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CHARACTERIZATION OF SCRATCH RESISTANCE OF COATINGS USING THE NANO-TECHNOLOGY[1]

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Abstract
Scratch resistance is a much desired characteristic for coatings in many applications. Characterization of scratch resistance of coatings scientifically is very important for improvement of coatings' tribological properties and development of high-scratching resistant coatings. Traditional empirical testing, such as crock-meter test, might not characterize the scratch resistance of coatings properly. In the mid-90s, the single-probe nano techniques were developed. The tests are carried out under well-controlled conditions, thus making it possible to study different scratching mechanisms under different test conditions. The scratching damages of coatings in the real-field vary from the light damages, such as mars (shallow and narrow scratches), to the medium and severe damages, such as rough trough, cracking, delamination and chipping. A Nano-Indenter equipped with a conical-shaped diamond tip was used to scratch the surface of coatings under a constant or increasing normal load to make artificial damages similar to the real ones, and then the scanning probe microscope was used to take the high-resolution images of the scratched surface, and examine and analyze the damages. We introduced micro mar resistance (MMR) to characterize coatings' ability against the light damage. In addition, we could identify different responses of coatings to the scratching stress, *i.e.*, elastic response, plastic deformation and abrasive wear, quantitatively. To characterize coatings' ability against the medium and severe damage, such as rough trough, cracking, delamination and chipping, a series of critical forces were used, at which the corresponding damage occurs. Using MMR and the critical forces, we can fully characterize scratch resistance of coatings.
Keywords: Scratch resistance; Mar resistance; Wear resistance and critical force for cracking.

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Introduction

Scratch resistance is an important and highly desired property for coatings in many applications, such as polymeric clear topcoats applied on the automobile bodies, which customers expect will have a long-lasting glossy looking and secured protective function. Consequently, the techniques of characterizing the scratch resistance have been pursued for long time to seek reliable laboratory test methods that can predict the performance of the coatings against scratching in their real-field applications and direct their further improvement.

Scratches are made by external stresses along the surface of the coatings with a tangential component as well as the normal load. Conventional hardness measured by well-established indentation tests is not a complete characterization of the scratch resistance. Instead, it is just a measurement of the materials' ability against a normal compressive stress. Some coatings are very hard, but they may have a poor scratch resistance due to their brittleness and/or weak toughness.

Early scratch tests could be listed from very primary ones, such as pencil test, which ranks the coatings as B, F, H, 2H, etc., to the instrumental ones, such as Taber test, crockmeter test, etc. Taber test, described in ASTM D-1044, employs abrasives of hard alumina particles embedded in a pair of rubber wheels weighted against a spinning test panel. Although it is still used in many applications, such as in the window tests for the auto industry, it was thought to be too harsh for many applications, such as clear topcoats. The crockmeter test (the device is manufactured by Atlas Materials Testing) is commonly accepted by the auto industry for the clear topcoats test. In the crockmeter test, a clear topcoat to be tested is applied over a black basecoat on a rigid panel and cured. The panel is immersed in dry Bon Ami cleaning powder and is secured on a test bed. In performing the test, a test probe covered with a fresh green felt pad is moved back and forth over a portion of the panel in ten double strokes so the panel is scratched in the area abraded by the probe. The panel then is cleaned in a stream of cold tap water and gently dried with a soft paper towel. The gloss is measured using a Byk 20^0 pocket gloss meter by slowly moving the meter across the panel, measuring gloss of both the unscratched and scratched sections. The result of the resistance against scratching is reported as percent of gloss retained. However, the surface configuration of a coat that has undergone the crockmeter test is different from that of the same coat that contained real scratches made in the application field, as shown in Figure 1. The quite different configurations indicate that the surface in the crockmeter test suffered different stresses and damages than actually encountered in the real field.

