Thermal Stability Studies of a Polyimide-Polytetrafluoroethylene Blend and Its Components

CHARLES R. DAVIS[1,*] and JEFFREY A. ZIMMERMAN[2]

[1]IBM, Thomas J. Watson Research Center, Yorktown Heights, New York 10598; [2]IBM, Microelectronics Division, Endicott, New York 13760

SYNOPSIS

Low-dielectric constant (ε_r) polymers, such as polytetrafluoroethylene (PTFE), are an important component of advanced electronic products that transmit data, since it is this physical property that largely determines a device's performance. For instance, the dielectric constant determines overall signal speed and proximity in that one circuit line can be placed to another, i.e., wiring density, while maintaining desired electrical characteristics. However, due to PTFE's inertness and intractability, significant challenges exist in the successful application of the polymer as an insulation material. One specific example is the lack of available methods to uniformly and controllably generate fine, high-density features in the neat fluoropolymer. Recently, it was reported that excellent structuring characteristics of PTFE can be achieved by sensitizing the fluoropolymer to excimer laser radiation using small quantities of an aromatic polyimide. An important physical property of the sensitization agent, in addition to interacting strongly with the laser's emitted energy, is suitable thermal stability due to PTFE's high-temperature processing requirements. Using multiple analysis techniques, the thermal decomposition behavior of PTFE, polyimide sensitizer, and resulting polymer blend have been evaluated. It was determined that the onset of decomposition for all systems is near or greater than 500°C. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymers are an important component in microelectronic devices, e.g., as insulation layers. Polymers having a low dielectric constant (ε_r) are especially critical since these materials participate directly in determining the performance of the electronic device. For instance, the insulator's dielectric constant determines the device's signal propagation speed, ss, as shown by the following equation:

$$ss \propto 1/\sqrt{\varepsilon_r}$$

In addition, the proximity that conductors can be placed with respect to one another, while maintaining desired electrical characteristics, e.g., impedance, is also determined by the insulating material's dielectric constant.[1,2] Specifically, the lower the dielectric constant, the closer conductors can be placed while maintaining a fixed impedance.

As a class of materials, the Teflon®[†] family, which includes most notably PTFE, offers the lowest dielectric constant values of commercially available neat polymers; e.g., PTFE's dielectric constant is about 2.1. Only the newest member to the Teflon family, Teflon AF®,[‡] has a lower dielectric constant, reported to be about 1.9.[3] In addition to their low dielectric constants, interest in Teflons as insulation materials, especially PTFE, is due to their high-thermal stability and excellent chemical resistance. However, Teflons have not gained wide acceptance in microelectronics applications due, in part, to pro-

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* To whom correspondence should be addressed.


[†] ®Teflon is a registered trademark of E.I. du Pont de Nemours Co., Wilmington, DE.
[‡] ®Teflon AF is a registered trademark of E.I. du Pont de Nemours Co., Wilmington, DE.

cessing difficulties including generating high-resolution structures, e.g., small holes, in the bulk polymer. An increasingly common and attractive method to microstructure some polymers is by excimer laser ablation.[4-7] However, not all polymers have the requisite molecular structure to inherently absorb high-energy UV photons emitted by excimer lasers and as required for ablation.

A quantitative evaluation identifying the interaction that a material has with UV energy of a specific wavelength is defined by its absorption coefficient, α_λ. Commercially available excimer lasers commonly emit in the quartz region of the UV spectrum, i.e., 193, 248, 308, and 351 nm, although there

have been recent publications on systems having an emission at 157 nm.[8,9] PTFE, whose structural repeat unit is

$$(- CF_2 - CF_2 -)_n$$
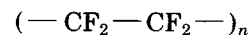
has only $n \to \sigma^*$ and $\sigma \to \sigma^*$ electronic transitions available. These are high-energy transitions requiring short wavelength radiation in order to achieve excitation. Thus, bulk structuring of PTFE is not observed with excimer lasers emitting in the quartz-UV since α_λ for the fluoropolymer at 193, 248, 308, and 351 nm is 0.[10-12] It is worthwhile noting that ablation of neat PTFE has been achieved using very


(a)

