTs, while it has increased after addition of functionalized CNTs. The reason for this is the state of dispersion of CNTs within the polymer matrix, as depicted in **Fig. 2(c)**. An interconnected network of CNTs increases the viscosity of polymers. But when functionalized CNTs are added to PBT, there is an increase in the MFI value, therefore a decrease in viscosity i.e. resistance to flow. Thus, it can be confirmed here that the functionalized CNTs are well dispersed within PBT matrix, as evident from the MFI results.

The crystallite size of the samples was calculated by Scherrer's equation using the XRD data and the average data is reported in **Table 2**, along with the thermal data. It can be seen from **Table 2** that the crystallite size reduces on addition of pristine CNTs; however, it shows a slight increase after addition of functionalized CNTs. This can be attributed to an increase in hardness of the composites, as evident from **Fig. 2(a)**. The extent of increase in hardness will impart brittleness to the matrix, which is caused by the clashing of heat barriers while solidification of the sample in injection molding. Better dispersion achieved after functionalization increases the number of nucleating centers within the polymer matrix. When these centers solidify, they lose heat in a very small span of time i.e. few seconds. The heat barriers of each nucleating center (i.e. f-MWCNT) clash with each other and hinder the solidification process, which leads to brittleness. Thus, it can be said here that PBT-fCNT composites containing large number of (-COOH) functional groups interact with the PBT matrix and make the composites brittle. The nucleating effect of the functionalized CNTs during the melt compounding may also be a contributing factor for its brittleness.

3.3 Thermal analysis of PBT and PBT/CNT composites by DSC

The melting and crystallization peaks of the polymer samples are shown in **Fig. 3**, while **Table 2** summarizes the thermal data obtained from DSC. It can be seen from the melting curve that the changes in melting temperature (T_m) values of the samples are not much significant.

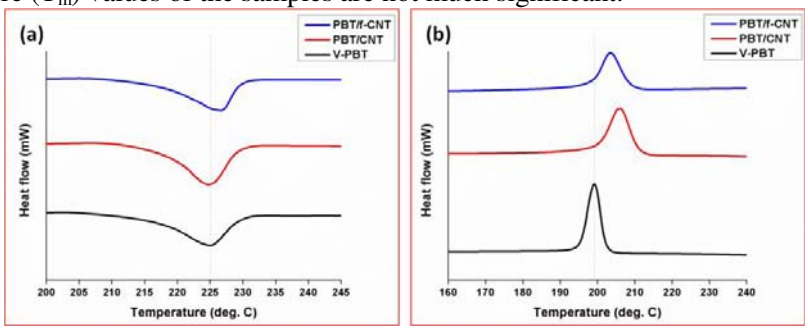


Fig. 3(a) Melting curves; **(b)** Crystallization curves of PBT and PBT/CNT composites

Table 2 Crystallite Size and Thermal data of the samples

Samples	Crystallite Size (Å)	Tm (°C)	Tc (°C)	ΔHm (J/g)	ΔHc (J/g)	% Xc
V-PBT	201.2	225	199.29	47.5	45.64	33.92
PBT/CNT	160.2	224.73	206.48	50.16	54.58	35.82
PBT/f-CNT	165	226.92	203.61	49.36	47.65	35.25

On the contrary, the crystallization temperature (T_c) of PBT-CNT composites increased by almost 7°C. Also, the % crystallinity of PBT increased after incorporation of CNTs, both pristine and functionalized. This indicates the fact that CNTs act as nucleating agents within PBT matrix, thereby improving the nucleating tendency of the polymer, also evident from increased values of crystallization temperature. The long fibrillar structure of CNTs provide ideal nucleation sites for polymer chains to tether and the crystal growth becomes easier when thermal driving force is available [9]. But a slight fall in crystallization temperature of PBT-fCNT suggests that the heterogeneous nucleation of PBT in this composite has led to the formation of more defect ridden crystalline lamella and less ordered crystals of PBT. After functionalization, the reduction in agglomeration and more uniform dispersion imparts crystallinity to the material but in a defect ridden manner [7,9]. This clearly will affect the properties of the composites.

