Raman Spectroscopy in Coatings Research and Analysis: Part II - Practical Applications

By Neil J. Everall, ICI Plc*

In this two-part tutorial, the use of Raman spectroscopy for characterizing and testing coatings is examined. Part I covered the type of information that can be obtained using Raman spectroscopy (August 2005 JCT CoatingsTech, page 38), and described how a coating is studied in a typical Raman experiment. In Part I we also discussed the thickness of the coating to be studied, and the influence of the substrate. In this section, we focus on examples that illustrate the capabilities and limitations of Raman spectroscopy.

APPLICATIONS AND EXAMPLES

Compositional Mapping

Perhaps the most obvious application of Raman spectroscopy to coating technology is compositional mapping, whereby a map or image of the composition of a coating can be built up in two or three dimensions. Raman mapping involves sequential acquisition of Raman spectra as a laser beam is incrementally rastered over a sample. An image over a sample size of a few (well-separated) Raman frequencies can then be constructed based upon the intensity (or some other parameter) of a Raman band as a function of position in the sample (Figure 3). Raman imaging involves defocusing the laser to illuminate a large 2D area of a sample, and then sequential acquisition of laser shots at distinct Raman frequencies (selected using a tunable filter). In principle, this is an attractive approach, and for simple, stable systems, where it is only necessary to record images for a few (well-separated) Raman frequencies, it can be very fast. However, if many Raman bands have to be analyzed and understood the coating chemistry, then it can take a long time to acquire images at all of the necessary frequencies. In addition, Raman imag-

ing requires a high power laser beam (to generate a reasonable power density at the sample when the beam is defocused), and it turns out that samples are more prone to thermal decomposition under global illumination than point illumination, due to the difficulty in con- ducting heat away from a "sheet" of hot material at the sample surface. There are also hybrid technologies available, where the laser is focused to a line on the sample; spectra are acquired simul- taneously at each point along the line, using a spectrograph/CCD (Charge-Coupled Device) camera combination, then the line is moved to a new point on the sample. Approaches to Raman mapping and imaging have been summarized in detail elsewhere.1-4,31

Many of the examples discussed in this tutorial involve measuring spatial variations in a property, so only a few of the examples of compositional mapping involving imaging will be given here. Table 1 summarizes the influence of manufacturing variables on the surface quality of paper laminates impregnated with melamine-formaldehyde (MF) and urea-formaldehyde (UF) resins.4 They used Raman microscopy to map the MF distribution as a function of the amount of UF that was added to the system. They showed that if the UF level was too low, then the MF tended to fill voids in the center of the laminate, leaving the surface MF-deficient and causing visible defects. Increasing the amount of UF prevented ingress of the MF into the body of the laminate, thereby in- creasing the MF concentration at the surface, giving fewer defects. Larsson et al. used confocal Raman axial profiling with a water-immersion objective to map ligand distributions in surface- treated chromatinized adhesive particle.43 They showed how accurate axial profiles of aliph, sulphophy, and dextr trans concentrations could be obtained from particles immersed in water. This proved that the sulphopropyl groups were confined to shells (~20 µm) shells on the surface of ~100 µm diameter bead, and allowed coating thickness to be assessed for different particle types. The power of Raman imaging and mapping was shown in a detailed study of the near-surface composition of a thermo- plastic elastomer (TPE) that was sprayed with a chlorinated poly( dimethylsiloxane) (CPO) to form a primer layer for subsequent painting.46 The TPO was a blend of ethylene- propylene rubber (EPR) and poly(propylene) (PP). The Raman im- aging showed separation of the TPO in distinct EPR and PP phases, with the EPR and CPO domains occurring on the surface. The authors suggested that the solvent carrier for the CPO spray was responsible for induced quantization of the TPO into its EPR and PP compo- nents. This work also highlighted the need for multivariate data processing to analyze the large volume of data that is generated in spectroscopic images (Figure 9).

