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Improvement of the adhesion between TiO_2 nanofilm and glass substrate by roughness modifications

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Abstract

An increase of the adhesion between soda-lime glass substrate and TiO_2 nanofilm was achieved by roughness modifications, treating the glass surface with acid or basic solutions. The study was organised through a D-optimal experimental design. The roughness (measured by AFM) and the weight loss were statistically analysed using MODDE 9.0 software. Subsequently, the correlation between the surface roughness and the adhesion (measured by scratch test) of the films was studied. The statistic analysis of the results indicates how the chemical treatments modify the roughness of the glasses and it was found that smooth surfaces enhance the adhesion of the films.

Keywords: Adhesion, TiO_2, nanoparticles, glass, roughness, D-optimal design.

1. Introduction

The advances in building materials are focused not only in the improvement of their technical and aesthetic properties, but also in the development of functional surfaces which can be utilized as architectural elements and indoor or outdoor furniture. Between these kinds of surfaces, anti-smog, self-cleaning and antibacterial glasses have been achieved by the use of coatings formed by TiO_2 nanoparticles [1]. However, although much progress has been obtained in the production of this class of glasses, there still are several limitations that make difficult their insertion on the market. One of these limitations is the low adhesion between the coatings and their glass substrates. Nowadays, the principal solutions to

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overcome this problem is the employment of pre-linked clusters [2], which involves both long experimental procedures and expensive reagents and the usage of silica pre-coated glasses as substrates [3,4], but these latter are employed principally to avoid ion diffusion. The proposal of this study was to enhance the adhesion by the modification of the glass roughness through simple chemical treatments, since previous reports indicate that rough glass or sapphire substrates promote the adhesion of Au coatings [5-7]. The experimental procedure was planned with using the Design of Experiments (DOE) technique, with the goal not only improve the adhesion by means of the roughness approach, but also accurately investigate which variables influence the glass roughness. By the DOE was also possible to determine at what levels these variables must be kept to get either rough or smooth surfaces. In particular, the experiments were carried out using a D-optimal design in order to examine the effects of the chemical solutions, their concentration and the treatment times on the final glass roughness. Based on the statistical results and scratch critical loads, the correlation between the roughness and the adhesion were obtained.

2. Materials and Experimental Methods

SAINT GOBAIN soda-lime float glasses were used as substrates. The experimental procedure used to carry out the chemical attack of the substrates is reported in detail in reference [8]. Images of two different zones of each treated sample were taken with an Atomic Force Microscope, AFM (Park Autoprobe CP, Park Scientific Instruments). All images were taken in non-contact mode using a 100 μm scanner, at a scan size of 5 μm. The roughness was expressed as Rms rough (root-mean-squared roughness, given by the standard deviation of the analyzed data) and R_{p-v} (referred to the maximum peak-to-valley distance within the analyzed area). Table 2 reports the experimental design, the measured roughness values and the weight loss. The statistical calculations and multiple regressions of the weight loss and AFM data were performed using the MODDE 9.0 [9] software. Representative attacked glasses were coated by dip coating with 5 layers of a commercial TiO_2 nanoparticles suspension provided by COLOROBBIA S.p.A., using a dipping rate of 85 mm/min. To obtain correlation between the roughness and the adhesion, the scratch critical loads of the coated glasses were measured. All the adhesion measures were made after the treatment at 110 °C for 1.5 h to evaporate the solvent, but any further treatment at higher temperatures (annealing) was performed.

2.1. Experimental design

A D-optimal design with three factors (two numerical plus one categorical) was used to identify the factors that influence the glass roughness. D-optimal design was used since this design could deal with qualitative factors easily. Based on a literature analysis, the chemical solutions (X_1), their concentration (X_2) and the treatment time (X_3) [10,11] were identified as control factors (Table 1). Temperature was set at a fixed value (37 °C) for all the experiments. The construction of an experimental plan through D-optimal design consists of defining levels, selection of the model that fits and choosing design points from a set of candidate points that was generated depending on the selected model [12]. As presented in Table 1, the numeric factors were varied over two to three levels, while the categorical factor contains 3 levels, i.e. three categories. The final D-optimal experimental plan contains a total of 21 experiments including three center points (Table 2). The experiments were carried out following the run order to avoid any systematic bias in the outcomes. The obtained model was evaluated for each response function and the experimental data (AFM roughness and weight loss) were analysed statistically using the MODDE 9.0 software.

