

Study of the Processing Chemistry of Polyimides with Thermogravimetry/Fourier Transform Infrared/Mass Spectrometry Techniques

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ABSTRACT: One of the fundamental aspects of the carbon fiber-reinforced, high-temperature polyimide composite AFR700B/T650-35, namely, the curing chemistry involved in the polyimide formation, was studied in real time with thermogravimetry/Fourier transform infrared (FTIR)/mass spectrometry (MS) evolved-gas analysis techniques. The off-gas reaction products identified by FTIR and MS essentially confirmed the literature polyimide curing mechanisms. However, the FTIR/MS data obtained could also accommodate a reversed curing chemistry in which the elimination of water from amide ester formation occurred first and was followed by the release of methanol from subsequent imidization. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2213–2224, 2002

Key words: polyimides; thermogravimetry; FTIR; mass spectrometry; processing chemistry

INTRODUCTION

Currently, carbon fiber-reinforced composites of polyimides are being used in aircraft engines and many space applications. When these composites are used in such applications, they must be capable of functioning at temperatures as high as 371¹ and up to 427°C.² At these high service temperatures, the thermal stability and thermal oxidative stability of the polymer matrix are of primary concern. Any thermal decomposition or thermal oxidative degradation could potentially affect their high-temperature applications.

For given monomer components and end groups, the stability of polyimides depends on the

processing chemistry involved.^{3,4} Thus, in addition to the composition, the monomer reactivity, associated reaction mechanism, and reaction kinetics must be considered when the resulting cured polymer structure is determined. The resulting structure highly influences the stability. For polymerization of monomeric reactants (PMR)-15, a 316°C polyimide, studies^{5,6} have shown the effects of monomer aging during storage and its curing schedule. Therefore, the performance of a polymer is intimately tied to the manner in which it is formed; that is, processing–structure–property interrelationships need to be established for the understanding and modification of the material properties.

Traditionally, infrared (IR) absorption spectroscopy, nuclear magnetic resonance spectroscopy, reverse-phase liquid chromatography, and gel permeation chromatography have been employed^{5,7} to follow the reactions of PMR-15 and the buildup of molecular weights. Unfortunately,

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these techniques lack the ability to monitor these reactions continuously. More recently, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and dielectric constants have been used^{5,6} to follow the polyimide reactions continuously. These techniques allow for the detection of the effects of these reactions through the heat of reaction with DSC, through rheology with DMA, and through ion mobility with dielectric constants. They are valuable in process control and useful for reproducibility checks. However, they lack the ability of positively identifying the reaction products when they are made. Hence, a need for the *in situ* monitoring of monomer reactions and subsequent polymerizations by direct reaction product identification exists.

Recently, Pan et al.⁸ successfully applied online thermogravimetric analysis (TGA)/Fourier transform infrared (FTIR) and TGA/mass spectrometry (MS) techniques to follow the various PMR-15 reactions. Using TGA permits heating the monomer mixture to reaction temperatures and following the evolution of condensation gaseous products by weight loss, whereas FTIR helps in identifying, at the same time, what these small gas molecules are. When large organic species are given off, they are identified with mass spectroscopy.

In this study, the same approach was applied to investigate the processing chemistry of high-temperature polyimide preregs of AFR700B, VCAP-75, and LARCTM-RP46. The curing time and temperature for off-gas productions were determined. The sequence of the evolution of these off-gases was then compared with that of the PMR-15 prepreg and the literature curing chemistry for these high-temperature polyimides. Processing chemistry based on this online off-gas monitoring was proposed. On the application side, this information would be useful for the establishment of proper processing conditions for part consolidations. For instance, the onset of a vacuum application to pull off evolved gases during curing and the subsequent application of pressure to minimize void formation in a consolidated part are two such important processing considerations for producing quality polymer composites.

EXPERIMENTAL

Material Selection

Three high-temperature polyimide preregs with glass-transition temperatures between 316 and

371°C were chosen for the processing chemistry study: AFR700B/T650-35, VCAP-75/glass fiber, and RP46/IM7. They were stored in a small freezer (−12°C) before use. Small pieces of the polyimide preregs were cut for thermogravimetry (TG)/FTIR or TG/MS measurements.

Characterization Techniques

Modulated DSC (TA2920 MDSC, TA Instruments, New Castle, DE) provided the DSC curve of the three polyimide preregs in nitrogen for the determination of endothermic and/or exothermic temperatures, which gave an indication of the release of absorbed moisture or residual solvent and the evolution of condensation reaction products. A thermomechanical analyzer (TMA943, TA Instruments) was used to measure the glass-transition temperature of the postcured AFR700B/T650-35 composite in air. TG/FTIR/MS techniques were used to monitor the off-gas released from prepreg samples during the curing process. The details of the TG/FTIR/MS setup are given elsewhere.⁸

RESULTS AND DISCUSSIONS

Short-Time Curing of the AFR700B/T650-35 Prepreg

AFR700B,⁷ an addition polyimide, was made from the following monomers: monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE), *para*-phenylenediamine (PPDA), and dimethyl ester of 4,4'-hexafluoroisopropylidene bisphthalic acid (HFDE) with methanol as a solvent. Reinforced with the 3K intermediate-modulus carbon fiber T650-35, the AFR700B/T650-35 prepreg was produced.

To explore the temperature ranges for off-gas evolution, we carried out a curing run of this AFR700B prepreg in TGA by heating it to 400°C at 10°C/min in nitrogen. The TGA weight-loss curves exhibited two major weight-loss peaks at 115 and 149°C with corresponding weight losses at 1.55 and 4.28%, as shown in Figure 1. In addition, a shoulder on a derivative thermogravimetry (DTG) curve appeared at about 250°C, and another minor DTG peak occurred around 340–350°C.

The FTIR temperature profile for the curing of the AFR700B/T650-35 prepreg to 400°C at 10°C/min in N₂ showed peak rates of evolution of CH₃OH (1033 cm^{−1}), H₂O (3715 cm^{−1}), and cyclo-

