EGA and Multi-Step Pyrolysis of Phenol Formaldehyde Resin by CDS Pyroprobe

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Application Note

Polymer

Abstract

This application note investigates the thermal decomposition of Bakelite, which is a thermosetting phenol formaldehyde resin, using EGA and multi-step pyrolysis GC-MS techniques.

Introduction

In the early 1900s, Leo Baekland discovered he could form a resin by controlling pressure and temperature applied to phenol and formaldehyde. Bakelite, or polyoxybenzylmethylengycolanhydride, became famous for being the first synthetic plastic[1].

In this application note, thermal characteristics of Bakelite resin were explored, first by performing Evolved Gas Analysis (EGA), followed by multi-step pyrolysis GC-MS. Finally, the reproducibility of single step pyrolysis at 700°C of this phenol-formaldehyde resin was explored.

Experiment Setup

The sample was first added into a DISC (Drop-In-Sample Chamber) tube and then analyzed using EGA as the first screening step. Using the information from this step, multi-step pyrolysis was performed. A reproducibility study was also performed on the resin at a setpoint of 700°C.

EGA

Pyroprobe with DISC		GC/MS	
Initial:	100°C	Column:	Fused silica (1m x 0.10mm)
Final:	800°C		
Ramp Rate:	100°C/min	Carrier:	Helium 1.25mL/min
Interface:	300°C	Split:	80:1
Transfer Line:	300°C	Injector:	360°C
Valve Oven: 300°C		Oven:	300°C
		Ion Source:	230°C

Multi-step Pyrolysis			
Pyroprobe with DISC		GC-MS	
DISC Chamber:	450°C 20s 700°C 20s	Column:	5% phenyl (30m x 0.25mm)
Interface:	300°C	Carrier:	Helium 1.25mL/min
Transfer Line:	300°C	Split:	40:1
Valve Oven:	300°C	Injector:	360°C
		Oven:	40°C for 2 minutes 10°C/min to 320°C
		Ion Source:	230°C
		Mass Range:	35-600amu

Single Step Pyrolysis
Pyroprobe with DISC

DISC Chamber:	700°C 20sec
Interface:	300°C
Transfer Line:	300°C
Valve Oven:	300°C

GC-MS

Column:	5% phenyl (30m x 0.25mm)
Carrier:	Helium 1.25mL/min
Split:	40:1
Injector:	360°C
Oven:	40°C for 2 minutes 10°C/min to 320°C
Ion Source:	230°C
Mass Range:	35-600amu

Results and Discussion

When subjected to a heating rate of 100°C/min from 100°C to 800°C, thermal decomposition of Bakelite appears to happen in multiple stages, the first large area of outgassing has a maximum temperature of 430°C, and a second area emerges at 480°C.

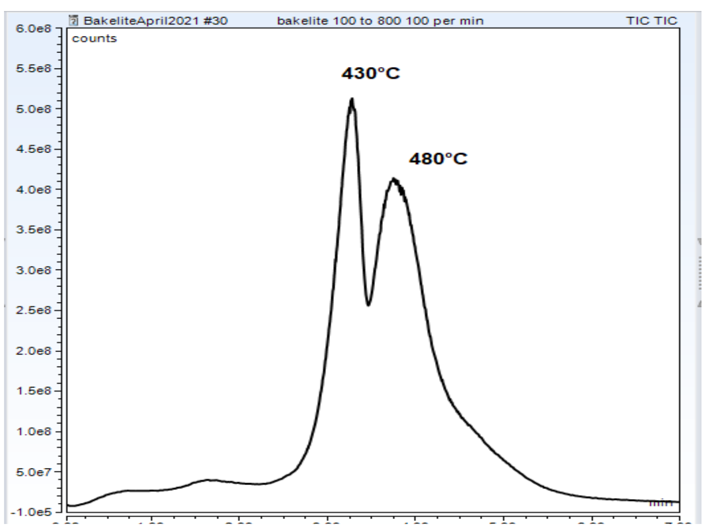


Figure 1. Evolved Gas Analysis of Bakelite from 100°C to 800°C at 100°C per minute ramp rate.

When the mass spectra under the first large peak is examined, m/z 43 is abundant, and the averaged spectra shows list library matches for carbohydrates. On the other hand, the mass spectra under the second peak has m/z 94, 107, and 121, which are associated with phenol and substituted phenols.

