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Thermal properties of PETI-5/IM7

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Abstract

The assigned glass-transition temperature, and the mechanism for the thermal decomposition of PETI/IM7 were obtained using DSC, DMA and TGA/FTIR/MS techniques. The assigned glass-transition temperature was shifted to a much higher temperature after the sample was cured. TG/MS/FTIR results indicated that water and NMP were released from the fresh sample during the staging step. NMP and CO_2 were the major products released from the sample during the curing step. The possible three-step mechanism of decomposition, which was only based on the gas evolution, was proposed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: PETI-5; Cure; Glass-transition temperature (T_g); Mechanism; TG/MS/FTIR

1. Introduction

NASA is developing the high-speed civil transport (HSCT). The nose and leading-edge temperatures of high-speed airplane will range from 375 to 4000°F (464–455 K), with temperatures of 300–3500°F (422–455 K) elsewhere. Polyimides are attractive for high-speed airplane application as the material used for the surface area because of its excellent thermo-oxidative stability and mechanical properties. But they are known for their inferior processability as compared to epoxies and bismaleimides.

Phenylethynyl-terminated polyimides have been developed at the NASA Langley Research Center [1]. Unlike linear polyimides, PETI phenylethynyl-terminated-imide-oligomers can be thermally cured to form cross-linked molecular structures, typically increasing resistance to solvents, glass-transition temperatures, and moduli of elasticity. The advantage of phenylethynyl-terminated polyimides over ethynyl-terminated polyimides is the higher reaction temperature of the phenylethynyl group compared to the ethynyl group. This higher reaction temperature provides a larger temperature range to melt-process these polymers [2]. Hergenrother et al. [3] made PETI-1 derived from ODPA and 3,4′-ODA endcapped with 3-APEB, PETI-2 using PEPA as the endcapper, PETI-4 derived from BPDA and 85 mol% of 3,4′-ODA and 15 mol% of APB endcapped with 3-APEB, and PETI-5 with PEPA. After studying the molding process and T_g, they found PERI-5 displayed better retention of tensile strength and modulus.

Hergenrother [1] continued to study the composite properties of the PETI-5 mixed with IM7 fiber using *N*-methyl-2-pyrrolidone (NMP) as the solvent. NMP must be removed from the polymer. Processability of the IM7/LaRC PETI-5 was excellent as evidenced by a cure cycle study in which five different cure cycles

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representing various heating rates and hold temperatures produced good-quality laminates and excellent mechanical properties. Hou et al. [4] found that the crystal-melting temperature and heat of fusion increased with the increasing of annealing temperature. Meanwhile, the volatile content in the sample decreased. The rheological behavior, the volatile depletion rate and the thermally induced crystallization of PETI were used to develop fabrication condition for void-free composites. The optimum molding condition is to fabricate for 1 h at 371°C under 1.38 Mpa (200 psi). The use of the combined technique of TG-FTIR to obtain information on volatility during degradation was investigated in this work to develop an understanding of the chemical and physical phenomena that determine the processing requirements of PETI-5.

2. Experimental

In this experiment, two samples (one fresh and one cured) were analyzed and compared. It was found that the cured sample is harder than the fresh one.

2.1. Experimental procedure

2.1.1. Assignment of the glass-transition temperature

TA 2920 modulated differential scanning calorimetry (MDSC) was employed to assign the T_g for the PETI-5 fresh sample. The sample was cooled to −50°C, then heated to 100°C at the rate of 3°C/min. TA 2980 dynamic mechanical analyzer (DMA) with a single cantilever was employed to determine the T_g the for PETI-5 cured sample. The frequency was 1 Hz and the sample was heated

