Fine textured composite low friction coatings with combined corrosion protection ability

C. Becker-Willinger, P. Kalmes, D. Bentz

INM – Leibniz Institute for New Materials
Campus D2 2, D-66123 Saarbruecken, Germany, nanomere@inm-gmbh.de

ABSTRACT

A new class of multifunctional low friction coatings combining a low coefficient of friction of $\mu < 0.1$ over 1 km sliding distance with high corrosion protection ability > 600 h in the neutral salt spray test on mild steel were developed. The coatings possess a fine textured composite morphology which is achieved during the spray application and thermal curing process. Flake type hexagonal boron nitride as solid lubricant with appropriate surface modification and a particle size in the submicrometer range was dispersed in a polyimide matrix together with high aspect ratio platelet shaped SiO_2 particles having a thickness in the range of 200-400 nm in order to improve the barrier properties against diffusion of corrosive substances. The fine textured morphology was proven by means of scanning electron microscopy on polished cross sections. The tribological properties of the resulting fine structured coatings were investigated in dependence on the boron nitride flake and the SiO_2 platelet content.

Keywords: low friction, lubricant, boron nitride, composite, corrosion protection

1 INTRODUCTION

Low friction coatings based on polymeric binders and solid state lubricants have restarted to draw attention in the recent past for the use in gears, bearings and other tribological systems for e.g. automotive applications or energy producing machinery in order to substitute lubricating grease or oil. One challenge in this approach is the optimisation of the low friction coatings towards the extremely low coefficient of friction of oil lubricated systems. Another required feature would be that the low friction coatings containing solid state lubricants should also provide sufficient corrosion protection when metals prone to corrosion are used in the tribological system without hydrophobic grease, which usually would hinder the access of water and in this way would prevent corrosion to start.

A lot of work has been done in the past on investigation of the tribological characteristic of polymers and polymer composite bulks [1]. Low friction coatings derived from polymeric binders and lubricants show increasing interest to be used in many different field of industry. An indication in this direction may be given by the fact that a lot of literature can be found mainly as patents. As inorganic type lubricants usually graphite, molybdenum disulfide, metals, alloys and hexagonal boron nitride are used. Organic polymer type lubricants such as e.g. polytetrafluoroethylene (PTFE) or high-density polyethylene (HDPE) also are possible candidates. The binders for these mostly particulate materials is based on different polymeric matrix materials and is selected depending on the requirements that act on the coating [2, 3].

High performance polymers, such polyimide (PI) are important binder matrices in the field of tribology and are widely used to fabricate low friction coatings [4-6]. Different functional fillers are dispersed in the polyimide matrices in order to improve the tribological performance of the resulting PI composites as well as the wear resistance [7]. Polymeric lubricants such as PTFE particles help to decrease and stabilize the friction coefficient of coatings at a low level, and further addition of hard fillers such as e.g. silicon carbide (SiC) significantly improves the wear resistance [8]. Interesting tribological properties could be achieved by the combination of nanoparticles derived from e.g. silicon nitride (Si_3N_4) and solid state lubricant such as PTFE into polyimide matrix [9]. Among the mechanisms of tribological modification, the improvement of mechanical surface properties [7] and the lubrication enabled by transfer film formation [9] are very important for the final tribological performance of such polymer matrix based composite coatings.

A drawback of solid state lubricants is their higher coefficient of friction compared to oil and the necessity to balance friction with controlled abrasion especially to enable to form a stable transfer film which is essential to realize lubrication. For example tribological coatings suitable for elastomer surfaces based on a polyurethane polymer and amorphous flake-type graphite particles were described [10]. A similar approach using uniformly dispersed particles of different nature in a polyimide binder material was investigated with a solid lubricant to produce wear resistant injection molded parts with tribological properties [11]. The matrix material was filled with low hardness layered silica to improve the mechanical stability of the composite material. Carbon fibers were added to control the wear. In addition polymer based low friction coatings are often equipped with hard filler particles to increase their mechanical strength [12].

