Estimating Nanoscale Surface Roughness of Polyethylene Terephthalate Fibers

Loránd Románszki, Szilvia Klébert, and Károly Héberger*

ABSTRACT: Quantitation of surface roughness is difficult, if subtle, but significant differences cause an uncommon variance. We used atomic force microscopy to measure the surface roughness of polyethylene terephthalate (PET) fibers before and after a 30 s plasma treatment of 300 W. Samples were measured multiple times at different locations, in four scan sizes. The surface roughness was expressed in terms of nine roughness parameters. Despite the large number of data, simple statistics was not able to detect significant differences in roughness before and after plasma treatment. A factorial analysis of variance (ANOVA) of the normalized data and a sum of ranking differences analysis using four types of data preprocessing and their factorial ANOVA confirmed that (i) the plasma treatment had roughened the PET fiber surface; (ii) the roughness increases with the scanned area in the measured range; and (iii) what the best roughness parameters are in discriminating between surfaces before and after treatment. Although the compared roughness estimators were on different scales, a roughness estimation of the nanoscale surfaces was feasible, where other methods fail. The presented methodology can be applied widely and unambiguously for highly different method comparison tasks.

1. INTRODUCTION

Plasma treatments of textiles and fabrics have been extensively studied in the last decade as the textile industry is continuously trying to fulfill the increasing demand of society in terms of enhanced hydrophobic or hydrophilic properties, better printability, intelligent filtration properties, flame retardation, biocompatibility, self-cleaning finishes, and so forth. 

For the preparation of textiles with functional coatings, surface modification is the most obvious and suitable technique. Several wet chemical methods are available to tailor surface properties but most of them bear several disadvantages like large chemicals and energy consumption, influence on the bulk properties of fibers, health and environmental hazard, and high cost. 

Plasma technologies offer a much greener possibility for surface modification as they are dry technologies without cooling water utilization, need minimum amount of chemicals, are energy efficient, and have no pollution effect. 

Furthermore, plasma treatments are restricted to the uppermost layer (10–20 nm) of the material without affecting the bulk properties. 

Obviously, plasma treatment of surfaces is carried out in nonthermal or cold plasmas, where the thermodynamic equilibrium is not reached. 

When a material is subjected to plasma treatment, chemical and morphological changes occur on the surface. Activation and cleaning are typical chemical processes during which the surface energy increases and the contaminations disappear, respectively. A typical morphological effect is etching, when the bulk material is damaged and gas-state by-products, usually atoms or small molecules, are eliminated from the surface, resulting in the change of the surface roughness. Usually all these processes take place simultaneously.

In our work, we studied the morphological changes of polyethylene terephthalate (PET) fibers induced by a plasma treatment [diffuse coplanar surface dielectric barrier discharge (DCSBD)]. The surface topography of untreated and treated samples has been characterized by atomic force microscopy (AFM), which can provide three-dimensional information about the surface morphology. According to a literature survey, the roughness of the surface significantly changes, usually increases, during plasma treatment because of the etching effect of plasmas. However, an already large initial roughness may even decrease after plasma treatment as a result of erosion of the asperities.

Our earlier investigations of cellulose fibers by AFM showed that a 30 s long plasma treatment caused a slight, but detectable roughness increase. However, the statistical significance could not be unequivocally ascertained. Interestingly, the roughness seemed to increase also with increasing...
scanned area. Therefore, in our current study we wanted to answer the following questions:

1. Is it possible to detect and quantify slight roughness changes by AFM, taking into account the relatively large variance of the measurement data?
2. What are the most relevant roughness parameters that can differentiate the two sets (treated and untreated) of samples?
3. Does the detection of roughness change become easier with increasing observation area (scan size)?

2. RESULTS AND DISCUSSION

2.1. Scanning Electron Microscopy and AFM. Plenty of examples can be found in the literature about the roughening effect of different plasmas on PET and other fibers. In this work, scanning electron microscopy (SEM) inspection found nanoscale damage of the PET fibers after being treated for 30 s in plasma (Figure 1). In particular, pits with elliptical openings, usually aligned to the fiber axis, and exfoliations were identified. However, this effect of the plasma treatment is hardly visible; therefore, the evaluation could be subjective and converting surface morphology changes into numbers is not easy.

In order to quantify the observed deteriorations, individual fibers were pulled out from samples of untreated and treated PET fabrics and scanned by AFM. The tip of the AFM cantilever is raster scanning downwards across the surface of the fiber from left to right. When the scanning parameters are set so that the feedback loop reacts quickly to the detected surface features, the deflection of the cantilever is minimal and the corresponding deflection image is poor in contrast, whereas the contrast of the height image is the best. On the contrary, when the scanning parameters are set to a slower feedback loop reaction, height image is poorer in contrast (as the tip is not closely tracking the surface), whereas the deflection image is sharper (as the cantilever is forced to deflect by the encountered surface irregularities). Both height and deflection images are recorded, but only height images are used in the analysis of the roughness data, as only these ones contain the needed point-by-point height information of the topography.

