

Study of Stability of High-Temperature Polyimides Using TG/MS Technique

WEI XIE, REBECCA HELTSLEY, XINHUA CAI, FUQUAN DENG, JIEMIN LIU, CHARLES LEE, WEI-PING PAN

Thermal Analysis Laboratory, Material Characterization Center, Department of Chemistry, Western Kentucky University, Bowling Green, Kentucky 42101

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ABSTRACT: The oxidative stability of the carbon fiber-reinforced composite of polyimide was examined, in real time, using the evolved gas analysis techniques. Off-gas degradation products suggested the onset temperature for chain scissions to be fairly low at about 190–220°C. Based on the off-gas products present and the trend of their release, the composite degradation mechanism appeared to be similar between 190 and 371°C, thereby marking 371°C to be the highest accelerated aging temperature for its long-term lifetime prediction. Beyond 371°C, different degradation mechanisms would apply. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1219–1227, 2002

Key words: thermal analysis; polyimides; TGA; degradation

INTRODUCTION

Currently, carbon fiber-reinforced composites of polyimides are being used in aircraft engines and many space applications. When these composites are utilized in such applications they must be capable of functioning in temperatures as high as 371°C^{1–4} up to 427°C.⁵ At these high service temperatures, the thermal stability and thermal oxidative stability (TOS) of the polymer matrix are of primary concern. Any thermal decompositions or thermal oxidative degradations could, potentially, affect their high temperature applications.

With regard to the assessment of polymer stability, Thermogravimetry Analysis (TGA) is usually employed to determine the temperature of initial weight loss, which can be viewed as the

onset of degradations. Moreover, it can be used to monitor continually the weight loss kinetics.^{6,7} Although the end results of thermal and/or thermal oxidative degradations in terms of weight loss are measurable by TGA, their degradation pathways are not readily assessable without the aid of an on-line evolved gas analysis. Once again, Thermogravimetric Analyzer/Fourier Transform Infrared Spectrometer (TG/FTIR) and Thermogravimetric Analyzer/Mass Spectrometer (TG/MS)^{8–10} offer the means of identifying, in real time, small gaseous products like CO₂, H₂O, CH₄, and CO, as well as large organic species.

The stability of polyimide composites has been studied extensively. Zhang¹¹ studied the thermal and oxidative stability of Cytec[®] 5260/IM7, a BMI composite, by TG/FTIR. In addition, the same BMI composite was later examined by Zhong¹² using TG/MS. Mass fragments including such large organic species as phenylisocyanate, methylphenyl isocyanate, benzosuccinimide, etc., were noted. The FTIR/MS data suggested the methylene group in the backbone to be the initiation site for degradation. More works on the thermooxidative stability of fluorinated polyimides at 371°C

Correspondence to: W.-P. Pan.

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had been done by Scola,¹³ who examined and compared the high-temperature performance of various fluorinated polyimides including 3F-PDA, 36F-PDA, AFR700B, and other PMR-type resins at 371°C and above. More recently, Alston¹⁴ investigated the thermal oxidative stability of several high-temperature polyimides using TG/FTIR. The presence of degradation products such as phenyl isocyanate, *p*-phenylene diisocyanate, and trifluoromethane in a 3F polyimide led them to propose the degradation initiation site to be either imide or fluorinated linkages. The proposition that the degradation in a 3F or 6F polyimide started at a fluorinated linkage agreed well with the theoretical bond order calculations by Lee.¹⁵ They found the C—CF₃ linkage to have the smallest bond order and thus, the largest C—C bond distance. Hence, this C—CF₃ linkage would be the initiation site of degradation.

In the present study, the stability of a postcured AFR700B/T650-35 laminate was determined using TG/MS. Thermal aging of this laminate was conducted in a nitrogen environment while thermal oxidative aging was carried out in air. Both dynamic and isothermal aging were conducted for stability study. Weight loss and off-gas evolutions were measured as a function of aging time and temperature. These MS off-gas profiles formed the basis of degradation pathway probe.

