REGENERATION OF THERMALLY RECYCLED GLASS FIBRE FOR COST-EFFECTIVE COMPOSITE RECYCLING: PERFORMANCE OF FIBRE RECYCLATES FROM THERMOSET COMPOSITES AND WITH SUBSEQUENT ReCoVeR TREATMENTS

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Abstract
This paper reported transformability of regenerating strengths of heat treated glass fibres (HTGFs) into recycled glass fibres (RGFs) from polyester composites at 500 to 600°C. The fibre recyclates were examined using scanning electron microscopic (SEM) and showed that the surface contains different types and amounts of thermal residues depending on treatment temperature. With additional washing step, the RGF surface is dramatically clean. The RGFs, with/without washing step, were further treated using ReCoVeR process, where strength of HTGFs can be recovered. The tensile results demonstrated that ReCoVeRed RGFs shows positive effect on strength enhancement but not as significant as HTGFs. However, higher strength was found on ReCoVeRed RGFs with additional washing step. The observation and discussion were detailed in this study.

1. Introduction

Due to excellent ratio between mechanical properties and production cost, glass fibres are widely used as composite reinforcements in automotive, wind turbine and leisure industries. The benefit derives increasing demands for glass fibre composites annually. For example, in 2012, there are 1 million tonnes of glass fibre composites being produced in Europe [1]. In global market, the production rate of glass fibre composite grows dramatically and reaches approximate 10 million tonnes per year. Within these glass fibre reinforced plastics (GFRPs), 65% are thermoset polymer. When the fibre composites reach their shelf life, the disposal of these products could be a challenge issue as the cross-linked nature of thermosetting polymer. For past decades, the disposal for these end-of-life composites always ends up landfill. However, as the green awareness keeps rising nowadays, the cost for landfill is increasing or forbidden by legislation. Therefore, it increases pressure on composite manufacturers, end users to find the solutions for reuses or recycle the fibre composites.

Over last decade, it has been demonstrated that the glass fibres can be successfully extracted from thermoset matrices with great conversion rate through various processes such as mechanically grinding, thermally, and thermo-chemically decomposition of polymer [2-6]. In mechanical grinding process, the size of the fibre recyclates is much shorter than their critical length and the contamination of resin residues limiting the recycled materials application as fillers in composites [7]. In terms of thermal and thermo-chemical recycling processes, they have been proven to retain length of the fibres originally embedded in matrix. The advantage brings the potential for the recycled fibres as reinforcements in composite system. As it is well-documented that glass fibres are sensitive to higher temperature environment [8, 9], severe strength reduction has been found on the fibre recyclates. For example, in thermal recycling process using fluidised-bed, the strength of the fibre recyclates could drop up to 90% compared to the pristine fibres [5, 6]. Therefore, at present, the recyclates are impossible to fully substitute pristine glass fibres in composite production.

It is well known that the commercial glass fibres contain a thin layer of silane coating. The material acts as a protective layer to increase environmental resistance of glass fibres and also assist the interfacial adhesion to polymeric matrices. It also has been reported [10, 11] that the silane coating could also be a healing agent for flaws on the glass fibre surface and thus increase the fibre strength. Referring to recycling process where high temperature is often employed, it is reasonable to suspect that the silane coating could be thermally degraded leading to lower mechanical performance of fibre recyclates. However, one may expect that the decrease on recycled fibre strength could be due to the fact that the fibres experience internal damage caused by exposure to high temperature environment. Furthermore, after thermal recycling process the surface fibre recyclates are often contaminated with degraded polymer [4, 12] and/or mineral fillers. The residues could be considered as flaws after any treatment applies to the recyclates for strength enhancement.

In this paper, the mechanical performance of glass fibres recycled from polyester matrix composites at elevated temperature was studied. The fibre recyclates were then treated with ReCoVeR treatments to investigate the transformability of strength increase in heat treated fibre to recycled fibres. The relationship between ReCoVeR treatment and surface morphologies was also investigated to address the thermal residues effect on the mechanical performance of the ReCoVeRed treated recycled fibres.

2. Experiments

2.1. Materials

The materials used in this study are Advantex® boron-free glass fibre rovings, with diameter of approximate 17μm, supplied from Owens Corning Vetrotex. In this study, two types of Advantex® glass fibres with different sizing were used: water or γ-aminopropysilane (APS). After glass fibres were produced from pilot scaled bushing process, water was applied to the glass which is called water sized fibres. The fibres have lower environmental resistance and are denoted as “unsized” fibres in our study. This fibre roving was used as comparison to chemically sized fibres to investigate the surface effect on recycled fibres from composite. In addition to another fibre roving which contains chemically sized fibres, once the glass fibres were produced 1 wt.% of hydrolysed γ-aminopropysilane (APS) solution was applied to the fibres through industrial sizing applicator which are referring to APS sized glass fibres in our study. After sizing process, both of the fibres were dried at 105°C for 24 hours.

