CATALYSED THERMAL DECOMPOSITION OF MATRICES FOR CLOSED-LOOP RECYCLING OF FIBRE REINFORCED THERMOSETS

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Abstract

An investigation into catalysed thermal decomposition of epoxy resin was carried out with the goal to improve the commercial viability of glass/carbon fibre reinforced thermoset recycling. Tensile strength degradation was initially established as a barrier in retaining the value of reinforcing fibres after thermal recycling. A variety of metal oxides were examined to find their ability at reducing the high operating temperatures currently limiting the reusability of recovered glass fibres. It is proposed that such a material could be integrated within an established recycling system, such as a fluidised bed reactor, facilitating an increase in glass/carbon fibre tensile strength. It was found through thermogravimetric analysis that copper (II) oxide, cerium (IV) oxide and cobalt (I,II) oxide nanopowders could reduce the second stage degradation onset temperature of epoxy resin by 59, 63 and 40°C respectively. When applied to glass fibre reinforced epoxy resin the temperature required for fibre liberation was reduced by up to 120°C. The strength of glass fibres recovered with the aid of the metal oxides showed some increase in strength but was less than expected given the notable reduction in conditioning temperature required for fibre liberation. All oxides reduced the thermal stability of IM7 carbon fibres resulting in amplified weakening of the fibres after thermal conditioning at just 400°C.

1. Introduction

Due to their extraordinary specific mechanical properties; carbon fibre reinforced plastics (CFRP) have found applications in the aerospace, automobile and sports industries. Production of virgin carbon fibres is expected to rise to 100 kilotons by 2018[1]. 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. Their low production cost and good specific mechanical properties have made GFRPs ideal materials to use in many engineering sectors; predominantly the renewable energy and transport industries [2, 3]. A consequence of this increase in demand in both glass and carbon reinforced plastics is a large amount of composite production waste and end-of-life products.

Increasing pressure through new government legislation is forcing the end-user to dispose of end-of-life composites in an eco-friendly manner. Unlike reinforced thermoplastics; thermoset based composites cannot easily be reused/recycled due to their polymer crosslinking. Many proposed recycling methods for both carbon and glass fibre reinforced thermosets (CFRT and GFRT respectively) involve liberation of the fibres from the matrix, followed by reuse in secondary composite components.

Fluidised bed systems have been shown to successfully recover carbon fibres from thermosetting resins by thermally degrading the matrix in air at around 550°C[4]. This process has several

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advantages such as; diminished char residue due to the presence of oxygen in the fluidising fluid, tolerance to mixed/contaminated materials and scalability. Carbon fibres recovered by means of the fluidised bed process can exhibit a tensile strength reduction between 25-50%[5]. The mechanism for PAN based carbon fibre strength loss during thermal condition is oxidation of the fibre surface. The degree of oxidation and fibre mass loss is dependent on, but not limited to, heating temperature and time of exposure[6]. As with CFRT, the fluidised bed has been utilised to degrade the thermoset matrix and liberate reinforcing glass fibres. The thermoset decomposition temperature, process time and surface damage caused during processing renders the glass fibres unusable in high strength components. *Feih et al.* reports a glass fibre strength loss of around 60% after just 8 minutes when heat treated at 550°C. This strength loss is increased to 70% after thermal conditioning at 600°C for 15 minutes [7, 8]. Although this process has been shown to successfully retrieve glass fibres; work must be carried out to develop an approach capable of reducing any/multiple thermal recycling limitations[9].

A novel method to aid the decomposition of thermoset matrices in fibre reinforced composites is underway by investigating the use of metal oxide catalysts. It is proposed that an oxide catalyst could potentially be integrated within a fluidised bed system to assist the combustion process, reduce operating conditions, and recover glass/carbon fibres with higher residual strength. Transition metal oxides are utilised in many organic reactions and are notable for their redox properties[10]. Three metal oxides were selected for thermal analysis; copper (II) oxide (CuO), Cobalt (II,III) oxide (Co_3O_4) and cerium (IV) oxide (CeO_2). These were selected based on; their published ability to aid polymer degradation, thermal stability, low health risks and cost. It was deemed essential that the metal oxides chosen must be able to be used commercially.

