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Thermal Degradation Investigation of Polyurethane Elastomers using Thermal Gravimetric Analysis – Gas Chromatography/Mass Spectrometry

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Thermal Degradation Investigation of Polyurethane Elastomers using Thermal Gravimetric Analysis – Gas Chromatography/Mass Spectrometry

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Abstract

The thermal degradation of two polyurethane elastomers was investigated via thermal gravimetric analysis coupled with gas chromatography/mass spectrometry. Decomposition occurs in a multi-step fashion with similar onset temperatures for both materials. Apparent activation energy plots were calculated inside Model-Free Kinetics software and utilized to construct conversion and isothermal conversion tables. These tables predicted material degradation as a function of temperature and time. Isothermal experiments were performed and found to be in good agreement with the predictions made from the Model-Free Kinetics software package. Volatile products evolved during the multistep decomposition were captured at various times and analyzed using the coupled gas chromatography/mass spectrometry system. This analysis demonstrated strong correlation between the degradation products and known decomposition mechanisms for polyurethanes.

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NOMENCLATURE

AMU	atomic mass unit
E_a	activation energy
DSC	differential scanning calorimetry
DTG	derivative thermogravimetric analysis
GC/MS	gas chromatography / mass spectrometry
K	Kelvin
MFK	model free kinetics
TA	thermal analysis
TDI	toluene diisocyanate
TG	thermal gravimetric
TGA	thermal gravimetric analyzer
wt%	weight percent

1. INTRODUCTION

1.1 Background

This report focuses on the thermal degradation of polyurethane elastomers commonly used to encapsulate electronic components. By characterizing the decomposition process, products, and kinetics, Sandia National Laboratories can gain a more complete picture about how these materials will behave under abnormal environments. Furthermore, this work bridges a gap uncovered during thermal modeling and simulation performed by Silva et al. as part of the W78 program. The elastomers in this investigation are listed in Table 1.

Table 1. Formulation of Conathane® EN-7 and EN-8 polyurethane elastomers

Material	Description	Components	References
EN-7	Polyurethane elastomer	Part A Isocyanate Prepolymer Part B Polyol *Iron acetylacetonate catalyst: 40 ppm	[1], [2]
EN-8	Polyurethane elastomer	Part A Isocyanate Prepolymer Part B Polyol *Iron acetylacetonate catalyst: 250 ppm	[1], [2]
Component weight mix ratios for both elastomers are: 100 Part A to 18.8 Part B *The iron catalyst comes pre-mixed with either Part A or Part B			

1.2 Polyurethane Elastomers

The following section examines two polyurethane elastomers synthesized through the general reaction mechanism presented in Figure 1. The complete structure was shown in previous work and Appendix A [1].

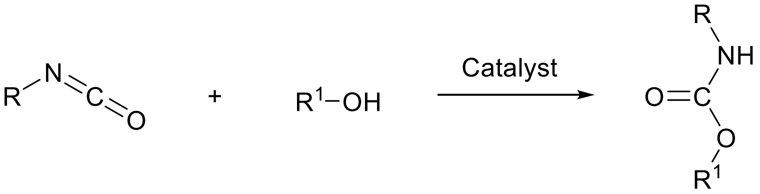


Figure 1. General formation of urethane linkages in polyurethane elastomers

1.2.1 EN-7 and EN-8

EN-7 is a commercial product developed by Conap, with assistance from Sandia, as a replacement for EN-4/5 due to toxicity concerns over the mercuric catalyst. Though the catalyst was replaced with iron acetylacetonate, the backbone of EN-7/8 still contains toluene diisocyanate (TDI) which is toxic and a suspected carcinogen in the free state [1].

The formula is a mixture of two parts, and the iron acetylacetonate catalyst is included in either Part A or Part B:

- Part A Isocyanate Prepolymer, contains 2,4-TDI capped polybutadiene diol with about 10% unreacted TDI
- Part B Polyol, 50/50 mix of 1,3-dihydroxy-2-ethylhexane and N,N'-(2-hydroxypropyl)aniline

EN-8 is identical in composition to EN-7 except for the higher concentration of catalyst, which enables EN-8 to be slowly cured at room temperature instead of the higher temperatures used in curing EN-7 [2]. Per the technical data sheet, the physical properties of both elastomers are nearly identical when processed as recommended.

1.3 Decomposition Mechanisms and Model-Free Kinetics

The primary decomposition mechanisms of polyurethanes take place at the urethane linkages and have been reported previously [3, 4]. It is generally accepted that there are three main mechanisms, which are represented with EN-7/8 in Figures 2 – 4.

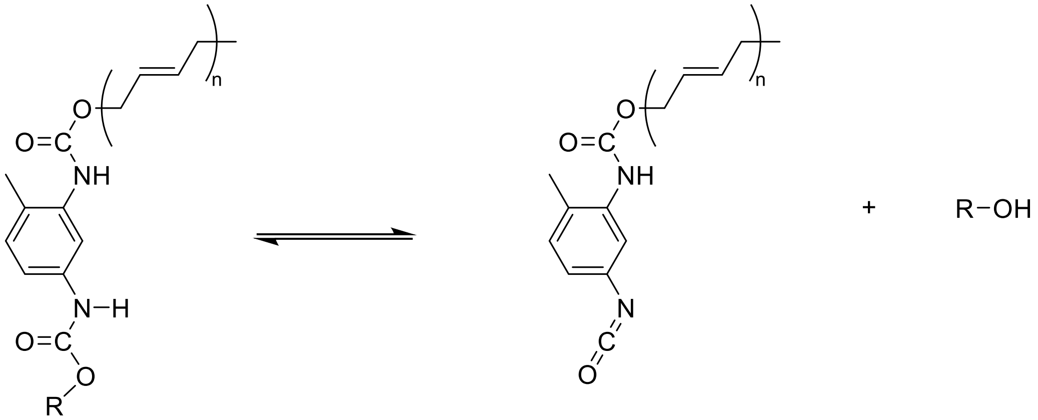


Figure 2. Dissociation of urethane linkage into isocyanate and alcohol

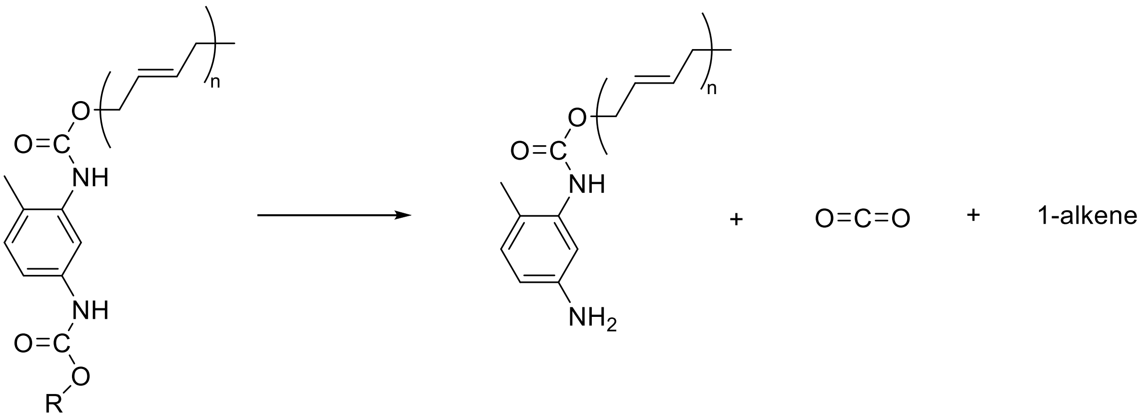


Figure 3. Scission at the urethane linkage to generate a primary amine, carbon dioxide, and a terminal alkene

