Impact of low-temperature plasma treatment parameters on wettability and printability of PLA film

JOANNA IZDEBSKA-PODSIADŁY[1]

[1]Warsaw University of Technology, Department of Printing Technology, Institute of Mechanics and Printing, Faculty of Production Engineering Warsaw, Poland

Keywords:
Biodegradable polymers, contact angle, plasma treatment, polylactide film, printability, wettability

Abstract
The paper investigates the influence of low-temperature plasma on selected properties of PLA films. Two different gases, oxygen and argon, were used in the study with variable activation parameters (activation duration of 2, 4, 6, 8 and 10 minutes and activation pressures of 0.4 and 0.5 mbar). The influence of the modification on the wettability of the substrate with distilled water, diiodomethane and three different flexographic inks (one water-based and two kinds of solvent-based) was analyzed. As a result of the studies, oxygen plasma activation was found to improve the wettability of the substrate more than the activation with argon. In addition, longer activation time has no significant effect on the contact angle when activated by argon plasma. On the other hand, when activated with oxygen, the lowest value of the contact angle was observed after the shortest activation time of 2 minutes. Moreover, the extension of the activation time caused a slight increase of the contact angle, although it was still very low in comparison with the contact angle noted before plasma treatment. Furthermore, it was found that the type of gas used for plasma modification has a much greater effect on wettability in solvent-based inks than in water-based ink.

Introduction

Wide use of the film in the packaging industry makes it necessary to be able to print advertising and information material on their surface. However, after refining most plastics there is a problem with the wettability and adhesion of printing inks, lacquers or adhesives. Adhesion is mainly dependent on the value of surface free energy expressed in mJ/m2, which is calculated by using the contact angle of the substrate with specified measuring fluids, i.a. distilled water, diiodomethane, glycerol or formamide. Different methods for calculation of surface free energy are available, e.g. Fowkes, Owens-Wendt, Van Oss-Chadhury-Good, Zisman, Neumann, etc. (Żenkiewicz, 2007, Izdebska-Podsiadły & Dörsam, 2017).

Getting the correct wettability of the substrate and adhesion to the applied layer is achieved by changing the properties of the top layer of the plastic as a result of its modification. Modification of the material can be accomplished by chemical and by physical methods (Izdebska & Thomas, 2016). Plasma treatment is one of the physical methods, and due to the properties of plastics, low temperature plasma is used.

Plasma, often referred to as the fourth state of matter, is formed by the action of electricity on matter. It is a gas containing a mixture of reactive species such as: electrons, ions and neutrals (Thiry et al., 2016). As a result of the action of plasma on the surface of the polymer, physical and chemical digestion takes place, cleaning the surface of organic pollutants and ablation (Kusano, 2013). This improves the adhesion and increases the roughness. In addition, there are also changes in the chemical properties of the surface layer that result in decrease in C-C and C-H bonds and change in properties such as hydrophilicity (Ebnesajjad & Ebnesajjad, 2014, Shentons & Stevens, 2001).

Various types of gas are used in plasma treatment, e.g. oxygen, nitrogen, argon, helium, carbon dioxide, fluorine, ammonia. The use of different gases causes various changes in the characteristics of the material, for example plasma operation with oxygen increases the surface free energy, while fluorine reduces the chemical reactivity. In conclusion, the following changes occur on the surface of the film during activation: removal of impurities, change of geometric structure of the surface (increase of its roughness),

formation of polar compounds on the surface leading to an increase of the surface free energy of the modified material (Wiącek et al., 2016, Hegemann et al. 2003).
Over the past several years, interest in biodegradable polymers that can be used in the packaging industry has increased considerably. The advantage of this type of polymers, unlike other polymers produced from petroleum, is their decomposition under aerobic conditions into water, carbon dioxide and other mineral components, and under anaerobic conditions into methane and biomass. One of the biodegradable materials is polylactide, also called polylactic acid or PLA. Other biodegradable films used in packaging include cellulose and starch. PLA is a material obtained from renewable raw materials such as maize, rice, potatoes, rye etc. Initially used mainly in medicine, it is increasingly used in the production of disposable packaging (Stepczyńska & Żenkiewicz, 2014). Polylactide, like polystyrene, is characterized by high rigidity and brittleness. It is similar to PET with regard to resistance to fats and oils. In addition, it is a highly polar and relatively hydrophobic material (Rasal et al., 2010, Xiao et al., 2015, Rong & Keif, 2007, Lagarón, 2011, Jiang & Zhang, 2011, Siracusa et al., 2008).
There are publications on plasma modification of the top layer, however most of them concern biomedical applications and only a few deal with commodity applications (Jordá-Vilaplana et al., 2014, Chaiwong et al., 2010, Bolbasov et al., 2014, Yang et al, 2002a & 2002b, Rocca-Smith et al., 2016, Moraczewski et al., 2015 & 2016, Kim & Masuoka, 2009, De Geyter et al., 2010, De Geyter, 2013, Pankaj et al., 2014, Hirotsu et al., 2002, Wan et al., 2006, Garcia-Garcia, 2014). In addition, according to the author's knowledge, none of the works investigates low-temperature, low-pressure plasma using argon and oxygen for PLA treatment under variable pressure, as it is done in the results presented in this paper. Moreover, beside determining the influence of activation on water and diiodomethane wettability, which allows the determination of surface free energy, the effect of activation on the wettability of the substrate with various flexographic inks was also investigated. It should be emphasized that due to the increasing importance of PLA and its various uses (medical and industrial) research of its properties and modifications should be continued.

