THE VIBRATIONAL SPECTROSCOPY OF BIOCOMPATIBLE POLYMERS

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Biodegradable polymers are currently used in drug delivery and tissue engineering, polycaprolactone (PCL) being one of the most widely used materials. PCL acts as a bioresorbable scaffold having the ability to stimulate tissue growth. Its surface and bulk structure affects the cell adhesion and the scaffold's lifetime. The surface coating by titanium nitride is applied to increase cell adhesion to the samples, and in the future — implants. The deposition of thin titanium nitride coatings on the fibrous scaffolds' surface enhances cell adhesion [1].At the same time, the process of coating the polymer scaffolds may modify its crystalline structure. Here, we aim at investigating the structural modifications in polycaprolactone coated with titanium nitride using Raman spectroscopy.

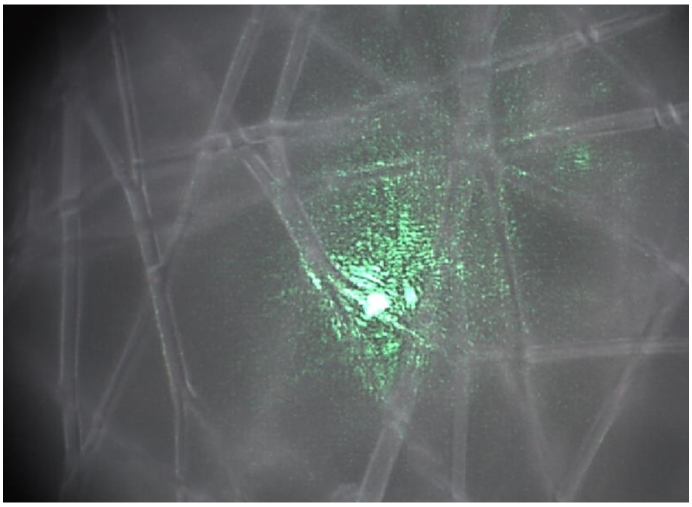

Figure 1. The fiber structure of the sample with green laser

The work was completed according to specifications: on one side of samples produced by the method of electrospinning from polycaprolactone (PCL) with a molecular weight of 80 000 had been deposited thin coating of TiN (titanium nitride) by magnetron sputtering [2]. One of the first goals is to evaluate whether it is possible to see differences that occur by changing the degree of PCL crystallinity depending on coating time from 0 to 240 seconds. Increasing the deposition time increases the amount of titanium nitride on the surface.

The method of Raman spectroscopy was selected for several reasons: the need for samples of small size, simplicity of sample preparation, access to a large amount of information, nondestructive and noncontact analysis. Raman spectroscopy is an optical spectroscopy based on the ability of the studied systems (molecules) to inelastically scatter monochromatic light. The sample is irradiated with a laser of 532 nm wavelength, and the Raman spectra is acquired using a Centaur U HR spectrometer; other lasers with wavelengths 405 nm (violet) and 785 nm (near-infrared) were used in a Renishaw Raman spectrometer. For each sample, at least two points were measured. Previous work showed the dependence of the width of the Raman peaks on the crystallinity of PCL.[2] We analyzed the Raman peaks at 2905, 2852, 1720, 1280, 1110 cm^{-1}, but only 2 peaks have information about crystallinity: 1110 cm^{-1} and 1280 cm^{-1}. The spectra were filtered to remove cosmic rays, the background was subtracted, then all the spectra were normalized and compared. The dependence of the full width at half-maximum from the samples with different coating times of titanium nitride was investigated. The results shown in Figure 2 demonstrate us that samples with longer coating time up to 120 s measured with 532 nm laser source have a smaller full width at half-maximum (FWHM), as seen in figure 2, consequently crystallinity of this samples is greater. At the coating time of 240 s the FWHM increases again.

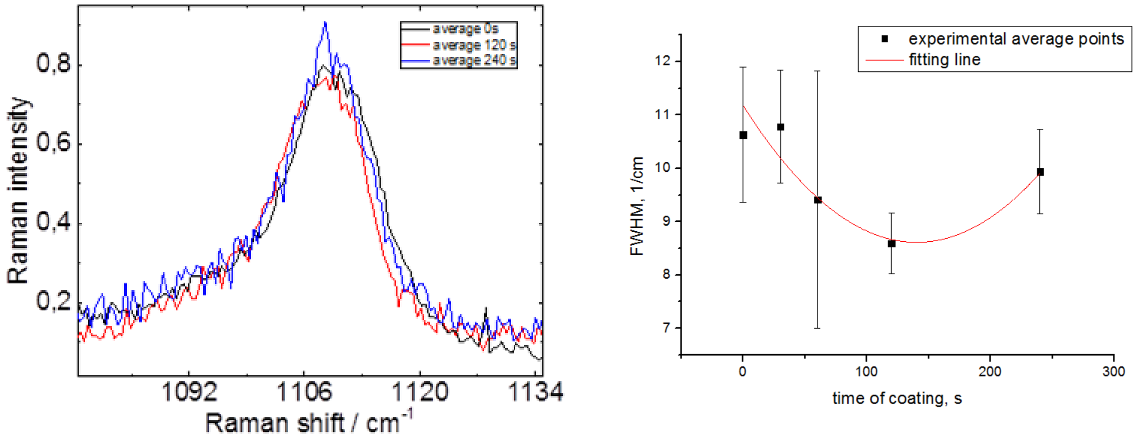

Figure 2. Left: Averaged Raman spectra in the region of the Raman peak ~1110 cm^{-1}.
Right: The dependence of the FWHM of the peak at 1100 cm^{-1}
on the coating time using green laser with wavelength 532 nm

Previous studies showed that longer coating times result in improved crystallinity of the scaffolds due to the preferential destruction of the amorphous regions of the polymer in the process of titanium deposition. Also, the heating of the polymer material during the treatment promotes the crystallization process. The increase of crystallinity of PCL fibers is known to lead to the increase in their Young's modulus and mechanical strength [3].

A more thorough evaluation and the comparison of the results with the crystallinity obtained by other characterization methods (such as differential scanning calorimetry (DSC), X-ray diffraction (XRD) and direct measurements of mechanical properties by uniaxial stretching) could establish Raman spectroscopy as a good alternative method for non-destructive testing of crystallinity and mechanical properties of PCL electrospun scaffolds. That is why further work will aim at correlating crystallinity and mechanical properties of PCL electrospun scaffolds obtained by different methods.

Acknowledgements. The authors thank I.N. Lapin from Tomsk State University, Russia, for performing Raman measurements with 785 and 405 nm excitation.

References

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