

DETERMINATION OF THE THERMAL DEGRADATION KINETIC PARAMETERS OF CARBON FIBRE REINFORCED EPOXY USING TG

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Abstract

In this work, a kinetic study on the thermal degradation of carbon fibre reinforced epoxy is presented. The degradation is investigated by means of dynamic thermogravimetric analysis (TG) in air and inert atmosphere at heating rates from 0.5 to 20°C min⁻¹. Curves obtained by TG in air are quite different from those obtained in nitrogen. A three-step loss is observed during dynamic TG in air while mass loss proceeded as a two step process in nitrogen at fast heating rate. To elucidate this difference, a kinetic analysis is carried on. A kinetic model described by the Kissinger method or by the Ozawa method gives the kinetic parameters of the composite decomposition. Apparent activation energy calculated by Kissinger method in oxidative atmosphere for each step is between 40–50 kJ mol⁻¹ upper than E_a calculated in inert atmosphere.

The thermo-oxidative degradation illustrated by Ozawa method shows a stable apparent activation energy ($E_a \approx 130$ kJ mol⁻¹) even though the thermal degradation in nitrogen flow presents a maximum E_a for 15% mass loss ($E_a \approx 160$ kJ mol⁻¹).

Keywords: epoxy/carbon, kinetic parameters, mass loss, TG, thermal degradation

Introduction

The use of high-performance thermoset polymers/carbon fibre composites has increased in recent years. A number of manufacturers are interested in the association of the composite lightness, the thermal stability and the good mechanical properties. Currently for structural applications, epoxy resins generally strengthened with glass or carbon fibres represent the basis of a large choice of organic matrices. The thermal use limit of these epoxy resins for a long time is situated under 180°C. It is necessary to be able to quantify the long-term thermal stability and durability of polymeric materials.

Ideally, the material would be monitored under use conditions for the desired lifetime. Nevertheless, the results must be available as fast as possible this is seldom economical. The solution is to study the accelerated ageing of polymers in order to obtain the kinetic parameters of decomposition such as the apparent activation energy and then to extrapolate results back to a typical use environment. For a good relation-

ship it is important to consider the degradation mechanisms under use conditions in the same way as that under the accelerated ageing conditions.

Thermogravimetric analysis (TG) is often used to determine decomposition reactions and to evaluate the thermal stability. The mass loss is controlled by the time in isothermal conditions or by the temperature during the heating rate. Changes in mass can be associated with solvent or water desorption/absorption, oxidation or reduction and decomposition. The inconvenience of isothermal condition is the time of tests which is excessively long, particularly, at low isothermal temperature. Dynamic TG tests tend to be shorter and the mechanism of degradation may be studied over a large temperature range with typical heating rate.

A previously work on polyimide polymer systems using thermogravimetric analysis compared several methods to calculate thermal kinetic parameters [1]. We have shown that Van Krevelen, Horowitz–Metzger, Coats–Redfern and MacCallum–Tanner methods give a similar apparent activation energy. All kinetic parameters calculated by using these methods show equally good agreement with the experimental data.

The aim of this paper is to investigate the thermal degradation of epoxy/carbon composite in dynamic conditions. The thermal stability is described by comparing the temperature when degradation begins or by comparing the mass loss at a chosen temperature when the tests are conducted in air or nitrogen atmospheres. Moreover, apparent kinetic parameters are determined. The activation energy have been evaluated employing Kissinger's method assuming first order reaction or the Ozawa's method which gives an estimated activation energy for the overall degradation.

Experimental

Material

The material investigated is an epoxy polymer (DGEBA) reinforced with UD carbon fibre (Tokyo Rope). The density of composite is 1.505 kg l^{-1} and the mass amount of fibre is about 55 mass%. These epoxy composite provided good thermal stability and a glass transition temperature up to 115°C is determined by modulated DSC.

Samples were reduced in powder for tests. The powder is dried at 55°C in vacuum during two weeks before the TG tests.

Thermogravimetric studies

Dynamic thermogravimetric runs were obtained with a Shimadzu TG-50 thermo-balance in dry inert or air atmosphere at a flow rate of 50 ml min^{-1} . The initial mass of the sample was about 10 mg.

