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Thermal Characterization and Model Free Kinetics of Aged Epoxies and Foams using TGA and DSC Methods

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Abstract

Two classes of materials, poly(methylene diphenyl diisocyanate) or PMDI foam, and cross-linked epoxy resins, were characterized using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), to help understand the effects of aging and "bake-out". The materials were evaluated for mass loss and the onset of decomposition. In some experiments, volatile materials released during heating were analyzed via mass spectroscopy. In all, over twenty materials were evaluated to compare the mass loss and onset temperature for decomposition. Model free kinetic (MFK) measurements, acquired using variable heating rate TGA experiments, were used to calculate the apparent activation energy of thermal decomposition. From these compiled data the effects of aging, bake-out, and sample history on the thermal stability of materials were compared. No significant differences between aged and un-aged materials were detected. Bake-out did slightly affect the onset temperature of decomposition but only at the highest bake-out temperatures. Finally, some recommendations for future handling are made.

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FIGURES

TABLES

NOMENCLATURE

TGA	Thermal Gravimetric Analysis
DSC	Differential Scanning Calorimetry
PMDI	Poly(methylene diphenyl diisocyanate)
MS	Mass Spectroscopy
MFK	Model-Free Kinetics
SNL	Sandia National Laboratories

1. INTRODUCTION

This report contains the results for the thermal characterization of various materials of interest for stockpile stewardship. Specifically, two poly(methylene diphenyl diisocyanate) PMDI foams and two epoxy resins were subjected to different heat-treatments and analyzed for signs of decomposition or aging. Of significant concern was determining what changes can be detected in materials when subjected to thermal treatments relative to virgin materials or unheated materials. The thermal treatments of interest are "bake-out" and "accelerated aging". Techniques used in this work include thermal gravimetric analysis (TGA), differential scanning calorimetric (DSC) and mass spectroscopy (MS).

Bake-out: This term refers to heating a sample at a specified temperature in order to induce a specific change. For example, a bake-out might drive out water from a sample. A bake-out is ideally performed at a temperature and for a time period which does not alter the inherent physical or chemical properties of the material and can be considered a reversible process.

Accelerated aging: This term refers to heating a specimen above ambient conditions for a specified time period to mimic the aging of a sample held at ambient temperatures for a much longer duration. Aging is typically considered an irreversible process due to physical or chemical changes in the material.

An open question remains regarding when bake-out turns to accelerated aging. In Section 3, results from TGA and DSC measurements are presented. These experiments were designed to help understand the factors or variables associated with long-term aging of materials and bake-out. The results are divided by material. A discussion follows the results.

Also in Section 3 of this work, the apparent activation energy for the thermal decomposition of various materials is compared. The premise of these experiments is that if a material undergoes an irreversible chemical change during a bake-out process, this change may be detectable in subsequent thermal decomposition measurements. For example, if one compares the decomposition properties of virgin PMDI foam with 30-year old PMDI foam, the onset temperature for decomposition, or total wt% loss might be different between the two materials. Similarly, by using a technique called "model-free kinetics" (MFK) the measured activation energy for decomposition of 30-year old foam might be different than virgin foam. This approach might also be applied in determining whether or not bake-out causes an irreversible chemical change, as reflected in a change in the activation energy for higher temperature decomposition reactions.

The materials investigated in this work include a PMDI foam from the stockpile referred to as FoamP. A newly synthesized foam with the same chemistry, but different density was used for comparison, referred to as FoamN. A composite fiberglass/epoxy resin was evaluated and is referred to as EpoxyP. For comparison, an epoxy resin with no fiberglass was fabricated and is referred to as EpoxyN. These samples, FoamP, FoamN, EpoxyP and EpxoyN were all subjected to "aging" at various temperatures for one or two months. Table 1 is provided to reference the nomenclature used in this report.

Table 1: Description and code of materials used in this study.	
Sample Code	Sample Description
FoamP	Foam from stockpile (> 20 years old)
FoamP@70C	Foam from stockpile heated to 70 °C for two month
FoamP@90C	Foam from stockpile heated to 90 °C for two month
FoamP@110C-1month	Foam from stockpile heated to 110 °C for one month
FoamP@110C-1month	Foam from stockpile heated to 110 °C for two month
FoamN	New foam made in 2012
FoamN@70C	New foam heated to 70 °C for two month
FoamN@90C	New foam heated to 90 °C for two month
FoamN@110C-1month	New foam heated to 110 °C for one month
FoamN@110C-1month	New foam heated to 110 °C for two month
EpoxyP	Epoxy with glass from stockpile (> 20 years old)
EpoxyP @70C	Epoxy from stockpile heated to 70 °C for two month
EpoxyP @90C	Epoxy from stockpile heated to 90 °C for two month
EpoxyP @110C-1month	Epoxy from stockpile heated to 110 °C for one month
EpoxyP @110C-1month	Epoxy from stockpile heated to 110 °C for two month
EpoxyN	New epoxy without glass made in 2012
EpoxyN@70C	New epoxy heated to 70 °C for two month
EpoxyN @90C	New epoxy heated to 90 °C for two month
EpoxyN @110C-1month	New epoxy heated to 110 °C for one month
EpoxyN @110C-1month	New epoxy heated to 110 °C for two month

2. EXPERIMENTAL METHODS

Data collection and processing:

Samples were aged in sealed vessels under an inert atmosphere for one or two months at the specified temperature.

Thermal gravimetric analysis (TGA) was performed using a Mettler-Toledo TGA1. Samples were prepared in 40 µL aluminum crucibles without a lid. Each sample was heated from 30 to 600 °C at 2, 5, 10 and 20 °C/min (β) under argon flowing at 40 ml/min. A Pfeiffer mass spectrometer (MS) was connected to the TGA and sampled the gaseous species. Three samples were run at each heating rate. Data collected by TGA was processed by comparing the onset temperature of decomposition and the temperature for a specified conversion (α) determined from the weight loss. Initial comparisons were performed at α = 10 and 50 wt%. Plots of temperature versus heating rate (β) for these two values of α provide a rough comparison between materials. Plotted are the mean of three runs with error bars for 95% confidence intervals.

Differential scanning calorimetry (DSC) was performed using a Mettler-Toledo 823e DSC instrument. Samples were prepared as above without lids. Each sample was heated from 30 to 600 °C at 2, 5, 10 and 20 °C/min (β) under argon flowing at 40 ml/min. Data were analyzed by taking the first derivative of the heat flow to find the peak value as a function of temperature. The peak was then plotted as a function of heating rate (β) for each sample. No error analysis was performed because peaks were not always found for every sample. DSC analyses were minimal due to the scatter in data. Trends were consistent with the TGA data and serve as an independent verification of the decomposition properties of the materials.

Model free kinetics

Apparent activation energies (E_a) were derived from the TGA data by comparing the percent conversion, or α, as a function of the temperature for different heating rate (β). This technique first developed by Vyazovkin is referred to as “Model-Free Kinetics” and assumes Arrhenius type behavior for the chemical reactions. The advantage of using model-free kinetics over traditional kinetic models is that complex reactions can be described without information regarding the elementary chemical steps or reaction order. This model assumes that the apparent activation energy of a reaction is a function of conversion and not heating rate. Theoretically, if the activation energy of a process can be measured, then predictions about the rate of a reaction at lower temperatures can be made. This approach grants one the ability to predict properties like thermal stability of a material, in lieu of performing the actual measurement, which might take too long. More information can be found in the literature [1-5] and Mettler-Toledo UserComm02 and UserComm08.

3. RESULTS

This section contains the experimental results of TGA and DSC experiments. The section is divided by analysis method and material.

TGA Analysis

Basic thermal gravimetric analysis was performed, coupled to a MS. The intent of these experiments was to measure the mass loss from each sample with increasing temperature and to identify any volatile species evolved during this process. Each sample is discussed separately.

Material FoamP

A set of ramp-hold-ramp experiments were performed to determine the onset temperature and weight loss (wt%) as a function of heating rate. Samples were heated from 30 – 200 °C then 200 – 400 °C with an isotherm segment in the middle. The heating rates used varied from 40, 30, 20 to 10 °C/min (Table 2). Mass spectroscopy was used to analyze the headspace while heating but the sensitivity was typically too low to distinguish between background volatile species. Below 200 °C, FoamP showed less than 1 wt% mass loss. Above 300 °C the up to 71 wt% loss was observed depending on the ramp rate. For these samples the onset temperature decreased with slower ramp rates, which is consistent with a decomposition process.

Step-hold TGA experiments (Table 5) were conducted on FoamP to determine the stability of the resin at specific temperatures. Samples were run in triplicates and a mass spectrometer was connected to analyze any detectable volatile species. The TGA traces for the old FoamP show a 2 wt% loss between 30 and 250 °C. Once a temperature of 250 °C was reached the foam began to lose more weight; nearly 14 wt% was lost by the end of the experiment, which was halted after 60 min at 250 °C. The accompanying mass spectra showed a significant rise in m/z = 30, 42 and 44 at 250 °C compared to the blank runs or samples EpoxyN and EpoxyP. These signals at m/z = 30, 42 and 44 remained elevated for the duration of the experiment. The increased ion count is consistent with the drop in mass measured by TGA. To conclude, FoamP loses mass at a slow rate until >170 °C. At 250 °C the part begins to lose significant mass and would likely continue to degrade if the experiment were run longer.

Table 2: Ramp-hold-ramp experiments for FoamP in argon.			
File Name	Ramp Rate (°C/min)	Onset Temp (°C)	Total mass loss (wt%)
JGC-07-019-1&2	40	331	71 ±11
JGC-07-019-3&4	30	330	67 ±2
JGC-07-019-5&6	20	326	69 ±5
JGC-07-019-7&8	10	315	66 ±6
Onset temperature and total mass loss are the average of two runs.			

Similarly, a set of step-hold TGA experiments were performed on FoamP@70C- foam aged at 70 °C for three weeks under nitrogen. The same heating profile listed in Table 5 was employed. Samples were run in triplicates and a mass spectrometer was connected to analyze any detectable volatile species. The triplicate TGA experiments showed a mass loss of < 1wt% up to 250 °C, slightly less than the un-aged old FoamP discussed above. Above 250 °C the foam loses nearly 14 wt% similar to the un-aged part. Similar results were seen for FoamP@110C and FoamP@130C- foam aged at 110 °C and 130 °C for three weeks in nitrogen. Higher fidelity experiments looking at the onset temperature and activation energy of decomposition are discussed in Section 3.