(b)
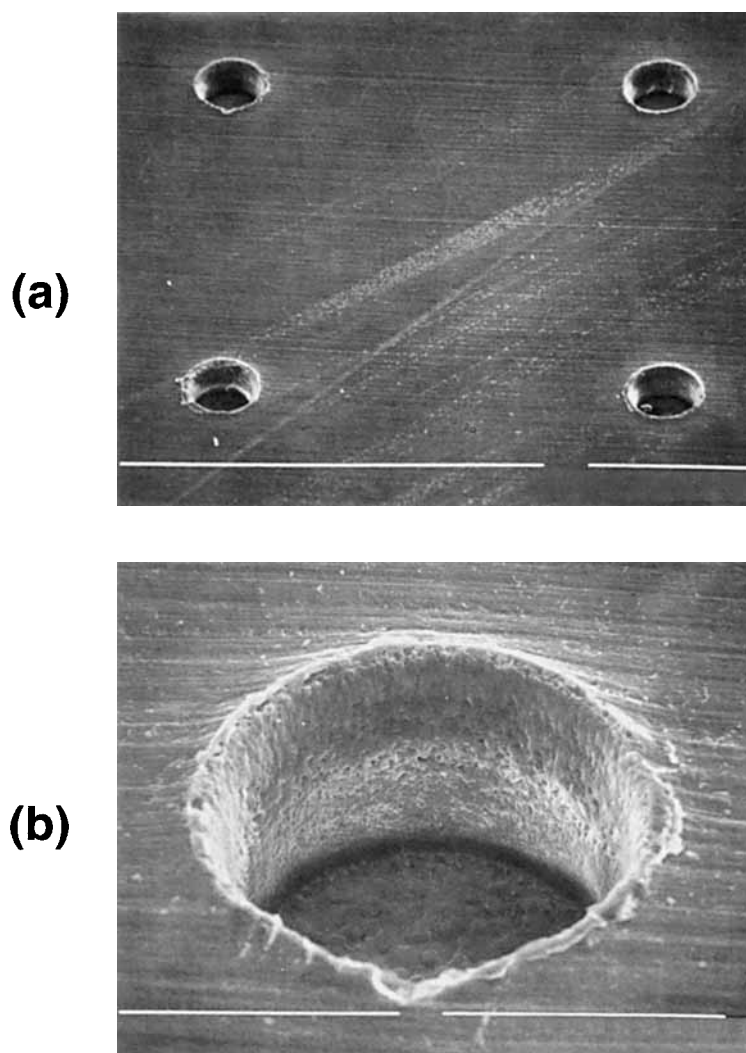
Figure 1   SEM photomicrographs of features ablated in PTFE containing 0.5% polyimide (wt/wt) using 308 nm and a fluence of 12 J/cm^2 at (a) low and (b) high magnification. Entrance hole diameter is $\approx$ 127 μm.

short pulses (e.g., femtosecond pulse width) providing high-intensity radiation where ablation is attributed to multiphoton absorption[13] or the use of shorter wavelength emissions, e.g., 157 nm.[8,9]

Sensitization and thus successful ablation of materials that are transparent at excimer laser emissions have been successfully demonstrated by investigators using compounds known as dopants. Dopants are typically low molecular weight, highly conjugated organics that have good UV-absorbing characteristics at the ablation wavelength of interest and have similar solubility to the transparent polymer matrix, e.g., poly(methyl methacrylate) (PMMA) and pyrene at 308 nm.[14-16] Although PMMA is not readily structured at 308 nm, upon the incorporation of small amounts of pyrene, ablation is easily achieved. However, commonly known dopants and sensitization techniques found in the literature are not compatible with UV-transparent polymers such as PTFE due the fluoropolymer's intractability and extreme processing requirements, e.g., high temperature.

Blending of polymers is of scientific and commercial value because it offers the opportunity to provide materials exhibiting a wide variety of interesting and desirable behaviors and properties. Often, blending is associated with the enhancement or variation of gross, physical characteristics of the final material over those of the individual components comprising the blend, for instance, improved mechanical properties. Davis et al.[10] and Egitto and Davis[11] recently reported the successful enhancement of an atypical, less commonly investigated physical property, α_λ, for PTFE through polymer blending by the addition of small quantities of an aromatic polyimide: biphenyl tetracarboxylic acid dianhydride–phenylene diamine (BPDA–PDA). BPDA–PDA's structural repeat unit is
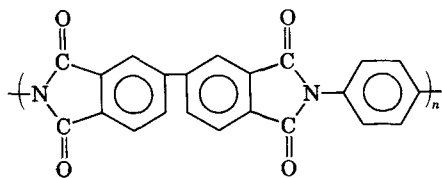
At 308 nm, α_λ for aromatic polyimides is on the order of 1×10^5 cm^{-1}.[5] Materials having α_λ of this magnitude are considered to have intense photon interaction. Thus, upon the incorporation of small quantities of polyimide into a matrix of PTFE, α_λ is suitably altered so that microstructuring of the fluoropolymer is readily achieved with excimer lasers

emitting in the quartz UV.[10,11] Egitto and Davis[11] reported that for enhanced excimer laser processing of PTFE the polyimide concentration (wt/wt) can be < 5%. For instance, at 308 nm and an emission fluence of 7 J/cm^2, optimum polyimide concentrations are near 0.2% (wt/wt). Figure 1 is a representative SEM photomicrograph of features formed in PTFE doped with 0.5% BPDA–PDA polyimide (wt/wt) using a XeCl excimer laser emitting at 308 nm and a fluence of 12 J/cm^2. The ablated features are well defined and exhibit a smooth wall profile, indicating excellent blend uniformity and homogeneity. It is noted that neat PTFE does not exhibit ablation behavior at these conditions. The purpose of this article is to discuss the thermal decomposition behavior of PTFE, BPDA–PDA polyimide dopant, and the resulting fluoropolymer–polyimide blend using thermal gravimetric analysis and pyrolysis/mass spectroscopy.

