Modification of the glass surface by DCSBD plasma discharge to improve adhesion of decorative gold

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Abstract. The present work, as one of the first scientific works, deals with the modification of the glass surface induced by DCSBD plasma discharge to increase the adhesion of decorative gold layers on glass products. In the study of such a modification, it was necessary to monitor the effectiveness of the modification of the glass surface, and subsequently it was necessary to test the resistance of the deposited gold layers in tests performed directly in operation. In the present work, the adhesion of gold to DCSBD-modified glass surfaces by plasma discharge was uniquely evaluated by image analysis.

1. Introduction

The main goal of the present work is to determine the effect of DCSBD (Diffuse Coplanar Surface Barrier Discharge) plasma on the adhesion of industrially applied decorative gold coating to the glass surface. Plasma modification is an environmentally friendly process, and it is assumed that its application can clean the glass surface [1-4]. Such plasma-chemical activation can be an effective tool to improve the adhesion test and thus eliminate product imperfections in the future. The following work also deals with the application of plasma to activate surfaces (also glass) and improve adhesion (also gold) [5-8]. When activating the surfaces of the material, changes in the contact angles of the test fluids and changes in the surface free energy can be observed [9,10]. These findings serve as proof that the performed plasma-chemical modification of the surface of the material will generate new results: under a suitably set experimental conditions, such changes may be possible that will show better resistance to abrasion and washing. The advantage of the DCSBD type plasma application is that it is easily generated in a laboratory or industrial atmosphere. Plasma is also qualified as atmospheric pressure plasma, cold plasma or nonthermal plasma and the time aspect (durability) of the implemented modification is also examined [11-14].

2. Materials and methods

2.1. Plasma treatment
To evaluate the experiment of the present work, glass samples / surfaces can be categorized into:
• without plasma modification; (unmodified)
• modified by DCSBD plasma; (modified)
All samples of glass in the present work were taken and processed (grinding and polishing) directly in the production in the glassworks RONA, a. s., Lednické Rovne, (SR). The plasma reactor KPR 200 mm, which is available at the Faculty of Industrial Technologies in Púchov, was used for the experiment. The reactor power was set at 375 W, using a planar ceramic dissector for DCSBD plasma discharge. Said dielectric was prepared for modification by gradually increasing the power, while pads for glass samples were placed on it. The exposure time of the DCSBD discharge was set at up to 30 s. The distance of the glass surfaces from the ceramic dielectric was determined to be 0.28 mm using washers. For surface modification, such a distance is reported in the literature [13,15,16] as ideal (0.3 mm). Modification of glass surfaces was always performed on the 2 largest surfaces of glass samples (adjacent and opposite sides). The glass samples moved sporadically during the modification. The technical description of the device is more precisely given in the work [17].

2.2. Actions performed by RONA a. s.

All samples of glass were subsequently delivered for processing - painting in the company RONA a. s. using a brush, a decorative gold coating was applied (horizontally and vertically) to samples without DCSBD plasma and to samples modified with DCSBD plasma. Subsequently, firing was performed at a temperature of approximately 520 ºC, for a duration of approximately 5 hours. The sample preparation was thus completed.

The samples were at RONA a. s. marked and subjected to two types of test (Figure 1, Table 1):

- Samples marked with numbers 1 and 2 were subjected to a washing cycle in an industrial dishwasher (using a standard detergent specified by the dishwasher manufacturer). Sample without plasma modification attached, unlabeled.
- Samples A and B were immersed in vinegar solution for 24 hours. Sample without plasma modification, unlabeled.

![Figure 1](image-url). Overview of glass samples after adhesion tests by washing and leaching.
Table 1. Overview of samples used in experiments

| Type of test (realized by RONA a. s.) | Sample marked as |
|--------------------------------------|------------------|
| Washing in an industrial dishwasher  | 1                |
|                                       | 2                |
| Leaching in vinegar solution (4 %)   | A                |
|                                       | B                |

