STUDY ON PROPERTIES OF COMPOSITES REINFORCED BY HEAT TREATED GLASS FIBRES SIMULATING THERMAL RECYCLING CONDITIONS

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In the present study, commercial chopped glass fibres were heat treated at 300°C, 450°C, 500°C and 600°C to imitate a composite thermal recycling process. The heat treated fibres were extrusion compounded and injection moulded with polypropylene to form composites. The heat treatment increased the susceptibility of the fibres to length degradation during the melt processing particularly at higher conditioning temperatures. Comparison with the Cox model revealed that the stiffness of the composite was affected by the reduced fibre length. The reduced fibre length did not significantly contribute to the reduction of the tensile strength and the impact strength. These properties were deteriorated by other factors such as the strength degradation of the glass fibres and the reduced fibre matrix interaction. Thus a post treatment which recovers the fibre strength and optimizes the fibre-matrix interface will be essential to produce thermally recycled glass fibre composites with high mechanical properties.

1 Introduction

Glass fibre composites are extensively used because they offer an advantageous ratio between costs and performance. The disposal of end-of-life composite products is difficult. Glass fibres and polymeric matrices are not bio-degradable. The disposal of composite waste in landfill is not desired because of environmental concerns. Thus reuse and recycling of these materials has become an immediate task and challenge.

Thermal recycling using a fluidised bed method is one promising approach for the recycling of glass fibres. However, the fibre strength is severely degraded by the fluidized bed process [1, 2]. Due to the need to chop up the input composite material the length of the fibre output is also discrete. Consequently, these recycled glass fibres are more suitable for discontinuous fibre composite applications rather than for continuous ones.

Melt processing of short fibre thermoplastic composites leads to fibre length degradation. Fibre-fibre interactions, fibre-melt interactions and fibre-processor surface interactions cause forces which break the fibres to shorter lengths [3]. The glass fibre strength is highly sensitive to elevated temperatures. A strength reduction of up to 90% was observed for fibres recovered using the fluidized bed process [1, 2]. Simple heat treatment of glass fibre bundles and single glass fibres also resulted in a significant strength reduction [4]. Due to their decreased strength, recycled glass fibres were expected to show larger fibre length degradation during melt processing than pristine glass fibres.

Discontinuous glass fibre polypropylene composites are suitable for high volume production and they can be used for semi-structural applications. The mechanical properties of glass fibre polypropylene composites are strongly influenced by the length distributions of the glass fibres. Thomason et al observed that the Young's modulus, tensile strength and impact resistance increase sharply with the fibre length up to a plateau [5]. Thus an enhanced fibre breakage of recycled glass fibres during processing could also lead to a reduction of the mechanical properties.

In the present study the mechanical properties and fibre length distribution of glass fibre polypropylene composites were investigated. Heat treated glass fibres and untreated glass fibres were used. The heat treatment conditions followed the conditions used for thermal recycling processes in order to understand the fibre length reduction when producing composites using recovered glass fibres.

2 Experimental

Extrusion compounding and injection moulding

The investigated composite materials consisted of 'SABIC® PP 579 S' Polypropylene (PP) and 'DS 2200-13P' glass fibre strands provided by 3B fiberglass company. The glass fibres were coated with a commercial sizing which is optimized for polypropylene composites. These materials (30wt% glass fibre by composite weight) were extrusion compounded using a 'Betol BC25' single screw extruder. The temperatures of the five different heating zones of the extruder were set to 170°C-220°C. The extruded material was drawn through a water bath and cut into pellets using a rotary cutter. The pelletized composite material was fed into a '25 ton Arburg Injection Moulder' to produce dog-bone shaped specimens with a geometry according to the ASTM 638 standard. 1% Polybond 3200 by weight of PP was added to the composites to improve the interfacial shear strength between the fibres and the PP.

Fibre heat treatment

The heat treatment of the glass fibres was performed prior to the extrusion compounding at 300°C, 450°C, 500°C and 600°C in a 'Carbolite CWF 12/13' furnace. The furnace was preheated for one 1h before the samples were inserted for 25min. The samples were then allowed to cool down in ambient air.

