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Case Study
Off-gas Analysis
Jordi Labs

Released by:
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CONFIDENTIAL

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Introduction

The thermal stability of a polymer is a vital consideration in many industrial processes. It is important to gain a clear indication of the types of chemical species which are evolved and the temperatures at which they are released to insure worker safety during manufacturing. With the large number of additives and copolymers available for industrial use; volatile components can pose potential hazards to those exposed to large quantities or over prolonged periods. In some industrial applications such as porous glass manufacturing polymers may be intentionally degraded to facilitate the formation of porous structures. Characterization of the degradation products is then used to assess potential worker safety concerns.

Evolved gas analysis (EGA) and thermal gravimetric analysis (TGA) are two methods which can be used to identify the decomposition profile of a polymer, revealing volatile substances which may be hazardous and providing an outline of at what temperatures those products might evolve. Pyrolysis Mass Spectroscopy is a complimentary method which provides enhanced identification of individual volatile species. When used in conjunction, these methods can allow for reliable guidelines for safe and proper use of a material. With this study, we aim to demonstrate that the methods of EGA, TGA and PYMS may be utilized in tandem to effectively analyze a mixed polymer system: identifying the temperatures as the individual components degrade and quantifying the relative mass composition of the polymer blend.

For this case study, the following sample was analyzed:

1. A 50:50 blend prepared from poly(vinyl pyrrolidone) (PVP) and polysulfone (PSU) standards

And the following tests were performed:

1. Thermogravimetric Analysis (TGA)
2. Evolved Gas Analysis (EGA)
3. Pyrolysis Mass Spectroscopy (PYMS)

Objective

The goal of this analysis was to perform TGA/EGA to determine the thermal weight loss profile of the polymer blend and to identify the individual components at each weight loss step.

Summary of Results

The thermal profile revealed no appreciable weight loss up to 375 ºC indicating the material can be used without significant polymer decomposition below this temperature. Above 375 ºC, two peaks were observed in both the EGA and TGA experiments which occurred at analogous temperatures and were identified as poly(vinyl pyrrolidone) (PVP) followed by polysulfone (PSU) degradants by EGA. Two potentially carcinogenic compounds, benzene and 1-vinyl-2-pyrrolidinone were identified as decomposition products at elevated temperature.

Individual Test Results

A summary of the individual test results is provided below. All accompanying data, including spectra, has been included in the data section of this report.

Sample Preparation

TGA

Approximately 20 mg of a prepared 50:50 polymer blend was analyzed by TGA by increasing the temperature from 100 °C to 700 °C at a ramp rate of 30 °C/min (matching the conditions of the EGA analysis). This process was repeated to produce an additional replicate run.

EGA

Approximately 0.6 mg of a prepared 50:50 polymer blend was heated from 100-700 ºC at 30 ºC/min while the mass spectrum was continuously recorded. No chromatographic separation mechanism is used in EGA analysis; however the summed mass spectra can be compared to a polymer/additive mass spectrum database.

PYMS

Analysis by PYMS was conducted using a single shot technique. The single shot experiment consists of heating a sample to a desired temperature while released species are cryogenically trapped and then analyzed by GCMS. Approximately 0.5 mg of the (vinyl pyrrolidone) (PVP) and polysulfone (PSU) standards were heated to 550 ºC and 650 ºC respectively.

Prominent peaks found in PYMS typically include fragments of the polymer as well as monomer, antioxidants and other additives. Sample peaks were compared with over 796,613 reference compounds using the NIST/EPA/NIH mass spectral search program.

Results

TGA

Across both replicates, the sample exhibited two weight loss steps and an average weight loss of 78.96% was observed. The residual weight observed after reaching 700 ºC is due to the presence of sulfur and nitrogen in the polymer structures. The individual steps had onset temperatures of approximately 350 and 478 °C. The TGA profile for replicate 1 is presented in **Figure 1**, along with the EGA profile. The major weight loss steps are summarized in **Table 1**.

EGA

The EGA profile of the sample consists of two peaks, as seen in **Figure 1**. The first evolved between 400-520 ºC, and the second evolved between approximately 500-700 ºC. The mass spectral data for the first peak is consistent with poly(vinyl pyrrolidone), whereas the summed mass spectrum for the second peak is consistent with polysulfone.

