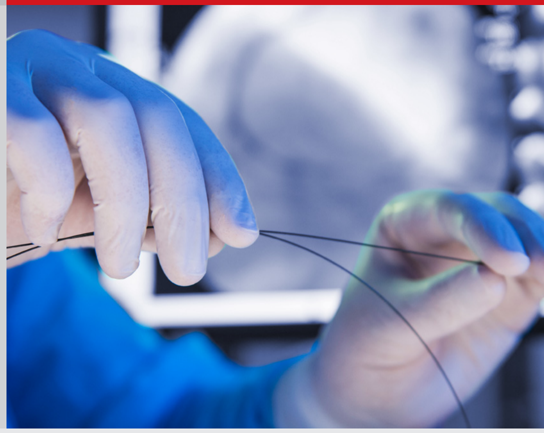
::: Application Report

Anton Paar



Advanced Mechanical Surface Testing

Biomedical applications 2: adhesion and scratch resistance by scratch testing

Introduction

The fast growing domain of mechanical testing of biomaterials demands ever more sophisticated measurement techniques. Researchers and developers are interested in knowing not only the mechanical properties of biological materials and biomaterials (hardness and elastic modulus) but also in adhesion and scratch resistance of many types of surface coatings applied to biomaterials. Knowing adhesion of functional coatings is primordial in order to ensure good biocompatibility of implants, improved osseointegration and generally long lifetime of many prosthetic or stent applications.

This application report summarizes the use of the scratch test technique for assessment of adhesion of functional surface coatings (hard or soft) and their scratch resistance. It is complementary to the application report dedicated to hardness and elastic modulus measurement using nanoindentation.

Scratch test method

The scratch technique is used for determination of adhesion of coated materials where the coating is usually providing a protective function. In biomedical applications, coatings are often used to decrease the coefficient of friction of joint implants (hard coatings), on bone implants for better osseo-integration (hydroxyapatite), or on stents for biocompatibility and drug elution (polylactic-co-glycolic acid, PLGA). All of these coatings have to be biocompatible and should adhere well to the substrate. Scratch testing is one of the few methods that can verify the adhesion of a coating and so ensure a sufficiently long lifetime of the implant.

Scratch tests on dental implant screws

Hydroxyapatite (HA) coatings are widely used for orthopedic and dental implants because of their advantages, which include increased contact surface for improved osseo-integration, and the fact that they are made of a similar material as the bone which facilitates bridging of small gaps between the implant and the surrounding bone. However the adhesion of the hydroxyapatite coating has to be verified in order to ensure the benefits of this surface treatment – without good adhesion the hydroxyapatite would detach from the (usually metallic) substrate and insufficient integration with the bone or fracture would occur.

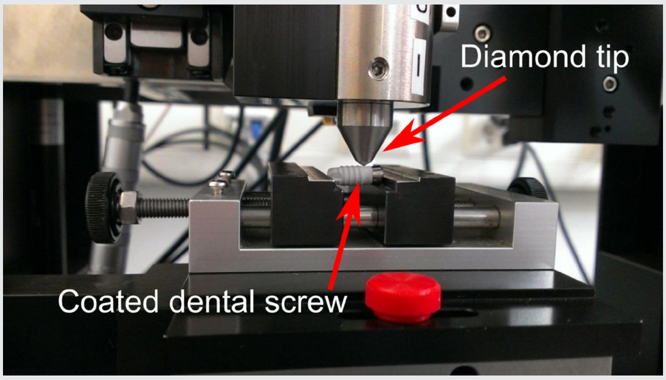


Figure 1 – Scratch test setup on a hydroxyapatite coated dental screw.

