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Adhesive and tribological behaviour of cold atmospheric plasma-treated polymer surfaces

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1. INTRODUCTION, OBJECTIVES

The present research deals with testing the reliability of polymer surfaces modified with Dielectric Barrier Discharge (DBD) source, atmospheric cold plasma process in polymer-polymer and polymer-metal contact-systems through revealing adhesive and tribological characteristics. The named process is suitable to modify the physical and chemical structures of polymer surfaces efficiently and thus change their surface characteristics including their adhesive and tribological properties. Two groups of polymers had been selected: the first is engineering polymers including PEEK, PET, PA6-E, and POM-C. The second is Polyolefin polymers and Fluorine polymer include PP, UHMW-PE (HD1000 and HD500), and PTFE due to the importance of these groups in sticking technique application also in industrial and medical applications, etc. In contrast, (S235-construction steel) has been utilised as the main metallic counterpart. We characterise the untreated, treated, contacted and tribologically tested samples by complex surface analytical, adhesive and tribological tests. The primary target is to find relationships between the parameters of plasma treatment and the induced surface chemical and physical changes as well as links between the adhesive and tribological characteristics that can form the basis of producing structures with reliable polymer-polymer and polymer-metal bonding.

The main aim of the research to describe (or/and find) the relation and useful data between the surface properties and the tribological behaviour of engineering polymers due to the effect of the DBD atmospheric plasma treatment. The objectives of this work are:

- Description of the sliding friction measurements of the different polymer/steel pairs using pin-on-disc tribometer apparatus under dry and lubricated conditions with treated and virgin polymer surfaces.
- Comparison of friction and wear behaviour of the selected engineering polymers in connection with their plasma treated surface. Surface energies, chemical composition, and surface topography are taken into consideration.
- Investigate the adhesive behaviour of the virgin, and DBD plasma treated polymers. Change in surface energies (polar and dispersive components); wettability is investigated. Adhesive bonding tests are performed with typical glueing materials selected for engineering polymers.
- Giving general connection between virgin and DBD plasma treated polymers concerning surface characterisation and tribological behaviour.
- Set the optimal condition and possibilities of DBD plasma treatment advantageous for the selected engineering polymers.

2. MATERIALS AND METHODS

The present chapter is introducing the materials and their preparations in addition to the engineering and scientific methods.

2.1. Materials and preparations

Experimental materials

Eight types of commercially available thermoplastic (semi-crystalline) polymers (distributed by Quattroplast Ltd., Hungary and produced by Ensinger GmbH, Germany) were used in bulk conditions (unfilled). The polymers are distinguished to two groups to facilitate comparison process: 1) Engineering polymers including PEEK, PET, PA6-E, and POM-C, and 2) Polyolefin polymers including PP, UHMW-PE (HD1000 and HD500), and PTFE.

Adhesives

The commercial adhesives with a controlled bond line thickness of 0.1 mm were applied following the manufacturer procedures (Henkel AG & Co., Germany), including: (i) Loctite 406 (Ethyl cyanoacrylate) with Loctite 770 (Primer-Cyanoacrylate-Aliphatic amine) as activator, (ii) Loctite 9466 (two-component epoxy), (iii) Loctite 330 (Acrylic-Urethane metacrylate ester), (iv) Loctite 3035 (Acrylic-Methacrylate).

Specimens preparation

For tribological tests, polymer specimens were machined into pins with a diameter of 10 mm and thickness of 4 mm. The surfaces were subsequently polished with wet SiC paper (grid numbers P1200 and P400) and felt sheet toward required surface roughness. The same surface preparation was applied for samples used in tribological tests, surface chemical composition, topography, and energy measurements except morphology scan and AFM measurements where extruded polymer surface was applied. However, adhesive test specimens were cut from extruded plates in a rectangular shape with dimensions: 25.4 mm x 100.0 mm x 2.0 mm and applied to the test with the virgin extruded surface. Before testing, all samples were cleaned in an ultrasonic bath with distilled water and 96% ethanol (Reanal, Hungary).

Steel surfaces (counterfaces) were first ground and polished with SiC abrasive paper (grid numbers 400 and 600) with grooves oriented parallel in a single direction. For tribological and adhesive tests, the average roughness of the steel plates was $R_a=0.72\pm0.02$ μm perpendicular to the grinding direction and $R_a=0.46\pm0.02$ μm parallel to the grinding direction (measured with SurfTest SJ-201, Mitutoyo, Japan). The steel specimens of adhesive tests have the same dimensions of polymer specimens as mentioned above. The surfaces were subsequently cleaned with Loctite SF 7063 (Henkel AG & Co., Germany) according to the supplier's technology.

2.2. Plasma treatment

The polymer surfaces were modified by cold atmospheric plasma treatment using a dielectric barrier discharge (DBD) equipment (manufactured by Roplass s.r.o., Brno, Czech Republic) operating under controlled air atmosphere (temperature 23°C, relative humidity 50%), as shown in Fig. 1. The plasma panel consists of two systems of parallel strip-like electrodes (with typical dimensions of: 1.5 mm wide, 0.5 mm thick, 1 mm strip to strip) embedded in aluminum oxide

matrix. The ceramic layer between the plasma and electrodes has a thickness of typically 0.4 mm. The plasma is ignited with a high frequency (10–20 kHz), high voltage with peak-to-peak values of 20 kV. The elementary discharge involves a diffuse surface discharge developed over the metal electrodes and a filamentary streamer discharge created between the electrodes giving its H shape. Visually homogenous plasma can be reached with increasing voltage and absorbed power as more and more elementary discharges are generated. The applied high voltage may give rise to the heating of the dielectric surface and the surrounding gas, too. In order to keep the system at the lowest possible temperature, oil is circulated over the system, which allows to keep the gas temperature around 320 K. The power of the DBD plasma system is set to 320 W, which provided a quasi-homogeneous diffuse plasma with air as process gas. The plasma treatment time is one minute for each polymer sample. The treatment time was decided to obtain the maximum surface modification according to early stage of surface energy investigations. The samples were stored in aluminum foil until further use. The following surface characterisation, adhesive and tribological testing were all done within 24 hours after the surface plasma treatment to fully include the effects of surface modification and under ambient air conditions ($T= 23^{\circ}\text{C}$, $H= 50\%$). Preliminary results revealed that the plasma-treated surfaces start to recover toward their original state after longer time (i.e., after two days).

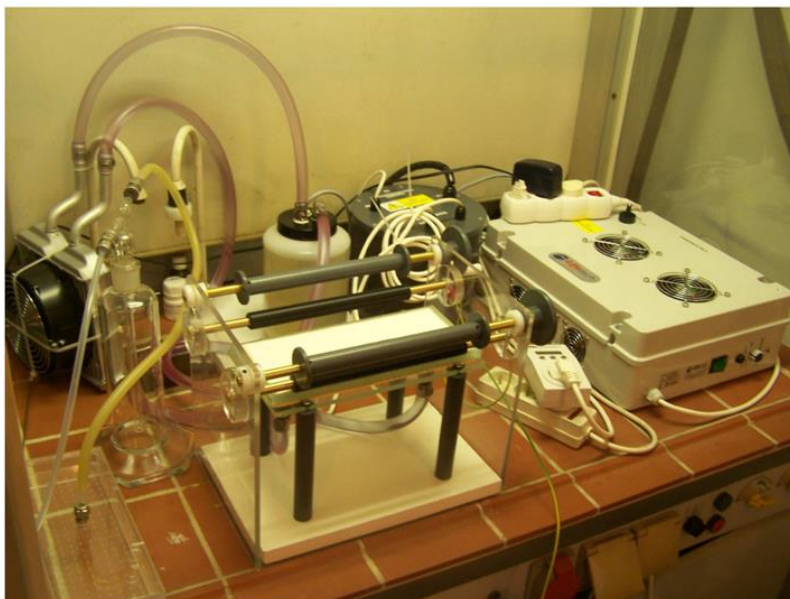


Fig. 1. DBD laboratory equipment which used for polymer surfaces treatment

2.3. Surface characterisation

Chemical composition

The X-ray photoelectron spectroscopy (XPS) was carried out on a XSAM 800 spectrometer (Kratos, Manchester, UK) equipped with a non-monochromatic Mg $K\alpha_{1,2}$ radiation source (1253.6 eV) operating under a fixed analyser transmission mode (chamber pressure $<10^{-7}$ Pa) to investigate the chemical composition of polymer surface. The pass energy was set at 80 eV for survey spectra (wide scan) and at 40 eV for high resolution (detailed) spectra. The wide scan spectra were recorded at 0.5 eV steps in the 50 to 1300 eV energy range while the detailed spectra were recorded at 0.1 eV steps for the respective main elements. As a reference, the C1s line for the hydrocarbon C-H_x component was set to a binding energy of 285 eV. The accuracy of binding energy

determination was ± 0.2 eV. The data acquisition and processing was performed with the Kratos Vision 2 software, applying a Shirley type background subtraction and decomposition of the peaks using a mixed Gaussian-Lorentzian shape of equal full-width-at-half-maximum. The quantitative analysis of the surface composition was based on integrated peak areas calculated by the XPS MultiQuant program and is expressed in at.-%, using experimentally determined photo-ionisation cross-section data and asymmetry parameters.

