

CHANGING THE SURFACE PROPERTIES OF ABS PLASTIC BY PLASMA

S. CHLUPOVÁ, J. KELAR, P. SLAVÍČEK*

Department of Physical Electronics, Masaryk University, Kotlařská 2, 602 00 Brno, Czech Republic

*ps94@sci.muni.cz

Abstract. The research deals with plasma treatment of acrylonitrile butadiene styrene plastic (ABS). The plastic was treated with Diffuse Coplanar Surface Barrier Discharge (DCSBD) and Gliding arc at atmospheric pressure. ABS was chosen because of its low price, wide use in industry. Samples were analyzed with contact angle measurement and the surface energy was determined as well. The results show that only a few seconds of plasma treatment can cause relatively large wettability change.

Keywords: plasma, surface treatment, DCSBD discharge, ABS plastic, contact angle, surface energy.

1. Introduction

In the last few decades acrylonitrile butadiene styrene (ABS) has attracted a lot of attention for its use in industry; well known are for example productions of protective helmets, small kitchen tools, toys such as dolls, cars and LEGO. The main reasons why ABS plastics are so favorite nowadays are its chemical structure, weathering, aging resistance and thermal properties. Thanks to the chemical composition, ABS belongs to the group of polystyrenes with high impact strength, it is also effectively stabilized against aging or fluctuations in temperature and humidity. Even though the ABS plastic was described chemically and we know its physical properties, it has not been described after plasma treatment very well.

In recent years, the nonthermal dielectric barrier discharge (DBD) at atmospheric pressure has been used extensively for surface treatment of polymers [1], [2]. Plasma treatment is environmentally friendly in comparison with chemical treatment [3]. Using this type of discharge has a lot of advantages, no vacuum is needed and samples can be treated at atmospheric pressure with easy setup, so it is a low-cost treatment method. We can use different gases, such as *He*, *Ar*, *N₂*. Polymers surface modification have been studied recently because of an improvement of physical properties [4]. However, polymers are appropriate for use in industry because of their low density, flexibility etc., their surface properties do not go hand in hand with demands regarding biocompatibility, wettability, adhesion and friction. This is the main reason we examined ABS; an appropriate surface modification can raise the use of this plastic. After plasma treatment, free surface energy is higher and wettability is better. In presented work we used two atmospheric pressure plasma sources, Gliding arc and Dielectric Coplanar Surface Barrier Discharge (DCSBD). This two sources were used due to their low cost because no vacuum is needed. DCSBD is a special type of DBD with a parallel arrangement of electrodes, which are located in the ceramic plate (serving as a part of dielectric barrier) and dielectric cooling oil [5], [6]. This special

type of non-isothermal plasma has been developed for wood, textiles, fibres, polymers treatment etc. [7], [8]. The purpose of this contribution is to show changes in wettability and free surface energy after the plasma treatment of ABS plastic.

2. Experimental part

Two types of treatments have been used for experiments. The first treatment was carried out with DCSBD and the second one with Gliding arc. These two methods were chosen for their industry applications and small costs.

2.1. DCSBD

DCSBD is an abbreviation for Diffuse Coplanar Surface Barrier Discharge. It is a special type of dielectric barrier discharge operating at atmospheric pressure and in many different gases including air. The scheme of coplanar arrangement of electrodes can be seen at Figure 1. The main purpose of this plasma source is plasma treatment of planar samples in the solid state. This type of barrier discharge has been developed by Cernak's group at the Department of Physical Electronics at Masaryk university and at Comenius University in Bratislava. This plasma source consists of parallel metallic electrodes embedded in ceramic and cooled by a cooling oil, see Figure 2. The cooling oil is necessary because of collisions between the charged particles, which heat the device. The ceramic can be heated by dielectric losses too. In addition to that, cooling oil is cooled by a water cooling system to the temperature about 16–20 °C. The frequency range of supply voltage is 15–50 kHz, the input power is in the range of 50–700 W, the voltage is up to 20 kV peak to peak and amplitude of discharge current is about 0.4 A. The advantage of DCSBD configuration is a large discharge area so big samples can be treated as well.