2. Experimental

2.1. Epoxy resin thermal decomposition

Epoxy degradation with and without various metal oxides present was initially carried using TGA in order to rank the catalysts performance. The catalysts effect on the decomposition onset temperature is particularly important when considering the effect this has on the fibre residual strength after recycling. CuO, Co_3O_4 and CeO_2 nanopowders were purchased from SIGMA-ALDRICH with particle size of <50nm (TEM), <50nm (TEM) and 21 nm (TEM) respectively. PRIME 27 Resin and PRIME 20LV extra slow hardener were supplied by Gurit. They were mixed at a weight ratio of 100:28 then, using a syringe, small droplets of the uncured epoxy were dropped onto non-stick plastic sheets. The epoxy disks were then cured following supplier instruction. Sample selection was then carried out by weighing the epoxy disks; any out with the range of 11.5-12.5mg were discarded. The samples were finally prepared for thermal analysis by applying a layer (≈20mg) of metal oxide in an Alumina TGA pan. In an attempt to keep a consistent interface area, the flat (underside) surface of the epoxy disk was then placed on top of the oxide layer.

In order to determine whether the metal oxides possess the ability to reduce the decomposition temperature of epoxy the samples were degraded under non-isothermal conditions. They were heated at a rate of 10°C/min from room temperature to 700°C in the presence of air, using a TA Instruments Q50. Further investigation of the effect of metal oxides was carried out by decomposing isothermally; showing the time and minimum temperature required for full epoxy degradation. In this case the sample was rapidly heated from room temperature to a variety of temperatures in the presence of air then held isothermally until the epoxy had fully decomposed.

2.2. Single E-glass fibre tensile testing

In order to estimate the recycling temperature reduction required to re-claim commercially valuable glass fibres, the effect of temperature and time on thermally conditioned glass fibres was found. Subsequent experimental work required the manufacture and recycling of GFRP therefore glass fibre

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bundles were taken from a pre-made mat; this ensured consistency with regards to fibre type throughout the single fibre tensile testing. E-glass fibre bundles were taken from a FORMAX tri-axial (0°/ -45°/+45°) 3 ply mat and thermally conditioned within a furnace in air ranging from 400 to 500°C for up to 240mins. Following this; 30 single glass fibres from each heating schedule were glued to 20mm gauge length card templates. The cross sectional area of each glass fibre was found by capturing an image of the fibre using an Olympus GX51 optical microscope then measuring its diameter using ImageJ software. The fibre cross section was assumed to be circular. Tensile testing of the glass fibres was performed using a Testometric M250-2.5CT with a 5N load cell at a strain rate of 1.5%/min following ASTM C1557-03.

2.3. Glass fibre reinforced epoxy preparation and decomposition

GFRP laminates were manufactured to find the effect of the catalysts on their recycling temperature and subsequent recovered fibre strength. The 3 layer FORMAX tri-axial mat described above was infused with PRIME 27 resin and hardener at a weight ratio of 60% glass fibre and cured as before. After curing, the laminates were cut into 60x60mm squares, having a thickness and mass of around 2mm and 6.7g respectively. A sample arranged similar to that of TGA was used whereby the GFRP sat on a metal oxide bed. To keep the ratio of catalyst to epoxy mass (5:3) consistent with the TGA experiments, 6.7g of each metal oxide was use since 60% weight of the GFRT was glass fibres. An iterative process was used to find the minimum epoxy decomposition temperature with each of the metal oxides applied. Each sample was initially heat treated at 500°C for 90mins; if the epoxy degraded allowing fibres to be recovered for testing the temperature was reduced by 10°C and a new sample was treated. Once the minimum temperature required for fibre liberation was found the conditioning time was reduced incrementally until both the minimum recycling temperature and time were determined. This process was repeated for each metal oxide. In an attempt to ensure consistency both in terms of the fibres tested and handling required to retrieve the liberated fibres; the fibres selected for testing were always from the middle layer of the recycled mat. Glass fibre sample preparation and testing was carried out as outlined above.