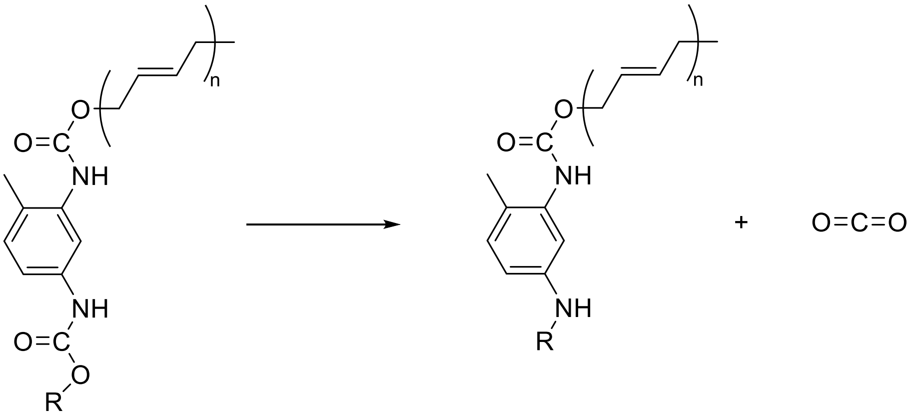


Figure 4. Scission at the urethane linkage to generate a secondary amine and carbon dioxide

The R group in Figures 2 – 4 is the same as the R^1 group in Figure 1; see the chemical structure of the polyols formulated in Part B of the polyurethane (section 1.2.1) for clarification. It is important to note that the reaction in Figure 2 is reversible, i.e. the isocyanate can react with the alcohol and reform the polyurethane linkage.

Rates of reaction are typically measured isothermally and fit to the Arrhenius equation for simple single-step reactions. Kinetic parameters such as the activation energy (E_a) and rate constant (k) are extracted from this analysis and provide insight into the energy barrier and speed of a given reaction. In a report by Colt and Cordaro there is a discussion of the Model-Free Kinetics (MFK), used to extract kinetic parameters [5]. Specifically, it discusses how calculating E_A numerically is more representative of a system with multi-step decomposition processes that vary in their contributions to the overall effective E_a. The polyurethane elastomers described in this report decompose in a multi-step fashion.

2. EXPERIMENTAL METHODS

The following section discusses experimental methods to collect and analyze data.

2.1 Thermal Degradation Analysis

The decomposition of the materials was investigated using a Mettler-Toledo thermal gravimetric analyzer with differential scanning calorimetry (DSC) capabilities (Instrument TGA/DSC3^{+}). Approximately 5 – 7 mg samples were contained in one of two pan types with no lid:

- A 40 µL aluminum pan
- A 70 µL ceramic alumina crucible

The solid elastomers were cut into small pieces to allow them to fit into the pans and crucibles. All samples were heated under a blanket of nitrogen flowing at 20 mL/min. Samples were heated from 35 to 600°C at rates of 0.5, 1, 2, 6, 8, 10, 12, 14, 16, 18, and 20 K/min. Samples used with the gas chromatography / mass spectrometer contained approximately 20 mg and were heated at a rate of 10 K/min from 35 to 600°C. Care was taken to be consistent with the crucible type and sample mass. As heating rates increase, the thermal conductivity of both the pan and sample materials play a larger role in the degradation onset. Onset temperatures shift to higher values for an alumina pan and for larger masses, when comparing to an aluminum pan and smaller masses, respectively.

2.2 Model-Free Kinetics

Mettler Toledo's "Model-Free Kinetics" software package was used to calculate the apparent activation energy of each material as a function of conversion (α), where α is equivalent to 100 – wt%. Curves at heating rates of 0.5, 1, and 2 K/min were used for the analysis [6].

2.3 Gas Chromatography / Mass Spectrometry

Gas chromatography/mass spectrometry (GC/MS) analysis was conducted on the exhaust gas from a TGA using an SRA IST16-Storage Interface and an Agilent GC/MS instrument (7890B GC / 5977B MSD). First, a preliminary TGA experiment was performed to determine the capture time intervals for storage in the IST16. Second, the IST16 was programmed to collect the gas samples at the predetermined time intervals. The IST16 uses a heated transfer line held at 150°C to capture the exhaust gas in a 250 µL storage loop. Third, the TGA experiment was repeated and up to 15 gas samples captured. Lastly, the 250 µL gas samples were sequentially injected onto the GC column and analyzed using the following parameters:

Injection: Inlet at 150^{o}C, split injection, 20:1
Oven: 40^{o}C for 3 mins, 10^{o}C/min to 310^{o}C then held for 10 minutes
Column: HP-5MS, (5%-phenyl)-methylpolysiloxane, 30m x 0.250mm x 0.25µm
MS Scan: Atomic mass unit (AMU) range 19-500, MS Source 230^{o}C, MS Quad 150^{o}C

3. RESULTS AND DISCUSSION

3.1 Understanding Results by Analysis Technique

3.1.1 Thermal Gravimetric Analysis

A report by Colt and Cordaro summarized the use of thermal gravimetric analysis (TGA) for understanding reaction mechanisms [5]. A brief description is extracted and provided herein. Thermal analysis (TA) using weight-loss as an indicator of reaction extent is called TGA. Thermal gravimetric (TG) curves collected show that varying the heating rate changes how the materials degrade. TG curves diverge from one another or intersect, called crossing-over, when the heating rate is significantly different and at low or high reaction conversions. Crossing-over of TG traces when comparing different heating rates occurs for one primary reason: Elementary reactions have different activation energies. In other words, competing mechanisms can turn on or off depending on the heating rate employed for thermal decomposition. A seemingly single-step decomposition trace could be representative of multiple individual elementary reactions, all having different kinetic parameters.

3.1.2 Derivative Thermogravimetric Analysis

Material degradation can be a complicated process that occurs in multiple steps. The steps are identified by their inflection points, where the rate of mass loss is at a maximum. In some cases, overlapping degradation steps are not clearly visible in TG curves and the inflection points are obscured. A plot of the first derivative of the TG trace (DTG) can help identify the degradation steps, as inflection points in the TG curves become local minima in the DTG trace. The minima are a useful aid in identifying multi-step decomposition processes [5].

3.1.3 Model-Free Kinetics

Apparent activation energies were calculated and plotted in the software as described in section 2.2. Potentially a combination of heating rates both high and low can be used, however the slower heating rates give better resolution for the degradation processes [7]. A broad range of heating rates can also lead to mechanistic changes that manifest in TGA curves crossing-over, resulting in mathematically nonsensical MFK analyses. Activation energy plots, from curves that did not cross-over, were further utilized to construct conversion and isothermal conversion (iso-conversion) tables. These tables are different methods of analyzing the elastomer’s decomposition but use the same three parameters: conversion, temperature, and time. Both methods can be used to understand degradation without having to perform the isothermal experiments.

3.1.4 Gas Chromatography / Mass Spectrometry

Observed degradation within TGA is better understood if the volatile products are known. These degradation products, contained in the exhaust gas of the TGA, were analyzed via GC/MS to identify the chemical species. Ideally, mass spectrometry data can lead to positive identification of all compound peaks in a chromatogram. More often, the mass spectrum library can match only a portion of the compounds and/or the match probability is low. The products successfully matched can then be used to support hypothesized or suspected degradation mechanisms. A few example chromatograms are provided in Appendix B and a comparison of direct injection versus IST16 storage is provided in Appendix C.

3.2 EN-7 and EN-8 Results

3.2.1 TGA in Nitrogen

The TGA curves in Figure 5 show the thermal degradation of EN-7 at four different heating rates. We immediately observe that the curves cross-over in the range of 75 – 55 wt% and that there is a shift in the onset temperatures of decomposition with heating rate. Both observations can be explained by the chemical reactions taking place in the material. Since these reactions happen over a period of time and activate with differing amounts of energy (i.e. fraction of molecules with energy necessary to overcome the barrier and react, a Boltzmann distribution of states), they are naturally dependent on the heating rate. Thus, when the heating rate is decreased, the maximum reaction rate occurs at a lower temperature because molecules spend more time at energy states necessary for reaction [8]. Also visible in the TGA plot, a single-step degradation process initiates at around 215°C while a multi-step process initiates around 390°C. The DTG curve, plotted for the heating rate of 2 K/min on the same figure, displays these initiation temperatures and number of steps more clearly.

