

Thermal Degradation of High-Temperature Fluorinated Polyimide and its Carbon Fiber Composite

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ABSTRACT: High-temperature polymers are being used for a broad range of applications, such as composite matrices for structural applications (e.g., high speed aircraft). Polyimides are a special class of polymers that meet the thermal and oxidative stability requirements for high temperature composite aerospace applications. A weight loss study was performed on a fluorinated polyimide resin and its carbon fiber composite in an effort to determine its thermal stability and degradation mechanisms. Experiments were conducted using a preheated oven and thermogravimetric analysis to obtain the weight loss. Regardless of the method used, the resin and com-

posite exhibited excellent thermal stability (less than 1% weight loss) below 430°C, regardless of 2–20 min of exposure. After 20 min of exposure at 510°C, the composite remained relatively stable with only 5.3% weight loss using the oven technique, whereas the neat polyimide sustained 12.6%. When degradation occurred, it was found to be the result of thermolysis and oxidation (to a lesser extent). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2254–2261, 2010

Key words: carbon fiber; composites; degradation; high-temperature materials; polyimides

INTRODUCTION

High-temperature polyimides are finding use in a variety of applications, from electronics to aerospace, because of their high thermal stability and excellent mechanical, chemical, and electrical properties.^{1,2} Additionally, fiber-reinforced high temperature polymer matrix composites are particularly attractive for aerospace structures because of their low density,^{2,3} high mechanical strength,^{2,4–10} high modulus,^{2,5,7–9} thermo-oxidative stability,^{2,8,9,11,12} excellent electrical properties,^{2,5,10,13} and superior chemical resistance.^{2,4,5,9,14} A variety of polyimide-based composites have been studied for use in aerospace applications.^{2,5,11,15} The phenylethynyl end-capped fluorinated polyimide is especially useful because of its environmental stability and high glass transition temperature (435 – 455°C).⁷ Because of its high dry T_g , the fluorinated polyimide is a good material to withstand the extreme service conditions experi-

enced by military aircraft and reusable space vehicles.

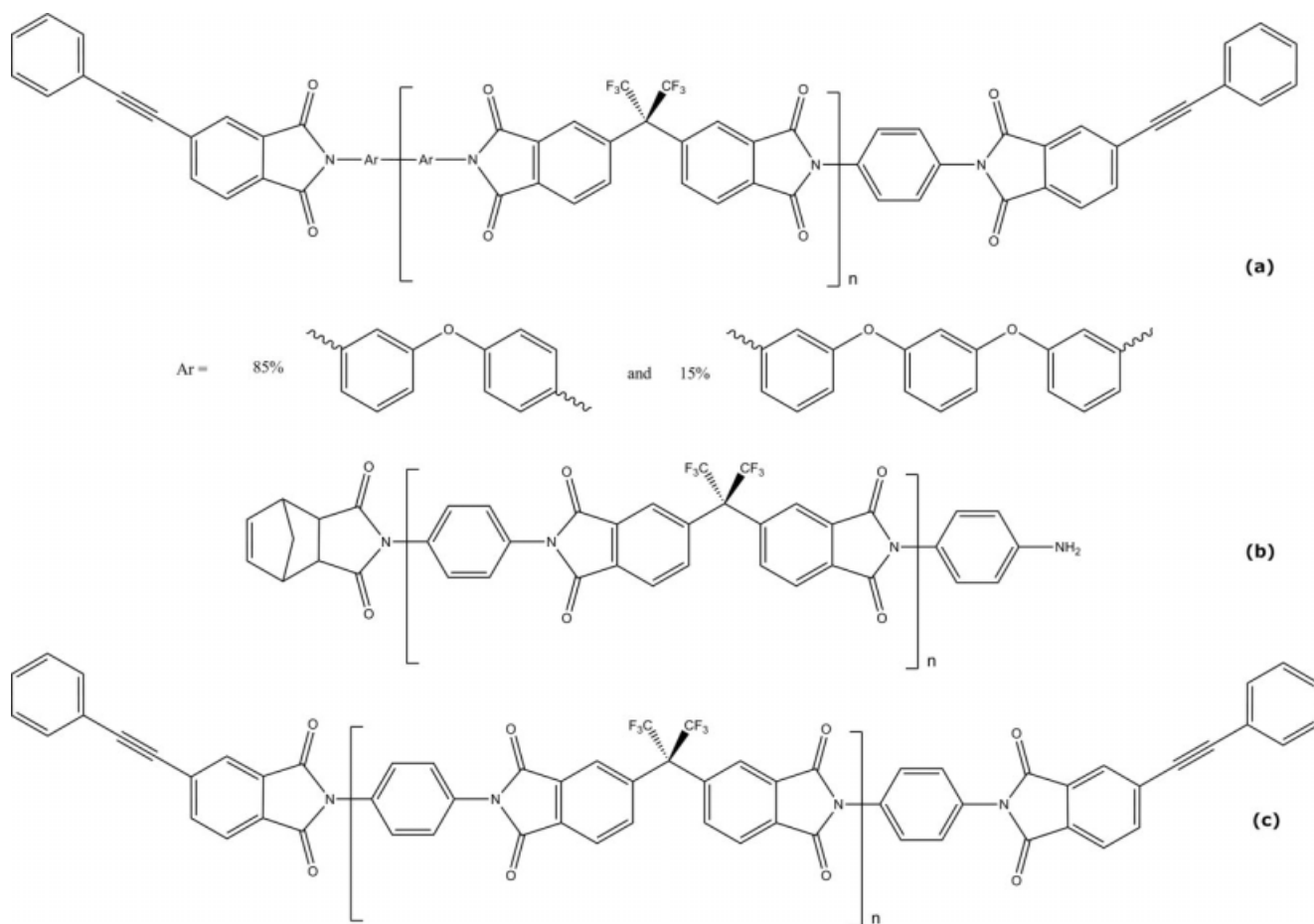
An area of concern for materials to be used in aerospace applications is the ability to withstand temperatures greater than 400°C with minimal degradation during long exposure times.^{2,16} In general, polyimides are the most thermally stable polymers because of their high T_g 's and high decomposition temperatures,¹⁵ but resistance to oxygen needs further study for the fluorinated polyimide composites because of some initial findings.^{12,17} Most composites will exhibit microstructural changes and degradation in properties when exposed to high temperatures.¹² Adding reinforcements to neat polyimide resin, such as carbon fiber, results in a lower weight loss because of a smaller amount of resin in the composite being subjected to degradation.^{17,18} This added stability is a result of the polyimide resin matrix only being able to oxidize or undergo other forms of degradation from the surface of the material. This allows the composite to withstand higher temperatures than the neat polyimide resin because of less neat resin material at the surface.¹²

