

The effect of load on the tribological property of polyacetal and metallographic observation

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Abstract

The effects of applied loads on the dry sliding wear properties of polyacetals were investigated using on a conventional plate-disc-type reciprocating sliding wear of tribometer against a hardened 100Cr6 stainless steel as a counterface. The frictional behaviours were determined at a fixed speed. The wear surfaces and wear tracks for the polyacetal samples was observed with an optical microscope when tested at various conditions. The results showed that the specific wear rate decreased with increasing the loads. The static friction coefficient of polyacetals/steel tribo-pairs under 50N load was about 0.74, but decreased to 0.26 for 200N load. Furthermore, wear surfaces and wear tracks observation exhibited that ploughing and cutting were responsible for wear behaviour at lower load, but adhesion and plastic deformation seemed to be dominant for the higher load because increasing normal load also led to a rise in temperature at the frictional surface.

Keywords: Polymer, Polyacetal, Dry sliding, Load, Wear, Friction, Worn surface, Ploughing, Cutting.

1. Introduction

Polymers can be used for sliding friction systems such as ball joints, crane guidance and, roller and gears without lubrication. The most commonly used for polymers are PTFE, PA, POM, PEEK. Among the range of thermoplastics, POM are typical thermoplastic polymers, which is exhibited good sliding properties for different sliding applications because they exhibits low friction, wear and good fatique and creep resistance. Therefore, these polymers has been widely used as self lubricating materials in many fields like manufacturing and otomotive industry, electronic appliance and construction industry [1-3]. POM can replace not only non-ferrous metals but also iron casting, steel casting and stainless steels lighter. In most cases, however, it is of primary concern to develop polymeric materials that possess low

friction and low wear properties under dry sliding conditions against smooth metallic counterparts [4, 5]. The transferred of polymer materials may deteriate or improve the service characteristics of a system due to adhesion between the contacting surfaces by directly taking part in a sliding operation. The transferred materials affect the friction coefficient and wear rate. Numbers of friction and wear behaviour of POM have been performed on the hardened steel counterface in a pin-on-disc, pin-on-ring or reciprocating pin-on-flat. They provide fundamental information about friction and wear mechanisms, consequently used for development of new materials or surface treatments [6, 7]. Friedrich et al.(1995) studied the friction and wear properties of high temperature resistant polymers, particularly polyetheretherketone (PEEK) under various testing conditions against smooth steel counterpart. It is reported that the coefficient of friction increased with increase in load. Wang and Li [9] found that the sliding velocity influenced the sliding wear of UHMWPE polymer to a greater extent than the applied load [10, 11]. They distinguished the wear loss in three different periods during the operating time viz. the wear loss in running-in period, steady-state period and severe wear period. However, it is reported that the wear rates of POM and UHMWPE could decrease with increasing sliding speed when the roughness of the mating surface was low [5]. Bohm et al. [12] revealed that HDMWPE clearly outperformed all of other polymers tested while PEEK indicated the poor wear performance. Seabra and Baptisa [13] found that UHMWPE-green was found to be the lowest frictional coefficient and good wear resistance among the food grade polymers like PTFE, UHMWPE, HMW-PE, PA 6, POM-C and PETP under sugar interface dry sliding conditions. It is concluded that, this polymer was one of the best option to match stainless steel because of the presence of green pigments. The friction coefficients changed with counterface roughness, an



optimal surface roughness of PETP/PTFE and POM-H which were lower than that of PA [14]. The wear rates were higher on rougher surfaces for PA. In case of PA 6G/oil, it strongly depended on the load and surface roughness. However, the wear resistance of PETP/PTFE and POM-H increased with increasing tensile strain at rupture. Samyn and De Baets [15] studied the friction of a commercial polyoxymethylene homopolymer (POM-H) on large-scale and small-scale reciprocating test rigs. No transfer was observed for small-scale tests, while a stable transfer film was developed under large-scale sliding with identical flash temperatures. Later work also showed that for a small scale tests, the calculated flash temperatures were between 60-180 °C that not revealed melting. Samyn et al. [16] reported that PET/PTFE sliding against the stainless steel developing the transfer layer on to the steel surface, which led to reduction in friction coefficient. There was no wear debris found for UHMWPE/carbon against stainless steel [17]. SEM examination indicated that polymer transfer of POM-C was initiated by mechanical interlocking of metal asperities into the polymer. The resulting wear debris particles were smeared into the roughness valleys and, finally the most of the metal surface was covered by the polymer [18].