After this EGA screening, temperatures were chosen for multi-step pyrolysis GC-MS based on the EGA peak positions. 450°C was first chosen as a pyrolysis temperature, which is the trough between the two EGA peaks. 700°C was the 2nd pyrolysis temperature, at which the resin is fully decomposed, provides detail of the chemical compounds evolving from each stage of thermal decomposition.

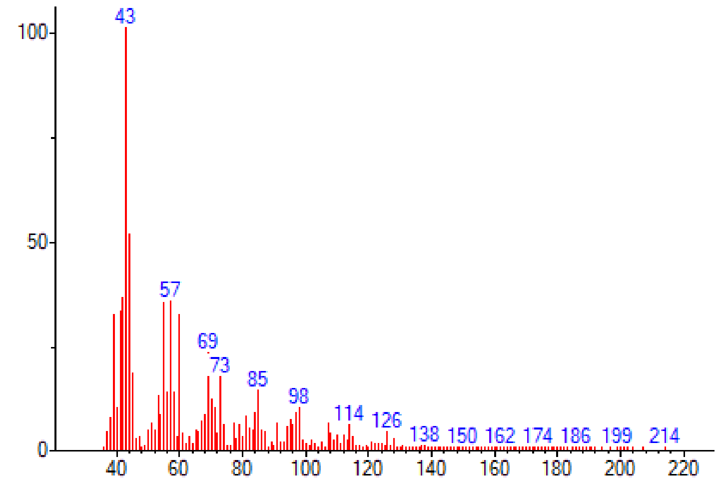


Figure 2. Mass spectrum of 430°C peak in Figure 1.

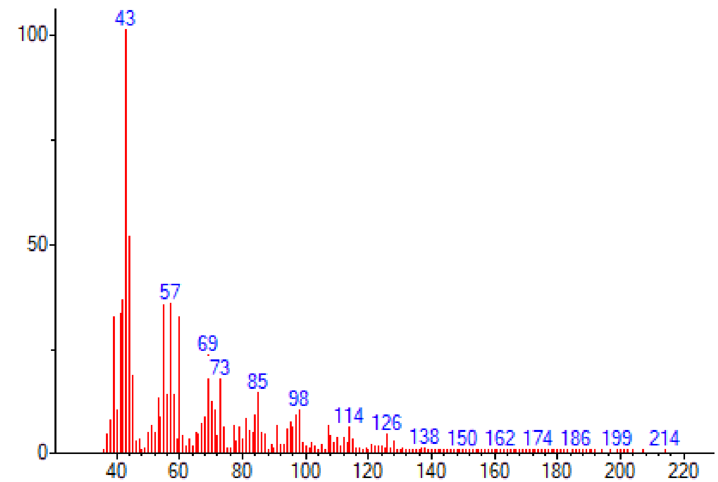
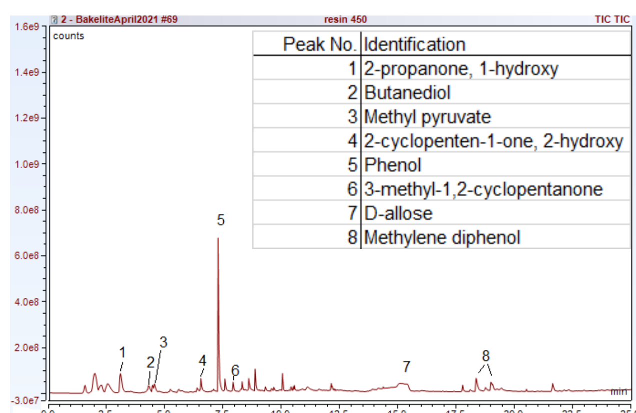


Figure 3. Mass spectrum of 480°C peak in Figure 1.



Peak No.	Identification
1	2-propanone, 1-hydroxy
2	Butanediol
3	Methyl pyruvate
4	2-cyclopenten-1-one, 2-hydroxy
5	Phenol
6	3-methyl-1,2-cyclopentanone
7	D-allose
8	Methylene diphenol

Figure 4. Pyrogram of Bakelite resin at 450°C.

As observed in the EGA, many of the compounds pyrolyzed at 450°C are oxygenated species, like aldehydes and ketones. These species have a high amount of m/z 43 in their mass spectra. This implies that alcohol groups from the resin are first released along with some scission of the phenol-formaldehyde bond.