Two similar polyimides, PETI-5 and AFR700B [Scheme 1(a,b)], have been studied for use in military and aerospace applications. Both exhibit good thermal stability, but the T_g for PETI-5 is 270°C and for AFR700B it is near 400°C, whereas the dry fluorinated polyimide studied here is 435–455°C.^{4,7,15}

Additional Supporting Information may be found in the online version of this article.

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Scheme 1 Chemical structures of PETI-5 (a), AFR700B (b), and fluorinated polyimide (c).

PETI-5 was selected for the high speed civil transport program in the early 1990's, but its low T_g made it difficult to use at the desired higher service temperatures.^{15,16} Despite the high T_g for AFR700B, the crosslinks from the endgroups are a weak link that decreases the overall strength because of their susceptibility to hygrothermal degradation.⁴ Initial studies with the neat fluorinated polyimide [Scheme 1(c)] showed excellent thermal stability, with a decomposition temperature of 524°C that resulted in 5 wt % loss.^{4,7} The added fluorinated polyimide stability comes from the combination of the perfluoromethyl substituents in the backbone of the oligomer (from AFR700B) and the phenylethynyl endcaps (from PETI-5).¹⁵

In this work, weight loss of the fluorinated polyimide and its corresponding polyimide carbon fiber composite under elevated temperature is examined. Weight loss as a function of exposure temperature and time was measured using thermogravimetric analysis (TGA) and by pre and post-weighing of specimens treated in an oven. Both techniques showed similar weight loss trends as a function of time and temperature, but TGA showed much greater weight loss because of greater surface area to

volume (i.e., small sample size). The neat polyimide resin and carbon fiber composite exhibited negligible weight loss at temperatures below 430°C for exposure times up to 20 min. This study serves to highlight the thermal stability and clarify the thermal degradation mechanism of this fluorinated polyimide and its carbon fiber composite for future use in high temperature applications.

EXPERIMENTAL

Materials

Fluorinated phenylethynyl-terminated imide oligomer and polyimide carbon fiber composite with 55 wt % carbon fiber concentration, T650-35/8HS/AFRPE-4 10 ply (4 mm thick), were obtained from Performance Polymer Solutions (Centerville, OH) and used as received.

Sample preparation

Fluorinated polyimide neat resin panels were prepared at NASA Glenn Research Center in a 10.2 cm × 10.2 cm steel compression mold to produce 2 mm thick panels. Resin pieces were cut into 3 and 6 mm squares

using a micromatic precision slicing machine. Composite pieces for testing were cut into 3 and 6 mm squares using a band saw. Resin and composite pieces were then placed in a vacuum oven at 70°C for a minimum of 24 h to dry before testing.

Weight loss testing

Oven aging of specimens was accomplished using a Barnstead Thermolyne 48,000 Furnace (Dubuque, IA). The furnace was heated to a targeted temperature from 250 to 510°C, in increments of 20°C under an air atmosphere. Samples (6 mm squares) were individually placed in the oven for 2–20 min time intervals in increments of 2 min, and a new sample was used for each time interval and temperature increment (140 total samples were tested). Weight loss measurements for all resin and composite samples were recorded and percent weight loss was calculated. Percent weight loss was calculated using eq. (1):

$$\% \text{ Weight loss} = \frac{\text{Sample initial weight} - \text{Sample final weight}}{\text{Sample initial weight}} \times 100 \quad (1)$$

TGA of polyimide resin and polyimide-carbon fiber composites was performed with a TGA Q50 Thermal Analyzer (TA Instruments, New Castle, DE). Samples (3 mm squares) were heated to targeted temperatures, from 250 to 510°C, in increments of 20°C and held for 20 min under an air atmosphere, unless otherwise noted, using the equilibrate method. Weight loss was determined as a function of time at increments of 2 min, from 2 to 20 min, to compare with results obtained from oven testing.

