

# The Use of XPS, FTIR, SEM/EDX, Contact Angle, and AFM in the Characterization of Coatings

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Coatings are applied to surfaces for a variety of reasons: to enhance their appearance, to protect the substrate, to augment the adhesion to other layers, or to functionalize them for further reactions. To evaluate the efficacy of the coating, it is often necessary to analyze the substrate and the coating to ensure that the needed characteristics are present. To this end, the use of x-ray photoelectron spectroscopy (XPS), contact angle, and atomic force microscopy (AFM) can provide information about the surface composition, its morphology, and its ability to be wetted with various solvents. Scanning electron microscopy with energy dispersive x-ray analysis (SEM/EDX) and Fourier transform infrared spectroscopy (FTIR) can provide a clear picture of the near surface components as well as the continuity of coatings. All of these aspects are valuable in evaluating a coating and essential when problems are encountered. The application of these techniques to the analysis of coatings is discussed.

**Keywords** coatings, failure analysis, scanning electron microscopy

## 1. Introduction

The characterization of coatings can be fundamental in evaluating their appearance, performance, and durability. There are increasing industrial and consumer demands for defect-free surfaces, better polymer/metal adhesion, and novel multilayer coatings. The use of surface analysis to investigate and pinpoint the cause of problems with these coatings can provide enabling knowledge for process control, product development, and troubleshooting. A number of the techniques available for surface analysis are sophisticated and not typically found in manufacturing facilities. These analytical tools are available elsewhere and should be used to characterize coatings in well-controlled experiments to gain the most information possible with the least number of samples. A number of techniques are discussed here. The sensitivity, analysis depth, spatial resolution, and information provided by each technique is outlined, and examples of typical applications are given.

The physics behind each of the techniques are not presented, as this information is available elsewhere (Ref 1-6). Each of the case studies is a real industrial example of applications of the surface analytical techniques, and for this reason many of the details about the samples are excluded (identifying information about the manufacturers). This lack of detail does not significantly compromise the presentation of the data.

## 2. Techniques

### 2.1 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is an excellent technique for analyzing the top 5-10 nm of a surface. XPS pro-

vides elemental composition with oxidation state information to sensitivities of 0.5 at.%. All elements except hydrogen and helium can be detected by XPS. This technique is commonly employed when adhesion problems are encountered or when the presence of a very thin film contaminant is suspected, which may not be amenable to scanning electron microscopy/energy dispersive x-ray analysis (SEM/EDX). The spot size for many XPS spectrometers is limited to a minimum of 150  $\mu\text{m}$ . There has been a new generation of XPS instruments introduced into the market, which have spatial resolutions of 1 to 2  $\mu\text{m}$ . Analysis is easiest on conductive samples, but the charging problems on insulating samples can be controlled by a combination of a flood gun and a metal screen over the sample. Survey scans provide the elemental composition of the surface, and high resolution scans of the various peaks provide information about the oxidation state of the element. This information can be very important when investigating the composition of oxide/metal layers, modified surfaces, and surface reactions.

XPS results presented here were collected using a Surface Science Laboratories Model SSX-100 XPS using aluminum  $K\alpha$  radiation, a 600  $\mu\text{m}$  spot size, and a 150 eV pass energy. Charging at the samples surface was controlled by the use of a flood gun.

### 2.2 Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis

SEM/EDX provides a pictorial representation of the surface with the elemental composition of chosen areas. EDX provides the elemental composition of the surface for elements from boron through uranium. The technique is sensitive for elements to approximately 0.1 wt % and can probe depths from 0.2 to 8  $\mu\text{m}$  depending on the energy of the electron beam used and the average atomic number of the sample. This technique is the workhorse of many analyses because of the power inherent in being able to provide a pictorial representation combined with an elemental analysis. With unknown samples, this is frequently the technique of choice for initial analysis. SEM/EDX does not provide oxidation state information as does XPS. SEM does

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provide spatial resolution of the surface down to the nanometer range particularly on field emission SEM. With the image, elemental maps of the same area can be acquired to aid in the analysis. SEM/EDX is also used to study cross sections of material. This can be invaluable in determining which layer in a multilayer material is giving rise to the defect. The sample can be mounted and polished carefully to expose the defect. From this approach, the layer of origin for the defect can be determined. Quite often SEM and optical microscopy are very useful complementary techniques.

