INVESTIGATION INTO THE USE OF METAL OXIDES FOR CATALYSED EPOXY RESIN DECOMPOSITION

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ABSTRACT

An investigation into catalysed thermal decomposition of epoxy resin was carried out with the goal to improve the commercial viability of glass fibre reinforced plastic recycling. A variety of metal oxides were examined to find their ability at reducing current limitations associated with thermal recycling methods such as high operating temperatures and exposure time to such environments. Thermogravimetric analysis (TGA) was utilised to determine the effect of copper (II) oxide (CuO), titanium (IV) oxide (TiO_2) and cerium (IV) oxide (CeO_2) on epoxy degradation. CuO and CeO_2 provided a reduction in second stage degradation onset temperature of around 60°C under a non-isothermal heating rate of 10°C/min; however, TiO_2 exhibited no such ability. Under isothermal heating conditions, at a temperature of 500°C, all metal oxides provided a reduction in full epoxy decomposition time. CuO yielded the fastest epoxy degradation, reducing it by 12 minutes compared to epoxy alone. The epoxy first and second degradation stage activation energies were found through a kinetic study; with and without the addition of the metal oxides. It was observed that CuO transformed the epoxy degradation into a one stage process at heating rates of 30°C/min and above. CeO_2 lowered the second stage activation energy however TiO_2 caused an increase in both cases. The reduction in epoxy thermal decomposition temperature and time presented by CeO_2 and CuO is believed to be sufficient justification for further investigation. Future work will focus on how the improvement in recycling conditions can translate into recovered glass fibre strength retention.

1 INTRODUCTION

In recent years there has been a large increase in the use of glass fibre as a composite reinforcement material; accounting for 90% of all fibre reinforced composites produced [1]. The annual global production of glass fibre composites is approaching 10 million tons; with thermoset based polymers accounting for 60% of the market [2]. Their low production cost and good specific mechanical properties have made them ideal materials to use in many engineering sectors; predominantly the renewable energy and transport industries [3,4]. A consequence of this increase in demand is a large amount of end-of-life products. Increasing pressure through new government legislation is forcing the end-user to dispose of end-of-life thermoset composites in an eco-friendly manner. The polymer cross-linking which occurs during thermoset curing results in a material which, unlike thermoplastics, cannot easily be thermally recycled. Factors such as energy consumption and the extensive damage to the fibres associated with current thermal recycling methods makes them not financially competitive compared to purchasing new material; meaning most waste is destined for landfill.

Thermal recycling processes involve the decomposition of the thermoset matrix at temperatures as high as 600°C. Energy can subsequently be recovered through full combustion of the gases produced as a result of this decomposition. [5]. The thermoset decomposition temperature, process time and surface damage caused during processing renders the fibres unusable in high strength components. *Feih et al.* reports a glass fibre strength loss of around 60% after just 8 minutes when heat treated at 550°C. This strength loss is increased to 70% after thermal conditioning at 600°C for 15 minutes [2,6].

Fluidised bed systems have been shown to successfully recover glass fibre from thermosetting resins; however, work must be carried out to develop an approach capable of reducing any/multiple thermal recycling limitations [7]. A closed-loop recycling system could be made cost effective by retaining the glass fibre mechanical properties, allowing them to be reused in high strength components. A novel method to aid the decomposition of thermoset matrices in glass fibre reinforced composites is underway by investigating the use of metal oxide catalysts. It is proposed that an oxide catalyst could potentially be integrated within a fluidised bed system to assist the combustion process, reduce operating conditions, and consequently recycle glass fibres with higher residual strength.