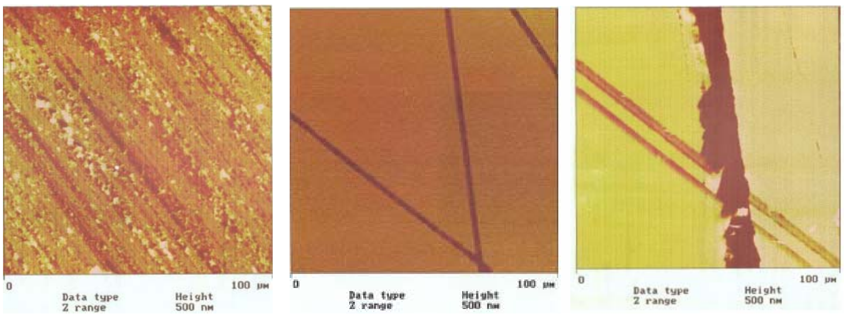


Figure 1: Comparison of surfaces of a same coat: Left: after crockmeter test; Middle: contains real mars (light scratches); Right: contains severe scratches.

ISSN 2179-3956

In the mid-90s, the single-probe nano techniques were developed. The tests are carried out under well-controlled conditions, thus making it possible to study different scratching mechanisms under different test conditions, and correlate scratch resistance of the tested coatings with their physical and chemical properties. In the tests, some used the atomic force microscope,[1-8] and others used a variety of homemade devices.[9-15] Commercial nano-indenters and nano-scratchers, such as Nano-Indenter XP made by MTS Systems Corporation and Nano/Micro Scratch Tester made by CSM Instruments, were developed around the late of 90's, and became more and more popular in the scratch testing.[16-19] These nano instruments are easy to use, offer flexible test conditions, and have greatly enhanced the capability of carrying out scratch measurements.

As an illustration, a Nano-Indenter XP of MTS equipped with a 90^0 conical-shaped diamond tip with a radius of 1 μm at its apex is used in the following measurements descriptions. The Indenter can perform both indentation and scratch tests with a normal force up to 500 mN and a penetration depth up to 2 mm. In the scratch tests, the Indenter can scrape the tested surfaces under a constant, increasing, or incremental load. A Scanning Probe Microscope (SPM), NanoScope IIIa, made by Veeco Metrology Group, is used in our lab to examine the damaged surfaces and analyze the scratching mechanisms.

Mar (shallow and narrow scratch) Resistance Measurement

Mars refer to the light surface damages. Since the degradation of coatings could be attributed to the existence of group of mars in many applications, study of coatings' resistance against light damage (mar resistance) merits attention. The depth of most mars ranges from a couple of dozen nanometers to several hundred nanometers, while the width ranges from a couple of hundred nanometers up to 2-3 micrometers. A single mar may not be readily noticeable. However, the existence of a group of such mars does degrade the appearance of coatings. Mar resistance is a complicated issue; it cannot be characterized with a single quantity. Usually a series of normal loads was used in the testing to measure the mar resistance of a tested coating under different loads.

Before the test, the samples are washed, if possible, in an ultrasonic bath with a mild solvent-free detergent, rinsed in a stream of cool tap water, gently dried with soft tissue, and then blown dry with high-pressure nitrogen gas to remove any dust and grease on the surface, which otherwise would effect the test results.

In performing the test, the tip first makes a pre-scan under a light load of about 10 μN or less to measure the surface profile along the line to be tested. The surface profile is stored and will be used to automatically correct subsequent data. During the scratching procedure, lateral motion, applied load, real-time penetration depth, and the frictional force encountered by the tip are recorded. Following the scratching, the tip will make a post-scan to measure the residual depth of the scratch. Curves of applied load, real-time penetration depth, residual depth, and frictional force *versus* the lateral movement of the tip can be plotted.

