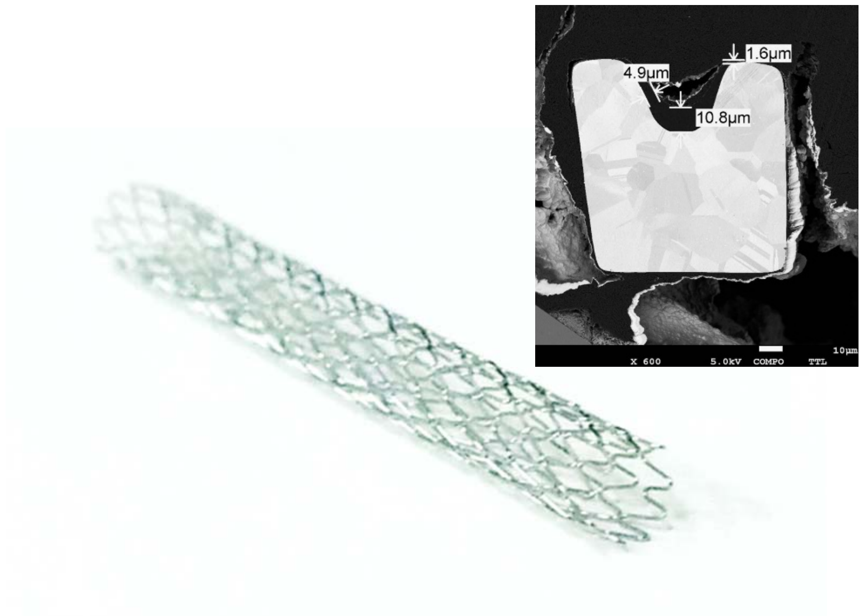
STENT COATING FAILURE USING NANO SCRATCH TESTING



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INTRODUCTION

Blood is carried through arteries away from the heart to other parts of body. Any weakening or blockage of these blood passageways may create significant risk to the patient's health and even become life threatening. A stent is a small mesh tube inserted into the lumen of blood vessels to treat narrow or weak arteries. Stent implantation becomes a widely used surgical procedure to support the inner wall of the artery and restore blood flow[i].

IMPORTANCE OF NANO SCRATCH TEST FOR STENT COATING EVALUATION

Drug–eluting stent is a novel approach in stent technology. It possesses a biodegradable and biocompatible polymer coating that releases medicine slowly and continuously at the local artery to inhibit intimal thickening and prevent the artery from being blocked again[ii]. One of the major concerns is the delamination of the polymer coating that carries the drug-eluting layer from the metal stent substrate. In order to improve the adhesion of this coating to the substrate, the stent is designed in different shapes. Specifically in this study, the polymer coating locates at the bottom of the groove on the mesh wire, which brings enormous challenge to the adhesion measurement. A reliable technique is in need to quantitatively measure the interfacial strength between the polymer coating and the metal substrate. The special shape and the small diameter of the stent mesh (comparable to a human hair) require ultrafine X-Y lateral accuracy to locate the test position and proper control and measurement of the load and depth during the test.

MEASUREMENT OBJECTIVE

In this application, the Nanovea Mechanical Tester, in Nano Scratch Mode, is used to evaluate the cohesive & adhesive strength of the polymer coating on the metal mesh of stent samples. We would like to showcase the capacity of Nanovea Mechanical Tester in performing nano scratch tests on stent samples *as thin as a human hair*.

Fig. 1: Nano scratch tip on the stent sample.

TEST CONDITIONS

1. **On the Regular Stent Samples:**

The stent was carefully fixed on the sample stage, with a thick metal wire inserted inside the stent tube as support during the nano scratch test. The Nanovea Mechanical Tester was used to perform the nano scratch tests using the test parameters summarized in Table 1, in order to evaluate the cohesive and adhesive strength of the polymer coating on the metal substrate of the stent sample.

Load type	Progressive
Initial load	0.05 mN
Final load	300 and 100 mN
Sliding speed	0.5 mm/min
Sliding distance	0.5 mm
Indenter geometry	Conical
Indenter material (tip)	Diamond
Indenter tip radius	20 µm
Temperature	24°C (room)

Table 1: Test parameters of the nano scratch measurements on the Regular Stent Samples.

2. **On the Grooved Stent Samples:**

The SEM image in Fig. 2 shows the cross section of the stent sample. The stent possesses a groove with a depth of ~30 µm. The polymer coating with a thickness of 10.8 µm is located at the bottom of the groove. Regular 60° conical diamond tips are not sharp enough to reach the bottom of the groove without touching the sidewall. Therefore, a sharp 40° conical diamond tip is used in this study (Fig. 3). The nano scratch tests were performed using the test parameters summarized in Table 2.