For illustration, typical height images are shown for both untreated and treated samples, in all four different scanning sizes, in the 3D color-coded, oblique view (Figure 2).

By a simple visual inspection of these images, obvious differences in the roughness of the untreated and treated samples can be unequivocally stated only in the case of the smallest, 4 μm² scan areas. Figure 3 summarizes the results of roughness measurements before and after the plasma treatment by presenting boxplot charts of nine roughness parameters as a function of the scanned area. Two general trends can be observed: (1) the mean of the individual roughness parameters is generally increasing with increasing scan area, apparently tending to, but at the scan areas of the experiments, not reaching, a plateau level (cf. ref 32); (2) the means after plasma treatment are generally higher in absolute value than the ones before the treatment. However, a conclusion about the roughening effect of the 30 s plasma treatment can be drawn only if the whole set of corresponding data is compared. The outcome of univariate Mann–Whitney tests is that the roughness parameters are significantly different at the 0.05 error level at the lowest scan size (4 μm²) only. At larger scan sizes, the roughening effect of the plasma treatment thus cannot be ascertained. However, the power of multivariate statistical analysis is evidenced in the following.

2.2. Effect of Roughness Parameters (Analysis of Variance of Normalized Raw Roughness Data, Table S1). Normalization (NOR) was unavoidable as all roughness parameters were on different scales. Figure 4 shows that a classical box and whisker plot cannot discriminate between the roughness parameters.

Therefore, we had to decompose the effect of factors by variance analysis. Table 1 summarizes the analysis of variance (ANOVA) results.

The plasma treatment (Fₚ) is highly significant: the roughness is considerably lower before treatment, irrespective of the chosen roughness parameter (Figure S1). Almost all roughness parameters are equivalent, except for the peak count (Figure S2). A post hoc least significant difference test

Figure 1. SEM micrographs of untreated (A) and plasma-treated (B) PET fabrics, 3000X magnification. Apart from some particulate, debris-like contamination, smaller and larger holes (ellipses) and exfoliations (arrows) are visible on the plasma-treated samples.

Figure 2. Representative 3D color-coded height maps of untreated, respectively, plasma-treated samples scanned at increasingly larger areas. Note that the height scale range is 160 nm for all images except for the two 4 μm² scans, where it is 80 nm.
differentiates peak count, but other post hoc tests (Bonferroni, Scheffé, etc.) do not. Levene’s test for homogeneity of variances is not significant, showing that all roughness parameters originate from the same distribution. Vertical bars denote 0.95 confidence intervals.

The coupling of the first two factors (plasma treatment and scan area) can be seen in Figure 5.

The line plot reveals smaller roughness for untreated samples: the red dotted line runs always above the blue solid line.

The tendency is clear: as the scan area increases, the roughness also increases.

At $F_2 = 25 \mu m^2$, the difference is not significant in $F_1$, but the mean before treatment (b, blue full circle) is lower than after treatment (a, red empty box), even in this case.

The conclusions are obvious: plasma treatment causes coarsening of the surface, and it is worth to consider a larger scan size for better differentiation between samples before and after treatment at least in this measurement scale.

The rudeness of the modeling is revealed in the normal probability plot of residuals, eq 6 (Figure S3).

Table 1. Univariate Tests of Significance for Normalized, Raw Roughness Measures (Sigma-Restricted Parameterization, Effective Hypothesis Decomposition)\textsuperscript{a}

| SS        | n  | MS         | $F$  | $p$      |
|-----------|----|------------|------|----------|
| intercept | 1  | 6.234      | 2566 | 0.000000 |
| $F_1$ (plasma treatment) | 1  | 0.05232    | 21.54| 0.000004 |
| $F_2$ (scan area) | 3  | 0.2810     | 115.7| 0.000000 |
| $F_3$ (roughness parameters) | 8  | 0.006202   | 2.553| 0.009469 |
| $F_1 \times F_2$ | 3  | 0.006431   | 2.647| 0.04797  |
| $F_1 \times F_3$ | 8  | 0.01575    | 6.484| 0.000000 |
| $F_2 \times F_3$ | 24 | 0.001620   | 0.6667| 0.8858   |
| $F_1 \times F_2 \times F_3$ | 24 | 0.001971   | 0.8114| 0.7245   |
| error     | 783| 0.002429   |      |          |

\textsuperscript{a}SS—sum of squared residuals, n—degree of freedom, MS—mean sum of squared residuals, $F$—Fisher criterion, $p$—theoretical probability. Significance at the 1% level is indicated in bold.
2.3. Sum of Ranking Differences Calculations. Sum of ranking differences (SRD) is able to compare and group the differently defined roughness parameters. The row average was selected as the benchmark. The scaling problem persists; hence, four types of data preprocessing has been carried out: NOR, rank transformation (RNK), range scaling (SCL), and standardization (STD).

