RECYLING CARBON FIBRE/EPOXY RESIN COMPOSITES USING SUPERCRITICAL PROPANOL

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Keywords: *recycling, carbon fibre, supercritical, propanol*

Abstract

Recycling high value carbon fibre from polymer composites using supercritical n-propanol is reported in this paper. The mechanical properties of the recycled carbon fibre were characterized using single fibre tensile tests. The surface properties were characterized using SEM, XPS and XRD. The actual bonding strength of the recycled carbon fibre with epoxy resin was measured using a single fibre pull out test. The decomposition products of epoxy resin was analysed using GC-MS.

The study shows that the recycled carbon fibre has very similar mechanical properties to the corresponding virgin carbon fibre. Although the surface oxygen has decreased somewhat this has not made a significant reduction to the interfacial bonding strength with epoxy resin.

1 Introduction

Recycling carbon fibre from polymer composites has attracted great attention due to its wide application in aeronautical and automotive industries and the large amount of off-cuts and end-of-life components produced. The majority of the polymer matrices with carbon fibres are epoxy resins. They are crosslinked polymers, which cannot be recycled by melting and remoulding without excessive degradation. To recycle high value carbon fibre, an effective method for decomposition of epoxy resin is desired.

In the last decade, a high temperature fluidized bed process has been successfully developed in our group [1-3]. Although this method can continuously recycle carbon fibre and recover the energy from the oxidation of epoxy resins, a chemical recycling process for both carbon fibre and epoxy resin is preferred. To this end, supercritical fluids have been used. A supercritical fluid is a substance simultaneously above its critical temperature and pressure. In the supercritical state, the fluid has a high diffusivity and solubility, which enables it to carry-out new chemical processes for decomposition and partial oxidation. Alcohols have convenient critical temperatures and pressures and may therefore be used to recycle waste polymer composites.

Supercritical methanol and ethanol have been used to recycle glass fibre reinforced polyester composites [4]. Propanol has been used in our previous study [5]. Ethanol and methanol did not work well when treating epoxy resin composites. However, propanol has shown much better performance, which may be due to its favorable oleophilic behaviour. Characterization of the recycled carbon fibre is described in this paper with a comparison with the corresponding virgin carbon fibre.

2 Experimental Section

2.1 Materials

Both the composites and virgin carbon fibre were supplied by the Advanced Composites Group Ltd (UK). The composite consisted of T600S carbon fibre and an amine cured bisphenol A epoxy resin. 1-Propanol was purchased from Aldrich, which was HPLC grade with a purity of 99.9%.

The epoxy resin used for single fibre pull out test was from Dow with a commercial name DW2.

2.2 Recycling process

A flow diagram of the recycling process is shown in Figure 1. The recycling was conducted in a flow reactor, in which the composite was put and

supercritical propanol was passed through for around 10 minutes at 300°C and 50 bar. The carbon fibre recycled was then taken out of the reactor for analysis. A picture of the recycling rig is shown in Figure 2.

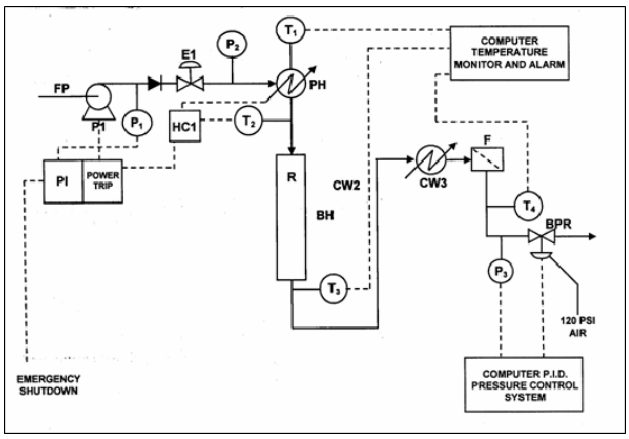

Fig. 1. A flow diagram for the process

Fig. 2. A picture of the recycling test rig.

2.3 Removal of size from the virgin fibre surface

The virgin carbon fibre had a thin layer of epoxy size on the surface. To remove the size, the fibre was soaked in acetone at room temperature for a week. After taking out of the acetone bath, the fibre was washed three times using fresh acetone in an ultrasonic bath. The fibre was then extracted using boiling tetrahydrofuran (THF) for 72 hours. During the extraction, the THF was changed twice. After extraction, the fibre was washed three times using fresh THF. Other researchers' work [6-9] was referenced and the carbon fibre manufacturer was consulted for the size removal procedure.

2.4 Surface characterisation

The XPS analysis was conducted using a Kratos AXIS ULTRA with a mono-chromated Al kα X-ray source (1486.6eV) operated at 15mA emission current and 10kV anode potential. Survey spectra in the range of 0-1400 eV were recorded for each sample with a pass energy of 80 eV and a step of 0.5 eV, followed by high resolution scanning over C1s range with a pass energy of 20 eV and a step of 0.1 eV. All spectra were recorded at a 90° take-off angle. Surface atomic composition was calculated using CasaXPS software with Kratos sensitivity factors.

