APPLICATION NOTE

FT-IR Spectroscopy

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Time Resolved FT-IR Analysis of Cyanoacrylate Curing

Introduction

Resins are used universally in the manufacture of a vast range of goods including electronics, disposable medical devices and even aerospace components. Most resins rely on the polymerization of monomeric components to form a solid layer which has high mechanical strength, and which strongly binds two surfaces in order to 'glue' them together. The polymerization reaction responsible for curing resins varies depending on the monomers used. This means that the curing process can differ significantly between formulations of resins in terms of time, strength, compatible materials and initiation conditions.

One of the most commonly used types of resin valued for their rapid curing and strength of bond are cyanoacrylates, otherwise known as 'superglues'. The monomeric components in this case are various esters of cyanoacrylic acid, most notably 2-methyl cyanoacrylate, 2-ethyl cyanoacrylate and 2-octylcyanoacrylate. Polymerization is catalyzed by basic surfaces of materials and moisture. This glue is rapidly cured when applied to materials such as wood but application on surfaces without moisture or surface hydroxyl bonds can take several hours. In these cases, the initiation of polymerization depends on atmospheric moisture and may require activating compounds for more efficient cure times.

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The basic mechanism for curing 2-ethyl cyanoacrylate is shown in Figure 1. Knowing the mechanism of the expected reaction can help with the interpretation of spectra.

Due to the wide range of resin formulations with different uses and physical properties, it's important to monitor and understand the mechanisms responsible for curing as well as their rates in order to optimize their efficient usage. This can be achieved using FT-IR which measures the change in spectral information as the resin cures. The PerkinElmer Spectrum 3™ FT-IR spectrometer (Figure 2) with a Universal Attenuated Total Reflectance (UATR) accessory may be used for this application. The data can be collected and analyzed with Spectrum™ Timebase software. Timebase allows you to view the profile of a changing reaction over long periods of time with respect to the absorbance. The three-dimensional data (absorbance, wavenumber and time) can be converted into a 2-dimensional profile which gives an overview of the changes over the entire reaction. The Spectrum 3 is capable of fast scanning with scan speeds suitable for analyzing rapid reactions.

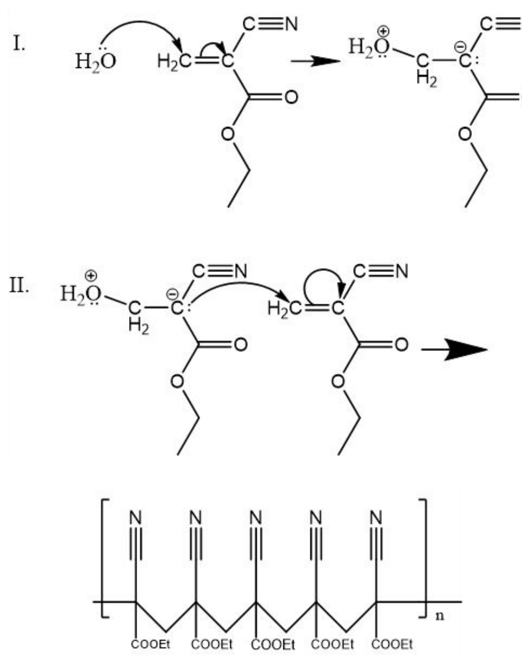

Figure 1. Mechanism of cyanoacrylate polymerization.

Figure 2. Spectrum 3 with UATR accessory.

Experimental

In each experiment samples were applied to a diamond ATR accessory and cured as a result of exposure to atmospheric moisture except for the rapid-scanning experiment. Data was recorded in Spectrum Timebase using consistent instrument settings across the experiments according to Table 1.

Formulation

Different formulations of cyanoacrylate adhesives were compared at room temperature for 16 hours each. One droplet was dispensed directly from the bottle onto a PerkinElmer diamond UATR. As soon as the droplet touched the ATR crystal the run was started. After 16 hours, the Gram-Schmidt profile of all samples indicated no further change in the spectral features of the resin, thus showing the reaction had finished.