Load type	Progressive
Initial Load (mN)	0.1
Final Load (mN)	300
Loading rate (mN/min)	300
Scratch Length (mm)	0.25
Scratching speed (mm/min)	0.25
Indenter geometry	40° cone
Indenter material (tip)	Diamond
Indenter tip radius (µm)	5

Table 2: Test parameters of the nano scratch measurements on the Grooved Stent Samples.

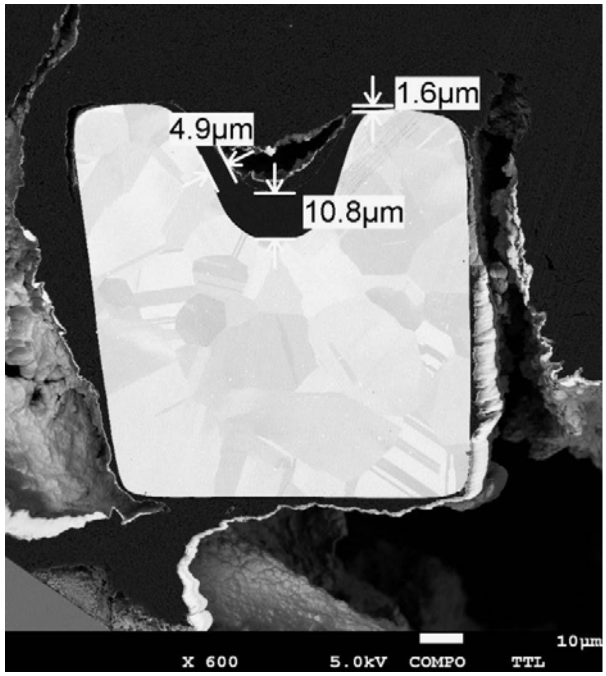


Fig. 2: Cross section of the Grooved Stent Sample.

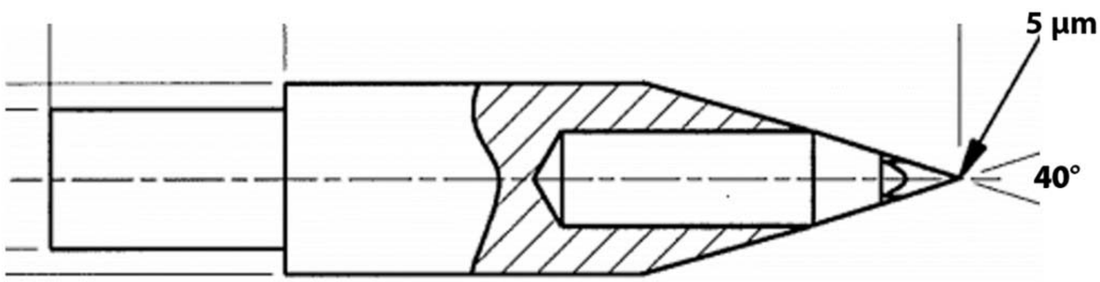


Fig. 3: Schematic of the diamond tip for the nano scratch test on the Grooved Stent Samples.

RESULTS AND DISCUSSION

The stent mesh has a diameter of 100 µm, which is comparable to that of a human hair. Therefore, precise position control is critical to locate the scratch test at the center of the stent mesh. The sample stage of Nanovea Mechanical Tester possesses a fine X-Y lateral accuracy as low as 0.25 µm, allowing users to pinpoint the test location under the integrated optical microscope and perform the nano scratch test under the scratch tip.

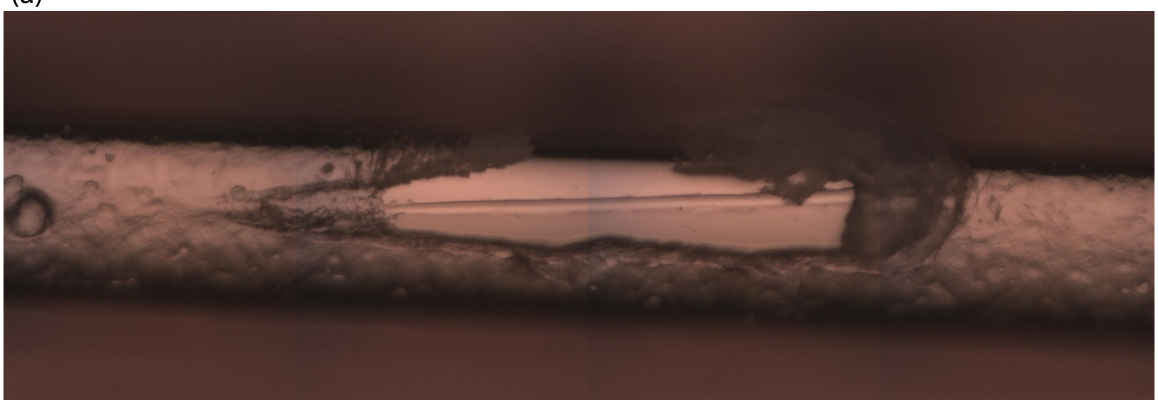
1. **Test results of the Regular Stent Samples:**