Mechanical testing

Uniaxial tensile tests were conducted using an 'Instron 5969' testing machine. All tests were performed with a head displacement rate of 1mm/min. A video extensometer was used to measure the strain.

Unnotched and notched impact test specimens were cut from the injection moulded tensile bars. The dimensions of the impact test specimens followed the ISO 179-1:2010(E) standard. The Type A notches were machined. All specimens were tested edgewise using a 'Tinius Olsen Impact 503' impact tester with a 25J hammer.

Fibre length distribution

The glass fibres were extracted from the injection moulded tensile test specimens by ashing in a 'Carbolite CWF 12/13' furnace. An 8hour ashing program with temperatures up to 650°C was used to burn off the PP completely.

For the fibre length measurement, the fibres were firstly suspended in water before adding a few drops of 85% glycerin to improve the dispersion of the fibres. An 'IDM FASEP' fibre length analysis system was used to analyze the length distribution of the dispersed fibres.

3 Results and discussion

Fibre length degradation

Figure 1 shows the length weighted average length of heat treated and untreated glass fibres in injection moulded tensile test specimens. Each datapoint represents more than 10000 fibres of one tensile test specimen. The results indicate an enhanced length degradation of heat treated glass fibres. The heat treatment at 300°C led to slightly shorter fibres in the composites. The heat treatment at 450°C and 500°C did not lead to a further drop of the residual fibre length. Glass fibres heat treated at 600°C exhibited the largest length degradation during melt processing.

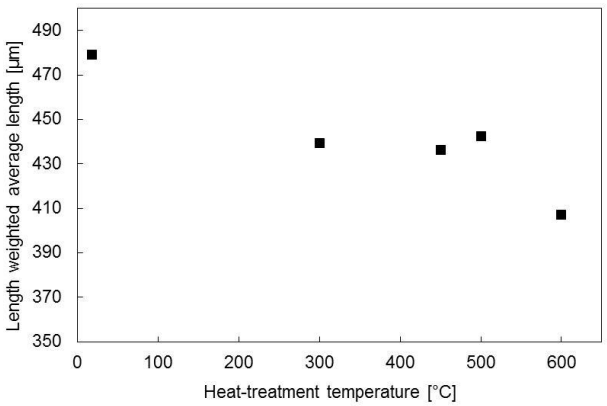

Figure 1. Length of untreated and heat treated glass fibres in injection moulded polypropylene

The enhanced fibre breakage of heat treated fibres can partly be attributed to their reduced tensile strength. Fibres are broken to shorter lengths in polymer melts due to buckling. According to the thin rod theory, the critical buckling radius is inversely proportional to the tensile strength [6]. Thus heat treated glass fibres are more susceptible to buckling. The heat treated glass fibre bundles were not broken up during the heat treatment or during handling operations. However, material was taken from the barrel of the extruder. Fibre bundles which were heat treated at 600°C showed a strong tendency to break up into a fluffy mat before reaching the melting zone in the extruder. In contrast, pristine glass fibre bundles dispersed at a later stage of the compounding process in the polymer melt.

Figure 2 shows the surface of a pristine glass fibre bundle. The surface is completely covered by the sizing. The sizing also acts as an adhesive between the fibres. In contrast, the heat treated glass fibres in Figure 3 are not covered by sizing and no sizing is visible between the fibres. The lack of sizing between the fibres allowed the bundles to break up before the melting zone in the extruder and form a fluffy mat as shown in Figure 4.

