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Tribological Properties of Nanosized Calcium Carbonate Filled Polyamide 66 Nanocomposites

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Abstract. For the purpose of developing high performance tribomaterials for mechanical sliding parts such as gears, bearings and so on, nanosized calcium carbonate (nano-$CaCO_3$) filled polyamide 66 (PA66) nanocomposites were investigated. The nano-$CaCO_3$ was a kind of precipitated (colloid typed) $CaCO_3$, and its average particle size was 40, 80 and 150 nm. Surface treatment was performed by fatty acid on the nano-$CaCO_3$ and its volume fraction in the nanocomposite was varied from 1 to 20vol.%. These nanocomposites were melt-mixed by a twin screw extruder and injection-molded. Tribological properties were measured by two types of sliding wear testers such as ring-on-plate type and ball-on-plate type one under dry condition. The counterface, worn surface and wear debris were observed by digital microscope and scanning electron microscope. It was found that the nano-$CaCO_3$ has a good effect on the tribological properties, although the effect on the frictional coefficient and specific wear rate is differed by the volume fraction and the type of sliding wear modes. This is attributed to the change of wear mechanisms, which is the change of form of the transfer films on the counterface and the size of wear debris. It follows from these results that PA66/nano-$CaCO_3$ nanocomposites may be possible to be the high performance tribomaterials.

Keywords: Nanosized calcium carbonate, Polymer nanocomposites, Tribological properties, Polyamide 66
PACS: 81.05.Qk, 81.40.Pq, 82.35.Np

INTRODUCTION

In recent years, polymer nanocomposites such as nanosized filler filled thermoplastic composites are attracting considerable attention from industry, because they may offer unique mechanical and physical properties that are not readily obtainable from conventional particulate filled ones. Among them, nanosized calcium carbonate (nano-$CaCO_3$) has been of great research interest[1)-5)]. In general, conventional typed $CaCO_3$, of which size varies from 1 to 50μm, has been used to reduce the cost of matrix polymer. On the other hand, nano-$CaCO_3$ is available for toughening polymer because of the dramatic increase in the interface between filler and polymer. Many reports have been presented on the preparation, characterization, rheological, and mechanical properties of nano-$CaCO_3$ filled polymer composites based on the commodity plastics, for example, polypropylene (PP), polyethylene (PE) and poly (vinyl chloride)(PVC)[1)-5)]. However, not many have been done on nano-$CaCO_3$ filled nanocomposites based on engineering plastic such as polyamide (PA), polyacetal (POM) and polybutylene terephthalate (PBT), which are widely used in the mechanical engineering applications, and very few, if any, on tribomaterials, which are used for mechanical sliding parts such as gears, bearings, and seals, of these nano-$CaCO_3$ filled nanocomposites based on engineering plastic. In our previous works, we investigated the mechanical and tribological properties of precipitated (colloid type) $CaCO_3$ filled polyamide composites (PA6/$CaCO_3$ and PA66/$CaCO_3$ composites) for tribomaterials[6), 7)]. It was found that the mechanical and tribological properties of PA6/$CaCO_3$ and PA66/$CaCO_3$ composites are improved by the surface treatment of $CaCO_3$, and these composites show the different tendencies according to the type of surface treatment. However, in our knowledge, there are no experimental data on the effect of the type (particle size) of nano-$CaCO_3$ on the tribological properties of these nanocomposites based on engineering plastic.

