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Thermal characterization of PMR polyimides

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Abstract

Polyimides are attractive for high temperature applications as the matrix resins, due to their excellent thermo-oxidative stability and mechanical properties. As composite materials for aerospace applications, they possess certain unique characteristics such as toughness, resistance to temperature and solvents as well as high tensile strength and modulus. A series of novel PMR polyimides based on substituted benzidines are examined and compared to the state-of-the-art PMR-15. The assigned glass transition temperatures and the mechanism for the thermal decomposition of four specific PMR polyimides are obtained, using thermal mechanical analysis and TGA/FTIR/MS techniques. Their thermal decomposition steps are proposed, identified and also compared to each other.

Keywords: Polyimide; TGA/FTIR/MS; Degradation mechanism

1. Introduction

The polyimide comprises one of the most stable and heat resistant polymer system. PMR polyimides (most noticeably PMR-15), prepared by polymerization of monomeric reactants, are high temperature polymers used as the matrix resins in fiber-reinforced composites for a variety of advanced aerospace applications [1,2]. As composite materials, they possess certain unique characteristics, such as good solvent resistance, high temperature performance and outstanding mechanical properties.

TGA/FTIR/MS techniques have often been used in the study of thermal degradation of materials. The technique allows for the simultaneous and continuous identification of evolved decomposition products as materials pyrolyzed. The result from TG/FTIR/MS data can suggest possible degradation mechanism.

The objective of this study is to examine a series of novel PMR polyimides based on substituted benzidines and compare them to the state-of-the-art PMR-15. The assigned glass transition temperatures are determined by thermal mechanical analysis (TMA). In addition, the thermal degradation mechanism of these PMR polyimides is proposed, using DSC and TGA/FTIR/MS techniques.

2. Experimental

2.1. Preparation of PMR polyimide resins

A series of novel PMR polyimides are formulated from 3,3′,4,4′-benzophenone tetracarboxylic acid dimethyl esters and nadic ester as the endcap

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with four different diamines; namely, 2,2′-dimethylbenzidine (DMBZ), 2,2′,6,6′-tetramethylbenzidine (TMBZ), 2,2′-bis(trifluoromethyl)benzidine (BFBZ) or methylene dianiline (MDA) in 50% methanol solution. The monomer solution were concentrated to syrup by heating, and then staged at 204°C for 2 h and 260°C for 30 min to afford imidized resin powders. The PMR polyimide oligomers are generally insoluble even in polar aprotic solvents such as *N*-methyl-2-pyrrolidinone (NMP); therefore, the molecular weights cannot be determined by GPC. The formulated molecular weight for PMR polyimides are listed as follows: DMBZ-15 = 1500 g/mol, PMR-15 = 1500 g/mol, BFBZ = 1824 g/mol, TMBZ = 1584 g/mol. The resin discs were processed from the imidized powders by compression molding at 315°C at 1500 psi for 2 h. The structures of four PMR polyimides are shown in Fig. 1.

2.2. TMA technique

The glass transition temperatures of PMR polyimides were measured by TMA on a TA Instruments 2940 Thermomechanical Analyzer, using expansion probe with 5 g load.

2.3. TG/MS technique

The non-postcured samples of PMR polyimides were placed in a ceramic pan and analyzed on an SDT (simultaneous TGA and DTA) 2960 interfaced to a Fisions VG Thermolab Mass Spectrometer by means of a heated capillary transfer line. The Fisons unit is based on quadruple design with a 1–300 amu mass range. The sample gas from the interface was ionized at 70 eV. The system operates at a pressure of 1×10^{-6} Torr. The samples were heated at 1°C/min from room temperature to 950°C in dynamic nitrogen atmosphere. The DTA reference was 10 mg of pure aluminum oxide. A NIST library database was used for MS analysis.

2.4. TG/FTIR technique

The sample was placed in the ceramic boat, and was heated in the TGA 951 at 1°C/min from ambient

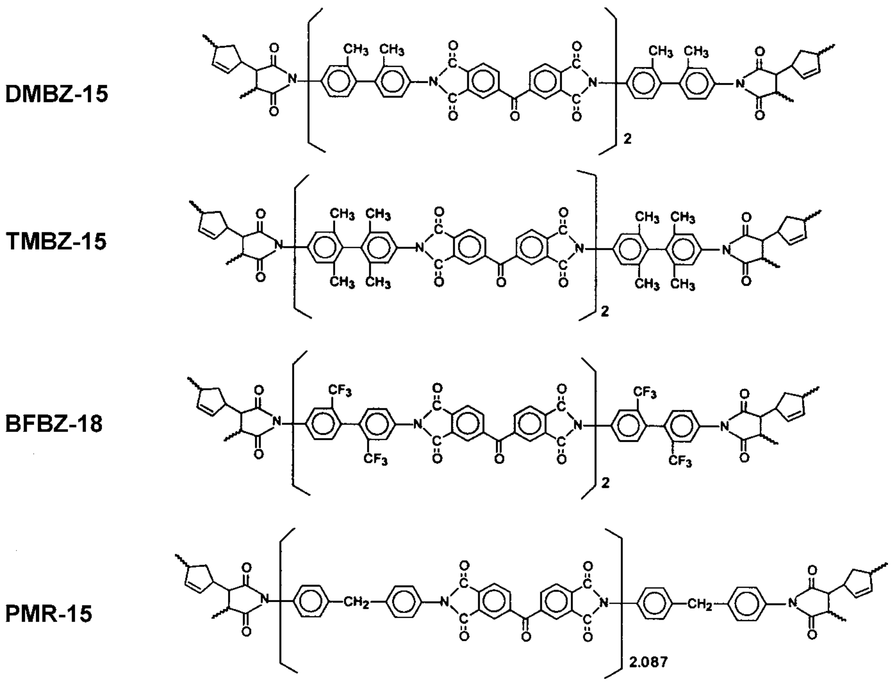


Fig. 1. Structures of PMR polyimides.