As an example, the results for normalized SRD calculations can be seen in Figure 6.

Peak count is indistinguishable from random ranking. Therefore, it was eliminated from further analysis. Other roughness parameters group together, \(R_z\) and \(R_{\text{max}}\) being located closest to the reference.

Similar SRD calculations have been completed for the other preprocessing methods (RNK, SCL, and STD; data not shown).

2.4. ANOVA of SRD Scores. Roughness parameters, except the peak count, were considered as factor 3, and four data preprocessing options as factor 4 with four levels: NOR, RNK, SCL, and STD (Table 2), see part 4.4. Sevenfold cross-validation assigned uncertainty values to SRD values in a repeated random manner. In this way, \(9\) (roughness parameters) \(\times\) \(4\) (preprocessing methods) \(\times\) \(14\) (repetitions) = \(448\) SRD values were calculated and the effects of factors and their interactions were decomposed.

After decomposition of the role of various ways to determine roughness by AFM, and the preprocessing methods, the effect of the latter is only significant at the 1% level, that is, it is reassuring that we have not incorporated artificial information by using data preprocessing.

The various ways to determine roughness (\(F_3\)) and its interaction with preprocessing (\(F_3 \times F_4\)) are highly significant, which can be seen in the next figure (Figure 7).

Based on the model, the following roughness parameters are recommended: (i) the vertical distance of the highest point from the lowest point (maximal height, \(R_{\text{max}}\)); (ii) the mean vertical distance of the five highest points and five lowest peaks (count)}

![Figure 5. ANOVA decomposition of two factors: plasma treatment, two levels, \(b = \text{before}, a = \text{after}\), and scan area, four levels, 4, 25, 45, and 64 \(\mu\text{m}^2\).](image)

![Figure 6. SRD (values, scaled between 0 and 100) for normalized roughness data. SRD [\%] values are plotted on the x axis and left y axis; the right y axis shows the cumulative relative frequencies of the random ranking distribution function (black curve). The 5% probability ranges (XX1), median (Med), and 95% (XX19) are also given.](image)

![Figure 7. Weighted means for roughness measures (\(F_3\)), effective hypothesis decomposition. An arbitrary dotted line separates the recommended roughness measures from the worse ones.](image)

Table 2. Univariate Tests of Significance for Factors 3 and 4 (Eq 6; Sigma-Restricted Parameterization, Effective Hypothesis Decomposition)\(^a\)

| SS      | MS   | \(F\)  | \(p\)  |
|---------|------|--------|--------|
| intercept | 64,680 | 1 | 64,680 | 166,700 | 0.000000 |
| \(F_3\)  | 4953 | 7 | 707.6 | 1823 | 0.000000 |
| \(F_4\)  | 4.005 | 3 | 1.335 | 3.441 | 0.01688 |
| \(F_3 \times F_4\) | 189.4 | 21 | 9.021 | 23.25 | 0.000000 |
| error   | 161.4 | 416 | 0.3880 |        |        |

\(^a\) SS—sum of squared residuals, \(n\)—degree of freedom, MS—mean sum of squared residuals, \(F\)—Fisher criterion, \(p\)—theoretical probability. Significance at the 1% level is indicated in bold.
points from the mean plane \( (10 \text{ points mean}, R_s); \) and (iii) the mean vertical distance of the five highest points from the mean plane \( (\text{average max. height}, R_{\text{zmax}}). \)

The worst parameter for expressing roughness is the vertical distance of the highest point from the mean plane, that is, the \( R_z. \)

It seems that the highest and deepest points are not symmetric; not the same roughness values are produced in case of positive and negative deviations from the mean plane.

The zigzag pattern in Figure 7 is arbitrary as it depends on the enumeration (ordering) of the roughness parameters. However, the significant differences in the means are real and the grouping is quite straightforward. A conservative Scheffé test amalgamates the three best roughness parameters into one group, the other parameters being significantly different from these three and from each other.

The residuals of model (6) follow a normal distribution in a much better way than the (normalized) raw data do (Figure S4).

As for the future studies, we plan to include other roughness parameters in the comparison.

3. CONCLUSIONS

The plasma treatment causes a significant increase of the surface roughness, irrespective of the different ways of expressing the measured roughness. Plasma treatment caused an increase (ca. 20%) in the normalized roughness (independently of the way it was given).

