Effect of carbon-nanotube length on friction and wear of polyamide 6,6 nanocomposites

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ABSTRACT

The friction and wear of polyamide 6,6 (PA66) nanocomposites containing 1 wt% of carbon nanotubes (CNTs) with different lengths were studied using a block-on-ring tribometer at different sliding velocities. CNT addition was found to increase storage modulus, loss modulus, and thermal conductivity of the composites, suggesting possible influence to their tribological properties. Tribotest results revealed a substantial effect of the length of CNTs and it was more at elevated temperatures. In the sliding tests performed at temperature below 110 °C the coefficient of friction (COF) tended to be decreased by CNTs addition, while it was slightly increased as the CNT length increased. However, at temperatures beyond 110 °C, the COF increased with the addition of CNTs and increased, even more, with longer CNTs. Wear resistance was also improved by long CNTs, and this improvement was particularly evident at elevated temperatures. TEM investigation of the sliding surface indicated that the improvement of wear resistance and the increased COFs observed at high temperatures could be attributed to the nematic alignment of CNTs along the sliding direction, which was more pronounced with longer CNTs. The marked reinforcing effect of long CNTs was also supported by the morphology of the transfer films and wear debris.

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1. Introduction

Polymer composites strengthened by reinforcing fibers and additives have successfully replaced traditional metal-based machine components during the last decades. Much effort has been made to improve the relatively inferior mechanical properties of monolithic polymers by selecting proper reinforcements and by tailoring the interfacial properties between the reinforcement and the matrix [1–3]. In particular, the tribological properties of the polymers have been improved significantly by intelligent material design with nanosized reinforcements and various sliding components, which had not been considered as a viable alternative to metallic components due to insufficient strength, have been successfully substituted by the polymer composites [4–6].

In order to improve the tribological properties of the polymeric composites, various fibrous reinforcements based on metals, ceramics, and polymers have been examined concerning their mechanical properties, wear resistance, thermal conductivity, electrical conductivity, and surface chemistry. In particular, special attention has been given to the properties of the sliding surfaces that are altered by the size and distribution of the reinforcements in the polymeric matrices. Sung and Suh [7] studied the effect of glass fibers orientation on the tribological properties of polymer-based composites. Kurokawa et al. [8] investigated the strength- and friction-induced noise propensity of the carbon fiber reinforced polyamide 12 (PA12). Zhang et al. [9] examined the effect of carbon fiber length on the wear resistance of epoxy composites. Kim et al. [10] studied the effect of humidity on the tribological properties of short glass fiber reinforced polyamide 6,6 (PA66). Hooke et al. [11] studied the friction and wear of nylon–glass fiber composites concerning the effect of thin interfacial layers on the composites. The main aspect shared by the above studies is the role of the fibrous components in the composites and the emphasis on the importance of the microscopic deformation of the sliding surface with reinforcing fibers.

Development of polymer composites with nano-size reinforcements is also remarkable if we take into account their enhanced material properties compared to the conventional composites [12]. Various reinforcements with different aspect ratios have been employed for the nanocomposites. Among them the improvement of the tribological properties using CNTs attracted much attention due to CNTs’ unusual properties [13,14] in terms of shear and elastic moduli, and thermal conductivity compared to other fibrous reinforcements. Strong influence of CNT dispersion within
The composite on friction and wear was also addressed by Bal and Samal [15], since the agglomeration during the processing and alignment of CNTs on the sliding surface can change tribological properties significantly [16]. Hwang et al. [17] also supported the importance of the CNT dispersion for the improvement of the tribological properties, while various processing techniques for the successful distribution of CNTs in the polymeric matrix were reported elsewhere [16,18]. The role of CNTs on various tribological properties of the friction layer has also been investigated. For instance, Cai et al. [19] studied wear resistance of the polyimide composites reinforced with CNTs and showed that a low friction level and improved wear resistance were achieved in the presence of CNTs. Other authors [20–23] also reported a similar improvement in tribological properties when CNTs were added into polymer matrices. They suggested that the topography of the sliding surface was changed by the presence of CNTs and that the reinforcement on the sliding surface played a crucial role in the tribological properties. However, the effect of the CNT length on the friction and wear of the polymeric composite and the behavior of CNTs on the sliding surface at elevated temperatures have not been fully understood.