EXPERIMENTAL

Materials

BPDA–PDA polyamic acid in N-methyl-2-pyrrolidinone (NMP), ≈ 15% solids, and TEF 30B, ≈ 60% solids PTFE, in an aqueous dispersion from E. I. du Pont de Nemours Co. and 40% aqueous solution of dimethylamine (DMA) from Aldrich were used as received.

Blend Preparation

Water is a nonsolvent for both BPDA–PDA polyamic acid and polyimide. To successfully introduce polyimide into PTFE, water compatibility is required since the PTFE component exists as an aqueous dispersion. Water compatibility of the polyimide is achieved by partially reacting the acid functionalities, typically about 33%, present on the polyimide precursor with amine. Once formed, the polyamic acid salt is freely added to the aqueous PTFE dispersion, at room temperature, using simple blade mixing:

Table I   Bake/Cure Cycle for Sensitized PTFE Dispersion

Temperature (°C)	Time (Mins)
100	60
200	60
320	120
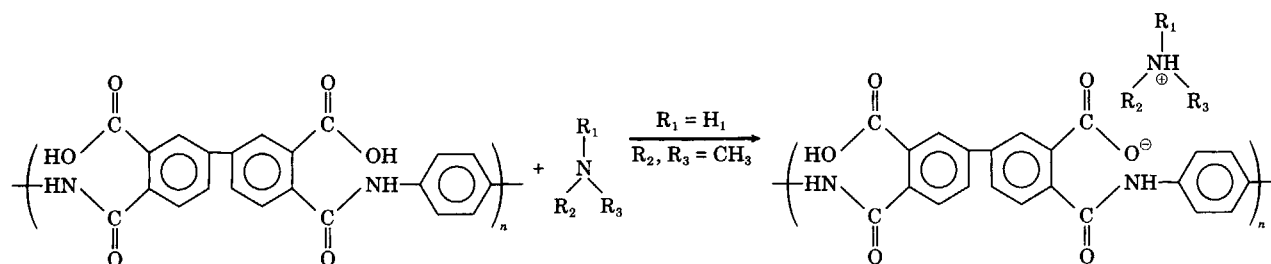
Continuous films of polyimide-doped PTFE are obtained by casting the sensitized dispersion onto an appropriate substrate, e.g., a metal, using a drawdown bar coater. Once applied, the coatings are baked, using a thermal-step cycle (Table I)[10] in a Blue-M high-temperature convection oven at ambient pressure, eliminating dispersion medium and surfactant and converting the polyamic acid/polyamic acid salt to polyimide. Sintering of the polyimide–PTFE coating is achieved by using high pressure and temperature (above the fluoropolymer's T_m), delivered by a Wabash flatbed press, resulting in a uniform polymer blend. Polymer blend compositions are prepared by appropriate ratioing of each constituent.

Analysis

Thermal characteristics of the polyimide blends and their homopolymer constituents were investigated using a Perkin-Elmer Series 7 thermal analyzer group (differential scanning calorimeter and thermogravimetric analyzer, DSC, and TGA, respectively) with air and N_2 atmospheres and an Extrel

FTMS 2000 Fourier transform ion cyclotron resonance mass spectrometer coupled with an in-house-designed pyrolysis cell. To enhance the detection sensitivity of the polyimide's thermal decomposition products, NMP was partially removed from the polyamic acid and polyamic acid salt samples, via high vacuum, prior to analysis by the mass spectrometer. In the mass spectra analysis, both positive (50 eV and 2 V trapping potential) and negative (5 eV and −2 V trapping potential) ion fragments were evaluated. Heating rates for the TGA, DSC, and FTMS were typically 10, 20, and 25°C/min, respectively.

RESULTS AND DISCUSSION

PTFE is a semicrystalline polymer that can be bulk processed, e.g., made to flow and exhibit excellent self-adhesion, using high pressures and thermal exposures exceeding its crystalline melt temperature, $T_m \approx 327$°C (Fig. 2). The observed lower, ambient temperature transitions are associated with crystal lattice changes. In addition to having a high T_m, the
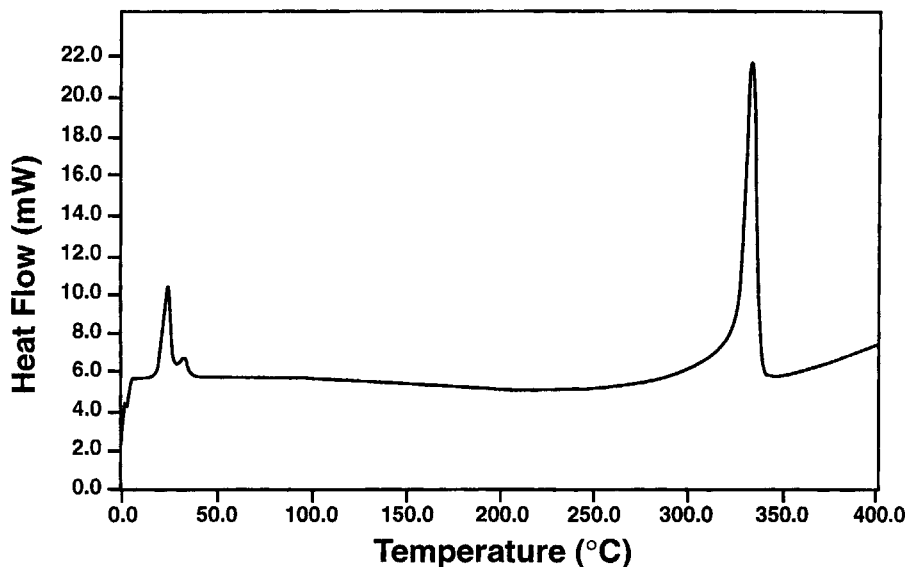

