LONG-TERM THERMAL STABILITY OF POLYIMIDE RESIN TRIA-X AND CARBO FIBER /TRIA-X COMPOSITE MATERIAL

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Keywords: Aromatic polyimide, Polymer matrix composite, Long-term thermal stability, Oxidation.

Abstract

Long-term thermal stability of polyimide resin “TriA-X” and carbon fiber reinforced TriA-X was evaluated. The neat TriA-X resin was exposed at 180 °C, 240 °C, and 270°C for 3000 h in air and at 270°C under reduced-pressure environment. The composite material was exposed at 240 °C and 270 °C for 3000 h in air. The neat resin showed excellent thermal stability at 180°C for 3000h. Although the weight loss and shrinkage of the resin at 270°C was significant because of oxidation, the composite material maintained the compression strength after the aging at 270 °C for 2000h. The degradation of TriA-X resin in air was mainly dominated by the oxidation of 4-phenylethynylphtnalic anhydride moiety which was the end group of TriA-X.

1. Introduction

Aromatic polyimide resins have excellent potential for matrix of composite materials applied in high temperature aplications. NASA Langley Reserch Center had developed PMR-15 [1-4] showing a high glass transition temperature of 340 °C. However, it is brittle and shows low oxidation resistance. Although another developed polyimide resin PETI-5 has high fracture toughness, the glass transition temperature is 80 °C lower than that of PMR-15 [5-8].

In order to combine high glass transition temperature, good mechanical properties, and formability to polymer matrix composite, Yokota et al. developed an amorphous, asymmetric, and addition-type imide oligomer “Triple-A” [9, 10]. The chemical structure of Triple-A polyimide had been revised and improved several times. The most advanced polyimide of Triple-A series, “TriA-X”, shows the world highest properties [11, 12]. The imide oligomer of TriA-X is derived from four monomers; pyromellitic dianhydride (PMDA), 2-phenyl-4, 4’-diaminodiphenyl ether (p-ODA), 9,9-bis (4-aminophenyl) fluorene (BAFL), and 4-phenylethynylphthalic anhydride (PEPA). Figure 1 shows the chemical structure of TriA-X imide oligomer. This imide oligomer shows low melt viscosity because of asymmetric structure ($|\eta^*|_{min}$=154 Pa・s). Furthermore, the cured resin has high glass transition temperature (T_g=370 °C) and excellent failure strain (>11%). The developed carbon fiber/TriA-X composite materials exhibits excellent mechanical properties at temperatures higher than 200 °C.

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When the high temperature polymer matrix composite is applied for aerospace applications, such as a commercial aircraft engine and a leading edge of supersonic aircraft, knowledge of long-term thermal stability is an essential information to predict its lifetime and durability. In this study, the neat TriA-X resin was exposed at 180, 240, and 270°C for 3000 h in air so as to understand the potential of TriA-X for long-term thermal stability and the degradation process in air. Furthermore, the stability of carbon fiber/TriA-X composite material was evaluated by a non-hole compression test after aging at 240 °C and 270 °C for 2100 h in air.