The detection and quantification of slight roughness changes can be accomplished by AFM even if a relatively large variance is present in the measured data.

The most relevant and recommended roughness parameters are the vertical distance of the highest point from the lowest point \( (\text{maximal height}, R_{\text{max}}); \) the mean vertical distance of the five highest points and five lowest points from the mean plane \( (10 \text{ points mean}, R_s); \) and the mean vertical distance of the five highest points from the mean plane \( (\text{average max. height}, R_{\text{zmax}}). \)

An increase in the observing areas will enhance the detection of small roughness differences in the studied scale.

The sum of (absolute) ranking differences method is able to find subtle differences and hence it can group the relevant parameters even when the classical statistical tools fail. The best and worst parameters can also be determined.

Although the compared roughness estimators were on different scales, a roughness estimation of the nanoscale surfaces was feasible, where other methods fail. The presented SRD coupled with ANOVA can be applied widely and unambiguously also for highly different method comparison tasks.

4. EXPERIMENTAL SECTION

4.1. PET Fabric and Plasma System. A DCSBD plasma system was used for surface treatment of the PET fabric, (ROPLASS s.r.o., Brno, Czech Republic) in ambient air. The nonthermal plasma panel consisted of two systems of parallel strip-like electrodes embedded in alumina matrix. The plasma was ignited with sinusoidal high frequency, 10–20 kHz, high voltage with peak-to-peak values of up to 20 kV. To keep the system at low temperature, cold oil was circulated over the electrodes. The discharge was operated in air at 300 W, which provided a quasihomogeneous diffuse plasma surface. Both sides of the fabric samples were treated for 0.5 min. The treatments were performed on a commercial PET fabric (55 g/m²). During the treatment, both sides of the samples were placed in the plasma. Before the treatment, the samples were thoroughly cleaned to remove any sizing agent.

4.2. Morphological Studies. Untreated and treated PET fabric samples were investigated by an EVO 40 scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany) at 20 kV acceleration voltage. To avoid any electrostatic charging, the samples were coated with a 10 nm thin gold layer.

4.3. Surface Roughness Measurements. The surface roughness of individual PET fibers, which were removed from the untreated and treated fabric, was measured by a Dimension 3100 atomic force microscope equipped with a Nanoscope IIIa controller (Digital Instruments/Veeco, Santa Barbara, California, USA) on 4, 25, 45, and 64 \( \mu \text{m}^2 \) areas using silicon cantilevers in contact mode with a \( 512 \times 512 \) pixel resolution. The main parts and the function of the Nanoscope are illustrated in Figure 8. The number of measurements for the above four scan sizes was 16, 11, 7, and 13 in the case of samples before plasma treatment, and 13, 15, 12, and 9 in the case of samples after plasma treatment. Known weaknesses and systematic errors of AFM scanning, such as tip convolution problems determined by tip radius and cone angle, no tracking of deep trenches and steep slopes, and so forth, were not taken into account in the data treatment.

Raw measurement files were processed using the Nanoscope software by first applying a third-order flattening. Nine widely used roughness parameters, see for example, ref 34, were determined, such as the

1. root mean square roughness (also \( R_q) \)

\[
R_q = \sqrt{\frac{\sum_{i=1}^{n} z_i^2}{n}}
\]

(1)

where \( z_i \) represents the distance of the \( i \)th point from the mean plane;

2. mean roughness, \( R_a \)

\[
R_a = \frac{1}{n} \sum_{i=1}^{n} |z_i|
\]

(2)
3. max. height, \( R_{\text{max}} \) the vertical distance of the highest point from the lowest point;
4. 10 points mean, \( R_p \) the mean vertical distance of the five highest points and five lowest points from the mean plane;
5. peak count, the number of peaks higher than the threshold value (here: 0.1 \( R_p \));
6. max. peak height \( (R_m) \), the vertical distance of the highest point from the mean plane;
7. average max. height \( (R_{\text{avm}}) \), the mean vertical distance of the five highest points from the mean plane;
8. max. depth \( (R_s) \), the vertical distance of the lowest valley from the mean plane;
9. average max. depth \( (R_{\text{avd}}) \), the mean vertical distance of the five lowest points from the mean plane.

For the multivariate statistical analysis, the last two parameters (max. depth and average max. depth), being negative numbers, had to be reversed, their opposite values (max. depth and average max. depth), being parameters derived from the AFM measurement data (see, e.g., ref 35) have not been included in the analysis. One of the excluded parameters was the (dimensionless) roughness factor \( (f_i \text{ or } r) \), defined as the ratio of the real (or rather, measured) surface area to the projected surface area. The roughness factor is relevant only in fields and applications where the real surface area is known, but this is rarely the case: for example, in electrochemistry and contact angle and wetting disciplines.45 In our case, however, roughness parameters used in the field of tribology, more relevant for the application of such fibers, have been considered.