Wettability

For surface energy values (wettability), contact angles were measured by static sessile drops, using the Surface Energy Evaluation (SEE) System apparatus (Advex Instruments, Czech Republic, the equipment is available at AKI, MTA). Double distilled water and diiodomethane (CH_2I_2) (Sigma-Aldrich, Reagent Plus 99% grade) were used as testing liquids deposited as 2 ml droplets by a Hamilton syringe. The contact angles were measured after stabilisation of the drop shape (typically after 5 sec) and are reported as an average of five measurements with standard deviation. From these measurements, the total surface energy together with polar and dispersive components are calculated following the Owens-Wendt method.

Morphology

The surface morphology of extruded polymer surfaces was analysed by scanning electron microscopy SEM (Carl Zeiss EVO, 40 XVP microscope, Germany) with heated tungsten source. Before the shots, samples were plated by gold to compensate the insulation properties of the plastics and avoid interference with the measurements. SEM resolution is 3 nm at 30 kV (SE and W), and 4.5 nm at 30 kV (BSD - XVP® mode) with 0.2 to 30 kV Acceleration Voltage. The magnification capability is 7 to 1000 000 \times , the field of view is 6 mm at the Analytical Working Distance (AWD); the X-ray Analysis is 8.5 mm AWD and 35° take-off angle.

Topography

The surface topography was evaluated from non-contact profilometry, using a 3D optical profilometer Coherence Correlation Interferometry (CCI) HD type (Taylor Hobson, Leicester, England, the equipment is available at Soete Laboratory, Ghent University) with an ultra-high precision closed loop piezoleless z-scanner having a resolution in z-direction of 0.1 Å. The white light illumination was produced from a Fibre lite DC-950 source and measurements were made at 50% light intensity. A surface area of $330 \times 330 \mu\text{m}^2$ was imaged by vertical scanning interferometry, with an objective lens at magnification 50X and numerical aperture= 0.55. The scanning arrays contained 2048×2048 pixels with a field-of-view= 330 μm , corresponding to a pixel size of 0.165 μm . The images were processed by Talymap software (Digiserve) to calculate the 3D surface roughness parameters according to ISO 25178, including S_a (average roughness), S_z (maximum height), S_{ku} (kurtosis), and S_{sk} (skewness). The roughness values were determined as average from three measurements at independent surface locations, with repeatability $S_a < 0.2$ Å.

2.4. Adhesive testing

Lap-shear tests were done according to DIN EN 1465 on single lap joints of polymer/polymer or polymer/steel pairs (bonded area $25.4 \times 12.5 \text{ mm} = 317.5 \text{ mm}^2$). The pairs were bonded by using

the apparatus was specifically designed for this purpose to ensure the accurate overlapping and bonding. The apparatus was made of PTFE to reduce the possibility of specimens sticking to the apparatus (knowing, the low sticking ability of PTFE). The commercial adhesives with a controlled bond line thickness of 0.1 mm were applied in the jig following the manufacturer procedures (Henkel AG & Co., Germany). The bonding area was maintained under a constant normal load of 5 N during curing. The prescribed amounts of glue are approximately 0.035 ml of Loctite 406 and 0.1 ml for the other structural adhesives, respectively. The test samples were glued immediately after plasma treatment and stored in aluminum foil until adhesive testing was done. For adhesive testing, the coupons were mounted in a universal mechanical tensile bench (Zwick Roell Z100, max. 100 kN, at Szent István University) and the heads were pulled at 1.3 mm/min following ISO 527-1 standard. The adhesive bonding force was determined as the maximum load on failure of the bond, and the adhesive shear strength was calculated as the average of five repeated measurements of force at failure per bonded surface area.

2.5. Tribological testing

The tribological tests were done on a pin-on-disc configuration according to the VI. wear test category of the German standard DIN 50322 using a dynamic tribotester constructed at Szent István University (Fig. 2) with polymer pin (diameter 10 mm, thickness 4 mm) mounted in a stationary holder and loaded against a rotating steel counterface (disc diameter 100 mm, thickness 12 mm). The counterfaces of standard and non-alloy steel with low carbon content (0.17 %) and tensile strength= 400-500 N/mm², grade S235 (Ferroglobus Ltd., Hungary) were applied for both adhesive and tribological testing. A homogeneous and parallel contact area is assured by aligning the polymer pin with a small bearing ball at the top and fixing it with a needle to avoid rotation during sliding. The polymer pin is mechanically loaded against the steel counterface through a dead-weight loading system. The radius of the frictional track can be selected by the position of the cross guiding rail and is fixed at 40 mm for each experiment. The friction force is measured from the bending moment induced to the pin under sliding and recorded by strain gauges. The wear is characterised by the drop-in height of the polymer specimen and is measured as the vertical displacement of the pin holder with a contactless proximitor. The temperature rise is measured by a thermocouple introduced in the polymer pin at 1 mm above the contact zone (i.e., the polymer bulk temperature). During testing, the friction coefficient μ , the vertical displacement (Δh = wear + deformation) and the temperature T are continuously monitored. The tribological results are calculated as an average of three repeated measurements. Two testing protocols were followed to study the sliding under mild conditions:

- sliding tests under “dry” conditions were performed by applying a sliding velocity $v= 0.05$ m/s and stepwise increasing contact pressures $p= 0.5, 1, \text{ and } 2$ MPa (i.e., pv -conditions 0.025, 0.05 and 0.1 MPa.m/s) over a sliding distance of 60 m (i.e., sliding time 20 min) for each load. The applied time per load level was experienced as sufficient to establish steady state sliding conditions. The total sliding distance was 180 m (i.e., total sliding time of 60 min),
- sliding tests under “run-out” lubrication conditions were performed, using commercial gearbox oil (SAE 80W90): a drop of oil (10 ml) was added onto the steel disc through a pipette in front of the polymer contact zone during a first sliding period (0.5 m distance), followed by the automatic cleaning of the lubricant layer by wiping the sliding track on the

steel surface with a sponge during a second sliding period (9.5 m distance). As such, (i) the first period of sliding corresponds to an oil-lubricating regime, while (ii) the second period of sliding is representative for a mixed or boundary lubrication regime, although the exact thickness of the lubricating oil film has not been further assessed due to its permanent change in thickness over time. The tests were run under a sliding velocity $v = 0.05$ m/s, contact pressure $p = 0.5$ MPa (i.e. pv -condition 0.025) and total sliding distance 10 m.

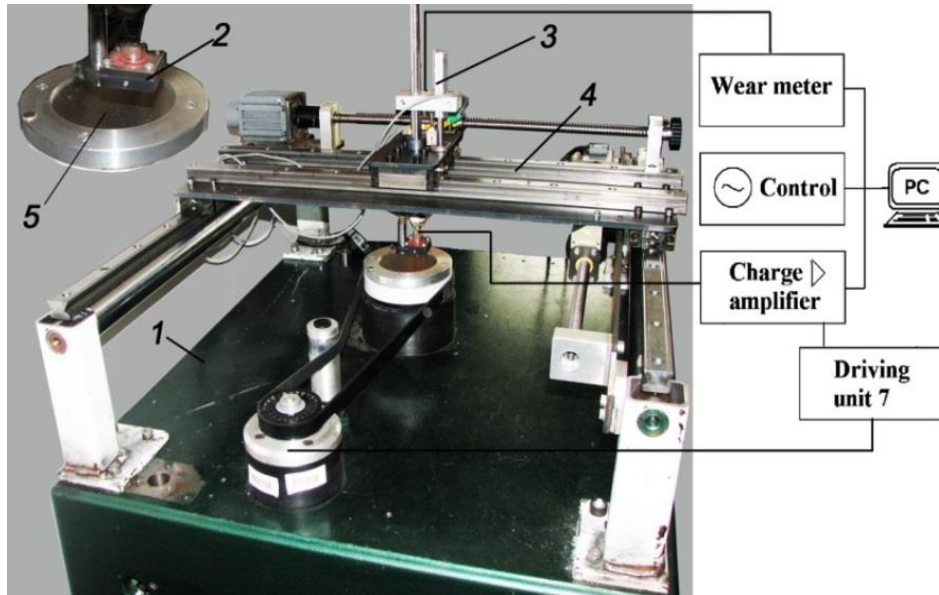


Fig. 2. Experimental set-up of the Pin on Disc tribotester: 1) base frame, 2) Pin holder, 3) loading head, 4) positioning rail, 5) rotating steel disc

3. RESULTS

The present chapter displays the most important achieved results and their discussion.

3.1. Surface characterisation

Surface characterisation is done according to the surface chemical composition, wettability, morphology, and topography which control the latter polymer's behaviour in adhesive and tribological measurements.

Chemical composition

Engineering polymers:

The changes in chemical surface composition after plasma treatment were monitored by XPS analysis of engineering polymer surfaces. The wide-scan spectra indicated three characteristic peaks at 285.0 eV (C1s), 533.2 eV (O1s), and 400.4 eV (N1s). The elemental composition (at.-%) before and after plasma treatment was calculated from high-resolution XPS spectra (Table 1 for PEEK). The presence of nitrogen on the pristine samples of some polymers presumably results during the preparation of the materials where the nitrogen atoms are covalently bonded to the carbon chain. After plasma treatment, the oxygen content has increased and carbon content has decreased (see ratio nO/nC), while some more atmospheric nitrogen may have further reacted with the activated surface of PEEK, PET and PA6-E whereas there is no presence of nitrogen can be observed on POM-C surfaces before and after treatment. The surface of pristine polymers is contaminated with a hydrocarbon layer that is typical for each polymer stored in ambient conditions and efficiently removed after plasma treatment. As a result of plasma treatment, polar groups were formed containing oxygen on the surface which can contribute to a hydrophilic improvement.

