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ANALYSIS AND DEVELOPMENT OF THE ADHESION OF STENT COATINGS

Abstract: The influence of the surface roughness on adhesion strength of polyurethane coating on stainless steel alloy (316LVM) is introduced. These coatings are one of the development directions in coronary stent production. One of the widely spread stent base material is the 316LVM, so in the presented study these materials were involved. The samples were prepared by etching and electro-polishing. The current density and polishing time were changed to create samples with different surface roughness. After electro-polishing polyurethane (Chronoflex®) coating was applied. The adhesion of the coating on different surfaces was tested by scratch test (nano indenter technique). The increasing surface roughness gives stronger adhesion. According to our experiments it was concluded that the coronary stents, treated by etching without polishing could cut out the balloons during expansion, therefore the surface roughness should be under this value. It is recommended to use an electro-chemical treatment that is resulting Ra=1.5-2.0 μm roughness.

1. Introduction

The significance of biomedical engineering is continuously increasing all over the world [1]. There has been a great leap forward in the field of surface treatments for metallic coronary stents to improve their biocompatibility. Stent coating is an important factor for stent design, influencing both angiographic and clinical outcomes [2,3]. The coating can protect the metallic surface of the stent from corrosion attack caused by the biological environment [4] though coatings in general have potential disadvantages relating to cracks and discontinuities, fluid seepage, and delamination [5].

However, usage of bare metal stents is widespread, in order to reduce non-desirable complications, new coatings have been developed. The hope of overcoming the natural roughness of bare metal was one of the first reasons to coat bare metal stents with polymers [6,7].

Non-biodegradable polymer coatings can serve as a shield against corrosion and also as a platform for improving the biocompatibility of the device [6,8,9] adhesion of such films to their substrates has been the subject of several studies [10]. E. Gallino et al. developed a process to coat the stainless steel surface from the biological environment by depositing an ultra-thin uniform, cohesive and adhesive plasma polymerized allylamine coating [4]. F. Lewis et al investigated the adhesion properties of fluorocarbon films of three different thicknesses deposited by plasma polymerization. Among the coatings with different thicknesses studied, only those with a thickness of 36 nm exhibited the required cohesion and interfacial adhesion to resist the stent expansion without cracking or delaminating. Otherwise, cracks were detected in the coatings having thicknesses equal or superior to 100 nm, indicating a lack of cohesion [11]. Polymeric coatings should be resistant during implantation and expansion of the stent [12]. The CSM Scratch Testers are ideal instruments for characterizing the surface mechanical properties of thin films and coatings [13]. S. J. Bull et al investigated scratch adhesion behaviour of relatively thick hard coatings on soft substrates thin hard coatings on hard substrates. The residual stress in the coating has been carefully determined and the quantification is expected to be more accurate [14]. D. Vodnick et al. used a new energy-based method has been proposed to quantitatively assess the interfacial adhesion of soft films on compliant substrates with complex geometries. The method utilizes a scratching technique to determine energy required to delaminate a unit of area of coating while taking into account energy lost to substrate deformation [15].

Widely spread technique is the scratch test to characterize the adhesive strength of the coating-substrate system. During the scratch test, the sample is displaced at constant speed and at a certain load, damage occurs along the scratch path. This load value is the critical load [16]. The critical load depends on coating adhesion, but also on several other parameters; some are directly related to the test itself whereas others are related to the coating-substrate combination [17,18].

In our study we submit the impact of the surface roughness on adhesion strength of polyurethane coating on 316LVM substrate exemplified with results of a complex materials analysis process.

2. Materials and methods

Samples: Stainless steel alloy (316LVM) tube slices were used as samples, which were produced by laser cutting in longitudinal direction at every 120 degree of a tube, which original measures were 1800 µm diameter and 120 µm wall thickness. Two small holes were placed at the ends of the tube slices to fix the samples without damage. The lengths of the specimens were 11 mm. This type of tube is already used in stent production.

Sample preparation: The laser cut process of the samples is followed by the surface preparation, which is extremely important for the coating's adhesion and the removing of the laser-cutting burr. The first step of the surface preparation is the etching. Etching was done by using etchant and ultrasonic agitation. The etchant was mixed from equal portion of HCl 35% w/w (hydrogen chloride) and HNO_3 65% w/w (nitric acid) which was diluted in 1:3 proportions (50 ml etchant mixed with 150 ml distilled water). Each etching process lasted for

5 minutes because this way the elimination of the oxide layer and burr, created by the laser cutting, was ensured.