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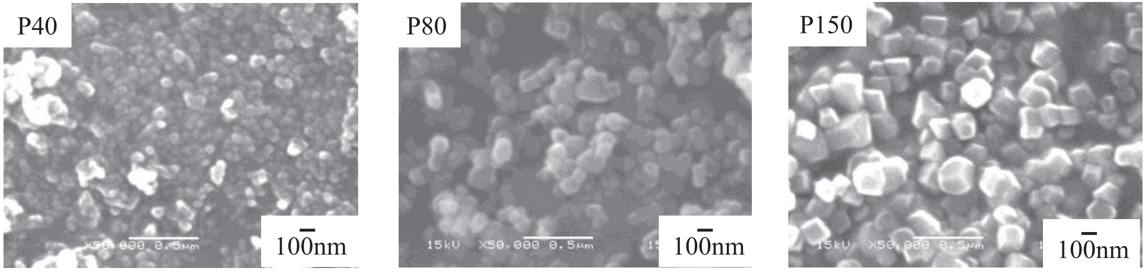
For the purpose of developing the new tribomaterials, we investigated the tribological properties of nano-$CaCO_3$ filled PA66 nanocomposites experimental in this study.

EXPERIMENTAL

The materials used in this study were three types of nanosized calcium carbonate filled polyamide 66 composites (PA66/nano-$CaCO_3$ nanocomposites). Polyamide 66 (PA66, Zytel 101L, Du Pont Ltd.) was used as the matrix polymer. The nanosized calcium carbonate (nano-$CaCO_3$, Shiraishi Kogyo Ltd., Japan) was a kind of precipitated (colloid type) $CaCO_3$ and its average particle size was 40 (P40), 80 (P80) and 150nm (P150). Surface treatment was performed by fatty acid on nano-$CaCO_3$ and its volume fraction in the nanocomposite was varied from 1 to 20vol.% SEM photographs of these nano-$CaCO_3$s are shown in Fig. 1 All the components which were dried for 12h at 90°C in vacuum oven were dry blended in the small plastic bottle, subsequently melt mixed at 85rpm and 270°C on a twin screw extruder (TEX-30, Japan Steel Works, Ltd., Japan). After mixing, the extruded strands of various PA66/nano-$CaCO_3$ composites were cut by a pelletizer, and were dried again at 90°C for 12h in vacuum oven. Various shaped samples for mechanical and tribological properties testing were injection-molded (NS20-A, Nissei Plastic Industrial, Japan). The molding conditions were as follows: cylinder temperatures of 270°C, mold (cavity) temperature of 100°C and the injection rate of $6cm^3/s$. Tribological properties were measured by two types of sliding wear testers such as ring-on-plate type and ball-on-plate type one under dry condition. The ring-on-plate type sliding wear testing by the tester (EFM-3-EN, Orientec, Co. Ltd., Japan) was conducted using plate specimens (30mm x 30mm x 3mm) at room temperature, normal load of 100N, sliding speed of 0.5m/s, and sliding distance of 3,000m in accordance with JIS K 7218a. In this testing, the type of contact is a full contact between the test specimen and counterpart. A carbon steel (S45C) ring with the surface finished by No.800 polishing paper was used as a counterparts. The tribological properties were evaluated by frictional coefficient μ and specific wear rate V_s. The specific wear rate is calculated by the weight of sample before and after testing. On the other hand, the ball-on-plate type sliding wear testing by the tester (HEIDON Type20, Shinto Scientific Co., Ltd., Japan) was conducted using plate specimens (30mm x 30mm x 3mm) at room temperature, normal load of 20N, sliding speed of 30mm/s and sliding distance of 200m. In this testing, the type of contact is an intermittent contact between test specimen and counterpart (ball). A high carbon-chromium bearing steel (SUJ2) ball (ϕ2.5mm) with the surface finished by No.800 polishing paper was used as a counterpart. The tribological properties were evaluated by frictional coefficient μ, wear loss V and specific wear rate V_s. The wear loss and specific wear rate is calculated by the height of sample measured by laser displacement sensor. The transfer film on the counterface, worn surface and wear debris were observed by scanning electron microscope (SEM, VE-8800S Keyence Co. and JSM-6360LA. JEOL Ltd., Japan).