### 4.4. Data Preprocessing

The samples were arranged in the rows, whereas the roughness parameters were arranged in the columns of a table (called input matrix in the fields of chemometrics). Data reduction has not been carried out, as no constant or highly correlated variables were present. On the other hand, the above roughness parameters spanned over considerably different scales; therefore, proper scaling was unavoidable, using the most prevalent scaling options: NOR, RNK, SCL, and STD.

The NOR, often confused with STD, scales each variable to unit length, that is, it divides each matrix element by the column Euclidian norm (L2-norm)

\[
x_{ij}^{\text{norm}} = \frac{x_{ij}}{\sqrt{\sum_{j} x_{ij}^2}}
\]  

(3) where \( i = 1, 2, \ldots, n \) is the number of rows (samples) in the input matrix.

RNK substitutes the numerical values with rank numbers (also column wise), the smallest number receives rank number one, the second smallest two, and so on.

SCL: all variables can be transformed to the \([0, 1]\) interval easily using the equation below

\[
x_{ij}^{\text{range scaled}} = \frac{(x_{ij} - \min(x_j))}{(\max(x_j) - \min(x_j))}
\]  

(4) where \( j = 1, 2, \ldots, m \) is the number of columns (roughness parameters) in the input matrix.

All values are forced within the range zero [for minimum(s)] and unity [for maximum(s)].

STD is carried out in two steps: (i) centering (column mean is subtracted from each matrix element) and (ii) each centered matrix element is divided by the standard deviation of the respective column. It is denoted by STD.

### 4.5. Sum of Ranking Differences

This technique was recently developed for fair method comparison and readily received general usage from chromatographic column comparison37 to multicriteria decision making.46 It can easily be perceived that an actual method that is “closer” to a gold standard (reference) is better than any other alternative. Here, the nine roughness parameters defined in part 2.3 have been compared by SRD. It is interesting to know, which one is the best among them, which ones are equivalent, and whether there are any significant differences among them. The SRD technique coupled with ANOVA can answer these questions easily.

Row-averages were used as the gold standard (benchmark) as the biases of different measurement techniques also follow normal distribution, which is a widely and unambiguously accepted empirical finding in analytical chemistry (e.g., laboratories are compared using z-scores39 with the assumption of normality in proficiency testing). After this data fusion operation, a column by column evaluation follows: the calculation of (absolute) differences between the standard and the individual vector rank-coordinates, and summation of the absolute differences for each sample. These values are the sum of the absolute ranking differences and are abbreviated as SRD. SRD values rank and group the individual roughness parameters.

The basic idea of SRD calculations is presented in ref 40 The SRD values are, in fact, Hamming or city block distances

\[
\text{SRD} = \sum \left| r_i - q_i \right|
\]  

(5) where \( r_i \) is the rank number of object \( i \) for the actual roughness parameter and \( q_i \) is the rank number of object \( i \) for the gold standard, here the row-average.

Generally, only the normalized SRD values (scaled between 0 and 100) are plotted on the \( x \) and \( y \) axes, that is, not the line lengths carry information, but line grouping and closeness of lines to zero [i.e., a “good” roughness parameter is closer to the gold standard (reference) than a “worse” one], and their overlapping with the distribution of SRD values for randomized rank numbers. The latter is also plotted to the right \( y \) axis; overlapping means that the respective roughness parameter(s) is (are) indistinguishable from random ranking. This randomization test is called comparison of ranks with random numbers and denoted as CRRN.41

Identical numbers in the input matrix may distort the ranking procedure; however, ranking with ties is also possible, using partial ranking:40 our visual basic application program for MS Excel is downloadable from: http://aki.ttk.mta.hu/srd.

All details, SRD distributions, and theoretical background are given in our earlier works.40–42

The only limitation for SRD procedure is the too small number of rows: though the algorithm starts at the row number of three, the probability of accidental decision is heightened, then. Empirical evidences suggest that above the row number of six, the random ranking is negligible.

The entire SRD procedure contains not only the calculation of Hamming, or city block distances, but involves two validation steps: (i) a randomization test as shown above and (ii) \( n \)-fold cross-validation. The computer code allows calculating 5- to 10-fold cross-validation in a stratified and in a random manner (repeated resampling). In this work, we used...
sevenfold cross-validation in a repeated random manner [also called Monte Carlo (re)sampling].