The composites used in this study are made in house using casting method. The matrix system was unsaturated polyester resin in styrene which is commonly used in industry. The glass fibre bundles (either unsized or APS sized fibres) were unidirectionally aligned in a casting mould. The polyester was firstly mixed with initiator, methyl ethyl ketone peroxide (MEKP), in the ratio of 100 to 1 by weight. The mixtures were then degased in a vacuum chamber for 10 minutes before pouring into the casting mould for 12 hours curing at room temperature. The composites were then post cured at 80^{o}C for three hours and then at 120^{o}C for two hours.

2.2. Composite recycling process

Carbolite high temperature muffle furnace was used for recycling process from 500 to 600^{o}C. It should be noted that the composite samples made of unsized and APS sized fibres were treated simultaneously in the same oven to keep consistency with identical thermal history. It should be noted that the composites were heat treated in the furnace from room to target recycling temperature which took approximate 45 minutes before isothermal time of 25 minutes. The purpose of the recycling process is to eliminate splash coming from degrading polymer which could potentially cause cross contamination to other samples in the same furnace and also minimise damage of the recycled fibres due to high thermal expansion coming from polymeric matrix.

2.3. Fibre cleaning process

Sonication was used to wash recycled fibres before ReCoVeR treatment in order to compare the fibres just being reclaimed from composites. The recycled fibre bundles were firstly sonicated in deionised water for 5 minutes using sonic bath (CAMLAB Transsonic T480/H) and, subsequently, were dried in oven at 90^{o}C for 15 minutes. The fibre bundles were further dried at room temperature for at least overnight before ReCoVeR treatments.

2.4. ReCoVeR treatment

Following up successful ReCoVeR treatment to enhance tensile strength of heat treated glass fibres [13], ReCoVeR 2 and ReCoVeR 4 were treated on recycled fibres. The first treatment is aiming to study transformability of strength increases in heat treated fibres to recycled fibres where ReCoVeR 4 is used to investigated the effect of thermal residues on the strength of ReCoVeR treated recycled fibres. It should be addressed that the APS sized fibres used in this study are the same as the ones with ReCoVeR study on heat treated fibres.

2.5. Characterisations

2.5.1 Scanning electron microscope (SEM)

Surface of treated glass fibres was characterised using HITACHI SU-6600 Field Emission Scanning Electron Microscope (FE-SEM). Well-isolated single fibres were meticulously separated from fibre bundle and were attached on carbon tape with extra care. Subsequently, the isolated fibres were coated with a thin layer of gold under Argon atmosphere using Edward S150 sputter coater before SEM examination. The magnification range of 3 to 4k times was used to record fibre images.

2.5.2 Tensile tests

The sample preparation and single fibre testing follow ASTM C1557-03 [14]. Single isolated fibres were firstly extracted from as-received, thermally recycled, or post-treated glass fibre bundles with extra care to minimise any physical damage to fibres. The fibres were then centred in a window made of cardboard frame and secured on the double sided tape as shown in Figure 1 in order to reduce further damage to fibre in following preparation process. Subsequently, Loctite™ Gel Superglue was applied to the cardboard close to the ends of window and therefore the testing gauge length is determined. In this study, the gauge length is 20mm which is also corresponding to the width of the window. Once the superglue was dried, the double sided tapes were removed.

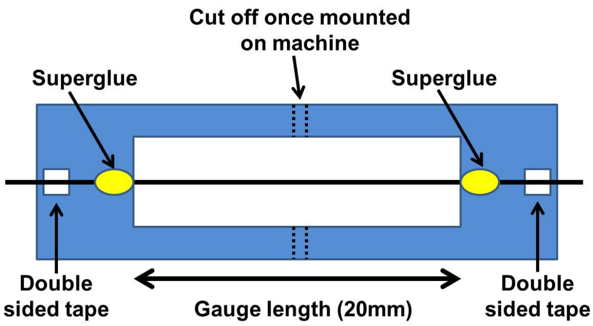

Figure 1. Schematic diagram of tensile sample preparation.