Table 1. Factors, their levels and the chosen responses.

Parameter	Code	Levels (Coded)		
Chemical solution	X_1	HCl (X_{1HCl})	NaOH (X_{1NaOH})	CH_3COOH ($X_{1CH3COOH}$)
Concentration[1]	X_2	A (X_{2A})	B (X_{2B})	-
Treatment time, min	X_3	30 ($X_{3\text{-}30}$)	120 ($X_{3\text{-}120}$)	240 ($X_{3\text{-}240}$)
Responses				**Code**
Rms roughness, nm				Y_1
$R_{p\text{-}v}$[2], nm				Y_2
Weight loss, %				Y_3

[1] A= High concentration, B = Low concentration. Concentration in % for HCl and CH_3COOH and in M for NaOH.
[2] $R_{p\text{-}v}$ = maximum peak-to-valley distance.

Table 2. Design matrix and measured responses.

Exp. No.	Run Order	Factors			Responses		
		Qualitative	Quantitative				
		(X_1), Chemical Solution	(X_2), Concentration	(X_3), Treatment time, min	(Y_1), Rms Roughness (nm)	(Y_2), $R_{p\text{-}v}$ (nm)	(Y_3), Weight loss, %
1	20	HCl	A	30	2.40	76.46	0.0000
2	5	HCl	A	120	4.83	102.70	0.0089
3	3	HCl	A	240	2.08	54.93	0.0059
4	18	NaOH	A	30	2.52	45.70	0.0008
5	8	NaOH	A	120	27.09	428.60	0.0015
6	9	NaOH	A	240	7.10	83.41	0.0050
7	1	CH_3COOH	A	30	6.00	90.84	0.0000
8	12	CH_3COOH	A	120	7.36	65.66	0.0000
9	2	CH_3COOH	A	240	1.49	17.75	0.0008
10	21	HCl	B	30	23.78	320.00	0.0050
11	14	HCl	B	120	4.30	46.19	0.0389
12	17	HCl	B	240	16.19	147.00	0.0016
13	6	NaOH	B	30	3.422	43.80	0.0028
14	15	NaOH	B	120	9.98	83.17	0.0072
15	19	NaOH	B	240	10.14	101.20	0.0042
16	7	CH_3COOH	B	30	1.974	38.39	0.0000
17	13	CH_3COOH	B	120	4.84	54.74	0.0000
18	11	CH_3COOH	B	240	10.16	77.78	0.0077
19	4	HCl	A	120	3.16	40.23	0.0000
20	10	HCl	A	120	13.27	126.4	0.0052
21	16	HCl	A	120	3.84	48.37	0.0034

Note: Table 2 only shows the results for the so-called "Zone 1" of each sample, since values measured for the Zone 2 were used to evaluate the homogeneity of the generated surfaces.

2.2. Statistical analysis of the data

The statistical analysis was carried out following three steps: (a) evaluation of the raw data; (b) regression analysis and (c) interpretation of the model. The evaluation of the raw data was focused on a general appraisal of regularities and peculiarities in the data. The regression analysis involves the calculation of the model, linking the input factors to the measured responses. In this work, the Multiple Linear Regression (MLR) method was used to explore the dependence of the responses on varied factors. For each response, the regression model was selected based on the analysis of the following parameters: the *goodness of fit* (R^2), which measures how the regression model fit the data; the *goodness of predictions* (Q^2), which estimates the predictive power of the model; the *model validity,* that measures the