Characterization

Optical microscopy of the resin and composite was performed with a Hirox 3-D Microscope (River Edge, NJ) using $\times 200$ magnification. Images of the cross-sections of each material were obtained after being exposed to 250, 370, 490, and 510°C for 20 min, along with an unaged control specimen. Scanning electron microscopy of the composite was conducted using an FEI Quanta 600 FE-SEM (Hillsboro, OR) at $\times 500$ and $\times 2000$ magnification. Degradation of the polyimide resin was investigated using a Netzsch TGA 209 F1 Iris (Burlington, MA) instrument that was coupled with a QMS Aeolos mass spectrometer (Selb, Germany) and a Bruker Tensor 27 FTIR (Madison, WI). Analysis was performed under air with a 20 mL/min flow rate, 20 mg sample size, and a 10°C/min heating rate (used to heat the sample to 800°C). The coupling system between

the TGA, FTIR, and MS was heated up to 200°C to prevent condensation of evolved gases.

RESULTS AND DISCUSSION

Oven weight loss

The weight loss of the polyimide resin and its carbon fiber composite provides insight into the stability of these materials at various time and temperature exposures. Figure 1(a) shows the percent weight loss as a function of temperature for the neat polyimide resin. At temperatures below 430°C, the weight loss is less than 1% for exposure times up to 20 min. This polyimide is able to withstand higher temperature environments (without degrading) than most other polymers because of its highly aromatic chemical structure and highly crosslinked network [Scheme 1(c)].² When exposure temperatures are above 450°C, the weight loss exceeds 1% after 14 min, especially at 490°C with exposure times greater than 10 min and 510°C with exposure times greater than 6 min. The decomposition temperature (T_d) for the polyimide resin, as shown in Figure 2(a),

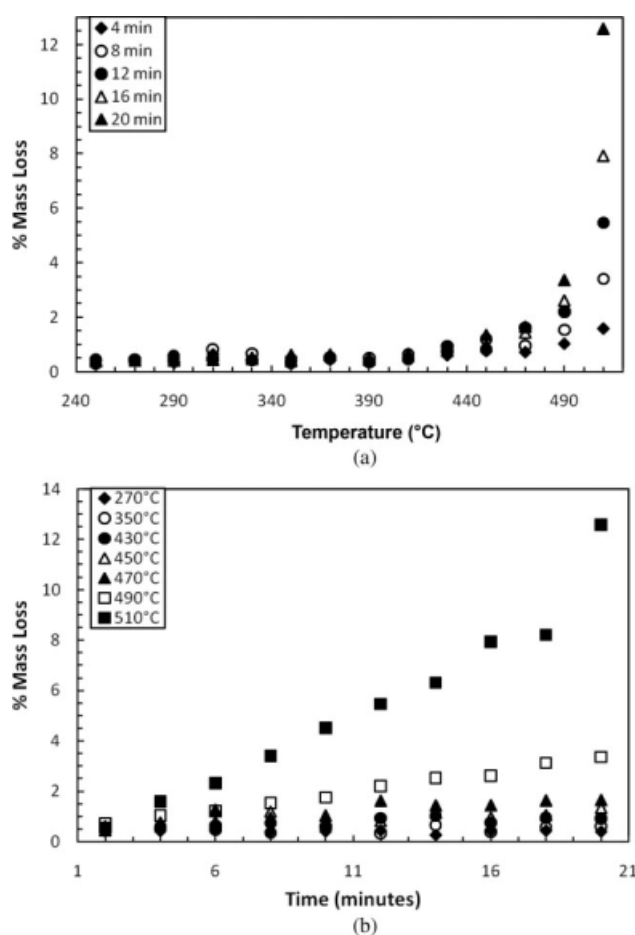


Figure 1 Polyimide resin weight loss in oven as a function of exposure temperature (a) and time (b).