Liu et al. [19] made an attempt to model the wear behaviour of three polymers such as UHMWPE, PA-6/UHMWPE and PA-6 using a regression analysis. It is reported that the contact pressure was the main controlling parameter for the wear process compared to other influencing parameters such as the sliding distance and speed. Sahin [20] studied the abrasive wear behavior of polyamides through the combination effect of load, speed, distance and grit size. Optimal process parameters, which minimized the wear resistance was the factors combination of L1, S2, G2 and D1 for both polymeric materials [21]. Sagbas et al. [22] studied the abrasive wear of POM under various testing conditions using central composite design (CCD) and artificial neural network (ANN). Sahin et al. [23] investigated the dy sliding wear behaviour of POM using on a conventional flate plate-disc-type reciprocating sliding wear of tribometer. Cylindrical shape of the samples from POM tested against a hardened smooth steel counter face. Frictional behaviours were determined at fixed speed under two different loads. The experimental results showed that static and dynamic coefficients of friction under 100 N normal load varied between 0.432 and 0.266, respectively. In addition, the coefficient of friction and specific volumetric wear rate decreased with increasing the load.

The literature review demonstrated that the sliding wear behaviour of POM polymers were studied. However, there are limited numbers of studies on the sliding wear of the polymers using the effect of lower loads, and roughness [1, 4, 14, 15, 24, 25, 26]. Therefore, aim of this work was to study the dry sliding wear behaviour of POM by experimental base under different loads changing from 50N to 200N at dry sliding conditions. Furthermore, the worn surface observations were carried out to find responsible mechanisms during the dry sliding wear of the polyacetals.

2. Experimental

2.1. Materials and Apparatus

The POM used in this present study, which was commercially available from Ertacetal Company. The charactersitics of the POM-C (Ertacetal-C, white) thermoplastic wear samples. This POM keeps its favourable mechanical properties up to 92°C. The experimental apparatus was a pin-on-flat wear-testing machine with a reciprocating motion. A pin specimen was fixed to a reciprocating stage or to a pin specimen holder by setting screws. The polymer bars were machined into small cylindrical shapes with lathe machine for the pinon-disc wear testing. The diameter of the pin specimen was 8 mm with 15 mm in length. The pin was then mounted in a steel holder in the wear machine so that it was held firmly perpendicular to that of the flat surface of the rotating counter disc. The specimen of 8 mm in diameter for POMs tested under different loads against smooth hardened steels. Chemical, physical and mechanical properties of to be tested materials were given in Table 1. The normal load was applied through a spring and lever.

Table 1. Chemical, physical and mechanical properties of POM-C materials

I OW C materials					
Some properties	Metric units	POM-C			
Density	gr/cm ³	1.41			
Shore hardness	N.mm ²	85			
Compressive	MPa	72			
strength at %5					
Elastic modulus	MPa	2800			

Friction force was measured with a strain-gauge detector installed on the wear-testing machine. POM was slid in a reciprocating motion against cold rolled steel AISI 42CrMo6 grinded to an average surface roughness, R =0.20 - 0.40 µm perpendicular to the sliding direction. For the tests, a polymer cylinder was positioned into a moving head and was slid on its side (line contact) against a fixed steel counterface plate. The steel counterface was fixed to a base plate. The cylindrical samples had a diameter of 8 mm and a length of 15 mm, while the steel mating plate sizes 58 x 38 x 4mm, which was heat-treated to give a surface hardness of 59-62 RC. The tests were carried out at 50N, 100 N, 150N and 200 N normal load, corresponding to 0.99, 1.98, 2.99 and 3.98 MPa contact pressures. The sliding velocity was 0.3 m/s over a sliding stroke of 15 mm. The total sliding distance of 2160 and



