Scanning Electron Microscopy Enhanced by Atmospheric Pressure Plasma

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Abstract: A gentle treatment of surfaces by an atmospheric pressure plasma is proposed as an analysis method combined with scanning electron microscopy (SEM). In particular, nonconductive and soft materials can be investigated by SEM in more detail, if this gentle plasma treatment is applied. In the study, we present an atmospheric pressure plasma jet 'hairline' which has been used for treatment of organic samples. The temperature profile and very low heating power of the hairline plasma has been characterized with Laser Schlieren Deflectometry. The plasma treatment reveals an intriguing crosslinking structure of the polymer network which cannot normally be approached with a conventional SEM. The microscopy has been provided by Secondary Electron Hyperspectral Imaging and by high resolution SEM.

Keywords: atmospheric pressure plasma, electron microscopy, LSD, organic materials

1. Introduction

Atmospheric pressure plasmas (APP) are used in versatile applications related to the surfaces, e.g. for thin film deposition, surface functionalisation, grafting, activation, cleaning or chemical etching. Many sources have been developed for a functional coating (e.g. barrier films, anticorrosion protection), adhesion improvement or even for wound healing [1, 2]. APP sources take part on the global technologic progress [3]. An unconventional approach with a different perspective on such applications is the use of stable and well-defined sources as a tool for material analysis. Here, we demonstrate how a gentle treatment improves scanning electron microscopy (SEM) of an organic materials. In particular, APP jets can be applied for this purpose because of their localized interaction with a sample (treated and non-treated areas can be controlled by an operator and compared in SEM) and because of a flexible operation at laboratory conditions (see Fig. 1).

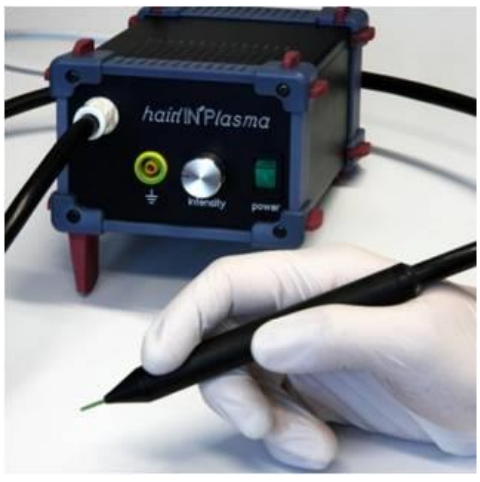

Fig. 1. Photography of the APP jet used for the local surface pre-treatment of samples in electron microscopy.

In biomedical applications, organic films which are biodegradable represent a hot topic for food science and implants production [4, 5]. Typical examples are polymers based on polyethylene oxide or polylactic acid. However, a highly resolved analysis of such materials is challenging because of their amorphous and smooth morphology combined with a sample sensitivity to the analytics. In particular, SEM at higher probe currents and voltages degrades the materials and an appropriate analysis cannot be provided. Hence, cryo-SEM or SEM with a low energy electron beam is required in this situation.

The latest progress in the field demonstrated the challenging analysis of soft materials by the modern electron microscopy. Secondary Electron Hyperspectral Imaging (SEHI) is the method successfully used for observing structural changes at the nanoscale of semicrystalline polypropylene, organic photovoltaics, and hierarchical biopolymers [5, 6]. The combination of SEHI and APP treatment represents an innovative promising approach which has never been applied for the characterisation of the class of biodegradable polymers, such as polylactic acid which is the polymer of focus of this study.

2. Materials and Methods

Thin film samples based on poly-lactic acid (PLA) has been prepared by plasma-assisted vacuum thermal deposition on a polished silicon wafer and they are described in [7]. Here, a smooth (RMS roughness < 10 nm) homogeneous sample has been chosen with thickness about 100 nm demonstrating the highest challenge for the morphologic investigation.

For the scanning electron microscopy of PLA samples, two microscopes have been used. The first one is a high-resolution SEM (JSM7500F by JEOL) with a field-

emission gun and secondary electron in-lens detector (maximum resolution of 1.0 nm at 15 keV). For the purpose of this study, the SEM has been operated at acceleration voltage of 2 kV. The samples have not been coated with any conductive films. The second SEM is Helios Nanolab G3 UC (by FEI) specifically designed for high resolution imaging at low voltages below 1 kV and capable of SEHI.

