Tribological Behaviour of Multi-Walled Carbon Nanotubes (MWCNT) Filled Polybutylene Terephthalate (PBT) Nanocomposites

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Abstract This paper focuses on evaluating the tribological properties of PBT/MWCNT nanocomposites at low CNT concentrations of 0.1, 0.2, 0.3, 0.4 and 0.5 wt%. The composites were prepared by melt-compounding and samples were tested in a pin-on-disc sliding configuration under different load conditions. It was found that the friction coefficient of the composites reduced with increasing CNT content, irrespective of the test load. Meanwhile, the specific wear rate of the composites first decreased and later increased with increasing CNT content. SEM of the worn out surfaces indicated that ploughing and peeling phenomenon of PBT was suppressed at lower CNT addition, but with increasing CNT content the surface seemed to be more damaged. The transfer film formed on the counter-face was also investigated by SEM. It was revealed that the PBT/MWCNT composites formed a thin and more uniform film as compared to the thick and grainy films deposited by virgin polymers. But at higher CNT concentrations, the transfer film once again became lumpy. These findings could be attributed to the presence of CNT agglomerates within PBT matrix at higher CNT concentrations due to non-uniform dispersion.

Keywords PBT/MWCNT composites ·
Tribological behavior · Specific wear rate ·
Friction coefficient · Transfer film · Wear debris

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1 Introduction

Polymers are gaining extensive importance over metallic parts in various tribological applications, owing to their low density, excellent wear resistance and ease of manufacturing [1–4]. The wear of polymeric parts such as gears and bearings is mostly dominated by abrasive mechanism. Thus, superior wear resistance is expected from such parts. In order to improve the mechanical and tribological properties of polymers, they are usually reinforced with various fillers such as montmorillonite [5], kaolin [6], nanosilica [7], talc/ calcium carbonate [8], graphene [9], glass fiber [10], carbon fiber [11], aramid fiber [12], wollastonite [13], carbon nanotubes [14], etc. For critical applications, such as in aerospace and defense, CNT reinforced polymer composites are gaining importance because of their superior properties. While the mechanical and thermal properties of CNT/polymer nanocomposites have been widely explored, a relatively small number of tribological investigations of polymer composites have been reported.

Chen et al. [15] investigated the tribological behavior of PTFE/CNT composites. It was observed that CNTs significantly increased the wear resistance of PTFE and decreased its friction coefficient by reducing the adhesive and ploughing wear of the composites. They reported that CNT served as spacers, thus, preventing direct contact between mating surfaces and giving minimum wear rate at 20 vol% of CNT. Dong et al. [16] reported that 1.5 wt% of CNT exhibited smallest wear rate and lower friction coefficient in epoxy/MWCNT nanocomposites. The significant improvement was attributed to great mechanical strength and very high aspect ratio of CNTs.

Yang et al. [17] studied the tribological behavior of PS/CNT composites under dry conditions. It was found that addition of CNT drastically reduced the friction and

improved the wear resistance of the composites. This was attributed to significant reinforcing and self-lubricating effect of CNT on the PS matrix. Thakur et al. [18] investigated the wear properties of HDPE/CNT nanocomposites with 0.05 wt% of CNT. It was found that the friction coefficient of the composites decreased even when the load increased. Similar trend was also shown by the wear rate of the composites. Meng et al. [19] reported that the friction coefficient and wear rate of PA-6 were reduced by addition of 1 wt% CNT under dry sliding condition. This was again attributed to the reinforcing effect, self-lubrication and excellent thermal conductivity of CNT.

PBT is increasingly gaining popularity in many tribological applications and is successfully replacing polyamides due to its better dimensional stability, especially in water and in mineral water, without cracking under load [20]. However, research on tribological behavior of PBT/CNT nanocomposites has not been found in literature so far, to the best of our knowledge. Since, CNTs are mechanically very strong and have a high aspect ratio, it is expected that introducing small amount of CNTs will significantly improve the tribological properties of PBT based nanocomposites also. To address this area, investigations have been carried out on PBT/MWCNT nanocomposites to evaluate their friction and wear behavior at low CNT concentrations.

