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Cite this article as:

Liu Yi, Xu Xiao-Zhou, Mo Song, Lan Bang-Wei, Zhu Cai-Zhen, Li Cui-Hua, Xu Jian, Fan Lin. Long-term Thermo-oxidative Degradation Modeling of a Carbon Fiber Reinforced Polyimide Composite: Multistep Degradation Behaviors and Kinetics[J]. *Chinese J. Polym. Sci.*, 2020, 38(11): 1202-1213. doi: 10.1007/s10118-020-2425-7

View online: <https://doi.org/10.1007/s10118-020-2425-7>

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Long-term Thermo-oxidative Degradation Modeling of a Carbon Fiber Reinforced Polyimide Composite: Multistep Degradation Behaviors and Kinetics

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Abstract This study aims to disclose the thermo-oxidative degradation behaviors and kinetics of a carbon fiber reinforced polyimide (CFRPI) composite for modeling of the long-term degradation process. The degradation behaviors were revealed through off-gas products analysis, and the overall kinetic interpretation was achieved from study of the mass-loss curves recorded under dynamic conditions. It was found that thermo-oxidative degradation of the CFRPI composite was a multistep process, which included four main reaction steps. Since most kinetic analysis methods were derived from simple reactions described by a single kinetic triplet, they cannot be applied reliably to such a process. Therefore, we firstly separated the four overlapped reaction steps by peak fitting of derivative thermogravimetric curves using Fraser-Suzuki equation considering the asymmetrical nature of kinetic curves, and subsequently analyzed each individual reaction employing Friedman method and experimental master-plots method. Four sets of kinetic triplets were determined to characterize the entire degradation process. The validity of four corresponding kinetic triplets was confirmed by perfect simulation of mass-loss curves recorded at both dynamic conditions used in kinetic analysis and entirely different isothermal conditions. Finally, modeling of long-term aging at 400 °C of the CFRPI composite was successfully achieved based on these kinetic triplets. The predicted mass loss and flexural property correlated well with experimental results. This study can serve as a basis for rapid evaluation of the long-term durability of the CFRPI composite in various application environments.

Keywords Polyimide composite; Thermo-oxidative degradation; Multistep process; Kinetics; Long-term aging modeling

Citation: Liu, Y.; Xu, X. Z.; Mo, S.; Lan, B. W.; Zhu, C. Z.; Li, C. H.; Xu, J.; Fan, L. Long-term thermo-oxidative degradation modeling of a carbon fiber reinforced polyimide composite: multistep degradation behaviors and kinetics. *Chinese J. Polym. Sci.* 2020, 38, 1202–1213.

INTRODUCTION

Polyimides with rare combination of excellent thermal stability in various environments, unique dielectric properties, high mechanical properties, and high solvent and radiation resistance unparalleled by most other kinds of polymers are widely used as matrix resins in fiber reinforced composites in aerospace industry.^[1–3] Especially, the carbon fiber reinforced polyimide (CFRPI) composites have been evaluated as structural and sub-structural materials in aircraft systems, *e.g.* engines, airframe, and wings.^[4] In such applications, the long-term durability of aerospace composite materials under service environments is the primary concern.^[5] The performance of composite materials would be compromised when they are exposed to high temperature and oxidation environment over a long period of time, which may possibly result in the failure of aircraft systems.^[6] Consequently, how CFRPI composites behave during their service life must be better understood when

considering CFRPI composites as a reliable material for aerospace application.

Many researchers studied the thermo-oxidative degradation of CFRPI composites isothermally below the glass transition temperature and tried to model mass changes and/or mechanical properties deterioration as a function of degradation time. Schoeppner *et al.* studied the thermo-oxidative behavior of the unidirectional G30-500/PMR-15 composite with different geometries during isothermal aging at 288 °C.^[7] It was found that the mass loss rates were dependent on the specimen geometry, implying the anisotropic nature of the degradation behavior. Empirical models based on weight loss surface fluxes, *i.e.* weight loss per unit surface area per unit of time, were successfully developed to predict the mass loss during long-term thermo-oxidative degradation.^[8] Many studies demonstrated that the thermo-oxidative degradation of CFRPI composites in isothermal aging conditions was a diffusion-oxidation process.^[9,10] To reduce the empiricism of models for prediction, characterization of oxygen diffusivity of each composite constitute, *i.e.* matrix, fiber, and interphase, was essential. Thus, Pochiraju *et al.* developed a model that enables long-term simulation of gaseous reactant diffusion in

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Received January 22, 2020; Accepted March 13, 2020; Published online June 15, 2020

degradation.

Thermogravimetric Analysis

TGA measurements were carried out under linear non-isothermal conditions from 400 °C to 800 °C with various heating rates of 0.5, 1, 1.5, 2, and 3 °C/min under air atmosphere at a flow rate of 40 mL/min to record the thermo-oxidative degradation behaviors. The experimental TGA curves with heating rates of 0.5, 1, 1.5, and 2 °C/min were used for kinetic analysis to characterize the thermo-oxidative degradation process, and the TGA curve with a heating rate of 3 °C/min was employed to validate the obtained kinetic parameters. Slow heating rates in TGA measurements were used to minimize the interfering mass and heat transfer phenomena occurring during the reaction. Meanwhile, isothermal TGA experiments were run at temperatures of 500, 600, and 700 °C in air, and the data of mass changes were used to further validate the kinetic parameters.

Long-term Isothermal Aging

The isothermal aging of the CFRPI composites was carried out in a THERMONCEPT KU40 air-circulating oven at 400 °C for 100 h. The oxidizing environment in the oven was guaranteed by providing a continuous supplement of air through the oven inlet. 120 Specimens were used in the experiment and all specimens were weighted within 0.0001 g accuracy with an OHAUS electronic balance before aging. The specimens were heated to 400 °C with a heating rate of 10 °C/min in flowing nitrogen. When the temperature reached 400 °C, the atmosphere of the oven was switched from nitrogen to air. Every 5 h, 6 specimens were removed from the oven and cooled in a desiccator. Then, 5 of the specimens were employed to record the corresponding mass loss, and to measure the flexural property on an INSTRON 3365 universal tester. The sixth specimen was used to examine the morphology of the thermally oxidized composite by a Hitachi SU8020 SEM instrument.