The profiles of room temperature cures shown in Figure 3 can be visually compared with one another to distinguish which formulations have the fastest cure completion and rates of cure. The diamond ATR has no notable basic surface chemistry that would initiate this polymerization, so relies upon atmospheric moisture.

Table 1. Parameters for formulation comparison experiment.

Resolution (cm^{-1})	8
Range (cm^{-1})	4000-600
Scan Speed (cms^{-1})	1.0

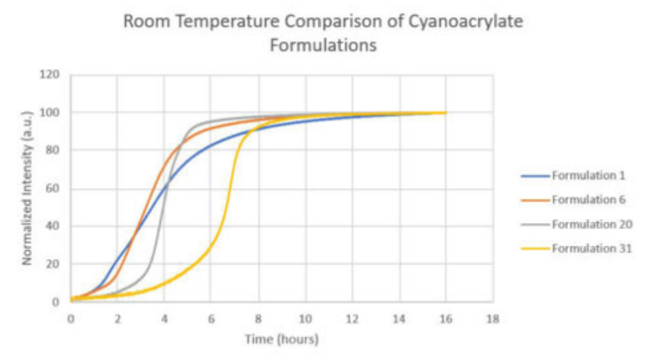

Figure 3. GS profiles of room temperature cures of different cyanoacrylate formulations.

Temperature

One of the formulations was used to compare curing rates versus temperature. One droplet of Formulation 1 was applied to a Specac heated Golden Gate ATR accessory which had equilibrated to the desired temperature, the run was started as soon as the sample was applied. A range of experiments were performed using 60, 80, 100 and 120 °C as the sample temperature.

Visual assessment of the curing profiles in Figure 4 immediately reveals the relationship between operating temperature and cure. This may be useful to those looking to optimize cure rates in different heated environments.

Application Size

Formulation 1 was also used to compare the change in the nature of the cure when different film thicknesses are applied to a substrate. The application sizes compared were as follows: a very small droplet from a dispense needle scraped with a spatula to give a thin layer, the same sized droplet as the other experiments and one very large application consisting of multiple droplets. All samples were applied to the heated ATR plate at 80 °C.

The differences in the cure rates and completion times shown in Figure 5 are affected by the rate at which atmospheric moisture can propagate through the sample until the reaction begins at the interface of the sample and ATR crystal. Therefore, this is a suitable method for determining the optimum thickness of layers or mass of resin used for an application.

Using Activators for Faster Curing

Formulation 1 was cured at room temperature on the UATR using a cyanoacrylate activator spray. Upon applying the activator, the sample cured within seconds as opposed to several hours when activators are not used. The reaction was monitored using a fast scan speed of 16 cms^{-1}.

Figure 6 shows the curing time using the activator to be extremely rapid, completing within little more than 1 second. Faster scanning speeds greatly improve the number of data points in this fast transition, providing a much more detailed analysis.

Spectral Changes

The spectral changes that occur within the samples over the course of the cure were the same across all the cyanoacrylate formulations. The easiest way to visualize the change in spectral features is to contrast the spectra taken over time with the first spectrum and last spectrum in the run as shown in Figure 7. Subtracting the initial spectrum of the uncured formulation from all subsequent spectra allows for easy visualization of the changing spectral features during the curing. Using this method, Figure 8 shows the increase and decrease of bands across time for the reaction of Formulation 1 at 80 °C.