Table 1. Elemental composition of pristine and plasma-treated PEEK surfaces determined from high-resolution XPS spectra

Sample		O (at.-%)	C (at.-%)	N (at.-%)	nO/nC
PEEK	Theoretical	13.63	86.35	0	0.158
	Untreated	25.3	73.4	1.4	0.345
	Plasma-treated	27.2	70.6	2.2	0.385

Polyolefin polymers and PTFE:

The elemental composition (at.-%) before and after plasma treatment was calculated from high-resolution XPS spectra (Table 2 for UHMW-PE HD1000). As unavoidable surface contamination, a small amount of oxygen and nitrogen could be detected on the pristine polyolefin polymer surfaces. Upon plasma treatment, the oxygen content increased with the parallel decrease of the carbon content indicated by the changes of nO/nC atomic ratios. This suggesting incorporation of oxygen-containing polar groups into the surface that provides reason to the better wettability.

The elemental composition of pristine PTFE surface is pretty close to the theoretical one (Table 3), while the nF/nC atomic ratio significantly decreases after plasma treatment which proves the significant defluorination ability of DBD plasma. Although the oxygen content also changed,

the moderate increase suggests a limited build-up of oxygen containing groups, comparing to other polymers.

Table 2. Elemental composition of pristine and plasma-treated polyolefin polymer surfaces determined from high-resolution XPS spectra

Sample		O (at.-%)	C (at.-%)	N (at.-%)	nO/nC
PE HD500	Theoretical	0	100	0	0
	Untreated	7.8	90.7	1.5	0.086
	Plasma-treated	24.9	71.4	3.7	0.349

Table 3. Elemental composition of pristine and plasma-treated PTFE surfaces determined from high-resolution XPS spectra

	O (at.-%)	C (at.-%)	F (at.-%)	nF/nC	nO/nC
Theoretical	0	33.3	66.6	2	0
Untreated	0.5	31.5	68	2.159	0.016
Plasma-treated	0.8	37.2	62.3	1.675	0.022

Wettability

The contact angle values of water (γ_w) and diiodomethane ($\gamma_{CH_2I_2}$) together with calculated surface energies of pristine and plasma-treated samples (after 24 h and 80 days) are summarised in Table 4 for PEEK and UHMW-PE HD1000, including total surface free energy (γ_{tot}) with its polar component (γ_{polar}) and dispersive component (γ_{disp}). After plasma treatment, the contact angle of all polymers decreases and the surface energy increases mainly due to an increase in polar component of polymer surfaces. The higher surface wettability after plasma treatment is in line with the presence of polar functional groups at the surface, as confirmed by the previous XPS data.

Table 4. Surface energy of pristine and plasma-treated polymer surfaces (after 24 h and 80 days) determined from contact angle measurements (Owens-Wendt method)

Sample		θ_w (deg)	$\theta_{CH_2I_2}$ (deg)	γ_{pol} (mJ/m ²)	γ_{disp} (mJ/m ²)	γ_{tot} (mJ/m ²)
PEEK	Untreated	70±1.5	30±6.4	6.1	44.3	50.4
	Treated (24 h)	29±2.2	29±3	26.4	44.9	71.3
	Treated (80 day)	48±3	35±2	17.4	40.1	57.5
	Δ 24h/80 day %			332/-34	1.4/-10	41/-19
PE HD1000	Untreated	87±0.4	47±1.9	1.9	36.2	38.1
	Treated (24 h)	35±2.3	35±5.8	24.7	42.2	67
	Treated (80 day)	53±4.6	43±6.1	16.8	38.2	55
	Δ 24h/80 day %			1200/-32	17/-9.5	76/-18

Morphology

The morphology of polymer surfaces was studied by scanning electron microscopy SEM from several positions for each polymer surface. Surface morphology has been examined for extruded polymer surfaces later have used for adhesive bonding tests. The magnitude of magnification was

3. Results

assigned depending on which level the surface morphology change can be detected. In spite of small parallel scars, and spherical surface impurities can be visible, the pristine surface of PEEK runs mostly smooth. However, there is some tiny unevenness on the right-hand side of the surface which gives a rough pattern (Fig. 3 left). On plasma treated sample, there are small areas formed on the molten surface, while the small parallel scars disappeared (sample orientation and measuring site were almost identical). The tiny small spheres and the brighter area in the upper right corner are made of more significant amounts of oxidised materials (Fig. 3 right). The surface roughness of all extruded polymer surfaces is increased after plasma treatment in line with PEEK behaviour except UHMW-PE.

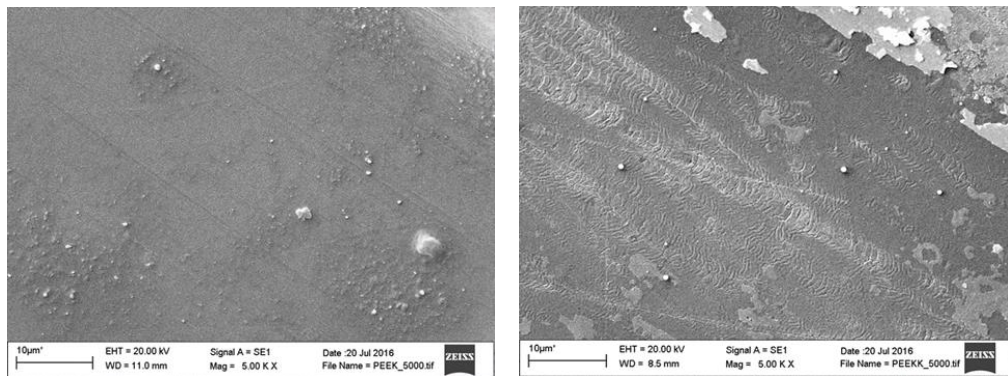


Fig. 3. Surface morphology of PEEK from scanning electron microscopy SEM, left: untreated, right: treated (5000X magnification)

The 10000X magnification (Fig. 4) points out that the unevenness of UHMW-PE pristine sample at this resolution is less, and apart from surface mechanical damage, the pristine sample surface is rougher than plasma-treated sample. During the treatment, very small micro-grooves were formed. This pattern appears to be repeated throughout the examined surface, suggesting that plasma-treated surface interaction occurs everywhere, the groove shape itself may depend on plastic properties and/or the degradation rates.

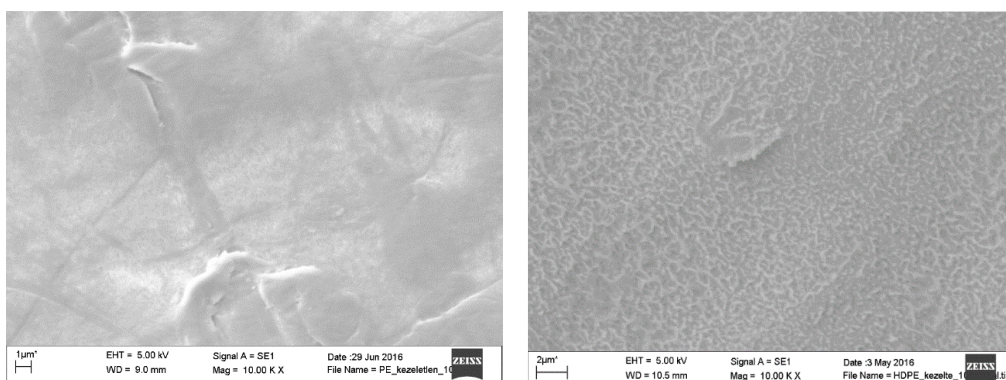


Fig. 4. Surface morphology of UHMW-PE from scanning electron microscopy SEM, left: untreated, right: treated (10000X magnification)

Topography

Engineering polymers:

The changes in surface topography of polished pristine and plasma-treated samples are illustrated by 3D non-contact profilometry surface scans of PEEK in Fig. 5. The polymer surfaces after

3. Results

plasma treatment are flattened due to removal of the top layer and “melting” of the surface asperities, while the original machining (polishing) grooves remain visible. The surface scans were repeated at 24 h and 800 h after plasma treatment, showing good stability in surface topography.

