DIFFERENT IMAGING TECHNIQUES FOR INVESTIGATION OF TREATMENT EFFECTS ON VARIOUS SUBSTRATE SURFACES

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Abstract: The different imaging techniques were used for measurement of the properties changes on substrate surfaces. In this paper we report about testing various treatment on different substrates following investigation and characterization of the advantages/disadvantages of these methods for future applications. We usually used flexible materials such as polyethylene terephthalate (PET) and poly-carbonate (PC) for treatment. We also used glass substrate and aluminum oxide (Al_2O_3) to determine the efficiency of oxide plasma etching. As imaging techniques mainly atomic force microscopy (AFM), scanning electron microscopy (SEM), contact angle measurement and a special method for examination of layer adhesion known as a scratch test were used.

Keywords: substrate treatment, cleaning, AFM, oxide plasma, contact angle, SEM

1. INTRODUCTION

The aim of this work is to find out an optimal process to clean substrate surface. However, a clean surface is not a guarantee that the next layers (it is used for the next step as an application layer or other layers) will have good adhesion to underlying substrate. Thus if we want to get a strong adhesion between the substrate and the first layer we need a surface treatment.

Nowadays, there are widespread diverse chemical methods for surface treatment. This is mainly due to easy application on the surface and the fact that it is the cheapest option. Unfortunately, many more serious problems as toxicity are appears with use of these methods. Chemical cleaning leaves plenty of impurities which are not good for the final cleaning process of substrate. Physical cleaning is other method (besides chemical methods) used for substrate preparation. Physical methods like oxide plasma treatment is environmentally friendlier and more useful in most cases.

We have used for basic cleaning of flexible and glass substrates different kind of alcohols, such as isopropyl alcohol (IPA), ethyl alcohol (EA) and methyl alcohol (MA). These alcohols have been used in combination with non-fiber cloth that can be considered as partly mechanical cleaning. Further, sodium hydroxide (NaOH) has been used to chemical treatment of flexible materials and oxide plasma enhanced by argon has been used for physical treatment.

Atomic force microscopy (AFM) has been used to obtain a surface morphology. The contact angle measurement was used to evaluate surface energies. To achieve quality review about the efficiency of treatments we needed to make the surface conductive. Thin copper layer was deposited by magnetron sputtering and consequently strengthen by electrochemical copper plating. Thus for these cases, we could use imaging SEM technique and a method for adhesion quality control.

2. RESULTS AND DISCUSSION

2.1. TREATMENT AND SUBSTRATE CLEANING TECHNIQUE

MECHANICAL AND CHEMICAL CLEANING GLASS SURFACES USING ALCOHOLS

The aim of these imaging procedures was to investigate contamination of the substrate surface by used alcohols for cleaning. The contamination of the surface is very important for applications of the next layers. We used the same glass substrates which were sonicated for 10 minutes in bath of each alcohol. Afterwards, they were dried with nitrogen (dried under gas flow and results was controlled by optical inspection) and put on the hotplate at 150°C for 10 minutes. Finally, all samples were closed into a box to prevent contamination by dust particles and placed in-to the AFM measurement equipment (SNOM/SPM NT-MDT N-Tegra). The measurement was performed in semi-contact mode.

Figure 1 shows surfaces of cleaned glass substrates after AFM measurement. Differences between Figure 1 (a, b) and Figure 1 (c) are visible at first sight. The highest peaks of glass surface have yellow colour and the lowest peaks are red. It means that in cases of cleaning surface by EA and IPA, the surface have more smaller impurities than in case of MA. The surface treated by MA contains more residual impurities which are illustrated by yellow or light yellow colour. These impurities have a larger volume than glasses cleaned by EA and IPA.