Dynamic runs were performed at a rate of 0.5, 1, 2, 5, 10 and $20^\circ\text{C min}^{-1}$ from ambient to 900°C .

The kinetic parameter of interest were the apparent activation energy E_a relating to the initial degradation of the composite. Numerous analytical methods are avail-

able in the literature to calculate E_a [2]. The values obtained from different methods are never identical but range closely enough to get an average value.

The general form of the kinetic expression used in analysing dynamic and isothermal TG data is based on n^{th} order reaction mechanism and in most cases, the temperature dependence can be satisfactorily described by the Arrhenius equation which is assumed viz.,

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) (1-\alpha)^n \quad (1)$$

α – conversion, n – reaction order, E – activation energy, A – pre-exponential factor of Arrhenius equation.

The Kissinger [3] method supposes a first order kinetic. This method allows the calculation of E_a from a point T_{max} which is the temperature at the maximum of the heating derive mass loss curve. Since the maximum rate occurs when $d\alpha/dt=0$ the Eq. (1) gives:

$$\left(\frac{d^2\alpha}{dT^2}\right)_{\text{max}} = 0 = \left(\frac{d\alpha}{dT}\right)_{\text{max}} \left[\frac{E}{RT_{\text{max}}^2} - \frac{A}{q} \exp\left(\frac{-E}{RT_{\text{max}}}\right) n(1-\alpha)_{\text{max}}^{n-1} \right] \quad (2)$$

Kissinger has shown that $n(1-\alpha)_{\text{max}}^{n-1} = 1$ and is independent of the heating rate. The logarithm expression of Eq. (2) is:

$$\ln\left(\frac{q}{T_{\text{max}}^2}\right) = -\frac{E}{R} \left(\frac{1}{T_{\text{max}}}\right) \quad (3)$$

The plot of $\ln(q/T_{\text{max}}^2)$ vs. $1/T_{\text{max}}$ has a slope of $-E/R$.

For each degradation step a sudden mass loss was observed and the activation energy was calculated. However, we have focused our attention on the first mass loss step which was related to initial degradation kinetic.

Results

Dynamic TG experiments in air or nitrogen flow at heating rate from 0.5 to 20°C min⁻¹ are shown in Figs 1 and 2. Mass is lost as temperature increases which slower rate yielding earlier degradation onsets. Mass loss is total in an oxidative atmosphere while the char yield obtained in nitrogen at 900°C is dependent on heating rate.

Both tests kinetic degradation presents several stages. In an inert atmosphere the first stage begins at 275 and ends at 415°C. The maximum rate is near 350°C and the corresponding mass loss at this temperature was about 7 mass% (Table 1). Nevertheless, the mass loss of the first step in inert flow is dependent of the heating rate. For this purpose Table 2 shows a mass loss between 9.5 to 14.2 mass% for experiments run from 1 to 20°C min⁻¹. The second step was attributed to a decomposition of the non-volatile residues formed in the first step. The mass loss of this second step was about 20 mass% with the end decomposition temperature at 625°C. For some experi-

