ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 9, Issue 12, June 2020

A Low-Cost Atmospheric Pressure Dielectric Barrier Discharge system For Hydrophilicity Enhancement of Polypropylene Films

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Abstract: ***Dielectric barrier discharges (DBDs), have found a several number of interesting industrial applications because they can produce non-equilibrium plasmas in a very simple and economic way that make it superior over other non-equilibrium atmospheric pressure plasmas. Most polymers are intrinsically hydrophobic, and thus do not adhere well to other substances. Treatment of these polymers by discharge plasmas modifies its surface without changing bulk properties. In this study, air and oxygen DBD plasmas have been used for enhancing the hydrophilicity of polypropylene (PP) surface. The plasmas are generated by an economic and simple system. PP surfaces have been exposed to plasmas for different times at a discharge power of 16 W for both air and oxygen plasmas. Surface characterization is achieved by measuring water contact angle (CA) before and after treatment, Diffused Reflectance-FTIR and scanning electron microscope (SEM). Contact angle measurements shows that the contact angle decreases with the increase in exposure time until reaching saturation at contact angle of about 20^o for air and oxygen plasma, but the saturation was reached in the case of oxygen plasma faster than air plasma at the same discharge power. SEM micrographs shows that air plasma cause cracks on polymer surface, also it shows confined spherulitic crystals with a fractal dendrite (FD) morphologies on the surface of oxygen plasma treated samples.***

Keywords: **Atmospheric pressure plasma; Contact angle; Dielectric barrier discharge (DBD).**

I. INTRODUCTION

Plasma is an ionized gas which has a collective behavior. With plasmas, especially low temperature plasmas, a wide variety of chemically active species can be produced which are more numerous and energetic than those produced by ordinary chemical reactions. This makes plasma a valuable tool in many industries such as microchip fabrication, textiles, food packaging and polymer treatment. Most types of low temperature plasmas are easily produced at low pressures. In contrast, atmospheric pressure plasmas are technically significant with regard to many industrial applications because there is no need for closed champers and vacuum systems to generate plasma in addition it can be integrated very well with production lines. [1]

Manuscript received: 27 May 2020
Manuscript received in revised form: 25 June 2020
Manuscript accepted: 10 July 2020
Manuscript Available online: 15 July 2020

Dielectric barrier discharge (DBD) is one of the most common methods for producing atmospheric pressure plasmas. This type of discharge is featured by the presence of a dielectric layer(s) in the gap between the electrodes that prevents arc formation. Because of the presence of the dielectric layer, this type of discharge operates with AC source. [2] The production of atmospheric pressure non thermal plasmas by DBD is very simple and does not need a vacuum system or a sophisticated power supplies as compared with corona discharge. [3] Other advantage of DBD is that, it can be scaled up to large industrial installations with high powers. [4] The applications of DBD are numerous, examples of these applications are surface treatment, [5–7] ozone production, [8] medical applications, [9] [10] environmental applications, [11] and plasma display panels.

Polypropylene polymer (PP) is one of the most common and most producible materials in the world. It is widely used in many industrial applications because of its favorable properties like lightweight, excellent mechanical properties, low cost production and easy to recycle. Despite these desirable properties, PP has a low surface energy which results in hydrophobic characteristics like poor printability, wettability and adhesion. Most of PP applications like painting, coating and packing require a good hydrophilic characteristic rather than a hydrophobic characteristic. For making a good use of PP the polymer surface must be treated to enhance its hydrophilic characteristics.

The techniques used for enhancing hydrophilic characteristics of PP surfaces are numerous. These techniques include mechanical, biological and physicochemical treatment. One of the most used physicochemical methods is called *gas phase methods*, this method uses a gas which contains active species such as ions, electrons, free radicals and excited molecules i.e. *plasma*. [12] The methods depending on plasmas for treatment is better than chemical ones because it is economic and environment friendly.

The plasma can change the surface of PP by two methods. It can change the Surface morphology of PP or the chemical composition of the surface by increasing the number of polar groups on the surface. [13, 14]

Different types of plasmas can be used to modify the surface of PP polymers. Examples of these types are DC glow discharge air plasma, [15] microwave induced argon plasma, [16] DBD helium and air plasma generated via pulsed high voltages, [17, 18] radio frequency plasma of air, nitrogen, oxygen, and ammonia. [19] Most of the methods listed above need either a vacuum system or a special high frequency power supplies for generating plasmas.