4.6. Analysis of Variance. Two types of ANOVA have been carried out:

(i) A factorial ANOVA was completed on the normalized raw (roughness) data with three factors (i) plasma treatment \(F_1\) with two levels [before (b) and after (a) treatment]; (ii) scan area \(F_2\) with four levels (4, 25, 45, and 65, all in \(\mu m^2\)); (iii) roughness parameters \(F_3\) with nine levels, see part 2.3. The number of repetitions were different, but on average 12. Hence, the model was

\[
\text{Roughness norm} = b_0 + b_1 F_1 + b_2 F_2 + b_3 F_3 + b_{12} F_1 F_2 + b_{13} F_1 F_3 + b_{23} F_2 F_3 \]

\[
+ b_{123} F_1 F_2 F_3 \quad (6)
\]

where \(b_0, b_1, b_2, \ldots, b_{123}\) and so forth, are constants. Altogether 885 roughness values were evaluated: 2 (treatment options) \(\times\) 4 (scan areas) \(\times\) 9 (roughness measures) \(\times\) \(\sim\)12 (repetitions).

The raw data can be found in Table S1.

(ii) A factorial ANOVA on SRD values: rescaling of the roughness parameters and ordering by SRD allows revealing more effects by factorial ANOVA.\(^{43}\) The first ANOVA coupling with SRD has already been published in 2014.\(^{19}\) Uncertainty values were assigned to SRD values by use of a sevenfold cross-validation as follows. Approximately 1/7th of the samples were removed with repetitions many times. SRD ranking of roughness parameters was completed on the training (approximately 6/7th) of the samples, that is, on the training sets, and the left-out part was simply ignored. As the number of samples during cross-validation is smaller, the variance is slightly overestimated (a conservative estimation).

Roughness parameters were considered as factor 3 also here \((F_3)\), except for the peak count that was excluded from further analysis. Four data preprocessing options were considered in SRD calculations \((F_1)\): NOR, RNK, SCL, and STD, see part 2.4. Sevenfold cross-validation multiplied by the SRD values many (14) times: in such a way 9 (roughness parameters) \(\times\) 4 (preprocessing methods) \(\times\) 14 (repetitions) = 448 SRD values were calculated and the effects of factors and their interactions were decomposed. The following model was considered

\[
\text{SRD} = a_0 + a_3 F_3 + a_2 F_2 + a_{34} F_3 F_4 \quad (7)
\]

All statistical tests and ANOVA calculations were carried out by STATISTICA (data analysis software system), version 7.1. StatSoft, Inc. (2005); www.statsoft.com.

## ASSOCIATED CONTENT

1. Supporting Information
   The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.9b04211.

   Original data set; effect of plasma treatment at two levels, before and after treatment; effect of various ways to determine roughness by AFM; and normal probability plots of residuals showing improper and considerably better modeling (PDF)

## AUTHOR INFORMATION

### Corresponding Author

Károly Héberger — Plasma Chemistry Research Group, Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences Centre of Excellence, 1117 Budapest, Hungary; orcid.org/0000-0003-0965-939X; Email: heberger.karoly@ttk.hu

### Authors

Lóránd Románszki — Functional Interfaces Research Group, Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences Centre of Excellence, 1117 Budapest, Hungary; orcid.org/0000-0002-6347-5228

Szilvia Klébert — Plasma Chemistry Research Group, Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences Centre of Excellence, 1117 Budapest, Hungary; orcid.org/0000-0002-3107-3371

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b04211

### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The authors thank the support of the National Research, Development, and Innovation Office of Hungary (OTKA, contract no. K 119269). This work was partially funded also by the National Competitiveness and Excellence Program, Hungary (NVKP_16-1-2016-0007).

