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Pender, K. and Yang, L. (2017) Investigation of the potential for catalysed thermal recycling in glass fibre reinforced polymer composites by using metal oxides. Composites Part A: Applied Science and Manufacturing, 100. pp. 285-293. ISSN 1359-835X , http://dx.doi.org/10.1016/j.compositesa.2017.05.016

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

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ARTICLE INFO

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_2 and Co_3O_4 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:

$$Me - O + Red \rightarrow Red - O$$

$$Me + Ox - O \rightarrow Me - O + Ox$$
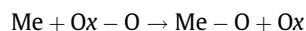
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Initially a reductant (Red) reduces the metal oxide surface $(Me - O)$. It returns to its original state after re-oxidation by an oxidant $(Ox - O)$ [11]. The result of this two stage reaction is the transfer of oxygen from one substance to another [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_3O_4) and cerium (IV) oxide (CeO_2) were selected in this investigation. CeO_2 can become non-stoichiometric at elevated temperatures, providing highly mobile oxygen vacancies through its fluorite structure [11,14]. Although CeO_2 is widely used as a catalyst (such as automobile catalytic convertors), 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_3O_4 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_3O_4 and CeO_2 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^2, 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 predominately 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_a. 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). $\beta = 1, 2, 5, 7$ and 10 °C/min were chosen with each sample type being heated from 25 to 700 °C in air.
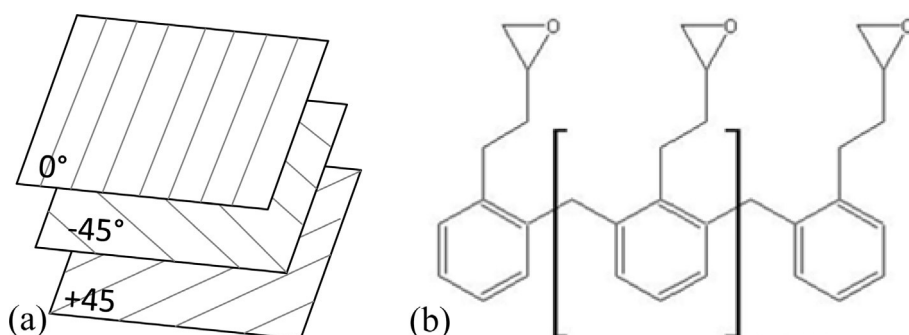

Fig. 1. (a) Schematic of 3-ply glass fibre mat (all fibres tested were taken from the −45° middle layer) and (b) structure of epoxy phenol novolac resin.
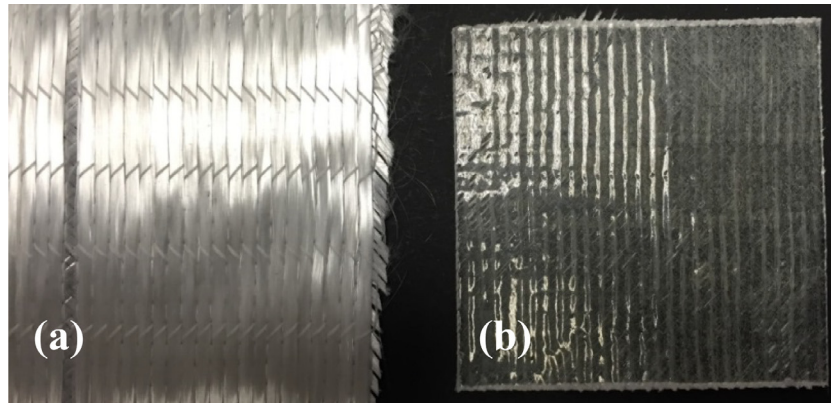
Fig. 2. Images of (a) the glass fibre preform and (b) GF-epoxy sample.

2.5. Thermal degradation of composites using furnace

Lab scale recycling of GF-epoxy was carried out within a furnace with an air atmosphere. Unlike a fluidised bed, this is a static and discontinuous process. This allowed for a simplified means of initial characterisation while still gaining valuable insight into the effect of the metal oxides on fibre strength retention and energy consumption in GF-epoxy recycling. The GF-epoxy plate sat on a 2.7 g bed of metal oxide nanopowder during heating in the furnace, ensuring consistency with TGA sample arrangement. An iterative process was employed to find the minimum epoxy degradation temperature and corresponding minimum treatment time, with each of the metal oxides applied. The treatment time is the duration the sample is heated and the minimum treatment time is defined as the shortest duration of heating required for glass fibre liberation from the matrix, at a given treatment temperature. Initially the minimum degradation temperature required for epoxy to degrade assisted by each metal oxide was found by heating for extended treatment times. The treatment time was then reduced incrementally until both the minimum temperature and treatment time were evaluated. In order to assess the effect of the metal oxides on fibre strength retention, the strength of glass fibres thermally recovered from the middle layer of the GF-epoxy plate with the application of the metal oxide catalysts was measured and compared to those without a catalyst.

In addition, the energy consumption of the furnace used during each epoxy degradation was found using an electricity meter. This allowed a comparison to be made between the catalysing capability of each oxide and both recovered fibre strength and the energy input required for recycling fibres.