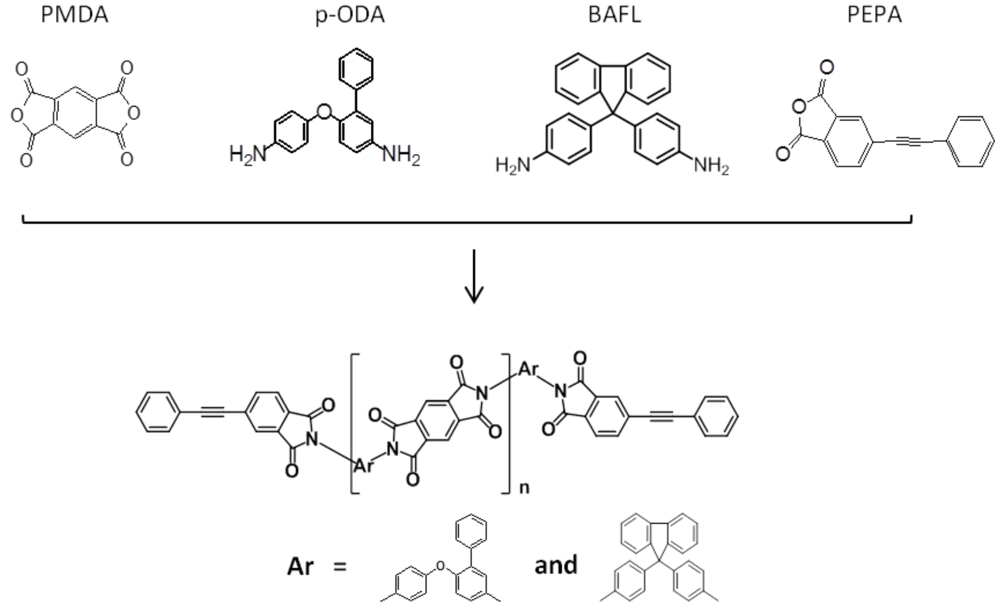

Figure 1. Chemical structure of the PMDA/p-ODA;BAFL/PEPA (TriA-X) imide oligomer

2. Experiments

2.1. Processing of the neat resin film

Three types of resin were prepeared for the isothermal aging test. Table 1 shows the molecular composition of these resins. TriA-X (B10) imide oligomer was prepeared by reacting two diamine monomers, p-ODA and BAFL, with one acid anhydride monomer: PMDA, and finally endcapping with PEPA. The molecular backbone of TriA-X, which was PMDA/p-ODA, was prepared so as to determine affects of the end group for the thermal stability. The imide oligomer was cured as a film (100mm × 100mm × 60~100μm) by using a hot press at 370°C for 1 hour under 1.4MPa. Furthermore, different TriA-X oligomers without BAFL (TriA-X (B0), n =1, 4, 7) in the degree of polymerization (*n*) were prepeared to evaluate effects of *n* for thermal stability. The forming of TriA-X (B0) film was more easily than that of TriA-X (B10) when *n* was high. This was the reason why the TriA-X (B0) was applied for the evaluation.

Table 1 Resin films for aging tests

Specimen Type	Degree of polymerization: *n*	Ratio of each monomer			
		p-ODA	BAFL	PMDA	PEPA
TriA-X(B10)	4	4.5	0.5	4.0	2.0
PMDA/p-ODA	---	5.0	0	5.0	0
TriA-X(B0)	1	2.0	0	1.0	2.0
	4	5.0	0	4.0	2.0
	7	8.0	0	7.0	2.0

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2.2. Fabricating of composite material

PAN-based carbon fiber (MR50R, Mitsubishi rayon co., Ltd.) was used as the reinforcement of composite. The fiber was immersed into the TriA-X(B10) imide oligomer by a prepreg coater. The prepregs then were stacked on a tool by hand lay-up. The stacking sequence was [90/0]4s. In this study, vacume hot pressureing (v-HP) molding was applied to fabricate the laminate plate. In v-HP molding, the prepreg was dired at 260 °C for 2 h, and cured at 370°C under 1.4MPa for 1 hour.

2.3. Long-term thermal aging tests

The formed resin films were exposed at 180°C, 240°C, and 270°C for 3000 h in air using a thermostatic chamber (PHH-201M, ESPEC corp.), and at 270 °C for 3000 h under reduced-pressure enviroment using a vacuum furnace (DQ-30SA, SATO VAC INC.). The pressure in the vacuum furnace was less than 1.0 Pa. The film was cut to 50 mm × 100 mm × 60~100 μm as an exposed specimen. The weight loss and shrinkage during aging were measured. Their intial values were determined by the film dried at 60°C for more than 4 h under a reduced-pressure.

In the case of composite materials, the laminate was cut to 15 mm × 82 mm × 2.5 mm (w × l × t). Cut specimens were exposed at 240 °C and 270 °C in air using PHH-201M for 2100 h. According to the literature [13], it took 120 h at 120 °C to dry a polyimide composite. In this study, the weight exposed for 100 h at respective aging temperature was set as the initial value.