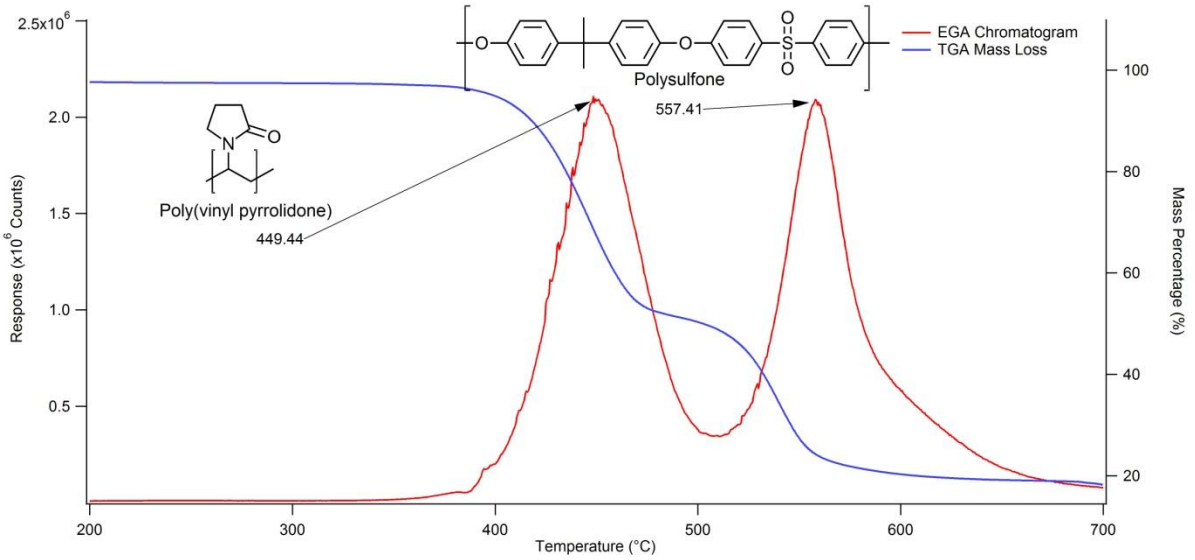

Figure 1 Combined thermal profile of the sample up to 700 ºC

Table 1. Summary of results for polymer blend				
Temperature (ºC)	**TGA**			**EGA**
	Sample weight loss (%)		**Average Loss (%)**	**Compound Observed**
	Rep 1	**Rep 2**		
100 to 477	44.43	44.61	44.52	PVP
477 to 700	34.54	34.39	34.47	PSU
Total weight loss	**78.91**	**79.00**	**78.96**	**-**

PYMS

While EGA is a useful technique for identifying polymeric components, the process does not involve any chromatographic separation to isolate specific degradants which may be produced as the polymer is heated. Pyrolysis mass spectrometry (PYMS) has the added advantage of providing a chromatographic separation to isolate individual chemical species but does not provide information on the temperature at which evolution occurs. Combining these methods provides a complete picture of the identity and temperature at which volatile species are released.

As an example, PYMS spectra for both PVP and PSU standards were obtained and are shown in **Figure 2** and **Figure 3**. The main degradants evolved from each polymer are identified. PVP degradation was found to result in release of 1-vinyl-2-pyrrolidinone among other components. This compound is suspected to cause cancer. Similarly, PSU degradation was observed to release benzene which is a known carcinogen. The EGA data was extracted using a mass associated with each species to provide a profile of the temperature of evolution for each compound as shown in **Figure 4**.