2.6. Thermal conditioning of glass fibres

The dependence of heating temperature and time on the E-glass fibre tensile strength was found. Single glass fibres were taken from the middle layer of the original preform and subsequently heated within a furnace in air ranging from 400 to 500 °C for up to 240 min.

The effect of physical contact with each of the metal oxides during heating on glass fibre strength was also investigated. Glass fibre bundles were manually separated in order to increase potential fibre exposure. The metal oxide powders were then layered over the fibres and heat-treated in a furnace for 25 min at 400 and 550 °C. A control sample was also prepared following this procedure with CuO without actually heating to account for possible additional damage to the fibres that could arise from the extra handling involved. After exposing the fibres to the metal oxides for 25 min, single fibre tensile strength was measure as described below.

2.7. Single glass fibre tensile test

All single fibre tensile testing was performed following ASTM C1557-03 and practice developed in [22]. 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. The diameter was then measured using ImageJ software. Tensile testing of the glass fibres was performed using a Testometric M250-2.5CT with a 5 N load cell at a strain rate of 1.5%/min at ambient conditions.

3. Results and discussion

3.1. Non-isothermal epoxy decomposition

Initially TGA was performed on each of the metal oxides in isolation at 500 °C in air. In all cases, there was a small mass loss of no greater than 2%. This mass loss was attributed to impurities in the metal oxide powder and not related to the metal oxide thermally decomposing. As expected no mass gain through oxidation was observed as all metals are at their highest oxidation state. The metal oxides appear stable when heated alone at the temperatures investigated.

Fig. 3(a) shows typical TGA thermograms obtained through non-isothermal degradation of epoxy at a heating rate of 10 °C/min. There is a negligible change to the initial degradation onset temperature for each metal oxides tested; all occuring in the narrow range of 333–338 °C. However, all oxides used in this investigation decreased the onset temperature for the second stage of epoxy degradation; with CeO_2, CuO and Co_3O_4 reducing by 63, 59 and 40 °C respectively. Moreover, CuO results in the largest initial mass loss during the first stage degradation compared to all other samples; exhibiting a loss of over 90% at just 400 °C. Fig. 3(b) shows that the rate of the initial epoxy degradation stage with CuO applied is more than doubled than that found in the same epoxy catalysed by the other two oxides. Both epoxy degradation onset temperature and rate are key parameters in determining its efficiency in facilitating thermal recycling of the composites. The results in Fig. 3 suggest that CuO is the most effective catalyst among the oxides selected in this work in terms of aiding matrix thermal degradation.
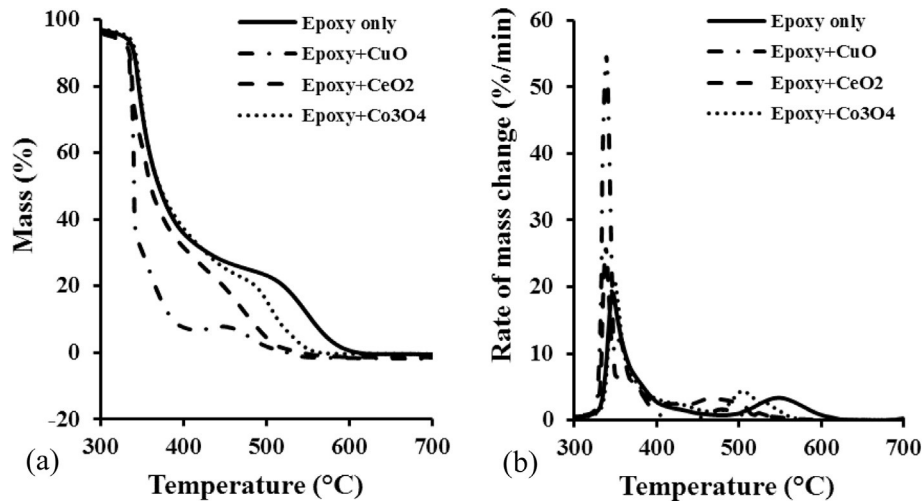
Fig. 3. (a) Comparison of TGA thermograms at a heat rate of 10 °C/min and (b) corresponding rate of mass loss for epoxy and epoxy with various metal oxides.

3.2. Isothermal epoxy decomposition

Fig. 4(a) shows a comparison of the TGA results obtained through isothermal degradation of epoxy at 500 °C. Epoxy exposed to CeO_2 and Co_3O_4 shows a similar two-stage decomposition process; an initial mass loss of around 90% followed by a decreased rate of mass loss until the epoxy fully degrades. Full decomposition occurs after 14 min for the sample with epoxy alone, while 5 and

4 min are required for complete epoxy degradation when CeO_2 and Co_3O_4 are used respectively.