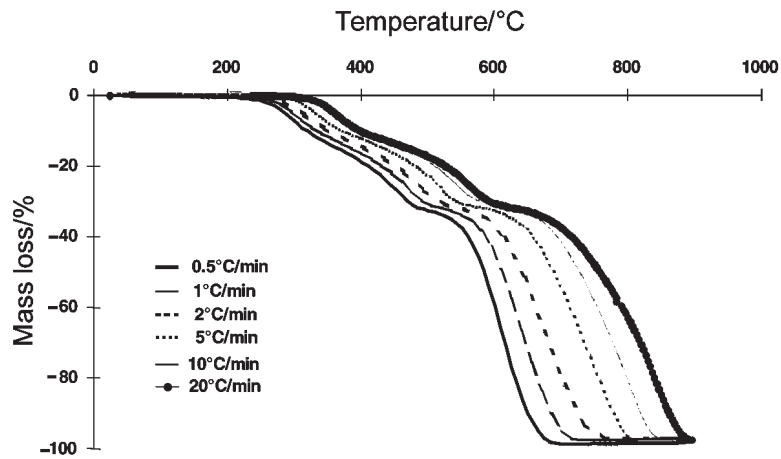


Fig. 1 TG of epoxy/carbon composite in air atmosphere

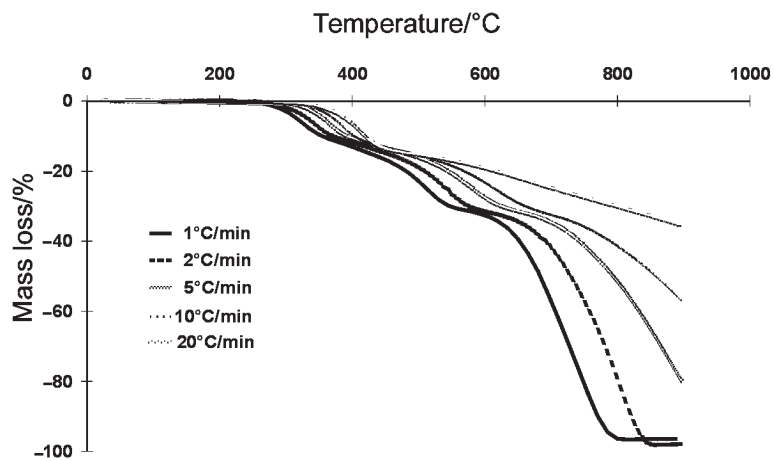


Fig. 2 TG of epoxy/carbon composite in nitrogen atmosphere

ments in nitrogen gas the derivative dynamic TG curve is not well defined particularly for the third stage. This third stage was principally attributed to the degradation of the carbon fibre [4] and represents the highest mass loss about 70 mass%.

Three stages were also observed for the dynamic thermogravimetric studies in oxidative conditions. The first step begins at about 250°C and the polymer loses 8 mass% of its initial mass. The second step shows a maximum rate near 500°C. The third step corresponds to the degradation of the residue with a rapid rate. The global mass loss of the later step is close to 70 mass% of the initial mass at 615°C.

Table 1 Mass loss (%) of carbon/epoxy composite for each step of dynamic TG in air or inert flow

Heating rate/ $^{\circ}\text{C min}^{-1}$	Nitrogen			Air		
	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3
0.5	–	–	–	10.5	22.4	67.1
1	9.50	21.4	69.0	9.0	22.4	68.6
2	10.00	21.4	68.6	6.2	24.7	69.1
5	11.90	18.1	–	8.1	21.4	70.5
10	11.39	8.8	–	8.5	20.0	71.4
20	14.20	20.5	–	10.0	20.0	70.0

Table 2 T_{max} and mass loss corresponding for each step of epoxy/carbon dynamic TG

Heating rate/ $^{\circ}\text{C min}^{-1}$	$T1_{\text{max}}$		$T2_{\text{max}}$		$T3_{\text{max}}$		
	$T/^{\circ}\text{C}$	mass loss/%	$T/^{\circ}\text{C}$	mass loss/%	$T/^{\circ}\text{C}$	mass loss/%	
Nitrogen	1	320	5.6	515	25.8	725	68.2
	2	343	6.0	544	25.0	800	79.1
	5	368	6.8	586	25.1	–	–
	10	387	7.4	613	24.6	–	–
	20	414	8.6	671	23.0	–	–
Air	0.5	296	6.7	452	26.5	609	64.7
	1	311	6.7	461	24.0	641	66.4
	2	315	5.3	465	21.5	675	66.8
	5	338	5.65	519	26.0	748	77.0
	10	352	4.9	541	24.0	800	80.9
	20	366	5.6	559	25.0	839	79.8

The Kissinger method was employed to obtain the apparent activation energy in air or nitrogen from several run with different heating rate (q). Figure 3 represents the Kissinger plots of the epoxy composite degraded in nitrogen flow. Table 3 summarises the values calculated in both atmospheres.