2 Materials and Methods

2.1 Materials

PBT in the form of granules (grade: PBT-R1-D0035, density: 1.31 g/cm^3) was procured from Sipchem, while the MWCNTs (purity: >98%, avg. OD: 25 nm, avg. ID: 15 nm, avg. length: 25 μm) were provided by Ad-Nano Technologies Pvt. Ltd., Karnataka. The CNTs were added to the PBT granules in fixed amounts of 0.1, 0.2, 0.3, 0.4 and 0.5 wt% and all the composites were prepared by melt-compounding technique. The coding for all the formulations of nanocomposites is given in Table 1.

Table 1 Codes and composition of the investigated samples

Sr. no.	Composition	Code
1	Virgin PBT	PBT 0
2	PBT + 0.1 wt% CNT	PBT 0.1
3	PBT + 0.2 wt% CNT	PBT 0.2
4	PBT + 0.3 wt% CNT	PBT 0.3
5	PBT + 0.4 wt% CNT	PBT 0.4
6	PBT + 0.5 wt% CNT	PBT 0.5

2.2 Wear Testing

The wear performance of both the virgin PBT and the PBT/CNT nanocomposites was evaluated at ambient temperature in a multi pass pin-on-disc configuration on a Wear and Friction monitor (Make: DUCOM, Model: TR-20LE-MI) under different load conditions of 20, 60 and 100 N. The pins with dimension 10 mm×10 mm×30 mm were used for experimentation purpose. The samples were first abraded with superfine SiC paper (grade 1500) for uniform contact, cleaned with acetone, dried and weighed prior to experimentation. The pin was continuously abraded for 3 min (i.e. multiple pass) against the SiC paper (grade 220) as counter-face at a speed of 200 RPM and track diameter of 80 mm. Three test results were averaged for each type of sample and then reported in this study.

2.3 Characterization

The worn surfaces of the samples, the transfer film on the SiC paper and the debris generated after wear testing were investigated by scanning electron microscope (Make: SEM-JEOL, Model: 6380A), while the morphology of the composites was observed with high resolution FEG-SEM (Make: Zeiss, Model: SIGMA HV). Prior to the study, the surfaces 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 Discussion

3.1 Friction Coefficient of PBT/CNT Nanocomposites

The variation of friction coefficient of PBT/CNT nanocomposites with different loads is shown in Fig. 1.

It is evident from Fig. 1 that the friction coefficient of PBT/CNT nanocomposites decreases with increasing CNT, irrespective of the test load. The lowest friction coefficient is observed for PBT 0.5 in all loading conditions. The reduction in friction coefficient of PBT 0.5 at 20 N load is approx. by 32%, as compared to virgin PBT. This difference further reduces at higher loads, where it becomes ∼10% at 60 N and ∼13% at 100 N loads. With respect to load, it can be seen that the reduction in friction coefficient of PBT 0.5 is approx. 4% and 7% as load increases from 20 to 60 N and further to 100 N. This reduction of friction coefficient with CNT content is almost linear, which indicates the fact that an increase in the surface area fraction of CNTs reduces direct contact between the composite surface and the counter-face, as also shown by other studies also [2, 15, 19]. This also suggests that CNTs
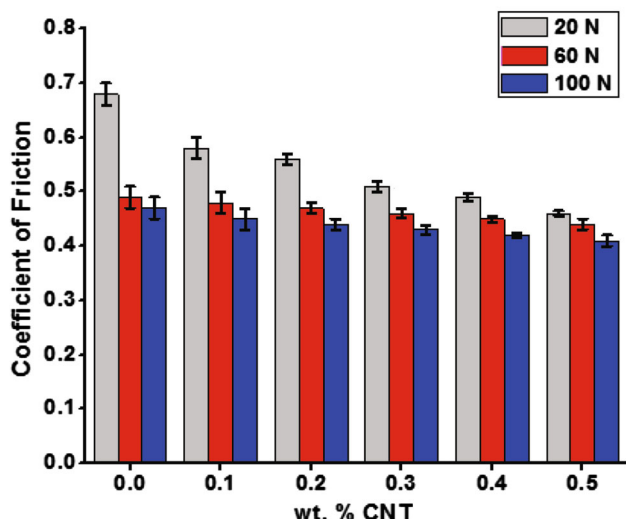
Fig. 1 Friction coefficient of PBT/CNT nanocomposites

