

Investigation of catalysed thermal recycling for glass fibre reinforced epoxy using fluidised bed process

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Abstract

An investigation of the effect of metal catalysts on thermal recycling of glass fibre reinforced epoxy was carried out within a fluidised bed system.. CuO nanopowder was integrated with epoxy to assess its ability at reducing the epoxy thermal stability and in turn reducing the typical temperatures required in thermal recycling for epoxy composites. It was found that the CuO was able to significantly accelerate the thermal degradation of the selected epoxy. The CuO loading of 5% weight of epoxy provided the largest reduction in thermal stability and activation energy of the second stage of decomposition. It was also demonstrated that the addition of CuO did not negatively affect epoxy mechanical properties or curing and, in fact increased the epoxy glass transition temperature. When applied to glass fibre-epoxy (GF-epoxy) recycling within the fluidised bed process, glass fibres were recycled at just 400 °C with a yield of up to 59%.

Keywords: Catalysis, Composites, Recycling, Thermosets, Waste

1. Introduction

The disposal of end-of-life composite products in an environmentally friendly and economically viable manner is one of the most important challenges currently facing the composites industry. The annual global production of glass fibre reinforced plastics (GRP) is exceeding 10 million tons; with thermoset based composites projected to account for approximately 50% of the market share of fibre reinforced plastic materials [1, 2]. Their low production cost and good specific mechanical properties have made GRP suitable materials in many engineering sectors; predominantly the renewable energy and transport industries [3]. A consequence of this increase in demand in GRP is a large amount of composite production waste and end-of-life products.

Historically composite waste streams were generally destined to landfill, which is a poor disposal strategy for materials requiring intensive energy input in their manufacture. It is currently already illegal to landfill composite waste in numerous EU countries due to the EU Directive on Landfill of Waste [4, 5]. Thermoset based composites cannot easily be reused/recycled due to their polymer crosslinking. Extensive research has been recently devoted into the development of composites recycling techniques, which have led to various recycling techniques [3, 6, 7]. Among them are thermal recycling methods, in which reinforcing fibres (e.g. glass and carbon fibre) are liberated by incinerating polymeric matrices, followed by reuse in secondary composite components. Recycled fibres tend to suffer property degradation to various extents depending on the specific techniques employed. In the case of glass fibres recycled from fluidised bed systems, significant strength loss has been reported which renders the recycled fibres unusable in high strength components [8-12]. It has been shown that the tensile strength of glass fibres recovered from the fluidised bed technique is highly dependent on recycling temperature; ranging from 50-

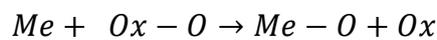
90% of the original fibre strength [13]. It is well understood that exposure time also influences the degree of thermal weakening of glass fibres [14]. The mechanism of thermal weakening of glass fibres is still under discussion in the literature, and there seems to be no consensus on the physical change(s) that occur in glass fibre that can account for the strength loss [11]. The proposed mechanisms can typically be divided into two categories, bulk or surface phenomenon. It is proposed that thermally conditioning glass fibres can lead to internal structural changes such as enthalpy relaxation [15, 16] and anisotropic relaxation [15]. Other studies suggest fibre weakening occurs due to the formation of surface defects/flaws when heated [17].

Fluidised beds are a widely used process in numerous industrial technologies, such as catalytic cracking, gasification, drying/cooling and pneumatic transport of powders, primarily due to their good heat transfer, thorough mixing ability and accurate temperature control [18]. It has been demonstrated that the fluidised bed process as a means of thermally recycling glass fibre reinforced thermosets has many advantages such as scalability, operation continuity, contaminant tolerance and processing dissimilar polymers [4, 19, 20]. The process involves thermally degrading the polymer matrix and liberating the reinforcement fibres, which are subsequently collected for reuses. Oxygen is present in the fluidising medium (typically air) in order to diminish char residue on the recycled fibres. High operating temperatures, excellent gas-solid heat transfer, a constant supply of oxygen and attrition allows for rapid decomposition of the polymer matrix in the fluidised bed process. The polymer volatiles can subsequently be fully combusted for recovering their energy.