The objective of the present work was to address the roles of different components in modifying the tribological performance of multifunctional fine textured polyimide composite coatings described in [13]. The final goal was to understand the interaction of the key particulate components in specific combinations and how the morphology of the resulting composite coatings, in particular the spatial arrangement and orientation of the flakes and platelets, is influencing the coefficient of friction.

2 EXPERIMENTAL

The investigations were based on Nanomer® low-friction coating composition (denoted: FTC1) consisting out of hexagonal boron nitride flakes (denoted: h-BN flakes) as solid lubricant, platelet type SiO_2 pigments having a TiO_2/ZrO_2 surface layer (denoted: LS platelets) as corrosion protection additive, silicon nitride hard filler particles (denoted: Si_3N_4 hard filler) and a perfluoropolyether co-monomer (denoted: FL co-monomer) incorporated in a polyimide matrix derived from Bis-aminophenylphenoxysulfone and Pyrromellitc-dianhydride. In order to understand the role of each of the additives in the polyimide matrix and later on the synergistic effects achieved by special combinations the following compositional variations were performed starting from FTC1 and systematically deleting one or more functional additives (Table 1).

sample	h-BN flakes / wt.-%	LS platelets / wt.-%	Si_3N_4 hard filler / wt.-%	FL co-monomer / wt.-%
FTC1	30	5	2.5	10
FTC2	30	-	-	-
FTC3	-	5	-	-
FTC4	-	5	-	10
FTC5	-	-	-	10
FTC6	30	-	-	10
FTC7	30	5	-	10

Table 1: Investigated compositions of polyimide type Nanomer® coatings with different additive combinations.

All chemicals were of analytical grade and used without further purification: Pyromellitic anhydride (PMDA, Acros Organics); 4,4´-bis(3-aminophenoxy) diphenyl sulfone (BAPPS, 95%, Alpha Aesar); N-Methyl-2-pyrrolidone (NMP, VWR); Fluorolink D10H (Solvay Solexis); Hexagonal boron nitride (h-BN, HeBoFill® 110, Henze Boron Nitride Products GmbH); Silicone Nitride M11-A (Si_3N_4 M11, H.C. Starck); Colorstream® T20-04 WNT Lapis Sunlight [LS] (MERCK KGaA PLS/Pigments (Darmstadt, Germany).

The formulations were prepared as described in [13], spray coated on stainless steel plates and cured in a temperature program up to 200 °C. The resulting coating thickness was 22 µm ± 5 µm and the roughness R_a = 0.44 µm ± 0.05 µm. The coating morphology was determined by Scanning Electron Microscopy (SEM), using a Quanta 400 F (FEI-Company) in the low vacuum modus (100 Pa) at 20.0 kV. For the cross-section analysis samples were embedded in epoxy resin and polished.

The tribology tests were performed according to DIN 50324 using a ball-on-disc tribometer (CSM Instruments, Switzerland; normal force F = 2 N, distance s = 1000 m, sliding speed v = 10 cm/s, radius r = 16 mm, counter body: 4 mm steel ball 100Cr6, medium: air). For investigations concerning the influence of mechanical stress on the corrosion protection ability of the coating measurements with a normal force of 5 N and distances of 100 m were carried out. The neutral salt spray corrosion test was performed according to DIN EN ISO 9227 in a corrosion testing apparatus, model 606/400 l provided by Erichsen GmbH Co KG, (Hemmer, Germany). The salt spray solution was a (50 ± 5) g/l sodium chloride solution with a pH of 6.5 to 7.2 at (25 ± 2) °C. This solution is sprayed into the test chamber at (35 ± 2) °C test temperature.

3 RESULTS AND DISCUSSION

3.1 Morphology

The morphology of the complete formulation sample 1 has been investigated by scanning electron microscopy (SEM) on polished cross-sectional areas of the coatings on stainless steel (Figure 1).

