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DEGRADATION OF FIBRE LENGTH DURING THE RECYCLING OF CARBON FIBRE COMPOSITES USING A FLUIDISED BED PROCESS

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SUMMARY: Carbon fibre is a valuable material and a thermosetting composite recycling process based on fluidised bed technology has been developed at The University of Nottingham. This paper describes the fluidised bed composite recycling process and a detailed investigation of one of the important qualities of recovered fibre, the fibre length distribution. A series of tests were performed to investigate the degree of fibre length degradation during the recycling process. This was done by taking batches of composite, each containing fibres of uniformly chopped carbon-epoxy prepreg scrap at different initial fibre length, then processing in the fluidised bed under the same conditions one at a time. Fibres with mean length from 5.9 to 9.5mm were recovered. Overall results show the longer the initial fibre length, the longer the average recovered fibre length, but also the greater the degree of length degradation. Initial characterisation of other properties of recovered carbon fibres have also been investigated, results shown the recovered fibre retain approximately 75% of their tensile strength whilst the Young's modulus is unchanged, and the surface condition is similar to the virgin fibre. The reasons for fibre length degradation are proposed and discussed; and the implication for re-use of the recovered fibres is also reviewed.

KEYWORDS: Composite Recycling, Carbon fibre, Fibre Length Distribution, Fluidised Bed, Prepreg

INTRODUCTION

Carbon fibre is a valuable material and during the manufacture of composite components from prepreg, a significant amount of material is wasted in offcuts. The European consumption of carbon fibre is currently about 2500 tonnes per year[1]. Of this about 80% is processed as prepreg and typically up to 40% are wasted as offcuts[2]. Currently these offcuts are landfilled, along with any scrap composite components, as there is no available recycling technology. Since carbon fibre consumption is growing at a rate of over 10% per annum throughout Europe there is an increasing requirement for an economic and environmentally responsible recycling route for in-process and post consumer scrap.

Fluidised bed recycling processes for composite materials have been under development at the University of Nottingham for a number of years. The initial work focused upon the recovery of glass fibre from scrap composites [3,4]. The process is now being applied to the recovery of carbon fibre [5]. It was found that useful glass fibres could be successfully recovered. Yet, the quantity of scrap glass fibre reinforced composites required to make the process economic does not exist at the present time. However, a smaller plant recovering carbon fibres has the potential to be economic, at lower scrap volumes, because of the higher value of the recovered carbon fibres.

The fibres recovered in the fluidised bed process are in the form of short discrete monofilaments of random orientation. They therefore lend themselves to re-use in applications requiring short fibres in a disperse form. Possible applications are as

reinforcement in moulding compounds, where short disperse fibres are required. Glass fibres recovered in a similar form to these carbon fibres have already been processed satisfactorily as a replacement for virgin glass fibre in a thermoset moulding compound. This has been described in our previous paper [3] and it is likely that recycled carbon fibre could also be used in this way. Alternatively, tissue or veil type products require disperse fibres and these have potential as a recycling route. Some promising initial trials have already been undertaken and further research is planned.

Fibre length is a key factor in determining the quality of recovered fibres and identifying applications for re-use. In short fibre reinforced plastic (SFRP) composites, for instance, the tensile properties of the composite is primarily dependent on the interfacial shear strength between the fibre and polymer matrix; the critical fibre length; the length distribution and the orientation of the short carbon fibre. Increasing the mean fibre length of the SFRP composite will increase the interfacial adhesion between the fibre-matrix, hence, the tensile strength of SFRP composite. Fu and Lauke [6] showed an increase of the mean fibre length from critical fibre length to 5 times or greater, enabled the short fibre composite to approach its theoretical strength. For maximum durability, the length of the fibre must exceed its critical length by a factor of 5 to 10 times [7]. Similarly fibre length is an important parameter in the production of veil.

Degradation of carbon fibre occurs during fluidised bed recycling and the manufacturing process of any potential uses. It is thus important to understand how much degradation occurs in the fluidised bed process and determine what length fibres can be recovered.