temperature to 950°C, under a flowing (50 ml/min) nitrogen (UHP grade). The DuPont 951 TGA interfaced to a Perkin Elmer 1600 series FTIR with a permanent silicon transfer line (length, 1 in.). The purge gas carries the decomposition products from the TGA through a 70 ml sample cell with KBr crystal windows. For detection of the decomposition products, the cell was placed in the IR scanning path and kept at 150°C by wrapped heating tape to prevent possible condensation. The IR detection range was 450–4500 cm^{-1}.

3. Results and discussion

3.1. TMA

Table 1
Glass transition temperature of polyimides

Resins	T_g (°C)	
	Non-postcured	Postcured[a]
DMBZ-15	366	391
TMBZ-15	333	401
BFBZ-18	269	404
PMR-15	276	350

[a] Resins were postcured at 315°C in air for 16 h.

TMA analysis on PMR polyimides (Table 1) showed that PMR polyimides based on substituted benzidines displayed much higher T_g's than that of PMR-15 ($T_g = 391$°C for DMBZ-15 and 401°C for TMBZ-15 and 404°C for BFBZ-18 compared to 350°C for PMR-15, after postcure at 315°C for 16 h in air). This phenomenon is attributed to the steric hindrance of pendent groups (CH_3 and CF_3) on the biphenyl rings, which creates higher rotational barrier during the glass transition phase [3]. After postcuring at 315°C in air for 16 h, all four samples shows significant increases in T_g, due to further crosslinking reactions.

3.2. Thermogravimetric analysis (TGA)

The weight loss curves are plotted in Fig. 2 for the four samples. Based on DTGA curves shown in Fig. 3,

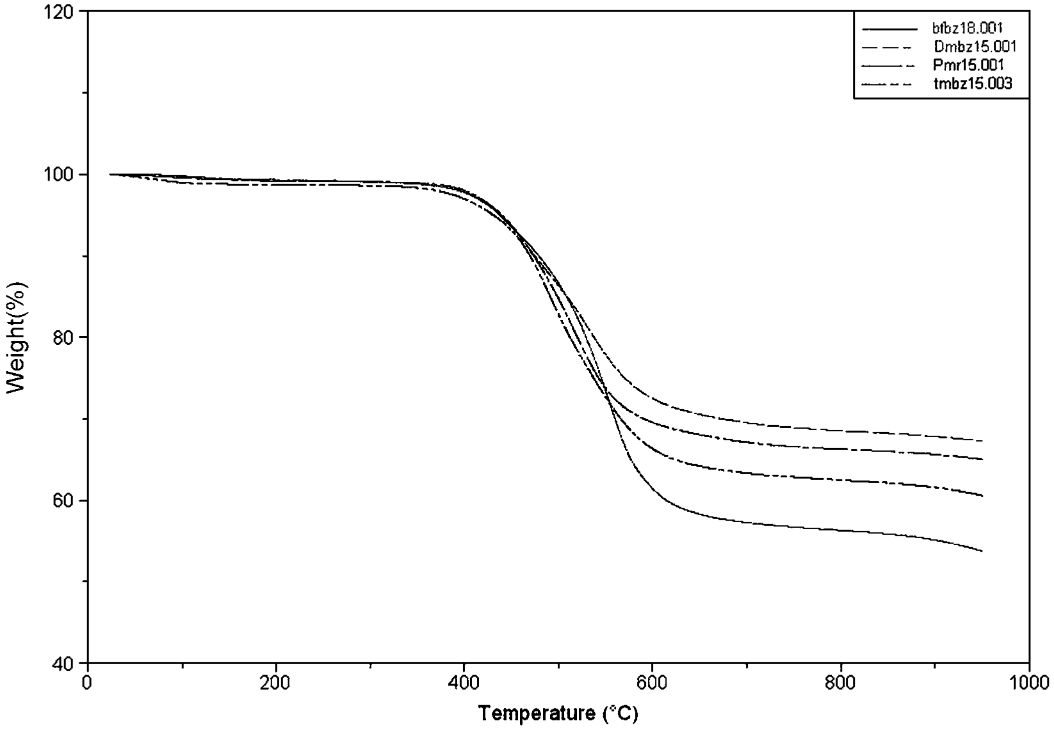


Fig. 2. TGA curves of four PMR polyimides.