The effective area of plasma produced by the DCSBD was 8 × 20 cm. The plasma thickness is about 0.3 mm. With the use of DCSBD adhesion, wettability etc can be changed. This type of discharge

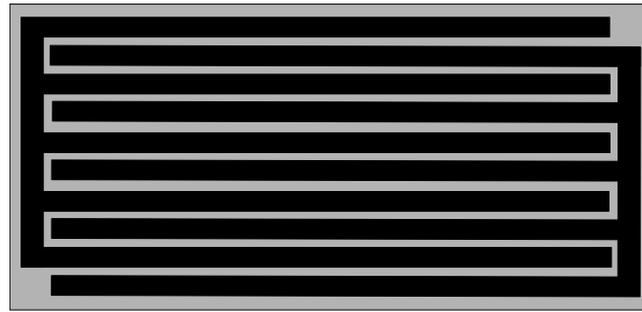


Figure 1. The coplanar arrangement of the electrodes

is used for changing material properties very often, for example if we want to change hydrophobic material to hydrophilic one. In presented work, power of 400 W and frequency of 15 kHz were used.

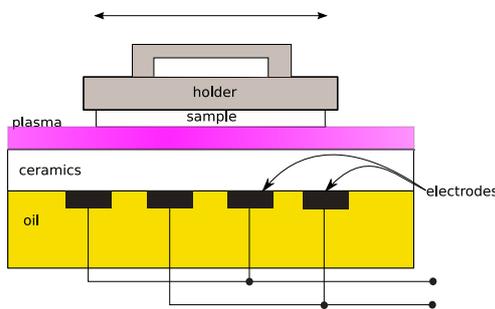


Figure 2. The scheme of the plasma treatment of the sample by the DCSBD

2.2. Gliding arc

The second type of plasma source used was Gliding arc. It is a commercial plasma source generating non-isothermal plasma. A discharge is excited between two corner electrodes made from different materials. A discharge is formed at the narrowest point, then it expands, slides along the electrodes and disappears. New discharge emerges immediately at the same initial place. The scheme of sample plasma treatment by Gliding arc can be seen at Figure 3.

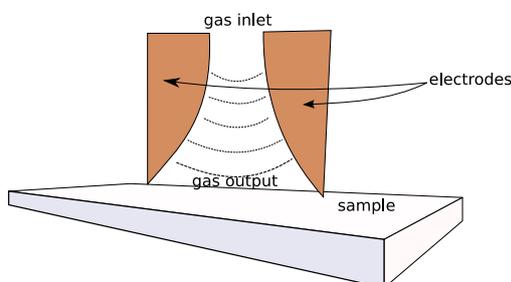


Figure 3. The scheme of the plasma treatment of the sample by the Gliding arc

The discharge journey is given by geometry of the electrodes, airflow and voltage. This plasma source operates at frequency of 40 kHz with the power approx. 500 W. The generator of high voltage produces voltage

up to 10 kV. The treatment width is approx. 50–60 mm. Gliding arc is not stable in time thanks to the plasma filaments which are moving constantly, and as the result of the fact that produced plasma is not as homogeneous as DBD.

2.3. Roughness

For the better comparison of these plasma sources we measured the change of roughness before and after plasma treatment. This physical property was measured using laser confocal microscopy to get an R_a coefficient, which is the arithmetic average of the absolute values of the profile height deviations from the mean line, recorded within the evaluation length. Simply put, R_a is the average of a set of individual measurements of the surfaces peaks and valleys. R_a can be calculated as

$$R_a = \frac{1}{L} \int_0^L |Z(x)| dx \quad (1)$$

L is the evaluation length and $Z(x)$ is the profile function.

