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Plasma Assisted Activation of Polylactic Acid Surface

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Abstract. Nowadays, the polylactic acid (PLA) is a very promising material which is biodegradable and can be made completely from renewable resources. It can replace not very ecological plastics in food packaging industry especially because of much faster degradation. Some applications require surface treatment to obtain better surface adhesion. Plasma treatment is more suitable way how to treat the PLA surface than wet chemical treatment because PLA degrades in environment with higher humidity and temperature. For PLA surface plasma treatment Diffuse Coplanar Surface Barrier Discharge (DCSBD) was used. DCSBD generates a low-temperature non-thermal plasma with power density ≈ 2 W/cm^2. Via water contact angle measurement we found out that with increasing input power and increasing treatment time the hydrophilicity of PLA surface improved. The water contact angle significantly decreased just after 2–3 s long plasma treatment. We have observed changes on PLA surface after plasma treatment during storage up to 7 days. The samples treated in plasma less than 10 s became more hydrophobic when stored. The samples treated 10 s and longer showed same hydrophilic properties during storage, or even better than were measured recently after plasma treatment. Polar component of surface energy increased by 100 % of the nontreated sample value. FTIR measurement had shown minor changes in spectra at wavenumber of 1650 cm^{-1}, which can correspond to –N–H, –C=O functional bonds or it can signify cross-linking of polymer chains. FTIR measurement confirmed that this change in FTIR spectrum was caused by plasma treatment of PLA surface and not the heat from the plasma reactor.

Introduction

Polymeric plastic materials such as polymethyl-methacrylate (PMMA), polytethylene terephtalate (PET) and polyester (PE) had replaced the traditional materials (e.g. wood, glass, etc.). The invention and the use of these materials led to higher level living standard, but it also brought problems with multiplying waste, whose degradation time is in order of hundreds or even thousands of years [*Scott*, 2000]. Polylactic acid (PLA) is a polymer completely biodegradable under certain conditions (higher humidity and temperature) within 0.5–2 years and it decomposes to water and carbon dioxide. PLA is made from renewable resources (e.g. corn starch); it has excellent optical and good mechanical properties [*Vergne et al.*, 2011]. Therefore is PLA very promising material and it can be widely used in food packaging industry. Due to biocompatibility of PLA the second most promising field are medicinal applications such as various implants, sutures or drugs encapsulation, where PLA after certain time harmlessly decomposes in the body [*Lasprilla et al.*, 2012].

In packaging industry as well as in medicinal application some specific modification of surface are needed (e.g. printing, special coatings, cell attachment and proliferation). PLA has poor adhesive properties, therefore pre-treatment is needed to increase the adhesion (or hydrophilicity) of PLA surface [*De Geyter et al.*, 2010]. Wet chemical treatment of PLA surface, especially at higher temperature is not possible because of the degradation. With plasma treatment we can exclude the wet chemical treatment and obtain more hydrophilic surface for further processing [*Kima et al.*, 2009]. PLA decomposes at ≈ 200 °C [*Kirk-Othmer*, 1998], therefore low-temperature non-thermal plasma is needed, where the temperature of electrons is high and the temperature of heavy particles (atoms, molecules, ions, etc.) is lower than 200 °C.

Diffuse Coplanar Surface Barrier Discharge (DCSBD) [*Šimor et al.*, 2002] generates low-temperature non-thermal plasma at atmospheric pressure. DCSBD consists of two ridge-shape strip-like electrodes printed on Al_2O_3 dielectric plate. Discharge is supplied by high-frequency (≈ 18 kHz) high-voltage (amplitude 10 kV). Power applied to the DCSBD is in orders of hundreds of watts up to 500 W. Power density of thin layer of plasma is ≈ 2 W/cm^2. DCSBD plasma treatment has been successfully used also for polymer surface activation [*Černák et al.*, 2011, *Homola et al*, 2012].

Experimental setup

Material

NatureWorks® PLA Polymer 4042D foil (NatureWorks LLC, USA) with thickness of 0.5 mm was cut to dimension of 2 cm × 5.5 cm. For plasma treatment we used two kinds of samples: a) PLA as received; b) PLA cleaned in ethanol and then ultrasonicated in distilled water (20 °C) for 2 min.

Plasma treatment conditions

Samples were attached to the carrier cart by vacuum pump. To immerse the sample sufficiently into plasma, the distance of sample surface from the discharge plate was set to 0.3 mm. The input power to discharge was 300 W, 350 W and 400 W. The plasma treatment time varied from 1 up to 60 seconds. The sample was treated in dynamic regime, where the sample was moved through plasma layer to obtain homogenous surface treatment.