The SEM/EDX data presented here were collected using the Hitachi S4500 field emission SEM (Nissei Sangyo, Ltd., Tokyo, Japan) equipped with a EDAX CDU LEAP Detector (EDAX, Mahwah, NJ) with a light element detector.

### 2.3 *Fourier Transform Infrared Spectroscopy (FTIR)*

FTIR provides information about the types of bonds present in a material and can often enable the analyst to pinpoint the exact material being used. If analysis of a coating or a defect shows the presence of only carbon or carbon, oxygen, and nitrogen, then it is often difficult for the manufacturer to backtrack in the process to identify the cause of a problem. FTIR can differentiate between compounds such as polyethylene and polypropylene whereas these materials will have identical elemental compositions to techniques such as XPS and EDX. There are a number of accessories available with FTIR, which broaden the scope of the instrumentation. These accessories include attenuated total reflection (ATR), diffuse reflection (DRIFTS), external reflection, and microscopy in both reflection and transmission modes. Use of the accessories allow the surfaces to be probed in a number of different ways. ATR allows the soft surfaces to be probed at depths from 0.5 to 1.5  $\mu\text{m}$ . This technique is ideal for probing deposits of polymer surfaces, gaging surface oxidation and determining material differences between the bulk and the surface of a material. DRIFTS can be used to probe the composition of finely ground powders. Surfaces can also be abraded with special disks to transfer surface material to a support on which it can be analyzed. This is a very useful option for surfaces which cannot be cut down for analysis but can be abraded. External reflection is an excellent technique for examining thin coatings (0.1 to 2  $\mu\text{m}$ ) on reflective supports. The samples can include both inorganic and organic coatings on reflective surfaces such as polished metals. The microscopic technique is excellent for examining very small areas of contamination, lack of adhesion, or formation of unknown crystalline substances. FTIR is at its most useful when used in conjunction with SEM/EDX because the probe depth of the techniques is often similar and the elemental composition supplied by the EDX can be invaluable in interpreting FTIR spectra.

The infrared spectra were collected using a Bruker IFS55 infrared spectrometer (Billerica, MA) equipped with a microscope. The accessories were Baseline model units from Spectra-Tech.

### 2.4 *Contact Angle*

Contact angle (CA) measurements probe the wettability of a surface with different solvents. Wettability is a very important

aspect of many surfaces, especially in coating applications, because the first step in being able to coat a surface is to ensure that the coating will actually wet the surface. A coating can often be applied to a surface, but the coating will bead-up and display a lack of adhesion if the surface is not wettable. Many surface modification methods involve changing the energy of the surface through oxidation. The change in the surface energy changes the wettability and enhances the adhesion of many coatings. Problems with coating adhesion can often be traced through the use of contact angle measurements especially if there are no apparent differences in the surface composition.

Contact angle measurements were collected using a Ramé-Hart Model 100 contact angle goniometer (Mountain Lakes, NJ) equipped with a micro-syringe attachment for measuring advancing and receding contact angles. The probe liquid used is Milli-Q water unless otherwise indicated.

### 2.5 *Atomic Force Microscopy (AFM)*

AFM is a technique for measuring surface topography. A probe is rastered across the surface and is deflected as it encounters features on the surface. The technique generates a topographical map from which average roughness data, line scans, histograms of heights, and fractal data can be derived. The method not only probes the physical aspects of the surface, but it can also be modified to measure any number of other characteristics, depending on the types of probes and the specialized techniques employed. The pictorial representations of the surfaces can be similar to those seen from SEM measurements, but AFM provides much more information in the Z-direction than SEM.

AFM data were collected using a Topometrix Explorer atomic force microscope (Santa Clara, CA) with standard tips in contact mode.

## 3. Applications and Case Histories

### 3.1 *Adhesion Problems and XPS*

A wealth of information can be obtained by analyzing both sides of a failed surface in conjunction with the cross section of the components. Typically both sides of the failed bond have similar compositions, and this composition enables the analyst and the manufacturer to determine the layer in which the bond has failed. If the bond is between metal and polymer and there is metal on both sides of the failed bond, the failure may have occurred in the metal/metal oxide layer. If there is a third component, such as an adhesive, present in the sample XPS analysis can help determine which of the two interfaces has failed. For these reasons, XPS is very useful in laminate analysis.