In order to aid thermoset matrix decomposition and reduce energy input, it is proposed that an oxide catalyst could potentially be integrated within a fluidised bed system to assist the

polymer combustion process. This technology could have the advantage of lowering the temperature required for thermal decomposition and therefore potentially decrease the energy consumption and running costs of the recycling process.

Metal oxides encompass a widely used category of solid catalyst with transition metal oxides being utilised in many organic reactions [21]. The following typical redox mechanism describes the catalytic oxidation reactions on metal oxides:



Initially a reductant (*Red*) reduces the metal oxide surface (*Me - O*). It returns to its original state after re-oxidation by an oxidant (*Ox - O*) [22]. The result of this two-stage reaction is the transfer of oxygen from one substance to another [23]. Oxidation of organic substances will occur as a result of the metal oxide donating a lattice oxygen, producing a vacancy on its surface [24]. The air stream in the fluidised bed process can therefore be responsible for re-oxidising the surface oxygen vacancy, facilitating a continuous redox cycle.

It was previously demonstrated that copper (II) oxide (CuO) could successfully reduce the thermal stability of epoxy [25, 26]. The application of CuO on GF-epoxy reduced the epoxy matrix decomposition temperature required for glass fibre liberation by 120 °C when recycling statically in a furnace. This resulted in lower energy input required for GF-epoxy recycling and higher glass fibre strength retention [25]. The mechanism for copper oxide catalysed decomposition of polymeric material is outlined in [26]. The catalytic effect of copper oxide initiates with the abstraction of tertiary hydrogen atoms producing radicals while reducing copper oxide. The RO and ROO radicals generated during these reactions accelerate the oxidation of polymer molecules.

A recycling system, based on a fluidised bed reactor, was developed in house and the effect of integrating CuO in such a method of recycling GF-epoxy was investigated. The present work gives an overview of the recycling process design and operation conditions. The effect of utilising CuO in the process to 1) facilitate composites thermal recycling 2) reducing energy consumption during recycling and 3) the impact on glass fibre strength retention has not been studied previously and was therefore investigated in this work.

2. Experiment

2.1 Materials

PRIME 27 epoxy resin (epoxy phenol novolac based) and PRIME 20LV extra slow hardener (cycloaliphatic and aliphatic amine based) was supplied by Gurit. CuO nanopowder was purchased from Sigma-Aldrich with nominal particle size of 50 nm. The epoxy was prepared by mixing the CuO nanopowder with the epoxy resin by hand, followed by ultrasonic mixing for 30 min to disperse the particles into the resin system. The hardener was added at 28% weight of the resin alone, then, after mixing till combined, the epoxy was placed in a vacuum chamber to degas for 10 min. Epoxy not containing CuO was prepared as above without the steps involving the addition and dispersion of CuO. The epoxy was room temperature cured for 24 h followed by post-cure treatment at 65 °C for 7 h. A Hitachi SU6600 scanning electron microscope (SEM) was used to observe the dispersion of CuO in the cured epoxy, as shown in Figure 1. Some agglomeration of the CuO is present in Figure1, however the dispersion does appear homogenous on the whole. The CuO particle size, measured using SEM, was found to approximate that given by the supplier.

Composite feedstock for the fluidised bed recycling process was prepared in-house. Two types of feedstock were prepared, 1) GF-epoxy and 2) GF-epoxy with CuO nanopowder integrated in the epoxy matrix at 5% by weight. To prepare the fluidised bed feedstock, a tri-axial 3-ply preform was impregnated with the epoxy using a hand layup method. The preform was supplied by Hexcel Reinforcements UK Ltd and had a $[0^\circ / -45^\circ / +45^\circ]$ layup, fabric mass of 1180 gsm and stitched using polyester thread. After impregnation, the epoxy cured at room temperature for 24 h followed by post-cure at 65 °C for 7 h. The cured laminates were then cut into 60 mm \times 15 mm, having a thickness and mass of 3 mm and 1.7 g respectively. The composite feedstock was cut to these dimensions to allow recovered fibres to be long enough to perform single fibre tensile testing. It was determined through a burn off test that the feedstock had a fibre weight fraction of approximately 60%. ‘PPG Fibre Glass Mat[®] 92 chopped strand mat’ (CSM), supplied by PPG Industries, was also used in this work in the preparation and testing of GF-epoxy tensile specimens.