The present work aims to improve the hydrophilicity of PP surfaces by using a simple and economic DBD plasma system running with a frequency of 50 Hz and uses cheap and available gases. The plasmas, air and oxygen DBD plasmas, used in treatment of PP are generated in a planar geometry system. Characterization of electric properties of DBD is estimated. Surface characterization by measuring water contact angle (CA) before and after treatment, Diffused Reflectance-FTIR and scanning electron microscope (SEM) are also included.

II. EXPERIMENTAL DESCRIPTION

A. The polymer

The polymer used in this study is a biaxially-oriented polypropylene (BOPP) films. It is obtained from a local company that produces packaging materials. The XRD of the film in 10 - 90o 2 theta range is shown in Fig. 1 and shows peaks at 14.1o, 17o, 18.6o and 25.66o which correspond to the isotactic biaxial oriented polypropylene polymer. [20]

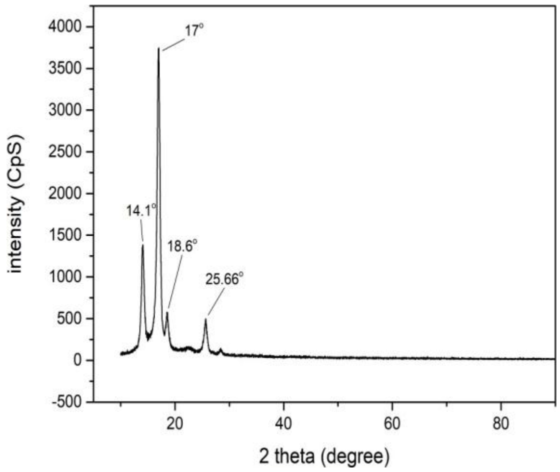

Fig. 1. X-ray diffraction diagram of the polymer film.

B. The DBD Plasma system

The experimental setup used for treatment of PP is illustrated in Fig. 2. Plasma is generated between two parallel plane electrodes. Each electrode has an area of 25×25 cm2 and the upper one is covered with a layer of ordinary glass with a thickness of 2 mm. The discharge gap measured from the lower surface of the dielectric to the lower electrode has a width of 2 mm. The electric circuit of the discharge consists of a high voltage power supply (0-15 kV) with a frequency of 50 Hz. A resistor R3 having a value of 255 kΩ is connected in circuit for protecting the power supply and discharge cell against any accidental arc formation. For measuring the voltage across the cell, a divider consists of two resistors *R1* and *R2* connected in series with a dividing ratio of 1:1000 is used. In order to display the current waveform on an oscilloscope, a resistor *R* = 100 Ω is connected in series with the cell.

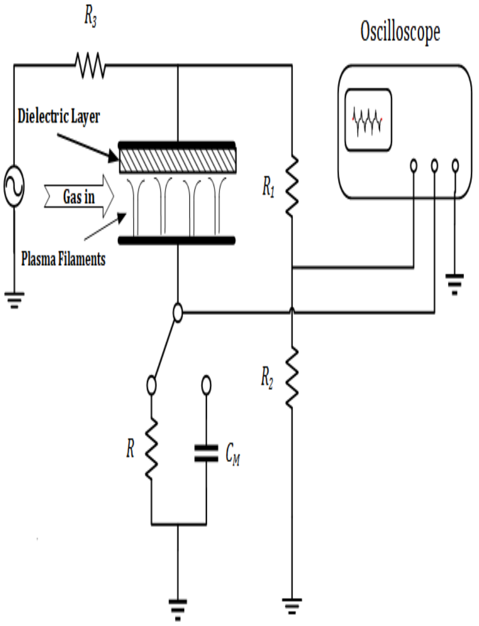

Fig. 2. Schematic diagram of the dielectric barrier discharge system.

III. RESULTS AND DISCUSSION

A. Electrical characterization of the discharge cell

The discharge cell was electrically characterized by two methods. The first one is accomplished by displaying current and voltage waveforms on the screen of a digital storage oscilloscope (IV characterization) and the second one by measuring the consumed discharge power at different applied voltages using Lissajous figures.

