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Can thermally degraded glass fibre be regenerated for closed-loop recycling of thermosetting composites?

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ABSTRACT

Commercially manufactured E-glass fibres were heat-conditioned to mimic the effects of thermal recycling of glass fibre thermosetting composites. Degradation in the strength and surface functionality of heat-treated fibres was identified as a key barrier to reusing the fibres as valuable reinforcement in composite applications. A chemical approach has been developed to address these issues and this included two individual chemical treatments, namely chemical etching and post-silanisation. The effectiveness of the treatments was evaluated for both thermal degraded fibres and corresponding composites. Drastic reduction was observed in the properties of the composites with the heat-conditioned preforms indicating thermally degraded glass fibres have no value for second-life reinforcement without further fibre regeneration. However, significant regeneration to the above properties was successfully obtained through the approach developed in this work and the results strongly demonstrated the feasibility of regeneration of thermally degraded glass fibres for potential closed-loop recycling of thermosetting composites.

1. Introduction

The disposal of end-of-life composite products in an environmentally friendly manner is one of the most important challenges currently facing the industrial and academic composites community. It is projected that by 2015 the total global production of composite materials will significantly exceed 10 million tons which, at end-of-life, will occupy a volume of over 5 million cubic meters [1]. Glass fibre reinforced composites account for more than 90% of all the fibre-reinforced composites currently produced. About 60% of this volume employs thermosetting matrix materials producing composites (GRP) that are difficult to recycle in an efficient manner [1]. The perspectives on this issue have been recently highlighted due to the accelerating growth in the use of such composite materials in transportation and wind energy sectors [2]. For instance, wind turbine applications have growth rates well into double figures with a predicted 6 million tons of GRP wind turbine blades to be produced globally over the coming decade [3]. Currently most of this material is destined for landfill at the end of its 10–25 year application lifetime. However the rapidly increasing cost and reducing availability of landfill, combined with increasing national and international legislation, means that such disposal of end-of-life composites is becoming economically and socially unacceptable. Clearly alternate methods for dealing with end-of-life composites are urgently required.

Although thermoplastic based composites are, in principle, intrinsically recyclable, the greatest challenge is with the larger fraction of thermoset based GRP composites. The infusible and insoluble high-density networks in molecular structure make thermosetting polymers ideal candidates for composites with more demanding performance required in areas such as aerospace and wind energy. The very same reason for their merits, however, has also been causing difficulties in recycling thermosetting composites. The 3D network structure does not result in the same reprocessability offered by thermoplastic polymers. Consequently, various techniques have been developed to recycle thermosetting polymers and these techniques have been seen to serve as the foundation of the recent development of thermosetting composites recycling [4]. A number of processes are available for recycling such composites [5,6]. Of these possible routes, thermal recycling is probably the most technologically advanced and has been piloted in the UK and Denmark. However, nearly all options deliver recycled fibres (which make up approximately 60% by weight of the composites) that suffer from a lack of competitiveness with pristine first-pass materials. A key factor in this equation is the huge drop in the performance of recycled glass fibre in comparison to its original state [5,7]. Consequently, recycled fibres have a very

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poor performance to cost ratio, and in most cases are considered unsuitable for reprocessing and reuse as a valuable reinforcement of composites. A breakthrough in this field could enable such recycled glass fibres to compete with pristine materials in many large volume composite applications. The development of an economically viable process for regenerating the properties of thermally recycled glass fibres would have major technological, societal, economical, environmental impacts. We are currently focusing on enabling cost-effective closed-loop recycling for glass fibre thermosetting composites. The following areas have been identified by us as major technical barriers that have to be overcome in order to achieve this goal. This includes fibre recycling technique, fibre strength regeneration, fibre surface reactivation and fibre reprocessing.

In this paper we report some recent developments in these critical areas with particular focus on strength regeneration and surface reactivation of thermally treated glass fibres. The aim of this study is to verify the concept of regenerating thermally degraded glass fibres for a potential closed-loop recycling of glass fibre thermosetting composites.

