ADHESIVE AND TRIBOLOGICAL CHARACTERISTICS OF POLYMER SURFACES TREATED WITH ATMOSPHERIC COLD PLASMA PROCESS

OTKA K 113039

Duration: 01/01/2015 – 31/03/2019 (4 years + 3 months extension)

Basic facts:

- the project followed the original workplan (reported annually)
- the planned basic research staff carried out the work, which was assisted occasionally by external experts and researchers.
- the obtained results were published internationally and disseminated to industrial partners as well.

Summary of published results with OTKA (NKFIH) ID and acknowledgement:

- conference articles:	5 pcs
- scientific articles without impact factor:	10 pcs
- PhD dissertation:	1 pc
- scientific articles with impact factor:	5 pcs
- summa impact factors:	14,8

Abstract of the research report:

In the research project, we investigated the surface treatment of engineering polymers (nine different types) by cold atmospheric plasma (DBD) technique:
1) General and HPM technical grade plastics: PEEK, PET, PA6-E, PA66, POM-C
2) Plastics from mass production: PP, UHMW-PE HD500 és HD1000, 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.

It was found that plasma treatment increases the polar functional moities on the surface for most of the polymers. As a result, the surface energy increases, the adhesion improves. Shear strength of the glued bonded surfaces improved for either polymer/polymer or polymer/steel bond pairs, although improvement varied in the function of the applied adhesive and the type of the polymer. We showed that the surface roughness of the treated polymers usually decreases. In combination of decreased roughness and increased surface energy (polar and dispersive components) the surface can exert higher oil retention capability that provides better friction than the pristine polymer.

The achieved results can be directly exploited in various industrial sectors such as design and application of mechanical parts, packaging, etc.

Detailed report

1. Materials and methods

1.1. Polymers

Eight types of commercially available thermoplastic (semi-crystalline) polymers (produced by Ensinger GmbH, Germany) were used in bulk conditions. The polymers are distinguished to two groups to facilitate comparison process: 1) Engineering polymers, and 2) Polyolefin polymers and PTFE. The properties of the materials are available from the distributor. The materials grouped:

1) General and HPM technical grade plastics: PEEK, PET, PA6-E, PA66, POM-C
2) Plastics from mass production: PP, UHMW-PE HD500 and HD1000, PTFE

1.2. Atmospheric cold plasma (DBD) treatment

The polymer surfaces were modified by cold atmospheric plasma treatment using a dielectric barrier discharge (DBD) equipment (the equipment is available at AKI, MTA) operating under controlled air atmosphere (Fig. 1.a). The plasma is generated with a high frequency (10–20 kHz), high voltage with peak-to-peak values of 20 kV. Visually homogenous plasma can be reached with increasing voltage and absorbed power as more and more elementary discharges are generated (Fig. 1.b). The power of the DBD plasma system is set to 320 W, which provided a quasi-homogeneous diffuse plasma with air as process gas.

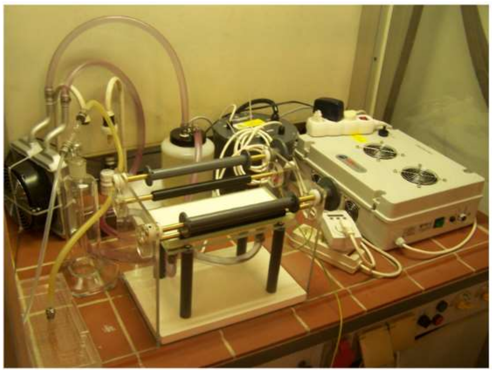


Fig. 1.a. DBD laboratory equipment used for polymer surfaces treatment

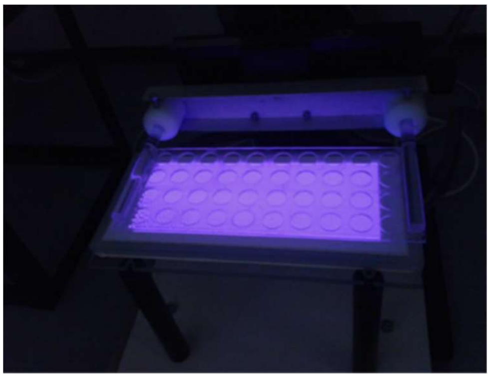


Fig. 1.b. homogenous atmospheric cold plasma in DBD plasma reactor with specimen holder above it

1.3. Surface characterization methods

- Chemical composition

The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a XSAM 800 spectrometer (Kratos, the equipment is available at AKI, MTA) equipped with a non-monochromatic Mg $Ka_{1,2}$ radiation source (1253.6 eV) operating under a fixed analyser transmission mode (chamber pressure$<10^{-7}$ Pa) to investigate the chemical composition of polymer surfaces.

