Characterization of Mar/Scratch Resistance of Polymeric Coatings: Part I

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This two-part article briefly reviews the development of mar/scratch characterization techniques, and focuses on single-probe tests with nano instruments which have been widely used recently. Quantitative measurements of micro mar resistance (MMR), different responses of the coatings to the marring stress (i.e., elastic response, plastic deformation, and abrasive wear), and critical forces for rough trough, cracking, delamination, and chipping are described, as are some complementary test methods. Statistical investigation of damage on samples used in real environments, combined with laboratory mar/scratch tests on these samples, could determine the force distribution curve in the lab which is approximately equivalent to the field conditions. The curve is useful for development of new coatings, and it can predict the weights of different damage modes that are likely to occur at the surface of the coatings in the field. The weights, combined with the quantification of the damage levels of different modes, allow calculation of a quantitative index to characterize the mar/scratch resistance of a coating in a specific environment comprehensively. To better understand the mar/scratch resistance behavior of tested materials, a detailed stress-strain study is needed, utilizing theoretical analysis and finite element modeling to complement the experimental measurements described here as an integrated approach.

INTRODUCTION

Mar/scratch resistance is an important and highly desired property for coatings in many applications, such as polymeric clear topcoats applied on automobile bodies, which customers expect to have a long-lasting glossy look while providing protection, and paints on thermoplastic olefin (TPO) that is being used more frequently as interior and exterior materials to replace metals. Consequently, techniques for characterizing mar/scratch resistance have been pursued for years in order to establish reliable laboratory test methods that can predict the performances of coatings against marring/scratching in their real-world applications and direct their further improvement.

Mars and scratches are made by external stresses along the surfaces of coatings with a tangential component as well as a normal component. Conventional hardness measured by well-established indentation tests is not a proper characterization of mar/scratch resistance. Instead, it is just a measurement of a material's ability against a normal compressive stress. Some polymeric coatings are very hard, but they may have a poor mar/scratch resistance due to their brittleness and/or lack of toughness.

Usually, mars/marring refers to the light surface damages encountered in the field; they are usually shallow and narrow, while scratches/scratching refers to medium to severe damages. The majority of the damage to topcoats applied on automobile bodies belong in the mar category. 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 visibly degrade the appearance of coatings. Scratches are more visible, and they may cause fracture and cracking, or even delamination and chipping.

Early mar/scratch measurement tests range from very basic ones, such as the pencil test, which ranks the coatings as B, F, H, 2H, etc., to instrumental ones, such as the Taber test, Crockmeter test, etc. The 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 (see *Figure* 1). Although it is still used in many applications, such as in window tests for the auto industry, it was thought to be too harsh for many applications of polymeric coatings, e.g., clear topcoats. The Crockmeter test was commonly accepted by the auto industry to test clear topcoats. Atlas Materials Testing manufactures the devices for this test. In the

Figure 1—Taber test.

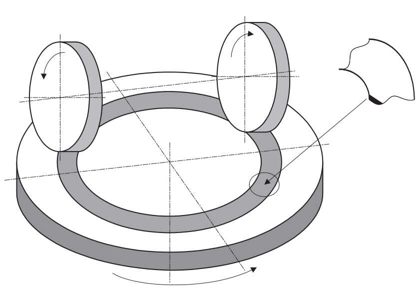

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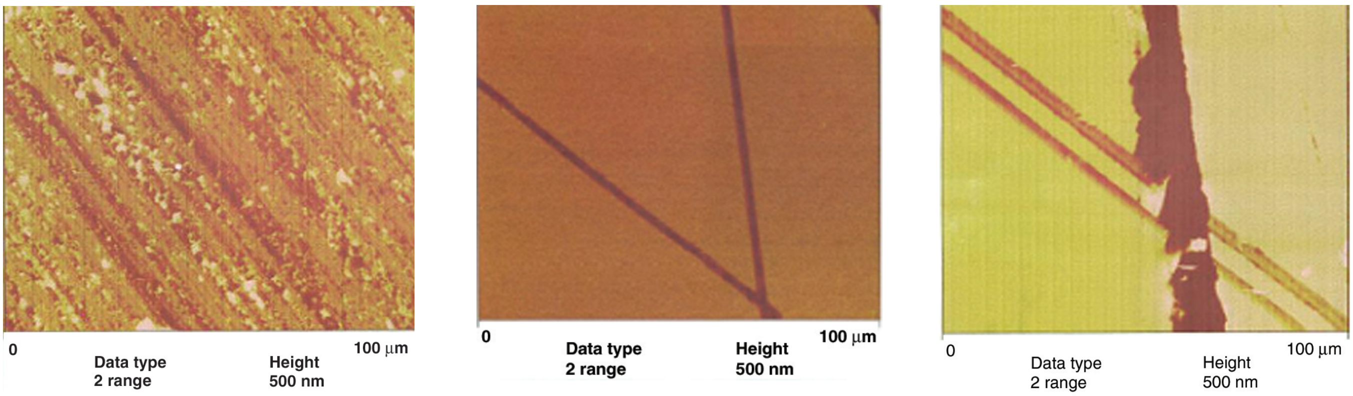
Figure 2—Comparison of the surface of a coat that has undergone the Crockmeter test with the surface of the same coat that contains real mars and scratches incurred in the application field.