Curing: Crystallinity in Polymeric Coatings

On occasion, one needs to character- ize crystallinity gradients in polymer films and coatings. For example, in order to achieve good adhesion between the polymer coatings and metal substrates used in car production, it is impor- tant to control the polymer crys- tallinity so as to retain an amorphous layer near the metal surface, while maintaining a reasonable level of crystallinity elsewhere to avoid compromising the mechanical performance of the coating. The critical changes can occur within just one or two microns of the metal surface, so excellent spatial resolution is required. Figure 10 shows a Raman line map, taken at one µm increments through a cross-section of a steel-polymer lami- nate. As one approaches the metal, the crystallinity falls dramatically (decrease in intensity of the 1096 cm-1 band over a distance of just 2 µm) with amorphous polymer at the metal interface. This result confirms that both the coating and the cur-forming processes have been controlled to produce an accept- able film structure both in the bulk and at the interface. Using imaging polar- ized confocal Raman microscopy, it is possible to map changes in polymer morphology, such as surface crystallinity, because the intensity of a Raman band depends on the orienta- tion of the laser and Raman fields and the orientation of the scattering unit.47 We have used this approach to map gradi- ents through the thickness of ultra- lowly-oriented PET films.48

Cure

UV CURE: Raman spectroscopy is ideally suited to studying the cure of re- active C=C groups. Figure 11 provides a simple example. In this case, an unsatu- rated polyester resin was cured using UV light and a cationic initiator, and a microtomed cross-section was then mapped with a Raman microscope to monitor consumption of the C=C double bonds. The resin was a bisphenol-A type epoxy containing reactive bisphenol-A diglycidyl ether (BDE) and cumylhydrogenated triphenyl methane (CHT) curing agent. Adapted from Figure 9 of reference 16, with permission of The American Chemical Society.

ANALYTICAL SERIES

Thermal Cure

In the paint industry, the drying (i.e., room temperature cure) of alkyd resin is a complex process involving cis-trans isomerization, C=C bond migration and crosslinking, and formation of peroxide and hydroperoxide species. While Raman can follow the C=C consump- tion and O-O-P formation, FTIR is far better suited to study thermal (i.e., thermal tempera- ture) effects of alkyd resins. In this example, the UV cure of an epoxy-acrylate resin containing a cationic acrylate functionality in the epoxy-acrylate isomer and confocal laser scanning microscopy (CLSM) to study filler distribution and cur of urethane- acrylate and ester-acry- late resins, although they neglected the effect of spherical aberration on the Raman depth resolution.46 Kim et al. combined Raman and AIR-FTR spec- troscopy to study the cure of a cationic acrylate to which an acrylate-functional- ized poly(dimethylsiloxane) (AP-PDMS) was added, and showed that there was an optimum level of AP-PDMS which resulted in improved surface cure and hardness.49 Unfortunately, it was not clear whether the authors could differ- entiate acrylate functionality in the PDMS from that in the ester-acrylate copolymer. Nichols and colleagues dis- covered several UV clearcoats in which spectral overlap made it difficult to resolve bands and so the quanti- tative cure profile.51 They showed how different derivatives could be used to improve band reso- lution and permitted quantita- tive cure profiling. They cut cross-sections and mapped cure at 10 µm intervals through the coat thickness, and compared situa- tions in which cure was limited by ei- ther UV penetration (as in Figure 8), or by oxygen inhibition. It was claimed that sufficiently high UV dose could overcome O2 inhibition at the surface, but that their cure monitor (10 µm) was not adequate to resolve any cure gradients which might be present within the first few microns of the coat. Raman microscopy is pre-eminent for monitoring spatial cure profiles, but cure kinetics can often be measured more easily using IR spectroscopy. For example, real-time IR spectroscopy has been pioneered by Becker for monitor- ing UV cure on the ms timescale.52 It would be difficult to obtain adequate spectral quality as rapidly using Raman spectroscopy.
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Many of the examples discussed in this tutorial involve measuring spatial variations in a property, so only a few examples of compositional mapping will be given. However, the discussion that follows provides the reader with examples of how Raman mapping can be used to study the chemical composition of coatings.

In this tutorial, two examples of compositional mapping will be given. In the first example, a UV-cure coating containing 2 parts by weight of urea-formaldehyde (UF) and 4 parts by weight of isocyanate-terminated polyester coating (UP) was studied. In this example, the UV-cure coating was studied with Raman spectroscopy to see if the UV light was able to penetrate into the coating. The UV light is attenuated as it penetrates into the coating, and this adversely affects the consumption of the isocyanate-terminated polyester coating. The cure profile is therefore 1, 2, or 3-dimensional. Raman spectroscopy can be used to study the curing process in a coating.