2 METAL OXIDE CATALYSTS

Mizuguchi et al. have shown the effectiveness of thermally excited Titanium (IV) oxide (TiO_2) as a catalyst for the decomposition of Polycarbonate (PC). PC chips were heated at 500°C for 30 minutes with and without TiO_2 present. A char residue was observed in the un-catalysed sample, most likely due to carbonisation, whereas the other contained no residue. Gas analysis, by means of mass spectroscopy, indicated complete decomposition of PC to H_2O and CO_2 [8]. *Shinbara et al.* also uses TiO_2 for PC decomposition, however, also states that thermoset plastics such as epoxy resin "can also be entirely decomposed…the decomposition occurs as efficiently as in the case of thermoplastic resins" [9]. A comparison between catalysed and un-catalysed epoxy was not carried out, hence it is still unclear whether the recycling conditions required for TiO_2 catalysed epoxy decomposition would favour increased glass fibre residual strength retention. A variety of other nonstoichiometric metal oxides have proven effective through the production of highly oxidative holes [9]. At elevated temperatures valence electrons within these materials are promoted to the conduction band, in turn creating an oxidative electron hole. The decomposition mechanism outlined by *Maki et al.* begins with the production of radicals through the capture of bonded electrons within the organic polymer by the oxidative holes. These radicals then propagate through the material, breaking the polymer chains, facilitating the complete combustion to yield H_2O and CO_2 [10].

Hong and Wang investigated the effect of copper oxides on the thermal degradation of epoxy resin due to reported delamination of printed circuit boards. It is thought that copper oxides accelerate the decomposition of polymer materials, resulting in reduced epoxy-copper bond strength. Two forms of copper oxides were investigated; cupric oxide (CuO) and cuprous oxide (Cu_2O). Thermogravimetric analysis (TGA) was carried out on the samples with the resulting derivative curves showing peaks occurring at lower temperatures for both samples containing copper oxides. It was later established that no conclusion could be made as to which copper oxide was more effective at catalysing the epoxy due to an inconsistency in specific surfaces [11]. *Allara and Roberts* outline the mechanism by which copper oxide catalyses the degradation of organic polymers. Carboxylic acids produced during oxidative decomposition of such materials react with the metal surface forming metal salts. It is hypothesised that this copper salt layer acts as catalytic surface creating free radicals which can migrate through the polymer matrix resulting in increased oxidation. These salts may also migrate through the polymer aiding the degradation through homogeneous catalysis [12,13].

Cerium (IV) oxide (CeO_2) is a widely used as a catalyst for reducing harmful exhaust gases produced by automobiles. It is able to achieve this due to its ability to undertake rapid redox cycles. Doping of CeO_2 has successfully improved its catalysing ability through increased oxide nonstoichiometry [14]. However at temperatures above 500°C, at low oxygen partial pressures, CeO_2 alone has been shown to become oxygen deficient (CeO_{2-x}). Work has not yet been carried out using CeO_2 as a catalyst for thermoset decomposition although it is believe that its surface reducibility at elevated temperatures could aid the combustion of epoxy [15].

Mizuguchi et al. recovered fibres from fibre reinforced plastics (FRP) through thermal activation of oxide semiconductors. Glass fibre fabric was impregnated with epoxy resin and sandwiched between two Cr_2O_3 coated honeycomb substrates to ensure good contact. Heat treatment was then carried out in a furnace, with full epoxy decomposition occurring after 10 minutes at 500°C. Characterisation of

recovered fibres was carried out through scanning electron microscopy (SEM), Rayman spectroscopy and X-ray diffraction showing no noticeable difference between virgin and recovered fibres (other than presence of sizing). It is concluded by the author that the recovered fibres need only be resized before reusing [8]. It is felt that mechanical characterisation of the recovered fibres must be carried out in order to determine whether the fibres can actually be reused. Exposure to such temperatures could result in glass fibres with low residual strength therefore having little value. Visually there appears to be little difference between virgin and recovered glass fibres using SEM, however, this does not necessarily indicate any retention in strength. Cracks (2 dimensional flaw consisting of an area across which bonds are broken) on the glass fibre surface could still be present but not observed using SEM [16]. It is these cracks which ultimately define the glass fibres strength; hence the similarity in the images obtained through SEM could be misleading. Mechanical characterisation of glass fibres recovered with and without the aid of the catalyst should be compared to virgin fibres to demonstrate how the difference in decomposition conditions translates into fibre strength retention.

