Effect of matrix morphology on the wear and friction behavior of alumina nanoparticle/poly(ethylene) terephthalate composites

Praveen Bhimaraj[a], David L. Burris[b], Jason Action[b], W. Gregory Sawyer[b], C. Gregory Toney[c], Richard W. Siegel[a], Linda S. Schadler[a],[*]

[a] Rensselaer Nanotechnology Center and Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, 110 8th Street, Troy NY 12180, USA
[b] Department of Mechanical & Aerospace Engineering, University of Florida, Gainesville FL 32611, USA
[c] Albany International Research Corporation, Mansfield, MA, USA

Abstract

The friction and wear properties of poly(ethylene) terephthalate (PET) filled with alumina nanoparticles were studied. The nanoparticle loading was varied from 1 to 10 wt.%. The nanocomposite samples were tested in dry sliding against a steel counterface. The results show that the addition of nanoparticles can increase the wear resistance by nearly 2× over the unfilled polymer. The average coefficient of friction also decreased in many cases. The nanocomposites form a more adherent transfer film that protects the sample from the steel counterface, although the presence of an optimum filler content may be due to the development of abrasive agglomerates within the transfer films in the higher wt.% samples. This study varied both crystallinity and weight percent of filler in a PET matrix in an attempt to separate the effects of nanofillers and crystallinity on the tribology.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Nanoparticle; Wear; Friction; Nanocomposite; Crystallinity; Tribology

1. Introduction

The tribology of nanoparticle filled polymers is of significant interest because of the ability of nanoparticles to alter the properties of the matrix and the surfaces involved while remaining as small defects in the matrix. Wang et al. observed that the addition of inorganic nanoparticles to polyetheretherketone (PEEK) led to the formation of what appeared to be a more coherent and tenacious transfer film on the steel counterface during wear [1–5]. This resulted in abated scuffing between the counterface and the composite, leading to simultaneous reduction in wear rate and coefficient of friction. Based on studies with polytetrafluoroethylene (PTFE) filled with ZnO nanoparticles, it was proposed that the nanoparticles act to strengthen the bond between the transfer film and the counterface [6]. Schwartz et al. measured the bond strengths of transfer films in detail and quantitatively showed that alumina nanoparticle filled polyphenylene sulfide (PPS) was more strongly bonded to the counterface than the neat resin [7].

Inorganic nanoparticles can also affect the tribology of polymers by changing the wear mechanism. Studies on polyoxymethylene (POM) filled with copper particles concluded that the wear mechanism in the composite filled with micron sized particles was primarily scuffing and adhesion, while wear of the nanoparticle-filled composite occurred by plastic deformation [8].

A critical factor controlling the tribology of polymers is their crystalline morphology. For instance, wear of PTFE occurs by disruption of the banded structure [9]. On the other hand, in polypropylene, spherulitic wear occurs by removal

* Corresponding author. Tel.: +1 518 276 2022; fax: +1 518 276 8554.
 E-mail address: schadl@rpi.edu (L.S. Schadler).

of thin films rather than by plucking of lamellae [10]. It has been shown previously that the addition of nanofillers alters the crystalline morphology of the polymer matrix and at times even results in formation of new crystal structures [11,12]. As the morphology changes due to the fillers, the tribological behavior is also expected to change. In a study on silica/nylon-11 nanocomposites, the improved friction and wear properties were attributed to changes in crystallinity and reinforcement content [13]. However, there have been no studies to date elaborating on the effect of nanoparticles on matrix crystallinity and subsequent effects on tribology.

In this study, we report on the tribological behavior of composites of poly(ethylene) terephthalate (PET) with nanosized Al_2O_3 additions. Most of the previous research on tribology of polymer nanocomposites focused on polymers such as PEEK, PTFE and more recently thermosetting polymers [14,15]. To the authors' knowledge, there has been no report on PET based nanocomposites. PET is one of the most widely used semi-crystalline polymers in the world. It finds applications in a variety of fields, ranging from fabrics and soft drink bottles, to magnetic recording tape substrates. Its wear and friction behavior are known to be affected by its crystallinity, under both dry and water lubricating conditions [16,17]. The coefficient of friction is reportedly only slightly dependent on crystallinity, although the wear rate increases monotonically with increasing crystallinity [16]. At lower crystallinities, wear occurs by adhesion, while at higher crystallinities, wear occurs predominantly by fatigue. In contrast, both hardness and strength increase with increasing crystallinity [18,19]. It is, therefore, of significant interest to investigate nanocomposites of PET and the effect of nanoparticles on matrix crystallinity and tribology.

