

The influence of fibre length and concentration on the properties of glass fibre reinforced polypropylene: 7) Interface strength and fibre strain in injection moulded long fibre PP at high fibre content.

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ABSTRACT

The mechanical performance of injection moulded long glass fibre reinforced polypropylene with a glass fibre content in the range 0-73% by weight has been investigated. The composite modulus exhibited a linear dependence on fibre content over the full range of the study. Composite strength and impact resistance exhibited a maximum in performance in the 40-50% by weight reinforcement content range. The residual fibre length, average fibre orientation, interfacial shear strength, and fibre strain at composite failure in the samples have been characterised. These parameters were also found to be fibre concentration dependent. The interfacial shear strength was found to be influenced by both physical and chemical contributions. Theoretical calculations of the composite strength using the measured micromechanical parameters enabled the observed maximum in tensile strength to be well modelled.

Introduction

Glass fibre reinforced polypropylene moulding compounds have been available for many years. Since their initial development this class of materials has experienced a rapid growth in their end use applications. This can be attributed to the relative ease of processing of such thermoplastic compounds combined with their clean and recyclable nature and an attractive price-performance ratio. However, as is typical with composite materials, we must contend with a balance of processibility to performance. To obtain a high level of processibility with these moulding compounds we must give up a certain level of the reinforcement efficiency of the fibres. Injection moulded composites often contain only relatively short fibres (i.e. shorter than the “critical” fibre length), oriented in complex and often non-optimal patterns. Moreover, extrusion compounding, the classical route for preparing such compounds becomes increasingly less attractive above a fibre content of 40-50% by weight of fibres due to increasing processing issues. Therefore the composite applications for these materials cannot be too demanding, where stiffness and strength criteria can be met with fibre weight fractions of 50% or less. This is low compared to “high performance” application where weight fractions of 70% or greater, of aligned, continuous fibres can be used, usually at the cost of accepting a lower level of processing efficiency such as lower throughput and higher associated costs.

In the past few years the growth in structural composite usage has resulted in the need for higher output manufacturing processes than have been used previously. This has provided the impetus for the development of techniques to produce long fibre (LF) reinforced thermoplastic, and particularly polypropylene (PP), matrix composites which possess both higher performance and mass processibility. The long (but discontinuous) fibre reinforced materials such as Glass Mat Thermoplastic (GMT) and LF-PP injection moulding pellets prepared by wire coating, cross head extrusion, or thermoplastic pultrusion techniques, have recently received much attention (1-12). In particular, the long-fibre reinforced pellets for injection moulding can give composites with many significantly enhanced properties in comparison with the more conventional “short-fibre” compounds (12). Much of the attention given to these materials focuses on the effects of fibre length, however due to the aligned nature of the fibres in the LF-PP moulding compounds it is possible to produce pellets with much higher glass fibre contents than those produced with extrusion compounding. The ability to produce such moulding compounds with high glass contents may enable the production of injection moulded composite components with significantly higher properties than were previously possible. However this would assume that the mechanical properties of these composites continue to increase with increasing fibre content. We recently (13) presented the results of a study of the structure-performance relationships in injection moulded LF-PP over a fibre content range of 0-73% by weight (0-0.5 volume fraction). The main results on mechanical properties are summarised in Figure 1 which shows the composite stiffness, strength and impact performance normalised to the PP values versus the fibre content. It can be seen that, although the composite modulus does increase linearly with increasing fibre content, both the strength and impact performance exhibit a maximum in the 40-50% by weight region. Of particular note is the performance at the highest fibre loadings where we see that, despite a large increase in composite modulus, the strength and impact performance has returned to levels close to that of unreinforced PP. It was further shown that these effects could not be fully explained by changes in residual

fibre length and orientation and it was suggested that further study of the level of fibre-matrix adhesion and fibre stress at composite failure was required. In this paper we present the results of a continuing study of this phenomenon.