2.4. Experimental procedure

Acrylonitrile butadiene styrene (ABS) was used for experiments. The ABS that was used is used primarily for edges of tables when it is ironed on the edges. This type of ABS is sold in long rolls so it was necessary to warm the plastic to make it straight and then make 5 cm x 2 cm samples. The experimental procedure starts with mechanically cleaning the sample with the mixture of cyclohexane and isopropylalcohol. After ten minutes when sample was dried it was plasma treated. The best way how to treat the sample on the DCSBD is to paste it on the holder as it can be seen in the Figure 2. The holder was specially made for this kind of plasma treatment on the 3D printer because we needed to keep the plasma layer thickness about 0.3 mm. On Gliding arc, the sample was pasted on the stand which is a part of a device delivered by company Electronic Diener. Samples were treated for 1 second, 3 seconds, 5 seconds, 10 seconds and 30 seconds. After this the sample was taken to a See system to analyze the contact angle and the free surface energy. the See system is a device developed by Advex Instruments, a spin-off company of Masaryk

University. The software provided can calculate the free surface energy on the basis of the most often used models. Ten drops of deionized water, ethylene glycol and diiodomethane were used for measurement. Used drop volume was 1 μl .

3. Results

3.1. Changing of surface energy

The dependence of water contact angle on aging time after plasma treatment of ABS plastic by both the atmospheric plasma sources is shown in Figures 4–7. Contact angle and surface energy changes were measured after plasma treatment with five different exposure time and with several different aging times, that means the time interval after the plasma treatment, and before contact angle measurement when samples were stored in the Petri dish in the laboratory, to avoid the change of temperature or humidity.

As it can be seen in the graphs, the exposure time, the aging time and the type of plasma source have a big influence on the samples hydrophilicity. To obtain the lowest contact angle, meaning the highest hydrophilicity of the surface, a longer exposure time was required. The plasma treatment of the ABS caused a big increase of the surface wettability. The water contact angle of the reference is 94.7 degrees, which means that the contact angle was greatly reduced by over 40 degrees. The ABS after plasma treatment was very hydrophilic.

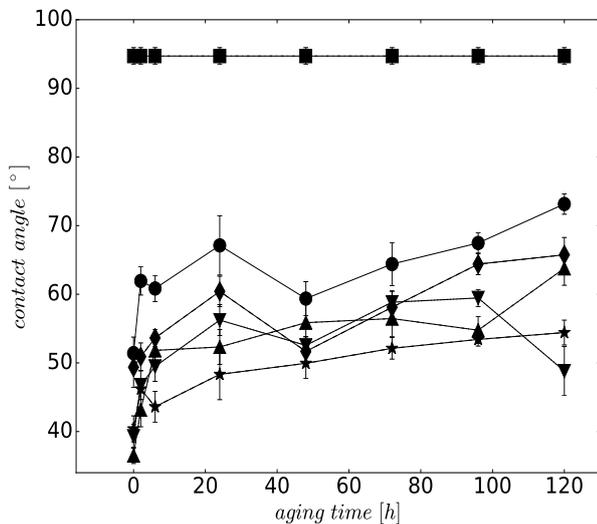


Figure 4. The water contact angle for ABS treated on the DCSBD with different exposure times, (●) 1 s, (◆) 3 s, (▲) 5 s, (▼) 10 s, (★) 30 s, (■) reference

As for the Gliding arc, we have better results in keeping the water contact angle low for a long time. After 5 days, the sample treated on DCSBD have the water contact angle over 50 degrees but for the Gliding arc we get the water contact angle of 45–50 degrees. We have the same results for the ethylene glycol. After 5 days, the sample treated by the Gliding arc had contact angle about 20 degrees, which is lower value

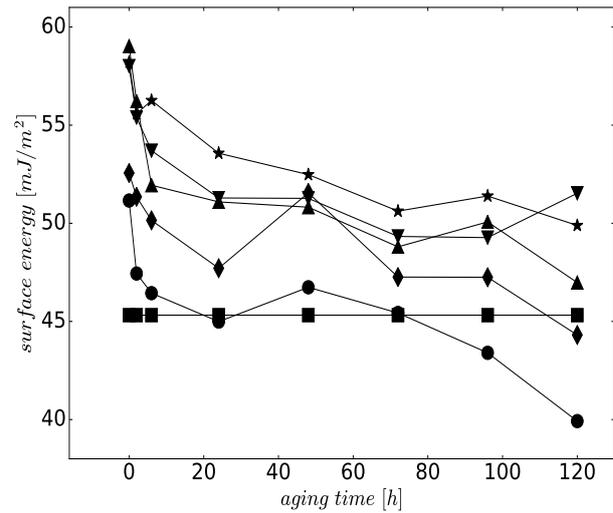


Figure 5. The surface energy for ABS treated on the DCSBD with different exposure times, (●) 1 s, (◆) 3 s, (▲) 5 s, (▼) 10 s, (★) 30 s, (■) reference