4320 m ensures steady-state condition. The wear pin was cleaned in acetone prior to and after the wear tests, and then weighed on a microbalance with 0.1 mg sensitiveness. Each test was performed with new track of disc. The specific wear rate (Ks) was then expressed on volume loss basis:

$$Ks = \frac{\Delta M}{\rho LFn} \left(\frac{mm^3}{N.m}\right) \tag{1}$$

Where M is the mass loss in test duration (gm), ρ is the density of composite (gm/cm³), F_n is the applied normal load (N) and L is the sliding distance (m). Three replicates were carried out for each material and results were averaged from the two test runs. **3.0 Results and discussion**

3.1. Wear rate

The experimental results of the adhesive wear of polyacetals at different conditions are shown in Table 2. The tests relevant to this table were carried out at a fixed speed, but indicated loads. The temperature at the frictional surfaces increased with increasing the load and the frictional heat on polyacetal can not be distributed in time due to the poor ability of heat transfer. The asperity summits became blunt and the spaces between asperities were filled in the running-in period which resulted in lower wear in the steady-state phase. The duration of the running-in phase was dependent on the test condition. It is evident from the figure that the wear rate decreased with increasing applied load, which could be explained with the fact that the wear rate is determined by the pv-value, where p stands for the load and v for the velocity. For example, the wear rates of the samples at loads of 50 N and 200 N varied from 0.61x10⁻⁶ and 1.533x10⁻⁶ mm³ / N.m. Samyn et al.[16] showed that the wear rates was ranged from 6x10⁻⁷ to 4x10⁻⁴ mm³ / N.m. However, typical wear coefficients obtained from pin-on-disc tests with POM pins against rotating steel disc were found to be around 2x10⁻⁶ to 4x10⁻⁶ mm³ / N.m in the available literature [4,10,31].

3.2. Effect of load

Fig.1 shows the influence of loads on the frictional and wear behaviour of polyacetal polymers at a constant speed of 0.3 m/s under different loads. It is observed that the weight loss increased more or less linearly due to increase the deformation of asperities at contacting points (Table 2). It is breaks off easily from the main body. However, the wear rate decreased with increasing the load because it is inversely proportional to the load and sliding distance. The temperature at the contacts rises decreased the shear strength of the polymer since the thermal softening of polymer occurred, which causes lower COF, and temperature also increased the real contact area by flowing across the counterpart surface. As a result of this, adhesion and transferring films became the dominant

wear type instead of abrasion and micro-cutting (see Fig.3).



Fig.1. Specific wear rate of polyacetal at a constant speed under different loads

Table 2. The experimental results of the dry wear rate of POMs under different load conditions

Loa d	Weight loss,gr	Specific wear rate (mm ³ /N.m) (10 ⁻⁶)	Average static COF	Averag e dynami c COF
50	0.02851	1.5330	0.74	0.33
100	0.04030	1.323241	0.42	0.30
150	0.0450	0.9850	0.36	0.28
200	0.03717	0.61023	0.26	0.25

3.3. Coefficient of friction

Table 2 shows the variations of coefficient friction with time for POM. The coefficient friction decreased with increasing the load, that is, it was varied from 0.74, 0.42, 0.33, and 0.26 for 50, 100 and 150 N, respectively. The high COF might be due to abrasive wear between the polymer and the surface of the counter face. The abrasive wear resulted in because of micro-ploughing action of the steel counter-face. The lowest static COF obtained was about 0.26 at 200 N load. The dynamic COF is 0.21-0.33 when the load is 50 N and decreased to 0.24 for higher load. The dynamic COF of POM-H at different conditions were about 0.78 and 0.60 at a fixed speed 0.3 m/s for 100 N and 200 N, respectively [16]. However, they measured the dynamic COF of about 0.33 under 200 N load at a speed of 1.2 m/s. The dynamic COF for POM-C, PEEK and PA6G (pv = 2 MPa.m/s) measured were about 0.20, 0.29 and 0.33, respectively [7].