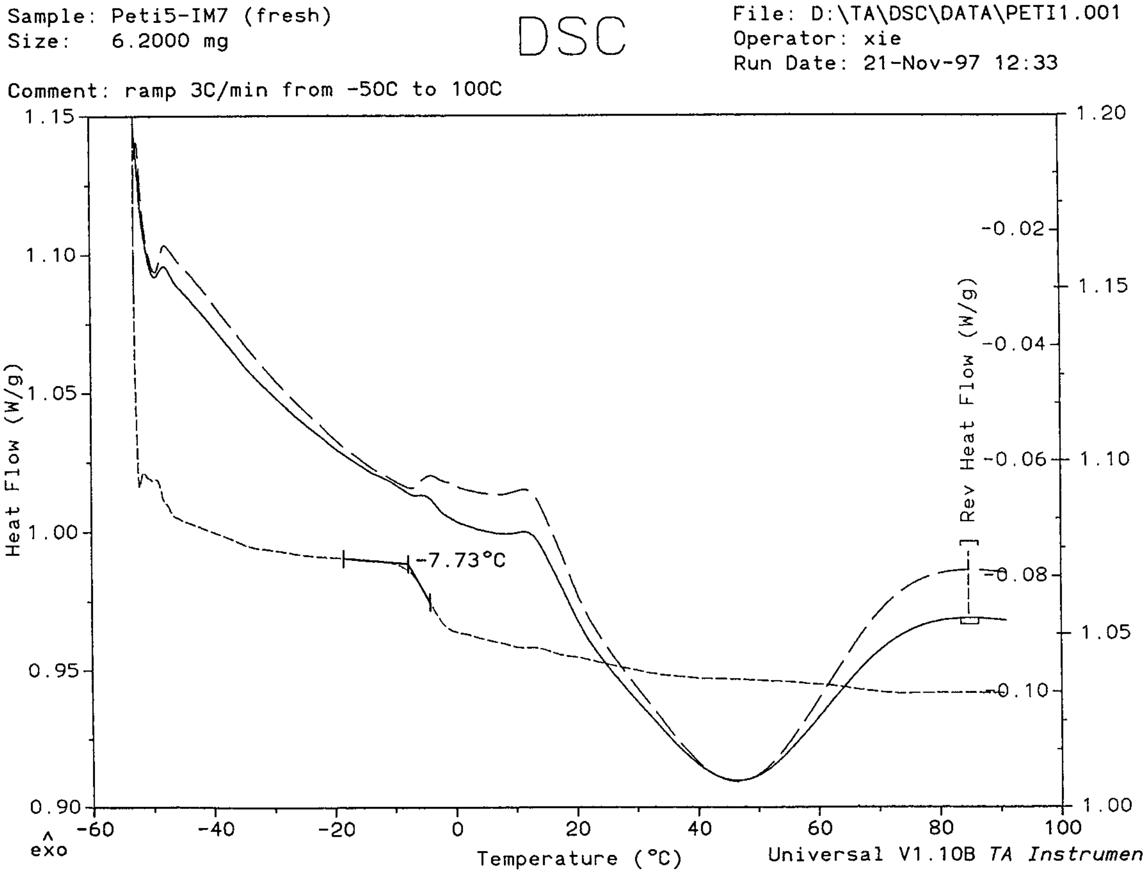

Fig. 1. The MDSC result for the PETI fresh sample.

from room temperature to 400°C at the rate of 5°C/min.

2.1.2. Determination of the decomposition kinetics parameters

A TA 2950 thermogravimetric analyzer (TGA) was used to determine the decomposition kinetics of the PETI-5 (cured) sample. The sample (about 50 mg) is heated to 900°C in UHP nitrogen at the flow rate of 50 ml/min. Four different heating rates (20, 10, 4, 2°C/min) were selected. The TA TGA kinetics analyzer software was used to analyze the result.

2.1.3. Studying the process of the staging and curing step, and the decomposition

The fresh sample was heated to 260°C at the rate of 1.55°C/min, held for 1 h at high vacuum (14.2 psi) (staging step), cooled and reheated to 371°C at the rate of 1.55°C/min; thereafter, the sample was held for 2 h in 100 psi (curing step) during the manufacture. The fresh sample was treated according to the same procedure in TG/MS and TG/FTIR, but only under ambient pressure, not under vacuum, in our laboratory. Then, the cured and fresh samples after being cured were heated to 900°C at the rate of 2°C/min in the TO/MS and TG/FTIR system to study the thermal-decomposition mechanism and the effect of vacuum on the curing process compared. All experiments, described above, were done in the UHP. The flow rate of nitrogen was 50 ml/min.

2.2. TG/MS and TG/FTIR techniques

The samples were analyzed on a TA2960 TGA/DTA (SDT) interfaced to a Fisons VG Thermolab mass spectrometer by means of a heated capillary transfer line. The capillary transfer line was heated to

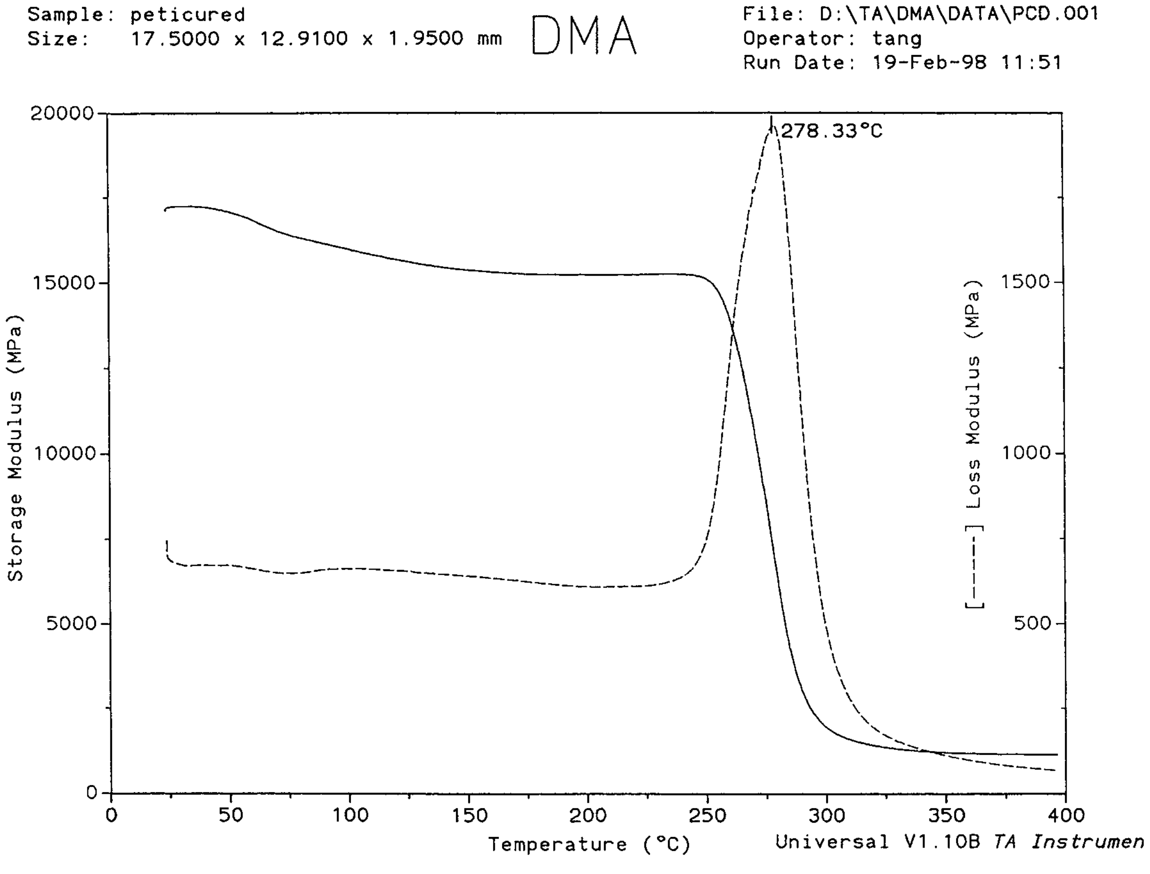

Fig. 2. The DMA result for the PETI cured sample.