In addition to stability determination and degradation mechanism examinations, an attempt to determine the highest accelerating aging temperature for long-term durability assessment was made for this AFR700B/T650-35 composite. In general, the lifetime of a polymer composite is estimated, on the basis of its weight loss, through accelerated aging. At elevated aging temperatures, it is easy to induce degradations and thus, a large measurable weight loss. If the degradation mechanisms remain the same over a given range of aging temperatures, one can determine the weight loss kinetics and then, estimate the corresponding aging time needed to produce the same weight loss at a lower aging temperature. If the degradation mechanisms change, this type of lifetime calculation based solely on weight loss kinetics could lead to misleading conclusions. In the absence of on-line degradation product identifications in the past, degradation mechanisms were, in general, assumed to stay the same for expediency sake. At the advent of evolved gas analysis by TG/FTIR and/or TG/MS, the off-gas degradation products are detectable, thereby providing the means of checking and verifying, in real time,

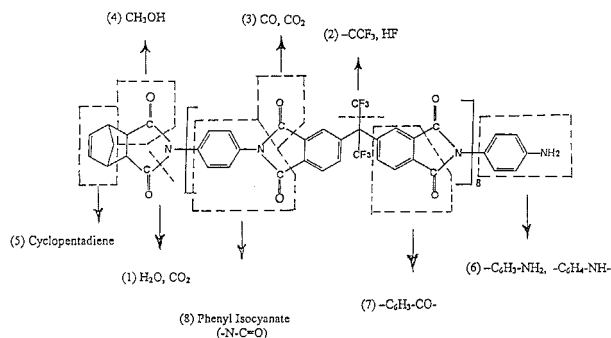


Figure 1 The structure of AFR700B/T650-35.

if the degradation pathways remain the same. Moreover, one can easily determine the aging temperature beyond which degradation mechanisms have changed and thus, define the maximum allowable accelerating aging temperature. To this end, the AFR700B/T650-35 composite was aged between 220 and 600°C followed by 4 h hold at the given aging temperature. Their off-gas degradation products were analyzed for accelerated aging temperature limit determination.

EXPERIMENTAL

Material Selection

The postcured AFR700B/T650-35 composite was employed for the polyimide stability study, which is made from NE, monomethylester of 5-norbornene-2, 3-dicarboxylic acid; PPDA, *para*-phenylenediamine; and 6FDE or HFDE, di-methylester of 4,4' hexafluoroisopropylidene bisphthalic acid using methanol as the solvent. Figure 1 displays its formulation. Reinforced with 3K intermediate modulus carbon fiber T650-35, the AFR700B/T650-35 prepreg was produced. The postcure conditions of AFR700B/T650-35 were shown in the Appendix. A Thermomechanical Analysis (TMA) measurement of this postcured laminate at 10°C/min gave its glass temperature at 417°C indicating that it has reached a T_g beyond 371°C. For TG/MS experiments, ground irregular shaped powders by the use of a metal file having a nominal size of 0.1–0.2 mm were employed.

Characterization Techniques

Thermomechanical Analyzer (TMA 943) measured the glass transition temperature of the postcured AFR700B/T650-35 composite in air.

TG/MS technique was used to identify the evolved gas species. The details of TG/MS set up were shown elsewhere.¹⁶

RESULTS AND DISCUSSIONS

AFR700B/T650-35 Composite Stability Study TGA Weight Loss

Regardless of the purge gas type, less than 3% weight loss in the composite occurred below 500°C at 10°C/min. In general, the largest weight loss rate took place at about 550–570°C in both nitrogen and air. Most of the off-gas products came about between 550 and 600°C. At 10°C/min, this composite lost 17% of its weight at 600°C in nitrogen, whereas the weight loss reached 35% in air. Thus, this composite lost more of its weight in air. Consequently, the composite is much more stable in nitrogen than in air. In other words, its thermal stability is greater than its oxidative stability. The composite lost 34% of its weight in air at 5°C/min. Compared to its 35% weight loss at 10°C/min, the heating rate did not appear to affect the composite weight loss kinetics at all.

The mass spectra of this composite were generated at 5°C/min in air, as seen in Figure 2. It is interesting that water ($m/e = 18$) had three peaks at 78, 311, and 500°C, respectively. Moreover, its first peak at 78°C appeared to be the major species given off below 100°C. The second water peak covered a broad temperature range between 230 and 455°C. The third one began at 455°C and extended to 600°C. These three water peak temperatures might vary, depending upon the heating rate used. Their presence, however, revealed the existence of three separate release mechanisms. The evolution of absorbed water or surface moisture was responsible for the first peak. The second peak might be due to oxidative degradations of the neat resin, while the third one might also involve carbon fibers.⁶ There was indication that residual methanol ($m/e = 31$) was given off shortly after heating started.