In the present test, the Indenter scraped the surface of a coated polycarbonate glazing system, a candidate for automobile windows, under ten pre-selected constant loads from 5, 6, ------ up to 14 mN, for a distance of 150 μm at a speed of 20 μm/s. It produced a group of ten parallel mars, with a pre-determined spacing of about 10 μm on the surface. After the scratching, the sample was washed again, but without the detergent, to remove any broken material, then the scratched surface was examined

ISSN 2179-3956

with the SPM. The upper part of Figure 2 shows the image of ten mars at the surface and their cross-section profile. The plot of the profile is made by the software in the SPM, based on the average values over about 400 selected data points along the mar. It allows us to measure the dimensions of the mars with great accuracy, thus calculating the micro mar resistance, MMR, quantitatively, which is defined as the normal force applied during the scratching divided by the cross-section area of the trough.(3)

$$MMR = F_N / A_{trough}.$$

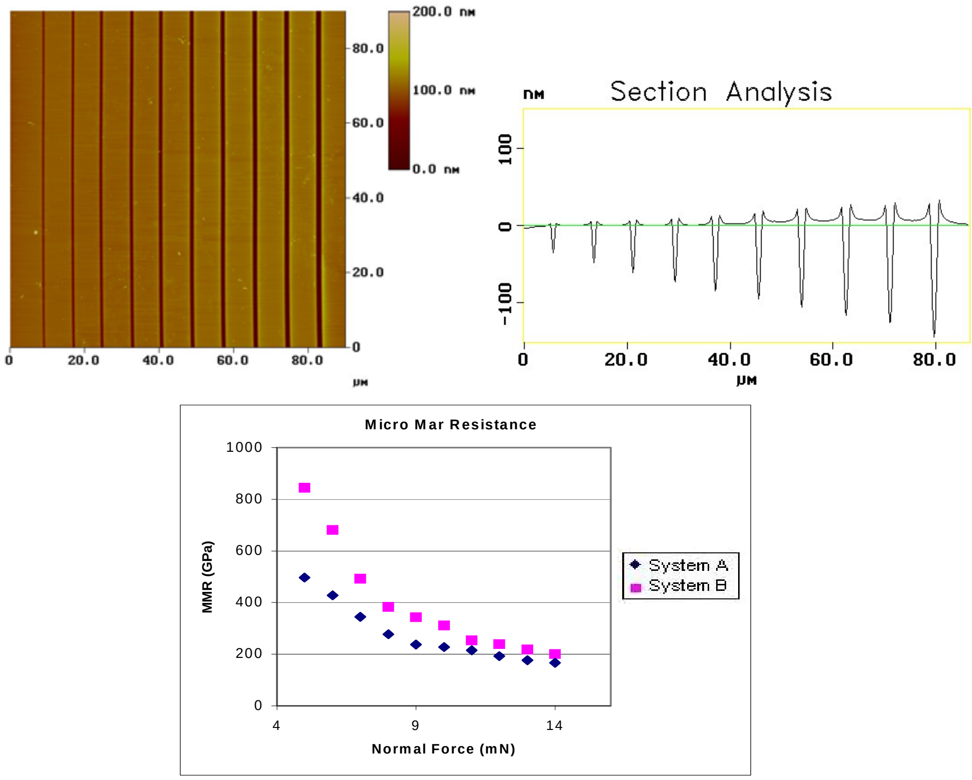


Figure 2: Upper: An image of ten mars, made under the 10 different constant loads from 5 to 14 mN, respectively, and their cross-section profiles. Lower: MMR versus the applied normal forces of two glazing systems.

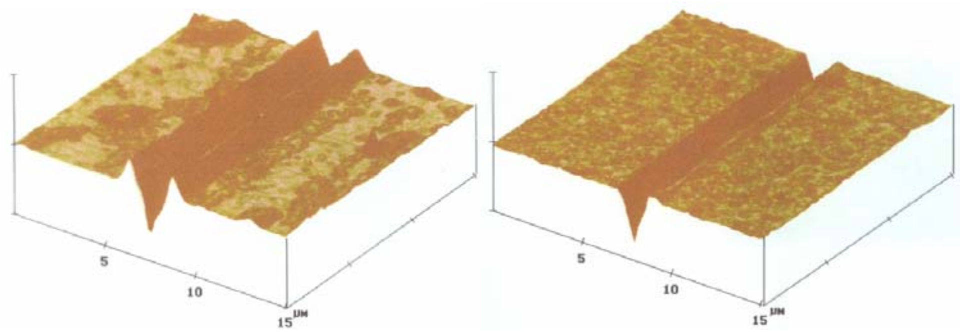
Using MMR, we can compare the mar resistance of different coatings clearly. MMR varies with the applied load, *i.e.* the penetration depth, so a group of values obtained under the different loads is needed to characterize it. The lower part of Figure 2 is a plot of MMR versus the applied normal forces of two coatings. MMR of coating B was much better than A's under the light normal forces, but it decreased more rapidly with the increasing normal force than A's. MMR of coating B was about the same as A's under the large normal forces.