The PLA samples have been treated with the 'hairline' APP jet developed at INP [8] (Fig. 2). The plasma source is characterized by a straight thin argon filament with the optical diameter of ca. 0.1 mm and length in the scale of cm. Hairline plasma is operated with electrical power between 0.1 and 0.5 W (excitation frequency 1 – 3 kHz despite DC voltage of -10 to -20 kV) and with the argon flow rate of 500 sccm. The treatment time was 30 s.

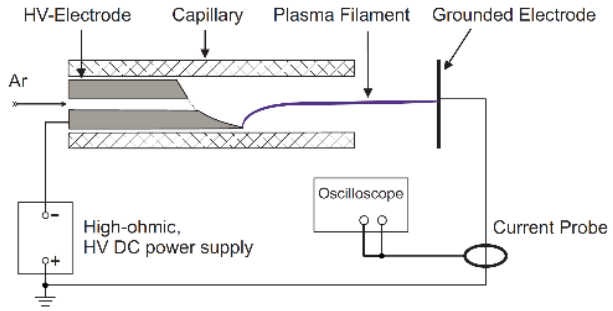

Fig. 2. Schema of the APP jet 'hairline plasma' [8].

3. Plasma characterisation

The energy balance of plasma treatment plays a crucial role for the resulting surface effects. Laser Schlieren Deflectometry (LSD) has been developed for the thermal characterisation of thin cold plasma filaments [9]. For the proposed application of APP in microscopy, the miniaturized plasma source (hairline plasma) is preferably considered. Hairline plasma has been analysed by LSD and the results are shown in Fig. 3.

The LSD analysis demonstrated the suitability of hairline plasma for treatment of PLA samples in the first approximation. Maximum temperature of the 10 ns lasting filament discharge is about 70 °C while the melting temperature of PLA is about 160 °C [10]. Assuming nonequilibrium chemistry, plasma – surface interaction can influence the surface structure partially also at lower temperatures. Hence, treatment time in order of seconds is suggested and interaction with softer parts and volatile components in the material could be expected.

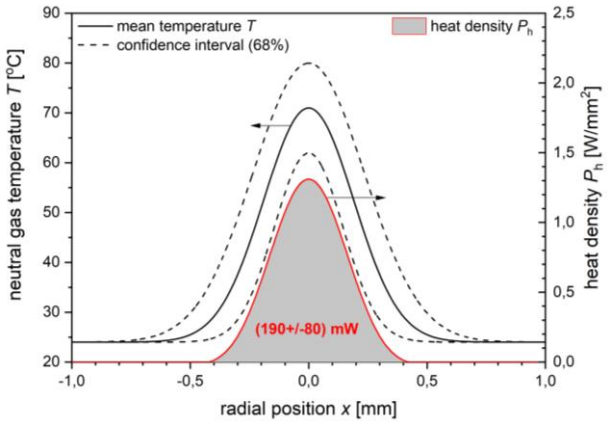

Fig. 3. Temperature and heat density profiles of hairline plasma obtained by LSD (Gauss model, δ_0=0.48 mrad, T_1=344 K, σ=270 µm, for details of LSD see [9]).

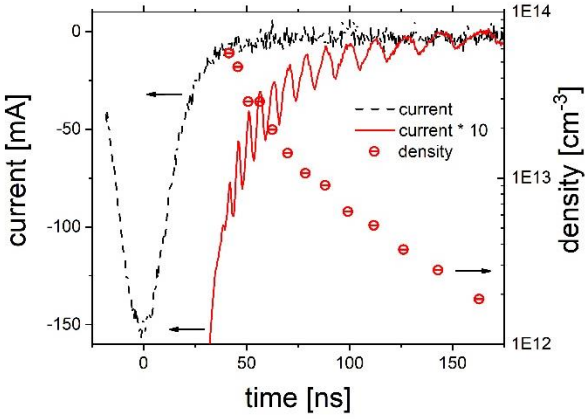

Fig. 4. Current signal and argon molecular ion density within the hairline plasma acquired by evaluating the plasma ion frequency [11].

