AP-103

QUANTITATIVE ANALYSIS OF EPOXY MIXING RATIOS USING PARTIAL LEAST-SQUARES ANALYSYS OF FTIR SPECTRA

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Published in International Labmate January 1991 Vol.16 XVI Issue 1

Abstract

ATR-FTIR (Attenuated Total Reflectance Fourier Transform Infrared) spectra of prehardened epoxies with varying amounts of hardener and resin (mix ratio) have been acquired on a Midac FTIR spectrometer. The spectra form a set of training spectra for partial least-squares (PLS) analysis which was then used to analyze a series of epoxies of unknown mix ratio. The PLS model predicted the unknown mix ratios for seven samples to an average of 0.1 part of hardener out of 11 parts (<1%).

Introduction

Mid range infrared spectra are rich with molecular structure information consisting mainly of rotational, vibrational, and bending motions for the constituent atoms. The numerous molecular motions of most polyatomic molecules afford a unique set of multiple and overlapping absorption bands in the fingerprint region of the infrared spectrum below 1600 wavenumbers, making infrared spectroscopy an important tool for positive identification of pure compounds. While the complexity of infrared spectra has served as an important qualitative tool it has, with a few exceptions, made quantitative analysis more difficult. Application of Beer's Law to complex absorption bands of unknown origin is unsettling at best. However, with the commercial production of the FTIR instruments over the pas decade and their attendant data acquisition systems, the quantitative analysis computation is being pushed aside.

The FTIR instrument compared with a traditional dispersive infrared spectrometer is faster (a spectrum is acquired in seconds rather than minutes), has greater sensitivity (which is increased by increasing the number of scans), and produces digitized data (most dispersive instruments do not). Unique advantages of the Midac is its small size, ruggedness, and high resolution capabilities. It rarely needs alignment, can easily be picked up and moved from place to place, and requires little bench space. The high speed and data system features of the FTIR instruments have led to the development and application of new statistical methods to FTIR spectra for quantitative analysis. Partial least-squares (PLS) analysis is one of the more significant developments.[1]

Partial least-squares analysis is one of several statistical techniques called factor methods. In factor analysis, the spectrum is reduced to a series of "subspectra" each with a corresponding weighing factor of loading. Factor analysis of FTIR spectra has been used for the characterization of materials such as coal, bauxite, manganese dioxide, and diesel fuel[2]. Through factor analysis, physical and chemical properties which manifest themselves in the infrared spectrum of a material may be calculated from the spectrum, such as the Cetane index and API gravity of diesel fuel.

Haaland and Thomas[3] give a lucid discussion of the PLS process as it applies to FTIR quantitative analysis, and Beebe and Kowalski[4] provide a graphical view. When properly performed the analysis rejects noise from the model, centers and weighs data appropriately, and fits all spectral information including both concentration and absorbance data. PLS has been applied recently to the FTIR quantitative analysis of borophosphosilicate films[5] detergent analysis[6], and to the prediction of octane numbers in gasoline[7]. Similar analyses are applied to food and cosmetic samples.

PLS analysis is well suited to the quantitative analysis of complex chemical systems which lack unique isolated absorption bands for the constituent components. One such system is the epoxy. Epoxy materials result from the reaction of a resin monomer containing at least two reactive epoxide rings with a hardener, usually a polyamine. The amine groups react with the epoxies affording a crosslinked polymeric system with exceptional mechanical and chemical properties. The physical properties of the epoxide are closely tied to the stoichiometry of the reaction, ie. the hardener/resin ratio. If it is too rich in hardener, the product will have shorter chains and fewer crosslinks, while a rich resin system leaves unreactive epoxy functional groups, and therefore changes the ensuing chemistry.

We have briefly studied the problem of determining epoxy resin-hardener mixing rations by integrating individual infrared peaks for the constituents of interest, and normalizing using an internal standard peaks, similar to the recent work of Cole and coworkers[8]. While Cole and coworkers were successful in their quantitative studies, our results were not very satisfactory. One system we evaluated contained a heavy loading of silica filler which obscured much of the spectrum. Another, which is described in this report, had few unique frequencies for the constituents and none proved satisfactory for quantitative analysis. However, the PLS analysis of this system provides data well within our required tolerance.

Our overall objectives were: 1. To determine the epoxy mixing ratio of a sample within minutes of preparation, the sooner the better. 2. Develop a process which could be performed on the plant floor by an unskilled operator. 3. To produce an analysis which could determine the hardener composition to within one half part out of eleven (optimum ratio is 11 hardener to 100 resin). Once the determination was made the instrument would then provide an immediate response to the operator, eg. go or no go.

Experimental

All analyses were performed on a Midac FTIR at 4 wavenumber resolution, with a room temperature DTGS detector. Higher resolution was evaluated briefly (up to 0.5 wavenumber is possible on the MIdac) but did not improve the analysis. However, gas analysis and other qualitative analyses would benefit from the higher resolution capability of the Midac.