Kinetic Analysis

Separation of overlapped reactions

In order to get an accurate kinetic interpretation of a multistep degradation process, the constituent reactions must be separated before kinetic analysis. The overlapped reactions occurring during thermo-oxidative degradation of CFRPI composite can be separated by simple peak fitting of the corresponding DTG curves using a mathematical function per assumed reaction. Considering the shape of DTG curves is regulated by the kinetics of thermo-oxidative degradation of CFRPI composite, the selection of fitting mathematical equations is quite important. The inappropriate use of fitting functions will force the kinetic parameters onto the DTG data, thereby diverging from the true kinetics and producing imprecise results. As demonstrated by Perejón *et al.* the Fraser-Suzuki function considering the asymmetrical nature of kinetic curves can fit properly any degradation curve that follows any reaction model.^[31] The Fraser-Suzuki function is as follows:

$$y = a_0 \exp \left[-\ln 2 \left(\frac{\ln \left(1 + 2a_3 \left(\frac{x - a_1}{a_2} \right) \right)}{a_3} \right)^2 \right] \quad (1)$$

where a_0 , a_1 , a_2 , and a_3 are amplitude, position, half width, and

asymmetry of the peak respectively.

Determination of the kinetic parameters

The individual reaction included in thermo-oxidative degradation of the CFRPI composites is gas-solid reaction, the degradation rate of which can be described as follows:

$$\frac{da}{dt} = A \exp \left(-\frac{E}{RT} \right) f(a) h(P) \quad (2)$$

where A is the pre-exponential factor, E is the apparent activation energy, R is the gas constant (8.314 J/(mol·K)), a is the extent of conversion, $f(a)$ is the reaction model, P is the partial pressure of the gaseous reactant, and $h(P)$ accounts for pressure dependence.^[32] For thermo-oxidative degradation of the CFRPI composite, the partial pressure of oxygen in the composite changes during degradation due to cracking.^[33] $h(P)$ takes complex forms, and cannot be considered as a constant value.^[34] The common kinetic analysis procedures do not explicitly involve the pressure dependence in Eq. (2). $h(P)$ may reveal itself in other kinetic parameters. Therefore, the obtained kinetic triplets in this study are apparent kinetic parameters, which include elements of both reaction and diffusion.

For thermogravimetric analysis, the mass dependence of a is defined as:

$$a = \frac{m_t - m_i}{m_f - m_i} \quad (3)$$

where m_i is the initial mass, m_t is the mass at time t , and m_f is the final mass at the end of the thermo-oxidative degradation process.^[35] Taking natural logarithms of both sides of Eq. (2), one obtains:

$$\ln \left(\frac{da}{dt} \right) = \ln [A f(a)] - \frac{E}{RT} \quad (4)$$

Eq. (4) denotes that if the process obeys only one reaction model $f(a)$ irrespective of heating programs, E could be calculated from the slope of the linear regression of the differential experimental data plotted as $\ln(da/dt)$ on $1/T$ at a specific a .^[36] That is known as Friedman method which allows to estimate E without identification of the reaction model $f(a)$ in advance.

After the apparent activation energy E is determined, the reaction model $f(a)$ and pre-exponential factor A should also be evaluated to get a complete kinetic triplet. The experimental master plot of the conversion rate at infinite temperature ($da/d\theta$) versus a can be plotted by calculating the values of $da/d\theta$ at each a according to the following equation:^[37]

$$\frac{da}{d\theta} = \frac{da}{dt} \exp \left(\frac{E}{RT} \right) \text{ with } \theta = \int_0^t \exp \left(\frac{-E}{RT} \right) dt \quad (5)$$

where θ is the Ozawa's generalized time referring to the reaction time needed to achieve a specific a at infinite temperature. Meanwhile, combining Eq. (2) and Eq. (5), a correlation between experimental master-plots and reaction model $f(a)$ can be expressed by Eq. (6):^[38]

$$\frac{da}{d\theta} = A f(a) \quad (6)$$

According to Eq. (6), if the degradation process can be described by a theoretical reaction model $f(a)$, the experimental master plot has the same curve shape with the $f(a)$ - a plot. By comparing the ideal reaction model (Table 1^[39]) curves normalized at $a = 0.5$ with the experimental master plots normalized at $a = 0.5$, the most appropriate kinetic model $f(a)$ can be

Table 1 The commonly used ideal reaction models.

Reaction model	Symbol	$f(a)$	$g(a)$
1. Order-based models			
Zero order	F_0	1	a
One-third order	$F_{1/3}$	$1.5(1-a)^{1/3}$	$1 - (1-a)^{2/3}$
Three-quarters order	$F_{3/4}$	$4(1-a)^{3/4}$	$1 - (1-a)^{1/4}$
First order	$F_1 (A_1)$	$1-a$	$-\ln(1-a)$
Second order	F_2	$(1-a)^2$	$(1-a)^{-1} - 1$
Third order	F_3	$(1-a)^3$	$[(1-a)^{-2} - 1]/2$
2. Nucleation models			
Avrami-Erofeev ($m \neq 1$)	A_m	$m(1-a)[- \ln(1-a)]^{1-1/m}$	$[- \ln(1-a)]^{1/m}$
3. Contraction models			
Phase-boundary-controlled reaction ($n \neq 1$)	R_n	$n(1-a)^{1-1/n}$	$1 - (1-a)^{1/n}$
4. Diffusion models			
One-dimensional diffusion	D_1	$1/(2a)$	a^2
Two-dimensional diffusion (Valensi)	D_2	$[- \ln(1-a)]^{-1}$	$(1-a)\ln(1-a) + a$
Three-dimensional diffusion (Jander)	D_3	$3(1-a)^{1/3}/[2[(1-a)^{-1/3} - 1]]$	$[1 - (1-a)^{1/3}]^2$
Three-dimensional diffusion (Ginstling-Brounshtein)	D_4	$1.5[(1-a)^{-1/3} - 1]^{-1}$	$[1 - (2a/3)] - (1-a)^{2/3}$
5. Random scission models			
$L = 2$	L_2	$2(a^{1/2} - a)$	$-\ln(1-a^{1/2})$
$L > 2$	L_n	No symbolic solution	—

identified. With the knowing of activation energy E and reaction model $f(a)$, the pre-exponential factor A can be deduced by Eq. (2).

RESULTS AND DISCUSSION

Multistep Thermo-oxidative Degradation of the CFRPI Composite

In this section, the experimental TG-IR measurements of polyimide resin, T800 carbon fiber, and CFRPI composite were carried out, and the results were discussed by comparing the thermo-oxidative degradation behaviors of these materials. The purpose of this section is to identify the individual reactions occurring during thermo-oxidative degradation.