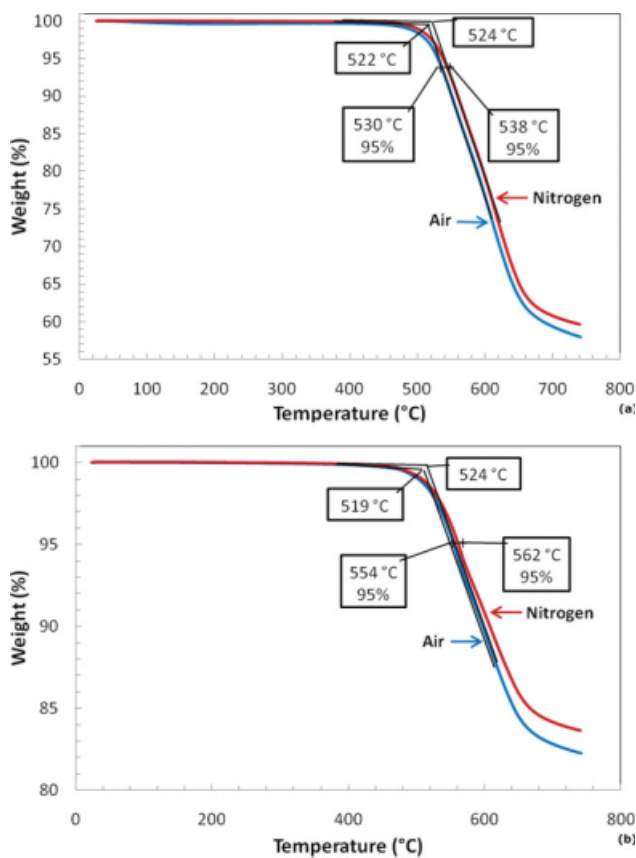


Figure 2 Weight loss as a function of temperature measured with a heating rate of 20°C per min. Decomposition temperature of polyimide resin (a) and polyimide composite (b) in air and nitrogen is shown at onset and 5% weight loss. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

is 522°C in air and 524°C in nitrogen. Furthermore, the resin has lost 5% of its weight at 529°C in air, whereas this same level of degradation does not occur until 538°C in nitrogen. The lower degradation temperature observed with an air atmosphere indicates a modest level of oxidation.¹⁹ This fluorinated polyimide can withstand up to 10 min at 510°C, just below its T_d , with only a 4.5% weight loss in air. A broader set of raw time and temperature data are shown in Supporting Information Table S1.

Oven-based weight loss shows an exponential trend up to 510°C [Fig. 1(a)], and this is expected to continue to higher temperatures. It is not until 430°C that any significant degradation is observed [Fig. 1(b)], which is expected when the temperature is below the polyimide's decomposition temperature of 522°C. A similar observation can be made when considering weight loss as a function of time at varying temperatures, as shown in Figure 1(b). At lower temperatures, regardless of time exposure (up to 20 min), there is minimal weight loss until 470°C. This data demonstrate the fluorinated polyimide's ability to withstand lower temperatures for longer durations

with little or no weight loss. Furthermore, this polyimide is able to withstand higher temperatures than PETI-5 [Scheme 1(a)] because of its low T_g (270°C) and a low decomposition temperature of 510°C.¹⁵ The lower stability in PETI-5 is due to differences in the backbone structure of the polyimide, such as the lack of CF_3 groups and the addition of ether linkages, that create other pathways for degradation to occur at high temperatures. AFR700B [Scheme 1(b)] has a similar structure to that of the fluorinated polyimide used here, except that AFR700B uses a nadic end-cap as the crosslinker. Both PETI-5 and AFR700B have high T_g 's, but AFR700B is not as thermally stable because of hydrolytic scission of its norbornene crosslinks.⁷ The superior thermal stability of the fluorinated polyimide (highest T_g and T_d) is due to its combination of the best features of PETI-5 (endcaps) and AFR700B (perfluoromethyl substituents).

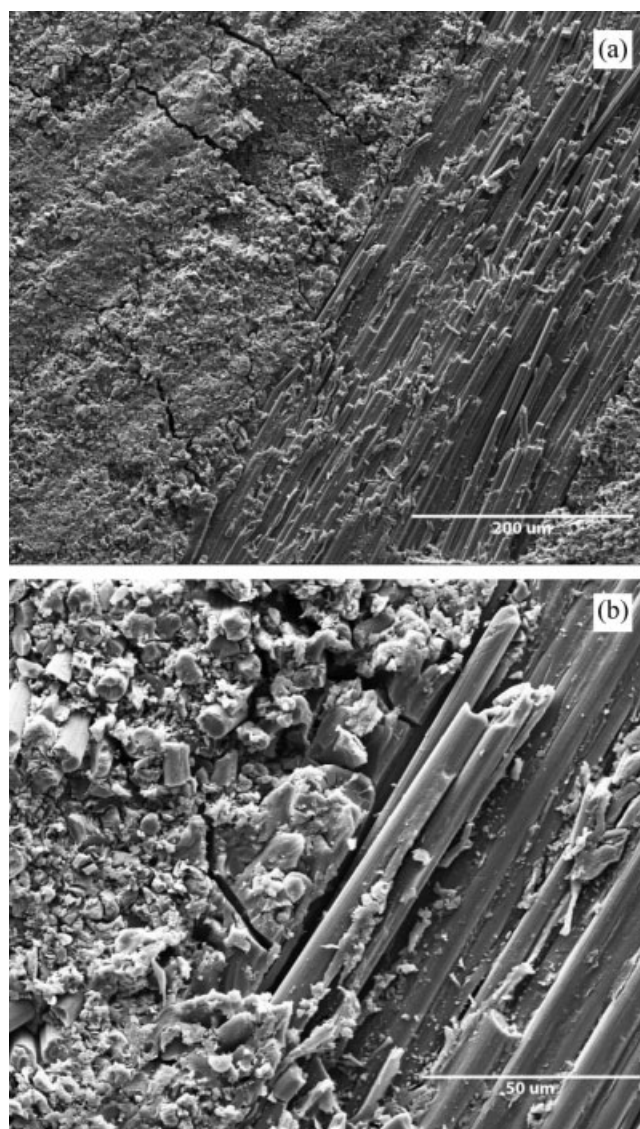


Figure 3 Scanning electron microscope images of polyimide composite cross-sections, after aging at 510°C for 20 min, at $\times 500$ (a) and $\times 2000$ magnification (b).

