

REAL TIME MONITORING OF ISOCYANATE CHEMISTRY USING A FIBER-OPTIC FTIR PROBE

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Introduction

The use of fiber-optic probes for spectroscopic reaction and process monitoring is emerging as a valuable tool in both academic and industrial laboratories^{1,2,3,4}. By combining the flexibility offered by fiber optics with the power of modern spectroscopic software, it is possible to develop real-time or near-real-time applications which actually enable the researcher to follow the details of a chemical reaction, and to determine reaction progress and end points directly. Detailed mechanistic studies of reactions are possible (Geiger), as well as process-related studies (Johnson).

Fiber-optic spectroscopic monitoring lends itself to in-situ studies of chemical reactions in solution and also during processes such as polymerization. Mid-IR spectroscopy in particular, because of its generally well resolved and well separated spectral features, can be used to develop robust reaction-monitoring strategies which are applicable under varying reaction conditions. This paper describes the use of fiber-optic mid-IR spectroscopy to follow the course of isocyanate reactions in solution and during a urethane polymerization reaction. In both reactions, the disappearance of the isocyanate group, $N=C=O$, provides a convenient spectroscopic marker which can be readily observed in the mid-IR where the asymmetrical $N=C=O$ stretch appears between 2250 and 2285 cm^{-1} , usually as a sharp peak and isolated from other spectral features. This offers the advantage that simple, robust peak-fitting and peak area calculations can be used to derive graphs of (remaining) isocyanate content versus time from a series of sequential mid-IR spectra – a procedure that is readily automated using modern spectroscopic software.

Experimental

Mid-IR spectra were obtained using a Remspec fiber-optic probe fitted with a zinc selenide ATR crystal. The probe was attached to a Bruker Vector 22 mid-IR spectrometer controlled by a desktop computer running OPUS software. The spectra were exported to GRAMS/32 software for interpretation using the GRAMS/32 peak-fitting routines and an additional program, Rempeak, which conveniently outputs a list of peak areas versus time in a format readable by most spreadsheet programs.

Solution Reaction of Isocyanate. A solution of a proprietary isocyanate compound (1 wt.% in ethyl acetate) was provided by an industrial partner. The mid-IR spectrum was recorded at a resolution of 4 cm^{-1} for a scan time of 30 s, then the solution (25 ml) was treated with an excess amount of tri-*n*-butylamine (5 ml, 99% pure from Alfa Aesar) and spectra were recorded every 60 s for a total of 80 minutes. The reaction was carried out at room temperature.

Curing of Synthetic Rocket Fuel with Urethane Binder. A simulated rocket fuel, comprising a urethane-based binder of undisclosed composition, was provided in uncured form by an industrial partner. The sample was held at a temperature of 55° C for approx. 27 hrs and mid-IR spectra were collected every two minutes by placing a Remspec fiber-optic probe with a zinc selenide ATR head in contact with the curing mass. During the experiment, two interruptions occurred: the first when cooling of the MCT detector failed for a short time, and the second when a software problem (since corrected) led to non-storage of collected data.

Results and Discussion

Figure 1 shows the mid-IR spectrum between 2200 and 2400 cm^{-1} for the solution reaction mixture as it evolves over approx. 20 mins. The tributylamine was added between the end of data collection for the first spectrum and the beginning of data collection for the second. The peak at 2340 cm^{-1} is the characteristic $C=N=O$ asymmetric stretch, and changes in the

intensity of this peak are clearly evident to the eye during the first ten minutes of the reaction. There are other, more subtle changes in the spectrum, but interpretation of these features was not attempted.

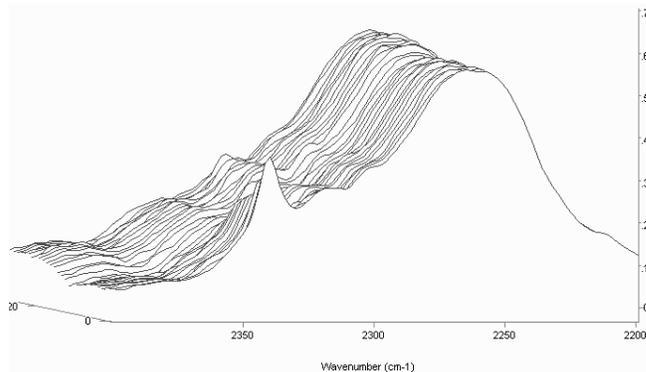


Figure 1. Mid-IR spectrum of isocyanate reaction mixture from 2200 to 2400 cm^{-1} plotted against time.

When the area of the peak at 2340 cm^{-1} is calculated for each spectrum, using Rempeak and the peak-fitting routines in GRAMS/32, the resulting plot (Figure 2) clearly indicates the loss of isocyanate as the reaction progresses.

After approximately 15 minutes, the isocyanate peak has virtually disappeared, indicating that the reaction is essentially complete. Without additional knowledge of the chemistry, it is not useful to speculate about the interpretation of other features in the spectrum. However, it is clear that the overall progress of the isocyanate reaction can be monitored in the mid-IR and that the resulting data can be interpreted using methods that lend themselves to automation.