Experimental

Owens Corning 174C-AD-3000 continuous glass fibres (nominal fibre diameter 20 microns) and Huntsman P4C6Z-059 polypropylene (MFI=35 g/10min) were used to produce LF-PP moulding compounds over a range of glass contents up to 73% by weight. The level of fibre-matrix interaction in this system was increased by the addition of 2% by weight of resin of Polybond 3200 coupling agent. The LF-PP moulding compounds were produced by a coating technique similar to that discussed by Bader and Bowyer (14). The continuous glass fibre strand was coated using a crosshead die attached to a 50 mm single screw extruder, which fed the polypropylene with a melt temperature of 230 °C. After water cooling the continuous strand was chopped into pellets of 12.5 mm length. These pellets were moulded into test bars on a 200-ton Cincinnati Milacron moulding machine. The cylinder heating zones had set point temperatures, rear 180 °C, centre 235 °C, front 221 °C, the nozzle temperature was set at 215 °C and the mould temperature was set at 65 °C. The mould was designed to produce a number of standard test specimens in one shot, all test bars and disks were single end gated.

Unless otherwise stated, all mechanical property testing was performed at 23°C and at a relative humidity of 50%. Tensile properties were measured in accordance with the procedures in ASTM D-638, using five ASTM Type I specimens at a crosshead rate of 5 mm/min (0.2 inches/min) and an extensometer gauge length of 50 mm (2 inches). Flexural properties were measured on five specimens in accordance with the procedures in ASTM D-790, at a crosshead rate of 2.5 mm/min (0.1 inches/min) and a span width of 50 mm (2 inches). Izod and modified Charpy impact properties were measured on ten specimens in accordance with the procedures in ASTM D-256 and ASTM D-4812. Fibre length and diameters were determined by image analysis and optical microscopy on fibre samples removed from the moulded bars after high temperature ashing. The fibre lengths of 500 fibres from each of three test bars were summed to obtain the fibre length distribution for each fibre concentration. Similarly, fibre diameters from 100 fibres from each of three test bars were determined to obtain the fibre diameter distribution. Measurement of fibre orientation was carried out on cross sections of the moulded tensile bars cut perpendicular to the flow direction as previously described (13).

Results and Discussion

The macro-method analysis used here to obtain values of the interfacial shear strength (IFSS) was originally proposed by Bowyer and Bader (14, 15) and an improved version has been extensively reviewed by Thomason (16-19). The macro-method has an enormous attraction in that it utilises data which are readily available from standard composite mechanical testing and requires only an extra determination of fibre length distribution, which is a common characterisation tool of those working with discontinuous fibre composites. The method is based on the Kelly-Tyson model for the prediction of the ultimate strength (σ_{uc}) of a polymer composite reinforced with discrete aligned fibres (20). This model can be simplified to the equation

$$\sigma_{uc} = \eta_0 (X + Y) + Z \quad (1)$$

where Z is the matrix contribution, X is the fibre contribution from fibres with length below a critical fibre length L_c , and Y is the fibre contribution from fibres with length above L_c where the critical fibre length (L_c) is defined by

$$L_c = \sigma_{uf} D / 2\tau \quad (2)$$

where σ_{uf} is the fibre strength, D is the average fibre diameter and τ is the IFSS. The Kelly-Tyson model assumes that all the fibres are aligned in the loading direction and the equation cannot be integrated to give a simple numerical orientation factor to account for the average fibre orientation. The common approach to this problem is to fit the experimental data using a simple numerical orientation factor (η_0). Bowyer and Bader extended the original Kelly-Tyson concept to model the stress-strain curve of the composite *prior* to failure (14, 15). The basis of their argument was that at any strain value (ϵ_c) there exists a critical fibre length $L_\epsilon = E_f \epsilon_c D / 2\tau$ where E_f is the Young's modulus of the fibre. Fibres shorter than L_ϵ carry an average stress = $L \tau / D$ and fibres longer than L_ϵ carry an average stress = $E_f \epsilon_c (1 - (E_f \epsilon_c D / 4L \tau))$. The composite stress at any strain level may then given by

$$\sigma_c = \eta_0 \left(\sum_i \left[\frac{\tau L_i V_i}{D} \right] + \sum_j \left[E_f \epsilon_c V_j \left(1 - \frac{E_f \epsilon_c D}{4\tau L_j} \right) \right] \right) + (1 - V_f) E_m \epsilon_c \quad (3)$$