act as solid lubricants and initiates self-lubrication when PBT/CNT nanocomposites slide against the counter-face [15].

During continuous sliding; 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; protecting the polymer matrix from being further destroyed [2]. Meanwhile, the worn out debris forms a lubricating layer on the counter-face, thereby reducing the abrasive action, and hence, the friction coefficient [21]. The effect of the nature of transfer film on tribological performance of PBT/CNT nanocomposites is explained further in detail. 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 [2, 22].

Further, it can also be seen from Fig. 1 that, the friction coefficient of the composites has reduced with an increase in load. This can be attributed to the combined effect of two competitive factors playing role in the nature of friction component between two surfaces. It is well known that the friction resulting from adhesion between polymer and counter-face equals to the product of shear strength of the polymer and the real contact area [2, 5, 23].

With an increase in the test load, the contact temperature between the pin and counter-face generally increases due to generation of localized frictional heat [10, 19]. This usually has two contradicting effects on the friction coefficient. On one hand, the shear strength of the polymer decreases with increasing contact temperature, which in turn reduces the friction coefficient for the sample. On the other hand, the elastic modulus of the polymer decreases at higher temperature, which results in an increase in the real contact area and consequently the friction coefficient increases.

Thus, the final change in the friction coefficient of the composites will be the result of these two competitive aspects [19, 23].

For the PBT/CNT nanocomposites under study, it is clear from Fig. 1 that the reduction of friction coefficient with increasing load can be attributed to the dominating effect of decreasing shear strength of the material at higher loads. The interfacial temperature between pin and counter-face is a crucial factor affecting the tribological characteristics [24]. With an increase in test load, the localized frictional heat tends to increase owing to the lower thermal conductivity of PBT. This causes softening phenomenon of the surface in contact and consequently plays an important role in reducing the friction coefficient, which has also been determined in previous studies [10, 21, 25].

3.2 Specific Wear Rate of PBT/CNT Nanocomposites

Figure 2 shows the specific wear rate of PBT/CNT nanocomposites with varying CNT content at different load conditions.

While the wear loss remains more or less same for all the CNT contents at 20 N load; it becomes minimum for PBT 0.2, reaching 3.8×10^{-3} mm^3/Nm, i.e $\sim$9% lower than virgin PBT. At higher loads, the reduction of specific wear rate becomes more significant and reaches minimum for PBT 0.3. The specific wear rate reaches 4.8×10^{-3} mm^3/Nm (i.e. $\sim$21% lower than virgin PBT) and 10.4×10^{-3} mm^3/Nm (i.e. $\sim$19% lower than virgin PBT) for PBT 0.3 at 60 N and 100 N loads, respectively. However; it can be seen from Fig. 2 that as the test load increases, the specific wear rate of PBT and its composites
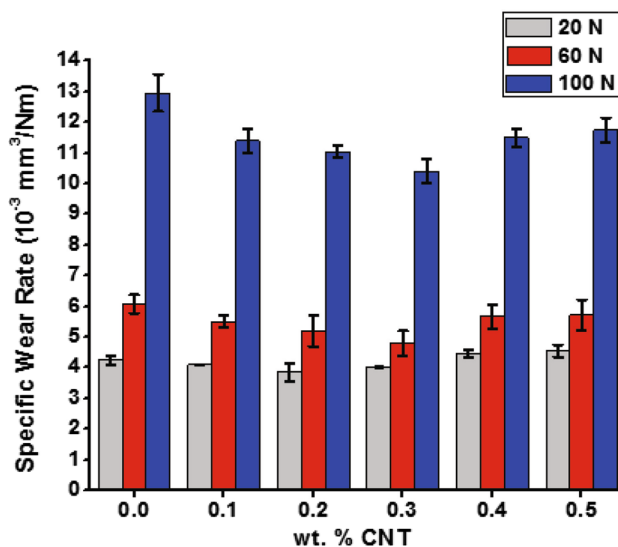

