# SLIDING PROPERTIES OF POLYIMIDE AGAINST VARIOUS STEEL AND DLC-COATED COUNTERFACES

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#### Abstract

Both polyimides and diamond-like carbon coatings are known for their good mechanical properties and chemical inertness. A lot of research is performed on their sliding behaviour against steel counterfaces, however little information is presently available on the performance of polyimides sliding against DLC. Small-scale tests are performed under 50 N normal load and 0.3 m/s to 1.2 m/s sliding velocity with St 37-2N, 42 CrMnNiMo8, 316L, DLC-coated and Si-DLC coated (DLN) counterfaces. It is concluded that only for a limited range of test parameters the coefficient of friction of polyimide/DLC is lower than for polyimide/steel, while wear rates of polyimide/DLC are continuously higher. DLC coatings are worn after sliding. Differences in friction are compared to surface energy measurements of the counterfaces, with low surface energy leading to low friction. Transfer consists of platelet-like particles on DLC and DLN counterfaces, while very few transfer was observed on 42 CrMnNiMo8 and smooth transfer on St 37-2N. Polyimide particles possibly act as abrasives, contributing to high wear sliding on diamond-like carbon coated counterfaces.

Keywords: Polyimide, diamond-like carbon, steel, friction, wear, transfer

#### **1. INTRODUCTION**

The effect of different counterface types on friction of graphite-fibre reinforced polyimides was previously discussed by Fusaro [1], including cobalt-based alloys, nickel-based alloys, glass, ferritic stainless steels, austenitic stainless steels and carbon steel. Differences in friction and wear were however most likely attributed to different surface roughness, varying between  $R_a$  = 0.006  $\mu m$  and  $R_a$  = 0.12  $\mu m$ inherent to the surface preparation process, rather than attributed to different counterface composition and interfacial interactions. Other researchers [2-4] have looked more closely to the effects of counterface surface roughness parameters, and usually as the counterface was made smoother the wear rate of the polymer sliding part was found to decrease while there is an optimum surface roughness for minimisation

in friction, depending on the interaction between adhesion and ploughing interaction. Two exceptions were found in the work of Swikert and Johnson [5] and the work of Dowson [6], showing that there is a minimum in wear for UHMWPE at  $R_a = 0.11 \ \mu m$  and 0.03  $\ \mu m$ respectively, and increased for lower surface roughness. According to Play [7], not only the average surface roughness, but the distribution of 13 independent roughness characteristics should be used for relationships between counterface roughness and tribological performance.

The purpose of this study is to investigate the influences of counterface composition on friction and wear of sintered polyimides, with identical surface roughness for each of the counterfaces contrasting with the work of Fusaro. Different steel grades are included in present research, together with two types of diamond-like carbon (DLC) coatings. During the past decades, surface properties have been tailored by the application of hard coatings for controlling corrosion of the metallic part, however only showing promise for low friction and wear for a selected amount of polymer sliding materials [8].

### 2. TEST SET-UP

A PLINT TE 77 High Frequency Friction Machine is employed for reciprocating sliding of polyimide cylinders against fixed counterface specimens (Figure 1) under 50 N normal load. With sliding frequencies between 10 Hz and 40 Hz and a sliding stroke of 15 mm, four velocities of 0.3 m/s, 0.6 m/s, 0.9 m/s and 1.2 m/s are selected over a total sliding distance of 15000 m. The contact zone is surrounded by a box with controlled atmospheric conditions at  $RH = 60 \% \pm 5\%$  and  $T = 23^{\circ}C.$  A piezoelectric force transducer measures the friction force and the combined wear of the polymer and counterface specimens is measured by a contactless displacement transducer. The real polymer wear is determined by weight measurements (balance, 0.0001 g) and diameter reduction (micrometer, 0.01 mm) measured two weeks after the sliding experiment to allow the content to return to water equilibrium conditions. Sliding temperatures are measured by a K-type thermocouple on the steel counterface, representing average bulk temperatures. Each test result is averaged from three runs.