3.4 Tensile properties of PBT and PBT/CNT composites

The tensile properties of virgin PBT and PBT/CNT composites are shown in **Fig. 4**. The figure demonstrates a decrease in tensile strength when PBT is reinforced with functionalized CNT. The strength of PBT-CNT can be seen as 57.22 MPa, i.e. approx. 5.5% higher than V-PBT (54.59 MPa) whereas for PBT-fCNT, the value is lower than both of them i.e. 51.01 MPa. The reason for this change can be attributed to increased hardness of the PBT-fCNT composites by approx. 10%. This induces brittle nature into the material, which is also reflected by the % elongation of PBT/f-CNT composite. An increase in % elongation of the composites after CNT addition can be attributed to the nano-reinforcing effect of CNT and CNT agglomerates within the polymer matrix [7,9-11]. Functionalization of CNTs promotes their homogenous dispersion and thus increases their tendency to nucleate the PBT matrix. This leads to *embrittlement* of the composite due to the thermal phenomenon explained earlier in **Section 3.2**. This fact can also be corroborated with the increase in hardness value.

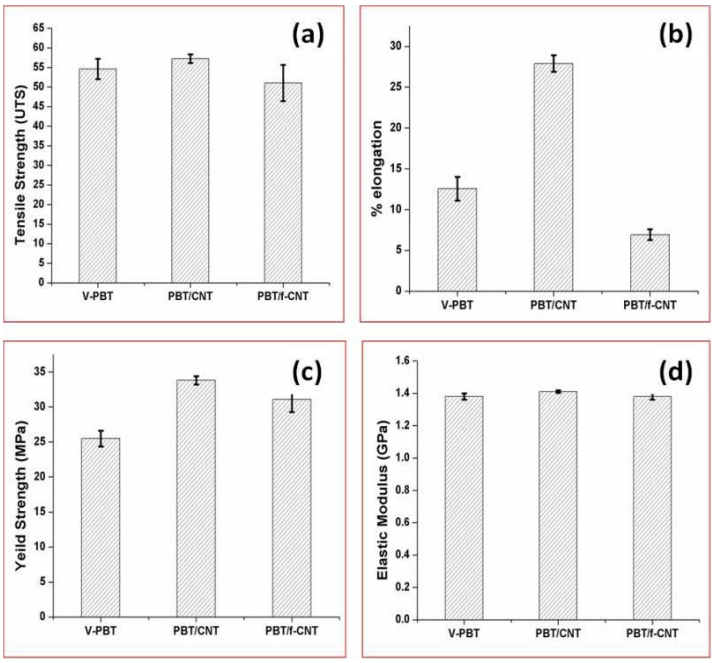


Fig. 4 Tensile properties of PBT and PBT/CNT composites

Though functionalization has improved the dispersion of CNTs within the PBT matrix, there are still chances of agglomeration of CNTs in small cluster sizes. The reinforcing effect of these agglomerates reduces owing to the fact that they also act as stress concentration points [9,12]. The negligible reduction in Yield strength of PBT-fCNT composite as compared to PBT-CNT composite also confirms the loss of ductility and increased brittleness.

3.5 Wear Performance of PBT and PBT/CNT composites

The specific wear rate of the samples tested at different loads is depicted in **Fig. 5(a)**, while their coefficient of friction is shown in **Fig. 5(b)**.

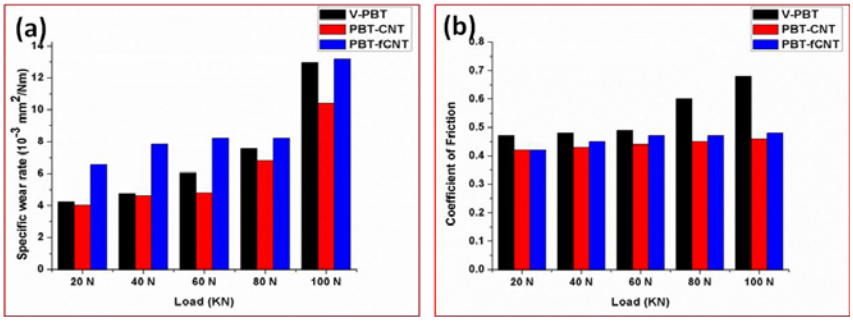


Fig. 5(a) Specific wear rate; **(b)** Coefficient of friction of PBT and PBT/CNT composites