2.2 Thermal analysis of epoxy degradation

Thermogravimetric analysis (TGA) was used to determine catalytic efficiency of CuO in reducing the decomposition temperature/time of epoxy. The amount of CuO nanopowder was chosen to be 0, 1.5 and 5% weight of epoxy. Epoxy disk specimens were prepared as outlined in 2.1. Epoxy samples in the range of 10.5-11.5 mg were used and TGA was performed using a TA Instruments Q50.

The impact of CuO on epoxy thermal stability was further assessed by evaluating its effect on the activation energy, E_a . There are a number of methods for determining the E_a from TGA data; in this investigation Kissinger’s differential method and Kissinger-Akahira-Sunrose (K-A-S) method were used [27, 28]. The analysis requires the epoxy to be decomposed at a

variety of heating rates; 1, 2, 5, 7 and 10 °C/min were chosen with each sample type being heated to 600 °C in air.

2.3 Assessing reusability of CuO

The reusability of CuO is important in assessing its potential as a catalyst for aiding epoxy decomposition. To do this, a relatively large quantity of bulk epoxy+CuO with 5% weight CuO was produced. This was heated in a muffle furnace at 550 °C for 1 h in air, until all epoxy had decomposed, leaving only the residual CuO. For clarity, the notation CuO(X) will be used, where X is the number of times CuO has been used to aid the decomposition of epoxy. After this first epoxy decomposition, the CuO(1) was collected from the furnace. To assess its catalytic activity, a fraction of the CuO(1) was then mixed with fresh epoxy to prepare epoxy+CuO(1) TGA samples, as described above. The remaining collected CuO(1) was then mixed with fresh epoxy to prepared bulk epoxy+CuO(1). Both TGA samples and bulk epoxy were prepared with 5% weight CuO throughout. The degradation process was repeated on the bulk epoxy+CuO(1) and the residual CuO(2) was again collected from the furnace and processed into epoxy+CuO(2) TGA samples. Figure 2 illustrates a flow chart of the methodology. TGA was performed on the various epoxy+CuO(X) samples at a heating rate of 1, 2, 5, 7 and 10 °C/min from room temperature to 600 °C in air. The effect of the number of previous uses on the ability of CuO to aid epoxy degradation was compared and quantified by calculating the activation energy of epoxy decomposition.

2.4 Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to investigate the effect of CuO content on the epoxy curing using a TA Instruments Q20. Uncured epoxy with 0, 1.5 to 5% weight integrated CuO were heated in the temperature range -10 to 180 °C, then cooled to -10 °C

and finally reheated to 180 °C all at a heating rate of 3 °C/min. The reaction enthalpy and glass transition of the cured material were characterised.

2.5 Epoxy tensile test

Epoxy tensile specimens were prepared in order to investigate the effect of incorporating CuO nanopowder on the epoxy tensile properties. The specimens were prepared and tested following ASTM D638-14. Epoxy with and without CuO integrated at 5% by weight was prepared as described in section 2.1. Using a syringe, the resin was transferred into a silicone rubber mould. An Instron 5969 testing machine equipped with a 50 kN load cell was used to perform the tensile test. The strain was recorded with an Instron 2663-821 video extensometer and the displacement rate was set to 1 mm/min.

2.6 GF-Epoxy tensile test

GF-epoxy tensile specimens were prepared in order to investigate the influence of incorporating CuO nanopowder, within the epoxy matrix, on the tensile properties of GF-epoxy. 16 layer of CSM, cut into 28 × 28 cm squares, were infused with epoxy under vacuum. The epoxy with and without CuO integrated at 5% by weight was prepared as described in section 2.1. The finished product gave a panel with a thickness of approximately 4 mm. Tensile specimens were then cut from the panel using a water jet cutter following ISO 527 and tensile tested as outlined in 2.5.

