

LARGE AREA SURFACE MODIFICATION INDUCED BY PARALLEL OPERATED MSE SUSTAINED GLOW DISCHARGES

C. Penache^a, S. Datta^b, S. Mukhopadhyay^c, A. Bräuning-Demian^d, P. Joshi^c, O. Hohn^a,

S. Schössler^a, T. Jahnke^a, H. Schmidt-Böcking^a

a) *J.W.Goethe University, 60486 Frankfurt am Main, GERMANY.*

b) *The Procter & Gamble Company, West Chester, Ohio 45069, USA.*

c) *Wright State University, Dayton, Ohio 45435, USA.*

d) *Gesellschaft für Schwerionenforschung mbH, 64291 Darmstadt, GERMANY.*

Abstract: A novel approach in the field of non-equilibrium plasma generation is the development of Micro Structured Electrode (MSE) arrays that can be operated at or near atmospheric pressure. The MSE-sustained discharges present a high density of electrons (10^{15}cm^{-3}) and metastable atoms (10^{13}cm^{-3}). The gas temperature immediately above the microstructure exceeds only slightly the room temperature. This study reports on the application of a microplasma array in the surface modification of plastic substrates. Detailed features of surface modification of plastics by means of MSE-sustained discharges are reported for the first time, utilizing both water contact angle and high resolution XPS analysis.

1. MSE MICROPLASMA ARRAY DESIGN

Microstructures using various types of geometry and electrode design were developed as a new and promising approach for low-cost high-pressure plasma sources [1-5]. Recent projects have explored the use of such devices for surface modification. The details of the MSE design were presented in earlier publications [6,7]. Briefly, these structures consist of a regular matrix of holes perforated in a thin composite sheet made out of two metallic foils separated by an insulator. The metal foils (electrodes) are typically 50-200 μm thick, with a dielectric layer thickness in the range of 50-250 μm . The holes, drilled through the metal-dielectric-metal composite, are typically 100-300 μm in diameter and are usually placed at a pitch (center-to-center distance) of 1.5 to 3 mm. The local electric field achieved in the vicinity of the microelectrodes is about 10^6 V/cm, strong enough for plasma generation at atmospheric pressure. Based on MSE arrays, stable direct current glow discharges were produced in noble gases (Ar, He, Ne), air and mixtures thereof, over a wide pressure range of several hundred mbar to 1 atmosphere. Discharge currents up to 20 mA per hole at moderate sustaining voltages around 200 V were measured. The MSE-sustained discharges provide non-thermal plasma that generates highly energetic electrons and free radicals without heating the gas. Therefore these devices are suitable for gas phase plasma chemistry and surface processing. Besides the ease of use, since expensive vacuum equipment is not required, these discharges offer a high density of active species. In many applications, particularly in surface modification, the free radicals generated are more important than the electrons and ions themselves.

2. SURFACE MODIFICATION OF POLYMER FILMS

Various experiments were carried out to explore the application of MSE arrays for surface modification. This paper describes the work carried out to improve the wettability of polyethylene films (PE) through surface modification induced by MSE-sustained discharges. A MSE module with

^a penache@ist.fhg.de

40x40 mm² active area and consisting of 196 parallel operated holes was used to induce surface modification on the polymer films. The diameter of the holes is 300 μm and they are positioned as a 14x14 hole array with 3 mm pitch. Due to the large number of microdischarges operating in parallel, the current per hole was usually maintained relatively low at 0.05 mA/hole and the operating pressure was kept under 1 atmosphere, to prevent the onset of thermal instabilities. The discharge current, gas flow and pressure as well as the distance between the MSE array and the polymer film substrate were varied during the experiments to understand how each of these parameters affect the degree of surface modification of the PE film. A sketch of the experimental set-up is given in figure 1.

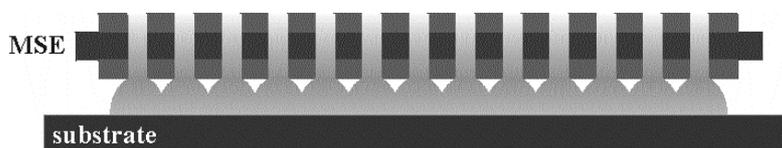


FIGURE 1. Schematic view of the experimental set-up.

Most of the measurements were done at 50 mbar using a mixture of Ar with 10% air as plasma gas. The degree of surface modification was studied using water contact angle (WCA) measurements. Chemical analysis of the surface was done using high resolution X-Ray photoelectron spectroscopy (XPS) and topographic analysis was performed using scanning white light interferometry. In addition to the data reported here, experiments were also done using a smaller array consisting of 36 holes at the same pitch, to investigate the extent of surface modification occurring in the lateral direction away from the array. In another set of experiments, surface modification of polypropylene (PP) films was studied to compare with the surface modification obtained on PE films. Results from these latter experiments will be reported in a subsequent publication elsewhere.