The nano scratch test was first performed with a linearly increased load to a maximum value of 300 mN. The full scratch track on the stent is shown in Fig. 4a. The failure behaviors at different critical loads are displayed in Fig. 4b and c, where critical load L_{c1}

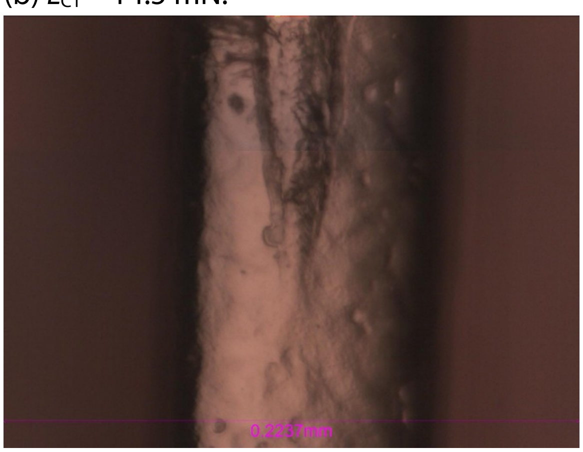
is defined as the load at which the first sign of scratch occurs, and L_{c2} is the load at which the coating is completely removed and the substrate is exposed. Fig. 3 plots the evolution of coefficient of friction (COF) and depth which provides more insight in the progression of coating failures during the scratch test.

It can be observed that the scratch on the coating starts to appear at L_{c1} of 14.5 mN as the first sign of coating failure. As the diamond stylus progressively penetrates into the polymer coating, the scratch grows wider and deeper. At the same time, the COF gradually increases from ~0.05 to ~0.7. When the critical load L_{c2} of 78.1 mN is reached, the coating completely delaminates from the metal substrate. As the normal load continues to linearly increase during the nano scratch test, the COF and depth remains relatively constant due to the solid support of the metal substrate against the diamond tip.

(a)



(b) $L_{C1} = 14.5$ mN:



(c) $L_{C2} = 78.1$ mN:

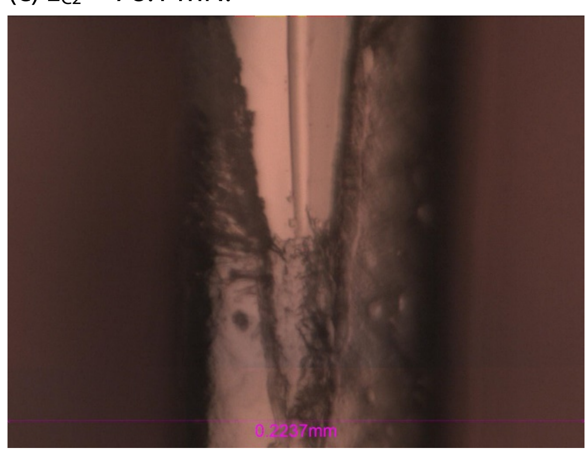


Fig. 4: The scratch track at different critical loads.

