Interfacial shear strength of nucleated short glass-fibre reinforced polypropylene

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Polypropylene and the short glass-fibre–polypropylene composite in the form of granules were each initially pre-mixed with a sodium benzoate nucleating agent in a dry blender and subsequently homogenized in a twin-screw extruder. The extrudate was masticated and compression moulded. The inherent fibre orientation K and the interfacial shear strength τ of the short glass-fibre–polypropylene composite were determined by use of the short fibre composite theories proposed by Kelly and Tyson and modified by Bowyer and Bader. The interfacial shear strength τ and orientation factor K values of 18 MPa/0.201 and 24 MPa/0.177 were obtained for the nucleated and the unnucleated composite, respectively. The nucleated composite showed decreased interfacial shear strength and increased orientation factor, as was expected. The interfacial shear strength of the unnucleated samples compared favourably with the literature values.

(Keywords: polypropylene; glass-fibre composite; composites)

INTRODUCTION

The rigidity and strength of polymers are enhanced by the incorporation of high-strength, high-rigidity and low-density reinforcing fibres. The excellent specific properties of these composites make them the preferred choice in applications where weight saving is highly desired. Polymeric composites are constituted of the matrix, the reinforcing fillers and the interface.

The matrix is viscoelastic and continuous and supports the rigid and elastic fillers which carry much of the applied load. The reinforcements are separated from the matrix by the interface. Semicrystalline polymers can be regarded as intrinsically reinforced polymers, where the crystallites act as the reinforcements and the continuous amorphous fraction is the matrix. Increasing the degree of crystallinity increases the modulus and the strength of the composite in accordance with the rule of mixture[1–3]. One way of improving the degree of crystallinity is by heterogeneous nucleation. Nucleated polymers form large numbers of small sized crystallites.

The transmission of the applied load through the matrix to the fibres depends on the state of the bonding between the matrix and the fibres. For short fibre composites, the load applied to the matrix is transferred to the fibres by shear at the interface[4–7]. The stronger the interfacial bonding, the more efficient the transfer of the applied load through the interface to the fibres. Fibre lengths must be greater than the critical length of the fibre in order to create an interfacial area large enough to permit the fibre to carry much of the applied load. The critical fibre length L_c is related to the radius of the fibre r, the interfacial shear strength τ and the average tensile strength in the fibre $\langle\sigma\rangle_f$ by the relationship:

$$\frac{L_c}{\langle\sigma\rangle_f}=\frac{r}{\tau} \tag{1}$$

The critical fibre length L_c is also related to the fibre modulus E_f and the ultimate strain of the composite ε_{cu} by the equation:

$$L_c=\frac{E_f\varepsilon_{cu}r}{\tau} \tag{2}$$

For a certain applied stress σ, the average tensile stress $\langle\sigma\rangle_f$ is assumed constant about the centre of the fibre[8–11]. Fibres with length L less than the critical fibre length L_c, will carry an average stress $\langle\sigma\rangle_f$ equal to half the maximum stress:

$$\langle\sigma\rangle_f=\frac{L\tau}{2r} \tag{3}$$

Fibres whose length exceeds the critical fibre length have an average stress related to the fibre modulus E_f and composite strain ε_c by the equation:

$$\langle\sigma\rangle_f=E_f\varepsilon_c\left(1-\frac{E_f\varepsilon_c}{2L\tau}\right) \tag{4}$$

Degradation of fibres by fracture during processing results in a distribution of fibre lengths in the composite system. Bowyer and Bader derived the stress–strain

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relationship for short fibre composites. They also determined the orientation factor K and the interfacial shear strength τ using the model proposed by Kelly and Tyson[8]. Since short fibre composites transfer stress from the matrix to the fibre by a shear transfer mechanism[12,13], knowledge of the interfacial shear strength τ and orientation factor K are important in their quantitative analysis.

The orientation factor K defines the average angle, θ, of the fibres with reference to a fixed 'load' direction. The values of the orientation factor vary from one, for highly oriented systems, $\theta = 0°$, to zero, for isotropic systems, $\theta = 90°$, depending on the processing techniques adopted. Compression-moulded samples are generally isotropic, with a K value of about 0.167[14]. The magnitude of the interfacial shear strength is an indicator of the efficiency of the reinforcement.