In this study, we have investigated the effect of the CNT length on the tribological properties of polymeric composites. This study was in part an effort to replace a metallic worm gear with a polymer composites. Particular attention was given to the behavior of CNTs on the friction layer as a function of CNT length and temperature at sliding interface, while the concentration of CNT was fixed at 1 wt%. Wear debris and distribution of CNTs on the sliding surface were also analyzed to investigate the changes in the wear mechanism induced by the length of CNTs and the temperature.

2. Experiments

The nanocomposite specimens studied in this work were prepared by reinforcing polyamide 6,6 (PA66, KN3311, KOLON Plastics Inc., Korea) with multiwall CNTs of three different lengths (S-CNT, M-CNT, L-CNT; JEIO Ltd.). The amount of CNTs in the composite is set to 1.0 wt%, which is equivalent to 14.9 vol%. The composition of the CNT was determined after a series of preliminary experiments to achieve optimum properties in terms of strength, friction level, and wear rate. The effects of CNT concentration on the properties of polymer composites studied by Yang et al. [24] and Wang et al. [25] also support the results from preliminary experiments. They reported that the best combination of mechanical and tribological properties was found when the polymer composite contains approximately 1.5 wt% of CNT and no further improvement was found beyond 1.5 wt%. The surface of the CNTs was treated with a base fluid to improve fiber opening during mixing. The dimensions of the CNTs used in this study are listed in Table 1 and the SEM micrographs of the studied CNTs are presented in Fig. 1. Mixing was carried out using a twin screw extruder (STS40HA, Korea EM Inc., Korea) operating at 200 rpm and at a temperature that was varied from 270 to 310 °C, from the feed zone to the die, to control the melt viscosity during mixing. The mixture was extruded as pellets for subsequent use in an injection molding machine (SELEX 120E, Korea). The cylinder and mold temperatures during molding were set to 300 and 80 °C, respectively, and injection was carried out at 80 bar. TEM observation revealed that CNTs were evenly distributed in the PA66 matrix.

Friction and wear of the composites were investigated using a block-on-ring type tribometer (BRW140, NeoPlus Inc.). Fig. 2 shows a schematic representation of the tribometer with the configuration of the ring and block specimens. The size of the

Table 1

Dimensions of the carbon nanotubes used in this study.

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<th>S-CNT</th>
<th>M-CNT</th>
<th>L-CNT</th>
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<tr>
<td>Length (μm)</td>
<td>1–3</td>
<td>5–20</td>
<td>25–40</td>
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<td>Diameter (nm)</td>
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Fig. 1. SEM images of carbon nanotubes used in this study before mixing.

Fig. 2. Schematic representation of the block-on-ring tribometer used in this study. A constant normal load was applied to the top of the block specimen.
block specimen (composite) was 16 mm (L) × 10 mm (W) × 5 mm (T) and the size of the ring was 45 mm (O.D.) × 20 mm (I.D.) × 12 mm (W). The ring specimen was made of S45C steel with an initial surface roughness of 0.15 μm. Before the tribotests, block specimens were ground using abrasive paper (#220) wrapped around the ring surface until the contact size was increased to 6 mm. The average surface roughness of the sliding surface of the block specimen was approximately 0.25 μm. The wear test was performed at 200 N and at sliding velocities in the range of 0.05–0.2 m/s. The test for friction and wear data was conducted at least five times at each set of test conditions. The wear rate was calculated as the wear loss divided by friction energy. During the tribotest the temperature of the ring surface was measured by inducing a light point contact of a K-type thermometer on the rotating ring surface. Temperature deviation between a static and a rotating disc was less than 1 °C.