validity of the model and the *reproducibility*, which represents the variation of the response of different tests performed at the same operative conditions, compared with the total variation of the response. The values of the previous parameters allow getting an overview of the regression model: R^2 could vary from 0 to 1, where 1 indicates a perfect model and 0 no model at all; Q^2 must have a value higher than 0.5. Moreover, R^2 should not exceed Q^2 more than 0.2-0.3 [13]. A value larger than 0.25 for the model validity indicates that there is no lack of fit in the data and the model error is in the same range that the pure error. Finally, a reproducibility value close to 1 indicates a high reproducibility [13]. Another tool used to determine the goodness of the model was the analysis of the residuals, since a good model should be characterized by normally distributed errors. This tool permitted to verify the normal behaviour of the residuals and detect deviating experiments.

During the interpretation of the model, it was determined whether the model could be used or eventually, pruning. The analysis of the regression coefficients and their confidence intervals permitted finding out the real effect of the factors on the measured responses, identifying which single factor or factors combinations influence the flat glass roughness. The study of the interactions between factors permitted to describe how the influence of one factor on the response depends on the level of another factor. In other words, there could be experimental cases in which the factor A has a positive effect on the response for a given level of factor B, while in a different level of B, the effect of A on the response is negative [14]. To determine the effect of interaction on the responses, interaction plots were used, which display the levels of one factor in the X axis and have a separate line for the means of each level of the other factor. The Y axis is the response.

3. Results and Discussions

3.1. Characterization

3.1.1. AFM roughness

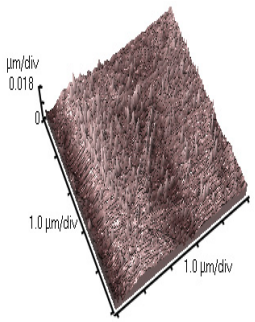

Figure 1. AFM image of the reference glass (Scan size = 5 mm).

The Rms roughness of the treated glasses is reported in Table 2. Compared with a reference glass (no treatment, Rms rough = 3.409 nm) it was observed that the chemical treatments modify the roughness, resulting in lower or higher roughness values. Figure 1 shows the AFM image of the reference glass. Samples 5 and 10 show the highest roughness values (27 and 24 nm, respectively). However, these surfaces were non-homogeneous due to the presence of residual particles formed as consequence of the chemical attack. This was confirmed by their highest R_{p-v} values (428 and 300 nm, respectively). Figure 2 shows the AFM images of sample 5, where it can be observed the residual particles that were formed

through the chemical treatment and the generated non-homogeneous surface. It was concluded that the chemical attack using NaOH 12M for 120 min or 3.7% HCl for 30 min promote the deposition of the residual particles in the glass surface, increasing the roughness (enhances the R_{p-v} value).

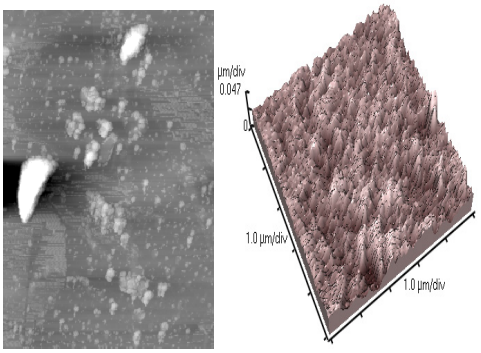

Figure 2. AFM images of sample 5 (Scan size = 5 mm).

Samples 12 and 15 also present high values of Rms rough, between 10 and 16 nm. This high roughness was still attributed to the presence of the formed residual particles, since the high R_{p-v} values of these samples vary from 101 to 147 nm. So, it was further confirmed that chemical treatments with 3.7% HCl for 240 min and NaOH 1.2 M for 240 min (low concentrations with long treatment times) induce high roughness values. Samples 6, 7, 8, 14 and 18 show "medium" values of Rms rough (5-10 nm), as well as "medium" values of R_{p-v} (50-100 nm). These samples present more homogeneous surfaces than the previous samples. These samples were treated with NaOH 12 and 1.2 M, 96% and 9.6% CH_3COOH. Finally, samples 4, 9, 11 and 16 present the lowest values of Rms rough ($\leq$ 5 nm), as well as the lowest values of R_{p-v} ($\leq$ 50 nm). These surfaces were the most homogeneous. Figure 3 shows the AFM of images sample 9.