TGA experiments with a 0.5 °C/min heating rate were performed up to 200 °C to mimic bake-out conditions. Also considered were size and surface effects for each sample. For FoamP, three different samples were analyzed; one piece with skin, one piece without skin, and multiple small pieces (Table 7). The one piece with skin and one piece without skin showed similar two-step weight loss profiles. Initially about 1.2 wt% is lost up to 80 °C followed by a flat-line. Above 180 °C both samples lost more weight—up to 2.5 wt% total. The crucible containing multiple pieces (w/o skin) displayed a more rapid initial weight loss followed by a flat-line and then further weight loss above 190 °C for a total of nearly 2.5 wt%. These data are consistent with a diffusion controlled process in which more surface area leads to quicker release of volatiles species.

Table 3: Ramp-hold-ramp experiments for FoamN in argon.			
Samples	Ramp Rate (°C/min)	Onset Temp (°C)	Total mass loss (wt%)
JGC-07-021-1&2	40	320	68.5±2
JGC-07-021-3&4	30	315	68.5±4
JGC-07-021-5&6	20	313	69±5
JGC-07-021-7&8	10	303	64±2
Onset temperature and total mass loss are the average of two runs.			

Material FoamN

A set of ramp-hold-ramp experiments were performed to determine the onset temperature and weight loss (wt%) as a function of heating rate. Samples were heated from 30 – 200 °C then 200 – 400 °C with an isotherm segment in the middle. The heating rates used varied from 40, 30, 20 to 10 °C/min (Table 3). Mass spectroscopy was used to analyze the headspace while heating but the sensitivity was typically too low to distinguish between background volatile species. As with FoamP, the onset temperature for mass loss decreased with slower ramp rates, which is consistent with a decomposition process. The total mass loss once ramped above 400 °C is nearly consistent, sample 7&8 being slightly lower. Overall, FoamN has an onset temperature for decomposition approximately 10 °C lower than FoamP. Both FoamP and FoamN show comparable mass loss upon heating to 400 °C in argon.

No step-hold TGA experiments were conducted on FoamN. Higher fidelity heating rate dependent experiments are discussed in part II.

TGA experiments with a 0.5 °C/min heating rate were performed up to 200 °C to mimic bake-out conditions. Also considered were size and surface effects for each sample. For FoamN, three different samples were analyzed; one piece with skin, one piece without skin, and crushed powder (Table 7). The sample with skin showed a gradual mass loss up to 80 °C like FoamP, of about 1.1 wt%. The 1-piece w/o skin and crushed powered both showed much faster initial weight losses of 1.3 wt% below 50 °C. All three show little weight loss between 90 and 170 °C. Above this temperature an additional 1.2 wt% loss is observed.

Material EpoxyP

A set of ramp-hold-ramp experiments were performed to determine the onset temperature and weight loss (wt%) as a function of heating rate. Samples were heated from 30 – 200 °C then 200 – 400 °C with an isotherm segment in the middle. The heating rates used varied from 40, 30, 20 to 10 °C/min (Table 4). Mass spectroscopy was used to analyze the headspace while heating but the sensitivity was typically too low to distinguish between background volatile species. No mass loss was observed until the temperature was increased from 200 to 400 °C. No correlation can be discerned between heating rate and the onset temperature for EpoxyP. Similarly, the total weight loss is inconsistent, which could be a result of the heterogeneity of the composite sample.

Table 4: Ramp-hold-ramp experiments for EpoxyP in argon.

Samples	Ramp Rate (°C/min)	Onset Temp (°C)	Total mass loss (wt%)
JGC-07-017-1&2	40	377	31.5±1
JGC-07-017-3&4	30	384	27.5±0.5
JGC-07-017-5&6	20	376	42.5±3
JGC-07-017-7&8	10	364	32.2±3

Onset temperature and total mass loss are the average of two runs.

Step-hold TGA experiments (Table 5) were conducted on EpoxyP to determine the stability of the resin at specific temperatures. Samples were run in triplicates and a mass spectrometer was connected to analyze any detectable volatile species. From 30 to 250 °C approximately 0.5 wt% mass loss was observed with a further 0.7 wt% decrease in mass as the sample is held at 250 °C for 60 minutes. Data from the MS were not significantly different than the blank background scan.

TGA experiments with a 0.5 °C/min heating rate were performed up to 200 °C to mimic bake-out conditions. Also considered were size and surface effects for each sample. For EpoxyP, three different samples were analyzed; one piece, multiple small pieces, and shredded pieces (Table 7). The one piece EpoxyP sample showed a steady weight loss up to 200 °C of 0.65 wt%. The multiple pieces and crushed samples showed a faster initial weight loss but one eventually gained back the lost mass while the one-piece sample lost a total of approximately 0.8 wt%. It appears that the higher surface area samples lose weight faster, consistent with diffusion of a gas or water from the material.

Material EpoxyN

Uncured epoxy was analyzed via TGA-MS and DSC (JGC-07-007): By TGA analysis, an 85 wt% loss was observed with an unset temperature near 200 °C and inflection point near 375 °C. Heating up to 800 °C did not show further mass loss. The results were similar in an argon or air atmosphere. In air, however, a large exothermic heat flow was observed via DSC near 550 °C. Signals detected by mass spectroscopy (and possible identities) were: 2 (H_2), 18 (water), 28 (N_2 or CO), 30 (NO?), 32 (O_2), 34 (H_2O_2), 36 (?), 38 (?), 40 (Ar), 42 (?), 44 (CO_2). The main difference between air and argon cover gas was the lack of a signal at m/z = 2 in air. No further work was done on the uncured EpoxyN resign.

No ramp-hold-ramp experiments were run on the uncured or cured EpoxyN.

Step-hold TGA experiments (Table 5) were conducted on EpoxyP to determine the stability of the resin at specific temperatures. Samples were run in triplicates and a mass spectrometer was connected to analyze any detectable volatile species. Up to 250 °C, a 0.5 wt% loss was observed. As the sample was held at 250 °C for one hour, an additional 0.5 wt% loss was measureable. No detectable species could be seen in the MS compared to the background signal.

TGA experiments with a 0.5 °C/min heating rate were performed up to 200 °C to mimic bake-out conditions. Also considered was size and surface effects for each sample. For EpoxyN, which does not contain any glass filler, multiple pieces were analyzed (Table 7). This material showed decreasing mass loss for all three samples of approximately 1 wt% from the beginning of the heating ramp.

Table 5: Step-hold TGA experiments.		
Temperature (°C)	Time (min)	Rate (°C/min)
30	10	Isothermal
30 – 70	2	20
70	30	Isothermal
70 – 90	1	20
90	30	Isothermal
90 – 110	1	20
110	30	Isothermal
110 – 130	1	20
130	30	Isothermal
130 – 170	2	20
170	30	Isothermal
170 – 250	4	20
250	60	isothermal
Performed on FoamP, FoamP@70 FoamP@110, FoamP@130, EpoxyN, EpoxyP		

Table 6: Results of step-hold TGA experiments[a]							
Sample	FoamP	FoamP @70	FoamP @110	FoamP @110	FoamP @130	EpoxyP[c]	EpoxyN[c]
Mass loss (wt%)	2; 14	1; 14	1; 14	1; 14	1; 14	1.2	1.0
Volatile species	m/z = 30, 42 and 44					None detected	
[a]Samples heated under argon as specified in Table 5 [b]Total mass loss at 170 °C; total mass loss after 1h at 250 °C							

Table 7: TGA/DSC of samples with a 0.5 °C/min heating rate to 200 °C.		
Sample	Mass (mg)	Sample Comments
EpoxyP	21.3	1 Piece
EpoxyN	14.0	Multiple pieces
FoamP	10.2	1 piece w/skin
FoamN	5.6	1 piece w/skin
EpoxyP	18.9	Small pieces (5)
EpoxyN	17.6	Multiple pieces
FoamP	13.5	1 piece, no skin
FoamN	5.8	1 piece, no skin
EpoxyP	18.4	Shredded
EpoxyN	18.0	Multiple Pieces
FoamP	6.7	Multiple pieces
FoamN	5.5	Smashed powder
All samples run in argon and repeated three times. (JGC-07-032)		

Table 8: TGA results with a 10 °C/min heating rate in argon.[a]			
Material	Mass loss (wt%)	Onset Temperature (°C)	Inflection point (°C)
FoamP:	83.60	312.10	341.81
FoamP@70:	80.34	309.26	339.61
FoamP@90:	79.88	309.62	340.23
FoamP@110 1 month:	82.05	310.23	340.20
FoamP@110 2 months:	80.59	308.79	341.45
FoamN	79.97	297.10	332.67
FoamN@70:	81.29	291.90	331.38
FoamN@90:	80.05	295.93	333.81
FoamN@110 1 month:	80.16	295.62	332.37
FoamN@110 2 months:	78.12	295.44	332.93
EpoxyP	31.89	369.81	381.91
EpoxyP@70:	34.36	368.28	380.09
EpoxyP@90:	35.42	366.04	379.29
EpoxyP@110 1 month:	31.78	369.57	382.00
EpoxyP@110 2 months:	33.50	369.84	381.19
EpoxyN	83.71	370.06	387.28
EpoxyN@70:	84.05	368.21	385.51
EpoxyN@90:	82.42	363.13	384.98
EpoxyN@110 1 month:	81.50	358.66	382.26
EpoxyN@110 2 months:	81.99	355.29	380.41
(a) Average of three triplicate experiments. No error analysis was performed due to low standard deviation.			

Variable β TGA

By varying the heating rate (β) and comparing the onset temperature of decomposition, information can be gained about the activation energy and thermal history of a material. All materials listed in Table 1 were evaluated. Plots of temperature versus heating rate (β) for all twenty materials are shown in Figure 1 to Figure 4. The two different conversions, or α, are 10 and 50% based on the total mass loss as measured by TGA. Figure 5 and Figure 6 plot the temperature versus β for the peak of the first derivative of heat flow measured using DSC.

Figure 1 is a plot of temperature versus β for α = 10% for FoamP, FoamN and the aged materials. These data show error bars significantly larger for β = 2 and 20 but the overall increase in temperature for larger β is clear. The spread for T as a function of β is slightly less for FoamN compared to FoamP as the material is aged. However, all materials have less than an eight degree spread in temperature for 10% conversion at different heating rates. FoamP consistently has the highest temperature versus β compared to the aged parts but the difference is within experimental error. When compared to Figure 2, which plots temperature versus β at α = 50%, some differences are noted. First, the spread in values for temperature versus β is larger for FoamP. The un-aged FoamP also appears at slightly higher temperatures compared to the aged FoamPs but FoamP@110-2months shows overlap with it. From these two figures, it appears that FoamN has a slightly lower thermal stability compared to FoamP, which could be due to a difference in polymer density. FoamN also seems less affected by aging albeit the differences in temperature versus β for FoamP are within the 95% confidence intervals for the triplicate measurements.