2.4. Thermogravimetric analysis of carbon fibre decomposition in air

As the strength reduction mechanism of carbon fibre during heating is associated with the oxidation of the carbon on the fibre’s surface; it was anticipated that the oxides may actually reduce strength retention by increasing carbon oxidation. Thermogravimetric analysis was performed on IM7 fibres in the presence of each oxide. The carbon fibre degradation onset temperature was found for each sample type by thoroughly mixing 3mg of chopped carbon fibre (around 5mm in length) with 22mg of each oxide nanopowder and heating at 5°C/min in air

3. Results and Discussion

3.1. Non-isothermal decomposition of epoxy resin using TGA

Figure 1(a) shows typical thermograms obtained through non-isothermal degradation of epoxy at a heating rate of 10°C/min. There is a negelagible change to the initial degradation onset temperature for each metal oxides tested; all occuring in the range of 333-338°C. All oxides tested however decreased the second stage degradation onset temperature; with CeO_2, CuO and Co_3O_4 reducing by 63, 59 and 40°C respectively. CuO facilitates the largest initial mass loss compared to all other samples; exhibiting a loss of over 90% at just 400°C. Figure 1(b) shows the rate of the initial epoxy degradation stage with CuO applied is more than doubled that of any other sample type. Although the thermograms produced by samples containing CeO_2 and Co_3O_4 show a reduction in temperature required for full epoxy decompostion; there is little divergence from epoxy only before 400 and 480°C respectively. Both epoxy degradation onset temperature and rate are key parameters in determining wether this techonolgy can be applied to fibre reinforced plastic recycling. These initial results suggest that CuO could be the most effective catalsyt for aiding GFRT decomposition.

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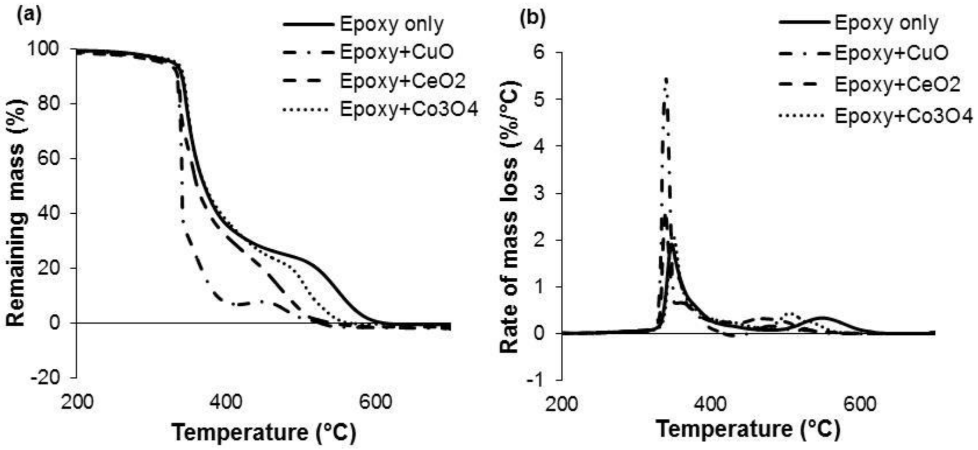