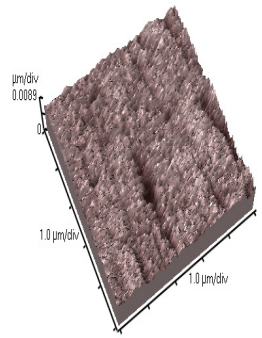

Figure 3. AFM image of the sample 9 (Scan size = 5 mm).

From the previous AFM observations, it was concluded that the chemical treatments that induce high roughness also promote the formation of residual particles, which contribute to increase the roughness of the surface. Furthermore, the attacked surfaces of these samples are not homogeneous. This could be a problem during the deposition of nanofilms, since a non-homogeneous surface decrease the adhesion of the coating. On the other hand, the chemical treatments that induce low roughness generate homogenous smooth surfaces, without the deposition of residual particles.

3.1.2. Weight loss

The weight loss of the glass substrates after the chemical treatment was determined. As shown in Table 2, all the glasses, except sample 11 (3.7% HCl for 120 min) present low weight loss (from 0 to 0.009%). This fact was attributed at the treatment with a 3.7% HCl, i.e., a chemical solution with low concentration. As presented in section 3.1.2, it was found that low concentrations promote an increase of the glass roughness, and consequently, could also promote a higher weight loss. The glasses that present the minimum weight lost are principally those attacked for low treatment times (30 min) or acetic acid.

3.2. Statistic analysis and interpretation

3.2.1. Rms roughness

The analysis of the raw data revealed high experimental reproducibility but a non-normal distribution, for this reason, a logarithmic transformation was applied. Eq. 1 shows the obtained regression model, which is characterized by meaningful values of R^2, Q^2, model validity and reproducibility (Table 3).

Table 3. Summary of fit of the regression model for Rms rough.

Parameter	Value
R^2	0.98
Q^2	0.90
Model validity	0.41
Reproducibility	0.99

$$Y_1 = 0.882358 + 0.0667097X_{1HCl} - 0.480168X_{1NaOH} + 0.413458X_{1CH3COOH} - 0.000448101X_3 - 0.315395X_{2A} + 0.315395X_{2B} - 0.00015077X_{1HCl}X_3 + 0.00264219X_{1NaOH}X_3 - 0.00249142X_{1CH3COOH}X_3 - 0.119654X_{1HCl}X_{2A} + 0.235417X_{1NaOH}X_{2A} - 0.235417X_{1NaOH}X_{2B} - 0.115763X_{1CH3COOH}X_{2A} + 0.115763X_{1CH3COOH}X_{2B} + 6.0817e^{-5}X_3X_{2A} - 6.0817e^{-5}X_3X_{2B} \quad \textit{Eq. (1)}$$

Eq. (1) shows two linear coefficients (X_{2A} and X_{2B}) and some interaction factors statistically meaningful ($X_{1CH3COOH}X_3$, $X_{1HCl}X_{2A}$, $X_{1HCl}X_{2B}$, $X_{1NaOH}X_{2A}$ and $X_{1NaOH}X_{2B}$). The negative sign of X_{2A} means that concentration A (high) has the effect of decreasing the roughness while the positive sign of X_{2B} indicates that this factor increases the Rms rough. Figure 4 shows the interaction plots for Rms rough. Plot 4a suggests that the effect of the chemical solution on Rms rough is dependent on the treatment time. This dependence is stronger when using NaOH and CH_3COOH but is negligible when using HCl. On the other hand, plot 4b indicates that the effect of the chemical solution on the response is dependent also on the concentration. This dependence is strong for HCl and CH_3COOH, while is low for NaOH.