2. Sample preparation

Poly(ethylene) terephthalate (grade: Crystar 3939) was obtained as pellets from DuPont. Alumina nanoparticles (average size: 38 nm) were supplied by Nanophase Technologies Corporation. The polymer pellets 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 atmosphere in a batch melt mixer (HBI SYSTEM 90, A HAAKE BUCHLER PRODUCT) at 260 °C and a screw speed of 50 rpm. As a control, the PET pellets alone were also mixed under the same conditions. The torque required to maintain the preset screw speed was continuously monitored. A drop in torque would imply a drop in viscosity of the polymer caused by degradation. However, the torque did not drop indicating that the polymer was not degrading [20]. Measurement of the intrinsic viscosity of unfilled polymer before and after the mixing process also suggests that the molecular weight did not drop as a result of processing. The dispersion of the particles was observed on thin sections of the nanocomposite using a JEOL CM-12 TEM (see Fig. 1).
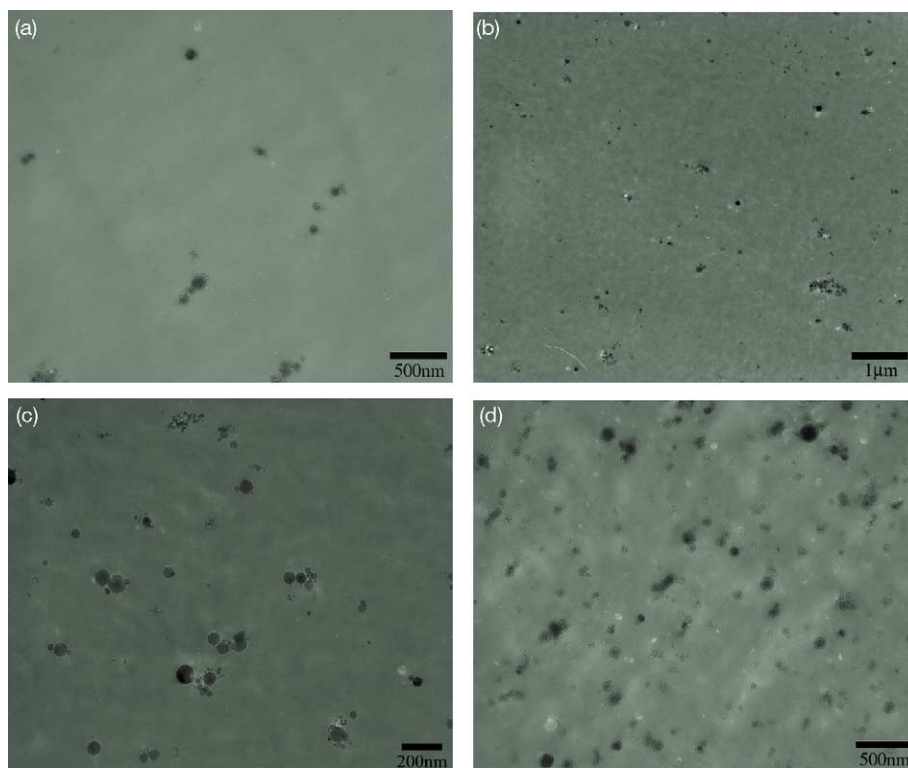

Fig. 1. Transmission electron microscopy images through sections of thickness ~70 nm of (a) 1 wt.%, (b) 2 wt.%, (c) 5 wt.%, (d) 10 wt.% of 38 nm alumina in PET. The nanoparticles are separated from each other. This dispersion state is maintained for loadings up to 10 wt.%.

Sections of thickness less than 70 nm were made from pieces of samples embedded in epoxy using a RMC Ultramicrotome and collected on a #200 copper grid after floating the sections in water. An acceleration voltage of 120 kV with an emission current of 24–26 μA was used to image the sections.

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 material obtained from melt mixing was cryogenically frozen, crushed, and dried in a vacuum oven at 150 °C for 24 h. 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 with ice 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, the samples were taken to melt under pressure in the mold and cooled down at specific cooling rates determined from a crystallization kinetics study. Samples of varying filler content were also prepared at two different crystallinity levels (20 ± 2% and 40 ± 2%); these samples will be referred to as iso-crystalline samples. The crystallinity of each sample was checked using a Mettler-Toledo 822e differential scanning calorimeter (DSC).