Before and after the tribotests, block and ring surfaces were examined using a laser confocal microscope (VK8710, KEYENCE). Wear particles were collected during the tribotests and their morphology was analyzed using a scanning electron microscope (Hitachi S-4300). The initial distribution of the CNTs in the block specimen and the realignment of the CNTs on the sliding surface after the tribotests were examined using a transmission electron microscope (FEI Tecnai 20, FEI Co.). Thermal conductivity of the composite specimen was measured using a laser flash method (LFA 457, NETZCH, Selb/Bavaria). Dynamic mechanical analysis (DMA Q800, TA Instruments) was also performed to measure storage and loss moduli following the ASTM D4065 procedure.

3. Results and discussion

3.1. Material properties of PA66+CNT composites

Materials properties that affect friction and wear of polymer-based composites, such as dynamic mechanical and thermal properties, were examined before analyzing the tribological properties of the nanocomposites. This is because the friction and wear of polymers and polymer composites are closely related to their phase transition [17,26], viscoelastic behavior [27], and thermal conductivity [17]. In this study the effect of CNT length on the material properties as a function of temperature was examined using different thermal analyses (TA), including dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and laser flash analysis (LFA).

Dynamic mechanical properties were measured up to 140 °C and are shown in Fig. 3. The largest storage modulus was obtained by mixing PA66 with CNTs, indicating that strength was improved by fiber reinforcement. Loss modulus also increased with CNTs due to the restricted molecular movement of PA66 in the presence of CNTs [28]. Glass transition temperatures of the monolithic PA66 and the composite containing CNTs were examined from the tan δ profile as a function of temperature. The peak damping capacity due to glass transition was found near 53 °C and it was approximately the same regardless of the content of CNTs, which indicated that CNTs have a negligible effect on the softening of the PA66 matrix. Melting temperatures were also measured by DSC during heating and cooling processes, and they were

![Fig. 3. Storage (a) and loss (b) moduli of monolithic PA66 and composites with CNTs. (c) Damping capacity (tan δ) was also compared to examine glass transition temperature.](image-url)
approximately 260 °C regardless of the presence of CNTs in the composites (data not shown).

The effect of CNTs on the thermal conductivity of PA66+CNT composites is shown in Fig. 4. It is evident that the thermal conductivity, which is measured by the laser flash method at three different temperatures, increases as a function of the CNT length. The higher thermal conductivity for longer CNTs suggests fast heat dissipation from the sliding surface and improved friction stability. The lower thermal conductivity at higher temperature is attributed to the Brownian motion of polymer chains, which decreases thermal energy transfer.

3.2. Tribological properties of PA66+CNT composites

The effect of CNTs on the friction level of the composites was examined at two different sliding velocities (0.05 and 0.2 m/s) under a load of 200 N. The COF changed as a function of the sliding distance and CNT length, as shown in Fig. 5. At low velocities the temperature of the ring surface increased up to approximately 70 °C, while a higher surface temperature (up to 190 °C) was measured at high velocities. A rapid rise of the COF at the initial stage was found; it was particularly pronounced at elevated temperatures owing to the larger friction heat at higher sliding velocities. This initial rise of the COF can be attributed to the increase of the contact area, as the sliding continues, because of initial adhesion of PA66 to the steel surface. A steady state friction level is observed after the initial stage and it indicates that the frictional force is produced by the sliding between the composites and the friction film present on the steel surface. At elevated temperatures, monolithic PA66 showed friction instability with a large fluctuation of the COF. On the other hand, in general, the composites with CNTs showed better friction stability. The friction

Fig. 4. Thermal conductivity of monolithic PA66 and its composites as a function of CNT length. The conductivity was measured at three different temperatures.

Fig. 5. The coefficient of friction and surface temperature of the ring as a function of sliding distance at two different sliding velocities: (a) 0.05 m/s and (b) 0.2 m/s.