Figure 1 Comparison of TGA thermograms at a heat rate of 10°C/min

3.2. Isothermal decomposition of epoxy resin using TGA

Figure 2(a) shows a comparison of the TGA results obtained through isothermal degradation of epoxy at 450°C. At this temperature only the un-catalysed epoxy fails to degrade within 15mins. Samples containing CeO_2 and Co_3O_4 produce similar thermograms; taking around 8mins to decompose. An initial large drop in mass also occurs in samples containing CuO which continues below zero, stopping at a mass of -20% and is followed by a rise to around 0% after 5mins where it finally plateaus. This pattern was typical for every isothermal heat treatment carried out containing CuO. Prior to epoxy degradation the TGA microbalance was zeroed with the CuO powder in the alumina pan; therefore, at these temperatures an explanation for such a phenomenon may be CuO reduction by carbon present in the epoxy. Furthermore, the mass loss below zero is (in all cases) smaller than the theoretic mass of oxygen within the CuO nanopowder used. It is known that copper will readily oxidise when heated in air which could explain the gradual rise in mass. At a treatment temperature of 400°C, Figure 2(b), only epoxy applied with CuO fully degrades within 15mins. CeO_2 provides an initial increase in rate of mass loss however, just like Co_3O_4, the residual mass after 15mins is the same as epoxy alone samples at around 28%. It was found that the minimum temperature required for epoxy in the presence of CuO to completely degrade using TGA was just 375°C, providing a 125°C reduction in decomposition temperature compared to epoxy alone.

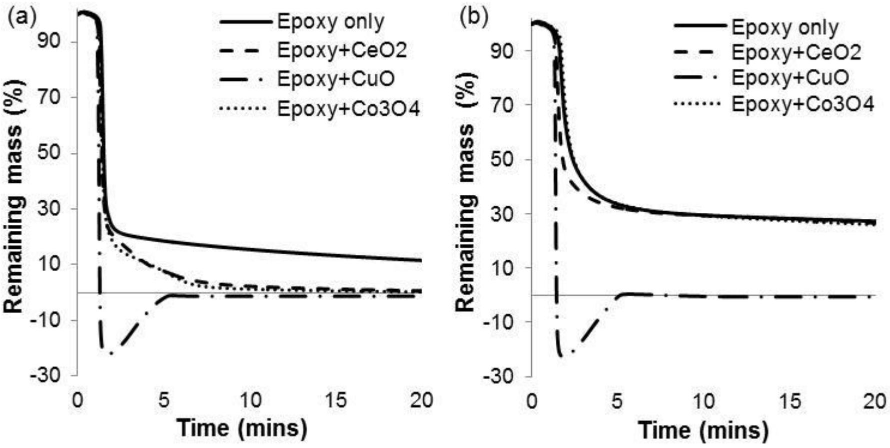

Figure 2 Comparison of epoxy resin decomposition time using the TGA isothermal heating program at (a) 450° (b) 400°C

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3.3. Effect of recycling temperature and time of E-glass fibre tensile strength

An investigation was carried out to establish the effect of the thermal conditioning parameters, temperature and time, on E-glass fibre strength. Figure 3 shows the relative residual single fibre tensile strength after heating at 400 and 500°C for up to 240mins. The error represents a 95% confidence limit. In close agreement with the literature, glass fibres are clearly susceptible to strength loss during thermally conditioning. Fibres exposed to a temperature of 400°C lost around 25% of their strength after 20mins and prolonged exposure of 120 and 240mins produced fibres with around 60% strength retention. When heat treated at 500°C for 20mins the glass fibre strength diminishes to 47% of its original value and finally plateaus at around 42% after a maximum of 60mins. Both conditioning temperature and time influence tensile strength retention, however, residual strength eventually plateaus at different values depending on treatment temperature. There is therefore a maximum expected tensile strength loss for a given recycling temperature, whereby prolonged heat expose may no longer effect residual strength. The rate of strength loss is greater for the higher conditioning temperature, with fibres heated at 500°C reaching this minimum residual strength faster than those exposed to 400°C. This data confirms the notion that reducing the typical recycling temperature of GFRT by means of catalysed epoxy degradation should yield glass fibres with increased strength retention.

