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Watching Paint Dry with FT-Raman Spectroscopy

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KEYWORDS

FT-Raman/paints & coatings, polymers, adhesives, resins/OMNIC, Macros\Basic, Series software.

INTRODUCTION

Many materials such as paints, adhesives, resins and polymers depend on a cure or polymerization stage during processing for their final physical properties. During this process, the bulk material undergoes chemical and physical changes often resulting in hardening or setting. Many different variables present during this polymerization stage will effect the final properties of the material. FT-Raman spectroscopy is often an ideal technique for monitoring these reactions and understanding the underlying chemistry.[1,2]

There are a number of reasons why it is important to follow the chemical and structural changes which occur during this reaction time. Failure mechanisms in all of these materials can often be attributed to a poor mix in the initial components or non-ideal conditions during the curing process. The development of new materials – stronger, faster setting epoxies or paints which do not require environmentally harmful solvents – requires an understanding of the process involved and an ability to identify changes that occur during the process.

FT-RAMAN ADVANTAGES

FT-Raman has a number of advantages for the measurement of polymerization and curing processes. Perhaps the most important reason is that FT-Raman is sensitive to important information which is difficult or impossible to obtain from other techniques. Carbon double bonds and other backbone structures in long chain molecules often show up very strongly in FT-Raman spectra. FT-Raman is also very sensitive to different isomers (*-cis* and *-trans* configurations) and to cross-linking and different packing structures between chains.

FT-Raman also uses near-infrared light to make direct non-destructive measurements of samples. This means that measurements are quick and easy to acquire. Normally the only preparation required is to place the sample in the beam. FT-Raman is generally done with near infrared light, therefore glass is transparent and is ideal for holding samples. Adhesives can be placed on disposable microscope slides, paint can be coated on glass or practically any other surface for study, and resins can often be studied in situ. This factor makes it very easy to perform experiments such as following polymerization reactions conducted at controlled temperatures and pressures.

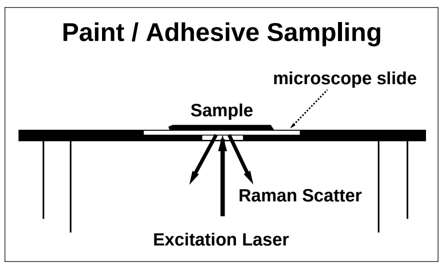

Figure 1

In addition, Nicolet has a sampling accessory that maximizes the benefits that the FT-Raman technique offers for curing and polymerization reactions. The FT-Raman flat plate accessory[3] allows the user to acquire a series of spectra taken from a single sample that represent how that sample changes over time. *(Figure 1)* The flat plate positions the sample so that spectra are collected through the bottom of a glass vessel or slide. The adhesive measurements in this study use a flat plate with a recess designed to accept a glass microscope slide. This allows the liquid materials to sit flat on the slide. After measurements are made on the curing process the sample can be easily discarded or used in aging and weathering tests.

AUTOMATING THE DATA COLLECTION PROCEDURE

It is very easy to automate the collection of data using OMNIC® Macros\Basic™ macro writing software. The simple example macro shown in Figure 2 collects a series of spectra representing temporal changes. A single spectrum can be collected in about 1 second at 4 cm^{-1} resolution. Since the curing process may take several hours to reach completion, spectra are collected at specific time intervals, improving the data quality.

In this example, the macro acquires a series of spectra, each taking 30 seconds to collect, at intervals of 2 minutes. The number of scans taken in each data collection is set in the *Collect Setup* field, the number of data collections is set in the *Start of Loop* field and the time interval between collections is set with the *Delay.*

In addition, data is automatically saved to disk by clicking that option in the *Collect Set-up* window. Saving data automatically gives each data set a short identifier and saves each time interval with an incremental file name. For example, file names might appear on the hard disk as glue0001.spa, glue0002.spa, glue0003.spa and so on. OMNIC also automatically stores the time of collection in the file header of each spectrum providing another reference.