2.4. Evaluation of mechanical properties of exposed composites

T_g of the composite was measured by a dynamic mechanical analyzer (DMA: Q-800, TA Instruments). In this measurement, the single cantilever beam test mode was applied. The specimen size was 10 mm × 40 mm × 2.2 mm (w × l × t). The tests was run from 30 °C to 450 °C at 4.0 °C/min with a cycling rate of 1 Hz and strain of 0.1 %.

Non-hole compressive (NHC) strengths and elastic modulus were measured on the composite materials exposed for 1100 h, 2100 h, and 3100 h. In this measurement, NAL-Ⅱ method [14] was applied. Figure 2 shows the jig used in NAL-Ⅱ method. Lower and upper grips are fixed to a specimen (15mm × 82mm × 2.5mm) using four screw bolts. Compressive load is applied to a speceimen through the grips. Gauge length is 10 mm, therefore strain gauges can be used to measure simultaneously.

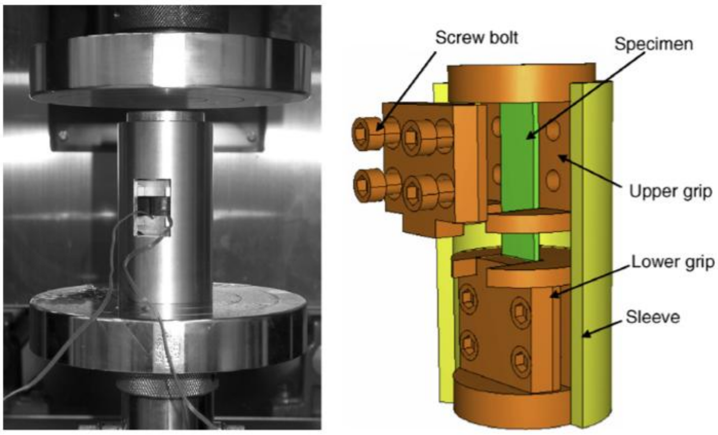

Figure 2 The jig used in NAL-Ⅱ method [10, 14].

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3. Reusult and discussion

3.1. TriA-X resin film

Figure 3 shows the weight loss of films as a function of the aging time. Furthermore, the shrinkage of the films were shown in Fig 4. As shown in Fig 3, the weight loss of TriA-X (B10) at 180°C was less than 0.5 %. The weight loss was significant with increase in temperature, which were 2.0 % at 240 °C and 8.9 % at 270 °C. This tendency agreed with the shrinkage as shown in Fig 4.

As shown in fig 3, the weight loss of TriA-X (B10) under reduced-pressure environment were negligible small compared with that in air. Furthermore, PMDA/p-ODA did not show apparent weight loss at 270 °C in air. These results indicated that the main reason of degradation of TriA-X(B10) was the oxidation on PEPA moiety which was the end group of TriA-X. Based on these results, the weight loss of TriA-X(B0) were compared on different degree of polymerization (*n*) as shown in Fig 5. As shown in Fig 5, the weight loss was small with increase in *n*. Since the molecular weight of the backbone (PMDA, p-ODA) becomes higher with increase in *n*, the concentration of PEPA moiety is relatively low when the *n* is high. Therefore, the result shown in Fig. 5 ensured that the oxidation of PEPA moiety was the main reason for the degradation of TriA-X.