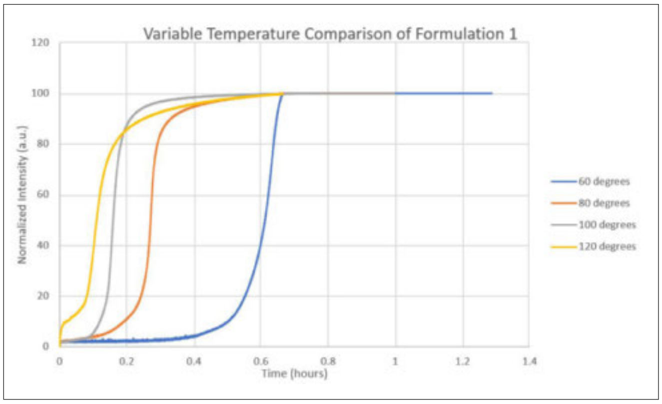

Figure 4. GS profiles of Formulation 1 curing at varying temperatures.

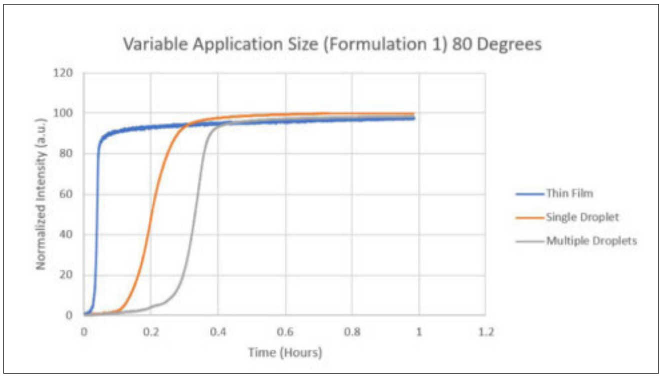

Figure 5. GS profiles of variable application sizes of Formulation 1.

Fast Scanning

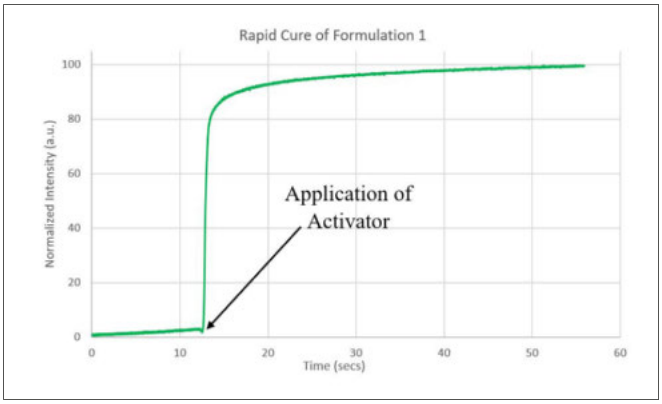

Figure 6. Profile of Formulation 1 cured with activator using fast scanning.