The second mass fragment examined was HCF_3 ($m/e = 70$), which started to evolve at 220°C. It reached a peak at 302°C. This finding was in agreement with the theoretical bond order calculation of Lee¹⁵ predicting $-\text{C}-\text{CF}_3-$ to be the weakest bond in a 6F polyimide. HCF_3 also displayed a second peak at 498°C. Shortly after the release of HCF_3 , HF ($m/e = 20$) was given off. Similar to the former, HF possessed two peaks as

well at approximately the same peak temperatures. Close to the initial presence of HCF_3 and HF, the second CH_3OH peak started to come off and continued to develop into a larger third peak with peak temperatures in proximity to those of H_2O , HF, and HCF_3 . Next, $-\text{C}_6\text{H}_3-\text{NH}_2$ or $-\text{C}_6\text{H}_4-\text{NH}-$ ($m/e = 91$) began to come off at about 250°C, indicating that the AFR700B end group, $-\text{C}_6\text{H}_4-\text{NH}_2$, may be vulnerable to oxidative degradation. It reached a peak at 300°C. Its release was complete at 366°C. At 275°C, the evolution of $-\text{C}_6\text{H}_3-\text{CO}-$ ($m/e = 103$) commenced. It possessed two peaks, one at 330°C, and the other at 500°C. Its first mass peak ended at 455°C. A single mass peak for cyclopentadiene ($m/e = 66$) at 500°C was seen. Its release started at about 450°C and continued on to 600°C, suggesting the vulnerability of the AFR700B NE end group to oxidative degradation. Carbon dioxide, CO_2 , at $m/e = 44$ began to show up at 250°C, and its evolution increased throughout the entire TGA/MS run. Its rate of release accelerated greatly at 450°C, hinting strongly the onset of carbon fiber oxidation. A comparison with the TG/MS evolve gas analysis of AFR700B neat resin may provide an insight to the onset point of carbon fiber involvement.

Several observations can be made from the above TG/MS evolved gas analysis. A number of off-gases were detected having peak rates of release close to 300–330°C. The presence of CH_3OH , H_2O , HCF_3 , HF, $-\text{C}_6\text{H}_4-\text{NH}_2$, and $-\text{C}_6\text{H}_3-\text{CO}-$ would suggest that extensive oxidative degradations had already taken place. The weight loss of AFR700B/T650-35 composite between 100 and 300°C was just 0.9% (2.2–1.3 = 0.9), which translated to a 3% neat resin weight loss at a 70/30 carbon fiber/resin weight content in the composite. After the initial loss of absorbed moisture, the polyimide resin would have undergone substantial degradations to produce a 3% weight loss. Thus, it is fair to say that at 300°C, oxidation has started and progressed to backbone chain scissions. It is also important to note that most off-gas products were given off in two stages. The second stage commenced at 450°C. Their evolutions picked up in speed and resulted in a second peak close to 500°C. Even though detailed degradation mechanisms for the second peak are not yet known, it is doubtful they were the same as the first peak. Moreover, their kinetics may be different. To complicate the situation further, new off-gases were seen in the elevated temperature region. Therefore, the use of elevated tem-

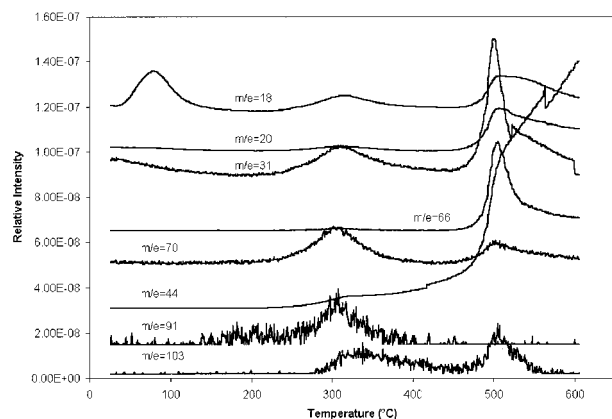


Figure 2 MS profile of AFR700B/T650-35 heated to 600°C in air at 5°C/min.

peratures above 500°C for accelerated aging would have serious limitations. It appeared that for durability assessment, long-term isothermal aging should be made at lower temperatures, which need to be determined experimentally.

Figure 3 showed the corresponding mass profiles for the AFR700B/T650-35 composite, when heated to 600°C in nitrogen at 5°C/min. A comparison of Figures 2 and 3 would shed some insight into the difference between aging in air/oxidative degradation and aging in nitrogen/thermal degradation. The summarized results at both air and nitrogen atmosphere were presented in Table I. First of all, the same mass fragments, i.e., at $m/e = 18, 20, 31, 44, 66, 70, 91,$ and 103 were present in both aging environments. It implied that the major degradation pathways involved might be similar. For $m/e = 18, 20,$ and 44 , little difference in the mass profile shape existed. For $m/e = 66, 70, 91,$ and 103 , their mass intensity