2.3. Image Analysis
Samples after testing in RONA a. s. were subjected to image analysis using ImageJ software to quantify the percentage of residual gold on the glass surfaces and thus determine the effectiveness of the adhesion to the glass surface after modification by DCSBD discharge. Photographs for image analysis were taken in *.RAW format on a Canon EOS 1200D digital SLR using Canon MACRO LENS EF-S 35mm and Canon EF LENS 50mm lenses. Manual focus mode was used, shooting parameters were set as follows: ISO 800, F4 aperture, 1/80 exposure, non-flash mode. The photos taken were converted to *.jpg format for the needs of ImageJ software, while the photos were modified with a standard image processing tool in the Windows 10 operating system (Sauna filter). A decorative gold coating was applied to two areas of the sample. Each such area was taken twice, while the second photo was taken by rotating the area by 180 degrees. The samples were additionally illuminated in the studio. The Threshold function has been applied using ImageJ software. It works with an image converted to an 8-bit display. Using this, it was possible to quantify the area on which the decorative gold coating had good adhesion and withstood the washing and leaching test (Figure 2).

2.4. Evaluation using a stereo microscope
Glass surfaces with decorative gold coating were observed using a STM 723 stereo magnifier. Photographs were taken using Impor 5.0 software, with the zoom ranging from min. 7 and max. 45 times. Most of the images taken were zoomed in at 10, 15 and 25 times.

2.5. Evaluation of contact angle
Two test liquids were selected to determine the value of the contact angle on glass surfaces unmodified and modified by plasma discharge: diiodomethane (MI) and distilled water (DW). The surface free energy and values of the polar and dispersive parts were calculated both for DCSBD plasma unmodified and modified glasses. The MATLAB® program was used in the calculations.

3. Results and discussion
To determine the change in wettability of the surfaces, the method of determining the value of the contact angle of the test liquid on the glass surfaces (before and after modification with DCSBD plasma) was chosen. In the case of the present work, the test liquids were diiodomethane (MI) and distilled water.
The values of the contact angles of 10 drops of diiodomethane are shown in the Figure 3 and the values of the contact angles of 10 drops of distilled water are shown in the Figure 4. All values obtained were tested for outliers according to the criterion (P > 0.05), none of which was marked as outliers.

**Figure 3.** Values of contact angles of diiodomethane (MI) drops on glass surfaces

**Figure 4.** Values of contact angles of distilled water (DW) drops on glass surfaces

On the surface of the glass without modification of DCSBD by plasma, the test liquids reached an average angle of 56.7 ° (MI) resp. 30.3 ° (DW). These values are confronted with the literature [9, 10]. Glass surfaces modified with DCSBD plasma become more hydrophilic after modification with DCSBD plasma. A drop in contact angle of almost 27 ° was observed with diiodomethane and 6 ° with distilled water. Average drop profile drops for (DI) in the image and for (DW) in the Figure 5.

An increase in surface free energy can be observed in glass samples modified by DCSBD discharge. The values of surface free energy, polar and dispersion component changes for plasma modified and unmodified surfaces are given in Table 2.
Figure 5. Graphical representation of the change in the profile of a diiodomethane drop and distilled water on the glass surface

Table 2. Values of surface free energy, polar and dispersive component on the surface of glass

|                              | Unmodified by DCSBD plasma | Modified by DCSBD plasma |
|------------------------------|----------------------------|--------------------------|
| Surface free energy (mJ.m⁻²) | 64.9 ± 3.2                 | 73.6 ± 2.3               |
| Polar component (mJ.m⁻²)     | 34.4 ± 3.2                 | 29.0 ± 2.3               |
| Dispersive component (mJ.m⁻²)| 30.5 ± 1.0                 | 44.5 ± 2.0               |

Observation of glass surfaces using an optical stereo magnifier (STM 723) provided the opportunity to monitor the adhesion of gold to glass surfaces. When observing the surfaces before the washing and leaching tests, it was possible to observe the coating of decorative gold as a continuous layer of gold on the whole surfaces of the glass up to its edges (as in Figure 6 on the right). The test by leaching in a vinegar solution degraded the layer of decorative gold only minimally. Reduced adhesion was observed only in the form of fine scratches (Figure 6 on the left), and exceptionally in the form of wider scratches, which most likely arose during sample handling after the leaching test (Figure 6 in the middle).