Although η_0 and τ are not generally known, values for these factors can be obtained if the composite stress (σ_{c1} and σ_{c2}) at two strain values (ϵ_{c1} and ϵ_{c2}) are known. The matrix contribution Z was calculated from an independent matrix modulus determination and used to calculate the ratio R of the fibre contributions at the two strains

$$R = \frac{\sigma_{c1} - Z_1}{\sigma_{c2} - Z_2} \quad R^* = \frac{X_1 + Y_1}{X_2 + Y_2} \quad (4)$$

Equation 3 was then used with an assumed value of τ to calculate the ratio R^* , the theoretical value of R . At this point the ratios R and R^* are independent of η_0 . The value

of τ is then adjusted until $R^*=R$ and that value of τ is used in Equation 3 to obtain a value for η_o (which is assumed to be the same at both strain levels).

Thomason has recently shown how the model can be improved by taking into account the non-linear stress-strain behaviour of thermoplastic matrices (16-19). For the matrix used in this study the stress contribution (in MPa) can be calculated for any strain level between 0-3% using

$$\sigma_{pp} = 0.75\varepsilon^3 - 6.34\varepsilon^2 + 21.01 \varepsilon \quad (5)$$

Furthermore the analysis method was extended to obtain a value for σ_{fm} the maximum fibre stress at composite failure. This can be obtained by inserting the composite breaking stress into the original Kelly-Tyson equation along with the determined values of τ and η_o . Consequently, this method gives values of the micromechanical parameters η_o , τ , σ_{fm} of any system. The relative simplicity and cost effectiveness of this approach makes it ideal as an industrial screening tool for product developers. Typical cumulative fibre length distributions from the samples in this study are shown in Figure 2. It can be clearly seen how increasing the fibre content of the compound leads to a reduction in the level of the average fibre length. The typical fibre length averages obtained from such distributions were previously shown to decrease approximately linearly with increasing fibre content. When the stress and strain values obtained from tensile testing are combined with the full fibre length distributions and applied in the procedure described above we obtain values for the parameters η_o , τ , σ_{fm} .

The results for η_o as a function of glass content obtained using this method are shown in Figure 3 where they are compared with values for average fibre orientation parameter obtained by optical analysis of polished composite cross sections and from back calculation using the composite modulus (13). Not surprisingly the macro-analysis values, which also use input data from mechanical testing, follow a similar trend to those obtained from the composite modulus. Some possible explanations for the difference between optically obtained values for η_o and values obtained through mechanical testing have been discussed previously (13). However, at this time, we have no definitive explanation for these differences.

The results for the IFSS are shown in Figure 4. The line in this Figure is simply a general guide to the eye. However it is clear that the IFSS appears to be decreasing with increasing fibre content. This general trend for a decrease in the apparent IFSS with increasing fibre content has been observed previously for injection moulded short fibre reinforced thermoplastics over a more limited range of fibre contents (10-40% by weight) (12, 17-19). The IFSS – fibre content relationship has been compared to a similar trend in the calculated values of residual compressive radial stresses on the fibres in these systems. These interfacial compressive stresses are a result of the differential in thermal expansion coefficients between the inorganic fibres and the organic polymer matrices. Although the trends have been shown to be similar, calculation of an interfacial strength contribution from the radial stress did require somewhat high values (0.4 – 0.7) of coefficient of friction between fibre and matrix. The extended glass content range of this study allows us to examine this relationship more rigorously. In Figure 5 the IFSS data are compared with a theoretical value of residual radial stress generated IFSS using a coefficient of friction of 0.6 and radial stress values calculated using the equations

proposed by both Nairn (21) and Piggott (22). It can be seen that it is possible to obtain an order of magnitude fit to the experimental data at any particular glass content by an expedient choice of the coefficient of friction. Nevertheless, the fit over the full fibre content range is not particularly good, and the value required for the fibre-matrix coefficient of friction is somewhat high. The implication of this result is that there must be more to apparent IFSS in this system than residual stresses alone.