3 EXPERIMENTAL

Epoxy degradation with and without various metal oxides present was initially carried using TGA in order to rank the catalysts performance. The catalysts effect on the decomposition onset temperature is particularly important when considering the effect this has on the glass fibre residual strength after recycling. In order to determine the effect of the metal oxides on the epoxy decomposition activation energy a kinetic study was carried out using data obtained from TGA. Three metal oxides were selected for thermal analysis; copper (II) oxide (CuO), titanium (IV) oxide (TiO_2) and cerium (IV) oxide (CeO_2). These were selected based on; their published ability to aid polymer degradation, thermal stability, low health risks and cost. It was deemed essential that the metal oxides chosen must be able to be used commercially. CuO, TiO_2 and CeO_2 nanopowders were purchased from SIGMA-ALDRICH with particle size of <50nm (TEM), <50nm (TEM) and 21 nm (TEM) respectively.

3.1 EPOXY SAMPLE PREPARATION

PRIME 27 Resin and PRIME 20LV extra slow hardener were supplied by Gurit. They were mixed at a weight ratio of 100:28 then, using a syringe, small droplets of the uncured epoxy were dropped onto non-stick plastic sheets. This created convex disks of epoxy with diameters around 6mm. This process was carried out multiple times on the same sheet; giving a large sample size to later choose from. The epoxy disks were then pre-cured at room temperature for 24 hours; allowing them to harden so they could then be moved without deforming. The samples were then post-cured at 65°C for 7 hours. The large sample size was initially visually analysed; discarding any epoxy disks which were deformed or did not appear to be in the correct diameter range. The final sample selection was then carried out by weighing the remaining samples; any samples out with the range of 11.5-12.5mg were discarded. This range was selected as the diameter and height of these samples fitted into the TGA pan well, leaving enough room for the inclusion of the metal oxide powder. The samples were finally prepared for thermal analysis by applying a layer (≈20mg) of metal oxide in an Alumina TGA pan. The flat (underside) surface of the epoxy disk was then placed on top of the oxide layer. The samples were arranged this way in an attempt to keep a consistent epoxy-catalyst interface area. TGA was performs using a TA Instruments Q50.

3.2 NON-ISOTHERMAL DECOMPOSITION

In order to determine whether the metal oxides possess the ability to reduce the decomposition temperature of epoxy the samples were degraded under non-isothermal conditions. They were heated at a rate of 10°C/min from room temperature to 700°C in the presence of air. Initially TGA was carried out on epoxy only in order to obtain a control in which to compare the catalysed thermal analysis against. This process was carried out twice to verify the reproducibility of the epoxy samples, therefore demonstrating any discrepancy between catalysed epoxy decomposition rates was not due to inconsistency in the epoxy itself.

3.3 ISOTHERMAL DECOMPOSITION

Further investigation of the effect of metal oxides was carried out by decomposing isothermally; showing the change in full epoxy degradation time. In this case the sample was rapidly heated from room temperature to 500°C (taking around 2 minutes) in the presence of air then held isothermally until the epoxy had fully decomposed.

3.4 KINETIC STUDY

A means of measuring the thermal stability of epoxy is calculating its decomposition activation energy; the minimum energy required to start the epoxy degradation. In theory a reduction in the activation energy in the presence of the metal oxides indicates the degradation is successfully catalysed. The catalysing capability of the metal oxides can be ranked by comparing their effect on the activation energy. A summary is given below outlining how the activation energy can be found from TGA data. Using a non-isothermal TGA heating programme the remaining epoxy mass can be plotted as a function of temperature assuming a linear temperature-time relation such that $\beta = dT/dt = constant$, where β is the heating rate. The rate of conversion is a linear function of the rate constant, k, (time dependent) and a function of conversion, α, (time independent);