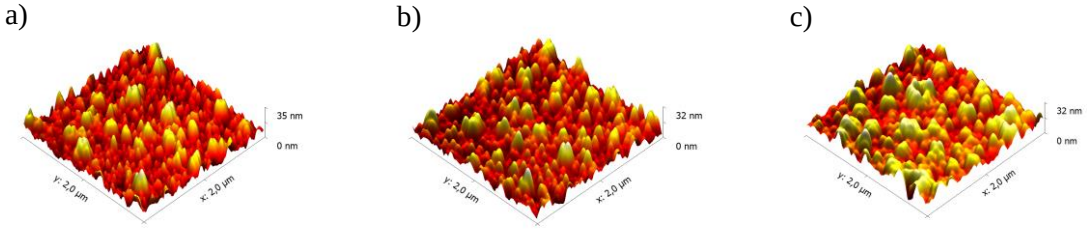
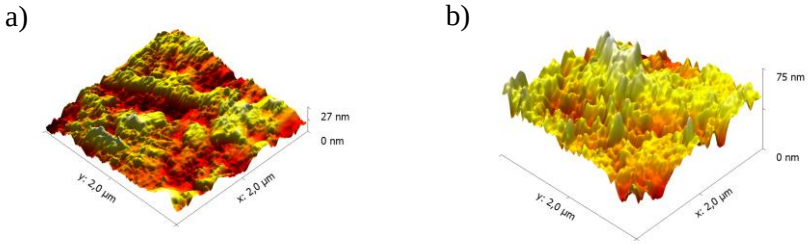


Figure 1: Cleaned glass surfaces imaged by AFM a) EA, b) IPA, c) MA.

DIFFERENCES BETWEEN CHEMICAL AND PHYSICAL TREATMENT FOR PET AND PC

Two different treatment techniques were used on two different substrates. Surfaces of PET and PC in Figure 2 (a) and Figure 2 (b) were treated with chemical solution of 20% mixed NaOH, the surface of that substrates is more non-homogenous than the surfaces treated by oxide plasma.

In addition, surface roughness of PC treated by NaOH is higher than plasma treated layer. This effect is due to non-conformal coating on the substrate how we can see in figure below. The plasma treated materials seem more uniform. According to the figures bellow, method of plasma treatment seems to be more suitable for surface preparation and promotes better adhesion.



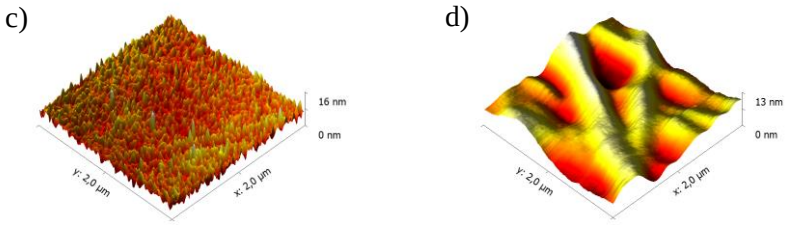


Figure 2: AFM images of NaOH treatment a) PET, b) PC) and plasma treatment c) PET, d) PC. [1]

2.2. METHODS FOR INVESTIGATION OF TREATMENT EFFECTS

CONTACT ANGLE MEASUREMENT AND EVALUATION OF SURFACE ENERGIES

Contact angles were measured with using sessile drop (10 µl) in equilibrium state. Two liquids (deionized water and ethylene glycol) with defined disperse and polar component were used to measure contact angle. The surface free energies were calculated and evaluated by the Owens-Wendt method.[2] The results values of these methods are shown in Table 1. Following formulas (1) – (4) were used for calculation. The surface tension of each phase can be split up into polar and disperse parts:

$$\gamma = \gamma^d + \gamma^p \tag{1}$$

Owens and Wendt extended by Fowkes [2,3] concept who was used to determine the cases where dispersion and hydrogen bonding forces may operate. They took the equation for the surface tension as their basis and combined it with a Young equation:

$$\gamma_{sl} = \gamma_s - \gamma_l \cos\theta \tag{2}$$

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\left[\left(\gamma_s^d \gamma_l^d\right)^{1/2} + \left(\gamma_s^p \gamma_l^p\right)^{1/2}\right] \tag{3}$$

Combining these two equations (2) and (3) we get an equation for a straight line which is written below (calculation for two liquid with polar and disperse component including data of measured contact angles):

$$\frac{\gamma_l(1+\cos\theta)}{2\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^p}\sqrt{\frac{\gamma_l^p}{\gamma_l^d}} + \sqrt{\gamma_s^d} \tag{4}$$

As a medium we used deionized water (DI) and ethylene glycol (EG). Droplets were applied on the surfaces of PET and PC which were treated by IPA, NaOH and by oxide plasma. [2,3]