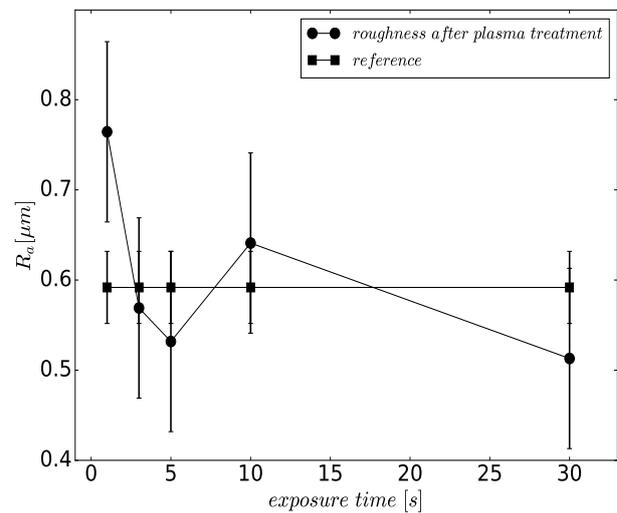


Figure 6. The roughness after the plasma treatment on the DCSBD

than on DCSBD. In the case of the diiodomethane, this difference is not that big because the contact angle after 5 days is about 45–50 degrees for both plasma sources.

3.2. Roughness after plasma treatment

The roughness was measured by the confocal microscope Olympus LEXT OLS4000. Coefficient R_a was calculated from area 646 x 646 μm . Results of roughness after plasma treatment are shown in Figures 6 and 9. Roughness results are the same for both plasma sources. We found with the confocal microscopy that we cannot change the sample roughness very significantly using DCSBD or Gliding arc.

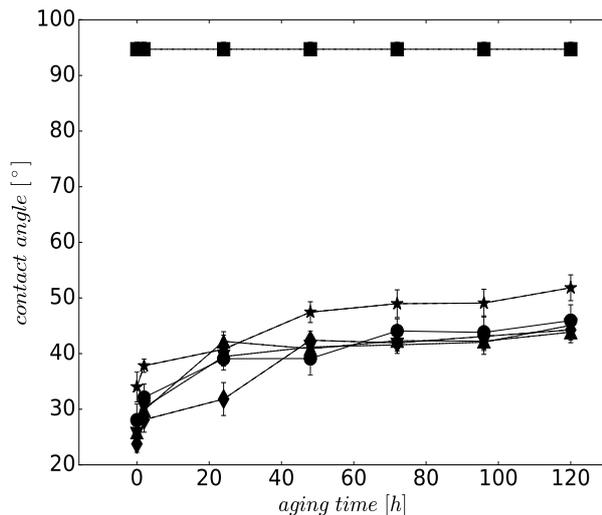


Figure 7. The water contact angle for ABS treated on the Gliding arc with different exposure times, (●) 1 s, (◆) 3 s, (▲) 5 s, (▼) 10 s, (★) 30 s, (■) reference

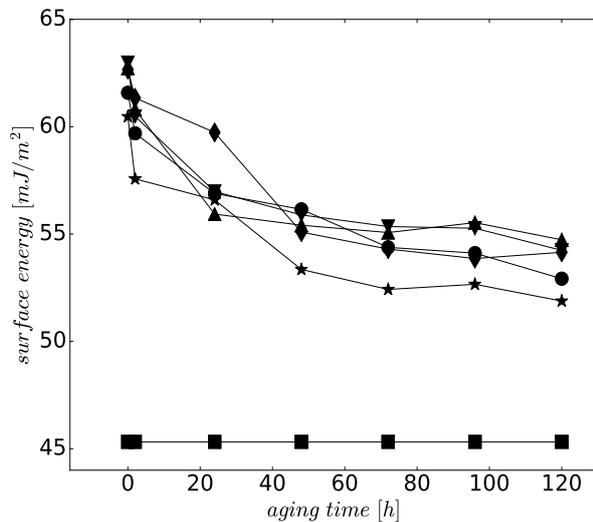


Figure 8. The surface energy for ABS treated on the Gliding arc with different exposure times, (●) 1 s, (◆) 3 s, (▲) 5 s, (▼) 10 s, (★) 30 s, (■) reference