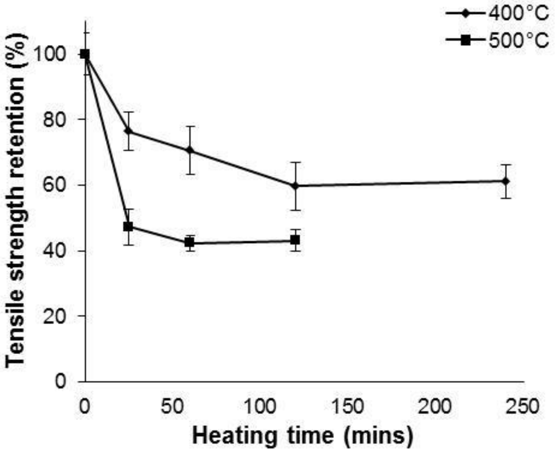

Figure 3 Strength of E-glass fibres after heat treatment at 400 and 500°C for a variety of conditioning times

3.4. Tensile strength of glass fibres recovered from GFRT

Table 1 gives the epoxy matrix decomposition temperature and time found qualitatively for each applied metal oxide. The un-catalysed GFRT control required a minimum recycling temperature of 500°C for 80mins in order to recover glass fibres for strength testing. CuO, CeO_2 and Co_3O_4 decrease the recycling temperature by 70, 50 and 50°C respectively.

Table 1 Summary of thermal conditioning parameters required for fibre liberation

Sample	Temperature (°C)	Time (mins)
GFRT only	500	80
GFRT+CuO	430	65
GFRT + CeO_2	450	60
GFRT+Co_3O_4	450	70

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The temperature required for the epoxy matrix to degrade when CeO_2 and Co_3O_4 are utilised is consistent with that observed using TGA under isothermal heating conditions; however, the treatment time required is considerably longer. According to TGA data CuO is demonstrably superior at reducing the epoxy degradation. This was not reflected when applied to GFRT recycling, requiring 430°C for 65mins to liberate fibres. It was believed that restricting the recycling time was limiting the potential temperature reductions that could be achieved when catalysing the epoxy matrix thermal degradation using CuO. By removing the time limitation it was found that fibres could be recovered at 380 and 400°C after 330 and 180mins respectively when using CuO.

Figure 4 shows the tensile strength of the glass fibres thermally recovered from GFRT with the use of the metal oxide nanopowders. With an as received tensile strength of 2.49GPa, considerable strength loss was sustained with and without each of the catalysed used. The tensile strength of fibres recovered without a catalyst at 500°C is 0.936GPa and closely correlates to that found for glass fibres directly heated at a similar schedule. Glass fibre tensile strength retention plateaued at around 42% after heat treating bundles at 500°C; when recovered from GFRT at the same temperature, fibre tensile strength retention is 38%. All catalysts tested are able to reduce strength loss during the epoxy matrix thermal decomposition. The highest strength retention provided by CuO, CeO_2 and Co_3O_4 are 1.11, 1.14 and 0.988GPa respectively. Although they provided a reduction in GFRT thermal recycling conditions, the retained strength in each case is lower than was suggested by the results from thermally conditioning bundles directly. With a linear treatment temperature-fibre residual strength relationship between 400 and 500°C for heated fibre bundles; the results from Figure 3 would suggest a recovered glass fibre tensile strength of 1.79, 1.63 and 1.60GPa when CuO, CeO_2 and Co_3O_4 are used respectively.