The manufacturer was trying to bond a polyvinyl chloride (PVC) molded piece to a second PVC piece using a PVC-based glue. This process had worked well in the past, but one particular lot of molded pieces was not adhering well. In instances where all of the materials are similar in composition, it is often difficult to determine the locus of the failure, but in this case the determination was successful by using XPS analysis.

PVC is typically loaded with additives, and one of these is often an organo-tin additive. At the surface of the molded PVC

piece away from the bond, tin was seen in significantly higher quantities than in the cross section. This difference is shown in Fig. 1 and indicates that blooming is occurring because the tin additive is migrating to the surface. XPS analysis of the bulk and the surface of the second sample showed no tin was present. No tin was present in the PVC adhesive. Tin was present on both sides of the failed bond area at levels similar to that seen on the surface of the molded part. Blooming of the tin additive to the surface of the polymer was interfering with the bonding of the two parts. Knowledge of the cause of the bonding failure helps the manufacturing facility trace the defective parts and correct the problem. This knowledge can also narrow the search for the cause of the problem. If the problem lies with one particular piece, the search for a solution can be concentrated in this area, and the problem solved more quickly.

In examining metal-polymer bonds, XPS can be exceptionally valuable. One such case can be found in metal/adhesive/foam composites. In this case, the composite was being applied to a support, and the bond between the metal and the foam was failing. There was no indication of the origin of the problem. A number of materials have to be investigated to find the source of the adhesion failure. In these cases the problem can be worked through step-by-step.

The first step is again to examine the failed interface to determine the locus of failure. This can assist in the examination of source materials. Once the locus of failure has been determined, materials from the failed lots can be compared with those from good lots. In this case, high silicon content was found at the interface of the failed bond and on the surface of the unbonded metal surface. Examination of a reference metal surface showed no silicon at the surface. From this information, the manufacturer was able to review the process and determine where the silicon contamination of the metal surface was occurring.

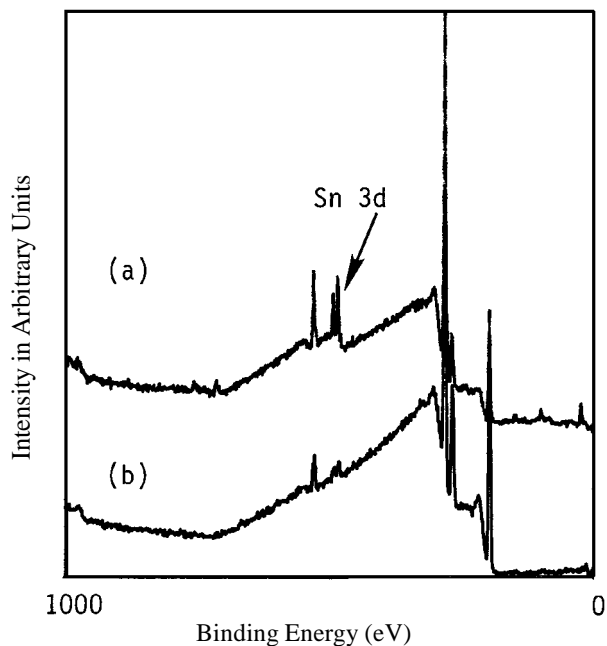
### 3.2 Surface Cracking and Coatings and SEM/EDX

SEM/EDX is a fairly common and valuable tool for examining coatings. Micrographs provide information about a wide variety of coatings including oxide thicknesses, crack propagation and its causes, defects in organic and metal coatings, as well as particle size and appearance.