Epoxy exposed to CuO, on the other hand, exhibited a completely different behaviour with initial massive weight loss of 120% followed by a rise to around 0% and final plateau after 5 min. This pattern could be explained by CuO reduction. Since the TGA microbalance was initially zeroed with the CuO powder and sample pan only, any mass loss below zero should be a result
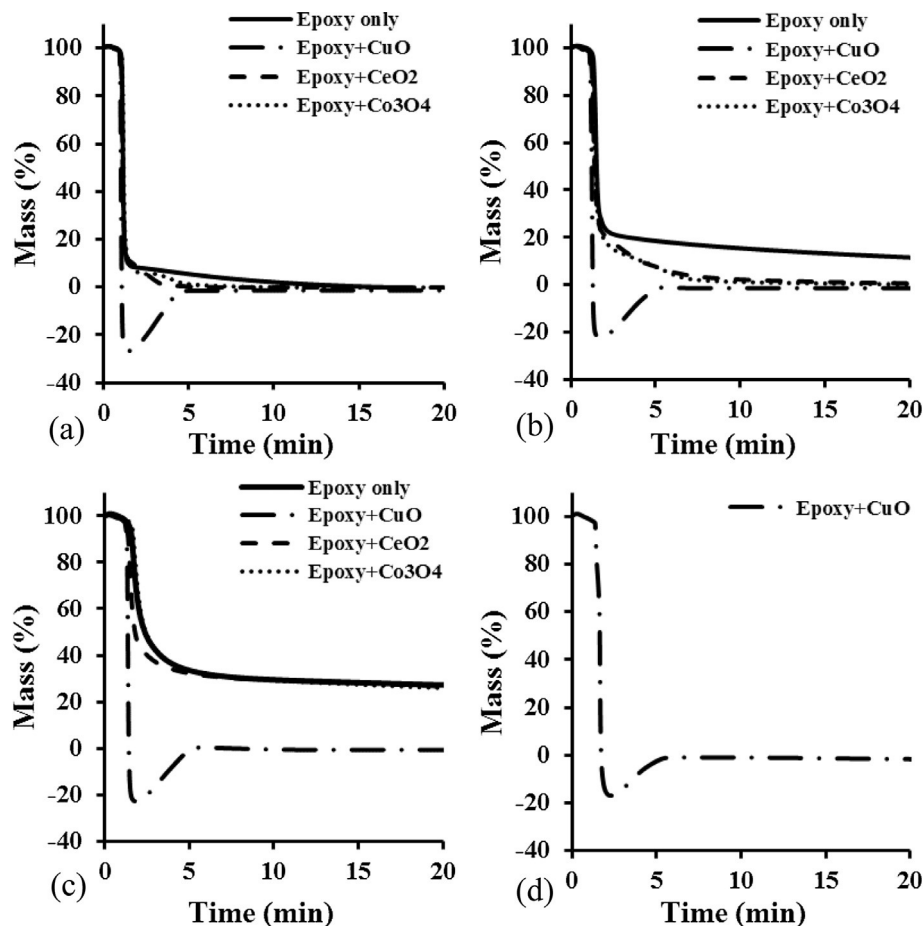

Fig. 4. Comparison of mass loss at a function of time in epoxy resin and epoxy resin with various metal oxides at (a) 500°, (b) 450 °C, (c) 400° and (d) 375 °C.

of CuO mass loss. Since thermal oxidation of the epoxy by CuO would cause CuO reduce to Cu_2O and/or Cu, this would result in a mass loss of CuO (relative to the initial sample mass) between 17% and 33% according to atomic weight change during this transition. The additional mass loss observed in Fig. 4 falls into this range and suggests that the rate of oxygen depletion in CuO is much faster than that in its re-oxidation. It is understood that both copper (I) oxide and copper can be oxidised to re-form copper (II) oxide by the hot air in the TGA furnace, which explains the subsequent weight gain in Fig. 4.

To test this assertion, epoxy applied with CuO was degraded using TGA in a nitrogen atmosphere. Fig. 5 shows the thermogram of the epoxy degrading isothermally at 500 °C. In this case, the additional mass loss from CuO reduction does not recover under nitrogen until the atmosphere in the TGA furnace was switched to air as shown in Fig. 5. Based on the above observation, it is reasonably safe to conclude that the mass loss behaviour below the origin in Fig. 4 should be a result of CuO redox reaction. On the other hand, similar behaviour is not observed when using CeO_2 and Co_3O_4. This could be another indication of their less catalytic efficiency.

In light of the behaviour of CuO in Fig. 4, it is plausible that the substantially greater mass loss of epoxy + CuO in Fig. 3a, between 350 and 450 °C, is the result of epoxy degradation facilitated by CuO and simultaneous CuO reduction. The extend of CuO contribution to the mass loss in this region could be estimated to be up to 20%, in agreement with that observed in Fig. 4.

When heating at 450 °C as shown in Fig. 4(b), only the uncatalysed epoxy fails to fully degrade within 15 min. Epoxy applied with CeO_2 and Co_3O_4 shows full degradation within approximately eight minuites. In contrast, the temperature reduction appears to have little effect on the catalysing performance of CuO, which produced near identical TGA therograms to that at 500 °C in Fig. 4(a). Further temperature reduction to 400 °C shows that only the epoxy in contact with CuO can fully degrade within 15 min as shown in Fig. 4 (c). It was found that the minimum temperature required for epoxy in the presence of CuO to degrade using TGA was merely 375 °C as indicated in Fig. 4(d). This has important implication in the energy reduction for thermal recycling as well as the strength preservation for recycled glass fibres.