Typical plots of the COF including static and dynamic as a function of the sliding times for POM under 100 N, 200 N contact loads at a fixed speed are envisaged in Fig.2 (a and b) respectively. The COF of the polymer/steel tribopairs was measured to be in the range 0.42 and 0.28 for static and dynamic component, respectively. Furthermore, the static and dynamic friction coefficients appeared to vary similarly as a function sliding distance or time, but the dynamic COF exhibited lower values than the static component, but indicated a stable behaviour with increasing the sliding distance (Fig.2). The static and



Proceedings of the International Symposium of Mechanism and Machine Science, 2017 AzCIFToMM – Azerbaijan Technical University 11-14 September 2017, Baku, Azerbaijan

dynamic friction coefficient plotted as a function of time in Fig.2 (b) under higher load, the static friction coefficient decreased at higher normal load. For example, the statistic and dynamic COF was about 0.28 and 0.21, respectively because the time to establish a steady-state friction shortened because of the frictional heat for the polymer, which increased the surface temperature. The literature indicated that transfer of the POM to the metal counterface led to an increase in the COF [25]. COF of POM-C sliding against AISI 100Cr6 steel was about 0.51, but decreased to 0.42 with the sliding speed of 0.05 m/s. The dynamic COF of POM at a reciprocating motion with polished steel slider was about 0.32 for POM. The materials were damaged rapidly when changed the sliding velocity from 0.42 to 0.84 m/s [30]. Therefore, the sliding velocity had a more obvious influence on the wear behaviour of POM-H than the nominal load.



Fig.2. Static and dynamic coefficient of friction as a function of sliding time for POM sliding at 0.3 m/s against the smooth steel. (a) 100N load, 16.4x10⁴ cycle, (b) under a 200 N load, 8.8x10⁴ cycle

3.4. Wear surface observations

In order to understand the differences among the polymers, wear surfaces and wear tracks for each one is taken from an optical microscope at a similar condition. The unworn specimen, worn polymer specimens, and counter-faces are examined using an optical microscopy. Fig.3 (a,b and c) show the polymer pin track and worn surfaces at different conditions when sliding against steel counterpart. Fig.3 (a) exhibits a quite rough surface because its only showing a manufactured roughness, not testing one, which is about $3 \mu m$ while Fig.3 (b) indicates an abrasive grooves over the sliding surface because the asperities in the steel counter face easily removed the material from the soft polymer by cutting action, but depth ness of the grooves varies from local place to place. However, Fig.3 (c) shows a relatively smoother surface than that of the previous sample because the polymers are cut by counter face disc, transferred to the steel surface and its surface is covered with the transferred polymer. That is to say, the debris particles pressed into roughness of the valleys. Thus, the traces of ploughings are not visible on the pin surface in this micrograph. Namely, ploughing and cutting are responsible for wear of the first case, but adhesion and plastic deformation seem to be dominant for the last case because increasing normal load also lead to a rise in temperature at the frictional surface. The decrease in the depth of scratches may probably be attributed to the formation of stable, adhesive and intact transfer film on the counter-surface [31, 32].





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Fig. 3. Wear track and wear surface of polymer specimens under two different loads of 0.30 m/s. (a) The pin surface before testing, (b) The pin worn surface tested at 100 N load, indicating abrasive grooves parallel to the sliding direction, (c) The pin worn surface tested at 200 N load, showing adhesive wear of delamination





Fig. 4. Wear surface of the polymer sample tested at: (a) 150 N, (b) 200 N

Fig. 4 indicates the wear surface of the polymer samples tested under loads of 150 N, 200 N, respectively. A similar surface topography was observed for both loads. The average surface roughness of the POM samples was measured when tested at 100N load test without and after the test. The average surface rouhghness was about 0.470 and $0.40 \ \mu m$, respectively. The surface roughness decreased about 15% due to machining the rough surface during the heavy loading. Fig. 5 shows the wear surface of counterpart, tested at 50 N load under low and higher magnification, respectively. This low magnification view indicates the thin films stretching across the abrasion grooves, and it is associated with ridge on sliding surface. The higher magnification also indicates polymeric materials are forced into the valleys between the ridges of the asperities and mechanically interlocks with the metal surface. Two dark lines also an indication of the transferred film is brown colour and adhered to the disc surface firmly. Mechanical anchoring and rolling effect is predominant for the lower load for POMs. This may be due to related to the debris formation, oxidation and surface roughness orientation during the rubbing process.