Identification of Different Responses to Scratching Stress

Analyzing the high-resolution images of the mars, the different responses of the coating to the scratching stress could be identified, thus making studying the different scratching mechanisms possible.(3) Figure 3 shows two different configurations of mars. Plastic deformation dominates in (a); two big shoulders sit on both sides of the ditch, indicating the material was displaced from the ditch to build these two shoulders during the scratching. Abrasive wear, *i.e.* mass loss, dominates in (b);

ISSN 2179-3956

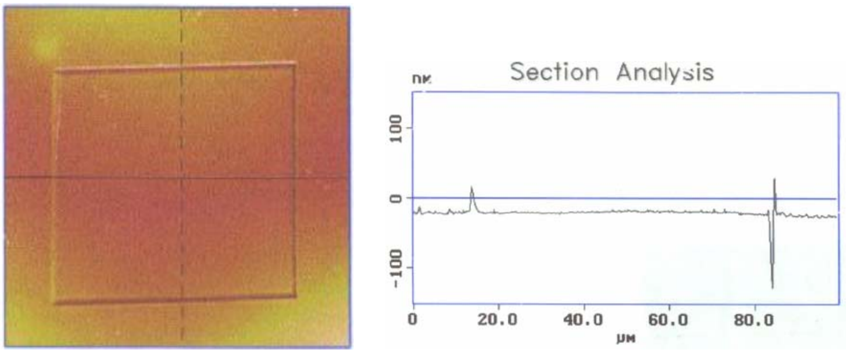
there are no shoulders and the material dug out from the ditch was broken from the surface and was washed away in the subsequent cleaning. Since mars are light damages, the abrasive wear discussed here does not necessarily mean fracture and cracking; it results in mass loss for sure.



(a) (b)

Figure 3: Two different mar configurations, (a) plastic deformation dominates, and (b) abrasive wear (mass loss) dominates.

Plastic deformation is reversible, if the material of the shoulders can be placed back in the ditch. An interesting test was carried out at the surface of a plastic dominant material, in which 512 vertical mars were made from the left side to the right side of an area of 70 by 70 μm. During the scratching, the left shoulder of the second mar filled up the ditch of the first mar, and the ditch of the second mar was made on the top of the right shoulder of the first mar, and so forth. The “healing” followed the "damaging". When the area scratching finished, only the left shoulder of the first mar and the ditch and the right shoulder of the last mar were left at the surface. The remaining area was almost completely restored, as shown in the image of Figure 4 (a) and its profile of 4 (b).



(a) (b)

Figure 4: After 512 vertical scratching from left to right, only the left shoulder of the first mar and the ditch and right shoulder of the last mar are remained at the surface. The upper and lower horizontal ditches in the image were made by the turning of the 512 scratching.

Most tested coatings showed a mixture of the responses, as shown in Figure 5. The total cross-section area of the two shoulders is less than the cross-section area of the ditch. In this case, the area of the two shoulders reflects the plastic deformation, and the difference between the total area of two shoulders and the area of the ditch reflects the abrasive wear, *i.e.* mass loss. Figure 6 is an illustration of how to calculate the micro mar resistance (MMR) and different responses of coatings to scratching stress, based on the dimensions of the scratch. The largest inverted triangle represents the cross-section area of the part of the tip that penetrated the

ISSN 2179-3956

surface during the scratching, which was calculated based on the real-time penetration depth and the shape of the tip. The difference between it, A_{scr}, and the cross-section area of the residual ditch, A_{dit1}, reflects the immediate elastic recovery; the difference between A_{dit1} and A_{dit2} reflects the viscoelastic recovery, if any. All the different responses, including plastic deformation and abrasive wear, can be calculated quantitatively, as shown in Figure 6.

