

Application News

No. A455

Spectrophotometric Analysis

Time-Course Analysis of Polyvinyl Chloride Adhesive by FTIR

Polymeric materials may undergo changes in composition or molecular structure due to such factors as mixing, heating, light exposure, etc. These changes may reach completion within a few seconds or may progress slowly over several hours. An FTIR is useful for conducting analysis of polymer composition and molecular structure, and LabsolutionsIR software, with its included time-course measurement program, permits tracking of sample peak changes over time. Although the program is suitable for tracking a gradual reaction, the included Rapid Scan feature is effective in cases where the sample reaction is completed within a few seconds.

Here, we introduce an example of measurement of the curing process of polyvinyl chloride resin adhesive using the time-course measurement program.

■ Sample - Polyvinyl Chloride Adhesive

The sample used here, a thermoplastic resin adhesive consisting of vinyl chloride - vinyl acetate copolymer resin dissolved in an organic solvent (acetone, cyclohexanone), is commonly used for bonding of vinyl chloride pipes, etc.

■ Time-Course Analysis Program

The Specac high-performance diamond ATR accessory (Golden Gate Diamond ATR), shown in the photograph of Fig. 1, was used for measurement. This unit is effective for measurement of adhesives, since its sample measurement component includes a tungsten carbide disk into which a diamond element is metal-bonded at high temperature. On the other hand, ATR attachments which rely on adhesive for fixing the prism in place are unsuitable for this analysis because dissolution of that adhesive due to contact with solvent, or removal of the cured adhesive could result in damage to the prism.

The analytical conditions are shown in Table 1. The time setting screen shown in Fig. 2 is used for setting the measurement interval. Since curing of a vinyl chloride resin adhesive takes about 20 minutes, a single measurement was set to be conducted every 30 seconds over a measurement period of 1800 seconds (30 minutes), assuming zero seconds for sample-drop onto the diamond disk.

Fig. 3 shows the ATR spectrum acquired using time-course measurement, in which measurements are conducted at fixed time intervals. The region from 2000 – 550 cm^{-1} is shown here as a 3D graph in which the XY axis represents time (sec) and wavenumber (cm^{-1}), and the Z axis represents absorbance. This permits observation of the sample reaction process over time.

Next, Fig. 4 shows the overlaid ATR spectra acquired at (0) minutes, 5, 10 and 30 minutes from the start of measurement, and the expanded region from 2000 – 550 cm^{-1} .

Due to the gradual decrease in the size of the peaks at 1708, 1357 and 1219 cm^{-1} , these peaks were thought to be derived from acetone. For reference, the ATR spectrum of acetone is shown in Fig. 5. The wavenumbers of these

3 peaks are close to those of the acquired spectra. Furthermore, once the solvents evaporate, water can be absorbed and is as is evident by the increase in the broad peak due to an O-H stretching vibration (in the vicinity of 3398 cm^{-1}). In addition, the C-Cl stretching vibration peaks at 692 and 609 cm^{-1} derived from the vinyl chloride resin also showed a gradual increase in size.



Fig. 1 Golden Gate Diamond ATR Accessory

Table 1 Instrument and Analytical Conditions

Instrument	: IRAffinity-1, Golden Gate Diamond ATR
Resolution	: 4.0 cm^{-1}
Accumulation	: 10
Apodization	: Happ-Genzel
Detector	: DLATGS

