Nanoscale Characterization of Coatings Surface Degradation with Tapping Mode Atomic Force Microscopy

by

Tinh Nguyen, Xiaohong Gu, Mark VanLandingham, Rose Ryntz[1], Diep Nguyen[2] and Jonathan Martin

Building and Fire Research Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899 USA

[1]Visteon Corporation, Dearborn, MI USA

[1]PPG Industries, Inc., Alison Park, PA USA

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NANOSCALE CHARACTERIZATION OF COATINGS SURFACE DEGRADATION WITH TAPPING MODE ATOMIC FORCE MICROSCOPY

Tinh Nguyen, Xiaohong Gu, Mark VanLandingham, Rose Ryntz[1], Diep Nguyen[2], and Jonathan Martin

National Institute of Standards and Technology, Gaithersburg, MD
[1] Visteon Corporation, Dearborn, MI
[2] PPG Industries, Inc., Alison Park, PA

e-mail: tinh.nguyen@nist.gov

Introduction

Surface characteristics of a polymer coating, such as gloss, and their changes with weathering depend strongly on surface topography and morphology. Therefore, data on early physical changes of coatings surfaces can provide valuable information for not only understanding the degradation mode but also for predicting long-term performance. Atomic force microscopy (AFM) is well suited for studies of early coatings degradation, as demonstrated recently [1-3]. This paper presents examples from the research in our laboratory on the use of both the phase and topographic imaging in tapping mode AFM (TMAFM) to investigate early surface physical degradation of coatings exposed to weathering environments. In tapping mode AFM, the probe is oscillated at a frequency near resonance. As the tip approaches the sample, the tip-sample interactions change the amplitude, resonance frequency, and phase angle of the oscillating probe. Detection of the amplitude and phase changes during scanning provides the topographic and phase images, respectively. Phase imaging in TMAFM is sensitive to both mechanical and chemical properties of the surface and tip-sample interactions.

Materials and Experimental Procedures

Thin and thick films applied to a substrate and thick free-standing films of automotive and industrial coatings were studied. Specific materials, preparation procedures, and degradation exposure conditions are given for each example. A Dimension 3100* Scanning Probe Microscope (Digital Instruments) operated in tapping mode and commercial silicon microcantilever probes were used. Both topographic (height) and phase images were obtained simultaneously using a resonance frequency of approximately 300 kHz for the probe oscillation and a free-oscillation amplitude of 62 nm ± 2 nm. The set-point ratio (the ratio of set point amplitude to the free amplitude) ranged from 0.60 to 0.80.

Results and Discussion

To provide long-term performance, automobile exterior coatings must resist degradation by sunlight. One example to demonstrate the utility of AFM for studies of automotive coatings photodegradation is illustrated in Figure 1. These are 5 μm x 5 μm AFM height images of a commercial clear polyurethane topcoat/pigmented polyurethane base coat applied to a plastic substrate before (top) and after exposure to 1500 kJ of ultraviolet (UV) radiation in an artificial weathering device (bottom) (1500kJ is the total amount of radiation impinging on the sample surface). The type and level of UV stabilizers, which are always used in both the top coat and base coat to provide their protection against UV light, are not known. In Figure 1, 3-D images are on the left, and 2-D images together with the line profiles and root-mean-square (RMS) roughness values are displayed on the right. The line profile and RMS roughness data (right, top) indicate that the coating surface before exposure was smooth with nanoscale roughness, with no evidence of pinholes or pits. After exposure, pits having sizes ranging from 150 nm to 400 nm in diameter and 2 nm to 5 nm in depth have developed on the surface of this sample.

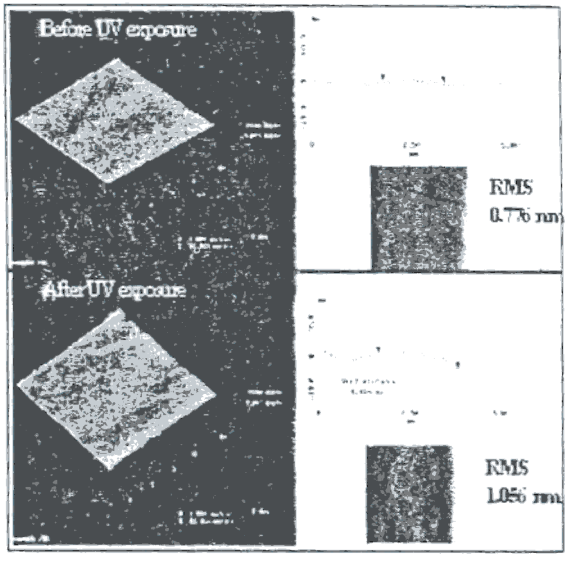

Figure 1. 5 μm x 5 μm, 3-D AFM height images (left) and 2-D images and line profiles (right) of a commercial polyurethane top coat/polyurethane base coat applied to a plastic substrate before and after exposure to 1500 kJ UV radiation.