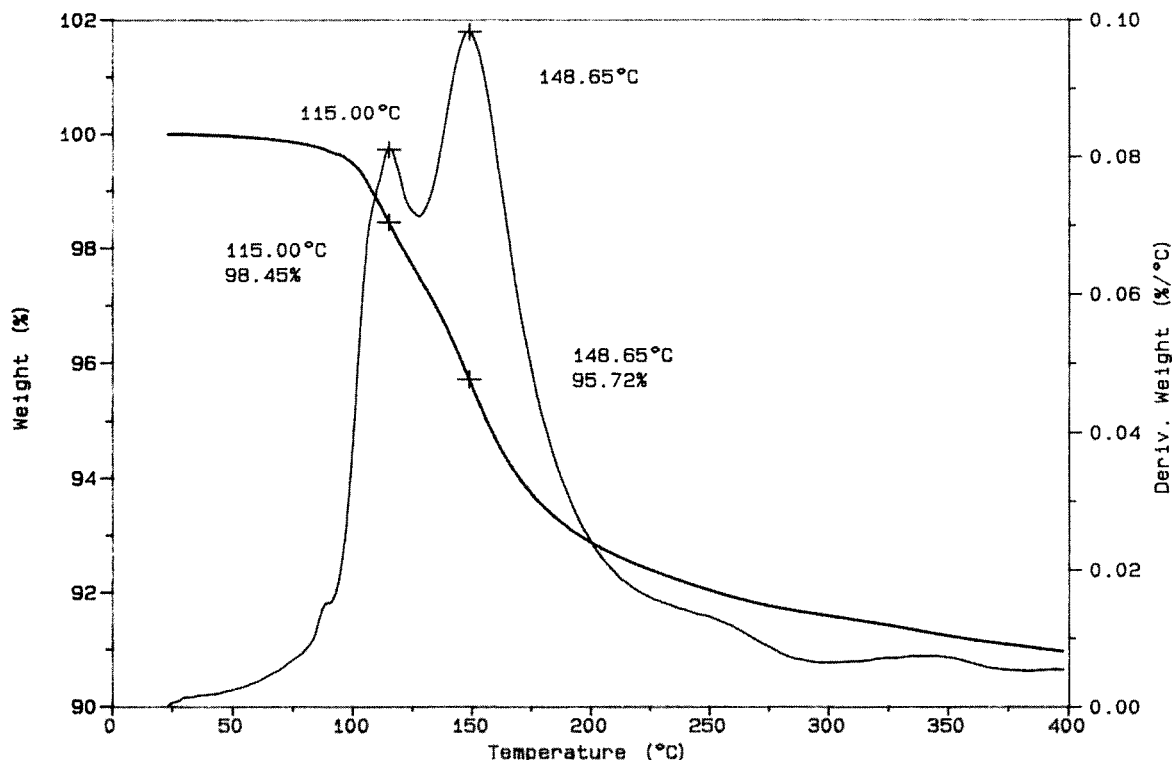


Figure 1 TGA profile of AFR700B/T650-35 heated to 400°C in nitrogen at 10°C/min.

pentadiene (663 cm^{-1}) at 176, 180, and 360°C, respectively, as seen in Figure 2. The corresponding MS temperature profile showed peak release rates of CH_3OH ($m/e = 31$ and 15), H_2O ($m/e = 18$), and cyclopentadiene ($m/e = 66$) at 150, 155, and 319°C, respectively, as illustrated in Figure 3. There was also a shoulder around 220–270°C for H_2O . In general, one can say that the MS data furnished the closest real-time cure reaction monitoring in comparison with FTIR data; this was also supported by the TGA weight-loss-rate data. The peak temperature for the AFR700B/T650-35 prepreg weight-loss rate was 149°C, in the proximity of the MS peak temperatures of 150 and 155°C, strongly suggesting that the release of CH_3OH and H_2O accounted for the rapid weight loss around 149°C. Overall, these real-time weight-loss, FTIR, and MS data indicated that the evaporation of the surface water and residual methanol solvent in the prepreg gave rise to a peak weight-loss rate at 115°C. It was then followed by the evolution of methanol and water at 150°C, the continuing loss of water from 220 to 270°C, and the formation of cyclopentadiene at 320°C. The detection of cyclopentadiene by TG/FTIR/MS was possible because no applied pressure was used, in contrast to autoclave prepreg

consolidation. When cyclopentadiene was formed via a reverse Diels–Alder reaction,⁹ it was given off and detected. As a result, it would be difficult to verify the existence of a reverse Diels–Alder reaction during prepreg autoclaving even if these TG/FTIR and/or TG/MS techniques were accessible.

The TG/FTIR/MS data obtained can also be used to determine the onset temperature for the release of vapors and gases from a TGA curing run. These onset temperatures, of course, depended on the detection threshold of the characteristic absorption bands. By and large, both methanol and water were given off at about 75–80°C, whereas the formation of cyclopentadiene started at about 245°C and ended at 355°C according to the MS data. FTIR indicated the ending of methanol evolution at approximately 270°C. For reasons unknown, it was difficult to ascertain the termination of water release from both FTIR and MS data.

A curing run of the AFR700B/T650-35 prepreg was also made with DSC from ambient temperature to 400°C at 10°C/min in nitrogen to determine if additional information could be obtained. The thermogram (Fig. 4) exhibited a minor endotherm at 100°C, a major higher temperature en-

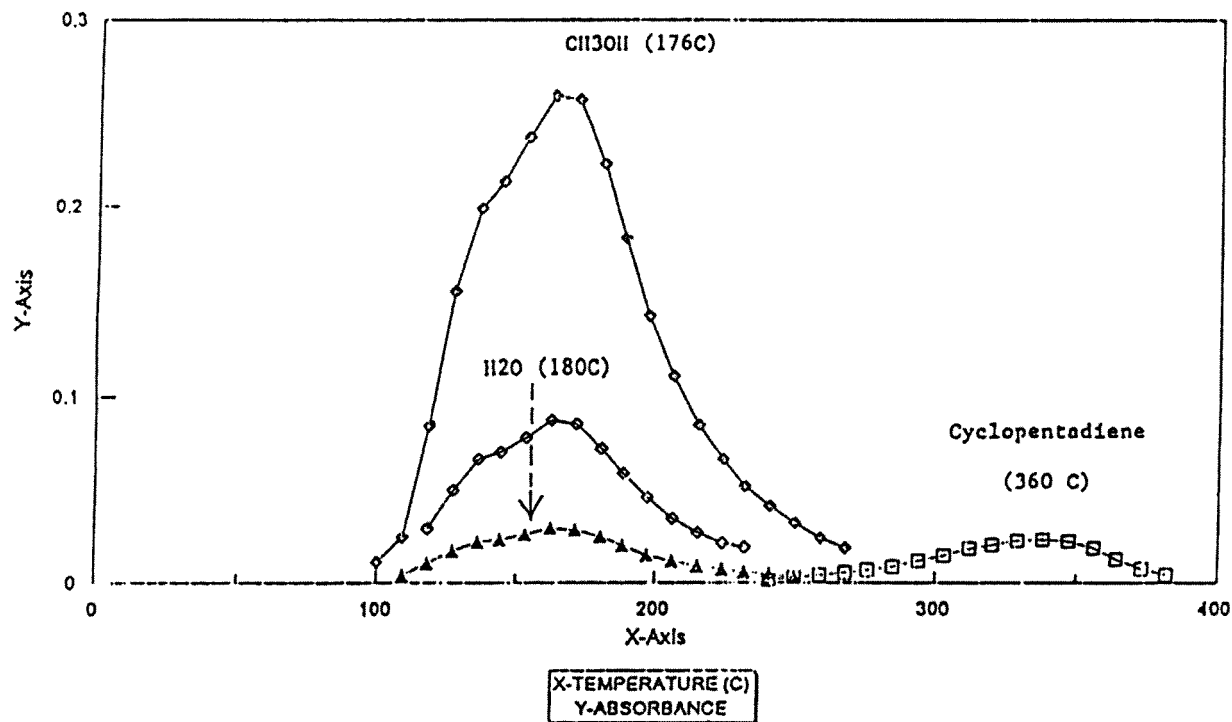


Figure 2 FTIR profile of AFR700B/T650-35 heated to 400°C in nitrogen at 10°C/min.