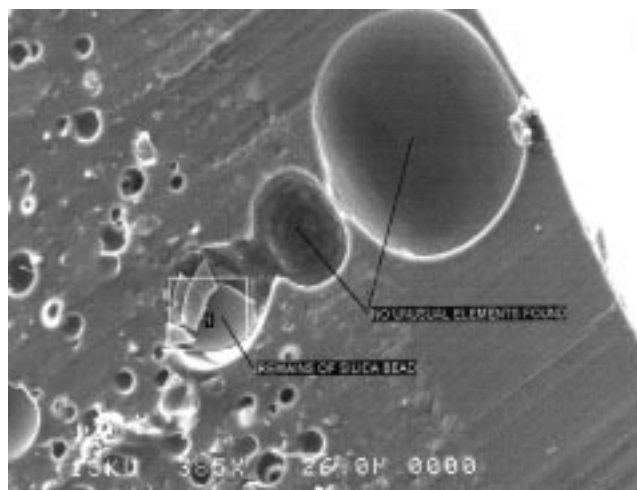
SEM/EDX is extremely useful in examining defects in coatings because with the current multilayer coatings it is extremely difficult to determine the source layer for many defects. The defect becomes apparent in the top layer, but the origins can be obscure. In Fig. 2, a micrograph of a coating defect is presented in cross section. The defect manifested itself as a pinhole in the coating. The sample was polished to expose the cross section of the defect, and in this manner the layer of origin for the defect was uncovered. As shown in the micrograph, the substrate is filled with hollow glass beads. Where the defects have occurred, a very large glass bead is present near the surface. It appears that the trapped gas in the bead expands when the sample is heatcured and forms bubbles in the subsequent layers. The gas in the uppermost layer of the coating escapes through the pinhole defect at the surface.

Frequently, novel coatings are developed, which impart useful functionality to a wide variety of parts. Although these coatings possess valuable properties, many of the problems lie in utilizing the functionality in a timely and cost effective man-

ner. Diamond coatings are among these novel developments. There is no doubt that diamond is an excellent material for use in electronic and wear-resistant coating applications. These applications for diamond coatings are possible because of the exceptional hardness, thermal conductivity, stability, and optical transmissivity of the material. The problem with these coatings occurs in attempting to adhere them to useful

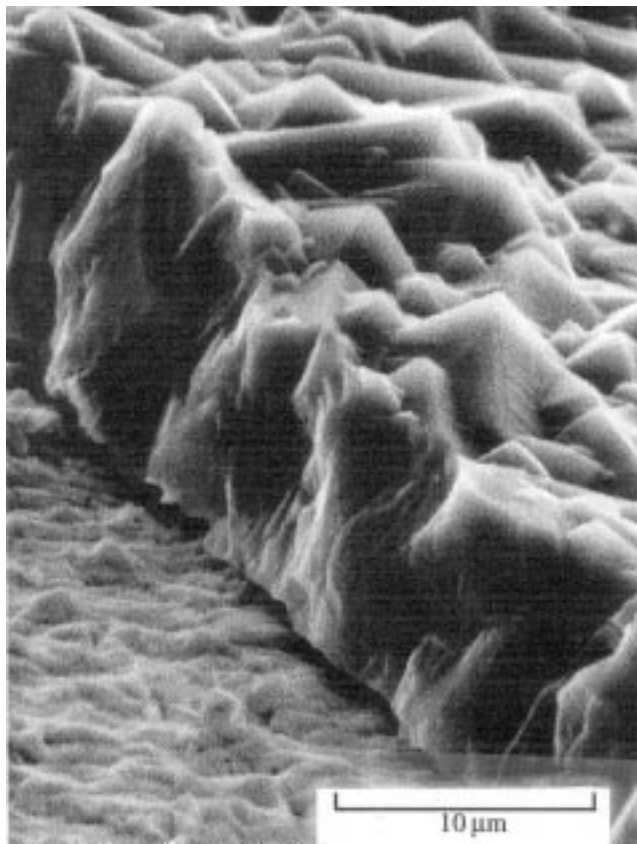


**Fig. 1** XPS spectra of the molded PVC piece (a) at the surface and (b) in cross section. The tin 3d<sub>3/2</sub> and 3d<sub>5/2</sub> at 493 and 485 eV binding energy are indicated. The peaks are much stronger in the spectrum of the surface than in the cross section.