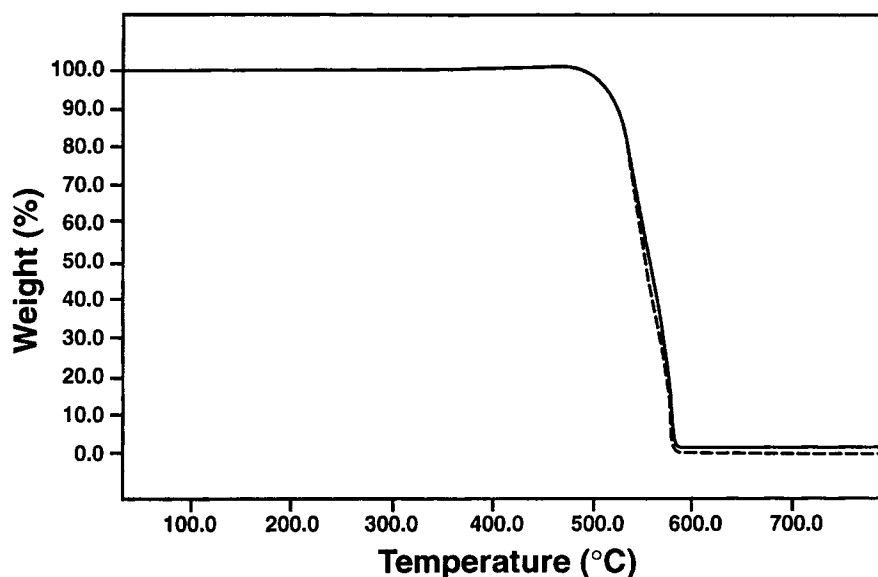**Figure 2**   Dynamic DSC scan of neat PTFE.

Figure 3   Dynamic TGA scan of neat PTFE (——) in air and (----) N_2 atmospheres.

onset of thermal decomposition for PTFE is also high.[17] Figure 3 is the dynamic TGA scan of neat PTFE in air and N_2. Under each atmosphere studied, the fluoropolymer's thermal and thermal–oxidative stability is excellent with the onset of decomposition found to be about 500°C. TGA data are found to be in excellent agreement with a more sensitive and structurally informative degradation technique, specifically, pyrolysis/mass spectroscopy. Figure 4 is a representative dynamic pyrolysis/FTMS scan of neat PTFE. As with TGA, the onset of degradation is found to occur near 500°C with the initial and primary degradation product being the tetrafluoroethylene monomer ion, $C_2F_4^+$, having an m/z of 100. Although other decomposition-product ions were formed, e.g., CF_3^+ (m/z = 69) and
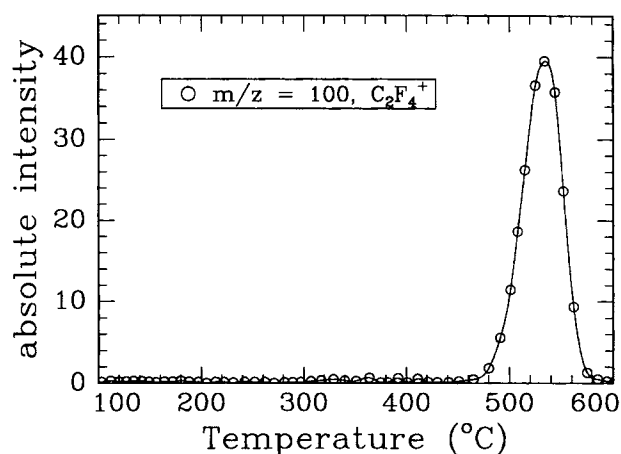
$C_2F_3^+$ (m/z = 81), in the present study, only the primary degradation-product ion associated with the onset of polymer decomposition is shown in the FTMS scan and included in the discussion.