3.3. Activation energy of epoxy decomposition

A summary is given below outlining how the Ea was found from TGA data. The F-W-O and K-A-S methods use the integral isoconversional principle; it is assumed that the reaction rate at constant extent of conversion is only a function of temperature. Eq. (1) gives the integral form of the reaction model.

$$g(\alpha) = \frac{A}{\beta} \int_0^T exp\left(\frac{-Ea}{RT}\right) dT \qquad (1)$$

It was derived by integration of the Arrhenius equation with the rate of conversion being a linear function of the time dependent rate constant and time independent conversion, α. A is the pre-exponential factor, R is the universal gas constant and T is temperature (absolute). Since Eq. (1) does not have an analytical solution, integral isoconversional methods typically make approximations of the temperature integral in linear form. The approximations given by the F-W-O and K-A-S methods are given in Eqs. (2) and (3) respectively.

$$ln(\beta_i) = Constant - 1.052\left(\frac{-Ea_\alpha}{RT_\alpha}\right) \qquad (2)$$

$$ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = Constant - \frac{-Ea_\alpha}{RT_\alpha} \qquad (3)$$

The index i denotes various temperature programs. These methods allow the Ea at various extents of conversion to be found by plotting $ln(\beta_i)$ vs $1/T_\alpha$ and $ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right)$ vs $1/T_\alpha$ for the F-W-O and K-A-S methods respectively [21].

As the F-W-O method was derived using the Doyle approximation, only conversions in the range of 20–35% can be used [23]. Fig. 6 shows the rate of change of mass for epoxy only degradation and clearly illustrates the thermal lagging effect caused by varying the heating rate. Ea is given as a function of conversion for the F-W-O and K-A-S methods in Fig. 7(a) and (b) respectively. It can be clearly seen that both methods exhibit a significant reduction in the Ea across the 20–35% conversion range of epoxy decomposition assisted by the selected oxides in this work. The two methods also yield similar Ea-conversion trends with the K-A-S method giving slightly higher values. Fig. 7 clearly indicates that epoxy degradation assisted by CuO has the lowest Ea and proves that CuO indeed possess the best catalytic efficiency among three metal oxides. The Ea of epoxy + CeO_2 and epoxy + Co_3O_4 are relatively constant across the conversion range analysed, however, epoxy + CuO and epoxy only clearly increase with conversion. This suggests alternative epoxy degradation kinetics, which could be further investigated using more complex autocatalytic models. Furthermore, the catalytic capability of CuO may decline with conversion as a result of reduction, leading to the observed rise in Ea.
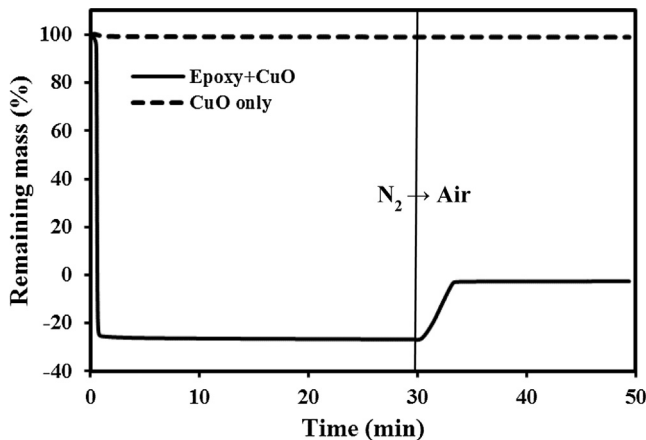

Fig. 5. Mass loss at a function of time at 500 °C in both CuO and epoxy with CuO in nitrogen between 0 and 30 min and in air between 30 and 50 min.
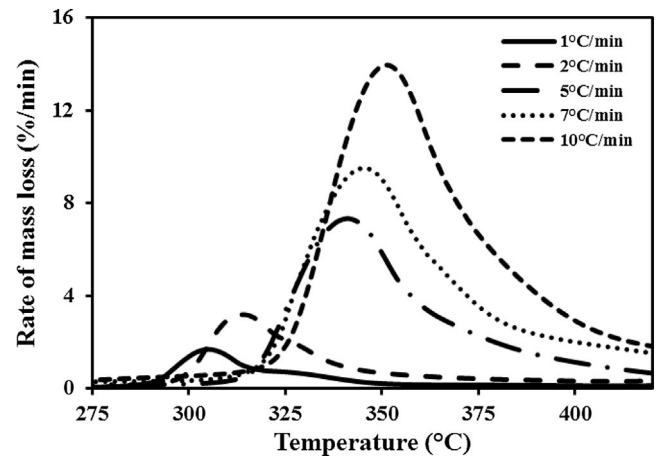