Curve-fitting of core XPS high resolution spectra was carried out on CasaXPS software. The line shape used was a Gaussian-Lorentzian product function with a Shirley type background. The G/L mix was taken as 0.5 for all peaks except the main graphitic peak, which was taken as 0.8 with a exponential asymmetric blend tail [10-12]. The adoption of asymmetric shape for graphitic carbon is due to the interaction of the positive core hole with the conduction electrons [13].

Scanning electron images for carbon fibres were taken using a JEOL 6400 microscope. The sample was mounted on an adhesive carbon layer stuck onto an aluminium stub and sputtered with a thin layer of gold. The acceleration voltage was 15 kV.

2.5 Single fibre pull out test

The interfacial bonding strength between fibre and epoxy resin was measured using a single fibre pull-out test. This method pulls a single fibre out of a microdroplet of resin. Care must be taken to make sure that the embedded length of the fibre is short enough to preclude fibre fracture below the surface. A schematic diagram for the single fibre pull out test is shown in Figure 2. The IFSS, τ, is calculated from the equation [14].

$$\tau = \frac{F}{\pi d L} \qquad (1)$$

where F is the peak debonding force minus the initial frictional force, d is the fibre diameter, and L is the embedded length.

2.6 Single fibre pull out test

The tensile properties of the carbon fibres were measured in accordance with BS ISO 11556. A single fibre was adhered on the window of a paper using epoxy glue. The gauge length was 20 cm. The single fibre underwent a tensile test on a Hounsfield frame with a crosshead rate of 1 mm/min. At least 20 samples were measured for one type of fibre.

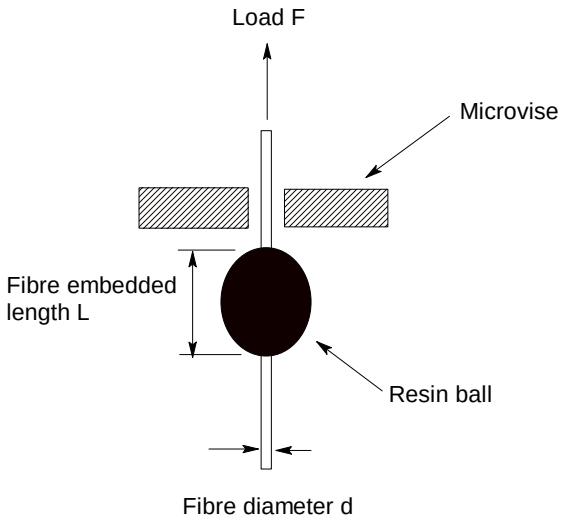

Fig. 2. A schematic diagram for the single fibre pull out test.

2.7 Analysis of decomposed products

The decomposed products of epoxy resin were analysed using a Fisons 8000 series gas chromatograph coupled to a Fisons MD800 mass spectrometer (Fisons Instruments, Loughborough, UK). The GC was fitted with a DB-5MS fused silica capillary column (50 m × 0.32 mm i.d., film thickness 0.25 μm).

3 Results and discussion

Figure 3 shows the composite prepreg fragments before recycling and the recycled carbon fibre. Figure 4 shows SEM images of the recycled and virgin carbon fibres. It can be seen that the surface of the recycled carbon fibre was quite clean except for some very small particles on the recycled fibre surface, which may be due to polymer residue.

The surface chemistry of the recycled carbon fibre was measured using XPS. The survey scans are shown in Figure 5a. There are three main elements on the surface, carbon (294 eV), oxygen (530 eV) and nitrogen (399 eV). The appearance of nitrogen on the surface indicates that the size on the surface has been removed. From the survey scan, the ratio of oxygen to carbon (O/C) was calculated. The O/C value decreased from 0.105 to 0.0876.

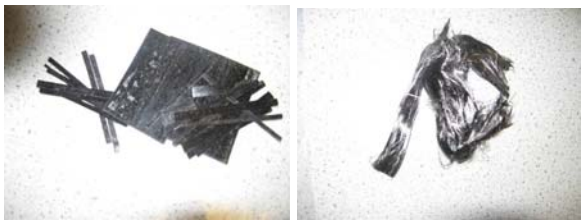

Fig.3. Pictures of polymer composites and the recycled carbon fibre.

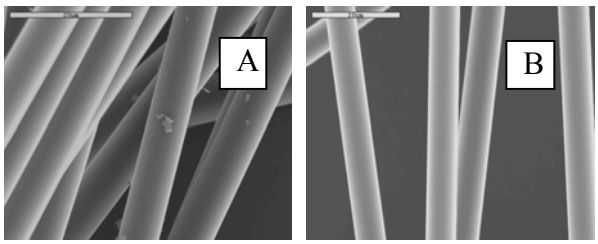

Fig.4. SEM images of recycled carbon fibre (A) and virgin carbon fibre T660S (B).