Materials and methods

Poly(lactic acid) film was purchased in the form of A4 sheets from Plastic Suppliers, Inc.. It was a commercially available film named Earth First PLA TCL with thickness of 50 microns. The values of film gloss at 60° and of haze were 115 G.U. and 3%, respectively. The mechanical properties of the material depend on the direction – their ultimate tensile strength was 98 N/mm2 for machine direction and 182 N/mm2 for transverse direction. The value of surface free energy of untreated film was specified as 38 mJ/m^2.

Film plasma treatment was carried out using Low Pressure Plasma Systems Diener Nano (Diener Electronic, Germany). Two kinds of gases were supplied to a vacuum chamber: pure oxygen (O2) or pure argon (Ar). Activation was conducted at the following fixed parameters: radio frequency 40 kHz, control pressure via gas, gas supply time 2 min. Such parameters as treatment time and power pressure were changed during the tests. Duration of plasma treatment was 2, 4, 6, 8 or 10 minutes depending on the sample. The power pressure was set to 0.4 or 0.5 mbar.

Contact angle was measured using DSA 100 device (Krüss, Germany). Distilled water and diiodomethane 99% CH_2I_2 (Sigma–Aldrich, Germany) as well as 3 flexographic inks were used as liquids. The characteristics of the inks are given in Table 1. The sessile drop techniques and the Tangent 2 method were used. 15 drops were deposited on each measured substrates at stable environmental condition with temperature 23 ± 1°C with needles of 0.5 mm in diameter. The contact angle values were measured 15 s after the drop deposition for both untreated and plasma treated samples. Moreover, all plasma-modified samples were tested immediately after activation. Reported values are the average of the measurements.

The surface free energy of PLA film and its polar and dispersive components were calculated with the Owens–Wendt method. This method requires the use of two liquids, one with a dominant polar component and the other with a dominant dispersive component. Therefore, distilled water and diiodomethane were used in this work as polar and dispersive components, respectively.

Table 1. Inks characteristics

	Ink 1	Ink 2	Ink 3
Trade name/ manufacturer	FlexiWet Chespa	Urania Chespa	Wiflex Chespa
Type of ink	water-based	solvent-based	solvent-based
Type of resin	Acrylic	PA	NC/PU
Viscosity [s] (Ford cup, 100 ml, Ø 4 mm)	18	18	18

Results and discussion

The contact angle with water is used in the tests as a basic parameter to determine the wettability of a material. The lower its value, the more hydrophilic it is, i.e. the wettability is higher. Wettability is one of the basic characteristics of plastics print substrates, which depend on the chemical composition and material morphology. Plasma treatment reduces the contact angle of water on PLA film from 76º to less than 36º (see Figure 1). Activation with oxygen plasma caused a larger reduction in contact angle with water than activation using argon gas. Nevertheless, it should be noted that the reproducibility of the results, i.e. the uniformity of changes in the surface of the film, was better for Ar plasma treatment.

Printing on plastics can be done using a variety of printing techniques, but flexographic printing is currently the most widely used one. Therefore, the PLA contact angle was measured using various flexographic inks, solvent-based inks using different resins and one water-based ink. The results are shown in Figure 1. The value of ink contact angle is used to determine the wettability of the substrate, a parameter closely correlated with its printability. If the ink does not properly wet the substrate, printing will not be possible. The inks may spill on the surface or form drops. The surfaces with a contact angle <90° are considered wettable, the lower the value, the better the wettability. The values of measured contact angles of water-based ink are greater than of solvent-based inks, resulting from the fact that water-based inks have higher levels of surface tension. This high level of surface tension is a consequence of high surface tension of water. For water-based inks the type of gas used for plasma activation had no significant effect on the wettability of the substrate. In case of solvent-based inks plasma activation with oxygen had a more favorable effect on wettability.

