

Soft ionisation analysis of evolved gas for oxidative decomposition of an epoxy resin/carbon fibre composite

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Abstract

Soft ionisation mass spectrometry was used to investigate the oxidative decomposition of an epoxy resin/carbon fibre composite using thermogravimetry (TG) coupled with mass spectrometry (MS). Through comparison between decomposition in air and in argon, it was recognized that the first step of the oxidative decomposition of the epoxy resins was similar to the decomposition in argon. During the devolatilisation process, the oxidative decomposition underwent a thermal decomposition leading to the formation of a large amount of volatile products which were subsequently oxidized into water and carbon dioxide. The gas produced in the thermal decomposition was not oxidized completely leaving some organic volatiles in the emissions. Using soft ionisation, the components of the evolved gases were identified by mass spectrometry.

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1. Introduction

Carbon fibre/epoxy resin composites have been widely used in aeronautical, automotive and sports goods industries. During the manufacture of these thermoset composites, a high scrap rate and significant amounts of off-cuts and rejects are generated, in contrast to the manufacturing of thermoplastic composites [1]. Together with end-of life components, the amount of waste carbon fibre composites has reached a significant level. At present time, the waste composites are mostly disposed of in landfill because there is no economic means of recycling the materials. This raises concerns regarding non-degradable wastes and also the loss of high value carbon fibre. An effective recycling process is therefore highly desirable in order to reclaim the high value carbon fibre and reduce the amount of waste going to landfill.

Recycling the thermoset polymer composites has been extensively studied, such as by pyrolysis (decomposition of the polymer matrix in the absence of oxygen) [2,3], chemical decomposition of the polymer matrix [4] and by using catalysts to decompose the polymer matrix [5,6] to form a mixture of organic chemicals. However, the above methods leave a layer

of char or non-decomposed matrix on the fibres. A further procedure is often needed to remove the impurities by oxidation in order to clean the recovered fibres [7]. Although these methods can recycle a fraction of polymer matrix, the value of the complex mixtures of organics produced from pyrolysis or catalytic decomposition has not been assessed. Oxidative decomposition of an epoxy resin matrix is an alternative method for recycling thermoset carbon fibre composites [8,9]. The oxidative decomposition is usually performed in a high temperature fluidised bed. The bed is set at a constant temperature between 500 and 650 °C. Scrap composites are then fed into the rig to decompose the polymer matrix at this temperature, and the fibres released are elutriated from the bed. This method produces clean fibres, which can be used without further treatment [9] and thermal energy from the oxidation of the matrix can be recycled [10].

Understanding the oxidative decomposition is essential to make use of the fluidised bed process to recycle carbon fibre. Although extensive research has been performed on the pyrolysis of epoxy resin in an inert gas atmosphere [11–13], the literature on the oxidative decomposition is scarce. Bishop and Smith [14] gave a review covering the literature up to 1966 for oxidative degradation of epoxy resin focusing on its thermal stability and oxidation mechanism. Recently, some work has been done on the kinetics of oxidative decomposition of epoxy resin using thermogravimetric analysis (TGA). For example, Chen et

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al. [15] investigated the decomposition kinetics of a bisphenol A type of epoxy resin in a nitrogen/oxygen atmosphere at various ratios. Regnier and Fontaine [16] investigated the features of the decomposition activation energy of the composite of the same type of epoxy resin reinforced with carbon fibre. In the above research, no attempts were given to identify the oxidative decomposition products.

For the high temperature fluidised bed process, it is important to identify the oxidative decomposition products and to determine the proportion of volatile organic compounds (VOC) in the emissions for the design of actual systems and for the control of potential emission problems. In this work, TGA was used to analyse the decomposition of epoxy resins at a fast heating rate, simulating the heating conditions in the high temperature fluidised bed. A mass spectrometer (MS) was coupled with the TGA in order to analyse the evolved gases during oxidative decomposition of the epoxy resin/carbon fibre composites. When using MS, the excited electrons for electron ionisation of the sample gas conventionally have energies of the order of 70 eV, which leads to extensive fragmentation of the ions produced. However, this high energy results in difficulties in identifying gas species generated in the decomposition of epoxy resins since the evolved gas is a mixture of gaseous species. In an attempt to overcome this problem, a soft ionisation technique was used to help identify the gas species, in which a much lower electron energy is used to ionise gas samples, thus much simplifying the identification work.