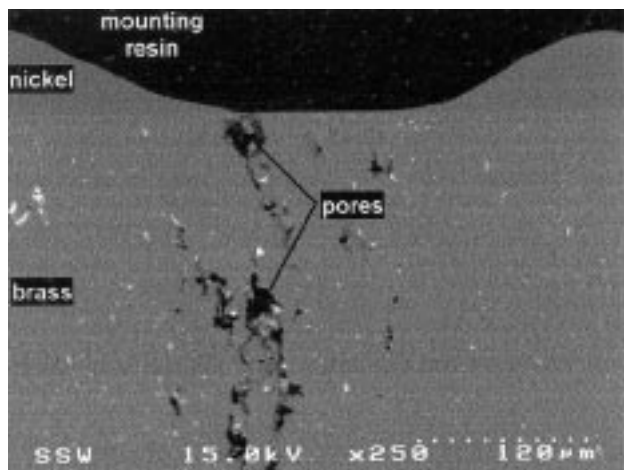


**Fig. 2** Scanning electron microscope micrograph of the cross section of a defect in a coated polymer surface. The cross section shows the broken silica bead in the substrate giving rise to the pinpoint defect at the surface of the coating. The micrograph was collected at 15 kV at a magnification of 385 $\times$ . (Art has been reduced to 60% of its original size for printing.)

substrates. Figure 3 shows a micrograph of a diamond coating on a tool bit. The micrograph shows that the edge of the diamond coating is not attached securely to the substrate but rather sitting on top of it. SEM provides a quick and useful check of the adhesion of such coatings to the substrates.



**Fig. 3** SEM of a diamond coating on a tool bit collected at 20 Kv at a magnification of 3270 $\times$ . The coating is approximately 7  $\mu\text{m}$  thick. (Art has been enlarged to 102% of its original size for printing.)

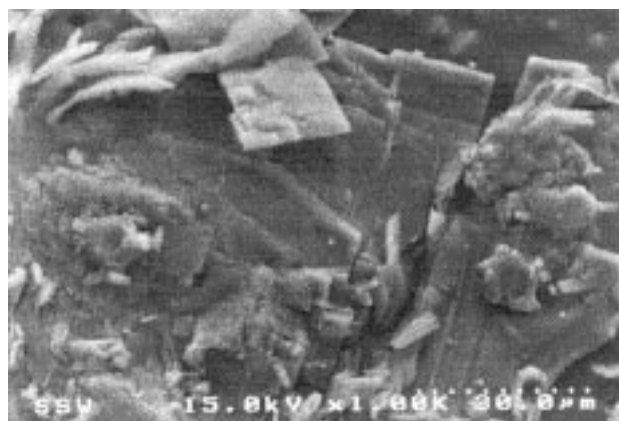


**Fig. 4** SEM backscattered electron image (BSE) showing the cross section of a defect in a nickel-coated brass piece. The porosity in the brass, which gives rise to the defect, is clearly seen in the cross-sectional image.

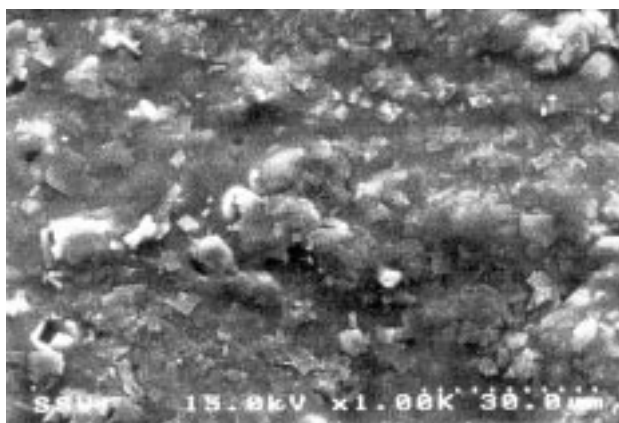
In this example, a nickel/chromium plating company was having a problem with pits in the plating of brass fixtures. Initial examination (plan view) of the pit showed that the coating was still intact in the pitted area and no contaminants were found. A portion of the samples were then mounted in a polymer resin and metallographically cross sectioned and polished to reveal the pitted area. SEM imaging of the pit in cross section showed a large amount of porosity within and at the surface of the brass substrate (Fig. 4). This porosity will cause an exclusion of the electric field at the pore opening, and thus the electro-deposition of the nickel plating is inhibited (Ref 7). Sufficient plating will occur, however, to seal off these pores. With this information and by working with the brass supplier, the manufacturer remedied the problem.