Figure 6. Observation of adhesion of decorative gold coating on glass surfaces after vinegar leaching test. Zoom in images: 7x, 25x and 45x

Larger differences can be observed when observing glass surfaces after the washing test than during the leaching test. The gold layer can be seen as a continuous layer (Figure 7 on the left). Differences can be observed in the reduced adhesion of gold at the edges of the sample (Figure 7). No such effect was observed in the leaching test. Significantly large areas of gold-free glass can be observed on the surfaces (Figure 6 in the middle and right). The gold probably did not have sufficient adhesion to the glass surface and was washed away by the pressure of the dishwasher water.
Figure 7. Observation of adhesion of decorative gold coating on glass surfaces after washing test in an industrial dishwasher. Zoom in images: 10x, 10x and 7x

The washing test was thus more demanding for the decorative coating of gold, while the reduction in adhesion could be observed with the naked eye. The washing test of samples 1 and 2 showed that the surfaces of the glass modified by DCSBD discharge did not show an improvement in the adhesion to the decorative gold coating. A decrease in the coverage of the glass surface with decorative gold coating on average 4.2% was recorded (Table 3). Values were obtained by evaluating 4 photographs for each sample (Table 4).

| Table 3. Results of image analysis for washing test (simplified form) |
|---------------------------|-----------------|-----------------|
| Type of test              | Glass type      | Average threshold [%] |
| Washing                   | Unmodified by plasma | 85.6           |
|                           | Modified by plasma (1 & 2) | 81.4           |
|                           | Difference       | -4.2            |

| Table 4. Results of image analysis (Threshold funcion) for washing test (full form) |
|---------------------------|-----------------|-----------------|-----------------|-----------------|
|                           | Glass type      | Average         | Photo no. 1     | Photo no. 2 sample rotated |
| Unmodified by DCSBD plasma| 85.6            | 86.6            | 84.6            |
|                           | 1.1             | 81.6            | 80.5            | 82.6            |
|                           | 1.2             | 85.1            | 85.5            | 84.7            |
| Modified by DCSBD plasma  | 83.4            | 88.3            | 87.9            | 88.6            |
|                           | 2.1             | 88.3            | 87.9            | 88.6            |
|                           | 2.2             | 70.7            | 72.7            | 68.7            |
|                           | 2               | 79.5            | Average 2.1 + 2.2 |

The leaching test of samples A and B showed that the DCSBD-modified glass surfaces did not show an improvement in adhesion to the decorative gold coating. Again, a decrease of 4.3% was recorded (Table 5). Values were obtained by evaluating 4 photographs for each sample (Table 6).
Table 5. Results of image analysis for leaching test (simplified form)

| Type of test | Glass type                         | Average threshold [%] |
|--------------|------------------------------------|-----------------------|
| Leaching     | Unmodified by plasma               | 95.3                  |
|              | Modified by plasma (A & B)         | 90.1                  |
|              | Difference                         | -4.3                  |

Table 6. Results of image analysis (Threshold function) for washing test (full form)

| Glass type                        | Treshold [%] | Photo no. 1 | Photo no. 2 (sample rotated) |
|-----------------------------------|--------------|-------------|-------------------------------|
| Unmodified by DCSBD plasma        | 95.3         | 94.7        | 95.8                          |
| A.1                               | 90.8         | 92.2        | 89.4                          |
| A.2                               | 90.7         | 91.9        | 89.5                          |
| Modified by DCSBD plasma          |              |             |                               |
| A                                 | 90.8         |             | Average A.1 + A.2             |
| B.1                               | 88.1         | 87.8        | 88.5                          |
| B.2                               | 94.0         | 93.5        | 94.6                          |
| B                                 | 91.1         |             | Average B.1 + B.2             |

4. Conclusion

In this work, the adhesion of decorative gold coating on glass surfaces was investigated to determine whether the pre-treatment of glass by surface modification with DCSBD plasma discharge will improve the adhesion. Based on the reduction of the values of contact angles of test liquids on glass surfaces after modification by DCSBD discharge, such an assumption was confirmed. The glass surfaces became more wettable after modification by DCSBD by plasma discharge. However, after the tests by washing in an industrial dishwasher and leaching in a vinegar solution, the improvement in adhesion was not confirmed. The evaluation of the adhesion of the layer of decorative gold on the surface of the glass, which in practice is carried out visually (pass/fail), was this time carried out using image analysis. The results of the adhesion of decorative gold coating on glass surfaces could thus be quantified. This is the first scientific work to use image analysis to determine the adhesion of gold to plasma-modified glass surfaces. The probably inhomogeneous effect of the DCSBD plasma discharge on the glass surfaces is also evidenced by the higher standard deviations from the method of measuring the contact angle for both test liquids. This can result in reduced adhesion of the decorative gold layer and is observed as just clear areas without gold coating. In the future, it will be necessary to introduce a more intense dynamic mode during the process of plasma modification of the glass surface. Further possible improvements in the expected results can be achieved by pretreating the glasses with an ultrasonic cleaner in combination with perfect degreasing of the surfaces with chemicals. In both cases, however, the results obtained will be more difficult to implement directly in the conditions of glass production.
References

[1] Sihelník S, Kelar J et al 2020 Atmospheric pressure plasma cleaning and activation of float soda-lime glass prior to lamination processing pp. 298-303, 10.37904/nanocon.2019.8769, ISSN 2694-930X.