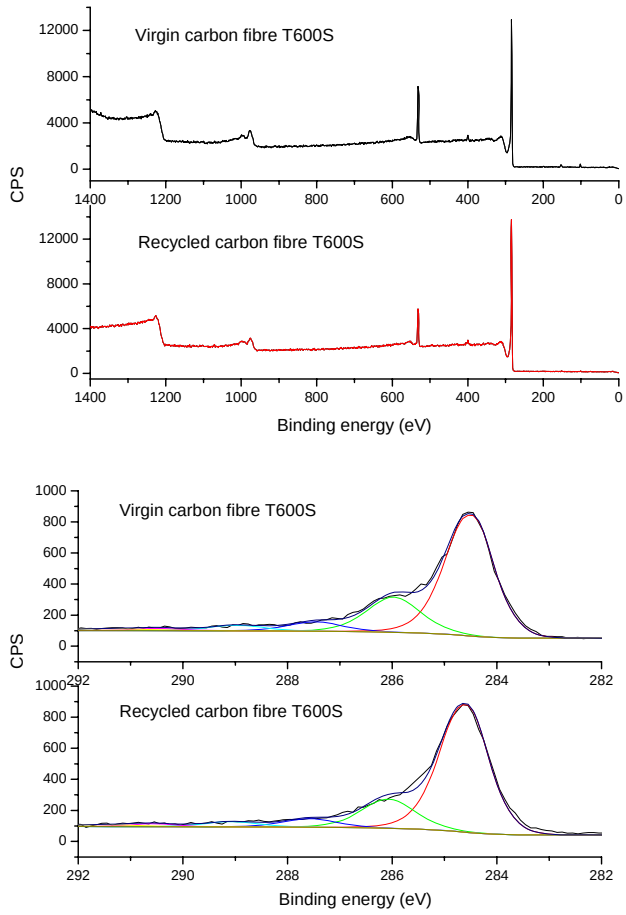

Fig. 5. XPS spectra for the recycled carbon fibre and virgin carbon fibre T600S.

The decrease may be the reaction of propanol with surface functional groups such as COOH and C-OH. The oxygenated groups on the surface were identified by their chemical shifts relative to the C-C binding energy using curve-fitting, as shown in Figure 5b. The percentages of the oxygenated groups are shown in Table 1.

Table 1. Oxygenated groups on the carbon fibre surface.

Chemical species	Virgin	Recycled
C-C	66.75	70.98
C-OH	21.25	17.71
C=O	5.66	5.17
COOH	3.40	3.16
CO_3^{2-}	1.16	1.48
π-π^*	1.78	1.50

As shown in Table 1, all of the three main kind of oxygenated groups (C-OH, C=O and COOH) have decreased.

In order to determine whether this small change has affected surface bonding strength with polymer, Interfacial shear strength with epoxy resin was measured using single pull out test. The results are given in Table 2.

Table 2. Interfacial shear strength (IFSS) for the carbon fibres with epoxy resin Hexcel DW2.

	IFSS (MPa)
Recycled fibre	59.7 ± 8.2
Virgin fibre	60.3 ± 6.7

It can be seen from Table 2 that there is a very small decrease in bonding strength but this is not significant given the scatter in the results.

Tensile properties of the recycled and virgin carbon fibres are listed in Table 3. Manufacturer's data are also shown. The recycled carbon fibre had a tensile strength and modulus close to the virgin carbon fibre.

Table 3. Comparison of tensile properties between recycled and virgin carbon fibres.

	Tensile strength (MPa)	Tensile modulus (GPa)
Recycled fibre	3884 ± 1236	219.93 ± 10.47
Virgin fibre	4017 ± 950	213.25 ± 11.63
Manufacture's data	4107	230

The decomposed products from epoxy resin were analysed using GC-MS, as shown in Figure 6. The approximate composition is given in Table 4. It shows clearly that the major products are phenol and substituted phenols.

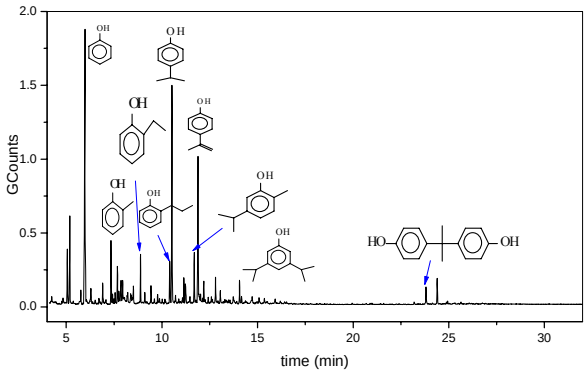

Fig. 6. GC trace for the decomposed products.

Table 4. Composition of the decomposed products.

Chemical species	Percentage
Phenol	34.9
p-isopropylphenol	26.4
p-isopropenylphenol	18.1
m-methylphenol	6.5
m-ethylphenol	4.7
The rest	9.4

Conclusions

It is feasible to recycle carbon fibre from its polymer composites using supercritical propanol. The recycled carbon fibre has comparable tensile properties with virgin carbon fibre. However, the surface oxygen has decreased to some extent. This decrease has not resulted in a significant reduction in the interfacial bonding strength with epoxy resin. The main decomposed products are phenol and substituted phenol.

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