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

The temperature dependence rate constant is given by the Arrhenius equation;

$$k = Aexp\left(\frac{-E}{RT}\right) \tag{2}$$

Where A is the pre-exponential factor, E is the activation energy, R is the universal gas constant and T is temperature (absolute). Combining (1) and (2) yields the following;

$$\frac{d\alpha}{dt} = Af(\alpha)exp\left(\frac{-E}{RT}\right) \tag{3}$$

For constant heat rate the extent of conversion can be analysed as a function of the temperature;

$$\frac{d\alpha}{dT} = \frac{A}{\beta}f(\alpha)exp\left(\frac{-E}{RT}\right) \tag{4}$$

There are many methods for determining the activation energy from TGA data; in this paper Kissinger's differential method is used. The analysis requires the epoxy to be decomposed at a variety of heating rates. In this investigation β=5, 10, 30 and 50°C/min were chosen with each sample type being heated from 25 to 700°C. This method is derived from eqn (4) under conditions of the maximum reaction rate. The temperature at which the maximum first derivative weight loss for each stage occurs (T_{max}) is found for the different heating rates. The following equation was used [17];

$$ln\left(\frac{\beta}{T^2{}_{max}}\right) = ln\left(-\frac{AR}{E}f'(\alpha_m)\right) - \frac{E}{RT_{max}} \tag{5}$$

The activation energy can be found from a plot of $ln(\beta/T^2{}_{max})$ against $1/T_{max}$, assuming $ln\left(-\frac{AR}{E}f'(\alpha_m)\right) = constant$.

4 RESULTS AND DISCUSSION

4.1 NON ISOTHERMAL DECOMPOSITION

Figure 1 shows typical thermograms obtained through non-isothermal degradation of epoxy at a heating rate of 10°C/min and decompostion onset temperatures can be found in Table 1. There is a negelagible change to the initial degradation onset temperature for all metal oxides tested; all occuring in the range of 333-338°C, which is comparible to that of only epoxy. TiO_2 appears to actually have adverse effects by increasing the second decomposition stage onset temperature; however, full epoxy degradation does occurs at a slighlty lower temperature. Both CeO_2 and CuO positively influence this onset temperature; decreasing it by 63 and 59°C respectively. The epoxy+CeO_2 thermogram may also indicate that the performance of CeO_2 is temperature dependant as there is only significant deviation from the epoxy only degradation above 400°C. CuO appears to facilitate a large initial mass loss, compared to all other samples, exhibiting a loss of over 90% at just 400°C. Both epoxy degradation onset temperature and rate are key parameters in determining wether this techonolgy can be applied to fibre reinforced plastic recycling. These initial results suggest that CuO could be the most effective catalsyt for aiding FRP decomposition.

	Degradation onset temperature (°C)	
	Stage 1	Stage 2
Epoxy only	337	519
Epoxy+CuO	333	460
Epoxy+CeO_2	335	456
Epoxy+TiO_2	338	530

Table 1: First and second stage epoxy degradation onset temperatures at a heating rate of 10°C/min