It is well known that the addition of the maleated PP “coupling agents” of the type used in this study frequently lead to improved mechanical performance in glass fibre reinforced PP. This improvement in performance is often attributed to the possible formation of chemical bonds across the fibre-matrix interface between the polymeric coupling agent and the silane coupling agents from the fibre sizing which is assumed to be chemically reacted to the fibre surface. Since the polymer coupling agent is added during the extrusion step with the glass fibres and the homopolymer PP, the availability of maleated groups at the interface to enhance the IFSS may well be proportional, among other things, to the ratio of the concentration of maleated molecules in the matrix to the glass fibre surface area in the composite. We have estimated this ratio using the fact that 1 g of composite contains

$$\frac{N_A (1 - W_f) C_{MPP}}{M_w} \quad (6)$$

Molecules of maleated PP, and contains a fibre surface area A_f of

$$A_f = \frac{4W_f 10^{21}}{\rho_f D} \quad nm^2 \quad (7)$$

Where N_A is Avogadro’s number, W_f is the fibre weight fraction, $C_{MPP} = 0.02$ is the weight fraction of maleated PP with molecular weight $M_w = 50,000$ in the PP matrix, ρ_f is the fibre density (kg/m^3) and D is the average fibre diameter in μm . The results of these calculations (solid line) are compared with the apparent IFSS (points) in Figure 6. It can be seen here that there exists a remarkable correlation between the trend observed in the calculated number of MPP molecules available per unit area of interface and the measured apparent IFSS. This result would appear to support the hypothesis that the MPP contributes significantly to the apparent IFSS through some adhesion mechanism. We do not mean to imply that all of the available molecules of MPP find a place at the interface. There will be many complex (mixing, diffusion, viscosity, time, temperature) relationships to consider in this process. However it does seem reasonable to assume that, if the processing conditions are kept constant, the probability of finding an MPP molecule at the interface will be directly dependent on the ratio of MPP matrix concentration to interfacial area in the system. To extend this analysis further what is required is a method to convert the calculated value of this ratio to a value of IFSS. In a previous publication (12) we compared the apparent IFSS of injection moulded short fibre PP with and without the addition of MPP across the 10-40% by weight fibre content range. We found that the apparent IFSS was increased by approximately 6.5 MPa by the addition of 2% by weight of MPP to the PP matrix. The MPP and PP in that study were the same as used here. Consequently we have also prepared a range of injection moulded long fibre PP samples without added MPP. The results for the tensile strength of these samples is compared with the samples with 2% by weight added MPP

in Figure 7. The large effect of the MPP on the tensile strength of these composites is clearly seen in this Figure. It is interesting to note that even the low performance of the samples without added MPP still appears to show a maximum in tensile strength in the 30-40% by weight glass fibre range.

The apparent IFSS for the samples with and without added MPP is compared in Figure 8. It can be seen here that the addition of 2% by weight MPP in this system also gives an increase in the apparent IFSS in the range of 2-18 Mpa depending on the fibre content. The difference with the previous study may well be explained by the differences in the chemical nature of the sizing layer on the fibres used in the two studies. The data in this Figure now allows us to “calibrate” the contribution of the ratio of MPP molecules to interfacial area to obtain a value for the contribution to the apparent IFSS. If we assume that the samples with no added MPP exhibit an IFSS made up solely of a physical contribution due to residual thermal stresses and interfacial friction then we can fit either the Piggott or Nairn model to the data to obtain a value of the interfacial coefficient of friction. The theoretical lines for both models with a friction value of 0.15 are also shown in Figure 8. It can be seen that, on this scale, there is little difference between the two models and that they both fit the experimental data for the samples with no MPP quite satisfactorily. Note that the addition of MPP to the matrix may result in improved fibre wetting which could in turn result in an increased coefficient of friction in the MPP containing composites. Notwithstanding this possibility we now further assume that the physical contribution to the apparent IFSS is unchanged by the addition of MPP and we use a value of 7.5 MPa for the contribution to IFSS of 2% MPP at 30% by weight glass fibre. This allows us to calculate the upper theoretical curve shown in Figure 8. It can be seen that, given the scatter of the IFSS data, we obtain a satisfactory fit of the theoretical curve to the apparent IFSS values. It is worth noting at this point that the presence of correlation in such complex systems does not necessarily imply causality. However, by using this approach we are apparently able to discriminate between the physical and chemical contributions to the IFSS in MPP modified glass fibre reinforced PP.