B. Characterization

The current and voltage waveforms for air and oxygen DBD plasmas are shown in Fig. 3 and Fig. 4 respectively. The applied voltages for both air and oxygen plasmas have a sinusoidal form with a frequency of 50 Hz and a peak voltage of 11.83 kV. The current waveforms are featured by the presence of humps, which corresponds to periods of time when the discharge is active. [21] The ends of these humps coincide with the maxima and minima of the applied voltage.

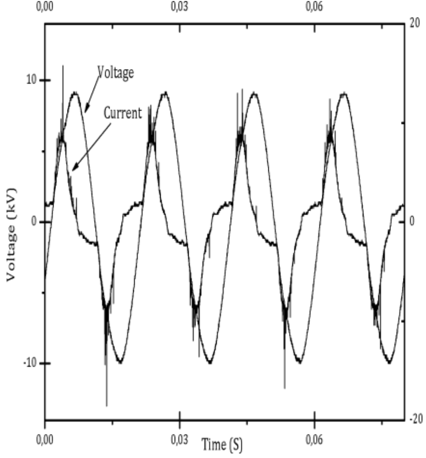

Fig. 3. Current and voltage waveforms for air DBD plasma.

Humps in the current waveforms for air and oxygen plasmas have spikes superimposed on it. These spikes result from current pulses resulting from discharge filaments. [22] The number of spikes in oxygen current waveform is larger than that of air for the same applied voltage which means that the number of discharge filaments in oxygen is higher than that of air.

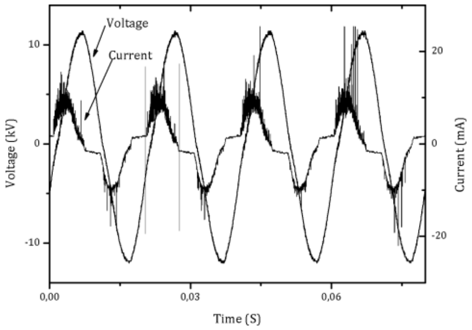

Fig. 4. Current and voltage waveforms for oxygen DBD plasma at a flow rate of 2 L min^{-1}

C. Consumed Power

A simple and reliable method for obtaining the power dissipated in the cell is by using the Lissajous figure method. [23–25] Lissajous figures are obtained by plotting the transmitted electric charge *Q* through the discharge cell as a function of the applied periodical voltage. The charge *Q* can be measured from the voltage drop across a measuring serial capacitor *CM*. For displaying Lissajous figure on oscilloscope, the resistor *R* in the setup is replaced by a capacitor *CM* of a capacitance 3.3 µF and running oscilloscope in *x-y* mode.

Fig. 5 shows two sets of Lissajous figures one for air plasma and the other for oxygen plasma at a flow rate of 2 L min^{-1}. It is noticed that the area enclosed by the figure increases with peak voltage, because as the voltage increases the power dissipated increases and hence the area of the figure increases.

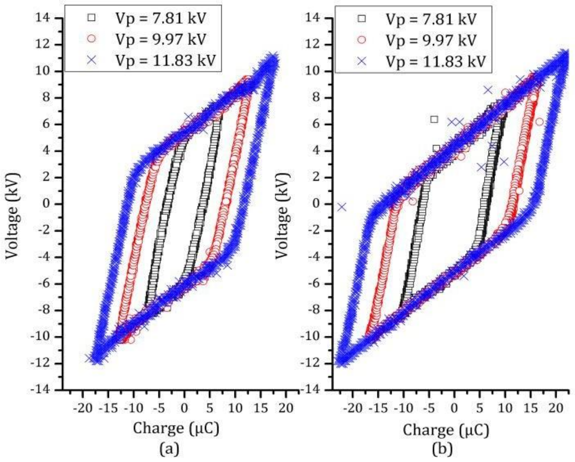

Fig. 5. Comparison between Lissajous figures for: (a) air and (b) oxy- gen at a flow rate of 2 L min^{-1} plasmas for different applied peak voltages.

