

# Measurement of Mar Resistance and Study of Marring Mechanism of Polymeric Coatings with Scanning Probe Microscope

Weidian C. Shen, Bin Jiang, and Frank N. Jones—Eastern Michigan University\*

## INTRODUCTION

The enormous technological importance of crosslinked polymeric surface coatings has engendered scientific interest in their tribological properties. One such property, resistance to marring, is a highly desired characteristic of coatings, especially for the coatings used in the automotive, glazing, and flooring industries.<sup>1-6</sup> The terms “mar” and “marring” are used to describe surface damage that is usually shallow and narrow. A single mar may not be readily noticeable, however, the existence of a group of mars does degrade the appearance of coatings.

We have used a scanning probe microscope (SPM) to examine mars in surface coatings on a panel cut from a used car. These mars might be made by car washing, polishing, etc. The depth of most of the mars ranges from a couple of dozen nanometers to several hundred nanometers, while the width ranges from a couple of hundred nanometers up to two micrometers. The length of the mars could be as long as a couple of dozen centimeters. Mar resistance is a measure of a material's ability to resist appearance degradation caused by small-scale mechanical stresses under a specific set of conditions. The severe damage resulting in visible, deeper, and wider trenches, in which coating fracture or even cracking is involved, is usually termed scratch and scratching. However, it is hard to set a clear demarcation line between the mars and the scratches. A statistical survey relating the damage to visibility and appearance was conducted by Lin and his colleagues.<sup>6</sup>

Our present work is concentrated on mar and marring, not scratch and scratching. Mar resistance is a complicated issue, and it depends on many factors, e.g., marring stress. To compare the mar resistance of different coatings, test conditions have to be specified. Even for a single coating, its mar resistance varies with the normal force applied during the marring, i.e., it varies with the penetrating depth of the tip into the coating. No single quantity can characterize it independently of marring stresses. To better characterize it, we have devel-

*A scanning probe microscope (SPM) equipped with a custom-made probe, consisting of a diamond tip and rectangular tungsten cantilever, was used to measure the mar resistance of crosslinked polymeric surface coatings at micron and submicron scales. The term “mar” is used to describe the surface damage of coatings, which may not be readily noticeable individually, however, the existence of many mars does degrade the appearance of coatings. Good mar resistance is a requirement for many coatings applications. With the unique high resolution of the SPM, the dimension of the mars can be measured with great accuracy, thus different responses of coatings to the marring stress, i.e., elastic recovery, plastic deformation, and abrasive wear, can be identified quantitatively. In addition, the dynamic process of marring, including viscoelastic creep, strain-hardening, micro-cracking, and surface fatigue, has also been studied with the SPM.*

oped a new test method by using an SPM equipped with a custom-made tip.<sup>7</sup> It is becoming more and more accepted in the coatings community as an appropriate method for measurement and characterization of marring.

SPM is the third generation of the scanning tunneling microscope (STM). STM was invented by Binnig and Rohrer at the IBM Zurich Research Laboratory in 1982.<sup>8</sup> It employs the quantum effect of electron tunneling and has achieved an exceptionally high resolution that is capable of observing individual atoms at the surface of the sample under study. It has been used widely to

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\*313 Strong Hall, Ypsilanti, MI 48197.

study a variety of samples. However, the samples for STM study must have at least moderate conductance in order to sustain the tunneling current. For this reason, the technique of STM could not have been applied to insulators. To deal with this limitation, the atomic force microscope (AFM) was developed in 1986, incorporating the principle of the scanning tunneling microscope and the stylus profilometer.<sup>9</sup> It could measure forces as small as  $10^{-9}$  N (1 nN) between atoms at the tip and atoms at the sample when the tip scans across the surface of the sample. Thus, atomic resolution has been achieved even on the insulating surfaces.