220°C, and the inlet port on the mass spectrometer was heated to 150°C. The Fisons unit is based on quadrupole design with a mass range of 1–300 atomic mass units (amu). The sample gas from the interface was ionized at 70 eV. The system operates at a pressure of 1×10^{-6} torr. A NIST library database for MS analysis is equipped in this MS system.

The sample was analyzed on a DuPont 951 TGA interfaced to a Perkin–Elmer 1650 FTIR with a permanent silicon transfer line (length 1 in). The UHP N_2 flow carries the decomposition products from TGA through a 70-ml sample cell with KBr crystal windows. The cell is placed in the IR scanning path for detection of the decomposition products and was kept at 150°C by wrapping it with a heating tape to prevent possible condensation. The other transfer line was kept at around 200°C. The IR detection ranges between 450 and 4500 cm^{-1}.

3. Results and discussion

3.1. Assigning the glass-transition temperature

Fig. 1 showed the MDSC result for fresh sample. The long-dash line represents the total heat flow. The solid line represents the nonreversible heat flow. It describes the thermal history. The short-dash line represents reversible heat flow. The extrapolated onset point method was used on this curve to determine the T_g for the fresh sample. The glass-transition temperature of the fresh sample is −7.7°C. From the DMA result (Fig. 2), we used the maximum peak temperature on the loss modulus curve to determine the glass-transition temperature. The glass-transition temperature for the PETI-5 cured sample is 278.3°C (DSC result also supports this value). As we know, T_g is the temperature at which large segments of the chain start

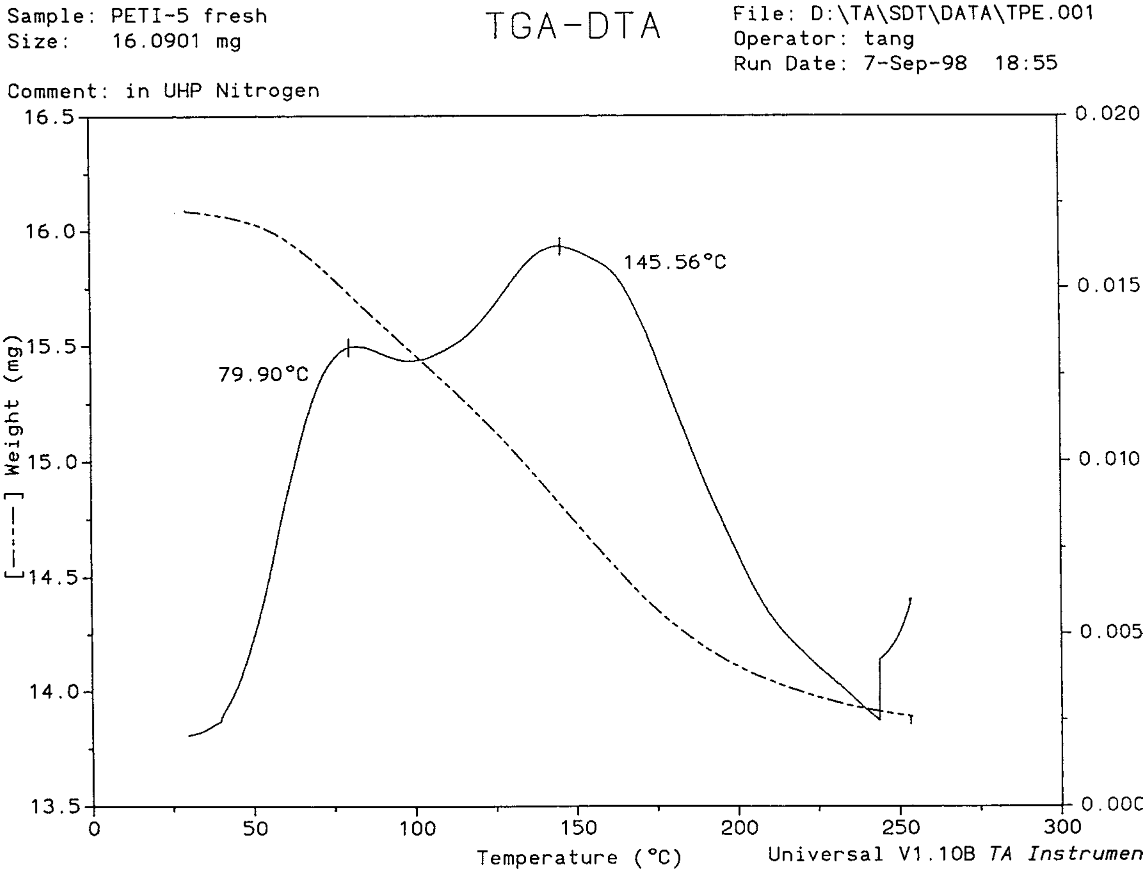

Fig. 3. The TGA result for the staging step of the fresh sample.

moving and the molecular mass of side chain is critical to the T_g. After being cured, the PETI-5 sample was cross-linked to a high degree. Its molecular mass of side chain was increased. Most of water and NMP were removed from the polymer, which becomes harder and more stable. The polymer chains were hard to move because they were cross-linked and entangled with each other. These results indicated that staging and curing steps improve the T_g for PETI-5 and make this polymer more suitable for airplane applications.