This paper describes the investigation of fibre length degradation during the fluidised bed recycling process, the importance of fibre length as one of the quality characterisation of the recycled fibre, which affects the potential fibre re-use application, hence the commercial viability of the carbon fibre recycling process.

FLUIDISED BED RECYCLING PROCESS

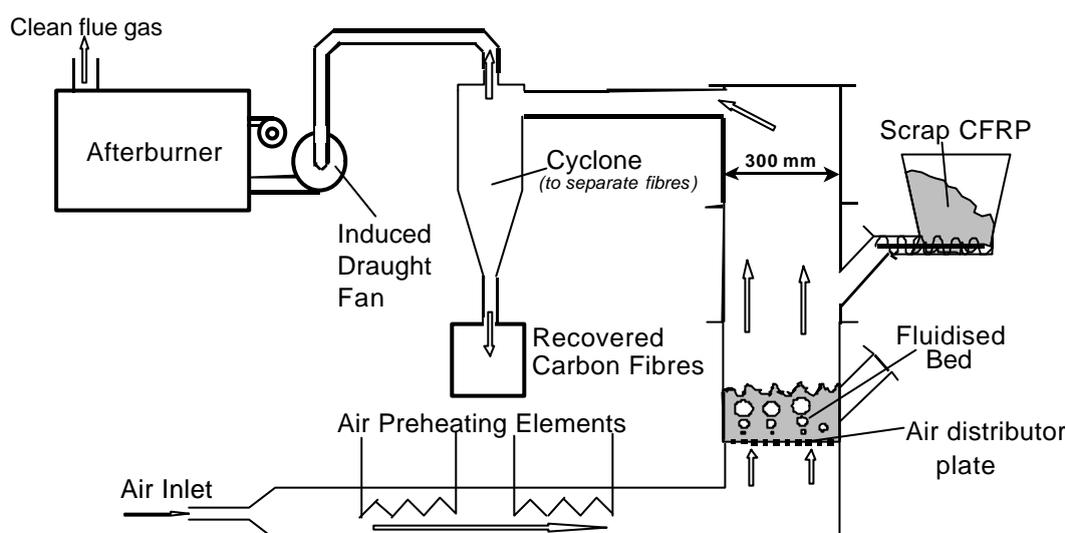
Thermosetting polymers cannot be recycled by remelting and depolymerisation processes are very difficult. The main value in scrap carbon fibre composites is therefore in the fibre. In the fluidised bed recycling process scrap material is fed into a bed of silica sand fluidised with heated air. The polymer in the composite volatilises, leaving clean fibres, which are released into the gas stream as individual monofilaments. The fibres are then separated from the gas stream in a cyclone for recycling. At the temperatures of 450-500°C at which the fluidised bed operates, the polymer does not fully oxidise. Combustion of the organic material is completed by passing the gas stream through a high temperature secondary combustion chamber where there is the potential to recover the energy in the polymer as heat.

A schematic view of the fluidised bed equipment is shown in Figure 1. The shell is formed by an assembly of three flanged stainless steel tubes. The bed comprises silica sand, with a nominal particle size of 0.85 mm, supported on a perforated stainless steel mesh. The upper two tubes comprise the freeboard where disengagement of the fluidising sand occurs. Fluidising air is preheated to a predetermined temperature in a ducting section containing electric resistance heaters (maximum rating 43 kW) situated before the fluidised bed. The air flow can be adjusted manually using a control valve and monitored using an orifice plate flow meter. Comminuted feed is stored in a hopper and introduced at a point above the hot fluidised bed. The performance of the fluidised bed process is dominated by the main operating parameters of bed temperature and fluidising velocity.

The temperature should be high enough to break down and volatilise the polymer, leaving clean fibres, but not too high to cause degradation or oxidation of the fibre. Although the process takes place in air, there is no significant oxidation of the carbon fibre. Other workers have also indicated [8,9] that at temperatures below 550° C, oxidation rates of carbon fibre in air are very low, resulting in a decrease in fibre diameter of less than 0.1µm per hour. The fluidising velocity controls the degree of agitation in the fluidised bed. This should be high enough to allow the fibres to be separated and elutriated from the bed but not too high to cause excessive fibre degradation.