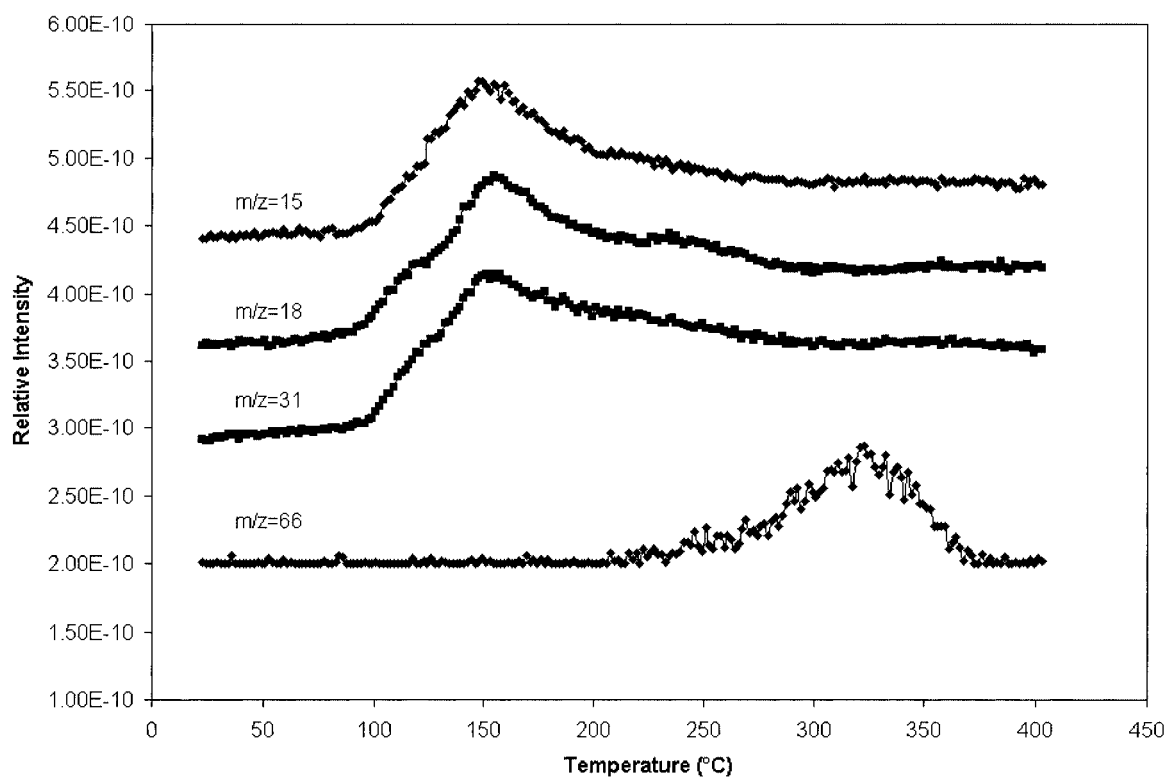


Figure 3 MS profile of AFR700B/T650-35 heated to 400°C in nitrogen at 10°C/min.

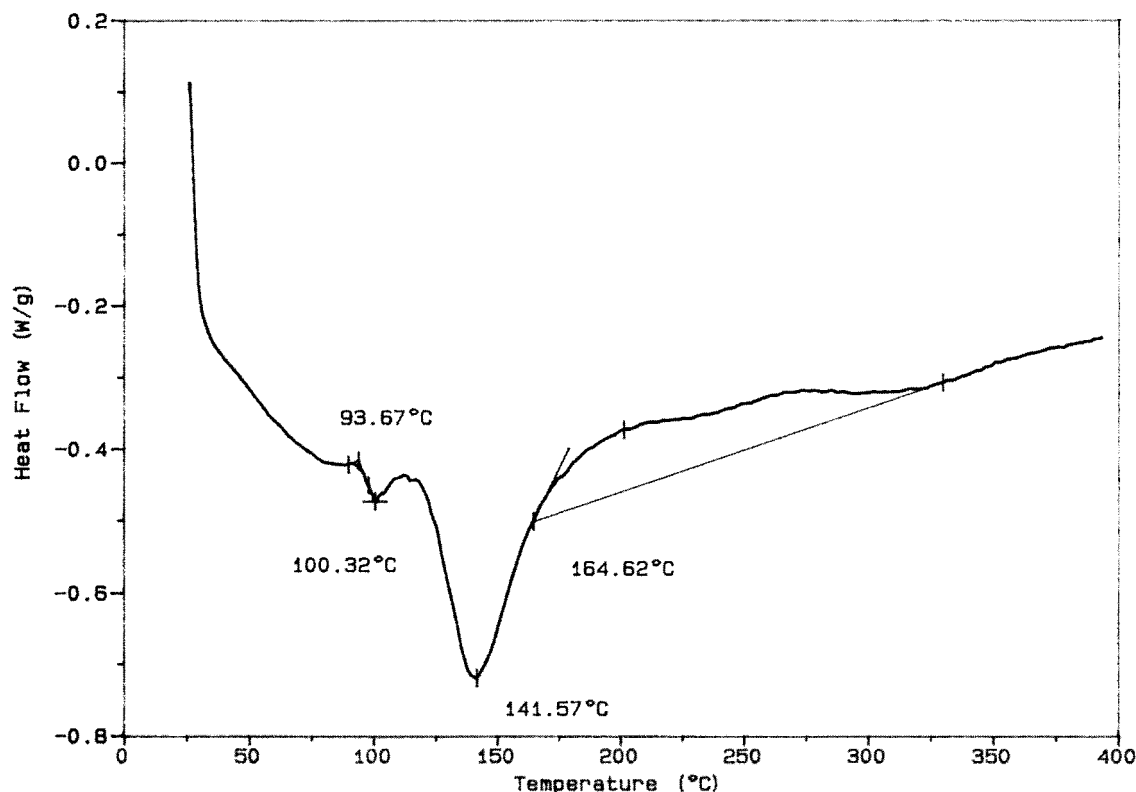


Figure 4 DSC curve of AFR700B/T650-35 heated to 400°C in nitrogen at 10°C/min.

dotharm at 142°C, and a broad exotherm from 165 to 325°C. The first endotherm appeared to be related to the evaporation of surface water. The second, large endotherm might have come from the combined effect of methanol evaporation (endothermic) and amic acid reaction (exothermic). The net result was endothermic because of the presence of a large amount of methanol solvent in the prepreg. For this reason, the heat of formation for the amic acid reaction could not be determined. Moreover, these DSC peak temperatures were fairly close to the TGA weight-loss-rate peak temperatures of 115 and 148°C, lending partial support to the origin of these weight losses. Following the second, large endotherm, a broad exotherm starting at 165°C and extending to 325°C was noted. The heat given off by imidization and subsequent crosslinking might be responsible for this broad exotherm. Its temperature range was certainly broad enough to cover those for both imidization and crosslinking.