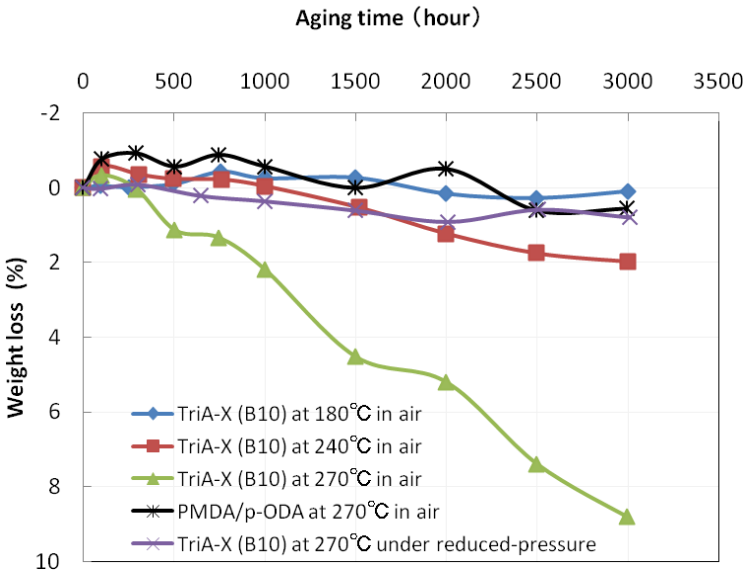

Figure 3 Weight loss of TriA-X (B10) and PMDA/p-ODA films exposed at 180°C , 240 °C, and 270 °C in air as a function of aging time.

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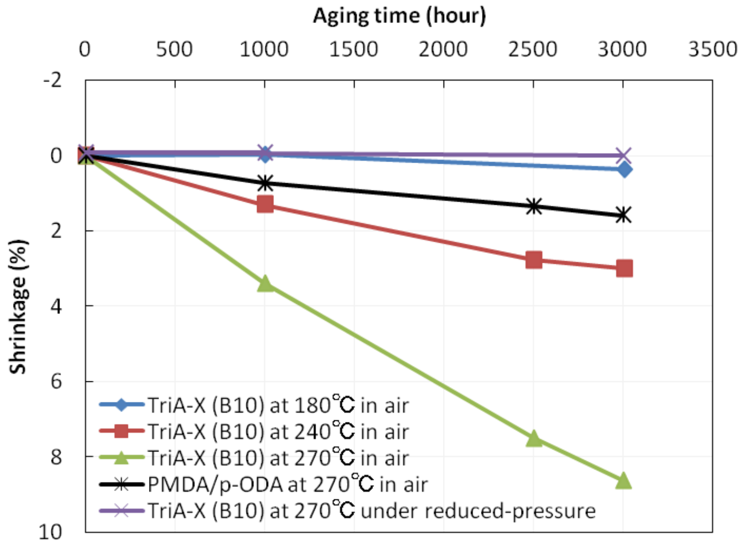

Figure 4 Shrinkage of surface area of TriA-X (B10) and PMDA/p-ODA films exposed at 180°C , 240 °C, and 270 °C in air as a function of aging time.

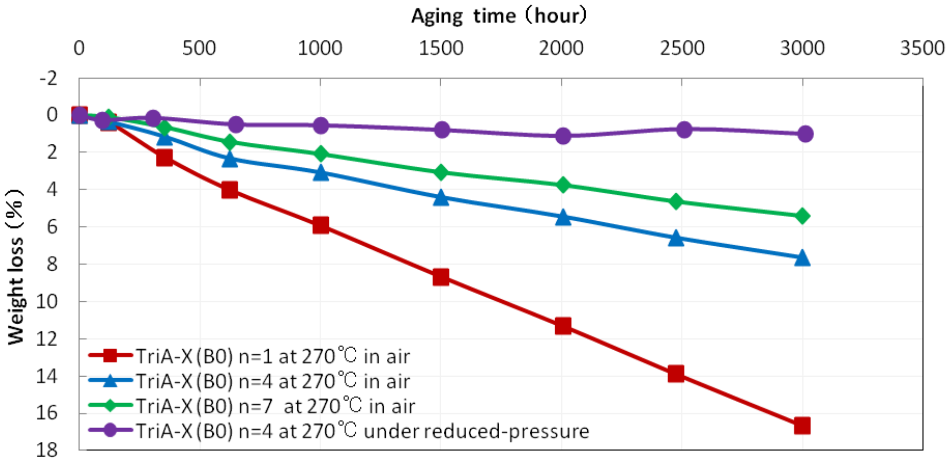

Figure 5 Weight loss of different TriA-X(B0) in the dgree of polymerizations (*n*).