Contact angle measurement

Contact angles were measured by a DSA30 device (KRŰSS GmbH, Germany) using droplets of volume 2 µl. Number of droplets used to calculate the average value of water contact angle (WCA) on one sample was 20.

Free surface energy evaluation

Free surface energy was determined by Owens-Wendt method by the medium of 2 liquids: water and diiodomethan. Volume of droplets used for surface energy evaluation was 2 µl and number of droplets of each liquid per sample was 15.

Fourier transform infrared spectroscopy

Chemical structure of non-treated and plasma treated PLA surface was evaluated by Fourier Transform Infrared (FTIR) spectroscopy in attenuated total reflectance (ATR) using *Bruker Optics Vector 22*, *MIRacle™ spectrometer* (PIKE Technologies, USA). As the ATR crystal diamond/ZnSe was used (45°incidence angle). Data were collected in range 4000–500 cm^{-1} with 10 scans for each sample and resolution 4 cm^{-1}.

Results

The WCA values of non-treated PLA samples was 70.8° ± 1.17° in the case of as received sample and 70.4° ± 1.18° in the case of cleaned sample. In Fig. 2 we see WCA values dependence on input power measured on the surface of PLA after DCSBD plasma treatment. As we can see the WCA remains almost the same by the as received PLA sample. Because 300 W plasma treatment seemed to

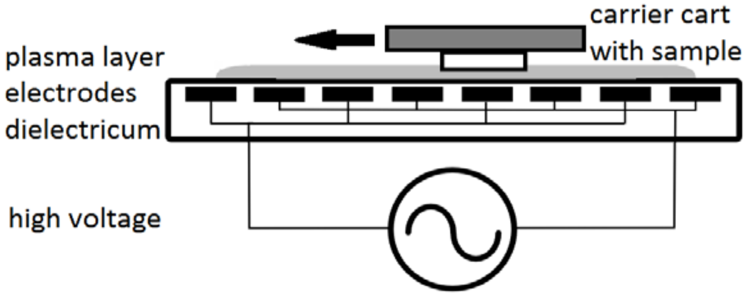

Figure 1. DCSBD discharge reactor in dynamic regime configuration [*Hergelová et al.*, 2012].

cause same changes as plasma treatment with higher input power, by further investigation of plasma treatment effect onto as received PLA sample input power of 300 W was used. WCA slightly decrease with increasing input power by cleaned PLA sample, hence we wanted to use the highest input power. But during PLA sample treatment at the input power of 400 W and longer treatment time (≈ 30 s) were the PLA samples overheated and then due to pumping of the sample attachment system unwanted degeneration of sample's shape occurred. Therefore we decided to use input power of 350 W by cleaned PLA sample.

Dependence of WCA on treatment time is in Fig. 3. As we can see by both samples, the WCA decreased to local minimum value after 2 or 3 s, than it slightly increased and at longer treatment time the values decreased to the global minimum of 53.2° ± 0.66° (as received) or 52.98° ± 1.22° (cleaned). First decrease of WCA to local minimum after 2–3 s was caused by new polar function groups formed on polymer surface. The consequent WCA values increase correspond to cross-linking of polymer chains via function groups formed deeper in the material after longer treatment time and functional groups formed on polymer surface. The WCA value global decrease after long treatment (30 s) and better hydrophilicity can signify polymer surface degradation and water

Free surface energy evaluation made from contact angle measurement showed increase of surface energy from 49.8 mJ/m^2 at non-treated sample to max. 57.0 mJ/m^2 after 10 s plasma treatment of as received PLA. In Fig. 4 we see that the disperse part of total surface energy after treatment remains at same level and the polar part increased by ≈ 100 %.

In the FTIR spectra in Fig. 5 we can see the more intensive peaks of PLA structure at the wavenumbers 1090 cm^{-1}, and 1748 cm^{-1}, which correspond to C=O bond, peak at 2947 cm^{-1} corresponding to $C–H_3$ and peak at 2995 cm^{-1} corresponding to C–H. Small changes occurred near the peak of C=O bond at 1748 cm^{-1}, as we can see in detail in Fig. 5 right. The peak at 1650 cm^{-1} was not visible after 3 s treatment, but with prolonging of the treatment time to 30–60 s the peak significantly increased.