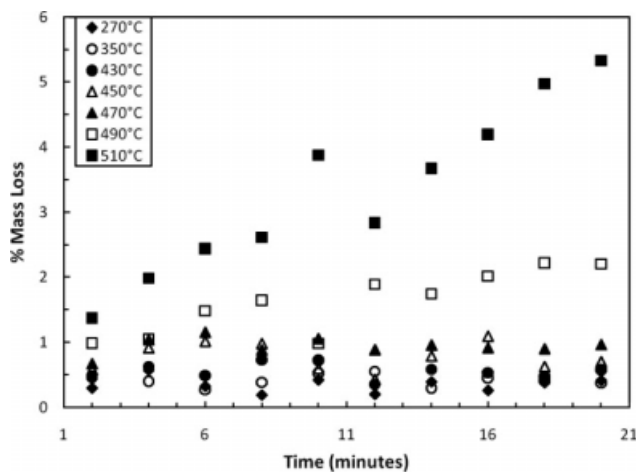


Figure 4 Polyimide composite weight loss in oven as a function of exposure time to various temperatures.

Adding carbon fiber to the fluorinated polyimide further enhances its thermal stability. The decomposition temperature of the polyimide containing 55 wt % carbon fiber, defined as the point at which 5% weight loss occurs, is 554°C in air and 562°C in nitrogen, as shown in Figure 2(b). This high degradation temperature allows the composite to withstand 510°C for up to 20 min and maintain weight loss below 5%. At temperatures below 470°C, weight loss is less than 1% regardless of the amount of exposure time. This enhanced thermal stability, relative to the neat polyimide, is a result of a strong fiber-matrix interface.²⁰ An elevated T_g (491°C) is evidence of this strong interaction. The adsorption of the polyimide to the carbon fiber surface delays decomposition because of prevention of air from permeating the interface.^{2,5,20–22} Figure 3 shows that