The dissociation of the urethane linkage into isocyanate and alcohol, Figure 2, is a reversible reaction reported to initiate between 200 to 250°C [3]. Little mass would be lost at these temperatures, since the degradation products are not volatile. The mechanism in Figure 3 is irreversible with the formation of carbon dioxide, a terminal alkene, and a primary amine. This mechanism could explain the degradation behavior initiated at 215°C. At higher temperatures, more reactions become energetically favorable, leading to the multi-step process visible above 390°C. It is probable that all three mechanisms in Figures 2 – 4 are occurring simultaneously along with secondary degradation reactions along the polymer backbone at these higher temperatures.

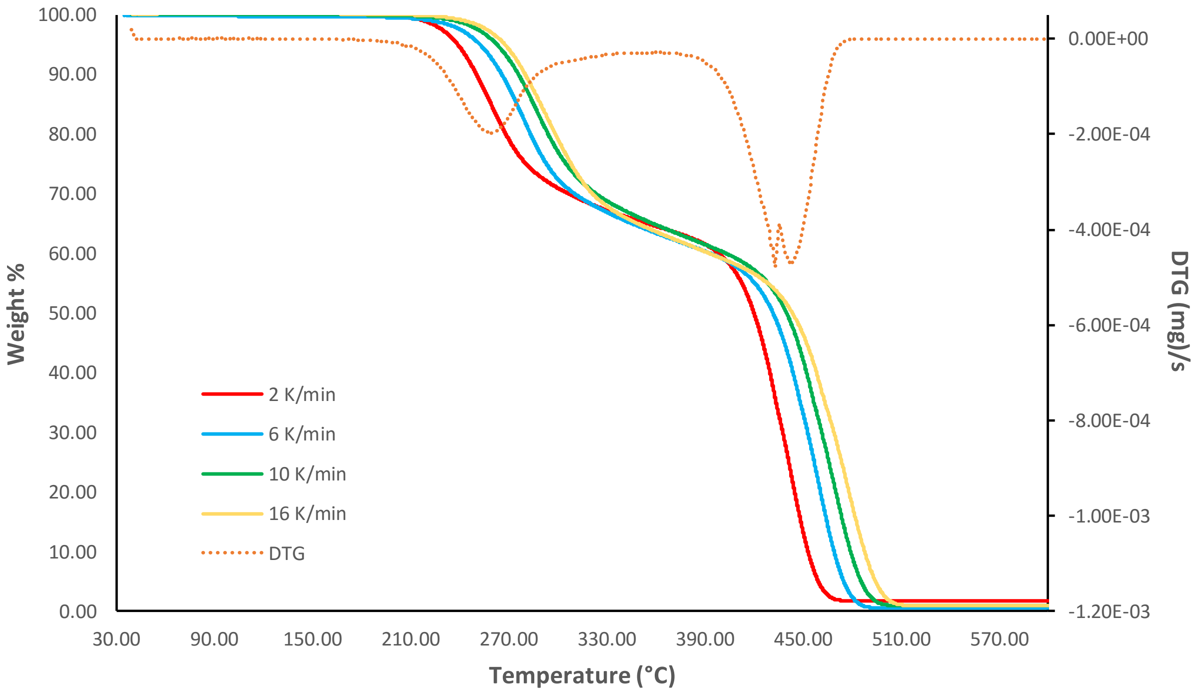


Figure 5. TGA of EN-7 with DTG curve

The thermal degradation of EN-8 occurs similarly to that of EN-7, shown in Figure 6. The trend in onset temperature with heating rate (via TGA) and degradation initiation temperatures (via DTG) are the same as for EN-7. The difference lies in the crossing-over behavior. EN-8 TGA curves cross over to a lesser extent than those of EN-7, which correspond to changes in the degradation mechanisms as discussed in section 3.1.1. However, it is not expected that the mechanisms would be significantly different since the chemical structures for both materials are identical with the possible exception of cross-link density.

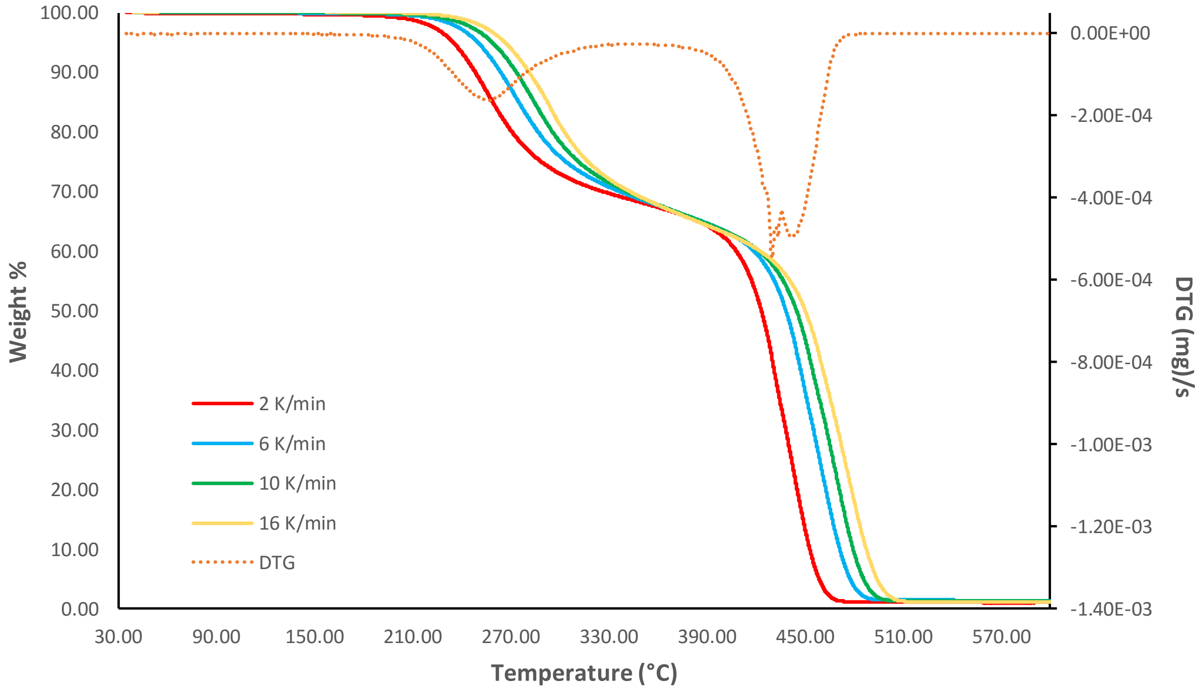


Figure 6. TGA of EN-8 with DTG curve

3.2.2 Model-Free Kinetics

The apparent activation energy curve as a function of conversion, Figure 7, was calculated for EN-7 from three heating rate curves (0.5, 1, 2 K/min) as stated previously. There are two distinct regions in the graph that correspond well with the first and second steps visible by TGA and have activation energies of approximately 130 kJ/mol and 270 kJ/mol.