The Power calculated using Lissajous figures at different applied peak voltages is shown in Fig. 6. The figure shows that the power increases by increasing the applied voltage. It also shows a slight difference in the power values of both gases and the value of power for air and oxygen plasmas are almost the same at peak voltage of 11.83 kV. Thus, for judging the effect of gas type on enhancing hydrophilicity of PP films the system is operated at a voltage of 11.83 kV since at that voltage the dissipated power in air and oxygen are almost equal.

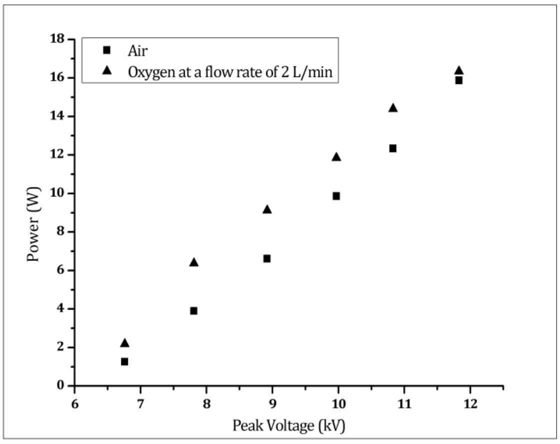

Fig. 6. Variation of discharge power with applied voltage (peak) for air and oxygen plasmas.

D. Contact angle (CA) measurements

For characterizing PP surface, the water contact angle (CA), which is a good test for polymer surface hydrophilicity, has been measured before and after treatment with air and oxygen plasmas. Contact angle measurement was done by analyzing digital images of water droplets on polymer surface using Drop Snake plug-in for the ImageJ program. [26, 27]

The variation of contact angle (CA) with exposure time for air and oxygen plasmas is illustrated in Fig. 7. It is observed that the contact angle decreases with increasing exposure time until reaching saturation at about 20^{o} in the case of air plasma treated PP films, but it takes a less time, two minutes, to reach saturation in the case of oxygen plasma treated samples.

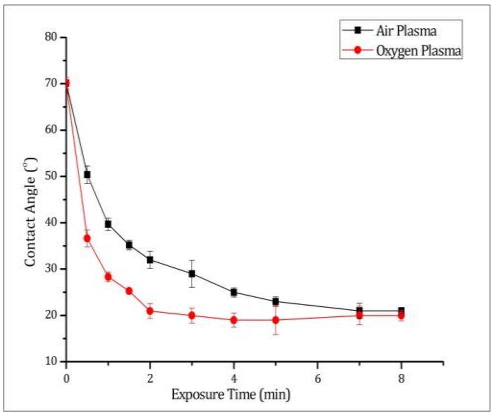

Fig. 7. Variation of contact angle (CA) with exposure time for air and oxygen plasmas.

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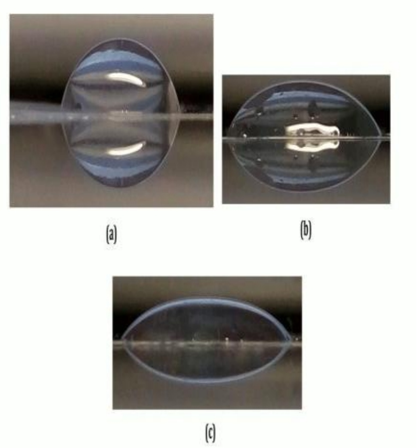

Fig. 8. Digital images of water droplets for PP film before plasma treatment (a), after two minutes of air plasma treatment (b), and after two minutes of oxygen plasma treatment (c)

The treatment of PP with air DBD plasma is less effective and takes a long time, seven minutes, to achieve the same result obtained by oxygen DBD plasma. This result can be interpreted by referring to current and voltage waveforms for air and oxygen plasmas (Fig. 3 and Fig. 4). These figures show that the number of filaments in the case of oxygen plasma is higher than that of air plasma, so treatment with oxygen DBD plasma takes less time as compared to air plasma