Comparisons between EpoxyP and EpoxyN at α = 10 and 50% are given in Figure 3 and Figure 4. In Figure 3 one sees that EpoxyP and EpoxyN have nearly identical T versus β curves despite EpoxyP containing fiberglass filler and being a decades-old part. The effects of aging on EpoxyN are more pronounced compared to EpoxyP. While both EpoxyN and EpoxyP have the highest T versus β curve, EpoxyN@110-2months drops nearly 20 degrees whereas EpoxyP@110-2months shows <5 °C decrease in temperature for 10% conversion at all β values. At α = 50%, Figure 4, the differences between all 10 materials decreases significantly compared to α = 10%. The overall trend, where EpoxyP and EpoxyN have the highest T versus β curves and EpoxyN@110-2 the lowest, is preserved but the spread between the high and low values narrows to <8 °C.

Tables 8 – 31 in the Appendix summarize all the TGA data obtained from variable heating rate thermal decomposition reactions for all aged, new and old parts.

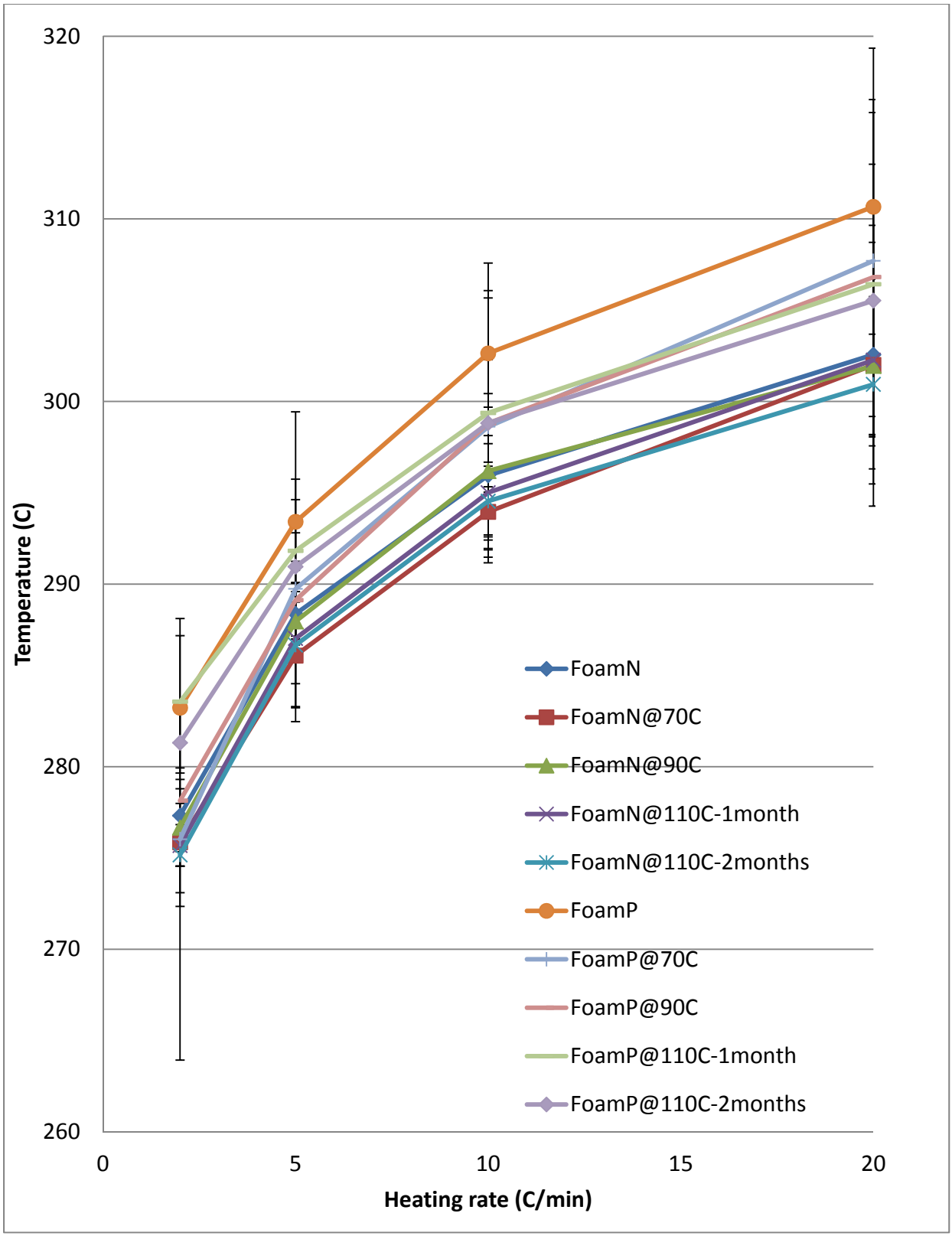

Figure 1: Averaged TGA data for foam materials at 10% weight loss. Means and 95% confidence intervals are plotted for three independent TGA measurements.

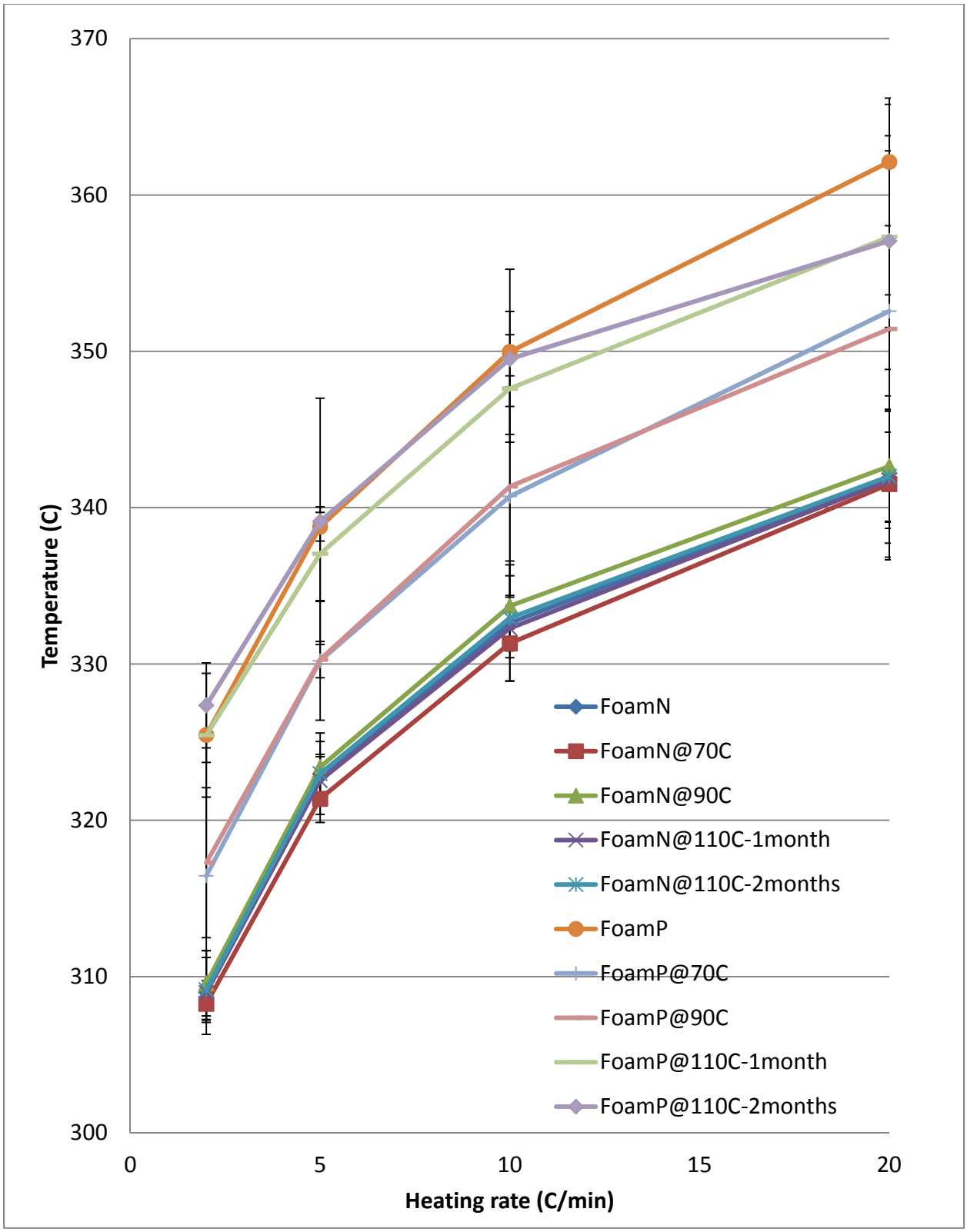

Figure 2: Averaged TGA data for foam materials at 50% weight loss. Means and 95% confidence intervals are plotted for three independent TGA measurements.