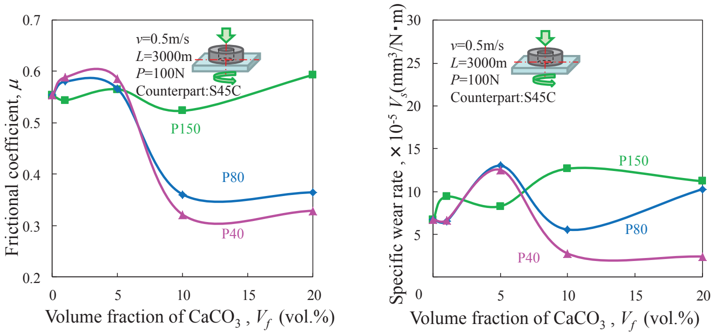
(a) P40 (b) P80 (c) P150

FIGURE 1. SEM photographs of various nano-$CaCO_3$ (×50000).

RESULTS AND DISCUSSION

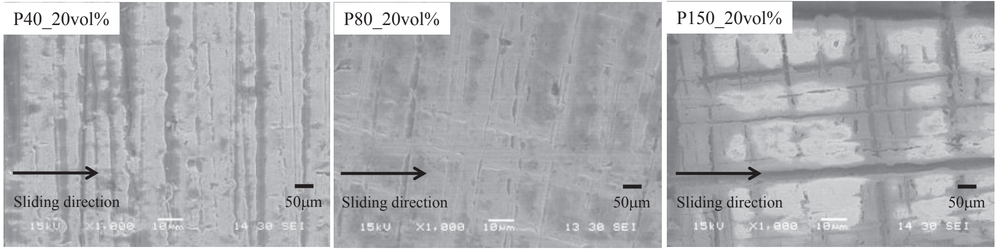
First, the tribological properties of various nanosized calcium carbonate (nano-$CaCO_3$) filled polyamide 66 (PA66) nanocomposites (PA66/nano-$CaCO_3$ nanocomposites) by ring-on-plate type sliding wear testing under dry condition are discussed. Fig. 2(a) and Fig. 2(b) show the influence of volume fraction of nano-$CaCO_3$ V_f on the frictional coefficient μ and specific wear rate V_s of PA66/nano-$CaCO_3$ composites, respectively. μ of all PA66/nano-$CaCO_3$ nanocomposites in the low V_f content less than 5vol.% has the almost same value, however μs in the high V_f content more than 10vol.% show the different behavior according to the type of the nano-$CaCO_3$. Although μ of P150 filled composite seems to be not highly influenced by V_f, μs of P40 and P80 filled ones decrease abruptly in the region of 5vol.% and 10vol.%. On the other hand, the influence of V_f on V_s has complex behavior according to the type of nano-$CaCO_3$. V_s of P40 and P80 filled composites shows the similar V_f dependence expect of high V_f

content (20vol.%) although V_s of P150 filled one increases gradually with increasing V_f. These results may be attributed to the change in the mode of wear mechanism by the type and volume fraction of nano-$CaCO_3$. This is because the tribological behavior of polymer composites and polymer nanocomposites are strongly influenced by their ability to form a transfer film on the counterface, the wear debris and the worn surface state of the materials, it is essential to observe these factors for understanding the mechanisms of their tribological properties[8),9)]. Fig. 3 presents SEM photographs on the surface of counterface after sliding wear testing by the ring-on-plate type sliding wear tester against various PA66/nano-$CaCO_3$ nanocomposites filled with high nano-$CaCO_3$ content (V_f=20vol.%): P40 (Fig. 3(a)), P80 (Fig. 3(b)) and P150 (Fig. 3(c)). The morphologies on the counterfaces after sliding wear test of all PA66/nano-$CaCO_3$ nanocomposites show the thin transfer films with shallow grooves in the direction of orthogonal to sliding direction overall. In particular, the thickness of transfer film increases with increasing the size of nano-$CaCO_3$ in the following order: P40<P80<P150. Fig. 4 shows SEM photographs of the wear debris after the ring-on-plate type sliding wear test of various PA66/nano-$CaCO_3$ nanocomposites with high nano-$CaCO_3$ content (20vol.%) against S45C ring: P40 (Fig. 4(a)), P80 (Fig. 4(b)) and P150 (Fig. 4(c)). The size of wear debris increases with increasing the size of nano-$CaCO_3$. The shape of wear debris changes with the size of nano-$CaCO_3$: first, those of P40 (Fig. 4(a)) are small granular and filamentary (roll) particles. Second, those of P80 (Fig. 4(b)) are long and thick rectangle particles. Third, those of P150 are big and thick granular particles. The tendencies of tribological properties mentioned above are thought to be due to the change of the mechanical properties and the internal structure such as the dispersibility of nano-$CaCO_3$ in the nanocomposites.