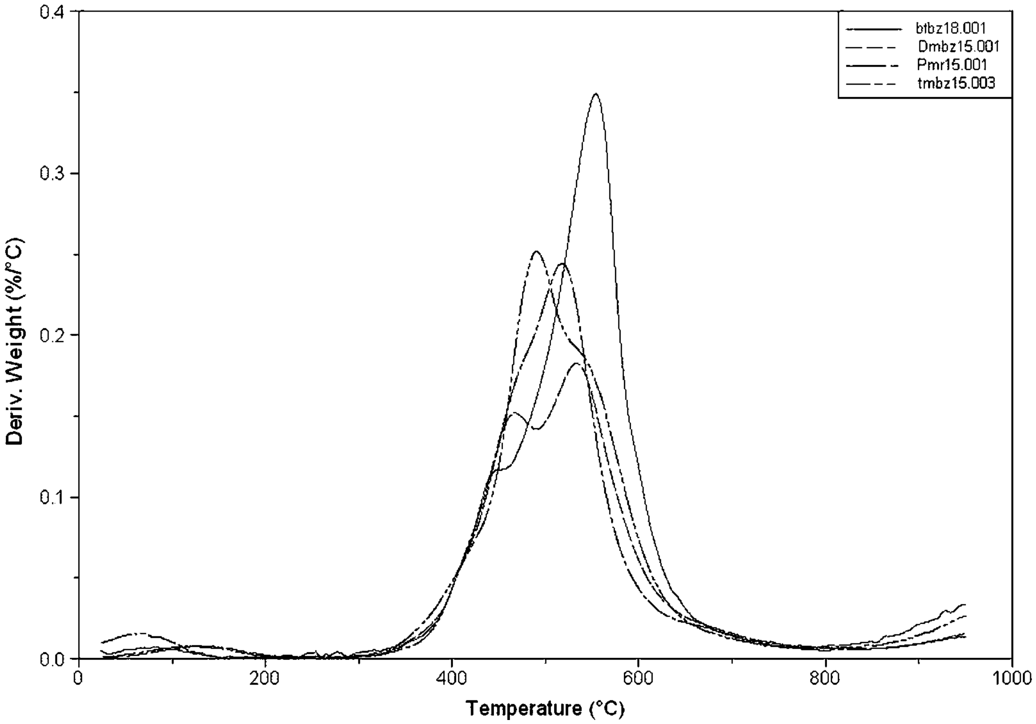


Fig. 3. DTGA curves of four PMR polyimides.

sample PMR-15 shows essentially a single stage reaction in UHP nitrogen. On the other hand, the decomposition of sample TMBZ-15, DMBZ-15, and BFBZ-18 are much more complex, the DTGA curve indicates a two-stage degradation process. It can be seen clearly that for TGA analysis in nitrogen the order of stability is PMR-5 > TMBZ-15 > DMBZ-15 > BFBZ-18, based on the peak of the first stage reaction of DTGA, which takes into account the little hump of DTGA curve in BFBZ-18.

These data indicate that the pendant groups on the biphenyl rings play an important role in the thermal stability of the corresponding resins. PMR-15, containing methylene dianiline, exhibits highest thermal stability, due to the presence of reactive benzylic hydrogens that are believed to form free radical upon cleavage of C–H bond, thus promoting additional crosslinking instead of degradation [4]. The methyl substituents in TMBZ-15 and DMBZ-15 cleave-off before the backbone ruptures. The poorer stability of sample BFBZ-18 is surprising, since it is well known that the CF_3 group is thermally more stable than CH_3 [5]. It is speculated that: (1) the electron withdrawing nature of the CF_3 reduces the reactivity of the diamine which produces oligomers with lower molecular weight which leads to poorer thermal stability; (2) the stronger C–F bond prevents the formation of free radicals for further reactions that tends to stabilize the resin.

3.3. Thermal degradation mechanisms of polyimides

TGA–MS and TGA–FTIR are very useful techniques employed in examining the detailed thermal degradation mechanism [5,6]. During TGA/MS/FTIR experiments, the releasing products from samples studied are simultaneously and continuously monitored by MS and FTIR. As shown in Fig. 4, the major products from decomposition of sample BFBZ-18 include HF, H_2O, CO_2, CO, HCF_3, COF_2, NH_3, and some aromatic derivatives. CO_2 is released in two stages: the first maximum rate of evolving CO_2 is around 531°C, and the second maximum rate is about 930°C. Although the evolution of CO_2 is even detected