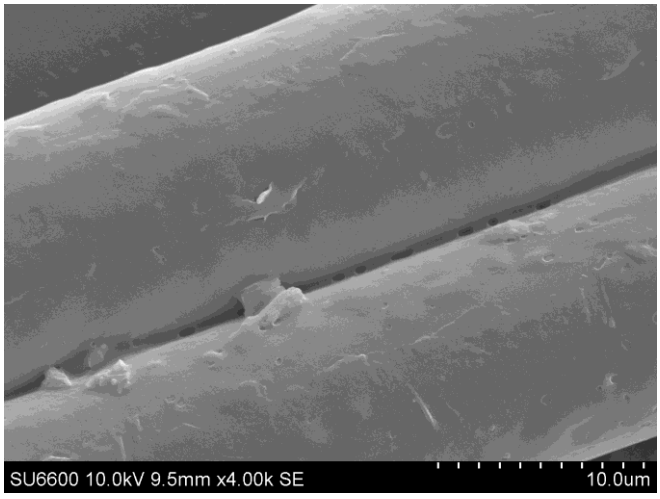

Figure 2. Pristine glass fibre bundle

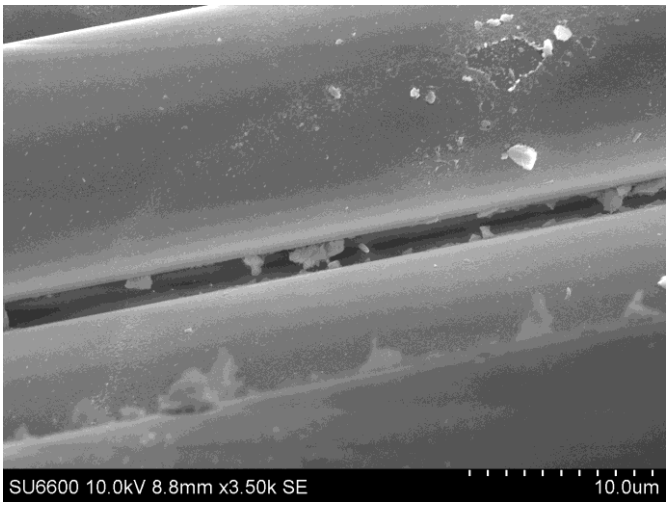

Figure 3. Glass fibre bundle heat treated at 600°C

Figure 4. Glass fibres heat treated at 600°C taken from the barrel of the extruder

Thomason compared the residual fibre length of pultrusion compounded glass fibre PP composites with extrusion compounded glass fibre PP composites after injection moulding. The pultrusion compounded composites were less susceptible to fibre length degradation during injection moulding than the extrusion compounded composites. This observation was explained by the arrangement of the fibres in the composite. The fibres in the pultrusion compounded composites were bundles when the material was fed into the injection moulding machine. In contrast, the fibre bundles in the

extrusion compounded composites were filamentized when the material was fed into the injection moulding machine. It was suggested that the central fibres in the bundles of the pultrusion compounded composites were protected against length degradation [5]. This hypothesis may also apply to the extrusion compounding process in the present study. Heat treated glass fibre bundles broke up earlier than pristine fibre. Thus the fibres at the centre of the heat treated bundles were less protected than fibres in pristine fibre bundles.

Stiffness

Figure 5 shows the Young's modulus (between 0% and 0.5% strain) of injection moulded polypropylene tensile bars that were reinforced with pristine glass fibres and heat treated glass fibres. Each datapoint represents the arithmetic average of ten tensile tests.

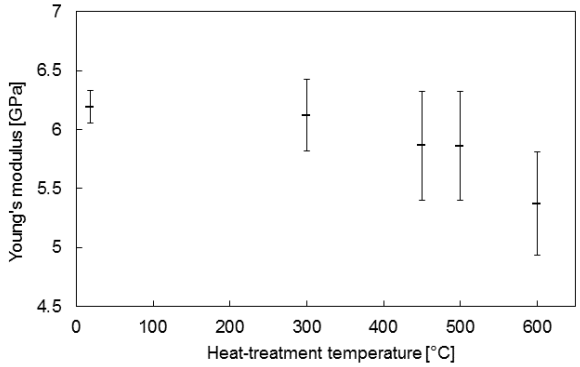

Figure 5. Young's modulus of untreated and heat treated glass fibre Polypropylene composites

The Young's modulus of short glass fibre polypropylene composites is mainly determined by the fibre content, fibre stiffness, fibre orientation, fibre length and matrix stiffness [5, 7]. It has been shown that the stiffness of glass fibres is not reduced by heat treatment [2, 8, 9]. Thus all properties mentioned above were constant in the produced composites except for the fibre length. Similar to previous work on discontinuous glass fibre polypropylene composites [10], the Cox-Krenchel equation (equation 1) was used to predict the stiffness of the composites which were produced in the current study.