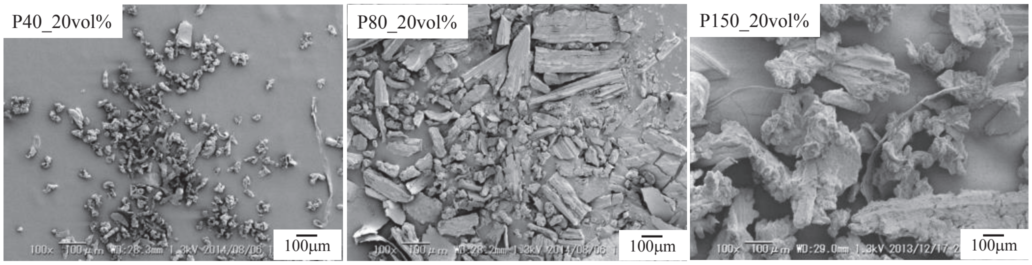
(a) Frictional coefficient (b) Specific wear rate

FIGURE 2. Influence of nano-$CaCO_3$ content on the tribological properties of PA66/nano-$CaCO_3$ nanocomposites by ring-on-plate type sliding wear test



(a) P40 (b) P80 (c) P150

FIGURE 3. SEM photographs of counterface of various PA66/nano-$CaCO_3$ nanocomposites by ring-on-plate type sliding wear test (x1000)



(a) P40 (b) P80 (c) P150

FIGURE 4. SEM photographs of wear debris of various PA66/nano-$CaCO_3$ nanocomposites against S45C by ring-on-plate type sliding wear test (x100)

Next, the influence of the size of nano-$CaCO_3$ on the tribological properties of PA66/nano-$CaCO_3$ nanocomposites was evaluated by ball-on-plate type sliding wear testing. Fig. 5 shows the relationship between the specific wear rate V_s and frictional coefficient μ of PA66/nano-$CaCO_3$ nanocomposites with high nano-$CaCO_3$ content (20vol.%). μ and V_s of PA66/nano-$CaCO_3$ nanocomposites decrease with decreasing the size of nano-$CaCO_3$. These results may be also attributed to the change in the mode of wear mechanisms by the size of nano-$CaCO_3$. Fig. 6 shows the image of digital micro-scope photographs of the counterface of bearing steel (SUJ2) ball as counterpart after the ball-on-plate type sliding wear testing of various PA66/nano-$CaCO_3$ nanocomposites with high nano-$CaCO_3$ content (20vol.%). The counterface of PA66/nano-$CaCO_3$ nanocomposites shows the different rough frictional surfaces according with the size of nano-$CaCO_3$. That of P40 shows the finely rough surface with shallow grooves parallel to sliding direction. On the other hand, that of P80 and P150 has the rough, wide and deep wounds on the bearing steel. In short, the larger the sizes of nano-$CaCO_3$ are, the rougher the roughness of counterface is. Fig. 7 shows SEM photographs of the wear debris after the ball-on-plate type sliding wear testing of various PA66/nano-$CaCO_3$ nanocomposites with high nano-$CaCO_3$ content (20vol.%) against SUJ2 ball. The size and the shape of wear debris change with the size of nano-$CaCO_3$, and these are big and thick flaky particles in the following order: P40<P80<P150.That is, the smaller the roughness of counterface and the sizes of wear debris are, the better the tribological properties such as frictional coefficient and specific wear rate become. These indicate that the roughness of counterface and the sizes of wear debris are closely related with the tribological properties in the intermittent contact wear mode (ball-on-plate type sliding wear test).