In the present paper we attempt to calculate the interfacial shear strength and the orientation factor for discontinuous glass-fibre reinforced polypropylene containing a sodium benzoate nucleating agent using the theoretical model proposed by Kelly and Tyson.

EXPERIMENTAL

Materials

Isotactic polypropylene Pro-Fax 6524 and short glass-fibre–polypropylene composite Pro-Fax PC-073 ($V_f \sim 12\%$) in the form of granules were supplied by Hercules Inc. Sodium benzoate was used as the nucleating agent. The composite and the homopolymer were respectively pre-mixed with 0.5% by weight of the nucleating agent by means of the tumble mixer. The pre-mixed samples were extruded by means of a twin-screw extruder model DSK 42/5 manufactured by Brabender Ohg Duisburg. The extruder has a screw zone 105 mm long, a screw channel depth of 6 mm, and a pitch of 30 mm.

Sample preparation

The unnucleated polypropylene and the composite containing no nucleating agent were used as the control samples. The control samples were pre-mixed and then extruded to ensure a uniform thermomechanical history for all the samples. *Table 1* shows the extrusion conditions for the samples. The extrudate in the form of continuous cylindrical rod was chopped into about 2–3 cm pieces and was subsequently granulated. The granulated samples were compression moulded into 145 × 145 mm sheets using a Two-speed hydro Pak hand press serial no. 6577, manufactured by Tangeys Ltd. Compression moulding was performed at a maximum mould temperature and pressure of 220°C and 1530 psi, respectively. Cooling was achieved by circulating cold water at 25°C per minute.

Table 1 Extrusion conditions for polypropylene (PP), nucleated polypropylene (NPP), glass-fibre reinforced polypropylene (GRPP) and nucleated composite (NGRPP)

Extruder section	PP	NPP	GRPP	NGRPP
Die-head temp. (°C)	220	220	225	225
Front-barrel temp. (°C)	215	215	220	220
Middle-barrel temp. (°C)	215	215	220	220
Rear-barrel temp. (°C)	210	210	215	215
Screw speed (rpm)	10	10	10	10

Mechanical testing

Tensile test specimens were cut from the samples by a laboratory table-type hand cutter fitted with a dumb-bell-shaped die. The test specimens were mounted in the Instron grips inside an environmental chamber. The specimens were all maintained at the temperature of testing for about 15 min before testing commenced. A 10% Instron strain gauge extensiometer no. 2630-015 was fitted to the central portion of the clamped specimen and was used to monitor the strain of the specimen. The samples were tested at a strain rate of $5.6 \times 10^{-4}\ s^{-1}$ at 23°C.

The fibre length distribution was measured by suspending the glass-fibre residue obtained from burning the composite in a solution of nylon 6,6[14]. The suspension was stirred and microscope slides were prepared by placing two drops of the suspension on a clean slide. After evaporation, a layer of fibres was firmly stuck to the surface of the slide. A microprojector was then used to measure the length of about 600 fibres.

RESULTS AND DISCUSSION

A mathematical model for the composite system was obtained by combining equations (3) and (4) as follows:

$$\sigma_c = KX + KY + Z \tag{5}$$

where X represents the contribution from fibres of length less than the critical length $L < L_c$, Y denotes the contribution from fibres whose length L is greater than the critical fibre length $L > L_c$ and Z is the contribution of the matrix in the system.

The terms X, Y and Z are more generally defined as follows:

$$X = \sum L_i V_i \frac{\tau}{2r} \quad \text{for } L_i < L_c \tag{6}$$

$$Y = \sum E_f \varepsilon_c \left(1 - \frac{E_f \varepsilon_c r}{2L_j \tau}\right) V_j \quad \text{for } L_j \geqslant L_c \tag{7}$$

$$Z = E_m \varepsilon_c (1 - V_f) \tag{8}$$

Equations (6)–(8) are combined to yield an equation for the strength of the composite similar to that derived earlier by Bowyer and Bader:

$$\sigma_c = K\left[\sum \frac{L_i V_i \tau}{2r} + \sum E_f \varepsilon_c \left(1 - \frac{E_f \varepsilon_c r}{2L_j \tau}\right) + E_m \varepsilon_c (1 - V_f)\right] \tag{9}$$

E_m was measured from the homopolymer without any nucleating agent. For a situation where the reinforcements nucleate the matrix, the matrix properties used in the calculation are those of the reinforced plastic. In this study both the nucleated and the unnucleated sample were used in the assessment of τ and K.