2. Experimental

2.1. Materials

The commercial composite was provided by Advanced Composite Group Ltd. in a prepreg form, containing 58% (weight) PAN based high strength carbon fibre Grafil 34-700 and 42% (weight) Bisphenol A-epichlorohydrin (DGEBA) type epoxy resin LTM26EL. The continuous carbon fibres in the composite had a diameter of 7 μm and were unidirectionally distributed in the sample. The DGEBA type epoxy resins are most widely used as the matrix of epoxy resin/carbon fibre composites. The prepreg had a thickness of about 0.2 mm. The sample size for TGA test was about 15 mg, which was cut into pieces of 2 mm \times 2 mm. The sample was then put into an open platinum sample pan of the TGA apparatus.

2.2. DTA-TG-MS analysis

The DTA-TG analysis was performed with a TA Q600 simultaneous differential thermal analyser coupled via a heated capillary to a HidenAnalytic HPR20 mass spectrometer. The ions were produced by an electron ionisation method, analysed using a quadrupole mass analyser and detected using a secondary electron multiplier (SEM). The decomposition experiments were conducted in an air or argon atmosphere at a flow rate of 100 $\text{cm}^3 \text{min}^{-1}$. Various heating rates were used to study the decomposition features of the epoxy resin. For simulating the heating conditions in a high temperature fluidised bed, the

Table 1
First ionisation energy for some species

Species	First ionisation energy (eV)
N ₂	15.58
O ₂	12.07
H ₂	15.43
Ar	15.76
CO ₂	13.77
CO	14.01
CH ₄	12.61
C ₂ H ₄	10.51
C ₂ H ₆	11.56

temperature was heated rapidly to 550 °C (300 °C min^{-1}) and then that temperature was maintained for 40 min.

2.3. Soft ionisation technique to identify gas components

For identifying the species evolved from the epoxy resin decomposition using the mass spectrometer, an electron energy of 15 eV was used with an emission current of 100 μA . This electron energy will not fragment organic species much and the m/z peaks correspond to the parent ions since the first ionisation energy of most organic species is around 9–15 eV and those of nitrogen and argon are higher than 15 eV [17]. The first ionisation energies of most organic species are reproduced and shown in Table 1. The first ionisation energy of oxygen is 12.6 eV, which will appear in the mass spectrum.

2.4. Evolved gas profile

After identifying the species produced, the multiple ion detection (MID) mode was used to monitor the evolved gas profile with time, using the MS to detect ions at particular m/z numbers. At this stage, an electron energy of 70 eV was used in order to have strong enough signals and to obtain fragmentation information. From the evolved gas profiles, concentrations of the various species were estimated.

3. Results and discussion

3.1. Characteristics of epoxy resin/carbon fibre composite decomposition

Fig. 1 shows heat evolution, mass loss and derivative mass loss (DTG) for the decomposition of an epoxy resin composite in air and argon with a heating rate of 10 °C min^{-1} . From the TG-DTG traces, it can be seen that the decomposition in argon had only a devolatilisation stage, which started at 320 °C and ended at 460 °C, and resulted in a mass loss of 27%. Since carbon fibre content in the composite was 58% (wt), there was up to 35% of the resin left on the fibre surface, most likely in the form of char. The decomposition in air underwent several stages. The devolatilisation process started and ended at the same temperatures as those in argon, and resulted in a comparable weight loss of 27%. The devolatilisation stage had two steps, corresponding to two peaks at 360 and 420 °C respectively as shown in the DTG

