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Use of Step Scan FT-IR and Multivariate Curve Resolution to Understand Aging of Propellant Binder as a Function of Depth into the Polymer Material

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Aging of Propellant Binder as a Function of Depth into the Polymer Material**

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Abstract

A sample of polymeric propellant binder was aged from 0 to 60 days at 95 oC and analyzed using FT-IR step scan photoacoustic spectroscopy. This technique has the ability of to obtain spectra of the polymer as a function of depth into the polymer material. Multivariate curve resolution was applied to the spectra data obtained to extract the contributions of the aged and un-aged spectral components form the spectra. It was found that multivariate curve resolution could efficiently separate highly overlapped spectra and yielded insights into the aging process.

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Introduction

Polymer aging has long been studied using mid infrared (IR) spectroscopy [1-14]. Kinetic information and pathways gleaned from the data can provide key insights into developing better antioxidants, crosslinkers and stabilizers. The progression of aging has often required that IR data be collected as a function of depth in order to gauge the rate of oxidation. Obtaining infrared spectral information as a function of depth within aged polymers can be quite challenging, especially if dramatic changes occur over micrometer scales. Typically, a microtome is needed to slice the polymer in order to yield samples that are thin enough to be examined using transmission infrared, however reliable microtome sampling can be difficult to achieve. The reproducibility of the microtome method is highly dependent on the polymer sample and skill of the microtommist. Further, the sample integrity comes into question, as the sample must be altered in order to perform the analysis. In one carefully executed study, it was shown that polymer oxidation could be induced by the microtome, the level of induced oxidation being dependent on the speed and type of blade used (15). Finally, samples yielded by this technique are not always easy to handle, as they are often quite thin (≤ 10 μm).

One promising method of nondestructive polymer interrogation is photoacoustic infrared spectroscopy. Using a photoacoustic (PA) detector in conjunction with a Fourier transform infrared (FT-IR) spectrometer provides a non-destructive technique that can greatly enhance the ease with which IR spectra are generated at various depths in the sample. Sampling depths from 10 to 100 microns can be easily obtained with PA FT-IR. In addition, PA FT-IR has the potential for estimating the depth at which chemical changes occur

Photoacoustic FT-IR spectroscopy works by modulating infrared radiation at acoustic frequencies and detecting the “sound” of the radiation that is returned from the sample of interest, using a microphone as the detector. Infrared adsorption by the sample causes a less intense “sound” and will be recorded as adsorption peaks in the infrared spectra. PA FT-IR can be run in standard rapid-scan mode or in step-scan mode. The advantage of step-scan mode is that in the absence of saturation all the infrared frequencies originate from the same depth. For standard rapid scan mode the higher infrared frequencies have a shorter penetration depth than the lower frequencies making interpretation on the IR spectra as a function of depth difficult. For the present study, all data was collected in step-scan mode.

The goals of this study were to 1) demonstrate the advantages of PA FT-IR in analyzing samples of an aged polymer material, and , 2) combine multivariate data analysis methods with PA FT-IR to determine the molecular components of aging within the hydroxyl terminated polybutadiene/dimeryl diisocyanate copolymer, chosen for this study This study presents PA FT-IR data acquired at different modulation frequencies for polymers aged from 0 to 60 days at 95 C. Also, data for polymers with varying amounts of anti-oxidant were analyzed to determine if anti-oxidant could be found in the material after oxidation of the material was well established.

A major goal of this study was to assess the ability of multivariate techniques such as principle components analysis (PCA) and alternating least squares (ALS) to extract chemical information from the data. In the literature to date only univariate analyses have been used to examine PAS FT-IR data. This type of analysis technique

requires that the data contain peaks that are can be attributed to a single component, which is not the case in many real world samples. In addition, using only single points for the data analysis discards information in the rest of the spectra that can give insight into chemical kinetics that is necessary to understand the system of interest. Both PCA and ALS can resolve pure component spectra from overlapped spectra and use all the data to maximize the information gained from a given data set.

Methods and Materials:

All FT-IR PA spectra were generated using a MTEC 300 photoacoustic accessory (MTEC Photoacoustic, Inc.), adapted to fit into a Bruker Equinox 55 step scan FT-IR. Step Scan modulation frequencies between 91 and 732 Hz were employed. Slower modulation frequencies probe deeper into the sample (~38 μm for 91 hz in typical polymers), while faster frequencies probe a shallower depth (~14 μm for 732 hz for typical polymers). Resolution was 8 cm^{-1} , aperture was 10 mm, and 128 scans were co-added for each experiment. All data were referenced to a glassy carbon black standard, supplied by the instrument manufacturer. An optical filter was employed that allowed the spectra to be under sampled by a factor of three, that is frequencies above 3800 cm^{-1} are rejected with an optical filter so no artifacts appear in the spectra due to undersampling. The instrument software displays both in-phase (IP) and in-quadrature (Q) spectra that can be combined to yield the magnitude spectra from the equation $M = ((\text{IP})^2 + (\text{Q})^2)^{1/2}$, where M is the magnitude spectrum, IP is the in-phase spectrum, and Q is the quadrature spectrum. The resulting magnitude spectrum is roughly equivalent to an absorbance spectrum.