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b)(a) Lower magnification(b) Higher magnification

Fig.5. Wear surface of counter-face plate under 50 N load at 0.30 m/s. (a) Lower magnification, indicating

mechanical encoring, (b) Higher magnification, showing tribo film formation

Fig.6 shows the wear surface of counterpart, tested at 150 N load at low and higher magnification, respectively. This figure reveals in a more clearly that the transfer film, which formed on the steel plate surface, is built up of more or less continuous thin layer. These are adhered preferentially on the asperity ridges of the ground metal counter-face. The sliding surface was found to heat up which was likely result in increased adhesion. Therefore, there were a more smooth surface obtained at higher load condition





b)(a) Lower magnification(b) Higher magnification

Fig.6. Wear surface of counter-face plate under 150 N load at 0.30 m/s. (a) Lower magnification, exhibiting a formation of transfer film on the wearing surface of the pin, (b) Higher magnification, exhibiting a transfer film on the surface

A similar surface appearance was also observed from the tested conditions, but various loads were applied on both pin and disc surfaces, as shown in Fig.7 (a,b), respectively. This micrograph shows the increase of wear scar width with the load. For example, it was about 0.8 mm when tested at 50 N load, but increased up to more or less 2.2 mm. However, it couldnot observed the same trend for 200 N load. It might be the formation of wear transfer layers because a brown colour was evident for that case. The transfer film formed on the counterpart surface with increasing the load occurs more smooth, thin, uniform, and tenacious





Fig.7. Wear surface of counter-face plate tested at: (a) 150 N, (b) 200 N

4. Conclusions

The following conclusions were drawn based on the experimental results for the frictional and wear properties of polyacetal-steel combinations.

- The experimental results showed that the wear rate of the polyacetals was influenced considerably by the load at increasing rate as approximately 2.5 times. The wear rates of the polymeric samples under the loads of 50N to 200N varied from 0.6102x10⁻⁶ to 1.533x10⁻⁶ mm³/N.m.
- 2. The friction coefficient of POM/steel tribo-pairs when tested at 50N and 200N load was measured to be in the range 0.74 and 0.26 respectively, but there was no significant changes occurred with the loads for the dynamic COF of 0.24-0.33.
- 3. Moreover, the wear surface observations by optic microscopy exhibited that ploughing and cutting were responsible for the wear behaviour of lower loads, but adhesion and plastic deformation seemed to be dominant for the higher load applications because the increasing normal load also lead to a rise

in temperature at the frictional surface of the tested polymeric samples.

References

- Huang T., Lu R., Wang H., Ma Y.& Tian J., Investigation on the tribological properties of POM modified by nano-PTFE, J.Macromolacular Sci.,Part B, Physics 50, 1235-1248 (2011).
- [2] Chen J., Ca Y.& Li H., Investigation of the friction and wear behaviour of POM/linear low-density polyethylene/ethylene/acrylic/acid blends, Wear 260, 1342-1348 (2009).
- [3] Sun LH., Yang ZG.& Li XH, Study on the friction and wear behaviour of POM/Al2O3 nancomposites, Wear 264, 693-700(2008).
- [4] Franklin S.E., Wear experiments with selected engineering polymers and polymer composites under dry reciprocating sliding conditions, Wear 251, 1591–1598 (2001).
- [5] Schwartz C.S.& Bahadur S., Studies on the tribological behaviour and transfer film counterface bond strength for polyphenlyene sulphide filled with nanoscale alumina particles, Wear 237, pp. 261-273 (2000).
- [6] Ziemiankski K.& Capanidis D., The mechanism of dry friction of polyoxymethylene against steel, Wear 82, pp. 317 (1982).
- [7] Kalácska G., An engineering approach to dry friction behaviour of numerous engineering plastics with respect to the mechanical properties, eXPRESS Polymer Letters, 7 (2),pp. 199–210(2013).
- [8] Friedrich K., Lu Z.&Mager A.M., Recent advances in polymer composites Tribology, Wear 190, pp.139–144. (1995).
- [9] Wang Y.Q.& Li J., Sliding wear behaviour and mechanism of ultra-high molecular weight polyethylene, Mater Science Engineering, A 266, pp. 155–160(1999).
- [10] Unal H., Sen U.& Mimaroglu A., Dry sliding wear characteristics of some industrial polymers against steel counterface, Tribology International 37, pp.727–732 (2004).
- [11] Watanabe M., The friction and wear properties of nylon, Wear 110, pp.379–188(1986).
- [12] Bohm H., Betz Sntonio M. Baptista., Tribological behaviour of food grade polymers against stainless steel in dry sliding and with sugar, Wear 253, pp.394–402 (2002).
- [14] Zsidai L., De Baets P., Samyn P., Kalacska G., Van Peteghem A.P.& Van Parys F., The tribological behaviour of engineering plastics during sliding



