

Tribological investigation of the effects of particle size, loading and crystallinity on poly(ethylene) terephthalate nanocomposites

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Abstract

The friction and wear properties of poly(ethylene) terephthalate (PET) filled with alumina nanoparticles were studied. The test matrix varied particle size, loading and crystallinity to study the coupled effects on the tribological properties of PET-based nanocomposites. The nanocomposite samples were tested in dry sliding against a steel counterface. The wear rate ranged from 2×10^{-6} to 53×10^{-6} mm³/Nm and the friction coefficient ranged from 0.21 to 0.41. Crystallinity was found to be a function of the processing conditions as well as the particle size and loading, while tribological properties were affected by crystallinity, filler size and loading. Wear rate and friction coefficient were lowest at optimal loadings that ranged from 0.1 to 10 depending on the crystallinity and particle size. Wear rate decreased monotonically with decreasing particle size and decreasing crystallinity at any loading in the range tested.

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1. Introduction

Polymeric nanocomposites continue to show unique tribological behaviors, with previous studies showing that the addition of nanoparticles can provide significant improvements in wear resistance [1–9] and in some cases a reduction in the friction coefficient. Three mechanisms have been proposed: (a) change in mechanical properties (modulus, strength and toughness), (b) change in morphology of the polymer (molecular weight, cross-link density for thermosets, crystallinity for semi-crystalline polymers), and (c) a direct effect of nanoparticles on the wear mechanism (e.g. improved adhesion of the transfer film). This study provides insight into the improved tribology of nanoscale alumina filled PET by separating the effects of crystallinity and nanoparticles, and by investigating the transfer films.

Our prior work [10] showed that the addition of 38 nm alumina nanoparticles to PET resulted in an optimum filler content of about 2 wt.% which provided a 50% reduction in wear rate and a 10% reduction in coefficient of friction. The results showed that the nanoparticles created a more adherent transfer film. In addition, through the use of iso-crystalline samples, it became clear that the improvements in wear rate were not entirely due to changes in crystallinity. The nanoparticles had an independent effect on the wear rate. This paper elaborates on those results showing the effect of particle size on the tribological behavior, and sheds light on the mechanism leading to more strongly adhered transfer films.

2. Experimental methods

Poly(ethylene) terephthalate (Grade: Crystar 3939) was obtained as pellets from DuPont. Alumina nanoparticles (average sizes: 17, 38 and 45 nm) were supplied by Nanophase Technologies Corporation. The polymer and nanoparticles were dried at 150 °C overnight in a vacuum oven prior to blending the composite. The composites were prepared by melt mixing the polymer pellets with the nanoparticles under an inert

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Table 1
Summary of tribological results for samples quenched and annealed under nominally identical conditions

Sample	Filler diameter (nm)	Filler loading (wt.%)	Wear rate (mm ³ /Nm)	Friction coefficient
1	N/A	0	17.5×10^{-6}	0.33
2	17	0.1	16.3×10^{-6}	0.29
3	17	0.5	11.1×10^{-6}	0.30
4	17	1	9.1×10^{-6}	0.31
5	17	2	9.4×10^{-6}	0.33
6	17	5	12.6×10^{-6}	0.39
7	38	1	12.9×10^{-6}	0.32
8	38	2	9.5×10^{-6}	0.30
9	38	5	16.3×10^{-6}	0.35
10	38	10	52.8×10^{-6}	0.37
11	45	1	13.2×10^{-6}	0.33
12	45	2	12.6×10^{-6}	0.31
13	45	5	27.0×10^{-6}	0.30

Variables are filler size and loading. Crystallinity was not controlled.

atmosphere in a Buehler batch melt mixer at 260 °C and a screw speed of 50 rpm. As a control, the PET pellets alone were also mixed under the same conditions. Measurement of the intrinsic viscosity of unfilled polymer before and after the mixing process suggests that the molecular weight did not drop as a result of processing.

Samples for wear tests were prepared by compression molding to dimensions of 6.3 mm × 6.3 mm × 12.7 mm. Prior to molding, the composite (and neat) material obtained from melt mixing was cryogenically frozen in liquid nitrogen, smashed with a BF hammer, and dried in a vacuum oven at 150 °C. The quenched and annealed samples were prepared by heating the powders in the mold to 290 °C under pressure for 5 min and then quickly cooled while still under pressure. The samples were then annealed at 120 °C in vacuum for 2 h to develop the crystal structure.