Figure 1 shows a typical UV-cure system. The UV light is attenuated as it penetrates into the coating, and this adversely affects the consumption of the isocyanate-terminated polyester coating. The cure profile is therefore 1, 2, or 3-dimensional. Raman spectroscopy can be used to study the curing process in a coating.

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Cure

UV CURE: Raman spectroscopy is ideally suited to studying the cure of reactive Cure Coatings. Figure 12 provides a simple example. In this case, an unsaturated polyester resin was used with UV light and a cationic initiator. A microtomed cross-section was then mapped with a Raman microscope to monitor consumption of the C=C double bonds. The cross-section was then mapped with a confocal microscope to analyze the large volume of data that is generated in spectroscopic images (Figure 9).

Figure 9—Near-surface distribution of poly(propylene), ethylene-propylene rubber, and chlorinated polyethylene in components, in a C=C-sprayed polyester composite. The C=C double bonds are colored red. Other bands are shown in green. The cross-section shows that the C=C double bonds are not completely reacted at the surface. The cure profile is therefore 1, 2, or 3-dimensional. Raman spectroscopy can be used to study the curing process in a coating.

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In the paint industry, the drying (i.e., room temperature cure) of alkyl resin is a complex process involving cis-trans isomerization, C=C bond migration and crosslinking, and formation of peroxide and hydroperoxide species. While Raman spectroscopy can follow the C=C consumption and O-O formation, with moderate spatial resolution, Raman spectroscopy is better suited to study the cure of C=C-sprayed polyester composite. The C=C double bonds are colored red. Other bands are shown in green. The cross-section shows that the C=C double bonds are not completely reacted at the surface. The cure profile is therefore 1, 2, or 3-dimensional. Raman spectroscopy can be used to study the curing process in a coating.

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Young's Modulus as a function of film thickness and drying time. Erich et al. combined NMR imaging and confocal Raman microscopy to monitor the penetration of drying films into allyl films. The NMR data were used to calculate the true sampling depth of the Raman probe, which was shown to be about 1.6 times deeper than the nominal focal point. This confirmed that fraction must be accounted for to correctly analyze the position of the drying front.

Perhaps surprisingly, it is also possible to use Raman spectroscopy to predict the viscosity of paint emulsions. To et al. used partial least squares (PLS) regression to predict viscosity over the range 20–350 mPa{s} with a precision of about 25 mPa{s}. The model used spectral features relating to chain length and styrene content which had positive and negative correlations with viscosity. Combined with the more obvious measurements of composition and extent of polymerization, this could be an interesting tool for on-line analysis and production control, particularly given the ease with which Raman spectrometers can be configured for process analysis.

Despite Raman spectroscopy’s advantages in terms of sampling and spatial resolution, sometimes the basis spectroscopy of the system dictates that IR spectroscopy is the preferred approach. There are, however, many common components of coating materials which can be analyzed with Raman microscopy associated with UV-cured films, which in turn gives important information on the adhesion between the resin and the fibers.

Norstrom et al. analyzed sol-gel organosilane solutions before and after air-drying using Raman spectroscopy. As an example, the PEEK spectrum. Presumably this interaction due to the chromophore, so only indirect information on the interaction with the glass was obtained. (Resonant Raman scattering occurs when the laser excitation wavelength falls near or equal to a band (or bands) of the chromophore). In another example of this effect, Li et al. showed how very thin ( < 5 nm) coatings of diamond could be detected on carbon-fibers using surface-enhanced Raman scattering (SERS) and the carbon fiber, which activated incident or engineered carbon coatings are hard, chemically inert, and bio-inert, it can be an important tool for monitoring the fiber size processing.