STM and AFM, now combined as SPM with multiple functions, have opened a new era of high-resolution microscopes. Conventionally, SPM, whose probe has a spring constant ranging from 0.06 N/m to 0.6 N/m, is used for non-destructive imaging. With a little modification, using a custom diamond tip to replace the conventional tip and using a custom tungsten cantilever to replace the conventional cantilever, the SPM can be used for controlled damaging in the marring tests. It can mar the surface of coatings under different normal forces and at different scraping rates, then examine the marred surface using a conventional high resolution probe with great accuracy. With the exceptional high resolution, SPM can also be used to study the marring mechanism. It can clearly distinguish the different responses of coatings to the surface stress, i.e., elastic response, plastic deformation, and abrasive wear, quantitatively.<sup>10,11</sup> We have tested different coatings and studied the correlation of their tribological properties and their surface structure. The dynamic process of marring, including viscoelastic creep,<sup>12</sup> strain-hardening, micro-cracking,

and surface fatigue has been studied with the SPM also.<sup>13</sup> The accumulated knowledge will provide useful information in developing high mar-resistant polymer coatings.

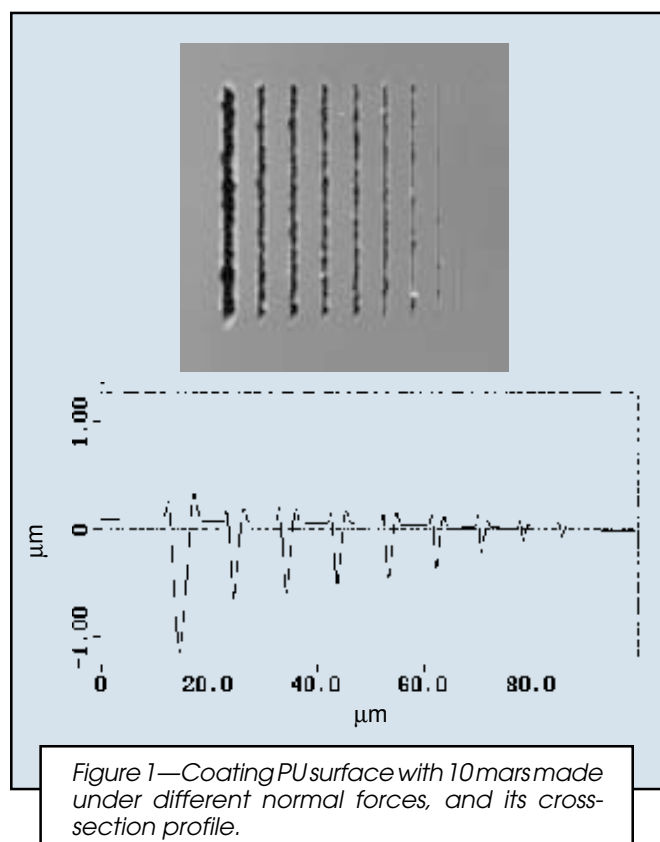
## EXPERIMENTAL

The SPM used in our tests was a Nanoscope IIIa manufactured by Digital Instruments. The custom-made probe consists of a diamond tip glued to a rectangular-shaped tungsten cantilever with epoxy resin. Our diamond tips are purchased from Imetra, Inc., Elmsford NY, whose manufacturer is in Switzerland. The tips of Imetra have well defined shape and sharpness. A  $90^\circ$  conical-shaped diamond tip with a  $1\ \mu$  radius at its apex was used in most of the tests described. The cantilevers are cut from tungsten foils, and their spring constants range from 400 N/m to 4000 N/m, three to four orders of magnitude larger than conventional SPM probes. The SPM equipped with such a probe is capable of making artificial mars, under well-controlled conditions, with the same dimensions as the mars encountered in the field.

The coating panels tested were cut into a  $10 \times 10\ \text{mm}^2$  piece by a shear cutter to fit the sample stage of the SPM. Before the test, the samples were washed 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 were blown dry with high pressure nitrogen gas.

In the micro mar resistance (MMR) measurement, the tip, under a fixed normal force ranging from about 50 micronewtons up to 2-4 millinewtons depending on the property of the tested coating, was moved laterally along the surface and made a single scrape of about  $70\ \mu\text{m}$  long. After the scraping, the tip was lifted and the sample was moved. A second mar was then made under an increased normal force, parallel to the first one at a distance of about  $10\ \mu\text{m}$ . After 5 to 10 mars were made under different normal forces, the marred sample was again washed in an ultrasonic bath without detergent, rinsed in a stream of cool tap water, gently dried with soft tissue, and blown dry with high-pressure nitrogen gas to remove the broken material. Then the marred surface was imaged with an SPM equipped with a conventional high-resolution tip. The dimensions of the mars were measured. The average values over 200-400 data points along the mar were used to calculate the MMR, which is defined as the normal force applied during the marring divided by the cross-section area of the trough, as well as the percentage of elastic, plastic, and abrasive response at different normal forces.