exhibited two peaks in air. The first peaks were smaller having a peak temperature close to 308°C, while the larger second peaks occurred at 500°C. The first peaks ended between 350 and 400°C. On the other hand, when the same composite was aged in nitrogen only a shoulder appeared around 408°C, which developed into a single peak at about 520°C. Moreover, for $m/e = 69$ ($-\text{CF}_3$), which is not shown in the figure, it was surprising to see that its release began as early as 120°C in both air aging and nitrogen aging regardless of the aging environment used. For $m/e = 66$ and 103 , their evolution took place at about the same temperature range (around 280°C) in air. However, their release in air diminished to nil at the end of the first peak and restarted to grow into a larger second peak. It would be difficult to ascertain the details of their degradation pathways on the basis of this MS data alone. Nevertheless, one could surmise that the composite degradation mechanisms started to change between 220 and 280°C, depending upon the aging environment used. Of course, one should bear in mind that this temperature range would vary with the heating rate during aging due to thermal lag. A smaller heating rate, which is closer to an isothermal aging, would decrease the temperature range for the onset of this degradation mechanism change.

Degradation Pathway Study

The off-gas products identified with the aid of MS were employed to probe the degradation pathways of AFR700B/T650-35 composite. Many gas products were detected during aging. Some of these off-gas products may be the intermediate

Table I Degradation Products of AFR700B/T650-35 in Both Air and Nitrogen Atmosphere with a Heating Rate of 5°C/min

Degradation Products	m/e	Peak Temperature (°C)					
		Air	N ₂	Air	N ₂	Air	N ₂
Water	18	78	78	311	320	500	510
HF	20			311		500	510
CH ₃ OH	31			311		500	500
CO ₂	44				320	500	510
Cyclopentadiene	66				470	500	510
HCF ₃	70			302		498	495
$-\text{C}_6\text{H}_3-\text{NH}_2/-\text{C}_6\text{H}_4-\text{NH}-$	91			300	420		500
$\text{C}_6\text{H}_3-\text{CO}-$	103			330		500	510

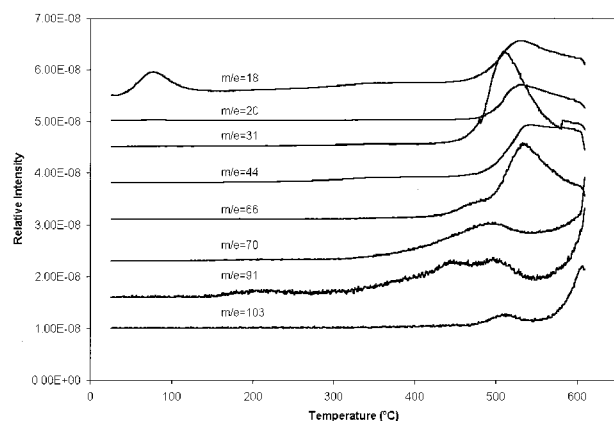


Figure 3 MS profile of AFR700B/T650-35 heated to 600°C in nitrogen at 5°C/min.

mass fragments produced by electron collisions in the mass spectrometer. For this degradation pathway study, only those ions and mass fragments related to and derivable from the AFR700B polymer structure (Fig. 1) were taken into consideration, including H_2O , CO , CO_2 , $-\text{CF}_3$, HF , CH_3OH , $-\text{C}_6\text{H}_3-\text{NH}_2$, $-\text{C}_6\text{H}_3-\text{CO}-$, $-\text{N}-\text{C}=\text{O}$ (phenyl isocyanate), and cyclopentadiene. Therefore, the emphasis was placed on the initial breakdown of the polymer backbone, instead of following the actual oxidation and subsequent reaction sequence leading to the various degradation products. Thus, this degradation mechanism study addressed mainly the onset of polyimide chain breakdown while leaving out the degradation pathway details.¹⁷ The motivation behind this approach was that once polymer chain breakdown commenced, those neat resin dominated composite properties would have deteriorated rapidly.