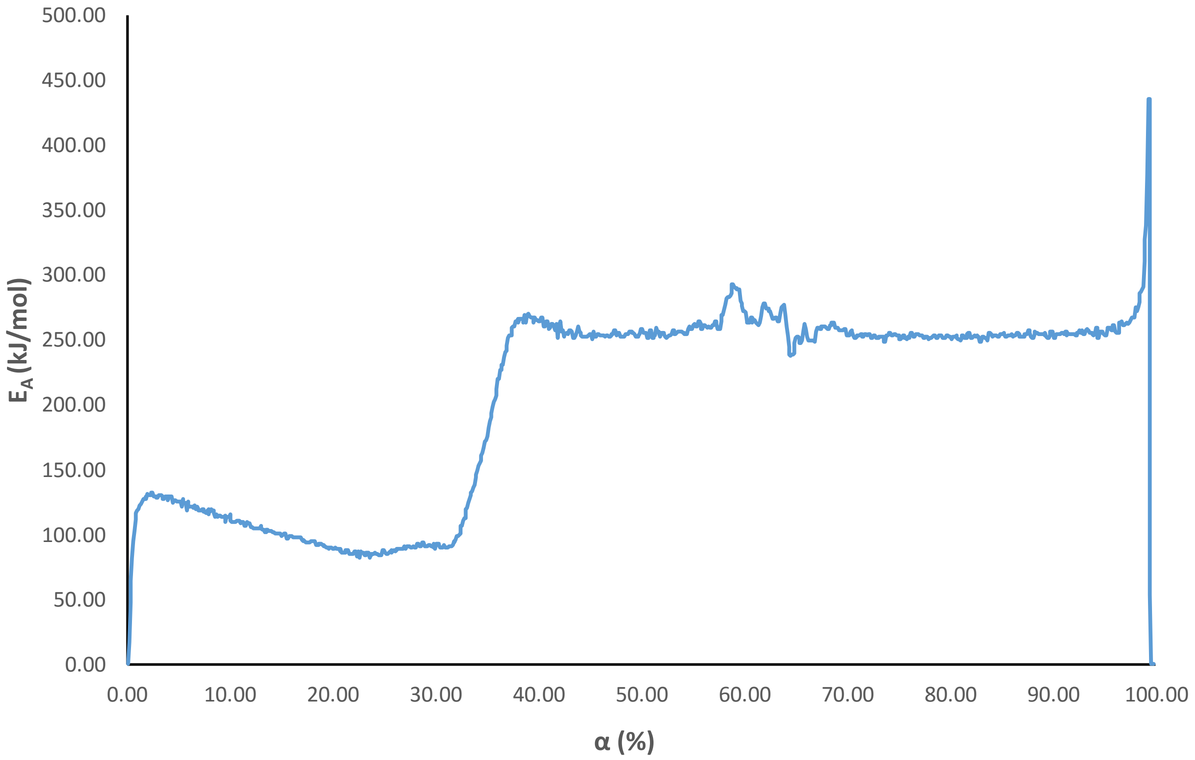


Figure 7. Apparent activation energy plot as a function of conversion for EN-7

The apparent activation energy curve was then used to construct the conversion and iso-conversion tables discussed in section 3.1.3, which are found in Tables 2 and 3 below. For example, if EN-7 is held at 250°C for 57 minutes it would lose 20 wt%. Without performing many isothermal experiments, this method allows the degradation of EN-7 in abnormal thermal environments to be estimated. It is important to understand that the results of the MFK analysis were obtained by using TGA curves at low heating rates, therefore the tables may not be a useful predictor of thermal behavior at high heating rates.

Table 2. Calculated conversions of EN-7 using MFK

Table Values: Time (min)		Temperature (°C)							
		150	**200**	**250**	**300**	**350**	**400**	**450**	**500**
α (%)	**2**	-	82	30	18	15	12	10	8
	5	-	148	33	20	15	12	10	8
	10	-	247	39	21	16	12	10	8
	15	-	341	46	22	16	12	10	8
	20	-	449	57	23	16	13	10	8
	25	-	644	81	28	17	13	10	8
	30	-	-	197	47	21	14	10	9
	40	-	-	-	-	356	26	12	9

Table 3. Calculated iso-conversions of EN-7 using MFK

Table Values: Temperature (°C)		α (%)							
		2	**5**	**10**	**15**	**20**	**25**	**30**	**40**
Time (min)	**5**	-	-	-	-	-	-	-	-
	10	445	445	445	446	447	449	458	475
	20	301	302	305	309	316	328	353	410
	40	229	239	249	256	265	278	307	388
	60	210	223	233	240	248	261	289	379
	120	190	204	214	221	228	238	264	366
	240	176	191	201	207	212	221	244	355
	480	165	180	189	194	199	206	227	346

The validity of the MFK modeling for EN-7 was tested by performing three isothermal experiments. Samples were inserted into the TGA at temperatures of 180, 200, and 250°C and held for 480, 247, and 60 minutes. Using Table 3 and interpolating, the expected conversions are 5, 10, and 20%. Figure 8, a plot of weight % versus time, shows good agreement for the MFK predictions at 180°C (α = 4%) and 200°C (α = 10%) and is close for 250°C (α = 22%).

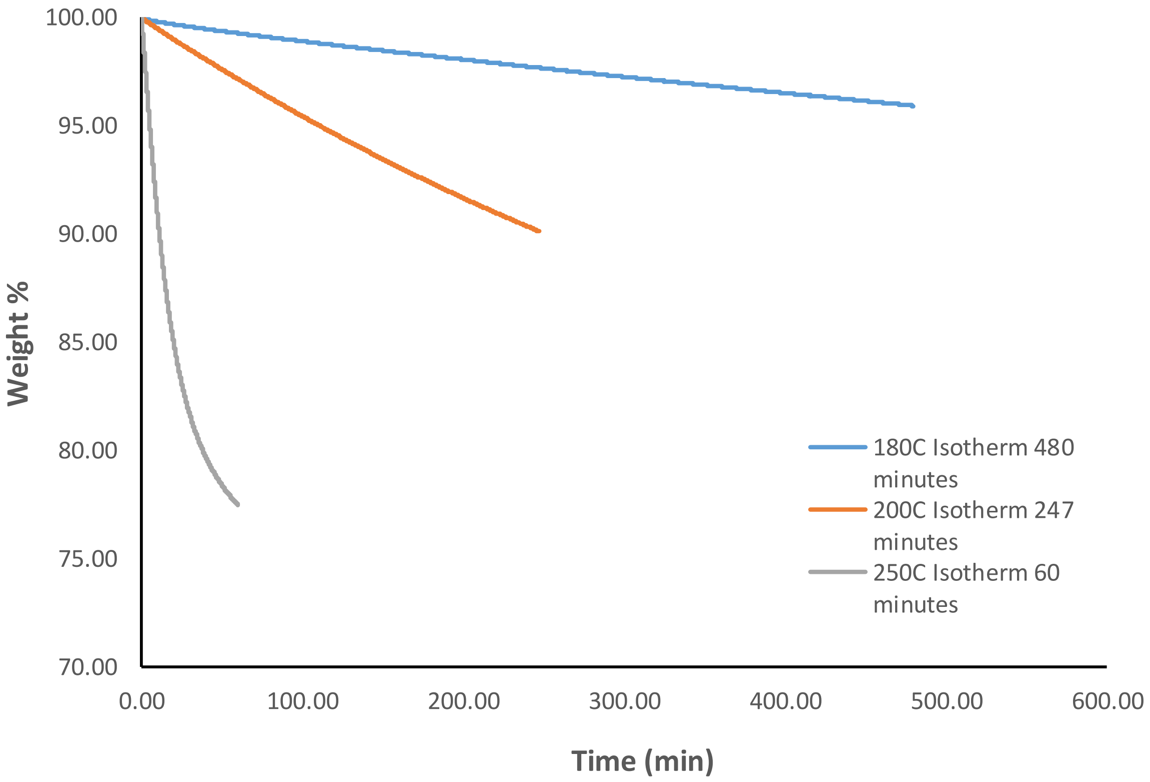


Figure 8. Conversion as a function of time for three isothermal experiments on EN-7

The apparent activation energy curve as a function of conversion, Figure 9, was calculated for EN-8 from the same heating rates as EN-7 (0.5, 1, 2 K/min). Again, there are two distinct regions in the graph that correspond well with the first and second steps visible by TGA and have activation energies of approximately 135 kJ/mol and 350 kJ/mol. Interestingly, the activation energies of the first degradation step are similar for both EN-7 and EN-8 but the activation energies (peak maximum) of the second degradation step differ by a substantial amount (80 kJ/mol). If the peak is ignored and a flat line fit through the data from 40 ≤ α ≤ 90, then the activation energy is 250 kJ/mol for both elastomers. This would indicate that, even though EN-8 requires more energy to activate the second degradation step, the elastomers degrade similarly after activation.