The curing rate affected the peak release temperatures of methanol and water mainly because of thermal lag. As a result, the 3°C/min heating rate resulted in lower water- and methanol-releasing peak temperatures. The FTIR profile

showed their occurrence at 128 and 130°C, respectively. Similarly, the MS profile gave rise to a methanol evolution peak temperature of 125°C and a peak temperature for cyclopentadiene formation at 314°C. Therefore, the prepreg heating rate exerted a dominating effect on the rate of gas evolution, which needed to be recognized. Although a single TGA 10°C/min ramp rate was generally used for expediency and determination of the curing temperature range, a slow heating rate comparable to commercial practice or, better yet, a real cure schedule may be required to examine the actual curing chemistry involved.

In summary, the overall TG/FTIR/MS results indicated the following curing chemistry paths for the AFR700/T650-35 prepreg at a 3°C/min heating rate: (1) the elimination of methanol through amic acid prepolymer formation at about 125°C; (2) the release of water from imidization at approximately 220°C; and (3) the thermal crosslinking of polyimide at 314°C via a reverse Diels-Alder⁹ reaction in which cyclopentadiene was formed, resulting in its detection in the absence of applied pressure in a thermogravimetric analyzer.

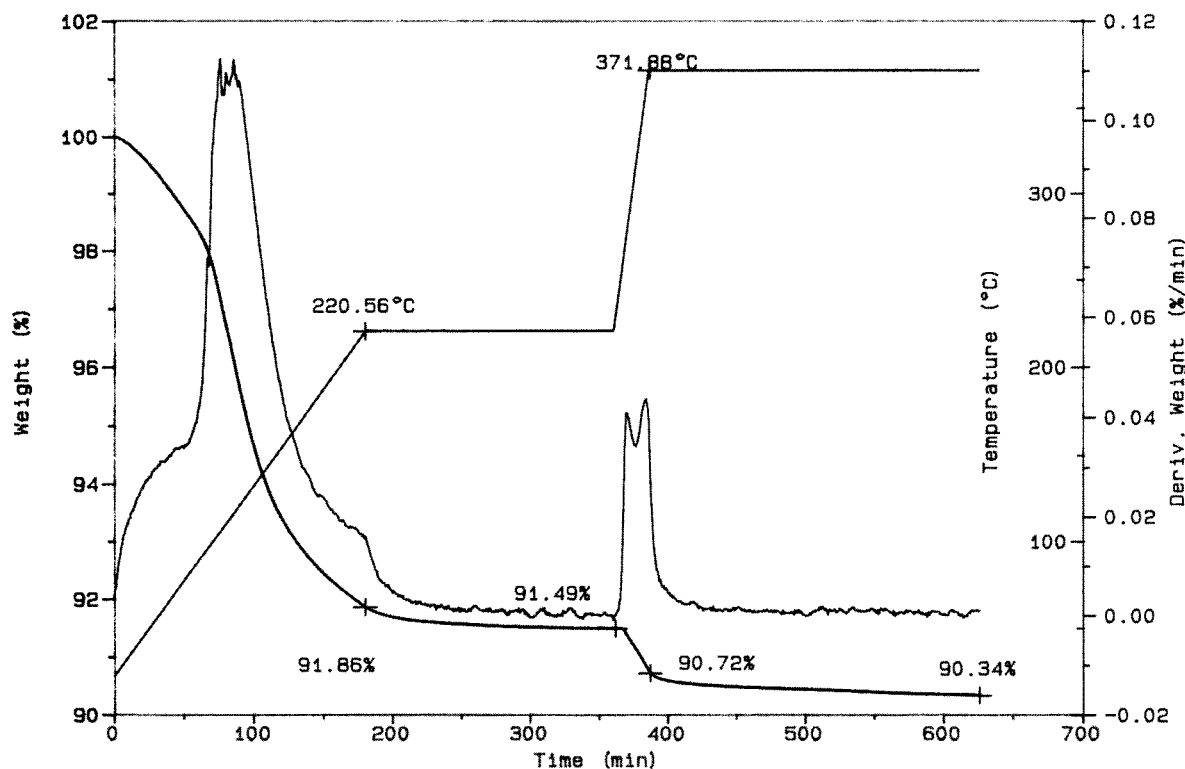


Figure 5 TGA profile of AFR700B/T650-35 based on the General Electric Aircraft Engines autoclave cure schedule.

Curing of the AFR700B/T650-35 Prepreg with an Autoclave Schedule

The AFR700B/T650-35 prepreg was cured in a thermogravimetric analyzer with the General Electric Aircraft Engines autoclave cure schedule. Because of equipment limitations, no application of vacuum and consolidation pressure was made. Thus, only the prepreg curing heat history was simulated. Furthermore, the slow cooling cycle during autoclave curing and its subsequent post-curing were eliminated in the interest of saving instrumentation use time. The absence of off-gas products during the cooling cycle and postcure period was assumed. Hence, the use of TG/FTIR and/or TG/MS would not yield additional information anyway. The actual cure schedule can be obtained elsewhere.¹⁰

Figures 5 and 6 show the corresponding TGA weight loss and MS profile for this 10-h plus curing run. TGA weight-loss data indicated a total weight loss of 9.66% at the end of the cure schedule. However, most of this weight loss took place in the first heating step from room temperature to 221°C at 8.14%. Little weight change occurred during 3 h at 221°C. Then, the second heating

stage from 221 to 372°C brought about another 0.77% weight loss. Thus, most off-gases should appear between room temperature and 221°C, with a small amount released between 221 and 372°C. Moreover, regardless of the TGA heating rate, the total prepreg weight loss was about the same. At 10°C/min to 400°C, the total weight loss was about 9.0%, whereas heating at 3°C/min produced a total weight loss of 11.0% when 400°C was reached. Because these total weight-loss values were fairly close to the 9.7% weight loss from the long-time cure, it might be surmised that most of the off-gases had been released. This small difference in total weight loss might have come from the initially absorbed moisture and residual solvent present in the various prepreg samples used.