A unique property of the plasma device used is the generation of high ion densities within small dimensions at atmospheric pressure (Fig. 4). By investigating electrical trace signals of ion acoustic waves from the plasma, the ion density can be distinguished and densities for molecular argon ions from $4 \cdot 10^{12}$ cm^{-3} up to 10^{14} cm^{-3} were measured within the pulse decay phase [11]. Molecular argon ions provide also a high kinetic energy and high mass for surface modifications. Further investigations indicate up to two orders of magnitude higher ion densities inside the main discharge for atomic argon ions.

4. Advanced Microscopy

Electron microscopy of the PLA sample without any plasma treatment is shown in Fig. 5. Evidently, the performance of both microscopes used is additionally limited by properties of the sample. The limits can be roughly illustrated by accessible magnification of this sample. In case of JSM7500F the maximum magnification was 7000, while the Helios achieved a contrasted image at 60000. Note, that a focus on small defects in the surface was helpful. Factor ten smaller magnification in Fig. 5.1b is obtained with a larger working distance (6.2 mm) compared to Fig. 5.2b (4.1 mm) and by a lower noise level in micrographs imaged by the Helios SEM designed for the high performance operation at low acceleration voltage. The micrograph in Fig. 5.2b suggests an existence of more crosslinked or crystallized domains in polymer structure of the PLA samples. However, the domains around the footprint of the polymer droplet (Fig. 5.2b) is not representative for the whole sample and the domains at a larger distance (>2 µm) cannot be resolved. Thus, the

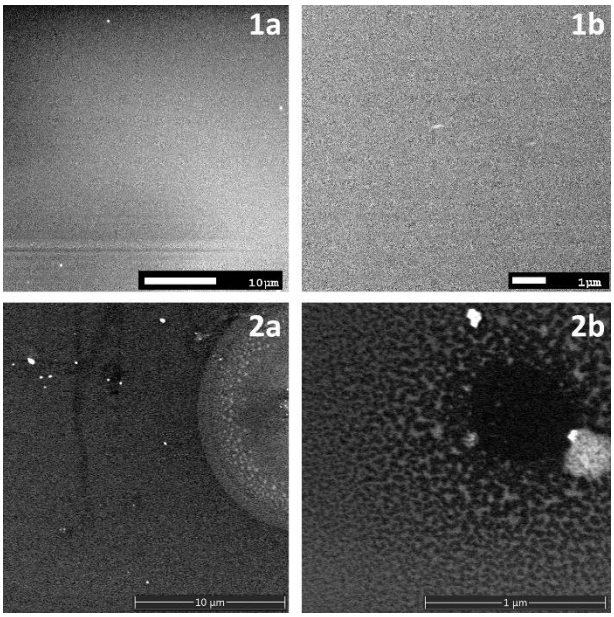

Fig. 5. SEM micrographs of the PLA sample (not plasma treated) at different scales (a – 10 µm, b – 1 µm) provided by JSM7500F (1) and Helios Nanolab G3 (2).

limitation by contrast and resolution motivates an application of plasma treatment for a deeper investigation of the PLA structure.

Indeed, the same PLA sample was treated by hairline plasma immediately before the SEM analysis. The SEM micrograph is shown in Fig. 6. In comparison to the untreated surface, the SEM magnification was increased to 80000 and highly resolved structure of PLA network was imaged as a result of the plasma treatment. We speculate that two fundamental mechanisms contribute to this result. The first is the selective sputtering of the upper surface layer. Due to this effect light molecular components which are expected in the plasma polymerized film can be removed from the material surface by plasma evaporation or chemical decomposition into volatile products. Finally, the large molecular structures remain and they can be visualized because of the modified surface topography. The nanodomain structure generated an interspace in the coating (dark areas) can also possibly indicate a coil-globule transition [11].

The second mechanism of the contrast enhancement is the charge transport and charge deposition. Compared with other APP, the hairline plasma is quite unique, for it generates a high amount of positive ions and even molecular argon ions with densities above 10^{14} cm^{-3} [12]. The microscopically structured non-conductive material binds the space charge depending on a local electric permittivity of molecular structure and surface topography. Thus, the charge distribution can enhance the surface contrasting and resolution during electron microscopy

The feasibility of the proposed method has been also tested by means of the other microscope JSM7500F. The obtained SEM micrograph of the same sample at the same location is displayed in Fig. 7. The observed nanoglobules are in an accordance with the previous SEM image (Fig. 6). Although the setting of both microscopes was similar (acceleration voltage 1 kV) Helios Nanolab achieved twice the resolution and four times the magnification for this sample.