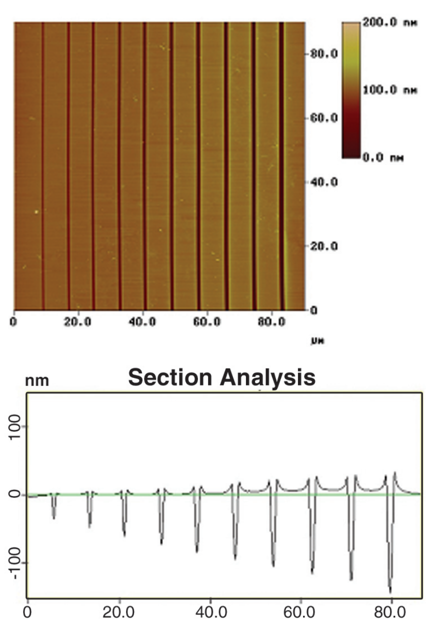


Surface after Crockmeter test | Real Mars | Real scratches

Crockmeter test, a clear topcoat 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. To perform the test, a test probe covered with a fresh green felt pad is moved back and forth over a portion of the panel in 10 double strokes so the panel is marred 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° pocket gloss meter by slowly moving the meter across the panel, measuring gloss of both the unmarred and marred sections. The result of the resistance against scratching and marring is reported as percent of gloss retained. However, the surface of a coat that has undergone the Crockmeter test is different from the surface of the same coat that contained real mars and scratches incurred in the application field, as shown in *Figure* 2. The quite different configurations indicate that the surface in the Crockmeter test was subjected to different stresses and suffered different damage than is actually encountered in the field.

Since the car wash is thought to be a major source of mars and scratches, a variety of laboratory devices and techniques have been developed to simulate a car wash, such as the Test for Wash Resistance and Scrub Resistance, described in ASTM D 2486 (USA), and Amtec Laboratory Car Wash, created by a DFO workgroup and approved by the DIN standardization committee (Germany). These tests were usually followed by a weight loss measurement or decrease in gloss measurement, giving an overall evaluation of the tested coatings. The results might or might not be consistent with the real applications. The essential shortcoming is that these tests could not distinguish various marring/scratching mechanisms, thus they can not be studied in detail to give clear directions on how to improve the performance of the tested coatings.

In the mid-90s, single-probe testing techniques were developed. The tests are carried out under well controlled conditions, thus making it possible to study different marring/scratching mechanisms under different test conditions, and to correlate mar/scratch resistance of the tested coatings with their physical and chemical properties. In the tests, some used the atomic force microscope,[1-9] and others a variety of homemade devices.[10-21] Commercial nano-indenters and nano-scratchers, such as Nano-Indenter XP by MTS Systems Corporation and Nano/Micro Scratch Tester by CSM Instruments, were developed around the late 1990s, and became increasingly popular for mar/scratch measurements.[22-27] These nano instruments are easy to use, offer flexi-



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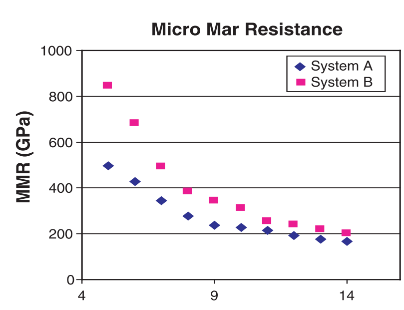
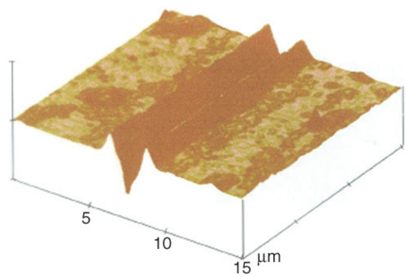


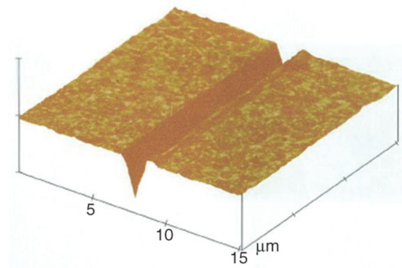
(b)

Figure 3—(a) An image of 10 mars, made under the 10 different constant loads from 5 mN to 14 mN, respectively, and their cross-section profiles. The MMR is then calculated as $MMR = FN/A_{trough}$. (b) MMR vs. the applied normal forces of two glazing systems.