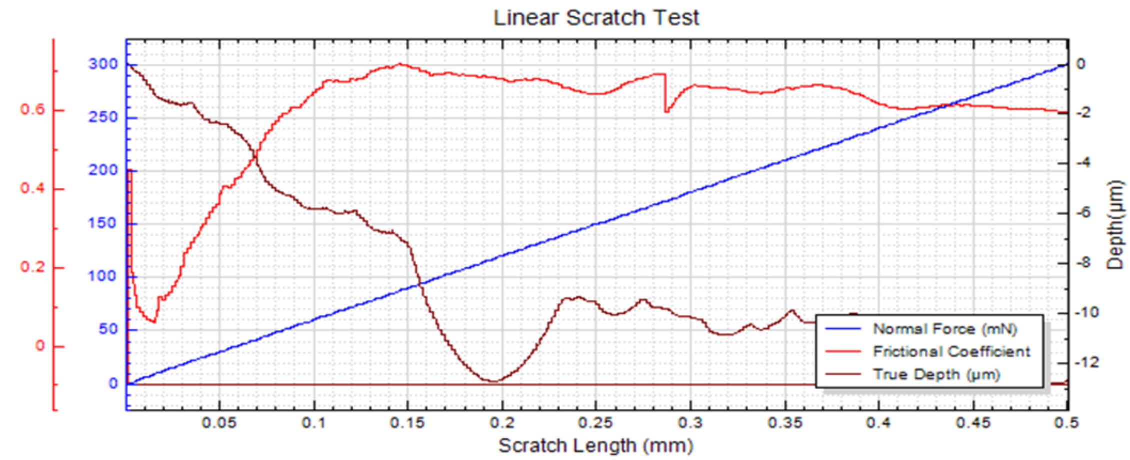
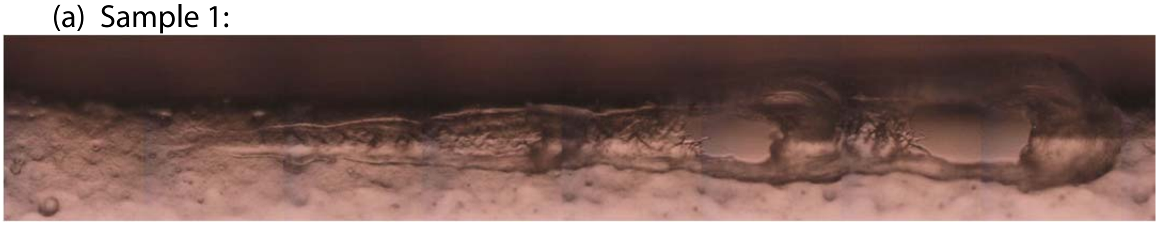


Fig. 5: Evolution of coefficient of friction and depth during the nano scratch test.

The failures during the scratch test up to 300 mN maximum load occurred at critical loads below 100 mN. In order to better quantitatively compare the cohesive and adhesive strength of the coatings to select the best candidate, we further performed the nano scratch test with a maximum load of 100 mN on two stent samples, namely Sample 1 and Sample 2.

Fig. 6 compares the scratch tracks of Sample 1 and 2 after the nano scratch tests. Sample 1 shows the first sign of scratch at a critical load L_{c1} of 13.2 mN, compared to 21.1 mN for that of Sample 2. The protective coating delaminates at 62.5 mN for Sample 1, while the coating of Sample 2 protects the metal substrate throughout the nano scratch test. The failures is also reflected in the evolution of COF and depth as shown in Fig. 7. When the diamond stylus penetrates and slides against the metal substrate, we can observe that the COF value peaks and the depth value slumps for Sample 1.

(a) Sample 1:



(b) Sample 2:

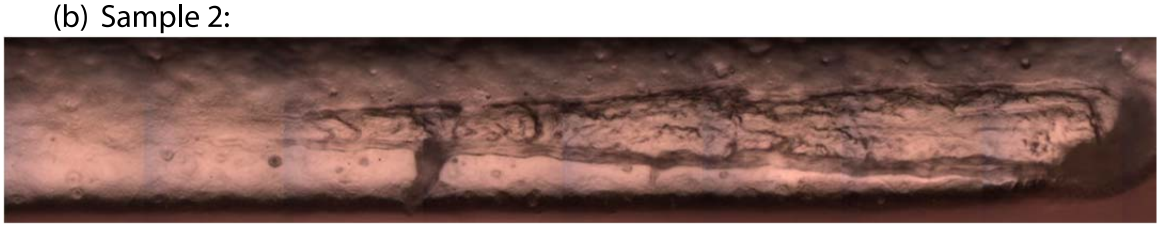


Fig. 6: The scratch tracks of Sample 1 and 2.