Equation 1 describes the stiffness E_C of the composite where η_O is the orientation factor, η_l is the length efficiency factor, V_f is the fibre volume fraction, E_M and E_f are the fibre matrix stiffness and fibre stiffness, respectively.

$$E_C = \eta_O * \eta_l * V_f * E_f + (1 - V_f) * E_M \quad (1)$$

Equation 2 provides the length efficiency factor where L stands for the average fibre length.

$$\eta_l = 1 - \frac{\tanh\left(\beta * \frac{L}{2}\right)}{\beta * \frac{L}{2}} \quad (2)$$

The factor β can be calculated with

$$\beta = \frac{2}{D}\sqrt{\left[\frac{2 * G_M}{E_f * \ln\left(\sqrt{\frac{r}{R}}\right)}\right]} \quad (3)$$

where D is the fibre diameter. E_f stands for the fibre stiffness, the factor r/R can be calculated with equation 5 and the shear modulus can be calculated with

$$G_M = \frac{E_M}{2 * (1 + \upsilon)} \quad (4)$$

where υ is the poison's ratio of the matrix.

$$\ln\left(\sqrt{\frac{r}{R}}\right) = \ln\left(\sqrt{\frac{\pi}{X_i * V_f}}\right) \quad (5)$$

X_i depends on the geometrical packing of the fibres. In accordance with previous work on discontinuous glass fibre polypropylene composites, a value of 4 was used for X_i.

To obtain the orientation factor, equation 1 was rearranged. An orientation factor of 0.64 was calculated from the data of the pristine glass fibre composite. This orientation factor was used to predict the stiffness of composites reinforcement with heat treated glass fibres. To calculate the composite stiffness E_C, a fibre stiffness E_f of 76.9GPa was used [11]. The stiffness E_M and the Poisson's ratio ν of injection moulded PP was measured to 1.6GPa and 0.45, respectively. A fibre diameter D of 13µm was quoted by the manufacturer. and a fibre volume fraction V_f of 12.8vol% were used as input data.

The predicted values from equation 1 are plotted in Figure 6 against the measurement data.

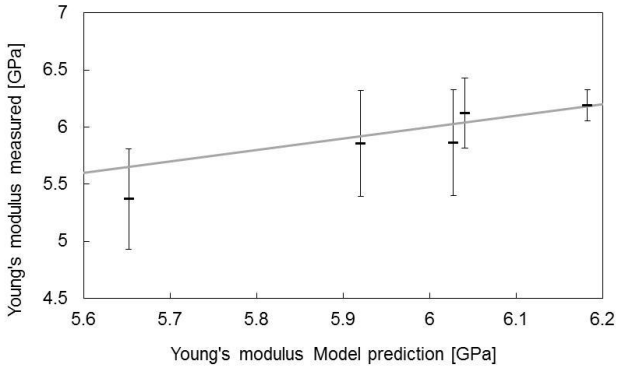

Figure 6. Measured Young's modulus versus model prediction

Figure 6 shows that the stiffness of the heat treated glass fibre composites can be predicted by the Cox-Krenchel equation. Ideally, all data would fall into the slope of unity which is drawn in figure 6. The discrepancy between measurement data and modelling data can be explained by measurement errors.

Thus, the reduction of the stiffness of the heat treated glass fibre composites can be explained by the enhanced fibre length degradation during melt processing.

Strength

Figure 7 shows that the tensile strength of the composites was significantly reduced due to the glass fibre heat treatment. The glass fibre heat treatment at 300°C caused a tensile strength reduction of more than 40%. A glass fibre heat treatment at higher temperatures caused a further drop of the tensile strength. The tensile strength of unreinforced PP was measured to 35.8MPa. Thus the tensile strength of the composite was identical with the tensile strength of unreinforced PP when the glass fibres were heat treated at 600°C.