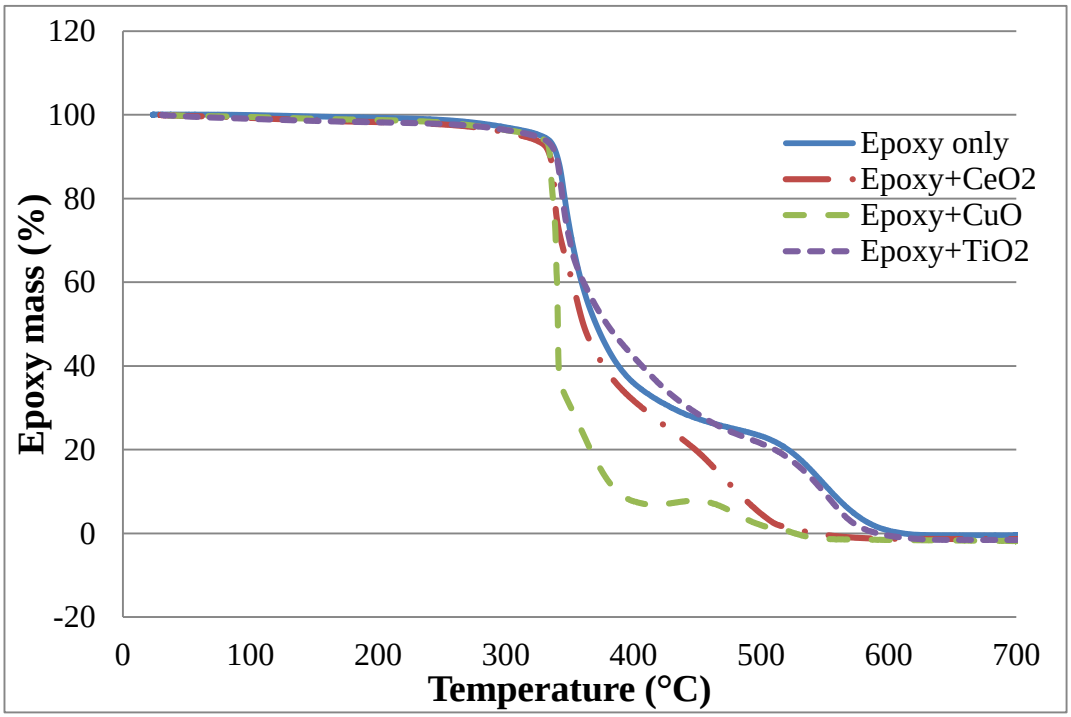

Figure 1: Comparison of TGA thermograms at a heat rate of 10°C/min

4.2 ISOTHERMAL DECOMPOSITION

Figure 2 shows a comparison of the TGA results obtained through isothermal degradation of epoxy for all metal oxides. All samples, except those containing CuO, show a similar two stage decomposition process; an initial mass reduction of around 90% followed by a decrease in rate of mass loss. Full decomposition occurs after 14, 8 and 6mins for epoxy only and samples containing TiO_2 and CeO_2 respectively. An initial large drop in mass also occurs in samples containing CuO which continues below zero, stopping at a mass of -20% and is followed by a rise to around -1.5% at 5mins where it finally plateaus. This pattern was typical for every isothermal heat treatment carried out containing CuO. Prior to epoxy degradation the TGA microbalance was zeroed with the CuO power in the alumina pan; therefore, at these temperatures an explanation for such a phenomenon may be CuO reduction by carbon present in the epoxy. Furthermore, the mass loss below zero is (in all cases) smaller than the theoretic mass of oxygen within the CuO nanopowder used. It is known that copper will readily oxidise when heated in air which could explain the gradual rise in mass. Finally, the inability to eventually rise back to 0% may be a result of copper (I) oxide formation; the lower oxide of copper. The exact cause for this phenomenon is currently not understood however it is clear from these isothermal TGA results that CuO has the ability to considerably increase epoxy degradation rate.