[2] Buček A, Brablec A et al 2017 Glass bond adhesive strength improvement by DCSBD atmospheric-pressure plasma treatment (International Journal of Adhesion and Adhesives) vol 78, pp. 1-3, ISSN 0143-7496.

[3] Cras J J, Rowe-Taitt C A et al 1999 Comparison of chemical cleaning methods of glass in preparation for silanization (Biosensors and Bioelectronics) vol 14, Issues 8-9, pp. 683-688, ISSN 0956-5663.

[4] DeRosa R L, Schader P A et al 2003 Hydrophilic nature of silicate glass surfaces as a function of exposure condition (Journal of Non-Crystalline Solids) vol 331, Issues 1-3, pp. 32-40, ISSN 0022-3093.

[5] Kvítek O, Bot M et al 2012 Gold nanoparticles grafting on glass surface (Applied Surface Science) vol 258, Issue 22, pp. 8991-8995, ISSN 0169-4332.

[6] Matsumae T, Kurashima Y et al 2019 Surface activated bonding of Au/Cr, Au/Ta and Au/Pt/Ti films after degas annealing for Si/sapphire gas cell (Microelectronic Engineering) vol 214, pp. 68-73, ISSN 0167-9317.

[7] Homola T, Matoušek J et al 2013 Plasma Treatment of Glass Surfaces Using Diffuse Coplanar Surface Barrier Discharge in Ambient Air. (Plasma Chemistry and Plasma Processing) vol 33, pp. 881-894.

[8] Li D, Xiong M et al 2020 Effects of low-temperature plasma treatment on wettability of glass surface: Molecular dynamic simulation and experimental study (Applied Surface Science) vol 503, ISSN 0169-4332.

[9] Tino R, Smatko L 2014 Modifying wood surfaces with diffuse coplanar barrier discharge plasma (Wood and fiber science: journal of the Society of Wood Science and Technology) vol 46, pp. 1-6.

[10] Kelar J, Shekargoftar M et al 2018 Activation of polycarbonate (PC) surfaces by atmospheric pressure plasma in ambient air (Polymer Testing) vol 67, pp. 428-434, ISSN 0142-9418.

[11] Prysiąznyi V 2013 Atmospheric Pressure Plasma Treatment and Following Aging Effect of Chromium Surfaces (Journal of Surface Engineered Materials and Advanced Technology) vol 2, pp. 138-145.

[12] Šulcová J, Papučová I et al 2020 Glass surface modification using diffusion coplanar surface barrier discharge (DCSBD) (Materials Science and Engineering) vol 776.

[13] Kováčik D, Ráhel J et al 2009 Diffuse coplanar surface barrier discharge -- basic properties and its application in surface treatment of nonwovens 3005-

[14] Al-Maliki H, Kalácska G The effect of atmospheric DBD plasma on surface energy and shear strength of adhesively monded polymer (Hungarian agricultural engineering) vol 31, pp. 52-58, ISSN 0864-7410.

[15] Arayananarakool R, Shui L et al 2011 A new method of UV-patternable hydrophobization of micro- and nanofluidic networks (Lab on a Chip) vol 11, pp. 4260-4266.

[16] Tan K T, White C C et al 2008 Fundamentals of Adhesion Failure for a Model Adhesive (PMMA/Glass) Joint in Humid Environments (The Journal of Adhesion) vol 84, Issue 4, pp. 339-367.

[17] Krmelová V, Janík R et al 2018 Operation of DCSBD plasma reactor in laboratory conditions (ZESZITY NAUKOWE WYŻSZEJ SZKOŁY ZARZĄDZANIA OCHRONĄ PRACY W KATOWICACH) vol 1(14), pp. 95-103, ISSN-1895-3794.

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