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

by Weidian Shen, Eastern Michigan University*

This two-part article (Part I was published on pages 54-60 in the March 2006 issue of JCT CoatingsTech) 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.

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 in Part I of this article (JCT CoatingsTech, March 2006) 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. Some complementary test methods are described in Part II.

Crack Density Measurement

In the testing of thermoplastic olefin (TPO), which is being used more often as interior and exterior material in automobiles,[7,19,20,44] it was found that the mar/scratch resistance methods described previously in Part I might not be appropriate. TPO is a very fragile material, easily damaged,[15,46] and the surface is relatively rough with fluctuations of up to several hundred nanometers. Due to the roughness of the surface (equivalent to the depth of most mars), it is hard to make a neat mar and calculate the micro mar resistance of it. Due to its fragile nature, the surface cracks as soon as the tip sticks into the surface, before scraping. To characterize its mar/scratch resistance behavior, an alternate method was proposed, in which the Nano-Indenter is used to scrape the surface of TPO under a relatively low constant normal load of a couple of milli-newtons. After the scraping, a Scanning Probe Microscope (SPM) is used to examine the scratch and measure the number of cracks per unit length. The density of the cracks is an indication of the material's toughness against the fracture. It also depends on the penetration depth during the scratching and the scraping speed. *Figure* 10 is a 25 µm by 25 µm image of a scratch made under 3 mN normal force, showing the cracks distributed on both sides of the ditch.

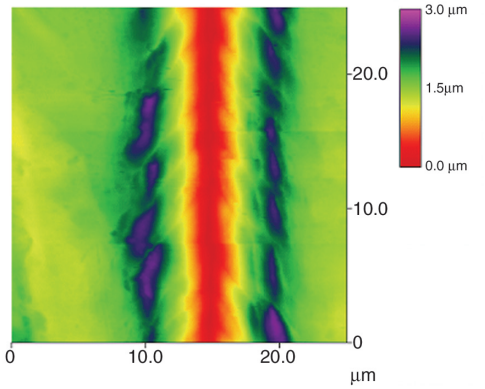
More than one dozen TPO samples with various components, prepared with different processing procedures, were examined. The average density of cracks of each sample, obtained from about a dozen images examined, varies from about 8 cracks per 25 µm to about 16 cracks per 25 µm.

Repeated Scraping Test

For the materials that may be subjected to the repeated scraping

*Surface Science and Nano-Tribology Laboratory, Coatings Research Institute, Ypsilanti, MI 48197.

Figure 10—Image of a scratch made under 3mN normal force, showing the cracks distributed on both sides of the ditch.



along the same trench in the applications, this test can provide a proper measurement of their mar/scratch resistance behavior in the applications; for example, the glazing material used for automobile side windows. The hard dust particles trapped between the window and the rubber seals may repeatedly mar and scratch the surface in the same trench when the window is rolled up and down.

In the repeated scraping test, the Nano-Indenter is used to scrape the sample surface along the same trench with a relatively low and constant load for several selected times. After the scrapings, images of the scratches are taken using the SPM for configuration study and the depths of the scratches are measured. The test results of two glazing materials, labeled as A and B, potential candidates for windows, are presented here as examples. In the test, their surfaces were scraped along the same trench under a constant load of 5 mN repeatedly for 5, 10, 20, 40, and 60 times at a scraping speed of 20 µm/sec. The measured depths of the mars after 5 and 10 scrapings on the surface of A were 60 nm and 90 nm, respectively; the measured depths of the mars after 5, 10, and 20 scrapings on the surface of B were 100 nm, 125 nm, and 135 nm, respectively, before the damages transited to the rough trough. The depths of mars on the surface of A were shallower than those at the surface of B after the same number of scrapings, which might be an indication that sample A is harder than B at the top layer. It was confirmed by the micro indentation hardness test that A, under a light normal force of 1.5 mN or 3.0 mN, was harder than B by about 35%.