### REFERENCES

1. Choudhary, U.; Dey, E.; Bhattacharya, R.; Ghosh, S. K. A brief review on plasma treatment of textile materials. Adv. Res. Text. Eng. 2018, 3, 1019.
2. Felix, T.; Trigueiro, J. S.; Bundaleski, N.; Teodoro, O. M. N. D.; Sério, S.; Debacher, N. A. Functionalization of polymer surfaces by medium frequency non-thermal plasma. Appl. Surf. Sci. 2018, 428, 730–738.
3. Haji, A.; Mousavi Shoushtari, A.; Mazaheri, F.; Tabatabaeyan, S. E. RSM optimized self-cleaning nano-finishing on polyester/wool fabric pretreated with oxygen plasma. J. Text. Inst. 2016, 107, 985–994.
4. Kan, C.-w. A novel green treatment for textiles: plasma treatment as a sustainable technology. https://www.crcpress.com/A-Novel-Green-Treatment-for-Textiles-Plasma-Treatment-as-a-Sustainable/Kan/p/book/9781439839447 (accessed April 24, 2019).
5. Penn, L. S.; Wang, H. Chemical modification of polymer surfaces: a review. Polym. Adv. Technol. 1994, 5, 809–817.
6. D’Agostino, R.; Favia, P.; Oehr, C.; Wertheimer, M. R. Low-temperature plasma processing of materials: Past, present, and future. Plasma Processes Polym. 2005, 2, 7–15.
7. Morent, R.; De Geyter, N.; Verschuren, J.; De Clerck, K.; Kiekens, P.; Leys, C. Non-thermal plasma treatment of textiles. Surf. Coat. Technol. 2008, 202, 3427–3449.
8. van Ooij, W. J.; Luo, S.; Datta, S. Surface modification of textile fibers and cords by plasma polymerization. Polymas Polym. 1999, 4, 33–55.
9. Erden, S.; Ho, K. K. C.; Lamoriniere, S.; Lee, A. F.; Yildiz, H.; Bismarck, A. Continuous atmospheric plasma oxidation of carbon fibres: influence on the fibre surface and bulk properties and adhesion to polyamide 12. Plasma Chem. Plasma Process. 2010, 30, 471–487.
(10) Kan, C.-W.; Man, W.-S. Surface Characterisation of atmospheric pressure plasma treated cotton fabric—effect of operation parameters. Polymers 2018, 10, 250.
(11) Bárdos, L.; Baránková, H. Cold atmospheric plasma: Sources, processes, and applications. Thin Solid Films 2010, 518, 6705–6713.
(12) Parvinzadeh, M.; Willoughby, J; Agrawal, P. Surface and Bulk Modification of Synthetic Textiles to Improve Dyebility. Textile Dyeing: InTech, 2011.
(13) Wrobel, A. M.; Kryszewski, M.; Rakowski, W.; Okoniewski, M.; Kubacki, Z. Effect of plasma treatment on surface structure and properties of polyester fabric. Polymer 1978, 19, 908–912.
(14) Lai, J.; Sunderland, B.; Xue, J.; Yan, S.; Zhao, W.; Folkard, M.; Michael, B. D.; Wang, Y. Study on hydrophobicity of polymer surfaces improved by plasma treatment. Appl. Surf. Sci. 2006, 252, 3375–3379.
(15) Paosawatyanyong, B.; Kamlangkla, K.; Hodak, S. K. Hydrophobic and hydrophilic surface nano-modification of PET fabric by plasma process. J. Nanosci. Nanotechnol. 2010, 10, 7050–7054.
(16) Gogolides, E.; Constantoudis, V.; Kokkoris, G.; Kontzamanis, D.; Tsougeni, K.; Boulouis, G.; Vlachopoulos, M.; Tserpi, A. Controlling roughness: from etching to nanotexturing and plasma-directed organization on organic and inorganic materials. J. Phys. D: Appl. Phys. 2011, 44, 174021.
(17) Modification of Polymer Properties; Jasso-Gastinel, C. F., Kenny, J. M., Eds.; William Andrew, 2016.
(18) Haji, A.; Semnani Rahbar, R.; Mousavi Shoushtari, A. Improved microwaved shielding behavior of carbon nanotube-coated PET film using plasma technology. Appl. Surf. Sci. 2014, 311, 593–601.
(19) Leroux, F.; Perwuelz, A.; Campagne, C.; Behary, N. Atmospheric air plasma treatments of polyester textile structures. J. Adhes. Sci. Technol. 2006, 20, 939–957.
(20) Poletti, G.; Orsini, F.; Raffaele-Addamo, A.; Riccardi, C.; Selli, E. Cold plasma treatment of PET fabrics: AFM surface morphology characterisation. Appl. Surf. Sci. 2003, 219, 311–316.
(21) Esena, P.; Riccardi, C.; Zanini, S.; Tontini, M.; Poletti, G.; Orsini, F. Surface modification of PET film by a DBD device at atmospheric pressure. Surf. Coat. Technol. 2005, 200, 664–667.
(22) Velas, A.; Junkar, I.; Cvejcar, U.; Kovac, J.; Mozetic, M. Surface modification of polyester by oxygen- and nitrogen-plasma treatment. Surf. Interface Anal. 2008, 40, 1444–1453.