Mass change observation

Fig. 1 shows the mass loss and rate of mass loss profiles of polyimide resin, T800 carbon fiber, and CFRPI composite. It can be seen that all specimens have been almost completely consumed. The starting temperatures of thermo-oxidative degradation of these materials were almost at about 500 °C, while the end temperatures exhibited some difference. The thermo-oxidative degradation of CFRPI composite finished at about 786 °C, which was higher than the end temperatures of both polyimide resin and T800 carbon fiber. The same result was also revealed by other researches, which was due to a synergistic effect between polyimide resin and carbon fiber.^[40] Derivative data shed some information of the numbers of reactions occurring during thermo-oxidative degradation. Each peak in the DTG curves associated with at least one reaction. For polyimide resin and T800 carbon fiber, main peaks at 581 and 743 °C were individually noticeable, indicating at least one reaction occurrence during thermo-oxidative degradation. For the CFRPI composite, a shoulder at about 562 °C, two main peaks at 616 and 759 °C, and a weak peak at 656 °C were clearly seen, revealing the occurrence of at least four overlapped reactions. Note that the temperatures of peaks on DTG curves of CFRPI composite were different from those of polyimide resin

and T800 carbon fiber, indicating that the thermo-oxidative degradation of CFRPI composite cannot be simply matched by the sum of the oxidation reactions of polyimide resin and T800 carbon fiber. Due to the complexity of the thermo-oxidative degradation process, the details of constituent chemical reactions are difficult to be ascertained only by analyzing the experimental TGA and DTG data, which need further study.

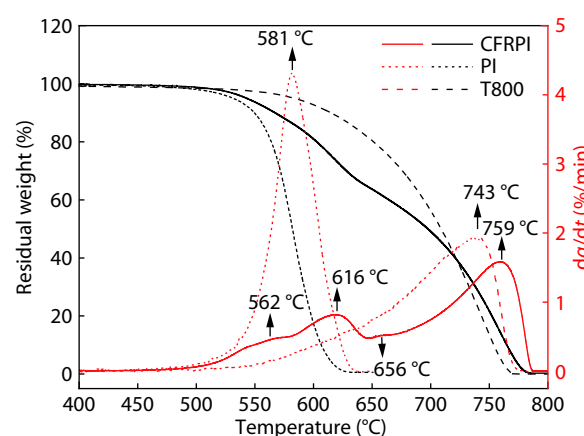


Fig. 1 Experimental TGA and DTG curves recorded for thermo-oxidative degradation of polyimide resin, T800 carbon fiber, and CFRPI composite under a linear heating rate of 2 °C/min.

Volatile products analysis

The species of the volatile degradation products identified with the aid of FTIR analysis were employed to probe the possible chemical reactions arising from thermo-oxidative degradation. Fig. 2(a) gives FTIR spectra of oxidation products for the polyimide resin heated from 400 °C to 700 °C under a linear heating rate of 2 °C/min. The main volatile oxidation products were oligomeric siloxane compounds (1028 cm^{-1}), CF_3H (1155 cm^{-1}), CO (2103 cm^{-1}), CO_2 (2368 cm^{-1}), and H_2O (3700 cm^{-1}).^[41,42] The signal intensity of these products was plotted as a function of temperature, as shown in Fig. 3(a). It can

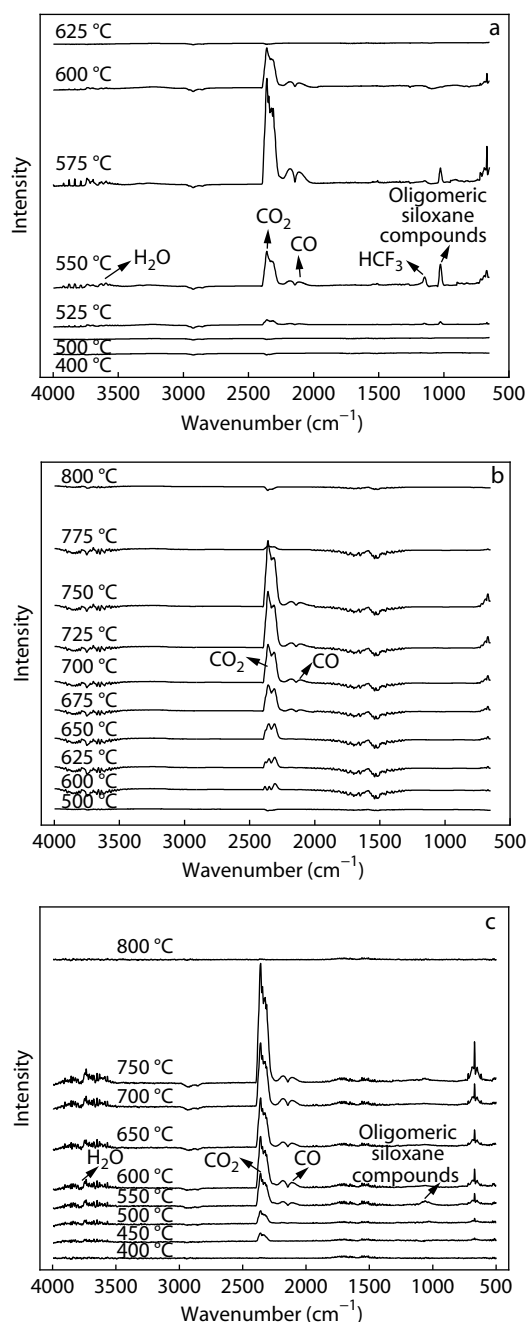


Fig. 2 FTIR spectra of volatile products collected during thermo-oxidative degradation of polyimide resin (a), T800 carbon fiber (b), and CFRPI composite (c).

be seen that two temperature domains appeared in the intensity profile. One temperature domain centered at 558 °C was related with evolution of CF_3H and oligomeric siloxane compounds, and another temperature domain centered at 578 °C was correlated with the release of CO , CO_2 , and H_2O . The reactions occurring during thermo-oxidative degradation of polyimide are related to its different functional groups. At lower temperatures, the major degradation pathway appeared to be the shedding of CF_3 groups and pyrolysis of the siloxane units; the higher temperature range probably showed degradation of imide groups and phenyl groups giving products of CO , CO_2 ,