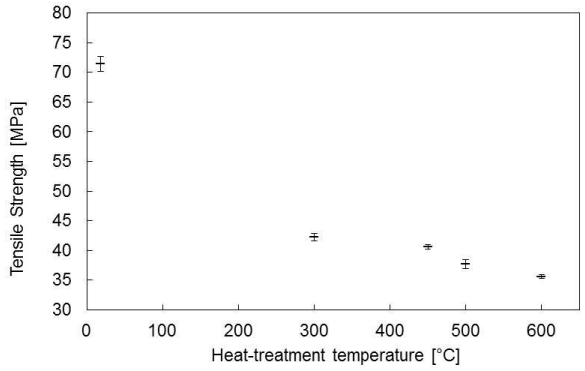

Figure 7. Tensile strength of untreated and heat treated glass fibre Polypropylene composites

The tensile strength of short fibre polypropylene composites is determined by the fibre strength, fibre orientation, fibre length distribution, interfacial shear strength (IFSS) and matrix strength [12].
The glass fibre heat treatment influenced the fibre strength and fibre length distribution in the composite. The IFSS might also have been influenced by the glass fibre heat treatment because of the degradation of the sizing.
It was observed that heat treatment even at 300°C leads to a significant deterioration of the glass fibre tensile strength [4, 9, 13].
Figure 8 and figure 9 show glass fibres that were found on the fracture surfaces of tensile bars. Glass fibres such as those in Figure 8 with a very smooth fracture surface were often found on the fracture surfaces of the heat treated glass fibre composites.
In contrast, most glass fibres on the fracture surfaces of the pristine glass fibre composites had a rough fracture surface with a small smooth mirror zone as shown in Figure 9.
Similar observations on the fracture surface of thermally treated glass fibres were reported by Feih et al.. Based on previous work by Shand [14], they showed that the mirror size correlates with the fibre strength and heat treatment temperature [9].

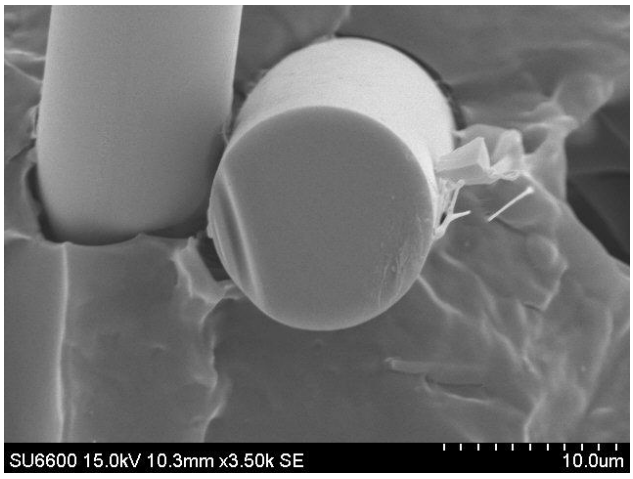

Figure 8. Fracture surface of heat treated glass fibre

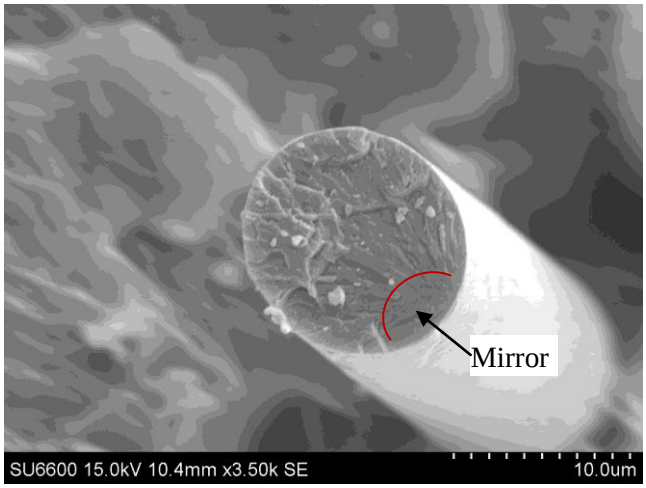

Figure 9. Fracture surface of pristine glass fibre

The IFSS might also have been influenced by the glass fibre heat treatment. A weight loss of 0.3% was observed after heat treatment at 300°C. This weight loss can be attributed to a sizing degradation. The heat treatment at 600°C led to a weight loss of 0.55%. The sizing degradation probably caused a reduction of the IFSS since the sizing of the pristine glass fibres was optimized for the interaction with polypropylene.