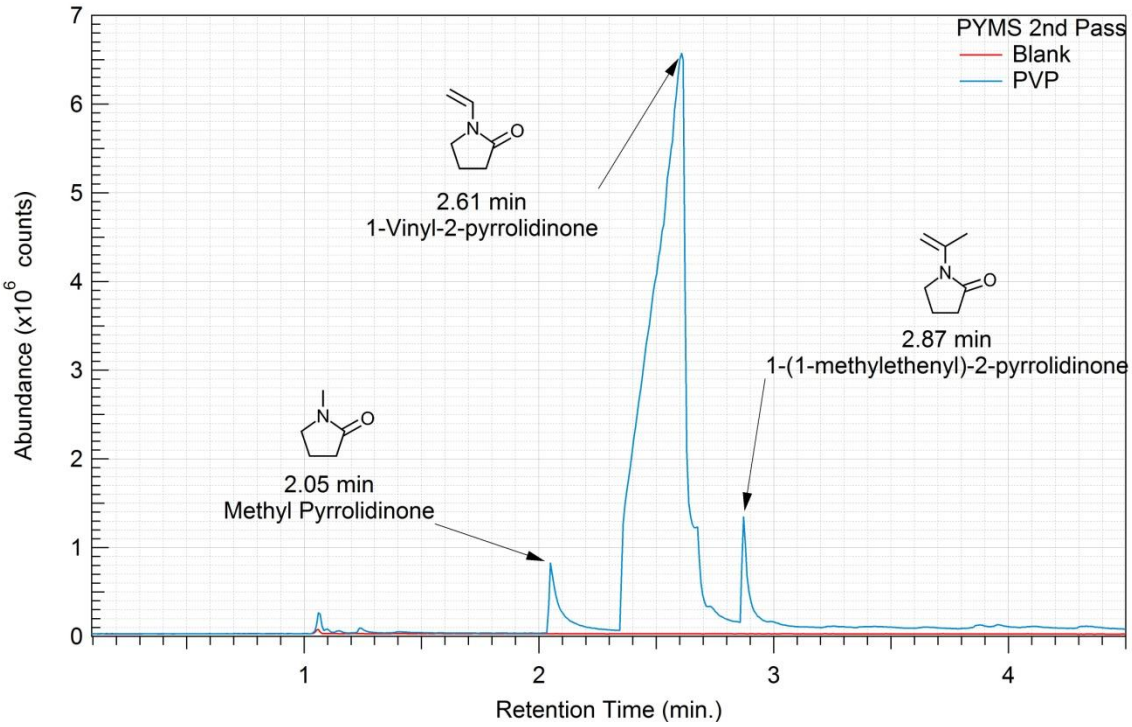

Figure 2: Degradation products of PVP seen by PYMS

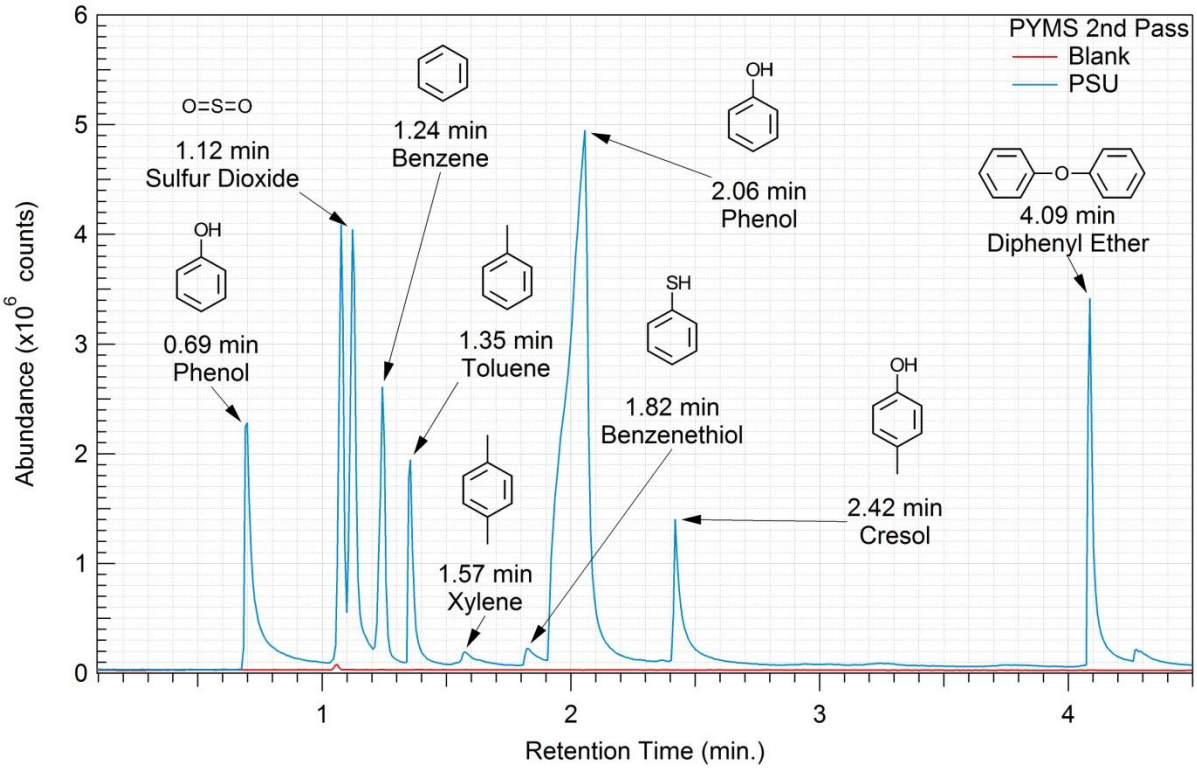

Figure 3: Degradation products of PSU seen by PYMS

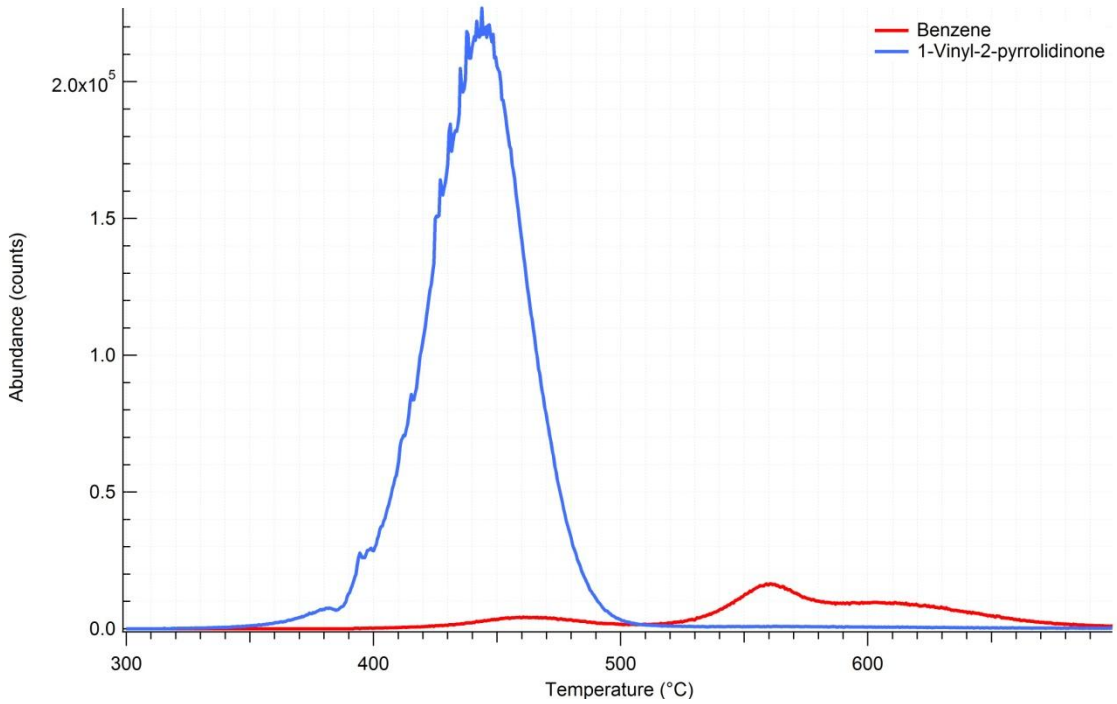

Figure 4: Temperature profile of Benzene and 1-Vinyl-2-pyrrolidinone evolution by EGA.

Analysis Conditions

EGA

The solid samples were analyzed using a Hewlet 6890 gas chromatograph in conjunction with a 5975B mass selective detector using a Frontier Laboratories double shot pyrolyzer model PY2020ID. Data acquisition was accomplished using chemstation software. Sample peaks were compared with over 796,613 reference compounds using the NIST/EPA/NIH mass spectral search program.

The following run conditions were applied for gas chromatographic analysis:

Sample Size = ~0.6mg
GC Temperature: 325 ºC
EGA Temperature: 100-700 ºC
EGA ramp rate: 30 ºC per minute
Detector Temperature: 315 ºC
Injector Split = 20:1
Mass Range: Low Mass = 18 High Mass = 800
Column = None (transfer line)

TGA

Analysis of the samples was accomplished using a TA 500 Thermogravimetric Analyzer in combination with TA Universal Analysis software. Approximately 10-20 mg of the sample was weighed into a platinum weigh boat for each analysis. Samples were run under a nitrogen atmosphere and heated from 100 °C to 700 ºC at 30 °C/min.

Closing Comments

Deformulation of an unknown material is intended to provide a best estimate of the chemical nature of the sample. All chemical structures are supported by the evidence presented but are subject to revision upon receipt of additional evidence. Additional factors such as material processing conditions may also affect final material properties.

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Jordi Labs specializes in polymer testing and has 30 years experience doing complete polymer deformulations. We are one of the few labs in the country specialized in this type of testing. We will work closely with you to help explain your test results and solve your problem. We appreciate your business and are looking forward to speaking with you concerning these results.

