**Investigation of catalysed thermal recycling of glass fibre reinforced epoxy**

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**Keywords:** recycling, glass fibre, themosets, catalysis, waste

**Abstract**

An investigation into catalysed thermal recycling of glass fibre reinforced epoxy was carried out to improve its commercial viability. CuO nanopowder was integrated with epoxy to assess its ability at reducing the epoxy thermal stability and in turn reducing the typically high thermal recycling temperatures required. It was found that the CuO at various loadings is able to 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.

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 ideal 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 strategies [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 is 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 split 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, primary due to their good heat transfer, thorough mixing ability and can operate at accurate temperatures [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. 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. The polymer volatiles can subsequently be fully degraded and their energy reclaimed.

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 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 () reduces the metal oxide surface (). It returns to its original state after re-oxidation by an oxidant () [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 decompostion 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 an industrial 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 never been studied and was therefore investigated in this work.

2. Experimental

E-glass fibres were obtained from a tri-axial 3-ply preform supplied by Hexcel Reinforcements UK Ltd. The preform had a [0°/ -45°/+45°] layup, fabric mass of 1180 gsm and stitched using polyester thread. PRIME 27 Resin (epoxy phenol novolac based) and PRIME 20LV extra slow hardener (cycloaliphatic and aliphatic amine based) were supplied by Gurit. CuO nanopowder was purchased from Sigma-Aldrich with nominal particle size of 50 nm.

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 itself. This was done to assess the ability of CuO to catalyse epoxy decomposition in the fluidised bed and facilitate glass fibre recycling at lower operating temperatures.

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 harder was added at 28% weight of the resin alone, then, after mixing till combined, the epoxy was placed in a vacuum chamber to de-gas for 10 min. This method approximates that outline in [27], where good dispersion of nanopowder in epoxy was observed. For feedstock containing CuO, the nanopowder was added at 5% weight of the total epoxy. Epoxy not containing CuO was prepared as above, minus the steps involving the CuO addition and dispersion.

To prepare the composite feedstock, the 3-ply preform was then infused with the epoxy at a weight ratio of 60% glass fibre using a hand layup method and cured following supplier instructions. The cured laminates were cut into 60 mm × 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.

3. Results and Discussion

## 3.1 Thermal analysis of epoxy decomposition

Figure 1 shows a comparison between epoxy degradation with and without the integration of CuO at 1 and 2°C/min using TGA.

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Figure 4 Epoxy degradation thermograms from TGA comparing epoxy only, epoxy with 1.5 and 5% added CuO at a heating rate of a) 1°C/min and b) 2°C/min

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 2 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 and fibres recycled at a lower temperature.

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Figure 2 Effect of CuO loading on 1st and 2nd onset and complete decomposition of epoxy

It should also be noted that the residual mass for epoxy+5% CuO samples is close to 4.8% as would expected if the CuO is not consumed during the process, suggesting the CuO can subsequently be recovered and reused. This is less clear in Figure 1 for epoxy+1.5% CuO due to such little CuO content.

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

|  |  |
| --- | --- |
|  | (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:

|  |  |
| --- | --- |
|  | (3) |
|  |  |

where β is the heating rate, α is conversion, denotes various temperature programs and m denotes the values related to the maximum rate. In the Kissinger method, at maximum rates, is plotted against giving rise to a straight line whose slope yields Ea [29].

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, :

|  |  |
| --- | --- |
|  | (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).

|  |  |
| --- | --- |
|  | (5) |

This method allows the Ea at various extents of conversion to be found by plotting vs .

Figure 3 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.

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Figure 3 Epoxy degradation thermograms from TGA illustrating the thermal lag caused by varying heating rate for a) epoxy only and b) epoxy with 5% added CuO

Figure 4 shows the straight-lines produced by the shift in temperature for each maximum rate; the gradient of which was used in the Kissinger method to calculate the Ea. As shown in Figure 3, the epoxy degradation has two degradation stages (giving two maximum rates) for all heating rates, therefore a value of Ea was found for each degradation stage to occur.

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Figure 4 Plot with straight lines of best fit used to find the first and second stage degradation Ea using Kissinger's method. From top to bottom; epoxy only, epoxy with 1.5% and 5% added CuO

Table 1 gives the Ea for all samples using Kissinger’s method, along with the correlation coefficients for the lines of best fit in Figure 4. It was found that that the Ea 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 [27]. However, Table 2 shows that the Ea of the second stage degradation is reduced with the integration of CuO, with 5% CuO loading showing the largest reduction in Ea 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 Ea is important to reducing operating conditions within the fluidised bed reactor.

Table 1 Ea found using Kissinger's method with the corresponding correlation coefficients for straight lines in Figure 3

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Ea (kJ/mol) | | Correlation coefficient | |
|  | Stage 1 | Stage 2 | Stage 1 | Stage 2 |
| Epoxy only | 118 | 101 | -0.9997 | -0.9925 |
| Epoxy+1.5% CuO | 145 | 84 | -0.9918 | -0.9627 |
| Epoxy+5% CuO | 140 | 80 | -0.9832 | 0.9876 |

The kinetics of the second stage of epoxy decomposition was further investigated using the K-A-S method, which allowed Ea at specific values of conversion to be found. Figure 2 shows a clear reduction in Ea across the second stage degradation with the integration of CuO. Samples containing 5% CuO loading again exhibit the lowest Ea with an average reduction in Ea across the studied conversion range of around 40% compared to epoxy alone. This decrease in second stage Ea along with the reduction in complete degradation temperature, shown in Figure 1, has real world implications and alludes to a lower energy input required for composites thermal recycling.

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Figure 5 Ea as a function of conversion for second stage degradation using K-A-S method

4. Concluding remarks

This work has successfully demonstrated the ability of CuO to reduce the thermal stability of epoxy-based composites and its potential for improving 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 Ea 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.

**Acknowledgments**

The authors gratefully acknowledge the financially supported from the Engineering and Physical Sciences Research Council through the Doctoral Training Partnership (EP/P504325/1). Appreciation is also given to the Advanced Materials Research Laboratory at University of Strathclyde for use of their facilities.

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