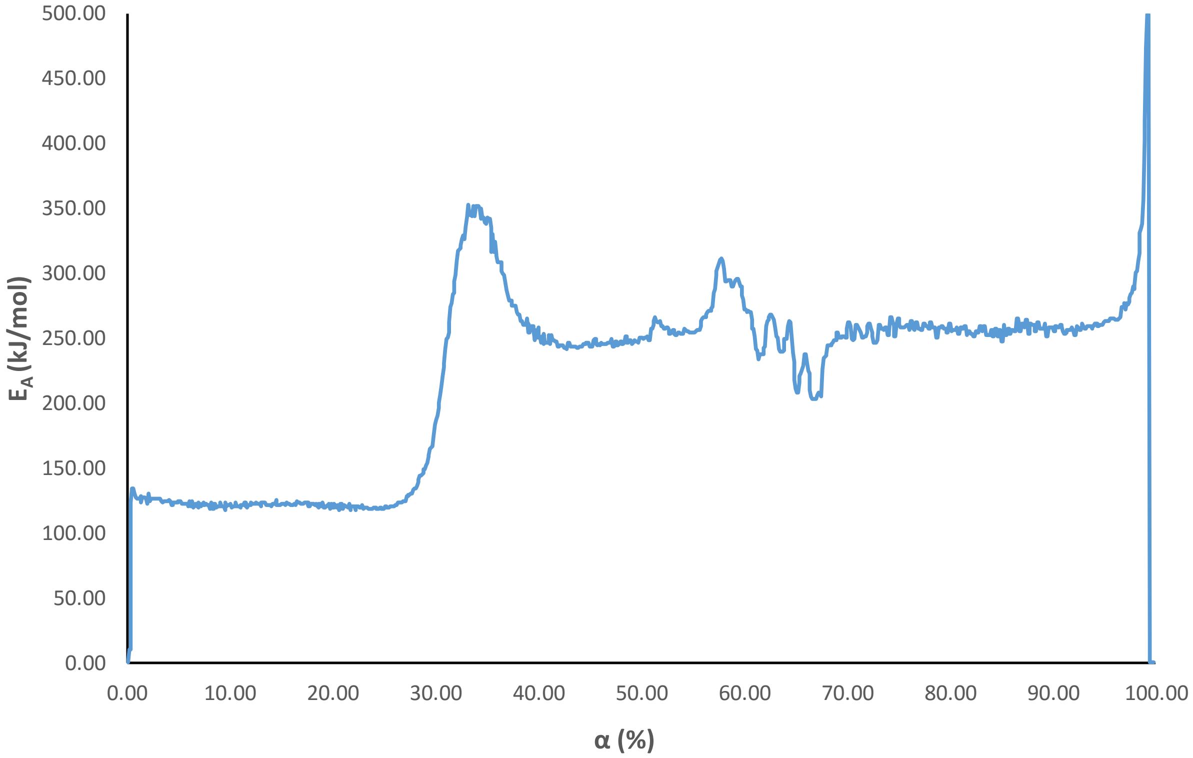


Figure 9. Apparent activation energy plot as a function of conversion for EN-8

The conversion and iso-conversion tables were constructed in the same method as those for EN-7, which are found in Tables 4 and 5 below. Compared to EN-7, if EN-8 is held at 250°C for 57 minutes it would lose only 14 wt%.

Table 4. Calculated conversions of EN-8 using MFK

Table Values: Time (min)		Temperature (°C)							
		150	**200**	**250**	**300**	**350**	**400**	**450**	**500**
α (%)	**2**	-	76	45	41	38	37	36	35
	5	-	121	48	42	38	37	36	35
	10	-	203	52	43	39	37	36	35
	15	-	328	59	43	39	37	36	35
	20	-	568	71	44	40	37	36	35
	25	-	-	109	47	40	37	36	35
	30	-	-	848	79	42	38	36	35
	40	-	-	-	-	723	48	36	35

Table 5. Calculated iso-conversions of EN-8 using MFK

Table Values: Temperature (°C)		α (%)							
		2	**5**	**10**	**15**	**20**	**25**	**30**	**40**
Time (min)	**5**	-	-	-	-	-	-	-	-
	10	-	-	-	-	-	-	-	-
	20	-	-	-	-	-	-	-	-
	40	324	326	328	331	335	345	365	417
	60	212	226	239	249	259	276	312	390
	120	187	200	212	221	232	247	286	374
	240	173	186	197	206	216	230	271	364
	480	163	175	185	193	203	216	258	355

The validity of the MFK modeling for EN-8 was tested by performing three isothermal experiments. Samples were inserted into TGA at temperatures of 180, 200, and 250°C and held for 345, 205, and 73 minutes, respectively. Using Table 4 or 5, the expected conversions are 5, 10, and 20%. Figure 10, a plot of weight % versus time, shows good agreement for the MFK prediction at 180°C ($\alpha = 5\%$) and is close for 200°C ($\alpha = 12\%$) and 250°C ($\alpha = 23\%$).

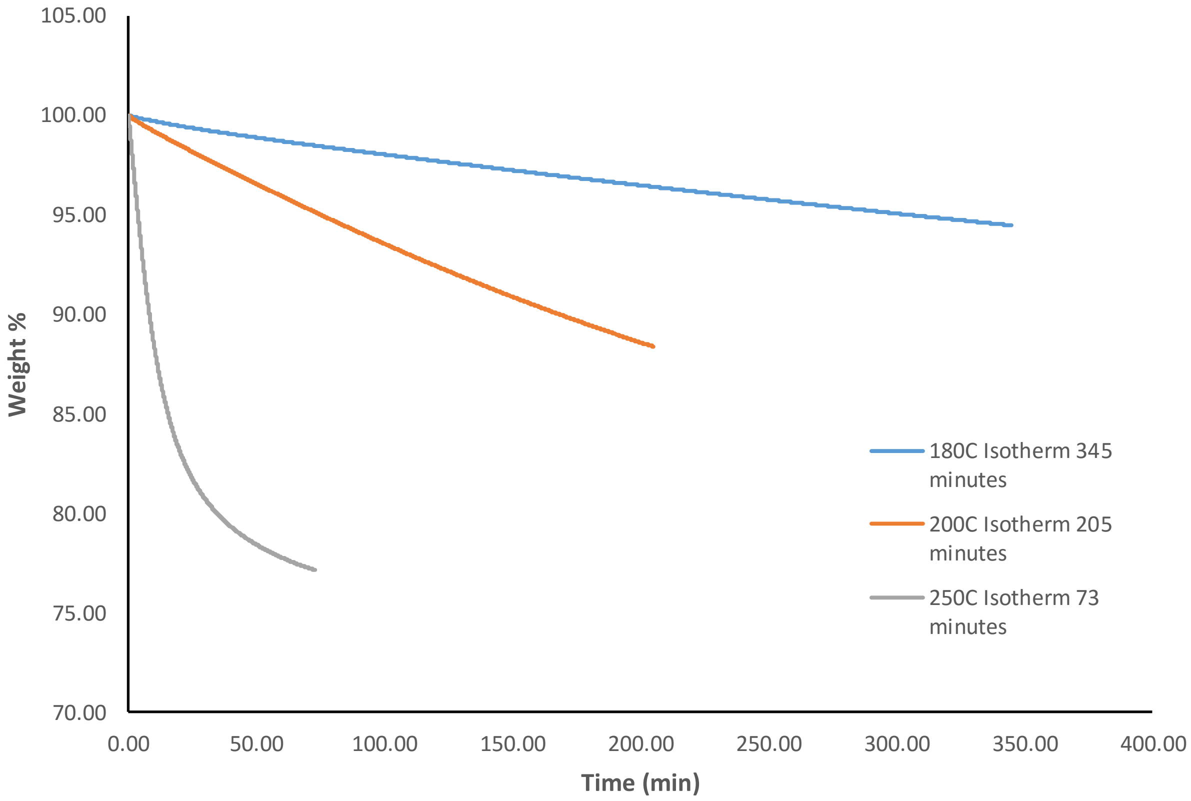


Figure 10. Conversion as a function of time for three isothermal experiments on EN-8

By comparing the MFK calculated conversions with the isothermal experiments' results for EN-7 and EN-8 it would appear that EN-8 is slightly more stable to degradation at higher temperatures (>200°C) and EN-7 is more stable at lower temperatures (<200°C), though the statistical significance of this has not been established. This observation correlates somewhat with the calculated activation energies as EN-8 had a higher E_a for the multi-step degradation.