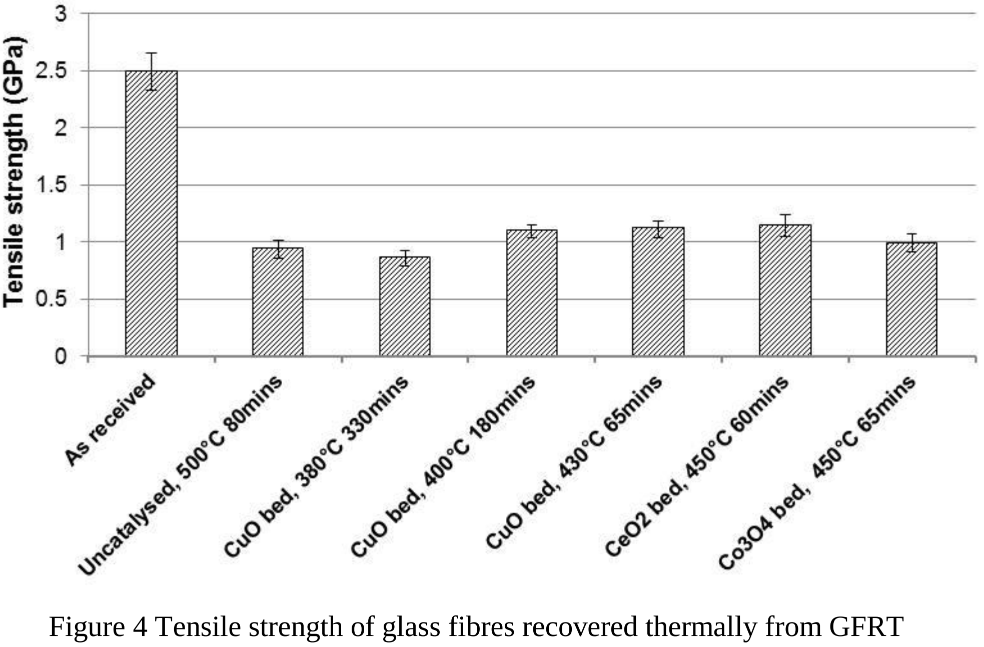

Figure 4 Tensile strength of glass fibres recovered thermally from GFRT

The cause of this lack in glass fibre strength retention is currently unknown. Unlike thermally conditioning bundles, these fibres had to be removed from the mat post-heat treatment. At this time the fibres are likely already weakened and have no sizing present to protect their surface from further damage caused during removal and subsequent sample preparation. For this reason some disparity between fibres recovered from GFRT and fibres directly thermally conditioned could be expected. This explanation may be unsatisfactory however when analysing the results of fibres recovered without a catalyst. As discussed, the strength of these fibres closely aligns with that of fibres heated in bundles under the same conditions. The handling of glass fibres recovered without a catalyst was the same as those with the metal oxides, suggesting that excess handling of the fibres is not a sufficient

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explanation for the lack in fibres strength retention. Although the retention is lower than expected, it has been shown that the metal oxides selected can yield glass fibre strength with increased tensile strength when recovered thermally within a furnace. Moreover, the temperature required to degrade the epoxy matrix and liberate fibres was reduced by up to 70°C while also decreasing recycling time.

3.5. Carbon fibre decomposition using TGA

TGA was used again to examine the thermal stability of carbon fibre in the presence of the metal oxides. Figure 5(a) shows the degradation thermograms of chopped carbon fibre with each metal oxide nanopowder applied. All catalysts clearly reduce the thermal stability of the carbon fibre with CuO again having the largest impact. CeO_2 and Co_3O_4 reduce the onset degradation temperature by around 50°C compared to CF alone whereas CuO has a much larger effect, reducing by around 130°C. It appears that the ability of the metal oxides tested to catalyse thermal decomposition of epoxy resin is intrinsically related to the degradation temperature of carbon fibre. It is known that the residual material present after the first stage of epoxy resin thermal degradation, referred to as coke, has a high carbon content. The beneficial ability of the oxides to catalyse the decomposition of such material appears to also increase the rate of carbon fibre oxidation. As the driving force behind carbon fibre strength degradation during heating is mass loss due to surface oxidation, the oxides may in fact have an adverse effect when applied to CFRP recycling.

The TGA data acquired clearly indicates that each of the metal oxides tested reduce the thermal stability of carbon fibre. In order to determine whether this adversely affects the tensile strength of the fibres; each metal oxide nanopowder was applied to the surface of IM7 carbon fibre bundles and heated at just 400°C for 25mins within a furnace in air. Single carbon fibre sample preparation and testing was again carried out as outlined above. Figure 5(b) shows the tensile strength of the fibres after the various heat treatments. Fibres thermally conditioned at 400°C in the absence of any metal oxide experienced no strength loss. As was suggested by the TGA results, all fibres applied with the metal oxide nanopowders experience a significant tensile strength loss. CuO has the most detrimental effect on fibre strength, reducing it by 46% relative to heat treated fibres alone. CeO_2 and Co_3O_4 have a similar impact by reducing strength by 20 and 24% respectively. In any respect all three metal oxide nanopowders tested reduce thermal stability of the carbon fibres tested and in doing so promote considerable fibre tensile strength loss. This is in stark contrast to the aim of reducing the temperature required for CFRP thermal recycling.