As shown in this study, the glass fibre heat treatment affected the fibre length distribution in the composite. The length weighted average fibre length varied between 400µm and 470µm. Previous work on a glass fibre polypropylene composite system with the same fibre content showed that the critical fibre length for the tensile strength is larger than 1mm [5]. Thus the observed variation of the fibre length did not significantly influence the tensile strength of the composite and the fibre length degradation cannot explain the sharp drop of the composite strength.

Thus the fibre strength degradation and potentially the IFSS are the main contributors to the tensile strength reduction of the composite. The enhanced fibre length degradation did not significantly contribute to the reduction of the composite tensile strength.

Strain at failure

It is reported [5, 7] that the failure strain of glass fibre polypropylene composites is influenced by the fibre content, fibre length and the interface properties.

Fu et al. [7] used equation 6 to describe the failure strain of short glass fibre PP composites where ε_C is the failure strain, l_m is the fibre length, r_f is the fibre radius and V_f is the fibre volume fraction. C_S is a constant which depends on the matrix properties, fibre properties and interface properties.

$$\varepsilon_C = C_S * \left(\frac{l_m * {r_f}^2}{V_f}\right)^{\frac{1}{3}} \quad (6)$$

Equation 6 was rearranged to calculate C_S. A value of 0.338mm^{-1} was obtained for C_S using the test data of the pristine glass composite with a fibre content of 12.8vol% as input data. The calculated value for C_S was used in equation 6 to predict the failure strain of the same glass fibre PP system with different fibre lengths measured in the present study.

Figure 10 shows the failure strain of glass fibre PP composites with pristine and pre-heated glass fibres. Each datapoint represents the arithmetic average of 10 tensile tests. For comparison, the calculated values for the failure strain are also plotted in figure 10.

The failure strain decreases at 300°C but increases at higher temperatures and recovered nearly to the value of pristine glass fibre composites.

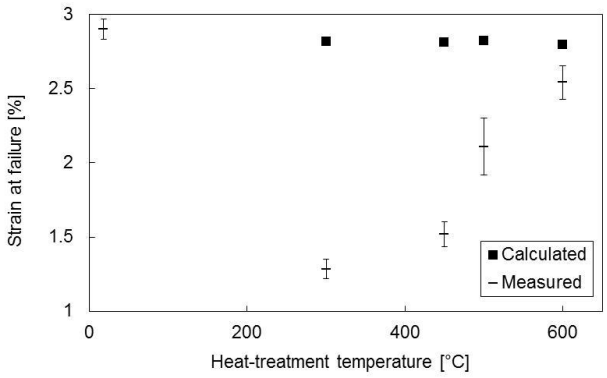

Figure 10. Predicted and measured strain at failure of the investigated glass fibre composites

The data in Figure 10 shows that the reduced length of heat treated glass fibres cannot explain the observed behavior of the failure strain. The glass fibre heat treatment at 300°C led to a length weighted average fibre length of 440µm. For this fibre length, equation 6 predicts a failure strain of 2.8% compared to the measured failure strain of 1.3%. In addition, higher heat treatment temperatures led to shorter fibres in the composite and higher failure strains. In contrast, equation 6 predicts a reduction of the failure strain.

A fibre length reduction as observed in this study only marginally influences the failure strain. Thus the system constant C_S changed due to the glass fibre heat treatment. The interface and the fibre properties changed due to the heat treatment.