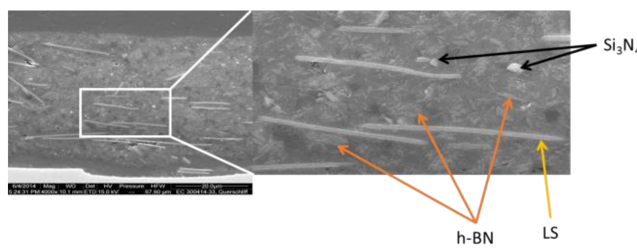

Figure 1: SEM micrograph from polished cross-section of FTC1 Nanomer® low friction coating on stainless steel.

As can be derived from Figure 1 the LS platelets are randomly distributed over the matrix and tend to arrange more or less in parallel orientation to the steel surface. The h-BN flakes seem to be quite well dispersed in the matrix in between the LS platelets and form only small agglomerates, which obviously could not be destroyed completely during the mixing process. The Si_3N_4 hard filler particles are used only in low concentration and also are randomly distributed over the matrix. Between the h-BN flakes and between h-BN flakes and LS platelets polymer type matrix can be observed indicating that a stack type layered structure might have been formed that is representing the fine textured composite morphology.

3.2 Tribological investigation

The investigation of the tribological properties of the different compositions from Table 1 on the macroscopic scale should give a first insight in some compositional relationships with respect to the fine textured morphology. In order to analyse the role of each particulate component dispersed in the polyimide matrix individual components have been omitted in a systematic way as shown in Table 1. As a frist approach in this direction Figure 1 shows the influence on the coefficient of friction derived from ball-on-disc tribometer for the addition of FL co-monomer and LS platelets to the polyimide matrix containing only h-BN flakes in comparison to the completely formulated FTC1 Nanomer® system.

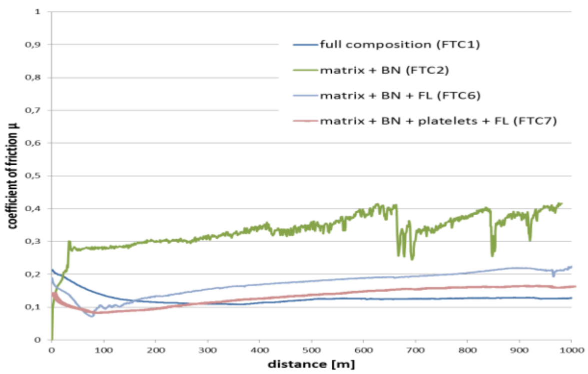

Figure 1: Coefficient of friction from ball-on-disc tribometer: Effect of addition of FL co-monomer and LS platelets to h-BN containing system FTC2 in comparison to FTC1 (loading parameters: 100Cr6 steel ball (d = 4 mm), v = 10 mm/s, F_N = 2 N, r = 15 mm).

The addition of FL co-monomer (FTC6) to polyimide matrix containing only h-BN flakes (FTC2) leads to a significant decrease of the coefficient of friction. This observation indicates that the FL co-monomer might not be completely bound to the polymer matrix during the thermal curing and cross-linking process. Furthermore it is interesting to note that going from FTC6 to FTC7 (= addition of LS platelets) results in a further decrease of the coefficient of friction over the whole sliding distance. This result indicates that some part of the loosely bound FL could also be localised at the platelet interface and in this way could act as a further sliding film.

As a second approach to understand the situation the comparison of single addition of LS platelets to the pure polyimide matrix (FTC3) and the combined addition of LS and FL co-monomer (FTC4) to the composite coating containing three types of additives FL, LS and h-BN (FTC7) and the completely formulated system FTC1 is shown in Figure 2.