Figure 4—Two different mar configurations: (a) plastic deformation dominates, and (b) abrasive wear (mass loss) dominates.



(a)



(b)

ble test conditions, and have greatly enhanced the capability of carrying out mar/scratch measurements.

As an illustration, a Nano-Indenter XP equipped with a 90° conical-shaped diamond tip with a radius of 1 µm at its apex was used in the measurements described. 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 mar/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 Digital Instruments, Veeco Metrology Group, was used to examine the damaged surfaces and analyze the marring/scratching mechanisms.

MAR RESISTANCE MEASUREMENT

Mar resistance not only depends on the properties of the coatings, but also depends on the test conditions. Since this is a complicated issue, mar resistance cannot be characterized with a single quantity. Usually a series of normal loads is used in the scraping to measure the mar resistance of a tested coating.

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.

In performing the test, the diamond 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 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.

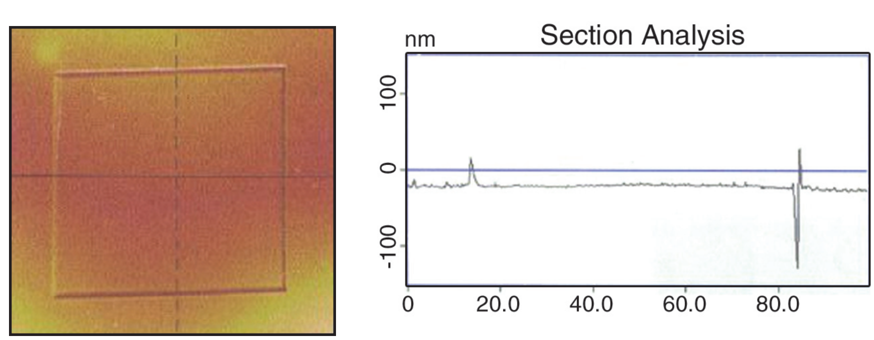
In the present test, the Indenter scraped the surface of a coated polycarbonate glazing system, a candidate for automobile windows, under 10 pre-selected constant loads from 5 mN, 6 mN, up to 14 mN, before the mar transited to the rough trough, which will be discussed later, for a distance of 150 µm at a speed of 20 µm/sec. It produced a group of 10 parallel mars, with a predetermined spacing of about 10 µm on the surface. After the marring, the sample was washed again, but without the detergent, to remove any broken material, then the marred surface was examined with the SPM. *Figure* 3a shows the image of 10 mars at the surface and their cross-section profiles. The plot of the profiles is made by the software in the SPM, based on the average values of 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 marring divided by the cross-section area of the trough as shown below,[4]

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

Using MMR, we can clearly compare the mar resistance of different coatings. MMR varies with the applied load, i.e., penetration depth, so a group of values obtained under the different loads is needed to present it. *Figure* 3b is a plot of MMR versus the applied normal forces of two systems. System A is the system used in *Figure* 3a. MMR of system B was much better than that of system A under the light normal forces, but it decreased more rapidly with the increasing normal force than system A's. MMR of system B was about the same as system A under greater normal forces.

For most of our tested crosslinked polymeric clear topcoats, MMR, as well as the micro-indentation hardness, is large at the very top layer, and decreases as the load increases and the tip begins to penetrate into the surface. This may suggest the existence of a hard crust at the top layer of these crosslinked polymer coatings, where the crosslink density may be higher due to the weathering effect.

Figure 5—After 512 vertical marrings from left to right, only the left shoulder of the first mar and the ditch and right shoulder of the last mar remained at the surface. The upper and lower horizontal ditches in the image were made by the turning of the 512 marrings.