Heat treated glass fibres fail at a lower stress and lower elongation than pristine glass fibres [9, 13]. This might have led to the sharp drop of the composite failure strain when the glass fibres were heat treated at 300°C. However, it does not explain the upward trend of the composite failure strain when the glass fibres were heat treated at higher temperatures. Higher heat treatment temperatures led to a further reduction of the fibre strength. It is likely that fibres failed before the peak load of the composite was reached. In addition, higher heat treatment temperatures also caused a further degradation of the glass fibre sizing. It is suspected that the sizing degradation led to a reduction of the IFSS. Thus stresses have probably not been transferred from the matrix to the fibres. These effects might have led to a matrix dominated failure which is similar to short fibre composites with low fibre contents [5, 15, 16]. The results of this study suggest that the failure strain of composites is not deteriorated by enhanced fibre breakage of heat treated glass fibres.

Impact properties

Figure 11 shows the unnotched and notched impact strength of pristine glass fibre composites and heat treated glass fibre composites. Each datapoint represents 10 impact tests.

The notched and unotched impact strength decreased sharply due to the glass fibre heat treatment. However, unnotched and notched impact strength increased slightly when the heat treatment temperature was increased from 300°C to 450°C and 600°C.

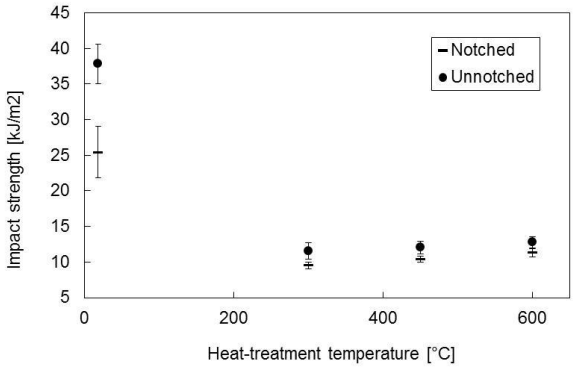

Figure 11. Impact strength of pristine and heat treated glass fibre composites

A study on injection moulded glass fibre polypropylene composites showed that the notched impact strength strongly depends on the aspect ratio of the fibres [5].

However, the observed reduction of the notched impact strength in the present study cannot be attributed to the enhanced fibre breakage of heat treated glass fibres during melt processing. The measured fibre length is clearly below the critical fibre length of the impact strength. A study on a comparable glass fibre PP composite showed that the critical fibre length for the impact strength is larger than 1mm [5]. Thus the measured fibre length reduction cannot explain the sharp drop of the impact strength after glass fibre heat treatment.

The reduction of the fibre strength is one likely reason for the decrease of the impact strength in this study. Thomason and Vlug [17] developed a model for the notched impact strength which considers

fibre fracture as energy dissipation mechanism. In this model, the fibre fracture energy is propertional to the square of the fibre strength.

In contrast to other work [5], the results of the current study do not exhibit a linear relationship between tensile strength and unnotched impact strength. When the heat treatment temperature was increased the tensile strength continued to drop while the unnotched and notched impact strength increased marginally.

The observations described above suggest that fibre fracture is not the predominant energy dissipation mechanism of heat treated glass fibre composites. The reason for the increase of the impact strength at higher heat treatment temperatures is not clear and requires further research.

4 Conclusion

The present study revealed that heat treated glass fibres are more susceptible to fibre breakage during melt processing.

However, it can be concluded that the enhanced length degradation of thermally recycled glass fibres was only relevant for the stiffness of the investigated fibre matrix system. The length of the fibres in the composite was significantly shorter than the critical fibre length of the impact strength and tensile strength. Thus the observed variation of the fibre length did not significantly influence these properties.

For different composites the additional fibre breakage might still be relevant. If the fibre length is closer to the critical fibre length of the mechanical properties, enhanced length degradation of thermally recycled fibres might have a detrimental impact on the mechanical properties of the composite.

Most of the mechanical properties of the investigated composites were deteriorated because of the strength loss and reduced fibre-matrix interaction of the thermally treated glass fibres.

Thus the strength recovery of the fibres and enhancement of the fibre matrix interaction are the most important issues which have to be adressed in order to maximise the mechanical performance of thermally recycled glass fibre composites.

Acknowledgement

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