FRICTION AND WEAR RESISTANCE OF PLASMAPOLYMERIC COATINGS APPLIED ON ELASTOMERS

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ABSTRACT

Using plasmapolymeric coatings on flat elastomer plates as well as on dynamic sealing components a significant reduction of friction was determined in the past [1-4]. Quantifying the improvement of wear resistance enhanced lifetime tests were performed as a function of the applied film thickness. The flat elastomer plates were coated with a plasmapolymeric film ($SiO_xC_yH_z$) in a plasma enhanced chemical vapor deposition (PECVD) process. The film thickness was varied from 0.7 µm to 4.0 µm approximately. The investigated elastomeric substrate material was acrylic rubber (ACM). The friction of elastomers was investigated using an Universal Material Tester (UMT3) system with oscillating pin-on-plate contact geometry. The counterpart in the tribological tests was a 100Cr6 steel ball with a diameter of 10 mm. The tribological tests were run dry in ambient conditions with a velocity of 200 mm/s with a stroke length of 11 mm. Different normal forces between 2 N and 40 N were used. The oscillating measurement setup was chosen to save test time subjecting premature wear. The tests were performed until the coatings were rubbed through to determine the lifetime. It was found that the set in of the wear depended on the film thickness. The set in of wear was detected at the steep rise of the coefficient of friction. The wear resistance increased with increasing film thickness. A minimum film thickness is required depending on the applied load. The load bearing capacity was increasing with increasing film thickness. The beneficial wear resistance of the plasmapolymeric coating depicts the improved lifetime in combination with reduced friction. The film deposition is available at low costs due to the scalable PECVD process. The coefficient of friction was in the range of 0.15 to 0.25. It revealed that the coefficient of friction was independent of the film thickness. Even in the worst case the determined wear rate was below 0.70 µm/km.

Keywords: plasmapolymeric coating, elastomer, friction reduction, wear resistance, energy saving.

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INTRODUCTION

The tribological properties of elastomers are of crucial interest for several industrial products like sealing rings or other elastomer devices. E.g. the reduced friction of sealing rings in an automotive application realizes the reduction of CO_2 emission due to energy saving. As well for some applications it is preferable avoiding grease or oil lubrication due to purity grade. Another reason might be the cost effectiveness. Improved wear resistance at emergency running in a dry case is also desirable. Wear and accordingly the lifetime of components is therefore of economic interest. The used plasmapolymeric coatings in this article are able to provide all these demands. The applied thin films realize low friction at low costs. The investigations regarding reduced dry and lubricated friction of flat elastomer plates using plasmapolymeric coatings were published by the authors in the past [1-3]. Moreover the reduction of friction on coated radial shaft sealings was demonstrated [4]. Consequently, this article focuses on the investigations of wear. For the developed chemical composition of the plasmapolymeric coatings to reduce friction of plastic and elastomeric materials a patent was issued [5].

EXPERIMENTAL DETAILS

Substrate Preparation

As substrate material acrylic rubber (ACM 380 DF) with 75-Shore-A hardness was used. Regarding a formula to convert Shore hardness into a Young's modulus the Young's modulus was estimated as 9.40 MPa [6]. The studied coated and uncoated elastomers were tested as flat plates with a size of 1 cm x 2 cm and a thickness of 2 mm. Before film deposition the substrates were cleaned using a wet chemical solution in an ultrasonic bath at 60 °C.

Film Preparation

The elastomer plates were coated with a plasmapolymeric coating ($SiO_xC_yH_z$). The film was prepared by plasma enhanced chemical vapor deposition (PECVD) using oxygen (O_2) and Hexamethyldisiloxan (HMDSO). The standard mixing ratio of the process gases was 1:3.7 (HMDSO:O_2). The Young's modulus of the plasmapolymeric coating determined by nanoindentation with a Berkovich indenter is 38.40 GPa [3]. A small part of measurements was made with a mixing ratio of 1:1 (HMDSO:O_2). Thereof the Young's modulus was found as 17.69 GPa [3]. The corresponding results are labelled in the case of confusion of dates. The chamber was evacuated to a base pressure below $1x10^{-2}$ mbar before starting the deposition process. The film deposition was carried out at approximately $2x10^{-2}$ mbar working pressure. For improved adhesion a thin interlayer between substrate and topcoat using HMDSO-nitrogen-plasma was applied. Prior to the deposition, the cleaned substrates were activated in a hydrogen-oxygen-plasma. In all steps a power of 1500 W was applied. The deposition process produced a homogeneous coating on the surface laterally as well as in depth vertically. During the deposition process samples were removed from the batch to get different film thicknesses approximately between 0.7 µm and 4.0 µm. Each time an activation was run proceeding the deposition process. The substrate temperature during the deposition process was below 37 °C.

