

TG-FTIR Analysis Novolac Polymer Resin

Sample Description

Novolac is a thermoplastic phenol-formaldehyde resin, which is typically used as a bonding agent in brake linings and abrasive grinding wheels. Other uses include electrical insulation, clutch facings, and a reinforcement agent and modifier for nitrile rubber. The polymer is primarily obtained using excess phenol and acid catalysts.

Novolac resin is generally cured with hexamethylenetetramine or p-formaldehyde to form cross-linked structures. The resin used in this study was not cross-linked.

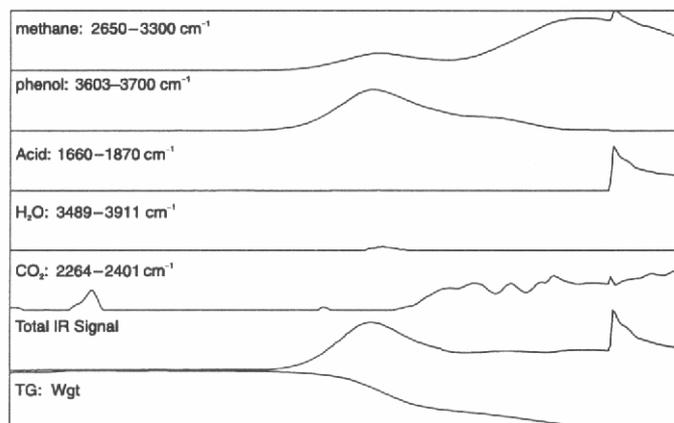


Figure 1: TG Weight Loss and FTIR Gas Profiles

Experimental

TG-FTIR analysis of a Novolac resin was performed using a Thermo Cahn TherMax 300. Nitrogen was used as the reaction gas, so the end-products of the decomposition are pyrolysis products rather than products of oxidative degradation. The temperature program began at 60°C, ramping at 25°C per minute to a final temperature of 800°C. FTIR spectra were acquired throughout the run at a temporal resolution of 6 seconds and a spectral resolution of 4cm⁻¹. A Thermo Mattson Galaxy spectrometer and TG-FTIR interface, equipped with a wide band MCT detector, were used for the FTIR analysis. The transfer line, high-temperature flow cell, and TG interface were held at 300°C for the duration of the run to prevent sample condensation. The sampling interface to the TG was the Patented Thermo Cahn Sniffer interface. The Sniffer is an eighth inch outside diameter inconel tube that is placed immediately above the sample cup. The location of the Sniffer minimizes the dilution effects of the TG reaction gases on the gases evolved by the sample. The evolved gases were transferred through the FTIR flow cell by a peristaltic pump with a flow rate of 40 millilitres per minute.

Analysis

The ability to profile specific gases is a primary advantage in FTIR detection of gases evolved during TG analysis.

The net absorbance calculations used here in multiple frequency ranges provided very specific evolved gas profiling. The evolved gas profiles for Novolac decomposition, shown in Figure 1, were calculated using a net absorbance from a local baseline calculation.

The baseline and peak values used for each gas in Figure 1 are listed in the table below.

Evolving Gas	Baseline Points (cm ⁻¹)	Peak (cm ⁻¹)
Carbon Dioxide	2401—2264	2361
Water	3911—3489	3750
Add	1870—1660	1759
Phenol	3700—3603	3655
Methane	3300—2650	3016

The trace labeled *Total ZR Signal* in Figure 1 follows the sum difference over time of infrared spectra from a baseline spectrum acquired at the start of the run. Intensities shown in the FTJR traces are proportional to infrared absorbance—not sample weight.”

Figure 2 represents a three dimensional plot of infrared absorbance spectra versus time. A 3D plot is useful for presenting the changes that occur in the infrared spectra over the course of the TG analysis. Each absorbance band along the

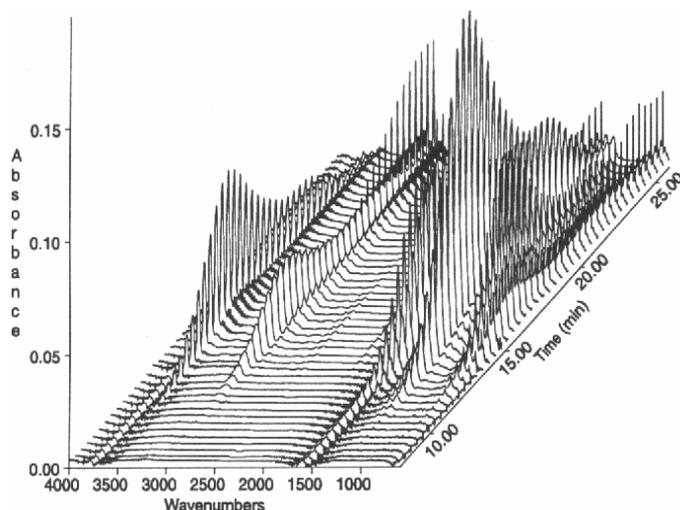


Figure 2: 3D Plot IR spectra Vs time

wave-number scale represents functional groups of the evolved gases.