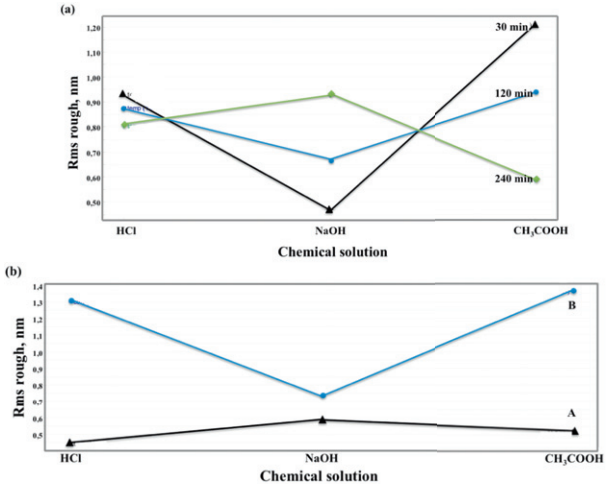

Figure 4. Interaction plots for Rms rough; (a) Chemical Solution/Treatment time; (b) Chemical Solution/Concentration.

3.2.2. $R_{p\text{-}v}$

The raw data for $R_{p\text{-}v}$ present high reproducibility and normal distribution (after the logarithmic transformation). The model obtained model presents good values of R^2, model validity and reproducibility, but a negative Q^2 value. From the analysis of residuals it was found that experiments 3, 7, 10 and 14 deviate from the normality and could be considered as possible outliers. By the removal of Exp. 14, a valid regression model (Eq. 2) with good values of R^2, Q^2, model validity and reproducibility (Table 4) was obtained:

Table 4. Summary of fit of the regression model for $R_{p\text{-}v}$.

Parameter	Value
R^2	0.96
Q^2	0.77
Model validity	0.70
Reproducibility	0.97

$$Y_2 = 1.88434 + 0.290091X_{1HCl} - 0.278292X_{1NaOH} - 0.0117993X_{1CH3COOH} - 0.000990806X_3 - 0.0458288X_{2A} + 0.0458288X_{2B} - 9.31669e^{-5}X_{1HCl}X_3 + 0.00247892X_{1NaOH}X_3 - 0.00238576X_{1CH3COOH}X_3 - 0.262307X_{1HCl}X_{2A} + 0.262307X_{1HCl}X_{2B} + 0.0294485X_{1NaOH}X_{2A} - 0.0294485X_{1NaOH}X_{2B} + 0.232858X_{1CH3COOH}X_{2A} - 0.232858X_{1CH3COOH}X_{2B} \quad \textit{Eq. (2)}$$

The $R_{p\text{-}v}$ parameter is influenced by two linear factors, the hydrochloric acid and the acetic acid, and by five interaction factors. The HCl has a positive effect, i.e., when using HCl the Rp-v parameter increases. On the other hand, a decrease in $R_{p\text{-}v}$ is obtained when using acetic acid. The interaction plots (Figure 5) suggested that, as in previous case, the effect of the chemical solution on $R_{p\text{-}v}$ is dependent on both the treatment time and the concentration. In particular, comparing these two plots it can be observed that the dependence of the chemical solution is stronger when varying the concentration.

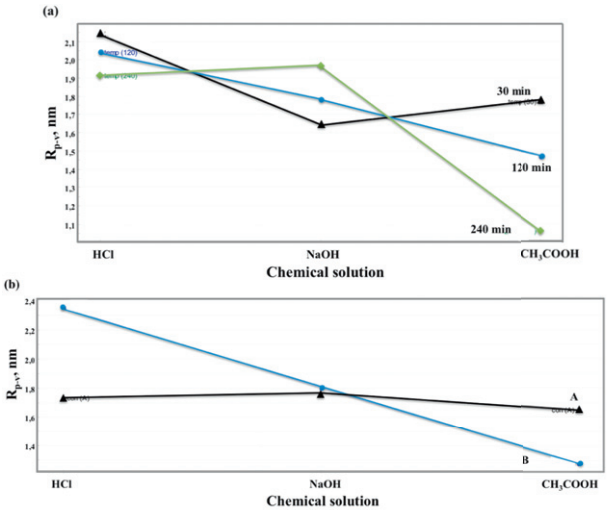

Figure 5. Interaction plots for R_{p-v}; (a) Chemical Solution/Treatment time; (b) Chemical Solution/Concentration.

