Evolved Gas Analysis and Multi-step Pyrolysis of Cyanoacrylate Glue

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Application Note
Polymer

Abstract
This application note demonstrates Evolved Gas Analysis (EGA) and Multi-step Pyrolysis (MSP) with GC-MS on cyanoacrylate glues.

Introduction
Cyanoacrylate adhesives, first patented in 1949[1] and marketed under the trade names Super Glue and Krazy Glue, bond nearly instantly to surfaces. The cyanoacrylate monomer polymerizes quickly in the presence of water, forming strong chains. While standard cyanaoacrylate glues can be nearly 100% cyanoacrylate, custom formulations also exist. As a powerful analytical tool in failure, competitor, and even forensic analyses, Evolved Gas Analysis together with Multi-step Pyrolysis is supportive of discovering chemical components in finished materials. In this application note, two formulations of cyanoacrylate glues were explored.

Experiment Setup
Two different glues, one of which is a liquid formulation of one brand, and the other is a gel formulation of a different brand, were applied to a glass slide and allowed to set before sampling. Pieces of each glue (100μg) were scraped from the glass slide using a kraft knife and loaded into individual DISC (Drop-In-Sample Chamber) tubes for analysis. Then, using the Pyroprobe Application Decision Making Tree[2] as a guide, a fused silica transfer line was used to connect the GC inlet to the MS detector in a preliminary EGA run. After which, a 30 meter long 5% phenyl capillary column was used for multi-step pyrolysis. A vent-free adapter was installed to enable a fast switch between the fused silica and the column without losing vacuum in the mass spectrometer.

EGA

Pyroprobe 6200 Autosampler	GC-MS
Initial: 50°C	Column: Fused silica (1m x 0.10mm)
Final: 1000°C	Carrier: Helium 1.25mL/min 80:1 split
Ramp Rate: 100°C per min	Injector: 360°C
Interface: 300°C	Oven: 300°C
Transfer Line: 325°C	Ion Source: 230°C
Valve Oven: 300°C	Mass Range: 35-600amu

Multi-Step Pyrolysis

Pyroprobe 6200 Autosampler	GC-MS
DISC:	Column: 5% phenyl (30m x 0.25mm)
350°C 30 sec	Carrier: Helium 1.25mL/min, 50:1 split
500°C 30 sec	Injector: 360°C
Interface: 300°C	Oven: 40°C for 2 minutes
Transfer Line: 325°C	12°C/min to 320°C (10min)
Valve Oven: 300°C	Ion Source: 230°C
	Mass Range: 35-550amu

Results and Discussion

EGA was first performed on the glues. In this fast screening technique, the DISC temperature was ramped up at 100°C/min from 50°C to 1000 °C and the GC oven was kept isothermally at 300°C. The results for both glues are shown overlayed in Figure 1. Two regions of interest were seen in each glue, the first region at between 200°C and 350°C, followed by a second region between 350°C and 550°C. When the mass spectra were averaged in the first regions and compared against a NIST library, the top match was for 2-cyanoethyl acrylate in both glues, and a search of the averaged mass spectra in the second region had a top match for polymethyl methacrylate in the polymer library. Figures 2 and 3 show the search matches from the gel glue. From these EGAs, it also can be seen that the liquid glue's first peak emerged at a slightly lower temperature than the gel glue, and the liquid glue had less methyl methacrylate than the gel glue.

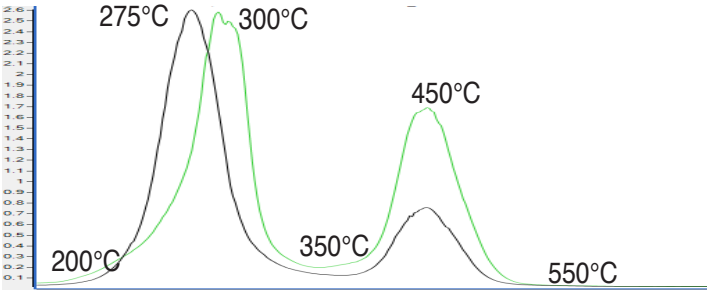


Figure 1. Evolved Gas Analysis of liquid glue (black), and gel glue (green) from 50°C to 1000°C at 100°C per minute.

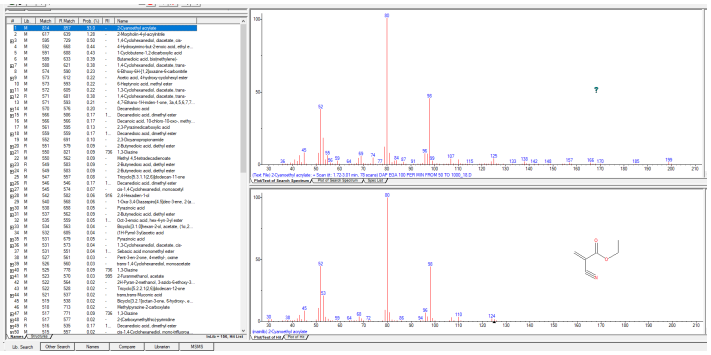


Figure 2. NIST Library match from the first Peak of the Gel Glue EGA from Figure 1.

