



Infrared Spectroscopy

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Time-Resolved FTIR studies of Adhesives and Paints

Introduction

Paints and adhesives, although dissimilar materials with different purposes, have a commonality that they are typically liquid phase starting materials that end up as solid materials after a drying or curing period.

Adhesives can permanently join surfaces together either by mechanical or chemical bonding. Mechanical bonding is the simpler and more common form of adhesion. The bond formed between the adhesive and the surface occurs when the adhesive works its way into the small pores of the surface as a liquid and then begins to dry. Chemical bonding is more complex and occurs by forming a compound between the chemicals of the two surfaces.¹

There are many different types of paints, but the main types are either solvent-based or water-based with an appropriate polymer system and functional additives present. The loss of water or solvent over time allows the material to dry into a stable state to perform the intended use.

Attenuated Total Reflectance (ATR) FTIR sampling methods are used extensively within the coatings and adhesives industries for the characterisation of raw materials and product formulations. These are mainly instant measurements of a sample after a drop of the material is placed onto the ATR crystal. This application note describes how these ATR measurements can be extended to monitor the changes taking place over time as the material dries or cures.

Experimental

The PerkinElmer Spectrum Two™ was equipped with a UATR (Universal Attenuated Total Reflectance) accessory (Figure 1). Diamond or disposable silicon ATR crystal elements were used for the time-resolved studies as will be described later.



Figure 1: The Spectrum Two FTIR Spectrometer with UATR Accessory.

Spectra are recorded by simply placing a drop of the sample onto the ATR crystal. As the sample is liquid, perfect contact with the crystal will be achieved without applying the pressure arm. A typical spectral measurement is performed over the spectral range 4000-450 cm^{-1} at a spectral resolution of 8 cm^{-1} , taking approximately 10-15 seconds. ATR spectra of 2 paint types, acrylic and enamel, are shown in Figure 2.

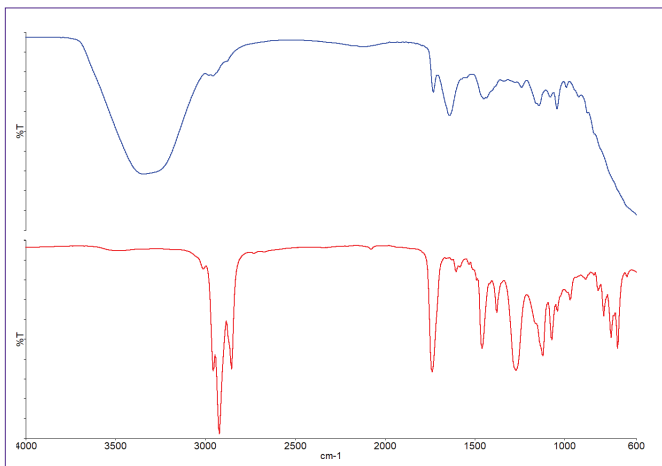


Figure 2: ATR spectra of acrylic (top) and enamel (bottom) paints.

It is clear from these spectra that the acrylic paint is water-based due to the presence of a broad -OH band around 3400 cm^{-1} , but the enamel paint is solvent-based. These spectra could be used as QC check spectra for a specific product formulation.

Time-Resolved Paint Studies

The Spectrum Timebase software allows multiple spectra to be run over a certain period of time. In these experiments spectra were collected every 10 seconds over a period of hours. A comparison of spectra recorded at the start and end of the experiments will show the spectral and chemical changes that have occurred.

Figure 3 below shows two spectra of a water-based paint at the start of the time base run time (red) and at the end (black). At the start of the experiment the materials within the formulation are solvated in the water and the water gives the most intense bands. As the water evaporates over time it is clear to see that the broad -OH band at 3400 cm^{-1} becomes less intense as the concentration of the other materials present increases. At the end of the experiment the water bands have virtually disappeared.

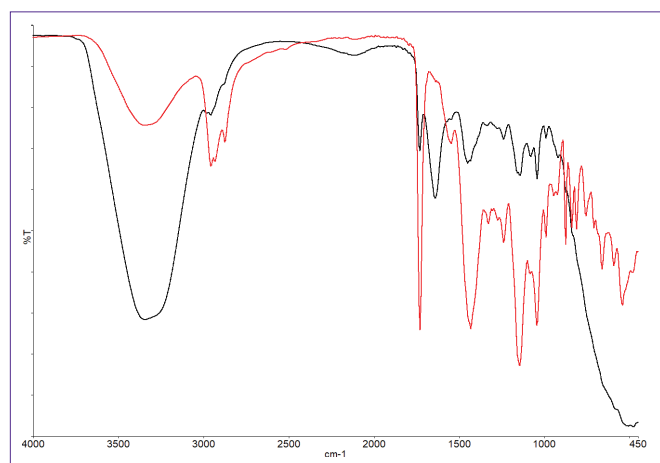


Figure 3: Spectra of water-based paint at start (black) and end (red) of run.

