EXAMINATION OF THE COATINGS OF CORONARY STENTS

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ABSTRACT

In our study the main properties of coated coronary stents are shown, such as foreshortening, recoil, surface features and failures and the expansion properties. The types and the effects of active and passive coatings are introduced. The results of our examinations with different coated coronary stents are shown as well.

KEYWORDS

coated coronary stent, passive coating, active coating

1 INTRODUCTION

In Hungary, the disease of the coronary arteries is one of the most frequent illnesses and it often leads to heart attack or early death. The treatment of these illnesses is a developing section, so it gives a lot of possibilities to the engineers as well. Therefore, there are numerous of new materials. Intravascular stents are small tube-like structures expanded into stenotic arteries to restore blood flow perfusion to the downstream tissues. The stent is mounted on a balloon catheter and delivered to the site of blockage. When the balloon is inflated, the stent expands and is pressed against the inner wall of the coronary artery. After the balloon is deflated and removed, the stent remains in place, keeping the artery open, so they help the blood to flow through [1]. Their function is to prevent restenosis in the coronary arteries. They are innovative devices, designed to be a minimally invasive treatment option for patients. This treatment results in shorter hospital stays [2].

2 MATERIALS OF THE COATINGS

The materials of stents are usually stainless steels, cobalt-chromium alloys, Mg-alloys, polymers or nitinol [2]. There exist coated and uncoated stents as well. In the expanded part of the artery, the chance of thrombosis is bigger, without stent as well, so it is practical to coat the stents. There are two main types of the coatings: passive and active coatings [3, 4].

Passive coatings. The main advantage of passive coated stents is that they are invisible for the ambient tissues. Passive coatings have to assure the optimal interaction with blood and

the wall of the artery. It has to inhibit the alluvium of the cells on the surface. Because of the complexity of the blood, it is really difficult to construct reliable passive coatings [5].

– *Precious metals.* Gold is a highly radiopaque and biocompatible material. Hence, coating stainless steel stents with gold enhances radio visibility and allows precise stent positioning [6]. In contrast to the expected effect, the rate of restenosis has grown at gold coated stents, but the pure gold Tentaur stents showed positive results [6, 7].

– *Oxide, nitride and carbide coatings (carbon, SiO_2, TiNOX, SiC).* Nowadays, these coatings are very prevalent, especially Diamond Like Coating (DLC) and TiNOX. The use of DLC coatings for implantable medical devices has been investigated with respect to bioresponse, corrosion resistance and the impact of device fabrication/operation upon coating integrity for stents. Revascularization with titanium-nitride-oxide – coated stents appears safe and effective in patients with de novo coronary artery lesions and that titanium-nitride-oxide–coated stents reduce restenosis and major adverse cardiac events compared with stainless steel stents of otherwise identical design [8, 9, 10].

– *Silicone and other polymers (PE, PP).* The chemical, material and mechanical properties of the synthetic polymers are variable on a wide range and easy to shape them.

– *Human polymers (phosphorylcholine, fibrin, elastin, hyalurons acid).* The phosphorylcholine is nonallergenic because it is a normal component of human cell membranes; it decreases platelet adhesion and, hence, thrombus formation; it elicits less adverse tissue response unlike other polymers, and thus creates potentially less chance of restenosis; and it may serve as a vehicle for local drug delivery [6], so human polymers could be active or passive coatings as well.

Active coatings. Active coatings obstruct the activation of the platelets. There are two types of active coatings: bonded drugs and radioactive coatings. The drugs were bonded by the help of some kind of matrix on the surface of the stent. Their main role is to obstruct the platelet-activation and the rise of antithrombotic effect. The bind of the drugs can be incorporation into a polymer, direct drug loading onto the stent, porous ceramics or PC-coatings. Without a carrier polymer the 40% of the agent gets lost during the expansion. There are two types of the binding of the drugs to the polymer: matrixing and conjugation. Matrixing means that the polymer and the drugs were mixed together, so the drug molecules has random place in the coating. There is no chemical bandage, so thus the agent-liberation is controlled only by the diffusion. The other way, conjugation means that there is a covalent bandage between the drug and the polymer. In the structural conformation, the molecules of the agent and the polymer have a regular order. The agent is able to get out from the polymer only when it dissolves, because of the chemical bandage. Dissolving of the polymer can occur by surface erosion or by the enzymes of the blood [11, 12, 13].

The five main groups of the drugs by their effect for the human system:

– Anti-proliferative (Colhicine, Paclitaxel)
– Anti-thrombins (Hirudin, Glicocalix)
– Immunomodulators (Sirolimus, Tacrolimus)
– Anti-migration (Probucol)
– Promote healing endothelization (NO donors).

The other method, called brachytherapy is an intravascular solution. Either of the methods is to implant emitter stents, but there is a big problem, called edge effect. Edge effect means that restenosis is bigger near to the edge of the emitter stent. Probably the reason for this is that the dose of emitting intensifies the intimal hyperplasia. Therefore, the so-called “cold”, not radioactive stent-edge and the so-called “warm”, radioactive stent-edge were tested, but they didn’t work [12].