Figure 1 ~ Schematic diagram of the fluidised bed test rig

Fluidised Bed Test Rig



METHOD

Cured unidirectional prepreg (Batch No.217CU, HT CF~ *Grafil* 34-700; Epoxy resin~LTM26EL; Resin by weight, $R_w=38\%$) was carefully chopped to different Initial Fibre Lengths (IFL) of 8, 10, 15, 20, and 25mm (± 1 mm). Each of the uniformly chopped prepreg samples was processed in the fluidised bed test rig under the same conditions one at a time. The operating condition in the fluidised bed test rig was at a fluidising velocity of 1m/s and a controlled temperature of 450°C with nominal bed sand particle size of 0.85mm. Samples of recovered fibre from each test were then dispersed carefully onto at least three petri dishes, and one image per dish was taken by a video camera. Each image was processed and the length distribution of the recovered fibres was measured and recorded in pixels by *Aphelion* image analysis software. This software ran a macro program, which can identify fibres by analysing different light intensity in the image; it is also capable of identifying crossed fibres and eliminating background dust. Finally, the data was transferred to spreadsheets, where the fibres that crossed the image frame and dust contamination were eliminated and the fibre length distribution graphs were plotted and analysed.

Control Test of the Image Analysis

A control test of the image analysis was done with different uniformly chopped carbon fibre lengths of 5, 10, 15 and 20mm. The results showed there were fibre breakages, due to the handling of fibre during the analysis resulting in 15% reduction in average fibre length by weight. Therefore, the image analysis technique gives a conservative estimate of the fibre length distribution.

RESULTS AND DISCUSSION

Figure 2 shows the general trend of the recovered fibre length distribution histograms for different IFL prepreg samples. When the IFL is 8mm, the recovered fibre distribution shows a negatively skewed type histogram, where the mean fibre length is biased to the longer recovered fibre length; For the 10 and 15mm IFL graphs, the recovered fibre length distributions show a twin-peak type histogram, where the higher peak is situated in between 35mm and the second lower peak occurs near the original IFL region; When the IFL is increased to 20 and 25mm, the recovered fibre length distribution shown an isolated-peak type histogram, similar to the 10 and 15mm IFL graphs, except a smaller isolated peak near the original IFL region. From these results, it can be deduced that the higher the IFL, the higher the fibre length degradation during processing, especially when IFL>10mm.

Table 1 ~ Summarised results of the fibre degradation investigation

IFL, mm	Average Fibre Length, mm		Fibres Counted N	Length Degradation, %	
	L _n	L _w		L _n	L _w
8	4.75	5.84	164	40.6	27.0
10	4.42	6.15	214	55.8	38.5
15	4.88	7.38	258	67.5	50.8
20	5.72	8.71	149	71.4	56.5
25	5.44	9.50	180	78.2	62.0

L_n = Fibre Length by Number; L_w = Fibre Length by Weight

Figures 3 and 4 summarise the test results and show that the longer the initial fibre length, the longer the average recovered fibre length, but also the greater the degree of length degradation. The number average fibre length, L_n is the mean fibre length based on the number of fibres measured; whereas the weight average fibre length, L_w is the mean fibre length based on the weight of the fibres sampled. The average fibre length by weight, L_w is more meaningful than the average fibre length by number, L_n , as it reflects the proportion of the total fibre content with any given length. The percentage fibre length degradation by weight was calculated by:

$$\text{Length.Degradation, \%} = \frac{(IFL - L_w)}{IFL} \times 100\%$$

Extrapolation of the graphs shown in Figures 3 and 4 suggested that fibre degradation is likely to be greater for initial fibre lengths above 25mm and it is unlikely that an average fibre length much above 10mm could be achieved from the process at the operating conditions currently used.

Recovered fibres are broken into smaller pieces due to sand particle abrasion at high temperature during the fluidised bed process; the wall roughness of the cyclone separator and fibre handling during the length distribution analysis. Possible improvements to reduce the degree of fibre degradation further may be achieved by control the fluidised bed processing parameters and the use of alternative fibre-gas separation devices.