3.2.3. Weight loss

The analysis of the raw data reveals that also in this case a logarithmic transformation is necessary to obtain a Gaussian distribution in order to improve the subsequent statistical analysis. The obtained model presented non-statistically meaningful values of R^2, Q^2, model validity and reproducibility; indeed, the residual analysis shows the presence of two possible outliers. Their removal permitted to have a statistically meaningful model (Eq. 3) for the weight loss.

$$Y_3 = -1.22896 + 0.6561X_{1HCl} + 0.530606X_{1NaOH} - 1.18671X_{1CH3COOH} - 0.014091X_3 + 0.0161826X_{2A} - 0.0161826X_{2B} - 0.00682767X_{1HCl}X_3 - 0.00672584X_{1NaOH}X_3 + 0.0135535X_{1CH3COOH}X_2 \quad \textit{Eq. (3)}$$

Eq. (3) indicates a meaningful statistically linear factor, the treatment time (X_3) and three interaction factors, $X_{1HCl}X_3$, $X_{1NaOH}X_3$ and $X_{1CH3COOH}X_3$. The linear factor, X_3, has a negative influence on the weight loss, i.e., maximizing the treatment time and remaining constant the other factors, a decrease of the weight loss is obtained. Regard the interaction effects, the interaction plot (Figure 6) for the weight loss revealed that the effect of the treatment time on the weight loss depends on the used chemical solution, especially at long times.

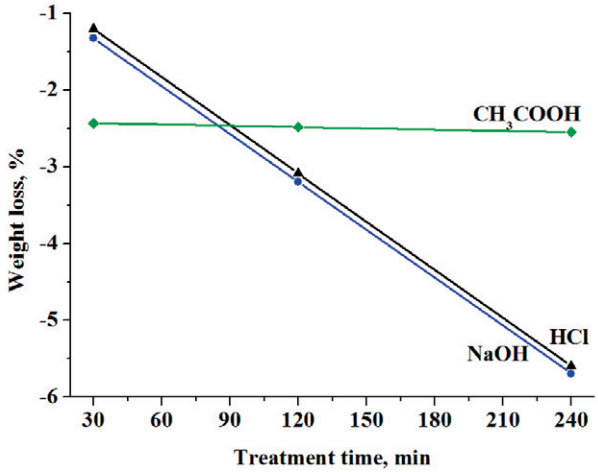

Figure 6. Interaction plot for Weight loss: Treatment time/Chemical solution.

3.3. Correlation between glass roughness and adhesion

Table 6 shows the chemical treatment, the roughness and the critical scratch loads of representative glass samples (highest, high, medium and low roughness).

Table 6. Roughness and scratch adhesion of some representative attacked glasses.

Description	Glass sample				
	Reference	Exp. 5	Exp. 12	Exp. 18	Exp. 9
Chemical treatment	No treatment	NaOH 12 M, 120 min	HCl 3.7 %, 240 min	CH_3COOH 9.6%, 240 min	CH_3COOH 96%, 240 min
Rms roughness, nm (Zone 1)	3.41	27.09	16.19	10.16	1.49
Rms roughness, nm (Zone 2)	3.40	12.91	11.01	11.40	1.46
R_{p-v}, nm (Zone 1)	36.13	428.60	147.00	77.78	17.75
R_{p-v}, nm (Zone 2)	48.11	93.07	161.90	91.65	41.49
Critical load [c], N	4.5587 ± 3.6840	3.3467 ± 1.5688	6.7027 ± 5.3309	3.2045 ± 2.7200	9.1659 ± 2.4068

[c] Defined as the load needed to form defects in the film, i.e., the beginning of the visible rings formed by the Rockwell tip.