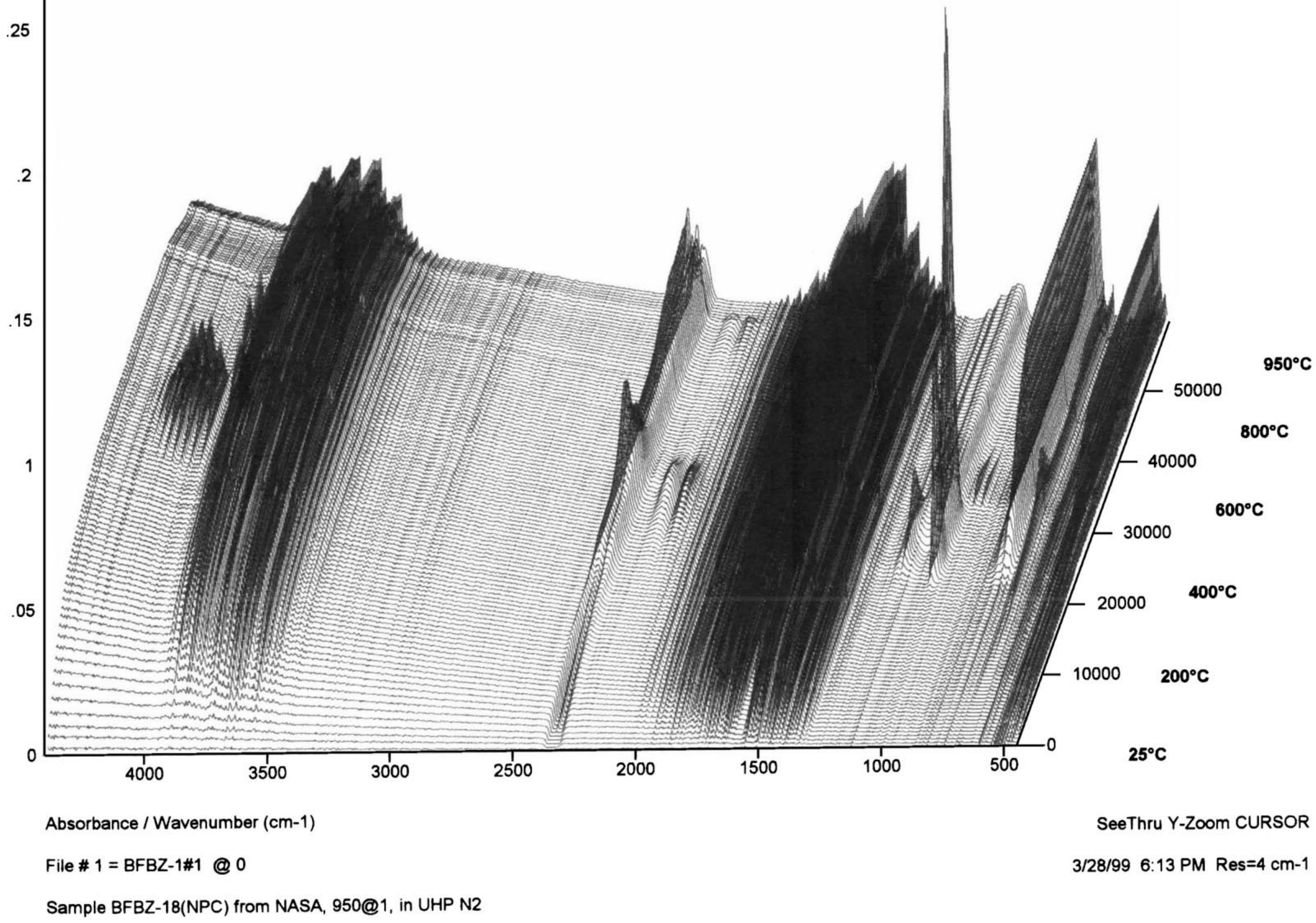
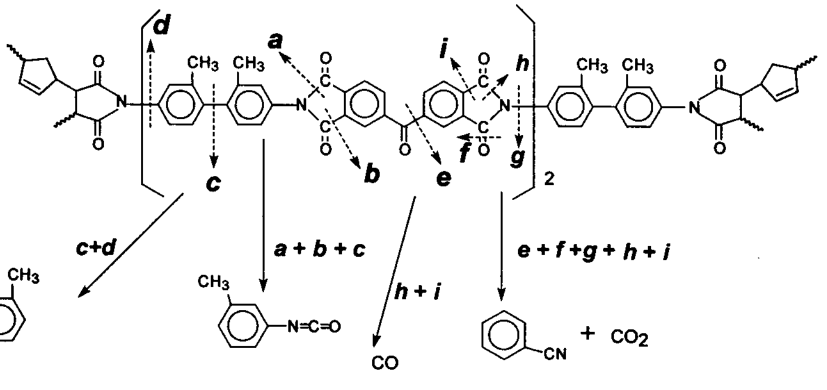


Fig. 4. 3D FTIR spectra of gases from the pyrolysis of BFBZ-18 at a heating rate of 1°C/min.

before CO under ultra-high purity (UHP) N_2 atmosphere, which seems indicates that both CO_2 and CO are the direct products from the decomposition of sample BFBZ-18. However, by examining MS results, the spontaneous conversion of CO directly to CO_2 can occur at the temperatures over 400°C [6]. The results illustrate that the degradation of the pendant groups has maximum intensity at 522°C, as indicated by the evolution of HCF_3, COF_2, and HF. At higher temperature around 601°C, the main chain starts to decompose and the product NH_3 is observed.