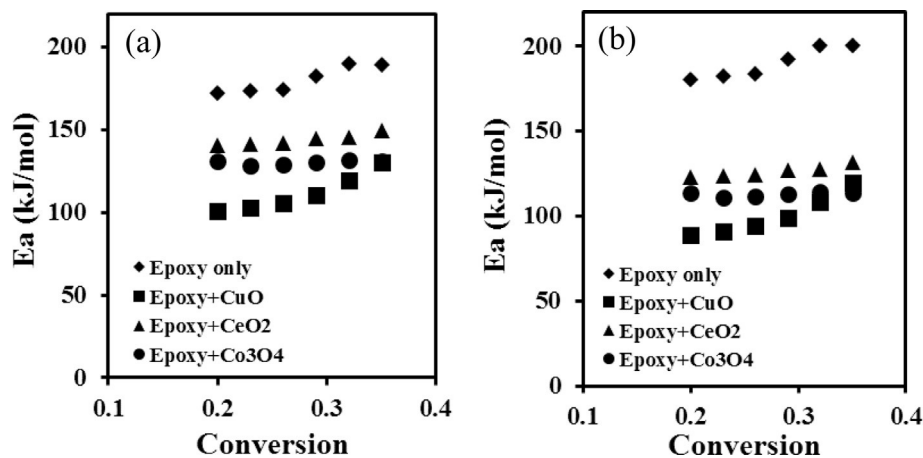**Fig. 6.** Effect of heat rates on rate of mass loss in epoxy.

Fig. 7. Calculated activation energy across 20–35% conversion using (a) F-W-O and (b) K-A-S methods.

These results agree well with those in Figs. 3 and 4. The F-W-O method gave 68, 36 and 50 kJ/mol for the average reduction in Ea (across 20–35% conversion) caused by CuO, CeO$_2$ and Co$_3$O$_4$ respectively. This has real world implications and alludes to a lower energy input required for composites thermal recycling.

3.4. Effect of metal oxides on composites recycling using furnace

Table 1 gives the epoxy matrix decomposition temperature and time found qualitatively for GF-epoxy samples degraded in the furnace in the presence of the metal oxides. In agreement with the results obtained from TGA, CuO provided the largest reduction in the required temperature for the epoxy matrix to fully degrade. CuO, CeO$_2$ and Co$_3$O$_4$ decrease the recycling temperatures by 120, 50 and 50 °C respectively. These results are consistent with those observed using TGA. Table 1 also shows that the heating period required is considerably extended as the temperature is reduced even including the case of the use of CuO. Such phenomenon may seem to be expected from typical temperature dependence of reaction kinetics. However, the results in Fig. 4 have clearly demonstrated that similar temperature reduction can hardly affect the period of epoxy degradation when highly efficient catalyst, such as CuO, is employed. It implies that the extended period of GF-epoxy decomposition observed in the furnace is likely to be caused by up-scaling effect compared to very small amount of epoxy samples used in TGA. It is reasonable to expect that such extended period of full matrix degradation could be minimised in a different recycling process such as fluidised bed, in which much smaller composite scraps will encounter agitated particles to give more effective interaction between them. Fig. 8 shows a comparison between GF-epoxy heat-treated with and without CuO. Both samples were heated at 380 °C for 330 min. It can be clearly seen that GF-epoxy degradation assisted with CuO returned with clean glass fibres as shown in Fig. 8(b) in contrast with its counterpart in Fig. 8(a).

Table 1 also shows that the total energy required to recycle each of the samples within the furnace, measured using an electricity meter. It can be shown that all metal oxides can reduce the energy consumption of the furnace by around 40% compared to uncatalysed GF-epoxy recycling. The values calculated are specific only to the furnace used in this investigation and may not be generalised for different operations. It should also be noted that the energy consumption of the furnace is likely dominated by its heat loss with little influenced from the exothermic reaction taking place inside. The calorific value of the GF-epoxy processed is likely to be around 12 kJ/g and therefore insignificant compared to the furnace energy consumption figures given in Table 1 [24]. The established furnace parameters (temperature and time) required for thermal decomposition therefore dictates the measured energy consumption. Nevertheless, a simple comparison of energy consumption between heating parameters should reflect the potential energy benefit from the employment of degradation catalysts.

Further investigation will be carried out in translating this technology to a large-scale process, such as a fluidised bed recycling system. The dynamic nature of the fluidised bed process could overcome the difficulties of solid-solid mass transfer in static operations as in furnace. The method of catalyst integration into the process could be achieved by incorporating an oxide into the fluidised bed reactor as (or as a constituent of) the fluidising medium. The fluidise bed process can also facilitates the continuous reuse of the catalyst. Even if relatively high quantities of oxides are initially required, the cost benefit of long-term reduction in operating conditions could be realised.

3.5. Effect of temperature and time on glass fibre strength

An investigation was first carried out to establish the effect of temperature and time on glass fibre strength. Fig. 9 shows the relative residual single fibre tensile strength after heating at various temperatures in the range of 400 and 500 °C for up to 240 min. The error represents a 95% confidence limit. In close agreement with the literature, glass fibres are susceptible to strength loss caused by heating. Fibres exposed to a temperature of 400 °C lost around 25% of their strength after 20 min. Prolonged exposure of 120 and 240 min led to approximately 40% strength retention. When heated at 500 °C, the glass fibre strength diminishes to 47% of its original value within the first 20 min and levels off at 42% within 60 min. Clearly, both heating temperature and time influence the fibre strength, however, the residual strength plateau
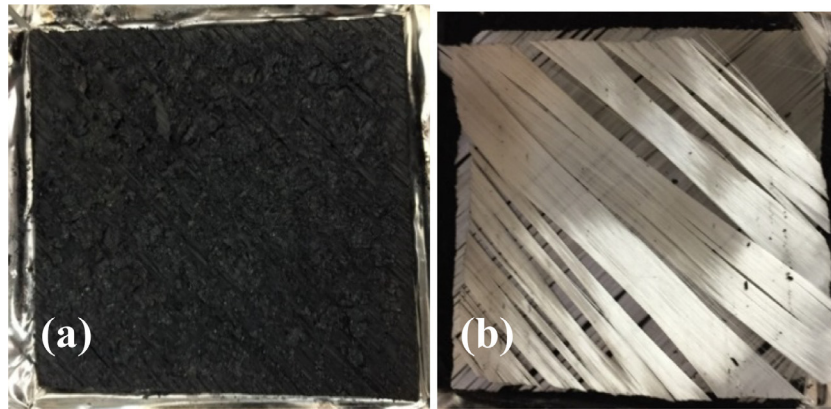
Table 1
Energy consumption required for fibre liberation by thermally degrading epoxy matrix with different temperature and duration.