Once absorbed or trapped moisture and residual volatile were driven off by heating, thermal, and/or oxidative aging of the AFR700B/T650 composite started. Figure 1 showed the potential chain breakdown sites: (1) the intermediate and complete oxidation of $-\text{C}_x\text{H}_y-$ or $\text{R}-\text{C}=\text{O}-\text{R}'$ producing H_2O and CO_2 ; (2) the loss of HCF_3 or $-\text{CF}_3$ from the $-\text{C}-\text{CF}_3$ bond of $\text{CF}_3-\text{C}-\text{CF}_3$ commencing at 220°C, which was the weakest bond (also a side chain) in AFR700B, to be followed by the break-off of $-\text{F}$ from $-\text{CF}_3$ to form a HF molecule; (3) the split off of imide carbonyl, $-\text{C}=\text{O}-$, by breaking the $-\text{N}-\text{C}$ single bond of $-\text{N}-\text{C}=\text{O}-$ and the $-\text{C}-\text{C}-$ single bond of the adjacent $-\text{C}-\text{C}_6\text{H}_3-$ group; (4) the break-off of a $-\text{CH}-$ attached imide carbonyl group from the norbornene ring to form CH_3OH ; (5) the loss of cyclopentadiene from the end norbornene

group; (6) the split off of the end aniline group, $-\text{C}_6\text{H}_3-\text{NH}_2$; (7) the break-off of $-\text{C}_6\text{H}_3-\text{C}=\text{O}$ from the phenyl imide ring; (8) the release of phenyl isocyanate, $\text{C}_6\text{H}_5-\text{N}-\text{C}=\text{O}$, from the phenyl imide group.

The release of these degradation products began at slightly different temperatures according to their relative stability. Some off-gases occurred at about the same temperatures suggesting the possibility that they were concurrent and competitive degradation processes. Nevertheless, it was quite interesting to note that these off-gas products were in general agreement with the degradation events reported by Alston¹⁴ for 3F and 6F polyimides.

Accelerated Aging Temperature Determination

Accelerated aging was usually the methodology adopted for assessing long-term durability of a composite. For a first-order approximation, expediency, and simplicity, weight loss, instead of composite property measurements, was used. The underlying principle involved was the hidden assumption that once a significant weight loss took place, polymer chain breakage followed resulting in property deterioration. Furthermore, the use of high accelerated aging temperatures to reduce the aging time needed and then, extrapolated to the lower service temperature required that the degradation mechanisms remained the same throughout the entire temperature range. Without the knowledge of degradation products occurring in real time and thus, the corresponding degradation mechanism, the weight loss kinetics was used, in the past, for service lifetime prediction. As a result, lifetime prediction was, in general, not accurate. With the aid of this TG/MS evolved gas analysis, the degradation products could be determined in real time. Consequently, one could use the off-gas products as a guide for assessing if similar degradation mechanism occurred. Simply stated, if the same set of degradation products were detected and also, given off at similar kinetics within a prescribed temperature range, the high-end temperature would, then, be the highest accelerated temperature allowable. The accelerated aging temperature for AFR700B/T650-35 composite was determined in 220–600°C by the following scheme.

The weight loss in AFR700B/T650-35 composite was heated at 5°C/min and 10 to 600°C in air as well as in nitrogen. The weight losses at 100, 200, 300, 400, 500, and 600°C were presented in

Table II The Weight Loss of Composites at Different Temperature

Heating Rate	Conditions	Weight Loss (%) at Different Temperature					
		100°C	200°C	300°C	400°C	500°C	600°C
5°C/min	Air	1.30	1.51	2.18	3.26	7.05	44.0
	Nitrogen	0.30	0.38	0.61	0.93	1.81	12.0
10°C/min	Air	0.29	0.43	0.78	1.31	2.98	34.8
	Nitrogen	0.54	0.65	0.79	1.17	2.60	16.5

Table II. The greater stability in an inert aging environment such as nitrogen was evident. The heating rate also affected the weight loss rate. In air, the larger the heating rate, the less the residence time at a given temperature, and the smaller the weight loss became.

Considering the case of aging in air at 10°C/min, the composite lost 1.31% of its weight upon reaching 400°C. Between 400 and 500°C, an additional 1.67% weight was lost. But, most of the weight loss occurred between 500 and 600°C amounting to 31.8%. Assuming a 70/30 carbon fiber/neat resin weight composition, the necessity of carbon fiber participation in oxidative degradations should be obvious. An examination of the corresponding MS profile for $m/e = 18, 20, 31, 44, 66, 70, 91, \text{ and } 103$ (see Fig. 4) revealed a declining intensity for most of the above mass fragments, except for CO_2 at $m/e = 44$. This also tended to support the contention that oxidation of carbon fiber was involved. If the AFR700B/T650-35 composite was heated to 600°C and then, allowed to cool down in ambient condition for about 20 min, one could see that all the above mass fragments including CO_2 decreased in in-

tensity. When AFR700B/T650-35 composite was aged to 600°C at 10°/min in nitrogen, a similar trend in its MS profile to that obtained in aging in air was seen. Another nitrogen aging of AFR700B/T650-35 composite was carried out to 600°C at 10°C/min and held at 600°C for 4 h. Its MS profile showed little effect from the additional 4-h 600°C hold. All the mass fragments continued to decline in intensity. Thus, both the weight loss and the MS profile seemed to indicate that 600°C was too high a temperature for accelerated aging.