3.2. Studying the mechanism of staging and curing, and the decomposition step

In the TGA (Fig. 3), there are two peaks in the DTG curve of staging step for fresh sample (at 79.90 and 145.56°C). From the TG/MS result (Fig. 4), the water curve (m/e=18) has two peaks at the same position. And ions for which m/e is 99, 98 and 71 have one peak at about 145°C. The first peak may be due to the loss of water absorbed and the second one is due to the loss of the water and NMP, which combined with PETI-5 by hydrogen bonding or was encapsulated by the long chain. For the curing step, only one peak, at 292°C, was observed in the DTG curve. From the TG/MS/FTIR result, we know this is due to the loss of residual NMP and CO_2. During the curing step, the side groups (C=O) reacted with each other and released CO_2. The PETI-5 molecule was cross-linked. The possible process of curing, based only on gas evolution, is shown in the Fig. 5.

Fig. 6 indicates the systematic shift in the rate maxima to lower temperatures with decreasing heating rates. The heating rate has a moderate effect on the variation of weight loss. Three DTG peaks were

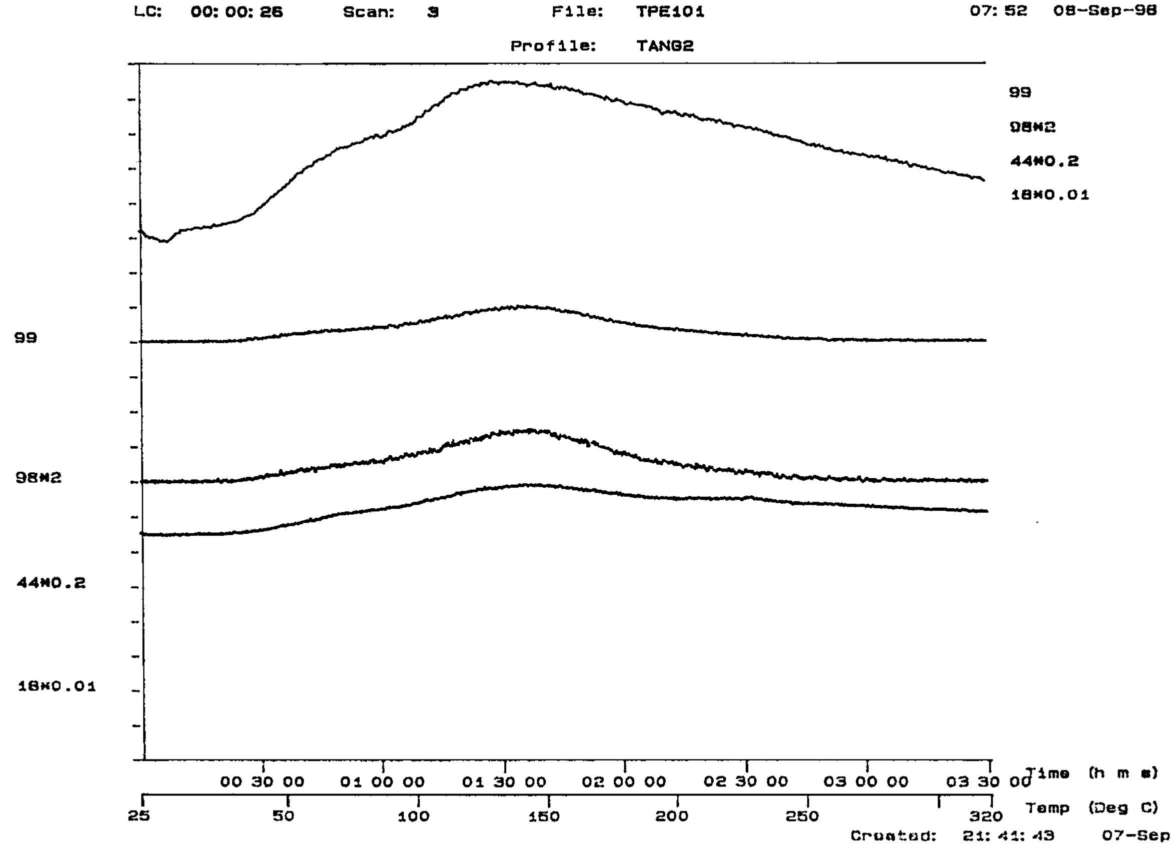

Fig. 4. The TG/MS result for the staging step of the fresh sample.