4. Conclusions

In conclusion for this study we can say that the plasma modification in the ambient air is very suitable for increasing the surface energy and decreasing the contact angle, so the surface has better wettability. The main result of this research is the comparison between two plasma sources. Both of them can change surface properties very well. Even though the samples treated by the Gliding arc have lower contact angle, differences are not very significant but the surface energy results show that the Gliding arc is a better choice for changing the surface properties of ABS. The roughness did not change enough to attract our attention any further.

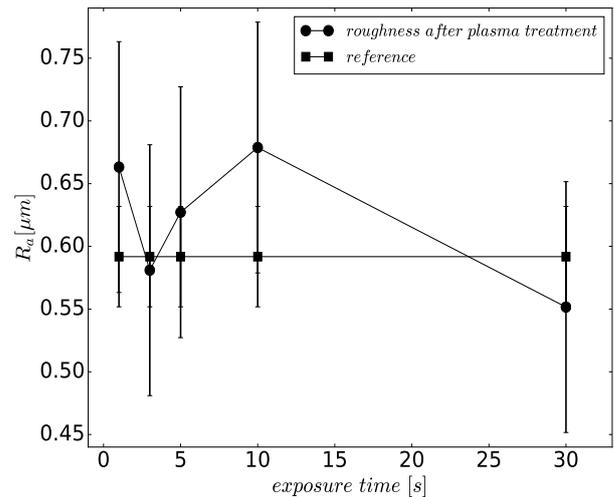


Figure 9. The roughness after the plasma treatment on the Gliding arc

Acknowledgements

This research has been supported by the project LO1411 (NPU I) funded by Ministry of Education Youth and Sports of Czech Republic.

References

- [1] D. Pappas. Status and potential of atmospheric plasma processing of materials. *J. Vac. Sci. Technol, A*, 29(2):20801–20817, 2011. doi:10.1116/1.3559547.
- [2] H.E. Wagner, R. Brandenburg, K.V. Kozlov, A. Sonnenfeld, P. Michel, and J.F. Behnke. The barrier discharge: Basic properties and applications to surface treatment. *Vacuum*, 71(3):417–436, 2003. doi:10.1016/S0042-207X(02)00765-0.
- [3] W. Cui, W. Liu, T. Wang, and Ch. Ma. The application of atmospheric pressure dielectric barrier discharge plasma on the cleaning of photovoltaic panels. *IEEE Transactions on Plasma Science*, 45(2):328–335, 2017. doi:10.1109/TPS.2017.2647991.
- [4] Z. Fang, X. Wang, T. Shao, and Ch. Zhang. Influence of oxygen content on argon/oxygen dielectric barrier discharge plasma treatment of polyethylene terephthalate film. *IEEE Transactions on Plasma Science*, 45(2):310–317, 2017. doi:10.1109/TPS.2016.2633063.
- [5] V.I. Gibalov and G.J. Pietsch. Dynamics of dielectric barrier discharges in different arrangements. *Plasma Sources Science and Technology*, 21(2):024010, 2012. doi:10.1088/0963-0252/21/2/024010.
- [6] M. Simor, J. Rahel, P. Vojtek, M. Cernak, and A. Brablec. Atmospheric pressure diffuse coplanar surface discharge for surface treatments. *Applied Physics Letters*, 81(15):2716–2718, 2002. doi:10.1063/1.1513185.
- [7] V. Prysiaznyhny and M. Cernak. Air plasma treatment of copper sheets using diffuse coplanar surface barrier discharge. *Thin solid films*, 520(21):6561–6565, 2012. doi:10.1016/j.tsf.2012.06.069.
- [8] T. Homola et al. Plasma treatment of glass surfaces using diffuse coplanar surface barrier discharge in ambient air. *Plasma Chemistry and Plasma Processing*, 33(5):881–894, 2013. doi:10.1007/s11090-013-9467-3.