Fig. 2 Specific wear rate of PBT/CNT nanocomposites

also increases significantly, agreeing with the fact that wear loss is directly proportional to load [10, 19, 26].

It can be seen from Fig. 2 that the specific wear rate of the PBT/CNT nanocomposites reduces at first and then increases with increasing CNT content, irrespective of the load. This indicates that the wear resistance of PBT improves because of CNT addition in small amounts. The loss of wear resistance at higher CNT concentrations can be attributed to the fact that as CNT content increases; the tendency to form agglomerates also increases, owing to the strong van der Waals' force of attraction between individual CNTs. To further explore the effect of CNT agglomerates on the tribological properties of PBT/CNT nanocomposites, micrographs of the cross-section and the worn surfaces of the composites are explained thoroughly in the next section.

3.3 Investigation on the Worn Out Surface of PBT/ CNT Nanocomposites

The SEM micrographs of some of the samples studied here are shown in Fig. 3. It can be seen that at low load of 20 N, the surface of virgin PBT shows wear tracks with mild ploughing and peeling marks, indicating abrasive action of counter-face on polymer [2]. But at higher loads of 60 N and 100 N, the polymer shows heavy plucking and scuffing marks, which can be attributed to the action of adhesive wear phenomenon [19]. On the contrary, the ploughing or scuffing phenomenon is suppressed for PBT/CNT nanocomposites, irrespective of the load. The worn out surface of the nanocomposites also appear relatively smoother. This observation agrees with the improved wear

resistance of PBT/CNT nanocomposites as seen from Fig. 2.

It is interesting to observe here that, though the wear resistance of the PBT/CNT nanocomposites reduces at higher CNT content, the worn out surface of these samples seem to be more or less similar to that of the composites with highest wear resistance. This can be attributed to the fact that as the sample wears off progressively; the polymer matrix wears down first, thus, exposing the embedded CNTs to slide against the counter-face. Owing to their extremely high strength and thermal conductivity, CNTs tend to carry most of the load and transfer heat and stress effectively [2, 19]. 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. These CNTs then can serve as solid lubricants to prevent direct contact between the two mating surfaces [15, 19], thereby reducing the friction coefficient, as evident from Fig. 1.