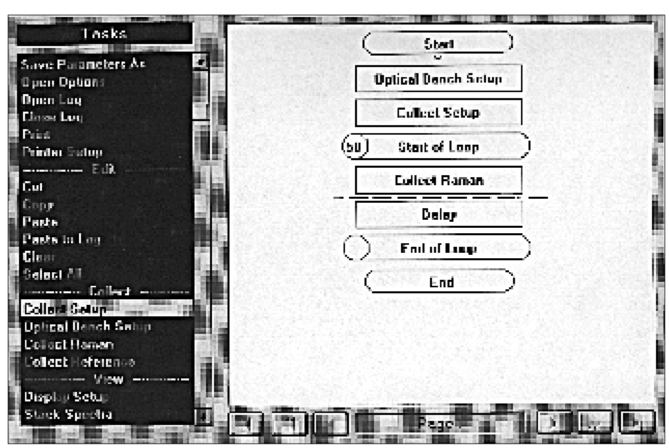

Figure 2

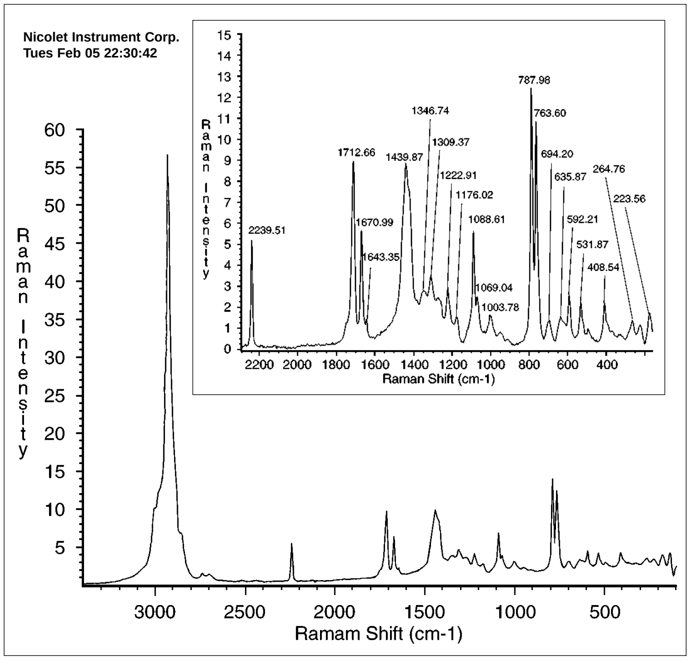

Figure 3a
Insert: expanded to show the symmetric C-C-C stretching at 788 cm^{-1} and 763 cm^{-1} and the C-C skeletal stretch at 1088 cm^{-1}.

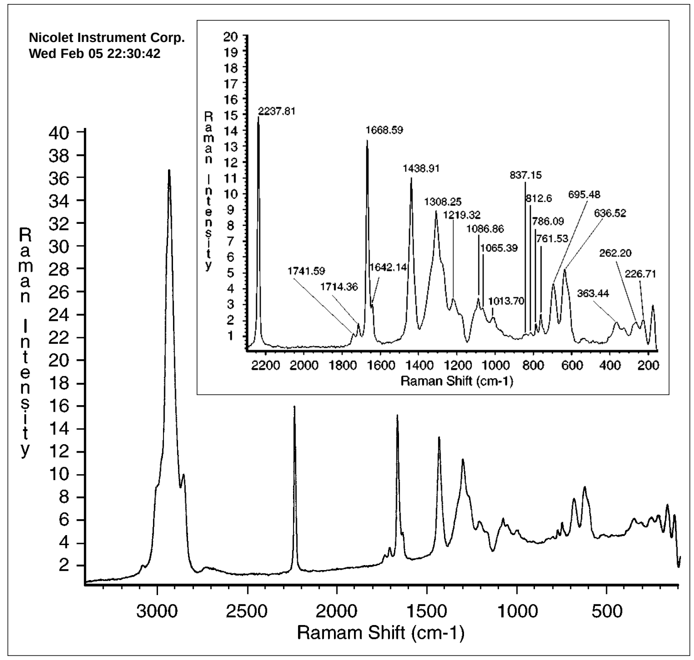

Figure 3b
Insert: expanded to show the C=C stretching band at 1668 cm^{-1}.