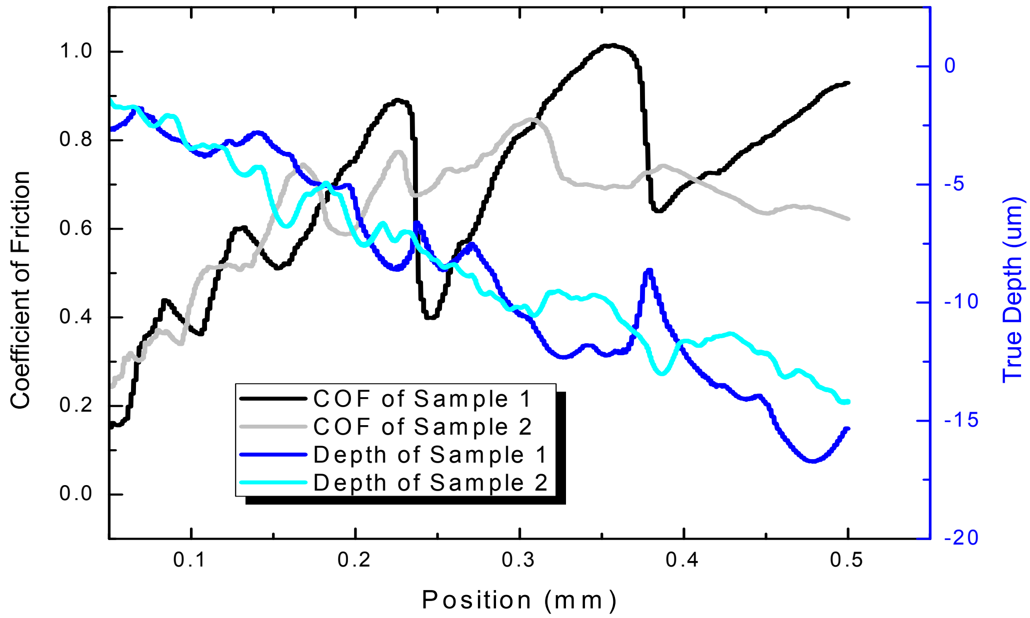


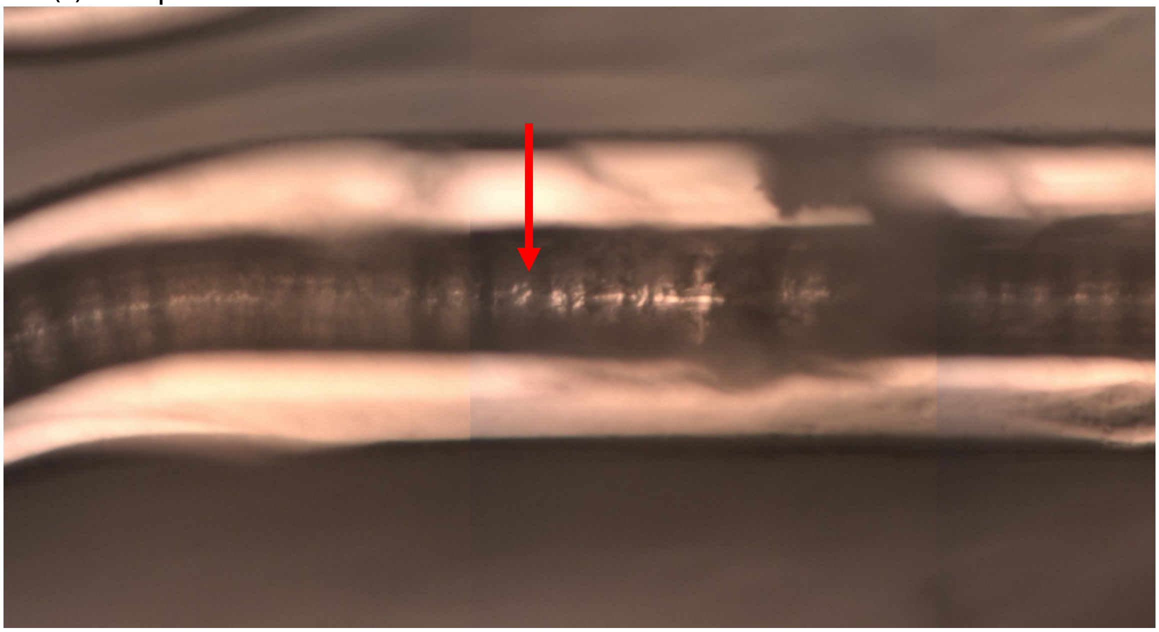
Fig. 7: Comparison of friction coefficient and depth during the nano scratch test.

2. **Test results of the Grooved Stent Samples:**

As shown in Fig. 2 and Fig. 8, the grooved stent mesh has a diameter of ~90 µm, which is comparable to that of a human hair. The groove has a width of ~50 µm and a depth of 30 µm. Such a special shape and small size bring tremendous challenge to the scratch test on the coating at the bottom of the groove. Precise position control is critical to locate the scratch test at the center of the groove. The nano scratch test was performed with a linearly increased load to a maximum value of 300 mN. The full scratch tracks on the grooved stents Samples 3 and 4 are compared in Fig. 8. The critical load L_c is the load at which the coating fails and the substrate is exposed. Fig. 9 plots the evolution of normal load and depth, which provides more insight in the progression of coating failures during the scratch test.