During a scratch test, the failure of the coating can be determined by optical microscopy, variation in penetration depth, acoustic emission or by the tangential frictional force between the tip and the sample. Scratch tests on a dental screw with a ~2 μm thin coating were performed using an Anton Paar Micro Scratch Tester with a 0.2 mm radius diamond and a 1 mm scratch length. The normal load was increased over 30 s from 0 N to 10 N. An example of the data recorded during such scratch tests is shown in Figure 2. Note that a Panorama image is almost always recorded for easier offline evaluation of the results and also for archiving purposes. The patented Panorama image is synchronized with the recorded signals (force, depth, acoustic emission, etc.) and saved with the measurement file.

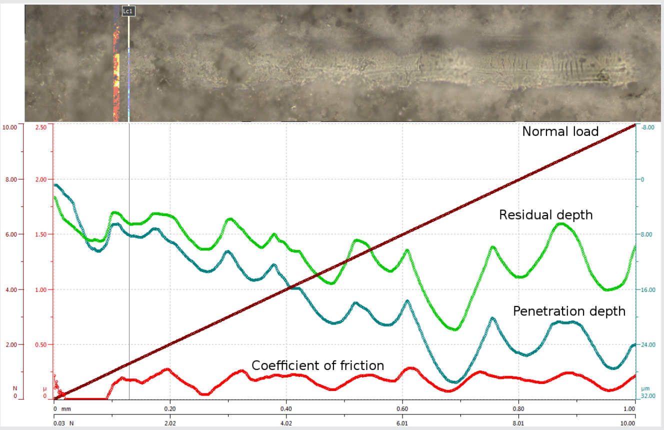


Figure 2 – Data recorded during a scratch test: penetration depth, residual depth after the scratch and coefficient of friction. This figure also contains the corresponding Panorama image.

Figure 3 illustrates an area corresponding to the critical failure (critical load, Lc1) in the scratch track. The coating was completely removed (shown by arrow) as the substrate (brighter area) was reached during the test. The critical load value was 1.2 N±0.1 N, which shows excellent repeatability in the test results.

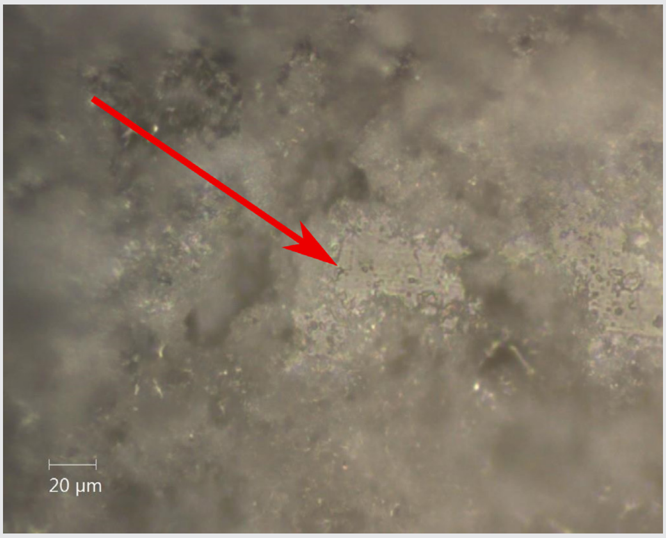


Figure 3 – Critical load area on the hydroxapatite coated dental implant.

Nanoscratch testing of drug eluting stents

Metallic stents are often employed in medicine for either drug delivery or as support for the walls of arteries (for example the coronary artery) which frees the (partially) clogged passage or simply reinforces the artery walls. Various alloys have been developed over time as well as special coatings, (some drug eluting), which aids healing and prevents the release of ions from the metallic stent. Similar to other coated biomaterials, the adhesion of the functional film is important for proper functioning of the stent. However, in comparison to many other implants, the coated parts of the stent are usually formed by mesh with wire diameter of ~50 µm and length ~300 µm (see Figure 4). The stent in the form of flat wire mesh must therefore be placed onto a flat support (e.g. a microscope slide) and glued carefully with epoxy to ensure good bonding to this support.