Instron 3342 tensile testing machine connected to a 10N load cell was used to measure tensile properties of the samples. Prior to the tests, the diameter of each sample was measured using OLYMPUS GX51 optical microscopy (OM) in order to determine fibre mechanical properties. In tensile test, the edges of window cardboard were carefully cut off once the sample was mounted on testing rig in the machine. The cross head speed is 0.3 mm/minute according to the gauge length of 20mm in order to follow strain rate of 1.5% strain/minute from standard method. The samples broke during mounting or too close to the edge of window were discarded. A total of 30 samples were tested for each condition and the results presented in this study are the averaged value with error bars indicating 95% confidence limit.

3. Results and discussions

3.1. Surface of recycled fibres

SEM images of APS sized fibres with/without various treatments were shown in Figure 2. The surface of pristine APS sized fibre is smooth and a thin layer of sizing coating can be clearly observed as red arrow indicated in Figure 2(a). In contrast, a larger amount of thermal residues were observed on the surface of recycled fibres at 500^{o}C than the ones at 600^{o}C as shown in Figure 2(b) and (c). The observation of contamination on the recycled fibres is repeatedly reported on recycling study on fibre composites [4, 12].

Figure 2(d) shows, as an example, the surface of recycled fibres (500^{o}C) after washing step. The washed fibres are significantly cleaner and smother than as-recycled fibres. The similar observation was also found in recycled fibres at 600^{o}C. The clean surface could be advantageous for any subsequent treatment on the fibres and minimise the flaw generation from thermal residues.

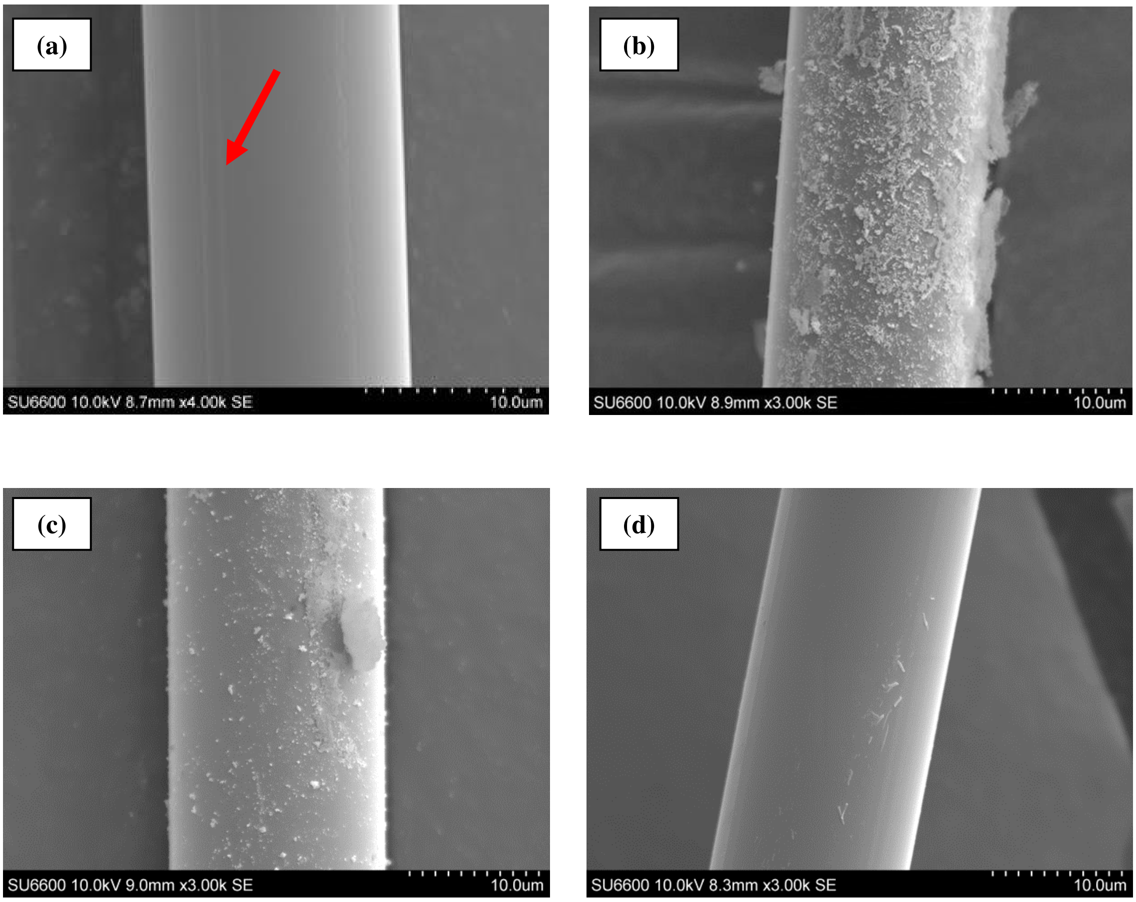

Figure 2. SEM images of APS sized fibres in (a) pristine state, recycled from polyester resin at (b) 500 and (c) 600°C. Image (d) shows the surface of recycled fibre at 500°C with cleaning step.