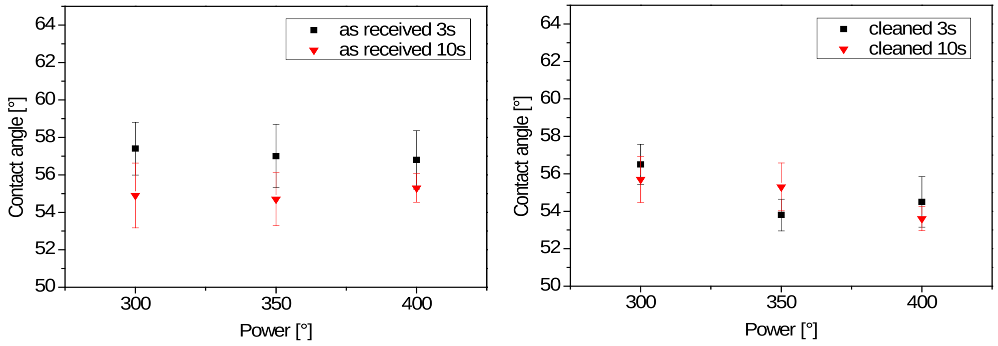

Figure 2. Water contact angle dependence on input power at treatment time 3 s and 10 s: left — PLA as received; right — PLA cleaned.

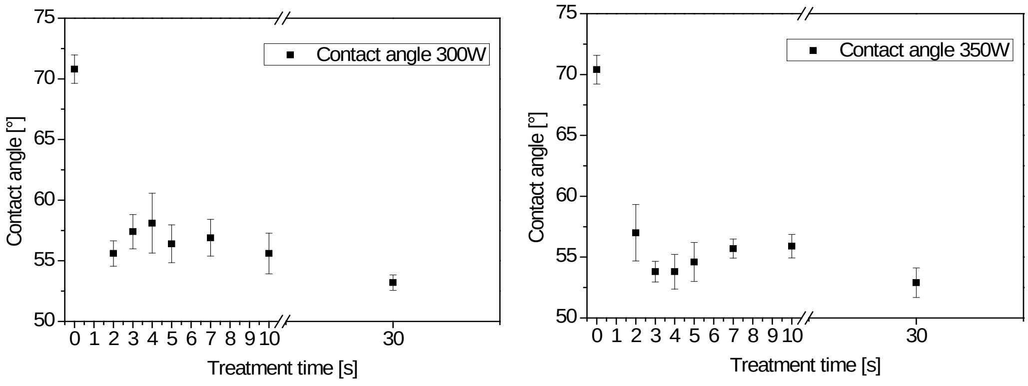

Figure 3. Water contact angle dependence on treatment time: left — PLA as received, input power 300 W; right — PLA cleaned, input power 350 W.

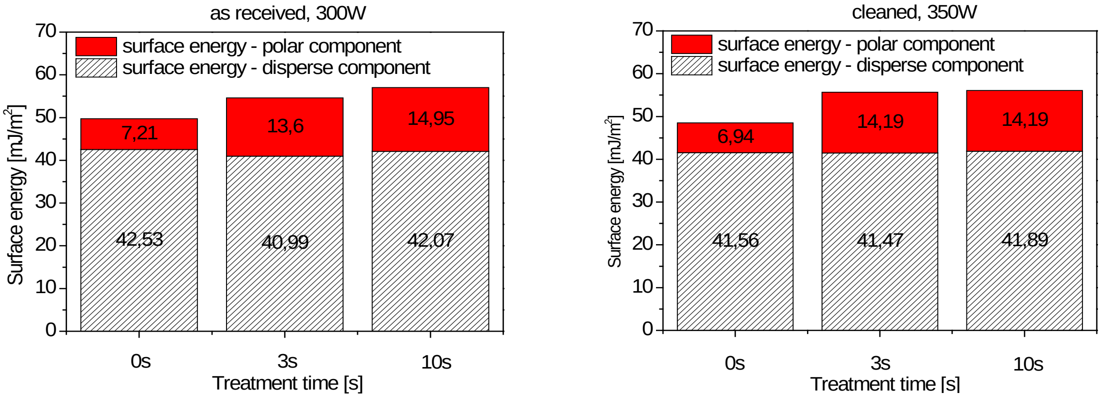

Figure 4. Free surface energy of PLA surface treated by DCSBD plasma: left — PLA as received, right — PLA cleaned.