- 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) were used as testing liquids deposited as 2 ml droplets by a Hamilton syringe. From these measurements, the total surface energy together with polar and dispersive components was 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, the equipment is available at AKI, MTA) with heated tungsten source. In addition to SEM investigations, the average surface roughness of extruded polymer surface was measured by atomic force microscopy (AFM).

- 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 piezoless z-scanner having a resolution in z-direction of 0.1 Å. The images were processed by Talymap software (Digiserve) to calculate the 3D surface roughness parameters according to ISO 25178, including Sa (average roughness), Sz (maximum height), Sku (kurtosis), and Ssk (skewness).

1.4. 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 × 12.5 mm= 317.5 mm^2). 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 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.

1.5. 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, 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/mm^2, 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. During testing, the friction coefficient μ, the vertical displacement (Δh= wear + deformation) and the temperature T are continuously monitored. 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, 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). 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.

2. Results

2.1. Surface characterisation

- Chemical composition

The wide-scan spectra (XPS) indicated three characteristic peaks at 285.0 eV (C1s), 533.2 eV (O1s), and 400.4 eV (N1s). For engineering polymers the elemental composition (at.-%) before and after plasma treatment was calculated from high-resolution XPS spectra (for engineering polymers Table 1.). 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 *n*O/*n*C), 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.

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

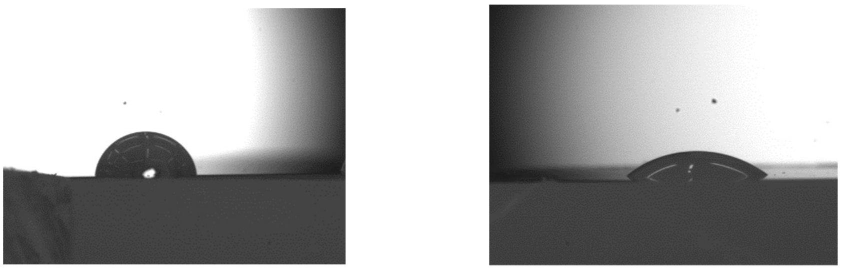
Sample		**O (at.-%)**	**C (at.-%)**	**N (at.-%)**	***n*O/*n*C**
PEEK	Theoretical	13.63	86.35	0	0.158
	Untreated	25.3	73.4	1.4	0.345
	Plasma-treated	27.2	70.6	2.2	0.385
PET	Theoretical	28.58	71.44	0	0.4
	Untreated	31.6	68.4	0	0.462
	Plasma-treated	36.2	62	1.9	0.584

PA6-E	Theoretical	12.5	75	12.5	0.167
	Untreated	12.8	74.5	12.5	0.172
	Plasma-treated	20.3	66.6	13.1	0.305
POM-C	Theoretical	50	50	0	1
	Untreated	39	60.9	0	0.64
	Plasma-treated	46.5	53.5	0	0.869

In case of treated polyolefin polymers and PTFE, 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 plasma treatment could effectively break up primarily the C-H, and C-C bonds, decreasing the corresponding C1 peak down to 17 at.-%, 46 at.-% and 48 at.- % for PP, UHMW-PE HD500, and UHMW-PE HD1000 respectively. While component peaks at 286.4, 288.2 and 289.3 eV indicating formation of new functional groups such as hydroxyl (OH), carbonyl (C=O), and carboxylic acid (O=C-O).

- Wettability

The contact angles and surface energies for pristine engineering polymers also UHMW-PE HD500, and UHMW-PE HD1000 are very similar due to their comparable chemical composition. After plasma treatment, the contact angle of all polymers decreases (Fig. 2) and the surface energy increases mainly due to an increase in polar component engineering polymers: PEEK 332%, PET 315%, PA6-E 360%, and POM-C 250%; polyolefin polymers and PTFE: PP 17700%, UHMW-PE HD500 854%, UHMW-PE HD1000 1200%, and PTFE 3650%). Polyolefin polymers and PTFE were observed a higher increase in surface polarity after treatment rather due to their hydrophobicity (although UHMW-PE polymers have lower contact angle than 90°, they are considered as hydrophobic) thereby low surface energy in the initial state. However, engineering polymers have higher surface energy after treatment due to their high surface energy in the initial state. The dispersive component slightly increases or remains almost constant for engineering polymer while moderately increases for polyolefin polymers. However, PTFE was observed the highest increase in dispersive component (46%).