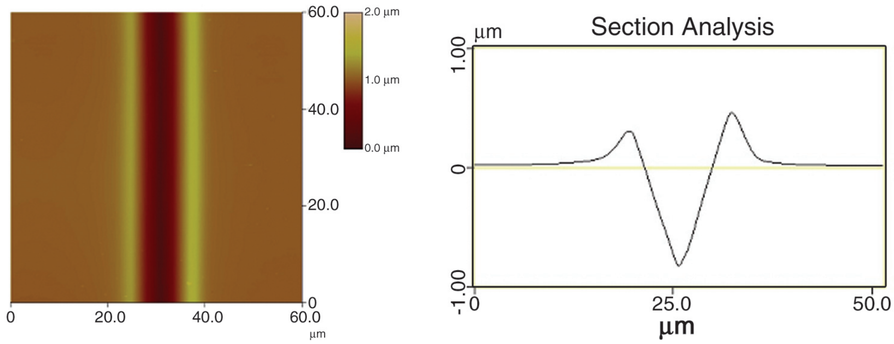


Analyzing the high-resolution images of the mars, the different responses of the coatings to the marring stress could be identified, thus studying the different marring mechanisms was possible.[4] *Figure* 4 shows two different configurations of mars. Plastic deformation dominates in (a): two big shoulders sit on both sides of the ditch, indicating the material was displaced from the ditch to build these two shoulders during the marring. Abrasive wear (i.e., mass loss), dominates in (b): 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; but it results in mass loss for sure.

Plastic deformation is reversible, if the material on 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 μm by 70 μm. During the marring, 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 marring 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* 5a and its profile in 5b.

Most tested coatings showed a mixture of the responses, as shown in *Figure* 6. 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—considering the compressibility of the tested coatings is no more than 5%—between the total area of two shoulders and the area of the ditch reflects the abrasive wear, i.e., mass loss. *Figure* 7 is an illustration of how to calculate MMR and shows three different responses of coatings to marring stress, based on the dimensions of the mar. The largest inverted triangle represents the cross-section area of the part of the tip that penetrated the surface during the marring, which was calculated based on the real-time penetration depth during the marring and the shape of the tip. The difference between it and the cross-section area of the residual ditch reflects the immediate elastic recovery plus the viscoelastic recovery, if any, during the time between the scraping and the imaging afterwards. The calculation of plastic deformation and abrasive wear was as described above.

Figure 6—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.

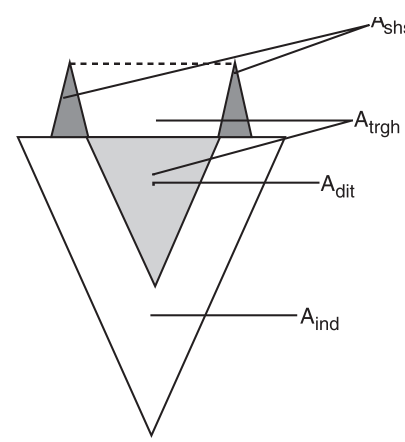


In the MMR calculation, the cross-section area of the ditch was used first to divide the applied force. Later, it was replaced by the cross-section area of the trough,[3,4] which is the cross-section area of the ditch plus the area between two shoulders, if any, based on the following consideration: Suppose two mars possess the same size 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 10 different normal forces were used. The results of MMR and the three responses to marring 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.[28-30] Other groups made the same efforts—Loubet studied the effect of strain rate in the scratching tests[31] and Krupicka examined the influences of scratch speed, contact geometry, and load on deformation response.[21]

A large portion of the tested coatings showed self-healing to different extents. This is attributed to viscoelastic recovery. Viscoelastic recovery is different from elastic recovery. It results in partial

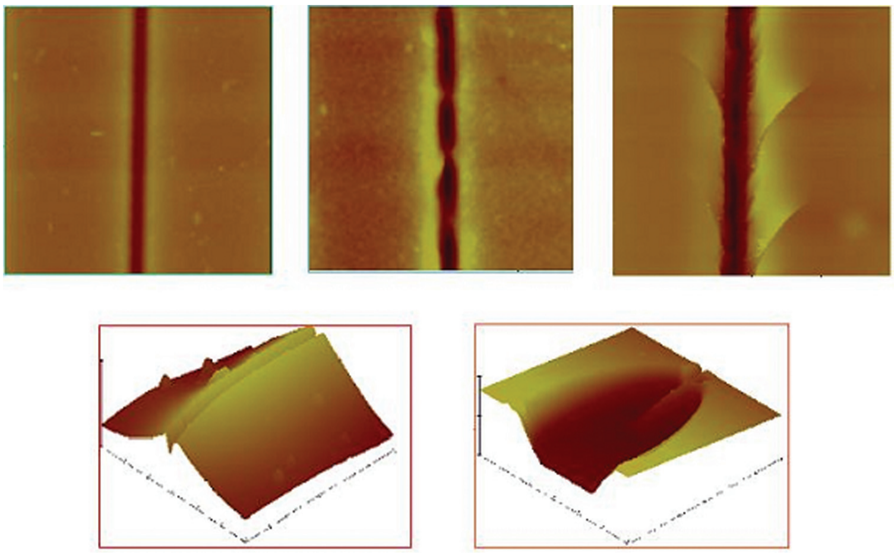
Figure 7—Illustration of how to calculate the MMR and three different responses of coatings to marring stress.