It can be seen here that the specific wear rate of PBT-CNT reduces considerably, irrespective of the test load applied. But when functionalized CNTs are added to PBT, the wear performance of the composites deteriorated significantly. This can be attributed to the increased hardness of the composite as explained earlier. Although there are no CNT agglomerates present in the matrix to act as defects, the poor interfacial adhesion between CNTs and PBT and the brittleness incorporated in PBT, causes the material to wear off more, as compared to PBT-CNT composite.

On the other hand, the coefficient of friction of both the types of PBT/CNT composites was found to be lower than that of virgin PBT. This can be attributed to the fact that the CNTs act as spacers and self-

lubricants during continuous sliding [13]. As the polymer surface wears out, the CNTs get exposed to the counter-face. These exposed CNTs bear most of the load and transfer heat and stress effectively, thus, protecting the polymer matrix from being further destroyed [14]. Meanwhile, the worn out debris forms a lubricating layer on the counter-face, thereby reducing the abrasive action, and hence, the friction coefficient [15]. This encouraging effect of CNTs is attributed to its exceptionally high strength and thermal conductivity that assists in suppressing the peeling and scuffing of polymer matrix [14,16]. These CNTs pulled out of the matrix can then serve as solid lubricants to prevent direct contact between the two mating surfaces [13,17], thereby reducing the friction coefficient. The SEM micrographs of the worn out surfaces of the samples are shown in **Fig 6**.

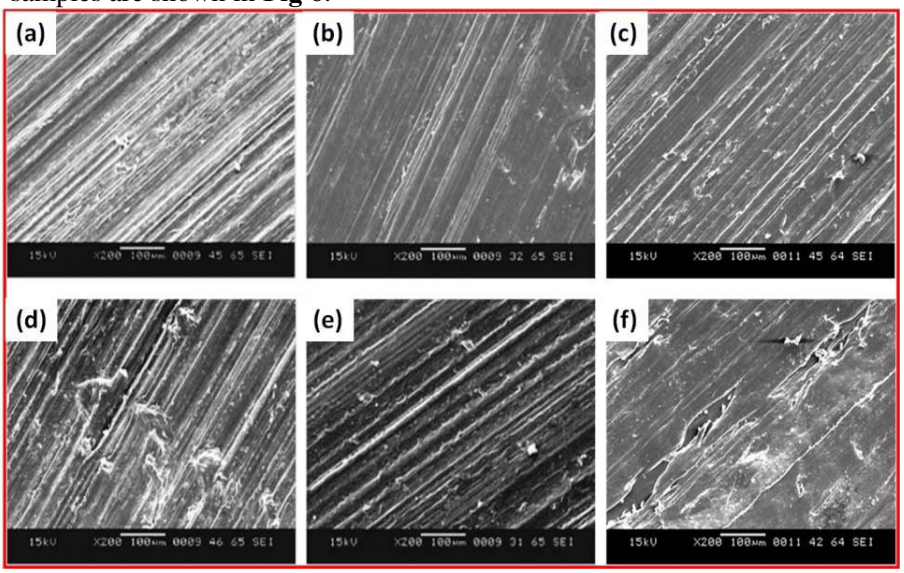


Fig. 6 SEM micrograph of worn surfaces of **(a)** V-PBT; **(b)** PBT-CNT; **(c)** PBT-fCNT at 20 N load and **(d)** V-PBT; **(e)** PBT-CNT; **(f)** PBT-fCNT at 100 N load