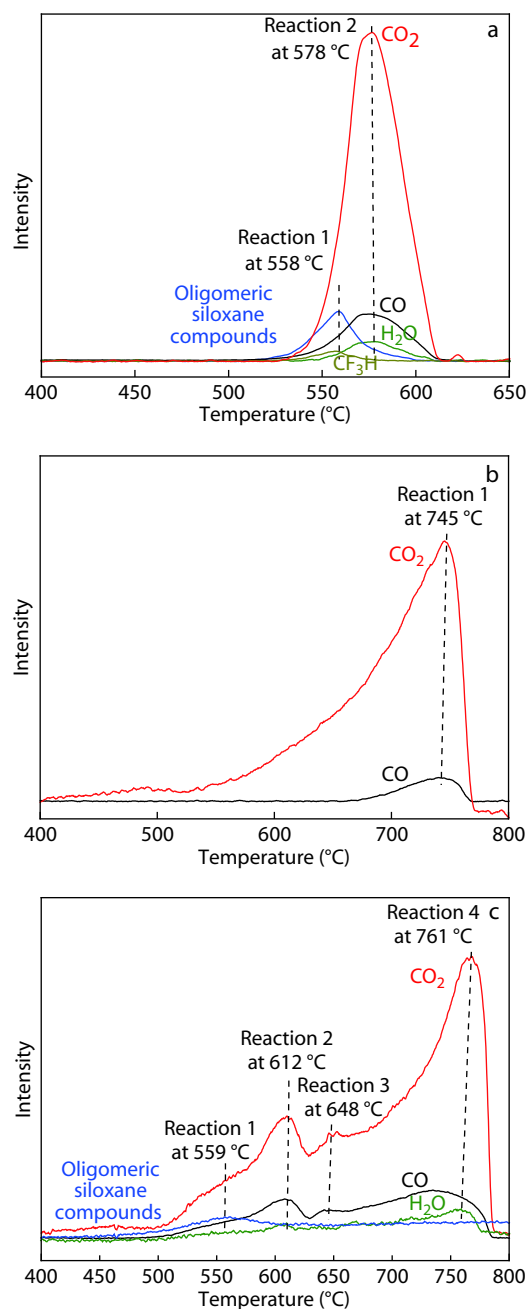


Fig. 3 Intensity profiles of volatile products for thermo-oxidative degradation of polyimide resin (a), T800 carbon fiber (b), and CFRPI composite (c).

and H_2O .^[43,44] Therefore, the thermo-oxidative degradation of polyimide resin was supposed to be controlled by two main reactions: degradation of instable side groups and main chain pyrolysis. The same research procedure was conducted on the thermo-oxidative degradation of T800 carbon fiber. The results are shown in Figs. 2(b) and 3(b). It was found that the main volatile products were CO and CO_2 ,^[45] and only one temperature domain centered at 745 °C existed, indicating the thermo-oxidative degradation of carbon fiber was mainly regulated by one reaction: carbon fiber oxidation. The thermo-oxidative degradation of carbon-fiber reinforced polyimide

composites was also studied. It was found that the oxidation products were oligomeric siloxane compounds, CO, CO₂, and H₂O, including the main oxidation products of both polyimide resin and T800 carbon fiber, as shown in Fig. 2(c). The relationship between signal intensity of such species and temperatures is shown in Fig. 3(c). Four temperature domains centered individually at 559, 612, 654, and 761 °C were noticeable. By comparing these temperature domains with those of polyimide resin and T800 carbon fiber, the intensity peaks at 559 and 612 °C were deduced to be related with pyrolysis of polyimide resin, and the intensity peak at 761 °C was proposed to be correlated with degradation of T800 carbon fiber. It is interesting to point out that, the signal intensity peak at 654 °C related with the evolution of CO₂, CO, and H₂O belonged to neither the pyrolysis of polyimide resin nor the degradation of T800 carbon fiber. Considering the interphase is also one component of composites besides polyimide and carbon fiber, such a peak was identified to be related with the degradation of the interphase. Colin *et al.* pointed that the radicals in the interphase arising from oxidation are scavenged by carbon fiber, making the interphase more thermally stable than matrix resin.^[46,47] Based on the above results, four chemical reactions were supposed to occur during thermo-oxidative degradation of CFRPI composite, which were related to side groups of polyimide, polyimide backbone, interphase, and carbon fiber, respectively.

Thermo-oxidative Degradation Kinetics of the CFRPI Composite

Separation of overlapped reactions

After identifying the reactions included in the thermo-oxidative degradation, the mass loss behaviors related with different chemical reactions were separated by peak fitting of experimental DTG curves (da/dt - T curves) using the Fraser-Suzuki function. During the peak fitting procedure, some constraints were introduced to diminish the deviation of results from intrinsic mass loss behaviors. The maximum rate of each reaction was fixed at the temperature at which the reaction fraction is almost constant.^[31] Meanwhile, the changes in parameter a_3 of Fraser-Suzuki function with the variation of heating rates must be small for a specific reaction.^[48] Based on the above constraining conditions, all da/dt - T curves for CFRPI composites were fitted by the Fraser-Suzuki function using a computer program Peakfit (Systat Software Inc.). As can be seen in Fig. 4, the overall da/dt - T curves are perfectly matched by the sum of the individual reactions. All fitting parameters yielded by the peak fitting of each experimental curves are shown in the Table 2. The relative contribution L (the area calculated under the fitted derivative curves) of the four reactions to the overall thermo-oxidative degradation process is 5.98%, 17.87%, 8.42%, and 67.72%, respectively. The contribution value of 67.72% corresponding to carbon-fiber weight content of the CFRPI