One particularly useful application of AFM for quantitative studies of coatings degradation is its ability to measure the enlargement and deepening of pits with exposure at the nanoscale level. This is demonstrated in Figure 2 for a 10 μm thick, clear acrylic-urethane coating applied to a CaF_2 substrate exposed for 6160 h in a xenon arc device at 70 % relative humidity (RH) and 50 °C. For these measurements, the AFM images were taken at approximately the same location after each exposure time using a special sample holder and procedure described in detail in Reference 2. It is interesting to observe that the pit depth increased nearly linearly with time, but pit diameter enlarged rapidly at first then slowed down. This kind of quantitative data is not only useful for kinetics studies of the degradation but also allows us to assess the pit sizes that start to influence the surface appearance.

AFM can also provide valuable information on surface microstructure changes caused by weathering. Figures 3 and 4 provide examples to demonstrate this capability. Figures 3a and 3b are the height and phase images, respectively, and Figure 3c displays the phase images at a higher magnification (the scan sizes are given in the figure caption). These images were taken from the air surface of a blend consisting of 70 % (mass fraction) poly(vinylidene fluoride) (PVDF) and 30 % copolymer of PMMA and poly(ethyl acrylate) (PMMA-co-PEA) before and after exposure to a xenon

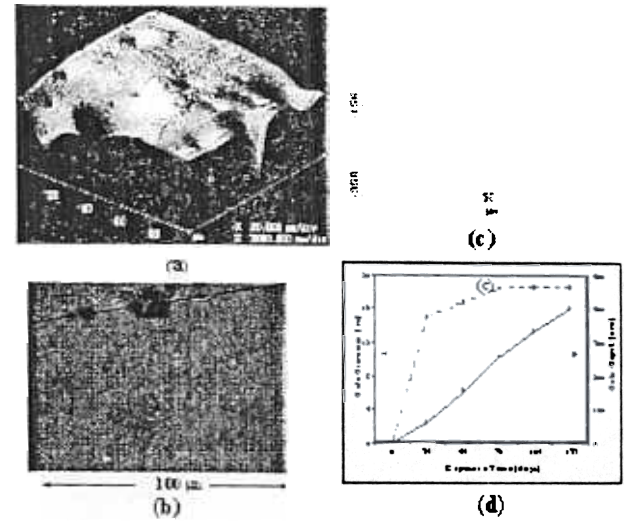

Figure 2. Imaging and measurement of pit enlargement and deepening by AFM for a clear acrylic-urethane coating exposed to a xenon arc lamp for 6160 h at 50 °C/70%RH condition; a) 3-D image, b) 2-D image with a line crossing two pits, c) corresponding line profile showing pit width and depth, and d) depth and diameter of the large pit as function of exposure time.

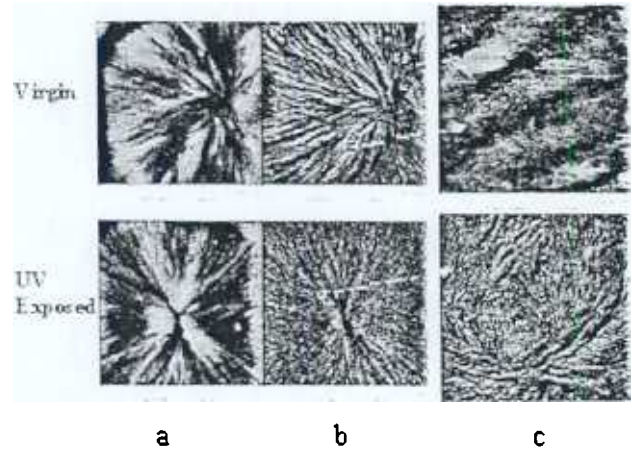

Figure 3. AFM images of 70/30 PVDF/PMMA-co-PEA air surface before and after exposure to UV light at 50 °C/9% RH for 7 months; a) 25 μm x 25 μm height images, b) 25 μm x 25 μm phase images, and c) 2 μm x 2 μm phase images.