It can be observed that as the normal load linearly increases during the scratch test, the diamond stylus progressively penetrates into the polymer coating, leading to deepening of the scratch track. When the critical load L_c is reached, the coating delaminates from the metal substrate. The coating on Sample 3 starts to fail at the critical load L_c of 126 mN, compared to 173 mN for Sample 4. The critical loads of different samples allow one to quantitatively and reliably evaluate and compare the quality of the test coating samples. The coating on Sample 4 possesses a higher L_c and adheres to the substrate at higher loads, making it a better candidate in this study.

(c) Sample 3:



(d) Sample 4:

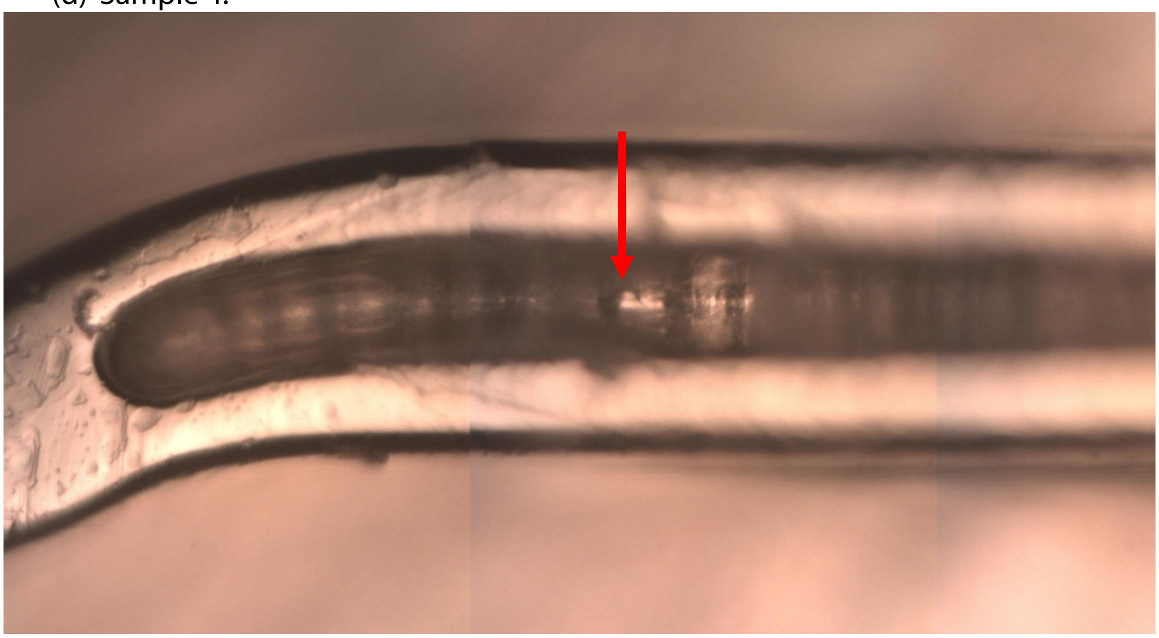
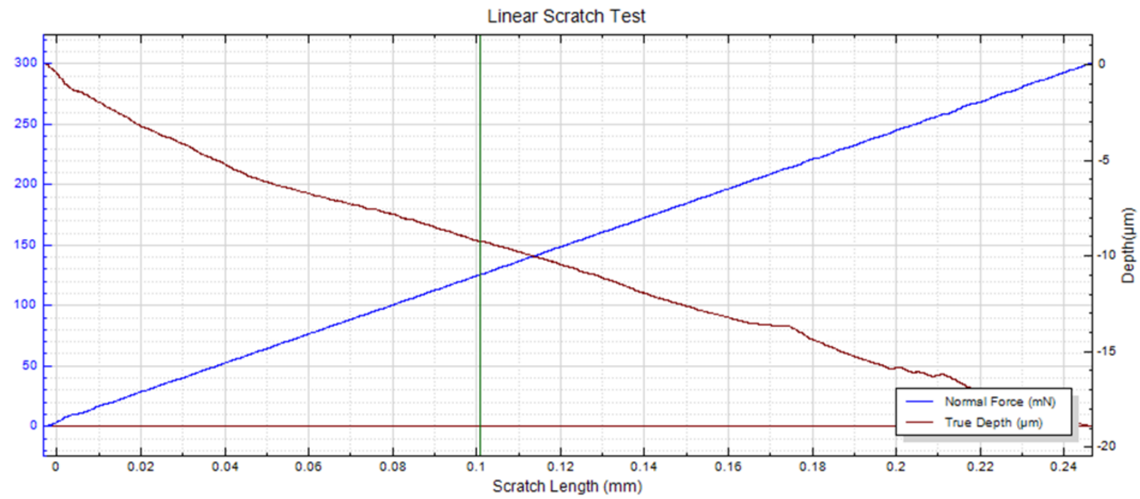


Fig. 8: The full scratch tracks of Grooved Stent Samples 3 and 4.