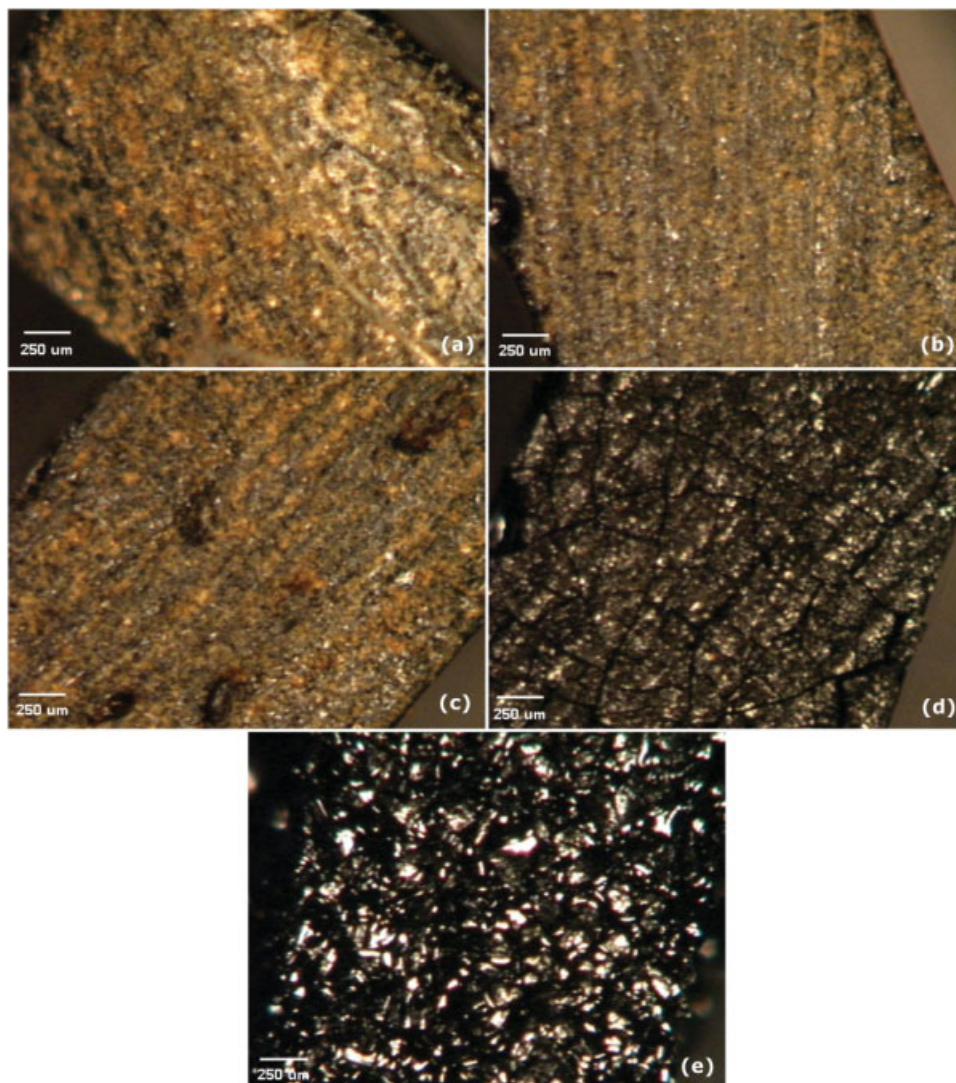


Figure 5 Optical microscope images for neat polyimide resin before aging (a) and aged at 250°C (b), 370°C (c), 490°C (d), and 510°C (e) for 20 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

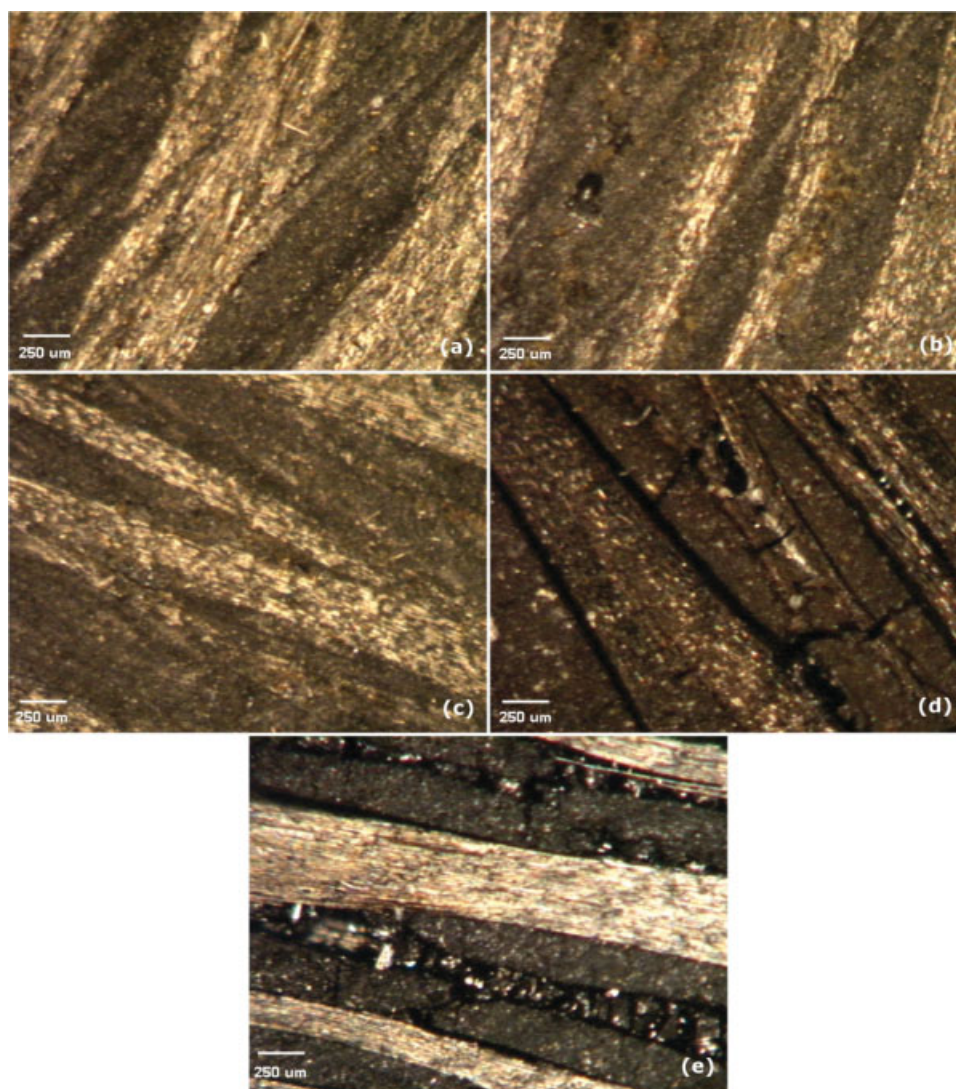


Figure 6 Optical microscope images for polyimide composite before aging (a) and aged at 250°C (b), 370°C (c), 490°C (d), and 510°C (e) for 20 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

this strong interaction remains after exposure to 510°C for 20 min. These cross-sectional images of polyimide composite, exposed to 510°C for 20 min, show the carbon fiber tightly interfaced with the matrix. Cracks in the polyimide are very apparent at both low [Fig. 3(a)] and high [Fig. 3(b)] magnification, but no significant gaps are observed where polymer meets fiber. When exposure temperatures are greater than 490°C the composite begins to show signs of weight loss greater than 1% at all studied exposure times, as shown in Figure 4. This result is not surprising because the temperature is nearing the decomposition temperature. A broader set of time and temperature weight loss data for the composite are shown in Supporting Information Table S2.