3.2.3 Gas Chromatography / Mass Spectrometry

The exhaust gas from the TGA setup was captured at user-defined time intervals and stored inside 250 µL heated sample loops by the SRA IST16. A graphic of these times is shown for both elastomers in Figure 11. The 15 separate gas samples were then individually injected onto a gas chromatography (GC) column. The column separated the chemical components before they were ionized and detected via the mass spectrometer. In contrast to in-situ MS or Fourier transform infrared spectroscopy (FTIR) techniques, the GC enables one to separate individual gaseous species for identification rather than detection of the entire gas-phase at a single time point. Better resolution of the volatile degradation products is expected.

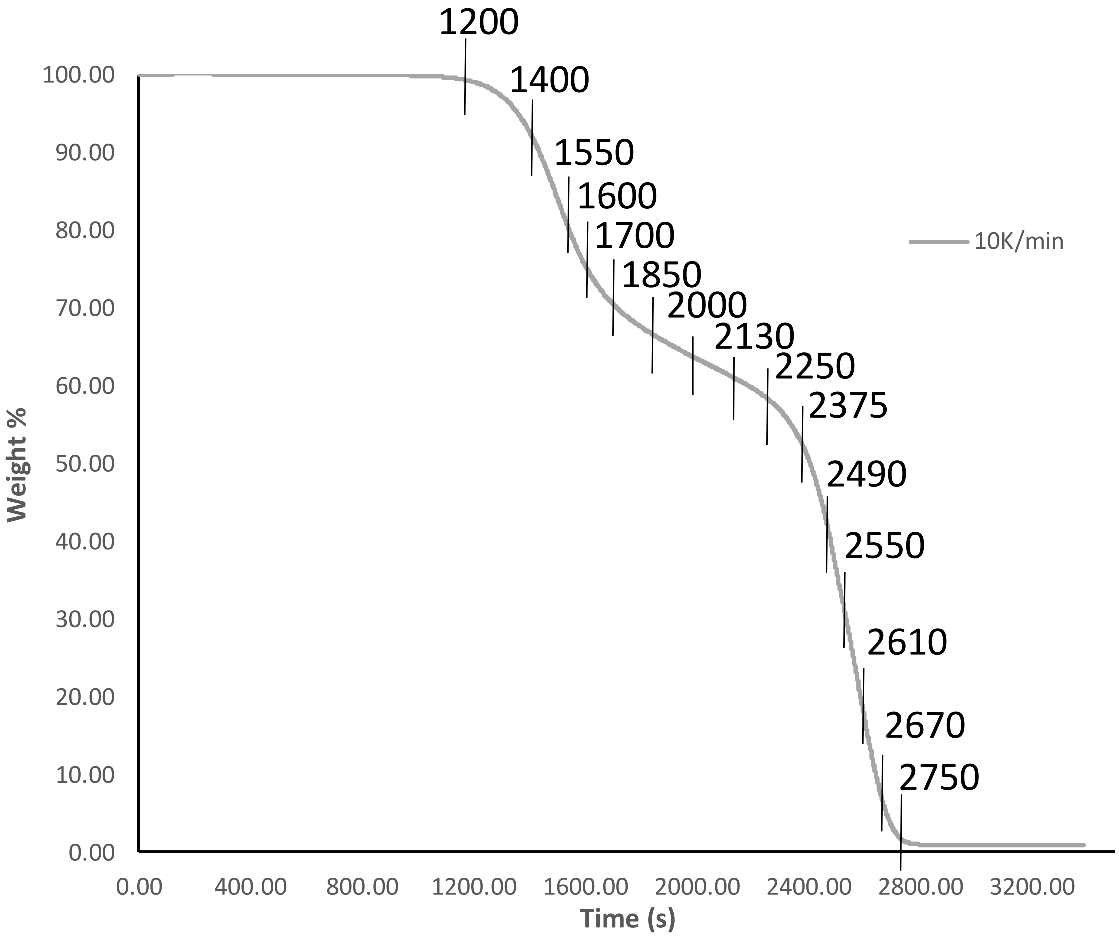
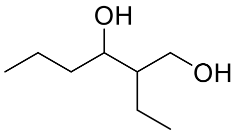
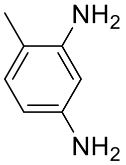
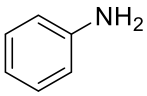
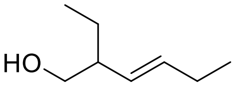
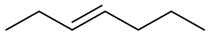
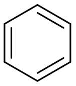
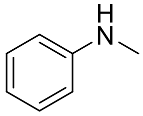
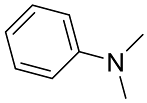
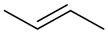
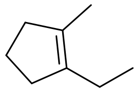


Figure 11. IST16 capture time intervals for EN-7 and EN-8 GC/MS analysis

A chromatogram, which contained peaks that represent decomposition products, was generated for all 15 time intervals listed in Figure 11. The fragmentation pattern and detected AMUs of each peak were compared against the Wiley 10th / NIST 2014 mass spectrum library to identify the chemical species. Many products were detected by GC/MS but could not be identified by the mass spectrum library. Chemical species that could be identified were then correlated to a degradation mechanism of the polyurethane elastomers. This information is displayed below in Table 6 for both materials. The table highlights those products that: could be matched to a mechanism, were a result of secondary degradation, or fall in a class of molecules (cycloalkenes, linear alkenes, etc.) that are likely products given the chemical structure of the elastomers. From this analysis, there is significant evidence to support the three mechanisms identified in Figures 2 – 4. The mechanism in Figure 2, dissociation of the urethane bond into alcohol and isocyanate, appears to occur first (lowest temperature) in agreement with published literature. This is due to the presence of an alcohol in the earliest time interval, 1200 s. There was no evidence of free TDI in the gas chromatograms, however isocyanates are highly reactive with any alcohols present and would reform the urethane linkage (the molecules are held in the storage loops at 150°C before injection onto the GC column). Ample confirmation of the mechanism in Figure 3 is provided by the detection of carbon dioxide, a primary amine, and linear alkenes in a majority of the time intervals. Lastly, the mechanism in Figure 4 becomes favored at 2130 s for EN-7, right at the onset of the second degradation step. Allan et al. noted there have been few reports of this mechanism, formation of a secondary amine and carbon dioxide, occurring to any great extent [3]. It is interesting to note that evidence of the mechanism in Figure 4 appears at 2250 s for EN-8, higher in temperature than EN-7.

Table 6. Thermal degradation products of EN-7 and EN-8 analyzed by GC/MS

Chemical name	Chemical Structure	Time Intervals (s)	Reaction Mechanism (Figure #)
1,3-dihydroxy-2-ethylhexane		1200, 1600, 1700, 1850	2
1,3-diamino-4-methylbenzene (Diaminotoluene)		1200, 1400, 1550, 1600, 1700, 1850, 2000, 2130, 2250, 2375	3
Aniline		1200, 2000, 2130, 2250, 2375, 2490	3
Carbon Dioxide	O=C=O	1400, 1550, 1600, 1700, 1850, 2000, 2130	3, 4
2-ethyl-3-hexen-1-ol		1550, 1600, 1700, 1850, 2000	2, 3
3-heptene		1550, 1600, 1700, 1850, 2000	3
Benzene		2130, 2250, 2375	secondary
N-methylaniline		2130[1], 2250, 2375, 2490	4
N,*N*-dimethylaniline		2130, 2250, 2375	secondary
Linear alkenes	Ex. 	1200, 1550 - 2490	3, secondary
Cycloalkenes	Ex. 	1200, 1700 - 2490	secondary

Note: Time intervals greater than 2,490 seconds not listed due to complexity of products evolved

[1] EN-7 only

4. CONCLUSIONS AND FUTURE WORK

This report analyzed the thermal degradation behavior of two polyurethane elastomers, EN-7 and EN-8, commonly used at Sandia National Laboratories. The elastomers were characterized using TGA-GC/MS with MFK to better understand their response to abnormal environments. This powerful tool provided a deeper understanding of degradation mechanisms and was able to predict material conversions.