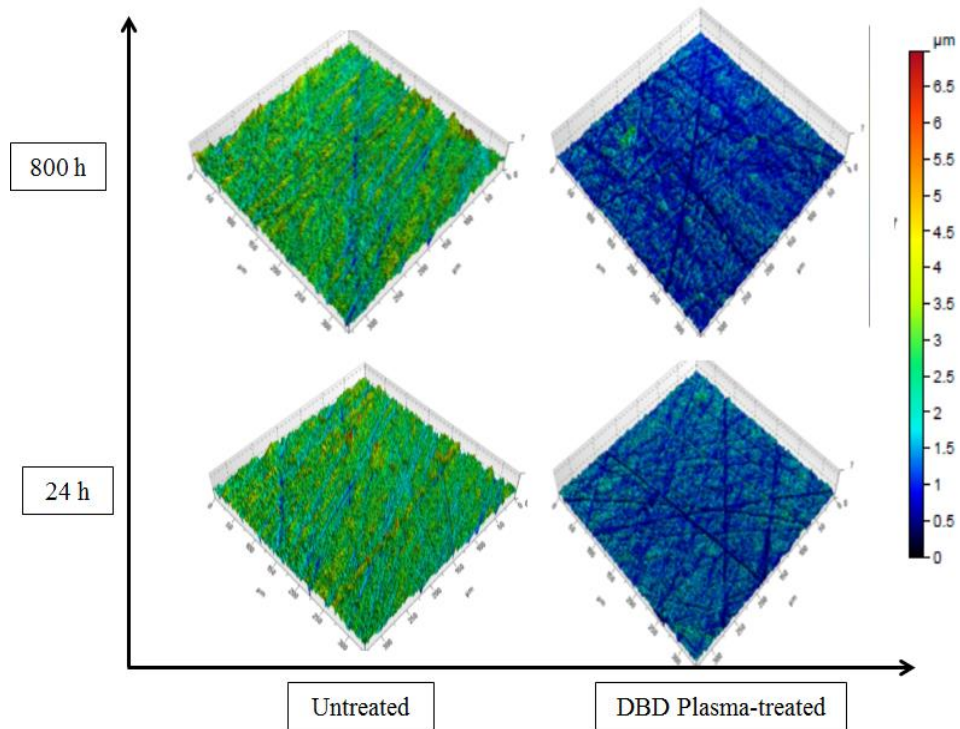


Fig. 5. Non-contact profilometry of pristine and plasma-treated samples ($330 \times 330 \text{ mm}^2$ surface area) for PEEK

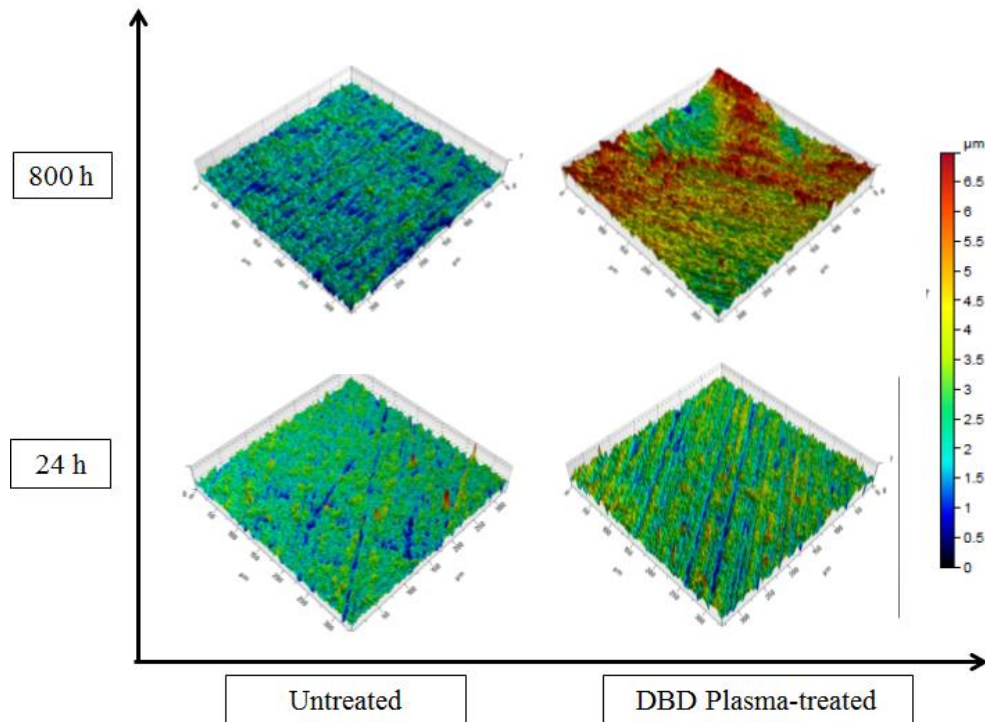


Fig. 6. Non-contact profilometry of pristine and plasma-treated samples ($330 \times 330 \text{ mm}^2$ surface area) for UHMW-PE HD1000

Polyolefin polymers and PTFE:

Surface topography of pristine and plasma-treated samples monitored by non-contact profilometry is illustrated by 3D surface scans for UHMW-PE HD1000 in Fig. 6. Due to the plasma surface treatment, an opposing trend can be observed in the topography of the particular polymers. The roughness somewhat increased for PP and UHMW-PE HD1000 and it increase with the time whereas considerable decrease occurred for UHMW-PE HD500 and slightly for PTFE.

Overall topographical results of both groups it can be observed that engineering polymers show a higher reduction in surface roughness and better stability with time function than polyolefin polymers and PTFE.

3.2. Effect of atmospheric DBD plasma on adhesive bonding

The shear strength (lap-shear tests) of pristine and plasma-treated polymer/polymer and polymer/steel joints is presented for PEEK (Fig. 7) and for UHMW-PE HD1000 (Fig. 8). In average, the statistical deviation (spread $\sigma\%$) on the shear strength (5 repetitions) significantly reduces after plasma treatment for all polymers. Overall, the tendency for adhesive-type of failure reduces after plasma treatment and changes into cohesive failure or adhesive-type failure with higher shear strength, after being an adhesive failure on one or two surfaces or cohesive failure in the adhesive layer. The pure cracking of the bulk polymer corresponds to highest shear strength in case of epoxy-type and cyanoacrylate adhesives on plasma-treated engineering polymer surfaces irrespective of the counterface. The highest shear strength for polyolefin polymers and PTFE was varied from adhesive to other and depending on the counterface. The increase in the shear strength of adhesively bonded joints is in line with the higher surface energy of polymer surfaces after plasma treatment.

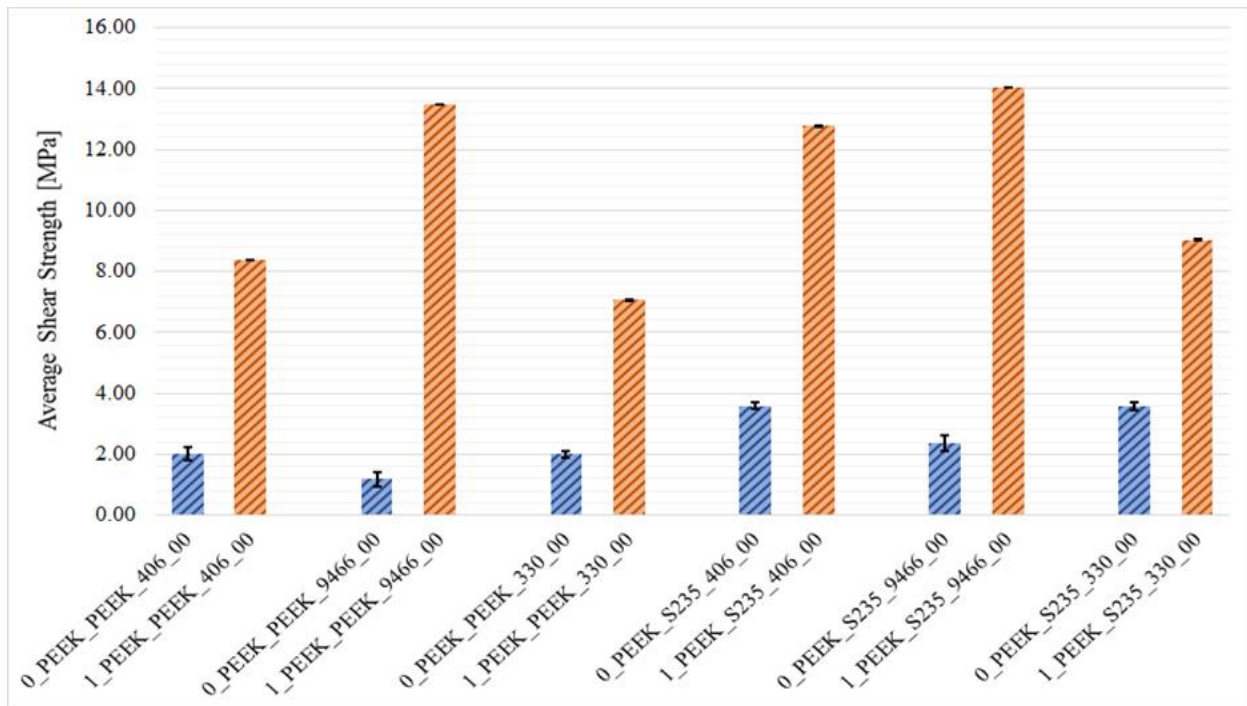


Fig. 7. Adhesive testing of polymer/polymer and polymer/steel couples after application of different adhesive types for pristine samples and plasma-treated samples for PEEK