Polymer samples were nominally 1 cm x 1 cm in area and 0.3 cm thick. In order to assess long term and short term variability, repeat samples were acquired in both back-to-back fashion and several days after the initial data was acquired. Theory behind the PA FT-IR technique has been covered extensively in the literature [16,17] and is not discussed in this manuscript.

Polymeric materials used in this study were supplied by Elf Atochem and Huls America Inc. and consisted of a hydroxyl terminated polybutadiene/dimeryl diisocyanate copolymer. Materials were aged at elevated temperatures, 95 C, for periods up to 60 days. A series of aged materials with anti-oxidant, 2,2'-methylene-bis(4-methyl-6-t-butylphenol), concentrations ranging from .25 to 1% by weight were investigated. A sample of the copolymer was also examined that had no anti-oxidant to obtain spectral information about the pure material.

Data analysis was performed on a Pentium 4[®] system using Matlab[®] 6.5 and a multivariate analysis program written in house. Data was prepared by normalizing all data to unit length and baseline correction as required.

Results and discussion:

Principle Component Analysis of the Data

PA spectra acquired at 732 and 183 Hz from samples aged for 0, 12, 24, 30, 36, 42, 48, 54 and 60 days are shown in Figures 1a and 1b respectively. Spectra have been length-normalized and baseline corrected. Estimated sampling depths are ~14 μm for the 732 Hz spectra ~38 μm for the 91 Hz spectra. The approximate depths are calculated from the equation, $2L = 2(D/\pi f)^{1/2}$, where f is the frequency (Hz) of modulation and D is the thermal diffusivity of the polymer, which for many polymers is estimated to be $1 \times 10^{-3} \text{ cm}^2/\text{s}$ [18]. The thermal diffusion length, L , is the decay after the signal has decayed to 63% of its original signal, e^{-1} . Both sets of spectra show an increase in the carbonyl stretching frequency at 1725 cm^{-1} and the growth of a shoulder band at 1775 cm^{-1} . The increase in these vibrational frequencies is expected for the oxidation of the material and is due to the formation of hyperperoxide acids within the polymeric material [14]. An increase is also seen in the band at 3400 cm^{-1} which would be consistent with a increase in the hydroxol group concentration as the polymer is oxidized. In addition to this increase in the bands corresponding to oxidation in the polymer, a decrease in the band at 3075 cm^{-1} is observed corresponding to the C-H stretch frequency of vinyl groups in the polymer backbone. This decrease in intensity is consistent with an oxidation mechanism as the reduced double bond of the vinyl group is oxidized to a carbonyl group. Finally, in both sets of data the C-H stretching region from 2970 cm^{-1} to 2820 cm^{-1} shows a distinct change from predominantly CH_2 groups with adsorption at 2924 cm^{-1} and 2853 cm^{-1} to an increase in CH_3 groups with bands growing in at 2970 cm^{-1} and 2853 cm^{-1} .

In order to understand the kinetics of oxidation that occurs as a function of depth, sections of the spectra presented above were analyzed by principle components analysis (PCA). Figure 2a shows the score plots from the PCA analysis for the C-H vinyl stretching band centered at 3075 cm^{-1} for the 732 Hz ($2L \sim 14 \mu\text{m}$) modulation frequency. The scores show a very dramatic change between samples 4 (30 days aging) and 5 (42 days aging). Examination of the spectra corresponding to these scores indicates that almost all the vinyl groups within the first 40 microns of the material are oxidized. Figure 2b shows the scores for the same data for the region between 2000 and 600 cm^{-1} . This plot shows that the most dramatic change in the spectra occurs between samples 5 (42 days) and 6 (50 days). While this does present the most dramatic change in the spectra the overall trend in the oxidation is more gradual for this region than with the C-H vinyl band. Thus the sudden oxidation of the vinyl band does not necessarily correlate to the dramatic changes in the other spectral regions indicating that the oxidation of the vinyl groups occurs at a different rate than does other species involved in the oxidation process.

Figure 3a shows the score plots for the for the C-H vinyl stretching band centered at 3075 cm^{-1} for the 418 Hz ($2L \sim 18 \mu\text{m}$) modulation frequency. The scores show a sudden change in the C-H vinyl band between 30 and 40 days, as was the case with the 732 Hz data. However, this data set also shows the oxidation requires 48 days to reach a steady state. Figure 3b shows the scores plot for the region from 2000 to 600 cm^{-1} shows a more gradual increase in the oxidation from 24 days to 48 days. This is a slightly

smoother transition than was seen for the 732 Hz data where changes were more stepwise.