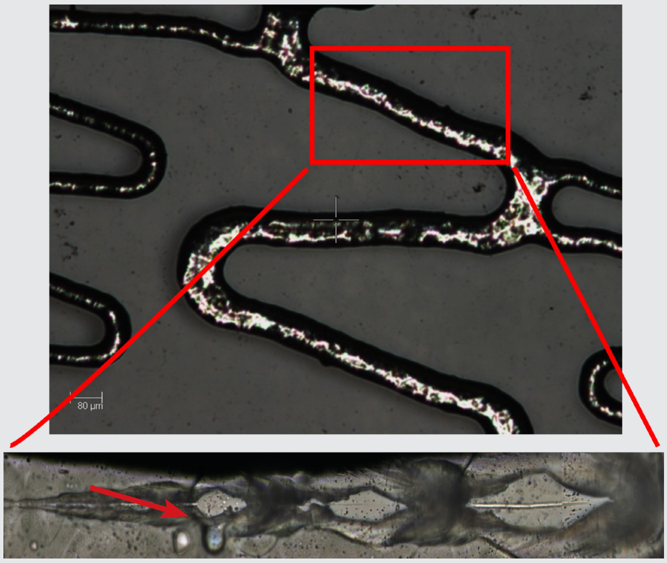


Figure 4 – Panorama image of typical scratch test performed along a coated stent. Arrow is showing the Lc1 area. Lc2 corresponds to full delamination of the coating (not shown).

In case of cylindrical stents, a special mounting jig has to be used: the stent is stretched on a metal pin with appropriate diameter so that the stent cannot slip on the pin. This assembly is then mounted on the standard friction table of the Nano Scratch Tester (NST) in such a way that selected wires of the stent lie parallel to the direction of the scratch. In both cases, the Nano Scratch Tester provides a reliable test method for estimation of adhesion of the coating by determination of optical critical loads on scratches performed on the stent's wires. The scratch tests in this application were done with a 2 µm radius diamond indenter on a 0.4 mm long line, with loads progressively increasing from 0.3 mN to 50 mN. Two critical loads were detected: the first (Lc1), corresponding to the first failure of the coating and the second (Lc2), corresponding to full delamination of the coating. An example of a Panorama image in Figure 4 illustrates a scratch test performed along a coated stent, showing the appearance of the first failure (critical load Lc1, marked by an arrow). After successfully overcoming the preliminary difficulties with fixing the stents (whether flat or cylindrical), the nanoscratch method yields very good results with the ability to evaluate the effects of manufacturing or storage on the adhesion of the coating, thus helping determine the lifetime of these important biomedical implants.

Table 1 Critical load values obtained from nanoscratch testing of coated stents.

		Sample 1	Sample 2	Sample 3
Lc1	Data : 1	28.94	14.46	17.76
[mN]	Data : 2	24.59	40.34	21.88
	Data : 3	15.55	11.45	14.01
	Data : 4		--.--	20.56
	Mean	**23.03**	**22.08**	**18.55**
	Std Dev	6.83	15.88	3.48
Lc2	Data : 1	39.96	29.49	23.60
[mN]	Data : 2	38.62	--.--	30.17
	Data : 3	25.47	18.81	--.--
	Data : 4		--.--	26.18
	Mean	**34.68**	**24.15**	**26.65**
	Std Dev	8.00	7.55	3.31

Scratch testing of angioplasty balloons

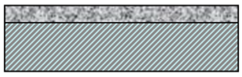
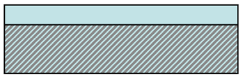
Angioplasty is used to open blocked arteries by inserting a catheter through a small puncture to the heart. The artery is then unblocked by inflating a tiny balloon (see Figure 5). There are many different types of angioplasty balloons commercially available. Some of the balloons are coated to increase their burst resistance and ensure that they withstand deployment during the angioplasty medical procedure. It is important to verify that the balloons resist puncture or scratching. The Nano Scratch Tester is one of the few suitable instruments that can perform such testing in a well-defined way.

Figure 5 – Sample preparation for Nano Scratch testing.