Since bulk processing conditions of PTFE can include temperatures exceeding the fluoropolymer's T_m, any additive incorporated into the polymer, e.g., excimer-laser dopant, must exhibit excellent thermal stability. Aromatic polyimides are well known for their attractive physical characteristics including excellent thermal and chemical resistance, outstanding mechanical properties, and excimer-laser structuring quality.[18-20] Figure 5 is a dynamic TGA scan of BPDA–PDA polyimide in air and N_2 atmospheres. In Figure 5, the starting material is the polyimide's precursor, specifically, polyamic acid in NMP. Pyrolysis/FTMS identifies that the initial and significant weight loss observed between about 100 and 200°C is due to the elimination of solvent and water, with the latter resulting from the intramolecular cyclodehydration reaction that converts polyamic acid to polyimide:
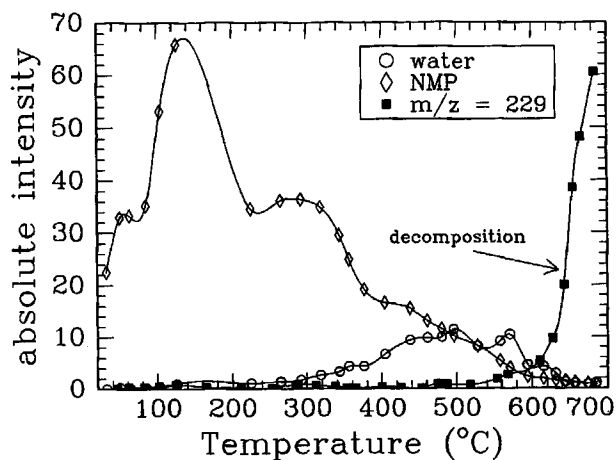

Figure 4   Dynamic pyrolysis/FTMS scan of neat PTFE.
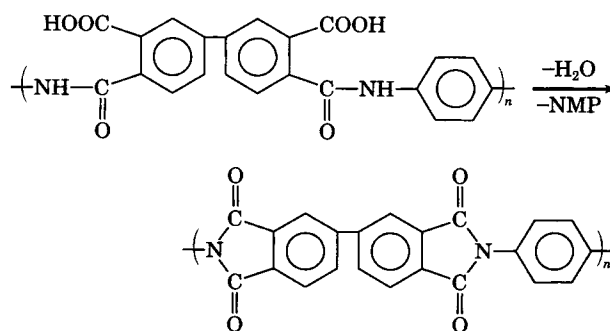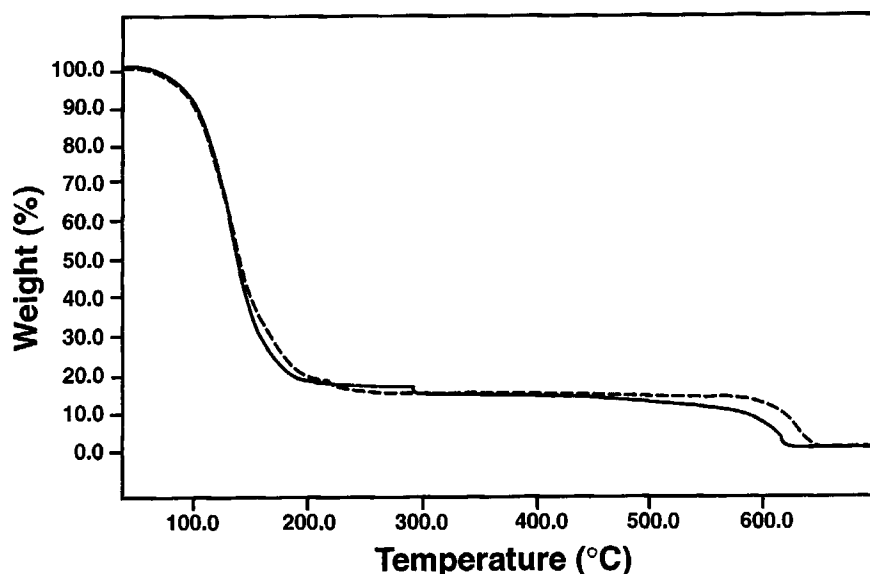
Figure 5 Dynamic TGA scans of BPDA–PDA polyimide (initial starting material is polyamic acid) in (——) air and (----) N₂ atmospheres.

Conversion of polyamic acid to polyimide is essentially complete at temperatures slightly > 200°C, as shown by the stable TGA base line, and is in excellent agreement with Snyder and Davis who used infrared spectroscopy to follow the cure behavior of BPDA–PDA.[21] In TGA analyses, imidization of the polyimide precursors occurred under N₂, at a heating rate of 3°C/min, until the final curing temperature of 400°C was reached. At that time, the heating rate was increased to 10°C/min and either the N₂ purge was continued or the atmosphere was changed to air. The polyimide's excellent thermal and thermal-oxidative stability is readily apparent with the onset of degradation occurring at temperatures, in either atmosphere, near 600°C and thus well in excess of that for PTFE.

Figure 6 is a pyrolysis/FTMS dynamic scan of the polyimide where the starting material is polyamic acid. Pyrolysis/FTMS data are in excellent agreement with TGA with the onset of degradation occurring near 600°C. The initial and primary decomposition product of the formed polyimide is a negative ion fragment having an m/z = 229. Presently, the chemical structure associated with the 229 ion is not yet assigned. Difficulties in identification of the m/z = 229 fragment are due to the large number of structural possibilities containing hydrogen, carbon, nitrogen, and oxygen. In addition, products formed by pyrolysis decomposition of aromatic polyimides do not proceed entirely by straight bond cleavage.[22] Also identified in the pyrolysis/FTMS spectrum are evolved solvent (NMP) and water (a

byproduct of the imidization process). The gradual release of NMP and water from the polyamic acid/polyimide system, during dynamic thermal decomposition analysis, has been previously noted.[22] In addition, this behavior has been previously observed for a number of polymers and is particularly important in polymer precursors processed with solvents. Typically, solvent desorption from the polymer occurs up to the decomposition temperature with additional solvent released once the structural integrity of the material is disrupted.[22]