Sol-Gel Sol-gel processes have been extensively studied with Raman spectroscopy, particularly for hybrid systems where it might be necessary to monitor the cure rate of a number of independent reactive systems in conjunction with the formation of both organic and inorganic networks. Pestel et al. investigated the UV cure kinetics of two different coating systems: trimethylolpropane trisethoxysilane and tetraethoxysilane, with additional vinyl and acrylate components. They followed the hydrolysis of the alkoxysilane and the crosslinking of the acrylate and vinyl groups, and correlated the degree of crosslinking with the surface hardness before and after more detailed analysis. There is also recent discussion of Raman spectroscopy with SiO2. Raman spectroscopy to study the polymerization of an epoxy-functionalized alkoxysilane (glycidoxypropylmethyldimethacrylate, or GPTMS). Cure was initiated with an amine that can catalyze both ring-opening of the epoxy and condensation of the silanol groups that result from hydrolysis of the methyol groups. The GPTMS was dissolved in water and the amine was added, and then the liquid was cast onto a hot plate and dried at a lower temperature, and then cured at 150 °C for an hour. The GPTMS:amine ratio was varied to investigate the effect on the cure chemistry. The Raman data proved that for high levels of amine catalyst, extensive ring-opening of the epoxy had occurred after drying (signifying complete cure). Cure with silane groups in conjunction with the formation of both organic and inorganic networks. This is a very nice example of how both the organic and inorganic components of a hybrid system can be monitored with Raman scattering. Characterizing the amine polymerization is a generally-applicable approach for the study of carbon-fiber reinforced composites. In some cases, one needs to study the fiber-resin interface in the presence of organic matrix. This can be achieved if the spectrum of the interface is much more intense than in the bulk. For example, when using a laser used resonance Raman spectroscopy to analyze stress-transfer in glass-fiber reinforced epoxy composites. Prior to forming the composite, the fibers were coated with a dicyclosilane or a urethane copolymer that was then cross-polymerized to yield a conjugated system of alternating double bond and triple bond units. This conjugated system, which show significant frequency shift under applied stress can be an important tool for monitoring the fiber size processing.

CARBON Raman spectroscopy is extremely sensitive to the different crystalline forms of elemental carbon can assume, and, as such, is one of the most widely used single wavelength techniques for in-situ analysis of carbonaceous material. Raman spectroscopy is well suited to detection of specific crystall forms of inorganic. Consequently, the authors

CORROSION SCIENCE Raman spectroscopy can be readly applied to study corrosion in situ. Bernard et al. used Raman microscopy to study the corrosion of iron that was protected with an epoxy-amine coating technology, diamond-like carbon (DLC) coatings, and polycrystalline diamond coatings, are hard, chemically inert, and bio-inert, it can be an important tool for monitoring the fiber size processing.

As well as being directly deposited, carbon can be formed as a by-product of other processes-for example, the implantation of plastic, heat treatment of sol-gels, and thermal annealing of metal-carbide ceramics. Raman spectroscopy is an invaluable tool for characterizing the carbon products by their different processes.
were able to detect the formation of elemental sulphur, FeOOH (goethite), and iron carbonate. Impedance spectroscopy showed that the films were in-depth polymerized polypeptide coatings on the metal. This work allowed the redox reactions to occur by measuring the frequency and shape of the Raman signal by about an order of magnitude, making subtle changes in the Raman (~1525 cm⁻¹) more noticeable. Raman spectroscopy is often superior to IR analysis for speciation of inorganic materials, but the sensitivity of SERS is not widely applicable as a routine analytical tool. First, not all metals and analytes give strong SERS spectra. A detailed discussion of the SERS mechanism is beyond the scope of this tutorial; the reader is referred to a recent review for more detail.⁷⁹,⁸⁰ Despite its sensitivity, SERS is not widely applicable as a routine analytical tool. First, not all metals and analytes give strong SERS spectra. A detailed discussion of the SERS mechanism is beyond the scope of this tutorial; the reader is referred to a recent review for more detail.⁷⁹,⁸⁰

CONCLUSIONS

This tutorial has attempted to illustrate the ways in which Raman spectroscopy can contribute to the study of coatings. An article of this length can only give a flavor for the possibilities, but the examples given and the literature cited will give a broad indication of what can be achieved. This discussion is far from exhaustive. For a number of existing technologies (such as sum-frequency generation and near-field Raman microscopy) we have chosen to omit settings on the ground of space considerations and a current lack of general applicability in the field. References


Figure 13—Possible configuration for obtaining SERS spectra of paint films on any surface, such as by depositing a thin (~10 nm) silver film onto the coating, one can generate SERS spectra by focusing the laser beam onto the silver.