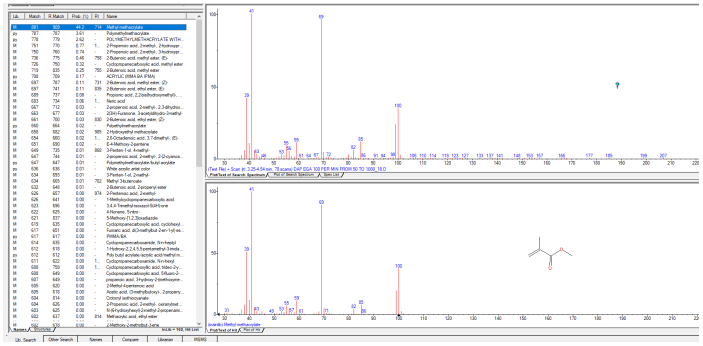
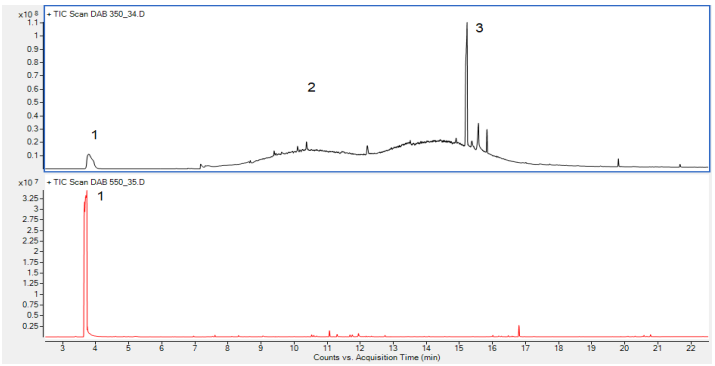


Figure 3. NIST Library match from the second Peak of the Gel Glue EGA from Figure 1.

The information from these EGAs were used to determine setpoint temperatures for multi-step pyrolysis. Temperatures chosen were to the right of each peak to be sure adequate energy was applied to thermally release each component. Therefore, 350°C, and 550°C temperatures were chosen for multi-step pyrolysis GC-MS.



Peak	Identification
1	methyl methacrylate
2	ethyl cyanoacrylate
3	Decanedioic acid, dimethyl ester

Figure 4. Multi-step pyrolysis of gel glue at 350 °C (top), and 550 °C (bottom).

Multi-step pyrolysis of gel and liquid glues are shown in Figures 4 and 5, respectively. At 350°C, the gel glue had a rise at the baseline between 8 and 15 minutes. When this region's mass spectra was averaged and compared against the NIST library, the top hit was Ethyl cyanoacrylate. In addition to this, a peak for Decanedioic acid, dimethyl ester, a plasticizer additive, was identified in CDS's additive library (Figure 5). This helps the gel glue remain elastic. In the 550°C step, there was a peak for methyl methacrylate, and when the mass spectra of the chromatogram is averaged and compared against CDS's polymer library, a top match was for Poly(methyl methacrylate) (Figure 6).

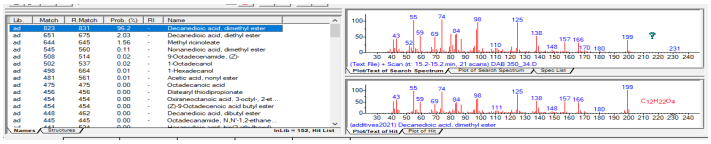


Figure 5. CDS Additive Library match from the Gel Glue at 350°C in Figure 4.

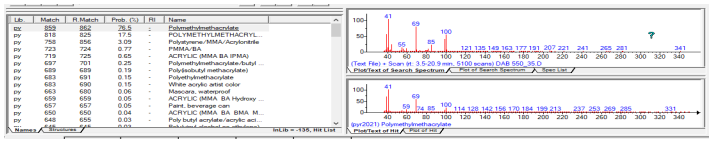
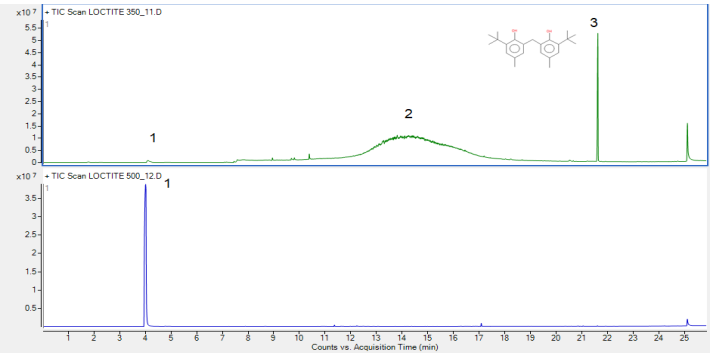


Figure 6. CDS Polymer Library match from the Gel Glue at 550°C in Figure 4.

Multi- Step Pyrolysis of the liquid glue is shown in Figure 7. Liquid glue also had an ethyl cyanoacrylate match for the baseline rise at 350°C, but the shape of this region differs slightly from the gel glue. This, plus the differences in the EGA's first peak could indicate a slightly different, cyanaoacrylate formulations.