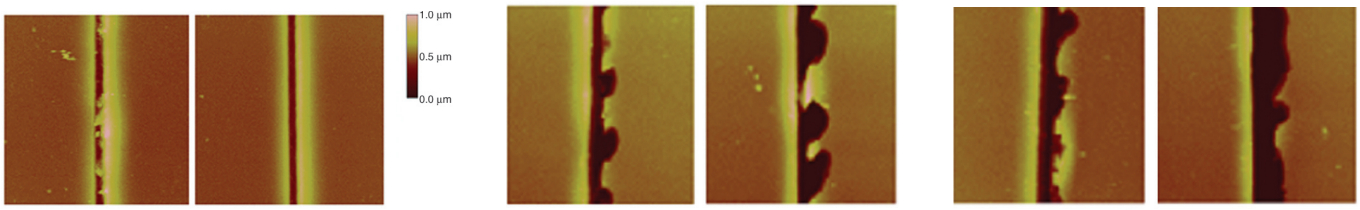
The images of the scratches showed that the damages of sample A belonged to the category of "mar" after 5 or 10 scrapings, then became "rough trough" after 20 scrapings, and chipping took place after 40 or 60 scrapings. In contrast, the damages of B stayed in the category of "mar" beyond 20 scrapings. However, when the chipping occurred after 40 and 60 scrapings, the damages on the surface of B were more severe (the chipped spots deeper and wider) than those on the surface of A. The selected images for illustration are shown in *Figure* 11. The results indicate while B is soft, it is more ductile, so it stayed in "mar" longer. On the other side, sample A is hard, but it may be brittle and was vulnerable under the increasing load, and the damage transited to rough trough earlier. The results are consistent with the results of the micro mar resistance and critical force measurements of A and B. Under the light loads, MMR of sample A is better than B, since B is soft and ductile, and the mars on the surface of B were deeper and wider. However, the critical force of transition from mar to rough trough of sample A was lower than that of sample B, since A is brittle, and its surface was easily broken under the increasing load.

Examining the dimensions of the chippings further suggests that the vulnerable layer of sample A, where the adhesion/cohesion was weak and it was easily chipped off, might be in the depth of 600–800 nm, while that of sample B might be in the depth of 1.4–1.8 µm. When the chipping took place on both surfaces, B suffered more severe damages than A.

Cross-Scratching Test

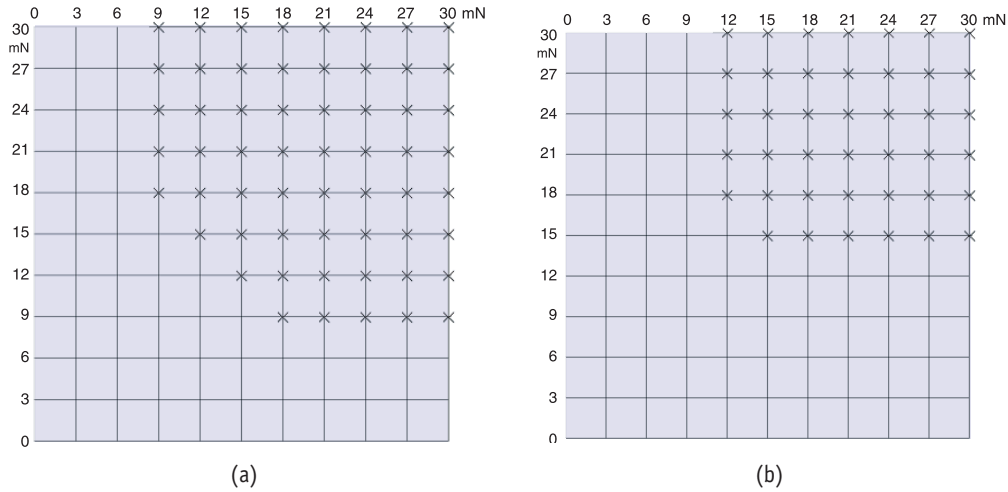
For the materials that may be subjected to cross-scratching in applications, the cross-scratching test can provide a proper measurement of their mar/scratch resistance be-

Figure 11—(a) After 20 scrapings, surface A (on the left) had a rough trough, while surface B (on the right) had a mar. (b) After 40 scrapings and (c) after 60 scrapings, both surfaces were chipped, but the chipped area on surface B (on the right), is bigger and deeper than surface A (on the left).