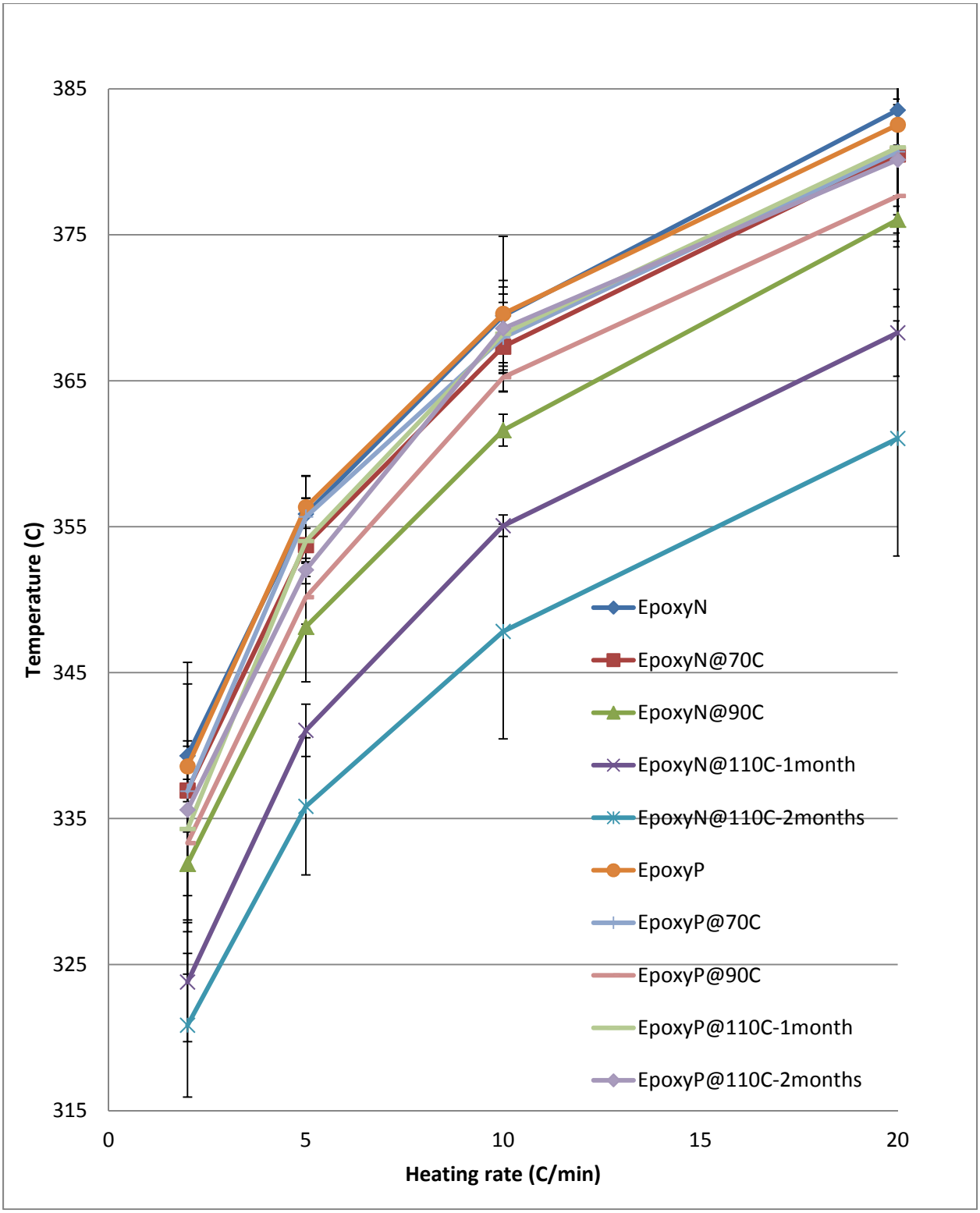

Figure 3**:** Averaged TGA data for epoxy materials at 10% weight loss. Means and 95% confidence intervals are plotted for three independent TGA measurements.

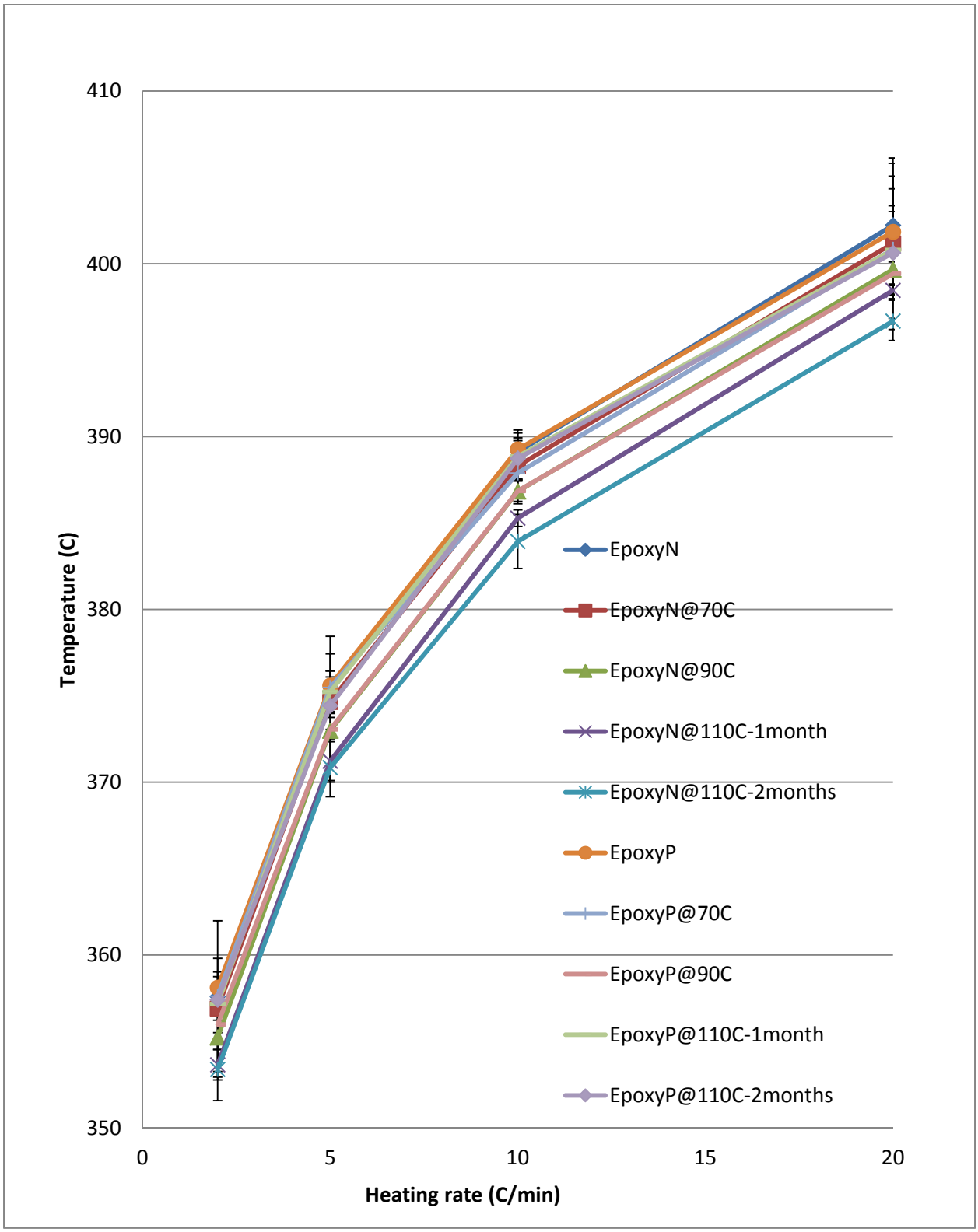

Figure 4: Averaged TGA data for epoxy materials at 50% weight loss. Means and 95% confidence intervals are plotted for three independent TGA measurements.

Variable β DSC

DSC was used as an alternative method to verify the trends found using TGA. The same twenty samples were analyzed using the same heating range and rates as employed in the TGA measurements. Experimentally, the maximum rate of heat flow out of the sample was recorded by taking the first derivative of the exothermic thermal decomposition of each material. For FoamP and FoamN, the data collected at $\beta = 2$ and 5 °C/min roughly correspond to $\alpha = 12 – 15$ and 20 – 30 % conversion based on temperature. At higher heating rates, the conversion increases but the spread in data are too large for a reasonable comparison. The peak temperature at $\beta = 2$ °C/min for EpoxyP and EpoxyN roughly corresponds to $\alpha = 15\%$ conversion. The observed "peak" temperature varied as a function of β more widely compared to fixed values of conversion, or α, as measured in TGA experiments. This large fluctuation is partially attributed to instrumental limitations, which are reported to be more accurate and precise at slower heating rates. At higher heating rates there is too much spread to make a correlation to α. Due to the large uncertainties associated with the DSC data, no further analyses were performed.

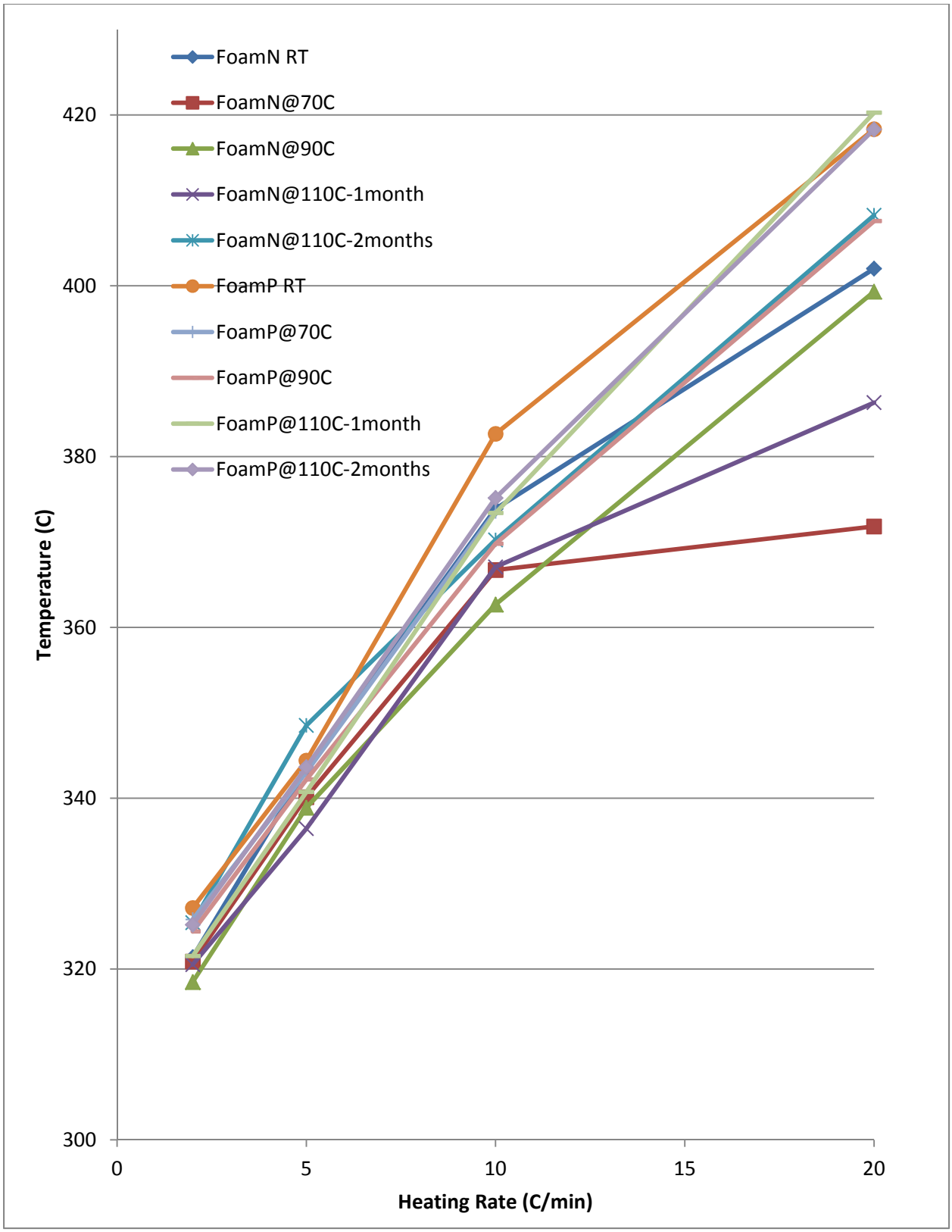

Figure 5: Temperature of peak calculated from the first derivative of heat flow using DSC. Mean of three experiments shown unless otherwise noted.