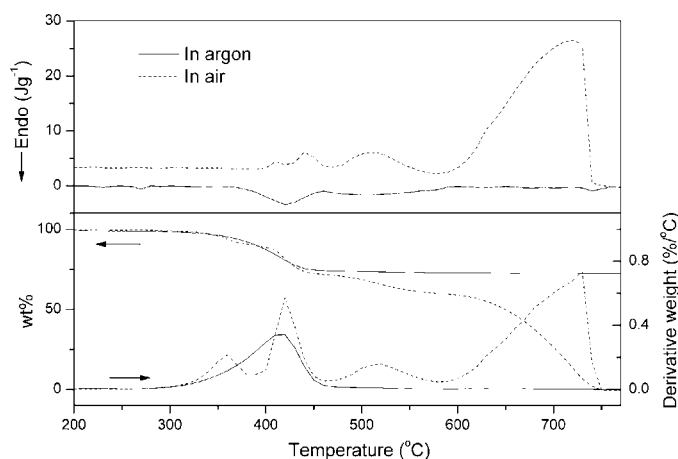


Fig. 1. TG and DTA traces for the decomposition of the epoxy resin/carbon fibre composite in air and in argon, with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

curve. Unlike the decomposition in argon, any char left on the fibre surface will be oxidized. This started at $460\text{ }^{\circ}\text{C}$ and ended at $580\text{ }^{\circ}\text{C}$, resulting in a mass loss of 15%. This process is slower compared with devolatilisation. The last stage was oxidation of the carbon fibre, corresponding to the strong peak at $730\text{ }^{\circ}\text{C}$ in the DTG curve. The weight loss for the last stage was 58% and corresponded well with the carbon fibre weight fraction for the composite.

From the DTA traces in Fig. 1, it can be seen that the decomposition in air was an exothermic process, while the decomposition in argon was endothermic. The peaks from the DTA and TG-DTG traces are listed in Table 2. For the decomposition in argon, the endothermic peak in DTA occurred at the same position as in DTG. For the oxidation in air, all the peaks corresponding to the decomposition of epoxy resin occurred earlier in DTG than in DTA. This suggests that oxidation of the evolved gases occurred later than they were released. Since the sample had a thickness of 0.2 mm , the oxidation of evolved gases on the surface heated the sample locally. This may be responsible for the appearance of two peaks during the devolatilisation in air.

Figs. 2 and 3 show the gas evolution profiles in the above experiment for the decomposition in air and in argon respectively. The evolution of four species appearing in the gas evolved was analysed. $m/z = 18$ and 44 were assigned to water and CO_2 , respectively, and $m/z = 2$ and 26 were from organic volatiles, the assignments of which were given in detail in the following sections. A lot less CO_2 were produced for the decomposition

Table 2
The peaks for the decomposition of an epoxy/carbon fibre composite in argon and air

	In argon		In air	
	DTG	DTA	DTG	DTA
Devolatilisation	420	420	360	410
	–	–	420	440
Char oxidation	–	–	510	520
Carbon fibre oxidation	–	–	730	730

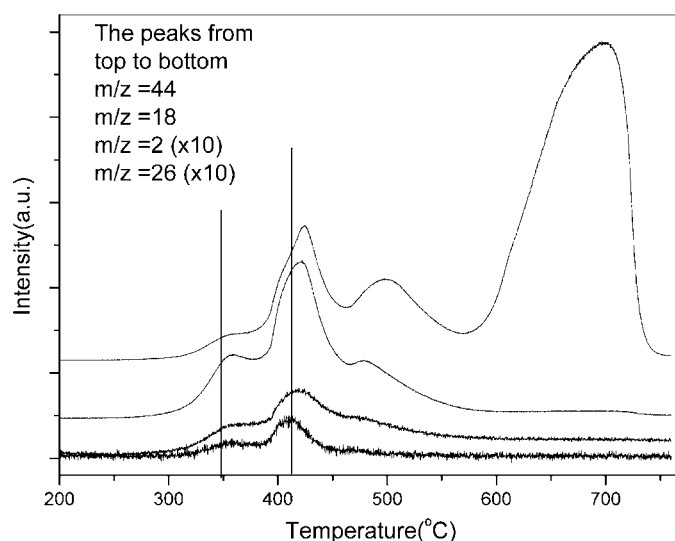


Fig. 2. MS evolved gas profiles for oxidative decomposition of the epoxy resin/carbon fibre composite with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

in argon comparing with the decomposition in air. In Fig. 2, the strong CO_2 peak at $730\text{ }^{\circ}\text{C}$ corresponded to the oxidation of carbon fibre. There were no peaks for $m/z = 2, 18$ or 26 during carbon fibre oxidation.