Sincerely,

Leland Martin

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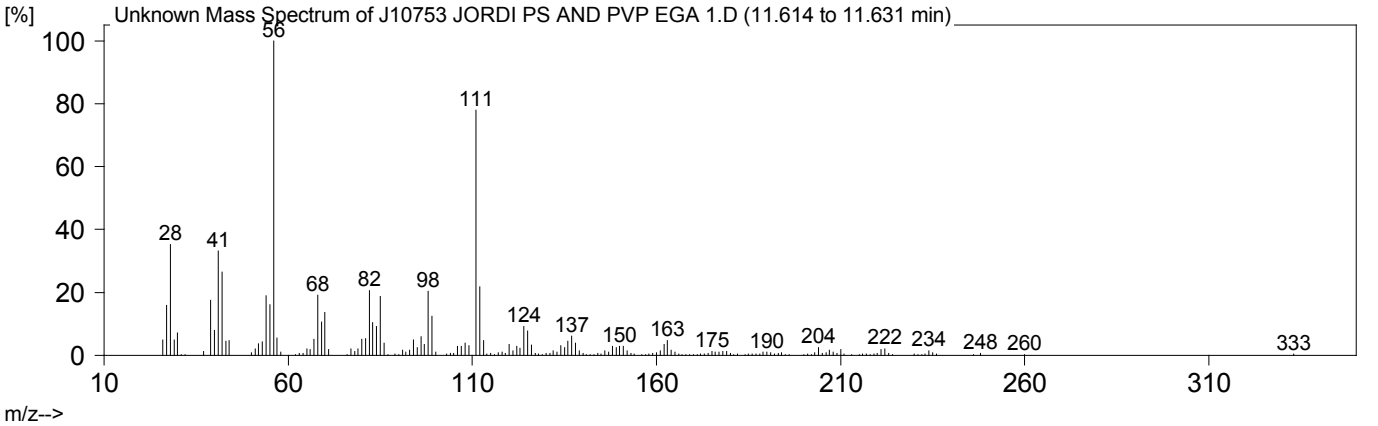
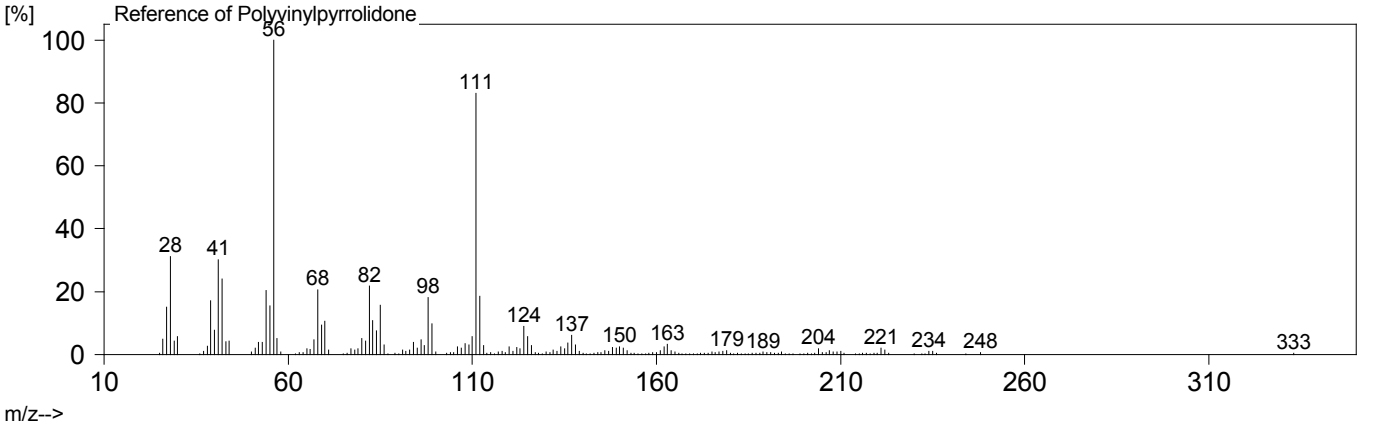
EGA Data