Experimental Setup

The friction coefficient of the coated and uncoated elastomers was investigated using an Universal Material Tester (UMT3) system [7] with oscillating pin-on-plate contact geometry (Figure 1). Elastomer plates were used as test material to see a fast wear reaction. Furthermore the testing of plates is not as expensive as real component tests are [8]. The tribological tests were performed dry without using lubricants under ambient conditions (relative humidity 40-50 %, room temperature 20-22 °C) with a velocity of 200 mm/s and a stroke length of 11 mm. For the first tests a standard normal force of 4.7 N was used which corresponds to an initial Hertzian pressure of 1.61 MPa. As mentioned above, the oscillating tests on plates were performed to intend a fast wear. Contrary to expectations test times over 140 h were needed. Due to these very long test times different normal forces between 2 N and 40 N were tried to find a suitable normal force for the lifetime investigations. The further experiments were performed with a normal force of 15 N corresponding to an initial Hertzian pressure of 2.37 MPa. In passenger cars characteristic initial pressures of radial shaft sealings are in the range of 2 MPa. The elastomer samples were glued on a 1.5 mm thick steel plate to be fixed in the UMT3. As adhesive a cyanoacrylate (Loctite Superglue Precision) was used. The steel plate was a VA steel (material number 1.4301) with a 3C surface. A 100Cr6 steel ball (DIN 5401, Grade 28, material number 1.3505) of 10 mm diameter was used as counterpart. Most tests were performed until the coatings were rubbed through. In addition some coated samples were tested different times and stopped before a failure occurred.

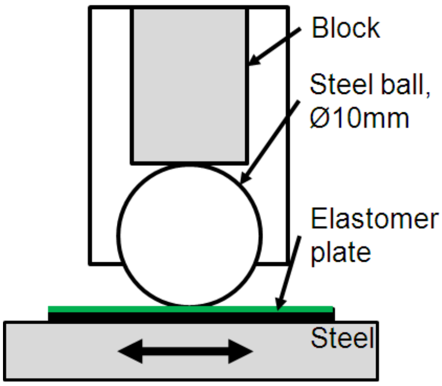

Figure 1. Schematic of the pin-on-plate contact geometry. Uncoated steel ball in contact with coated or uncoated elastomer plate. The flat elastomer plate is glued to a steel plate and is oscillating.

To investigate the film thickness of the intact coatings after the tribological tests, scanning electron microscopy (SEM) and focused ion beam (FIB) measurements were done. For these measurements a FEI Helios Nanolab 600 was used. The samples were evaporated with gold due to electrical conductivity. The FIB cuts were made at 30 kV using a gallium liquid metal source and a small protective platinum patch with approximately 1 µm thickness.

THEORY

Investigations with glass spheres against smooth transparent elastomeric plates revealed that there was no continuous sliding of the rigid asperities against the rubber surface under all conditions [9-10]. For instance, above a critical velocity so called Schallamach waves were observed. Those waves of detachment were observed as small folds of the elastomer across the contact area during sliding. Also it was found that the molecular attraction forces have to be taken into account regarding the deformation of the contacting partners [10-11]. The magnitude of the energy dissipation due to deformation during sliding is increasing due to adhesion [10]. Beside the interfacial bonds the viscoelastic loss properties have to be considered [10].

In summary, the shape of worn elastomers, e.g. roll formation, rubber bulge or so called angels hair, result from adhesive contact and viscoelastic deformation during sliding at sufficient velocities. Reducing the friction of elastomers a plasmapolymeric coating [1-4] with separating behavior was applied for the investigations in this article. That is equivalent to decreased adhesion between counterpart and coated elastomer surface. It is expected that the occurrences of waves of detachment were decreased due to the plasmapolymeric coatings.

Regarding investigations of Moore [12] sharp textures on the rubber surface were also connected to adhesional friction and are causing abrasional wear. Rounded textures on the rubber surface were attributed to hysteresis and are causing fatigue wear [12].