For the decomposition in air, the patterns of all the four gas evolution profiles were similar except that CO_2 profile had a strong peak corresponding to carbon fibre oxidation. However, the peaks corresponding to the organic volatiles were $10\text{ }^{\circ}\text{C}$ to the left of those for water and CO_2 at both positions for the devolatilisation stage, which indicates that they were released earlier than water and CO_2 . In contrast, for the decomposition in argon as shown in Fig. 3, the positions of all the peaks were within $1\text{ }^{\circ}\text{C}$, indicating that they were produced simultaneously.

To simulate the heating conditions in a high temperature fluidised bed, heating rates up to $300\text{ }^{\circ}\text{C min}^{-1}$ were used to in

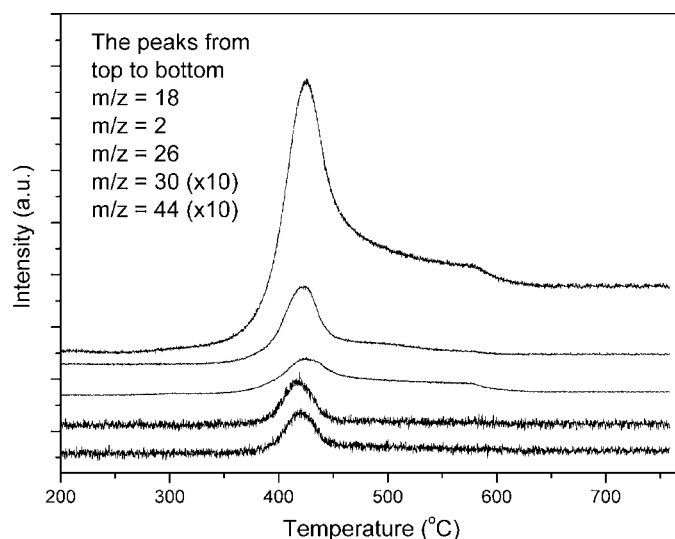


Fig. 3. MS evolved gas profiles for decomposition of the epoxy resin/carbon fibre composite in argon with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

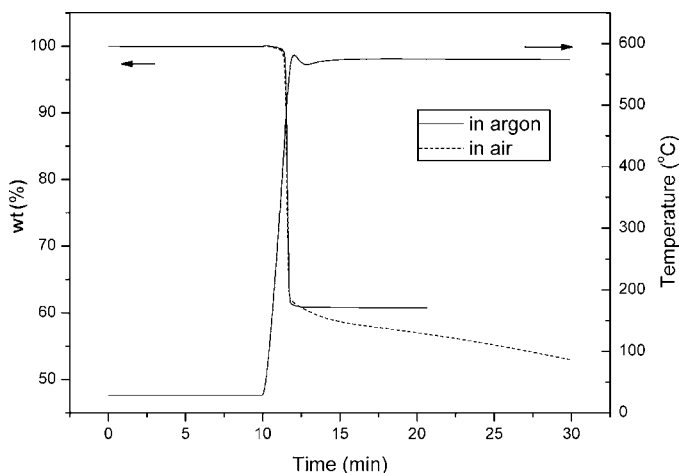


Fig. 4. TGA traces of the epoxy resin/carbon fibre decomposition in argon and in air with a heating rate of $300\text{ }^{\circ}\text{C min}^{-1}$.