2.7 Fluidised bed recycling process

Figure 3 shows a schematic of the in-house fluidised bed recycling process. The polymer matrix was thermally decomposed within the fluidised bed reactor, which was fabricated from a stainless steel pipe with a diameter of 210 mm. The height of the reactor freeboard

was 1 m to encourage disengagement of the fluidised sand within the reactor and avoid excessive sand entrainment into the separation section of the process. Silica sand with nominal particle size 0.5-1 mm was used as the bed medium, which sat on a distributor plate with a porosity of around 10%. The distributor plate was comprised of two perforated stainless steel plates sandwiching a 0.4 mm aperture mesh to contain the sand. The composite was fed into the reactor through an access pipe, located just above the expanded sand bed.

The fluidising air was supplied to the reactor via a centrifugal fan. The fan allowed the flow rate to be varied with a relatively constant static pressure rise. The fluidisation velocity was regulated by controlling the fan speed and the flow rate was measured with a velocity transmitter. Before entering the reactor, the air was preheated and recycling temperature of the bed was regulated via PID control. To avoid overheating, temperature limit controllers were used to monitor the heater inlet and outlet temperatures.

The fluidising airflow was sufficient to entrain the released glass fibres from the bed and into the reactor freeboard. An induced draft fan was used to draw the glass fibres and polymer volatiles from the freeboard and to keep the reactor under a slight negative pressure. The glass fibres were recovered from the gas stream using a cyclone separator. The cyclone was based on a high efficiency Stairmand model. A mesh based filter was located between the cyclone separator and induced draft fan caught any fibres which passed through the cyclone without separating from gas stream.

2.8 Recycling GF-epoxy using fluidised bed

Only the fluidised bed temperature was varied when investigating the effect of CuO on GF-epoxy recycling. The feed rate, static bed height and fluidisation velocity remained constant

throughout testing at 0.85 g/min, 150 mm and 1.5 m/s respectively. Composites were fed into the fluidised bed at the stated feed rate for 60 minutes, after which the system was ran for a further 15 minutes without feeding any more composite. After processing, the recycled fibres were weighed and the bed cleaned of any residual fibres in order to not contaminate subsequent tests. The yield efficiency of fibres recycled from GF-epoxy using the fluidised bed system, with and without integrated CuO, was evaluated at various temperatures. Since the fibre weight fraction of the composite feedstock was 60%, the following equation was used to evaluate the yield efficiency for each test.

$$Yield\ efficiency = \frac{Mass\ of\ recycled\ GF}{Mass\ of\ composite\ input \times 0.6} \times 100 \quad (1)$$

2.9 Single glass fibre tensile test

All single fibre tensile testing was performed following ASTM C1557-03. Card tabs were cut out of 250 g/m² grade paper. Double-sided tape was placed on the paper tab approximately 1 mm away from the cut out window. The glass fibres were placed on top of the double-sided tape and Loctite Gel Superglue was applied to the fibres at the upper and lower edge of the window. The tensile strength of at least 30 single glass fibres from each heating schedule was characterised at 20 mm gauge length. The cross sectional area of each glass fibre was assumed circular and found by capturing an image of the fibre using an Olympus GX51 optical microscope under 500× magnification. The diameter was then measured using ImageJ software, ensuring a consistent length scale throughout. The accuracy of fibre diameter measurement using the Olympus GX51 optical microscope and ImageJ analysis software was previously investigated by comparing these with values measured using SEM. All diameter measurement using optical microscopy fell within ±0.2 µm of those obtained using the SEM. Tensile testing of the glass fibres was performed using a Testometric M250-2.5CT with a 5 N

load cell at ambient conditions. After mounting in the tester, the card window sides were cut and testing was carried out at a strain rate of 1.5 %/min.