To prepare samples of equal crystallinity (iso-crystalline), the samples were taken to melt under pressure in the mold and cooled down at specific cooling rates determined from a crystallization kinetics study. Three crystallinity levels (20, 30 and 40%) were studied. The crystallinity of each sample was measured using a Mettler-Toledo 822e differential scanning calorimeter (DSC). None of the samples had more than 2% variation from the nominal value.

Wear and friction tests were conducted on a custom linear reciprocating tribometer. This tribometer with detailed uncertainty analyses for friction coefficient and wear rate are discussed in detail in Schmitz et al. [11,12]. Briefly, the sample is pneumatically loaded via electro-pneumatic valves, a pneumatic cylinder and a linear thruster, against a steel counterface. The pin sample is mounted directly to a six-channel load cell which reacts to all forces and moments on the sample. The steel counterface is mounted directly below the pin sample on a reciprocating linear table driven by a stepper motor. The attached computer data acquisition system monitors the forces and displacements continuously. Tests were conducted on 347 stainless steel counterfaces that were sanded with 600 grit paper to an average roughness of $R_a = 0.1\text{--}0.2 \mu\text{m}$; additional details of the experimental procedure can be found in Bhimaraj et al. [10] The quenched and annealed samples were tested with a normal force

of 340 N (8.5 MPa), while the iso-crystalline samples were tested at a lower load of 250 N (6.3 MPa) due to the reduced yield stress of the 20% crystalline samples. The mass loss due to wear was measured and wear rates are reported from single point observations of volume loss (mass loss/density: mm³) per load (N) per sliding distance (m), and the coefficient of friction is an average value over the entire test. The crystallinity of the nanocomposite was calculated by taking the ratio of the measured heat of fusion to the theoretically calculated heat of fusion of completely crystalline PET of the same mass.

3. Results

Samples of varying filler size and loading were quenched and annealed under identical conditions and therefore have uncontrolled nanoparticle induced crystallinities (the results for the samples in this matrix are listed in Table 1). The wear rate is plotted versus filler wt.% in Fig. 1 for alumina–PET nanocomposites with 17, 38 and 45 nm average alumina diameter. The 17 nm particles reduced the wear rate of PET by 48% at 1 wt.% loading, the 38 nm particles reduced the wear rate of PET by 46% at 2 wt.%

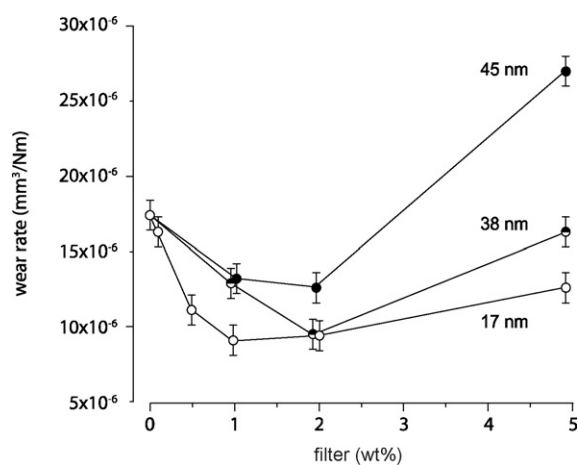


Fig. 1. Wear rate plotted vs. filler wt.% for alumina–PET nanocomposites with three filler sizes. Samples are quenched and annealed; crystalline fraction is not controlled.

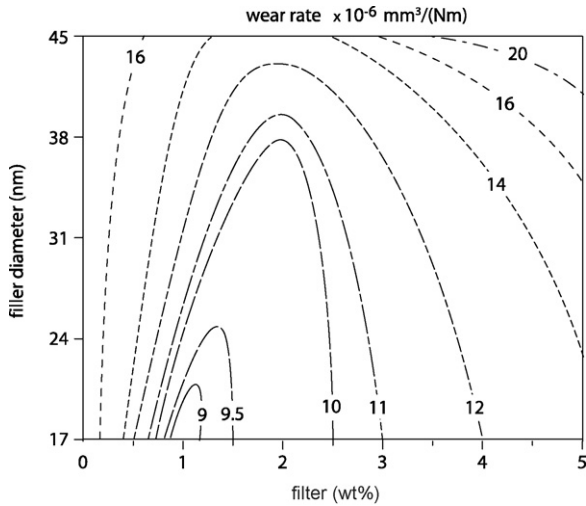


Fig. 2. Contour plot of wear rate vs. filler wt.% and filler diameter. Samples are quenched and annealed; crystalline fraction is not controlled.