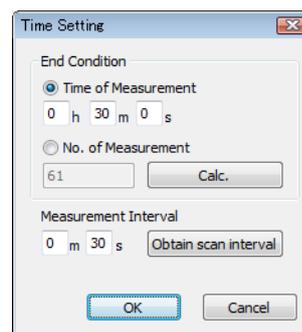


Fig. 2 Parameter Settings Screen

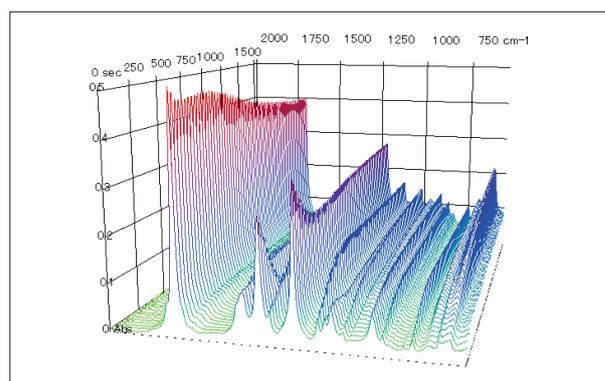


Fig. 3 3D Time-Course Measurement Graph

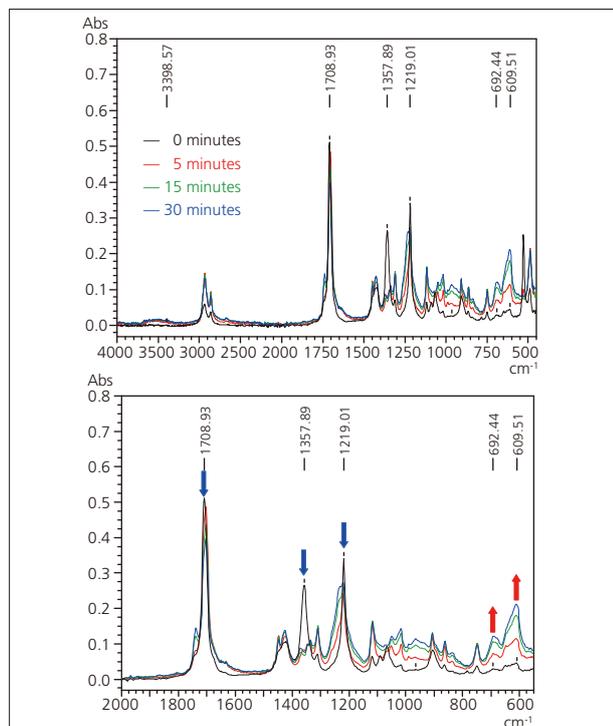


Fig. 4 FTIR Spectra and Expanded Region from 2000 cm⁻¹ to 550 cm⁻¹

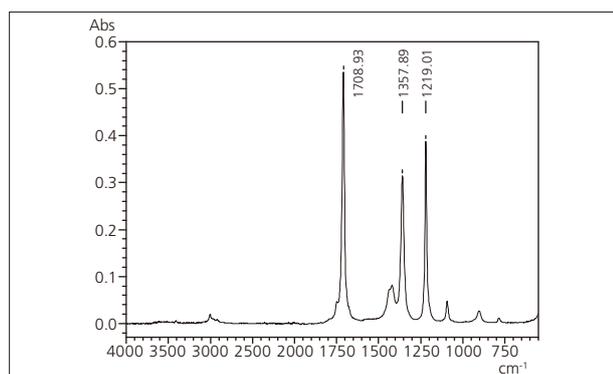


Fig. 5 ATR Spectrum of Acetone

■ Peak Change Analysis Using 2D Time-Course Data

Time-course measurement also permits the graphic display of absorption changes in peaks of interest as 2D time-course data. The graph of the absorption changes displayed for selected wavenumbers is called an SAC (Selected Absorption Curve). Here, we focused on the three peak area values at 1708 cm⁻¹, 1219 cm⁻¹ and 609 cm⁻¹, which exhibited remarkable changes in Fig. 4. The respective calculated results are displayed in Fig. 6. The X-axis displays the time (sec) and the Y-axis the peak area values.

The peak due to the C=O stretching vibration in the vicinity of 1708 cm⁻¹ (baseline: 1800 – 1550 cm⁻¹) becomes large relatively quickly, and then gradually decreases in size. While the skirt of the peak from vinyl acetate resin at 1740 cm⁻¹ and the C-Cl bands at the lower wavenumbers become larger due to the curing process, the acetone peak gradually becomes smaller due to volatilization.

The peak in the vicinity of 1219 cm⁻¹ (baseline: 1300 – 1150 cm⁻¹), becomes smaller due to volatilization of acetone and other organic solvents, but the peak due to the C-H bending vibration of the vinyl acetate-vinyl chloride copolymer resin visibly increases over time.

Thus, there are two processes associated with the increase and decrease of area values for the peaks at 1219 cm⁻¹ and 1708 cm⁻¹. The vinyl chloride resin peak in the vicinity of 609 cm⁻¹ (baseline: 663 – 580 cm⁻¹) that is associated with the C-Cl stretching vibration, however, becomes larger over time. Then, we calculated the curing reaction rate using the peak area value of the C-Cl stretching vibration in the vicinity of 609 cm⁻¹, assuming a reaction rate of 0 % at the start of measurement and the completion of the curing reaction 30 minutes later. Assuming A as the peak area of the C-Cl stretching vibration at 609 cm⁻¹ which increased as the curing reaction progressed, A₀ as the peak area of the uncured substance (0 minutes) in the vicinity of 609 cm⁻¹, and A₃₀ as the peak area of the fully cured substance (30 minutes) in the vicinity of 609 cm⁻¹, the curing reaction rate X (%) was calculated according to the following expression.

$$X (\%) = (A - A_0) / (A_{30} - A_0) * 100$$

The calculated results are shown in Fig. 7. As described above, not only peak height, but peak area values and peak ratios also, can be displayed using the 2D time-course data, in addition to the complex calculation results shown here. Furthermore, not only can these 2D time-course data be displayed during measurement, they can also be extracted from the 3D data after completion of measurement.

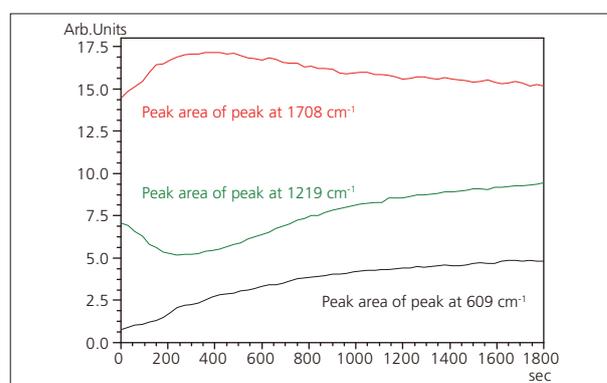


Fig. 6 2D Time-Course Graph of Peak Areas

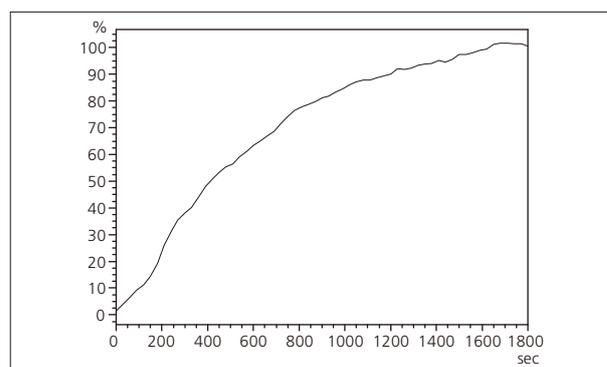


Fig. 7 Reaction Rate of Polyvinyl Chloride Adhesive

■ Conclusion

Here, we introduced an example of time-course measurement of the polyvinyl chloride resin adhesive by FTIR. It was demonstrated that when measuring a sample in which the reaction proceeds gradually, this type of time-course measurement effectively provides a variety of data, including peak height, peak area, as well as reaction rate.