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3.2. MR50R/TriA-X

Figure 6 presents the a DMA trace of the MR50R/TriA-X(B10) composite. The storage modulus (*E'*), loss modulus (*E''*), and *tan δ* are ploted as a function of temperature. The glass transition temperatue (T_g) was determined from *E'* by setting up tangents to the linear portion of the curve before and after the modulus drop off. As a result, the T_g of the MR50R/TriA-X(B10) was 374°C that was close to that of the TriA-X (B10). This result implied that the matrix was totally cured.

Figure 7 shows the weight loss of the MR50R/TriA-X (B10) composite at 240 °C and 270 °C in air. Furthermore, Fig 8 and 9 presents the NHC strength and elastic modulus of the composite after aging at 240 °C and 270 °C. Although the weight of composite tended to decrease at 240 °C and 270 °C in air as well as the film, the compressive strength and elastic modulus were maintained at least for 2100 h at 270 °C in air. In general, the oxidation reaction of a composite material progresses from the surface. In this study, the surface of specimen was 90° ply which rarely beared the longtitudinally compression stress. Therefore, the reason why the compressive properties were maintained for 2100 h at 270 °C might be that the degradation of composite progressed only at the surface ply.

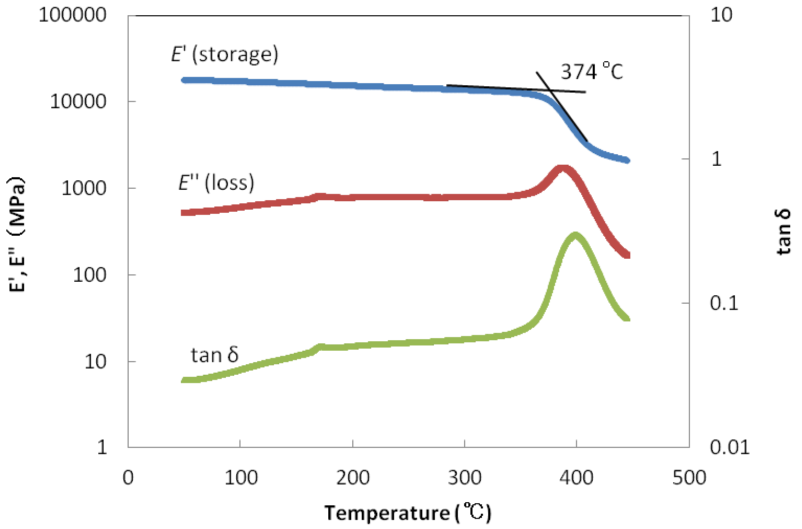

Figure 6 Dynamic mechanical snalysis (DMA) traces of a MR50R/TriA-X (B10) composite.

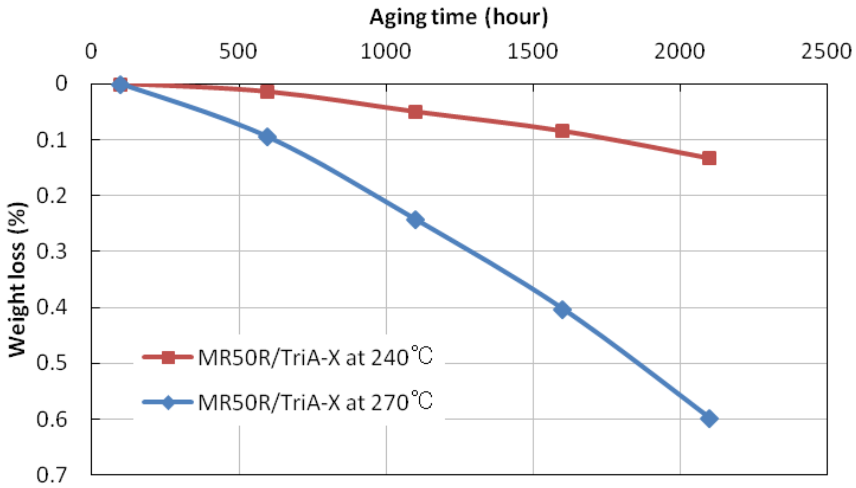

Figure 7 Weight loss of MR50R/TriA-X (B10) on aging tests at 240 °C and 270 °C in air.