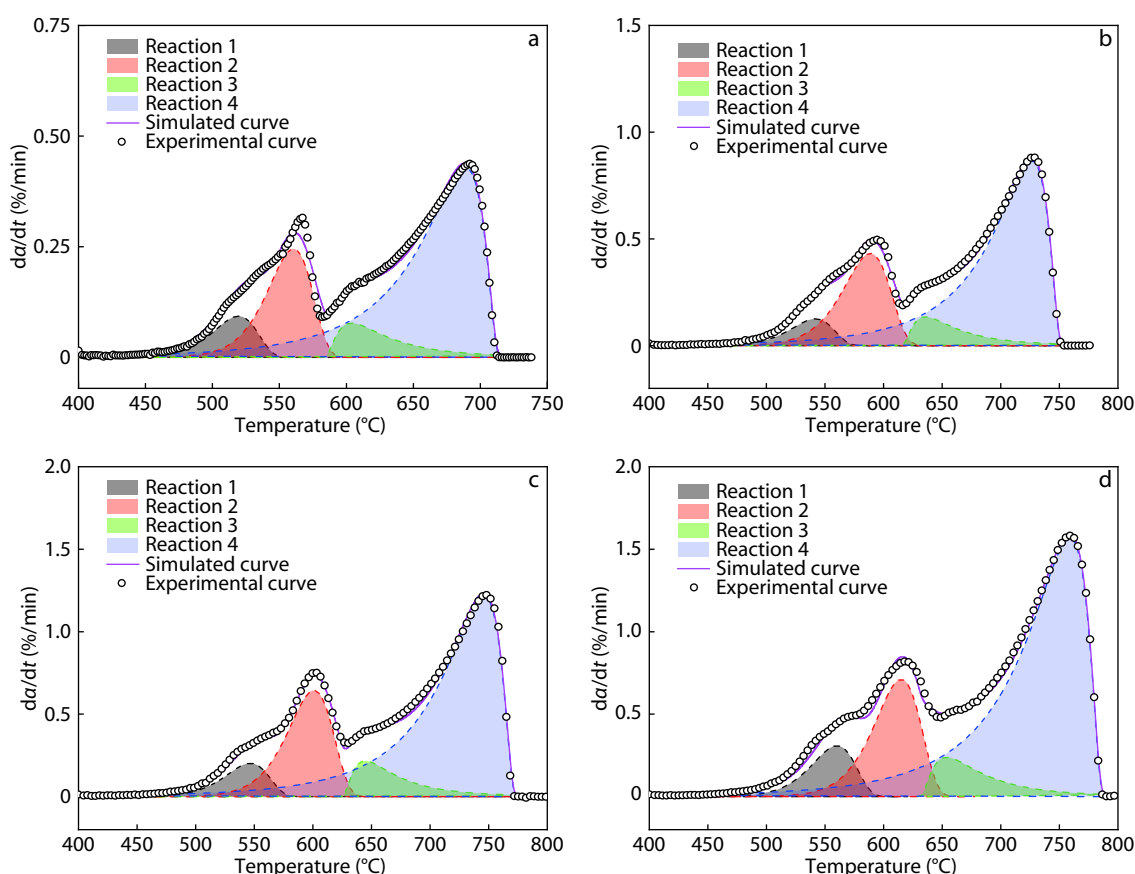


Fig. 4 The peak fittings of experimental DTG curves obtained at different heating rates: 0.5 °C/min (a), 1 °C/min (b), 1.5 °C/min (c), and 2 °C/min (d), using the Fraser-Suzuki function by assuming four reactions included in the thermo-oxidative degradation of CFRPI composite.

composite translated to about 60% volume fraction in the composite, which correlates well with the measured value. At the same time, the obtained contribution L of each separated reaction was not sensitive to the variation of heating rates according to Table 2. That proves the rationality of assumption

Table 2 Fitting parameters obtained by peak fitting of experimental DTG curves using Fraser-Suzuki function for thermo-oxidative degradation of CFRPI composite.

	Heating rate (°C/min)	a_0	a_1	a_2	a_3	L	r^2
Reaction 1	0.5	0.09	519.44	38.84	−0.35	6.79	0.9903
	1	0.13	541.80	42.33	−0.36	5.05	0.9974
	1.5	0.20	546.59	43.29	−0.36	5.57	0.9965
	2	0.31	560.11	44.02	−0.36	6.51	0.9974
Reaction 2	0.5	0.25	560.48	39.18	−0.36	18.06	0.9903
	1	0.43	588.74	46.74	−0.36	19.18	0.9974
	1.5	0.64	600.83	45.02	−0.36	18.43	0.9965
	2	0.71	614.97	46.41	−0.36	15.82	0.9974
Reaction 3	0.5	0.08	604.02	40.56	0.92	9.13	0.9903
	1	0.13	635.72	39.94	0.92	7.98	0.9974
	1.5	0.22	644.74	39.47	0.92	8.58	0.9965
	2	0.24	653.79	45.23	0.92	8.00	0.9974
Reaction 4	0.5	0.43	688.82	50.65	−0.92	66.02	0.9903
	1	0.87	726.43	50.81	−0.92	67.79	0.9974
	1.5	1.21	746.01	53.76	−0.92	67.41	0.9965
	2	1.57	758.91	57.19	−0.92	69.67	0.9974

of four chemical reactions occurring during thermo-oxidative degradation.

Calculation of apparent activation energy E

The weight loss curves of each separated reaction under different heating rates in the conversion α range of 0.10 to 0.90 were then constructed by integrating and normalizing the differential curves obtained by the peak fitting procedure. These constructed curves were subsequently analyzed by Friedman method for the calculation of the activation energies E . Fig. 5 shows Friedman plots of $\ln(da/dt)$ versus $1/T$ for each of the constituent reactions of CFRPI composites in the conversion range of 0.10 to 0.90 in steps of 0.10. The calculated E and corresponding Pearson's correlation coefficients (r) are summarized in Table 3. Obviously, all the slopes of these Friedman plots indicated good parallelism for the entire conversion α range (0.10–0.90), and the variation amplitude of the values of E for each reaction was quite small. The difference between the maximum E value and minimum E value (ΔE) was less than 10% of the average value for each individual reaction, which happens in the case of the single-step reaction. The average E values of 161.87, 127.37, 158.38, and 148.99 kJ/mol were respectively estimated for the four reactions during thermo-oxidative degradation of CFRPI composite. Note that the values of E did not increase as the thermo-oxidative degradation advances. For example, the average E value of reaction step 1 was higher than that of reaction step 2. That

