Surface changes of poly-L-lactic acid due to annealing

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Abstract. Surface modifications are very important part of both current cutting-edge research and modern manufacturing. Our research is focused on poly-L-lactic acid, which is biocompatible and biodegradable polymer that offers applications in modern medicine. We observed morphological changes of the surface of metalized samples due to annealing and studied effect of modifications on total surface area and pore surface and volume. We observed that annealing of non-metalized samples had most pronounced effect up to the 70°C, after which all observed parameters dropped significantly. Metallization has changed behaviour of the samples significantly and resulted in generally lower surface area and porosity when compared to non-metalized samples.

1. Introduction
Surface of material plays very important part in it functional properties and final use and therefore modifications of various substrates are thoroughly researched. Many methods ranging from lithography through micro-printing to plasma treatment are implemented in both cutting-edge research and modern manufacturing processes [1-4]. This paper will focus on application of self-organization as this process is currently very attractive for research for several reasons. First, emergence of order from disorder is fascinating subject on its own. Second, practically every biological structure was created due to self-organization and therefore understanding mechanisms behind these processes can significantly help us understand existence of life [5-8]. Finally, self-organization has potential to revolutionize every aspect of technology and manufacturing as it offers way to improve properties of materials on macro-scale due to carefully organized structure on nano-scale, which is practically impossible to achieve by any other process [9-11].

In this paper we would like to present our work on unveiling mechanism behind self-organization due to metallization and subsequent thermal annealing of poly-L-lactic acid, a biocompatible and biodegradable polymer with promise of applications in medicine. Combination of these two methods is used for altering morphology of this polymer and formation ripple-like structures [12-14]. Modification of surface includes chemical and physical changes which both have very important role in bioapplications as they are crucial for cell growth [15]. Careful examination of the changes in total surface area, pore volume and area [16] gives us valuable data for better understanding what occurs during this modification.

2. Experimental
Biopolymer poly-L-lactic acid (PLLA, density 1.25 g•cm-3, glass transition temperature Tg = 60°C, crystallinity 60-70 %, thickness 50 µm, Goodfellow, Ltd., UK) was used in the presented experiments. Gold layers were deposited from Au target (99.999 %) by diode sputtering technique (BAL-TEC SCD 050 equipment, Switzerland). Typical sputtering conditions were: room temperature, sputtering times
10–300 s, argon (purity 99.997 %) pressure of about 5 Pa, electrode distance of 50 mm, electric current of 20 mA. Part of the samples were annealed at 60°C for 60 min (BINDER thermostat, Germany) and then cooled to room temperature in air.

Surface morphology and roughness of the samples were examined by means of atomic force microscopy (AFM). The AFM images were taken on VEECO CP II setup (Veeco, USA) in a tapping mode. Si probe RTESPA-CP with the spring constant 20–80 N•m⁻¹ was used. Roughness (Ra) represents the arithmetic average of the deviations from the centre plane of the sample [17].

Properties of porous CNPs (total surface area, total pore volume and pore size distribution) of were determined using a Colter SA 3100 (Beckman Colter) analyzer. The results were obtained by evaluation of the shape of BET isotherms of nitrogen absorption and desorption [16].

3. Results and discussion

Our samples preparation is shown in Figure 1. Pristine PLLA was sputtered with gold to form metal nanolayer on the surface. Part of these samples was studied as-sputtered, the rest was subsequently annealed. For AFM scans samples were treated only from one side, for surface area and porosity measurements both sides of the material were treated to achieve uniformity of the surface for this method.

Figure 2 shows AFM scans of PLLA samples. As-sputtered sample have smooth surface with few protruding “spikes”, which are more prominent on the sample with thinner metal layer. These structures are either impurities on the polymer surface or crystals that grew through the surface. This morphology changes drastically after annealing. Smooth surface is replaced by wrinkles formed over the surface. Size of the wrinkles directly depend on amount of sputtered gold. We can also observe preferential orientation of the wrinkles, which is particularly prominent on samples with 10 nm thick gold layer.

Figure 3 shows surface area, pore volume and surface as obtained by BET isotherms of nitrogen absorption and desorption. We observed that pristine PLLA has small total surface area and porosity. These properties significantly increase due to annealing above glass transition temperature peaking at 70°C. These changes are probably due to uneven expansion of polymer and formation of pores inside the material. At this temperature, longer polymer chains are still capable of holding the structure during annealing therefore we can observe this large change in both total surface area and porosity. On the other hand, on the samples annealed at higher temperatures (80 and 90°C) we observed sharp drop of both surface area and porosity when compared to samples treated at lower temperatures. We assume that after this temperature material viscosity is either low enough to compensate for thermal caused expansion or longer polymer chains are not capable of holding pores open. Both of these effects, or their combination, lead to one observed effect: pores are not present in material after cooling back to room temperature and measurement.
To compare, we also tested metalized samples. They showed in general lower both surface area and porosity when compared to their non-metalized counterparts. We assume that changes in material due to annealing are transformed into wrinkling on the surface thanks to the metal layer. We also observe sharp increase in total surface area for the sample with thickest metal layer, while porosity remains very similar to samples with thinner metal layers. In this case surface structure is responsible for this additional surface, while porosity changes only slightly.

This change of behaviour led us to the idea of principle behind wrinkle formation. We assume that there is some residual stress in the polymer, probably from manufacturing process, which is responsible for wrinkle formation. To support this assumption we prepared four samples with carefully marking their original orientation on the polymer foil. These samples were subsequently sputtered with gold layer and annealed with various combinations of deviations from original orientation to rule out that orientation of the samples during either sputtering or annealing have any effect on the final wrinkle orientation. Afterwards samples were arranged so that they had same orientation as in the original polymer foil and observed by means of AFM. Observed orientation of wrinkles differed by less than 10° from each other and therefore orientation during sample preparation has no significant effect on final wrinkle orientation, therefore reason behind ripple-like structure formation must be intrinsic property of polymer foil: most probably internal stress from manufacturing process as we suggested. This corresponds well with our findings. Material directly from manufacturing has low porosity in comparison with annealed samples. Annealing allows release of the internal stress from rearrangement of polymer and formation of pores as shown in Figure 3. Higher temperatures (more than 80°C) may allow release of stress by creep or flow of polymer chains in addition to pore formation (and their subsequent collapse), therefore observed increase is significantly smaller. In comparison to this, metal allows another mechanism of stress release: by wrinkling. Due to different thermal expansion coefficients of PLLA and gold local instabilities appear during annealing that force polymer rearrangement, resulting in release of internal stress. This corresponds well with observed almost non-existent porosity of metalized samples.

Figure 2 Afm scans of as-sputtered (left) and annealed (right) samples with 10 and 40 nm thick gold layer.
Figure 3 Graph showing total surface area, pore volume and surface obtained by evaluation of BET isotherms

4. Conclusion

Annealing of samples causes significant changes to surface morphology and porosity of PLLA. Annealing of pristine PLLA resulted in significant changes to both surface area and porosity of the samples, while most pronounced change was on samples treated at 70°C. Higher temperatures caused collapse of polymer structure and porosity sharply dropped. On the other hand metalized samples had only small changes in porosity after annealing but we observed increase of surface area due to wrinkling, especially on samples with thicker gold layer. Based on the obtained data, we suggest that both increase in porosity and wrinkling are mechanisms of stress release that is inherent to original polymer foil and originates probably from manufacturing process. These data offers us insight into this mechanisms and base for other experiments with PLLA.

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6. References

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