(a) (b) (c)

Figure 12—Two groups for a total of 20 scratches; each of them was 1000 µm long made under a linearly increasing force from 0 to 30 mN, in a pair of orthogonal directions, and made a matrix with a spacing of 100 µm. An "x" mark was used to indicate the observation of the chipping at the intersections.



havior in the applications. For example, in the glazing material used for automobile windshields, the overlap area swept by two rubber wipers blades may be cross-scratched by the hard dust particles trapped between the windshield and the rubber blades.

Again, samples A and B are used as examples to describe the cross-scratching test. The 1000 µm long scratches were made with the Nano-Indenter under a linearly increasing force from 0 to 30 mN at a scraping speed of 20 µm/sec. Two groups of a total of 20 scratches were made in a pair of orthogonal directions, which made a matrix with a spacing of 100 mm as shown in *Figure* 12. After the scratching, all the intersections were examined by the SPM, and a mark "×" was used to indicate the observation of the chipping at the intersections.

There were more chipped intersections on the surface of A than on the surface of B. The chipping began to take place under the lighter loads on surface A than on surface B. However, as soon as the chipping began to take place at the intersections of surface B, the damage was more severe than that of surface A. *Figure* 13 shows two pairs of images. One was taken at the intersection of (12 mN, 15 mN), where the chipping took place only on the surface of A; the other was taken at the intersection of (27 mN, 24 mN), where the chippings occurred on both surfaces, and the chipped spot on the surface of B was bigger and deeper. The results gave further support to the repeated scraping test. Due to the brittleness of the top layer of sample A and ductility of sample B, the intersections on the surface of A began to chip first. Under the increasing loads, chipping took place at the intersections of surface B too. The vulnerable layer of B is deeper, thus the chipped pieces on the surface of B were thicker and bigger than those of A.

Due to the variety of coatings/materials properties and variety of their application conditions, continuous development of characterization methods to provide reliable and dependable characterization for the real applications is necessary.

INVESTIGATION OF APPLICATION ENVIRONMENTS BY MAR/SCRATCH MEASUREMENTS

In this section, we will look at the process of designing, engineering, and developing mar/scratch resistant coatings/materials for a specific application. Investigating the application environments is the necessary first step. This will be carried out by an intensive statistical survey of the damages on the surfaces of the samples, which have been used in the application environment, plus the mar/scratch measurements on these used samples.

For this procedure, the previously mentioned coated glazing material for automobile side windows, which is under development by Exatec LLC, a joint venture of GE and Bayer, is used here again as an example.

Exatec has a large collection of used windows from cars and trucks driven in various U.S. states as well as abroad, and the samples were cut from different parts of the windows. An optical microscope, equipped with a CCD camera, and a Scanning Probe Microscope were used to examine the damaged surfaces of the samples.

The practical application environment is very complicated, and the damages can be caused by a variety of culprits. For example, damages on the side window surfaces can be made by brush bristles in car washing, sand and stone particles on roads, salt particles in winter, as well as the dust particles trapped between the window and the rubber seals as mentioned above. Consequently, the configurations of the damages are much more diversified. However, as an approximation, all of the damages can be classified into five categories: mar, rough trough, cracking, delamination, and chipping, as described above. Based on the intensive statistic survey, the weights of occurrence of the five distinguishable damages are, as an illustration, 75%, 15%, 6%, 3%, and 1%, respectively.

Carrying out a laboratory test with the Nano-Indenter and SPM on the samples of the used windows, as previously described, the measured critical forces for rough trough, for cracking, for delamination and for chipping were 20 mN, 30 mN, 40 mN, and 50 mN, respectively. Thus, the distribution of the forces encountered by the windows in real field conditions could be approximately equivalent to a force curve in the laboratory, as plotted in *Figure* 14. The area under the line between F=0 to F=20 mN is 0.75, i.e., 75%; the area under the line between F=20 mN to F=30 mN is 0.15, i.e., 15%; and so forth. The total area under the line is 1, i.e., 100%, and the force distribution function P is normalized. Here, an assumption was made for simplicity that the forces distribute uniformly between F=0 to F=20 mN, between F=20 mN to F=30 mN, and so forth. If the damages are classified into more and more modes, by measuring the weights of occurrence of each mode and their corresponding critical forces, a smooth force distribution curve can be obtained eventually, such as shown in *Figure* 15. The curve is very useful. If it is heavily weighted on the light side, it indicates material in the applications will mostly suffer from light invading forces, having only narrow and shallow mars at its surface. Thus, marring will dominate and it will not be necessary to enhance its resistance against the severe damages. On the other hand, if the force curve is weighted on the heavy side, it indicates that the material will mostly suffer from severe damages (i.e., cracking, delamination and chipping) and it would make no sense to concentrate on improving its micro mar resistance.