3. Results and discussion

3.1 Thermal analysis of epoxy decomposition

Figure 4 shows a comparison between epoxy degradation with and without the integration of CuO at 1 and 2 °C/min using TGA. There is little change to the first stage degradation; however, both the second stage onset temperature and complete decomposition temperature are significantly reduced by the application of CuO. Figure 5 gives a comparison of these temperatures for all CuO loading (at 1 °C/min) and it can be seen that the higher CuO content results in a larger reduction in thermal stability. On average, the complete decomposition temperatures drops by 36 and 60 °C for 1.5% and 5% respectively. CuO is clearly able to decrease the thermal stability of the residue present after the initial degradation of epoxy. It follows that the operating conditions of the fluidised bed could be reduced to recycle fibres at a lower temperature. It should also be noted that the residual mass for epoxy+5% CuO samples is close to 4.8% as would be expected if the CuO was not consumed during the process, suggesting the CuO can subsequently be recovered and reused. This is less clear in Figure 4 for epoxy+1.5% CuO due to such little CuO content. The reusability of CuO is further investigated in section 3.3.

3.2 Epoxy degradation activation energy

A summary is given below outlining how the E_a can be found from TGA data. The temperature dependence of the reaction rate is typically parameterized through the Arrhenius equation:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

where k is the rate constant, A is the pre-exponential factor, R is the universal gas constant and T is temperature. The Kissinger equation below can be derived from Equation (2) under conditions of the maximum rate:

$$\ln\left(\frac{\beta}{T_{m,i}^2}\right) = \ln\left(-\frac{AR}{E\alpha}f'(\alpha_m)\right) - \frac{E_a}{RT_{m,i}} \quad (3)$$

where β is the heating rate, α is conversion, i denotes various temperature programs and m denotes the values related to the maximum rate. In the Kissinger method, at maximum rates, $\ln(\beta/T_{m,i}^2)$ is plotted against $1/T_m$ giving rise to a straight line whose slope yields E_a [28]. The K-A-S method uses the integral isoconversional principle; it is assumed that the reaction rate at constant extent of conversion is only a function of temperature. Equation (4) gives the integral form of the reaction model, $g(\alpha)$:

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E_a}{RT}\right) dT \quad (4)$$

It was derived by integration of Equation (2) with the rate of conversion being a linear function of the time dependent rate constant and time independent conversion. Since Equation (4) does not have an analytical solution, integral isoconversional methods typically make approximations of the temperature integral in linear form. The approximations given by the K-A-S method is shown in Equation (5).

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \text{Constant} - \frac{-E_a\alpha}{RT_{\alpha}} \quad (5)$$

This method allows the E_a at various extents of conversion to be found by plotting $\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right)$ vs $1/T_{\alpha}$ [28].

Figure 6 shows the degradation thermograms for epoxy only and epoxy+CuO at 1, 2, 5, 7 and 10 °C/min. The thermal lag caused by varying the heating rate is clearly illustrated, with decomposition occurring at lower temperatures when slower heating rates are used.

3.2.1 Kissinger's method

Table 1 gives the temperature at the peak rates used to create the plots given in Figure 7. Figure 7 shows the straight-lines produced by this shift in temperature for each maximum rate; the gradient of which was used in the Kissinger method to calculate the E_a . As shown in Figure 6, the epoxy degradation has two degradation stages (giving two maximum rates) for all heating rates, therefore a value of E_a was found for each degradation stage to occur.

Table 2 gives the E_a for all samples using Kissinger's method, along with the correlation coefficients for the lines of best fit in Figure 7. It was found that the E_a for the first stage of degradation increased with the integration of CuO for both loadings. This phenomenon was also reported by *Zabihi and Somayyeh* and was attributed to CuO nanoparticles in the epoxy matrix leading to an increase in the crosslinking density [30]. However, Table 2 shows that the E_a of the second stage degradation is reduced with the integration of CuO, with 5% CuO loading showing the largest reduction in E_a of 20%. This suggests that CuO is able to catalyse the thermal degradation of the residual char typically present after the first stage of epoxy degradation without compromising the epoxy thermal stability at lower temperatures. Given it is the char residue that requires typical high GF-epoxy recycling temperatures, reducing its degradation E_a is important to reducing operating conditions within the fluidised bed reactor.