BPDA–PDA's excellent thermal stability is a reflection, in part, of the high ring content in its mo-

Figure 6 Dynamic pyrolysis/FTMS scan of BPDA–PDA polyimide (initial starting material is polyamic acid).
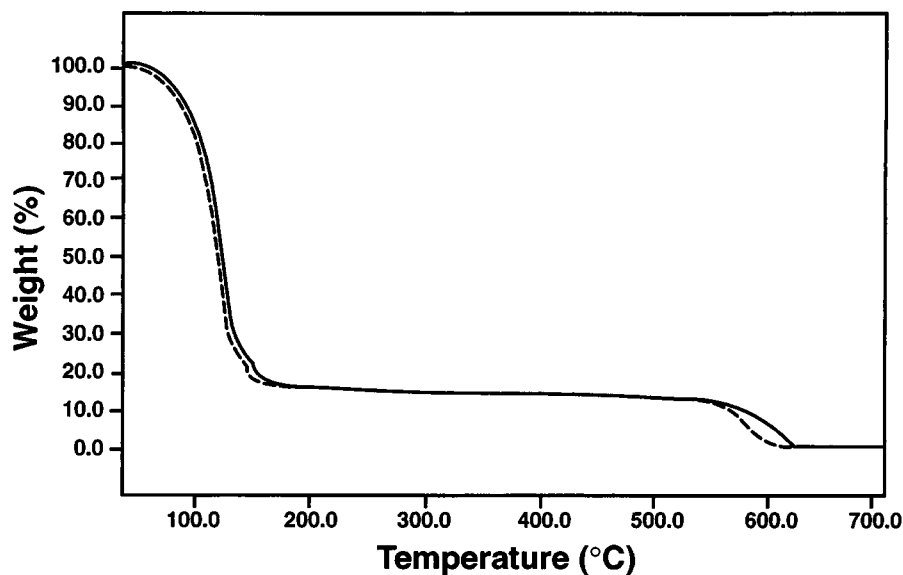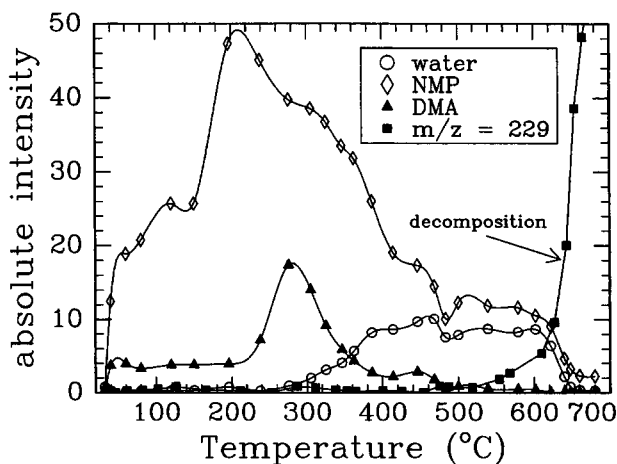
Figure 7 Dynamic TGA scans of BPDA-PDA polyimide (initial starting material is polyamic acid salt) in (———) air and (— — —) N_2 atmospheres.

lecular structure. In addition, the high aromatic ring content also provides extensive electronic conjugation in the molecule, resulting in the polymer's strong UV absorption coefficient, α_λ, including those at lower energies (longer wavelengths), e.g., 308 nm. As the materials' conjugation length increases, a hyperchromic effect and bathochromic shift in λ_{max} occurs. Thus, BPDA-PDA shows a significant absorption at 308 nm. α_{308} for BPDA-PDA has been experimentally determined to be 1×10^5 cm^{-1}.[10] This is in excellent agreement with Liu et al. who investigated the absorption coefficient of other aromatic polyimides.[5] Therefore, polyimides have the requisite thermal stability and absorption coefficient to behave effectively as a UV-sensitization agent for PTFE.

However, unlike early doping studies of UV-transparent materials where the host polymer and sensitization agent had similar solubility, ensuring even and uniform dopant incorporation, PTFE's chemical inertness presents a sensitization challenge. PTFE is commercially available in three states: (1) powder, (2) skived, and (3) aqueous colloidal dispersion. A polymeric dispersion can be described as discrete, individual particles, whose size is typically 1 nm to 1×10^3 nm, dispersed in a liquid medium and stable over a long period of time.[23] Of the three available forms, the dispersion most closely resembles that of a solution and offers an excellent vehicle to uniformly incorporate a dopant. However, PTFE and polyimides are insoluble and the chal-

lenge of forming an even and uniform blend is presented. In addition, water (the medium for the PTFE dispersion) is a nonsolvent for polyimides and their respective polyamic acids. However, by partially reacting the polyimide precursor's acid functionalities with an organic base such as an amine, e.g., DMA, the organic salt of the polyamic acid is formed. Once formed, the polyamic acid salt can be freely added to the aqueous PTFE dispersion.[10,11] Thus, the polyamic acid salt is used as the vehicle for introducing the polyimide-UV sensitizer