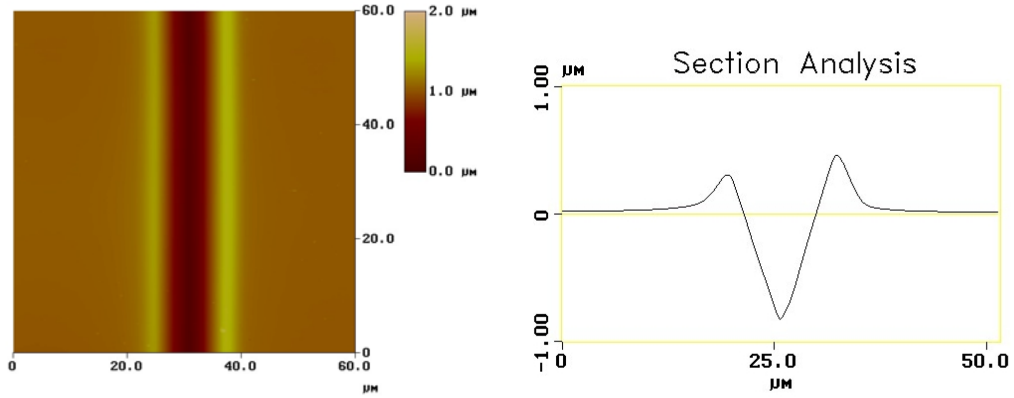


Figure 5: Mixture of the responses, plastic deformation and abrasive wear (mass loss). The cross-section area of the two shoulders is less than the cross-section area of the ditch.

In the MMR calculation, the cross-section area of the ditch was used first to divide the applied force. Later, it was replaced by the cross-section area of the trough,[2,3] which is the cross-section area of the ditch plus the area between two shoulders, if any, based on the following consideration.

Suppose two mars possess the same size of ditch, but one has two shoulders and the other has none. Due to the larger topographic fluctuation of the surface, the damage of the first sample will be more visible. To make the MMR more consistent with the visual judgment and other optical evaluations, the cross-section area of the trough was used to replace the cross-section area of the ditch in the calculation of MMR.

It should be pointed out that the mar resistances obtained above are not universal. The measurement was carried out under specific test conditions, although ten different normal forces were used. The results of MMR and the responses to scratching stress, *i.e.*, elastic recovery, plastic deformation and abrasive wear, depend not only on the normal load, but also on the shape and sharpness of the tip, scraping speed, and other conditions. Briscoe and his group did intensive study on dependence of the surface damage modes on contact mechanics variables, *i.e.* load, included angle of the spherical and conical tip, scratch speed, *etc.,* for several selected polymeric materials, and introduced a map to illustrate the relationship.[20, 21]