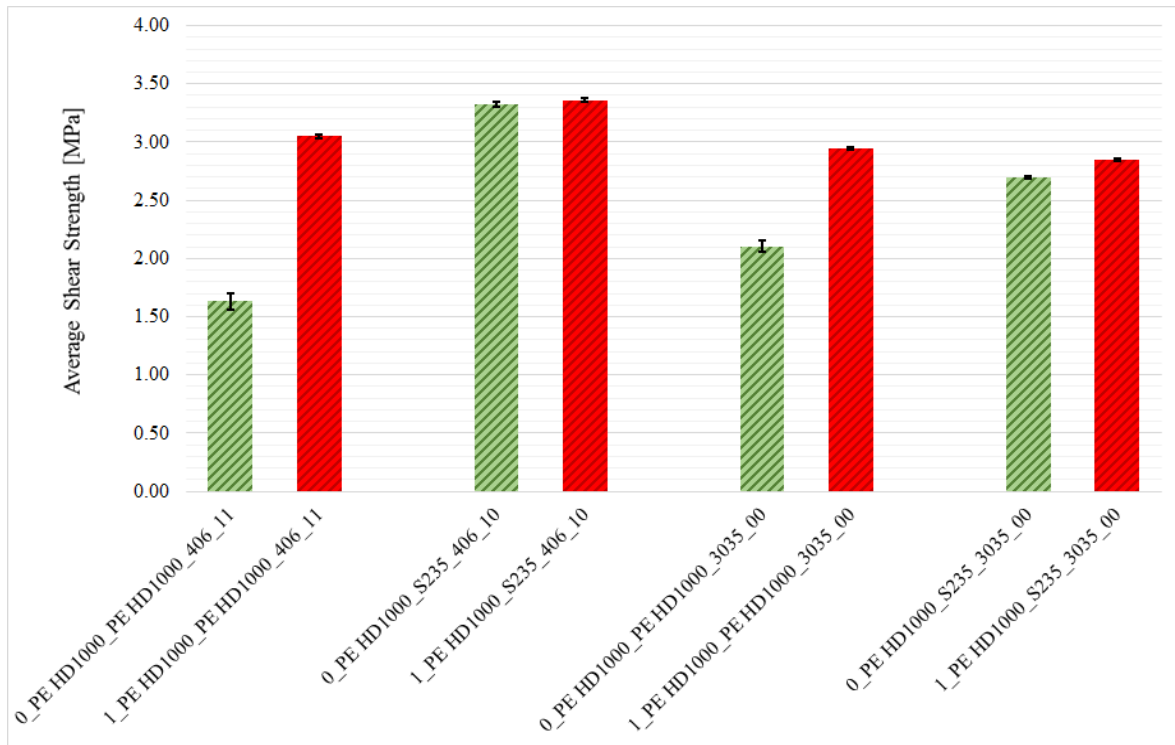


Fig. 8. Adhesive testing of polymer/polymer and polymer/steel couples after application of different adhesive types for pristine samples and plasma-treated samples for UHMW-PE HD1000

3.3. Effect of atmospheric DBD plasma on tribological behaviour

Effect of atmospheric DBD plasma on tribological behaviour of engineering polymers

Dry sliding tests

The average values for coefficients of friction μ are summarised in Fig. 9 during dry sliding tests of pristine and plasma-treated samples under different normal loads. The coefficients of friction and wear were determined from three repetitions with a statistical variation of $\pm 2.5\%$ on pristine and $\pm 1\%$ on plasma-treated samples. The coefficients of friction for all pristine surfaces show significant running-in phenomena with a peak value during the first couple of meters, which can be explained by the presence of a contaminating hydrocarbon layer on the untreated polymers. The plasma-treated polymer surfaces present lower friction than pristine polymers, except for the PEEK at highest normal load. It can be observed, however, that the differences in coefficients of friction between untreated and plasma-treated polymers become smaller at high loads. The observations for lower friction after plasma-treatment are in contrast from what would be expected from the higher surface energy and adhesive strength of plasma-treated surfaces, which would both imply a higher coefficient of friction. In parallel, it has also to be considered that the lower roughness of plasma-treated polymer surfaces can either increase or decrease the coefficients of friction.

The wear and deformation Δh of the pristine samples gradually increases at higher loads and wear of PEEK is lower than wear of PET, PA6-E, and POM-C respectively at all load levels, regardless the vertical displacement (in opposite to the higher friction for PEEK and POM-C than PET and PA6-E) confirming the mechanical strength and stiffness in combination with smaller

contributions of deformation for PEEK. An estimation of wear and deformation under each normal load was made from the slope of the graph. After the plasma treatment and sliding under highest load level, the Δh values for PET, PA6-E, and POM-C increase (in opposite to the lower friction after plasma treatment) while they remain almost similar for PEEK (in opposite to the higher friction after plasma treatment). The bulk temperatures of the polymer samples closely follow the trends for coefficients of friction for PEEK, PET, and POM-C, while opposite trends have been noticed with higher temperatures corresponding to the lower friction after plasma treatment for PA6-E. The latter can be understood by the reduction in heat conductivity of the plasma-modified surface layer in case of PA6-E.

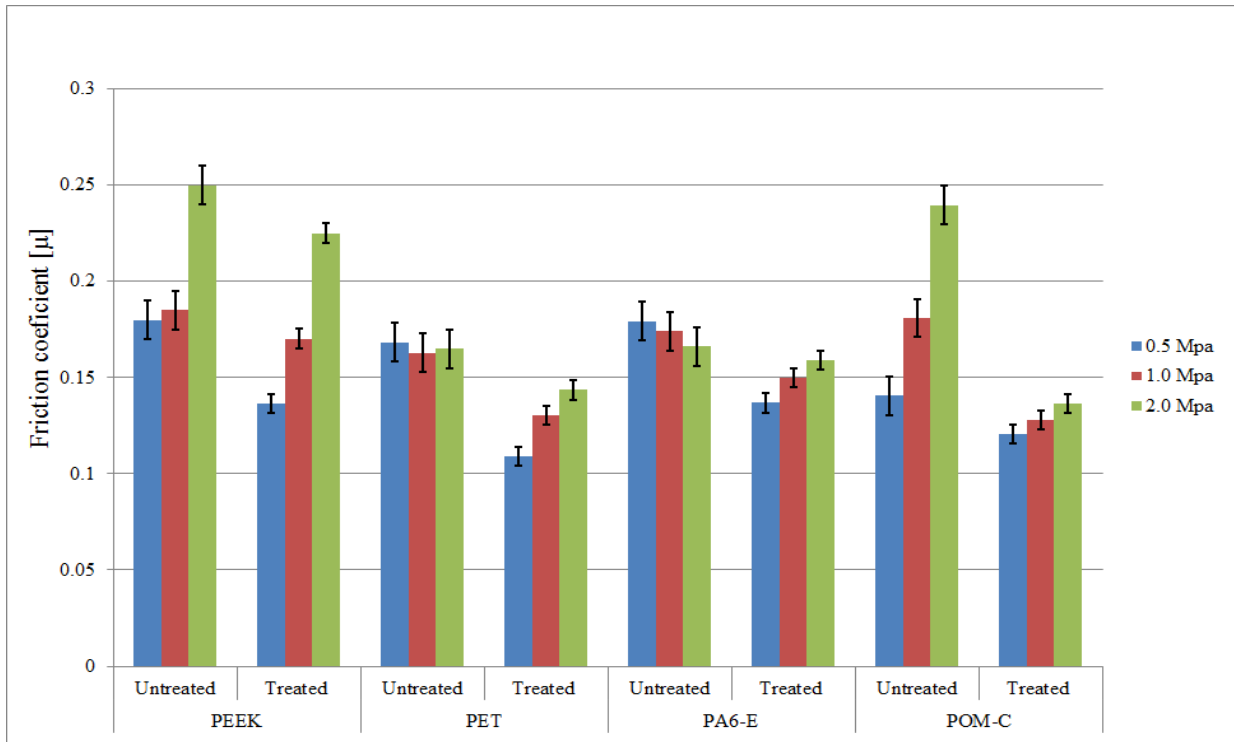


Fig. 9. Tribological testing under dry sliding conditions at 0.5, 1, and 2 MPa: summary of average coefficients of friction for engineering polymers

Lubrication run-out tests

The maximum and average coefficients of friction (Fig. 10) are lower than previous tests under dry sliding at 0.5 MPa. The presence of a thin lubricating film efficiently demonstrated differences in tribological properties between untreated and treated polymer samples. After application of an oil droplet during the first period of sliding, low coefficients of friction (<0.05) with almost no differences between different samples are observed through the lubrication action of an oil film. After cleaning the sliding track, friction remains lower than under dry sliding conditions while different behaviour occurs between pristine and plasma-treated samples: the lubricating effect responsible for low friction of plasma-treated samples lasts for longer sliding times. The lower friction under “run-out” lubrication conditions can be attributed to the better retention of the oil in the sliding interface in case of plasma-treated surfaces: the surface energy (and mainly the surface polarity) of the plasma-treated polymer surfaces is significantly higher than the pristine surfaces and, therefore, favourably enhances the adsorption of the hydrophobic (polar) oil lubricant on the polymer surface and entrapment in the interface.