Figure 8 Dynamic pyrolysis/FTMS scan of BPDA-PDA polyimide (initial starting material is polyamic acid salt).
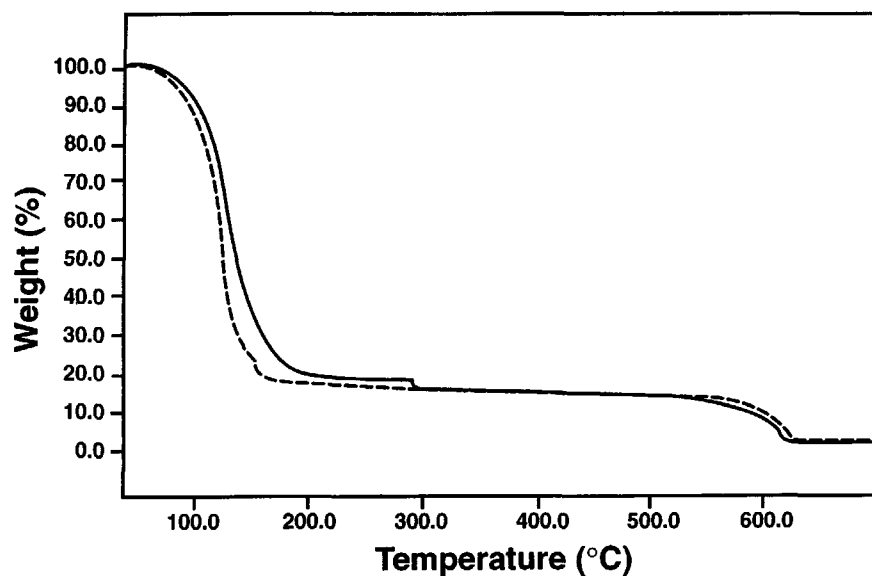
Figure 9 Dynamic TGA scans of BPDA–PDA polyimides where initial starting materials are (——) polyamid acid and (----) polyamic acid salt.

into PTFE. Therefore, the thermal stability in question is not that of polyimide formed from polyamic acid, but that formed from the polyamic acid salt.

Figure 7 is another dynamic TGA scan of BPDA–PDA polyimide in air and N₂ atmospheres. However, the starting material for this scan is the polyamic acid salt in NMP. The characteristic thermal behavior seen for neat polyamic acid, as previously

shown in Figure 3, is repeated, i.e., the thermal stability of the polyimide formed from the salt precursor is found to be similar to that for the acid with the onset of degradation occurring at temperatures, in either atmosphere, near 600°C, and again well in excess of that for PTFE. Figure 8 is a pyrolysis/ FTMS dynamic scan of the polyimide formed from the salt precursor. As seen in the TGA scan, the onset of degradation occurs at ≈ 600°C. Again, the
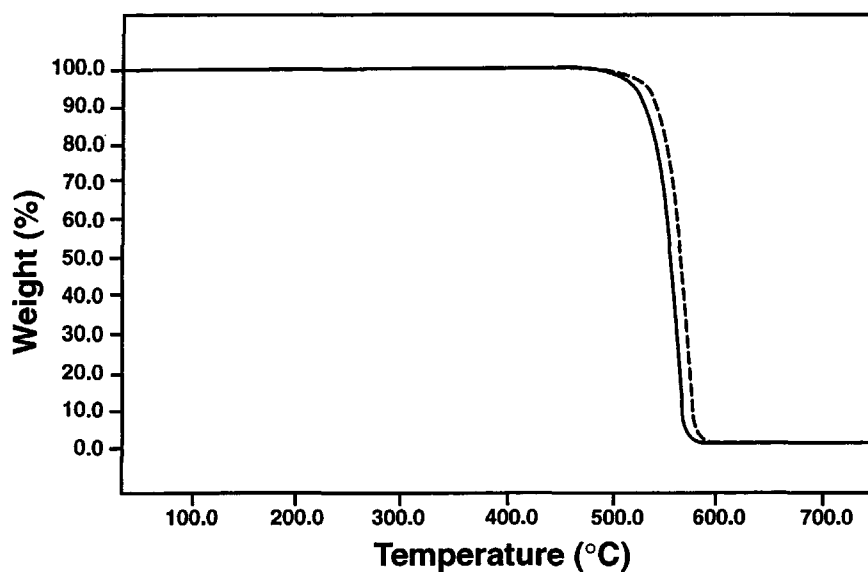
Figure 10 Dynamic TGA scan of PTFE containing 5% polyimide (wt/wt) in (——) air and (----) N₂ atmospheres.
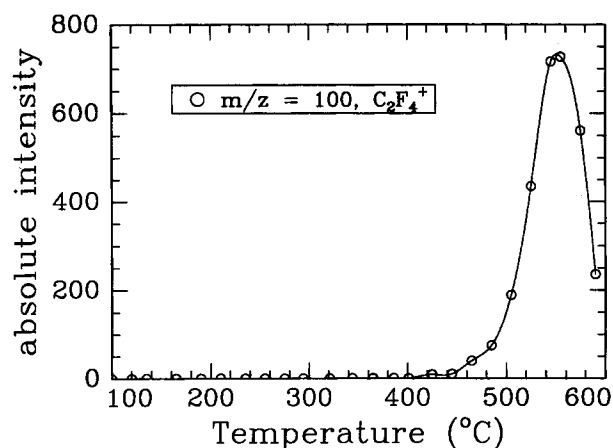
**Figure 11** Dynamic pyrolysis/FTMS scan PTFE containing 5% polyimide (wt/wt).