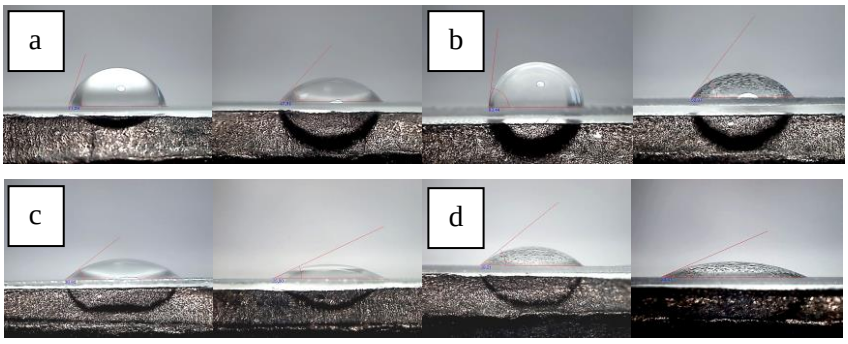


Figure 3: Different liquids drops on the surfaces – cleaned by IPA a) PET: DI, EG; b) PC: DI, EG) and treated by oxide plasma c) PET: DI, EG; d) PC: DI, EG.

Figure 3 shows that plasma treatment has the biggest influence on contact angles of both materials. Their contact angles were reduced more than two times. However, all these changes are clearer from Table 1, shown below. That table contains measured contact angles of both liquids but also their polar and dispersive component. From them were counted all total energies.

Calculations of polar, dispersive and total component of surface energy								
Treat	**Sample**	**θ DI [°]**	**θ EG [°]**	**Polar** $k = dy/dx$ **[√mJ.m^{-2}]**	**Dispersive** $q = y_1 - k \cdot x_1$ **[√mJ.m^{-2}]**	$k^2 = \gamma_s^p$ **[mJ.m^{-2}]**	$q^2 = \gamma_s^d$ **[mJ.m^{-2}]**	**Total energy** $\gamma_s = \gamma_s^d + \gamma_s^p$ **[mJ.m^{-2}]**
IPA	PET	68,35	45,82	4,16	4,31	17,31	18,58	35,84
	PC	80,47	52,05	2,71	4,94	7,33	24,37	31,71
Plasma	PET	34,18	21,34	7,04	3,46	49,63	11,98	61,61
	PC	38,51	23,88	6,73	3,59	45,30	12,91	58,20
NaOH	PET	69,25	39,73	3,65	4,96	13,36	24,64	38,00
	PC	75,75	52,46	3,45	4,44	11,89	19,68	31,58

Table 1: Results from surface energies calculation [1].

USING SCRATCH TEST FOR EVALUATION OF LAYERS ADHESION

There are several methods for investigation of layers adhesion. This technique has been proved to be suitable for finding out which treatment can be used. Choice of the treatment method depends on the material. In this case, special flexible materials were measured, namely PET and PC. Requirement of scratch technique is that there must be layer on the surface. The method is based on a scratch diamond indenter penetration into the layer of the applied coating under constant or increasing force towards the substrate. The conductive layer was a copper layer fabricated by cathode sputtering and subsequent intensification layer by electrochemical plating.

Figure 4 shows two graphs with three curves representing treatment applied on the surfaces. We can compare the results to evaluate which pretreatment of the substrate surface appears to be the best within the adhesion. Each of these curves introduce progress of the scratch. In Figure 4 (a) is shown blue curve representing substrate with NaOH treatment. A rapid drop of the penetration depth is caused by peeled off copper layer from substrate. It is a reason why we can say which treatment is appropriate and which is not. Layer prepared on NaOH pretreatment is inconvenient for PET substrate due to the low adhesion to substrate.