The same major degradation products are observed with all the other three samples, DMBZ-15, TMBZ-15, and PMR-15, including water, CO, CO_2, CH_4, and NH_3 and some aromatic derivatives which are identified as phenyl isocyanates [6] which overlaps with CO_2 near 2358 cm^{-1}, as shown in Figs. 5–7. Water is evolved at all temperature from very low temperature about 100°C to the very high temperature 950°C, this indicates that at least part of it must be a genuine degradation product and not just adventitious moisture. The pendant methyl groups in TMBZ-15 and DMBZ-15 are released as CH_4 which reaches the maximum intensity at 479°C for TMBZ-15 and 436°C for DMBZ-15. As for PMR-15, the generation of CH_4 at 521°C is derived from $-CH_2-$ group of methylene dianiline. As an indication of the main chain degradation, NH_3 is observed at maximum intensity at temperature 557°C for TMBZ-15, 531°C for DMBZ-15, and 514°C for PMR-15.

Two steps decomposition of sample TMBZ-15, DMBZ-15, and BFBZ-18 could be concluded from TGA/FTIR/MS data. In the first step, the end groups and side groups are broken from the main chain to produce CO, CO_2, water, and either fluorinated products or CH_4. And then the main chain of polyimide undergo thermal degradation while releasing NH_3, CO, and CO_2. Compared the pathway of CO which directly arise from imide ring, the pathway of CO_2 is more complicated. Several mechanisms have been suggested previously [6]: (1) amic acids which may form either from incomplete imidizationor hydrolysis of imide rings; (2) decomposition of the isoimides derived from the rearrangement of imides; (3) unreacted anhydrides. However, Fig. 8 shows that the IR spectra of cured DMBZ-15 neat resin showed that most of labile –OH and –NH stretches at 3500 cm^{-1} are diminished due to the cyclization of polyamic acids and the unreacted dianhydride (C=O at 1852 cm^{-1}) present in the molding powders has disappeared, except the symmetrical carbonyl (C=O) stretch at 1778 cm^{-1} and unsymmetrical carbonyl stretch at 1715 cm^{-1}. It is also difficult to explain the rearrangement of imides to isoimides during the TGA–FTIR experiment. Furthermore, TGA/MS could identified other aromatic fragments included phenyl isocyanates which overlapped with the very strong CO_2 absorption, and benzonitrile ($m/e = 103$), toluene ($m/e = 91, 92$) as shown in Scheme 1. The detection of benzonitrile by TGA–MS strongly confirmed the cleavage of carbonyl group (C=O) in the imide rings into oxygen radicals which could be combined with CO to form CO_2. Similar degradation products have been verified recently by high resolution pyrolysis GC–MS [8] on thermoplastic polyimides with identical backbones. Therefore, the most



Scheme 1.