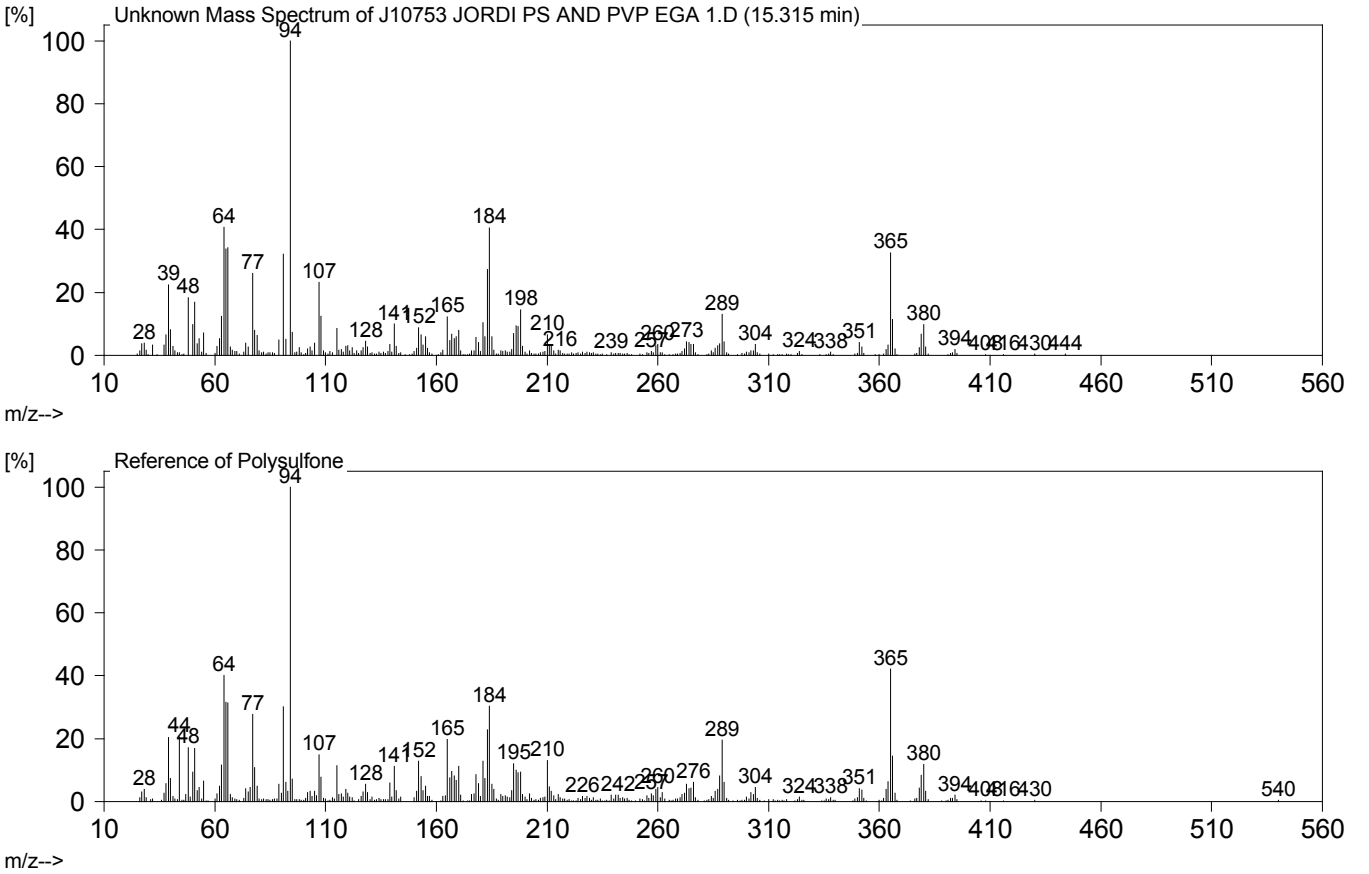
F-Search Results --- Mass Spectrum Comparison