3 TESTING METHODS

For the expansion of the passive coated stents two in vitro methods were tried. At the first method mid-air expansion was used and at the second method the stents were expanded in an in vitro system and during the examination physiological tincture were flown through it. The balloons were expanded above their nominal pressure (to 20 bars), simulated the clinical use of them. Before, during and after expansion the coating was examined mostly on the curves and it was analysed by different methods (stereomicroscope, scanning electron microscope and energy dispersive x-ray microanalysator). Different methods were assembled for the examination of fatigue properties of the coatings.

BiodivYsio^{TM} *stent.* The material of this stent is stainless steel, 316L, coated with phosphorilcoline. The struts have rectangle shape and they are rounded. The nominal diameter of this stent is 3 mm and the nominal length is 15 mm. Mid-air expansion was used (Fig. 1, 2). Before expansion, the coating of this stent had a good quality; the whole coating was uniform. After expansion the coating of the stent peeled off (Fig. 3, 4).

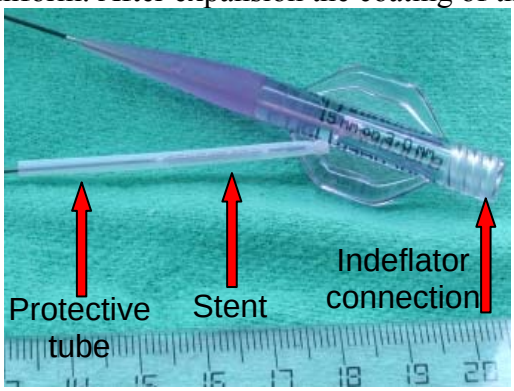

Figure 1. The stent transport system

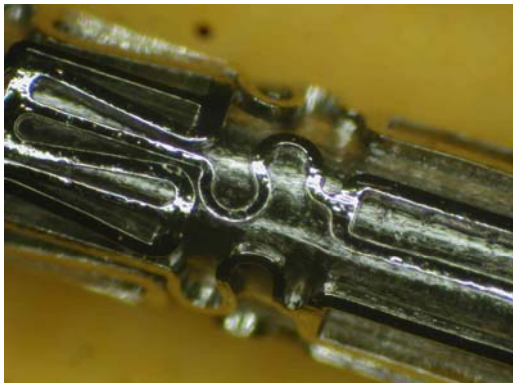

Figure 2. Before expansion

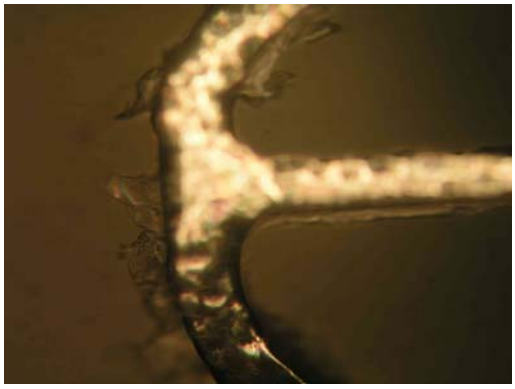

Figure 3. After expansion; the coating slivered off, N=100×

Figure 4. After expansion, the peeled off coating, N=100×

The foreshortening (4.13 %) and recoil (3.63 %) were measured and gave correct values, but after expansion the uniformity of the coating was broken: the coating was peeled off from the surface, because the expansion was done in mid-air.

Tecnic Carbostent^{TM}**.** The material of this stent is stainless steel, 316LVM, coated with carbon film. The struts have rectangle shape and they are rounded. The nominal diameter of this stent is 3 mm and the nominal length is 30 mm. The coating was examined and no damage was found. The expansion was done by an ultrasonic resonator, which uses the energy of the ultrasonic concentrating to the stent. In the places exposed to the biggest change of form parallel splitting occurred on the carbon coating, the coating did not remain uniform, and small pieces were separated (Fig. 5, 6).