Each sample and background was scanned 10 times and ratioed. The conditions used for acquisition of the spectra were similar to those expected to be used in the real system, ie., the spectrometer was not purged and samples were prepared in ambient air. The viscous resin hardener mixtures were pored directly onto a 45 degree ZnSe crystal of a Spectra-Tech horizontal ATR accessory.

The Midac FTIR hardware and software operations are carried out with the bundled software Spectra Calc from Galactic Industries. This is an excellent software system allowing on the one hand, complete access to all data and most hardware operations, and on the other hand, is simple to use with mouse or keyboard menu selections, or direct operations through easily written macros or customized programs. Dozens of useful data and system utility programs ar included and easily accessed. Galactic PLSplus software was used for data analysis on this problem. Our procedure is summarized as follows:

1. A training set of 10 spectra of different mixing ratios was acquired on samples prepared by weighing on a four place balance. About 30 grams of resin and 3 grams of gardener were used to produce the different mixing ratios, which covered the range of values anticipated during in-plant sample preparation. The training set of spectra are significantly larger than the number of unknowns, the larger the better[9].

2. Immediately after weighing, the samples were stirred vigorously for 3 minutes. During this process, a reference spectrum of the ATR crystal against air was acquired and stored. The ATR crystal plate was removed and washed thoroughly with acetone between analyses.

3. Once the calibration spectra are acquired, the data are processed by PLSplus. A data file is created which defines concentration information about the training spectra. This file is accessed PLSplus which then calculates a specified number of factors (subspectra) and fits these to concentration data.

4. The next step is to determine the optimum number of factors to use to fit the data. Some factors may only contain noise and using an excess of factors over-determines the system. The factor optimization process is accomplished using a program called PRESS (Predictive Residual Error Sum of Squares). PRESS removes one spectrum from the group of training spectra and then calculates the prediction error for this spectrum using the remaining spectra as the training set. This process is automatically

5 repeated, sequentially removing one spectrum at a time until all have been used. Each iteration evaluates the error based upon the number of factors used up to the total number of factors. PRESS then produces a prediction error as a function of the number of factors used. Generally there is a minimum error produced by the optimum number of factors for the system. Use of too few factors underdetermines the system, and an excess overdetermines it.

> Once the calibration is complete, one moves to the predictive stage. The spectrum of an unknown is acquired as above, and the resin and hardener concentrations are immediately calculated from the PLS model. Acquisition of the spectrum and calculations require significantly less than one minute.

Results and Discussion

One of the first problems we faced was that our ATR effective pathlength was too long for the sample. Several peaks below 1600 wavenumbers had absorption values above 2.0 absorbance units, making this data unreliable. In general we try to operate below 1 absorbance unit where significant light is still reaching the detector and Beer's Law is more likely to be followed. In certain analyses (EPA 418.1 Total Petroleum Hydrocarbons) the Midac is linear beyond 1.5 absorbance units, which speaks to its good energy throughput and high signal-to-noise ratio. Although the PLSplus software allows selection of multiple regions for analysis, we elected to use the hydrocarbon C-H stretching region for analysis. Our desire to avoid water vapor in the air and moisture in the sample was another reason for choosing the C-H stretching region.

While the pathlength problem could be circumvented with another geometry crystal, the results obtained with this cell proved to be satisfactory, *vide infra*.

If we look at the spectra for the individual components and that for the optimum mixture of the two components, we see that the hardener spectrum has a peak somewhat isolated but riding on the right shoulder of the resin C-H stretching region. The resin spectrum sits on the rather broad ill-defined hardener spectrum.

We can also look at the plot of the training set data calculated using PLSplus versus the mixing ratios as weighed. The results show that PLSplus does a reasonable job of fitting the data. We did not analyze the variability in the data, however one experimental problem possibly explains some to this variation. The resin sample used to prepare our standards is contained in a one gallon can. The resin contains a high percentage of solids which tend to settle to the bottom of the container. Each time a sample was acquired the container was stirred vigorously but the high viscosity and opacity of the resin left some uncertainty about the homogeneity of the sample.

Approximately two weeks after the calibration was established a set of seven "blind" samples were analyzed using the training set of data described above. One point was used to reestablish the baseline for the samples and the analysis proceeded identically as described above. With the exception of the first sample that was run, all FTIR determined values fell within 0.1 unit of their prepared values. The average of the deviations for the seven samples is 0.1 hardener unit. The agreement between the prepared mixture and the FTIR predictions is excellent and well within the requirements of the analysis. This data speaks well for the stability and reproducibility of the Midac spectrometer, since a considerable time passed between calibration and analysis. No alignment or other procedures were performed (except for alignment of the Spectra-Tech ATR accessory).

Conclusions

In a rather simple series of experiments, FTIR/PLS analysis has provided data superior to that we had obtained using more traditional methods of analysis. Once the calibration is established, it is a simple matter to evaluate new systems. The method is fast providing important information quickly so that corrections to processes may be made before significant damage is done. The method is applicable to a wide variety of sample types, including liquids, solids, gases, films, pastes, etc.

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