2. Experimental

2.1. Materials

Boron-free E-glass fibres supplied by Owens Corning Vetrotex were used for micromechanical tests including single fibre tensile test and microbond test described below. The fibre roving was produced on a pilot scale bushing and was received as 20 kg continuous single end square edge packages. The roving had a nominal tex of 1200 and a single fibre diameter of 17.4 ± 1.3 μm. The molten fibres had all been hyperquenched by water spray before they were coated with a normal rotating cylinder sizing applicator containing a 1% γ-aminopropylsilane (APS) hydrolysed solution in distilled water. The room temperature mechanical properties of these fibres have been reported in somewhere else [8]. 'SABIC® PP 579 S' polypropylene (PP) compounded with 1 wt% maleic anhydride grafted polypropylene (MaPP) was used as the matrix to demonstrate different levels of adhesion with both thermally and chemically conditioned glass fibres. It would be indeed more consistent to use the same matrix for a model composite to investigate the effect of different fibre treatments developed in this work. However, it was thought that using other readily available materials should not jeopardise the main purpose of conveying the concept of closed-loop composites recycling. The composite materials in this study consisted of 'PPG Fibre Glass® Mat 92 chopped strand mat' (CSM) supplied by PPG Industries and IN-2 epoxy infusion resin supplied by Easycomposites. Using virgin CSM gives the advantages of maintaining the original form of the CSM in terms of fibre length, orientation and fibre content after different treatments. This limits the dependence of the composite properties only to the variables related to glass fibres themselves. The chemicals used to treat thermally degraded fibres included ACS reagent 48% hydrofluoric acid (HF) and γ-aminopropyltriethoxysilane supplied by Sigma Aldrich.

2.2. Thermal treatment

Heat conditioning of glass fibres intended for micromechanical testing was carried out in a Carbolite LHT6 furnace in the temperature range 450–600 °C. The chosen temperatures cover a typical range required in thermal recycling techniques such as pyrolysis and fluidised bed. The conditioning procedure within a comprehensive study of thermal effect on fibre strength loss has been detailed in [1]. Heat treatment of CSM was carried out in a furnace at a temperature of 500 °C for 30 min. The preform of total 16 layers of 28 cm × 28 cm CSM was placed in a metal tray, which could be inserted in the furnace as shown in Fig. 1. This facilitated sample handling for the subsequent chemical treatment and vacuum infusion process. The preform was placed in the furnace at room temperature followed by a temperature ramp at 10 °C/min before it reached 500 °C. After the heat treatment, the preform was cooled to room temperature outside the furnace and subject to chemical treatments if required.

2.3. Chemical treatment

It is known that heat-treated glass fibre suffers significant strength loss [1,5,9,10]. In order to regenerate its strength, 1 v% HF aqueous solution was employed to treat degraded fibres. Approximately 100 mg 15 cm long glass fibres were immersed in 300 ml HF solution for up to 2.5 min. The HF-treated fibres had been repeatedly rinsed with deionised water before they were dried in an oven at a temperature 110 °C for 20 min. When such treatment was applied to the heat-treated CSM, the immersion time was extended up to 10 min to compensate for the relatively lower amount of HF solution (3 L) with respect to ~300 g glass fibres. Approximately 2% of fibre diameter was lost after the treatment of the CSM. The drying process was extended up to 24 h to ensure complete drying of the preform and this was confirmed by monitoring the weight change during drying. It has been reported that thermally degraded glass fibre also loses its original surface coating [10] and may even end up with a dehydroxylated surface [11]. In order to reactivate surface functionality after heat and/or HF treatment, the fibres were fully immersed in 1 v% APS solution for 15 min. The APS solution was prepared with deionised water at its natural pH value. The aqueous solution was aged for 24 h before use. The condensation of silane deposition on the glass surface was achieved through the drying process at a temperature of 110 °C for 15 min. In the case of CSM, this stage was extended up to 24 h. When weak heat-treated preforms were handled through the above chemical treatments, extreme care was taken to minimise disruption to the original CSM in terms of fibre length, orientation and fibre content.

Fig. 1. Photo of 16 layers of chopped strand mat heat-conditioned in the furnace. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)