During the run the software will generate a Gram-Schmidt profile that gives an overall indication of the changes in the total spectral absorbance. Additional profiles can be generated to monitor specific spectral bands of interest. These profiles indicate when there are no longer any spectral changes occurring, examples shown in Figure 4 for the water and carbonyl peaks.

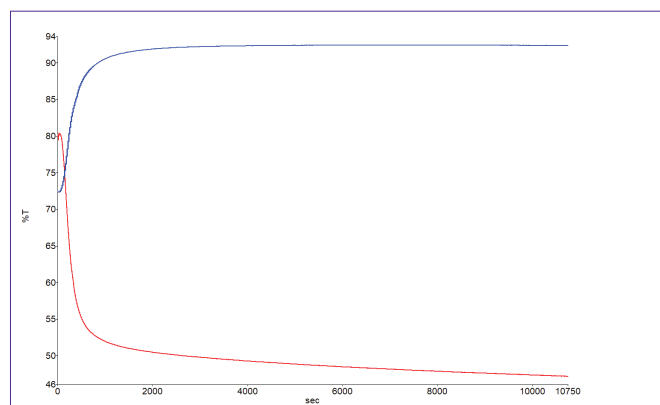


Figure 4: Band profiles for water 1640 cm^{-1} (blue) and carbonyl 1730 cm^{-1} (red).

The profiles show a rapid initial loss of water that slows down and has only minor losses after 6000 seconds.

A similar experiment was performed on a solvent-based paint. The spectra obtained from the start and the end of the experiment are shown in Figure 5 with the major differences being in the hydrocarbon peak at just below 3000 cm^{-1} and the carbonyl peak at around 1730 cm^{-1} .

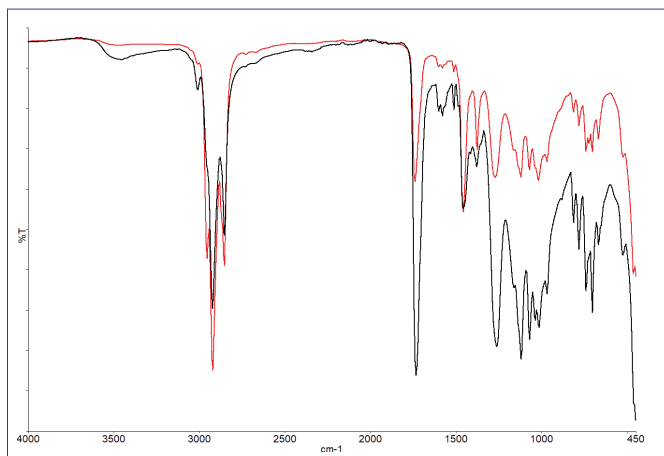


Figure 5: Spectra of Solvent based paint at start (red) and end of run (black).

Profiles for the hydrocarbon (2955 cm^{-1}) and carbonyl (1734 cm^{-1}) are shown in Figure 6. The hydrocarbon peak decreases as the solvent evaporates and the carbonyl peak increases as more of the bulk materials come into contact with the ATR crystal. These plots are consistent with a hydrocarbon solvent being used in the formulation.

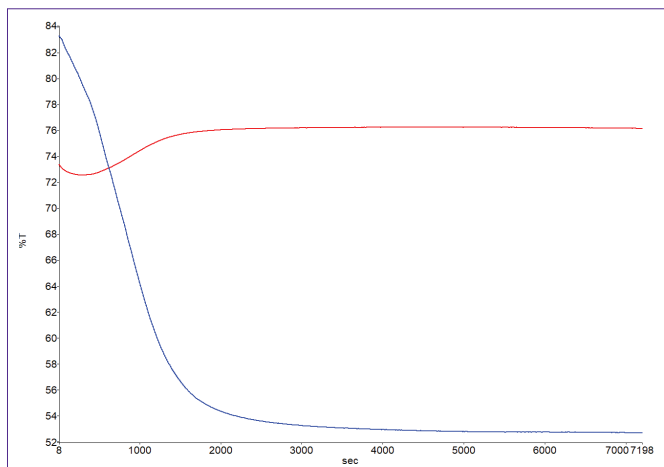


Figure 6: Band profiles for hydrocarbon 2955 cm^{-1} (red) and carbonyl 1734 cm^{-1} (blue).

The loss of solvent appears to be almost complete after about 5000 seconds.

Time-Resolved adhesives studies

Many types of adhesives cure very quickly when in the presence of atmospheric moisture to form a very strong bond. The chemical changes can be monitored using ATR accessories. However, the purpose of the adhesive is to stick to surfaces and performing these experiments on a “multi-use” ATR crystal element can require aggressive cleaning processes that can damage the crystal or the ATR top plate. Using disposable silicon ATR crystals is a new approach that is much more suitable for these experiments and are low cost. The Specac Arrow Silicon ATR consumable slides are shown in Figure 7 and can be used on the Spectrum Two UATR accessory for these types of experiments. At the end of the experiment when the adhesive has cured then the ATR crystal slide can be removed and replaced with another one. The slide can either be disposed of or retained if further measurements are required.