The kinetic parameters calculated in air flow present activation energy values higher than E_a obtained in nitrogen flow. A difference of 40 kJ mol^{-1} was observed in favour of the oxidative atmosphere for the first step for equivalent mass loss and for the second step by a superior activation energy of 50 kJ mol^{-1} for the decomposition in air. These results suggest a different comprehensive degradation mechanism in which an oxidative stage was involved as supported by complete observed mass loss.

Kiefer *et al.* [4] mentioned that the sample preparation had an effect on the kinetic results. It does seem that the kinetic parameters are divided into two groups, however, depending whether or not the sample contained fibres. He observed that the resin is affecting the fibre. In order to compare kinetic parameters derived in different

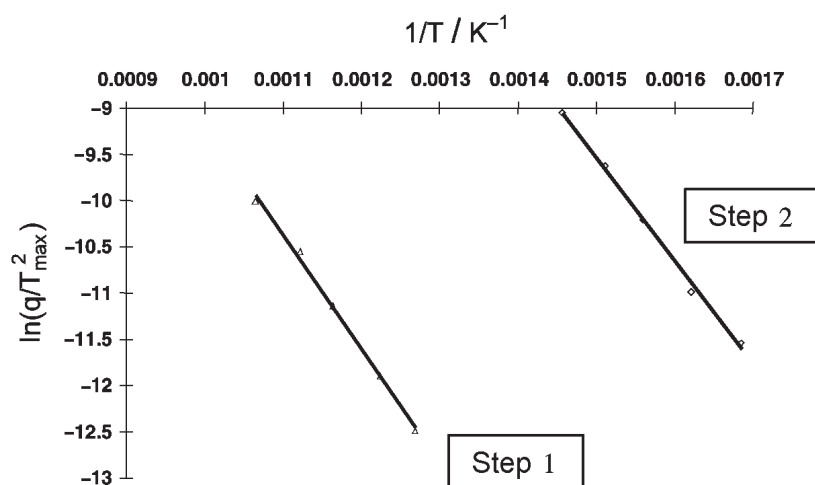


Fig. 3 Kissinger plots of epoxy/carbon composite in nitrogen

conditions he recommended to assign uncertainties to the quantities $\ln A$ and E . In this study the T_{\max} was determined with good precision but experiments at low heating rate until $2^{\circ}\text{C min}^{-1}$ presents some difficulties to determine precisely this value in air flow. For Abate *et al.* [5], at lower heating rate the chain scission was higher than branching and crosslinking rates in nitrogen. In an oxidative atmosphere, the degradation were due to several processes which were simultaneous at low scanning rates.

Table 3 Kinetic parameters calculated from Kissinger equation for the degradation of epoxy/carbon composite in nitrogen and air flow

Atmosphere	$q/^{\circ}\text{C min}^{-1}$	$a=E/R$	$\ln A$	r^2	$E_a/\text{kJ mol}^{-1}$
Nitrogen	1–20	11.1	7.1	0.9962	92
		12.3	3.2	0.9960	103
		15.9	15.9	0.9954	132
Air	0.5–20	18.5	12.7	0.9840	154
		12.9	1.2	0.9944	108

However the activation energy estimated at about 108 kJ mol^{-1} for the third step in air and corresponds to the degradation of carbon fibres. These results are in accordance with the literature [6].

A variation of the procedure shown above can be used to evaluate a dependence of the apparent activation energy on the extent of conversion. We employed an advanced isoconversional method which is based on the assumption that the reaction model is independent of the heating rate and calculate an overall apparent activation energy from the dynamic TG data. Using the method of Ozawa [7], the rate of mass loss can be represented by the equation:

$$\frac{d\alpha}{dT} = \frac{A}{q} \exp\left(\frac{-E}{RT}\right) g(\alpha) \quad \text{or} \quad g(\alpha) = \int_0^\infty \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{q} \int_0^T \exp\left(\frac{-E}{RT}\right) dT = \frac{AE}{qR} p(x) \quad (4)$$