The examples in Figure 6 to Figure 8 illustrate the scratch results obtained on three such balloons; one uncoated and two coated (see Table 2). For the scratch testing, the balloons were deflated and attached to glass slides with water-soluble glue (to allow future removal for burst tests).

The scratch tests were performed using the Nano Scratch Tester with the following parameters: spherical diamond indenter with 20 µm radius, load from 5 mN to 500 mN, scratching speed 1 mm/min, and a scratch length of 1 mm. Scratching of the uncoated PET balloon resulted in rupture of the balloon wall at ~420 mN. The coated balloons showed no rupture of the PET substrate and only the rupture of the coating was observed. The failure (critical load) of the Si-filled urethane coating was observed at ~295 mN whereas the urethane clear coat failed at ~350 mN.

Table 2 Tested angioplasty balloons

Balloon variant	**Balloon structure**
Uncoated single-wall PET balloon (21 µm)	
Si-filled urethane coated (4 µm) PET balloon	
Urethane clear coat (9 µm) coated PET balloon	

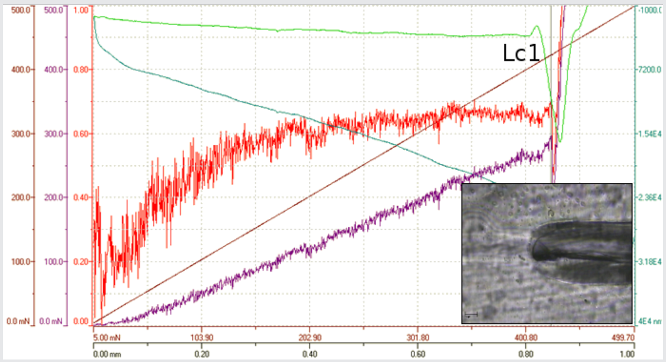


Figure 6 – Scratch data and image of the uncoated balloon failure.

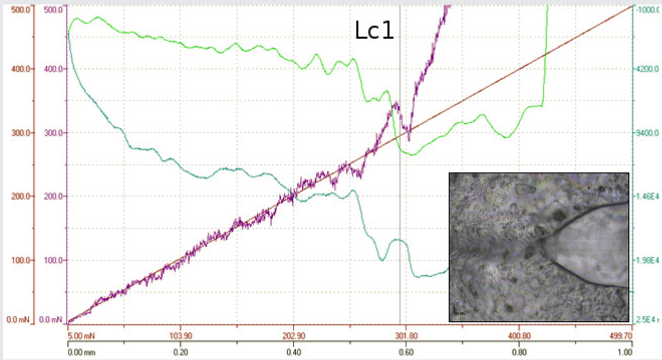


Figure 7 – Scratch data and image of the Si-filled urethane coated balloon failure.

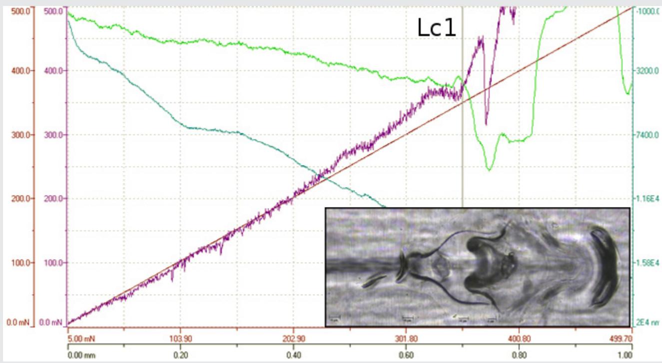


Figure 8 – Scratch data and image of the failure of the urethane clear coat on the balloon.

The burst results performed on the same balloons showed that burst pressure was higher for the coated balloons: the burst pressure for the uncoated balloon was 10 atm whereas it increased to ~13 atm for the coated balloons. Despite the apparently lower critical load, the coated balloons better resisted the scratch damage. While the uncoated PET was punctured at ~450 mN, both coated PET balloons resisted failure up to 500 mN since only the coating failed - but not the pressure-bearing PET substrate. These results were also confirmed by comparison of penetration depth (corrected across surface topography thanks to pre-scan/post-scan procedure), which was higher on the uncoated sample (more extensive damage). The Nano Scratch Test results are therefore very important for estimation of the effect of protective coatings on angioplasty balloons.