3.2. Tensile results

3.2.1 Recycling temperature effect

Figure 3 shows the strength of recycled fibres at elevated temperature. The results of unsized fibres were shown here as comparisons. It can be clearly seen that the recycled fibres have approximate 70% strength reduction to pristine glass fibres (APS sized ones). As temperature increases, the recycled fibres at 600°C show slightly increase in strength compared to the ones at 500°C. This could be due to the selection of fibres for tensile testing. The weakest fibres might break during sample preparation so that the relatively stronger fibres remain and past the tests. The results of strength reduction on thermally recycled fibres are comparable to other recycling studies on glass fibre composites [4-6]. In terms of unsized fibres, similar behaviour to recycled APS sized fibres is obtained. This may indicate that the APS coating is missed after thermal recycling process and the reinforcing effect (around double increase in strength with APS sizing) has no longer existing on the fibre. However, the thermal residues which are caused by degraded APS may remain on the fibre surface and may affect any treatment to recover strength of the recycled fibres.

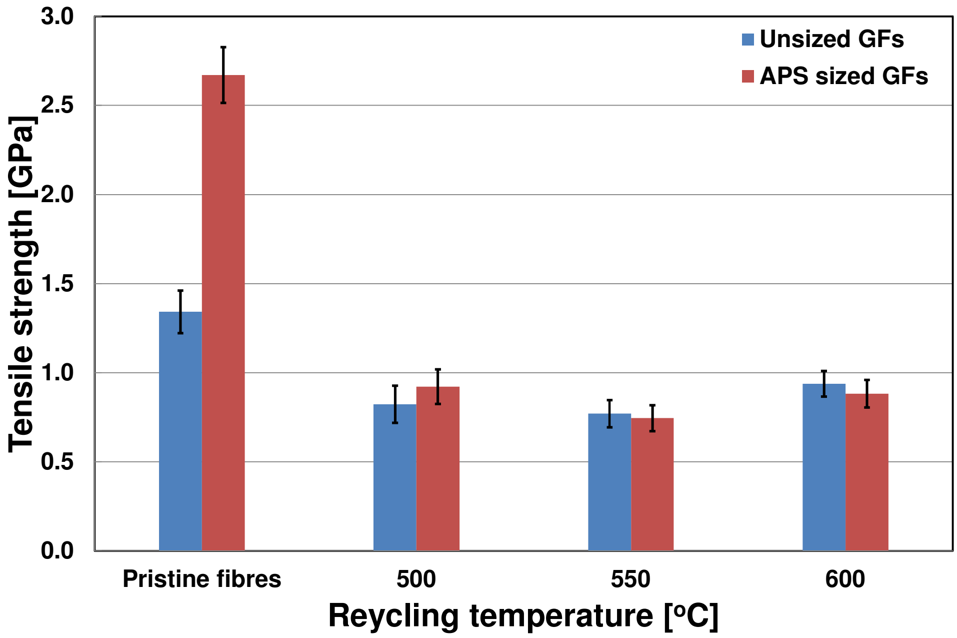

Figure 3 Tensile strengths of recycled unsized and APS sized glass fibres from polyester resin at elevated temperature.

3.2.2 ReCoVeRing effect

The tensile results of ReCoVeR treated fibres were shown in Figure 4. Unlike heat treated glass fibre, the finding of over double increase in strength using ReCoVeR 2 treatment could not be replicated on recycled fibres. One of possible reason could be due to thermal residues shielding the reinforcing effect on fibres. The residues could act as flaws and remain on the surface after ReCoVeR process. The flaws could introduce stress concentration during deformation on fibres so that the fibre breaks at lower strength.