Both EN-7 and EN-8 were shown to decompose in a multi-step fashion with similar onset temperatures. Apparent activation energies were calculated using the MFK software, then further utilized to construct conversion and isothermal conversion tables. Excellent agreement was found between the MFK predictions and the isothermal experiments when conversional data was compared. This agreement demonstrates the applicability of MFK in modeling the degradation of polyurethane elastomers under a variety of thermal design requirements, so long as the requirement falls within the broad thermal range investigated herein.

Degradation mechanisms for polyurethanes, previously described in the literature, were applied to the thermal behavior of the elastomers. The mechanisms were validated by identification of the volatile degradation products with GC/MS. It was not possible to identify every chemical species, but a reasonable amount of confidence could be obtained.

This report raises several questions for future investigation. First, both elastomers should be further evaluated to determine if the differences in their thermal stability (measured by conversion, α) is statistically significant, especially for temperatures $\geq 200°C$. TGA measurements, on elastomers in a partially confined state, could be performed to understand the degradation response in a closed environment.

The IST16 was instrumental in the successful linking of TGA measurements to GC/MS analysis. It was capable of automating the storage of gas samples and sequentially injecting them onto the GC column. Future effort should focus on validating its performance with other materials (i.e. a foam that also contains TDI, different polyurethane elastomers, etc.).

5. REFERENCES

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APPENDIX A: MOLECULAR STRUCTURE

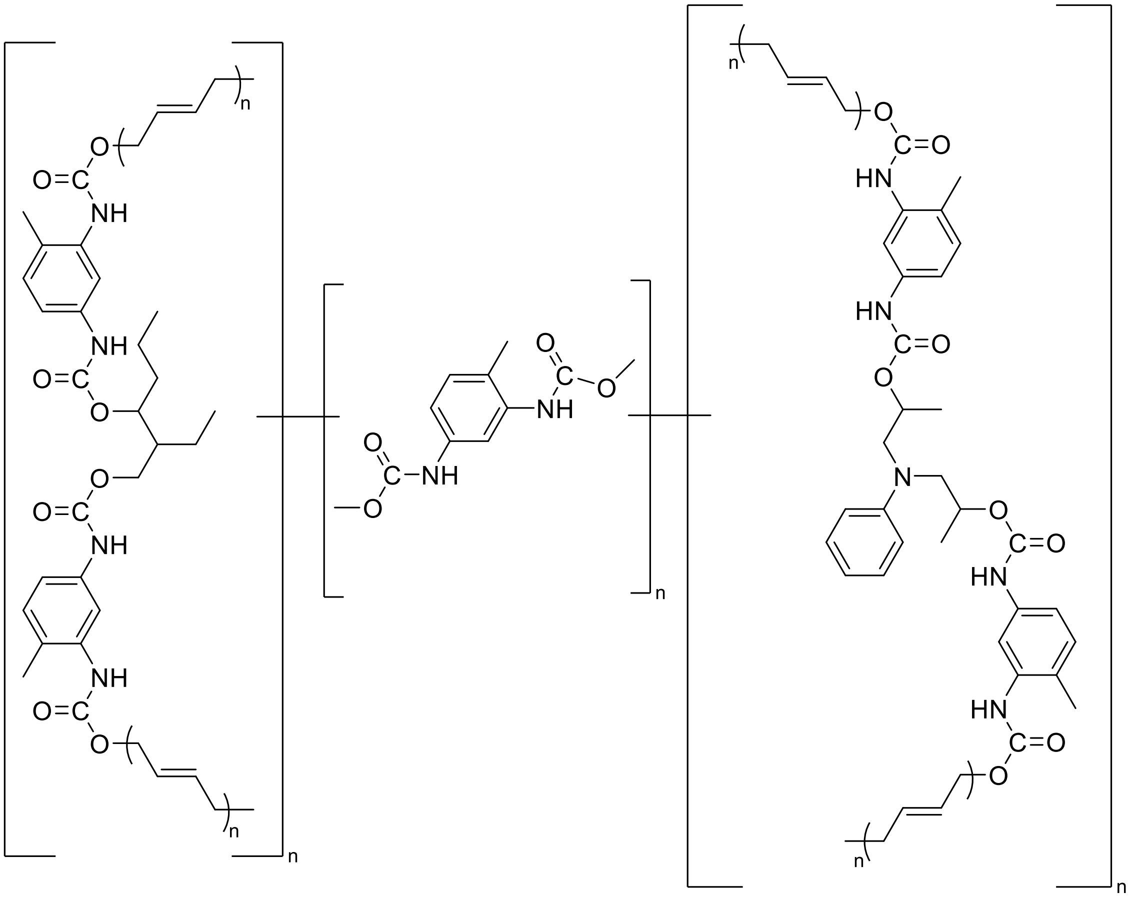

Figure A-1. Molecular structure of EN-7 and EN-8

APPENDIX B: EXAMPLE GAS CHROMATOGRAMS

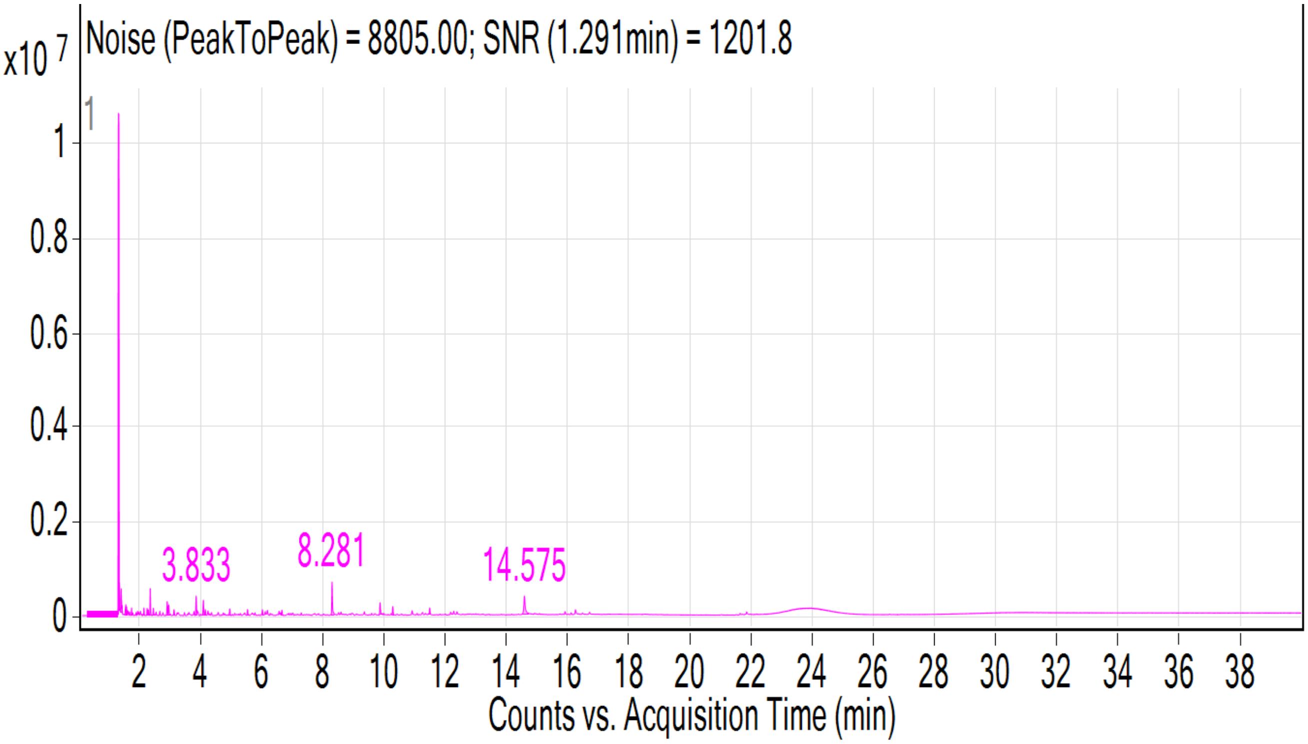

Figure B-1. Gas chromatogram of decomposition products from EN-7 captured at 2375 s