ISSN 2179-3956

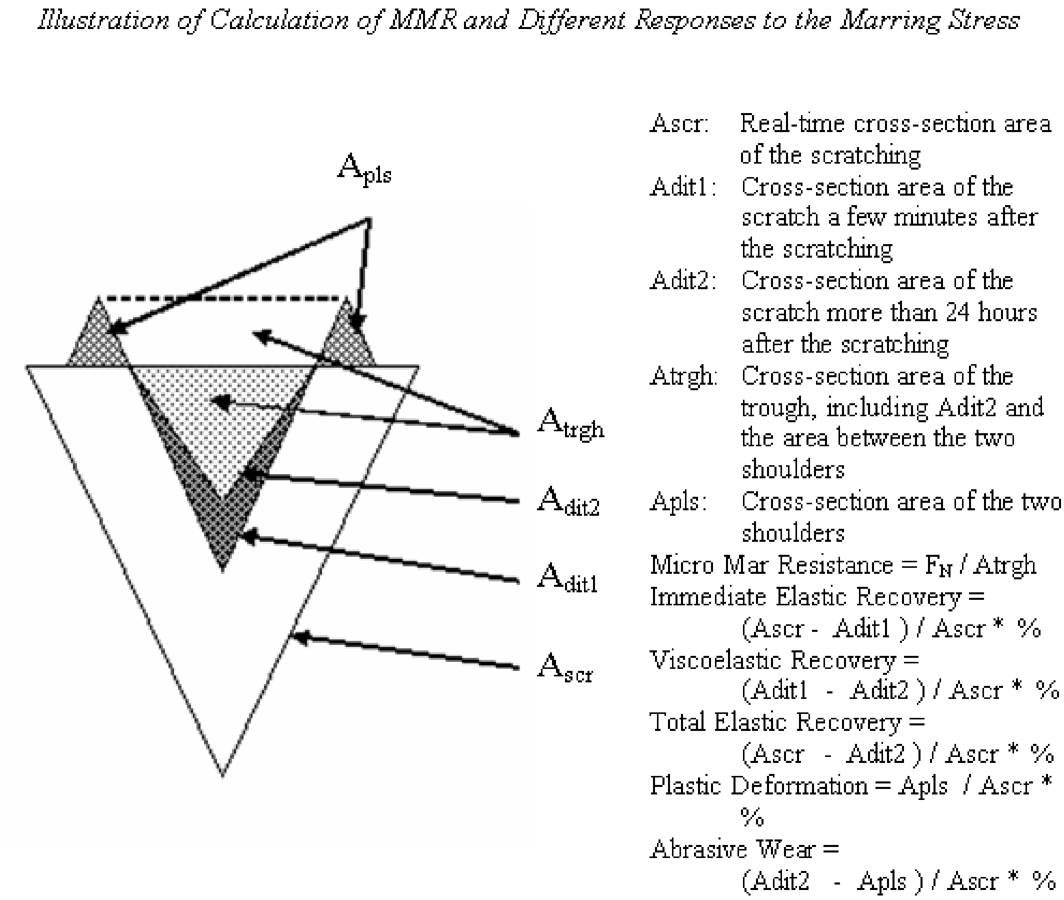


Figure 6: Illustration of how to calculate the micro mar resistance (MMR) and different responses of coatings to scratching stress.

Other groups made the same efforts, *e.g.* Loubet studied the effect of strain rate in the scratching tests,[22] and Krupicka examined the influences of scratch speed, contact geometry, and load on deformation response.[15]

A large portion of the tested coatings showed a self-healing to different extents. This is attributed to viscoelastic recovery. Viscoelastic recovery is different from elastic recovery. It results in partial or complete recovery of a scratched surface within a time frame from several minutes to several hours, while the elastic recovery occurs immediately after the marring tip moves over the surface. The viscoelastic recovery in the scratch tests of polymer coatings has been observed and studied by quite a few groups, and it mainly correlates to the glass transition temperature, Tg, of the coating.[6, 22-25]

Critical Forces Measurements

Mars are the light damage, made by the scraping under relatively low normal forces. They are usually fairly neat, consisting of a ditch with a smooth bottom and two, if any, well-shaped shoulders on both sides of the ditch, thus the micro mar resistance (MMR) is a reasonable characterization for the coatings' ability to resist the scratching stresses. Scraping the surface with an increasing normal force, the bottom of the ditch, as well as the ridges of the two shoulders, becomes rough. The neat mar becomes a rough trough. MMR is no longer an appropriate characterization

ISSN 2179-3956

since the cross-section area of the trough, used in the calculation of MMR, begins to change erratically along the rough trough. As the normal force increases further, cracking may show up in the surface of the coatings. Under the continuously increasing normal force, delamination may take place if the penetration depth of the tip reaches the interface and the stress generated by the scraping tip exceeds the adhesion strength. Increasing the force further more may result in the delaminated top layer being chipped off, piece-by-piece, from the surface. Figure 7 shows the five typical distinguishable damage modes, observed in the scratching tests.(26-28) Most scratching damages on the surface of the coatings used in the real field might be approximately classified into these five modes. Depending on the properties of the coatings, as well as testing/application conditions, the coatings may or may not show all the five modes, or even more configurations.