(a) Sample 3:



(b) Sample 4:

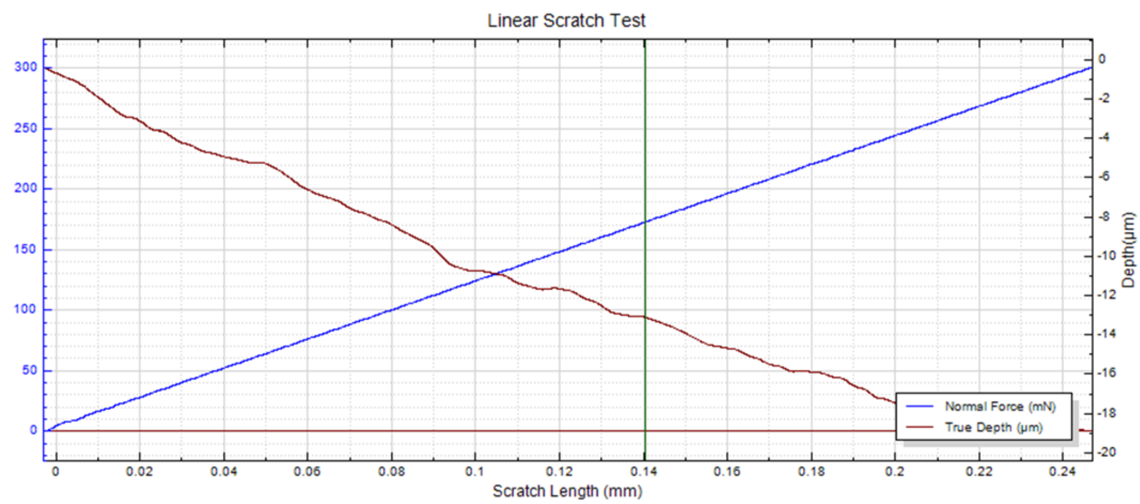


Fig. 9: Evolution of normal load and depth during the nano scratch test on the Grooved Stent Samples. Note: The vertical green line indicates the location where the polymer coating fails.

CONCLUSION

In this study, we showcased that Nanovea Mechanical Tester evaluates the cohesive and adhesive strength of the polymer coatings on the regular and grooved stent samples using nano scratch technique. The groove on the stent is 50 µm wide and 30 µm deep, making it extremely challenging to locate and test the polymer coating at the bottom of this groove. The fine X-Y accuracy at 0.25 µm for the sample stage of Nanovea Mechanical Tester allows us to precisely pinpoint the test location on the stent meshes of a diameter comparable to a human hair. By applying linearly increased loads in a controlled and closely monitored fashion, we can identify the critical load at which typical cohesive and adhesive coating failure occurs. It provides a superior tool to quantitatively evaluate and compare the intrinsic quality of the coating and the interfacial integrity of the coating/substrate system on a very small sample of a special shape.

The Nano, Micro or Macro modules of the Nanovea Mechanical Tester all include ISO and ASTM compliant indentation, scratch and wear tester modes, providing the widest and most user friendly range of testing available in a single system. Nanovea's unmatched range is an ideal solution for determining the full range of mechanical properties of thin or thick, soft or hard coatings, films and substrates, including hardness, Young's modulus, fracture toughness, adhesion, wear resistance and many others.

To learn more about Nanovea Mechanical Tester or Lab Services.