Wear and friction tests were conducted on a reciprocating tribometer. The schematic is shown in Fig. 2. The sample was pneumatically loaded against a steel counterface and controlled via an electropneumatic valve. The normal load and friction forces were measured with a six-channel load cell mounted directly above the pin sample. The steel counterface

was mounted directly below the pin sample on a reciprocating linear table driven by a stepper motor. The attached computer data acquisition system monitored 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 $R_a = 0.1$–0.2 μm. The quenched and annealed samples were tested with a normal force of 340 N, corresponding to a contact pressure of 8.6 MPa, and average reciprocating speed of 25 mm/s. The iso-crystalline samples were tested at a lower load of 250 N (contact pressure of 6.3 MPa) due to the reduced yield stress of the 20% crystalline samples. In order to obtain significant wear loss at reasonable testing time, these samples were tested at a higher velocity of 73 mm/s. The tests were conducted to a total sliding distance of 7.5 km. The mass loss due to wear was measured and wear rates were reported from single point observations of volume loss (mass loss/density: mm^3) per load (N) per sliding distance (m). Error bar for wear rates indicated are measured from five samples at a single data point. The coefficient of friction was obtained by dividing the frictional force by the normal force. Scatter in data is from standard deviation in coefficient friction in a single sample over the entire testing time.

The fraction of crystalline polymer in the nanocomposites was calculated by taking the ratio of the measured heat of fusion to the theoretically calculated heat of fusion [21] of a completely crystalline PET of the same mass. The mass of the polymer in the composite was used for these calculations.
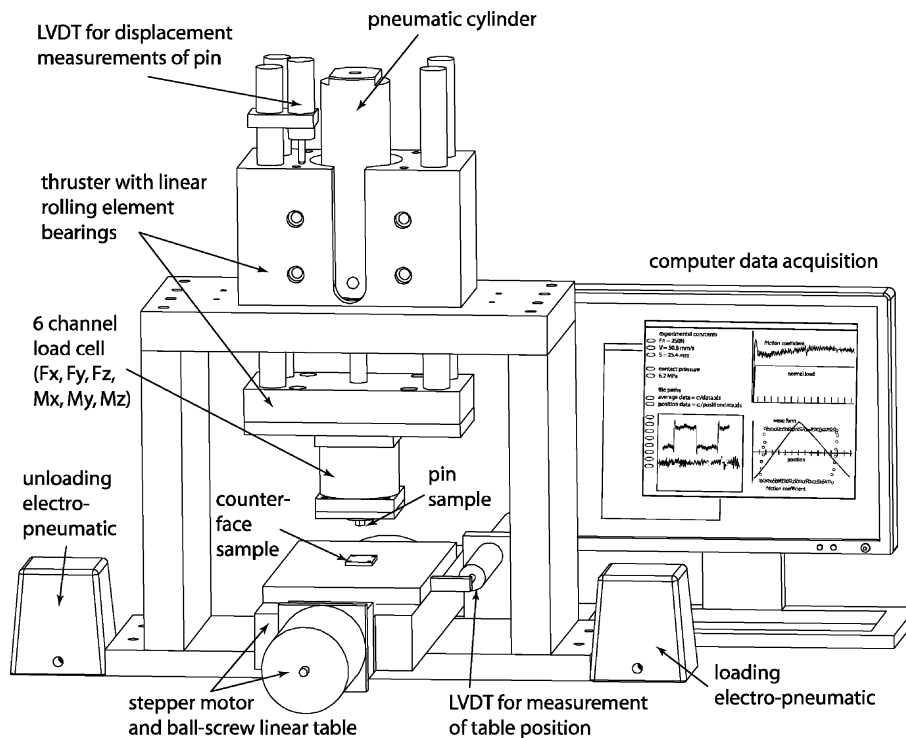

Fig. 2. A Schematic of the reciprocating tribometer used in this study.

3. Results

TEM micrographs representing the dispersion of the nanoparticles in the nanocomposites are shown in Fig. 1. The nanoparticles appear well separated and distributed within the PET matrix at all loadings.