For a new sample under development, carrying out a test in the lab using the force curve to measure critical forces for different damage modes can be used to predict the weights of different damage modes that might occur on the surface of the sample in the field. Suppose the critical forces of the new sample for rough trough, for cracking, for delamination, and for chipping are measured to be F_1, F_2, F_3, and F_4, respectively. The area under the curve between 0 and F_1 is the occurrence weight of mars, the area under the curve between F_1 and F_2 is the occurrence weight of rough trough, and so forth, as shown in *Figure* 16, which avoids a time-consuming field test. The greater the critical forces, lighter will be the damages the material will experience.

Using the occurrence weights of the different damage modes at the surface of a sample, plus the quantifications of the damage levels of different modes, a comprehensive mar/scratch resistance index can be calculated,[46] which will be discussed later.

QUANTIFICATION OF DAMAGES BY MARS AND SCRATCHES

The damages or appearance degradation of the clear topcoats, thermoplastic olefin, coated glazing materials for windows, etc., by mars and scratches is usually judged by vehicle owners on visibility of the damages. Different mar/scratch damage modes have different visibilities. Lin and his colleagues carried out a survey by having several dozen people examine the scratches

Figure 13—(a): Intersection of (12 mN, 15 mN) at surface A began to be chipped (b): Intersection of (12 mN, 15 mN) at surface B showed no chipping. (c) and (d): Intersections of (27 mN, 24 mN) at both surfaces were chipped, but the damage on surface B shown in (d) is more severe (with the chipped area bigger and deeper) than surface A, shown in (c).

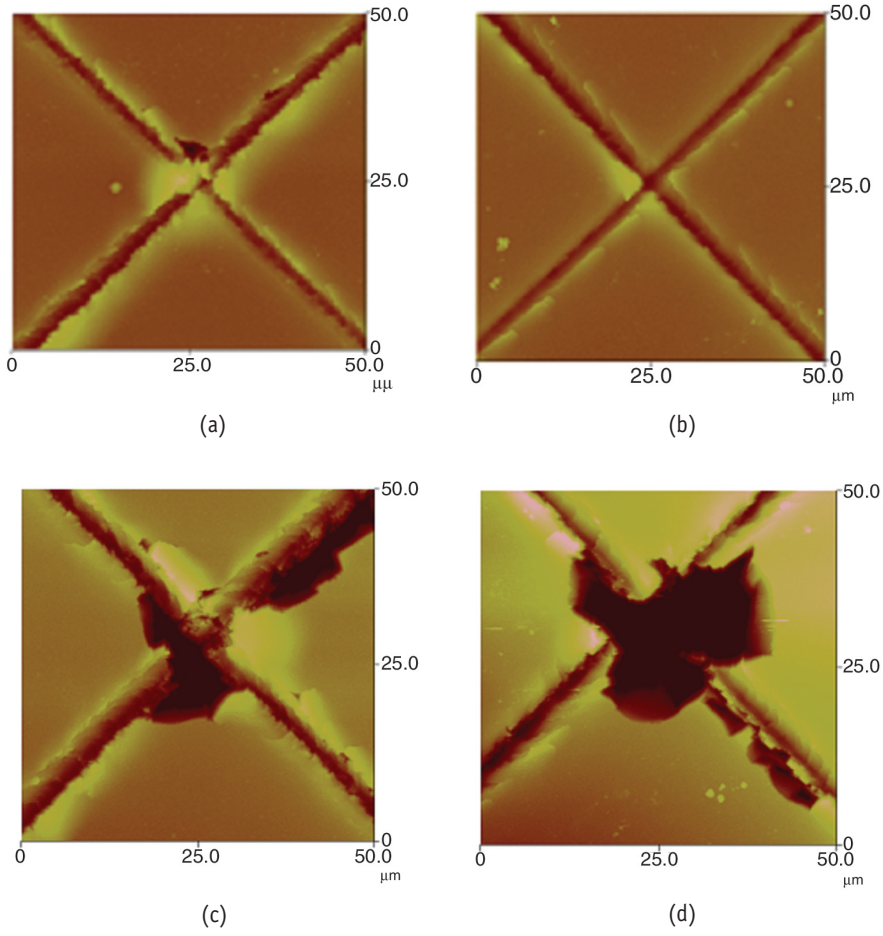
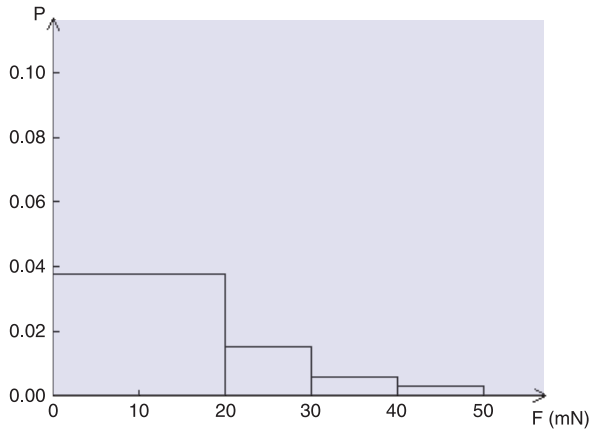