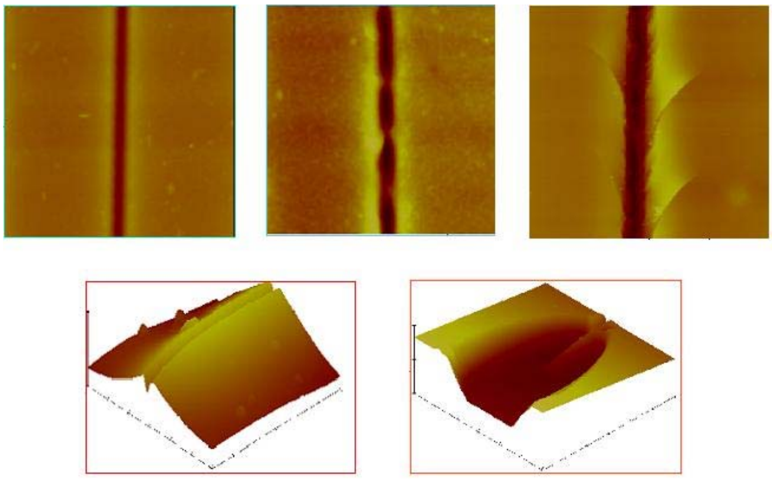


Figure 7: Five distinguishable damage modes, mar, rough trough, crack (upper from left to right), delamination and chipping (lower left and right).

To characterize the coatings' ability to resist the medium to severe damages, measurements of critical forces are widely used. In the present study, the critical force for rough trough, at which a neat mar transits to a rough trough, as well as the critical force for cracking, for delamination and for chipping, if any, will be measured, using the Nano-indenter to scrape the surface of sample under an increasing normal load. As the damage mode transits to the next more severe mode, the real-time penetration depth, as well as the depth of the residual ditch, becomes rougher, and the frictional force encountered becomes more fluctuated, which provide the evidences of the transition points. The scratched surface will be further examined by Scanning Probe Microscope to confirm the transitions, and determine the corresponding critical forces. Usually, several scratches are made under a selected increasing force. The average values of the measured critical forces will be used in the results.

Figure 8, taken from the website of MTS Nano-Indenter, shows the damage of a surface by scratching with an increasing normal load transited from a mild mode to a severe mode, after the tip has moved a distance of 220 μm, and the real-time penetration depth reached about 5000 nm. Knowing the starting force and the ending force of the linearly increasing load in the test, the critical force at the transition point could be calculated.

ISSN 2179-3956

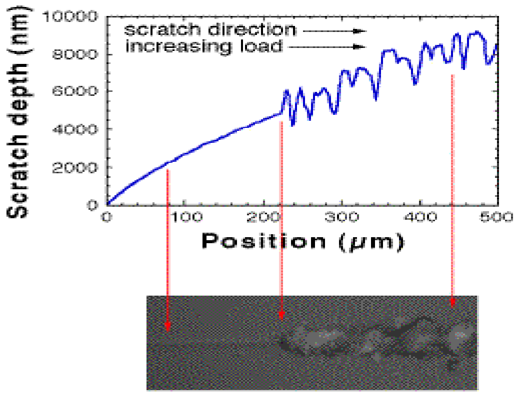
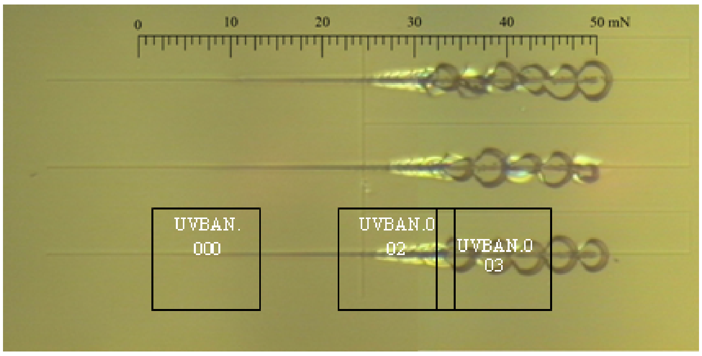