The linear relationship between the load-bearing contributions $(X + Y)$ and the experimentally analysed fibre contributions $(\sigma_c - Z)$ was used in the determination of the interfacial shear strength in accordance with the procedure established by Bowyer and Bader[16] and Nielsen *et al.*[17] for strain levels ranging from 0.1% to 2.5%. The shear strength is adjusted until the best straight-line fit is obtained by least squares methods. The slope of the best straight-line fit gives the orientation factor.

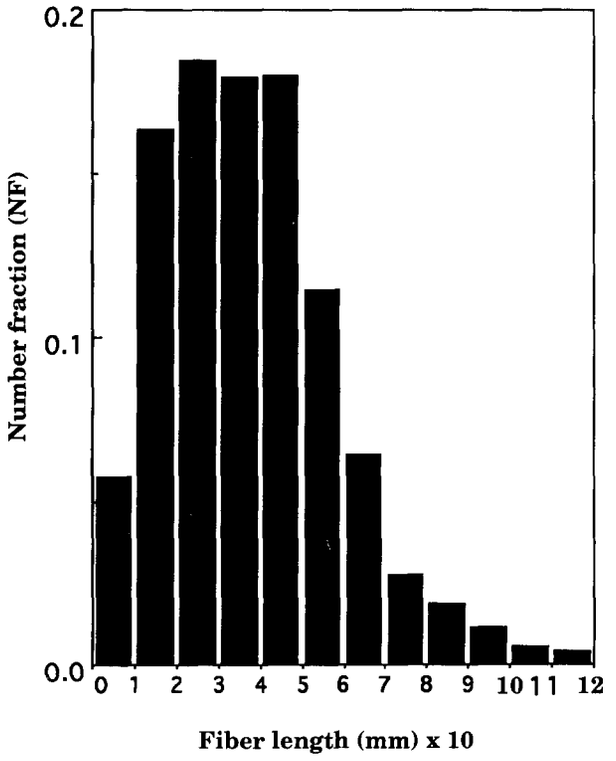

Figure 1 Fibre length distribution

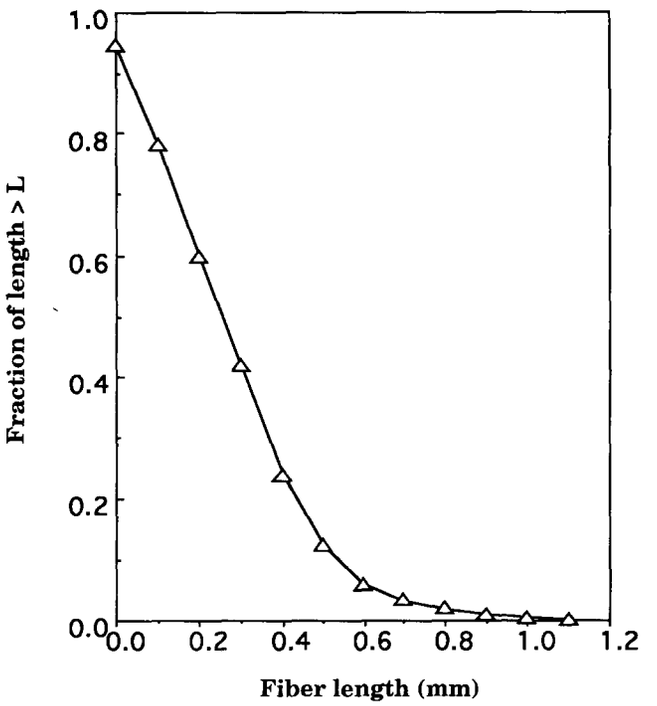

Figure 2 Cumulative fibre length distribution

Figures 1 and *2* show the fibre length distribution and the cumulative fibre distribution, respectively. These figures and the data in *Table 3* show that the longest fibre in the composite after extrusion, mastication and compression moulding is 1.2 mm. About 40% of the fibre lengths studied were less than 10% of the 3 mm length of fibres originally used in reinforcement, demonstrating how severely the fibre lengths were degraded during processing.

The tensile properties of the nucleated and unnucleated homopolymer and the composite at 23°C (*Table 2*), were used in the analysis. The ultimate strength of the nucleated and unnucleated polypropylene was calculated at 10% strain. As expected, the nucleated samples were slightly more rigid and less extensible than the unnucleated ones.