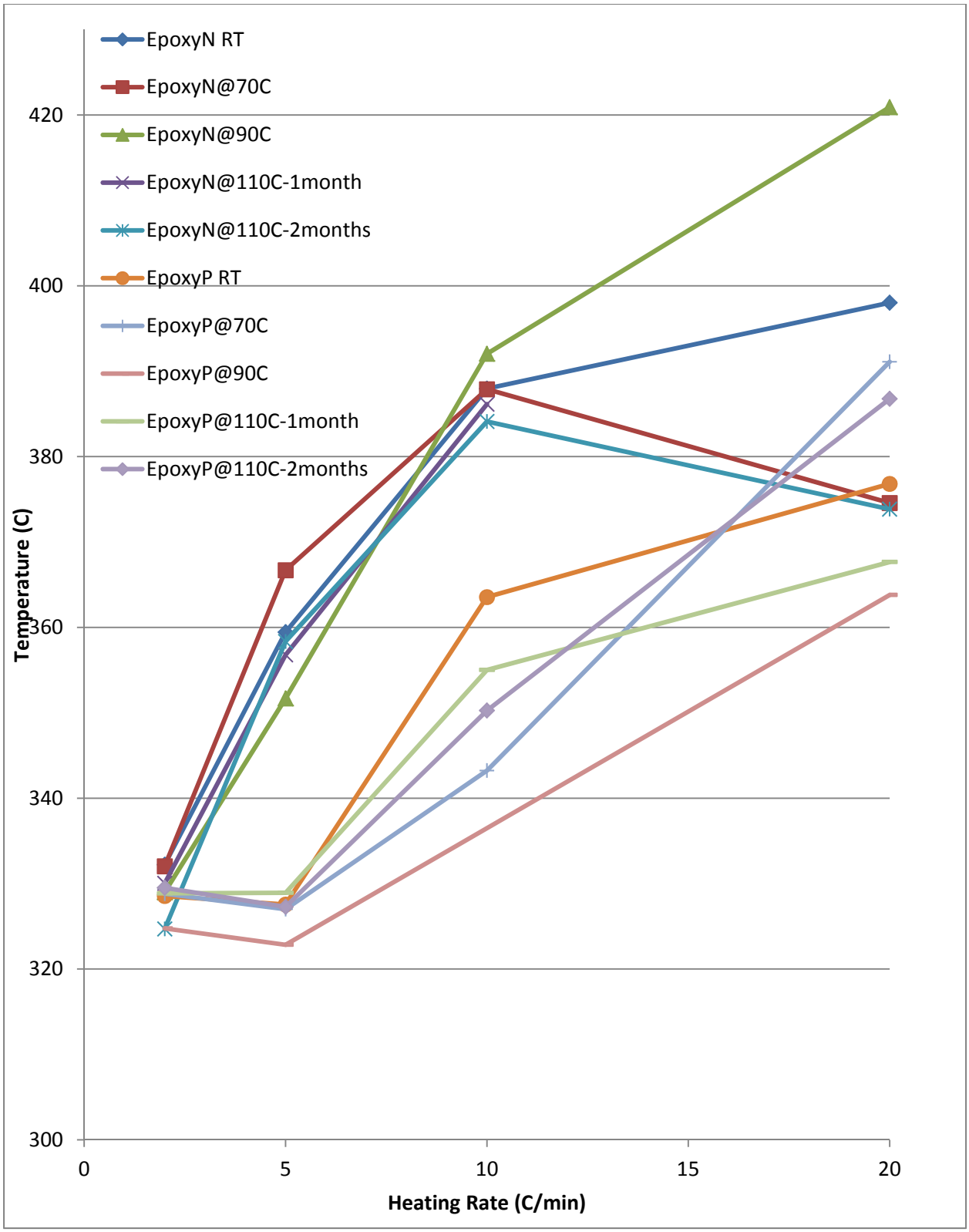

Figure 6: Temperature of peak calculated from the first derivative of heat flow using DSC. Mean of three experiments shown unless otherwise noted

Model Free Kinetics

Plots of the apparent activation energy (E_a) for the decomposition reaction of all materials from Table 1, as a function of α are shown in Figures 7 – 10. The variable TGA data presented above can be considered a slice at α = 10 or 50%, whereas these curves represent the integrated data over the entire decomposition reaction. In each figure the un-aged material is plotted in red. When overlapped, the largest differences between E_a are observable at low or high values of α. At α > 80% for all materials, the deviations are likely due to poor fits of the numerical regression used in analyses and not any actually chemical differences.

For FoamN, the E_a is nearly identical for α = 30 – 70% but some modest deviations are observed at α < 10%. Specifically, FoamN@90 and FoamN@110C-1month show lower apparent activation energy profiles than FoamN, which could be attributed to aging. However, this difference is lost for FoamN@110C-2month. Differences in E_a for FoamP are seen in Figure 8. Compared to the un-aged sample in red, the aged samples have a higher apparent activation energy except for FoamP@70C, which crosses at α = 45%. These data are not inconsistent with the variable β TGA data presented (Figures 1 and 2) above but do not elucidate any more information regarding the effects of aging. FoamP@110C-2months has a higher activation energy than the un-aged FoamP for the duration of α.

Plots of E_a versus α for EpoxyN and EpoxyP are given in Figures 9 and 10. For the most part, only modest differences are observed for all α except at α < 10%. Where there is deviation, for example EpoxyN, the differences are not consistent; EpoxyN@110C-1month has a lower apparent activation energy than EpoxyN but for EpoxyN@110C-2months it is the opposite. EpoxyP@110-1month and 2months at α < 10% both appear to have lower E_a compared to EpoxyP but the differences are modest.

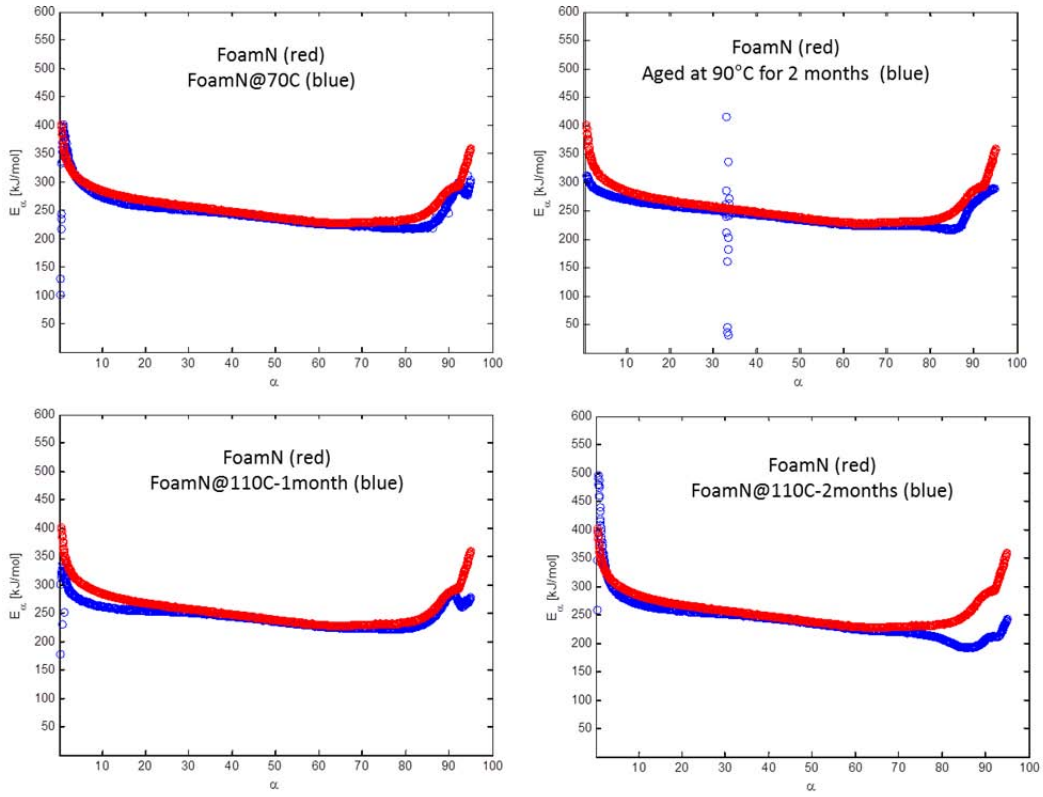

Figure 7: Apparent activation energy as a function of conversion (α) for FoamN.