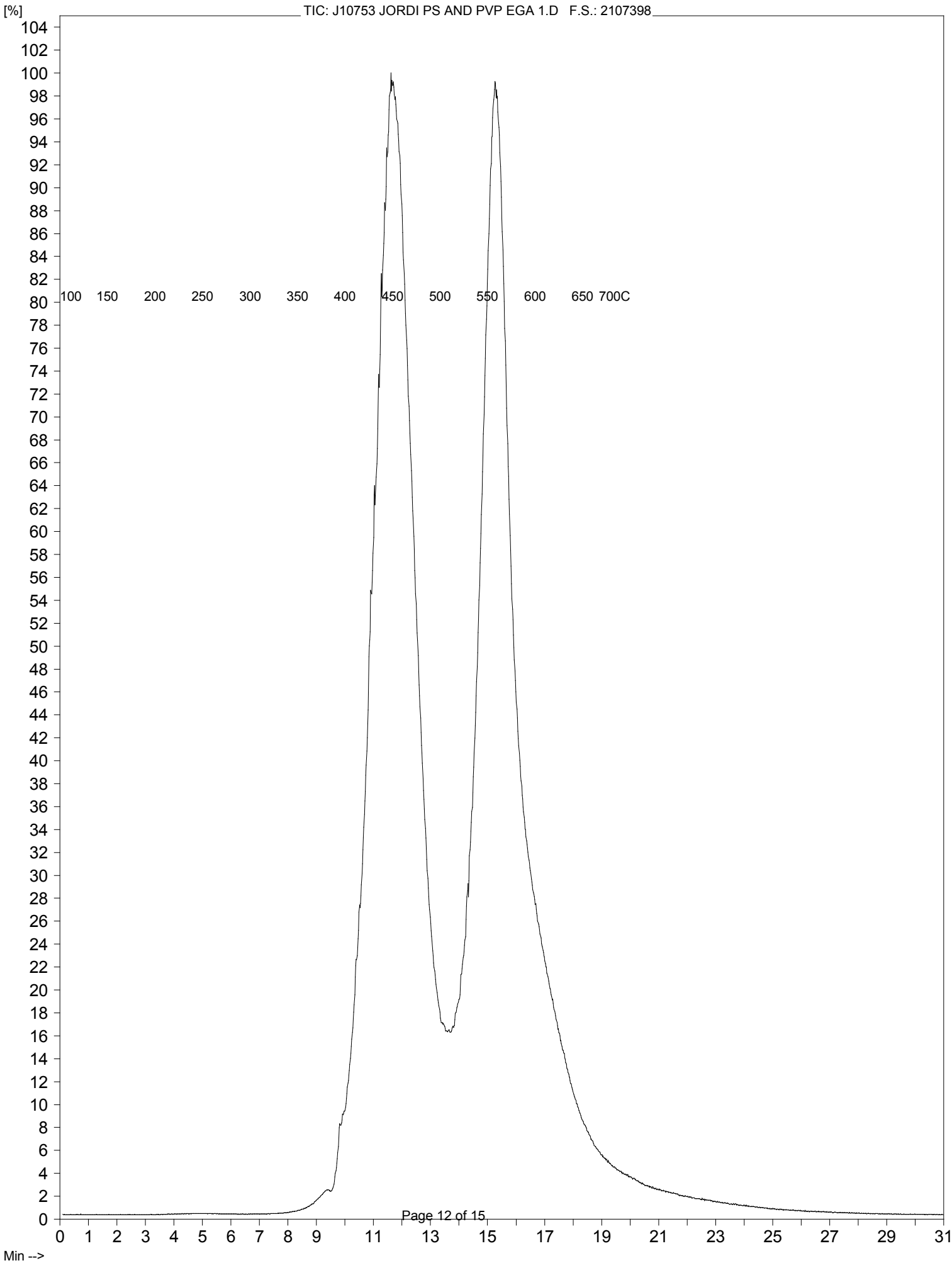


	Compound	Polymer / Additive	Entry ID	Rt Idx	Rt Time	MW	Qual [%]
1		Polyvinylpyrrolidone		-	11.73	-	99
2		PVP30K		-	11.74	-	91
3		Polyvinylpyrrolidinone (PVP) K-120 (13-		-	17.75	-	81
4		n-Vinylpyrrolidone/Vinyl Acetate		-	11.95	-	64
5		Chimassorb 7.5-9min		-	8.98	-	41
6		n-Vinylpyrrolidone/Vinyl Acetate		-	11.95	-	41
7		Irganox 565		-	8.75	-	36
8		Butyl Palmitate		-	2.11	-	36
9		Nylon 6 [Poly(caprolactam)]		-	12.11	-	36
10		Poly(vinyl acrylamide)	SP2 Cap #39	-	9.79	-	35
11		SP^2 #27 Cryoground Nylon 6 (Polycapro		-	12.18	-	33
12		Irganox 1098		-	9.61	-	32
13		SP^2 Nylon 6 [Poly(caprolactam)] Pellet		-	12.29	-	31

F-Search Results --- Mass Spectrum Comparison



	Compound	Polymer / Additive	Entry ID	Rt Idx	Rt Time	MW	Qual [%]
1		Polysulfone		-	15.26	-	95
2		Polysulfone		-	15.91	-	81
3		Poly(P-Phenylene ether sulphone)		-	16.66	-	49
4		Purple Gloves		-	12.51	-	19
5		Phenoxy Resin		-	11.68	-	18
6		Phenoxy Resin		-	13.03	-	18
7		HighFive Gloves		-	12.46	-	18
8		Poly(vinyl acetate)		-	12.11	-	17
9		Vinyl Chloride/Vinyl Acetate 17		-	12.33	-	17
10		Vinyl Chloride/Vinyl Acetate Hydroxylpr		-	12.23	-	16
11		Vinyl Chloride/Vinyl Acetate/Vinyl Alcol		-	12.17	-	16
12		Poly(vinyl alcohol)1		-	11.80	-	15
13		Polyvinyl chloride carboxylated		-	12.19	-	15