FTIR data showed the release of water and methanol peaked at 115°C shortly after curing started. This 115°C peak temperature lies within the 105–117°C peak temperature range for the TGA weight-loss rate, thereby suggesting water and methanol as the major off-gases from prepreg curing. Their releases tapered off when the prepreg reached 221°C. Therefore, for prepreg au-

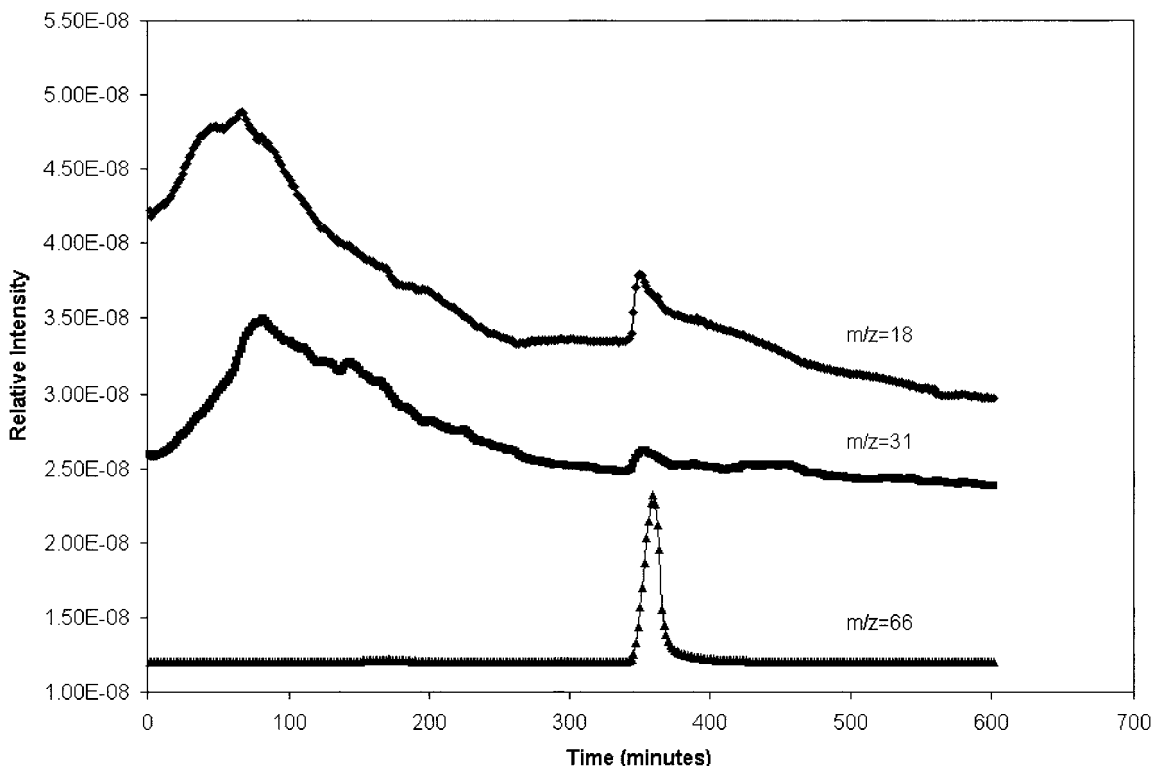


Figure 6 MS profile of AFR700B/T650-35 based on the General Electric Aircraft Engines autoclave cure schedule.

toclaving, the application of vacuum should be extended to 221°C to minimize bubble or void formation. A much smaller FTIR peak occurred for both water and methanol at 283°C. In addition, the loss of cyclopentadiene produced an FTIR peak at 286°C. All these events took place in the second heating stage from 221 to 372°C at 5.9°C/min. Two observations can be made: (1) the releases of methanol and water was not complete even after 3 h at 221°C and (2) the presence of cyclopentadiene confirmed the crosslinking of AFR700B via a reverse Diels–Alder reaction.⁹

Very little additional weight loss occurred after the second heating step, suggesting that the curing reactions and crosslinking were almost complete. To retain the cyclopentadiene formed in the prepreg for crosslinking, the application of pressure for part consolidation should be made after 221°C. The use of 221°C to time both the vacuum cutoff and application of consolidation pressure is, in fact, practiced by the industry for AFR700B prepreg autoclaving.

The MS profile showed results similar to those of the FTIR profile. The MS peak intensity temperatures differed slightly from the FTIR peak temperatures. If the formation⁹ of amic acid pre-

polymer (resulting in the release of methanol), followed by imidization (producing water), was complete by 221°C, the presence of a second set of methanol and water peaks in FTIR and MS at higher temperatures would be surprising. If these reactions were not complete, higher reaction temperatures (260–290°C) might be required to increase the polyimide mobility to advance the reactions further. If so, one would wish to know whether additional reactions could be advanced at even higher temperatures close to the top post-cure temperature of 399°C. To test this hypothesis, we made a longer and higher temperature cure of the AFR700B/T650-35 prepreg with TGA/FTIR/MS by adding onto the aforementioned General Electric cure schedule a third heating step, also at 5.9°C/min, to 427°C. No additional methanol or water was detected, suggesting that either the amic acid prepolymer formation and imidization reaction had been completed below 427°C or an additional reaction sequence not involving off-gas productions was still taking place.

The close proximity of the FTIR and MS peak temperatures for methanol and water rendered the determination of this AFR700B prepreg curing reaction sequence somewhat difficult. They

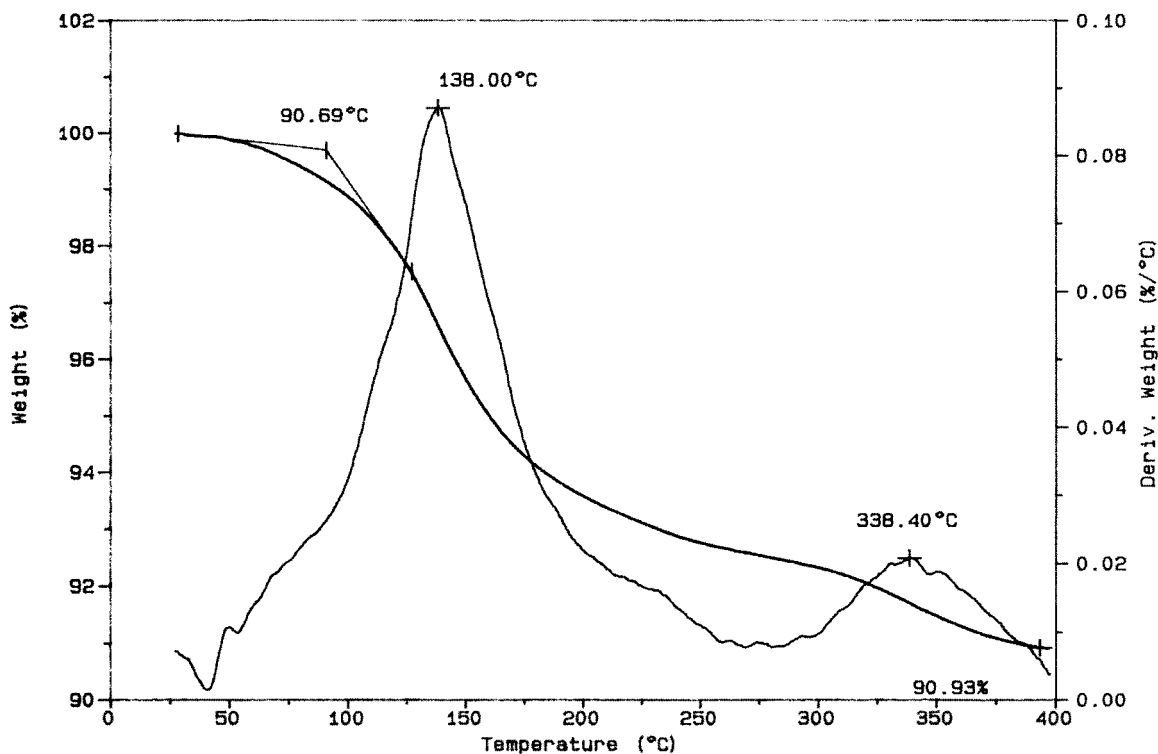


Figure 7 TGA profile of RP46/IM7 heated to 400°C in nitrogen at 10°C/min.