More than 200 coatings of different formulations have been tested with this method. Over 20% showed self-healing to different extents, mainly depending on their glass transition temperature,  $T_g$ . This is attributed to viscoelastic creep. Viscoelastic creep is different from elastic recovery; it results in partial or complete recovery of a marred surface within a time frame from several minutes to several hours,<sup>14,15</sup> while the elastic recovery occurs immediately after the marring tip moves over the surface. To study the viscoelastic creep in detail, we



imaged the marred surface continuously, immediately after the scratching, at a time interval of 10 minutes up to several hours when the recovery was almost complete and stored the data in a computer. Later, we plotted the dimension of mar versus time and studied the recovery rate, recoverable part, and unrecoverable part for the mars made under different normal forces.

To study the strain hardening, micro cracking, and surface fatigue, we marred the coating surface with an increasing number of scrapings in the same channel at a fixed normal force. The depth of ditch was measured, and the morphology at the bottom of the ditches was examined after each scraping. It provided direct experimental evidence for strain hardening, micro crack generation and propagation, and surface fatigue of a polymeric coating on the micron and submicron scales, when it undergoes marring.

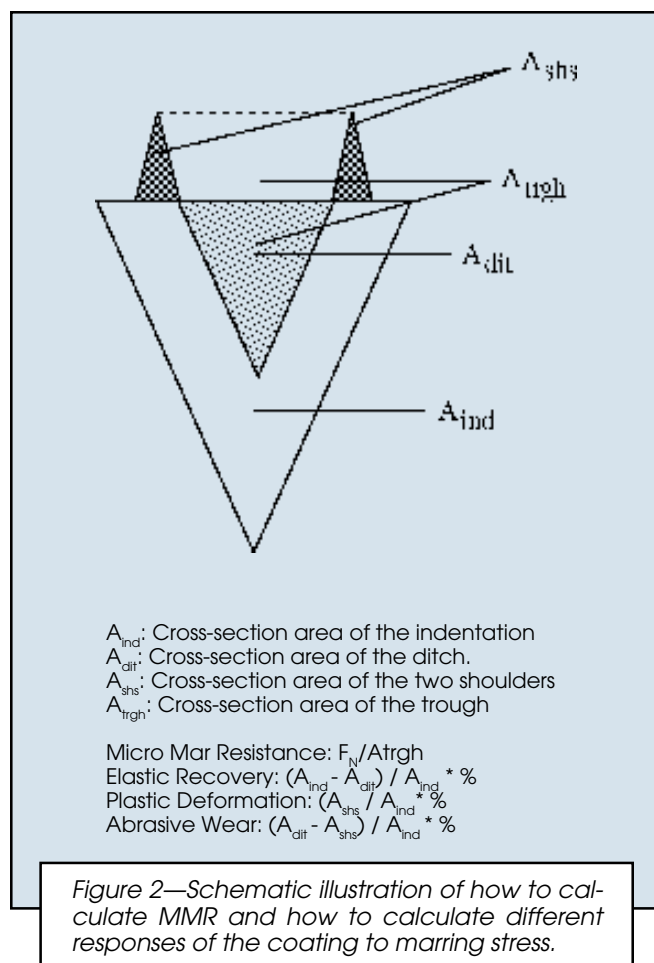
## RESULTS AND DISCUSSION

### Mar Resistance Measurement and Marring Mechanism Study

Figure 1 shows a cross-section profile of 10 mars made in the surface of an experimental PU coating, a polyurethane coating obtained from DuPont in two components, coded RKR94550 and RK7018, which were mixed in our laboratory just before the films were cast. The 10 mars in the surface were made under normal forces of 49, 92, 126, 169, 212, 254, 298, 338, 385, and 421  $\mu\text{N}$ , respectively. MMR, defined as normal force used in scraping divided by the cross-section area of the trough, is used to characterize the coating's resistance against marring. Thus, the polyurethane coating has an MMR of 2.6, 1.3, 1.0, 0.54, 0.37, 0.33, 0.27, 0.26, 0.25, 0.11 GPa under the increasing normal forces.