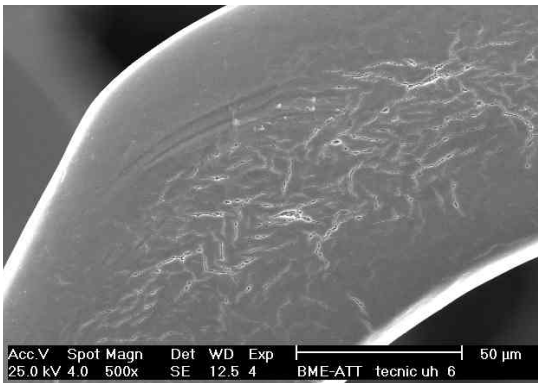

Figure 5. After fatigue test, splitting of the coating

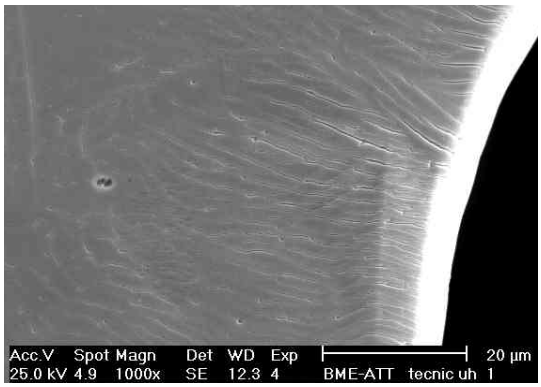

Figure 6. Spalling of the coating, after fatigue test

4. COATING EXPERIMENTS

Coating of sheets. Electro polished and non-treated sheets were silanised. They were cleaned with isopropyl alcohol and were placed to the desiccator for 10 minutes, above the mixture of dimethyldichlorsilane and methyltrichlorsilane. The silicone coating was applied to the silanised surface. Two types of the tincture were made for the silanised sheets: the adhesive was thinned with toulene, 1:1 and 1:2 relations. Dipping method was used. After drying, the coatings were examined by different methods. The coatings of the 1:1 relation, non-treated sheets were not suitable: the coating was not uniform, flow lines and solidifications occurred and these properties would influence the flow parameters. The coatings of the 1:2 relations, non-treated sheets resulted in better surface quality, but the coatings were concentrated to the central line of the sheet. The electropolished sheets with 1:1 relation coating showed good quality, but there were airlocks between the coating and the surface. The 1:2 related mixture gave better surface properties: smooth surface, less airlocks and thinner coating.

Coating of stents. The coatings were prepared only for electropolished stents, because the examinations with the sheets showed that with electro polishing far better results can be obtained. Three Tentaur stents were cleaned with isopropyl alcohol and were placed to the desiccator for 5 minutes, above the mixture of dimethyldichlorsilane and methyltrichlorsilane. The period of silanisation was reduced, because the silanised layers were too thick. Figures 7 and 8 shows that the coatings were not smooth, they were concentrated to the centres of the struts and they formed drops. The drying of the coatings was done by hanging, so it is needful to rotate the stent during the drying. There were solidification at the nodes as well, but there were not uncoated sections and the coating remained smooth and uniform.

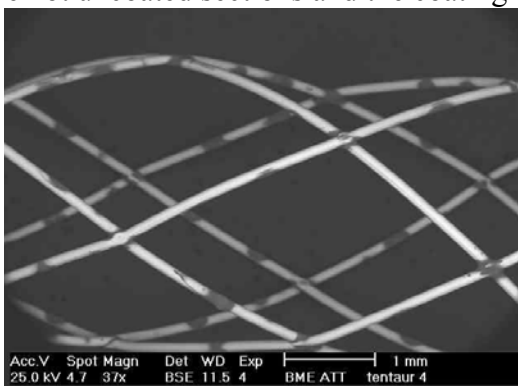

Figure 7. The concentrating of the silicone coating

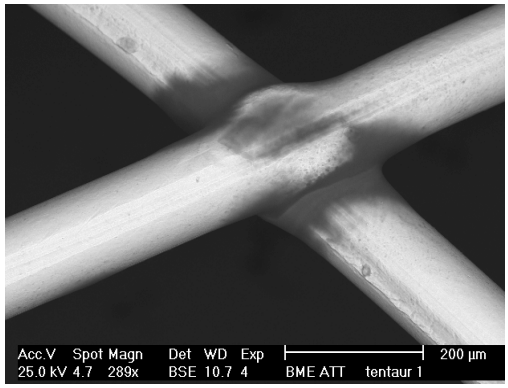

Figure 8. The silicone coating were thicker on the nodes

5. CONCLUSIONS

Before expansion the most frequent surface failures were pits, scratches, and small shrinkage of materials originated from the manufacturing and finishing processes, therefore the coating was not smooth. After expansion the coating was examined mostly on the critical curves, slip lines occurred, grain boundaries were outlined, so the roughness was grown locally, but the coating did not change significally.

Altogether the examined coatings had only minor injuries because of the expansion and the fatigue tests. The exception is only the phosphorylcholine-coated stent, but probably the peeled-off coating was arisen about the mid-air expansion.

In the ultrasonic-resonator one carbon-coated stent were examined and assessable that it was strained only on the critical curves: the coating was cracked and small peaces were separated.

Silicone coating was prepared for Tentaur stents. Before coating it is necessary to electro polish the surface, so that surface failures, which originat from the manufacturing processes can be decreased. The sterile and dust free environment is crucial to produce a suitable coating. In our opinion silicone coating could be a suitable coating, but it is necessary to find the right viscosity. The viscosity of our coating was good, but the coating technology was inefficient. It is practical to mix the silicone coating with drugs.

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