Adhesion of ZrO_2 coating on artificial knee prosthesis

In the search for new and more performant artificial prostheses, zirconia (ZrO_2) coatings have recently been introduced in the fabrication processes. These coatings are intended to prevent oxidation of the metallic (usually Ti6Al4V, CoCr or Zr-based alloys) load-bearing substrate and also to decrease the coefficient of friction. However, as with other coatings, the adhesion of the ZrO_2 layers has to be determined in order to ensure sufficient reliability of the prosthesis. The thickness of these ceramic coatings is in the range of units of micrometers (usually ~3 to ~5 µm) and since they are quite hard, one of the most suitable techniques to test the adhesion of these coatings is the scratch test method. The commonly applied procedure is to use the Revetest scratch tester with 200 N maximum load to induce failure at the ceramic coating-substrate interface due to shear stresses. In the present study we tested two samples with 5 µm thick ZrO_2 coatings deposited on Zr-based alloy substrate.

The particular interest of this study was to determine whether the zirconia coating adheres well on two different geometries of a knee implant: on the flat part and on the curved part (see Figure 9). The scratch tests were performed using the Revetest scratch tester with diamond indenter with 0.2 mm radius, with the force progressively increasing from 1 to 100 N on a distance of 3 mm. The effect of geometry on the normal force application and measurement could be neglected since the Revetest scratch tester uses active force feedback, ensuring the same force profile on both flat and curved surfaces. Similarly, the true penetration and residual depths were recorded thanks to the pre-scan/post-scan procedure.

Figure 9 – Knee prosthesis coated with a zirconia (ZrO_2) layer on the flat part (left) and on the curved part (right).

The results of the scratch tests revealed that there was a minor difference between the critical loads of the zirconia layer on the flat and curved regions. The first critical load (Lc1, partial delamination by adhesive failure) was slightly higher on the curved surface whereas the second critical load (Lc2, full delamination by ploughing) was slightly higher on the flat surface. The effect of the geometry on the adhesion of the ZrO_2 coating has therefore been proven to be only minor.

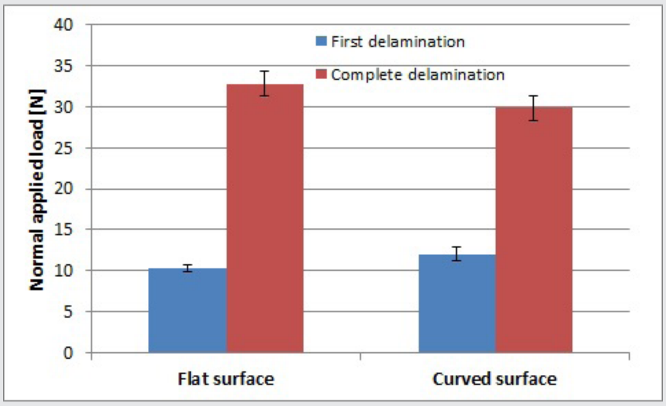


Figure 10 – Comparison of Lc1 and Lc2 on flat and curved areas of knee prosthesis.

Summary

Over the past several decades, a growing interest in better understanding the mechanical properties of biomaterials, bio-inspired materials, and biological materials has been seen. Although some characterization techniques were available, new and more advanced ones were needed. The scratch testing method belongs to these new characterization techniques, which is used for adhesion measurement of functional surface coatings. The advances in adhesion testing (including Panorama and prescn/postscan procedures) now readily allow for testing of adhesion and scratch resistance of many types of surface coatings which are used for improvement of osseo-integration or for reducing friction and wear. Scratch testers allow for fast and simple characterization of new functional coatings, of their adhesion and scratch resistance in well controlled manner.

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