Figure 14—Force distribution plot based on study of a sample, which has been used in the field with the weights of the occurrence of mar, rough trough, cracking, delamination, and chipping being 75%, 15%, 6%, 3%, and 1%, respectively; and its critical forces for rough trough, cracking, delamination, and chipping being 20 mN, 30 mN, 40 mN, and 50 mN, respectively, in the laboratory test.



made on a panel and found the scratches with fracture were much easier to notice than the scratches with pure plastic deformation.[41] Loubet's group did a similar study and had the same conclusion.[25] Since the visibility is judged by eye, which is an optical instrument, efforts have been made by several groups to quantify the damages by mars and scratches using optical evaluations, such as quantifying the light scattered from a deformed polymer surface,[11] characterizing the scratch deformation using surface optical reflectivity,[12] characterizing the scratch visibility by image analysis,[15] measuring scratch visibility using optical imaging,[47] etc.

Quantification of damages depends on the requirements of the applications. For the present example of coated glazing material for auto windows, considering that an object will be clearly sharp if viewed through an undamaged window and will be milky or cloudy if viewed through a damaged window, measuring the haze level increase to quantify the different damage modes is adequate. On the other hand, when developing new topcoats are applied to automobile bodies, using an optical reflection measurement will be adequate.

A Haze-Gard Plus instrument made by BYK-Gardner, as shown in *Figure* 17, was used to evaluate the degrading visibility of different damage modes by measuring the haze level increase. In the measurement, the transparent specimen is illuminated at normal incidence, and the transmitted light is measured photo-electrically by an integrating sphere. Haze is caused by wide-angle scattering. According to ASTM D 1003, haze is the percentage of transmitted light that deviates from the incident beam by more than 2.5° on average. When the total transmittance is measured, the sphere's normal outlet is closed, and when haze is measured, the normal outlet is opened. Increase of haze of a transparent sample reduces the contrast of an object viewed through the transparent sample and results in a milky or cloudy appearance of the object.

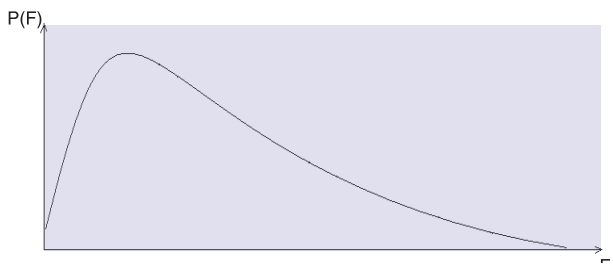
The measured haze levels of the samples with mars, rough troughs, cracks, delamination, and chippings were 0.04, 1.49, 3.52, 6.98, and 16.6%, respectively, as shown in *Figure* 18. As the damage mode passed from mar to trough to cracking to delamination and to chipping, the haze level increased dramatically. This indicated that the cracking, delamination, and chipping made more severe damage visible to eye examination. We used 0.04, 1.49, 3.52, 6.98, and 16.6 as quantitative damage levels of mar, rough trough, cracking, delamination, and chipping, respectively.