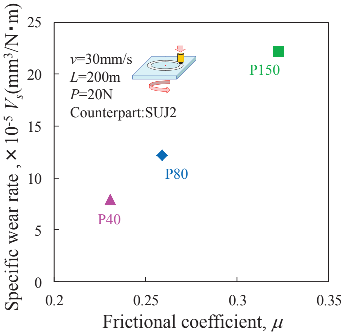
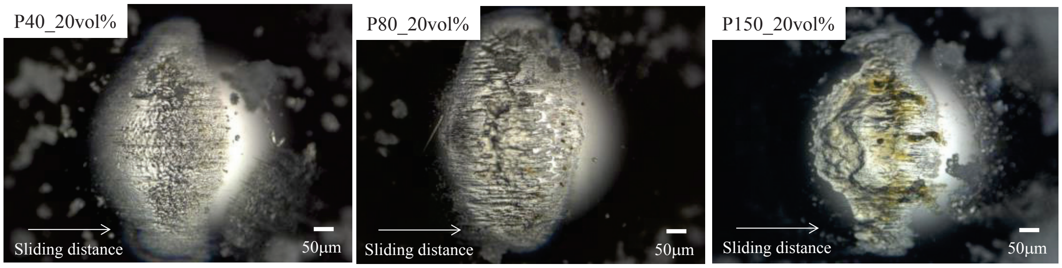
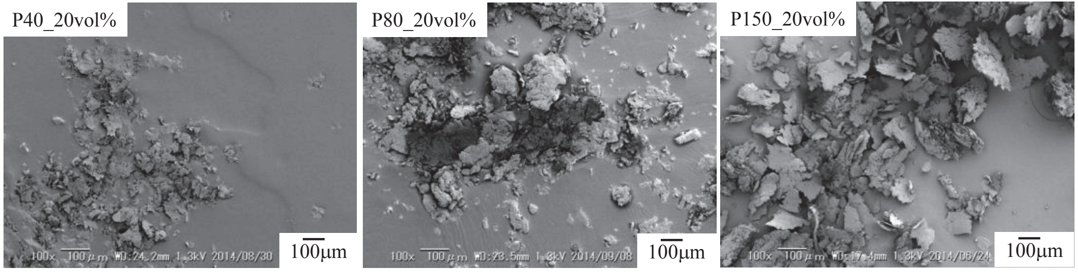


FIGURE 5. Influence of nano-$CaCO_3$ content on the tribological properties of PA66/nano-$CaCO_3$ nanocomposites by ball-on-plate type sliding wear test



(a) P40 (b) P80 (c) P150

FIGURE 6. The image of microscope photographs of counterface of various PA66/nano-$CaCO_3$ nanocomposites by ball-on-plate type sliding wear test(x300)



(a) P40 (b) P80 (c) P150

FIGURE 7. SEM photographs of wear debris of various PA66/nano-$CaCO_3$ nanocomposites by ball-on-plate type sliding wear test against SUJ2 (x100)

CONCLUSION

For the purpose of developing the new tribomaterials, we investigate the tribological properties of nano-$CaCO_3$ filled PA66 nanocomposites experimental in this study. It was found that nano-$CaCO_3$ has a good effect on the tribological properties, although the effect on the frictional coefficient and specific wear rate is differed by the volume fraction and the sliding wear modes. The smaller the sizes of nano-$CaCO_3$ are, the better the tribological properties becomes. This is attributed to the change of wear mechanisms, which is the change of form of the transfer films on the counterface and the size of wear debris. In particular, P40, which the size of nano-$CaCO_3$ is 40nm, is the effective for modifying the tribological properties of PA66. It follows from these results that PA66/nano-$CaCO_3$ nanocomposites may be possible to be the high performance tribomaterials.

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