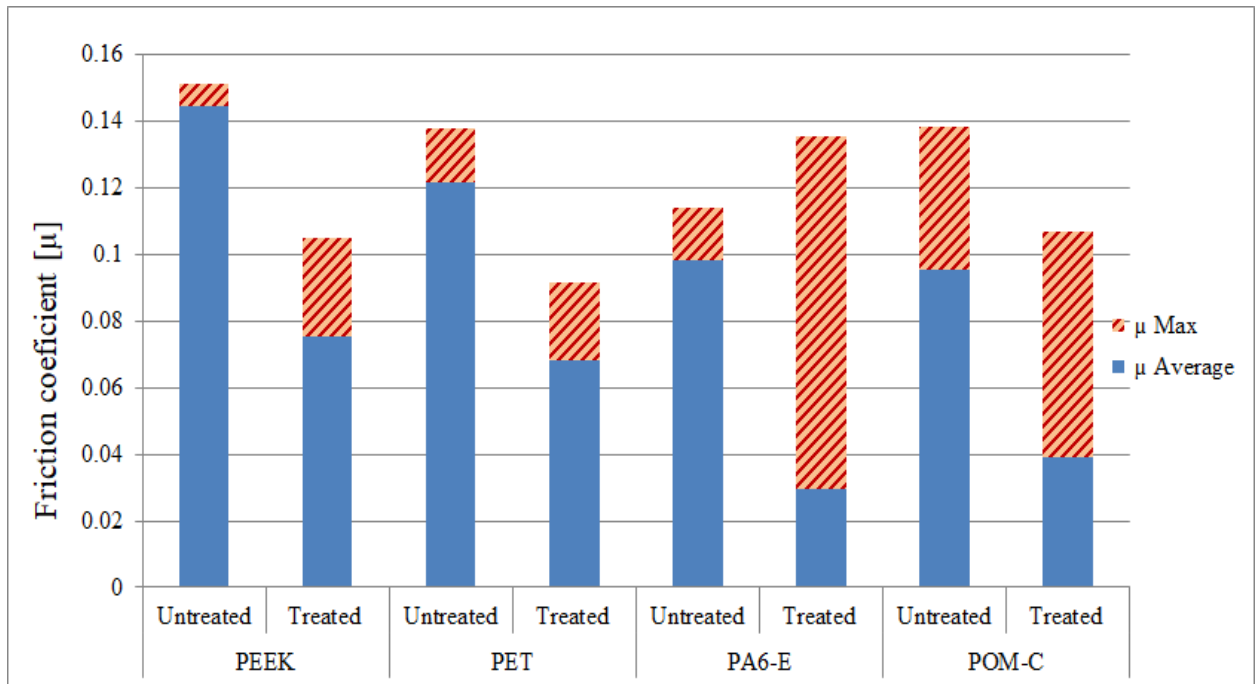


Fig. 10. Summary of average and maximum coefficients of friction of tribological testing under lubricated sliding and run-out conditions at 0.5 MPa for engineering polymers

Effect of atmospheric DBD plasma on tribological behaviour of polyolefin polymers and PTFE

Dry sliding tests

The average values for coefficients of friction μ are summarised in Fig. 11 during dry sliding tests of pristine and plasma-treated samples under different normal loads. The coefficients of friction and wear were determined from three repetitions with a statistical variation of $\pm 2.5\%$ on pristine and $\pm 1\%$ on plasma-treated samples. Similar to engineering polymers, the coefficients of friction for all pristine surfaces show running-in phenomena with a peak value during the first couple of meters; however, the peak values are smaller compared to engineering polymers attributed to the lower mechanical properties. This phenomenon can be explained by the presence of a contaminated hydrocarbon layer on the untreated polymers. The friction coefficient of PP is higher compared to other polymers concerning the high mechanical strength and stiffness (deformation component of friction), providing higher sliding resistance. The coefficient of friction of the pristine PP and PTFE shows a similar behaviour, where it is increasing with rising the load. At low load, the friction was considerably higher after plasma treatment as compared to pristine PP and PTFE, while at higher load (1 Mpa and 2 Mpa) coefficient of friction tends to become roughly identical to coefficient of friction of pristine surface. Due to the high wear rate for PP and PTFE increase the load causes a wear off of treated layer and the friction of the pristine and the treated surface become identical. Regardless the slight higher friction coefficient of UHMW-PE HD1000, the friction coefficient of pristine UHMW-PE HD (500 and 1000) are mostly similar. The effect of the increased surface energy and adhesion after plasma treatment resulted in a slight increase in the friction coefficient at all load levels for UHMW-PE HD (500 and 1000). The higher friction suggests that the treated layer did not wear off even at high load, which was confirmed by the correspondent curve. Similar to friction, wear is also much less for UHMW-PE HD (500 and 1000) than for PP and PTFE at all load levels which is indicated to the better mechanical strength and

stiffness of UHMW-PE HD (500 and 1000). The bulk temperature of pristine polymers is pretty similar and following the trends of the coefficient of friction except for UHMW-PE HD1000, where it is showing slight opposite trends with lower temperatures for treated surface corresponding to the higher friction which can be attributed to the heat barrier properties of the DBD plasma modified layer as mentioned before. Therefore, the generated heat by friction is accumulated in the contact zone and the counter-surface somewhat better than in bulk.

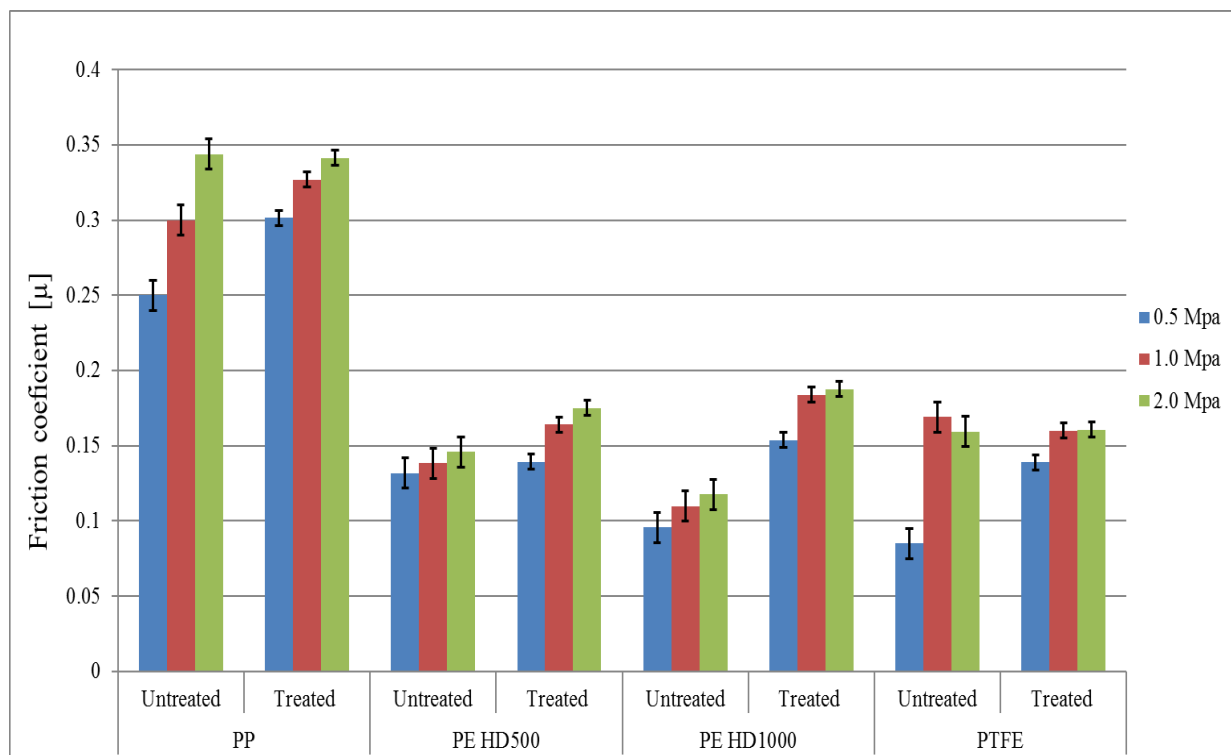


Fig. 11. Tribological testing under dry sliding conditions at 0.5, 1, and 2 MPa: summary of average coefficients of friction for polyolefin polymers and PTFE

Lubrication run-out tests

The maximum and average coefficients of friction are presented in Fig. 12. Application of an oil droplet during the first period of sliding resulted in an identically low coefficient of friction (<0.05) irrespectively of the type of sample and treatment owing to the lubricating action of the oil film. In spite of removing the oil from the sliding track, coefficients of friction remain considerably lower than dry sliding conditions ones where friction coefficient of pristine PP remains higher than other polymers in parallel with the tendencies under dry sliding conditions, concerning the higher stiffness as mentioned earlier. The lower friction can be ascribed to the oil retention ability of the polymer surface. However, a combination of the modified microgeometry and the increased surface energy of the plasma-treated polymers favourably enhances the adsorption of the oil lubricant on the polymer surface and entrapment in the interface resulted in lower coefficient of friction for PP, PTFE, and UHMW-PE HD500. During “run-out” the mixed friction regime approaches toward the boundary lubrication, and with decreasing thickness of the lubricant layer, the friction became stabilised at a lower level as compared to the pristine sample. The oil retention ability of treated UHMW-PE HD500 surface can also be detected, but it is much less apparent as compared to PP and PTFE. However, treated surface of UHMW-PE HD1000 was observed a slightly higher friction which is in line with topographical results, indicated to increase the surface

3. Results

roughness of UHMW-PE HD1000 upon plasma treatment. The higher surface roughness provides higher number of naked spots within the mixed lubrication which directly engaged with the countersurface developing junctions in the interface, and this required higher shear strength thereby higher friction. The high surface roughness was noted for PP as well but did not influence the friction behaviour due to the higher wear rate of PP which led to removing the treated layer during the first period of the sliding distance, although presenting of lubrication. In parallel, the considerable fluctuations in the friction indicate the effect of the varying layer of the lubricant.