When a composite was heated to an aging temperature at a relatively large heating rate as 10°C/min, not necessarily all the degradation products that could be given off were released due to its short residence time. If they could be given off at a lower aging temperature with the aid of a holding period at the lower aging temperature, an equivalent heating history or aging temperature with regard to degradation events could then be established. An attempt to determine the equivalent aging temperature was made by heating AFR700B/T650-35 composite according to the heat history listed below:

1. heated in air to 600°C at 10°C/min
2. heated in air to 500°C at 10°C/min and held for 1 h at 500°C
3. heated in air to 427°C at 10°C/min and held for 4 h at 427°C
4. heated in air to 371°C at 10°C/min and held for 4 h at 371°C
5. heated in air to 316°C at 10°C/min and held for 4 h at 316°C
6. heated in air to 260°C at 10°C/min and held for 4 h at 260°C
7. heated in air to 220°C at 10°C/min and held for 4 h at 220°C.

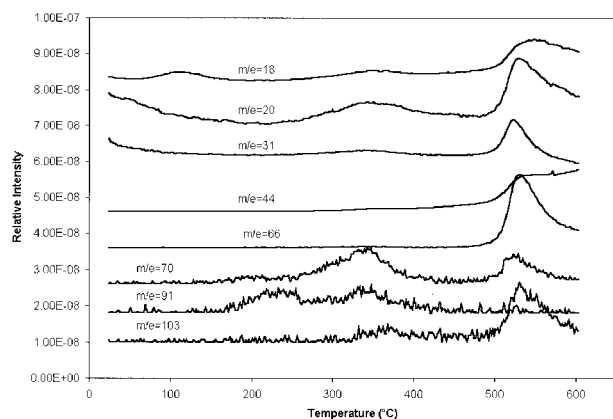


Figure 4 MS profile of AFR700B/T650-35 heated to 600°C in air at 10°C/min.

As the aging temperature was decreased from 600 to 220°C, its holding time should be lengthened exponentially. It was, however, held at a 4-h

interval for saving MS instrument time. This 4-h hold time also kept the holding time a constant in aging temperature reduction experiments.

The MS profiles for $m/e = 18$ (H_2O), 44 (CO_2), and 69 ($-\text{CF}_3$) were investigated for the accelerated aging temperature determination according to decreasing aging temperature. The MS profiles at 500 and 600°C aging showed essentially the similar release trend of H_2O , CO_2 , and $-\text{CF}_3$. Water possessed three peaks. Carbon dioxide gave rise to a plateau first, which was followed by a peak at elevated temperature. The mass species, $-\text{CF}_3$, had two peaks with the second peak at a greater intensity than the first. Their evolution was almost identical, except for the slightly continuing upward turn of CO_2 between 500 and 600°C in the 600°C aging. On the other hand, CO_2 intensity leveled off shortly after reaching 500°C for the 500°C aging. With regard to $-\text{CF}_3$, the former reached a second peak at 520°C, whereas the latter also attained to a second peak shortly after reaching 500°C, the target aging temperature. Because this 500°C aging temperature was so close to the peak temperature in the former at 520°C, the release of $-\text{CF}_3$ would have almost attained its peak. Hence, it was reasonable to expect that given additional aging time at 500°C, a peak in $-\text{CF}_3$ intensity would be and was, in fact, observed. Due to the close resemblance of the release of these off-gases, one can surmise that the 600°C aging in air could be substituted with a 500°C aging and 1 h hold at 500°C.

If the aging temperature was further lowered to 427°C but augmented with a 4-h hold at 427°C (Fig. 5), the release of H_2O , CO_2 , and $-\text{CF}_3$ still retained similar characteristics as those seen for the 600°C aging and the 500°C aging with 1-h

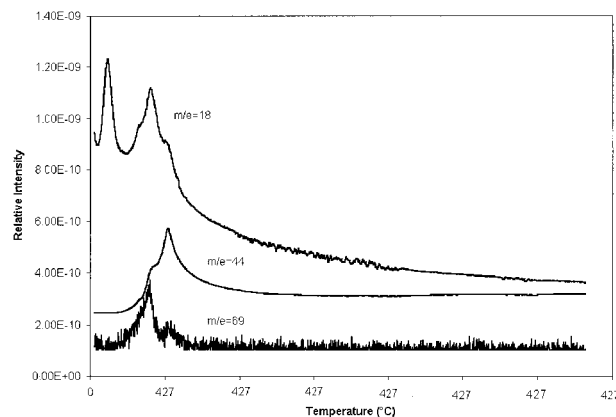


Figure 5 MS profile of AFR700B/T650-35 heated to 427°C in air at 10°C/min and hold for 4 h.