loading, and the 45 nm particles reduced the wear rate of PET by 28% at 2 wt.% loading. In all cases wear rate is lowest with 1–2 wt.% filler loading for the compositions tested. Contours of constant wear rate are plotted versus filler size and loading in Fig. 2 to facilitate the visualization of trends (these contour plots are created from 12 data points). For any given loading, as filler size increases, wear rate increases. The optimum loading tends to increase with increased filler size.

Friction coefficient is plotted versus filler wt.% in Fig. 3 for alumina–PET nanocomposites with 17, 38 and 45 nm mean alumina diameter. The 17 nm particles reduced the friction coefficient of PET by 12% at 0.1 wt.% loading, the 38 nm particles reduced the friction coefficient of PET by 9% at 2 wt.% loading, and the 45 nm particles reduced the friction coefficient of PET by 9% at 10 wt.% loading. Contours of constant friction coefficient are plotted versus filler size and loading in Fig. 4 to facilitate the visualization of trends, and are created from 12 data points.

In order to isolate the effects of the nanoparticles and crystallinity, iso-crystalline nanocomposite samples of 20, 30 and

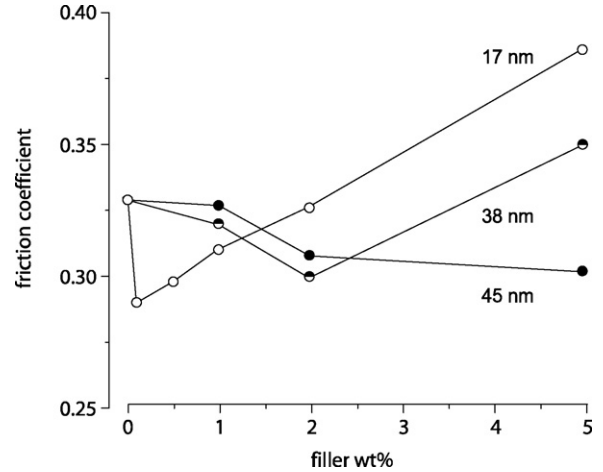


Fig. 3. Friction coefficient plotted vs. filler wt.% for alumina–PET nanocomposites with three filler sizes. Samples are quenched and annealed; crystalline fraction is not controlled.

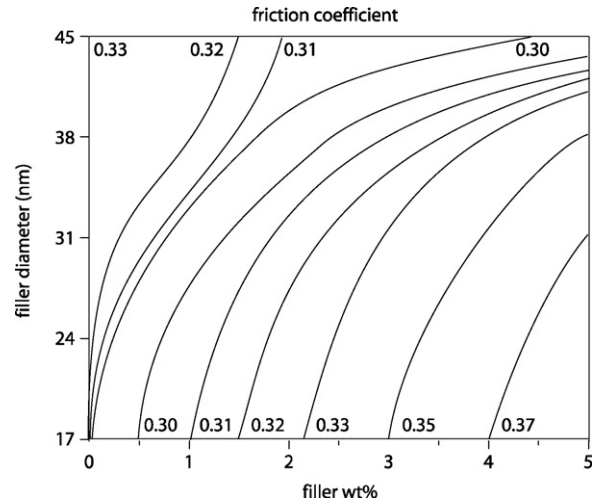


Fig. 4. Contour plot of friction coefficient vs. filler wt.% and filler diameter. Samples are quenched and annealed; crystalline fraction is not controlled.

Table 2
Summary of results for 38 nm alumina filled iso-crystalline samples

Sample	Crystallinity (%)	Filler loading (wt.%)	Wear rate (mm ³ /Nm)	Friction coefficient
14	20	0	4.6 × 10 ⁻⁶	0.36
15	20	1	1.9 × 10 ⁻⁶	0.31
16	20	2	2.9 × 10 ⁻⁶	0.35
17	20	3	2.4 × 10 ⁻⁶	0.41
18	20	5	2.0 × 10 ⁻⁶	0.33
19	30	0	6.7 × 10 ⁻⁶	0.23
20	30	1	2.3 × 10 ⁻⁶	0.26
21	30	2	5.0 × 10 ⁻⁶	0.25
22	30	5	5.5 × 10 ⁻⁶	0.26
23	30	10	9.8 × 10 ⁻⁶	0.25
24	40	0	10.0 × 10 ⁻⁶	0.21
25	40	1	9.3 × 10 ⁻⁶	0.27
26	40	2	4.3 × 10 ⁻⁶	0.31
27	40	3	5.7 × 10 ⁻⁶	0.37
28	40	5	6.0 × 10 ⁻⁶	0.33

Crystallinities were observed to vary less than 2% from the nominal value in all cases. Crystallinity and loading are varied.