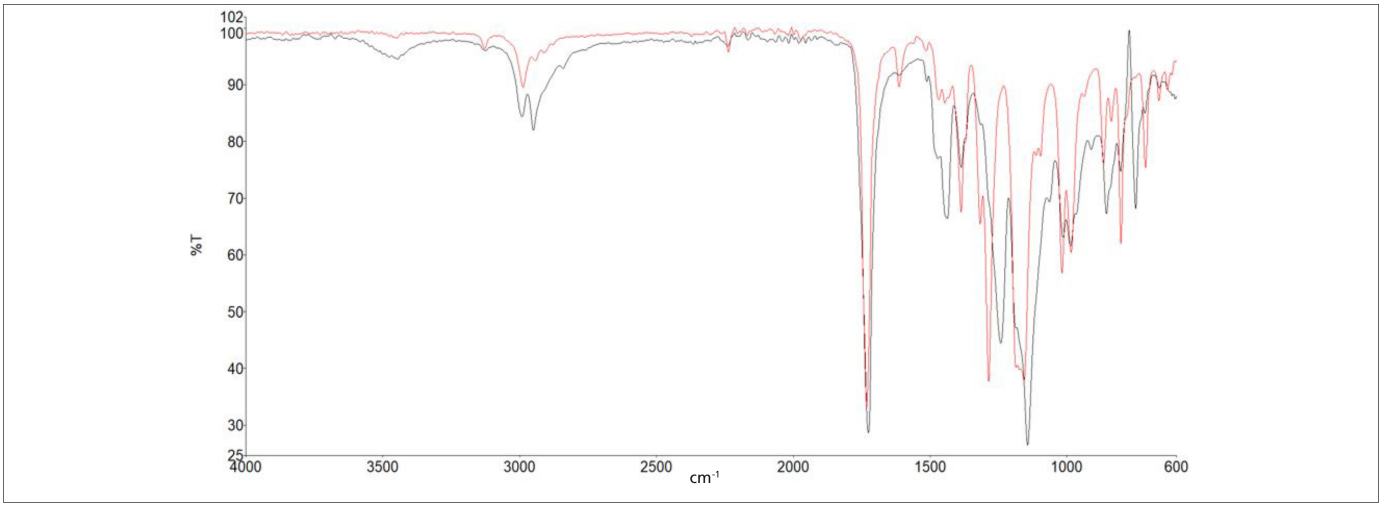

Figure 7. Contrasting spectra of Formulation 1 before (black) and after curing (red).

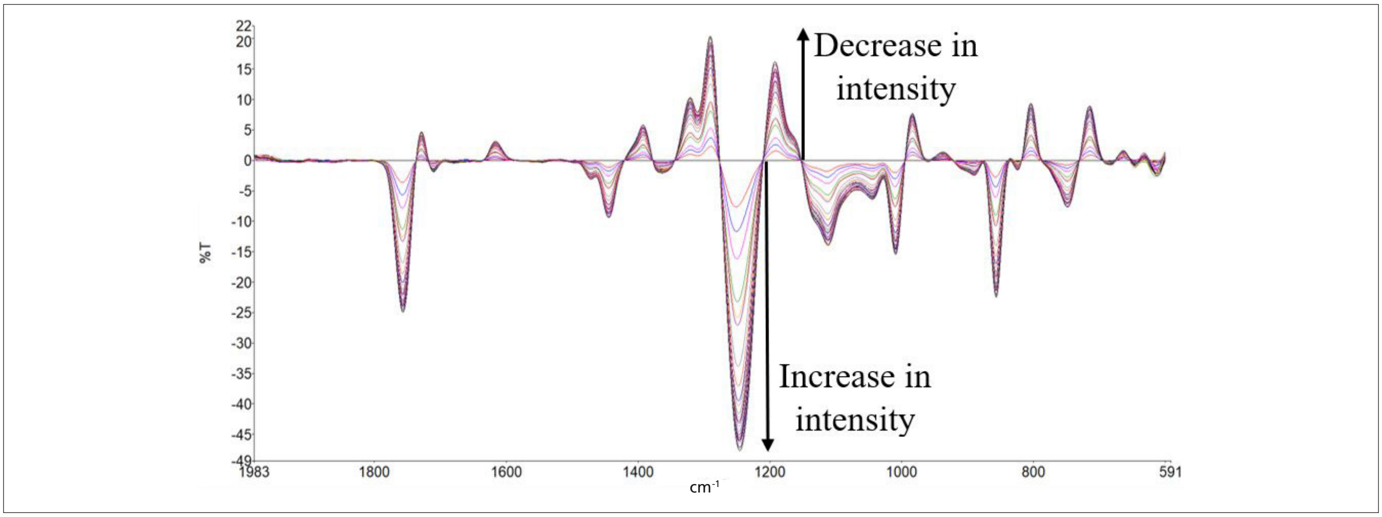

Figure 8. Selected spectra taken during the cure processed to highlight changes in spectral bands.

Conclusion

It is often necessary for manufacturers to compare many aspects of resin curing. It has been demonstrated that an FT-IR method for this allows for many dimensions of analysis. The PerkinElmer Spectrum 3 FT-IR spectrometer with UATR accessory and Spectrum Timebase software provides the tools for data collection and analysis so that variables may be compared and for spectral analysis by contrast of the spectra of cured and uncured samples. Fast scanning methods displayed here are useful for the analysis of rapidly-proceeding reactions and kinetics.

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