3. ANALYTICAL TOOLS AND METHODS

Water Contact Angle (WCA) measurements were done using a video contact angle measurement tool, Model 2500XE, made by AST Inc. 100% pure water from Baker Chemical Company was used for the measurement. Drop size was kept constant at 0.065 μl and built-in software was used to do curve fitting to accurately obtain the left and right contact angles made by the water droplet with the substrate. WCA measurements were done in several regions within the substrate area to determine uniformity of surface modification across the PE substrate directly opposing the MSE array. Untreated PE has a rather high WCA of about 110 degrees. If the surface is rendered wettable through plasma treatment, the WCA will decrease in value. WCA measurements were also done in regions of PE just outside of the MSE array position, to determine degree of lateral extension of surface modification as a function of current density, MSE-PE distance and time of treatment.

X-Ray Photoelectron Spectroscopy (XPS) measurements were done using a Kratos AXIS Ultra XPS unit. Mono-chromatized Al K_α X-ray line with a spot size of 55 μm and pass energy of 80 eV was used for enhanced spectral resolution. XPS allows to monitor and map the concentration of various elements on a surface as well as the chemical state of that element with respect to its bonding to other elements. Carbon and oxygen concentrations on treated and untreated surfaces, as measured by XPS, showed if the wettability change in PE was caused by oxygen incorporation. In addition, for each sample, XPS spectra were taken in positions on PE sample that corresponded to the location of a hole in the MSE as well as in positions on PE that fell between two adjacent holes of the MSE array, in steps of 750 μm. This allowed to obtain the detailed variation of oxygen concentration and incorporation across the PE substrate as a function of MSE hole location.

Scanning White Light Interferometry was done using a three-dimensional surface structure analyzer (Zygo, New View 5000). This measurement of surface topography indicates the presence of surface etching caused primarily by high-energy ions. The atoms on metastable states and the UV radiation are playing an important role too.

4. RESULTS

The PE films are normally hydrophobic, with a WCA value of about 110 degrees. When PE films are exposed to an oxygen containing plasma, the film is rendered hydrophilic and wettable, primarily due to oxygen incorporation leading to the formation of functional groups such as carboxyl and hydroxyl groups at the surface. For a PE film which was exposed to MSE-generated plasma at about 50 mbar pressure for 5 min, using a mixture of 10% air in Ar, the water contact angle was found to decrease from the original 110 degrees to about 40 degrees. The modification was found to be permanent whenever the substrate is placed at the anode or the cathode side.

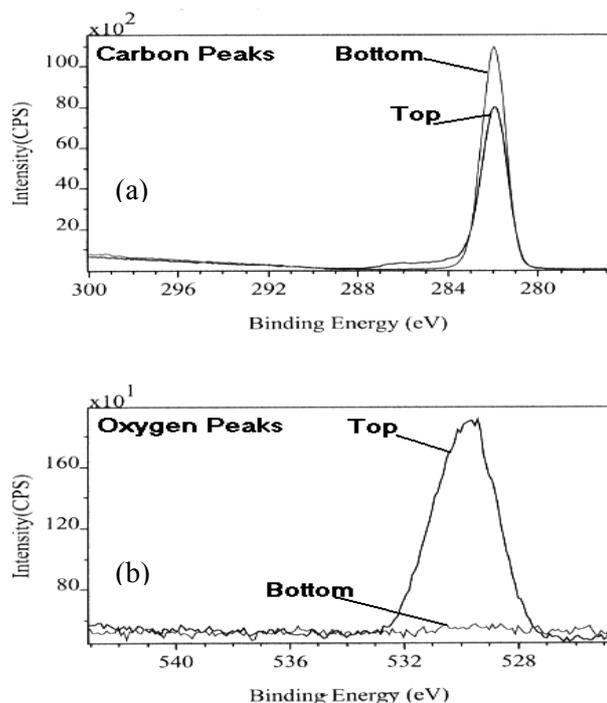


FIGURE 2: XPS Spectra of treated and untreated PE film: (a) carbon and (b) oxygen concentrations on treated (top) and untreated (bottom) surfaces. Distance MSE-PE 4 mm.