Repeatability

Figure 5 shows the spread of the mean fibre length by analysing at least 3 samples from each recovered fibre test. The result shows the consistency of the fibre length image analysis that has now been achieved, and this gives confidence to the results.

Figure 2 ~ Histograms of mass fraction verses recovered fibre length for different initial fibre length tests

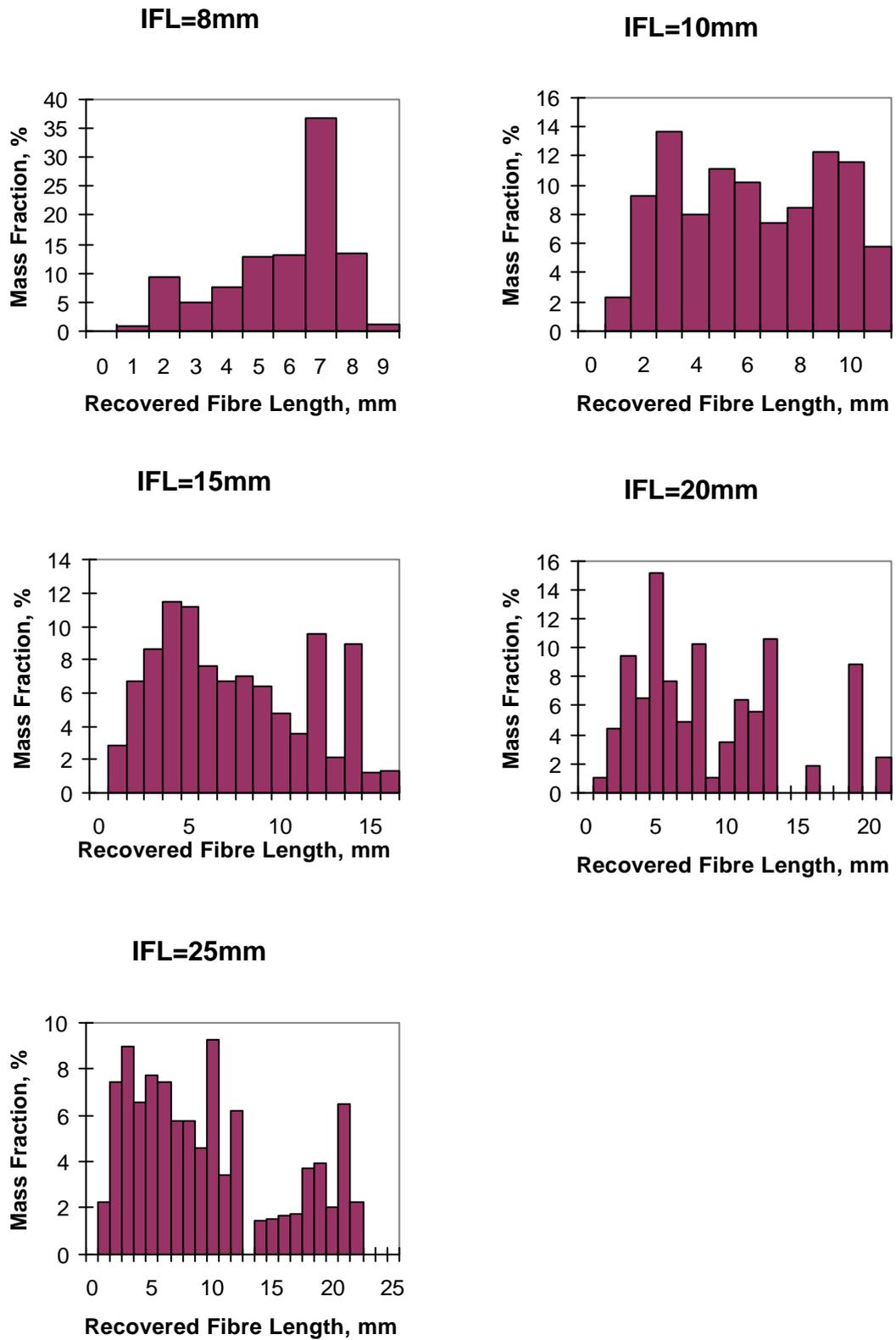


Figure 3~ Average recovered fibre length (by number, L_n and by weight, L_w) versus initial fibre length