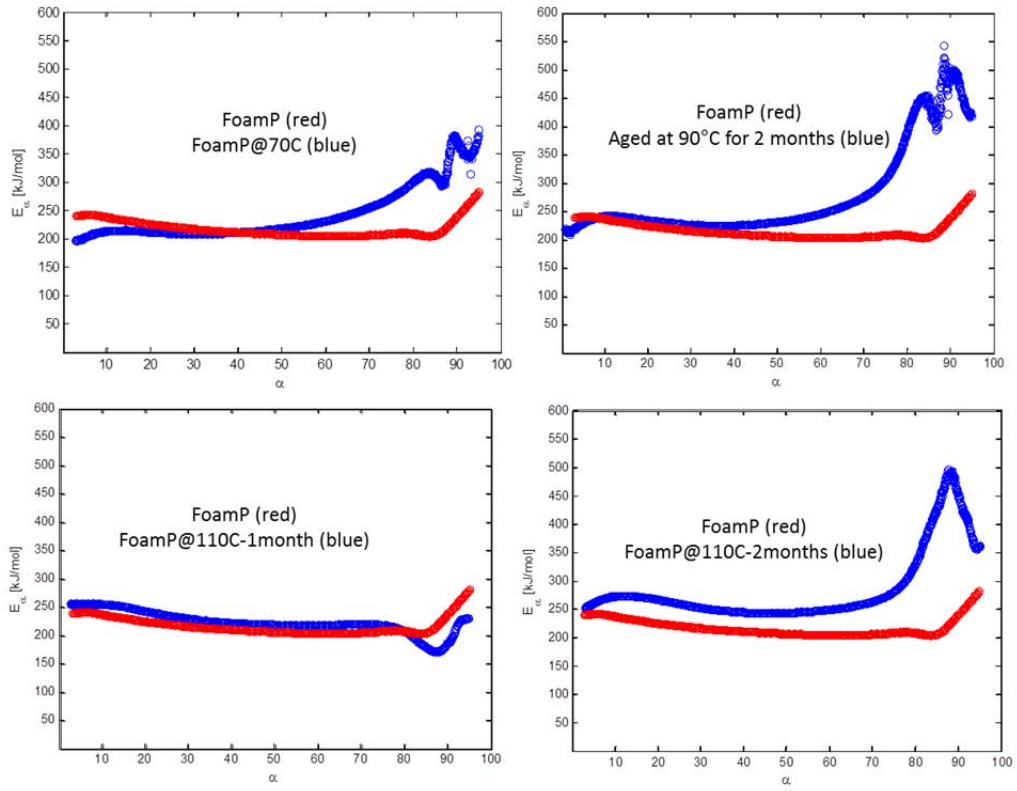

Figure 8: Apparent activation Energy versus conversion (α) for FoamP.

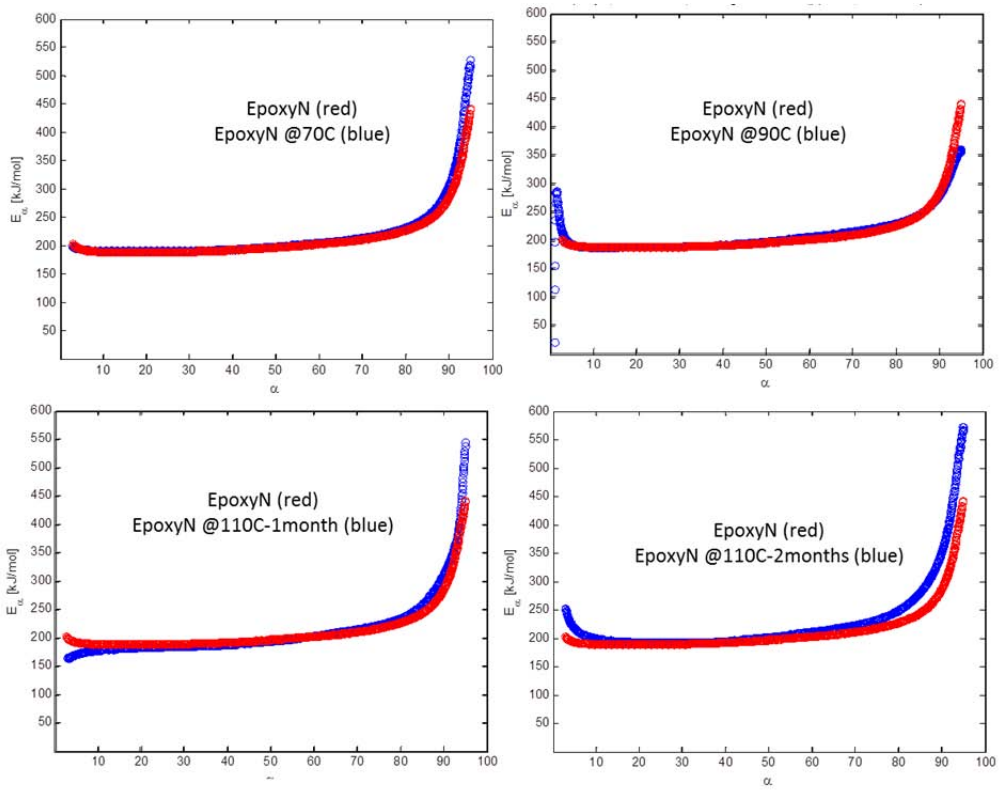

Figure 9: Apparent activation energy versus conversion (α) for EpoxyN.

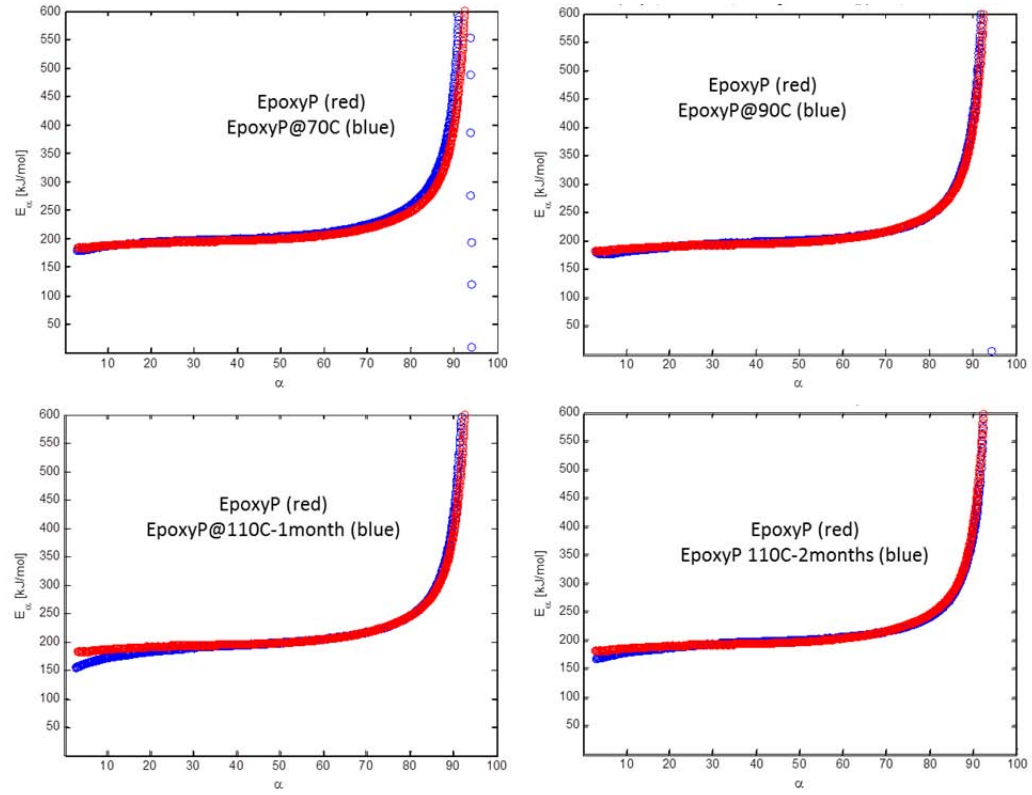

Figure 10: Apparent activation energy versus conversion (α) for EpoxyP.

4. DISCUSSION

Three analytical methods were used to probe changes to materials brought about by heating. Thermal gravimetric analysis (TGA) was used to record weight loss as a function of temperature. Mass spectroscopy (MS) was used to record any volatile species released during the TGA experiments. Differential scanning calorimetry (DSC) was used to measure the heat flow in or out of a sample as a function of temperature. By performing these measurements on materials of different thermal histories, subtle differences were observed.

Step-hold TGA-MS experiments (Table 5) show the mass loss associated with different temperature jumps beginning at 30 °C and ending at 250 °C. The results are listed in Table 6 for some of the materials. Of the materials tested, FoamP showed the greatest mass loss (< 2wt% below 170 °C) likely due to water desorption. No significant signals were observed in the mass spectrometer until 250 °C, at which point decomposition likely begins. EpoxyP and EpoxyN showed only minor weight losses up to 250 °C with no detectable gases seen in the attached mass spectrometer. Work reported in SAND2013-6519 shows that most of the mass loss at lower temperatures is water and CO_2.

A summary of the TGA burn-off experiments can be found in Table 8. In these experiments the sample was heated at 10 °C/min from 30 to 600 °C. Step-hold experiments showed less than 1.5 wt% loss prior to the onset of decomposition. The mass loss given in Table 8 is for the thermal decomposition in argon and the onset temperature is measure of when mass loss begins for a given heating rate. The inflection point, determined from the first derivative of the mass-loss curve, indicates the point of greatest rate of change for mass loss. Differences in these values may indicate a materials' fatigue due to aging. Only minor differences between aged and un-aged parts were recorded. For example, the total mass loss from the virgin FoamN was comparable to all other FoamNs aged at 70, 90 or 110 °C for up to two months. Only FoamP and EpoxyN showed minor decreases in the mass loss upon accelerated aging. The onset temperature for thermal decomposition does show some modest trend downward with aging. FoamP, FoamN and EpoxyN all display a decrease in the onset temperature for decomposition suggesting that accelerated aging, even at 70 °C, might decrease the upper thermal stability of these materials relative to un-aged materials. No change in the inflection point for any of the materials was observed suggesting that the fundamental chemical decomposition reactions for each material are not affected by aging. It should be noted that FoamP and FoamN are not the same density polyurethane. Therefore, any differences in their thermal decomposition behavior cannot be attributed solely to new and old foams.

DSC results, obtained simultaneous in TGA experiments or using a separate instrument were inconclusive. Exothermic heat flows were observed upon thermal decomposition of all samples but quantitative data were not obtained. In Part II, a look at the 1st derivative of the DSC heat-flow curves is compared along-side variable heating rate TGA experiments. The loss of mass with temperature for samples, DSC analysis may be invalid without considering the heat of vaporization in the heat flow measurement.

The premise of the MFK experiments was that if a material undergoes an irreversible chemical change during a bake-out process, this change may be detectable in subsequent thermal decomposition measurements. For example, if one compares the decomposition properties of virgin PMDI foam with 30-year old PMDI foam, the onset temperature for decomposition, or total weight loss might be different between the two materials. Similarly, by using model-free kinetics one can determine the activation energy as a function of conversion for the decomposition of 30-year old foam and compare these data to virgin foam. This approach might also be applied in determining whether or not bake-out causes an irreversible chemical change, as reflected in a change in the activation energy for higher temperature decomposition reactions.