Figure 2 presents the XPS spectra of the MSE-plasma treated PE and the corresponding untreated (control) PE surface. Figure 2(a) shows the carbon concentration on the treated and untreated surface while figure 2(b) shows the oxygen concentration on the same two surfaces. Correlating the measured change in the WCA with the data from figure 2(b) it can be concluded that the increase in wettability of the PE surface after MSE-plasma treatment is due to incorporation of oxygen groups on the surface. The relatively lower concentration of carbon on the treated surface as compared to the untreated surface is due to the higher concentration of oxygen relative to carbon on this surface, after plasma treatment. It is important to note that the actual surface area of the holes in the MSE array is two to three orders of magnitude smaller than the total surface area of the PE film that was modified by the MSE-plasma. Yet, the wettability of the PE film, as measured by the WCA method, seems uniformly increased over the entire surface. The variation of WCA as a function of distance between the MSE and the PE film sample is shown in figure 3. All samples were treated for 5 min with 10% air in argon at a flow rate of 50 sccm and a total pressure of 50 mbar. In one series, the PE sample was facing the cathode surface of the MSE while in the second series, the PE sample was facing the anode surface of the MSE. As the MSE-PE distance is decreased from 11 mm to 4 mm, the WCA values of the treated surface decreases, as expected, indicating increasing wettability as the plasma source is brought closer to the substrate. However, at MSE-PE distances less than 4 mm, it was noticed that the WCA values for the PE surface facing the cathode actually increases i.e. wettability decreases, as the plasma source is brought closer to the substrate. It is also observed that for the treatment condition where the PE surface faces the cathode at a distance of 1mm, white spots are observed on the PE film corresponding

to the location of the MSE holes across the PE substrate. This was not observed for the samples facing the anode at short MSE-PE distances. Figure 4 shows the variation of WCA as a function of MSE-plasma treatment time, when the MSE-PE distance is maintained constant at 4 mm. The WCA is found to decrease as the treatment time increases from 0.5 min to 10 min and in this range of treatment time no saturation effect is observed.

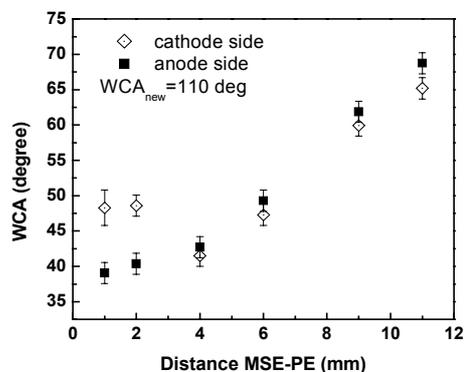


FIGURE 3. WCA variation in of plasma treated film with the MSE-PE distance.

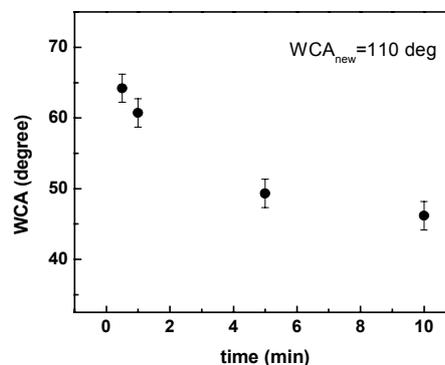


FIGURE 4. WCA variation of treated PE film surface, as function of treatment time.

Although WCA measurements indicated uniform surface modification across the PE film sample, it was expected that high resolution XPS analysis would provide more accurate data in terms of uniformity of oxygen concentration across the PE surface. In particular, this analysis is important for understanding whether the oxygen content on treated PE film varied in the region between adjacent MSE holes. To this end, extensive mapping of the oxygen content was performed using a small spot XPS unit, starting at a given hole position and moving towards the adjacent hole position while measuring the oxygen content at discrete intervals of 750 μm on the PE film.

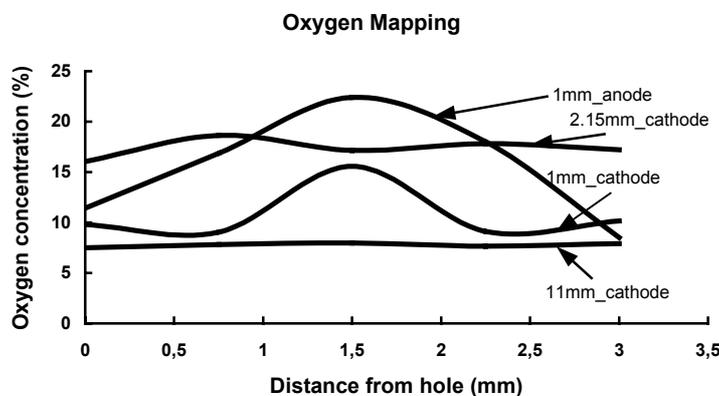


FIGURE 5. High resolution oxygen mapping on treated PE film as a function of MSE-PE distance and location between MSE hole positions.