were seen in the 98–115°C range, below 221°C, and also between 262 and 283°C, above 221°C. Thus, it became less certain, at least on the basis of the evolved-gas study, if the amic acid prepolymer reaction with the elimination of methanol, followed by imidization with the loss of water and crosslinking by a reverse Diels–Alder reaction or a Michael addition reaction, was the preferred curing mechanism. It appeared that amide ester formation with the loss of water, followed by imidization with the loss of methanol, could fit the FTIR/MS as well. The latter would produce a prepolymer with a larger molecular weight (the molecular weight was 776 for the amide ester prepolymer and 748 for the amic acid prepolymer) and, therefore, a higher viscosity for the subsequent imidization reaction to overcome. To resolve this uncertainty concerning the curing reaction sequence, independent investigative methods such as NMR⁷ (hopefully in real time) and isothermal gas chromatography/MS might be required.

The TG/FTIR/MS data from the long-time cure schedule were compared with data obtained at 3 and 10°C/min. Even though the various curing reaction steps, that is, amic acid prepolymer formation (or amide ester formation) followed by

imidization and crosslinking, were identified, their peak temperatures were different, depending on the heating rate and, therefore, the rate of cure. The larger the heating rates were, the greater the peak reaction temperatures were. For instance, FTIR showed the initial release of methanol and water to be at 115°C for the long-time cure, 128–130°C for the 3°C/min heating rate, and 176–180°C for the 10°C/min heating rate. Therefore, the use of test results obtained at large curing rates to draw conclusions should be made with caution.

Short-Time Curing of the LARC RP46/IM7 Prepreg

The curing of the RP46/IM7 prepreg in nitrogen was examined with TGA/FTIR and TGA/MS from room temperature to 400°C at 10°C/min. The monomer reactants for RP46 were NE, 3,4'-oxydianiline, and dimethyl ester of 3,3,4,4'-benzophenonetetracarboxylic acid. The prepreg was produced with the reinforcement of IM7, an intermediate-modulus carbon fiber.

The TGA weight-loss data exhibited a major weight-loss-rate peak at 138°C, a weak shoulder at 230°C, and a minor peak at 338°C, as seen in Figure 7. Again, the total weight loss at 400°C

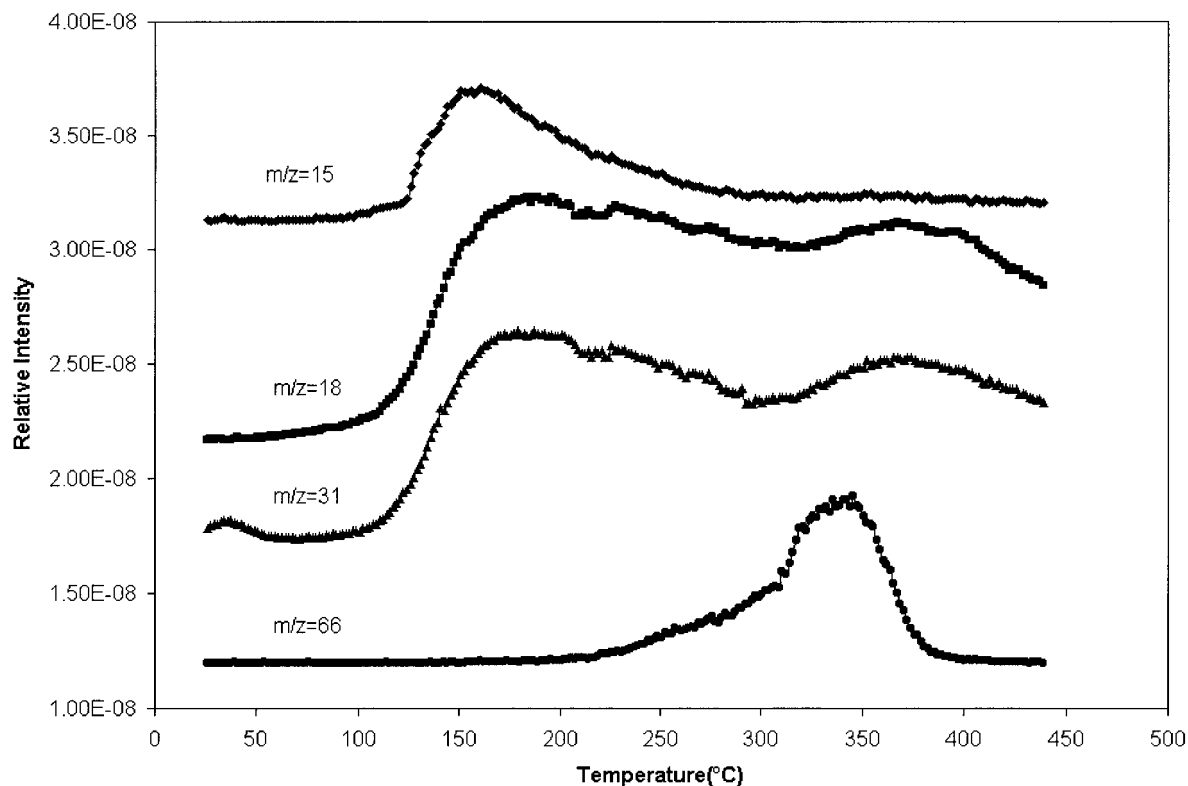


Figure 8 MS profile of RP46/IM7 heated to 400°C in nitrogen at 10°C/min.

was about 9.1%, similar to that seen in the AFR700B/T650-35 prepreg. It seemed to indicate that as long as the monomer functional groups remained the same, they would undergo similar reaction sequences, thereby giving off the same off-gas products. A DSC run was made under experimental conditions identical to those of the TGA run. The DSC curve's main features were an endothermic peak at 138°C, a broad exotherm between 165 and 325°C, and an exotherm at 342°C. The endothermic peak temperature was, in fact, identical to the first weight-loss-rate peak temperature of 138°C, strongly suggesting the release of water and methanol vapors. The exotherm at 342°C corresponded to the TGA peak temperature at 338°C.