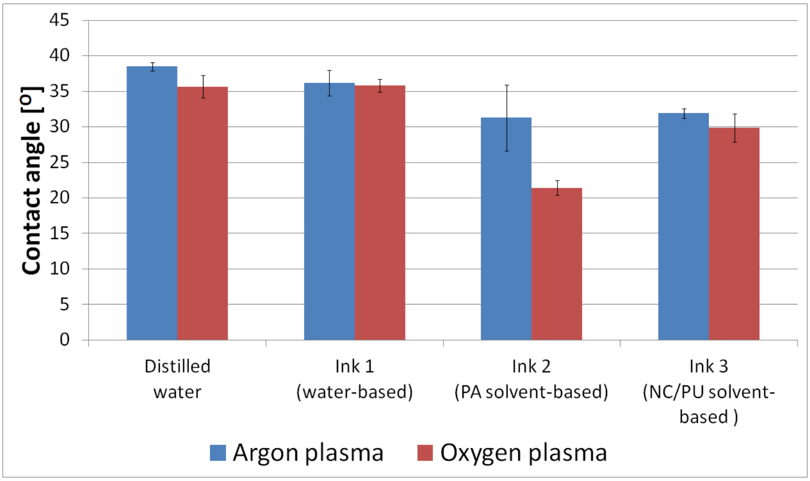

Figure 1: Contact angle with different liquids for PLA film treated with plasma for 4 minutes at pressure level 0.4 mbar in relation to the type of gas used

Analyzing the impact of the activation time on the contact angle with water (Figure 2), it was found that the type of gas used for the plasma activation has an important influence on the wettability achieved. With oxygen plasma activation, the smallest contact angle was achieved for the shortest activation time. This change lies in functional properties of the surface – increased proportion of hydroxyl and carboxylic groups on the surface. Longer activation time had an adverse effect, but a very large increase in activation time causes the contact angle to decrease again. The changes in surface topography are observed at that time resulting in improved wettability. In the case of argon plasma treatment, the smallest contact angle value was obtained while using the longest (10 minutes) activation time. However, in this case the differences between the contact angles with water obtained at different substrate modification times are small and vary between 40.1° and 44.8°.

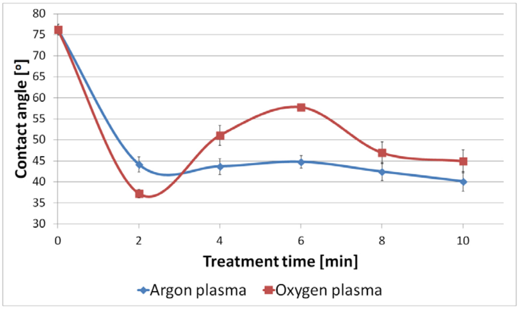

Figure 2: Contact angle with water for PLA film treated with plasma at pressure level 0.5 mbar in relation to the type of gas and the treatment time

The plasma pressure had a significant effect on the contact angle (see Figure 3). When using plasma with oxygen the differences were much higher than for argon plasma. However, regardless of the type of gas, it was found that the lower pressure value used for low pressure plasma allows for lower contact angle values.

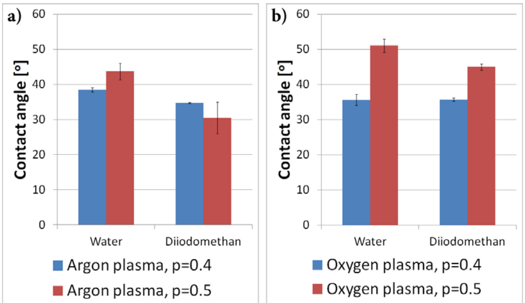

Figure 3: Contact angle with water and diiodomethane for PLA film treated for 4 minutes at different pressure level and with different plasma a) argon, b) oxygen.

The surface free energy (SFE) value of non-absorbent substrates is an important parameter used in industrial practice to determine the suitability of a particular substrate for printing. Polymers with the lowest SFE values are polyolefins and due to low level of wettability require substrate activation before printing or refining. In the case of biodegradable substrates this value is much higher, nevertheless they are still activated in order to improve the printing properties, adhesion of the ink or glue to the substrate, or to clean the surface. The determined value of SFE of unmodified PLA was close to that of the manufacturer (39.5 mJ/m^2). As a result of plasma treatment, it grew to over 60 mJ/m2. The described above contact angle analysis shows that the best results were obtained for oxygen plasma activation at lower pressures, but the SFE value for argon plasma at the same pressure was only minimally lower.