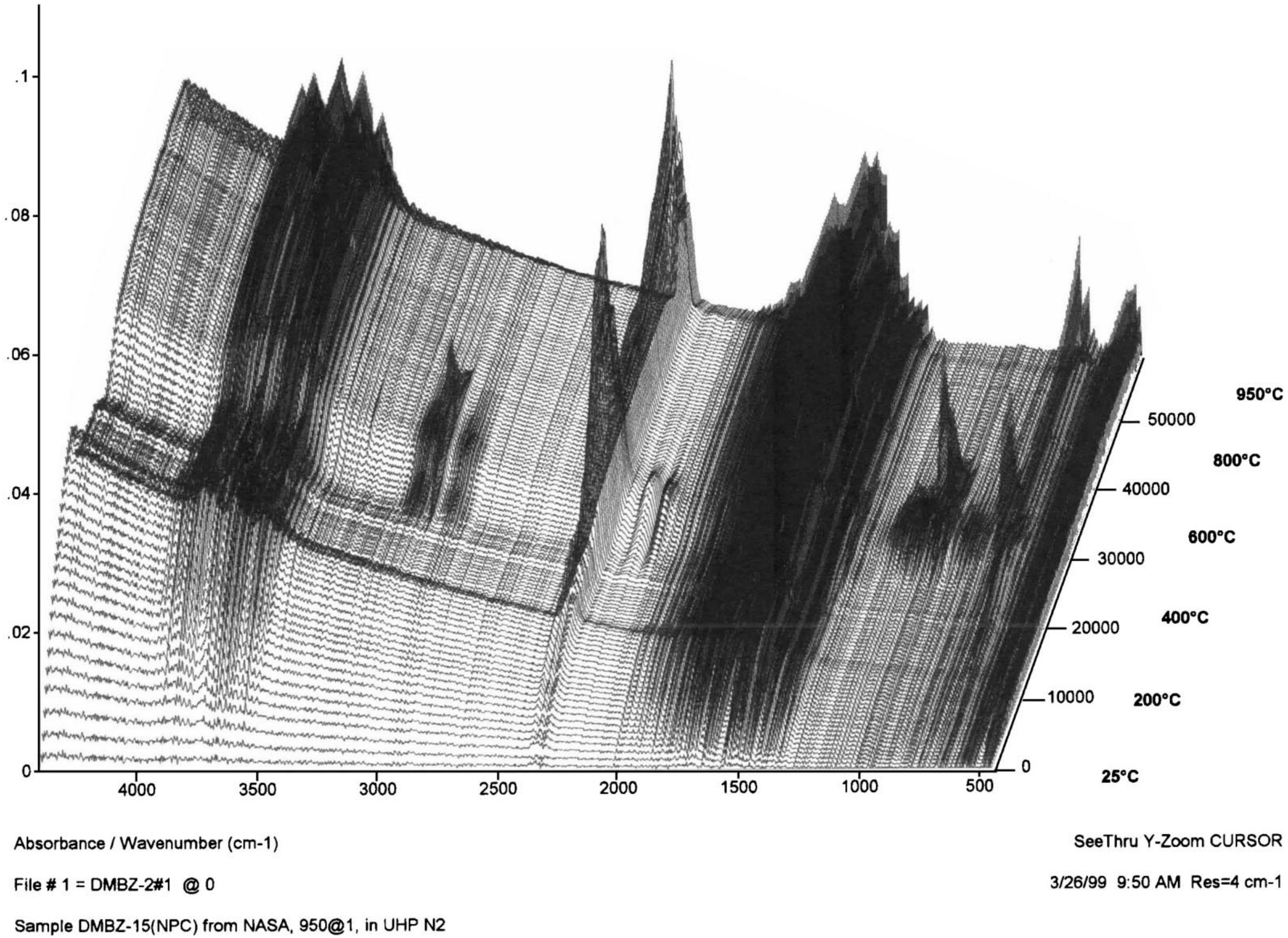


Fig. 5. 3D FTIR spectra of gases from the pyrolysis of DMBZ-15 at a heating rate of 1°C/min.

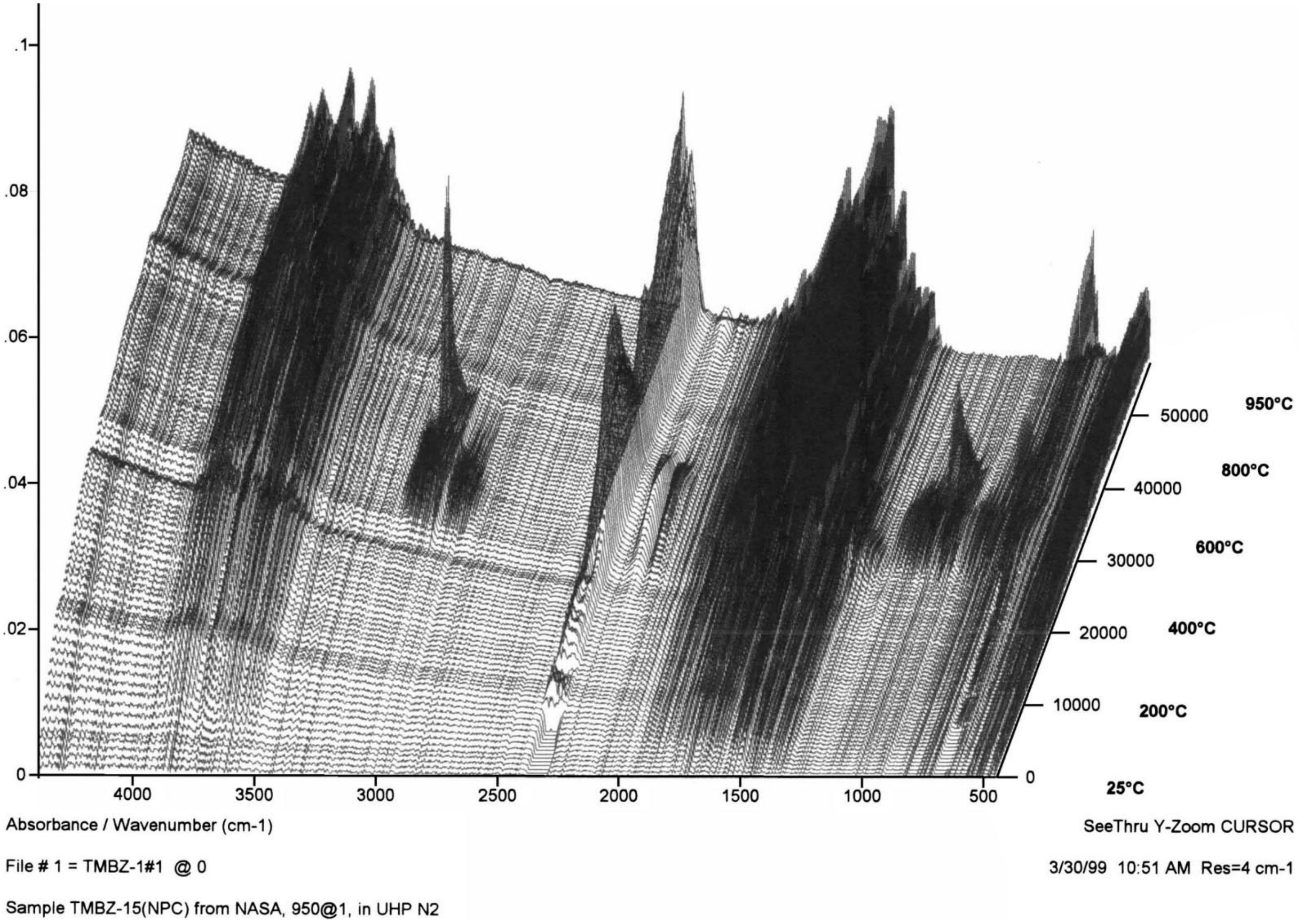


Fig. 6. 3D FTIR spectra of gases from the pyrolysis of TMBZ-15 at a heating rate of 1°C/min.