Contrary to the PC substrate, NaOH treatment seem to be the best as shown Figure 4 (b). The layer does not contain any errors or violation in form of rapid decreases as it was in case PET. [1]

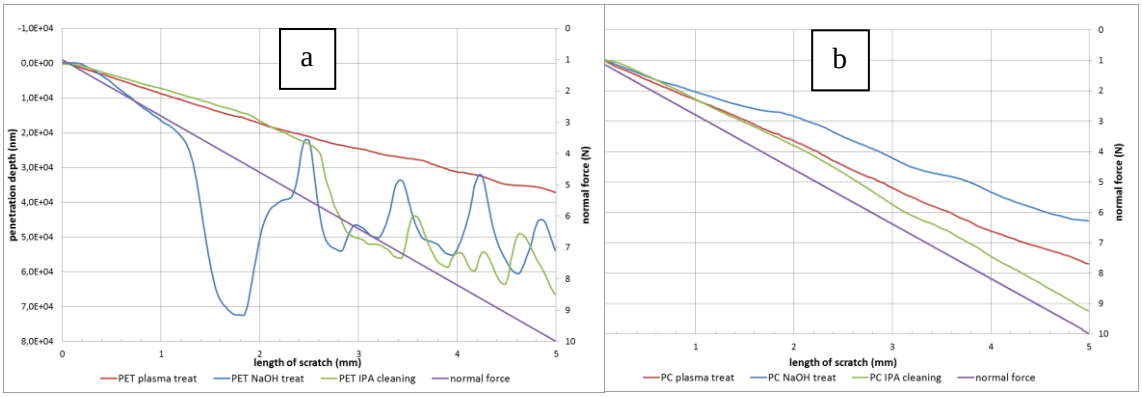


Figure 4: Results from scratch test characterization of layer adhesion between Cu layer and flexible substrates a) PET, b) PC. [1]

SEM INVESTIGATION OF DIFFERENT SUBSTRATE SURFACES

Scanning electron microscopy is one of the usually used technique for finding of some small areas on substrate surface. They are the subjects of our interest. Especially, it is really interesting technique when we want to do any modification with the surface and if we need to get results quickly. Otherwise, we cannot obtain an overview of the surface energies or the surface morphology.

Figure 5 shows several images which show that the SEM technique is better than AFM in that case. The main reason is that AFM technology have a range limitation in Z axis.

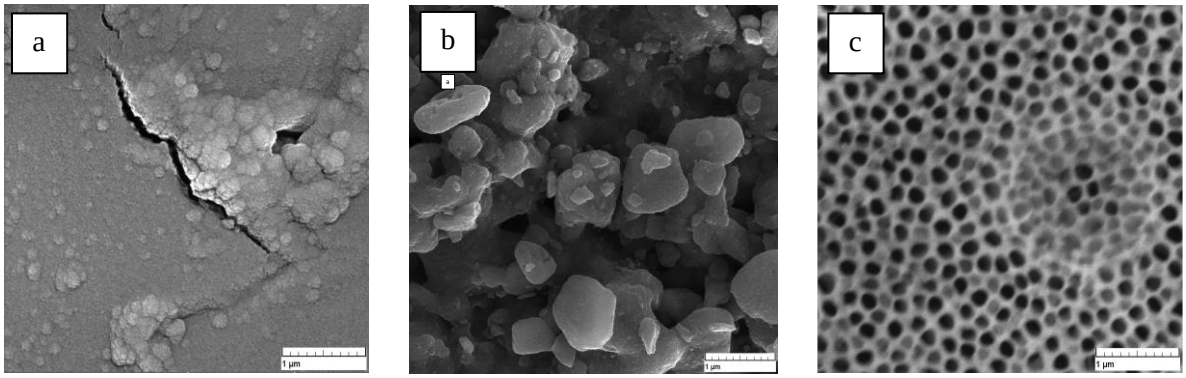


Figure 5: Different surfaces of the substrates: a) Cu layer by magnetron sputtering, b) TiO_2 particles, c) alumina treated by plasma.

3. CONCLUSIONS

The aim of this review paper was to show several techniques for detect changes on treatment substrates. We have used a few methods to obtain quantify and quality results for examination effects of these treatment. There is shown possible use of AFM for evaluation of cleaning effectiveness of different cleaning solvents. IPA and EA will be used as cleaning agent for next applications with substrates, because they do not contain any residual impurities as in case of MA. Oxide plasma turned out to be the best way was how make surface preparation for next applications of coatings or thin layers. Results were achieved by using different techniques as AFM, contact angle measurement and finally by scratch test. The SEM technique shows that it is a proper method for evaluation of surfaces with unknown range of Z axis, e.g. surfaces with different kind of particles, cracks or holes.

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