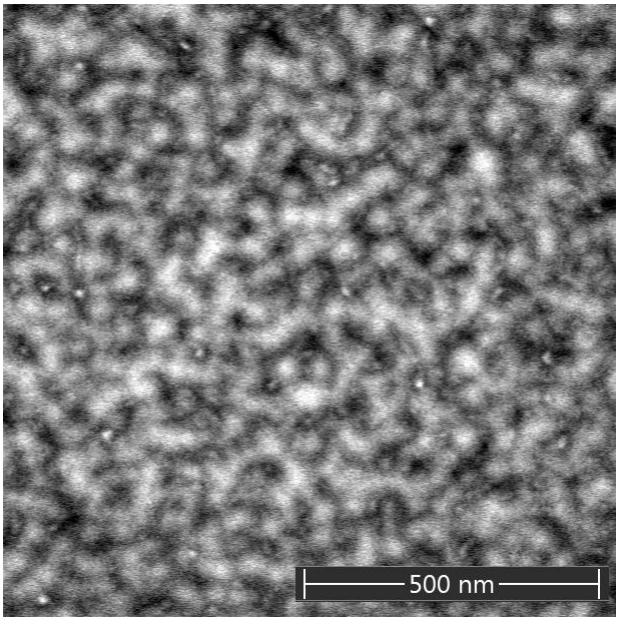

Fig. 6. SEM micrograph of the PLA sample (treated by hairline plasma) at magnification of 80 000 provided by Helios Nanolab G3, FEI.

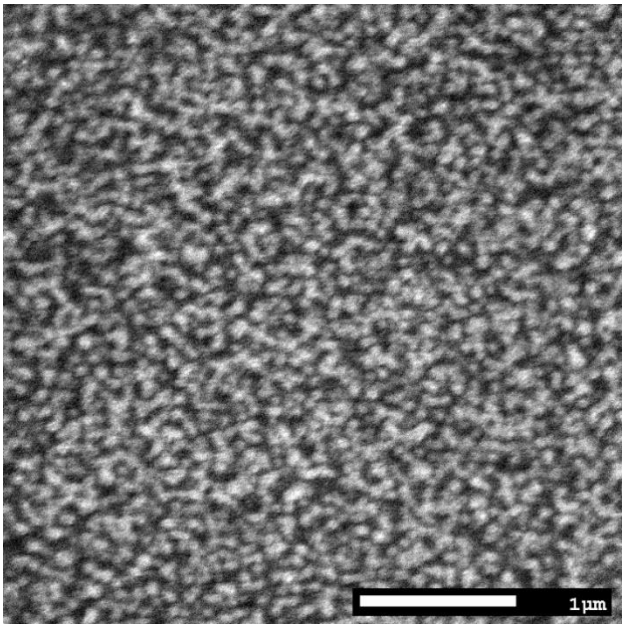

Fig. 7. SEM micrograph of the PLA sample treated by hairline plasma, magnification 20 000, JSM7500F JEOL.

5. Conclusion

The SEM analysis combined with the plasma treatment demonstrated PLA globules with diameter about 30 nm which are more crosslinked (light areas in the SEM micrographs). Additionally, small grains with diameter about 10 nm have been observed isolated in the surface.

SE microscopy has been performed on a sample of extremely small surface roughness (comparable with polished silicon wafer) and is sensitive to prolonged electron beam irradiation. Despite these barriers, plasma treatment using a 'hairline plasma' helped to reveal nanoscale molecular structure variations by electron microscopy. This was demonstrated by two SEMs. Based on these results we suggest the appropriate plasma treatment as a preparation method at the morphologic analysis of non-conductive surfaces.

Additionally, Laser Schlieren Deflectometry (LSD) was successfully applied for the spatial resolved characterisation of the hairline plasma. Thus, the specific thermal properties (maximum temperature 70 ^{o}C and heat power 190 mW) where considered for the application on the PLA sample.

6. Acknowledgement

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