Regarding the ravel structure of the molecule chains of elastomers a plasmapolymeric coating provides a very similar configuration. One fulfilled demand is keeping the elasticity of the elastomers. Another fact is the strong adhesion of coating to the elastomeric substrate due to the similar configuration. In combination with a slightly harder version of plasmapolymeric topcoat in relation to the hardness of the elastomer the wear resistance is increasing. Plasmapolymeric coatings reveal chemical resistance and can be used at low and high temperature. The used deposition technology PECVD allows series-production to realize low costs. As well the film deposition at products with 3D geometries like rotary shaft sealing or others is easily possible.

RESULTS AND DISCUSSION

The tribological tests proofed a reduction of friction of the plasmapolymeric coated elastomers in comparison to the uncoated one (Figure 2).

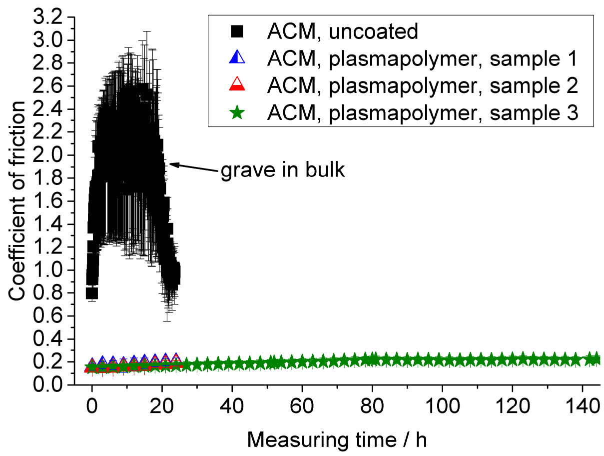

Figure 2. Coefficient of friction of uncoated as well as plasmapolymeric coated elastomeric substrates versus measuring time at 4.7 N. At all three coated samples the film thickness was 2.2 µm.

Comparing the friction results after one minute a reduction by 81 % of the coefficient of friction µ of the uncoated elastomers from 0.80 to 0.15 using plasmapolymeric coatings could be observed. In the uncoated case the counterpart removed elastomeric material continuously. Due to that pile-up the movement was carried out in a grave. In the coated case the counterpart deformed the samples viscoelastically without creating a grave due to avoiding macroscopic abrasion. The results of the three coated samples demonstrate the reproducibility. The first experiments were performed 24 h due to the expectation of fast coating collapse. Nevertheless the measurements demonstrate that the coating withstand an oscillating test with a normal force of 4.7 N more than 144 h. The test was stopped after 144 h to reconsider the testing conditions.

Due to the long measuring time different normal forces were tested to find a suitable normal force for lifetime tests (Figure 3). The Young's moduli of the different samples are indicated in the legend. Increasing the normal force the coefficient of friction is increasing. Depending on the increasing stiffness of the plasmapolymeric coating the slope is decreasing. The uncoated ACM exhibited the lowest stiffness. Comparing 1 µm and 4 µm film thicknesses it was observed that the coefficient of friction is independent of the film thickness.

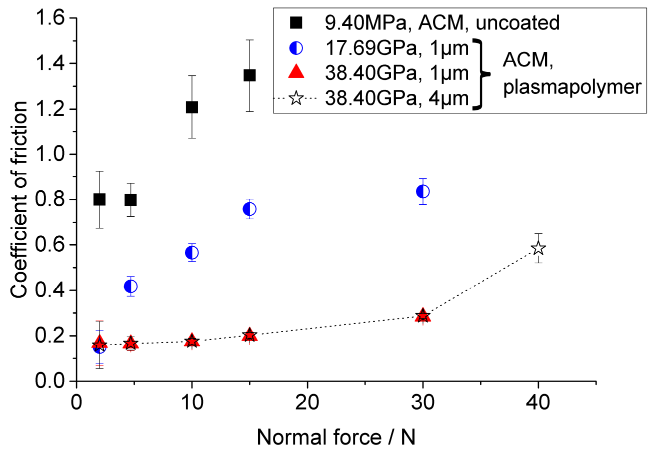

Figure 3. Coefficient of friction of uncoated as well as plasmapolymeric coated elastomeric substrates at increasing normal force after a measuring time of five minutes. The Young's moduli are labelled.

All coated samples revealed a reduced friction in comparison to the uncoated ones at all forces. Due to wear the softer plasmapolymeric coating (Young's modulus 17.69 GPa) revealed less friction reduction. Consequently, there were no further investigations into wear resistance of that soft type. In contrast the harder coating withstand tests up to a force of 30 N. Depending on these results 15 N were chosen intending further lifetime tests to achieve shorter test times.