Figure 12—Comparison of IR and Raman spectra of a TiO₂(35 nm)/SiO₂(15 nm) thin film on a polycarbonate substrate. The NCO/COH ratio was 2:1, to act as an excrescence of coated NCO/COH. The asymmetric NCO stretching is strong in the IR but in- visible in the Raman. The symmetric NCO bond is visible (1525 cm⁻¹) but is heavily perturbed by the amide II band of urethane and urea groups. Samples kindly provided by M. Diaz, ICI PLC.

POLYMERS AND COATINGS

Raman spectroscopy is often superior to IR analysis for speciation of inorganics. Raman scattering is more sensitive than IR, making subtle changes in weak position easily visible. Raman spectrometers make easy access to low frequency modes (0–400 cm⁻¹), which are critical for differentiating crystal forms. For example, exact matches between NMR and Raman bands confirm the structure of the material. The asymmetric NCO stretch is strong in the IR but invisible in the Raman. The symmetric NCO bond is visible (~1525 cm⁻¹) but is heavily perturbed by the amide II band of urethane and urea groups. Samples kindly provided by M. Diaz, ICI PLC.

SERS from coating

SERS, one needs to control the angle of incidence of the laser beam and the angle of collection of the Raman scatter. Campion has summarized the effect of varying the incident and collection angle and polarization, and the polarization, on the detected Raman signal. According to this analysis, using incident and collection angles of approximately 60° can boost the Raman signal by a factor of 1000. Magnification. Emission using a Raman microscope with a high numerical aperture objective results in a near-field image and collection radiation with a wide range of angles, so it is optimized for detecting thin layers on metals.

THIN COATINGS ON METALS

Under certain conditions, the Raman spectrum can be used to detect the presence of a polymeric coating. For example, a thin layer of polyvinyl alcohol (PVA) on a metal allows the detection of the Raman bands of the polymer. This information can be used to monitor the phase composition and related this to the state of the c-BN layer. The authors mapped the c-BN crystallization effects at the surface, making interpretation difficult. Third, the metal—adsorbate interaction is strong for molecules on the metal surface (up to 10⁹ M⁻¹ cm⁻²). SERS is not widely applicable as a routine analytical tool. First, not all metals and analytes give strong SERS spectra. A detailed discussion of the SERS mechanism is beyond the scope of this tutorial; the reader is referred to a recent review for more detail.⁷⁹,⁸⁰ Despite its sensitivity, SERS is not widely applicable as a routine analytical tool. First, not all metals and analytes give strong SERS spectra. A detailed discussion of the SERS mechanism is beyond the scope of this tutorial; the reader is referred to a recent review for more detail.⁷⁹,⁸⁰

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were able to detect the formation of elemental sulphur, Fe$_2$O$_3$, and Fe$_3$O$_4$. After bubbling H$_2$S through a solution in which a coated steel coupon was immersed, the corrosion products at the solution/film interface were identified as FeS$_2$ and p-tricalcium phosphate (TCP). In the coating, with the TCP/HA ratio increasing towards the metal surface, this attributed to differential cooling rates, with fast cooling at the metal favoring TCP. Hence, Raman microscopy allows one to adjust the film deposition to produce a thick enough layer of HA to prevent resorption of the underlying TCP. Raman measurements were ideal for this study since they can differentiate these materials quite easily compared with X-ray diffraction (XRD), for example. The acid soluble, bioactive and can be reabsorbed (an undesirable effect since it weakens the joint). Thus, Raman microscopy is highly sensitive to crystal size, where small changes in crystal diameter give a large change in the surface/volume ratio. As an example, Wemminghaus and colleagues applied micro-Raman spectrophotometry to characterize cubic boron nitride (c-BN) thin films deposited on silicon substrates. Prior measures on c-BN crystals of known size established the relationship between position and asymmetry of the 260 cm$^{-1}$ Raman band. Prior cali-
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**References**