For most of the crosslinked polymer surface coatings tested, the MMR, as well as micro indentation hardness (MIH), decreases with the increasing normal forces, i.e., decreases with the penetration depth. As mentioned previously, mar resistance is a complicated issue. It depends very much on the test conditions, such as applied normal force. Mar resistance of a single coating is probably best characterized by measuring it under different normal forces. We usually measure it under 5 to 10 different normal forces and provide a set of data to characterize it. The decrease of MMR and MIH with depth suggests the existence of a hard crust at the top layer of the crosslinked polymer coatings. It may be associated with the higher crosslink density at the top layer due to an aging effect.

As can be seen in the profile, there are two shoulders on both sides of the ditch, which reflect the plastic deformation. The material was displaced from the ditch to build up the shoulders during marring. In most cases, the total cross-section area of two shoulders is less than the cross-section area of the ditch. Since the polymer coatings are not compressible material, the difference between the total cross-section area of two shoulders and the cross-section area of the ditch is attributable to



the abrasive wear. Some material was abraded from the surface in the marring. We found the debris along the marred surface wherever abrasive wear occurred, which made the subsequent imaging with the conventional tip difficult. After the marring, we washed the samples again to remove the debris, then took an image of the marred surface. Figure 2 is a schematic illustration of how to calculate the MMR and different responses of the coating to marring stress. The cross-section area of the trough is the cross-section area of ditch plus the cross-section area between two shoulders, if any. To be more consistent with the optical evaluation and visual judgment of the coating surface, the cross-section area of the trough is used to calculate the MMR instead of the cross-section area of the ditch.

Different coatings possess different mar resistances as well as show distinguishably different responses to marring stress. We list our test results for a PE coating, comprised of a polyester resin made in our laboratories crosslinked with a monomeric methylolated melamine formaldehyde resin under acid catalysis; the PU coating, as mentioned earlier; and an AC coating, a commercial one-component automotive clearcoat obtained from DuPont and coded "Gen-3," which is presumed to be based on special acrylic polymers crosslinked, at least partly, with alcoholated melamine-formaldehyde resins, tested under a normal force of 126  $\mu\text{N}$  for a comparison. Although the PU and AC coatings are much harder than the PE coating, the PE coating shows a much better

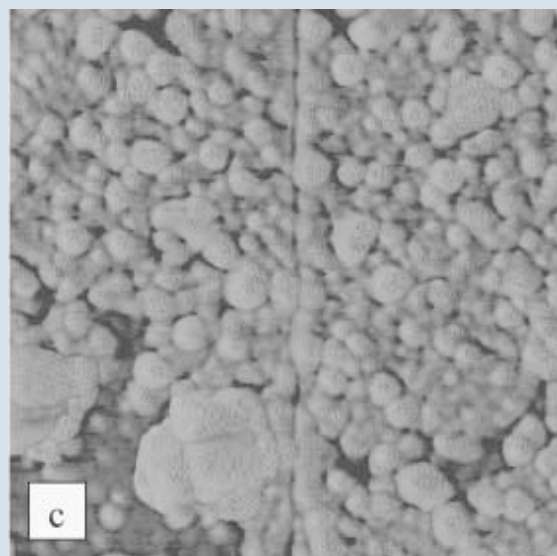
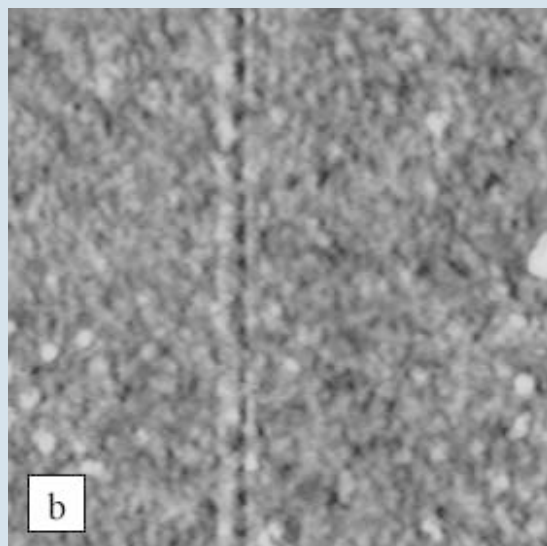
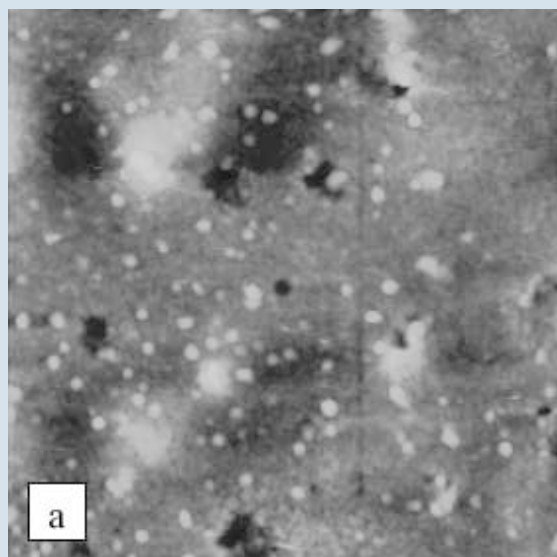