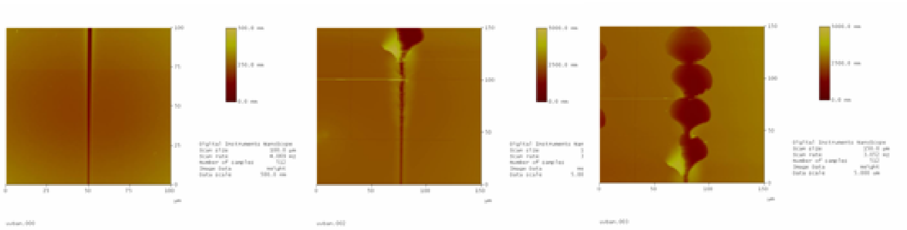
Figure 9: Real-time penetration depth in a scratching versus the lateral scraping distance.

In the development of a glazing material, the critical force measurements were carried out on an inorganic-organic hybrid hard coating, containing Si, O, H, and C, produced by plasma enhanced chemical vapor deposition (PECVD) on a siloxane/acrylic/polycarbonate composite, in our lab, which is a potential candidate to replace glass windows in the automobile industry due to its much lighter weight and extremely high impact resistance. The measured values of the critical forces in three sets of scratches were well within a deviation of 3% or less, which, in turn, verified the validity of the measurements. Of course, the heterogeneities of the coatings and inhomogeneous interfaces in some samples will cause large deviation of measured critical forces. Figure 10 is an illustration, showing the optical picture of three scratches made by Nano-indenter under an increasing load up to 50 mN and three SPM images in the selected area along lower scratch.

Progressive load (0-50 mN) tests

Optical and AFM images of an increasing load scratch on a sample





Sample	F-Mar	F- Rough trough	F- Cracking	F-Delamination	F-Chipping
UV	0-20/25mN	20-25mN	25-30mN	30-32mN	32mN+

Figure 10: Illustration of the increasing (progressive) load scratching test.

ISSN 2179-3956

As mentioned above, depending on the properties of the coatings/substrates and the testing/application conditions, the coatings/substrates may or may not show all the five damage modes. Classifying the scratching damages into five categories is not universal. Lin and his colleagues simply classified the damages in automotive clear coatings into two categories, *i.e.* plastic flow and fracture, and measured one critical force at the transition point.[29, 30] Courter and Kamenetzky used critical load I, at which the first crack occurs, and critical load II, at which the first severe cracking and delamination occur, to characterize the scratch resistance of coatings.[31]

We have to be aware of that the measured values of the critical forces depend on the testing conditions, including the shape and sharpness of the tip, scraping speed, rate of the normal load increase, *etc*. Sung and his colleagues investigated the dependence of critical force on the test conditions.[19] They found that if F_{crt} is the critical force for cracking measured when the Indenter is operated in the increasing force mode during the scratching; using the same constant force at F_{crt} to scrape the coating may not cause any cracking, and the values of measured critical forces may increase with the increasing scraping speed, too.

Essentially, it is the critical strain, not the critical force, and the strain rate, that determine the transition point from one damage mode to another. However, it is hard to measure the strain and its rate directly at this point. Critical forces measurements under selected conditions provide useful characterization of the mar/scratch resistance of coatings.

Summary

The nano instruments can perform the scratching tests under well-controlled conditions, which are used popularly in the scratch resistance characterization these days. As an illustration, a Nano-Indenter XP of MTS, combined with a Scanning Probe Microscope (SPM), is used to measure the micro mar resistance, the different responses of coatings to scratching stress, *i.e.* elastic recovery, plastic deformation and abrasive wear, quantitatively, and the critical forces for rough trough, cracking, delamination and chipping, which give a full spectrum of characterization of the scratch resistance behavior of coatings. One has to be aware of that all the measurement results are obtained under certain testing conditions. The damages of scratching essentially are the stress-strain problem. The strain and its rate are determined by the applied stresses in the tests, as well as by the properties of the coatings themselves. They, in turn, manifest the variety of the morphologies of damages. Theoretical analysis and finite element modeling can complement the experimental studies to gain fundamental understanding of the scratch resistance behavior of the coatings.

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ISSN 2179-3956

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