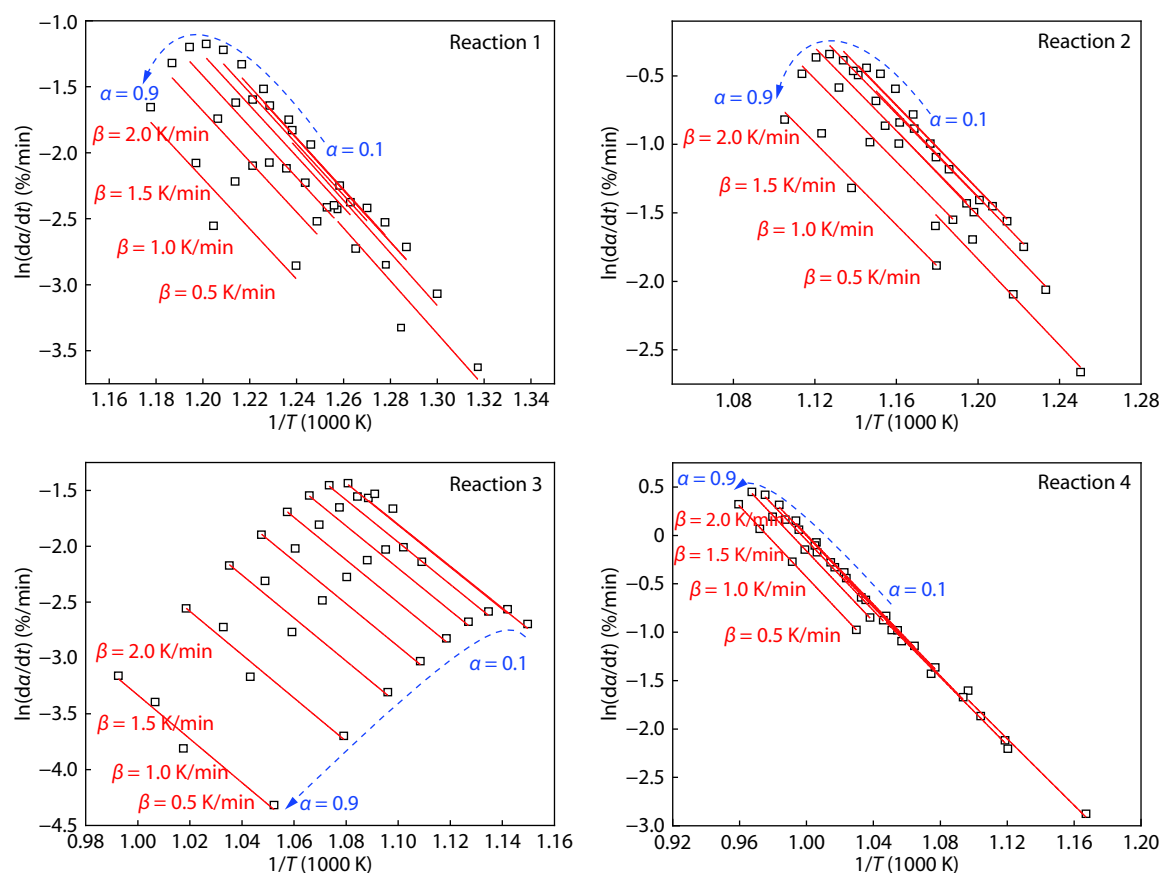


Fig. 5 Friedman plots of $\ln(da/dt)$ versus $1/T$ of each separated reaction in the conversion range of 0.10 to 0.90 for thermo-oxidative degradation of CFRPI composite.

Table 3 Apparent activation energy at each conversion value as well as the corresponding correlation coefficient calculated by Friedman method for thermo-oxidative degradation of CFRPI composite.

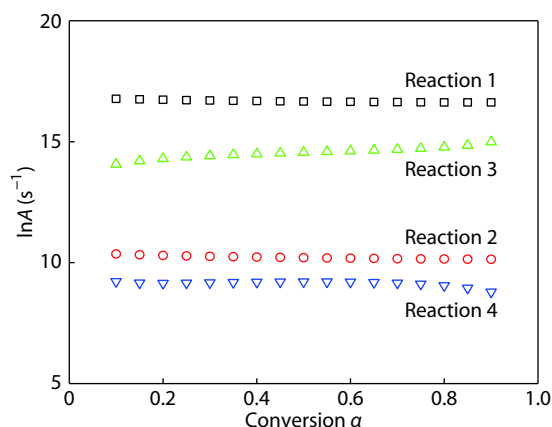
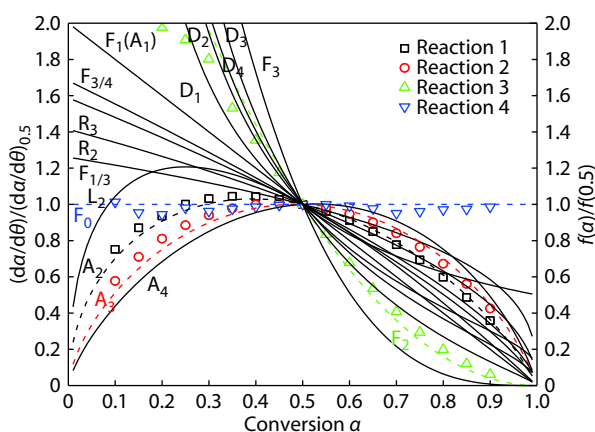
α	Reaction 1		Reaction 2		Reaction 3		Reaction 4	
	r	E_a (kJ/mol)	r	E_a (kJ/mol)	r	E_a (kJ/mol)	r	E_a (kJ/mol)
0.10	−0.9427	166.31	−0.9863	130.43	−0.9748	155.74	−0.9883	142.86
0.20	−0.9463	165.68	−0.9871	129.22	−0.9752	156.02	−0.9950	145.88
0.30	−0.9408	163.04	−0.9872	128.38	−0.9757	157.20	−0.9972	147.62
0.40	−0.9402	162.14	−0.9871	127.77	−0.9758	157.04	−0.9983	148.80
0.50	−0.9397	161.42	−0.9869	127.21	−0.9764	158.49	−0.9989	149.69
0.60	−0.9392	160.68	−0.9866	126.64	−0.9768	159.09	−0.9993	150.58
0.70	−0.9386	160.20	−0.9862	126.08	−0.9779	159.20	−0.9996	151.13
0.80	−0.9385	159.30	−0.9859	125.72	−0.9798	161.30	−0.9997	151.93
0.90	−0.9381	158.10	−0.9854	124.88	−0.9836	161.36	−0.9998	152.41
Average	—	161.87	—	127.37	—	158.38	—	148.99

was because the obtained E value could not be considered simply as the intrinsic activation energy barriers of a reaction but was also affected by the contribution from other reaction steps and diffusion of gaseous reactant.^[32]

Determination of reaction model $f(a)$ and pre-exponential factor A

Besides the apparent activation energy E , also the reaction model $f(a)$ and pre-exponential factor A should be provided for a complete kinetic description of the constituent reactions. The average activation energies and degradation rate data of the constituent reactions for thermo-oxidative degradation of CFRPI composites were employed to calculate the values of $da/d\theta$ at each conversion α according to Eq. (5). The comparison between experimental master plots obtained for each individual reaction and the commonly used ideal reaction model curves was conducted and shown in Fig. 6. It was found that the ideal nucleation and nuclei growth models could fit the shapes of experimental master plots of the reactions 1 and 2, and reactions 3 and 4 followed the order-based models. All reactions showed some deviations from the ideal models, which was because the ideal models are proposed assuming a totally homogeneous sample.^[49] After the determination of reaction model $f(a)$, the values of $\ln A$ at each α were calculated by Eq. (4)

as shown in Fig. 7. According to Fig. 7, the values of $\ln A$ were almost constant and irrespective of α , which indicates the precise kinetic interpretation of the CFRPI composite. All thermo-oxidative degradation kinetic triplets of CFRPI composite are summarized in Table 4.