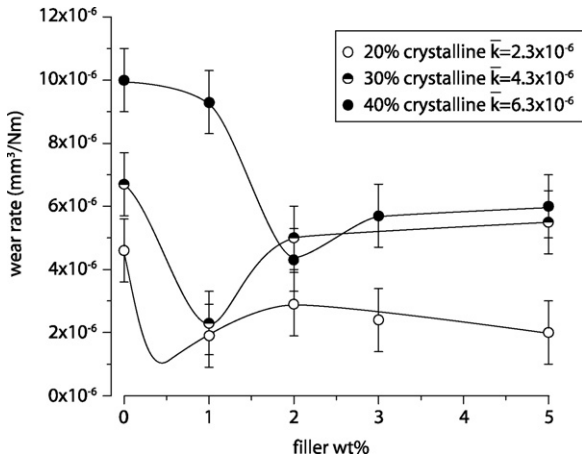


Fig. 5. Wear rate plotted vs. filler wt.% for iso-crystalline alumina–PET nanocomposites. Alumina filler is 38 nm in diameter on average. Crystallinity is controlled to within 2% of the nominal value.

40% crystallinity were created and tested with various nanoparticle loadings. Table 2 shows the results for all of the samples tested in this matrix. Wear rate is plotted versus filler loading for nanocomposite samples having crystallinities of 20, 30 and 40% in Fig. 5. The wear rate of the 20% crystalline unfilled PET sample was 50% less than that of the 40% crystalline unfilled PET sample. Fig. 5 also demonstrates an effect of the nanoparticles that is independent of crystallinity. At 40% crystallinity, the wear rate is reduced 57% with 2 wt.% 38 nm alumina. At 30% crystallinity, the wear rate is reduced 66% with 1 wt.% 38 nm alumina. At 20% crystallinity, the wear rate is reduced 59% with 1 wt.% 38 nm alumina. Contours of constant wear rate are plotted versus filler loading and crystallinity in Fig. 6. The optimum loading for reduced wear rate tends to increase slightly with increasing crystallinity and in all cases there is an optimum loading between 0 and 3 wt.%. At a given loading, as crystallinity increases, wear rate increases. Friction coefficient is

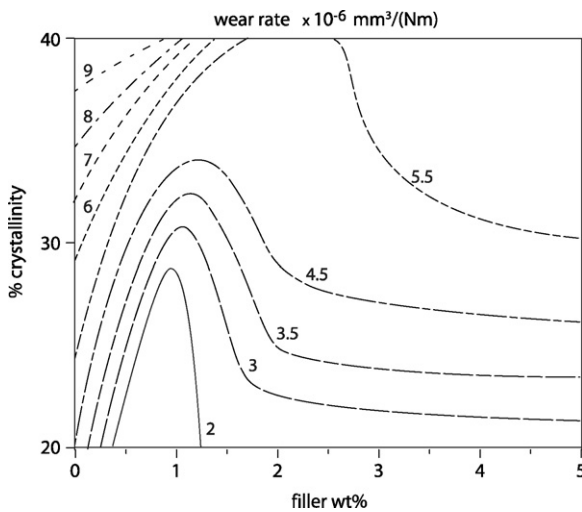


Fig. 6. Contour plot of wear rate vs. filler wt.% and crystalline fraction. Alumina filler is 38 nm in diameter on average. Crystallinity is controlled to within 2% of the nominal value.