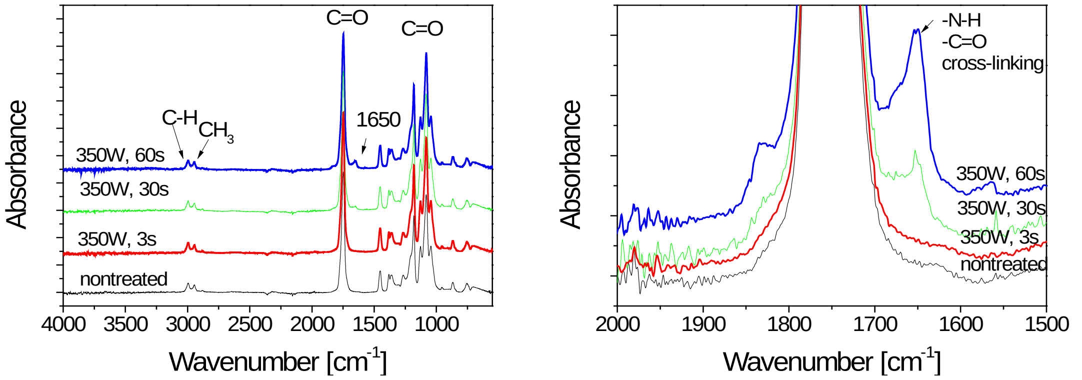

Figure 5. FTIR spectra of DCSBD plasma treated surface of cleaned PLA, input power 350 W: left — whole spectrum; right — detail of the peak at the wavenumber of 1650 cm^{-1}.

Ageing effect was studied via contact angle measurement and FTIR analysis. In Fig. 6 we can see changes in water contact angle measured on plasma treated PLA surface during storage after 1, 3, and 7 days. Trend of ageing depends on plasma treatment time. With longer treatment time the WCA increased less during storage, what can be well seen in Fig. 6 right. Free surface energy evaluation of the PLA samples of both types treated 10 s showed, that after 1 and 3 days of storage the total surface energy and its components remain the same. Little decrease by 3 mJ/m^2 was observed after 7 days of storage.

We studied ageing effect also via FTIR analysis. Measurements had shown the same changes in spectra at wavenumber 1650 cm^{-1}, which were mentioned previously. In contrast with Fig. 5 right, in Fig. 7 the peak at 1650 cm^{-1} of stored PLA sample treated 3 s increased after 6 days, but the peak of 30 s long treatment stayed at same level as immediately after treatment.

To ensure, that observed changes were caused by plasma, we heated PLA samples to 60 °C. No changes in FTIR spectra were observed.

Discussion

On the basis of the free surface energy increase, especially the polar component, and decrease of WCA after DCSBD plasma treatment we expect that new polar function groups were formed on PLA surface. This new functionality can be caused by oxygen built in the top of PLA surface, as it was detected previously by the DCSBD plasma treatment of other rigid polymers [e.g. PMMA, *Homola et al.*, 2012]. FTIR measurements didn't show significant changes in spectra made before treatment, after treatment and during storage. It means that the structure of PLA surface didn't change and that polymer structure was not destroyed by DCSBD plasma treatment. Little changes were measured also because plasma affected much thinner layer of PLA surface than was measured via FTIR-ATR