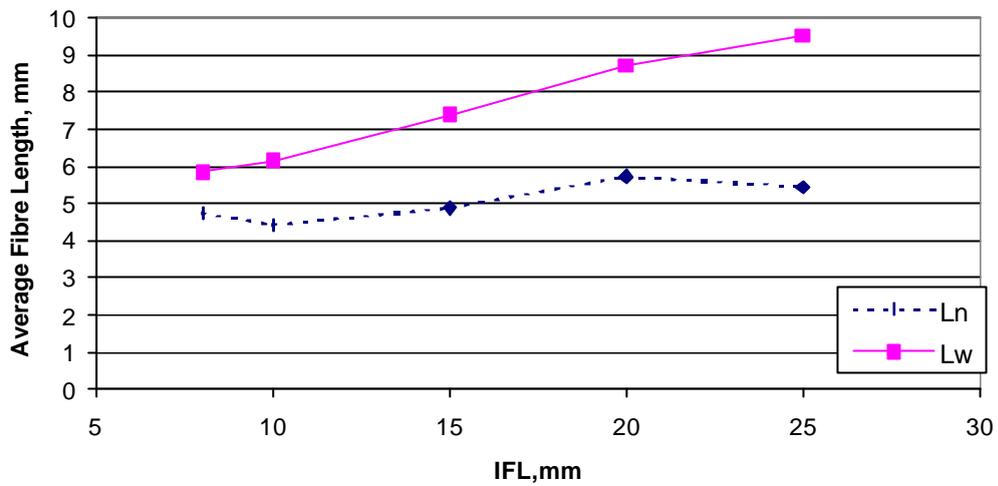


Figure 4 ~ Average recovered fibre length degradation (by number, L_n and by weight, L_w) versus initial fibre length

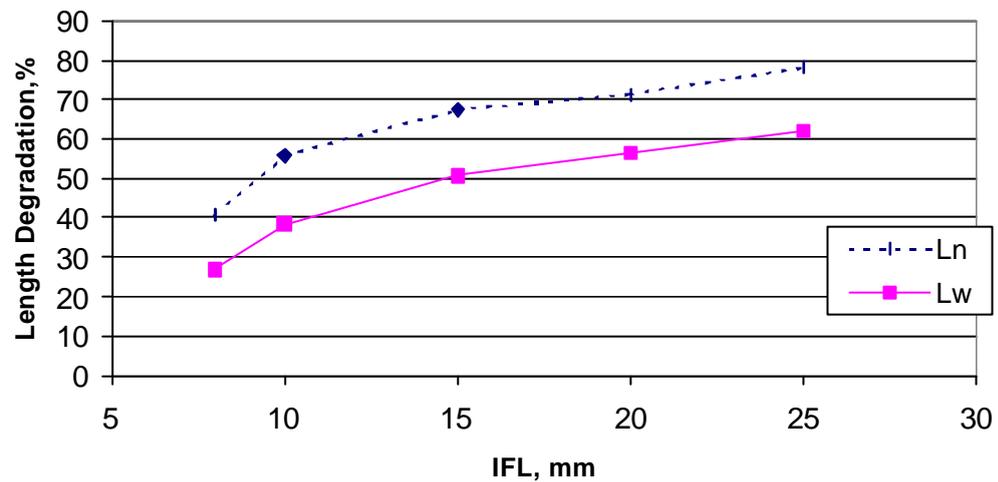
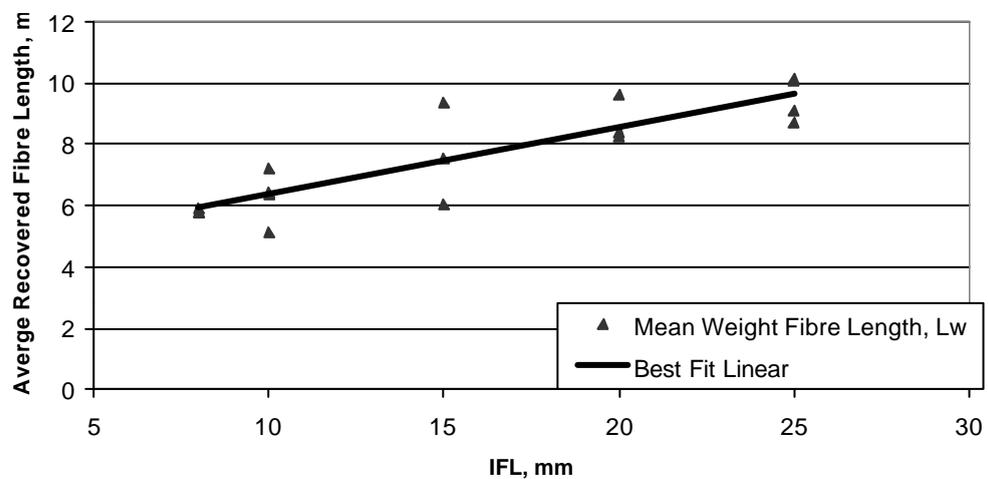