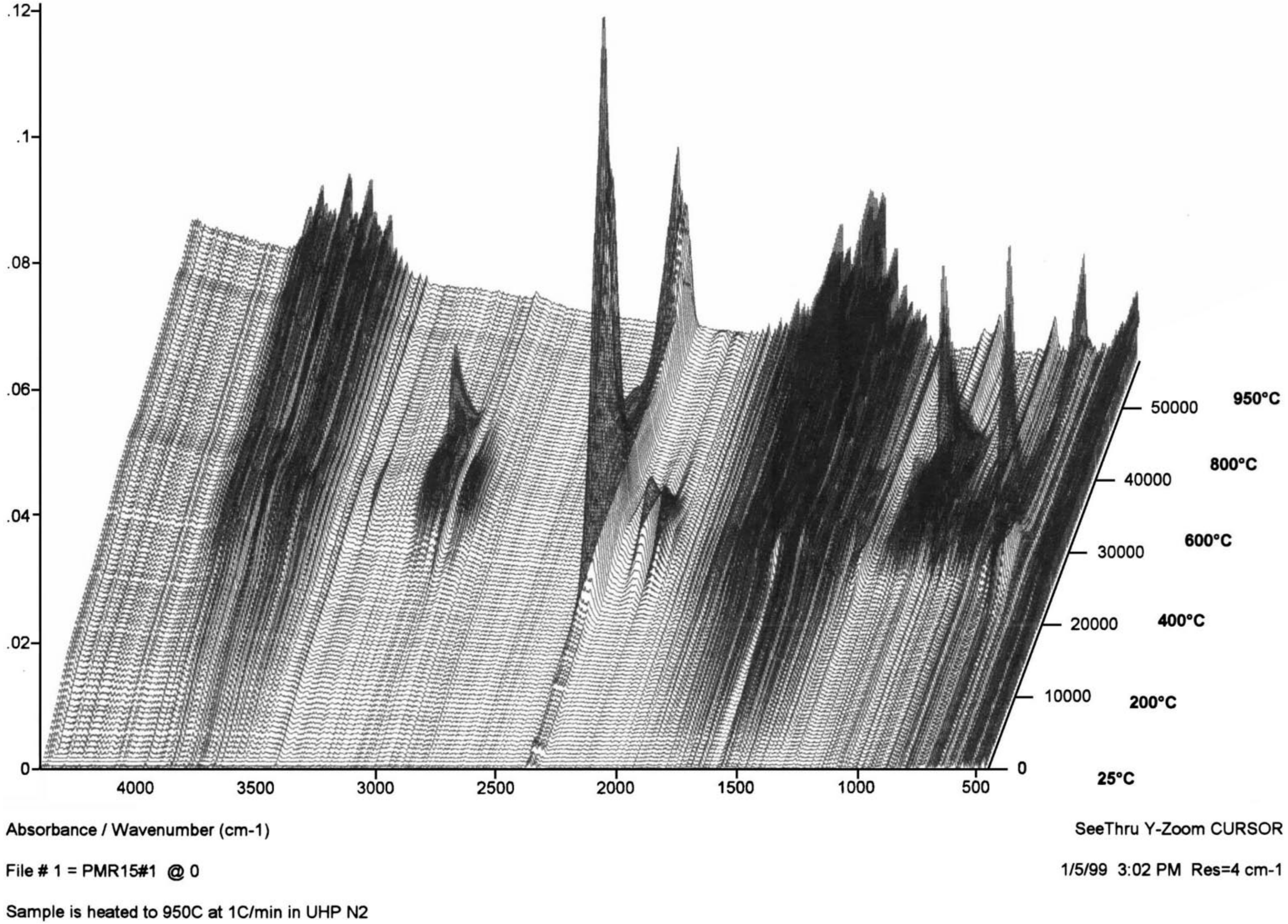


Fig. 7. 3D FTIR spectra of gases from the pyrolysis of PMR-15 at a heating rate of 1°C/min.