The logarithmic function of Eq. (4) gives:

$$\log g(\alpha) - \log p(x) = \log \frac{AE}{qR} \quad (5)$$

$\log(AE/qR)$ is independent of temperature even though $\log g(\alpha) - \log p(x)$ depends on it. To a first approximation $\log p(x)$ is a linear function of $1/T\alpha$ if x is sufficiently high, $\log g(\alpha)$ vs. $1/T\alpha$ should be linear. So the Ozawa method is based on the following expression,

$$\log g(\alpha) \cong \log \frac{AE}{R} - \log q + \log p\left(\frac{E}{RT}\right) \quad (6)$$

and uses Doyle's approximation for $\log p(E/RT)$. If $20 < E/RT < 60$, the integral $p(x)$ could be expressed as

$$\log p\left(\frac{E}{RT}\right) \cong -2.135 - 0.457 \frac{E}{RT} \quad (7)$$

and

$$\log g(\alpha) \cong \log\left(\frac{AE}{R}\right) - \log q - 2.135 - 0.457 \left(\frac{E}{RT}\right) \quad (8)$$

Differentiating Eq. (6) at constant conversion,

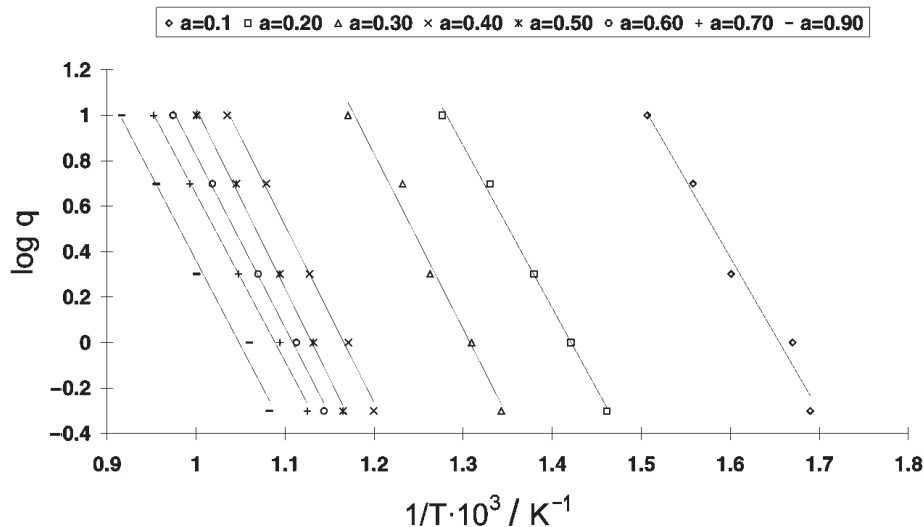


Fig. 4 Arrhenius plots of dynamic TG experiments in air of epoxy/carbon composite

$$E = \frac{R}{0.457} \frac{\log\left(\frac{q_1}{q_2}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \quad (9)$$

The activation energy could be obtained from a plot of $\log q$ vs. $1/T$ for α constant. Moreover, $\log A$ could be calculated from the intersection of the Y axis.

$$\log A = \log q + \frac{0.457}{RT} + 2.315 - \log E + \log R + \log g(\alpha)$$

Table 4 Activation energy and correlation coefficient of epoxy/carbon calculated from dynamic TG runs

α	Air		Nitrogen	
	$E_a/\text{kJ mol}^{-1}$	R^2	$E_a/\text{kJ mol}^{-1}$	R^2
0.03	119.0	0.9919	97.0	0.9928
0.04	114.0	0.9813	110.0	0.9982
0.05	129.0	0.9947	100.0	0.9886
0.06	120.5	0.9855	119.0	0.9982
0.07	134.0	0.9979	109.0	0.9912
0.08	127.0	0.9866	131.0	0.9993
0.10	124.0	0.9902	142.0	0.9942
0.11	124.0	0.9951	161.0	0.9868
0.13	112.0	0.9946	161.0	0.9767
0.14	117.0	0.9975	150.0	0.9839
0.16	112.0	0.9933	143.0	0.9898
0.20	130.0	0.9982	115.0	0.9911
0.22	136.0	0.9989	115.0	0.9946
0.25	144.0	0.9972	110.0	0.9954
0.27	139.0	0.9865	113.0	0.9982
0.30	140.0	0.9912	119.5	0.9999
0.35	133.0	0.9954	138.0	0.9995
0.40	142.0	0.9980	129.0	0.9997
0.45	141.0	0.9982	117.0	0.9995
0.50	144.0	0.9989	111.0	0.9997
0.60	138.0	0.9987	99.0	0.9983
0.70	134.0	0.9987	102.0	1.0000