3.2.2 K-A-S method

The kinetics of the second stage of epoxy decomposition was further investigated using the K-A-S method, which allowed E_a at specific values of conversion to be found. Figure 8 shows a clear reduction in E_a across the second stage degradation with the integration of CuO. Samples containing 5% CuO loading again exhibit the lowest E_a with an average reduction in E_a across the studied conversion range of around 40% compared to epoxy alone. This decrease in second stage E_a along with the reduction in complete degradation temperature, shown in Figure 4, alludes to a lower energy input required for composites thermal recycling.

3.3 Reusability of CuO

Figure 9 compares the effect of re-using CuO, up to three times, on its ability to aid thermal decomposition of epoxy. Multiple uses results in little deviation from the degradation thermogram obtained from epoxy containing fresh CuO. Table 3 gives the E_a for each sample found using the Kissinger method as described in section 3.2. As would be expected from Figure 9, there is a relatively consistent reduction in second stage E_a , indicating that the performance of CuO is not diminished when utilised repeatedly.

3.4 Effect of CuO nanopowder on epoxy properties

3.4.1 Epoxy cure

Table 4 gives the reaction enthalpy (ΔH) and glass transition temperature (T_g) of all samples under investigation. There is relatively little variation in both the enthalpy of the cure and T_g of the cured samples. The absolute reaction enthalpy decreases with CuO content, however, when normalised to epoxy mass only (i.e. disregarding CuO mass in sample) the enthalpy is essentially constant with CuO loading. T_g does tend to rise with CuO content which may

suggest higher crosslink density, although, the increase is slight and no firm conclusion can be drawn. It can be established, however, that the inclusion of CuO in the epoxy does not negatively affect the cure of the epoxy.

3.4.2 Epoxy and GF-epoxy tensile properties

Table 5 gives the tensile properties of the epoxy and GF-epoxy systems. The properties of neat epoxy approximate those found in other studies [31-33]. Considering the error (95% confidence), integration of CuO nanopowder, at 5% weight loading, does not appear to affect the average tensile strength or modulus of the epoxy. However, Table 5 shows that the addition of CuO nanopowder reduces the strain at break of epoxy indicating an increase in the brittleness of the epoxy system. The incorporation of CuO at 5% weight loading does not have a significant impact on the resulting tensile properties of GF-epoxy, as shown in Table 5. It appears that the effect of CuO has on the brittleness of the epoxy itself is not realised in the overall tensile properties of GF-epoxy, although the same may not hold for matrix-dominated properties such as interlaminar shear strength. This mechanical data, the calorimetry study of epoxy cure and kinetic study in section 3.2, suggest that the addition of CuO to aid epoxy thermal decomposition should not significantly affect the epoxy thermal or mechanical properties at typical operational temperatures.

3.5 Glass fibre recycling using fluidised bed

3.5.1 Effect of CuO on recycled fibre yield

Figure 10 gives the obtained fibre yields when recycling GF-epoxy in the fluidised bed at 400, 450 and 500 °C and compares the results with and without integrated CuO. It is clear that the application of CuO significantly improves the yield efficiency of recycled glass fibres, particularly at lower temperatures. When recycling at 400 °C the yield increases from

6% to 40% when using CuO. As would be expected, the yields appear as though they will converge at higher temperatures since the epoxy rapidly thermally decomposes without the need for an oxidising catalyst. This could be confirmed by recycled at higher temperatures, however, this work is centred on reducing the temperature required for recycling.

It is important to discuss the factors affecting the yield efficiency. There are two explanations for glass fibres not being successfully collected and therefore reducing the yield efficiency; 1) they were unable to exit the reactor and 2) inefficiency in the cyclone separator. The former is likely a result of fibres not becoming liberated from the matrix. This is due to the epoxy matrix not decomposing sufficiently because the required temperature was not achieved or inadequate time was given before ending testing. Almost no residual GF were found in the sand bed after recycling at 500 °C with CuO, suggesting that the cyclone separator has an upper limit of around 70% yield efficiency. The cyclone separator efficiency is independent of CuO presence in composite material therefore discrepancy between yields (for a given temperature) is the result of improved rates of fibres exiting the bed. It appears CuO can facilitate epoxy decomposition within the fluidised bed, increasing fibre liberation, in turn improving yield efficiency at lower operating conditions.