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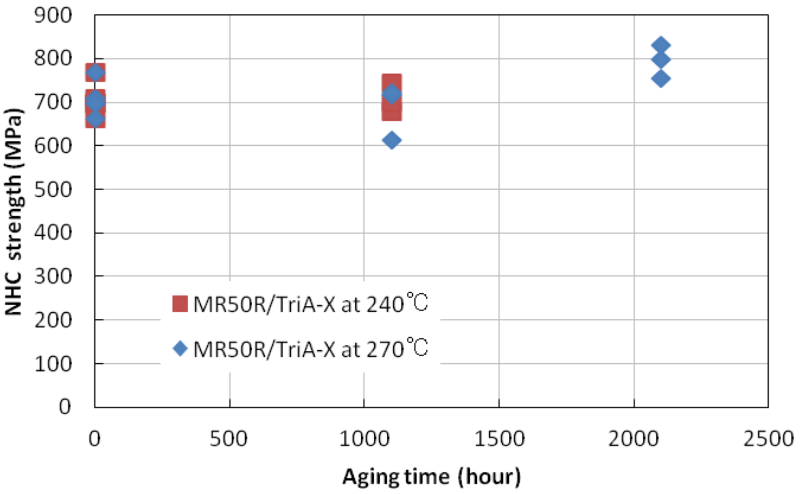

Figure 8 NHC strength of MR50R/TriA-X (B10) after aging tests at 240 °C and 270 °C in air.

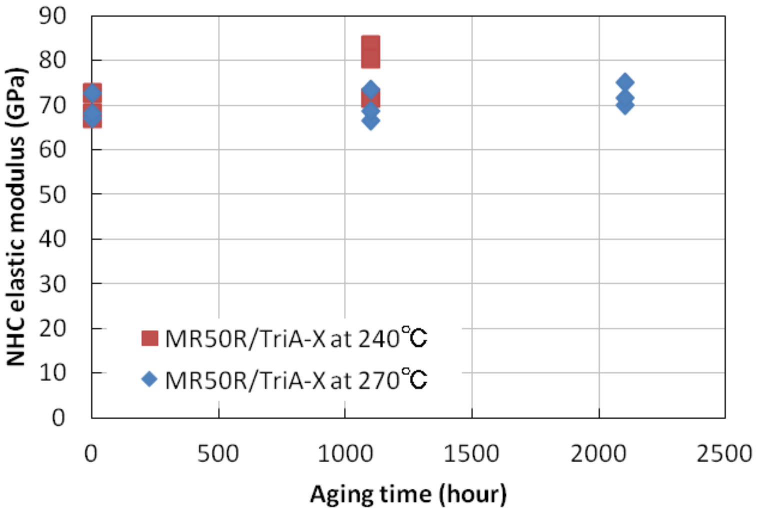

Figure 9 NHC elastic modulus of MR50R/TriA-X (B10) after aging tests at 240 °C and 270 °C in air.

4. Conclusions

This study evaluated the long-term thermal stability of a polyimide resin “TriA-X” at 180 °C, 240 °C and 270 °C. Furthermore, the thermal stability of carbon fiber/TriA-X composite material was evaluated by the non-hole conmpression test after aging at 240 °C and 270 °C. The TriA-X resin indicated high thermal stability at least for 3000h at 180 °C. The weight loss and shrinkage of TriA-X became significant at 270 °C. This degradation was mainly caused by the oxidation of the end group of TriA-X, which was 4-phenylethynylphtnalic anhydride moiety. Although the weight of composite decreased by the oxidation at 240 °C and 270 °C, the compression strength was maintained at 270 °C at least for 2100 h.

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