Atomic Force Microscopy in Coatings Research

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Atomic force microscopy (AFM) is a well-established technique for imaging in the micro- and nanoscale, which is leveraged by many industries to gain fundamental understanding of products and other systems of interest [1,2]. In the coatings industry, AFM allows researchers to probe coating morphology and composition at the level of detail required to solve today's most challenging problems [3]. AFM is especially useful as a complementary technique to, and in tandem with, electron microscopy due to their varied contrast mechanisms. This paper highlights the utility of AFM in coatings research, as applied by PPG towards new product development. A major goal of the paper is to explain the unique industrial perspective on AFM research to aid in fostering collaboration between industry, academia and instrument manufacturers.

AFM is useful, in the perspective of industrial coatings research and development, for investigating both the surface morphology of coatings as well as mapping the nano-mechanical properties of the material both at the surface and in cross-section. Many modern coatings products consist of multiple layers to provide optimal performance to the customer. The specific thicknesses, morphologies and mechanical properties of those layers and their interfaces is critical to their functioning as designed. In particular, determining the surface profile of coatings at the nanoscale is a challenging analytical endeavor that is readily accomplished via AFM. Additionally, obtaining sufficient contrast via electron microscopy in the organic portions of coatings systems is frequently challenging. While advanced electron imaging techniques such as energy filtered transmission electron microscopy can allow for clear resolution of disparate polymer phases, AFM provides an excellent opportunity to investigate these phases as well as to probe their individual mechanical properties.

This paper will present two case-studies that highlight the utility of AFM in coatings research at PPG. In the first, a polyester powder coating system was investigated in tandem with TEM to determine the nano-structural effects of commonly used additives. Cross-sectional analysis via nano-mechanical mapping was employed to probe the nanoscale domain formation. In the second, the nanoscale morphology of an automotive clearcoat is probed to investigate the surface features present and understand how it may relate to dirt retention and release.

To investigate the nanoscale effect of additives commonly used in powder coating systems, a generic powder polyester resin was extruded together with commonly used additives, such as flow modifiers. A fundamental study was designed in which additives were added individually and in combination with one another to better understand the effects on nanoscale morphology. The samples were extruded, sprayed and cured onto steel substrates. The films were then removed from the panels mechanically and prepared in cross-section via ultramicrotomy using a diamond knife. Brightfield TEM was carried out on the electron-transparent slices collected from the ulltramicrotomy preparation, while the resulting blockface was characterized using a Bruker Icon AFM and commercially available tips. Interestingly, a synergistic effect was observed, in which a combination of flow additives gave rise to nanoscale domains within the material; no individual additive component gave rise to these domains when used in isolation. This result highlights the complexity of modern coatings systems, which employ a variety of additives to achieve desirable rheological and physical properties. The specific identity of the domains is not yet fully understood, but their presence in the generic system indicates that they may play a role in the performance of many powder coatings systems.

To study the nanoscale morphology of a commercially available automotive clearcoat sample, the sample was analyzed as-made, with no additional preparation. The sample was sprayed onto a steel panel atop a typical, commercially available automotive coating stack (electrocoat, primer, basecoat, then clear). The sample surface was analyzed using a Bruker Icon AFM and commercially available tips. Automotive clearcoats are designed with both functional and aesthetic considerations in mind. Specifically, they are designed to be very smooth in order to provide a high-gloss finish; this generally also provides benefits to avoidance of dirt retention. Upon investigation of the commercially available clearcoat surface, nanoscale features were discovered that were not expected. These do not have an adverse effect on appearance but may affect how cleanable the surface is as well as the weatherability of the coating. AFM studies are continuing to determine the time evolution of these features following field testing, a task for which AFM is well-suited.

The insights provided by AFM in these case-studies allow for better fundamental understanding of coatings systems. These cases also highlight how AFM is useful in industrial coatings applications both as a complementary tool to TEM for determining polymeric nanoscale structural features as well as for probing the nanoscale morphology of coatings surfaces. Fundamental understanding of coating structures and morphologies at the nanoscale is critical to the development of next generation coating systems and AFM closely supports the efforts of research and development chemists across business units at PPG.

[1] S Yamamoto *et al*, Journal of Catalysis **159** (1996), p. 401.
[2] G Smith in “Industrial Metrology”, (Springer-Verlag, London)
[3] T Nguyen *et al*, Proceedings of the 9th International Conference on Durability of Building Materials and Components (2002), 9DBMC paper 93.

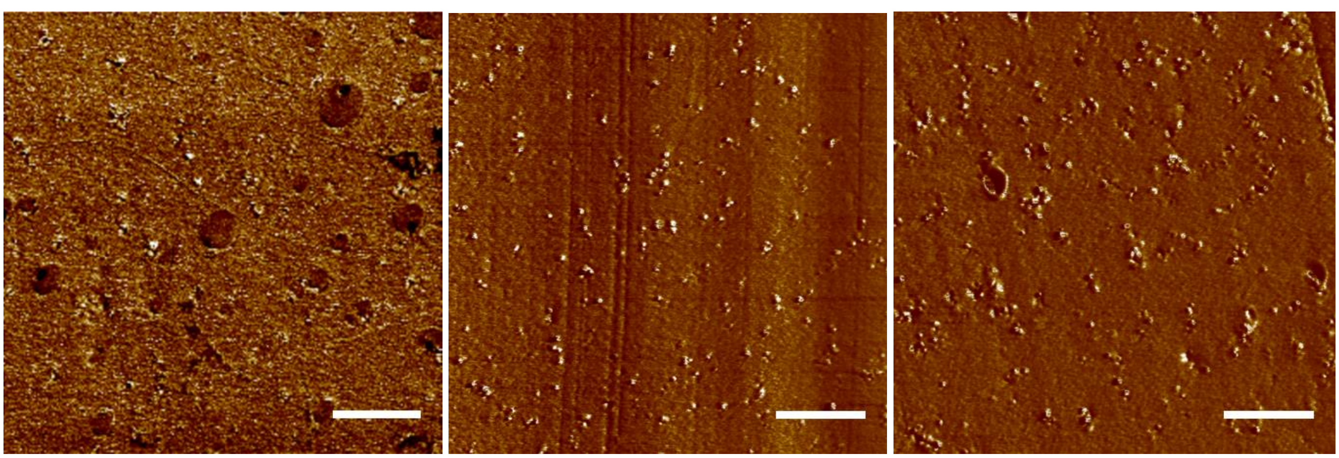

Figure 1. AFM modulus map images of ultramicrotome prepared powder coating samples. All additives (right) and individual additives: air-release additive (center) and flow additive (right). Scale bar is 1 micron.