Figure 5 ~ Regression analysis of the effect of the computational image analysis on different samples of each initial fibre length test



TENSILE PROPERTIES OF THE RECOVERED CARBON FIBRE

The method for strength and modulus testing of carbon fibre is based on BS ISO 11566:1996 ~ “Carbon fibres– Determination of the tensile properties of single-filament specimens”, and method B (from section 8.2.2) is used for the modulus calculation.

A Lloyd JJ M30K tensile testing machine was used for the testing single carbon fibre filaments. A datalogger was connected to the machine, where the tension load and the extension of the filament during the test could be recorded. A single carbon fibre filament is glued on to a specimen mounting with epoxy resin. After drying, the specimen mounting is carefully aligned with the loading axis of the tensile testing machine and clamped in the grips. A 5N load cell (with a load range of 5 to 0.1N± 0.0001N) is used, and the crosshead speed is set to 1mm/min. Both sides of the specimen mounting are cut carefully at the mid-gauge point, to leave the carbon fibre filament suspended in between the grips of the testing machine. The datalogger is initiated as the carbon fibre filament is loaded until failure. At least 20 carbon fibre single-filaments were tested for each carbon fibre sample.

It was found that carbon fibres recovered at a fluidised bed temperature of 450°C retain approximately 75% of their tensile strength, whilst the Young’s modulus is unchanged (See Table 2).