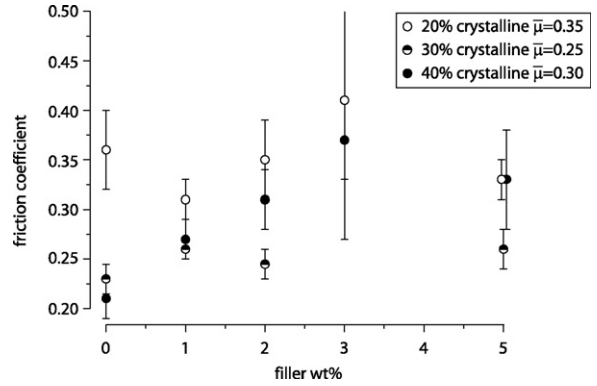


Fig. 7. Friction coefficient plotted vs. filler wt.% for iso-crystalline alumina–PET nanocomposites. Alumina filler is 38 nm in diameter on average. Crystallinity is controlled to within 2% of the nominal value.

plotted versus filler wt.% for 20, 30 and 40% crystalline samples in Fig. 7.

4. Discussion

There are a number of hypotheses regarding the mechanisms for reduced wear and friction in filled polymer systems, including various models based on rule-of-mixtures of tribological behaviors [13]. The role of transfer films in reducing wear has led to theories that wear reductions are due to increased adhesive strength of the protective films [14]. While there is no current consensus on any one theory, there are two features which typically accompany low friction and wear; small wear debris and uniform transfer films. This led to speculation by Bahadur and Tabor that the fine wear debris, and regulation of the wear debris size is responsible for the uniform transfer films [15]. Several aspects of these transfer films were investigated to clarify their role in this system.

The transfer films of the 30% crystallinity samples were examined using secondary electron microscopy and the images were analyzed to estimate the transfer film coverage. Fig. 8 shows the analysis method and transfer film coverage plotted versus filler wt.%. The unfilled transfer film is patchy, but as particle loading increases the coverage increases.

As previously described, the tenacity of the film adhesion is thought to be one mechanism of increasing wear resistance. The polar component of surface energy of a polymer has been shown to promote adhesion to steel [16]. The polar hydroxyl groups on the surfaces of the alumina nanoparticles were hypothesized to increase the polar component and possibly facilitate transfer to the steel. Contact angle measurements with water (H₂O) and diiodomethane (CH₂I₂) were made to calculate surface energies of the 30% crystallinity samples (Fig. 9 shows the dispersive and polar components). The polar component increases by more than 100% with 10 wt.% nanoparticle loading.

Lap shear tests were performed on quenched and slow cooled samples of various particle loadings. The load at adhesive failure is plotted versus filler wt.% for crystalline and amorphous samples in Fig. 10. The amorphous samples have 80% higher adhesive strength than the crystalline samples, which may

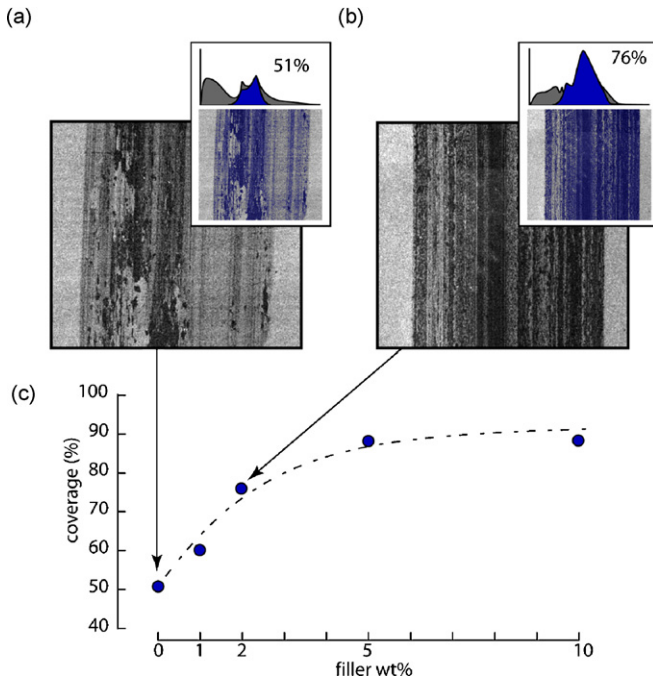


Fig. 8. Secondary electron analysis of transfer film coverage for 30% iso-crystalline samples. (a) Unfilled PET, (b) 2 wt.% 38 nm alumina filled PET, and (c) transfer film coverage plotted vs. filler wt.%.

explain the increased transfer film uniformity and the trend of reduced wear with decreased crystallinity.