Untreated Treated

Fig. 2. Water contact angle of PA6-E before and after plasma treatment

- Morphology

As seen on the 5000X magnification e.g. of PA6E sample (Fig. 3), the surface formed trenches contain further smaller pores (5000X magnification) which provide rougher surface. Generally it can be concluded that plasma treatment concentrates on certain points although it has a degrading effect on the entire surface. This structure is not similar to the initial sample, so some other effect can control this process, such as the ratio of amorphous crystalline phases. Oxidised materials were formed as well which are seen as bright areas on the right side of the image.

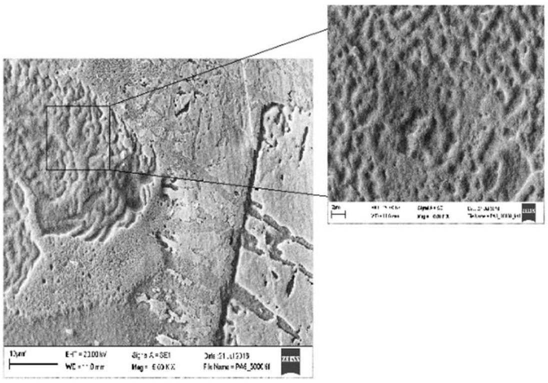


Figure 3. Surface morphology of plasma treated PA6-E from scanning electron microscopy SEM (5000X and 15000 magnification)

AFM roughness results typically agreed with SEM findings where the surface roughness of polymer surfaces is increasing due to DBD plasma treatment except UHMW-PE, which is shown a reduction in the surface roughness.

- Topography of polished surfaces

The polymer surfaces after 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. The initial Sa (average roughness) values of PEEK and PET are mostly close, while PA6-E and POM-C have pretty far values despite their similar preparation method before plasma treatment. For engineering polymers, the surface roughness values Sa (average roughness) and Sz (maximum height) reduced, where Sa (average roughness) decreased -44%, -52%, -67%, and -26% for PEEK, PET, PA6-E, and POM-C respectively, PA6-E exposes the higher reduction in the surface roughness parameters due to plasma treatment. Sku (kurtosis) greater than 3 for all the surfaces shows the sharp roughness peaks which appear to be reduced after the plasma treatment.

For material group 2. the initial Sa values of PP, UHMW-PE HD1000, and PTFE are almost identical being around 0.5 μm, while UHMW-PE HD1000 has 1.2 μm Sa value, despite their similar preparation method before plasma treatment. Such difference in the roughness could be expected considering the dissimilar surface hardness and strain capability of the particular polymers. 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 (Sa 67%)

and UHMW-PE HD1000 (Sa 25%) whereas considerable decrease occurred for UHMW-PE HD500 (Sa -68%) and slightly for PTFE (Sa -11%).

2.2. 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 were measured. In average, the statistical deviation (spread σ%) on the shear strength (5 repetitions) significantly reduces after plasma treatment for all polymers, that is about 15% for pristine PEEK to 1% for plasma-treated PEEK; about 8% for pristine PET to 1% for plasma-treated PET; about 9% for pristine PA6-E to 3% for plasma-treated PA6-E; about 9% for pristine POM-C to 1% for plasma-treated POM-C. Also the increase of the shear strength were found in most cases. As an example figure 4 shows the results of PEEK with different gluing materials.