Results

Some of the components produced are easy to identify from the FTIR spectra. For example, Figure 3 is the spectrum obtained at 3.61 minutes into the run, and is easily identified as carbon dioxide.

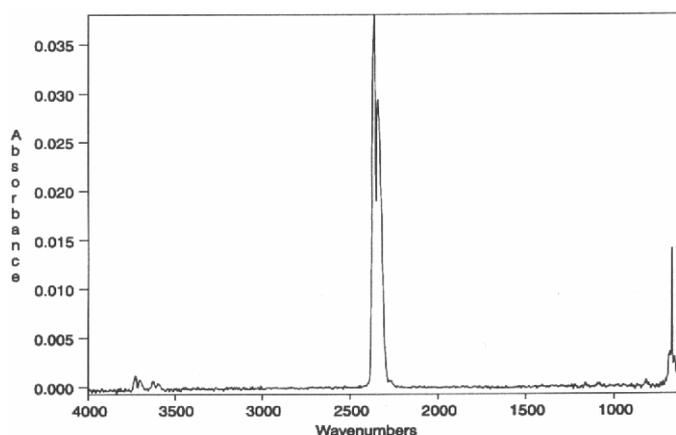


Figure 3: Carbon Dioxide at 3.61 Minutes

Other more complex spectra can be identified by spectral library search. The spectrum that compares to the major weight loss centred at 360 °C (Figure 4) was searched against the Aldrich Vapor Phase library. This spectrum is identified as phenol (Figure 5).

*Conversion to weight requires know the edge of the extinction coefficient, and a calculation of weight by the Beer-Lambert law. This type of quantitation generally requires calibration curves generated at the same temperature and pressure using the same flow cell as used in the TG analysis.

The band at 3649 cm^{-1} is due to the phenolic O—H stretch, and the band at 1182 cm^{-1} to the C—O stretch. The 1601 cm^{-1} absorbance band is caused by aromatic ring deformation, while the band around 3025 cm^{-1} to aromatic C—H stretch. The weight loss is due to non-polymerized phenol in the resin.

The area of steady weight loss above 500 °C corresponds to decomposition of the base polymer. A variety of gases are generated in this phase of the decomposition.

Figure 6 is the spectrum obtained at 25.26 minutes into the run. Spectral library search identified the best fit as methane. While methane is clearly a component in the evolved gases, comparison of the library spectrum with the raw data suggests the presence of other compounds.

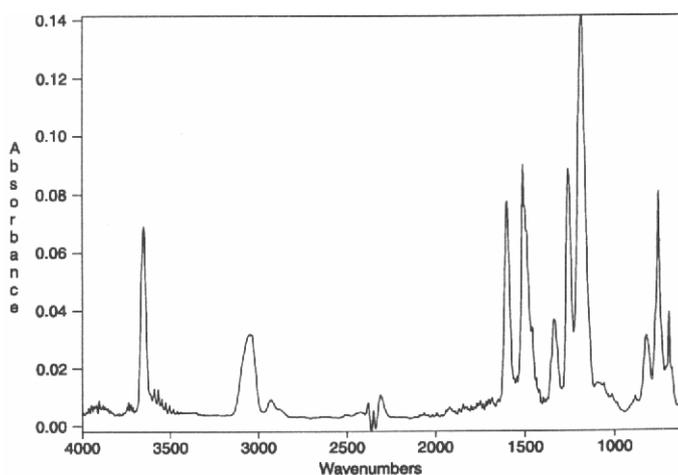


Figure 4: spectrum acquired major weight loss at 360°C.

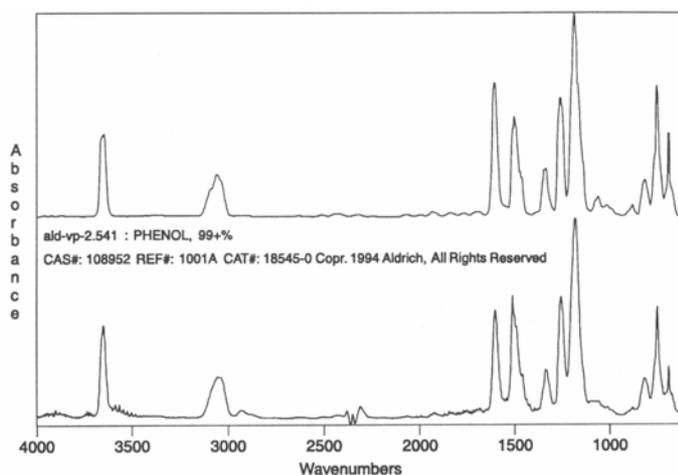


Figure 5: Spectrum Identified as Phenol with Spectral search.