Examples of the recorded friction data at 15 N are shown in Figure 4. A significant improvement of the wear resistance could be observed comparing uncoated and plasmapolymeric coated elastomeric substrates. The measuring time till the samples were worn was increased. The uncoated sample was rapidly worn in the first minutes. The coated ones withstand several hours dry rapid testing.

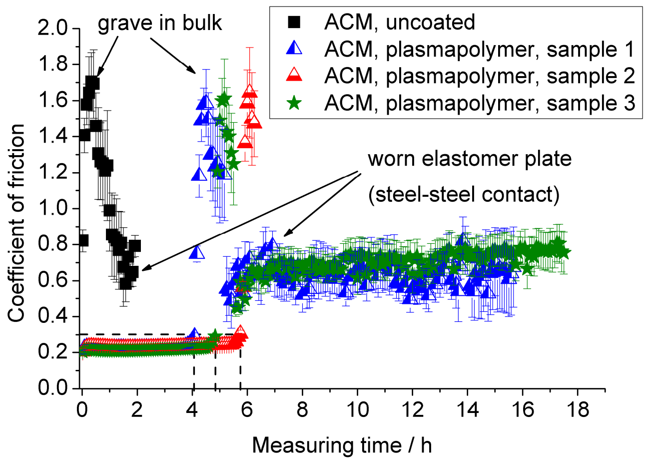

Figure 4. Coefficient of friction of uncoated as well as plasmapolymeric coated elastomeric substrates versus measuring time at 15 N. Film thickness was 2.2 µm. The limit of µ=0.3 until film was lost and the regarding measuring times were marked with dashed lines.

Evaluating the wear rate the measuring times at which the films revealed high wear were determined. The used limit of the coefficient of friction of µ=0.3 was indicated in the graph (Figure 4).

Analog the used limit of the uncoated substrates was µ=0.6 after a raised coefficient of friction. That's once the 2 mm substrate plate were rubbed through and there was a steel-steel contact. An intermediate determination of a wear track in the uncoated as well as coated case would have the significant influence of the compression set.

The film thickness deposited on the elastomeric substrates was varied. At least three samples for each film thickness were investigated. The measuring time till set in of wear was evaluated (Figure 5). Regarding the used tribological contact of dry steel ball versus oscillating elastomer plate at normal force of 15 N it was found that a minimum film thickness of approximately 2 µm is necessary improving the wear resistance significantly. That means the load bearing capacity was increasing with increasing film thickness. Concerning the minimum wear resistance an increase of the measuring time till set in of wear was observed at increasing film thickness (Figure 5). Unfortunately, there were varying results concerning the time above a film thickness of 2.2 µm. Nevertheless an improvement of the wear resistance due to the plasmapolymeric coating has been revealed. The found measuring time till set in of wear was increasing with increasing film thickness.

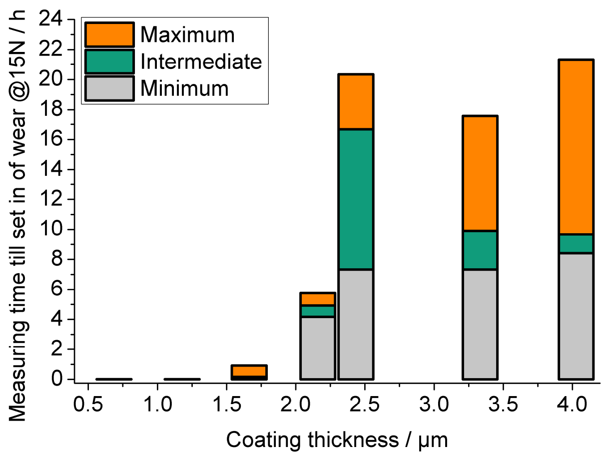

Figure 5. Measuring time at set in of wear versus the applied film thickness at 15 N.

The reason for the varying results at identical film thickness is not clear. The coefficient of friction was independent of the film thickness as well as reproducible at samples with the same film thickness (Figure 6). The room temperature was between 20 and 22 °C. The relative humidity was ranging between 40 and 50 %. The level of the coefficient of friction was not increased before the films were worn (compare Figure 4). That means there was no obvious contamination of the coating surface due to relative humidity or others. Every time a complete new counterpart was used. Samples as well as counterparts were cleaned prior testing.