E. Diffused Reflectance-FTIR Characterization

Diffused Reflectance-FTIR is used for characterizing PP films in order to show if any chemical changes are produced by plasma. FTIR spectrum for untreated, treated for 2 minutes with air plasma and treated for 2 minutes with oxygen plasma PP samples is shown in Fig. 9 which shows an obvious difference between the spectra of untreated and plasma treated samples. A broad peak appears between 3650 and 3300 cm^{-1} this peak is attributed to the OH stretching vibrations. [28] The hydroxyl (-OH) group is a polar group which interacts easily with water molecules via hydrogen bonds this results in improving of hydrophilicity of the polymer surface. Returning back to the spectrum, a peak with wave number of 1643 cm^{-1} appears in the treated samples, this beak belongs to the (C=C) stretching vibration. [14,29]

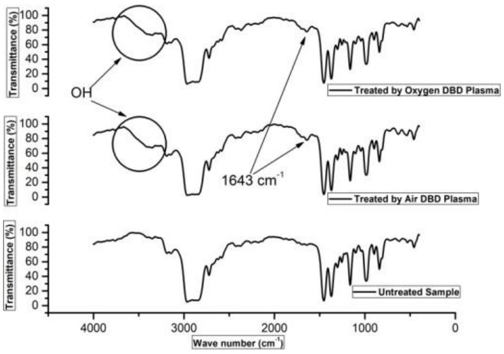

Fig. 9. Diffused Reflectance-FTIR spectrum for untreated, treated for 2 minutes with air plasma and treated for 2 minutes with oxygen plasma PP samples.

F. Scanning Electron Microscope (SEM) Characterization

The surfaces of the untreated, air plasma treated, and oxygen plasma treated PP films were examined by scanning electron microscope. The image of the untreated sample (Fig. 10) shows a smooth surface compared with treated samples which show appreciable morphological changes on the sample surface. In the case of air plasma treated sample, some cracks with a dimension of 17.5 μm are produced on the surface also the image shows increasing in the roughness of the surface (Fig. 11). SEM image (Fig. 12) of the oxygen DBD plasma treated surface shows spherulitic crystals which have fractal dendrite (FD) morphologies. [30] These crystals have the same crystalline morphology as that which results from the confined crystallization of polymers. [31].

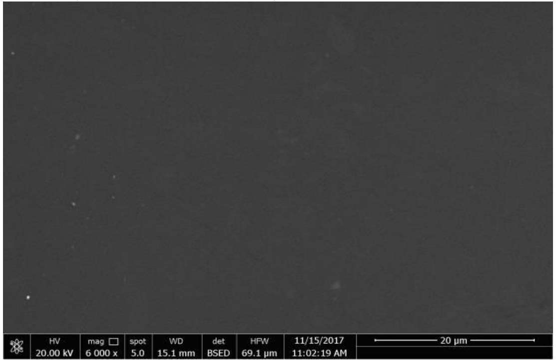

Fig. 10. Scanning electron microscope image for the untreated polypropylene sample.

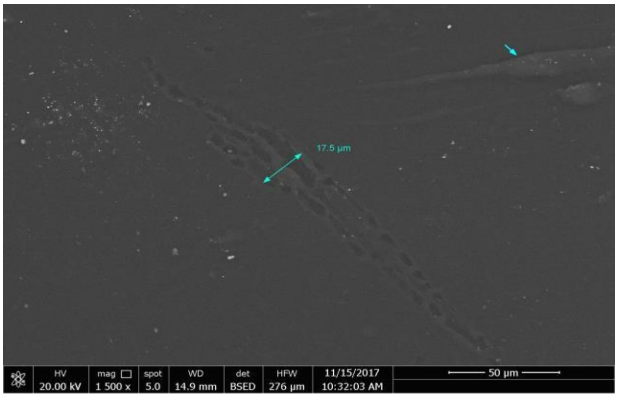

Fig. 11. Scanning electron microscope image of polypropylene film after two minutes of treatment with air plasma.

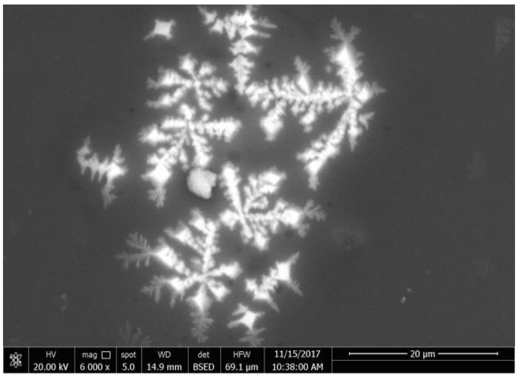

Fig. 12. Scanning electron microscope image of poly-propylene film after two minutes of treatment with oxygen plasma.