The composite not only exhibits lower weight loss with the addition of carbon fiber, but also it enhances other properties.¹⁷ Carbon fiber acts as a protective

barrier for the resin in the composite to prevent exposure to destabilizing elements. This protection allows the resin to withstand higher temperatures while also increasing the strength, thermal oxidative stability, and higher strength to weight ratio than their metal counterparts.¹⁹ The barrier from the carbon fiber also delays the decomposition of the polyimide resin within the composite. This is supported by the optical micrographs shown in Figures 5 and 6. There is no change in the neat resin or composite at the lower temperatures as seen in Figures 5(b,c) and 6(b,c). The light areas in the composite are the carbon fiber, whereas the darker areas are the resin. At 510°C, the neat resin [Fig. 5(e)] has qualitatively degraded more than the resin within the carbon fiber composite [Fig. 6(e)]. Also of note, is the delayed degradation at the interface between the carbon fiber and resin in the composite. This observation further reinforces the idea that

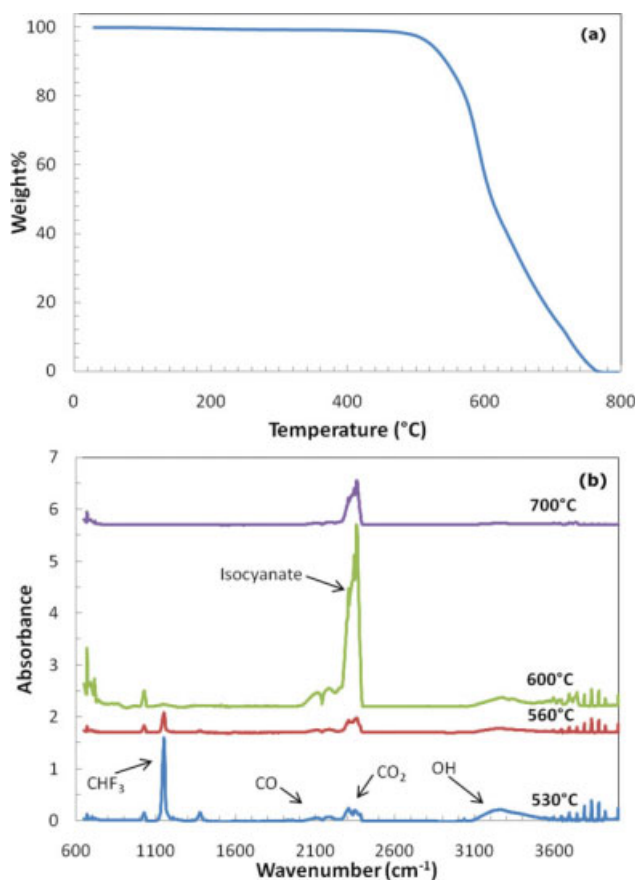


Figure 7 Polyimide weight loss as a function of temperature in air measured with a TGA-IR system (a). FTIR spectra of degradation products collected during heating (b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the composite material has a strong fiber-matrix interface, thus resulting in good thermal stability up to 20 min. The carbon fiber in the composite also prevents structural defects from occurring at higher temperatures, as seen from the images taken at 490°C [compare Figs. 5(d) and 6(d)].

Mechanism of polyimide degradation

Previous studies have focused on how similar PMR (polymerization of monomer reactants) type polyimides degrade at high temperatures in an attempt to predict the long-term, high-temperature performance.^{8,19} There are two different pathways that degradation occurs for these polyimides. One degradation route is through the cleavage of the C–N imide bonds that leads to a direct loss of CO, CO₂, and low levels of ArNCO. The second degradation pathway is from the loss of CF₃ and F from the two CF₃ linkages in the backbone of the polyimide, which is independent of the loss of CO and CO₂. Figure 7 shows the

loss of the CF₃ and NCO bonds using a combination of TGA and infrared spectroscopy for the fluorinated polyimide resin exposed to temperatures from 530 to 700°C in air. At lower temperatures, the major degradation pathway appears to be a loss of CF₃ linkages (CHF₃ has characteristic peak at 1150 cm⁻¹) from the backbone of the polyimide, whereas there is minimal loss of CO and CO₂. The higher temperatures primarily show loss of the NCO chemical bonds (isocyanate stretching is at 2340 cm⁻¹) with the CF₃ intensity decreasing as exposure temperature increases. These results suggest that both degradation pathways are independent of each other, but it is interesting to note that the breakdown of the backbone via NCO bonds occurs at much higher temperatures than the decomposition temperature of the polyimide resin material.