Figure 1: Reciprocating tribotester

# **3. TEST MATERIALS 3.1 Polyimide wear samples**

Mechanical properties of Vespel SP sintered polyimides are given in Table 1. As unfilled base polymer from polycondensation between pyromellitic dianhydride (PMDA) and 4,4' diamino diphenyl ether (ODA), moulding resins with initial grain size diameter of 10 µm to 20 µm are compacted towards 100 µm grains for improved flow characteristics in the sintering mould. Resins are 40% imidized and have a crystalline content between 25-50%, based on X-ray diffraction analysis. Cylindrical shapes (Ø 5 mm x 15 mm) are obtained from subsequent sintering phases own to industrial proprietary [9]. Thermal analysis of the polyimide samples shows no degradation up to 450°C and an endothermic reaction at 180°C due to dehydratation [10]. From its thermal stability and high strength, pv-limits up to 0.87 MPa.m/s or 1.7 MPa.m/s [11] are reported. Samples are cleaned with acetone before sliding.

# 3.2 Sliding counterfaces

High-alloy steel (40 CrMnNiMo8), carbon steel (St 37-2 N), stainless steel (316L), diamond-like carbon (DLC) and Si-doped diamond-like carbon or diamond-like nanocomposite (DLN) coated counterfaces are used, with properties given in Table 2. All surfaces were polished to  $Ra = 0.05 \ \mu m$  as shown on a SEM image in Figure 2. A plasma assisted CVD technique was used for deposition of the coatings. The DLC coating (black colour) has a hydrogen content of 30 at % and a thickness of 1.2 µm in combination with a Si interlayer of 10 nm for better adhesion. The DLN coating (grey colour) contains 15 at % silicium and 7 at % oxygen with a hydrogen content between 20 at % to 35 at %. The addition of Si is mainly advantageous for reduction in internal stresses and better thermal stability [12]. Its structure consists of two interpenetrating networks: an amorphous diamond-like (a-C:H) and a glass-like (a-Si:O), respectively stabilised by hydrogen and carbon. The Si<sub>:</sub>O content can be changed by variation of the type of siloxane precursor and changes the overall sp<sup>3</sup> hybridisation character of the DLC coating into a  $sp^2$  hybridisation with a lattice structure distortion induced by Si-C and Si-O-C bonds.

	Tensile strength	Elongation	Flexural strength	Elasticity modulus	Compressive s 1% strain	trength (MPa) 10 % strain	Thermal conducti vity
	(MPa)	(%)	(MPa)	(MPa)			(W/m°)
SP polyimide							
at 23°C	72.0	7.5	82.7	2480	24.1	112.4	0.29
at 260°C	36.5	7.0	44.8	1448			

Table 1. Sintered polyimides (Vespel SP) wear samples

# Table 2. Test counterfaces

	Density (g/cm <sup>3</sup> )	(Micro) Hardness (GPa)	Elasticity modulus (GPa)	Thermal stability (°C)	Coating thickness (µm)	Friction against steel	Wear rate against steel (10 <sup>-15</sup> m <sup>3</sup> /Nm)			
St 27 2 N	Composition in w%: $C \le 0.17$ , $Si = 0.03 - 0.30$ , $Mn = 0.20 - 0.50$ , $P \le 0.04$ , $S \le 0.04$									
St 57-2 IN	7.80	3	210	200	-	0.70	> 50			
High al-	Composition in w%: C = 0.43, Si = 0.30, Mn = 1.50, Mo = 0.20, Ni = 1.10, Cr = 2.00									
loy steel	7.85	5	210	200	-	0.70	> 50			
21.61	Composition in w% : C = 0.03, Si = 1.00, Mn = 2.00, Mo = 2.0-3.0, Ni= 10.0 – 14.0, Cr = 16- 18									
310L	7.90	2	210	200	-	0.60	4 - 15			
DLC	Composition : a-C:H									
	1.80 - 2.10	20-30	160	300	1.2	0.10 - 0.20	5-10			
DIN	Composition : a-C:H / a-Si:O									
DLIN	2.10	13 - 17	130	400	1.5	0.05 - 0.10	20-40			