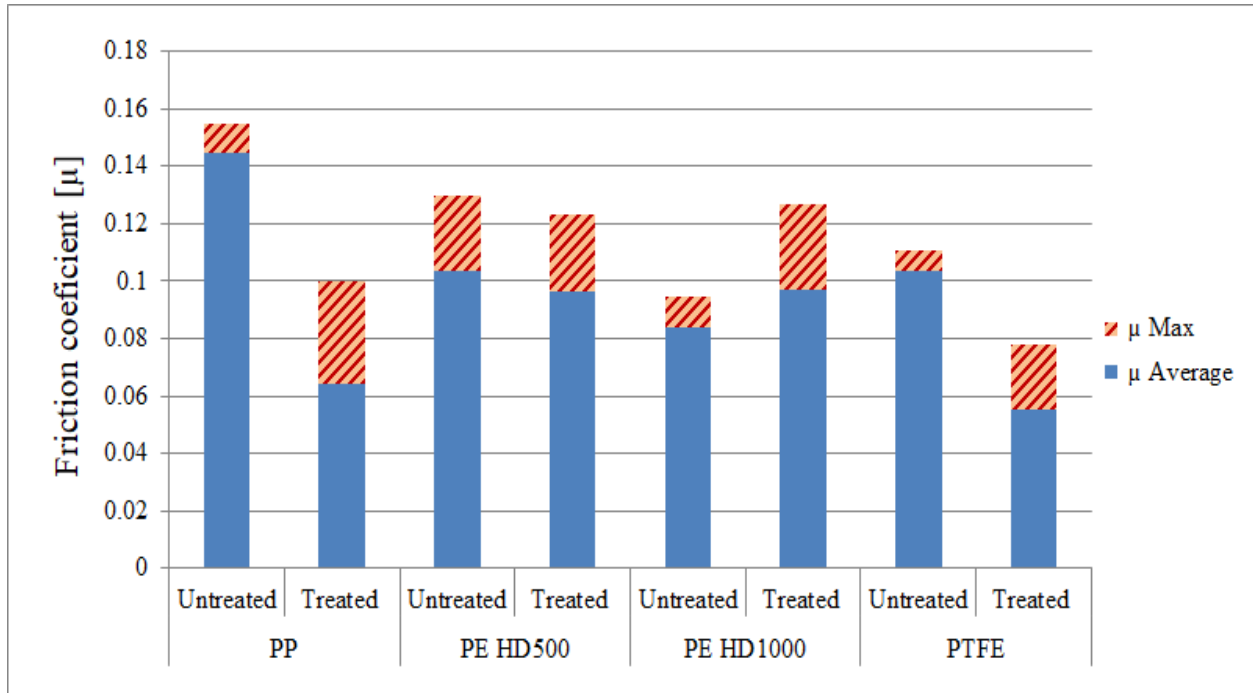


Fig. 12. Summary of average and maximum coefficients of friction of tribological testing under lubricated sliding and run-out conditions at 0.5 MPa for polyolefin polymers and PTFE

4. NEW SCIENTIFIC RESULTS

In this section the unique results investigated in my test systems are shown.

1. Surface chemical composition and wettability

Concerning the effects of DBD plasma treatment on chemical composition and wettability of polymer surfaces:

I stated that in case of PEEK, PET and PA6-E, the oxygen and nitrogen content increased while the carbon content decreased. For POM-C the oxygen content increased but no nitrogen presence was detectable besides the decreasing carbon content. The treated surfaces can be characterised by the formation of carboxylic acid and ester bonds by oxidation, especially for the aromatic PEEK and PET. Altogether I confirmed that the relative carbon content decreased with a parallel increase in overall oxygen content. The formation of polar groups containing oxygen on the surface can contribute to a hydrophilic improvement after plasma treatment. The surface energy of the treated surfaces increased, which influences both the adhesive as well as tribological behaviour.

In case of the examined polyolefin polymers and PTFE, I detected the formation of new functional groups such as hydroxyl, carbonyl and carboxylic acid, but in smaller rate compared to the examined engineering polymers.

2. Surface topography characteristics

In case of identical plasma treatments, I proved that the effect of the DBD plasma treatment on the surface topography can be bi-directional. The roughness of the original extruded smooth surfaces (R and S roughness in nano-scale) increased in parallel with the chemical modification of the surfaces following Kostov's theory, whereas the roughness of the machined and polished surfaces (R and S roughness in micron scale) decreased because of the "melting" effects (except for UHMW-PE HD1000) following Salapare's theory.

3. Adhesive bonding response to atmospheric DBD plasma treatment

I have stated the followings on the base of shear strength tests of polymer/polymer and polymer/steel adhesively bonded overlap joints (DIN EN 1465):

In case of DBD treated polymers, the shear strength of the bonded joints increased and the statistical deviation (spread $\sigma\%$) on the shear strength significantly reduced from 8-9% to around 1% for all polymers tested, regardless of the applied adhesive. In this case the technical reliability of bonded joints is significantly improved by the plasma treatment.

Concerning the DBD treated polymer surfaces the highest increase in shear strengths of the adhesive bonds were performed in case of epoxy adhesive. This is the result of the reactivity of the epoxy adhesive toward the carboxylic groups at the polymer surface after plasma treatment forming a strong adhesive bond. I stated that the untreated surfaces performed de-bonding failure on the surfaces under shear tests, while the treated polymers suffered more complex failure: de-bonding, cohesive failure in the adhesive layer and cracking in the bulk polymer occurred.

I found that among the polyolefins for the PP and UHMW-PE HD500 the increasing shear strength due to DBD plasma treatment can be concluded, however for UHMW-PE HD1000 and for PTFE the effect is barely perceptible. This phenomenon relates to the chemical composition of the

surfaces and the lower mechanical strength (lower E modulus and higher strain capability) of the matrix materials, too.

4. Tribological behaviour under dry sliding conditions for engineering polymers

In my dry sliding tribology systems, I have stated that:

At low pv load level (pv 0.025 MPa x ms⁻¹) the DBD treatment can decrease the friction coefficients of engineering polymers, in spite of the increased surface energy. This can only be true in Archard's friction theory if the decrease of deformation component of friction force is more significant than the increase of the adhesive component of friction. As a result of DBD treatment of machined and polished polymer surfaces I proved the decrease of the deformation component of friction via decreased surface roughness using 3D topography.

I proved with my measurements that the increase of " pv " load level, i.e. the increase of the real contact area, can reach a transition " pv " border, when the adhesive component of friction becomes dominant in accordance with the experienced higher surface energy of treated surfaces and the resulting friction of DBD treated polymer surfaces can exceed the virgin untreated ones. That transition " pv " load level can be measured identically for each polymer types.

5. Tribological behaviour under dry sliding conditions for polyolefin polymers and PTFE

I stated that the phenomenon introduced in 4 is not valid for polyolefin polymers and PTFE under the applied low " pv " load conditions (pv 0.025 MPa x ms⁻¹). The friction of treated polymer surfaces was higher compared to the virgin ones. When applying Archard's theory to this phenomenon, it is explained by dominant adhesive component of friction against the decreased deformation component of friction. The normal load is low but due to minor E modulus of polymer matrix, the occurred real contact area is large enough for higher adhesion.

6. Tribological behaviour under "run-out" oil lubrication conditions

With oil lubricated polymer/steel sliding pairs in mixed friction systems, I proved for the tested engineering polymers, polyolefins and PTFE (except UHMW-PE HD1000) that DBD treatment can enhance the lubricant retention and can cause lower friction. This is explained by the increased surface energy (polar and dispersive components both) of the DBD treated surfaces.

I concluded in my mixed friction sliding systems that the positive oil retention effect of DBD treatment can be limited by the increased surface roughness. In case of UHMW-PE HD1000 the surface roughness increased due to plasma treatment, thus the higher deformation component of friction (dry asperity contacts) dominates over the improved lubricating effects causing higher friction of the plasma treated surface compared to the untreated one.

5. CONCLUSIONS AND SUGGESTIONS

In conclusion, cold atmospheric DBD plasma treatment of polymer surfaces may induce favourable tribological properties for precision sliding components under mild conditions, especially under oil lubrication. In addition, the adhesive bonding of DBD plasma-treated polymers can sustain higher strength, especially for engineering polymers. After the DBD treatment of studied polymer surfaces under optimised conditions in air atmosphere, comparable effects on surface characterisation, adhesion, friction, and wear have been observed as follows:

The XPS measurements indicate the effects of surface oxidation with formation of polar functional groups and carboxylic acid moieties. The contact angle measurements show a significant reduction in WCA values thereby higher surface wettability for all polymers due to the developed polar groups.