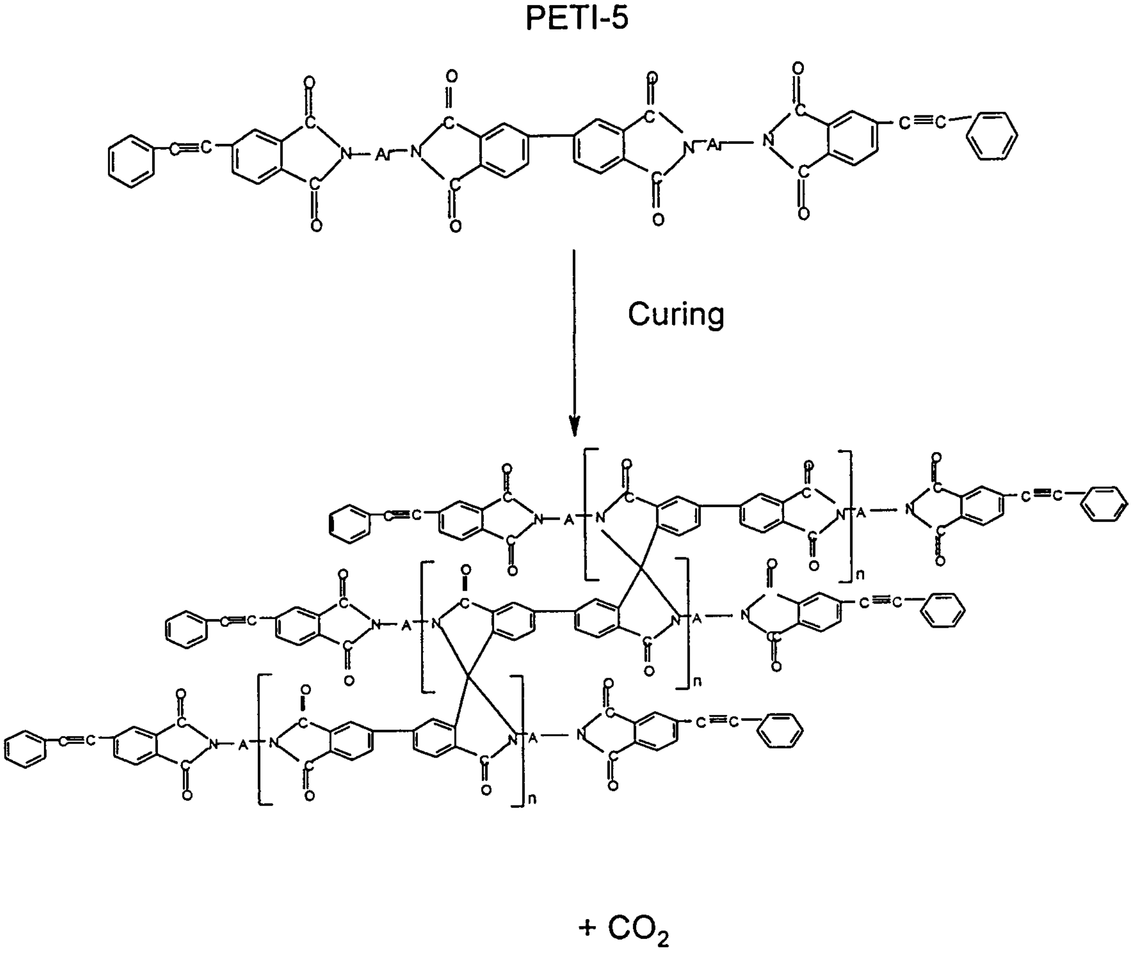

Fig. 5. The possible mechanism for the curing process.

identified. Table 1 shows the kinetic parameters at different conversion levels. After studying these and TG/MS/FTIR results (Figs. 7 and 8), the kinetics of decomposition for PETI-5 cured sample can be divided into three different stages. The activation energy and the logarithm of the pre-exponential factors at conversions of 1 and 2% are very similar. During this step, the residue of H_2O and NMP was

Table 1
Kinetics parameters at different conversion levels

Conversion (%)	Activation energy (kJ/mol)	Log (pre-exponential factor) (1/min)	60 min Half-life temperature (°C)
1.0	49.19	3.304	217.1
2.0	47.86	2.488	291.8
5.0	159.9	9.355	466.3
10.0	259.5	15.49	504.7
15.0	247.4	14.63	506.8

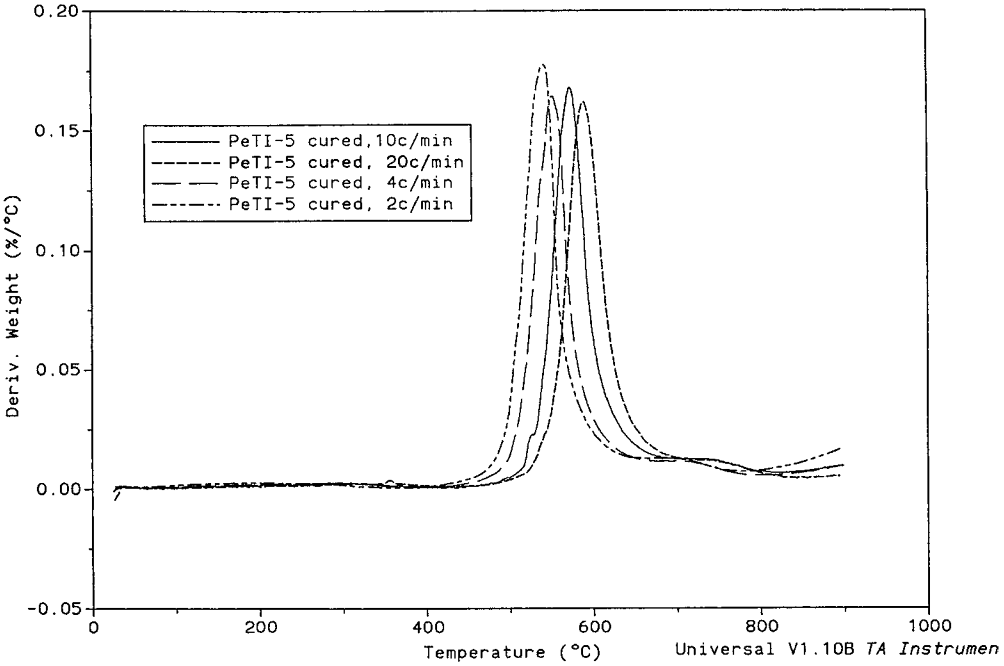

Fig. 6. The DTG curves for the decomposition step of the cured sample at four different heating rates.