**Fig. 7** The plots of $\ln A$ calculated according to Eq. (4) against α for the corresponding four reactions contributing to the overall thermo-oxidative degradation of CFRPI composite.**Fig. 6** Comparison of the ideal reaction model curves normalized at $\alpha = 0.5$ (solid lines) with experimental master-plots normalized at $\alpha = 0.5$ (symbols) of the four constituent reactions whose overlapping constitute the overall thermo-oxidative degradation process of CFRPI composite.**Table 4** Kinetic triplet of each individual reaction contributing to the overall thermo-oxidative degradation of CFRPI composite.

	Reaction 1	Reaction 2	Reaction 3	Reaction 4
E (kJ/mol)	161.87 ± 2.60	127.37 ± 1.67	158.38 ± 1.95	148.99 ± 2.93
$f(a)$	A_2	A_3	F_2	F_0
$\ln A$ (s^{-1})	16.67 ± 0.05	10.22 ± 0.07	14.54 ± 0.23	9.13 ± 0.11
Contribution L (%)	5.98 ± 0.70	17.87 ± 1.25	8.42 ± 0.47	67.72 ± 1.30

Validity of obtained kinetic parameters

The validity of obtained kinetic parameters depends on whether the modelling of mass loss behaviors based on these parameters shows good correspondence with the experimental results. Modeling of the thermo-oxidative degradation process was conducted based on the integral form of Eq. (2) with equation that defines the linear temperature procedure, i.e. $\beta = dT/dt$, as shown in Eq. (7):

$$\int_0^{\alpha} \frac{1}{f(a)} da = \int_0^T \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) dT \quad (7)$$

The left side of Eq. (7) is expressed by the following equation:

$$\int_0^a \frac{1}{f(a)} da = g(a) \quad (8)$$

which can be solved according to the specific reaction model shown in Table 1. The right side of Eq. (7) does not have an analytical solution, but can be solved with very high accuracy using an approximation equation expressed as follows:^[50]

$$\int_0^T \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) dT \approx \frac{AE}{\beta R} \exp\left(-0.37773896 - 1.89466100 \ln \frac{E}{RT} - 1.00145033 \frac{E}{RT}\right) \quad (9)$$

Eqs. (8) and (9) allow one to correlate the mass loss of a single reaction with the temperature. The mass loss of the CFRPI composite during thermo-oxidative degradation can be obtained by overlapping the mass loss of the four constituent reactions. Fig. 8 shows the comparison between the simulated results and experimental results of mass changes of the CFRPI composite heated from 400 °C to 800 °C in air with heating rates of 0.5, 1, 1.5, 2, and 3 °C/min, respectively. The simulated curves had excellent agreement with the experimental curves, indicating the modeling captures the adequate features of the thermo-oxidative degradation of CFRPI composite. The validity of the obtained kinetic parameters was further verified by predicting the mass changes of the composite under isothermal TGA conditions. Fig. 9 shows the mass-loss curves simulated for CFRPI composite exposed isothermally at 500, 600, and 700 °C as well as the corresponding experimental curves. Noticeably, both the predicted curves and experimental ones match perfectly. This indicates that neither contribution nor kinetic triplet of each constituent reaction changes with conditions of thermo-oxidative degradation, which makes it possible to perform long-term thermo-oxidative degradation modeling.

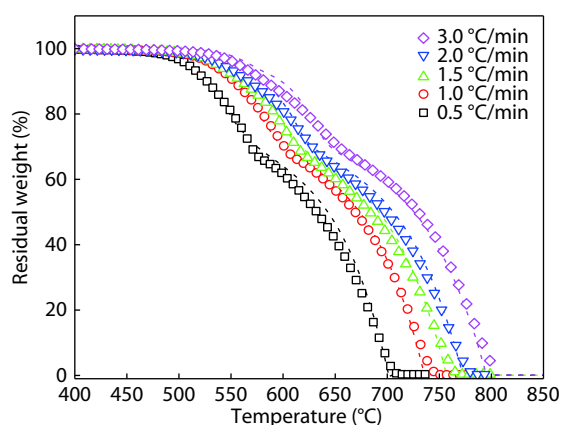


Fig. 8 Comparison between the simulated results (dash lines) and experimental results (symbols) of the mass changes for the thermo-oxidative degradation of CFRPI composite under different linear heating rates.

Long-term Thermo-oxidative Degradation Modeling

The feasibility of long-term thermo-oxidative degradation modeling of the CFRPI composite based on the obtained kinetic

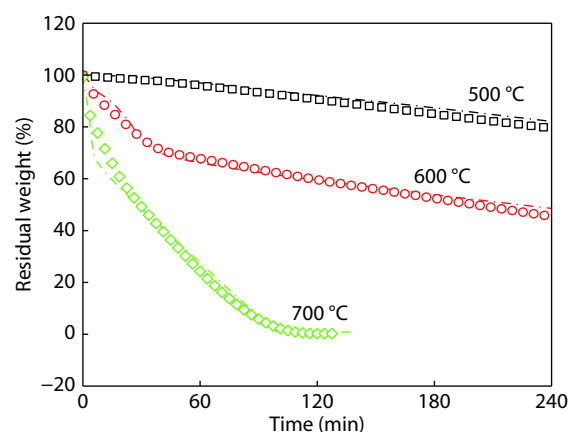


Fig. 9 Comparison between the simulated results (dash lines) and experimental results (symbols) of the mass changes for the thermo-oxidative degradation of CFRPI composite under isothermal TGA conditions.