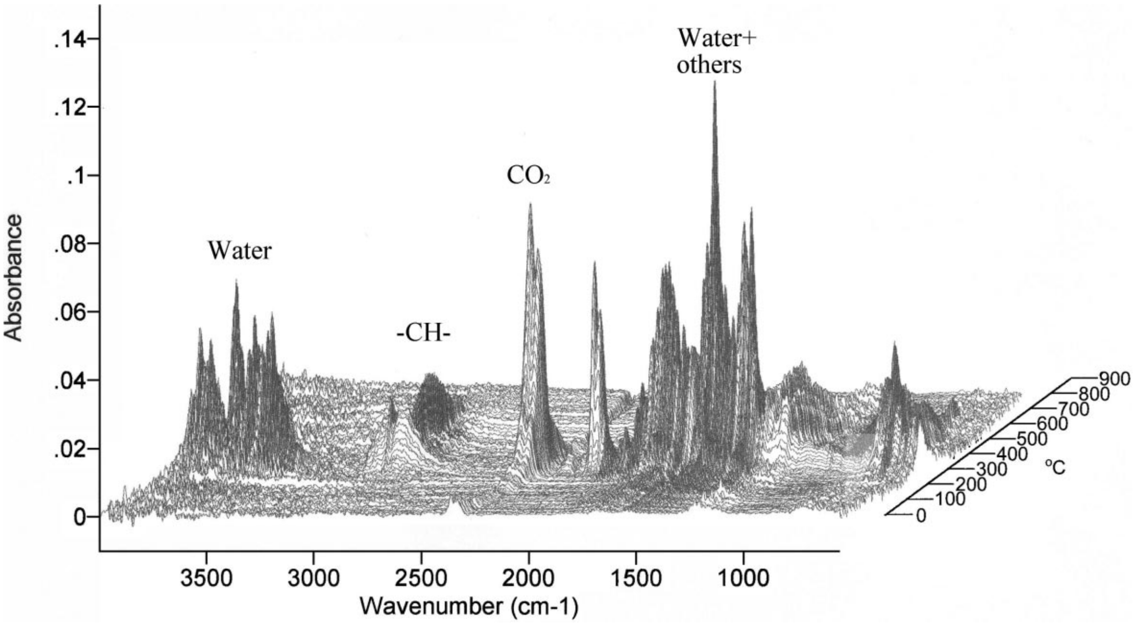


Fig. 8. 3D FTIR spectra of gases from the pyrolysis of DMBZ-15 neat resin.

reasonable explanation for the source of CO_2 is from the pyrolysis of hydrocarbon polymers which produced CO_2 and water. In fact, TGA–FTIR spectra of epoxy 8552 (Fig. 9) shows the evolution of CO_2, even though the epoxy contains no –COOH or imides. Therefore, it is very likely that CO_2 is a general degradation product of hydrocarbon pyrolysis and it is derived from the further oxidation of CO with free

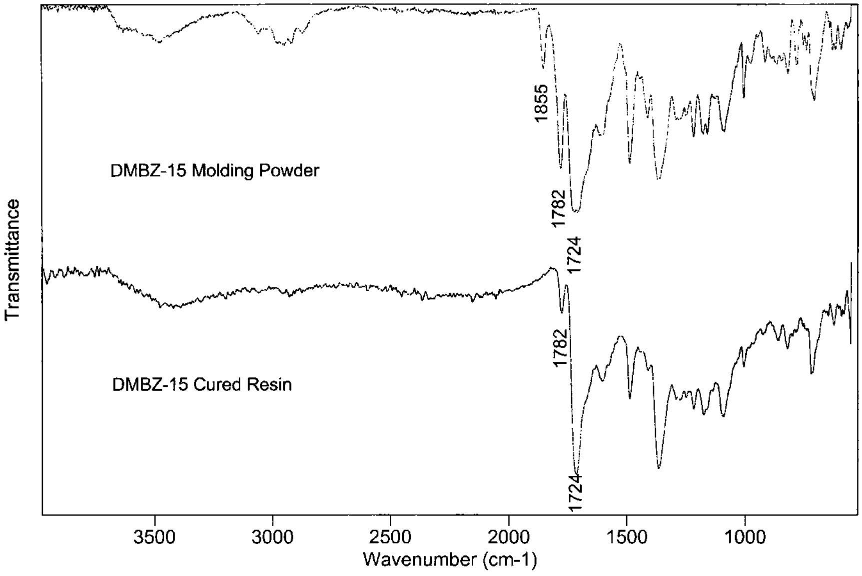


Fig. 9.

oxygen radicals, since the CO_2 background in FTIR under nitrogen was negligible. Although the intensity of CO_2 appears much stronger than that of CO in FTIR; in reality, there are substantial amount of CO evolution, since the extinction coefficient of CO_2 ($\varepsilon = 82\,\mathrm{l/mol\,cm}$) is 340-fold higher than that of CO ($\varepsilon = 0.24\,\mathrm{l/mol\,cm}$) [7]. Furthermore, TGA–MS could not identify any degradation product derived from the nadic endcap, although previous report indicated that cyclopentadiene was detected by pyrolysis GC–MS on PMR polyimides under various degree of cure [9]. However, additional aromatic fragments from polyimides need to be confirmed to clearly understand the degradation mechanism. Besides TGA experiment, isothermal aging on these PMR polyimides will be conducted to assess the long-term thermo-oxidative stability of these resins.

4. Conclusions

1. Pendant groups on the biphenyl rings creates steric hindrance which increases the rotational barrier for PMR polyimides based on substituted benzidines; thus resulting in higher T_g's.
2. Thermogravimetry shows that the thermal stability is in the order of PMR-15 > TMBZ-15 > DMBZ-15 > BFBZ-18. It is speculated that the more stable CF_3 substituent prevents the cleavage of C–F bond to form free radicals for further reactions which leads to more stabilized cured resins, as in the case of benzylic in PMR-15 and CH_3 groups in TMBZ and DMBZ, respectively.
3. The PMR-15 sample shows one step degradation behavior, but TMBZ-15, DMBZ-15, and BFBZ-18 samples illustrate more complex decomposition behaviors.
4. Carbon monoxide (CO) is the direct degradation products from imide rings and carbon dioxide (CO_2) is produced through the further combination of CO with oxygen radicals during pyrolysis of hydrocarbon polymers.

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