Sample	Temperature (°C)	Time (min)	Furnace energy consumption (kJ)
GF-epoxy only	500	80	64,200
GF-epoxy + CuO	380	330	20,200
	400	180	6030
	430	65	3720
GF-epoxy + CeO$_2$	450	60	4000
GF-epoxy + Co$_3$O$_4$	450	65	4090

Fig. 8. Image of (a) GF-Epoxy after heat treatment at 380 °C for 330 min without CuO (b) GF-Epoxy after identical heat treatment with CuO.
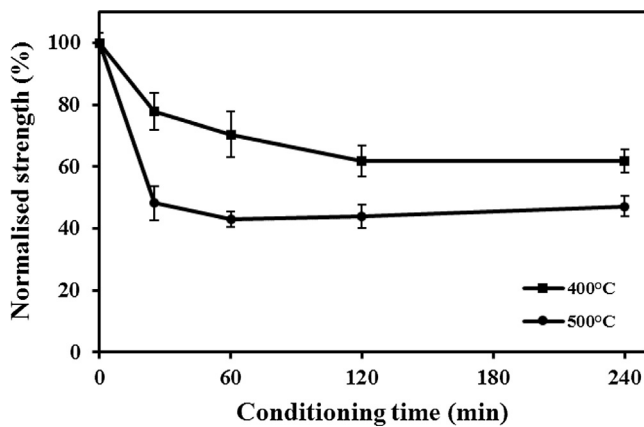

Fig. 9. Strength loss of glass fibres after heat treatment at various temperatures and times.

Fig. 10. Tensile strength of glass fibres recycled from GF-epoxy composites with the aid of the metal oxides.

increases in value with decreasing treatment temperature as seen in Fig. 9. The rate of strength loss is generally greater for high treatment temperatures; suggesting that composite recycling time is more detrimental to fibre strength retention at higher temperatures. Overall, these data confirm the notion that reducing the typical recycling temperature/time of GF-epoxy by means of catalysed epoxy degradation could yield glass fibres with significantly increased strength retention.

3.6. Strength of thermally recycled glass fibres

Fig. 10 shows the tensile strength of the glass fibres thermally recycled from GF-epoxy with the use of the metal oxides studied in this work. These results are compared to the strength of fibres after directly heat-treating glass fibres at the same temperature and time, as indicated in Fig. 9. Strength loss was sustained in all cases given an as received strength of 2.55 GPa. The GF-epoxy only sample heated at 500 °C yielded fibres with a strength of 0.94 GPa, which is lower than was observed for glass fibres directly heated at a similar schedule. This suggests that the additional processing and handling involved in manufacturing and retrieving fibres from the degraded GF-epoxy may have resulted in additional fibre damage.

Despite the high anticipation for potential strength retention indicated by the results obtained from direct fibre heat-treatment, the use of metal oxides showed much less effect on improving strength retention of recycled fibres as seen in Fig. 10. The average tensile strength of glass fibres recycled using CuO, CeO$_2$ and Co$_3$O$_4$ are respectively 1.11, 1.14 and 0.99 GPa giving
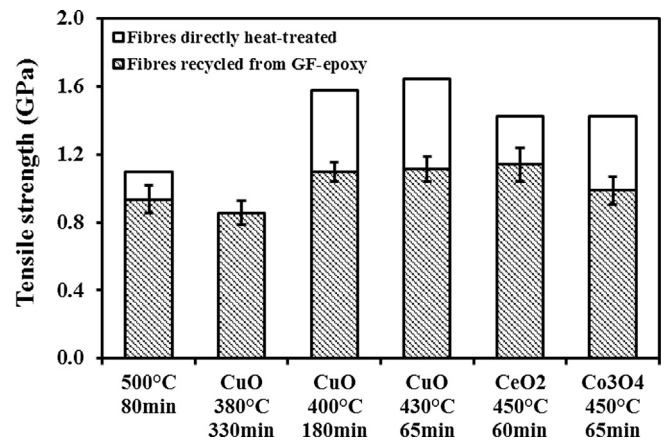
the maximum 21% strength recovery. Two possibilities may account for this under-delivered performance in strength recovery.