As mentioned above, the quantitative mar/scratch resistance index of a coating in a specific application can be obtained by multiplying the weights of different damage modes occurring on the surface of the coating in the application to the corresponding quantitative damage levels, then adding them together.[46] For the present example, the index of the material of the windows used in the application is calculated below. The calculation is based on the weights of occurrence of mar, rough trough, cracking, delamination, and chipping being 75, 15, 6, 3, and 1%, respectively, and their quantitative damage levels are 0.04, 1.49, 3.52, 6.98, and 16.6, respectively:

$$Q = \sum_{i=1}^{5} Wi * Di = 0.75 \times 0.04 + 0.15 \times 1.49 + 0.06 \times 3.52 + 0.03 \times 6.98 + 0.01 \quad 16.6 = 0.8395.$$

The smaller the index, the better the material performs in mar/scratch resistance behavior. If the damages are classified into more and more modes, the index will be, eventually, calculated through integration,

Figure 15—Force distribution curve; if we classify the damages into more and more modes, and measure their corresponding critical forces, ideally we will obtain a smooth force distribution curve.



$$Q = \int_{F=0}^{\infty} P(F)D(F)dF$$

where P(F)dF is the normalized weight of the damage caused by a force between F and F + dF, and D(F) is a function of F, representing the quantitative damage level.

The quantitative index comprehensively evaluates mar/scratch behavior of a coating in a specific application, which is very useful in developing new high mar/scratch resistant coatings and avoiding time-consuming field tests.

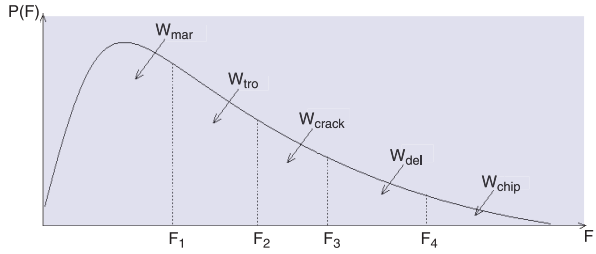
FUNDAMENTAL UNDERSTANDING OF MAR AND SCRATCH RESISTANCE

A lot of effort has been made in mar/scratch resistance studies to correlate the resistance to coatings' physical properties, such as hardness, elastic modulus, shear yielding strength, tensile strength, toughness, frictional coefficient, glass transition temperature, etc., and correlate the resistance to coatings' chemical components, such as crosslink type, crosslink density, pigments, etc.[7,17,19-22,31,48,49] There are no simple general commonly accepted correlations. One reason for the difficulties is the multiple modes/mechanisms of marring/scratching. Changing one physical property may reduce the damage of one mode, but increase the damage of another mode. For example, increasing the hardness of a coating surface could eliminate the damage under the light stresses, thus improving the micro mar resistance significantly. However, the hard coatings are sometimes brittle. As soon as the force exerted by an invader exceeds the critical force for cracking, severe and highly visible damage occurs. On the other side, reducing the yield strength makes coatings soft and ductile, and they suffer more plastic deformation under marring stress. However, cracking sometimes does not show up even when the scratches go very deep.

As stated, improving the mar/scratch resistance of a coating depends on its application environments. If it will mostly suffer from light invading forces and marring will dominate, it will not be necessary to enhance its resistance against the severe damages; if the coating will mostly suffer from severe damages (i.e., cracking, delamination, and chipping), it is not necessary to concentrate on improving its micro mar resistance.

Use of nano instruments in mar/scratch characterizations which employ the single-probe technique under well-controlled testing conditions makes the measurements reliable and reproducible. The micro mar resistance and critical forces can be measured with good accuracy. However, one has to notice the test conditions, and be aware that the damages in marring and scratching essentially are stress-strain problems. External force generates stress that causes strain. As strain increases at a certain rate, the deformation/damage experiences elastic deformation, plastic deformation, fracture, cracking, delamination at the interface—in sequence. The strain and its rate determine the morphologies of damages. However, the stress and strain are difficult to measure directly. The measurable MMR and critical forces are used for characterization, which are useful and reasonable. However, the testing conditions should be considered when the test results are used.