The coefficient of friction data is plotted versus sliding distance for the five different filler contents; this is shown in Fig. 3. The 1 and 2 wt.% composites have slightly lower average coefficients of friction than the unfilled material, with the minimum coefficient of friction obtained at 2 wt.%. On further increase in filler content, the coefficient of friction increased, with the 10 wt.% sample displaying the highest value. The time averaged coefficient of friction versus filler content and the standard deviation of the fluctuations in the coefficient of friction during the tests is shown in Fig. 4.
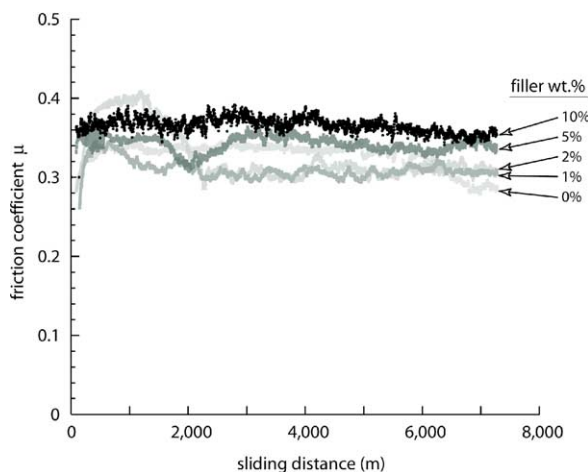

Fig. 3. Friction coefficient versus sliding distance for the PET composites (normal load: 340 N, sliding speed: 25 mm/s).
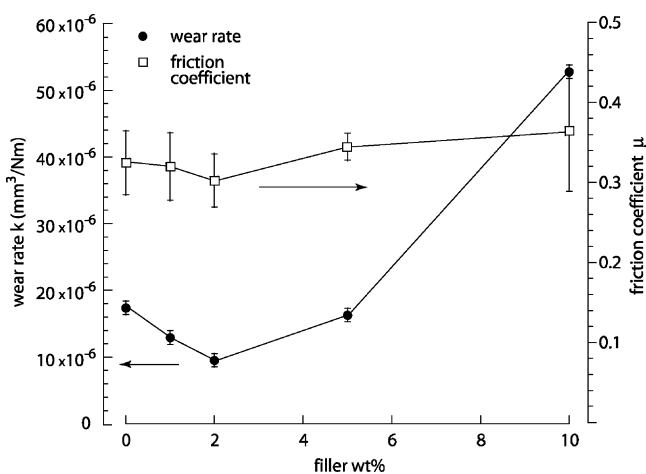

Fig. 4. Variation in wear rate of the PET and average coefficient of friction plotted against loading of 38 nm alumina. Wear rate decreases for low loadings with optimum filler content at 2 wt.% (normal load: 340 N, sliding speed: 25 mm/s). The error bars on the wear rate are the experimental uncertainty, while for those for the coefficient of friction represent the standard deviation of the measurement during the experiment.

The wear rate for the quenched and annealed samples is also shown in Fig. 4. At low filler concentrations, the wear rate decreased with increasing filler concentration. The minimum wear rate is obtained at 2 wt.% and is half the wear rate of the unfilled sample. Thereafter, the wear rate increases with increasing concentration and at 10 wt.% is higher than the wear rate of unfilled polymer.

The transfer films formed by these samples were examined with an optical microscope (micrographs are shown in Fig. 5). Inspection of the transfer films shows that the neat PET forms a thin layer with parts of the counterface being bare. The nanofilled samples form more coherent and uniform transfer films with increasing filler content.

4. Discussion

An optimum filler content for wear has been observed for several polymer-nanoparticle systems and is frequently less than 10 wt.% [1–5,15]. This is in contrast to micron-particle filled systems in which the optimum filler content is typically 30 vol.% [23]. In the quenched and annealed samples the wear rate and friction coefficient trends are similar with minima at 2 wt.%. The introduction of nanoparticles not only improved the wear resistance of PET, but also slightly reduced the coefficient of friction. The coherency and uniformity of the transfer films formed by the nanocomposites act to protect the sample from the hard asperities on the steel couterface.