Another reason to employ MFK experiments is to enable thermal stability predictions at lower temperatures. Reactions which may take too long at a given temperature could be predicted if the activation energy is known (based on Arrhenius theory). In practice, however, different reaction mechanisms operate at different temperatures which calls into question the accuracy of extrapolating measured apparent activation energies to different temperature regions. The MFK experiments performed in this study revealed only minors effects of aging. The differences in T versus β curves for EpoxyP and EpoxyN suggest two things. First, EpoxyN appears more susceptible to aging compared to EpoxyP. This difference could be due to incomplete curing of EpoxyN, lack of a glass-filler, or attributed to a 30-year difference in age between the two materials in which EpoxyP has already "aged". Second, these results show that the temperature spread for α is larger at 10% versus 50%. When α = 50% the decomposition process of all ten materials nears convergence, indicating that the thermal decomposition process for all materials is nearly independent of aging. This second point demonstrates the need to understand initial rates of reaction at lower temperatures, where differences between materials are most significant.

5. SUMMARY

Four sets of materials were evaluated using thermal degradation techniques. From these experiments, the main conclusion is that if kept under 90 °C, no significant chemical changes could be detected by TGA or DSC. These data, primarily obtained from TGA experiments show only minor differences between aged and un-aged materials. FoamP compared to FoamN is of different density but both show similar trends upon accelerated aging. The nature of off-gassing or water-loss was not quantitatively determined using TGA-MS experiments due to low instrument sensitivity.

EpoxyP compared to EpoxyN is a composite with a glass fiber and therefore shows significantly less mass loss upon thermal decomposition. However, the onset temperature for decomposition is similar for both EpoxyP and ExpoyN suggesting that EpoxyP has not aged. Interestingly, EpoxyN showed some minor susceptibility to accelerated aging as measured by the drop in onset temperature for decomposition. This observation implies that EpoxyP will not age any more in the next 30 years whereas as new Epoxy may undergo aging. However, since EpoxyP contains a glass fiber it is difficult to make a conclusive prediction.

Other experiments and more extensive bake-out procedures remain to be developed for the handling of these materials. Even at 70 °C, a slight decrease in the onset temperature is observed suggesting that FoamP will continue to age over the next 30 years.

Future experiments should include:

1) Comparing foams of equal density
2) Making a composite epoxy/glass similar to EpoxyP
3) Performing step-hold experiments on aged epoxy materials
4) Repeating mass spectroscopy experiments with improved sensitivity
5) Reanalyze variable heating rate TGA data at $\alpha = 1 - 5\%$
6) Continue MFK analyses with different numerical solutions to determine effects on fit

6. APPENDIX

Tables containing the data used to plot Figures 1 – 6 are given below.

Table 9: Averaged TGA data for FoamN with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	75.19	3.56	304.17	2.02	304.17	2.02	277.32	0.50	288.75	0.60	296.43	0.63	308.99	0.67	333.97	0.82
5	76.34	0.52	288.75	0.29	317.14	1.39	288.37	0.31	300.65	0.35	308.93	0.33	322.78	0.36	349.04	0.46
10	76.00	0.51	296.42	1.36	325.79	1.12	295.95	1.12	308.97	1.07	317.74	1.02	332.62	0.93	359.96	0.63
20	76.54	0.49	303.18	2.24	334.93	1.50	302.56	1.77	316.57	1.76	325.97	1.66	341.91	1.31	370.61	0.64

Table 10: Averaged TGA data for FoamN@70C (aged at 70 °C for two months) with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	76.93	0.47	305.31	2.29	305.31	2.29	275.87	0.33	287.21	0.31	295.23	0.28	308.26	0.25	333.34	0.59
5	77.37	0.99	287.86	0.51	317.41	1.25	286.09	0.39	298.62	0.40	307.15	0.38	321.38	0.38	347.63	0.60
10	78.40	1.24	294.26	0.29	323.91	1.61	293.96	0.34	307.03	0.26	315.99	0.21	331.32	0.23	359.54	0.41
20	76.74	0.39	302.72	0.95	333.96	2.07	302.00	1.11	315.98	1.11	325.45	1.11	341.51	1.17	371.38	1.23

Table 11: Averaged TGA data for FoamN@90C (aged at 90 °C for two months) with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	74.67	2.13	304.55	0.71	304.55	0.71	276.67	0.53	288.73	0.50	296.71	0.48	309.57	0.52	334.98	0.76
5	77.34	0.75	289.75	0.38	317.88	0.86	287.96	0.52	300.68	0.53	309.23	0.46	323.40	0.41	350.49	0.71
10	78.24	0.02	296.54	1.14	326.61	0.33	296.19	0.87	309.61	0.86	318.61	0.81	333.71	0.72	362.01	0.73
20	77.96	1.51	302.09	1.08	335.18	0.81	301.95	0.95	316.46	0.84	326.16	0.82	342.65	0.88	372.48	0.88

Table 12: Average TGA data of FoamN@110C (PMDI foam aged at 110 °C for one month) with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	76.00857	1.43	282.04	38.43	282.04	38.43	275.69	0.29	287.69	0.29	295.89	0.23	308.98	0.19	334.17	0.65
5	76.25	0.46	289.20	0.96	317.00	1.32	287.02	0.93	299.70	0.90	308.27	0.71	322.55	0.38	349.54	0.37
10	73.97	2.68	296.81	0.90	324.42	0.26	295.00	0.78	308.24	0.81	317.18	0.84	332.28	0.84	360.50	0.76
20	78.77	2.27	302.60	1.19	334.08	0.91	302.26	0.77	316.22	0.87	325.64	0.92	341.75	0.77	371.59	0.69

Table 13: Averaged TGA data for FoamN@110C-2 months (PMDI foam aged at 110 °C for two months) with variable heat rates (30 to 600 °C)

Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	67.74	0.81	304.92	0.68	304.92	0.68	275.17	0.71	287.41	0.64	295.77	0.56	309.15	0.52	334.20	0.51
5	72.16	1.15	288.41	0.75	317.49	0.06	286.66	0.86	299.77	0.81	308.53	0.72	322.98	0.65	349.94	0.54
10	73.77	1.67	295.46	0.74	327.02	0.34	294.54	0.53	308.26	0.52	317.49	0.48	332.94	0.36	361.88	0.10
20	76.13	0.47	301.19	0.77	334.30	1.62	300.94	0.69	315.53	0.81	325.37	0.91	342.01	1.07	372.34	1.16

Table 14: Averaged TGA date for FoamP RT with variable heat rates (30 to 600 °C)

Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	77.46	0.13	316.10	1.72	316.10	1.72	283.23	0.08	300.25	0.28	309.87	0.36	325.46	0.44	442.41	2.76
5	81.17	0.57	302.16	0.48	330.33	0.76	293.41	0.58	312.05	0.35	322.76	0.32	338.78	0.23	439.08	1.83
10	80.30	0.59	312.34	0.28	341.81	0.10	302.64	1.24	322.25	0.98	333.59	0.92	349.97	1.32	440.44	4.83
20	81.17	0.30	320.37	0.62	353.19	0.23	310.66	1.29	331.72	0.81	344.05	0.67	362.12	1.02	452.49	4.99

Table 15: Averaged TGA data for FoamP@70C (aged 2 months at 70 °C) with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	67.16	1.82	313.81	2.33	313.81	2.33	276.02	3.02	291.61	2.40	301.64	2.39	316.45	2.31	342.83	4.75
5	76.66	1.06	298.93	0.56	327.25	1.72	289.74	0.77	305.91	0.81	316.26	0.85	330.20	0.95	352.69	1.35
10	77.83	0.88	309.40	1.83	339.61	1.19	298.62	1.86	315.61	1.89	326.51	1.81	340.72	1.75	361.76	2.01
20	80.84	1.06	318.59	1.17	352.29	1.75	307.70	0.25	325.31	0.20	337.05	0.11	352.57	0.26	374.99	1.54

Table 16: Averaged TGA data for FoamP@90C (aged 2 months at 90 °C) with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	71.49	0.16	310.64	2.80	310.64	2.80	278.14	1.26	293.30	1.25	303.02	1.31	317.29	1.20	344.75	2.37
5	75.79	0.80	299.59	0.86	328.49	1.48	289.12	0.53	305.74	0.45	316.33	0.42	330.28	0.29	352.50	0.93
10	76.75	0.55	309.78	1.31	340.23	2.61	298.81	1.71	315.72	1.73	326.91	1.63	341.35	1.77	363.16	1.97
20	77.61	0.60	317.92	2.12	351.07	2.86	306.81	3.13	324.26	3.24	336.03	3.07	351.43	3.09	373.35	3.96

Table 17: Averaged TGA data for FoamP@110C-1month (aged 1 month at 110 °C) with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	76.43	0.48	313.50	2.32	313.50	2.32	283.55	0.90	299.67	0.81	309.17	0.78	325.44	0.99	473.18	2.28
5	80.18	0.80	300.79	0.43	328.38	0.79	291.82	0.70	310.27	0.60	321.19	0.58	337.05	0.75	443.42	8.79
10	79.44	0.30	310.73	1.17	340.20	0.34	299.37	0.73	319.29	0.92	331.27	0.89	347.62	0.86	444.18	3.35
20	79.81	0.65	318.57	1.90	351.35	1.96	306.42	2.53	327.02	2.36	340.02	2.13	357.32	2.12	446.66	9.31

Table 18: Averaged TGA data for FoamP@110C-2months (aged 2 months at 110 °C) with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	75.16	0.51	314.15	1.70	314.15	1.70	281.31	0.42	299.34	0.54	309.66	0.60	327.35	0.68	467.33	4.22
5	77.91	0.47	301.09	0.92	329.54	1.08	290.95	2.12	310.65	1.87	322.11	1.71	339.12	1.97	453.96	10.14
10	76.96	1.41	310.14	1.36	341.45	0.26	298.81	0.95	319.57	0.78	331.97	0.71	349.51	0.76	463.15	9.42
20	77.65	1.30	315.89	1.70	349.22	1.99	305.52	1.87	326.07	1.68	339.07	1.60	357.06	1.44	458.77	4.66