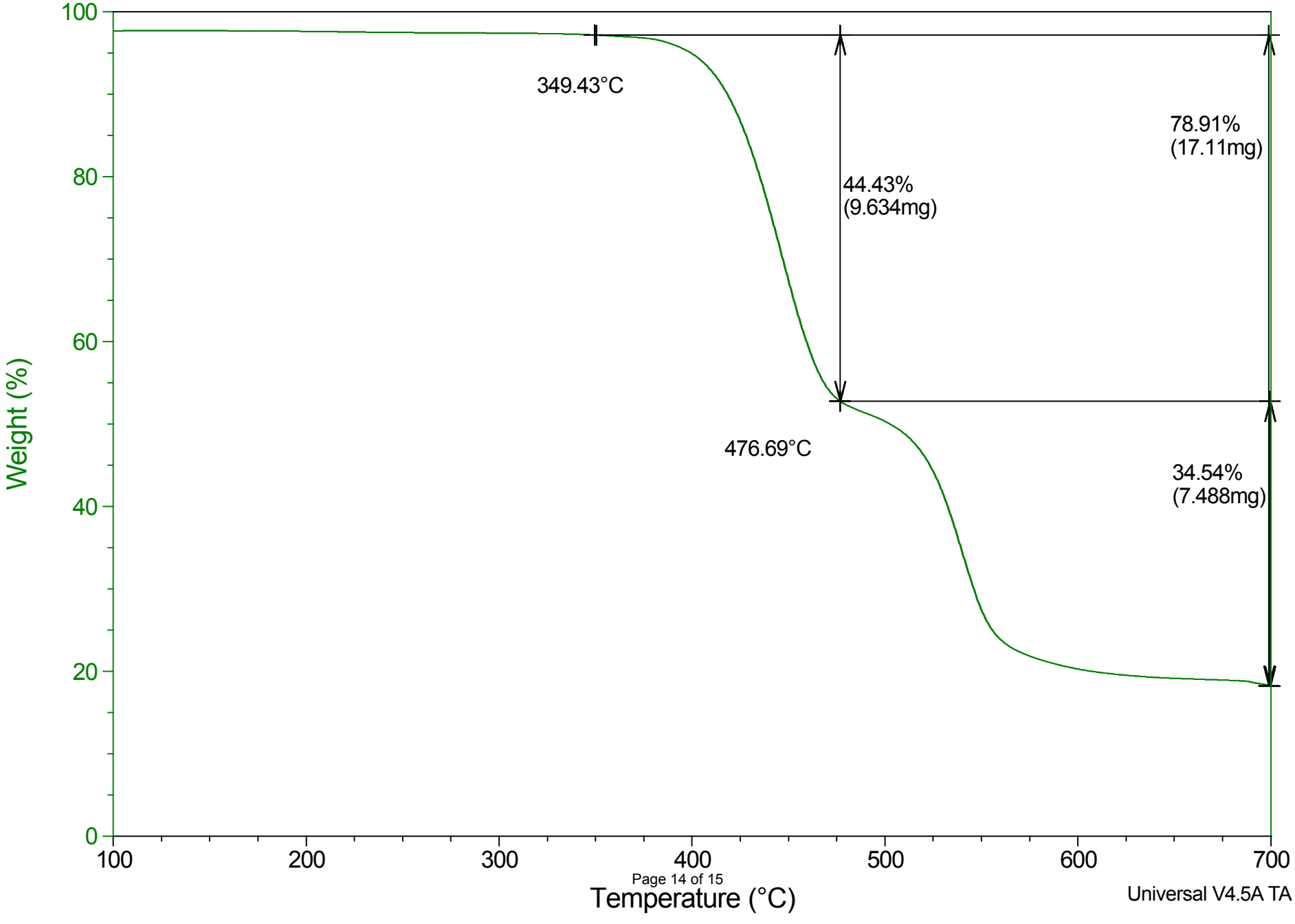

[%]
TIC: J10753 JORDI PS AND PVP EGA 1.D F.S.: 2107398
100 150 200 250 300 350 400 450 500 550 600 650 700C
Min -->

TGA Data

Sample: Polysulfone-PVP blend
Size: 21.6810 mg
Method: Ramp
Comment: 11.196 mg Polysulfone 11.134 mg PVP

TGA

File: R:...\TGA\Polysulfone PVP blend.003
Operator: JNW
Run Date: 18-Feb-2016 21:37
Instrument: TGA Q500 V20.13 Build 39



Universal V4.5A TA Instruments

Sample: Polysulfone-PVP blend
Size: 17.0290 mg
Method: Ramp
Comment: 8.896 mg Polysulfone 8.728 mg PVP

TGA

File: R:...\TGA\Polysulfone PVP blend.004
Operator: JNW
Run Date: 18-Feb-2016 22:57
Instrument: TGA Q500 V20.13 Build 39