The wear rate and coefficient of friction both increase at loadings higher that 2 wt.%, with the 10 wt.% filled nanocomposite displaying the poorest properties. This phenomenon of optimum filler content has been observed for several systems; however, an explanation for why the wear of the nanocomposite increases beyond an optimum filler content is lacking. Fig. 6 is a representative high magnification SEM micrograph of the transfer film formed by the 10 wt.% loaded PET sample. The micrograph reveals the presence of agglomerates that are neither observed in the sample before testing nor in the transfer films formed by the 1 and 2 wt.% composites. These agglomerates may be responsible for increased third body wear. It is hypothesized that the phenomenon of optimum filler content is a result of the competitive effects of transfer film development and the formation of abrasive aggregates. Such aggregates are not seen on the wear surfaces indicating that the aggregates are formed in the transfer film due to continuous shear. With increasing filler loading, the ease of formation of these aggregates in the transfer film is enchanced due to the reduced interparticle distance in the parent sample.

Though the transfer film character is an important factor affecting the wear of polymers, the question that needs to be answered is whether the observed change in properties is due to the improvement in the transfer film alone. Another important factor affecting tribology of polymers is crystallinity. Fig. 7 shows the variation in crystallinity with filler content. The nanocomposites have lower crystallinities than the un-
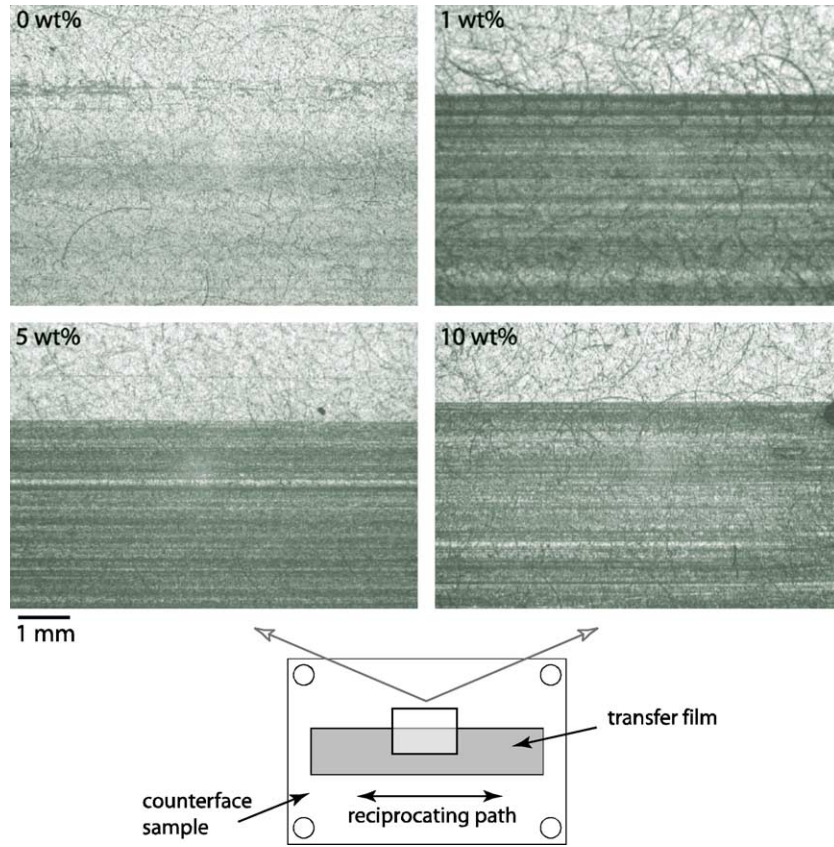
Fig. 5. Optical micrographs of transfer films formed by the nanocomposites compared to the neat sample. The region observed is indicated in the schematic below the figures. The control forms a scarce transfer film as opposed to the uniform and coherent transfer films formed by the filled samples.

filled samples. Fig. 8 shows the variation in wear rate with crystallinity for these samples. There is reasonable correlation between the wear rate and crystallinity except for the 10 wt.%, indicating that the change in crystallinity on addition of the nanoparticles could be contributing to the observed change in properties. To separate the contribution of crystallinity and filler wt.% iso-crystalline samples at two levels of crystallinity were evaluated.