When the test load increases, severe adhesion can be observed for all the samples. More scuffing and plastic deformation marks appear on the surface, which becomes significant at higher CNT concentrations [5]. At higher loads, the loss of material is promoted by weakened structure of polymer matrix owing to the increased localized frictional heat [14]. As explained briefly in Sect. 3.1, the reduction of shear strength of the material is dominant for PBT/CNT nanocomposites under study. Due to sliding action against the counter-face, the already weakened
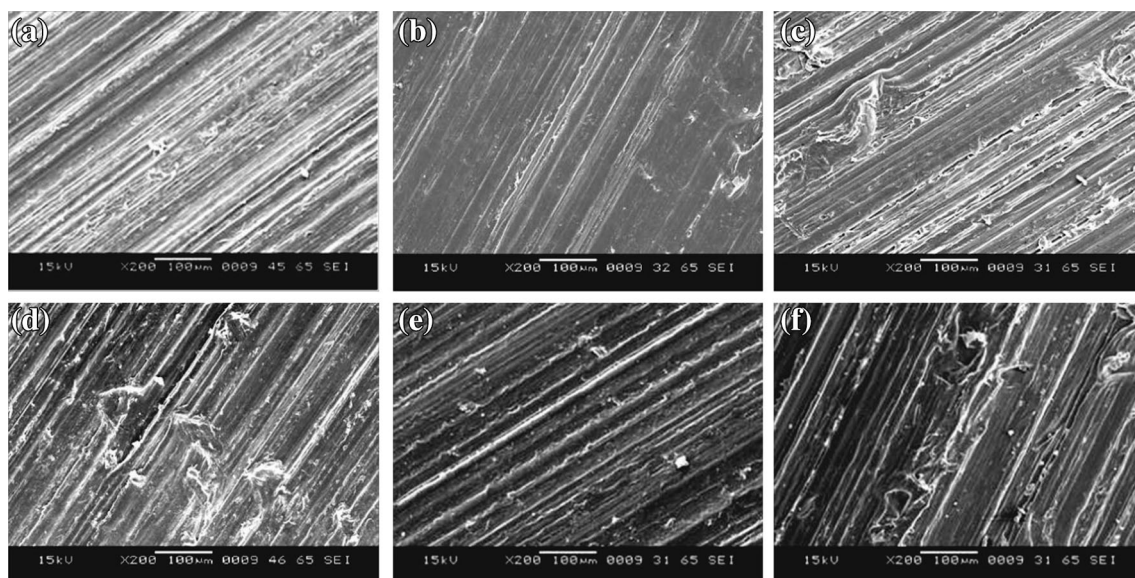

Fig. 3 SEM micrograph of worn surfaces of **a** PBT 0, **b** PBT 0.3, **c** PBT 0.5 at 20 N load and **d** PBT 0, **e** PBT 0.3, **f** PBT 0.5 at 100 N load

matrix material gets easily separated and the worn surface appears to be more damaged at higher loads.

Also, the loss of wear resistance with increasing CNT content has been hypothesized due to the formation of CNT agglomerates at higher concentrations, as mentioned in Sect. 3.2. To verify the presence of CNT agglomerates or clusters within the PBT matrix, morphology of the composites has been studied. It can be confirmed from Fig. 4 that as CNT concentration increases, the tendency of the CNTs to form agglomerates become prominent. This can also be the reason for the worn out surfaces of the composites appearing significantly damaged at higher loads. If the CNT agglomerates get pulled out from the matrix during sliding against the counter-face, then they tend to leave behind nano/micro-voids and defects in the PBT matrix [14]. This further weakens the structural integrity of the surface and hence may cause loss of wear resistance at higher CNT concentrations, also depicted by Fig. 2.

3.4 Study of Transfer Film Formed and Wear Debris Generated by PBT/CNT Nanocomposites

The capability of polymer matrix to form a thin and uniform transfer film on the counter-face during sliding plays an important role in the wear of polymer [14]. Figure 5 shows the SEM micrographs of selected samples. It can be observed here that a thick and incoherent transfer film is formed for virgin PBT, while, a relatively uniform and thin transfer film is formed for PBT/CNT composites. A uniform transfer film prevents direct contact between the composite surface and counter-face, therefore, resulting in lower friction coefficient and improved wear resistance, as seen from Figs. 1 and 2. A high specific surface area is obtained when the CNTs are well dispersed in polymer matrix. This improves the interfacial adhesion between PBT and CNTs and, thus, promotes the formation of a thin transfer film [19].