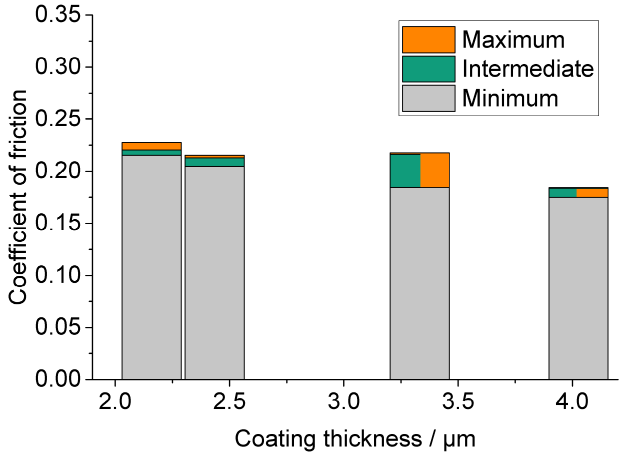

Figure 6. Coefficient of friction of plasmapolymeric coated elastomeric sub-strates versus applied film thickness at 15 N after measuring time of five minutes.

The adhesion between plasmapolymeric coating and elastomeric substrate was excellent in all cases. The surface texture as well as the roughness was identical regarding conditions of production. All samples were cut out of one bigger elastomeric plate and were cleaned the same way. The samples were coated in the same deposition process with high homogeneity. The observed friction results revealed statistically deviation. At the actual state it is only clear that the plasmapolymeric coating revealed an improved wear resistance with an observed minimum and maximum.

Assuming that the wear is increasing proportional at increasing measuring time a linear wear rate was calculated for the uncoated case as well as for each film thickness of the plasmapolymeric coatings. The linear wear rate of the uncoated ACM elastomer was 112 µm/km at 4.7 N and 1755 µm/km at 15 N. The linear wear rate of the plasmapolymeric coating for film thicknesses over 2 µm at 15 N was plotted in Figure 7. The determined wear rate was below 0.70 µm/km in the worst case. In the best case a wear rate of 0.16 µm/km was found at 2.4 µm film thickness.

Jacoby et al. published a linear wear rate of 1-2 µm/km investigating a plasmapolymeric coating with hardness gradient of 1 µm thickness [13, 14]. It has to be noted, that the testing conditions were different. Jacoby et al. stretched a coated elastomer plate using a 29 cm steel ball on the backside. The stretched samples were slided against steel plates using a normal force of 30 N. An initial Hertzian pressure of 0.32 MPa has to be assumed.

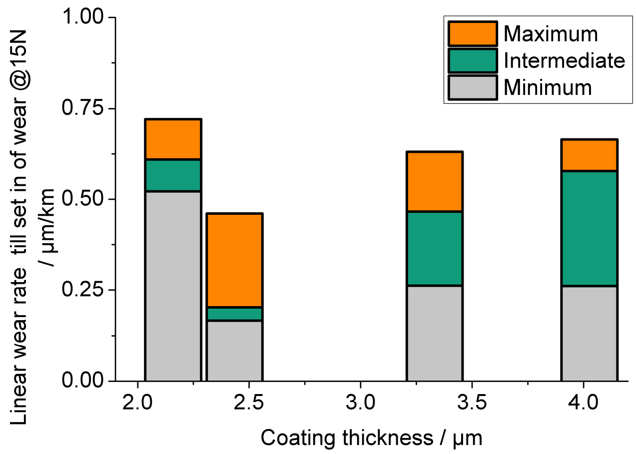

Figure 7. Linear wear rate determined by set in of wear at increasing film thickness in the range from 2.2 µm to 4.0 µm. Normal force was 15 N.

A comparison of the wear rates determined using set in of wear of the plasmapolymeric films and FIB investigations on intact films is plotted in Figure 8. Analog to the previous calculation of the wear rate the abraded film thickness observed by FIB due to remaining film thickness was divided by the travelled distance due to measuring time assuming linearity. The evaluation via FIB on intact films revealed decreasing amount of wear at ongoing measuring time and therewith a decreasing wear rate. At the beginning of the tribological test the main part of the wear occurred. That's corresponding to a running in behavior.