Table 19: Averaged TGA data for EpoxyN at RT with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	78.29	0.12	351.55	1.69	351.55	1.69	339.30	0.25	345.44	0.14	349.64	0.09	357.60	0.06	374.02	0.29
5	79.51	0.34	355.61	0.28	368.74	0.05	355.87	0.65	362.59	0.39	367.04	0.30	375.25	0.30	390.94	0.45
10	78.75	0.28	370.31	0.18	387.28	2.00	369.45	0.61	376.33	0.39	380.90	0.29	389.12	0.16	404.54	1.07
20	82.64	0.59	385.66	0.63	399.60	0.91	383.55	0.78	390.59	0.67	395.07	0.59	402.22	0.53	416.55	0.60

Table 20: Averaged TGA data for EpoxyN@70C (aged at 70 °C for 2 months) with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	76.9806	0.72	349.91	0.05	349.91	0.05	336.92	0.19	343.85	0.10	348.40	0.10	356.91	0.17	374.22	0.51
5	78.59	0.70	353.75	0.34	368.37	1.34	353.74	0.29	361.11	0.20	365.87	0.15	374.65	0.14	391.58	0.39
10	79.53	0.97	368.51	0.94	385.51	0.81	367.34	0.34	374.89	0.25	379.77	0.25	388.30	0.22	404.46	0.27
20	80.92	0.31	383.49	1.56	397.78	0.55	380.50	1.34	388.42	0.86	393.41	0.72	401.18	0.46	416.31	0.35

Table 21: Averaged TGA data for EpoxyN@90C (aged at 90 °C for 2 months) with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	75.38	0.22	349.00	0.03	349.00	0.03	331.90	0.55	340.33	0.25	345.66	0.14	355.23	0.07	373.61	0.27
5	78.08	0.56	348.80	0.33	366.73	0.04	348.14	0.05	357.31	0.06	362.96	0.07	372.98	0.02	391.49	0.18
10	77.39	0.29	362.66	0.53	384.98	3.61	361.61	0.27	371.02	0.05	376.77	0.02	386.83	0.18	404.46	0.87
20	79.75	0.86	380.79	0.49	398.03	0.10	376.04	0.37	385.39	0.21	391.09	0.19	399.67	0.21	415.22	0.58

Table 22: Averaged TGA data for EpoxyN@110C-1month (aged at 110 °C for 1 months) with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	75.89	0.60	348.18	0.03	348.18	0.03	323.79	1.02	335.76	0.51	342.46	0.36	353.65	0.22	374.16	0.20
5	76.79	0.16	344.44	0.22	366.76	1.70	341.04	0.45	353.04	0.28	359.89	0.23	371.22	0.28	390.84	0.30
10	76.25	0.56	359.02	0.80	382.26	3.21	355.07	0.18	367.11	0.13	374.00	0.10	385.28	0.12	404.51	0.03
20	79.20	0.03	375.29	1.39	395.42	1.20	368.29	0.74	380.98	0.46	388.07	0.36	398.46	0.07	415.51	1.41

Table 23: Averaged TGA data for EpoxyN@110C-2month (aged at 110 °C for 2 months) with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	73.25	0.37	346.53	0.90	346.53	0.90	320.84	1.23	334.11	0.67	341.48	0.47	353.38	0.45	374.99	0.57
5	74.91	0.37	342.80	1.02	370.18	2.44	335.84	1.18	350.64	0.66	358.53	0.45	370.84	0.42	391.35	0.11
10	75.86	0.61	356.45	2.51	380.41	1.41	347.82	1.84	363.39	1.30	371.67	1.04	383.93	0.39	403.60	0.09
20	76.65	0.49	373.17	0.97	394.68	2.53	361.04	2.01	377.11	1.24	385.47	0.81	396.68	0.04	415.33	0.66

Table 24: Averaged TGA data for EpoxyP at RT with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	28.54	0.96	351.10	0.39	351.10	0.39	338.57	0.35	345.77	0.15	350.21	0.15	358.11	0.16	376.43	0.28
5	30.67	0.25	357.10	0.59	368.89	1.43	356.34	0.16	363.34	0.16	367.63	0.29	375.59	0.46	393.17	0.87
10	30.53	2.49	369.92	1.09	381.91	0.94	369.59	1.33	376.72	0.77	381.11	0.47	389.26	0.28	406.31	0.35
20	28.51	0.34	383.05	1.68	398.04	0.83	382.54	1.40	389.70	1.23	394.06	1.18	401.85	0.99	416.22	0.48

Table 25: Averaged TGA data for EpoxyP@70C (aged at 70 °C for 2 months) with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	28.24	2.31	352.01	1.14	352.01	1.14	336.88	2.21	344.58	1.60	349.31	1.24	357.62	1.09	375.98	1.31
5	28.89	1.57	356.36	0.74	368.07	0.68	355.67	0.71	362.87	0.71	367.29	0.69	375.48	0.74	393.40	0.99
10	31.16	2.38	368.23	0.39	380.09	1.15	367.96	0.60	375.14	0.22	379.57	0.26	387.89	0.33	404.78	0.37
20	30.04	1.13	381.53	2.36	397.57	0.73	380.70	2.66	388.27	2.06	392.84	1.74	400.84	1.32	414.90	0.95

Table 26: Averaged TGA data for EpoxyP@90C (aged at 90 °C for 2 months) with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	28.80	1.67	350.84	1.27	350.84	1.27	333.32	1.52	341.88	1.19	347.18	0.99	355.98	0.76	374.49	0.65
5	29.69	0.58	352.43	0.84	366.95	0.77	350.17	1.45	359.02	1.15	364.24	0.85	373.05	0.76	390.84	0.97
10	33.33	1.35	366.08	0.28	379.29	0.70	365.24	0.25	373.29	0.11	378.03	0.03	386.85	0.15	404.70	0.19
20	32.46	1.17	378.61	0.57	394.42	1.75	377.66	0.87	385.87	0.52	390.73	0.33	399.42	0.36	414.71	0.58

Table 27: Averaged TGA data for EpoxyP@110C-1month (aged at 110 °C for 1 month) with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	26.74	2.29	351.19	1.15	351.19	1.15	334.28	2.49	343.16	1.63	348.45	1.17	357.17	0.66	375.98	0.24
5	29.24	1.04	355.85	0.53	369.13	0.86	354.01	0.73	362.16	0.59	366.90	0.41	375.23	0.30	392.88	0.41
10	29.65	0.36	369.61	0.30	382.00	0.20	368.22	0.68	376.05	0.45	380.56	0.34	388.85	0.34	405.95	0.35
20	30.67	0.98	382.15	1.13	395.30	1.33	380.98	0.83	388.59	0.79	392.97	0.78	400.80	0.64	416.16	0.68

Table 28: Averaged TGA data for EpoxyP@110C-2months (aged at 110 °C for 2 months) with variable heat rates (30 to 600 °C)																
Heating Rate	wt% loss	stdev	onset point	stdev	inflection point	stdev	10% conversion	stdev	20% conv	stdev	30% conv	stdev	50% conv	stdev	75% conv	stdev
2	29.61	0.16	353.10	0.39	353.10	0.39	335.60	0.31	343.86	0.12	348.99	0.05	357.42	0.04	375.52	0.25
5	26.92	1.49	354.44	0.79	368.90	0.73	352.04	0.11	360.66	0.23	365.92	0.21	374.42	0.11	391.51	0.17
10	31.60	0.89	369.80	0.74	381.19	0.66	368.58	0.71	376.12	0.60	380.59	0.47	388.73	0.30	405.50	0.06
20	31.57	2.06	382.04	0.75	394.96	1.94	380.14	0.94	388.08	0.79	392.62	0.95	400.63	1.11	416.11	0.88

Table 29:Mean and SD of three experiments measuring the peak heat flow via DSC for new epoxy (EpoxyN) with variable heating rates (300 to 600 °C)

Heating Rate	EpoxyN RT	SD	EpoxyN@70C	SD	EpoxyN@90C	SD	EpoxyN@110C-1month	SD	EpoxyN@110C-2months	SD
2	332.21	0.35	332.03	0.49	329.00	0.51	330.03	1.96	324.69	3.48
5	359.45	13.94	366.70	7.55	351.68	13.39	356.78	7.41	358.35	17.44
10	387.96	5.75	387.89	3.43	392.04	7.50	386.14	0.63	384.11	14.83
20	398.02	15.73	374.57	7.11	420.92	#DIV/0!	#DIV/0!	#DIV/0!	373.84	39.58

Table 30:Mean and SD of three experiments measuring the peak heat flow via DSC for epoxy part (EpoxyP) with variable heating rates (300 to 600 °C)

Heating Rate	EpoxyP RT	SD	EpoxyP@70C	SD	EpoxyP@90C	SD	EpoxyP@110C-1month	SD	EpoxyP@110C-2months	SD
2	328.54	0.77	328.81	1.15	324.75	1.11	328.85	1.87	329.51	1.03
5	327.55	1.50	327.00	0.76	322.84	1.24	328.92	0.72	327.28	0.76
10	363.55	3.39	343.23	19.70	303.00	3.64	355.02	23.08	350.27	10.68
20	376.81	3.29	391.10	#DIV/0!	363.80	11.73	367.66	6.09	386.77	10.50

Table 31:Mean and SD of three experiments measuring the peak heat flow via DSC for new foam (FoamN) with variable heating rates (300 to 600 °C)										
Heating Rate	FoamN RT	SD	FoamN@70C	SD	FoamN@90C	SD	FoamN@110C-1month	SD	FoamN@110C-2months	SD
2	321.39	0.46	320.88	3.70	318.48	5.51	320.52	0.83	325.43	3.85
5	343.39	2.63	340.12	2.57	338.89	3.22	336.44	2.24	348.52	3.85
10	373.88	3.06	366.72	3.83	362.68	0.62	367.08	4.20	370.25	5.73
20	402.01	5.99	371.82	5.89	399.32	0.01	386.32	27.32	408.25	19.59

Table 32:Mean and SD of three experiments measuring the peak heat flow via DSC for Foam part (FoamP) with variable heating rates (300 to 600 °C)										
Heating Rate	FoamP RT	SD	FoamP@70C	SD	FoamP@90C	SD	FoamP@110C-1month	SD	FoamP@110C-2months	SD
2	327.15	0.45	325.80	2.82	324.40	6.12	321.52	0.38	325.19	0.32
5	344.41	1.61	343.06	2.02	342.19	2.00	340.73	2.82	343.64	2.17
10	382.66	1.09	373.56	3.93	369.79	3.15	373.39	3.62	375.16	9.81
20	418.34	10.37	#DIV/0!	#DIV/0!	407.57	0.76	420.26	4.93	418.31	#DIV/0!

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