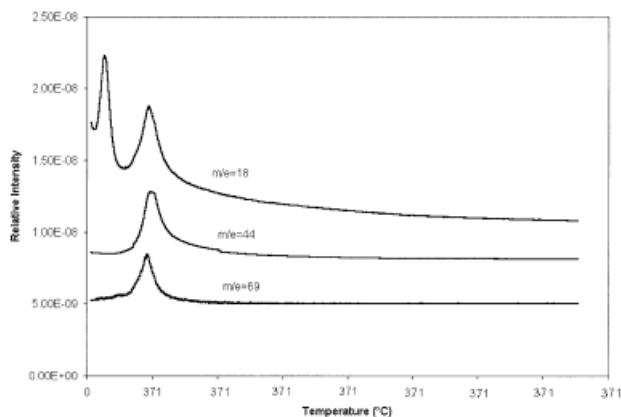


Figure 6 MS profile of AFR700B/T650-35 heated to 371°C in air at 10°C/min and hold for 4 h.

hold at 500°C. The major effect of this lowered aging temperature was to decrease the intensity of the third water peak, the carbon dioxide peak and the second $-\text{CF}_3$ peak. The lack of adequate thermal energy at 427°C to sustain certain degradation processes became evident. Consequently, their peak intensity was greatly reduced. If this aging temperature lowering trend continued, it could reach a point that no peaks would appear. The aging of AFR700B/T650-35 composite at 371°C in air with a 4-h hold confirmed such a trend. Figure 6 clearly indicated that 371°C was too low a temperature to initiate those degradation reactions involved in giving rise to the next peak for water, carbon dioxide, and $-\text{CF}_3$.

By the same reasoning, the preceding peak intensity of H_2O , CO_2 , and $-\text{CF}_3$ could be reduced by continued decreasing aging temperature. This trend was, indeed, noted for aging at 316, 260, and 220°C, respectively. In aging at 220°C, the intensity of the second peak for water, the first peak for carbon dioxide, and the first peak for $-\text{CF}_3$ was all small. Extrapolating further downward to a lower aging temperature like 190°C, one could potentially eliminate the second water peak. Thus, for the production and release of water between 190 and 371°C the decomposition pathways involved were probably similar. Therefore, the limit of its accelerated aging temperature would be 371°C. Beyond 371°C, a different set of water degradation mechanisms would have been started. So, to keep the water degradation mechanism similar for long-term lifetime prediction its accelerated aging temperature should be smaller than 371°C. The accelerated aging temperature limit for carbon dioxide and $-\text{CF}_3$ was only slightly different from that for water. For

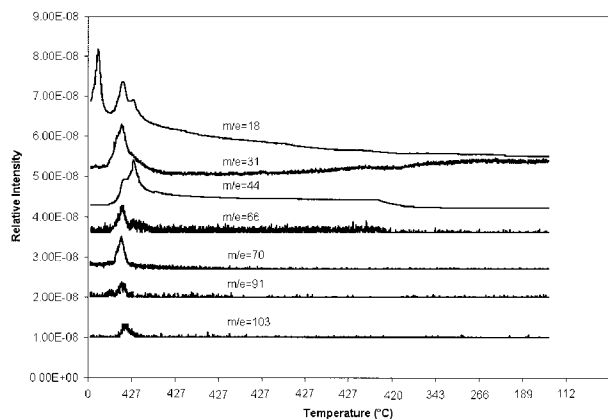


Figure 7 MS profile of AFR700B/650-35 heated to 427°C in air at 10°C/min, hold for 4 h, and then cooled down to 127°C at 1.8°C/min.

simplicity, 371—C could be applied to all these three degradation off-gases. Hence, any accelerated aging temperatures between 190 and 371°C could be used for AFR700B/T650-35 composite.