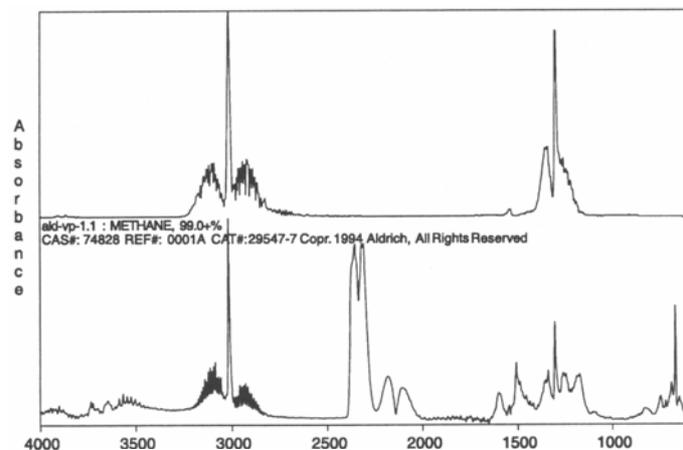


Figure 6: Methane spectrum acquired 25.26 minutes into the run.

Further examination of the spectrum indicates some phenol is still being generated (Figure 7).

The pyrolysis products of the sample at higher temperatures include substantial amounts of carbon dioxide and carbon monoxide. This continues as a trend throughout the rest of the run.

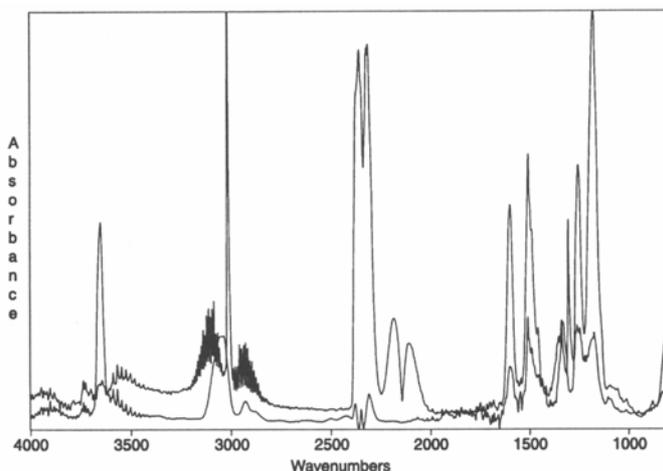


Figure 7: Overlay of Phenol (360°C) and spectrum as 625°C.

At 750°C another small weight loss occurs. This is barely discernible on the weight loss curve, but can be seen in the dW/dT curve (Figure 8). The infrared traces clearly show evidence of the presence of an organic acid.

The library search (Figure 9) identifies this compound as benzoic acid, which was probably the acid catalyst used in the formation of the Novolac resin.

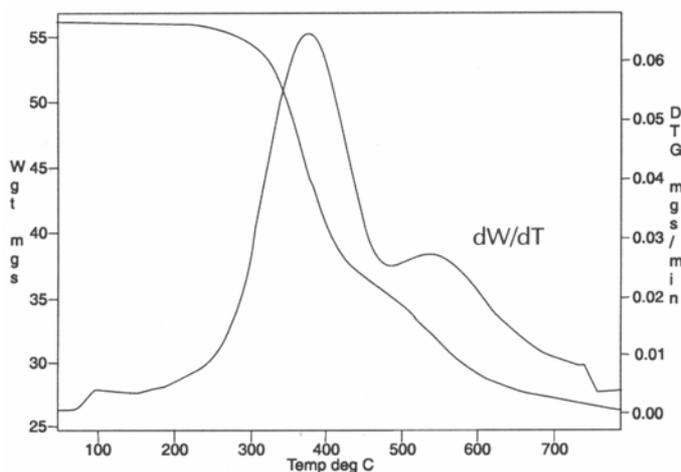


Figure 8: Minor Weight loss at 750°C evident in dW/dT curve.

Summary

Specific gases can be identified by using FTIR detection of the gases evolved during a TG analysis. By analyzing the spectra of the evolved gases from a Novolac sample, five specific gases were identified: carbon dioxide, water, acid, phenol, and methane.

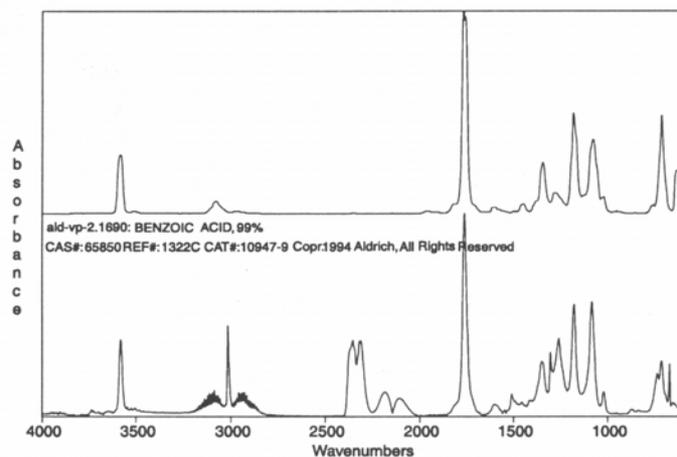


Figure 9: Spectrum Identified as Benzoic Acid with spectral library search