Fig. 6. The average friction coefficient and surface temperature of the ring measured at two different sliding velocities: (a) 0.05 m/s and (b) 0.2 m/s.
level was more stable when L-CNTs were used, suggesting an improved high-temperature resistance.

The average COF, obtained after the initial rise and fall of the friction level, and the surface temperature of the steel ring are plotted in Fig. 6 as a function of the CNT length. At low velocities (Fig. 6(a)) the ring temperature did not change much because of the small amount of heat accumulation at the sliding surface, while the COF decreased when CNT was mixed with the PA66 owing to the contact area occupied by CNTs on the composite surface. The regaining of the friction level by longer CNTs is attributed to the improved reinforcing effect of the long CNTs on the composite surface. While the temperature of the sliding interface was increased because of the high sliding velocities (Fig. 6(b)) the thermal conductivity of the composite played, instead, an important role in determining the tribological properties. This is indeed supported by the lower surface temperature owing to the improved thermal conductivity reported for the composites with longer CNTs. The lower COF of the monolithic PA66 indicates partial melting of PA66 at elevated temperatures. On the other hand, the friction level slightly increased as a consequence of the enhanced thermal conductivity and the improved reinforcement of the composite surface because of the longer CNTs.

Fig. 7. Wear rate of the block specimens plotted as a function of the surface temperature on the ring surface.

The wear rate of the monolithic PA66 and the PA66 composites reinforced with CNTs was examined as a function of temperature, which was controlled by the sliding velocity change from 0.05 to 0.2 m/s. At the initial stage of sliding the friction heat produced at the sliding interface caused a rapid temperature increase, and it was leveled off in a range of temperature from 60 °C up to 173 °C. Fig. 7 shows the wear rate normalized by the sliding distance and normal load. The graph indicates that the wear amount increases as the surface temperature increases and that the increase becomes remarkable at temperatures beyond 110 °C. The pronounced wear rate at elevated temperatures is attributed to the softening of the PA66 asperities at the sliding interface, while comparable wear amounts regardless of CNT length at temperatures below 110 °C indicate that the wear rate is not affected by softening of PA66.

In particular, composites with longer CNTs showed a much lower wear rate at elevated temperatures compared to monolithic PA66 or the composite with shorter CNTs showing less than half of the wear amount observed with L-CNTs. The pronounced reinforcing effect at elevated temperatures indicates a dissimilar wear mechanism when the temperature increases beyond 110 °C. At lower temperatures the wear amount does not rely on a thermally activated process but athermal molecular action plays a more important role, and it is similar regardless of the presence of CNTs in the composites. On the other hand the wear rate at elevated temperature is substantially affected by the length of CNTs in the PA66 composite due to dissimilar thermal conductivity, indicating a wear process based on a transient transfer of wear particles to and from the friction films.

The wear mechanism was further examined by analyzing the morphology of the wear debris collected during the sliding. Fig. 8 shows the micrographs of the wear debris obtained during the sliding at two different velocities. At low temperatures, the shape of the wear debris was flaky and the morphology was similar regardless of the presence of CNTs. The flaky wear debris indicates that the debris is produced by the delamination of the polymer films transferred to the ring surface [29]. A smooth detached surface on one side of the flake supports the delamination mechanism. On the other hand, at high temperatures the shape of the wear debris changed. When PA66 contained no CNTs, the granular debris was observed. This indicates that the partially molten asperities at the sliding interface are attached shortly on

Fig. 8. SEM images of wear debris obtained during the sliding tests using PA66, PA66+S-CNT, and PA66+L-CNT specimens at two different sliding velocities.
Fig. 9. The SEM images of (a) sliding surfaces of block specimens and (b) steel rings after the sliding tests under 200 N and at 0.2 m/s. Arrows indicate the sliding directions.