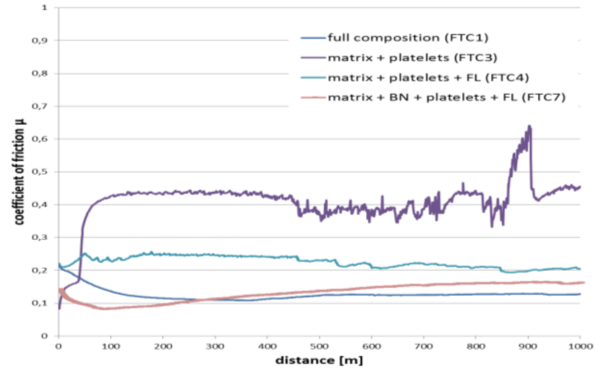

Figure 2: Coefficient of friction from ball-on-disc tribometer: Effect of addition of FL co-monomer and h-BN flakes to LS platelet containing system FTC3 in comparison to FTC1 (loading parameters: 100Cr6 steel ball (d = 4 mm), v = 10 mm/s, F_N = 2 N, r = 15 mm).

It can be derived from Figure 2 that the presence of LS platelets in the polyimide matrix does not seem to have positive effect on the coefficient of friction. The further addition of FL co-monomer results in lower friction values as could be expected in the case that the FL would only be loosely bound to the polyimide matrix. To finally achieve a conclusion concerning the role of the FL co-monomer Figure 3 shows the different systems containing the co-monomer and also the different particulate additives.

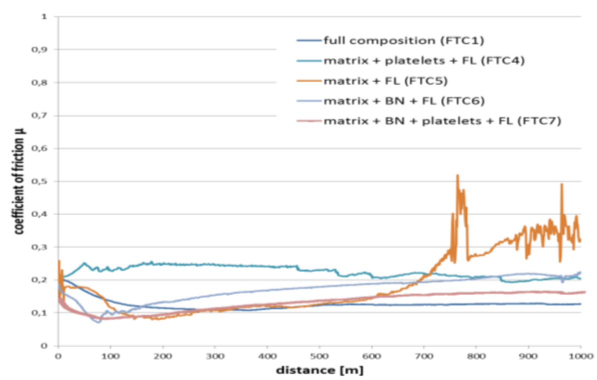

Figure 3: Coefficient of friction from ball-on-disc tribometer: Effect of addition of LS platelet and h-BN flakes to FL co-monomer containing system FTC5 in comparison FTC1 (loading parameters: 100Cr6 steel ball (d = 4 mm), v = 10 mm/s, F_N = 2 N, r = 15 mm).

From Figure 3 it can be derived that again only the combination of the three components h-BN flakes, LS platelets and FL co-monomer leads to low coefficient of friction over the whole sliding distance. The comparison with the fully formulated composite FTC1, which only contains 2.5 wt.-% Si_3N_4 hard filler in addition, reveals that this step leads to a homogenisation of the trend of the coefficient of friction up to 1000 m sliding distance. Only in the initial phase of the sliding experiment (from 0 m to

100 m) FTC1 shows a higher coefficient of friction value compared to FTC6 and FTC7. From this observation it can be concluded that the Si_3N_4 hard filler particles increase the wear resistance of the resulting coatings without negatively influencing the coefficient of friction when they are dispersed in low concentration. In this direction a regular particulate shape of the hard filler particles would help to keep the debris formation on a low level.

3.3 Corrosion behaviour

As the initial intention was to add corrosion protection effect in a low friction coating by addition of high aspect ratio barrier platelets the corrosion behaviour has been investigated at first on coated mild steel plates after ball-on-disc tribometer test (Figure 4).

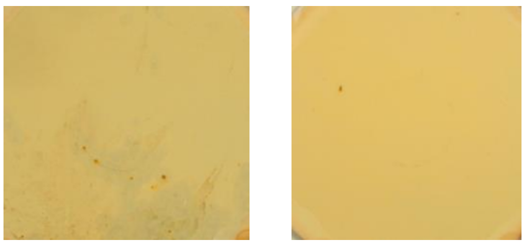

Figure 4: Coatings on mild steel for compositions FTC6 (0 % LS, left) and FTC7 (5 % LS, right) after tribometer test and 600 h neutral salt spray test.