At higher loads, it is observed that the scuffing became dominant, leading to remarkable rise in specific wear rate, as explained in Sects. 3.2 and 3.3. Severe adhesion at higher loads forms a thick and uneven transfer film for virgin PBT. While the transfer film remains non-uniform even for the PBT/CNT nanocomposites at higher test loads, it relatively become thin as CNT concentration increases. But it is also observed that as the CNT content increases; the transfer film become progressively lumpy. This can be attributed to the fact that presence of CNT agglomerates at higher concentrations causes large worn fragments to separate out from the sliding surface, thereby, forming a lumpy transfer film [5, 14]. This is also indicated by the size of the wear debris generated for PBT/CNT nanocomposites.

The generation of fine wear debris is known to be associative of increased wear resistance of polymer and its composites [14, 19]. Figure 6 shows SEM micrographs of wear debris of a few samples, representing the trend followed by all the samples, irrespective of the load.

It can be observed here that the size of wear debris becomes smaller at first as the CNT content increases up to 0.3 wt%. This confirms the fact that the CNTs that are getting pulled out of the PBT matrix forms fine wear particles. These fine particles get easily embedded between the peaks and valleys of the counter-face and thereby effectively protect the composite surface from direct contact [14, 15]. On the contrary, the increased wear debris size for composites with higher CNT concentrations indicate that when the CNT agglomerates are pulled out due to the sliding action of counter-face, they tend to tear off large chunks from the matrix as well. This leaves behind voids in the composite surface and leads to the formation of an uneven transfer film, hence, increasing the specific wear rate.

4 Overall Discussion

The friction coefficient and the specific wear rate of PBT matrix reduces with CNT addition, which ascertains the fact that the CNTs are an effective reinforcement for PBT and act as solid lubricants to avoid direct contact between polymer matrix and the counter-face. However, loss of wear resistance at higher CNT concentrations indicate non-
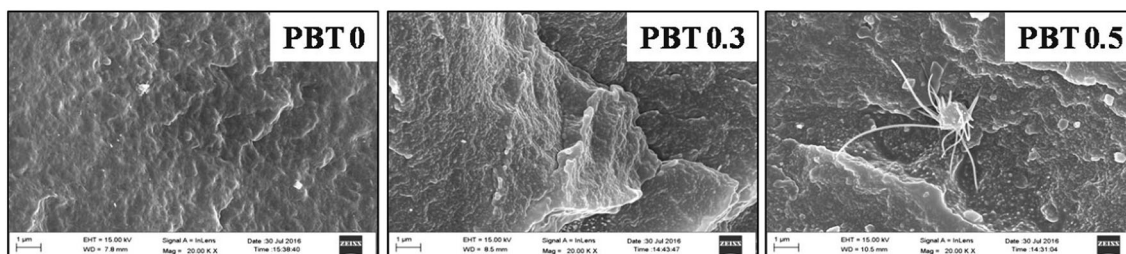

