

# Investigation of the potential for catalysed thermal recycling in glass fibre reinforced polymer composites by using metal oxides



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## ABSTRACT

An investigation into catalysed thermal recycling of glass fibre (GF) reinforced epoxy was carried out to improve its commercial viability. Strength degradation was established as a key barrier in retaining the value of fibres after recycling. Several metal oxides were examined to assess their ability at reducing the high operating temperatures currently limiting the reusability of recovered fibres. It is proposed that such a material could be integrated within a thermal recycling system facilitating an increase in fibre residual strength while reducing energy consumption of the process. It was found that CuO, CeO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> were able to significantly accelerate the thermal degradation of epoxy. When applied to GF-epoxy, both the temperature and time required for fibre liberation were significantly lowered, reducing energy consumption by approximately 40%. The strength of fibres recovered with the aid of the metal oxides was increased, with the full potential for the strength retention yet to be achieved.

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## 1. Introduction

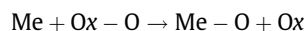
The disposal of end-of-life composite products in an environmentally friendly and economically viable manner is one of the most important challenges currently facing the composites industry. The annual global production of glass fibre reinforced plastics (GFRP) is exceeding 10 million tons; with thermoset based polymers accounting for 60% of the market [1]. Their low production cost and good specific mechanical properties have made GFRP ideal materials in many engineering sectors; predominantly the renewable energy and transport industries [2]. A consequence of this increase in demand in GFRP 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 [3,4]. 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 [2,5,6]. 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 [7,8]. It has found that the tensile strength of glass fibres recovered from the fluidised bed technique is highly dependent on recycling temperature and time; ranging from 50% to 90% of the original fibre strength [9].

In order to mitigate such strength loss 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. The reduction in operating conditions may also facilitate recovery of fibres with higher strength retention and commercial value.

Metal oxides encompass a widely used category of solid catalyst with transition metal oxides being utilised in many organic reactions [10]. The following typical redox mechanism describes the catalytic oxidation reactions on metal oxides:



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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) [11]. The result of this two stage reaction is the transfer of oxygen from one substance to another [12]. Oxidation of organic substances will occur as a result of the metal oxide donating a lattice oxygen, producing a vacancy on its surface [13]. The air stream in the fluidised bed process can therefore be responsible for re-oxidising the surface oxygen vacancy, facilitating a continuous redox cycle.

Three commercially available metal oxides including copper (II) oxide (CuO), cobalt (II, III) oxide (Co<sub>3</sub>O<sub>4</sub>) and cerium (IV) oxide (CeO<sub>2</sub>) were selected in this investigation. CeO<sub>2</sub> can become non-stoichiometric at elevated temperatures, providing highly mobile oxygen vacancies through its fluorite structure [11,14]. Although CeO<sub>2</sub> is widely used as a catalyst (such as automobile catalytic converters), its effect on thermoset plastic decomposition has not been reported. It has been demonstrated that CuO can reduce the thermal stability of epoxy, however, testing was limited to just 350 °C [15] and full epoxy decomposition (required for GFRP) was not investigated. Co<sub>3</sub>O<sub>4</sub> has been shown to catalyse the degradation of polymers and oxides organic compounds such as alcohols and CO [16–18]. The effect of these metal oxides on facilitating composites thermal recycling, reducing energy consumption during recycling and promoting fibre strength retention has not been studied and was therefore investigated in the present work.

## 2. Experimental

### 2.1. Materials

E-glass fibres were obtained from tri-axial (0°/–45°/+45°) 3-ply preform supplied by Hexcel Reinforcements UK Ltd. PRIME 27 Resin (epoxy phenol novolac based) and PRIME 20LV extra slow hardener (cycloaliphatic and aliphatic amine based) were supplied by Gurit. Fig. 1 shows the lay-up of the preform and the chemical structure of epoxy phenol novolac resin. CuO, Co<sub>3</sub>O<sub>4</sub> and CeO<sub>2</sub> nanopowders were purchased from Sigma-Aldrich with particle nominal size of 50 nm, 50 nm, and 21 nm respectively. It is understood that nanoparticles are intrinsically difficult to fluidise therefore the metal oxides could not simply be integrated within such a recycling system in this form. However, nanopowders were selected for this phase of the investigation to ensure good contact with composite materials.