It can be seen that at low load of 20 N, the surface of virgin PBT shows wear tracks with ploughing and peeling marks, indicating abrasive action of counter-face on polymer [14]. But at higher load of 100 N, the polymer shows heavy plucking and scuffing marks, which can be attributed to the action of adhesive wear phenomenon [17,18]. On the contrary, the ploughing or scuffing phenomenon is suppressed for PBT-CNT composite. This observation agrees with the improved wear resistance of PBT-CNT sample. This helps to restrain the peeling off of PBT matrix during the sliding action of the counter-face. In addition, it can also be speculated here that the CNTs that are released from PBT matrix during sliding may have been transferred to the contact zone of the composite surface and the counter-face. At higher loads, it was observed that the scuffing became dominant, leading to remarkable rise in specific wear rate, as explained earlier. This can be attributed to the fact that brittleness of the surface and poor interfacial adhesion between CNTs and PBT causes large worn fragments to separate out from the sliding surface, thereby, leaving behind a more damaged surface [17, 19, 20].

CONCLUSIONS

The mechanical and tribological properties of virgin PBT were successfully compared with the PBT/CNT composites incorporated with pristine as well as functionalized CNTs. An increase in the intensity of O-CH_2 bond from FTIR proves that the CNTs have hydrogen bonded with the PBT matrix. Also, the inclusion of CNTs facilitated the crystallization of PBT and therefore led to higher crystallinity

in the composites. The increase in the hardness of the composites was credited to improved dispersion of CNTs within the PBT matrix. The formation of interconnected network of pristine CNTs was indicated by the reduced MFI value of functionalized CNT reinforced composite. However, addition of functionalized CNTs also induced brittleness in the composite, which was evident in the reduction in tensile strength and % elongation of the composites. During wear, the peeling and scuffing phenomenon observed for virgin PBT was suppressed after CNT addition but its extent increases after adding functionalized CNTs. This can be attributed to the increase in hardness of PBT after incorporation of functionalized MWCNTs.

REFERENCES

[1] Loos M 2015 *Carbon Nanotube Reinforced Composites* CNR Polymer Science and Technology Elsevier Inc.
[2] Chen Y and Mitra S 2008 *J. Nanosci. Nanotechnol.* **8** 5770-5775
[3] Wang Y et al 2006 *J. Am. Chem. Soc.* **128** 95-99
[4] Georgescu C and Deleanu L 2012 *Proceedings of 15th International Conference on Experimental Mechanics* Portugal, Paper ref.: 3014
[5] Szeteiová K *Automotive Materials: Plastics in Automotive Markets Today* (Slovak University of Technology, Bratislava)
[6] Deshmukh G S et al 2011 *Trans. Indian Inst. Met.* **64** 127-132
[7] Kim J Y 2011 *Poly(butylene terephthalate) Nanocomposites Containing Carbon Nanotube* (Advances in Nanocomposites – Synthesis, Characterization and Industrial Applications) ed Dr. Boreddy Reddy (InTech) chapter 31 pp 707-726
[8] *Handbook of Thermoplastic Polyesters: Homopolymers, Copolymers, Blends and Composites* ed S Fakirov Wiley 2005
[9] Defeng W et al 2008 *Polym. Eng. Sci.* **48(6)** 1057-1066
[10] Coleman J N et al 2006 *Carbon* **44** 1624-1652
[11] Kwiatkowska M et al 2006 *Rev. Adv. Mater. Sci.* **12** 154-159
[12] Alam A K M et al 2016 *Polym. Compos.* **37** 1-9
[13] Chen W X et al 2003 *Tribol. Lett.* **15** 275-278
[14] Zhang X R et al 2015 *Adv. Compos. Mater.* **24** 147–159
[15] Hollander A E and Lancaster J K 1973 *Wear* **25** 155–170
[16] Briscoe B J et al 1988 *Wear* **124** 177–194
[17] Chopra S et al 2017 *Trans. Indian Inst. Met.* **70(3)** 801-807
[18] Meng H et al 2009 *Compos. Sci. Technol.* **69** 606–611
[19] Cho M 2008 *Mater. Trans.* **49** 2801–2807
[20] Mu B et al 2009 *Polym. Compos.* **30** 619–628