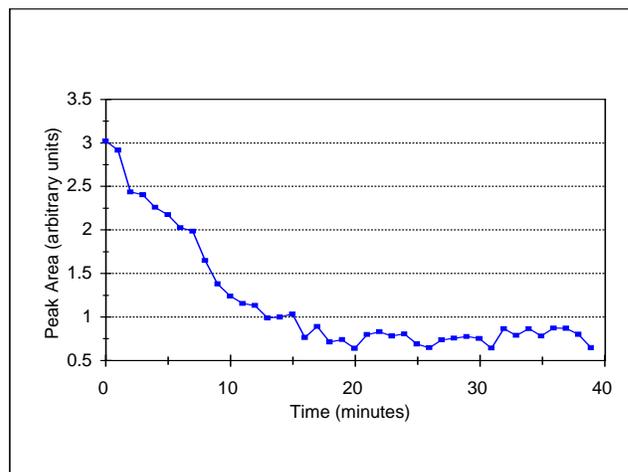


Figure 2. Peak area versus time for the isocyanate peak at 2340 cm^{-1}

In the case of the curing of simulated rocket fuel with urethane binder, the reaction extended over a much longer time scale and required heating. In practice, this type of cure can take over a week. The lab. reaction was run for 800 hours, and the isocyanate peak at 2250 cm^{-1} was monitored by collecting the mid-IR spectrum every two minutes. After the data collection was complete, the peak area at 2250 cm^{-1} was calculated for each spectrum and a graph was drawn of peak area versus reaction time. Selected spectra and the final graph are shown in Figures 3 and 4, respectively.

Again, it is clear that the disappearance of the isocyanate peak provides a valuable spectroscopic marker for the progress of the reaction.

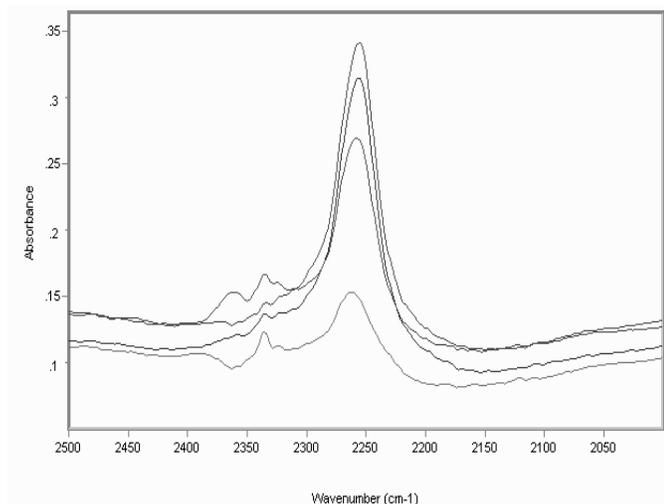


Figure 3. Mid-IR spectrum of simulated rocket fuel, from 200-2500 cm^{-1} showing isocyanate peak at 2250 cm^{-1} at time=0 (large peak), 50, 150, 950 minutes (small peak) from start of cure

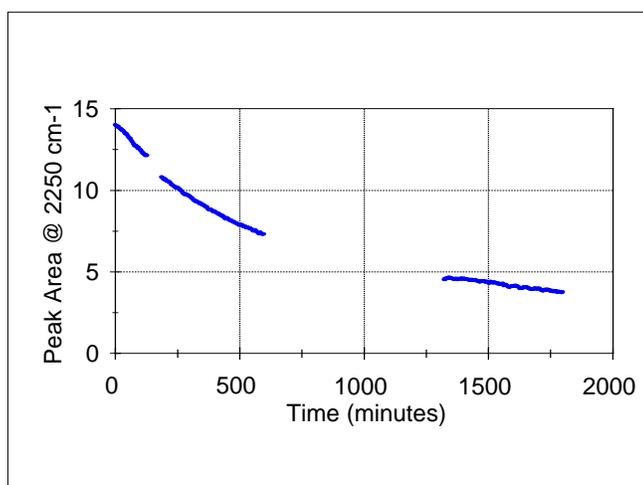


Figure 4. Peak area at 2250 cm^{-1} versus time from start of cure for urethane polymer mixed with simulated solid propellant

Conclusions

We have demonstrated the utility of mid-IR spectroscopy as a tool for monitoring the reactions of isocyanates, both in solutions and in polymerization reactions as a semi-solid mass cures. The distinctive asymmetrical $\text{N}=\text{C}=\text{O}$ stretch is a particularly convenient spectroscopic marker in these reactions, and can be used to determine the extent of reaction even when the detailed chemistry of the system is not understood. The fiberoptic ATR probe, combined with the capabilities of modern spectroscopy software, make it possible to use mid-IR spectroscopy as means of real-time, in-situ reaction monitoring.

References)

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