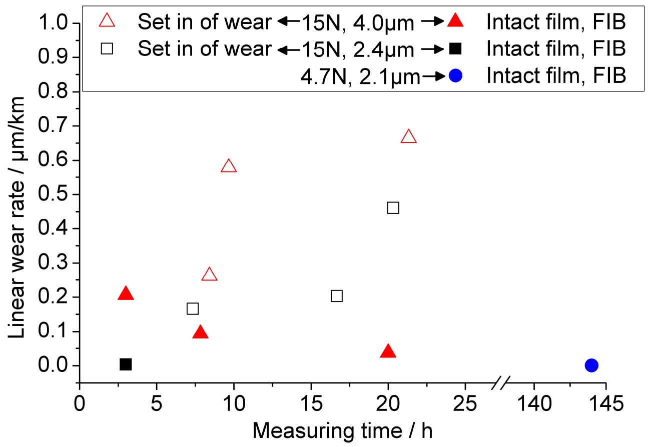

Figure 8. Linear wear rate of worn and intact films. The worn coatings were evaluated regarding set in of wear. In the case of the intact films the cross-sections were investigated using FIB.

Regarding the tests running until film was lost an increasing wear rate at increasing measuring time was found (Figure 8). It has to be noticed, that there might be no linearity of the wear rate. Regarding a comparison of values it is necessary to indicate the measuring time. The possible minimal wear rate of the samples is indicated by the investigations using FIB (Figure 8).

Using the former standard normal force of 4.7 N (1.6 MPa initial Hertzian pressure) at the dry rapid testing the FIB investigations revealed only 44 nm abrasion of the plasmapolymeric coating (film thickness 2.2 µm) in 144 h measuring time statistically. Consequently, a linear wear rate of $0.4(3)\cdot10^{-3}$ µm/km was determined. Figure 9 shows the plasmapolymeric coated tool traces on the elastomeric substrate. The tool traces were in direction of oscillation (bottom-up). The polished asperities on the hills represent the occurred wear of the plasmapolymeric coating. The lower areas are without any traces of wear. Figure 9 also shows the preparation for the FIB investigation. The raised rectangular bar from left to right in the middle of the picture was the protective platinum patch to prepare the cross-section measuring the remaining film thickness of the plasmapolymeric coating.

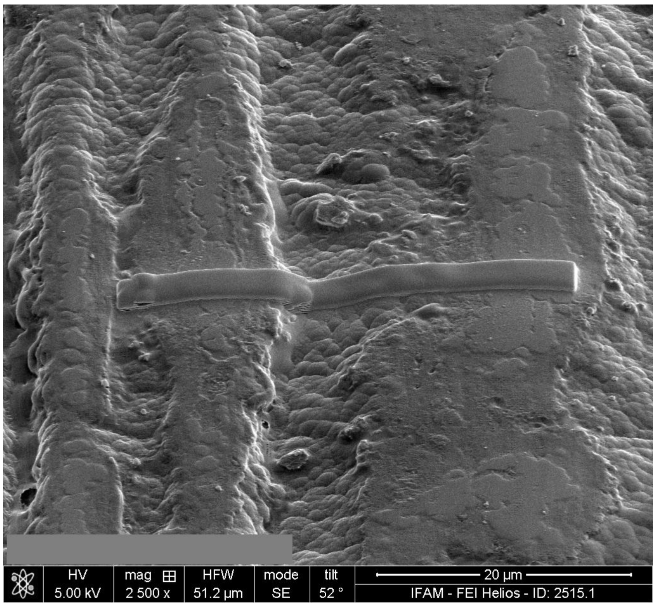

Figure 9. SEM picture before FIB bombardment. Abrasion of the asperities are illustrated. The tribological oscillation was in direction of the tool traces (bottom-up).

CONCLUSIONS

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The results demonstrate that the application of a plasmapolymeric coating on elastomer substrates reduces friction as well as wear. A reduction by 81 % of the coefficient of friction of the uncoated elastomers from 0.80 to 0.15 using plasmapolymeric coatings could be achieved. It was revealed that the coefficient of friction was independent of the film thickness. Regarding the dry oscillating test method an improvement of the wear resistance due to the plasmapolymeric coating of 3 to 4 orders of magnitude lower was found. The linear wear rate was evaluated by films rubbed through as well as FIB investigations on intact films. Depending on the test method the wear rate varied. Using the tribological test with 15 N until the plasmapolymeric coating was rubbed through a wear rate of only 0.16 µm/km was determined. Regarding the used load and testing conditions a suitable minimum film thickness has to be applied. In the case of 15 N 2 µm film thickness is needed for a significant wear reduction. Investigating intact films using FIB a lowest linear wear rate of 0.0371(5) µm/km occurred. After 144 h testing at a normal force of 4.7 N the FIB investigations on the intact film revealed a linear wear rate of $0.4(3)\cdot 10^{-3}$ µm/km.

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