Figure 16—Prediction of the weights of different damages that will occur in the real application for a sample, whose measured critical forces for rough trough, cracking, delamination and chipping are F1, F2, F3 and F4, respectively, in the laboratory test.



Nano instruments provide accurate measurements in forces, displacements, etc. in micro and nano scale. Their drawback in the mar/scratch tests is limited scraping speed, which is much slower than that in real applications. Some homemade devices have made progress in overcoming this limitation, making the tests more realistic.[16,50] Nano instruments tests may also be complemented by traditional field-simulation tests to give the full spectra of characterization in some instances. Another approach to improve the understanding of the mar/scratch resistance is

Figure 17—A Haze-Gard Plus instrument made by BYK-Gardner used to measure the haze level increase, thus evaluating the degrading visibility and quantifying the different damage modes.

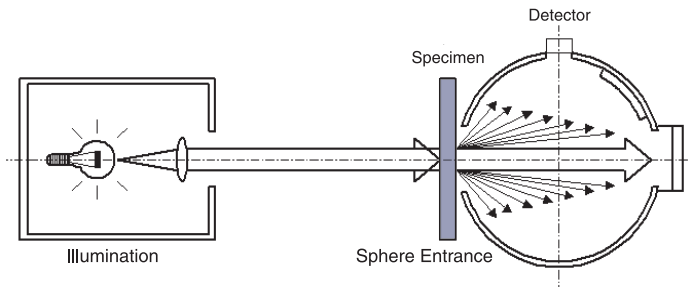
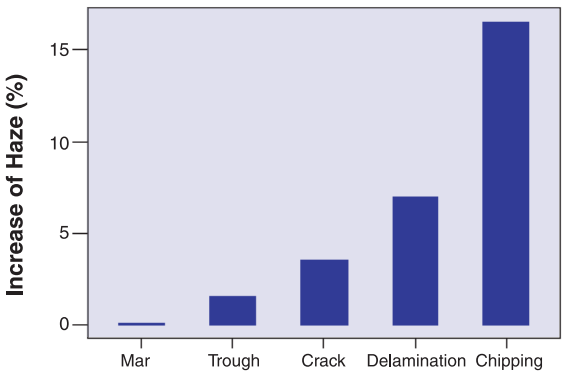


Figure 18—Measured haze levels of the mars, rough troughs, cracks, delaminations, and chippings were 0.04, 1.49, 3.52, 6.98, and 16.6%, respectively.



theoretical analysis and finite element modeling, which was successful for the hardness and elastic modulus studies in the indentation tests, but lacked in the scratching tests due to its complicated nature. Several groups have already tried this,[50] combined with experimental studies, as an integrated approach to investigate mar/scratch resistance.

SUMMARY

The nano instruments can perform the marring/scratching tests under well-controlled conditions, which are popular in mar/scratch resistance characterization today. As an illustration, a Nano-Indenter XP of MTS, combined with a Scanning Probe Microscope, is used to measure micro mar resistance, the different responses of coatings to marring 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 mar/ scratch resistance behavior of coatings). Selecting test methods should depend on the application conditions. Some complementary test methods, such as crack density measurement, repeated-scratching test, and cross-scratching test are described, too. Employment of the mar/ scratch tests, combined with the statistical survey of the damages on samples used in the field, can determine a laboratory force distribution curve that is equivalent to the force distribution curve encountered by coatings in real application, which can be used to predict the weights of different damage modes that will occur at the surface of a new coating if it is used in the field. Using the curve to find the weights of different damages, plus the quantifications of the damage levels of different modes, a quantitative index can be obtained to comprehensively characterize the mar/scratch resistance behavior of coatings in a specific application. One has to be aware that all the measurement results are obtained under certain testing conditions. The damages of marring/ scratching essentially are a 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 further fundamental understanding of the mar/scratch resistance behavior of polymeric coatings.

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