Fig. 10. TEM images of the sliding surfaces of PA66 composites with CNTs. Surface of the PA66 + S-CNT specimen tested at (a) low and (b) high velocities. Sliding surface of PA66 + L-CNT tested at (c) low and (d) high velocities. The insets in the micrographs show magnified images of the CNTs distributed on the sliding surface. Arrows indicate the sliding directions of the ring against the composite specimens.
the steel surface and are removed by the subsequent deformation due to the relative motion of the asperities on the sliding surfaces. The morphology of the wear debris changed to a roll shape when the composites contained S-CNTs. This is because S-CNTs reinforced the wear debris at elevated temperatures and produced rolls when the softened composite surface was removed, while the bonding of the transferred films was strong enough to remain on the steel surface [30]. Flaky wear particles were observed again when the composite contained L-CNTs. The flaky wear debris appeared partly because of the lower surface temperature due to high thermal conductivity and partly due to the strong reinforce-
ment by L-CNTs, which was supported by the substantial reducti-
on of the wear rate.

Sliding surfaces of the block specimen and the transfer films produced on the ring surface during the sliding at high temperatures are examined and are shown in Fig. 9. Heat-affected surfaces of the block specimen exhibited different morphologies due to different interfacial strengths. Monolithic PA66 showed rough surfaces after sliding, indicating the formation of relatively small granular wear particles. Lumpy ring surfaces observed after the sliding tests also supported the formation of small granular shape of wear debris. When PA66 contains S-CNTs, the sliding interface appears to be reinforced and both the ring and block exhibit smoother sliding surfaces. In this case the surfaces of the block specimen showed narrow strips, which supported the roll formation during the sliding at elevated temperature. PA66 with L-CNT, on the other hand, maintained smooth surfaces after the sliding tests, indicating the effective reinforcement of the heat-affected surface layers of the block specimen by L-CNTs and the development of the uniform transfer layer on the ring surface.

Distribution of the CNTs in the PA66 matrix was examined using a transmission electron microscope. A thin layer was obtained from the sliding surface of a block specimen using a focused ion beam technique. Fig. 10 shows TEM micrographs of the sliding surfaces of the PA66 composites with S-CNTs and L-CNTs after the sliding tests at low and high velocities. In the case of low velocity sliding of PA66 with S-CNTs, the CNTs were randomly distributed and no realignment of the CNTs was observed. However, CNTs were realigned along the sliding direction during the tests at high velocity. This is attributed to deformation of the softened PA66, which induces the CNTs to align themselves along the sliding directions. Realignment of CNTs in the PA66 matrix during the sliding was particularly conspicuous in the case of the composites with L-CNTs. The nematic alignment of the L-CNTs on the sliding surface appears to play an important role in producing the flaky wear debris and in improving wear resistance by reinforcing the sliding surface [31,32]. The low wear rate of PA66 with L-CNTs is, therefore, achieved by the nematic alignment of the CNTs [33], which reinforces the sliding surface, and by increased thermal conductivity, which reduces the temperature at the sliding interface.

4. Conclusion

In this study we have investigated the effect of nanotubes on the tribological properties of PA66 composites. Particular attention was given to the effect of the length of CNTs on the friction, and wear, as well as the associated wear mechanism at elevated temperatures. Results indicated that the reinforcing effect of CNTs in PA66 composites was pronounced in the case of sliding at elevated temperatures and a detailed list of the findings obtained from this study is given below.

1. Storage modulus and thermal conductivity increased when CNTs were added to PA66.

2. The friction coefficient decreased when PA66 contained CNTs and showed a stronger influence of the CNT length at elevated temperatures.

3. Wear rate was rapidly increased at surface temperatures beyond 110 °C and the high-temperature wear was significantly influenced by the length of CNTs.

4. The improved wear resistance of PA66 with CNTs is attributed to the nematic alignment of the CNTs on the sliding surface and the reduction of the surface temperature due to their high thermal conductivity.

References