the thermogravimetric analysis. The earlier occurrence of the organic volatiles was more clearly shown when a fast heating rate was used. Fig. 4 shows the mass loss curve of the decompositions at $560\text{ }^{\circ}\text{C}$ in air and in argon with an initial heating rate of $300\text{ }^{\circ}\text{C min}^{-1}$. The corresponding evolved gas profiles are shown in Figs. 5 and 6. For the decomposition in air, there were still two processes (devolatilisation and char oxidation), but these two processes were not separated clearly with the char oxidation starting before devolatilisation has finished during the rapid temperature ramp. After 6 min, all of the char was oxidized and the carbon fibre started to be oxidized. Due to the fast heating rate, gases were produced in a short time interval. Thus, they are less diluted in the carrier gas, resulting in stronger peaks than those at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Therefore, more species were detected. For the oxidative decomposition, it is clearly shown in Fig. 5 that the organic species were released 0.5 min earlier, while all of the organic volatiles were released simultaneously for the decomposition in argon as shown in Fig. 6.

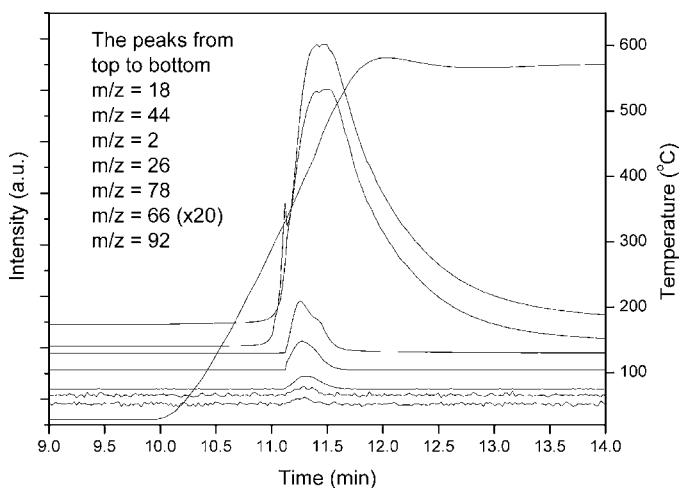


Fig. 5. MS evolved gas profiles for the oxidative decomposition of epoxy resin/carbon fibre composite with a heating rate of $300\text{ }^{\circ}\text{C min}^{-1}$. An electron energy of 70 eV was used for the detection.

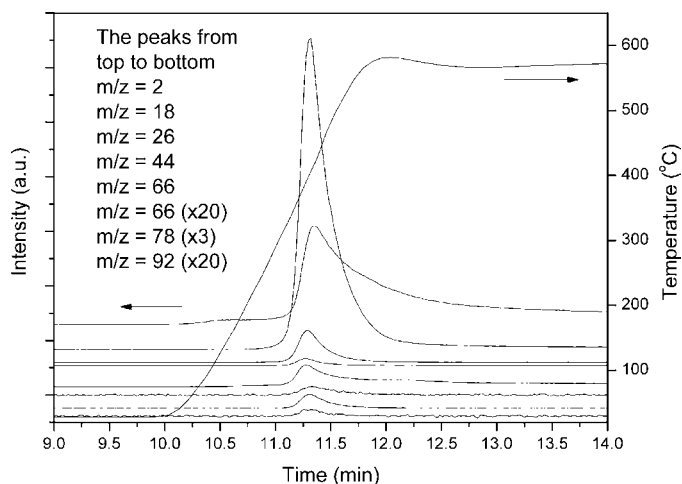


Fig. 6. MS evolved gas profiles for the decomposition of epoxy resin/carbon fibre composite in argon with a heating rate of $300\text{ }^{\circ}\text{C min}^{-1}$. An electron energy of 70 eV was used for the detection.

It can be seen that all of the gases were produced simultaneously for the decomposition in argon. However, water and CO_2 were released later than organic volatiles when oxygen was present. This indicates that the first step of the oxidative devolatilisation was the same as the decomposition in argon, which may be termed as ‘thermal decomposition’. In the thermal decomposition, a large amount of organic volatiles were produced. When oxygen was present, some of the organic volatiles were oxidized subsequently reducing the fraction of emissions. This was also indicated by the later occurrence of the exothermic peaks than the weight loss peaks as shown in Table 2.