**Figure 2:** SEM images (500 x) of original sliding surfaces with roughness  $Ra = 0.05 \mu m$ 

# 4. FRICTION AND WEAR RESULTS

Figure 3 shows the on-line registration of friction and vertical displacement for sintered polyimides against various counterfaces under 50 N, 0.3 m/s, plotted as a function of sliding distance. The evolution of steady-state friction and wear for different sliding velocities is shown in Table 3. For uncoated steel counterfaces, high-alloy steel leads to the highest friction at each sliding velocity. These observations for polyimides are contradicting to general laws outlined in Uetz and Wiedemayer [13], pointing that high counterface hardness should cause lower polymer friction on smooth surfaces. Stainless steel shows different frictional

tendencies than carbon and high-alloy steels, where friction stabilises in the latter cases and progressively diminishes on stainless steels. Friction on DLC coatings is higher than for uncoated steel and fluctuates strongly with sliding distance, although identical surface preparation and smooth roughness is applied. Unstable interaction between the polyimide cylinder and the counterface is correlated to severe coating wear and breakthrough. For the 0.9 m/s and 1.2 m/s sliding velocities, there is a sudden drop in friction at the end of the test preceded by high vibrations. For DLN coated steel, polyimide friction is lower than for uncoated and DLC coated counterfaces under 0.3 m/s to 0.9 m/s, although it seems that sliding

becomes less stable compared to uncoated counterfaces. This is related to variations in the transfer film morphologies as illustrated in Figure 6. For the 1.2 m/s sliding velocity, there is a remarkable increase in friction for DLN counterfaces, tending towards DLC counterface friction where overload situations cause coating failure. Compared to sliding of engineering polymers against DLN [14], the polyimide/DLN sliding couple performs reasonably good with lower friction than polyamide/DLN and more stable friction than POM-H/DLN and internal oil lubricated polyamide/DLN. However, PETP+PTFE/DLN shows lower and stable friction due to benefits of the PTFE internal lubricants allowing for beneficial transfer.



Figure 3: On-line friction and wear measurements

counterraces								
Counterface type	0.3 m/s		0.6 m/s		0.9 m/s		1.2 m/s	
	μ	mm <sup>3</sup> /m						
High alloy steel	0.51	7.7	0.41	12.2	0.36	12.5	0.40	18.5
St 37-2 N	0.43	7.2	0.35	11.0	0.31	12.3	0.33	15.2
316L	0.41	9.1	0.33	12.7	0.30	14.4	0.13	5
DLN	0.40	9.2	0.32	13.0	0.29	16.0	0.45	17.3
DLC	0.61	10	0.55	18.1	0.70	10.0*	0.80	5.3*

Table 3. Test results for friction ( $\mu$ ) and wear (mm<sup>3</sup>/m) of polyimide against different counterfaces

\* test prematurely stopped after 4500 m due to coating wear

Wear rates of polyimide cylinders are relatively higher against high-alloy steel than for carbon steel. Stainless steel counterfaces provide continuously higher wear rates of polyimide compared to steel. It seems therefore that low friction obtained on stainless steel not necessarily implies low wear rates. DLC and DLN coatings provide continuously higher wear rates compared to uncoated steel, with breakthrough of the DLC-coating under the highest sliding velocities. Therefore, the tests were stopped prematurely under 0.9 m/s and 1.2 m/s. Disregarding overload conditions, it seems that relative friction and wear values obtained against different counterfaces show good reproducibility for the various sliding velocities applied on a high-frequency tribotester.

#### 5. COUNTERFACE SURFACE ENERGY MEASUREMENTS

Dynamic contact angle measurements are performed using water and diiodomethane drop tests on a Dataphysics system (Figure 4), that allow for determination of both a polar energy and a dispersive energy component γp component  $\gamma_d$ . The counterfaces are mechanically ground ( $R_a = 0.20 \ \mu m$ ) and polished ( $R_a = 0.05 \mu m$ ) identically to those used in sliding tests and are cleaned with acetone, as surface cleanliness and preparation influence the measurements. The drop geometry is logged for 20 seconds with 40 measurements per drop and each water or diiodomethane drop test is repeated on three locations to ensure the statistical validity. The drop geometry is fitted according to the Laplace-Young method and analysed with the Owens-Wendt method for low energy surfaces. Reference values are chosen from Ström et al. [15] for water ( $\gamma_d =$ 21.80 mN/m and  $\gamma_p = 51.00$  mN/m) and Janczuk et al. [16] for diiodomethane ( $\gamma_d = 50.42 \text{ mN/m}$ and  $\gamma_p = 0.38$  mN/m). Results of a drop test are shown in Figure 5, showing that contact angles slightly decrease towards steady-state obtained after 3 seconds. Differences in drops on steel, DLC and DLN surfaces are shown in Figure 6. Steady-state contact angles together with polar and dispersive surface energies of the different counterfaces are given in Table 4.