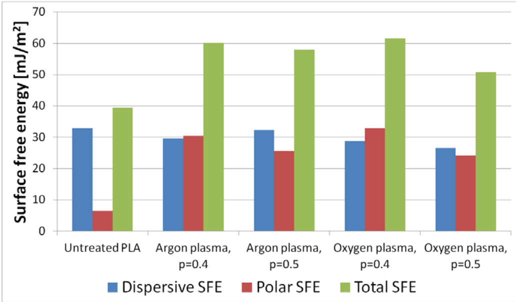

Figure 4: Surface free energy and its polar and dispersive components for PLA film treated with different plasma for 4 minutes.

Conclusions

As a result of the conducted studies it was found that oxygen plasma activation when selecting the optimal modification time leads to stronger improvement of the wettability of the substrate than activation with argon. Nevertheless, it should be emphasized that both types of gas allow significant reduction of the contact angle of PLA with water and various printing inks. Additionally, the duration of surface treatment has no significant effect on the contact angle with water when activated by Ar plasma. On the other hand, when activated with oxygen, longer activation time exceeding 2 minutes increases the value of the contact angle. Furthermore, it has been found that the type of gas used for plasma modification has a much greater effect on wettability for solvent-based inks than for water-based inks. However, there was no significant effect of the gas type on the SFE value of the PLA film, only the type of gas influenced the polar and dispersion components. Moreover, SFE value depended on the pressure at which activation was performed. Regardless of the plasma activation conditions a significant change in SFE and its polar component was observed which results in better wettability of the PLA substrate and in consequence, printability.

Acknowledgements

The author would like to thank professor Edgar Dörsam and IDD team from Institute of Printing Science and Technology, Darmstadt University of Technology, for providing access to the laboratory and equipment, and excellent work atmosphere.

Funding

This work was supported by the financial help from WUT Development Program by the European Union within the European Social Fund.

References

1. Bolbasov E.N., Rybachuk M., Golovkin A.S., Antonova L.V., Shesterikov E.V., Malchikhina A.I., Novikov V.A., Anissimov Y.G., Tverdokhlebov S.I. (2014) Surface modification of poly(L-lactide) and polycaprolactone bioresorbable polymers using RF plasma discharge with sputter deposition of a hydroxyapatite target. Materials Letters, 132, 281–284.

2. Chaiwong A., Rachtanapun P., Wongchaiya P., Auras R., Boonyawan D. (2010) Effect of plasma treatment on hydrophobicity and barrier property of polylactic acid. Surface & Coatings Technology, 204, 2933–2939.

3. De Geyter N. (2013) Influence of dielectric barrier discharge atmosphere on polylactic acid (PLA) surface modification. Surface & Coatings Technology, 214, 69–76.

4. De Geyter N., Morent R., Desmet T., Trentesaux M., Gengembre L., Dubruel P., Leys C., Payen E. (2010) Plasma modification of polylactic acid in a medium pressure DBD Surface & Coatings Technology, 204, 3272–3279.

5. Ebnesajjad S. and Ebnesajjad C. (2014) Plasma Treatment of Polymeric Materials. Chapter 9 In Surface Treatment of Materials for Adhesive Bonding. William Andrew.

6. Garcia-Garcia, D. et al. (2014) Surface modification of polylactic acid (PLA) by air atmospheric plasma treatment. European Polymer Journal, 58, 23–33.

7. Hegemann A., Brunner H., Oehr Ch. (2003) Plasma treatment of polymers for surface and adhesion improvement. Nuclear Instruments and Methods in Physics Research B, 208, 281–286.

8. Hirotsu T., Nakayama K., Tsujisaka T., Mas A., Schue F. (2002) Plasma surface treatments of melt-extruded sheets of poly(l-lactic acid). Polym Eng Sci, 42, 299–306.

9. Izdebska J. and Thomas S. (Eds.) (2016) Printing on polymers. Fundamentals and Applications. Elsevier.

10. Izdebska-Podsiadły J. and Dörsam E. (2017) Effects of argon low temperature plasma on PLA film surface and aging behaviors. Vacuum, 145, 278–284.

11. Jiang L. and Zhang J. (2011) Biodegradable and Biobased Polymers. In Kutz M. (ed.) Applied Plastics Engineering Handbook. Elsevier.

12. Jordá-Vilaplana A., Fombuena V., García-García D., Samper M.D., Sánchez-Nácher L. (2014) Surface modification of polylactic acid (PLA) by air atmospheric plasma treatment. European Polymer Journal, 58, 23–33.