Figure 4a shows the score plots for the C-H vinyl stretching band centered at 3075 cm^{-1} for the 183 Hz ($2L \sim 26\text{ }\mu\text{m}$) modulation frequency. Unlike the spectra acquired at 732 Hz ($2L=14\text{ }\mu\text{m}$) the scores show a gradual change in the C-H vinyl band between 30 and 48 days. In addition the raw spectra of this band show that 15% of the C-H vinyl band intensity is still left after 60 days of oxidation. Thus, at the 183 Hz modulation more of the unreacted vinyl groups are being probed. Figure 4b shows the scores plot for the region from $2000\text{ to }600\text{ cm}^{-1}$, which show a gradual increase in the oxidation from 24 days to 48 days. This is a smoother transition than was seen for the 732 data where changes were more stepwise.

Figure 5a shows the score plots for the C-H vinyl stretching band centered at 3075 cm^{-1} for the 91 Hz modulation frequency. Again the scores show a very gradual change in the C-H vinyl band between 30 and 48 days. In addition the raw spectra of this band show that 15% of the band intensity is still left after 60 days of oxidation just as the 418 Hz data showed. Figure 5b shows the scores plot for the region from $2000\text{ to }600\text{ cm}^{-1}$ shows a very smooth transition for oxidation from 24 days to 48 days.

A rapid change in oxidation rate is seen at approximately 30 day aging, most dramatically in the high-energy region of the infrared spectra. Oxidation that is occurring at times earlier than 24 days is therefore more likely to be occurring at sites that are not the vinyl groups. It is likely that the increase in the carbonyl band that is seen between 24 and 30 days is due to the formation of the degradation products of the antioxidant. Thus, the sudden decrease in the vinyl band from 30 to 42 day time frame is likely due to depletion of most of the antioxidant material in the first 12 microns of the material. The more gradual decrease in the C-H stretch frequency of the vinyl groups at increasing thickness indicates that consumption of the antioxidant deeper into the material is diffusion limited by consumption of the antioxidant closer to the surface.

Repeatability of the Data:

Repeat data were acquired for both the 183 Hz and 418 Hz modulation frequencies for 0, 12, 24, and 30 days for both samples. Two repeat samples were acquired for each of these days and they were acquired on different days. Additionally, repeats at 48 and 54 days were acquired for the 418 Hz modulated data. Figures 6a and 6b show PCA analysis of the one set of data and repeats acquired at 183 Hz and 418 Hz for the $2000\text{ to }600\text{ cm}^{-1}$ region. While some drift is seen occurring from day to day in the instrument the data shows that the spectra are very reproducible overall.

Multivariate Curve Resolution using Alternating Least Squares of the Data:

Multivariate Curve Resolution (MCR) is another multivariate technique that can be used for analysis of complex spectral data. Unlike PCA where the outputs of scores and factors can be abstract and difficult to interpret without factor rotation, MCR outputs meaningful spectra and concentration results when the proper constraints are applied. Starting points for the analysis are the spectra aged at 0 days for each of the respective frequencies and the spectra of the 732 Hz sample aged at 60 days since it was assumed

this gave the best estimate for the spectrum of the aged polymer. For all data shown the concentration matrix (relative concentrations in this case) was constrained to be non-negative since the least amount of either spectral shape that could be present was zero. For all cases the estimated spectra were also constrained to be non-negative since negative going spectra have no physical meaning. This gave reasonable estimates of pure component spectra. In order to assess the difference in oxidation kinetics at different depths difference spectra are calculated by subtracting the higher frequency data (shorter pathlength) from the lower frequency data (longer pathlength). Subtractions were performed on raw data sets after baseline correction; these data sets were then normalized.