Figure 4: Test equipment for surface energy measurements



Figure.5.



Figure 6: Drop tests on different counterfaces, (a) carbon steel St 37-2 N, (b) DLC and (c) DLN

Countorfoco turo	Contact	angle (°)	Surface energy γ (mN/m)			
Counterrace type	water	diiodomethane	polar	dispersive	total	
High alloy steel	42.1	39.8	24.14	34.94	59.09	
St 37-2 N	49.5	41.3	20.78	34.38	55.16	
316 L	68.9	42.1	9.75	35.09	44.84	
DLN	72.9	44.5	7.71	34.58	42.29	
DLC	57.8	43.2	16.80	33.99	50.79	

Table 4. Surface energies of different counterfaces

According to the Dupré equation, the work of adhesion  $W_A$  between polyimde SP and respective counterfaces X is calculated from Formula (1)





**Figure 7:** Relation between work of adhesion and coefficient of friction for different counterfaces (sliding velocities  $\blacklozenge$  0.3 m/s  $\circ$  0.6 m/s  $\blacktriangle$  0.9 m/s)

There should be a general trend for a solid of higher surface energy to have higher friction than one of lower surface energy for sliding under adhesive conditions. Plotting the coefficients of friction against counterface surface energy or work of adhesion (Figure 7) shows that previous rule is valid for DLN, St 37-2 N, stainless steel and HA. DLC however presents relatively higher friction than expected from its surface energy as effects like coating removal and increase in roughness contribute to unstable sliding and higher deformation component of friction.

#### 6. TRANSFER FILMS

Although polymers and DLC coatings are reported to develop a transfer film, the macroscopic polyimide transfer should be more important than the microscopic graphitisation of the DLC-coating located on the roughness peaks, and the properties of the polyimide transfer film will govern the performance of the tribological system. The counterfaces are studied by optical microscopy to reveal different morphologies of polyimide transfer, as shown in Figure 8. For HA-steel, no polymer transfer is

observed under low sliding velocities and very few polyimide into the roughness grooves is observed at higher velocities. The lack of transfer film formation is an indication of high friction. As e.g. discussed by Jintang et al. [17] complex chemical reactions between polymer, transfer and metal occur on the frictional depending on the counterface interface. composition. The cohesiveness at the interface between bulk metal and transfer film is governed by the formation of e.g., organometallics, while other researchers [18] recently described the hypothesis of a "n-p-n semiconductor" structure at the friction interface. They suggested that the impetus for adsorption could be the formation of "p-n junctions" that are favoured by the incorporation of foreign atoms. Another hypothesis is that reactive Cr, Ni, Mo or Mn sites on HA-steel are obviously sensitive to tribo-chemical oxidation during sliding and alter the bonding between the polymer transfer film and the metal surface. As demonstrated by Flint et al. [19] the nature of the oxide coat is influenced by the molybdenum content affecting adhesion. Smooth St 37-2 N steel results in coarse island-like transfer near the borders of the stroke and no transfer film in the centre of the stroke under 0.3 m/s, progressively gaining homogeneity at higher sliding velocity. The film becomes thinner under 0.9 m/s, covering the entire sliding stroke. For 316L stainless steel, plate-like polyimide particles homogeneously dispersed over the entire sliding area are observed. Transfer on diamond-like carbon coatings consists of an island-like film over the entire sliding area. The polyimide flakes for DLN are thinner and smoother compared to DLC, while also the surface fraction covered by polyimide is larger compared to steel and DLC. Separated flakes coalescence at higher sliding velocities into continuous shearing bands parallel to the sliding enhanced direction. partially by higher temperatures. Near the reversals of the sliding stroke, large island-like particles are sheared as the debris mobility is limited against the borders: particles remain in the contact interface between polyimide and counterface during reversal of the sliding motion, while they are immediately removed in the centre of the stroke. Coarse transfer particles are observed on DLC, with surface striations due to coating removal. Also for soft coatings, it was observed by Benabdallah [20] that the coating was removed after sliding against polymers. For present hard