Electro-polishing (EP) was applied on the etched and dried samples. The composition of the electrolyte was H_2O + H_3PO_4 88% w/w (phosphorus acid) + H_2SO_4 96% w/w (sulphuric acid) with the same rate. To reach different surface roughness the polishing parameters were changed.

The surface area of the tube slices was 73.68 mm^2. The base material particles issued by laser cutting process, have exfoliated by the etching. Then the following electro-polishing have resulted a smooth surface.

The coating: By using the dipping technology a passive, i.e. even surface polyurethane coating was created. The etched and electro-polished tube slices were coated in three layers by a 2% solution of Chronoflex® polyurethane. The coatings were prepared from a not mixed and evenly dried solution on room temperature.

Measuring of the surface roughness: Evenness and smoothness of surface of the tube slices was influenced by the electro-polishing parameters in order to examine the relation between the surface roughness and the adhesion (0.01 A/mm^2 and 30 s, 60 s, 90 s, 120 s, 150 s). The current density of the electro-polishing was chosen to be 0.01 A/mm2 because the further augmentation of the electricity in the case of such sample had caused a rough surface and the foaming of the electrolyte. The decrease of the current significantly increased the necessary time for polishing because the elimination of the greater roughness summits has higher time consumption. In the course of electro-polishing one of the tube slice holes was used to grip and we hang the samples into the electrolyte to polish. Then the surface roughness of the samples was examined with Zeiss LSM 510 META confocal microscope, so thus an objective and numerical result was received regarding to the average roughness. Before applying the coating, the effect of the different electro-polishing parameters on the surface roughness was examined on the surface treated samples. The samples were examined with equal settings at the same location, i.e. in the middle of the sample. Both the external and the internal surfaces of the samples were examined which is important because the stent is fabricated from the same type of tube, so it must be determined the two surfaces.

The measuring of the adhesion of the coatings: The adhesion of the coating on different surfaces was tested by scratch test (nano indenter technique), because this method is appropriate for such a small devices, as stents. A CSM Micro Combi Tester (MCT) was used to examine the coating's adhesion. In the process the MCT pulls a diamond Rockwell indenter along a straight line with a controlled normal force (FN) on the sample's surface. During this, the frictional force, the acoustic emission and the needle's penetration depth are registered. The evaluation is based once on the optical microscopy analysis of the scratches and secondly on the order of the coating's typical scaling methods to the normal force value on a given section.

The indenter's loading was increased from 0.04 N to 1.5 N according to the linear program of 2.09 N/min loading rate, the indenter's moving speed was 10 mm/min as well as it was set at the pre-experiments. The length of the scratches varied between 2.5 mm and 7 mm.

Examination of coating topography: The topography of the coated samples was examined by atomic force microscopy (AFM). AFM was used in contact mode to analyse the samples.

3. Results

The examination results show that the increasing electro-polishing time decreases the surface roughness until a certain limit in both inner and external surfaces. Figure 1a shows the results of the electro-polishing. One can see in Figure 1a reaching 150 s the sample's surface becomes smooth and the surface roughness does not decrease further; thus the external surface was considered significant because this territory attaches with the vascular wall and gets the highest level of stress as well. The parameters that are belonging to lowest surface roughness are 0.01 A/mm^2 and 90-150 s. These parameters give 1.2 µm average surface roughness. However to achieve a better adhesion of the coating a rougher surface was needed than the lowest roughness.

The surface topology was evaluated according to pictures created by a confocal microscope once in normal mode and then in inverse mode. The comparison of them shows clearly that quite a lot of pits exist on the surfaces that cannot be removed even with electro-polishing. This means that the coating is going to be thicker at these which phenomenon is not disadvantageous; moreover, it can correct the surface's adhesion with filling the hole by shape closing (anchoring effect).

Earlier experiences show that the etching in itself is not suitable as a stent surface treatment process, because the high surface roughness can cause damage of the balloon. The coating has a smoothing effect because the coating layer which is adhered to the sharp edges makes them rounded. Chronoflex® polyurethane coating was applied in 3 layers made from a 2% solution on the surface of the etched and electro-polished tube slices. Untreated samples were also involved, but the coating did not fully cover its surface due to the sample's high surface roughness, so it was excluded from further examinations. The 90-150 s electro-polishing times result closely the same surface roughness therefore 30 s, 60 s and the 90 s electro-polished samples were examined by scratch test.