The variation in wear rate and coefficient of friction versus filler content for the 20% iso-crystalline samples is shown in Fig. 9. The nanofilled samples all have lower wear rates than pure PET, and the minimum wear rate occurs at 1 wt.% loading. The coefficient of friction of the nanofilled PET is not significantly different from the unfilled sample. In the 40% iso-crystalline samples, the addition of nanofillers reduced the wear rate with the minimum at 2 wt.%; however,
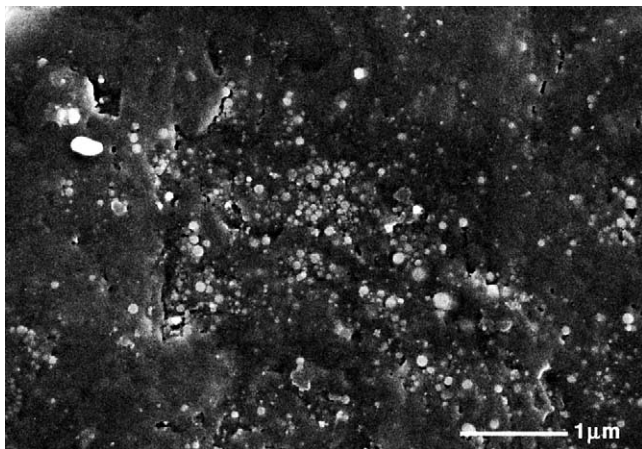

Fig. 6. SEM micrograph shows agglomerates of nanoparticles in transfer film formed by 10 wt.% filled composite.
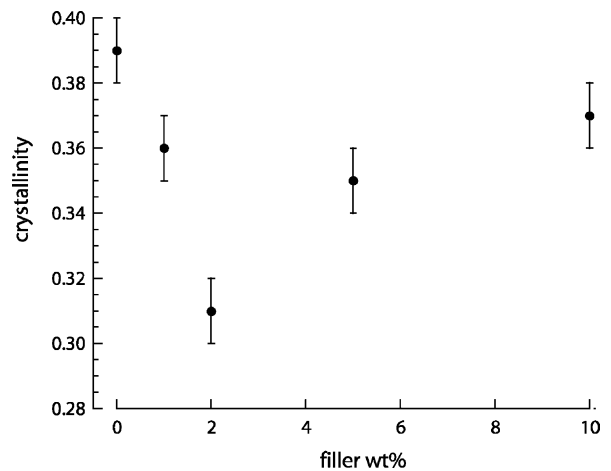

Fig. 7. Crystallinity as measured from DSC plotted against filler content.
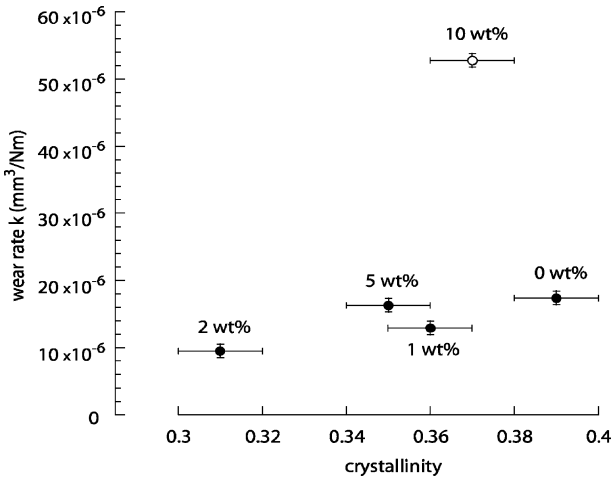
Fig. 8. Plot of wear rate against crystallinity for nanocomposites. With the exception of the 10% filled sample, which performed poorly, there appears to be a linear relationship between the wear rate and crystallinity.

the coefficients of friction of the filled samples are all higher than those of the unfilled samples (Fig. 10). The results of all experiments are summarized in Table 1.

A comparison of the isocrystalline data leads to the following understanding. First, the data is in keeping with the previously observed effects of crystallinity on coefficient of
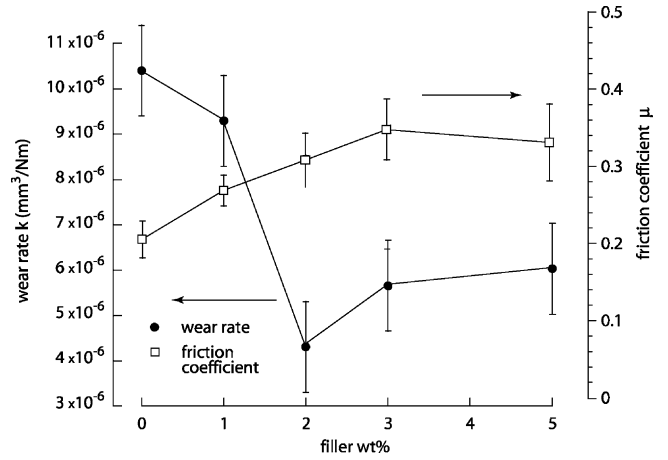