Figure 9 compares the values for experimental composite strength with those obtained from the Kelly-Tyson theory using the new values for the apparent IFSS shown as the solid line in Figure 8 and the previously obtained average fibre lengths and orientation factors (13). Although we still do not obtain complete agreement, the fit of theory to experiment is vastly improved by the use of the IFSS values obtained by the above method (13). Notwithstanding this improvement it is clear that we still do not obtain a perfect fit of theory with experiment. The final variable which must be dealt with is the value of σ_{fm} – the fibre stress at composite failure. It is common practice to assume that $\sigma_{fm} = \sigma_{uf}$ and to use a fixed average value for the fibre tensile strength in the Kelly-Tyson calculation of composite strength; the data in Figure 9 were generated using a fixed average fibre breaking stress of 2 GPa (13). If we assume a value of fibre modulus $E_f = 72$ GPa this would occur at a fibre elongation of approximately 2.8% which far exceeds the failure strain of many of the composites in this study. Given that it is difficult to imagine a scenario where the individual fibre strain is higher than the applied composite strain it seems unlikely that composite failure is *initiated* by fibre failure in this case. The macro-model used here also outputs a value for σ_{fm} and these data are shown in Figure 10. It can be seen that the stress in the reinforcing fibres at composite failure is reduced almost linearly as the fibre concentration increases. It is interesting to note that the implication of these results is that it is indeed most unlikely that fibre failure was the initiating cause of composite failure in most of the samples in this study. Only at

fibre contents below 20% by weight does the fibre stress level reach values which are in the region of the average fibre failure stress quoted above. Following the discussion above we have converted these values of fibre stress into fibre elongation and these are compared with the experimental composite failure strains in Figure 11. It can be seen that there is an excellent direct correlation between these two variables which indicates that fibres which are longer than L_c (and are aligned with the loading direction) are strained to approximately the same level as the composite itself. If we now use values for σ_{fm} calculated from the composite failure strain in the Kelly-Tyson model we obtain the values shown in Figure 12. The curves in Figure 12 are obtained from curve fitting quadratic equations using the least squares fitting method. It can be seen that we now obtain a good fit between theory and experiment.

Conclusions

In this investigation of the mechanical performance of injection moulded long glass fibre reinforced polypropylene over a fibre content range of 0-73% by weight we have found that composite strength and notched impact performance show a maximum in performance in the 40-50% by weight fibre content range. At higher fibre content these properties decreased significantly and approached the unreinforced polypropylene performance at the highest fibre content of 73% by weight. This experimentally observed maximum can be adequately modelled using existing theories if the data on the fibre content dependence of the prerequisite micromechanical parameters are fully available. Average fibre length in these composites decreases linearly with increasing fibre content, as does fibre strain at composite failure. Average fibre orientation parameter also appears to decrease with increasing fibre content although the observed trend appear to be dependent on the measurement technique and in all cases the results are subject to high levels of experimental error. Interfacial shear strength in this composite system is a yet more complex phenomenon and has been analysed by assuming both a physical and chemical contribution. In both cases a dependence on fibre content is observed. The physical contribution to the interfacial strength can be well modelled based on the assumption of the existence of a residual interfacial compressive strength that decreases approximately linearly with increasing fibre content. The chemical contribution to the apparent interfacial shear strength was found to be proportional to the concentration of the maleated polypropylene coupling agent molecules available per unit area of interface in the composite. Results indicate that a thorough understanding of the failure of this type of material may be better found with a strain based failure criterion as opposed to a stress based failure criterion.

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