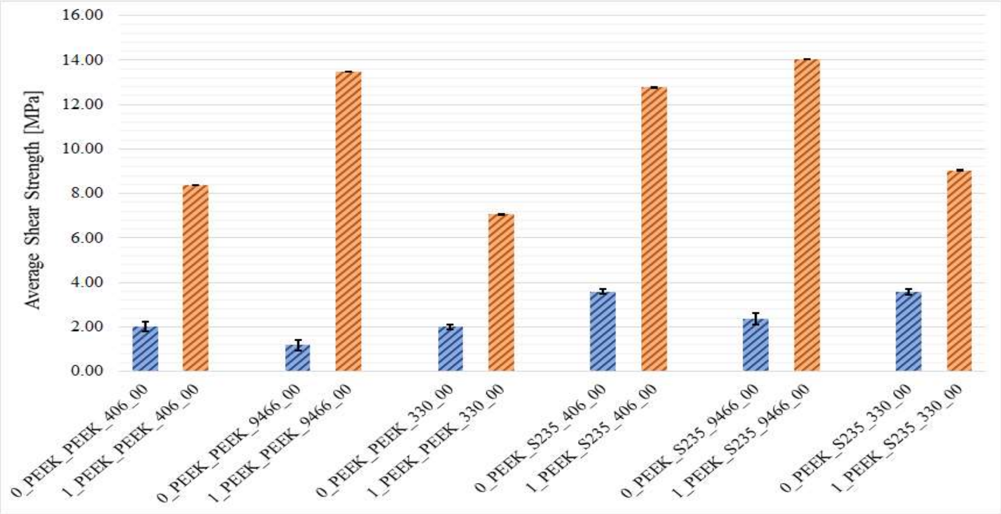


Figure 4. Adhesive testing of polymer/polymer and polymer/steel couples after application of different adhesive types for pristine samples and plasma-treated samples for a) PEEK

The observations of failure type for the adhesive bonds are documented in our previous articles, either presenting adhesive failure on one or two surfaces (1), cohesive failure in the adhesive layer (2), or cracking in the bulk polymer (3). 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. The pure cracking of the bulk polymer corresponds to highest shear strength in case of epoxy-type and cyanoacrylate adhesives on plasma-treated surfaces for PEEK and PET, irrespective of the counterface. In case of adhesive failure on dissimilar surface pairs (polymer/steel), it was observed that the glue most easily releases from the polymer surface and remains sticking on the steel surfaces. Regardless of the adhesive type and counterface, the plasma treatment improves the adhesive bonding compared to the pristine samples. The higher surface polarity after plasma treatment highly contributes to better adhesive bonding.

2.3. Effect of atmospheric DBD plasma on tribological behaviour

- Dry sliding tests

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. Overall, the friction for pristine PEEK and POM-C are slightly higher compared to pristine PET and PA6-E for the same normal loads, which can be attributed to the higher mechanical strength and stiffness of PEEK, providing higher sliding resistance (the surface properties of PEEK and PET can be considered as similar based on surface energy values, but the more complex aromatic structure of PEEK compared to PET may induce higher rigidity at molecular level). Whereas, the lowest mechanical properties of POM-C may play a similar role to increase the real contact area (RCA) with load increasing implies higher friction. The coefficients of friction do not (significantly) decrease with increasing the normal loads, which is an indication that softening mechanisms and temperature rise do not influence the sliding processes Therefore, it can be assumed that mechanical interactions and surface interactions are dominating effects. 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. According to Archard's theory of friction, F_f the friction force equals the sum of an adhesion force component F_a and a deformation force component F_d: under low loads, the deformation component is generally smaller than the adhesion component ($F_d<F_a$).