Figure 3—Images,  $1\ \mu\text{m} \times 1\ \mu\text{m}$ , of AC, PU, and PE with a nano scratch at their surfaces are shown in (a), (b), and (c) respectively.

mar resistance than the PU and AC coatings. It is due to the fact that the PE coating has a greater elastic recovery. The tip stuck deeper in the surface of the PE coating under the same applied normal force; however, the indentation recovered immediately after the tip moved over. In contrast, the PU coating has a significant plastic deformation, and the AC coating has a significant abrasive wear. Table 1 shows the MIH, MMR, and their different responses under a normal force of  $126\ \mu\text{N}$ .

The mar resistance and different responses of a coating also depends on the marring condition, such as the normal force used in the marring. The MMR as well as a percentage of elastic recovery, plastic deformation, and abrasive wear varied with the normal force applied in marring.

The correlation between the structure of coatings and their mechanical properties was explored. Images of  $1\ \mu\text{m} \times 1\ \mu\text{m}$  at the surface of the AC, PU, and PE coatings were taken using the SPM equipped with the conventional high-resolution tip. They showed three distinguishable polymer domain structures. A nano scratch with a depth of a couple of nanometers, which is much smaller than the mars in the MMR tests, was made at their surface, and the response of the polymer domains to the nano scratching was examined. Figure 3a is the image of the AC coating showing the small particles sitting at the top of the continuous matrix phase. In the nano scratching, the tip easily removed the small particles. This observation may relate to the brittleness of coating AC, as reflected in its tendency to undergo abrasive wear. Figure 3b is the image of the PU coating showing string shaped polymer domains. In the nano scratching, these domains realigned themselves along the scratch as the tip moved over the surface, similar to the shoulders of plastic deformation in the marring test. Figure 3c is the image of the PE coating with its polymer domains much larger than those of the ACs and PUs. In the nano scratching, the domains were hardly removed or broken, but were displaced from their original positions. After the tip moved past, they returned back to their original positions, making the left over path zig-zag-shaped, which may be attributable for the great elasticity of the PE coating in the marring test.

Mar resistance of polymeric coatings depends on a number of factors, such as chemical components, molecular weight, crosslink material and its density, additives, and processing procedure, etc. In addition, the mechanical properties of coatings vary with the depth and age. A scratching test performed at the top surface at nano scale does not necessarily represent the performance in marring test at micro and submicron scales. An intensive study is needed before any conclusive statement can be made.

### Viscoelastic Creep Study

To study viscoelastic creep, the diamond tip was replaced by a regular tip after the marring, and the imaging started within 15 min. It was observed that the total cross-section area of the shoulders, as well as the cross-section area of the ditch, decreased with time. The material was removed from the shoulders to fill up the ditch.