### 3.3 SEM/EDX Analysis Coupled with FTIR

Many coatings problems can be analyzed using a combination of SEM/EDX and FTIR. The SEM/EDX provides the elemental



(a)



(b)

**Fig. 5** SEM micrographs of good and bad coated parts. (a) The surface of sample A, the bad part, showing the very large (10 to 30  $\mu\text{m}$  square) crystals on the surface. Figure (b) is a micrograph of the surface of sample B, the good part, showing small flat particles (approximately 3  $\mu\text{m}$  square) at and just beneath the surface.

composition and the micrographs, while the FTIR is able to provide more specific molecular information.

In a recent instance, a company manufacturing coated molded rubber parts was finding an unsightly white residue on the surface of their coated parts. This residue had not been previously encountered. The manufacturer was able to provide examples of a part which met their specifications for appearance as well as the part with the unsightly residue. The white residue was believed to arise from defective coating material.

The samples were analyzed first using SEM/EDX to determine the appearance of the residue on a microscopic level and to obtain the elemental composition. The micrographs of the surfaces are presented in Fig. 5(a) and (b). From Fig. 5(a), the micrograph of the surface of the good part, small crystals can be seen lying at and just under the surface of the coating. Figure 5(b) shows that the crystals are from 10 to 100× larger and lie on the surface of the material. The EDX results are presented in Table 1. Both the crystals and the matrix material were analyzed by EDX for Sample A, the defective surface, and the small crystals on Sample B, the reference part were also analyzed. The presence of significant quantities of sulfur in the crystals on the surface of sample A was surprising, and the origin of such material at the surface was unable to be hypothesized. In this case, the manufacturer was unable to provide guidance.

Sample A was then analyzed using FTIR-ATR. The sample was pressed against a germanium crystal, and a spectrum was collected. The spectrum was compared to that collected from Sample B and found to be quite different. A library search of the spectrum of sample A gave a good match for benzothiazylsulfide, a sulfur-rich accelerant used in rubber processing. Figure 6 shows a comparison of the spectrum of sample A and the benzothiazylsulfide. The match was consistent with the type of material being molded and the elemental composition, as measured by EDX. The unsightly appearance was caused by the presence of the accelerant in crystalline form at the surface. The accelerant had migrated through the rubber and the coating to the surface of the molded, coated part.

### 3.4 FTIR of Deposit Defects

A manufacturer of decorative lacquer-coated metal parts was having a problem with the formation of a grayish-white deposit on the surface of the part. It was very important to the manufacturer that the surface of the part be defect free. SEM/EDX analysis of the problem showed the deposit to consist mainly of sodium, carbon, and oxygen with low concentrations of other elements. The elemental composition did not point to a single cause of the problem, so microscopic FTIR analysis was employed. The clear lacquer coating was analyzed first and determined to be of a polyacrylic-type material,

**Table 1** Elemental composition of the surfaces

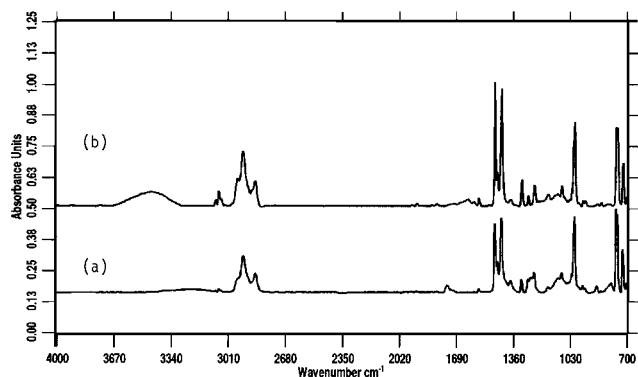
| Sample            | Elemental composition, at. % |     |     |     |      |
|-------------------|------------------------------|-----|-----|-----|------|
|                   | C                            | O   | Zn  | Si  | S    |
| a, large crystals | 80.6                         | 2.3 | 0.8 | ... | 16.3 |
| a, matrix         | 86.9                         | 9.9 | 0.4 | 1.9 | 0.9  |
| b, small flakes   | 86.7                         | 7.6 | 0.3 | 0.6 | 4.8  |