parameters was studied in this section. The CFRPI composite specimens were isothermally aged at 400 °C in air atmosphere for 100 h, and the corresponding weight loss and flexural strength were measured every 5 h. Meanwhile, the morphologies of the CFRPI composites at different thermo-oxidative degradation states were observed. Fig. 10 shows the

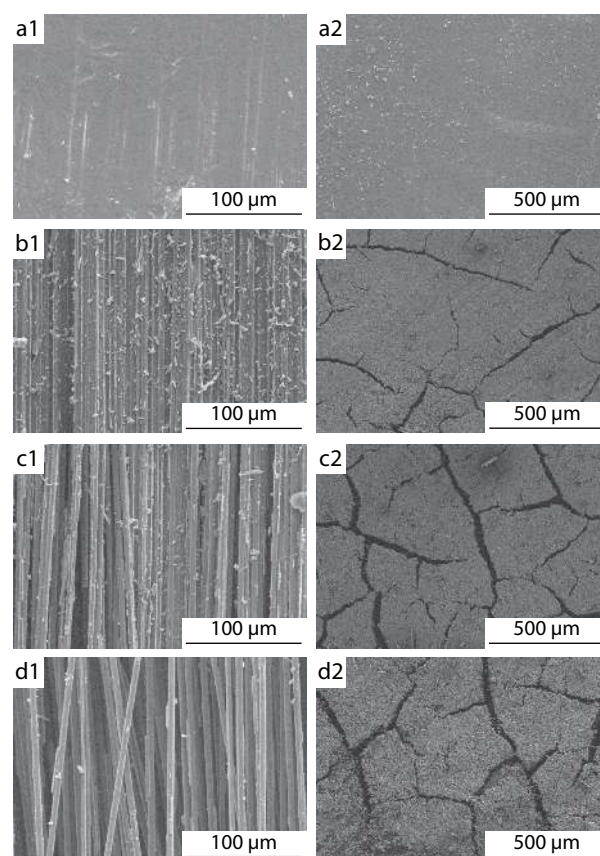


Fig. 10 The vertical-sectional (a1–d1) and cross-sectional (a2–d2) images of the CFRPI composite specimens isothermally aged at 400 °C for 0 h (a1, a2), 25 h (b1, b2), 50 h (c1, c2), and 75 h (d1, d2).

vertical-sectional and cross-sectional images of the composite exposed at 400 °C for 0, 25, 50, and 75 h. With the increase of the aging time, the polyimide resin on the surface gradually disappeared, leaving the carbon fiber exposed. However, the carbon fiber was not completely naked and some resin still tightly interfaced with it. This observation demonstrates that the interphase exhibited better thermo-oxidative stability than matrix resin, which correlates well with the supposed sequence of the reaction steps during thermo-oxidative degradation. During aging, microcracks grew and distributed across the thickness of the composite specimen, which was mainly due to the shrinkage mismatch between carbon fiber and polyimide resin caused by thermo-oxidative degradation.^[51] These microcracks enhanced the diffusion of the air into the interior of the composite,^[52] increasing the gaseous reactant pressure in the composite. This observation indicates that the long-term thermo-oxidative degradation of the composite at 400 °C was regulated by both gaseous diffusion and chemical reactions. Such a process can be characterized by the obtained apparent kinetic parameters, which include elements of both reaction and diffusion. The predicted results and experimental results of the weight loss during the long-term aging at 400 °C showed good correspondence with each other as shown in Fig. 11. The retention of the flexural strength was also predicted, supposing the relationship between weight loss of polyimide resin in composite and deterioration of flexural strength is highly linear. The results are also showed in Fig. 11. It can be seen that the retention rates of the flexural strength obtained by prediction correlated well with that measured by the experiment. The successful prediction of weight loss and flexural strength deterioration of the composite indicated the precise modeling of long-term aging process. It should be noted that the kinetic parameters used in modeling are only effective for the corresponding composite system studied, because they are peculiar for the chemical composition of the polyimide and type of carbon fiber. Nevertheless, this procedure can be likewise extended to other CFRPI composite systems. This study can serve as a basis for rapid evaluation of the long-term durability of aerospace CFRPI composites in various application environments.

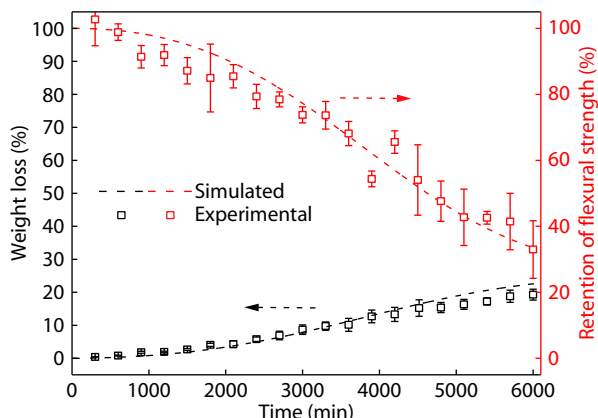


Fig. 11 The comparison of predicted results and experimental results of weight loss and retention of flexural strength for CFRPI composite isothermally aged at 400 °C in air.

CONCLUSIONS

The purpose of this study is to establish an inter-relationship among thermo-oxidative environment (temperature and time), mass loss behavior, and mechanical property deterioration of CFRPI composite on the basis of degradation kinetics. The thermo-oxidative degradation of the CFRPI composite was monitored by TG-IR measurements. The results of volatile products analyses indicated that the CFRPI composite decomposed in air through four independent reaction steps. The mass loss related to each reaction was firstly separated by peak fitting of the DTG curves using nonsymmetrical Fraser-Suzuki mathematical function, and the kinetic triplets were subsequently obtained by kinetic analysis of the separated reactions employing the Friedman method and experimental master-plots method. After validating the obtained kinetic parameters by reconstruction and prediction of TGA curves, modelling of long-term aging process of the CFRPI composite at 400 °C on the basis of these kinetic parameters was successfully achieved. The predicted weight loss and flexural property correlated well with the experimental results. However, further refinement will be necessary. The expression of $h(P)$ related with oxygen diffusion needs to be further understood, and incorporated into the kinetic analysis procedure. Thus, the modelling will become more accurate and hold great promise for successful application in lifetime prediction of the aircraft systems fabricated by CFRPI composites.

ACKNOWLEDGMENTS

The authors express their sincere thanks to Prof. Caihong Xu for her assistance on the synthesis of siloxane-containing polyimide resin.

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