Fig. 10. Effect of nanoparticles on wear and friction of PET matrix of $40 \pm 2\%$ crystallinity.

friction and wear resistance of homogeneous PET; namely, increased crystallinity causes a decrease in wear resistance. Secondly, the nanoparticles do contribute to increasing the coefficient of friction and any reduction in coefficient of friction is due to changes in the matrix which is in keeping with the hypothesis on the effect of hard particles. The decrease in coefficient of friction for the nanocomposite is a result of the effect of nanoparticles on crystallinity. Third, the effect of
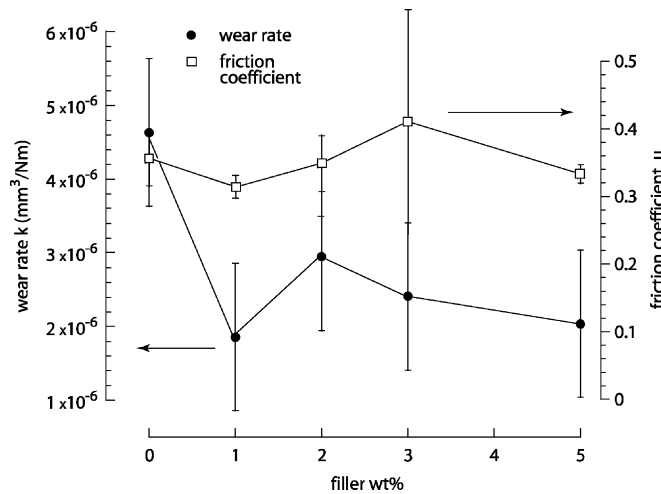

Fig. 9. Effect of nanoparticles on wear and friction of PET matrix of $20 \pm 2\%$ crystallinity.

Table 1
Summary of calculated average wear rates and friction coefficients for the PET/38 nm alumina composites on 347 stainless steel counterfaces

Filler content (wt.%)	Wear rate (mm³/Nm)			Friction coefficient		
	$F_n = 340$ N; $v = 25$ mm/s	$F_n = 250$ N; $v = 73$ mm/s		$F_n = 340$ N; $v = 25$ mm/s	$F_n = 250$ N; $v = 73$ mm/s	
	Same processing	$\theta_c = 20\%$	$\theta_c = 40\%$	Same processing	$\theta_c = 20\%$	$\theta_c = 40\%$
0	1.74E−5	4.6E−6	1.0E−5	0.33	0.36	0.21
1	1.29E−5	1.9E−6	9.3E−6	0.32	0.31	0.27
2	9.50E−6	2.9E−6	4.3E−6	0.30	0.35	0.31
3	–	2.4E−6	5.7E−6	–	0.41	0.37
5	1.63E−5	2.0E−6	6.0E−6	0.35	0.33	0.33
10	5.28E−5	–	–	0.37	–	–

nanoparticles is not limited to altering the matrix crystallinity. It is clear that the nanoparticles alone contribute significantly to the reduction in wear rate. The mechanism for this contribution is not clear, but is probably related to improving the transfer film.

5. Conclusions

1) Wear resistance of PET increases nearly 2X with the addition of 2 wt.% 38 nm alumina particles, with a 10% decrease in average coefficient of friction.
2) Wear resistance of PET increases on addition of nanoparticles at low loadings irrespective of the crystallinity of the polymer matrix. Coefficient of friction is affected both by crystallinity and nanoparticles.
3) The improvements in the friction and wear characteristics are attributed to the formation of a more coherent and adherent transfer film by the nanofilled composites.
4) It is hypothesized that the optimum filler content is the result of a competition between the transfer film development and the rate of abrasive aggregate development.

Acknowledgements

References

[1] Q. Wang, J. Xu, W. Shen, W. Liu, An investigation of the friction and wear properties of nanometer Si_3N_4 filled PEEK, Wear 196 (1996) 82–86.

[2] Q. Wang, Q. Xue, W. Liu, W. Shen, J. Xu, The effect of particle size of nanometer ZrO_2 on the tribological behavior of PEEK, Wear 198 (1996) 216–219.

[3] Q. Wang, J. Xu, W. Shen, Q. Xue, The effect of nanometer SiC filler on the tribological behavior of PEEK, Wear 209 (1997) 316–321.