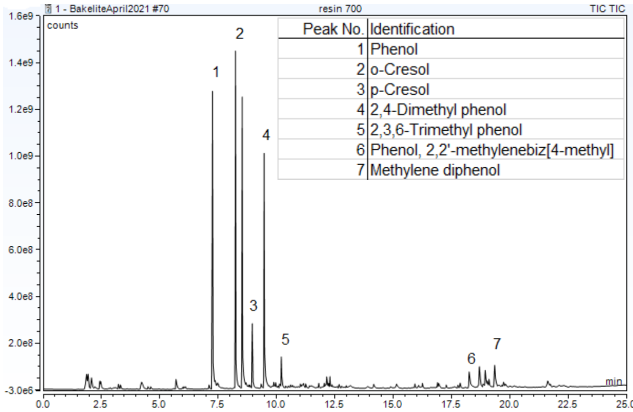


Figure 4. Pyrogram of Bakelite resin at 700°C after 450°C run

When pyrolysis of 700°C follows 450°C, phenols, and methyl substituted phenols emerge, including larger resin fragments, like methylene diphenols, as shown in Figure 4. No secondary pyrolysis products were observed due to the unique pulsed heating design to prevent large temperature gap between the sample and the heating elements.

After understanding the pyrolysis mechanism, 700°C was chosen since EGA data supports that the resin is completely decomposed at this temperature. RSD study was performed on 5 replicates of resin pyrolyzed with single-step pyrolysis at 700°C. Peak Area Ratios of 4 individual phenols to their combined total area were compared. RSDs were around 2% for the 3 largest peaks, while RSD for the smallest peak was under 10%.

Table 1. Peak Area Ratios of Phenolics in Bakelite Resin at 700°C.

	Peak Area Ratios			
	Phenol	o-Cresol	p-Cresol	Trimethylphenol
Rep 1	44.7	25.0	27.8	2.5
Rep 2	44.7	25.0	27.8	2.5
Rep 3	44.8	25.6	27.1	2.5
Rep 4	43.4	25.5	28.2	2.8
Rep 5	45.6	24.2	28.1	2.1
AVE	44.7	25.0	27.8	2.5
RSD%	**1.71**	**2.31**	**1.59**	**9.90**

Conclusion

The latest version of the Pyroprobe from CDS Analytical including easier sample preparation and introduction with the new DISC and sample tubes. The data from the Pyroprobe on challenging samples is highly reproducible for quantification study. With the available of multiple techniques, this instrument is capable in kinetic studies of polymer thermal degradation.

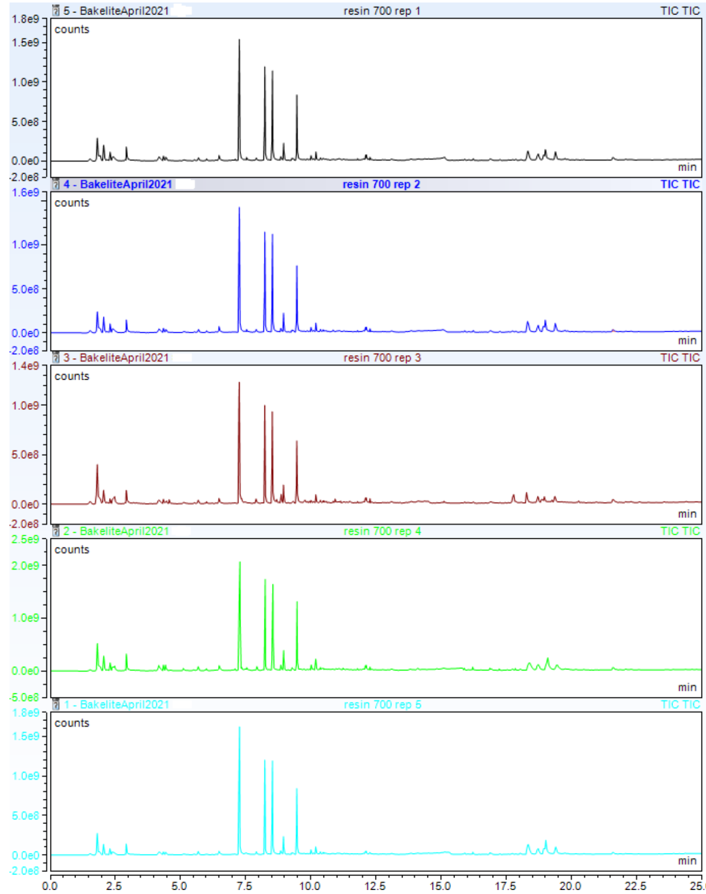


Figure 5. Replicates of Bakelite resin at 700°C.

References

1 Chandrasekaran, C., Technoeconomic Aspects of Nonrubber Linings-Glass, FRP, and Lead, in Anticorrosive Rubber Lining, 2017.