Table 2 ~ Tensile Properties of the Recovered Fibres

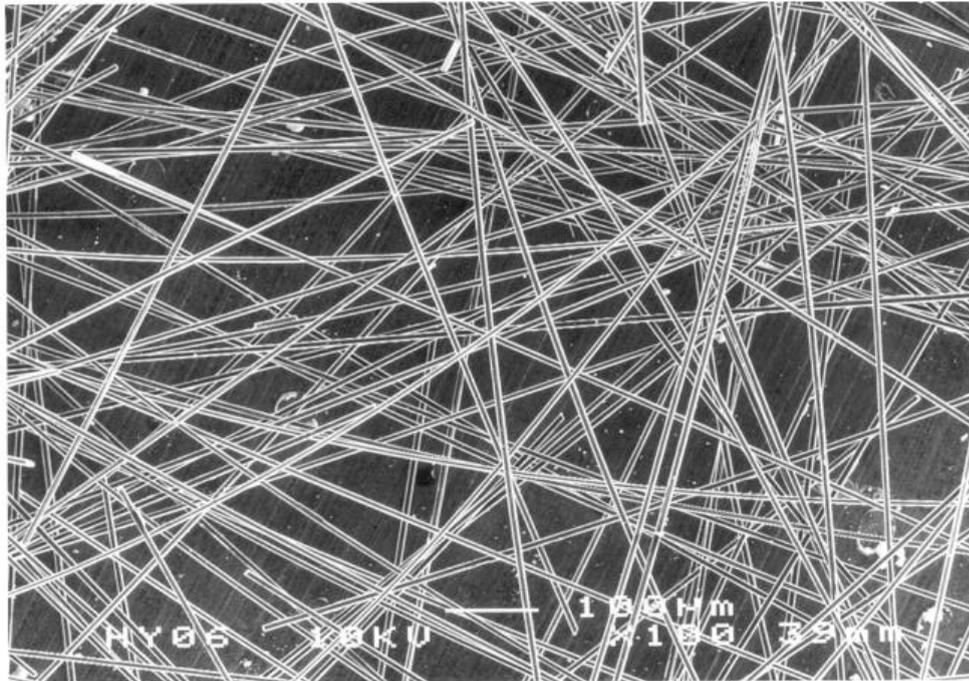
	Tensile Modulus, GPa	Tensile Strength, GPa
<i>Grafil 34-700 CF</i> [Manufacturers Data]	234	4.5
<i>Virgin Grafil 34-700 CF</i> [Measured]	241.9 [Average]	4.09 [Weibull Scale Parameter]
<i>Recovered Grafil 34-700 CF</i> [Measured]	243.2 [Average]	3.05 [Weibull Scale Parameter]

Carbon fibre is a brittle material, and fails due to the worst internal or external surface flaws. Therefore, a large variation in load applied at carbon fibre filament failure is expected, depending on the severity and the number of flaws within the specimen gauge length. The failure strength therefore has to be based on statistical analysis. Weibull distribution is a well-known method for fibre strength estimation [10]. The Weibull scale parameter is the maximum strength of 63% of the weakest fibres in the population.

SURFACE ANALYSIS BY SEM AND XPS

There are no detectable reduction in fibre diameter due to oxidation and the surface chemistry of fibre recovered remain very similar properties to virgin fibre, despite the use of air to fluidise the bed. SEM observations show that relatively clean fibres are recovered from the fluidised bed test rig, except that there are some traces of polymer matrix residue on the surface of a few fibres. See *Figure 6* By comparing the peaks on the XPS spectra, the recovered carbon fibres from the fluidised bed process show very similar surface chemistry properties to the virgin carbon fibre surface.

Figure 6~ Randomly distributed recovered carbon fibres from unidirectional prepreg



CONCLUSIONS

The investigations have shown that the carbon fibre length degradation in the fluidised bed recycling process is proportional to the initial fibre length of the scrap feed. Fibres initially of 8mm length are degraded by 28% to 5.9mm; whilst fibres of 25mm initial length are degraded by 61% to a mean fibre length of 9.5mm. The trends observed suggest that, under the current processing conditions, it is unlikely that the recovered fibres would have a mean fibre length much above 10mm, whatever the initial fibre length. The results have two implications. Firstly, they allow the recovered fibre length to be predicted from the length distribution of fibre in the scrap feed. This will guide optimal scrap preparation. Secondly, the maximum practical fibre length of about 10mm will influence the potential reuse applications for the recovered fibre.

Potential Reuse Applications of Recovered Fibre

Today, milled and chopped carbon fibres are commercially available from carbon fibre manufacturers. Standard lengths for milled and chopped carbon fibre are 300µm and 6mm respectively. Recycled fibre can be used as partial or full replacement of virgin fibre. Typical applications include moulding compounds, tissue or veil type products and reinforcement for concrete structures [11]. High electrical conductivity is another advantage of carbon fibre, and tissue products are often used to provide electrical screening. Further investigations are being carried out for the best suitable applications for recovered carbon fibre.

Future Work

Further work is being undertaken to investigate the effects of alternative processing conditions in the fluidised bed, separation techniques and recovered fibre handling to reduce degradation and increase other qualities of the recovered fibre, such as tensile properties and surface conditions. This will further improve the reinforcement potential of the recovered fibres and hence the commercial viability of the fluidised bed recycling process.

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