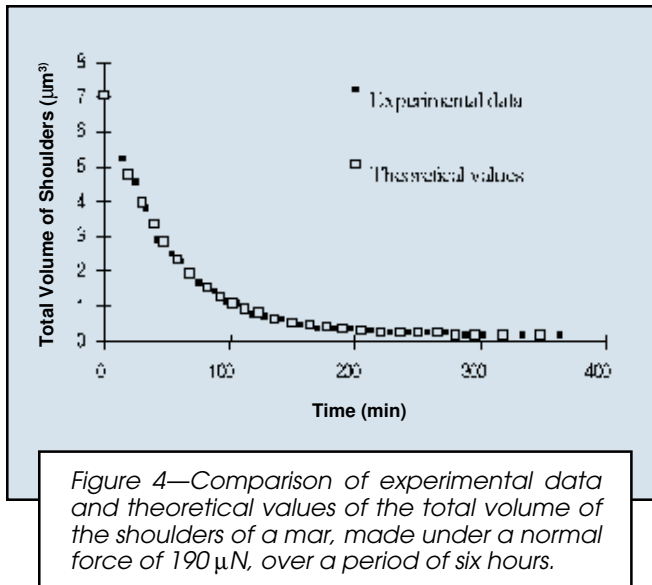


Figure 4—Comparison of experimental data and theoretical values of the total volume of the shoulders of a mar, made under a normal force of 190  $\mu\text{N}$ , over a period of six hours.

The total volume of the shoulders at time  $t$ ,  $V(t)$ , consists of a recoverable part by viscoelasticity,  $V_{\text{vis}}(t)$ , and an unrecoverable part of permanent plastic deformation,  $V_{\text{pla}}$ . The decrease of the volume of recoverable part  $dV_{\text{vis}}(t)$  in a small time interval  $dt$  is proportional to  $\delta t$  as well as the existing volume of the recoverable part  $V_{\text{vis}}(t)$ , thus we have

$$dV_{\text{vis}}(t) = -k V_{\text{vis}}(t) dt \quad (1)$$

where  $k$  is a proportionality constant. Through simple integration, we have

$$V_{\text{tot}}(t) = V_{\text{vis}/\text{ini}} \cdot e^{-kt} + V_{\text{pla}} \quad (2)$$

where the integration constant  $V_{\text{vis}/\text{ini}}$  is the initial volume of the recoverable part immediately after the marring.

Figure 4 is a plot of the measured total volume of shoulders of a mar, made under a normal force of 190  $\mu\text{N}$  at the surface of an acrylic polyol/hexamethylene diisocyanate (HDI) coating obtained from Bayer Corporation, over a six-hour period, and the theoretical predicted value, with the recovery rate  $k=0.02/\text{min}$ ,  $V_{\text{vis}/\text{ini}}=6.86\mu\text{m}^3$ , and  $V_{\text{pla}}=0.21\mu\text{m}^3$ . They agreed with each other very well.

Through the study, it was found that the rate  $k$  is independent of the size of mars made under different normal forces and is determined by the properties of the coating and influenced by temperature and humidity. Immersing the coating in water for a few minutes will greatly promote recovery.

Table 1—Micro Indentation Hardness (MIH), Micro Mar Resistance (MMR), and Responses to Marring Stress of Three Coatings at 126  $\mu\text{N}$ .

|    | MIH<br>(MPa) | MMR<br>(GPa) | Elastic<br>% | Plastic<br>% | Abrasive<br>% |
|----|--------------|--------------|--------------|--------------|---------------|
| PE | 9.2          | 3.5          | 97           | 1            | 2             |
| PU | 76           | 1.0          | 57           | 43           | 0             |
| AC | 53           | 0.64         | 21           | 14           | 65            |

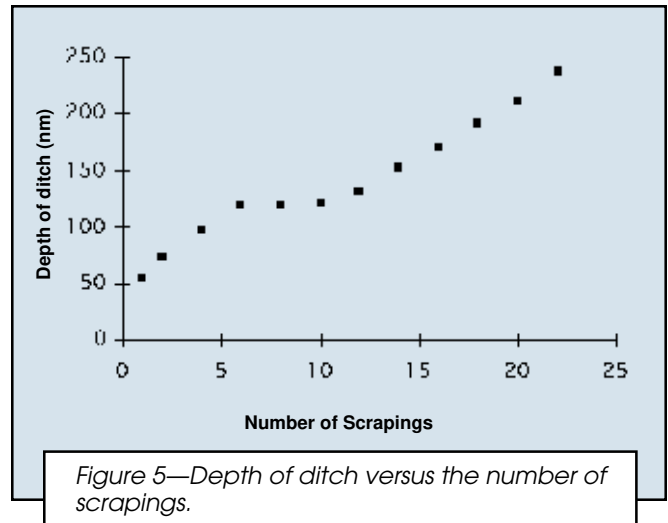


Figure 5—Depth of ditch versus the number of scrapings.