The presence of the optimum loading is clear in wear rate measurements, but does not appear in transfer film coverage measurements. Consistent with Bahadur and Tabor's theory on the role of fillers [15], which contends that smaller wear debris reduces wear rates, the nanoparticles used in this study are thought to have two primary functions in the composite; to nucleate crystallization during processing, and to deflect cracks, compartmentalizing damage within encapsulated regions. In

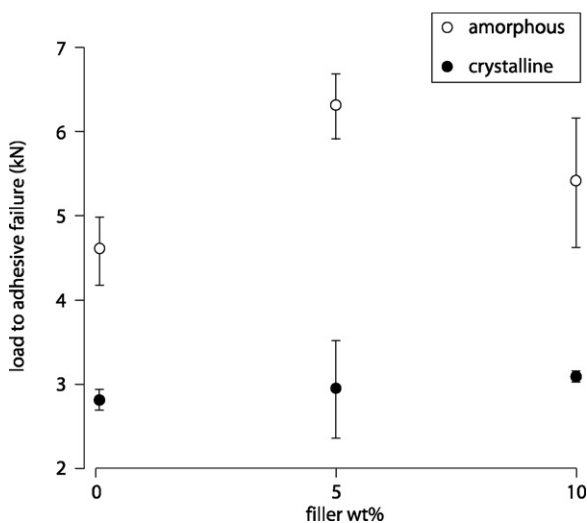


Fig. 9. Results of lap shear tests for rapid quenched (amorphous) and slow cooled (crystalline) samples. Load at adhesive failure is plotted vs. filler content for nominally identical tests.

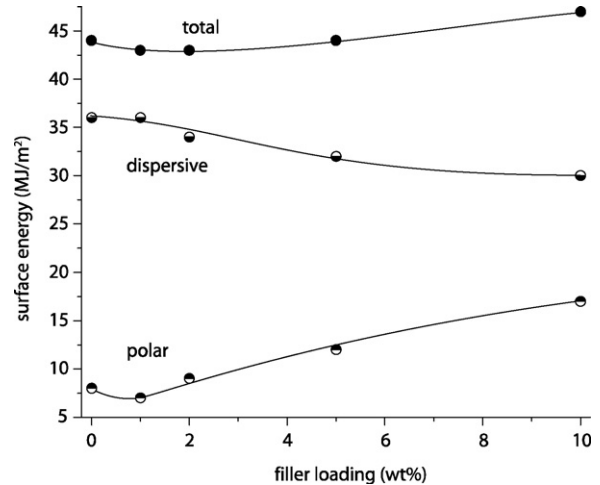


Fig. 10. Results of surface energy measurements for 30% iso-crystalline samples. Surface energy is plotted vs. filler wt.%.

either case, it is logical that smaller particles outperform larger particles—at a given loading smaller particles increase both the number of nucleation sites and surface area available for crack deflection. There is a limit to the effectiveness of nanoparticles, which is thought to be related to dispersion.

As the crystallinity of the sample increases, toughness, and more specifically, ductility are reduced, reducing the ability of the surface to accommodate the impacts and high strain rate events that typically occur in dry sliding. The improved fracture toughness of the unfilled 20% crystallinity sample over the 10 wt.% filled 40% crystallinity sample must have been sufficient to overcome the detrimental effects of a thicker, patchier transfer film.

5. Conclusions

- (1) Smaller particles were found to be more effective in reducing wear rate and friction coefficient than larger particles. For 17 nm alumina, wear rate was decreased by 48% at 1 wt.% loading, and friction coefficient was reduced by 12% at 0.1 wt.% loading. For 45 nm alumina, wear rate was reduced by 28% at 2 wt.% loading, and friction coefficient was reduced by 9% at 10 wt.% loading.
- (2) The optimum composition for reduced wear rate and friction coefficient increased as the particle size increased.
- (3) Crystallinity had a separate effect on the wear rate and friction coefficient. Unfilled samples of 20 and 40% crystallinity had wear rates and friction coefficients of 4.6×10^{-6} and 10.0×10^{-6} mm³/Nm, and 0.36 and 0.21, respectively. Wear rate increased monotonically with crystallinity at all filler loadings and friction coefficient was lowest for 30% crystalline samples on average.
- (4) The optimum loading was found to depend on the crystallinity of the sample, increasing monotonically with increased crystallinity.

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