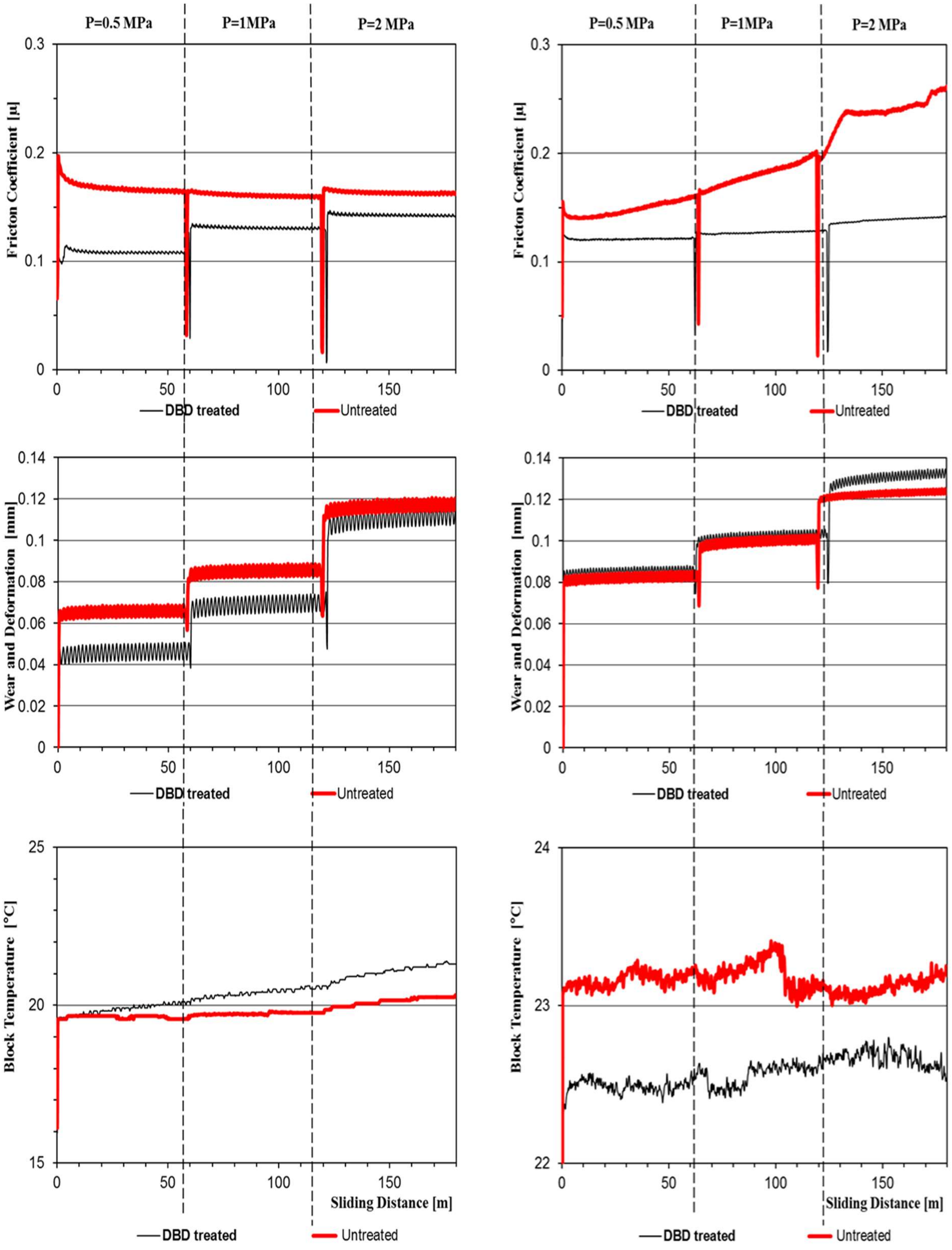


Figure 5. Dry friction results of PEEK(left) and PET (right)

From present results, however, it can theoretically be assumed that the lower friction for plasma-treated polymers under low loads should be attributed to the smaller contributions of a deformation component. The reduction in surface roughness for plasma-treated polymers can confirm that the deformation component near the surface asperities of the polymer should likely be reduced. At low loads, a smaller real contact area of the plasma-treated polymer surfaces can exist through the effects of plasma treatment.
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). It can be also remarked that the static deformation of all polymers was decreased during increase of the load. However, the measurements of Δh are only an indicative measurement for a couple of events over short sliding distances, including (i) heat expansion that counteracts the "real" wear, and (ii) creep that cooperates with the "real" wear. As a consequence of higher friction of plasma-treated PEEK under highest load, the thermal expansion should there be at highest and suppresses the wear at most. Thus, higher "real" wear than indicated by measurements under highest load can also be expected for the plasma-treated PEEK.

- Lubrication run-out tests

The maximum and average coefficients of friction (figure 6.) 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. (figure 7. examples of PEEK and PET) 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 of the plasma-treated polymer surfaces is significantly higher than the pristine surfaces and, therefore, favourably enhances the adsorption of the hydrophobic oil lubricant on the polymer surface and entrapment in the interface. However, more periodic fluctuations in friction occur after removal of the oil from the sliding track: the latter typically indicate friction instabilities within the mixed lubrication regime and can be attributed to dynamic changes in layer thickness of the remaining lubricant.

3. Conclusion and scientific results

3.1. Surface chemical composition and wettability

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 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.