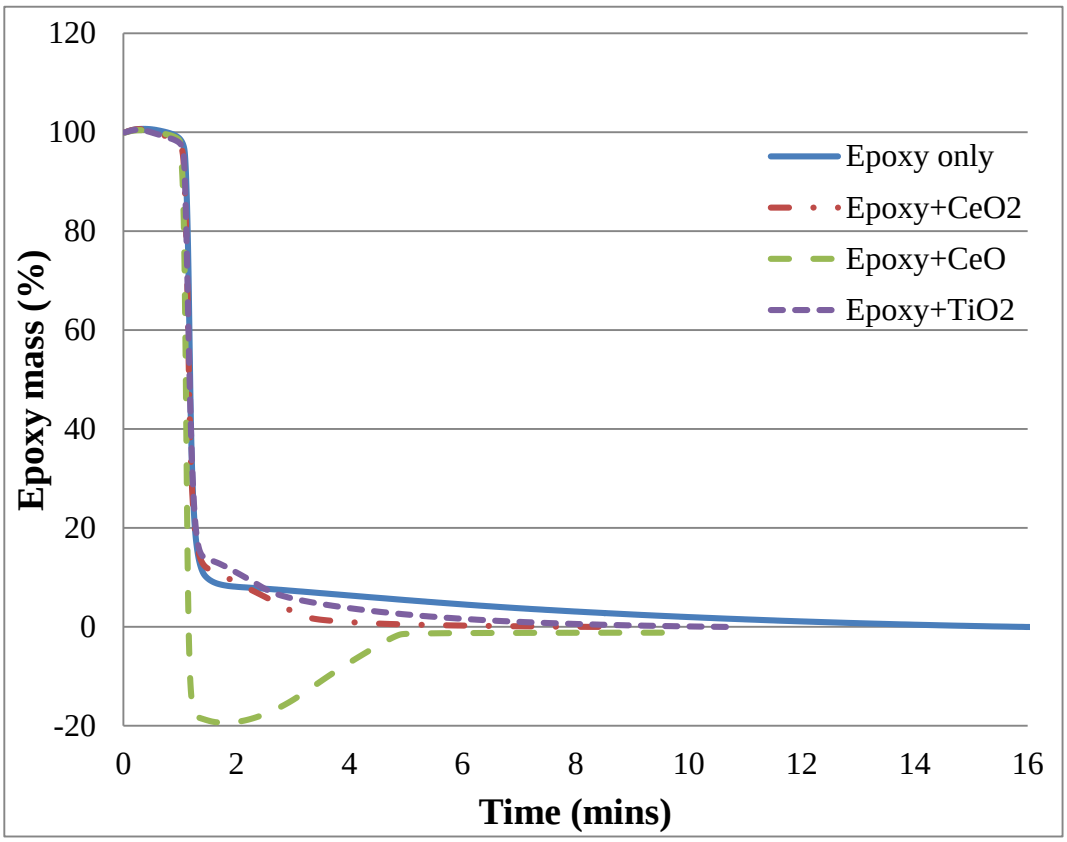

Figure 2: Comparison of epoxy resin decomposition time using the TGA isothermal heating program

4.3 KINETIC STUDY

In order to calculate the activation energy of epoxy decomposition following the method outlined above, the heat rate must affect the temperature at which the maximum mass loss rate occur. As expected, these temperatures increased with heat rate due to the lagging effect; Figure 3a shows an example of this effect on the epoxy only samples. During testing it was found that, as in the case with isothermal heating program, CuO transformed the epoxy degradation into a one stage process at heat rates of 30 and 50°C/min. This is illustrated in Figure 3b by the single peak mass loss rates during the degradation process. As a result of this a second stage activation energy could not be found for CuO catalysed samples.