Figures 7a and b show the ALS estimates of the spectral and concentration components respectively for the 732 Hz data between 2000 and 600 cm^{-1} . Pure component spectra in Figure 7a are well resolved and show distinct differences between the un-oxidized and oxidized components. For the oxidized component the carbonyl band is broader with a shoulder at 1780 cm^{-1} . In addition, many of the bands in the un-oxidized spectra below 1650 cm^{-1} diminish or loss fine structure altogether. This is supported by the estimates of the relative concentrations of the two components shown in Figure 7b, which shows that essentially none of the un-oxidized component is left in the system after 60 days. This is not surprising, since the oxidized spectra at 60 days were used as the starting point in the MCR analysis. However, as was discussed in the PCA section, the C-H stretching band of the vinyl group at 3075 cm^{-1} completely vanishes for this data set so assuming that the spectra at 60 days estimates the oxidized polymer is not an unreasonable assumption. Data in Figure 7b shows that the oxidation begins to increase after 12 days but shows the most dramatic increase after 42 days of aging. This is in agreement with the PCA analysis of the C-H stretching band of the vinyl group and the period after 42 days likely corresponds to the loss of almost all antioxidant in the first ~ 14 μm of the material. Thus, the oxidation tracked in the first 42 days is likely dominated by the kinetics of oxidation of the antioxidant and after 42 days of aging the kinetics of polymer oxidation take over. Attempts to use MCR to resolve the pure component spectra of the antioxidant from that of the oxidized polymer were unsuccessful. Possible reasons for this are that too few spectra were acquired at different aging times or that the 8 cm^{-1} resolution used in these experiments does not allow the MCR to distinguish a third highly overlapped species.

Figures 8a and b show the MCR estimates of the spectral and concentration components respectively for data between 2000 and 600 cm^{-1} comprising the difference between the 418 and 732 Hz data. The data described by the estimates of concentration and pure spectral component in Figure 8 arise from the region in the polymer between 14 and 18 μm (2L). Again the spectral components are well resolved in Figure 8a with similar changes in features that were seen in the 732 Hz data in Figure 7a. Estimates of the relative concentration matrix, however, are different for this data compared to the 732 Hz data. Figure 8b shows a significant increase in the oxidized band is seen after 12 days of aging but the increase in the oxidized levels off after 42 days of aging. The apparent halt to the oxidation of the material after 42 days is likely due to the formation of an oxygen impermeable skin on the surface of the polymer [14]. This is consistent with the kinetics observed at 732 Hz where an increase in the oxidation rate was observed after 42 days, which is likely due to the formation of the “skin” on the surface of the polymer. In

addition, $15\% \pm 2\%$ (1 standard deviation) of the un-oxidized component is left after 60 days of oxidation compared to 0 % for the 732 Hz data (this was determined by ratioing the estimated concentration of the un-oxidized component after 60 days aging to the estimated concentration at 0 days). This indicates that even at ~ 18 μm depth in the sample some of the material is protected from oxidation. Uncertainties in the relative amount of un-oxidized polymer left were obtained by calculating the spread in the $\hat{C}$ vector for the un-oxidized component for 48 through 60 days (the time at which the reaction is assumed to have leveled off). It should be noted that only relative comparisons can be made when comparing the $\hat{C}$ matrix across frequencies. Absolute comparisons cannot be made since pathlength and therefore spectral intensities change for each of the frequency data sets. Thus, the resulting values of the $\hat{C}$ matrix cannot be directly compared.

Figures 9a and 9b show the estimated concentration matrix for difference data between 183/418 hz and 91/183 Hz respectively (pure component spectra were similar to what was seen in Figures 7a and 8a). As with the difference data between 418 and 732 Hz the data in Figure 9 shows an increase in oxidation after 12 days of aging and a leveling off of the oxidation after 42 days. Again the halt in the oxidation is likely due to the formation of an oxidized skin nearer the surface of the sample that is impassible to oxygen. The relative amount of un-oxidized component for the 183 and 91 Hz data is $10\% \pm 5\%$ and $18\% \pm 3\%$ respectively. These values are calculated exactly as was done for the difference data between 418 and 732 hz.

Depth Profiling at Different Antioxidant Concentrations

Figures 10a and 10b show the show the estimated relative concentration matrix for 732 and the difference of the 183/732 Hz data on polymer samples with .25 % antioxidant. Both data sets show an increase in oxidation after 14 days and a leveling off of the oxidation kinetics after 30 days. While the initial onset of the oxidation is equivalent to what was seen in the 1% antioxidant data the oxidation terminates more quickly than with the 1 % antioxidant data. For the 732 Hz data the 1% antioxidant data shown in Figure 7b shows an increase in oxidation out to 60 days. All the difference data presented in Figures 8b, 9a and 9b show that the oxidation does not level off until after 42 days of aging. The leveling off of the oxidation kinetics at 30 days for the .25% antioxidant data indicate that the oxygen impermeable skin is formed ~ 12 days earlier with .25 % antioxidant. Also, since the 732 Hz sample shows a leveling off of the oxidation kinetics it is likely that the skin forms much closer to the surface than with the 1% antioxidant samples.

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Figure 1a

Figure 1b

Figure 2a

Figure 2b

Figure 3a

Figure 3b

Figure 4a

Figure 4b

Figure 5a

Figure 5b

Figure 6a

Figure 6b

Figure 7a

Figure 7b

Figure 8a

Figure 8b

Figure 9a

Figure9b

Figure 10a

Figure10b

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