arc lamp at 50 °C/9%RH condition for 7 months. These samples were prepared by casting the blend in isophorone solvent on a glass plate by a draw down technique, followed with heating at 220 °C in an air-

circulated oven for 10 minutes. Cast glass plates were removed from the oven and slowly cooled to ambient temperature (24 °C). At low magnification (Figures 3a and b), both the height and phase images before and after exposure show the large crystal structure of the crystalline PVDF material. The higher magnification phase image of the unexposed sample (c, top) shows that the spherulite surface was covered with a layer of non-crystalline material. However, this layer was essentially removed after exposure, revealing the fine lamellae structure (c, bottom). This well-organized crystal structure on the UV-exposed surface may be due to crystal growth or rearrangement of the lamellae, or both, resulting from UV light irradiation. The presence of a crystalline structure on the surface after exposure may explain the excellent UV resistant characteristics of PVDF-based coatings.

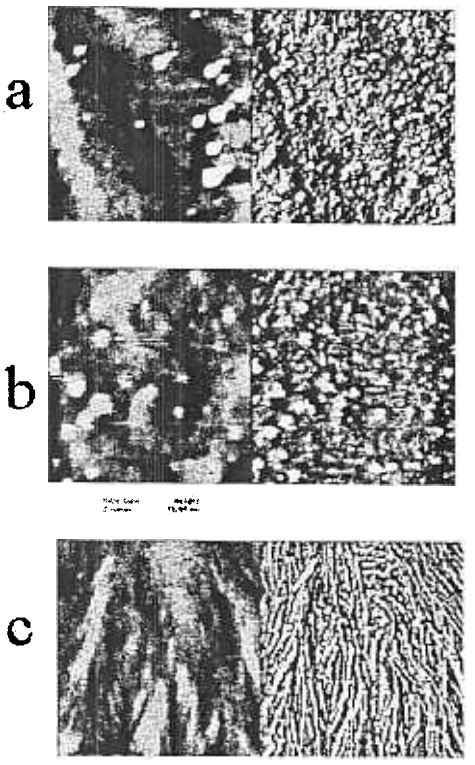

Figure 4. 1 μm x 1 μm AFM height (left) and phase (right) images of a 75 μm thick free-standing film of 70/30 PVDF/PMMA-co-PEA interface sample before and after exposure in UV light at 50 °C/75 %RH for two months; a) before exposure, b) after exposure, interface facing down, and c) after exposure, interface facing up toward the UV source.

The sample for Figure 4 images is similar to that of Figure 3, except the surface that was in contact with the glass substrate during film application and heating (designated as the interface) was investigated. This interface sample was obtained by lifting the film from the glass substrate after 10 minute immersion in boiled water. This sample was exposed to UV light at 50 °C and 75 % RH for approximately two months. After exposure, the face-down interface (as in the case the coating is still applied to the substrate) (Figure 4b) has not shown any evidence of degradation. However, the amorphous material on the interface that was facing toward the UV light source during exposure was mostly removed, exposing the fine lamellae structure. From AFM results shown in Figure 4 and contact angle and spectroscopic data presented previously [4], it is reasonably certain to conclude that the amorphous acrylate copolymer is preferentially enriched at the film/substrate interface and this enriched amorphous layer may explain the good adhesion of acrylic-modified PVDF coatings.

AFM results of polyester hydrolysis in alkaline and epoxy photodegradation will also be presented.

Conclusions

AFM results for a variety of coating samples exposed to weathering conditions have demonstrated that tapping mode AFM is a powerful technique for not only detecting nanoscale surface changes, but also for providing quantitative information on pitting process and revealing surface microstructure change of polymer coatings due to degradation.

**Certain commercial products or equipment are identified so as to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by NIST, nor does it imply that it is necessarily the best available for the purpose.*

References

1. X. Gu, D. Raghavan, T. Nguyen and M. VanLandingham, Polym. Deg. Stab., 2001, 74, 139.
2. M. VanLandingham, T. Nguyen, E. Byrd, and J.W. Martin, J. Coat. Techn., 2001, 73, no. 923, 43.
3. S. Biggs, C. Lukey, G. Spinks, and S-T. Yau, Prog. Org. Coat., 2001, 42, 49.
4. X. Gu, T. Nguyen, D. Nguyen, and M. VanLandingham, Proceedings, Annual Meeting of the Adhesion Society, 2002, p 497.