The FTIR profiles for the RP46/IM7 prepreg showed a peak temperature of 162°C for both methanol and water release. The peak temperature for cyclopentadiene formation occurred at 356°C. With the application of the 25°C thermal lag due to the FTIR gas cell residence time and signal averaging, these two peak temperatures became 137 (162 – 25) and 331°C (356 – 25), very close to the TGA weight-loss-rate peaks at 138 and 338°C, respectively. Thus, the evolution of

methanol and water was responsible for the first TGA weight-loss-rate peak and the DSC endotherm, whereas cyclopentadiene formation was accountable for the last TGA weight-loss-rate peak and DSC exotherm. The corresponding MS profiles (Fig. 8) exhibited a peak at 140°C for methanol according to the $m/e = 15$ intensity data. The intensity for water at $m/e = 18$ was very broad, so it was difficult to determine its peak temperature. The peak temperature for cyclopentadiene at $m/e = 66$ was 342°C, not too far from the thermal lag corrected FTIR peak temperature of 331°C.

On the basis of the TG/FTIR/MS and DSC information, for RP46/IM7 prepreg curing, the overall analysis seemed to suggest the following: (1) the release of methanol and water between 100 and 280°C with a peak at 138–140°C for both, indicating the loss of absorbed moisture and residual methanol as well as that from the formation of imidized prepolymer, and (2) the formation of cyclopentadiene between 200 and 400°C with a peak within 310–350°C. Thus, the prepolymerization and thermal crosslinking reaction sequence proposed by the National Aeronautics and Space Administration (NASA) LARC group¹¹ was

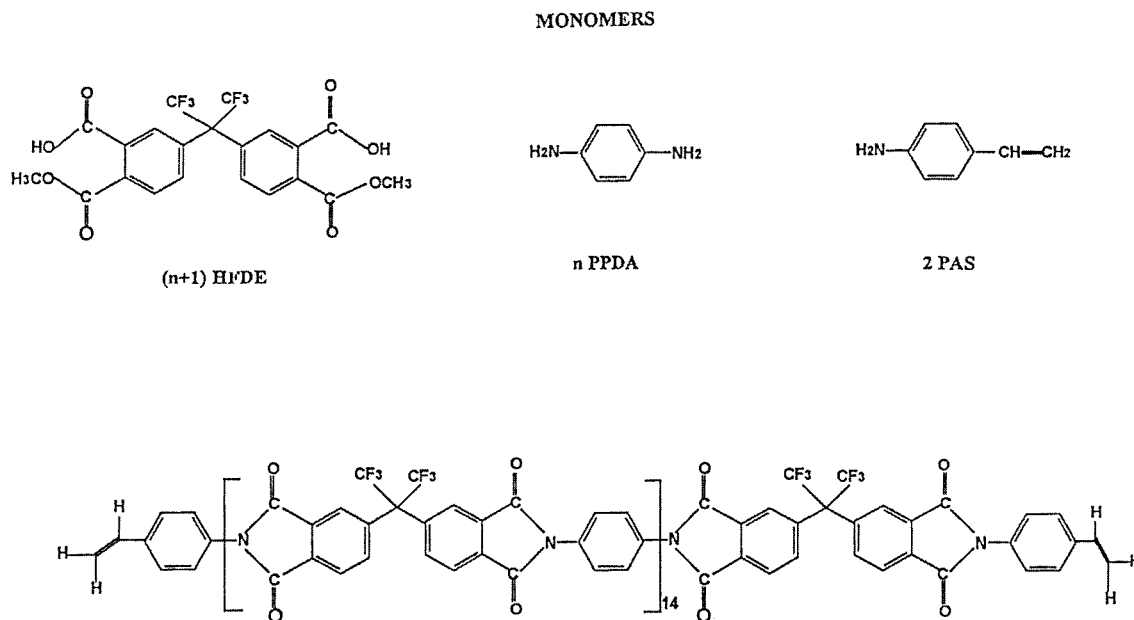


Figure 9 Schematic structure of VCAP-75.

confirmed by this real-time evolved-gas analysis. They essentially followed the curing reaction paths of the AFR700B/T650-35 prepreg. However, this evolved-gas analysis was not capable of probing the endo–exo isomerism reaction because no off-gases were generated and given off.

Short-Time Curing of the VCAP-75/Glass Fiber Prepreg

Even though it is a hexafluoro polyimide like AFR700B, VCAP-75 (Fig. 9) has a different set of end groups. It was formulated in methanol with $(n + 1)$ mol of HFDE, n mol of PPDA, and 2 mol of *para*-aminostyrene (PAS), where $n = 14$. VCAP-75 was capped with a vinyl group at both ends. Because of this end capping, its crosslinking did not involve the reverse Diels–Alder reaction. Hence, no cyclopentadiene was detected.

A short-time curing run of the VCAP-75/glass fiber prepreg was made with TGA at 10°C/min from room temperature to 400°C in nitrogen. The TGA weight-loss rate (Fig. 10) exhibited a peak at 149°C, almost identical to that for AFR700B/T650-35. There was a distinct shoulder between 180 and 225°C. At about 300°C, there was another minor shoulder. The first peak at 149°C was probably related to the evolution of methanol and water. The large shoulder was believed to be due to the release of water. At the end of the curing run, this prepreg lost a total of 10.3% of its

weight, fairly close to the losses for AFR700B/T650-35 (9.0%) and RP46/IM7 (9.0%).

The DSC curve of the VCAP-75/glass fiber (Fig. 11) had as its major features a large endotherm with a peak temperature of 142°C and a tailing shoulder extending to about 240°C. This DSC curve resembled the weight-loss-rate curve well. Furthermore, their first peak temperatures (142 vs 149°C) were fairly close to each other. The tailing shoulders also extended out to similar ending temperatures (240 vs 225°C). The evaporation of methanol and water was the main source of its large endotherm. Because of the large amount of water produced ($n = 14$ for the repeating backbone structure) from the condensation reaction, the large heat of evaporation would overtake its heat of reaction, thereby resulting in the tailing shoulder of the endotherm. As a result, no exotherm could be observed in the DSC curve.

