

Polymerization cure rates using FT-NIR spectroscopy

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Figure 1. Antaris II MDS FT-NIR analyzer with integrating sphere (1a). The prepared samples were placed on top of the window over the integrating sphere, similar to what is shown in 1b, for the duration of the experiments.



Introduction

Rate of reaction is an important parameter in chemical processes. The speed of reactions and the extent of completion often govern the viability of certain processes and determine the suitability of these reactions for commercial purposes.

One area of particular interest lies with polymerization processes. Polymerization is the general term for processes that bind single chemical units into long chains. These long chains can also cross-link to form large networks of interlocking three-dimensional structures. Plastics, epoxy-type resins and various glues and adhesives are examples of materials that are formed through polymerization processes. Fourier transform near-infrared (FT-NIR) spectroscopy can be used to study reaction rates and is used here specifically to monitor polymerization of three types of commercially available adhesives.

Often polymers require two components: a monomer with a reactive center and a curing agent. The reactive center on the monomer may be an epoxy, alkene or alkyne, acrylate, carbonyl or other functional group. The curing agent initiates or catalyzes the polymerization process through cationic or anionic addition or some other free-radical mechanism. Three polymer adhesives were the subject of this study: 1) an epoxy resin, where the epoxy functional group on the monomer is bound to amines in the curing agent; 2) a methyl acrylate adhesive, where addition to the alkene functional group is catalyzed by a free radical initiator; and 3) a cyanoacrylate adhesive, containing a similar alkene functional group, but is instead catalyzed by the presence of water vapor in air.

Near-infrared spectroscopy takes advantage of the vibrational overtones and combination bands present in nearly all complex molecules. Light from an FT-NIR analyzer impinges on the sample, causing molecular vibrations at characteristic frequencies. The light is then collected by the analyzer and is displayed as spectra. Specific substances result in unique spectra that can be used for identification or quantification. For the current study, spectra of three polymer precursors were taken at various intervals during polymerization. Peak heights at specific frequencies were measured during the experiments as a demonstration of the analyzer's ability to monitor polymer cure rates.

Experimental

Sample 1: A two-component epoxy resin (Spolchemie, Czech Republic) was obtained and mixed according to the manufacturer's recommended protocol. Samples of the activated mix were collected and prepared for analysis with a Thermo Scientific™ Antaris II™ MDS FT-NIR (Figure 1). Spectra were collected for approximately 55 hours, during which the epoxy moieties were chemically altered by nucleophilic attack from the amines in the curing agent.

Sample 2: A two-component acrylate base adhesive (UHU GmbH & Co, Bühl, Germany) was obtained from the manufacturer and mixed according to the recommended protocol. The transparent viscous acrylate copolymer contained a mixture of polymethylmethacrylate and methylmethacrylate monomers and was activated by free radicals generated from dibenzoylperoxide in the powdered curing agent. Samples of this acrylate-based adhesive were prepared for FT-NIR analysis as in sample 1. Spectra were collected for approximately 20 hours, during which the alkene functionalities disappeared through an additional mechanism.

Sample 3: A rapid-setting cyanoacrylate-based adhesive (Alteco, Osaka, Japan) undergoes anionic polymerization promoted by the presence of water vapor in air. As in sample 2, the carbon-carbon double bonds of the alkenes disappear as polymerization progresses. Samples of this material were analyzed with the Antaris FT-NIR without any preparation. While the reaction time is rapid, complete polymerization requires several hours, so the samples were analyzed for approximately 20 hours.

Data acquisition: The samples above were placed on a 0.5mm thick polyethylene film covering the integrating sphere. The signal contribution of the polyethylene film was ignored in the data analysis obtained from the samples. The samples were covered with aluminum foil to allow for beam reflection. Spectra were collected between 4000 and 10000 cm^{-1} ; scan resolution was set to 4 cm^{-1} and Norton-Beer apodization was used. The internal gold flag of the integrating sphere was used as the background. Simple baseline-corrected peak heights were measured at appropriate frequencies and monitored throughout the reactions.

Results and discussion

Sample 1: Figure 2a shows an overlay of spectra collected during the polymerization of the epoxy based resin in the region between 4488 – 4588 cm^{-1} . The absorption band at 4528 cm^{-1} associated with the epoxide group is shown to decrease in intensity throughout the data collection. The baseline-corrected peak height of the 4528 cm^{-1} band was plotted as a function of time (Figure 2b). The plot demonstrates that the peak height rapidly decreases in the first 1000 minutes (approximately 17 hours) essentially reaching its limit in approximately 2000 minutes (33 hours). This indicates that the reaction and curing process is complete in this time.