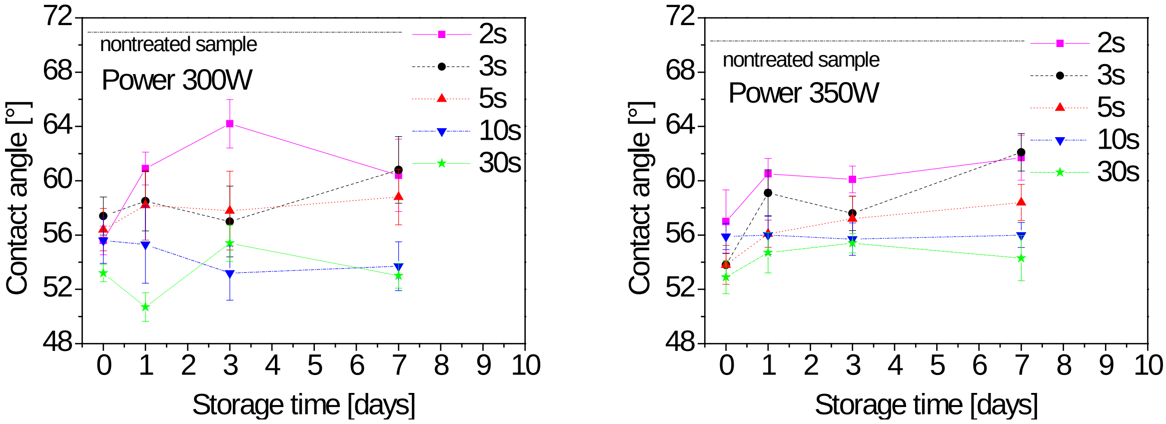

Figure 6. Changes in water contact angle on plasma treated PLA surface during storage in laboratory air : left — PLA as received, input power 300 W; right — PLA cleaned, input power 350 W.

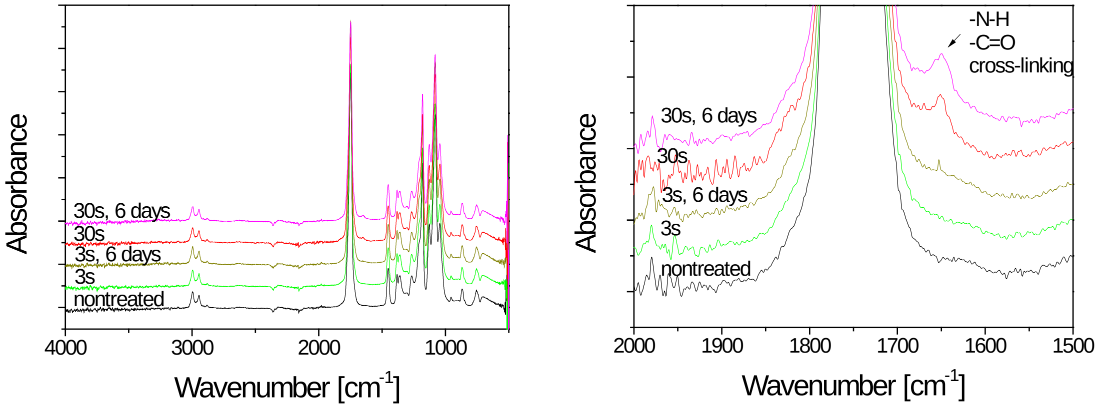

Figure 7. Ageing effect — FTIR spectra of DCSBD plasma treated surface of cleaned PLA, input power 350 W: left — whole spectrum; right — detail of the peak at the wavenumber of 1650 cm^{-1}.

technique. With FTIR-ATR measurement we obtained not only surface measurements but also unaffected volume measurements.

FTIR measurement had shown small increase of peak at wavenumber 1650 cm^{-1} after plasma treatment. This peak increased with longer treatment time. It can correspond to –N–H or –C=O functional bonds, of which –C=O is more probable, but both are at the end of appearance interval [*Milata et al.*, 2008]. After longer treatment time (30 s) was the peak formed right after plasma treatment and no changes were observed after 6 days of storage. This can be characteristic of cross-linking, where during longer treatment the polymer chain is cut and C=C bond is formed [*Yang et al.*, 2008]. After short treatment time (3 s) this peak was not formed. But due to post-treatment processes after 6 days of storage the peak at 1650 cm^{-1} appeared again.

Conclusion

We have studied the hydrophilic properties and chemical changes on PLA surface treated with low-temperature non-thermal plasma generated by DCSBD at atmospheric pressure. Water contact angle measurement had shown decrease of water contact angle with increasing input power and treatment time by both types of samples — as received and cleaned. FTIR measurement showed small increase of peak at wavenumber 1650 cm^{-1}, which can correspond to –N–H or –C=O functional bonds. It can also signify cross-linking of polymer chains after plasma treatment or partial change from L isomers to D isomers (as received is P(L)LA).

Total free surface energy increased after plasma treatment from 49.8 mJ/m^2 to ≈ 57.0 mJ/m^2 after 10 s plasma treatment. Increase of polar component of surface energy by 100 % indicates the presence of polar functional groups on PLA surface after DCSBD plasma treatment.

Trend of ageing effect depended on treatment time. With increasing treatment time the hydrophobic recovery of PLA surface was slower and the PLA surface treated longer than 10 s was even more hydrophilic during the storage. FTIR measurement had shown post-treatment processes especially by the samples with shorter plasma treatment (3 s). Further chemical analysis using XPS is needed to entirely understand the processes on PLA surface during plasma treatment and during the storage of treated samples.

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