Thermogravimetric analysis

Weight loss measured using TGA, of the fluorinated polyimide resin and composite, was performed as an alternative to oven aging. Figure 8 shows weight loss of the neat polyimide resin for temperatures

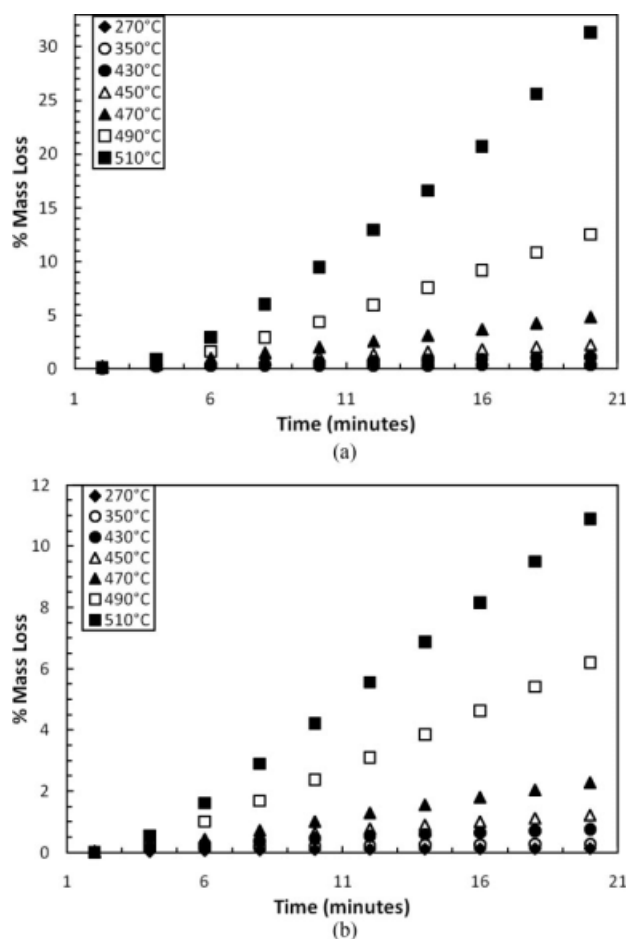


Figure 8 Polyimide resin (a) and carbon fiber composite (b) weight loss, measured with TGA, as a function of exposure time to various temperatures.

ranging from 250 to 510°C and 2 to 20 min hold times once each temperature was reached. When compared with Figure 1(b), it is clear that the TGA gives a much higher weight loss, relative to oven aging, for temperature exposures over 450°C. This discrepancy between oven and TGA is likely due to several factors, of which sample size is one of the most significant. TGA requires a much smaller sample, which results in better heat transfer compared to the oven due to greater surface area to volume ratio.²¹ Another issue with the oven is that opening, to place a sample inside, lowers the actual temperature and therefore less time is spent at the exposure temperature. The air flow over the sample in the TGA may also be enhancing weight loss. The oven technique is more reliable for small exposure times (2–10 min) because the TGA takes 6–8 min to reach the required test temperature and therefore gives a distorted weight loss. These factors cause the carbon fiber composite to show enhanced weight loss with TGA as well, as shown in Figure 8(b).

An examination of weight loss as a function of temperature for the polyimide resin [Fig. 8(a)] shows little loss before 450°C. It should be noted that both TGA and oven testing produce the same general weight loss trends as a function of time and temperature. At lower temperatures, regardless of exposure time, there is no visible difference in weight loss before 450°C. At higher temperatures, the TGA gives a clearer separation between test conditions relative to the oven. Much like neat polyimide, the composite shows little weight loss below 450°C [Fig. 8(b)], where the amount of exposure time begins to yield appreciable degradation. These trends are the same as those found with oven aging (Fig. 4), except for the higher weight loss at 510°C. Weight loss for a broader set of times and temperatures, measured with TGA, are shown in Supporting Information Tables S3 and S4 for neat polyimide and its composite, respectively.

CONCLUSIONS

Very little degradation (<1% weight loss) was observed for a fluorinated polyimide and its carbon fiber composite, when exposed to temperatures below 430°C. Beyond 470°C, both neat resin and carbon fiber-filled composite displayed relatively linear weight loss as a function of time, but this linear slope grew exponentially with temperature. TGA of the polyimide, done in air and nitrogen, suggests that oxidation is a relatively minor factor in the degradation process. Infrared spectroscopy performed during degradation confirmed that fluorinated species are the first to leave, followed by isocyanate groups at much higher temperature (~600°C). The polyimide composite shows a higher thermal stability compared to the neat polyimide resin for the exposure times studied

here. When exposed to 510°C for 20 min, the composite had a maximum weight loss of 10.9% using TGA and 5.3% using an oven, whereas the neat polyimide had a maximum weight loss of 31.3% and 12.6% for TGA and oven, respectively. The TGA method gives a more accurate weight loss for exposure times greater than 10 min, whereas the oven technique appears more useful when exposure times are less than 10 min. We found that for exposure times up to 20 min the composite shows better thermal stability; however, long term aging at lower temperatures of similar composites frequently showed the opposite effect.¹⁸ Both polyimide resin and composite were found to undergo thermolysis and modest oxidation during degradation. Future work for the fluorinated polyimide will include improved crosslinking and protection of thermally sensitive side groups (e.g., $-\text{CF}_3$). With a better understanding of degradation conditions and mechanism, improvements can be made to these high temperature materials. There will be a continual need for composites with ever higher thermal stability, especially as aircraft travel at ever increasing speeds.

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