IV. CONCLUSION

In this study the hydrophilicity of polypropylene (PP) films were improved by plasmas generated by a simple and economic DBD system running at atmospheric pressure with air or oxygen gases. The results showed that the contact angle decreases with increasing the plasma exposure time for air and oxygen. The treatment with oxygen plasma takes a less time (2 min) to reach the lowest measured contact angle (20o) as compared with air plasma treatment which takes 7 min to reach the same angle. The Diffused Reflectance-FTIR spectra for the treated samples show the presence of hydroxyl (-OH) functional group on polymer surfaces. The morphology of the polymer surface affects its hydrophilicity, so a SEM imaging of the surface was performed. SEM images show that air DBD plasma causes small cracks on the surface, while oxygen DBD plasma causes a formation of confined spherulitic crystals with fractal shapes on the surface. The formation of these crystals on polymer surface by oxygen DBD plasma is very interesting and needs further investigations.

REFERENCES

[1] R.A. Wolf, Atmospheric Pressure Plasma for Surface Modification, John Wiley & Sons, 2012.

[2] U. Kogelschatz, Dielectric-Barrier Discharges: Their History, Discharge Physics, and Industrial Applications, Plasma Chem. Plasma Process. 23 (2003) 1–46. Doi:10.1023/A: 1022470901385.

[3] A. Fridman, Plasma Chemistry, Cambridge University Press, 2008.

[4] U. Kogelschatz, B. Eliasson, Fundamentals and applications of dielectric barrier discharges, in: HAKONE VII Int Symp High Press. Low Temp. Plasma Chem., Greifswald, 2000.

[5] R. Mix, J. Friedrich, A. Rau, Polymer Surface Modification by Aerosol Based DBD Treatment of Foils, Plasma Process. Polym. 6 (2009) 566–574. doi:10.1002/ppap.200950009.

[6] K.G. Kostov, T.M.C. Nishime, L.R.O. Hein, A. Toth, Study of polypropylene surface modification by air dielectric barrier discharge operated at two different frequencies, Surf. Coat. Technol. 234 (2013) 60–66. doi:10.1016/j.surfcoat.2012.09.041.

[7] M. Chiang, K. Liao, I. Lin, C. Lu, H. Huang, C. Kuo, J. Wu, Modification of Hydrophilic Property of Polypropylene Films by a Parallel-Plate Nitrogen-Based Dielectric Barrier Discharge Jet, IEEE Trans. Plasma Sci. 38 (2010) 1489–1498. doi:10.1109/TPS.2010.2045769.

[8] U. Kogelschatz, Advanced Ozone Generation, in: S. Stucki (Ed.), Process Technol. Water Treat., Springer US, Boston, MA, 1988: pp. 87–118. doi:10.1007/978-1-4684- 8556-1_9.

[9] P. Rajasekaran, C. Opländer, D. Hoffmeister, N. Bibinov, C.V. Suschek, D. Wandke, P. Awakowicz, Characterization of Dielectric Barrier Discharge (DBD) on Mouse and Histological Evaluation of the Plasma-Treated Tissue, Plasma Process. Polym. 8 (2011) 246–255. doi:10.1002/ppap.201000122.

[10] U. Kogelschatz, Silent discharges for the generation of ultraviolet and vacuum ultraviolet excimer radiation, Pure Appl. Chem. 62 (1990) 1667–1674. doi:10.1351/pac199062091667.

[11] C.A. Aggelopoulos, Atmospheric pressure dielectric barrier discharge for the remediation of soil contaminated by organic pollutants, Int. J. Environ. Sci. Technol. 13 (2016) 1731–1740. doi:10.1007/s13762-016-1009-0.

[12] A.S. Hoffman, Surface modification of polymers: Physical, chemical, mechanical and biological methods, Macromol. Symp. 101 (1996) 443–454. doi:10.1002/masy.19961010150.

[13] N.S. Kasalkova, P. Slepicka, Z. Kolska, V. Svorcik, Wettability and other surface properties of modified polymers, in: Wetting Wettability, InTech, 2015.