The first one is the actual thermal loading experienced by the fibres during GF-epoxy recycling inside the furnace. Fig. 11 shows a comparison of surface temperature of GF-epoxy samples with
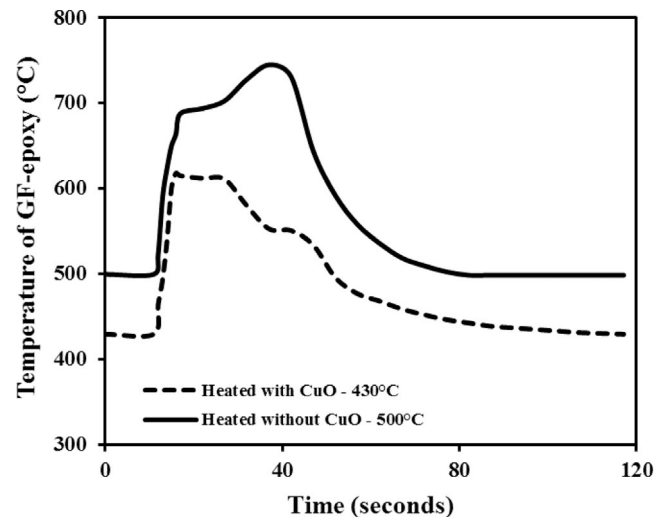

Fig. 11. Temperature measured directly on GF-epoxy composites surface during thermal recycling in furnace.

and without the presence of CuO. The temperature was measured by an independent thermocouple placed directly on the GF-epoxy during thermal recycling in the furnace. As it can be seen in Fig. 11, the surface temperature of the GF-epoxy increases substantially in both cases before it gradually drops down to corresponding set temperatures. Although the metal oxides increase the rate of epoxy decomposition, this did not result in transitory heating of fibres beyond that experienced in uncatalysed samples during recycling. The fibres recycled using CuO, however, experienced over 550 °C for 35 s with a maximum temperature of 620 °C. This sharp temporary rise in temperature is due to the exothermic nature of epoxy decomposition. The effect of this rapid thermal loading on the glass fibre strength was further investigated by heating glass fibre bundles at 600 °C for 15, 30 and 60 s within the same furnace. Inserting the fibres into the pre-heated furnace posed a challenge when heating for such short time periods. The fibres should be introduced without opening the main furnace door to avoid cooling and ensure an accurate thermal loading. This was achieved by rapidly lowering the fibre bundle in through the furnace chimney, which was originally installed to allow flue gas to escape. A precise conditioning temperature was attained by installing an independent thermocouple next to the fibres, as shown in Fig. 12.

Fig. 13 shows a dramatic reduction in fibre strength of around 40% and 50% after exposure to 600 °C for merely 15 and 30 s respectively. It is therefore clear that the brief increase in thermal loading caused by the epoxy can cause substantial weakening of the fibres. By recycling statically within the furnace, the rise in temperature as the epoxy degrades could not be adequately regulated. Simply halting energy input when the furnace temperature is above the set point is insufficient and consequently results in significant fibre weakening. The overshoot may be better controlled within a dynamic process such as a fluidised bed reactor. This allows a more responsive means of temperature control and could distribute areas of localised heating. This will be investigated further by examining processing parameters such as feeding rate and feedstock size when metal oxides are integrated in a fluidised bed recycling system.

The other possible explanation for the lack in strength retention could be related to sizing degradation, which may have also been promoted by the metal oxides. Fig. 14 presents the results obtained from TGA with glass fibre with and without the presence of the oxide catalysts. It is clear from Fig. 14 that all the metals oxides indeed also greatly facilitate the sizing degradation. It is interesting
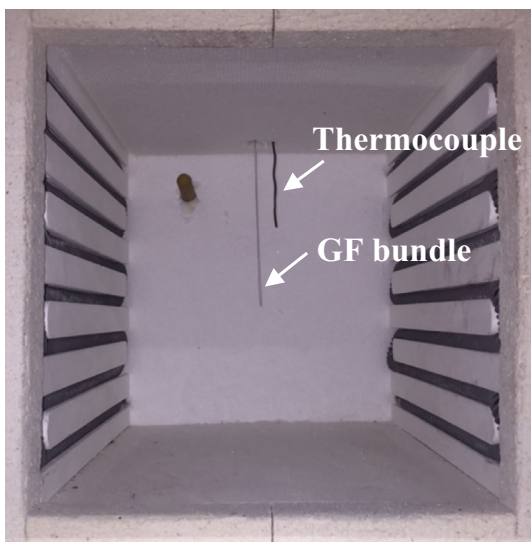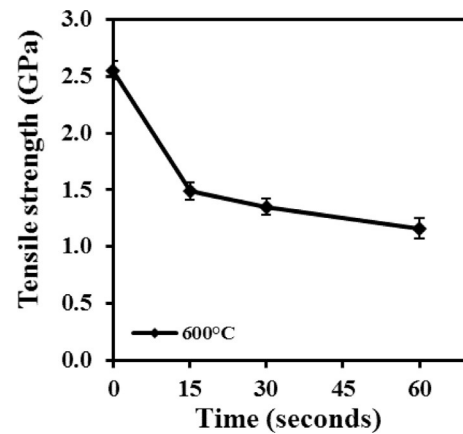
Fig. 13. Tensile strength of glass fibres after heating at 600 °C for a short period (less than a minute).
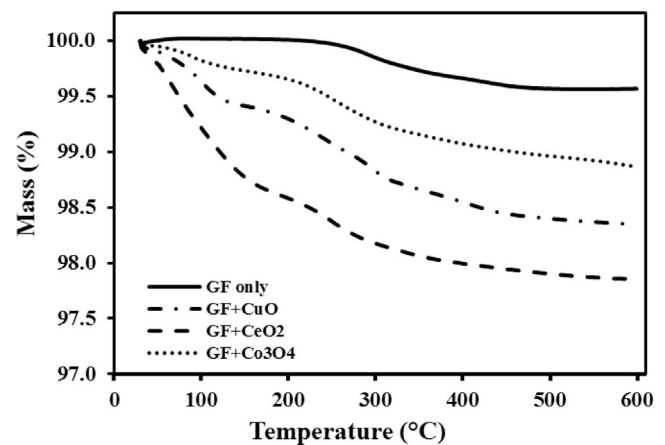
Fig. 14. Mass loss of glass fibres assisted by metal oxides as a function of temperature.