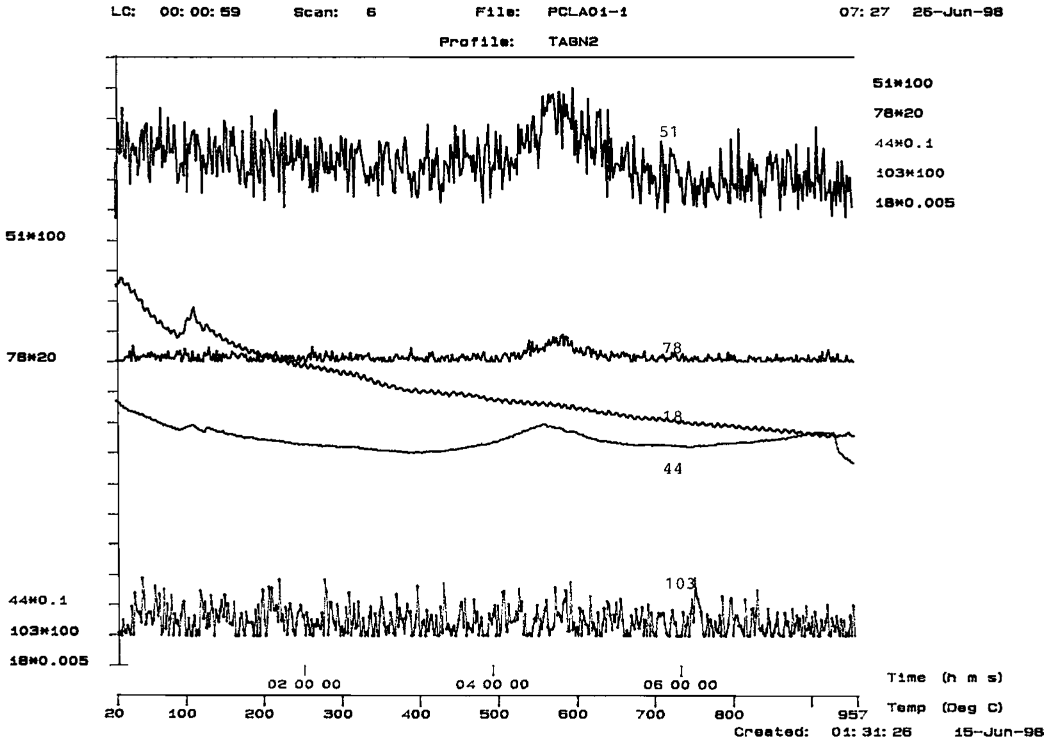

Fig. 7. The TG/MS result for the decomposition step of the cured sample.

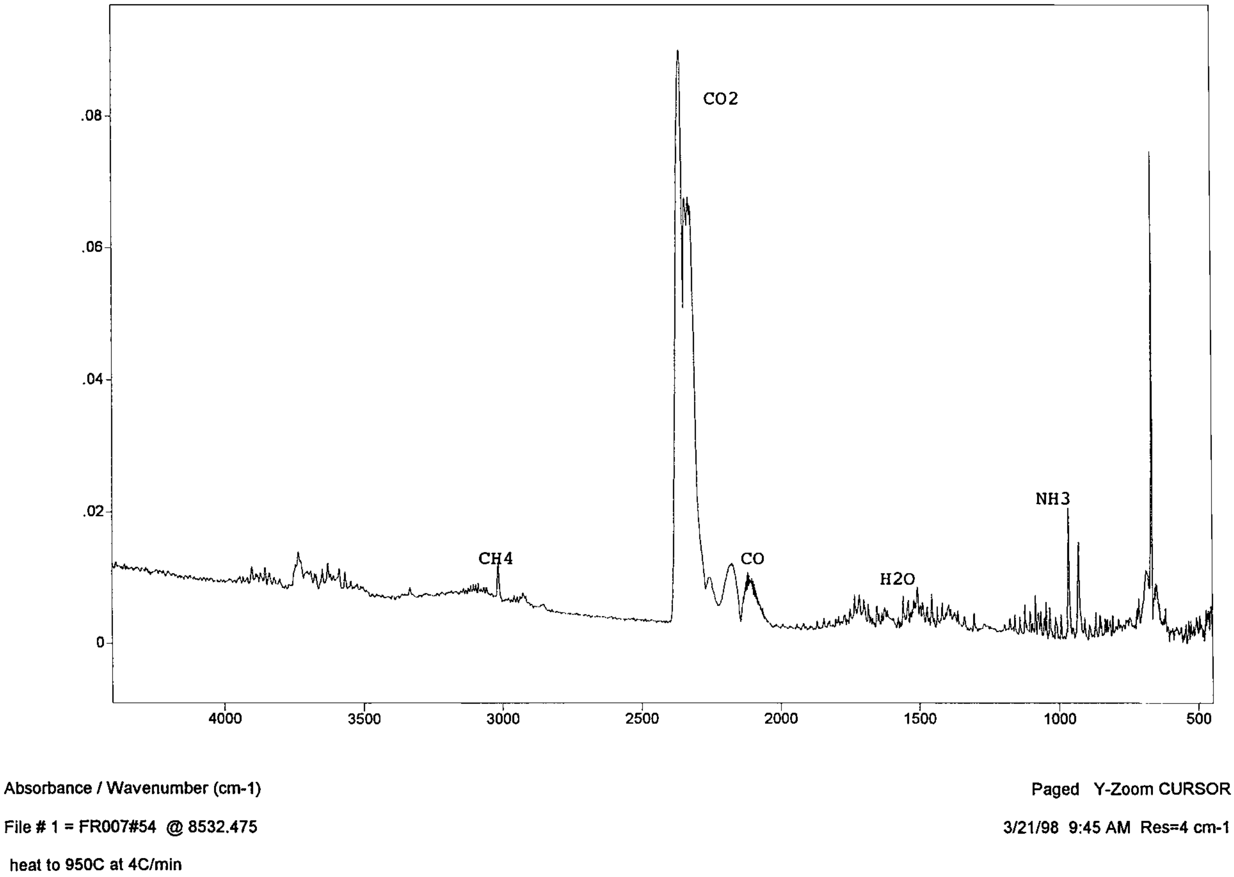

Fig. 8. The TG/FTIR result for the decomposition step of the cured sample.