The interfacial shear strength and orientation factor obtained for the unnucleated and the nucleated composite were 24 MPa and 0.177 and 18 MPa and 0.201, respectively (*Table 4*)[18]. The interfacial shear strength τ obtained for the unnucleated polypropylene was 24 MPa. This value compared favourably with the 26 MPa obtained earlier by Kassouf[15] and the 24 MPa reported by Bowyer and Bader[19]. The interfacial shear strength τ obtained for nucleated glass-fibre reinforced polypropylene 18 MPa was lower than that for the unnucleated composite 24 MPa. Although the stress–strain data for the nucleated and the unnucleated composites were different, the difference was not large enough to affect the analysis. Note that the matrix

Table 2 Tensile properties for polypropylene (PP), nucleated polypropylene (NPP), glass-fibre reinforced polypropylene (GRPP) and nucleated composite (NGRPP) at 23°C

Sample ID	Young's modulus, E (GPa)	Ultimate strength, σ^* (MPa)	Ultimate strain ε^* (%)
NGRPP	2.50	41.80	2.50
GRPP	2.43	41.20	2.67
NPP	1.18[a]	27.30[a]	10[a]
PP	1.08[a]	26.73[a]	10[a]

[a] Property at 10% strain
* Ultimate properties

Table 3 Fibre length distribution

S/N	Length, L (mm)	Frequency, ϕ	Number fraction, NF	Number fraction of fibre ($L > L_c$)
1	0–0.10	32	0.0570	0.9430
2	0.11–0.20	91	0.1630	0.7800
3	0.21–0.30	103	0.1840	0.5970
4	0.31–0.40	100	0.1790	0.4180
5	0.41–0.50	101	0.1800	0.2380
6	0.51–0.60	64	0.1140	0.1240
7	0.61–0.70	36	0.0640	0.0590
8	0.71–0.80	15	0.0270	0.0320
9	0.81–0.90	7	0.0180	0.0199
10	0.91–1.00	6	0.0110	0.0092
11	1.01–1.10	3	0.0054	0.0038
12	1.11–1.20	2	0.0036	0.0023

Table 4 Results of the theoretical analysis for the nucleated and unnucleated polypropylene and the composite using stress–strain data at 23°C

Property	NGRPP (nucleated matrix)	GRPP (unnucleated matrix)	GRPP (nucleated matrix)
τ (MPa)	18.00	24.00	24.00
$L_c \times 10^4$ m	5.280	4.240	4.240
$\sum(V_i L_i) \times 10^4$ m $L_i < L_c$	2.550	1.650	1.650
$\sum(V_j L_j) \times 10^4$ m $L_j > L_c$	1.672	2.570	2.570
K	0.201	0.177	0.180

Table 5 Variation of critical fibre length with strain in unnucleated glass-fibre reinforced polypropylene (GRPP)

ε (%)	$L_c \times 10^4$ m	$\% > L_c$	L_c/D
0.100	0.158	100.0	1.58
0.500	0.792	97.6	7.92
1.000	1.583	85.2	15.83
1.500	2.375	74.3	23.75
2.000	3.167	58.0	31.67
2.500	3.958	43.3	39.58
2.668	4.224	37.3	42.24

Table 6 Variation of critical fibre length with strain in nucleated glass-fibre reinforced polypropylene (NGRPP)

ε (%)	$L_c \times 10^4$ m	$\% > L_c$	L_c/D
0.100	0.211	100.0	2.11
0.500	1.056	94.30	10.56
1.000	2.111	78.80	21.11
1.500	3.167	58.00	31.67
2.000	4.222	37.30	42.22
2.500	5.228	23.04	52.22
2.668	–	–	–

contribution to the total composite property was about 30%.

A higher average L/D ratio was obtained for the fibres in the nucleated composite NGRPP (*Tables 5* and *6*) in agreement with the mechanism of fibre fracture proposed by Richard and Lewis[20]. The presence of the nucleating agent minimized not only the fibre–fibre contact but also reduced the number of fibres per unit volume in contact with either the barrel wall of the extruder and/or the screw. One would expect the nucleated composite to bear more load, but the nucleating agents may act as points of heterogeneities in the composite. They tend to reduce the bonding efficiency and disrupt the shear transfer mechanism. They therefore reduce the interfacial shear strength, increase the tensile strength and Young's modulus and reduce the ultimate strain (*Table 4*).

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