The amount of epoxy resin transformed into CO_2 can be calculated using the area for the CO_2 peak corresponding to carbon fibre oxidation at around $700\text{ }^{\circ}\text{C}$ as the amount of carbon fibre in the sample was known. The amount of carbon in the epoxy resin that was transformed into CO_2 can be calculated from the total area of the first three peaks ($350\text{ }^{\circ}\text{C}$, $430\text{ }^{\circ}\text{C}$ and $500\text{ }^{\circ}\text{C}$) at the trace of $m/z=44$ as shown in Fig. 2. The amount of carbon that was transformed into organic volatiles will be the difference between the total carbon in the epoxy resin and the carbon oxidized. The organic volatiles based on the epoxy resin can then be calculated using Eq. (1).

$$x = 1 - \frac{A_2 m_1}{A_1 c m} \quad (1)$$

where x is the percentage of epoxy resin converted to organic volatiles, A_1 the area of the peak carbon fibre oxidation ($700\text{ }^{\circ}\text{C}$), A_2 the total area of the peaks at 350 , 430 and $500\text{ }^{\circ}\text{C}$, c the carbon content of the epoxy resin (obtained using elemental analysis), and m_1 is the mass of carbon fibre in the sample, and m_2 is the mass of epoxy resin in the sample. Since the overlapping part between the peaks at 500 and $700\text{ }^{\circ}\text{C}$ were much smaller compared with A_1 and A_2 , complex peak splitting technique were not adopted. The lowest point between the two peaks was used as the end point for calculation of the areas, which led to less than 1% error.

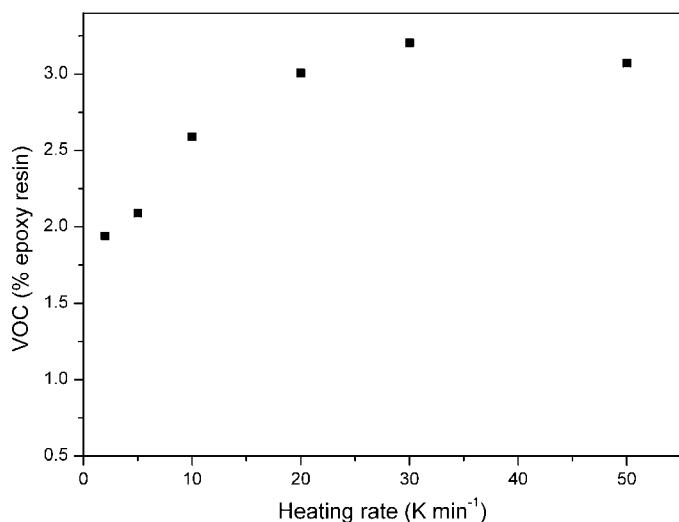


Fig. 7. The amount of volatile organics in emission based on epoxy resin vs. heating rate for oxidative decomposition of the epoxy resin/carbon fibre composite.

In order to estimate the volatiles produced with a very fast heating rate, as in a fluidised bed, various heating rates were used to decompose the composite. The amount of organic volatiles based on the epoxy resin was calculated using the above method. Fig. 7 shows the amount of organic volatiles against heating rate. For a heating rate of $2\text{ }^{\circ}\text{C min}^{-1}$, the epoxy resin transformed into volatiles was 1.8%. With the increase of the heating rate, the amount of volatiles also increased. However, the volatiles produced levelled off at around 3% for higher heating rates. At a fast heating rate, the amount of organic volatiles was produced in a shorter time interval, but oxygen supply was not increased. Hence oxygen may be in a state of deficiency. It can thus be inferred that the amount of epoxy resin transformed into volatiles is around 3% for a very fast heating rate such as in a fluidised bed.