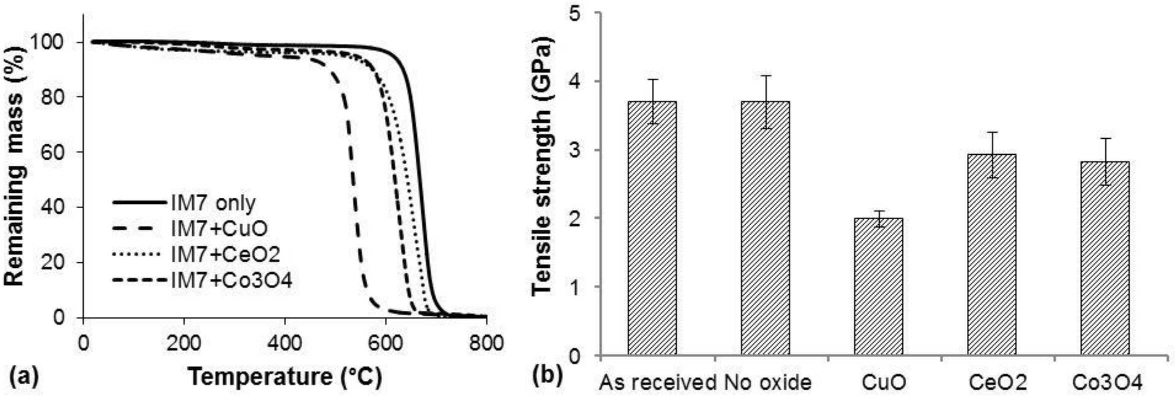

Figure 5(a) Effect of metal oxides on thermal stability of IM7 fibres (b) Tensile strength of IM7 fibres after thermal conditioning in the presence of metal oxides

4. Conclusions

Through non-isothermal TGA it was found that the application of CeO_2, CuO and Co_3O_4 had no notable effect on epoxy resin first stage degradation onset temperature however reduced the second

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stage by 63, 59 and 40°C respectively. Using an isothermal heating schedule it was found that all metal oxides fascillated full epoxy decompostion at 450°C. The minimum temperature required for epoxy in the presence of CuO to completely degrade was just 375°C, providing a 125°C reduction compared to epoxy alone. The effect of thermal conditioning temperature and time on E-glass fibre tensile strength was established. Both parameters impact recovered fibre strength with retention dropping to around 60 and 42% when heating for 120mins at 400 and 500°C respectively. This suggests that reducing the recycling temperature of GFRP by means of catalysed epoxy degradation could recover glass fibres with higher retained strength. The application of CuO, CeO_2, and Co_3O_4 to GFRT laminates successfully reduced the epoxy matrix decompostion temperture required for glass fibre liberation by 70, 50 and 50°C respectively, with similar conditioning times. Although the strength of glass fibres recovered with the use of the catalysts were higher than those liberated without; the retained stength was lower than was suggested by previous heat treated fibres with similar conditioning parameters.

It was thought that metal oxides could also be used to assist CFRP thermal recycling. TGA data shows that CuO, CeO_2 and Co_3O_4 reduce thermal stability of IM7 fibres by decreasing the degradation onset temperature by around 130, 50 and 50°C respectively. When applied to the carbon fibre surface during thermal conditioning at 400°C for 25mins CuO, CeO_2 and Co_3O_4 reduce tensile strength by 46, 20 and 24% respectively. In accordance with the strength loss mechanism outlined in the literature, it is thought that the metal oxides increase oxidation of the carbon fibre surface resulting in weakening of the fibres. As a result it is recommended that these metal oxides should not be utilised within a CFRP thermal recycling system to aid matrix decomposition.

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