The FTIR profile of the VCAP-75/glass fiber prepreg displayed a 171°C peak temperature for methanol as well as water. With the 25°C thermal lag inherent in the collection of FTIR data at 10°C/min taken into account, the real peak temperature for these two off-gases was 146°C (171 – 25), which was not too different from the 149°C peak temperature for its weight-loss rate. Hence, the evolution of both methanol and water definitely made up the major portion of this weight-loss-rate peak. Again, the identical peak temperature of 146°C for both methanol and water made

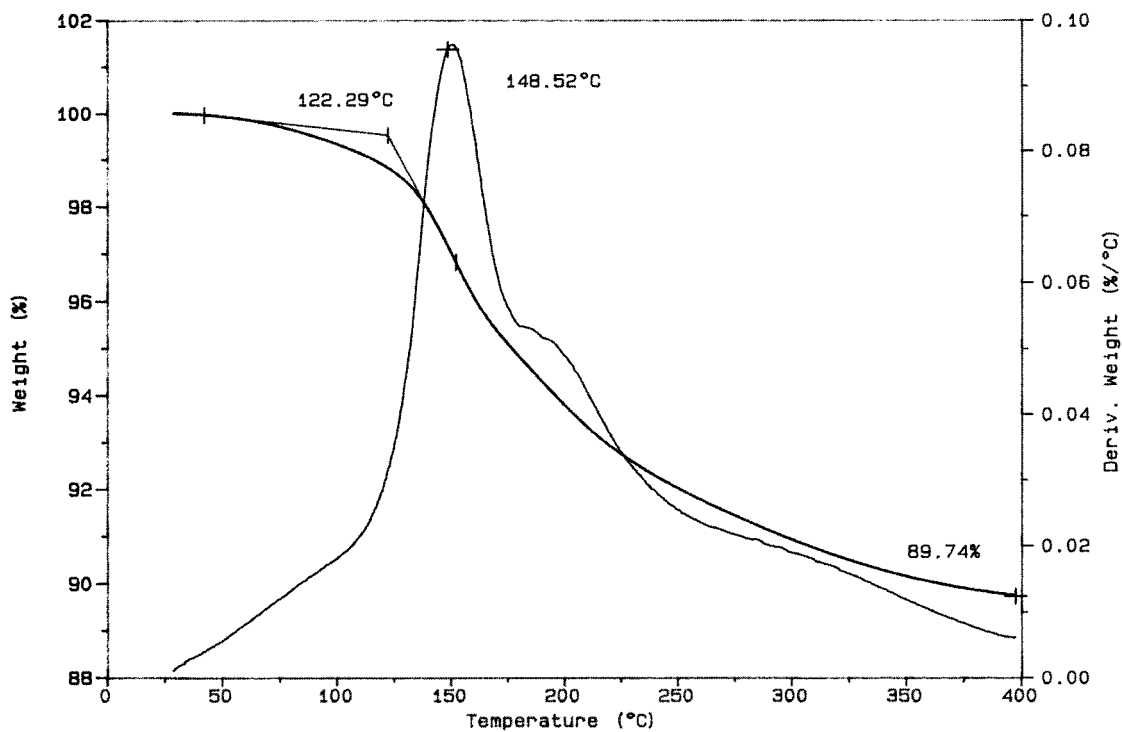


Figure 10 TGA profile of VCAP-75 heated to 400°C in nitrogen at 10°C/min.

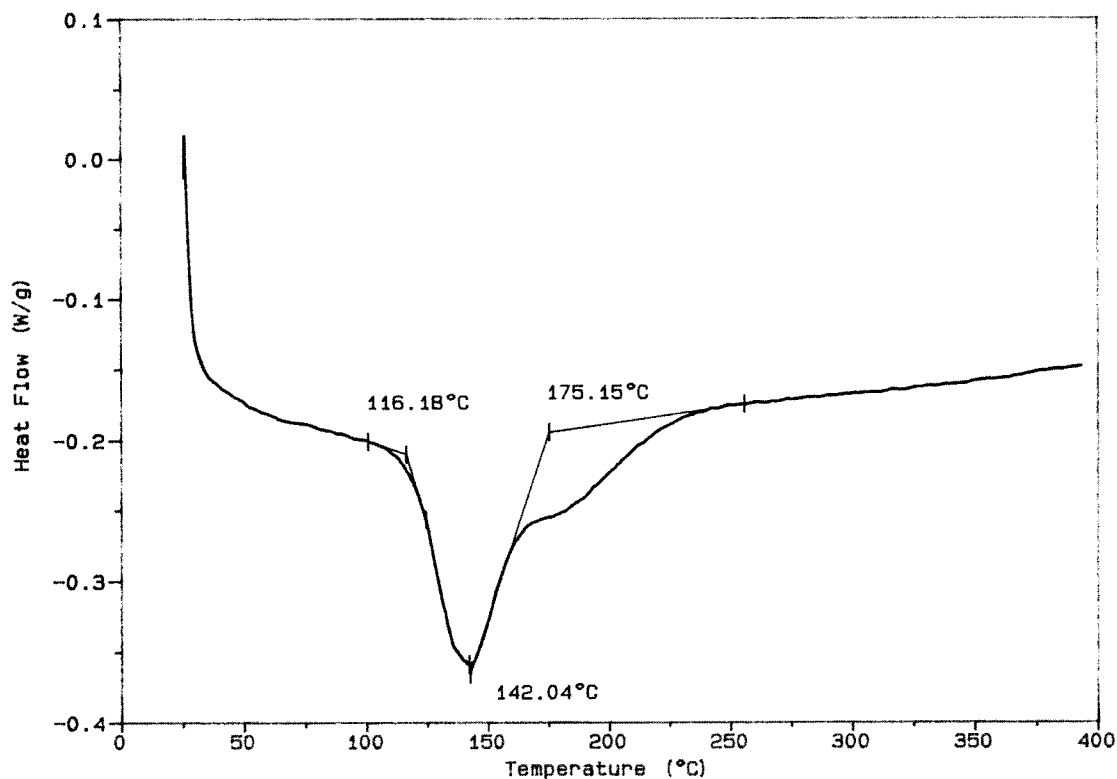


Figure 11 DSC curve of VCAP-75 heated to 400°C in nitrogen at 10°C/min.

the assignment of the imidization prepolymer reaction sequence difficult. They could fit either an amic acid formation/imidization reaction path or an amide ester formation/imidization curing sequence. The FTIR profile for water covered a temperature range of 110 and 240°C with a nominal peak temperature of 171°C. Between 200 and 240°C, its water absorption intensity appeared to have leveled out slightly, resulting in a minor shoulder. This shoulder might have derived from the imidization reaction releasing condensation water in the process. No cyclopentadiene with $m/e = 66, 65, \dots$ was detected by MS, which was consistent with its end-capping chemistry.

CONCLUSIONS

Overall, the *in situ* monitoring of the major curing reactions involved in a high-temperature polyimide with TG/FTIR and TG/MS was successfully demonstrated, although both techniques might involve some thermal lag, depending on the TGA heating rate. In essence, the thermal curing of the polyimides studied proceeded in the following fashion: (1) the elimination of methanol from amic acid prepolymer formation, (2) the release of water from subsequent imidization, and (3) thermal crosslinking.

These polyimide curing reaction steps are in agreement with the literature. However, the FTIR/MS data obtained could also accommodate an alternative, that the elimination of water from amide ester formation was followed by the release of methanol from subsequent imidization. When an NE end-capping monomer was used, cyclopentadiene was detected, thereby confirming the contention that the final crosslinking proceeded through a reverse Diels–Alder reaction.

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