The surface morphology investigations of extruded surfaces show an increase the surface roughness of the plasma-treated polymer surfaces except for UHMW-PE where the roughness was decreased and remains almost same for POM-C. The 3D topographical measurements indicate a reduction in surface roughness of the originally polished polymer surfaces (except PP and UHMW-PE HD1000) due to flattening of the surface asperities while the machining grooves remain present.

The adhesive shear strength of polymer/polymer and polymer/ steel joints increases after plasma treatment. Epoxy-type glue system has the highest shear strength for engineering polymers. Whereas, the glues systems of polyolefin polymers and PTEF were showed a varying strength depending on the countersurface. Besides the strength improvements, the reliability of the joints could also be improved this manifested by the much smaller standard deviation of the measured values and alteration of locus failure from adhesive failure type to cohesive failure in the adhesive layers' type or pure bulk crack in some cases.

The coefficients of friction for engineering polymers under dry sliding conditions are lower than pristine samples at low “ pv ” factor, while it may become higher under more severe sliding conditions. On the other hand, the coefficients of friction of polyolefin polymers and PTEF are higher than pristine samples at low “ pv ” factor, while coefficients of friction may become identical to coefficient of friction of pristine surfaces under more severe sliding conditions due to wear off the treated layer (especially for PTFE and PP). The deformation and wear (Δh) was varied for all polymer surfaces depending on the bulk mechanical properties. The bulk temperature is following the coefficient of friction behaviour except for PA6-E due to the low heat conductivity after treatment. As a unique feature, the coefficients of friction under oil-lubricated conditions remained low during “run-out” conditions for the plasma-treated samples (except UHMW-PE HD1000), as a lubricating layer was retained in the sliding interface. UHMW-PE HD1000 was showed higher coefficient of friction due to the high surface roughness after plasma treatment.

As a follow up to this research, further investigations and activities may be required to cover the most critical effects of atmospheric DBD plasma on polymer surfaces and tribology. I suggest the following desirable points:

Investigate the effect of DBD plasma on other materials (presently are trendy) such as amorphous, polymer composites, biopolymers, 3D printed polymers. Using a dynamic specimen movement during DBD plasma treatment instead of the liner which was used. Measuring surface low-frequency modes by Raman spectroscopy and different light wavelength absorption by FTIR. In addition to single lap joints, others joint types can be utilised such as thick adherend, double lap Joint, strap Joint, and scarf Joint. Testing of special adhesives developed for polyolefin type polymers (e.g., Yparex or Plexar). Investigate the polymer tribological behaviours under constant load for dry sliding conditions, repeating the tests under water “run-out” or “continuous” lubrication conditions and “continuous” oil lubrication conditions. In addition, the oil “run-out” lubrication testes may be repeated for three normal loads similar to dry tests. Testing the effect of atmospheric DBD plasma on polymer surfaces tribological behaviour under different test configurations and standards.

6. SUMMARY

In summary, eight commercial polymers were used in this research. Polymers were distinguished into two groups: 1) Engineering polymers including PEEK, PET, PA6-E, and POM-C, and 2) Polyolefin polymers and PTFE including PP, UHMW-PE HD500, UHMW-PE HD1000, and PTFE. Cold atmospheric DBD plasma treated the polymers for 1 min. The main objective of the research is to investigate the effect of DBD plasma on the polymers surface characterisation, adhesive bonding, and tribology. XPS was utilised to investigate the surface chemical composition. Contact angles and wettability were measured by static sessile drops, using (SEE) System apparatus. The surface morphology of polymer surfaces was analysed by SEM, AFM and 3D surface topography. The adhesive bonding was examined by lap-shear tests on single lap joints of polymer/polymer and polymer/steel pairs. The tribological tests were done by a pin-on-disc apparatus under dry (3 normal loads) and “run-out” lubrication (constant normal load) conditions.

The results show that DBD plasma can enhance the polar functional groups and carboxylic acid moieties in the polymer surfaces. The surface hydrophilicity was improved in parallel with contact angle reduction. However, polymer hydrophilicity is declined after 24 h from plasma treatment towards the initial state without reaching the original state of pristine samples. The surface morphology shows high surface roughness of extruded surfaces after treatment except for UHMW-PE and POM-C. The 3D topography is showed a reduction in the roughness parameters of plasma treated polymer surfaces due to surface flatten after melting the surface asperities except for PP and UHMW-PE HD1000 where they have a higher surface roughness after treatment.

The shear strength of polymer/polymer and polymer/steel adhesively bonded joints is improved of different adhesive systems in parallel with surface energy improvements. In general, DBD plasma treatment is favourable to improve the adhesive bonding for engineering polymers. The epoxy-type glue system was exposed the highest shear strength for engineering polymers. Whereas, the glue systems of polyolefin polymers and PTFE were varied depending on the counter surfaces. The statistical deviation of (5 repetitions) the shear strength is significantly reduced due to plasma treatment.

At low $p\nu$ factor, the coefficients of friction for treated engineering polymers are much lower than pristine surfaces under dry sliding conditions, while the coefficient of friction may become higher under more severe sliding conditions particularly for PEEK. On the other hand, the coefficients of friction of treated polyolefin polymers and PTFE is higher than pristine ones at low $p\nu$ due to the improvements in friction adhesive components, however, they have become identical at higher $p\nu$ for PP, PTFE due to the wear off of treated layer. Wear was varied depending on the mechanical properties of the bulk material. The bulk temperature has almost similar behaviour to the coefficient of friction curves except for PA6-E due to the low heat conductivity after treatment.

Under lubrication “run-out” conditions the coefficients of friction of treated polymer surfaces are significantly lower than pristine samples except for UHMW-PE HD1000 due to the high surface roughness of UHMW-PE HD1000 after treatment.

7. THE MOST IMPORTANT PUBLICATIONS RELATED TO THE THESIS

Refereed papers in foreign languages:

1. **Al-Maliki, H.**, Kalácska, G., Keresztes, P., and De Baets, P. (2015): Adhesion of polymer surfaces: brief review, *Mechanical Engineering Letters, SZIE*, 12, pp. 43-49.
2. **Al-Maliki, H.**, Zsidai, L., Keresztes, R., and Kalácska, G. (2016): Shear strength of polypropylene bonded joints using pristine and DBD plasma treated surface, *Mechanical Engineering Letters, SZIE*, 14, pp. 71-77.
3. Károly, Z., Klébert, Sz., **Al-Maliki, H.**, and Pataki, T. (2016): Comparison of NPIII and DBD plasma treatment in terms of wettability of PTFE and PA6, *Scientific Bulletin Series C: Fascicle Mechanics, Tribology, Machine Manufacturing Technology*, 30, pp. 47-50.
4. Szakál, Z., Zsidai, L., **Al-Maliki, H.**, Odrobina, M., and Kári-Horváth, A. (2016): Shear strength behaviour of adhesive bonded polymer and steel surfaces, *Scientific Bulletin Series C: Fascicle Mechanics, Tribology, Machine Manufacturing Technology*, 30, pp. 110-115.
5. **Al-Maliki, H.**, Zsidai, L., Samyn, P., Szakál, Z., Keresztes, R., and Kalácska, G. (2017): Effects of atmospheric plasma treatment on adhesion and tribology of aromatic thermoplastic polymers, *Polymer Engineering & Science*. (IF= 1.449*). DOI: 10.1002/pen.24689
6. **Al-Maliki, H.**, and Kalácska, G. (2017): Friction behavior of engineering polymers treated by atmospheric DBD plasma, *Periodica Polytechnica Mechanical Engineering*, 61(4), pp. 303-308.
7. **Al-Maliki, H.**, and Kalácska, G. (2017): The effect of atmospheric DBD plasma on Surface energy and shear strength of adhesively bonded polymer, *Hungarian Agriculture Engineering*, 31, pp. 52-58.
8. Sukumaran, J., Keresztes, R., Kalácska, G., **Al-Maliki, H.**, Neis, P. D., and De Baets, P. (2017): Extruded and injection moulded virgin PA 6/6 as abrasion resistant material, *Advances in Tribology*, 2017.
9. **Al-Maliki, H.**, Károly, Z., and Klébert, Sz. (2017): Surface morphology and chemical composition of PP and PETP treated by atmospheric plasma, *Mechanical Engineering Letters, SZIE*, 15, pp. 47-55.
10. **Al-Maliki, H.**, Kalacska, A., & Sukumaran, J. (2017): 3D Topographical evaluation by using the coherence correlation interferometry (CCI) technique for engineering polymers treated by DBD plasma, *Scientific Bulletin Series C: Fascicle Mechanics, Tribology, Machine Manufacturing Technology*, 31, 2-6.
11. **Al-Maliki, H.**, and Kalácska, G. (2018): Tribological behaviour of polymers in term of plasma treatment: A brief review, *Hungarian Journal of Industry and Chemistry*. (Accepted).
12. **Al-Maliki, H.**, Károly, Z., Klébert, Sz., and Kalácska, G. (2018): Surface characterization of Polytetrafluoroethylene treated by atmospheric plasma, *International Review of Applied Sciences and Engineering*, 09(1). (Accepted).