### Study of Strain Hardening, Micro Cracking, and Surface Fatigue

In the study of strain hardening, micro cracking, and surface fatigue, a 245  $\mu\text{N}$  normal force was applied to the tip, as the tip moved laterally to mar the surface. One-scrap marring, two-scrap marring, up to a 22-scrap marring was executed in the same path, respectively, on the surface of a coating supplied by Bayer Corporation. The coating was made by crosslinking a mixture of acrylic and polyester polyols with a mixture of polyisocyanates. It showed a micro phase separation; the round-shaped domains of the dispersed phase embedded in the continuous matrix phase.

Figure 5 shows a plot of depth of the ditches versus the number of the scrapings. The first single scraping made a ditch of 54 nm deep, and one more scraping increased the depth by about 20 nm. The rate of increase in depth decreased with the additional scrapings, and the depth reached a saturated value after six scrapings. However, as the scraping was repeated at the same trench, the depth began to increase again after 10 scrapings at a roughly constant rate of 10 nm per scraping.

To analyze the coating under repeated scrapings, a model proposed by Johnson<sup>16</sup> for indentation analysis was used. The coating under scraping consists of three zones, (1) a core immediately underneath the tip that is under hydrostatic pressure, (2) a plastic zone that surrounds the core, and (3) a large elastic hinterland that surrounds the plastic zone. In this analysis, the material around the ditch did not reach its plasticity limit after a single scraping. Thus, continuous scraping increased the depth of the ditch and caused further plastic deformation. However, the increase of the depth after each additional scraping decreased due to the hardened walls of the ditch that had been worked plastically in the previous scrapings. After six scrapings in the test, the material surrounding the ditch had reached its plasticity limit and could not be further deformed; a rigid-plastic zone was fully established. The stress exerted by the tip was transmitted,

through this rigid plastic deformed zone, to the large hinterland zone. Under the reduced stress over the large zone, the hinterland was elastically deformed, and it recovered immediately after the tip moved over. When equilibrium was reached, a saturation depth was obtained. Although the equilibrium was reached, fatigue processes would be expected to lead to wear eventually, as a result of the repeated plastic working. Due to the sufficiently high hydrostatic pressures, the materials immediately adjacent to the tip were prevented from cracking. Instead, cracks were generated in the subsurface, and they did not propagate and emerge at the bottom of the ditch after the first several scrapings. However, the continuous repeated scraping provided the energy for crack propagation and promoted surface fatigue. After 10 scrapings, the cracks began to emerge at the bottom of

the ditch and formed a broken fragile surface. Thus, the tip began to remove the weakened surface, layer by layer, at a roughly constant rate of 10 nm per scraping.

The images at the bottom of the ditch after different numbers of scrapings support this analysis. *Figure 6a* is the image of the coating surface before scraping. It consists of a continuous matrix phase and dispersed phase. The bright round-shaped spots protruding at the top surface are the domains of the dispersed phase, which are embedded in the continuous matrix phase. *Figure 6b* is the image at the bottom of the ditch after the first scraping. Some dispersed phase domains were removed away by the tip; the others were squeezed into the surface to different extents. After six scrapings, only a few domains of the dispersed phase remained at the surface. Most of them were either swept off or squeezed into the