to see that CeO_2 proves to be most effective in promoting degradation of the sizing. The exact sizing composition is proprietary and cannot be made readily available. Nevertheless, it implies that catalytic efficiency of these selected metal oxides is also dependent on targeted polymers. Fig. 15 shows a comparison of the strength of
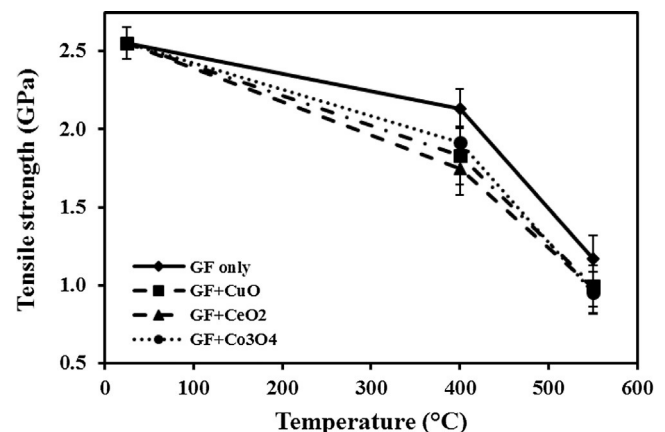
Fig. 12. Furnace arrangement for short thermal loading to glass fibre bundle.

Fig. 15. Tensile strength of glass fibres after direct heat-treatment with metal oxides at different temperatures.

glass fibres after heating in direct physical contact with each of the oxide catalysts. No reduction in the strength of fibres applied with CuO was observed when they did not undergo any elevated temperatures. This simply rules out the possibility of the mechanical effect of application of the oxides on fibre strength. At elevated temperatures, however, lower strength is exhibited by fibres heated in the presence of all the metal oxides. It is interesting to point out that the rate of strength loss presented in Fig. 15 seems to correlate with the results in Fig. 14. The more efficiently an oxide catalyst is able to promote sizing degradation, the more strength loss is caused by that oxide. As temperature of the heat-treatment continues to increase, fibre strength presented in Fig. 15 tends to converge regardless of the type of the oxides and their presence. This observation shares the similarity with that in [20], where it showed the effect of sizing degradation on the difference in strength loss of heat-treated glass fibres diminished as higher temperatures (e.g. 500–600 °C) are reached. This supports the observation from Fig. 15. However, the additional strength loss caused by the oxides does not seem sufficient to account for the total strength retention reduction shown in Fig. 10. Consequently, the lower-than-expected strength retention could be attributed to the effect underpinned by both factors discussed above.

4. Conclusions

This investigation has successfully demonstrated the ability of CuO, CeO$_2$ and Co$_3$O$_4$ to reduce the thermal stability of epoxy-based composites and their potential for improving thermal recycling process and fibre strength retention. It was found that CuO is superior at promoting epoxy decomposition; enabling full degradation at just 375 °C. The kinetic study found that all metal oxides tested reduce the activation energy in epoxy degradation. CuO provided the largest decrease in epoxy thermal stability; reducing the average activation energy by up to 90 kJ/mol.

The applicability of the metal oxides on GF-epoxy thermal recycling was established in terms of recycling temperature, energy consumption and recycled fibre strength. CuO, CeO$_2$, and Co$_3$O$_4$ successfully reduced the epoxy matrix decomposition temperature required for glass fibre liberation by 120, 50 and 50 °C respectively, while reducing recycling time by around 20 min. This was followed by around a 40% reduction in energy consumption when recycling with the oxides. CuO and CeO$_2$ exhibited superior performance, capable of increasing strength retention by 20%.

It was found that the thermal loading on fibres within GF-epoxy during recycling increased conciderably above the target recycling temperature due to exothermic epoxy decompostion. It was demonstrated that similarly brief high temperature treatments could significantly weaken fibres and is likely the predominant contributor to the lack in recycled fibre strength. Direct application of metal oxides on glass fibres during heat treatment caused greater weakening than was observed through thermal effects alone and it was confirmed that the metal oxides under investigation increase sizing degradation during heating. Consequently, sizing removal faciliated by the catalysts may also contribute to diminished fibre strength retention.

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