Fig. 4 Morphology of PBT/CNT composites showing state of CNT dispersion
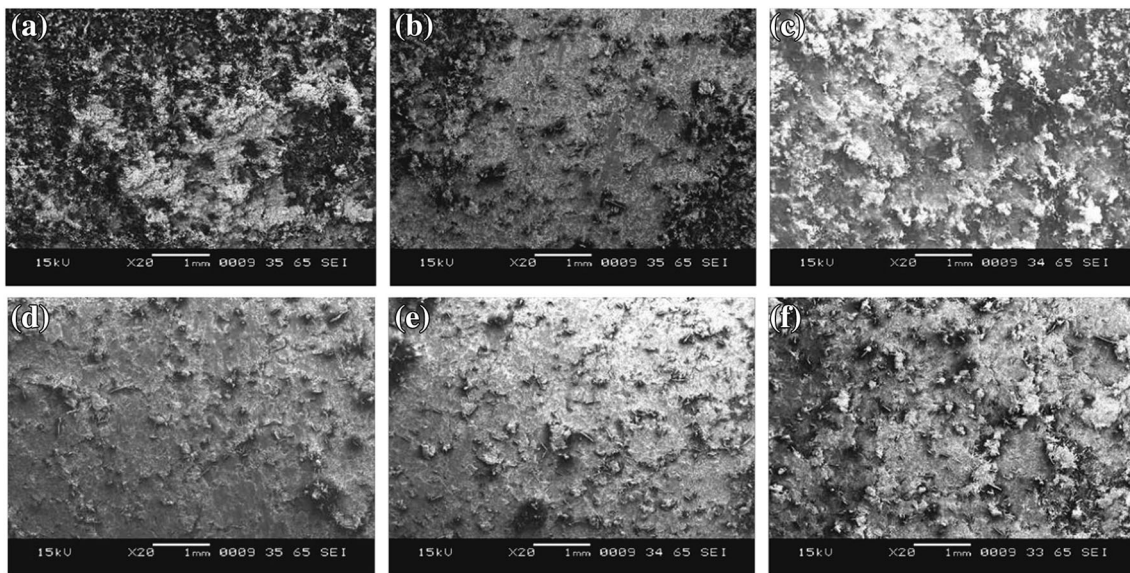
Fig. 5 SEM micrograph of transfer film deposited by **a** PBT 0, **b** PBT 0.3, **c** PBT 0.5 at 20 N load and **d** PBT 0, **e** PBT 0.3, **f** PBT 0.5 at 100 N load
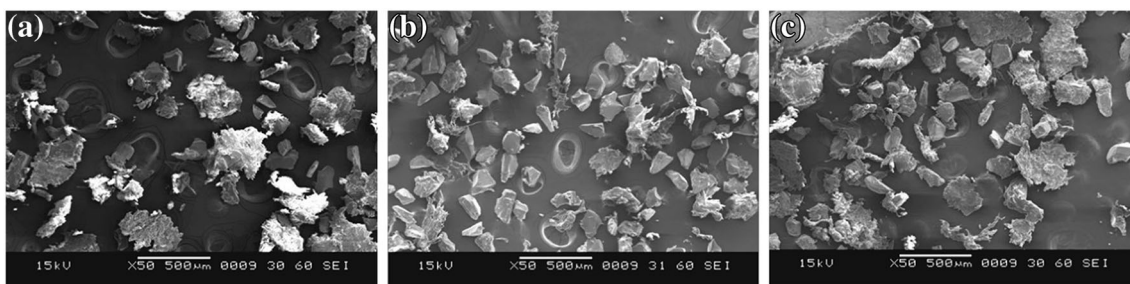

Fig. 6 SEM micrograph of wear debris generated by **a** PBT 0, **b** PBT 0.3 and **c** PBT 0.5 at 100 N load

uniform dispersion of CNTs in PBT matrix, also supported by morphological investigations. With an increase in test load, the friction coefficient of the composites reduces as the decrease in shear strength of material become dominant. On the contrary, a significant rise in the specific wear rate at higher loads confirms that the wear loss is directly proportional to load.

A smooth and uniform transfer film observed after CNT addition in small quantities is responsible for the reduction of wear loss of PBT. But presence of CNT agglomerates at higher CNT concentrations, lead to the formation of thick, lumpy and uneven transfer film that causes the loss of wear resistance, irrespective of the test load. The generation of small wear debris particles and relatively smoother worn out surface for PBT/CNT nanocomposites with low CNT concentrations indicates the dominance of abrasive wear phenomenon. While, formation of large wear debris particles and more damaged surface confirm the action of adhesive wear phenomenon on PBT/CNT nanocomposites at higher CNT concentrations.

5 Conclusions

A systematic investigation of the tribological properties of PBT/CNT nanocomposites with varying CNT content was successfully carried out. The composites with CNT weight percentage of 0.3 gave enhanced wear performance due to the self-lubricating action of CNTs. Moreover, the peeling and scuffing phenomenon observed for virgin PBT was suppressed after CNT addition. Thus, from the results and overall discussion it could be concluded that low CNT content in PBT matrix proved helpful in improving the wear resistance of PBT/CNT nanocomposites.

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