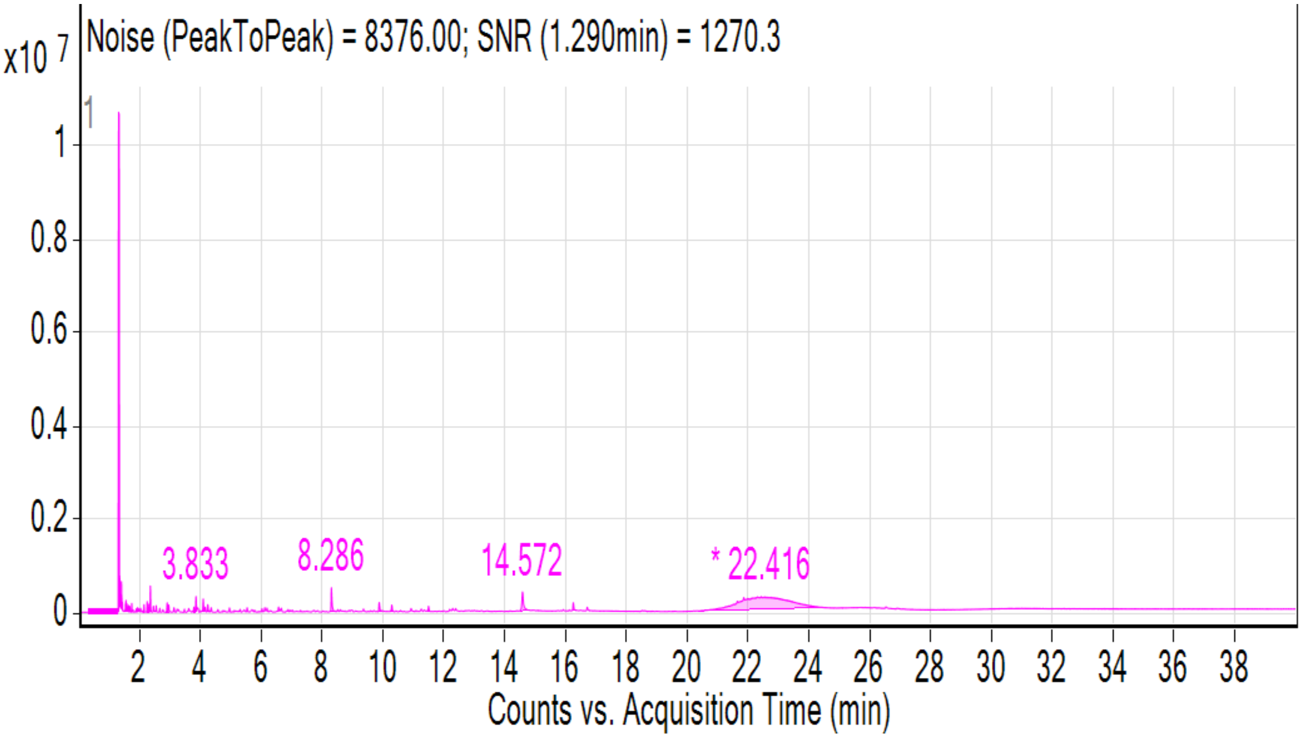

Figure B-2. Gas chromatogram of decomposition products from EN-8 captured at 2375 s

APPENDIX C: COMPARISON OF IST16 STORAGE VERSUS DIRECT INJECTION FOR GC/MS ANALYSIS

During the TGA-GC/MS characterization, exhaust gas is stored inside the IST16 storage loops before injection onto the GC column. Since the TGA experiment must finish and all samples stored before sequential injection, exhaust gas can spend anywhere from 26 – 630 min inside the storage loops which are held at 150°C. This environment could provide enough time to significantly alter the products via: secondary decomposition reactions, other side reactions of isocyanates, and from the reversible reaction that reforms the urethane linkages. To understand this behavior, a comparison of GC/MS data was performed at the same time intervals for two samples: exhaust gas that was stored in the IST16 for 411 minutes and exhaust gas that was directly injected onto the GC column. These results are shown in Figure B-1 below. As suspected, it appears there are some reactions occurring inside the storage loops which is evident based on the broad peak at 24 minutes in the chromatogram. Furthermore, it was necessary to bake out the storage loops after each experiment in order to remove side products and provide a clean baseline in the gas chromatogram (i.e. remove the broad peak seen at 24 minutes from becoming an artifact in future runs). Additionally, the data suggest that less compounds were detected in the stored exhaust gas versus the directly injected gas. It is not certain whether this is a result of reformation of the urethane linkages, additional side reactions of isocyanates, secondary decomposition reactions, or a combination of all three.

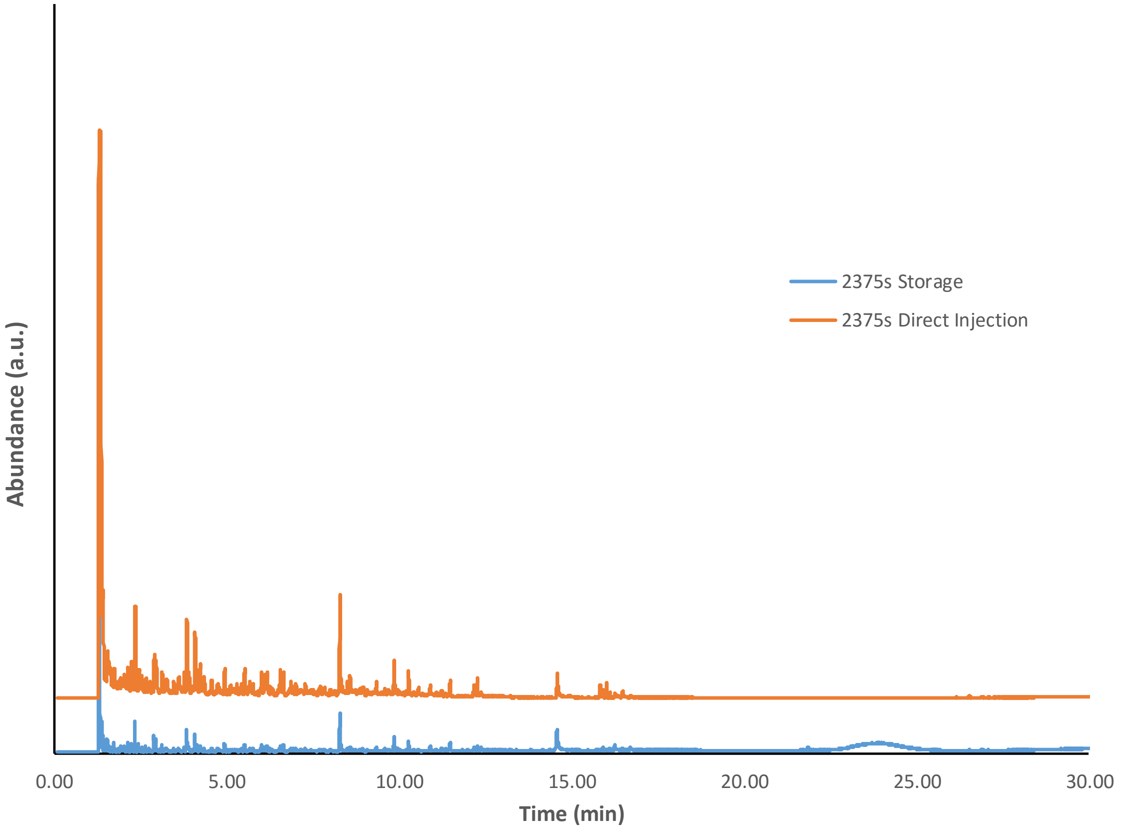

Figure C-1. Comparison of gas chromatograms obtained via direct injection onto column and IST16 storage before injection for EN-7

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