Figure 7: The Specac Arrow™ Silicon ATR crystal mounted in a Spectrum Two UATR.

In each experiment one droplet of adhesive was placed onto the Specac Arrow Silicon ATR crystal and spectra collected using the Spectrum Timebase software at 8 cm^{-1} resolution over a period of several hours. Spectra recorded at the start and end of the experiment and during the experiment are shown in Figures 8a and 8b. The initial spectrum identifies the adhesive as being water-based.

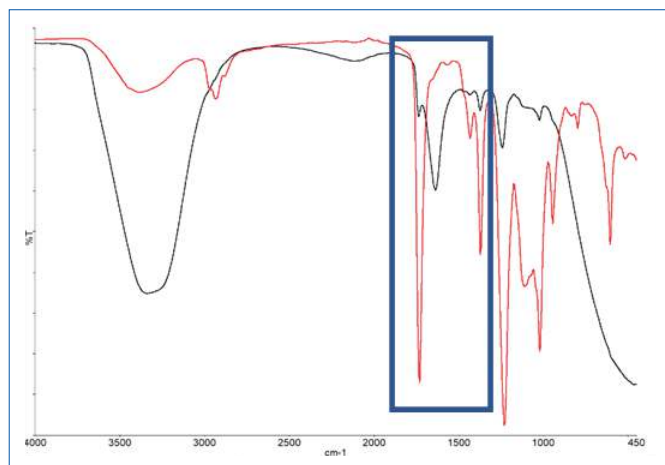


Figure 8A: Spectra of adhesive at the start of the experiment (black) and end of the experiment (red).

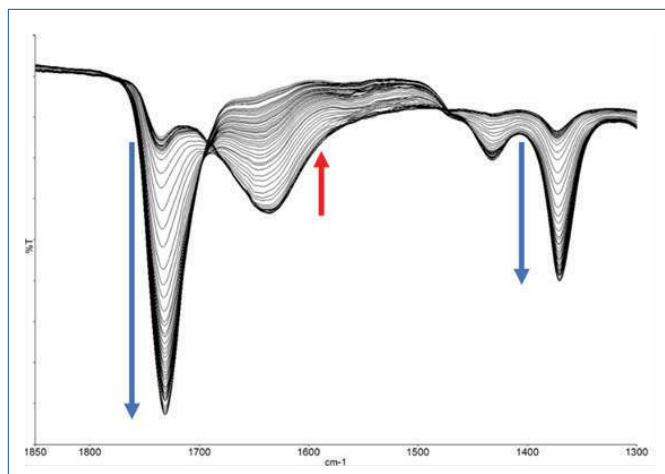


Figure 8b: Expanded region showing increase and decrease of spectral bands during the experiment.

The broad OH peak at just below 3500 cm^{-1} decreases significantly which identifies that the water has evaporated, and the material has solidified. The intensity plots of the water band and the polymer system are shown in Figure 9.

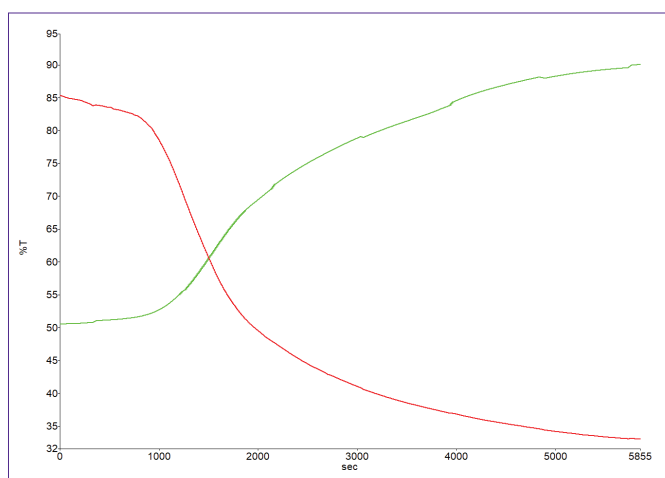


Figure 9: Band profiles for -OH 3400 cm^{-1} (green) and carbonyl 1734 cm^{-1} (red)

It is clear from this data that even after 100 minutes the adhesive is not yet fully cured despite the material feeling quite solid.

Conclusion

Monitoring how paints and adhesives dry/cure by FTIR takes very little sample preparation and is fast and simple. The disposable ATR crystals allow a low-cost analysis of the strongest adhesives which would be extremely difficult to remove and could result in damage to the ATR. These experiments could easily be extended to see how the rates of curing of the paints and adhesives are affected by different environmental conditions, such as temperature and humidity.

References

1. Permabond, <https://www.permabond.com/resource-center/in-english-doc-how-do-adhesives-work/>, (accessed June 22, 2022).