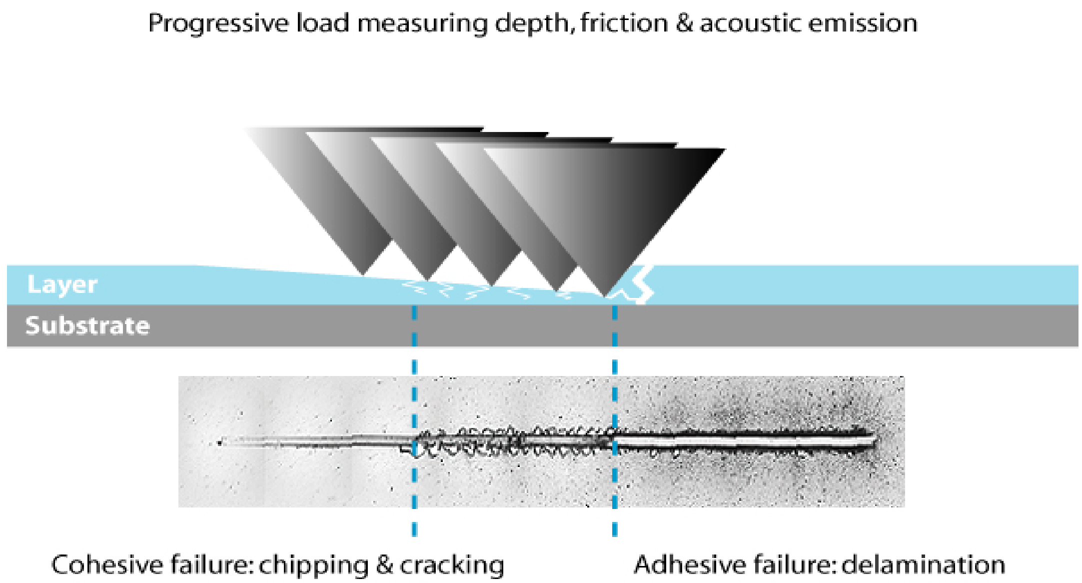
APPENDIX: MEASUREMENT PRINCIPLE

Principle of scratch test

The scratch testing method is a very reproducible quantitative technique. Critical loads at which failures appear are used to compare the cohesive or adhesive properties of coatings or bulk materials. During the test, scratches are made on the sample with a sphero-conical stylus (tip radius ranging from 1 to 200 μm) which is drawn at a constant speed across the sample, under a constant load, or, more commonly, a progressive load with a fixed loading rate. Sphero-conical stylus is available with different radii (which describes the "sharpness" of the stylus). Common radii are from 20 to 200 μm for micro/macro scratch tests, and from 1 to 20 μm for nano scratch tests.

When performing a progressive load test, the critical load is defined as the smallest load at which a recognizable failure occurs. In the case of a constant load test, the critical load corresponds to the load at which a regular occurrence of such failure along the track is observed.

In the case of bulk materials, the critical loads observed are cohesive failures, such as cracking or plastic deformation of the material. In the case of coated samples, the



lower load regime results in conformal or tensile cracking of the coating which still remains fully adherent (which usually defines the first critical load). In the higher load regime, further damage usually comes from coating detachment from the substrate by spalling, buckling or chipping. Fig. 10 illustrates the principle of scratch testing.

Fig. 10: Principle of scratch testing.

Comments on the critical load

The scratch test gives reproducible quantitative data that can be used to compare the behavior of various coatings. The critical loads depend on the mechanical strength (adhesion, cohesion) of a coating-substrate composite but also on several other parameters: some of them are directly related to the test itself, while others are related to the coating-substrate system. The parameters that determine the critical loads are summarized in Table 3.

Test specific parameters	Sample specific parameters
Loading rate Scratching speed Indenter tip radius Indenter material	Friction coefficient between surface and indenter Internal stresses in the material for bulk materials Material hardness & roughness for coating-substrate systems Substrate hardness and roughness

	Coating hardness and roughness Coating thickness

Table 3: List of parameters that determine the critical loads.

Means for critical load determination

Microscopic observation

This is the most reliable method to detect surface damage. This technique is able to differentiate between cohesive failure within the coating and adhesive failure at the interface of the coating-substrate system.

Tangential (frictional) force recording

This enables the force fluctuations along the scratch to be studied and correlated to the failures observed under the microscope. Typically, a failure in the sample will result in a change (a step, or a change in slope) in coefficient of friction. Frictional responses to failures are very specific to the coating-substrate system in study.

Acoustic emission (AE) detection

Detection of elastic waves generated as a result of the formation and propagation of microcracks. The AE sensor is insensitive to mechanical vibration frequencies of the instrument. This method of critical load determination is mostly adequate for hard coatings that crack with more energy.

Depth Sensing

Sudden change in the depth data can indicate delimitation. Depth information pre and post scratch can also give information on plastic versus elastic deformation during the test. 3D Non-Contact imaging such as white light axial chromatism technique and AFMs can be useful to measure exact depth of scratch after the test.

Other possible measurements by Nanovea Mechanical Tester:

Hardness and Young's Modulus, Stress-Strain & Yield Stress, Fracture Toughness, Compression strength, Fatigue testing and many others.

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[i] http://www.nhlbi.nih.gov/health/health-topics/topics/stents

[ii] http://www.scielo.org.mx/scielo.php?script=sci_arttext&pid=S1405-99402006000300008