released. The end groups and side groups were separated from the main chain at first. This explains why the first peak for ions 91 and the peak for ion 44 occurred before the other peaks. At the same time, the long chains were separated into the shorter chains.

In the second step, the chains of intermediate lengths were decomposed into small molecules by the heat. Most of the weight loss occurred during this period. From the TG/FTIR result, we can identify CH_4, water, CO, CO_2 and NH_3 (Fig. 8). The third step may be attributed to a continuous degradation of the chain. In this step, the chain is decomposed into much shorter chains and only a little of volatile materials is released. The possible mechanism is shown in Fig. 9.

Fig. 10 shows the TGA result for decomposition of the fresh sample (after curing). The peak in DTG curve is at 570°C. It is similar to the result for cured sample. But, the TG/MS result (Fig. 11) indicates that ions 91 and 103 cannot be identified. All other ions are the same. This indicated that the fresh sample, after staging and curing without vacuum, can have thermal stability similar to the cured sample, but the degree of curing for the fresh sample is lower than that for the cured sample. Vacuum is helpful during the curing process.

4. Conclusions

From the results of the study reported in this paper, the following observations can be made:

- The glass-transition temperature for the cured sample is much higher than that for the fresh sample.

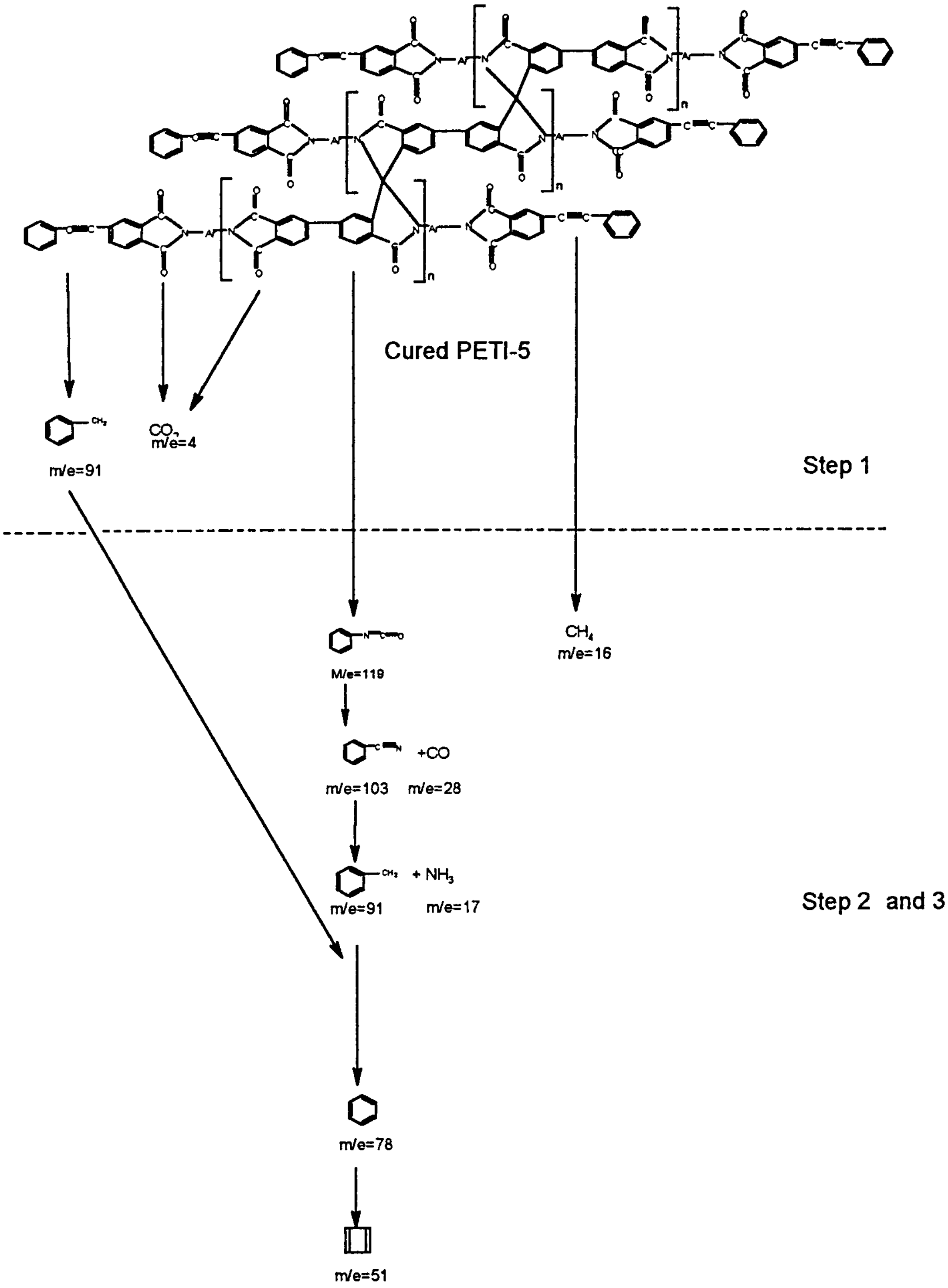

Fig. 9. The possible mechanism for decomposition.