Constant mass loss lines are determined by measuring the temperature at a given mass percent for each rate. In Fig. 4 the Arrhenius type plots of dynamic TG runs are

shown for mass ranging from $\alpha=0.1$ to 0.9 in air flow. Table 4 summarises the activation energy and the correlation coefficient on the overall mass loss from 3 to 70 mass% in air and inert flow. The results indicate an acceptable correlation coefficient always superior to 0.975.

Figure 5 shows the energy dependencies evaluated from the thermal degradation of epoxy/carbon composite in nitrogen and air.

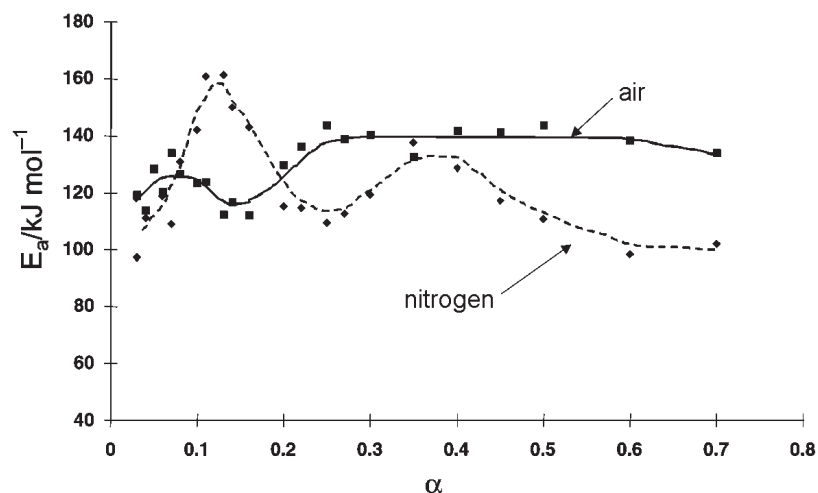


Fig. 5 Epoxy/carbon E_a calculated from dynamic TG in air and nitrogen flow

In nitrogen atmosphere, the evolution of activation energy is noted by a lower value in the beginning of the degradation. The initial E_a required to initial decomposition was about 100 kJ mol^{-1} . When 10% mass of composite is lost the activation energy increases to a maximum value of about 160 kJ mol^{-1} . This is followed by a decrease from 160 to 100 kJ mol^{-1} in the region $0.25 < \alpha < 0.7$. This decrease corresponds to the transition region between the first and the second step in the mass loss. For conversion $\alpha > 0.3$ the activation energy is characterised by the decomposition of carbon fibre.

The thermal degradation of composite in air presents a different behaviour. The initial energy dependence is a little bit superior and was estimated about 120 kJ mol^{-1} . The energy slowly decreases to a minimum value of 110 kJ mol^{-1} at $\alpha=0.15$ and then rises to about a stable value of 140 kJ mol^{-1} in the region $0.25 < \alpha < 0.7$.

Discussion

The thermal degradation of epoxy polymers is usually illustrated by one or two mass loss steps. Previous studies in our laboratory [8] have shown that the initial degradation of epoxy material induces a dehydration of hydroxyl functions. Then the aliphatic polyether area corresponding to the polyaddition of oxirane functions was decomposed. This new chemical structure of degraded epoxy presents a new conju-

gated carbons. The decomposition of this network corresponds to the second mass loss step in TG experiments.