### 2.2. Composite manufacturing

The composites used throughout the study were manufactured in house. The epoxy resin and hardener were mixed at a weight ratio of 100:28 according to recommendation of the supplier. The 3-ply preform was then infused with the epoxy at a weight ratio

of 60% glass fibre and cured following suppliers instructions. The cured laminates were cut into 60 × 60 mm<sup>2</sup>, having a thickness and mass of 3 mm and 6.7 g respectively. Fig. 2 shows the preform next to a typical GF-epoxy sample after curing.

### 2.3. Thermogravimetric analysis

#### 2.3.1. Epoxy degradation

Thermogravimetric analysis (TGA) was used to determine catalytic efficiency of the metal oxides in reducing the decomposition temperature/time of epoxy. Cured epoxy disks in range of 11.5–12.5 mg were used for TGA. The samples were prepared for thermal analysis by applying a 20 mg layer of metal oxide in an alumina TGA pan. The epoxy disks rested on this oxide layer and TGA was performed using a TA Instruments Q50. The samples were degraded under both non-isothermal and isothermal conditions. For the former, a heating rate of 10 °C/min from 25 to 700 °C in the presence of air was used. Isothermal decomposition involved rapidly heating samples from room temperature to a variety of temperatures in the presence of air then holding isothermally for 15 min.

#### 2.3.2. Glass fibre sizing degradation

It has been demonstrated that the removal of glass fibre sizing after heating can contribute to fibre strength loss above purely thermal weakening [19]. Without surface protection, the fibres are more susceptible to damage caused by mechanical handling [20]. As the commercial sizing on the fibres likely comprises predominantly of a polymeric film former, TGA was used to determine whether the metal oxides used had an impact on the sizing degradation. The mass of glass fibre is typically much greater than the sizing applied. In order to obtain accurate TGA results, a relatively large quantity of fibres was used. 250 mg of glass fibres (chopped to approximately 5 mm) were mixed with 180 mg of metal oxide and heated from 25 to 600 °C within an alumina beaker. TGA was performed using a NETSZCH STA 449 F1 Jupiter, which provides the ability to analyse larger quantity of samples.

### 2.4. Kinetic study of epoxy

The impact of the metal oxides on epoxy thermal stability can be ranked by comparing their effect on the activation energy, E<sub>a</sub>. In this investigation, two analytical methods were used: Flynn-Wall-Ozawa method (F-W-O) and Kissinger-Akahira-Sunrose method (K-A-S) [21]. Each method requires the epoxy to be decomposed at a variety of heating rates (β). β = 1, 2, 5, 7 and 10 °C/min were chosen with each sample type being heated from 25 to 700 °C in air.

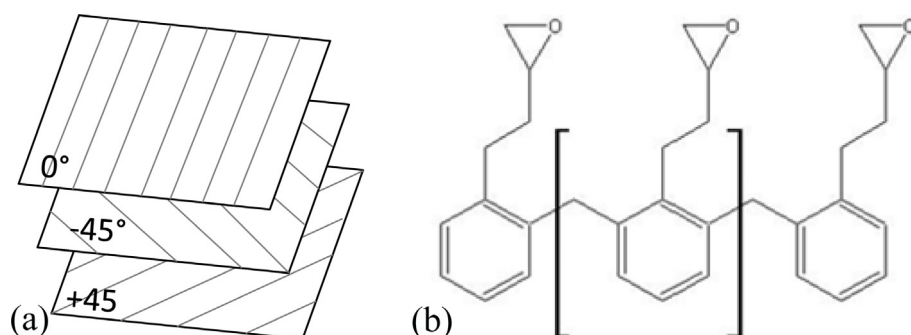


Fig. 1. (a) Schematic of 3-ply glass fibre mat (all fibres tested were taken from the –45° middle layer) and (b) structure of epoxy phenol novolac resin.

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