3.2. Identification of evolved gas species using soft ionisation

As is well known, electron impact ionisation in mass spectrometry can produce extensive fragmentation of molecules, giving a large number of positive ions of various masses that are less than that of the parent ions. This is clearly shown in Fig. 8, showing the mass spectra for the decomposition of the epoxy resin/carbon fibre composite under an atmosphere of argon, which were detected using ionisation energies of 25 and 70 eV respectively. When the ionisation energy was 25 eV, the peaks at low m/z values were very strong, but the peaks at high m/z values were very weak. When the ionisation energy was increased to 70 eV, the peaks at m/z 's greater than 78 were not detectable. This constitutes a problem for analysing gas mixtures in the epoxy resin decomposition. In order to analyse the evolved gases, a lower ionisation energy should therefore be used. Table 1 lists the first ionisation energies of some species [17]. As can be seen, nitrogen and argon have ionisation energies higher than 15 eV. However, most of the organic species have ionisation energies

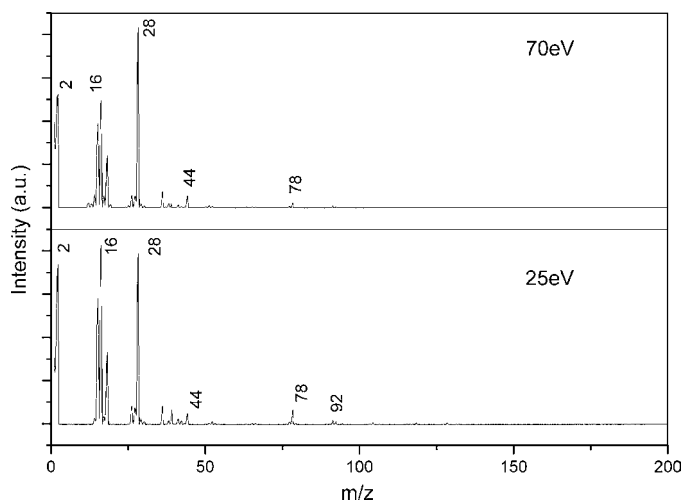


Fig. 8. Mass spectra of the decomposition of the epoxy resin/carbon fibre composite in argon detected using higher ionisation energy. The peaks for argon have been subtracted.

lower than 15 eV. Therefore, an ionisation energy of 15 eV was used to avoid extensive fragmentation.

Fig. 9 shows the mass spectra of the decomposition of the epoxy resin/carbon fibre composite in argon and air with an ionisation energy of 15 eV. It can be seen that m/z values greater than 78 were detected, and most of the ions can be considered as parent ions due to lower fragmentation. The spectrum of the gas evolved under an atmosphere of argon was much more complex than that under an atmosphere of air. For the decomposition in air, all the m/z peaks appeared in the mass spectrum for decomposition under argon but the intensities are different. This further justifies that the first step of the oxidative decomposition is the same as the decomposition in argon. Some of the volatiles produced in the thermal decomposition were oxidized into water and CO_2 .

Since hydrogen has a first ionisation of 15.43 eV, it was not detected. Due to the low sensitivity of CO_2 , the intensity was very low. However, a peak at $m/z = 2$ appeared when an ionisation

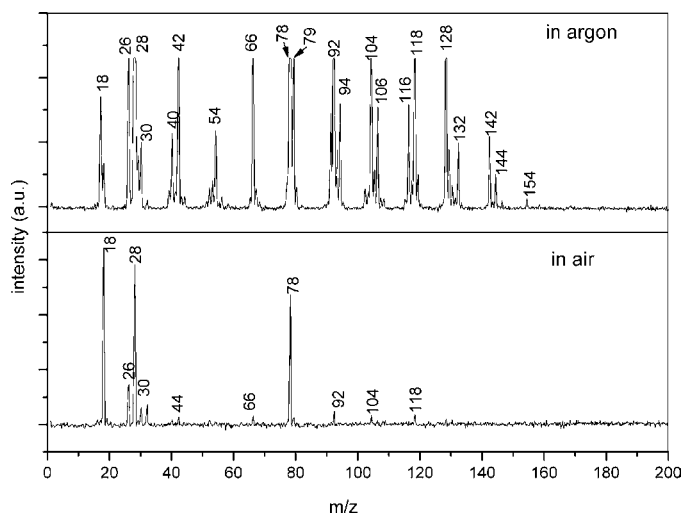


Fig. 9. Mass spectra of the evolved gas of the oxidative decomposition of epoxy resin/carbon fibre composite detected using an electron energy of 15 eV.