The scratching techniques were defined (the loading program and the indenter radius) which can examine the sensitive layers in the MCT machine's mN measuring domain. At pre-experiments indenters with a 10 µm or 50 µm radius were used, but in these cases the coatings immediately peeled off and the needle started to scratch the 316 LVM raw material too. Finally, a diamond indenter with 200 µm tip radius was used for the measurements.

During the scratch tests, the average normal force was measured what can cause the laceration of the coating. The indenter forced to penetrate into the coating by this force (FN) which is normal to the plane of the coating.

The coating of 30 s electro-polished tube slice (by 0.01 A/mm^2) started to lacerate at FN=0.36 N average normal force, but according to Figure 1b the increasing electro-polishing time (which means smaller surface roughness) cause decreasing normal force. We can conclude that decrease of the surface roughness come with the decreasing of the coating adhesion. One can see in Figure 1b the normal force which is belongs to the 90 s electro-polished samples is FN=0.2 N.

One can see in Figure 2a the 60 s electro-polished (the average surface roughness is 1.48 µm) and coated surface of a tube slice. This picture has been captured when the normal force has reached the critical value what is necessary to lacerate the coating. Figure 2a shows the indenter remove the coating but do not harm the surface of the substrate. So the measured value is not affected by the substrate, it is represent only the adhesion of the coating.

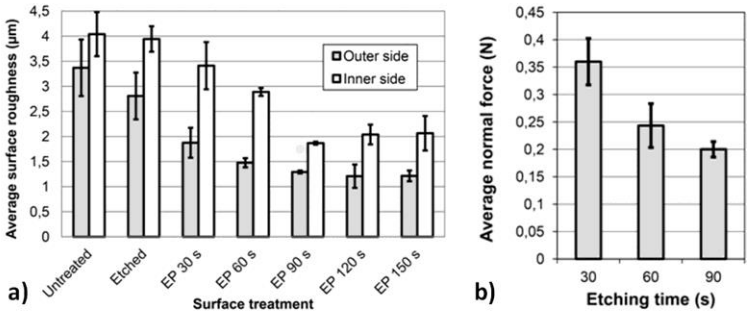

Fig. 1 a) The average outer and inner roughness of the differently electro-polished samples b) Normal force where the coating is peeled off during the scratch test (200 µm radius; 2,09 N/min loading rate)

The etchant attacks primarily the significantly prominent roughness peaks and grain boundaries, so we do not recommend using the simply etched surfaces because it can damage the balloon. The atomic force microscopic image (Figure 2b) shows clearly, that the surface roughness of the etched samples cannot significantly decreased by the coating especially in the case of high surface level differences. Figure 2b shows a simply etched sample which is coated in 1% polyurethane solution with 3 layers. The grain boundaries are still recognizable over the coating in the form of through of wave.

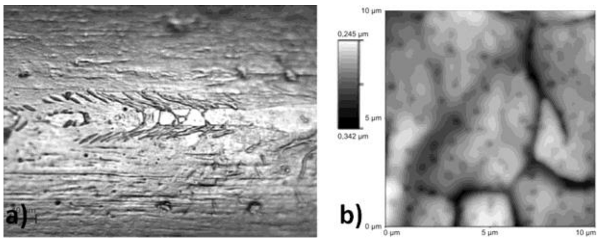

Fig. 2 a) The damaged coating after scratch test (FN=0.25 N) (Scratch direction: left to right; indenter radius: 200 µm; EP parameters: 0.01 A/mm2 and 60 s) b) AFM contact mode image of coated (1% PUR solution 3 times) sample

The surface roughness resulted by etching is too high, that is why it is not admissible. Further electro-polishing is necessary to remove the highest surface peaks.

4. Conclusion

At diagnosing the maximum roughness, it is necessary to take into consideration the requirements of the stent-production technology as well. According to our experiments, those stents that have been treated simply by etched might cut out the balloons during expansion. The coating itself cannot palliate significantly the sharp edges. Besides this, the electro-polishing through the evolved oxide layer makes the surface more resistance against corrosion, thus the surface becomes passive.

In virtue of this, considering both the Chronoflex® coating's adhesion characteristics and the potential maximum useable with material detaching requirements of the stent production technology, in order to reach the strongest adhesion of the stent coatings, it is expedient to use an electrochemical treatment of an Ra=1,5-2,0 µm rated roughness on the external surface. To reach the suggested surface roughness in case of 316LVM substrate is necessary 5 minutes chemical etching and electro-polishing (0.01 A/mm^2; 30 s).

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