Only the composition FTC6 containing no LS platelets shows blister formation and starting corrosion on the wear track from the tribometer test, whereas the FTC7 with LS platelets is still stable. In order to see the possible subsurface migration an artificial scribe has been introduced in coating FTC7 on mild steel and exposed to neutral salt spray test (Figure 5).

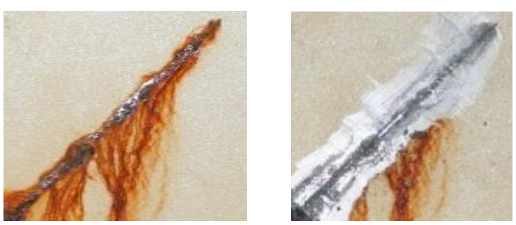

Figure 5: Sample FTC7 after 1200 h neutral salt spray test, red rust formation at artificial scribe (left), coating at artificial scribe mechanically removed with scalpel.

The investigation of the corrosion behaviour near the artificial scribe reveals that the subsurface migration is minimal and the rust index can berated with $R_i = 1$ indicating a remarkable corrosion protection effect.

4 CONCLUSIONS

The Nanomer® low friction coatings represented by the composition FTC1 show a fine-textured morphology with stacks of h-BN flakes and LS platelets as well as spacings in between consisting of polymer matrix ligaments. Macro scale friction experiments with ball-on-disc tribometer indicate that especially the compositions containing combinations of h-BN flakes, FL co-monomer and LS platelets show the lowest coefficient of friction and the lowest wear. The comparison of these findings with the results from the morphological analysis led to the hypothesis that the significant synergistic decrease of coefficient of friction may be due to formation of quasi micro-sliding layers localised in the spacings between h-BN flakes and LS platelets. In order to prove that hypothesis investigation of local friction behaviour should give further indication that loosely bound FL co-monomer may be enriched at the LS platelet surface. In addition transfer film formation process has to be investigated more in detail especially also concerning thickness, morphology and chemical composition of the transfer films obtained for the different coating compositions. Both steps would be part of future work. On the other hand the Nanomer® low friction coatings show a very interesting balance between low friction behaviour and wear resistance combined with corrosion protection ability, which makes these types of coating materials suitable for practical uses in industrial applications.

REFERENCES

[1] W. Brostow et al., J. Mat. Educ. **32**, 273-290 (2010).
[2] T. Mang, et al., “Lubricants and Lubrication”, Wiley&Sons, 2.Ed. 2007, pp. 694 - 703.
[3] H. Czichos, K.-H. Habig “Tribologie-Handbuch“, Vieweg, 3. Ed. 2012, pp.413.
[4] Li, C. and F. Yan, Wear, 2009, **266** (7–8), p. 632-638.
[5] Samyn, P., et al., Tribol. Intern., 2006, **39** (6), p. 575.
[6] Kitoh, M. and Y. Honda, Thin Solid Films, 1995, **271** (1–2), p. 92-95.
[7] Satyanarayana, N., et al., Tribol. Lett., 2007, **27** (2), p. 181-188.
[8] Demian, C., et al., Surf. Coat. Techn., 2013, **235,** p. 603-610.
[9] Su, F., S. Zhang, J. Appl. Polym. Sci., 2014, **131** (12), p. n/a-n/a.
[10] US 4694038, R.A. Burns, J.W. VanWyk, The Boing Company, 20 October 1986.
[11] US 5789523, D.E. George, J.S. Bloom, T.P. Feist, DuPont, 9 July 1996.
[12] US 20040229759 A1, A. Joseph et al., Jet-Lube Inc., 15 May 2003.
[13] WO 2013/092835 A1, C. Becker-Willinger, F. Hollmann, C. Kasper, INM gGmbH, 21.12.2011.