[14] L. Kravets, A. Gilman, M. Yablokov, V. Elinson, B. Mitu, G. Dinescu, Surface and Electrochemical Properties of Plasma-Treated Polypropylene Track Membrane, Plasma Process. Polym. 10 (2013) 603–618.

[15] K.N. Pandiyaraj, V. Selvarajan, R.R. Deshmukh, C. Gao, Modification of surface properties of polypropylene (PP) film using DC glow discharge air plasma, Appl. Surf. Sci. 255 (2009) 3965–3971.

[16] J. Lai, B. Sunderland, J. Xue, S. Yan, W. Zhao, M. Folkard, B.D. Michael, Y. Wang, Study on hydrophilicity of polymer surfaces improved by plasma treatment, Appl. Surf. Sci. 252 (2006) 3375–3379.

[17] F. Massines, G. Gouda, A comparison of polypropylene-surface treatment by filamentary, homogeneous and glow discharges in helium at atmospheric pressure, J. Phys. Appl. Phys. 31 (1998) 3411.

[18] N.-Y. Cui, N.M. Brown, Modification of the surface properties of a polypropylene (PP) film using an air dielectric barrier discharge plasma, Appl. Surf. Sci. 189 (2002) 31– 38.

[19] N.V. Bhat, D.J. Upadhyay, Plasma-induced surface modification and adhesion enhancement of polypropylene surface, J. Appl. Polym. Sci. 86 (2002) 925–936.

[20] F.J. Díez, C. Alvarińo, J. López, C. Ramírez, M.J. Abad, J. Cano, S. García-Garabal, L. Barral, Influence of the stretching in the crystallinity of biaxially oriented polypropylene (BOPP) films, J. Therm. Anal. Calorim. 81 (2005) 21–25. doi:10.1007/s10973-005-0739-x.

[21] T.C. Manley, The electric characteristics of the ozonator discharge, Trans. Electro- chem. Soc. 84 (1943) 83–96.

[22] S. FUJI, N. TAKEMURA, Electrical Characteristics of the Ozonizer, in: OZONE Chem. Technol., AMERICAN CHEMICAL SOCIETY, 1959: pp. 334–343. doi:10.1021/ba- 1959-0021.ch045.

[23] K.-P. Francke, R. Rudolph, H. Miessner, Design and operating characteristics of a simple and reliable DBD reactor for use with atmospheric air, Plasma Chem. Plasma Process. 23 (2003) 47–57.

[24] G. Nersisyan, W.G. Graham, Characterization of a dielectric barrier discharge operating in an open reactor with flowing helium, Plasma Sources Sci. Technol. 13 (2004) 582.

[25] Z. Falkenstein, J.J. Coogan, Micro discharge behavior in the silent discharge of nitrogen-oxygen and water-air mixtures, J. Phys. Appl. Phys. 30 (1997) 817.

[26] A.F. Stalder, G. Kulik, D. Sage, L. Barbieri, P. Hoffmann, A snake-based approach to accurate determination of both contact points and contact angles, Colloids Surf. Physicochem. Eng. Asp. 286 (2006) 92–103.

[27] D.L. Williams, A.T. Kuhn, M.A. Amann, M.B. Hausinger, M.M. Konarik, E.I. Nesselrode, Computerized Measurement of Contact Angles, (n.d.) 11.

[28] [28] G. Socrates, Infrared and Raman characteristic group frequencies: tables and charts, John Wiley & Sons, 2004.

[29] R. Morent, N. De Geyter, C. Leys, L. Gengembre, E. Payen, Comparison between XPS- and FTIR-analysis of plasma-treated polypropylene film surfaces, Surf. Interface Anal. Int. J. Devoted Dev. Appl. Tech. Anal. Surf. Interfaces Thin Films. 40 (2008) 597–600.

[30] C. Yu, Q. Xie, Y. Bao, G. Shan, P. Pan, Crystalline and Spherulitic Morphology of Polymers Crystallized in Confined Systems, Crystals. 7 (2017) 147. doi:10.3390/cryst7050147.

[31] R.M. Michell, A.J. Müller, Confined crystallization of polymeric materials, Prog. Polym. Sci. 54–55 (2016) 183–213. doi:10.1016/j.progpolymsci.2015.10.007.