initial and primary degradation product is the negative ion fragment having an $m/z = 229$. However, in addition to the loss of NMP and water during the imidization process, the amine used to generate the aqueous compatible polyamic acid salt, i.e., DMA, is also eliminated.

Thus, polyimide thermal stability is not sacrificed as a result of forming the organic salt adduct necessary for sensitizing PTFE. This is confirmed in Figure 9, which is a representative TGA scan, in N_2, of polyimide formed by polyamic acid, and polyamic acid salt. It is readily apparent that the resulting polyimides have identical thermal responses. Figure

10 is a representative TGA scan of a polyimide–PTFE blend in air and N_2 atmospheres, specifically, 5% polyimide (wt/wt). It is clearly seen that the blend exhibits the expected high-temperature stability, characteristic of its individual components, with the onset of degradation in both environments occurring at about 500°C. Figure 11 is a representative pyrolysis/FTMS scan of the same blend with the onset of decomposition agreeing well with the TGA data. In the FTMS scan, the major decomposition ion has an $m/z = 100$, which, as with neat PTFE, is indicative of $C_2F_4^+$, the tetrafluoroethylene monomer. Figure 12 is a TGA scan of neat PTFE and a 5% (wt/wt) polyimide–PTFE blend in N_2. The similarity of the thermal responses are readily apparent. The thermal behavior of the polyimide–PTFE blend, as followed by TGA and pyrolysis/ FTMS, is not surprising since the components are immiscible and nonreactive and the fluoropolymer is the major component and less thermally stable than is the polyimide; i.e., since the thermal stability of PTFE is less than that of the aromatic polyimide used for UV sensitization, the blend's thermal response will be driven by the fluoropolymer component.

SUMMARY

The thermal behavior of a polyimide–PTFE blend and its individual components were investigated using TGA and pyrolysis/mass spectroscopy. The
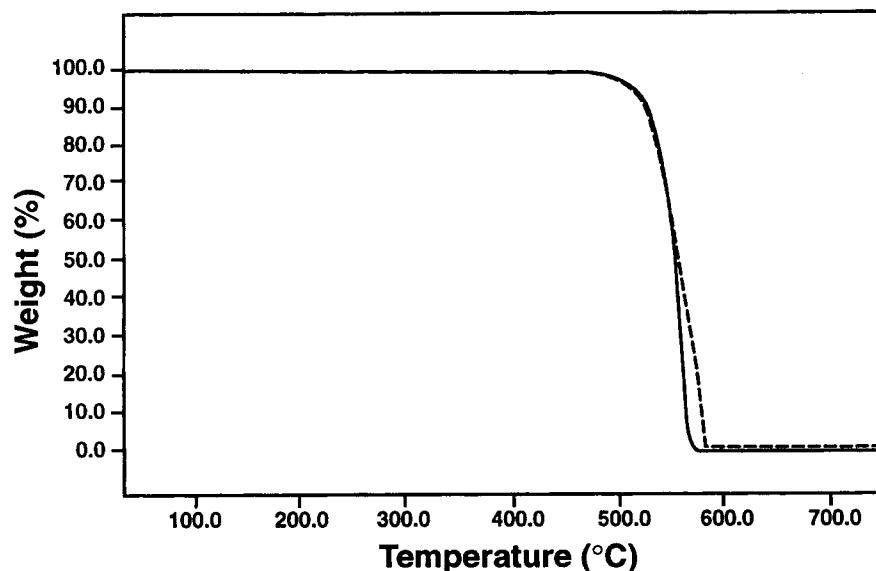
Figure 12 Dynamic TGA scan of (———) neat PTFE and (– – – –) PTFE containing 5% polyimide (wt/wt).

blend and its components exhibit high thermal and thermal-oxidative stability. For instance, in air and N_2 atmospheres, onset of thermal degradation for PTFE and BPDA–PDA polyimide, regardless of whether polyamic acid or polyamic acid salt (required to generate a uniform and homogeneous blend) was the precursor, is near 500 and 600°C, respectively. Finally, since the two polymers composing the blend are immiscible and nonreactive, the resulting material's thermal response mimics that of neat PTFE. This is not surprising since the major component of polyimide–PTFE blends, for enhanced excimer laser processing, is PTFE, typically 95% minimum (based on results of Egitto and Davis, at 308 nm and laser fluences of about 7 J/cm^2, maximum ablation rates for PTFE are achieved at polyimide concentrations of about 0.2% [wt/wt]).

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