Water, carbon dioxide, and tri-fluoro carbon functional group ($-\text{CF}_3$) were analyzed for the determination of accelerated aging temperature limit in this study. The primary reasons were two-fold: (1) water and carbon dioxide were the major off-gases from oxidative and thermal degradations; and (2) the tri-fluoro carbon fragment arose from breakage of the weakest bond, $\text{F}_3\text{C}-\text{C}-\text{CF}_3$, in AFR700B. Even though only present at a very small intensity, the presence of $-\text{CF}_3$ would signal the onset of continuing degradations, and thus, an important event. The other mass fragments such as $m/e = 20, 31, 66, 70, 91$, and 103 behaved in a similar fashion. A more complete MS profile (Fig. 7) for $m/e = 18, 20, 31, 44, 66, 91$, and 103 for the aging of AFR700B/T650-35 composite in air at 427°C, held at 427°C for 4 h, and then, cooled down to 127°C at 1.8°C/min was obtained. During cooling, the mass fragments continued to decrease in intensity, some more drastically than others. Thus, the inclusion of a cooling period after its isothermal aging at 427°C brought about little unexpected mass intensity changes. The more complete MS profiles for isothermal aging at 371, 316, and 220°C were obtained; however, they provided no new information.

Based on the aging of AFR700B/T650-35 composite at 600, 500, 427, 371, 316, 260, and 220°C, the above analysis of the off-gas products seemed to indicate that its accelerated aging temperature should be limited to 371°C. Beyond 371°C, its

degradation mechanism would have changed. It was the first time that an *in situ* chemical analysis made such a limit temperature determination possible.

CONCLUSIONS

The use of TG/MS evolved gas analysis technique to study the thermal and oxidative stability of AFR700B/T650-35 composite successfully identified, in real time, some of the important off-gas products during aging, such as H_2O , CO , CO_2 , HCF_3 , HF , CH_3OH , $\text{C}_6\text{H}_5\text{NH}_2$, phenyl isocyanate, cyclopentadiene, etc. In general, they were given off in two separate temperature ranges, having the first peak temperature between 300–330°C and the second peak temperature at about 500–520°C. The higher temperature peak was much greater than the first one, suggesting the participation of carbon fiber in the composite.

The onset temperature for the release of these degradation products from chain scissions was surprisingly small at about 190–220°C. Furthermore, up to this point the composite degradations proceeded in a similar fashion, regardless of the aging environment used. Beyond 220°C, oxidative degradations gaining in speed started to deviate from thermal degradations, resulting in a larger weight loss, and hence, a less stable composite.

The TG/MS evolved gas analysis also provided a convenient means of probing if the thermal oxidative degradations under accelerated aging conditions proceeded according to a similar degradation mechanism by examining the degradation off-gases and their kinetics. When the release of these off-gas products from varying aging temperatures followed the same trend, their degradation mechanisms were deemed to be the same. For the AFR700B/T650-35 composite, its degradation mechanism between 190 and 371°C was found to be similar. Thus, the highest accelerated aging temperature for its long-term lifetime prediction would be 371°C. This marked the first time that an accelerated aging temperature limit was determined according to real-time degradation products.

The use of these evolved gas analysis techniques for studying degradation mechanism detail, and hence, composite stability has some limitations. Due to the large number of mass fragments present in MS, it was difficult to assign chemical structure to some. Moreover, they appeared simultaneously, making detailed degrada-

tion pathway determination a challenging task. Lastly, some nonvolatile chemical intermediates produced from thermal oxidative degradations would escape detection by evolved gas analysis. Thus, complimentary techniques such as temperature programmable FTIR and NMR may prove useful in monitoring those chemical structures.

In this composite stability study, the emphasis had been placed on its chemical origin instead of mechanical performance. It would be most useful to relate any major chemical changes including chain scissions to composite mechanical property changes. To do so requires the knowledge of oxygen diffusion and heat transfer into a large mechanical property composite specimen. In the ideal case, one would wish to establish an interrelationship among aging environment/temperature/time, the state of chemical degradations, and mechanical property change. Because mechanical property measurement usually involves large composite specimens, it is of paramount importance to be able to determine its corresponding chemical changes during aging and its effects on property to gain a basic understanding of the composite stability.

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APPENDIX: THE POSTCURE CONDITIONS OF AFR700B/T650-35

1. Heat from room temperature to 232°C in 1 h 34 min.
2. Hold at 232°C for 4 h.
3. Heat from 232 to 316°C in 1 h 15 min.
4. Hold at 316°C for 16 h.
5. Heat from 316 to 343°C in 50 min.
6. Hold at 343°C for 4 h.
7. Heat from 343 to 357°C in 25 min.
8. Hold at 357°C for 4 h.
9. Heat from 357 to 371°C in 25 min.
10. Hold at 371°C for 4 h.
11. Heat from 371 to 385°C in 25 min.
12. Hold at 385°C for 4 h.
13. Heat from 385 to 399°C in 25 min.
14. Hold at 399°C for 10 h.
15. Cool from 399 to 343°C in 50 min.
16. Cool from 343 to 66°C in 1 h 40 min.

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