[4] Q. Xue, Q. Wang, Wear mechanisms of polyetheretherketone composites filled with various kinds of SiC, Wear 213 (1997) 54–58.

[5] Q. Wang, Q. Xue, W. Shen, The friction and wear properties of nanometer SiO_2 filled polyetheretherketone, Tribol. Intl. 30 (3) (1997) 193–197.

[6] F. Li, K. Hu, J. Li, B. Zhao, The friction and wear characteristics of nanometer ZnO filled polytetrafluoroethylene, Wear 249 (2002) 877–882.

[7] C.J. Schwartz, S. Bahadur, Studies on the tribological behavior and transfer film-counterface bond strength for polyphenylene sulfide filled with nanoscale alumina particles, Wear 237 (2) (2003) 261–273.

[8] L. Yu, S. Yang, H. Wang, Q. Xue, An investigation of the friction and wear behaviors of micrometer copper particle- and nanometer copper particle-filled polyoxymethylene composites, J Appl Polym Sci 77 (2000) 2404–2410.

[9] K. Tanaka, Y. Uchiyama, S. Toyooka, The mechanism of wear of polytetrafluoroethylene, Wear 23 (1973) 153–172.

[10] K. Tanaka, Y. Uchiyama, Friction, wear and surface melting of crystalline polymers, in: L.-H. Lee (Ed.), Advances in Polymer Friction and Wear, Polymer Science and Technology 5B, Plenum Press, New York, 1974, pp. 499–531.

[11] J. Zheng, R.W. Siegel, C.G. Toney, Polymer crystalline structure and morphology changes in nylon-6/ZnO nanocomposites, J. Polym. Sci. Part B: Polym. Phys. 41 (10) (2003) 1033–1050.

[12] X. Liu, Q. Wu, Q. Zhang, Z. Mo, Phase transition in polyamide-66/montmorillonite nanocomposites on annealing, J. Polym. Sci. Part B: Polym. Phys. 41 (1) (2003) 63–67.

[13] E. Petrovicova, R. Knight, L.S. Schadler, T.E. Twardowski, Nylon 11/Silica nanocomposite coatings applied by the HVOF process. II. Mechanical and barrier properties, J. Appl. Polym. Sci. 78 (2003) 2272–2289.

[14] M.Q. Zhang, M.Z. Rong, S.L. Yu, B. Wetzel, K. Friedrich, Improvement of tribological performance of epoxy by the addition of irradiation grafted nano-inorganic particles, Macromol. Mater. Eng. 287 (2) (2002) 111–115.

[15] G. Shi, M.Q. Zhang, M.Z. Rong, B. Wetzel, K. Friedrich, Friction and wear of the nanometer Si3N4 filled epoxy composites, Wear 254 (2003) 784–796.

[16] Y. Yamada, K. Tanaka, Effect of the degree of crystallinity on friction and wear of poly(ethylene) terephthalate, Polym. Mater. Sci. Eng. 50 (1984) 462–465.

[17] Y. Yamada, K. Tanaka, Effect of the degree of crystallinity on the friction and wear of poly(ethylene terephthalate) under water lubrication, Wear 111 (1) (1986) 63–72.

[18] T. Asano, F.J.B. Calleja, A. Flores, M. Tanigaki, M.F. Mina, C. Sawatari, H. Itagaki, H. Takahashi, I. Hatta, Crystallization of oriented amorphous poly(ethylene terephthalate) as revealed by X-ray diffraction and microhardness, Polymer 40 (1999) 6475–6484.

[19] J.M.G. Cowie, Polymers: Chemistry & Physics of Modern Materials, 2nd ed., Stanley Thornes (Publications) Limited, UK, 1991, pp. 321–361.

[20] M. Paci, F.P. La Mantia, Competition between degradation and chain extension during processing of reclaimed poly(ethylene) terephthalate, Polym. Degrad. Stab. 61 (1998) 417–420.

[21] R.L. Miller, in: J. Brandup, E.H. Immergut, E.A. Grulke (Eds.), Polymer Handbook, Fourth ed., Wiley-Interscience, New York, 1999.

[23] S. Bahadur, D. Gong, The action of fillers in the modification of the tribological behavior of polymers, Wear 158 (1992) 41–59.

Further reading

[22] G. Shi, M.Q. Zhang, M.Z. Rong, B. Wetzel, K. Friedrich, Friction and wear of low nanometer Si3N4 filled epoxy composites, Wear 254 (2003) 784–796.