Figure 11 shows an image of glass fibres which remained in the sand bed after recycling at 400 °C. The fibres shown in Figure 11(a) are from GF-epoxy only composites, whereas those shown in Figure 11(b) had CuO incorporated within the epoxy matrix. It is clear there is substantially more residual char present on the fibres processed without CuO present; they are too heavy to leave the bed, and hence why they cannot be recovered at such a low temperature. In contrast, the fibres processed with CuO are significantly cleaner with little sign of residue. These fibres are clearly liberated from the epoxy matrix and should be able to

leave the bed given enough time. Recycling GF-epoxy with CuO at 400 °C was therefore repeated. In this case, the additional run time (above the first 60 minutes of material input) was increased from 15 to 45 minutes while the total material input remained constant. The resulting yield efficiency was found to be 59%, the same as recycling at 500 °C without the addition of CuO.

For scaling up the recycling process, it is proposed that the catalyst could in fact be included within the recycling system as a permanent constituent of the fluidised bed particles. Under these conditions, the CuO would be under a redox cycle, where it is reduced by epoxy molecules then re-oxidised by the high temperature fluidising air stream [23]. Given the dramatic reduction in temperature required to recycling GF-epoxy using the metal oxide catalyst, even if relatively high quantities of oxides are initially required, the cost benefit of long-term reduction in operating conditions might be realised.

3.5.2 Strength of recycled glass fibres

Figure 12 shows the tensile strength of the recycled fibres for the various conditions investigated, where the error represents a 95% confidence limit. The tensile strength of the virgin glass fibre was found to be 2.55 ± 0.08 GPa. The recycling temperatures used in the fluidised bed process do not appear to influence the tensile strength of the recycled fibres. It is widely understood however that glass fibre strength loss increases with the conditioning temperature [25]. The lack in such a trend in Figure 12 suggests the strength loss is primarily dominated by mechanical damage, as fibres are processed through the fluidised bed recycling system. Reducing the temperature required for the epoxy decomposition does not appear to have the added benefit of increasing the strength retention of fibres recycled in the fluidised bed used in this work.

The surface of fibres recycled in the fluidised bed was further inspected under high magnification SEM, as seen in Figure 13. The presence of apparent damage was ubiquitous on the surface of recycled fibres in the form of scratches and depressions. No such features were observed on the surface of glass fibres simply thermally conditioned within a furnace at the same temperature, suggesting the damage is a result of mechanical attrition during recycling.

4. Conclusions

This work has demonstrated the ability of CuO to reduce the thermal stability of epoxy-based composites and its potential for improving energy efficiency of the thermal recycling process. CuO was integrated in the epoxy before curing with loadings of 0, 1.5 and 5% weight of epoxy being investigated. Through TGA, it was shown that the temperature required for complete epoxy decomposition was reduced by 60 °C on average when 5% CuO loading was used. The kinetic study found that the use of CuO reduces the activation energy of the second stage of epoxy decomposition when analysing with both Kissinger's and K-A-S methods; again the higher CuO loading providing the larger reduction in thermal stability. It was also shown that the effectiveness of CuO is not diminished with repeated uses. Using DSC, it was demonstrated that the integration of CuO did not negatively affect the epoxy cure with T_g actually increasing with CuO loading. The tensile strength and modulus of epoxy was not changed with the inclusion of CuO at 5% weight loading.

GF-epoxy composites were thermally recycled using an in-house developed fluidised bed recycling system and the effect of CuO on fibre recycling temperature, yield efficiency and strength assessed. Yield efficiency increased drastically from 6% to 40% when recycling with CuO at 400 °C; this was further improved to 59% when increasing recycling time. This is

close to the apparent maximum yield efficiency of the system of around 70%. Reducing the required recycling temperature does not appear to increase fibre strength retention, because of extensive mechanical damage sustained during the recycling process.

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