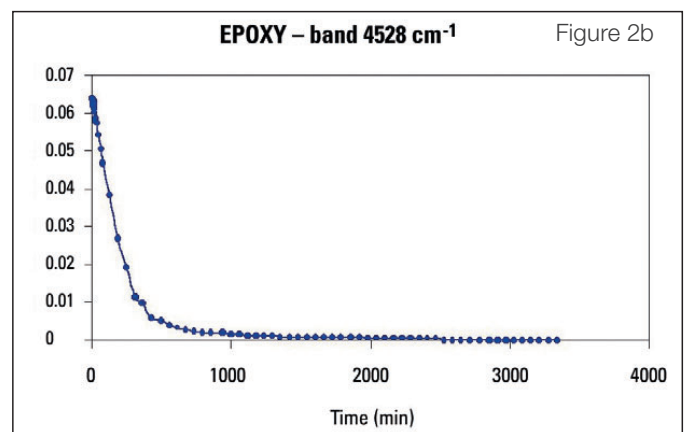
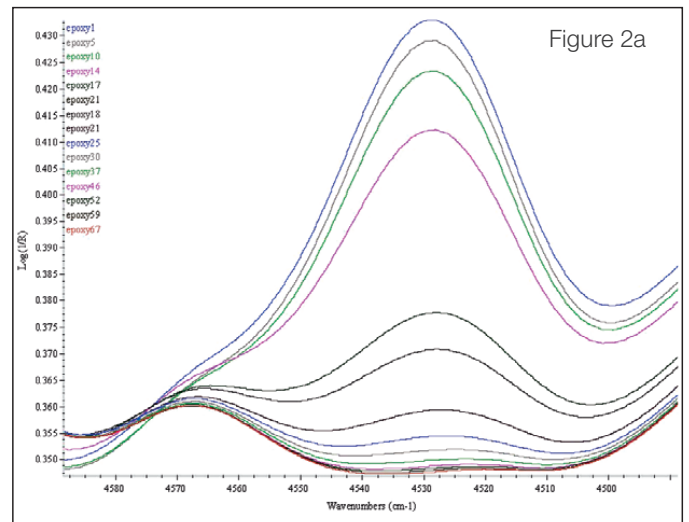


Figure 2. Overlay of spectrum showing decrease in absorption band at 4528 cm^{-1} over time (2a). Plot of the baseline-corrected peak height as a function of time (2b). The peak clearly diminishes over time as the epoxide group disappears during the polymerization process.

Sample 2: Figure 3a shows the overlaid spectra between 6103 and 6234 cm^{-1} . Here the band at 6167 cm^{-1} decreases as the polymerization progresses. This band is associated with the first overtone C-H stretch of an alkene. The baseline-corrected peak height of this band was also plotted as a function of time (Figure 3b). This plot shows a rapid decrease in peak height for the first 50 minutes, followed by a gradual decrease out to approximately 1200 minutes (20 hours). It should also be noted that the shape of the plot indicates there may be two or more chemical mechanisms accounting for the decrease in peak height.

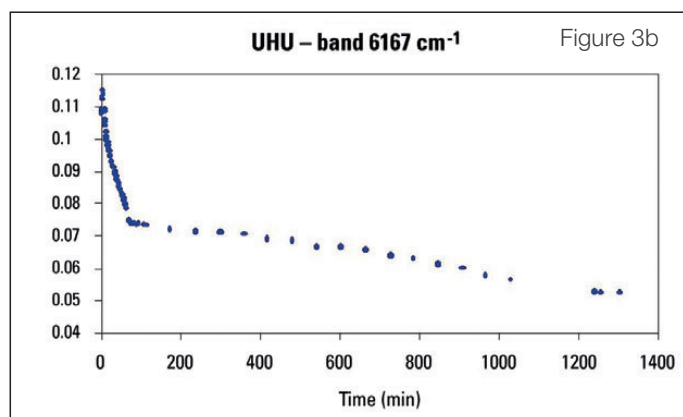
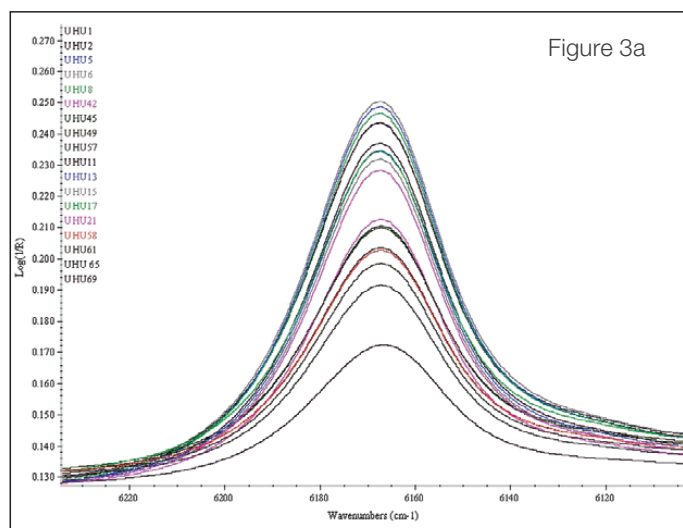