Peak	Identification
1	methyl methacrylate
2	ethyl cyanoacrylate
3	2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-] phenol

Figure 7. Multi-step pyrolysis of liquid glue at 350 °C (top), and 550 °C (bottom).

Additionally, liquid glue had no decanedioic acid, dimethyl ester, but instead has a peak for 2,2'-methylenebis[6-(1,1-dimethylleth-yl)-4-methyl-] phenol, an antioxidant identified in CDS's additive library (Figure 8). Like the gel glue,the run at 550°C had a top match for poly(methyl methacrylate) in the polymer library (Figure 9).

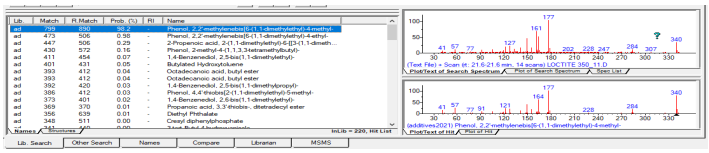


Figure 8. CDS Additive Library match from the Liquid Glue at 350°C in Figure 7.

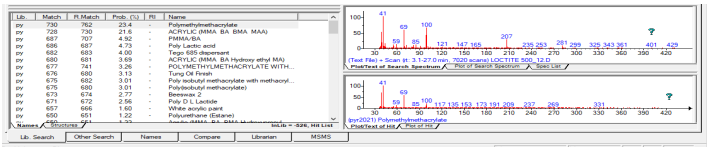


Figure 9. CDS Polymer Library match from the Liquid Glue at 550°C in Figure 7.

The amount of poly(methyl methacrylate) in the gel glue was quantified. To make the calibration curve, a calibration stock solution was first prepared by dissolving poly(methyl methacrylate) in dichloromethane, resulting in a final polystyrene concentration of 2.2 μg/μL. Aliquots of 2, 3, 4, and 5 μL stock solution with an absolute mass of polystyrene at 2.16, 4.32, 6.48. and 8.64 μg respectively were added to individual DISC tubes. The solvent was allowed to dry, and then each calibration standard, and the gel glue was pyrolyzed at 550°C. The area of methyl methacrylate plotted against the absolute mass of poly(methyl methacrylate), which resulted in a R^2 of 0.98 (Figure 10). Using this calibration curve, 0.10 mg of gel glue was found to have 7.7 μg of poly(methyl methacryate), a concentration of 77 μg/mg, and liquid glue was found to have 4.4 μg, or 44 μg/mg of poly(methyl methacrylate).

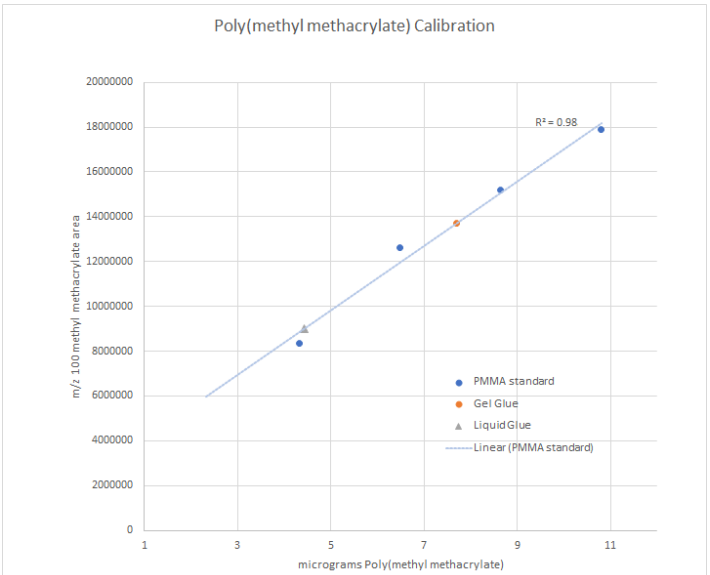


Figure 10. Poly(methyl methacrylate) Calibration with unknowns plugged in.

Conclusion

Both glues contained cyanoacrylates and methyl methacrylate. The difference in poly(methyl methacrylate) amounts could explain the difference in consistency between liquid and gel. The analyses indicated differences in the cyanoacrylate makeup, one glue had an anti-oxidant additive,while the other had a plasticizer additive. By applying a calibration curve, the amout of poly(methyl methacrylate) in each glue was quantified.

Evolved Gas Analysis plus Multi-step Pyrolysis GC-MS was useful in distinguishing between different "super glue" formulations, thermally separating analytes of 2 simplified chromatograms. These two techniques provide essential information for polymer identification. An EGA screening step provides quick information and serves as a guide for multi-step pyrolysis, which in turn provides in-depth information of polymeric materials. Finally, a calibration curve provided quantitative information about the chemical components.

References

1. Alan E. Ardis, "Preparation of monomeric alkyl alpha-cyano-acrylates", issued 19 April 1949, assigned to B.F. Goodrich Company.

2. Pyroprobe Application Decision Making Tree., CDS Analytical, 2021.