A_{ind} : Cross-section area of the indentation
A_{dit} : Cross-section area of the ditch
A_{shs} : Cross-section area of the two shoulders
A_{trgh} : Cross-section area of the trough

Micro Mar Resistance: F_N/A_{trgh}
Elastic Recovery: $(A_{ind}–A_{dit})/A_{ind}$ * %
Plastic Deformation: A_{shs}/A_{ind} * %
Abrasive Wear: $(A_{dit}–A_{shs})/A_{ind}$ * %

Figure 8—Five distinguishable damage modes: mar, rough trough, crack, delamination, and chipping.



or complete recovery of a marred surface within a time frame ranging 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 mar/scratch tests has been observed and studied by quite a few groups[7,16,19,31-36] and it mainly correlates to the glass transition temperature, T_g, of the polymer coating.[7,16,19,31,35,36]

CRITICAL FORCES MEASUREMENTS

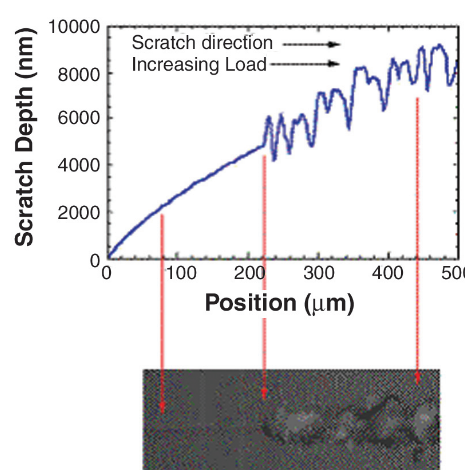
Mars are the light damages made by scraping under relatively low normal forces. They are usually fairly neat, consisting of a ditch with a smooth bottom and two, if any, well-shaped shoulders on both sides of the ditch. Thus, the micro mar resistance is a reasonable characterization for a coating's ability to resist mechanical stresses. Scraping a coating's 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 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 coating. 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 may result in the delaminated top layer being chipped off, piece-by-piece, from the surface. *Figure* 8 shows the five typical distinguishable damage modes, observed in the marring/scratching tests.[37-40] Most scratching damages on the surfaces of coatings used in the field can 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 five modes.

To characterize a coating's ability to resist 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, are 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 fluctuates more, which provides the evidence of the transition points. The mar/scratch is further examined by a Scanning Probe Microscope to confirm the transitions and determine the corresponding critical forces. Usually, several mars/scratches are made under a selected increasing force. The average values of the measured critical forces are used in the results.

Figure 9, taken from the MTS Nano-Indenter website, shows the damage of a surface by scratching. With an increasing normal load, the damage transitioned from a mild mode to a severe mode after the tip had 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.

In the development of a glazing material, the critical force measurements were made 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. This 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 six 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 sam-

Figure 9—Real-time penetration depth in a scratching vs. lateral scraping distance.



ples will cause large deviations of measured critical forces.

Depending on the properties of the coatings/materials and the testing/application conditions, the coatings/materials may or may not show all the five damage modes. Classifying the marring/scratching damages into five categories is not universal. Lin and his colleagues classified the damages in automotive clear coatings into two categories—plastic flow and fracture—and measured one critical force at the transition point.[41,42] 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.[43]

Again, one has to be aware that the measured values of the critical forces depend on the testing conditions, i.e., the shape and sharpness of the tip, scraping speed, rate of the normal load increase, etc. Sung and her colleagues investigated the dependence of critical force on the test conditions.[27] 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, then 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.

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 force measurements under selected conditions provide useful characterization of the mar/scratch resistance of coatings.

OTHER MEASUREMENT METHODS

Measurements of micro mar resistance, the different responses to marring stress—elastic recovery, plastic deformation and abrasive wear, and critical forces for rough trough, cracking, delamination, and chipping—described here in Part I, are commonly used in characterization of mar/scratch resistance of coatings. However, selecting a characterization technique must be based on the properties of the tested materials as well as their application conditions. In Part II of this article (to be published in JCT COATINGSTECH, April 2006) some complementary test methods will be described. CT

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