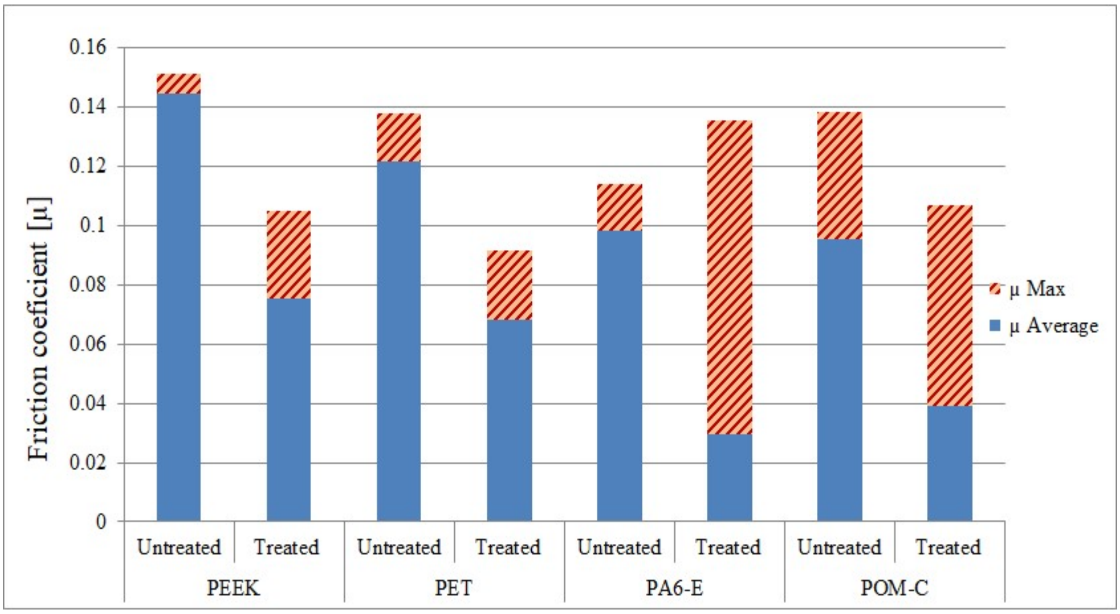


Figure 6. Summary of average and maximum coefficients of friction of tribological testing under lubricated sliding and run-out conditions at 0.5 MPa for engineering polymers

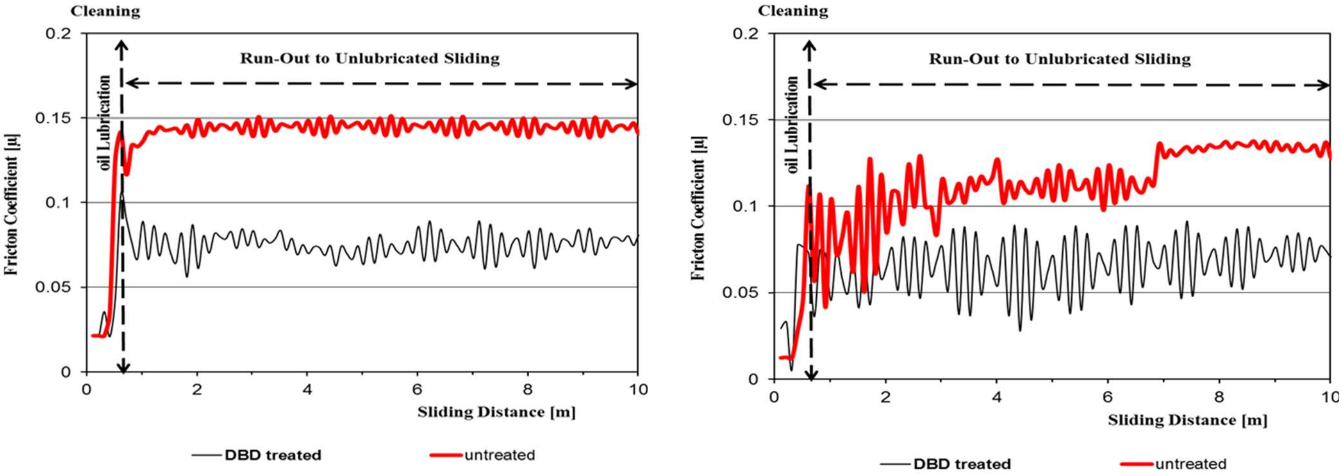


Figure 7. PEEK (left) and PET (right) oil run-out test results at 0.5 MPa

In case of the examined polyolefin polymers and PTFE, the formation of new functional groups such as hydroxyl, carbonyl and carboxylic acid were detected in slight degree.

3.2. Surface topography characteristics

In case of identical plasma treatments, 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.

3.3. Adhesive bonding response to atmospheric DBD plasma treatment

In case of DBD treated polymers, the shear strength of the bonded joints increased and the statistical deviation (spread σ%) 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. 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.

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 of the matrix materials, too.

3.4. Tribological behaviour under dry sliding conditions for engineering polymers

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 we proved the decrease of the deformation component of friction via decreased surface roughness using 3D topography.

The increase of "*pv*" load level 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.

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

With oil lubricated polymer/steel sliding pairs in mixed friction systems, we found 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. We also concluded in our mixed friction sliding systems that the positive oil retention effect of DBD treatment can be limited by the increased surface roughness.