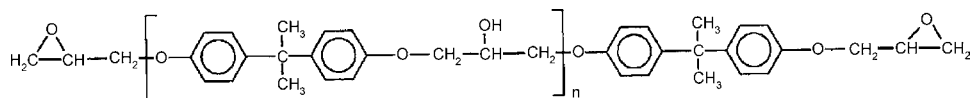


Fig. 10. The structure of uncured epoxy resin (DGEBA).

energy of 70 eV was used as shown in Fig. 8, and this peak was very strong compared with the peaks at other positions except for water and CO₂. The peak at $m/z=2$ was thus attributed to hydrogen.

Lee [11] and Bishop and Smith [12] have studied in detail the decomposition of DGEBA type epoxy resin under an atmosphere of nitrogen. The structure of the uncured resin is shown in Fig. 10. They identified the organics with molecular weight less than 100. Their assignments are reproduced in Table 3, in which the species with a molecular weight greater than 100 were deduced by the aid of the molecular structure of the epoxy resin in this work and the work of Pielichowski and Njuguna [18]. In their work, the possible degradation routes of epoxy resin were summarised, i.e. homolytic cleavage of bisphenol-A unit, heterolytic cleavage of the bisphenol A unit and cyclisation product of the glycidyl ether side chains to yield C₆H₅-O-C₃H₃ or C₆H₄-O-C₃H₄. As has been discussed previously, the first step of the oxidative decomposition was the same as the decomposition under argon. The decomposition products were subsequently oxidized leaving some traces of organic species. Therefore, the peaks in the mass spectrum for the oxidative decomposition were assigned to the same species as those corresponding to the decomposition under argon, which are given in Table 4. It can be seen that the organic volatiles from the emissions of oxidative decomposition contained various compounds. With the help of the identification of the organic volatiles and their proportions in the emissions, a post oxidation

Table 3
Assignments of each m/z for the decomposition of epoxy resin/carbon fibre composite under an atmosphere of argon

m/z	Possible molecules
18	Water
26	Ethyne
28	Ethylene
30	Ethane
40	Allene
42	Propylene
44	Carbon dioxide
54	Unknown
66	Cyclopentadiene
78	Benzene
92	Toluene
94	Phenol
104	Styrene
106	Ethylbenzene
116	3-Propynylbenzene
118	Allylbenzene
128	Ethynlstyrene
132	C ₆ H ₄ OC ₃ H ₄
142	Isopropylstyrene
144	Isopropylethylbenzene
154	Biphenyl

Table 4
The assignments of the peaks in the mass spectrum for oxidative decomposition of the epoxy resin

m/z	Possible molecules
2	Hydrogen
18	Water
26	Ethyne
28	Carbon monoxide and ethylene
30	Ethane
44	Carbon dioxide
66	Ethyl chloride
78	Benzene
92	Toluene
104	Styrene
118	Allylbenzene

process may be designed to reduce hazardous gases to the environment during recycling carbon fibre from epoxy composites using oxidative decomposition process.

4. Conclusions

In this work, the decomposition products of a DGEBA type epoxy resin/carbon fibre composite was analysed using DTA-TG-MS. By comparison with the decomposition under an inert gas atmosphere, it is found that the first step of the oxidative decomposition is similar to that for the decomposition under an inert atmosphere. A number of organic species are produced by thermal decomposition and these species are subsequently oxidized into water and CO₂. However, the oxidation is not complete, leaving some 3% of the resin as organic volatiles in the emissions. Therefore, the emissions from oxidative decomposition of epoxy resin/carbon fibre composites should be controlled carefully. Soft ionisation provides a mass spectrum, in which most of the peaks in the spectrum are molecular ions. This is useful for the recognition of the organic species with the aid of recognition work under nitrogen since the first steps for the two decompositions are similar.

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