coatings, the adhesion between coating and substrate is important for the coating performance and improves when the relative difference in hardness and internal stresses between coating and substrate decreases. Therefore, the adhesion on steel substrates is better for soft DLN coatings than hard DLC coatings.





**Figure 8:** Optical microscopy of different counterfaces with polyimide transfer, (a) highalloy steel, (b) St 37-2N, (c) 316L, (d) DLN, (e) DLC

# 7. FRICTION AND WEAR MECHANISMS

As polyimide and DLN structures are both characterised by C-C bonds, they show higher structural compatibility than a polyimide/steel combination. Therefore it is observed that wear debris adheres easily on DLN coatings over the entire contact area, however not consisting of a smooth film but rather plate-like transfer particles.

Unlike its compatibility, there is no homogeneous transfer own to the brittle nature of polyimides which does not allow for orientation and easy shear of the molecules. Homogeneous transfer films formed by sintered polyimides are rarely observed due to the lack of surface plastification. Only at temperatures above 180°C, exceeding a secondary transition temperature (no real glass temperature), partial molecular re-arrangements allows for smooth transfer. Sliding against coatings, wear debris remains for several sliding periods in the polyimide/coating contact area and agglomerates into larger particles with local conversion of polyimide/coating into smooth polyimide/polyimide contacts. As the load carrying capacity of the transferred particles is limited, they cause the friction to decrease only under low loads. The high wear rates in sliding against DLN are however attributed to tearing interaction and the abrasive action of transferred particles, as it is known that polyimides do not perform well under abrasive conditions. The higher surface energy for DLC coatings imply high adhesive sliding forces during initial sliding, which result in large wear particles torn out of the polyimide surface. Together with the

high internal stresses, they cause high friction. It is important that also the DLC coating is attacked by abrasive wear of polyimide, explaining its unfavourable performance under high load / high sliding velocity. In sliding experiments with steel, wear debris is partially washed out of the contact zone or forms a more continuous transfer film. The lack of transfer on high-alloy steel or in the centre of carbon steel represents the lower structural compatibility between polyimides and its counterface.

# 8. CONCLUSIONS

From sliding experiments of sintered polyimides against different steel counterfaces and diamond-like carbon coatings, it can be concluded that:

Si-doped DLC (DLN) counterfaces give the lowest friction for 0.3 m/s to 0.9 m/s. Higher sliding velocities however cause instabilities.

Polyimide wear rates after sliding against DLC or DLN are higher compared to steel counterfaces.

The coefficient of friction gradually increases for increasing work of adhesion, however higher friction on DLC coatings is observed as the coatings is catastrophically worn after sliding.

Transfer on DLC and DLN coatings consist of plate-like polyimide particles, while a smooth film is observed on St 37-2 N steel. Also for stainless steel, rather plate-like polyimides transfer is found which is favourable for low friction but higher friction compared to carbon steel.

Hypothesis about the friction and wear mechanisms against diamond-like carbon coatings should take into account the compatibility between an amorphous coating and a polymer structure, both consisting of a carbon-carbon network. Due to their high stiffness and difficult orientation of the aromatic structures, plate-like polyimide transfer particles act as abrasives for the polyimide sliding cylinder.

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### ACKNOWLEDGEMENTS

Surface energy measurements were made in cooperation with K. Van Acker from Vito (Mol, Belgium). We thank ing. W. Van Daele and ing. M. De Waele for assistance in SEM and optical microscopy. Bekaert Dymonics is acknowledged for coating depositions. This research has been financially supported by the FWO (Flemish Research Fund G.0295.01) and the Ghent University Research Board (BOF 01109098).