13. Kim M. C. and Masuoka T. (2009) Degradation properties of PLA and PHBV films treated with CO2-plasma. Reactive & Functional Polymers, 69, 287–292.
14. Kusano Y. (2013) Atmospheric pressure plasma processing for polymer adhesion: a review. The Journal of Adhesion, 755–777.

15. Lagarón J.-M. (2011) Polylactic acid (PLA) nanocomposites for food packaging applications. Chapter 17 in Multifunctional and nanoreinforced polymers for food packaging edited by J.-M. Lagarón. Woodhead Publishing Limited.

16. Moraczewski K., Rytlewski P., Malinowski R., Żenkiewicz M. (2015) Comparison of some effects of modification of a polylactide surface layer by chemical, plasma, and laser methods. Applied Surface Science, 346, 11–17.

17. Moraczewski K., Stepczyńska M., Malinowski R., Rytlewskia P., Jagodziński B., Żenkiewicz M. (2016) Stability studies of plasma modification effects of polylactide andpolycaprolactone surface layers. Applied Surface Science, 377, 228–237.

18. Pankaj S. K., Bueno – Ferrer C., Misra N. N., Milosavljević V., O'Donnel C. P., Bourke P., Keener K. M., Cullen P. J. (2014) Applications of cold plasma technology in food packaging. Trends in Food Science & Technology, 35, 5–17.

19. Pankaj S.K., Bueno-Ferrer C., Misra N.N., O'Neill L., Jiménez A., Bourke P., Cullen P.J. (2014) Characterization of polylactic acid films for food packaging as affected by dielectric barrier discharge atmospheric plasma. Innovative Food Science and Emerging Technologies, 21, 107–113.

20. Rasal R.M. et al. (2010) Poly(lactic acid) modifications. Progress in Polymer Science 35, 338–356.

21. Rocca-Smith J.R., Karbowiak T., Marcuzzo E., Sensidoni A., Piasente F., Champion D., Heinz O., Vitry P., Bourillot E., Lesniewska E., Debeaufort F. (2016) Impact of corona treatment on PLA film properties. Polymer Degradation and Stability, 132, 109–116.

22. Rong X. and Keif M. (2007) A Study of PLA Printability with Flexography. TAGA Proceedings, 605–613.

23. Shentons M.J. and Stevens G.C. (2001) Surface modification of polymer surfaces: atmospheric plasma versus vacuum plasma treatments. J. Phys. D: Appl. Phys. 34, 2761–2768.

24. Siracusa V. et al. (2008) Biodegradable polymers for food packaging: a review. Trends in Food Science & Technology, 19, 634–643.

25. Stepczyńska M. and Żenkiewicz M. (2014) Effects of corona treatment on the properties of the surface layer of polylactide. Polimery, 3, 59, 220–226.

26. Thiry D. et al. (2016) Plasma diagnostics for the low-pressure plasma polymerization process: A critical review. Thin Solid Films, 606, 19–44.

27. Wan Y., Tu C., Yang J., Bei J., Wang S. (2006) Influences of ammonia plasma treatment on modifying depth and degradation of poly(l-lactide) scaffolds. Biomaterials, 27, 2699–2704.

28. Xiao L. et al. (2015) Poly(Lactic Acid) – Based Biomaterials: Synthesis, Modification and Applications. Available from: cdn.intechopen.com/pdfs/26368/InTech Poly_lactic_acid_based_biomaterials_synthesis_modification_and_applications.pdf. [Accessed: 15th April 2017].

29. Yang J., Bei J.Z., Wang S.G. (2002a) Enhanced cell affinity of poly(d,l-lactide) by combining plasma treatment with collagen anchorage. Biomaterials, 23, 2607–2614.

30. Yang J., Shi G.X., Wang S.G., Bei J.Z., Cao Y.L., Shang Q.X., et al. (2002b) Fabrication and surface modification of macroporous poly(l-lactic acid) and poly(l-lactic-co-glycolic acid) (70/30) cell scaffolds for human skin fibroblast cell culture. J Biomed Mater Res, 62, 438–446.

31. Żenkiewicz M. (2007) Methods for the calculation of surface free energy of solids, J. Achiev. Mater. Manuf. Eng., 24 (1), 137–145

JOANNA
IZDEBSKA-PODSIADŁY

Joanna Izdebska-Podsiadły is an assistant professor at the Warsaw University of Technology in Poland. Her area of research includes ink modification, films surface treatment and flexographic printing.

j.izdebska@wip.pw.edu.pl