friction investigated with small-scale specimens, Wear 253, pp. 673–688 (2002).

- [15] Samyn P. & De Baets P., Friction of polyoxymethylene homopolymer in highly loaded applications extrapolated from small-scale testing, Tribology Letters, Vol. 19 (3), pp. 177-189(2005).
- [16] Samyn P. & De Baets P., Wear transition and stability of polyoxymethylene homopolymer in highly loaded applications compared to small-scale testing, Tribology International 40,pp. 819-833 (2005).
- [17] Samyn P.& De Baets P., Friction and wear of acetal. A matter of scale, Wear 259, pp.697-702 (2005).
- [18] Mergler Y.J., Schaake R.P.& Huis in't Veld A.J., Material transfer of POM in sliding contact, Wear 256, pp.294–301 (2004).
- [19] Liu C.Z., Ren L.Q., Tong, J., Joyce T.J., Green S.M.% Arnell R.D., Statistical wear analysis of PA-6/UHMWPE alloy, UHMWPE and PA-6, Wear 249, pp.31–36 (2001).
- [20] Şahin Y., 'Wear analysis of polyamide based on a statistical approach, Int. J. Mater. & Product. Technol. (IJMPT), 54 (1/2/3), pp.108-114 (2015).
- [21] Şahin Y., 'Analysis of abrasive wear behavior of PTFE composite using Taguchi's technique', Cogent Engineering, 2, pp. 1-15 (2015).
- [22] Sagbas A., Kahraman F.&Esme U., Modelling and predicting abrasive wear behaviour of POM using respondse surface methodology and neural networks, Metabk 48 (2), pp. 117-120(2009).
- [23] Şahin Y., Pauw J.D., Sukumaran J.,&Patrick D.B., Sliding friction and wear of polyoxymethlyene

polymer, Synergy International Conferences -Engineering, Agriculture and Green Industry Innovation, Godollő, Hungary, October 12-15, 2015.

- [24] Marcus K.,&C., The sliding wear of ultrahigh molecular weight polyethylene in an aqueous environment, Wear 178, pp. 17-28 (1998).
- [25] Sun L.H., Yang Z.G.& Li X.H., Study of the friction and wear behaviour of POM/Al2O3 nano composites, Wear 264, pp. 693-700 (2008).
- [26] Cai H.C.& Yan F.Y., Investigation of tribological properties of Al2O3-polyimide nanocomposites', Polym. Test., 22, pp. 875-882 (2003).
- [27] Kurukawa M., Uchiyama Y., Iwai T.& Nagai S., Tribological properties of Polyoxymethylene composites against aluminium, Journal of Tribology, 25, pp. 661-669 (2003).
- [28] Hu X., Tribological behaviour of modified polyacetal against MC nylon without lubrication, Tribology Letters 5, pp. 313-317(1998).
- [29]Mens J.W.M.& Gee A.W.J., Friction and wear behaviour of 18 polymers in contact with steel in environments of air and water, Wear 149, pp.255-268 (1991).
- [31].Goyal, R.K.; Jagdale, P.A. & Mulik, U.P., Thermal, mechanical, and dielectric properties of polystyrene/expanded graphite nanocomposites, J. Appl. Polym. Sci. 111, pp. 2071-2077(2008).
- [32] Goyal, R.K.& Yadav, M., Study on wear and friction behavior of graphite flake-filled PTFE composites, J. Appl. Polym. Sci. 127, pp.3186-3191