DATA ANALYSIS AND DISPLAY

Performing an FT-Raman analysis involving a number of spectra collected over time generates a vast amount of data. In this respect, it is analogous to a GC/IR data collection. Therefore, it is important to have software tools capable of interpreting data from the different aspects of groups of spectra as well as individual spectrum that may be of interest to the user.

In this example, we look at the data collected from an adhesive sample using the macro described previously. A similar approach can be used to analyze paint samples, polymer cures and polymerization reactions. FT-Raman allows corresponding information to be drawn from the study of these other chemical systems.

Figure 3 shows spectra from the start and end of the data collection, the first (3a) and last (3b) spectrum in our series. These two measurements reveal that although the basic structure of the adhesive remains the same throughout the data collection, some major changes occur. Some bands disappear while others shift or grow. However, this type of analysis contains no information about how these changes occur. Nor can it give any clue as to whether these changes are part of a single process or whether there are several simultaneous processes occurring, each independently causing changes in the spectrum. For this information, we need to examine the spectra collected at each time interval between the start and end of the reaction.

For example, the physical appearance of the adhesive would suggest that the reaction is complete within the first few minutes as the material becomes hard to the touch and undergoes a slight change in color. However, if one looks at the changes that occur in the spectra it is immediately clear that they do not finish changing for several hours – reactions are still occurring long after the first minutes.

Using spectral mapping tools such as the waterfall displays and contour maps*, available in OMNIC Series software, allows us to look at the change in the data over time and emphasizes those regions where change is occurring. Figure 4 shows a waterfall display of the first 15 minutes of the data collection. The waterfall display is a 3-dimensional representation of the data with the x and y dimensions representing the normal wavenumber vs. intensity scale and the z-axis representing time. The origin represents the start of the experiment for the time (z) axis.

This format illuminates the rate at which spectral changes occur. It also distinguishes between the different processes that occur during the cure by graphing band changes based on time. In Figure 4, the first process begins at the start of the cure and is finished within the first 15 minutes, with bands increasing rapidly in intensity, then leveling off and remaining stable over the remainder of the experiment. This technique allows us to track events such as the release of

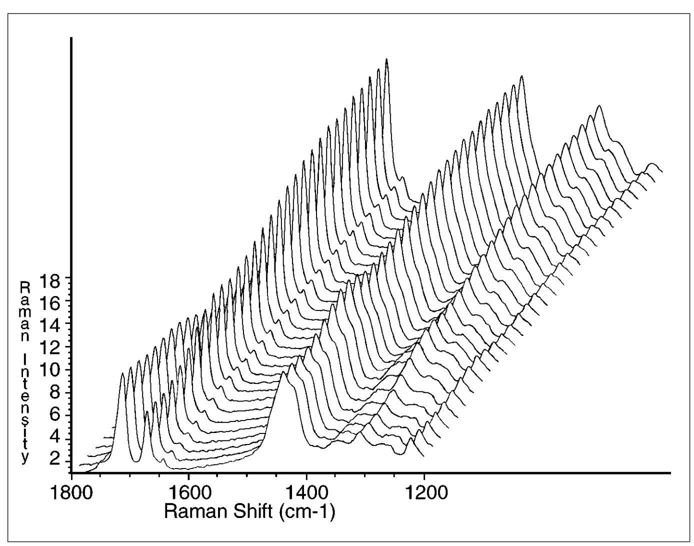

Figure 4

solvents or the onset of initiation reactions within the mixture.

The second process identified in the mixture changes at a fairly even rate throughout the experiment. This process is characterized both by bands reducing in intensity and by new bands forming. These changes may be attributed to the slower process of molecular bonds breaking in the mixture and of new bonds forming as molecular chains form 'cross-links' and the material adopts a hard rigid structure.

Some of the more notable peak changes can be seen in Figures 3a and 3b. The peaks at 788 and 763 cm^{-1} seen in Figure 3a are due to symmetric C-C-C stretching. As the adhesive dries, these bands gradually disappear, as seen in Figure 3b. The C-C skeletal stretching bands at 1088 cm^{-1} also decrease as the curing process proceeds. Another part of the cure process is the formation of C=C. The C=C stretching band can be seen in the initial adhesive spectrum (Figure 3a) but at a slightly shifted value of 1671 cm^{-1}. As the adhesive cures and C=C bonds are formed, this peak grows and shifts slightly.