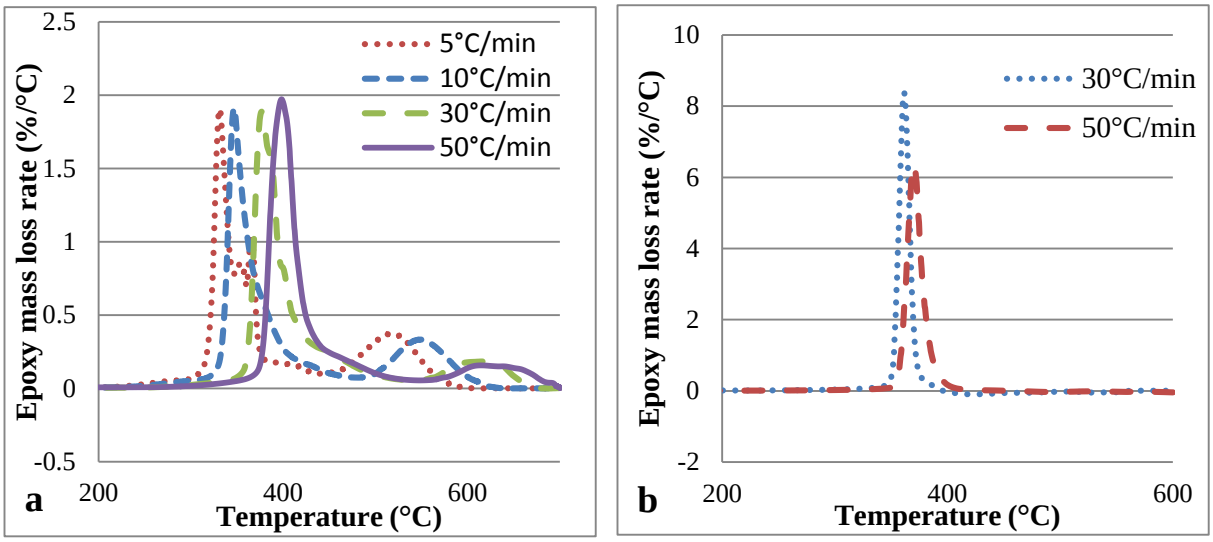

Figure 3: a) Example of temperature shifting effect due to change in heat rate for epoxy only samples b) CuO facilitating a one stage degradation process at heating rates of 30 and 50°C/min

The activation energies determined experimentally are given in Table 2 as well as the correlation coefficient for the line of best fits used during the analysis. An increase in first stage degradation activation energy was found in all samples containing metal oxides. Although CuO exhibits the largest rise, its ability to transform the degradation into a one stage process, at hate rates of 30°C/min and above, is promising for the overall degradation rate. Epoxy only and epoxy+TiO_2 samples display comparable second stage activation energies of around 130kJ/mol whereas CeO_2 reduces this to 107kJ/mol. In agreement with the non-isothermal TGA results above, TiO_2 shows relatively low catalysing capabilities whereas CeO_2 only has a positive effect at temperatures around 400°C and over.

Sample	Stage	Activation energy (kJ/mol)	Correlation coefficient
Epoxy only	1	109	-0.994
	2	130	-0.993
Epoxy+CeO_2	1	141	-0.998
	2	107	-0.992
Epoxy+CuO	1	157	-0.999
Epoxy+TiO_2	1	137	-0.998
	2	133	-0.931

Table 2: Epoxy degradation activation energies

5 CONCLUSIONS

Epoxy resin was decomposed in the presence of three metal oxides (CuO, TiO_2 and CeO_2) in order to determine their effect on degradation onset temperature and rate. Of the materials tested CuO appears to be the most successful at reducing these factors. Using TGA at a heating rate of 10°C/min CuO provided the highest first stage degradation rate while reducing the second stage onset temperature by around 60°C. At heating rates of 30°C/min and above the epoxy degraded in one stage with the application of CuO. Under isothermal conditions, at 500°C, CuO provided the highest reduction in epoxy decomposition time. CeO_2 has also shown the ability to aid epoxy decomposition, however, with less success than CuO. There appears to be a temperature dependency associated with CeO_2 performance; no real effects on epoxy degradation were observed till a temperature of around 400°C was reached under non-isothermal heating conditions. Moreover, the kinetic study indicated a reduction in second stage activation energy (compared to epoxy alone) which was not apparent in the first stage. The application of TiO_2 provided no advantage under non-isothermal heating and increased the activation energy for both stages of decomposition. A slight reduction in degradation time was observed under isothermal degradation however the results suggest that TiO_2 is the least effective at catalysing epoxy decomposition. The results obtained warrant further investigation into the application of CuO and CeO_2 during glass fibre reinforced epoxy degradation. The apparent reduction in recycling conditions these metal oxides provide could yield residual glass fibres with increased strength retention and higher commercial value.

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