and the spectrum is shown in Fig. 7(a). Spectra of the white deposit showed peaks in the region from 1960 to 2300  $\text{cm}^{-1}$ , which are consistent with the presence of cyanide, isocyanate, or nitrile groups. A representative spectrum is shown in Fig. 7(b). Depending on the area analyzed, the peaks varied significantly in intensity and position, indicating that there are a number of reaction products present in the deposit, but they all have a similar set of functional groups.

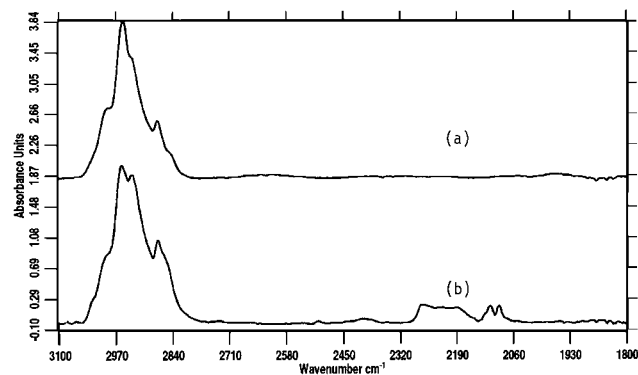
On presenting data to the manufacturer, the process chemicals were found to become trapped within the porosity of the coating and to bleed out later as a complex mixture of caustic and cyanide reaction products. This scenario was consistent with the SEM/EDX results and with the FTIR spectra of the deposits. Because SEM/EDX is not particularly sensitive to nitrogen, it was not surprising that it was not seen in the EDX spectra. The problem was attributed to cyanide bleed out. The process was modified and the defect was corrected.

### 3.5 AFM and the Measurement of Weathering in Coated Metals

Atomic force microscopy is a powerful technique for the gathering of roughness statistics from a variety of surfaces.



**Fig. 6** FTIR-ATR spectra of the surface of (a) sample A, the bad coated part, and (b) the library spectrum of benzothiazylsulfide.



**Fig. 7** Microscopic FTIR spectra of (a) the clear coating on the metal and (b) the white deposit on the surface of the finished piece. The peaks occurring between 1960 and 2300  $\text{cm}^{-1}$  indicate the presence of cyanide, isocyanate, or nitrile groups.

Figure 8 shows a typical two-dimensional representation of a weathered, coated painted surface. This sample was obtained from a manufacturer of painted metal materials. The surfaces became much rougher during weathering tests, and the manufacturer needed a numerically valid and statistically significant measure of the roughness of the surface as a function of changes they were making to the coating. Initially, more than thirty 10  $\mu\text{m}$ -square areas on a single sample were examined, and the roughness data were calculated to determine the variability encountered over the surface. After the variability of a single sample was determined, a smaller number of areas on subsequent samples were probed and roughness results were averaged. AFM also allows a number of additional calculations to be made on the scans such as line scans, bearing ratios, and peak/valley measurements. Although pictorial representations of the surface can be obtained from the SEM micrographs,

AFM allows calculations to be made, which can provide quantitative information about the samples.

### 3.6 Contact Angle and Surface Modification

Contact angle measurements are dissimilar from the other techniques discussed in this paper. SEM/EDX, AFM, XPS, and FTIR measure either the elemental composition, the molecular bonding, or the topography of the materials. Contact angle measures a property of the material, the wettability. Two samples investigated using all of the other techniques can have very similar elemental compositions, molecular bonding, and surface topography, and perform differently in their application. Typically, performance problems are manifested by a lack of adhesion between the coating and the substrate. If the materials have similar compositions and topographies but different adhesion properties, contact angle provides a probe to measure the wettability of the surface. The wettability of the surface is determined by the composition of the outer monolayer of the material, and this layer can be difficult to analyze if it differs significantly from the near surface composition. Wettability problems are most common in the polymer industry where adhesives, paint, and metallized coatings often fail to adhere to polymer surfaces. These problems are also seen when coating metal surfaces.