Once the chemistry of a reaction process is understood, or bands are identified which change in the curing process, other spectral software tools can be used to follow the reaction rate. The intensity of a spectral band in FT-Raman is directly proportional to the concentration of the molecular bond in the sample. Therefore, if we calculate the peak height or peak area of a specific band in each FT-Raman spectrum in the series, we can make a plot of band intensity vs. time to show the reaction rate.

Figure 5a shows the peak ratio of the carbonyl band at 1710 cm^{-1} against the C-H stretching region. This plot shows that the amount of carbonyl character decreases considerably during the first 30 minutes of the reaction and then begins to stabilize. In Figure 5b, we can see the cyano peak at 2240 cm^{-1} changing with respect to the C-H stretching region. As can be seen in this plot, the intensity of the cyano band increases considerably during the process but stabilizes after around 80 minutes.

Normalizing these plots by ratioing them with a relatively constant band (in this case, a C-H stretch) removes any changes in the spectra which are due only to the change in the physical nature of the sample.

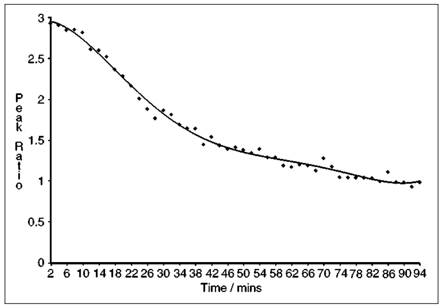

Figure 5a

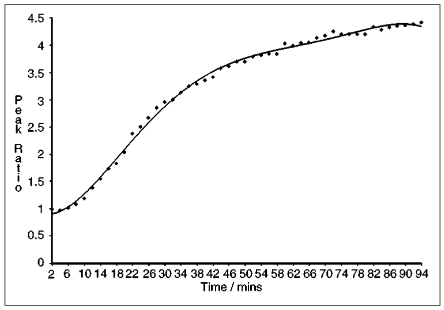

Figure 5b

Band heights and areas can be calculated within the OMNIC Macros\Basic language either as each spectrum is collected or by processing a data set separately after collection. Since OMNIC is Microsoft® Windows® compatible, it supports dynamic data exchange (DDE) of results into other Windows compatible programs. In this case, we have used Excel to produce data plots.

CONCLUSIONS

FT-Raman is an excellent tool for looking at slowly varying chemical processes such as paint or glue hardening, polymerization reactions and polymer cures. FT-Raman shows specific molecular information for these systems which is not obtainable from other laboratory techniques and provides sampling advantages that make collection both fast and simple. Optimized sampling accessories can make analysis of viscous or changing materials both easy and cost effective.

In addition, time-saving macros can be written to automate spectral collection and analysis simplifying the monitoring of the curing process. Spectral mapping tools like waterfall and contour displays offer an excellent way to display and analyze the large amount of data generated when following a real time chemical reaction. Results can then be exported using DDE to other Windows compatible programs for analysis.

REFERENCES

1. G. Ellis, M. Claybourne, S.E. Richards "The application of Fourier Transform Raman Spectroscopy to the Study of Paint Systems," *Spectrochimica Acta*, **46A**, 227 (1990)
2. C.J. deBakker, G.A. George, N.A. St John, P.M. Fredericks "The kinetics of the cure of an advanced epoxy resin by Fourier transform Raman and Near-IR spectroscopy," *Spectrochimica Acta*, **49A**, 739 (1993)
3. Nicolet product sheet, FT-Raman Sampling Geometries, P/N 169-716000

NOTES

* A contour plot is a 3-dimensional representation of data where time and wavenumber are represented as the x and y axes of a square plot. The intensity of a spectral band at different points on this square plot is represented using a 'contour line' which joins all points of the same intensity, or more commonly, using different colors to represent different intensities. This is analogous to a topographical map which represents height using a contour line or color.

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