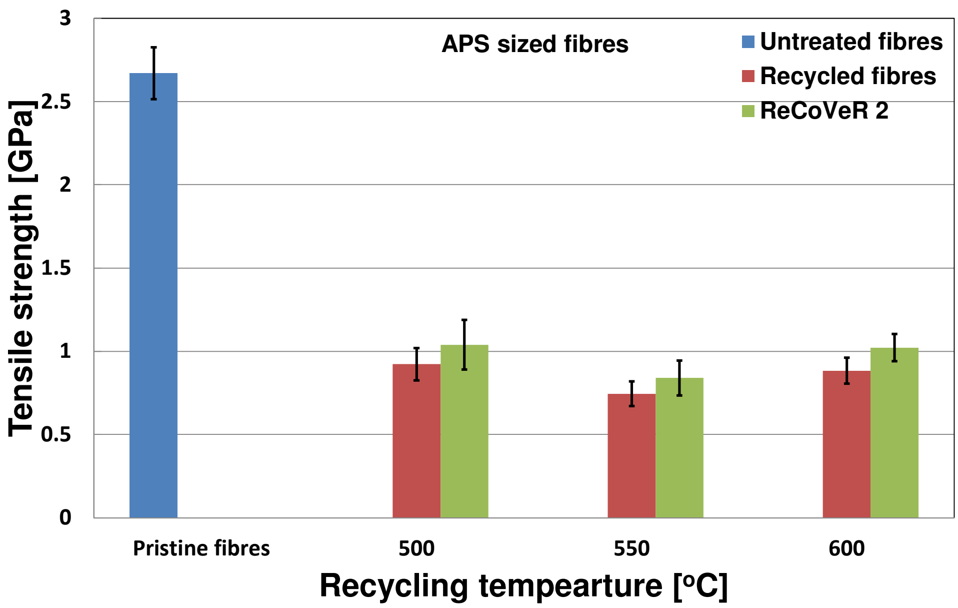

Figure 4. Tensile strengths of recycled APS sized glass fibres with/without ReCoVeR 2 treatment at elevated temperature.

3.2.3 Fibre cleaning effect

Figure 5 shows the difference in strength of fibres experiencing an additional washing step before ReCoVeR treatment. The treatment used in this study is another ReCoVeR treatment which can successfully increase the strength of heat treated glass fibres. As it can be seen in the figure, the general trend for both unsized and APS sized fibres shows the fibre strength increases with addition of washing step. Although the increment level strength is still far from recovering recycle fibres to pristine ones, the observation shows that ReCoVeR treatment could be affected by the fibre surface. The result showed in here may also provide another concept for recovering any types of recycled fibres, such as carbon fibres, for fibre composite reapplications.

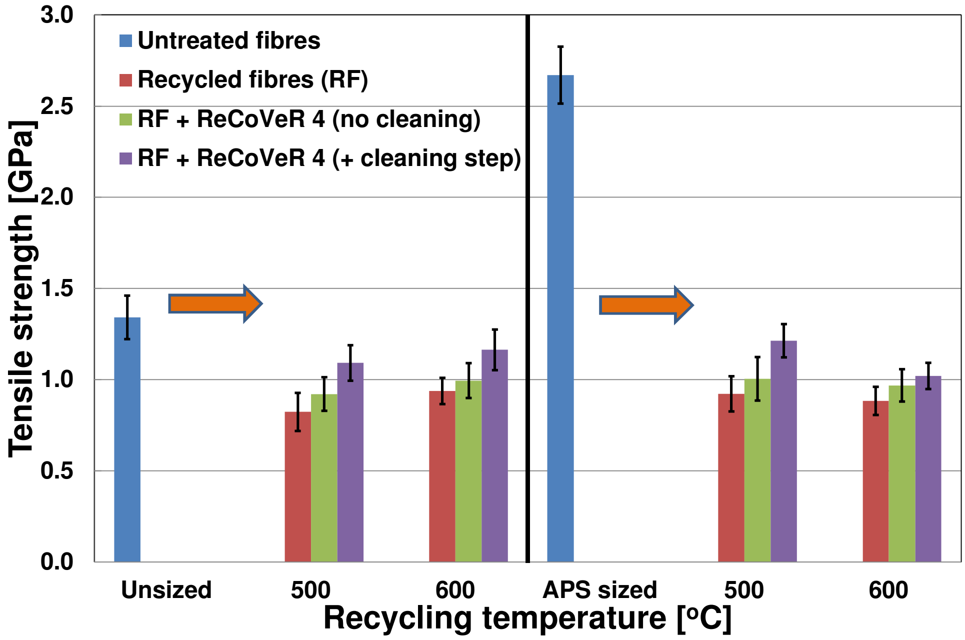

Figure 5. Tensile results of pristine, thermally recycled, ReCoVeR treated fibres with/without additional cleaning steps for unisized and APS sized fibres.

4. Conclusions

The strength of recycled glass fibres at 500 to 600°C was presented in this study. An approximate 70% reduction of strength in recycled fibres was found regardless recycling temperatures. After ReCoVeR treatment was applied to the recycled fibres, it was showed that the fibre strength did not achieve the same level as thermal conditioned glass fibres. However, if additional washing step was implemented before ReCoVeR treatment for recycled fibres, the strength is higher than the ones without washing.

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