Phosphating, annealing, and solvent cleaning are used in industry to increase the wettability of metal surfaces to make them suitable to accept coating materials. These processes change the wettability and hence the contact angle of the surface of the metal either by adding a hydrophilic material to the surface, as in phosphating, or by removing a hydrophobic material from the surface, as in annealing and solvent cleaning. Many metal surfaces have extremely thin films of lubricants and rolling oils remaining on the surface, which cannot be seen but will change the wettability of the metal surface. Contact angle is even more surface sensitive than XPS because it probes only the outer monolayer of material at a surface.

In the example, a set of four samples of polymer plaques had different adhesion properties when a coating was applied. Two of the samples exhibited good adhesion properties, and two samples were poor. The surfaces of the samples were analyzed by XPS, and the elemental composition is presented in Table 2. The samples had very similar compositions except for higher oxygen and silicon concentrations at the surface of the two good samples. The difference did not appear to be great enough to explain the adhesion properties.

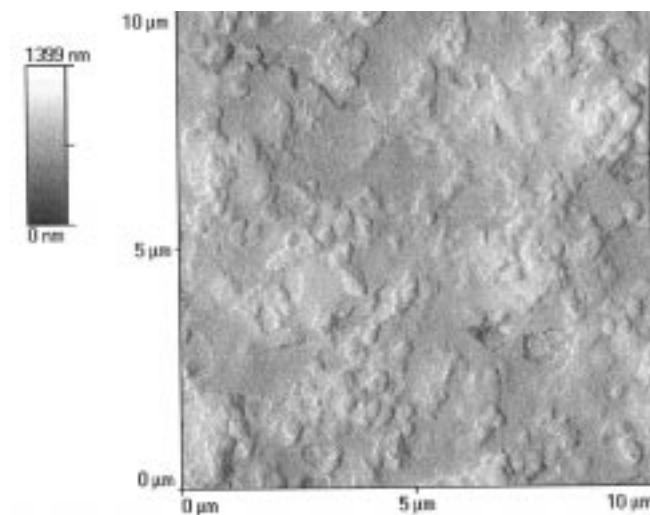
The advancing and receding contact angles of the samples were measured using water as the probe liquid and are presented in Table 3. The advancing contact angles for all of the samples were very similar. The differences were seen in the receding contact angles where the good samples had values from 20 to 25° lower than the poor samples. The receding contact angle is a good indicator of the amount of modification at a polymer surface and is a good measure of the wettability. In this example the determination of the surface composition was not enough on its own to pinpoint the problem, and a measure of the surface wettability was necessary.

**Table 2 Elemental composition of polymer plaques by XPS**

| Sample | Elemental composition, at. % |      |     |     |     |     |
|--------|------------------------------|------|-----|-----|-----|-----|
|        | C                            | O    | S   | Si  | Na  | N   |
| Good 1 | 85.1                         | 11.4 | 1.3 | 0.6 | 1.7 | ... |
| Good 2 | 84.6                         | 10.3 | 1.3 | 0.5 | 1.7 | 1.6 |
| Poor 1 | 90.7                         | 5.7  | 0.6 | ... | 0.8 | 2.3 |
| Poor 2 | 85.7                         | 9.5  | 1.8 | ... | 3.0 | ... |

**Table 3 Contact angle measurements of polymer plaques**

| Sample | Advancing and receding angles, in degrees |          |
|--------|---|----------|
|        | Advancing                                 | Receding |
| Good 1 | 91  | 45       |
| Good 2 | 90  | 51       |
| Poor 1 | 89  | 73       |
| Poor 2 | 92  | 73       |



**Fig. 8** AFM two-dimensional representation of the surface of a weathered, painted metal surface. The micrograph shows a 10  $\mu\text{m}$  square area from which average roughness, average peak height, maximum peak height, and a height histogram can be generated.

## 4. Summary

We have presented an overview of some surface analytical techniques which can be used to characterize coatings. A number of industrial examples of the application of these techniques in solving coatings problems are also included to highlight the capabilities of each of the techniques. Industrial coating problems often require the use of one or more analytical techniques to completely elucidate the cause.

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