Figure 5 shows the data of oxygen content at two adjacent hole positions (0 mm and 3 mm) and in the region between them, for MSE-PE distances of 1 mm, 2.15 mm, and 11 mm for the cathodic treatment and for MSE-PE distance of 1 mm for the anodic treatment condition. It can be seen that for MSE-PE distance of 1 mm, in both anodic and cathodic treatment, the oxygen content is actually higher in positions between the MSE holes than at the hole locations. Moreover, the concentration of oxygen is higher for anodic treatment than for cathodic treatment. In contrast, the oxygen concentrations for MSE-PE distance of 2 mm is relatively uniform at the hole positions as well as between hole positions. This indicates that, at shorter distances, there is a competition between oxygen incorporation and surface etching. Etching is more pronounced closer to the discharge location in the holes, leading to a lower oxygen concentration at the hole position compared to the region between holes.

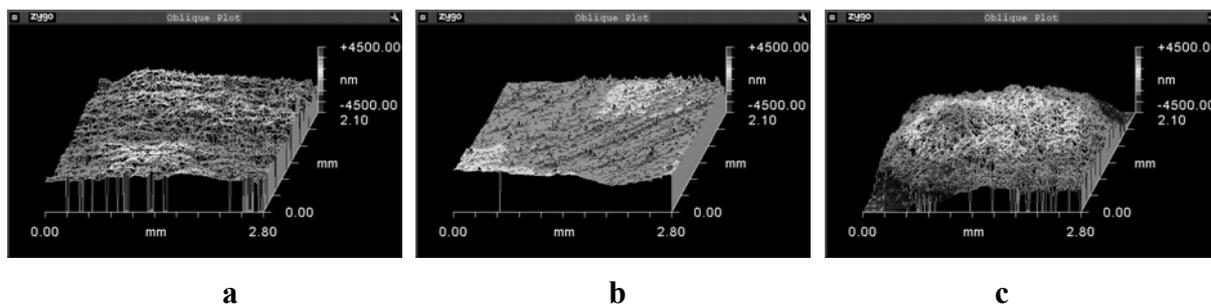


FIGURE 6. Interferometric images showing the surface structure of a new sample (a) and of samples treated at the cathode (b) respective anode side (c).

Etching is also more pronounced for cathodic treatment than for anodic treatment. This observation is further supported by interferometric analysis of the surface which shows an extremely smooth surface for cathodic treatment while the anodic treatment retains the surface roughness of the original film sample (see figure 6). When the MSE-PE distance is increased to 11 mm, relatively little incorporation of oxygen is observed on the PE surface, explaining the very small decrease in WCA when the MSE-PE distance is increased during treatment.

5. CONCLUSIONS

The study performed here provides interesting conclusions regarding the use of MSE-arrays for surface modification of polymeric film substrates. We show that surface treatment is feasible with such electrode arrays, leading to physical and chemical modifications of the polymer surface. The degree of uniformity observed in the treatment is quite surprising, given that the area of the MSE discharge is several orders of magnitude smaller than the actual area of the surface treated. The process is non-thermal, as evidenced by the absence of any visual thermal stresses in the polymer film. The degree of surface modification is a function of the treatment time as well as the distance between the electrode array and the polymer surface. However, there is a clear competition between oxygen incorporation and surface etching that is quite pronounced at very short distances between the MSE array and the polymer substrate, especially when the polymer surface faces the cathode of the MSE array. A manuscript detailing other aspects of this study is currently under preparation.

ACKNOWLEDGMENTS

The authors like to thank Dr. M. Miclea from ISAS Dortmund, Germany for the interferometrical analysis. This work was supported by: Bundesministerium für Bildung und Forschung (BMBF), Verein Deutsche Ingenieure (VDI) and Graduiertenförderung Land Hessen. Partial support of this study by Procter and Gamble through a research grant to Wright State University is gratefully acknowledged.

REFERENCES

- [1] K.-H. Gericke, H. Schmidt-Böcking, German Patent DE 196 05 226 C2, 1996.
- [2] M. Roth, T. Haas, M. Lock, K.-H. Gericke, A. Bräuning-Demian, L. Spielberger, H. Schmidt-Böcking, Proc. of 1st Int. Conf. on Microreaction Technology, Springer, Berlin, 1998, pp. 62-9.
- [3] K. H. Schoenbach, W. W. Byszewski, F. E. Peterkin and A. N. Dharamsi, US Patent No. 5 686 789, 1997.
- [4] C. H. Kruger, T. G. Owano and C. O. Laux, IEEE Trans. on Plasma Science, **25**(5), 1997, p. 1042.
- [5] P. F. Kurunczi and K. H. Becker, Proc. of HAKONE VII, 2000, Greifswald, 2000, pp 491-5.
- [6] A. Bräuning-Demian, L. Spielberger, C. Penache, H. Schmidt-Böcking, Proc. of the XIII GDA, Glasgow, 2000, pp. 426-9.
- [7] C. Penache, C. Gessner, A. Bräuning-Demian, P. Scheffler, L. Spielberger, O. Hohn, S. Schössler, T. Jahnke, K.-H. Gericke and H. Schmidt-Böcking, SPIE Proc. **4460**, 2002, pp. 17-25.