In an oxygen-containing atmosphere, the radicals formed during the initiation reaction react rapidly with oxygen to develop a new polymer radical. The peroxide radical is more thermally stable than the polymer degraded in the absence of oxygen. The decomposition energy is generally about 100 kJ mol^{-1} and thus inhibits the structure breakdown. The peroxide radical degradation occurs through network scission that produces low molecular mass species able to vaporise. Brown and Kashiwagi [9] explained the stabilising effect of oxygen. The oxygen attacks hydrogen activated groups to form a hydroperoxide which undergoes a β scission and gives a hydroxy-terminated polymer and products which contain carbonyl functions. Oxygen also promotes random scission. This process is accompanied by elimination of different chemical species (water, ester...). Another mechanism [10] includes an irreversible formation of PO_2^* which traps oxygen in the polymer structure after rearrangements and eliminates a typical molecule (methyl pyruvate) but the amount of the vaporised molecule seems to exceed the maximum theoretical yield.

The activation energy dependence on the degradation in nitrogen shows clearly in Fig. 5 that the degradation of epoxy cannot be described by a single value of activation energy. The first step of mass loss accounts for $\alpha=0.1$ of the initial mass. The apparent activation energy for this step illustrates an increase from 100 to 160 kJ mol^{-1} at $0.03 < \alpha < 0.12$. Degradation starts at the weak linkages whose concentration is high at low extents of degradation. Therefore, the network breakdown of epoxy controls the overall degradation rate. At $\alpha=0.12$ E_a is about 160 kJ mol^{-1} . This value gives us an estimate for the effective activation energy degradation limited by initiation [11]. According to TG data (Fig. 2), $\alpha=0.12$ corresponds to the beginning of the second step. Once the initiation reaction has produced sufficient number of reaction centres, the network scission becomes the rate controlling step and the apparent activation energy decreases to 110 kJ mol^{-1} in the region $0.12 < \alpha < 0.3$. The third step of mass loss $\alpha > 0.3$ seems to be assigned to the carbon fibres decomposition. This process is accompanied by a decrease of E_a down to a value of 100 kJ mol^{-1} .

For a degradation in air and according to the reaction of oxygen, the delayed decomposition starts as the decomposition of polymer peroxide (PO_2^*) to polymer radical (P^*). The overall rate of degradation should be determined by the rate of both formation P^* occurring from PO_2^* and network scission. The observed apparent activation energy dependence is consistent with the occurrence of degradation pathways. For $0.02 < \alpha < 0.1$ E_a does not really vary. The increase in apparent E_a reflects a decrease contribution of the alternative pathway (formation of P^* from PO_2^*) to the overall degradation rate. For $0.25 < \alpha < 0.7$, the apparent E_a is about 140 kJ mol^{-1} . The increase in the activation energy is associated with the increasing contribution of degradation initiated by network breakdown to the overall degradation rate.

Conclusions

The determination of the kinetic parameters using TG experiments have been studied to explain the stabilising effect of oxygen on the thermal degradation of a carbon fibre reinforced epoxy. Kinetic analysis suggests that the initial rates of degradation in nitrogen and air are respectively controlled by evaporating low molecular mass species forming a new conjugated carbon polymer and by the degradation of peroxide radical. The formation of the peroxide radical is reversible. An increase of temperature should favour the reverse reaction: the peroxide radical is decomposed to oxygen and a new radical. The activation energy of these processes are determined to be 100 kJ mol^{-1} for the evaporating low molecular mass species forming a new conjugated carbon polymer and more than 130 kJ mol^{-1} for the degradation of peroxide radical.

At the second stage the thermal degradation is controlled by the polymer network scission in both nitrogen and air. The influence of the gaseous atmosphere does not affect the apparent activation energy. The activation energy of degradation initiated by network scission in nitrogen is estimated to be 160 kJ mol^{-1} . This value gives a rough estimation for a similar process in air. The degradation apparent E_a initiated by network breakdown in air is in accordance and is about 140 kJ mol^{-1} .

The later decomposition stage corresponds to the thermal degradation of the carbon fibre. The activation energy was estimated to be 100 and 140 kJ mol^{-1} in nitrogen and air, respectively.

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