(23) Boria, G.; Anderson, C. A.; Brown, N. M. D. Surface treatment of natural and synthetic textiles using a dielectric barrier discharge. Surf. Coat. Technol. 2006, 201, 3074–3081.
(24) Károly, Z.; Kalácska, G.; Sukumaran, J.; Fauconnier, D.; Kalácska, A.; Mohai, M.; Klebert, S. Effect of atmospheric cold plasma treatment on the adhesion and tribological properties of polyamide 66 and poly(tetrafluoroethylene). Materials 2019, 12, 658.
(25) Szabo, O. E.; Csázas, E.; Koczka, B.; Toth, A.; Klebert, S. Enhancing the accessibility of starch size and cellulose to enzymes in raw cotton woven fabric by air-plasma pretreatment. Text. Res. J. 2016, 86, 868–877.
(26) Edwards, N. M. W.; Best, E. L.; Connell, S. D.; Goswami, P.; Carr, C. M.; Wilcox, M. H.; Russell, S. J. Role of surface energy and nano-roughness in the removal efficiency of bacterial contamination by nonwoven wipes from frequently touched surfaces. Sci. Technol. Adv. Mater. 2017, 18, 197–209.
(27) Liu, Y.-C.; Xiong, Y.; Lu, D.-N. Surface characteristics and antistatic mechanism of plasma-treated acrylic fibers. Appl. Surf. Sci. 2006, 252, 2960–2966.
(28) Vasilević, J.; Gjorgjievska, M.; Tomašić, B.; Orel, B.; Jerman, I.; Mozetič, M.; Velšek, A.; Simonic, B. The surface modification of cellulose fibres to create super-hydrophobic, oleophobic and self-cleaning properties. Cellulose 2015, 20, 277–289.
(29) Wang, W. Y.; Jin, X.; Wang, B.; Bian, L. N. Effects of oxygen-plasma treatment time on the properties of UHMWPE fiber. Adv. Mater. Res. 2013, 781–784, 2605–2608.
(30) Haji, A.; Rahbar, R. S.; Shoushtari, A. M. Plasma assisted attachment of functionalized carbon nanotubes on poly(ethylene terephthalate) fabric to improve the electrical conductivity. Polymery 2015, 60, 337–342.
(31) Mandolino, C.; Lertora, E.; Gambaro, C. Effect of cold plasma treatment on surface roughness and bonding strength of polymeric substrates. Key Eng. Mater. 2014, 611–612, 1484–1493.
(32) Ganti, S.; Bhushan, B. Generalized fractal analysis and its applications to engineering surfaces. Wear 1995, 180, 17–34.
(33) Binnig, G.; Quate, C. F.; Gerber, C. Atomic force microscope. Phys. Rev. Lett. 1986, 56, 930–933.
(34) Gademaw, E. S.; Koura, M. M.; Maksoud, T. M. A.; Elewa, I. M.; Soliman, H. H. Roughness parameters. J. Mater. Process. Technol. 2002, 123, 133–145.
(35) Bhushan, B. Surface roughness analysis and measurement techniques. In Modern Tribology Handbook; Bhushan, B., Ed.; Principles of Tribology; CRC Press: Boca Raton—London—New York—Washington, D.C., 2001; Vol. 1.
(36) Wenzel, R. N. Resistance of solid surfaces to wetting by water. Ind. Eng. Chem. 1936, 28, 988–994.
(37) Nowilk, W.; Heron, S.; Bonose, M.; Tchapl, A. Separation system suitability (SS): A new criterion of chromatogram classification in HPLC based on cross-evaluation of separation capacity/peak symmetry and its application to complex mixtures of anthraquinones. Analyst 2013, 138, 5801–5810.
(38) Lourenco, J. M.; Lebensztajn, L. Post-Pareto Optimality Analysis with Sum of Ranking Differences. IEEE Trans. Magn. 2018, 54, 8202810.
(39) Youden, W. J. Statistical Manual of the Association of Official Analytical Chemists. Statistical Techniques for Collaborative Test, 8th ed.; AOAC International: Gaithersburg, MD, USA, 1997.
(40) Héberger, K. Sum of ranking differences compares methods or models fairly. TranC. Trends Anal. Chem. 2010, 29, 101–109.
(41) Héberger, K.; Kollár-Hunek, K. Sum of ranking differences for method discrimination and its validation: comparison of ranks with random numbers. J. Chemom. 2011, 25, 151–158.
(42) Kollár-Hunek, K.; Héberger, K. Method and model comparison by sum of ranking differences in cases of repeated observations (ties). Chemom. Intell. Lab. Syst. 2013, 127, 139–146.
(43) Lindman, H. R. Analysis of Variance in Experimental Design; Springer Verlag: New York, NY, 1992.
(44) Héberger, K.; Kolarević, S.; Kračun-Kolarević, M.; Sunjog, K.; Gačić, Z.; Kljačić, Z.; Mitrić, M.; Vuković-Gačić, B. Evaluation of single cell gel electrophoresis data: Combination of variance analysis with sum of ranking differences. Mutat. Res., Genet. Toxicol. Environ. Mutagen. 2014, 771, 15–22.