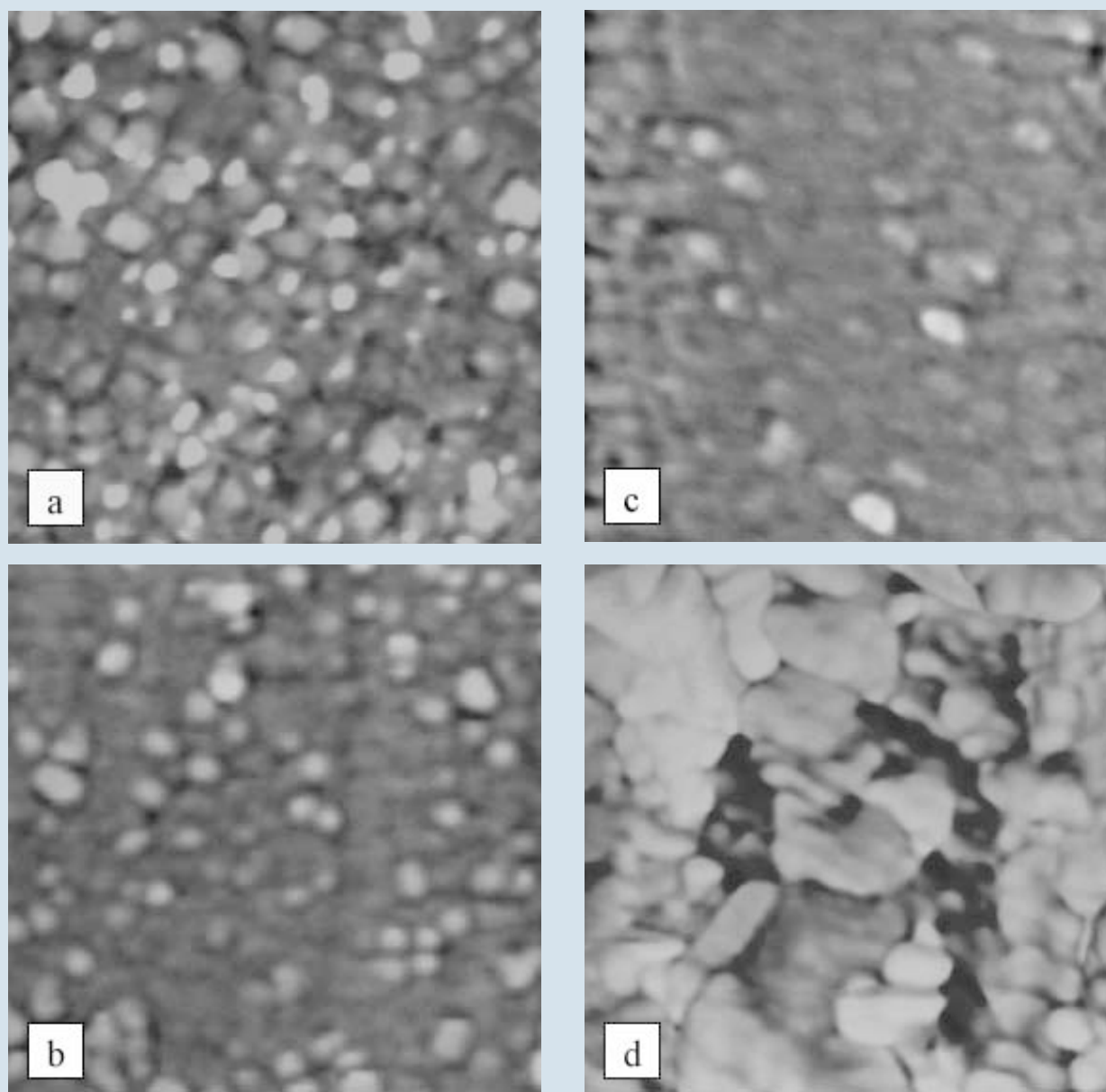


Figure 6—Images, of  $0.64\text{ }\mu\text{m} \times 0.64\text{ }\mu\text{m}$ , of the surface before scraping, and at the bottom of the ditch after 1, 6, and 10 scrapings are shown in (a), (b), (c), and (d), respectively.

continuous matrix underneath. At this stage the surface was pretty smooth and firmly compressed, but no cracks emerged at the surface yet, as shown in *Figure 6c*. *Figure 6d* is a typical image for the bottom of the ditch after more than 10 scrapings. The cracks emerged at the bottom of the ditch, forming a broken matrix phase with squeezed dispersed domains embedded in it.

## SUMMARY

We have used an SPM equipped with a custom-made probe to measure mar resistance and identify different responses of polymeric surface coatings to marring stress, as well as study the dynamic process of marring, such as viscoelastic creep, strain hardening, micro crack developing, and surface fatigue. The knowledge gained will be very helpful in understanding the marring mechanism and developing high mar resistant surface coatings. The SPM has been proved to be a very useful instrument in studying mechanical properties of coatings at micron and submicron scales.

## ACKNOWLEDGMENTS

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