As observed in Table 6, the coated reference glass shows a non-homogeneous low adhesion (C.L. = 4.5587 ± 3.6840 N). In this sample, when using high loads the coating is detached from the surface. Regards the adhesion between very rough surfaces and TiO_2 coatings, sample 5 (highest roughness) present one of the lowest scratch adhesion, with a C.L. value of 3.3467 ± 1.5688 N. Its non-homogeneous rough surface does not improve the adhesion, since the scratch C.L. of sample 5 is lowest that the scratch C.L. of the reference glass. Despite the C.L. value, this high roughness seems to promote a slightly enhancement of the adhesion, as the coating remain attached to the substrate also when high loads were applied, contrary to the reference glass. Experiment 12, which presents a non-homogeneous and rough surface (high roughness group), has a relatively high adhesion (C.L. = 6.7027 ± 5.3309 N), however, with a high standard deviation. Therefore, this chemical treatment is not convenient for the pre-treatment of

nano-coated glass substrates. Moreover, the film begins to detach over the track, but is not completely removed from the substrate. The fact that a high roughness does not improve the adhesion could be attributed to the combination of roughness and the increase of the water contact angle of the attacked surfaces. This combination often results in air pockets being trapped between the solid and liquid (the composite solid-liquid-air interface), thus leading to a significant decrease in the solid-liquid adhesion [15].

As shown in Table 6, medium values of roughness (3.2045 ± 2.7200 N; Exp. 18) do not improve the adhesion of TiO_2 coatings (compared with the reference glass). As in the previous case, the coating is slightly detached from the substrate. From Table 6, it is clear that Exp. 9 has the highest adhesion, since presents a critical load of 9.1659 ± 2.4068 N. This high value was correlated to its homogeneous smooth surface. Moreover, this sample shows one of the lowest variability of the adhesion from the sample set. In Exp. 9, the film is not detached from the substrate; only the marks of the Rockwell tip are formed (like defects, Figure 7). Moreover, as an interesting characteristic of the substrate, this glass shows low weight loss (Table 2).

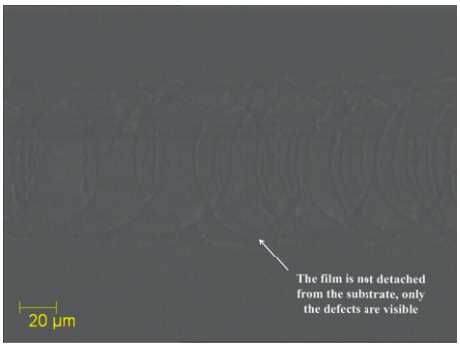

Figure 7. Scratch test of the Exp. 9.

4. Conclusions

From the AFM observations it was found that chemical treatments with HCl, NaOH and CH_3COOH, very concentrated or diluted for 30, 120 and 240 min modify the glass roughness. From the D-optimal design and the statistic analysis of the data, the linear and interaction factors that influence the roughness and the weight loss were investigated. Furthermore, this analysis permitted to determine how these factors modify the responses, i.e., which factors or factors combinations promote the increase or decrease of the roughness or weight loss. This information is of great importance when working with industrial processes, since it offers the possibility of working with combinations of different chemical attacks depending on the availability of the resources and the disposition of time to get the desired results. From the scratch measurements, it was found that smooth and homogeneous surfaces enhance the adhesion between the glass substrates and nano TiO_2 coatings. On the other hand, contrary to previous reports [5], in this case rough surfaces did not improve the adhesion. Possibly, the high roughness does not enhance the adhesion due to the formation of air pockets being trapped between the solid and liquid (the composite solid-liquid-air interface) when depositing the liquid nanoparticles, thus leading to a significant decrease in the solid-liquid adhesion.

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