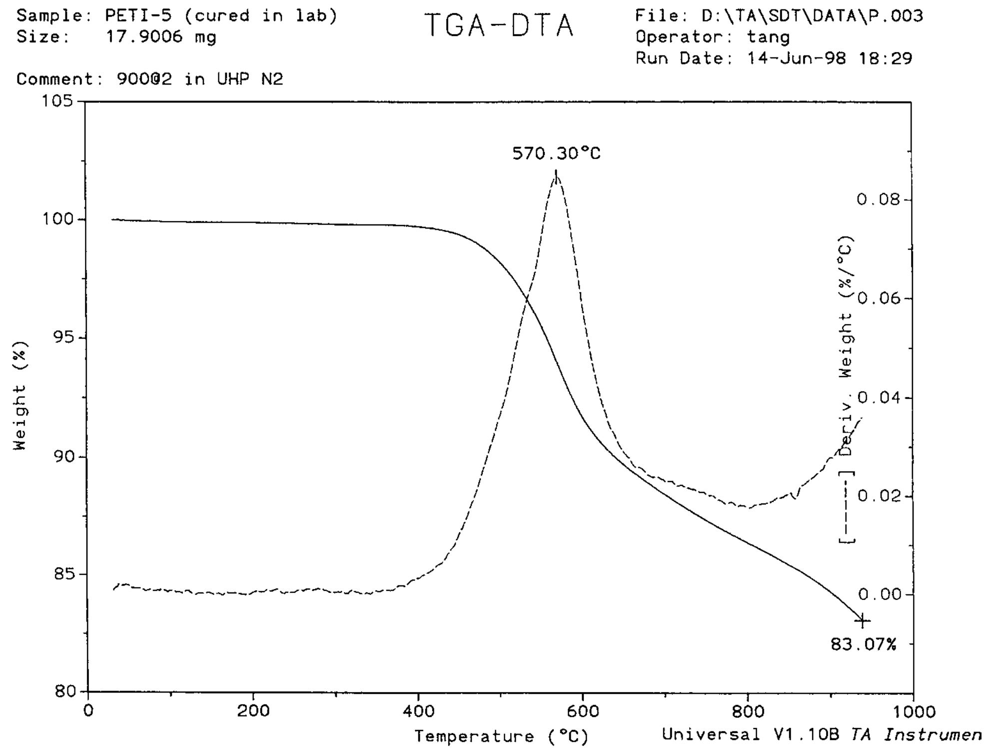

Fig. 10. The TGA result for the decomposition step of the fresh sample after being cured at the heating rate of 2°C/min.

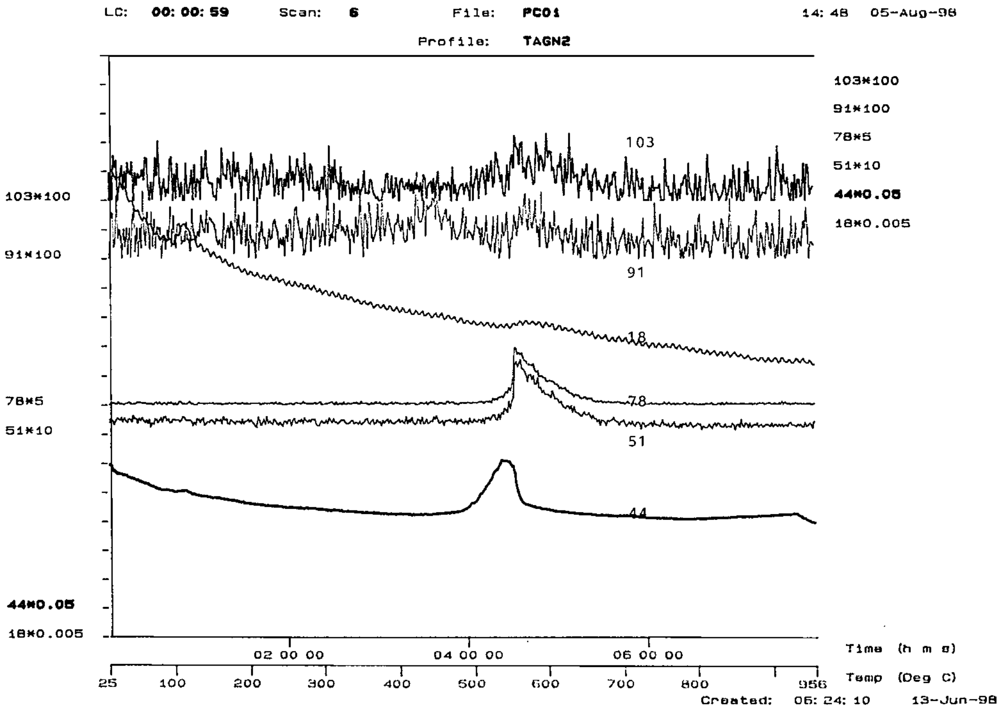

Fig. 11. The TG/MS result for the decomposition step of the fresh sample after being cured.

- A three-step mechanism for decomposition of cured sample is proposed and the kinetics parameters calculated.
- The TG/MS/FTIR results indicates that water and NMP are released during the staging step, NMP and CO_2 are released from the sample during the curing step.
- Vacuum is helpful to the degree of curing.

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