Figure 3. Overlay of spectrum in the range between 6103 and 6234 cm^{-1} for acrylate-based adhesive showing a decrease in peak height over time (3a). Plot of the baseline-corrected peak height as a function of time (3b) indicates the loss of alkene groups is initially rapid, followed by a slower gradual decrease.

Sample 3: Figure 4a shows the overlaid spectra of one absorption band in the range between 4450 and 4590 cm^{-1} . As expected, the peak at 4495 cm^{-1} diminishes as the polymerization progresses. Similar results were seen with bands at 4742 and 6208 cm^{-1} . The peak heights at 4495 cm^{-1} were plotted over time (Figure 4b). The plot indicates that the polymerization rapidly occurred in the first few minutes and was essentially complete by 800 minutes (approximately 13 hours). This is expected behavior for this type of rapid-setting adhesive.

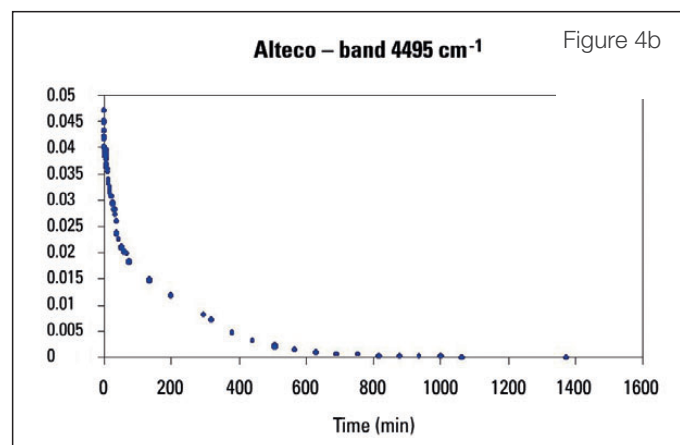
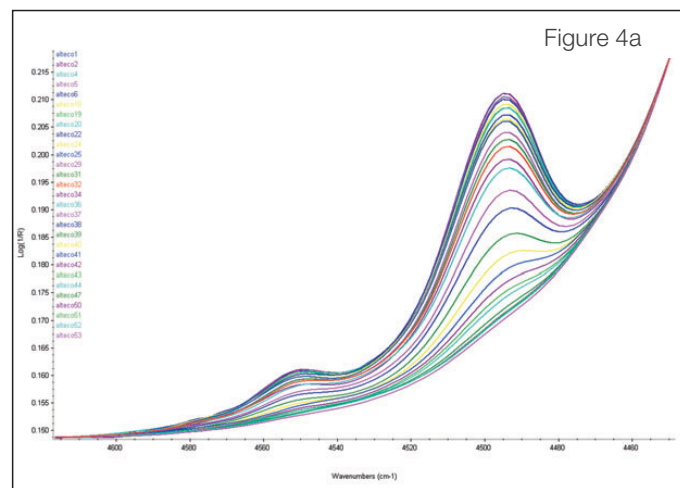


Figure 4. Overlay of spectrum in the range between 4450 and 4590 cm^{-1} for rapid polymerizing cyanoacrylate adhesive (4a). Plot of the peak at 4495 cm^{-1} as a function of time (4b) graphically demonstrates the rapid decrease in peak height associated with the rapid polymerization of this material.

Conclusion

The Antaris II FT-NIR analyzer was successfully used to monitor and track the chemical reaction rates of three polymerization reactions. An epoxy type polymer was shown to gradually cure with the loss of essentially all of the reactive groups by 2000 minutes. Polymerization of an acrylate-based adhesive was also monitored with the Antaris analyzer, with the reaction essentially complete within 1200 minutes. Finally, functional groups of a rapid-setting cyanoacrylate adhesive were shown to decrease as polymerization progressed, with the reaction essentially complete within 800 minutes. These examples clearly demonstrate the value of using the Antaris II FT-NIR analyzer to monitor reaction rates and observe reaction completion..

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