Cellulose (2008) 15:561–569
DOI 10.1007/s10570-008-9204-x

Cellulose man-made fibre reinforced polypropylene—correlations between fibre and composite properties

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Received: 30 October 2007 / Accepted: 7 February 2008 / Published online: 21 February 2008

Abstract A series of viscose fibres from the tyre cord type varying in mechanical parameters and titre were compounded with polypropylene to produce fibre reinforced composites. Single fibre strength is analysed in detail and conclusions are drawn with respect to effective strength values in composite applications. Composites were analysed in terms of tensile and impact properties. Correlations between single fibre and composite properties are studied. High fibre elongation leads to favourable composite impact properties via high composite elongations at break. Using water as a plastisizing agent increasing fibre elongation, notched Charpy impact strength can be improved by more than 50%. Using a modified rule of mixtures and a shear lag model for the composite modulus it was shown how a titre reduction improves the composite stiffness by an increased interfacial area. A direct fibre-composite strength correlation was not found.

Keywords Cellulose fibres · Injection moulding · Mechanical properties · Rayon · Reinforced polypropylene · Viscose

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Introduction

Cellulose man-made fibres such as viscose and lyocell find their main applications in the textile industry. However, the viscose process, for instance, can be set up in such a way as to produce a technical cellulose fibre with tenacities above 50 cN/tex, moduli around 1300 cN/tex and elongations well above 10%. This kind of viscose fibre, called cellulose tyre cord yarn, is preferentially used for reinforcing high speed tyres, where the usual polyester reinforcement lacks dimensional stability under cyclic loading at elevated temperatures.

In order to examine if the range of applications for these kind of fibres can be extended, the possibility of reinforcing highly hydrophobic thermoplastics such as polypropylene (PP) with cellulose man-made fibres has been studied recently (Weigel et al. 2002; Paukanillio et al. 2003, 2004; Ganster et al. 2006; Ganster and Fink 2006). First attempts in this direction have been made by Amash and Zugenmeier (1998, 2000) for model composites. Rayon tyre cord yarn has been used in this laboratory (Weigel et al. 2002; Ganster et al. 2006; Ganster and Fink 2006) on a larger scale to develop PP-based composites for automobile applications. Using a suitable compounding technology, composites with remarkable mechanical properties competing with short glass fibre reinforced PP and PC/ABS blends were obtained. With moderate fibre loads of 20 to 30%, strength and modulus were roughly tripled with

respect to the pristine PP and, quite different from natural fibre reinforced PP, notched impact strength was more than doubled, giving advantages even over glass reinforced PP.

In the present paper, a more detailed account is given for the strength properties of the standard cellulose tyre cord yarn Cordenka 700 as a function of length of testing and Weibull parameters are determined and compared to glass fibre values from the literature (Phani 1988). A variety of fibres from the tyre cord type made available by Cordenka GmbH with different diameters and fibre characteristics are used to reinforce a standard PP block copolymer by the double pultrusion method developed earlier (Gassan et al. 2003). Injection moulded test specimen are investigated with respect to strength, modulus, elongation at break and impact properties. Correlations between fibre properties, in particular elongation and break, with composite tensile and impact properties are studied.

Experimental

Materials

Cellulose fibres

All fibres used in this study are produced by Cordenka GmbH Obernburg, Germany. The fibres vary in terms of titre and mechanical properties and are all spun by variants of the tyre cord yarn process. Sample code and fibre titre as calculated from the number of filaments and cable titre data from the manufacturer are given in Table 1. The nominal diameter for the fibres using a fibre density of 1.5 g/cm^3 therefore ranges between 6 μm (T9) and 23 μm (T34). RT700 represents the standard super 3 material with which most of the earlier results (Weigel et al. 2002; Ganster et al. 2006; Ganster and Fink 2006) were obtained. The remaining fibres are produced by special test set-ups with increased spinning efficiency.

Table 1 Sample code and titre of fibres used in this study

Material	Sample code	Titre (dtex)
RT700	Std	1.8
610F3.4	T34	3.4
610F1.8	T18	1.8
610F0.9	T9	0.9
665	S2	1.8
Super 1	S1	1.8

Matrix materials

The polypropylene (PP) used in this study is a light flowing block copolymer suited for injection moulding applications as shown in Table 2, where some manufacturer's data are listed. For coupling the cellulose fibres to the PP matrix, maleic anhydride grafted polypropylene (MAPP) has been used as the coupling agent with a high MFI and a graft level >1 wt% (see Table 2).

Methods

Single fibre mechanical testing

Single fibre measurements were performed using a Zwick Z 020 universal testing machine (Zwick Co., Germany) with a 10 N load cell, various clamp separations (see text) and a testing speed of half the clamp separation per minute. For the Weibull analysis of Cordenka RT700, 100 filaments have been tested for each clamp separation. The other fibres were measured with a clamp separation of 20 mm, 10 mm/min testing speed, and the number of filaments was 30. The measurements were performed in an air conditioned laboratory at 23 °C and 50% relative humidity.

Single fibre measurements on dry fibres could not be carried out due to the fast equilibration with ambient humidity. However, fibre bundle testing gave an increase in strength and modulus of dried fibre bundles (6 h at 110 °C) of approximately 20% and 10%, respectively, compared to the conditioned ones, while elongation was decreased by 15%.

Compounding

A pultrusion technique was applied with a conventional co-rotating twin screw extruder (Haake Rheocord 9000 PTW 25) equipped with a coating die assembly to cover a number of (continuous) filament tows of rayon tyre cord yarn with the molten matrix-coupling agent mixture which was premixed before fed into the extruder

Table 2 Matrix polymer and coupling agent used in this study with selected manufacturer's data

Trade name	Abbreviation	Producer	MFI (g/10 min)	Strength (Mpa)	Modulus (Gpa)
Stamylan P 412MN40	PP	Sabic	37 at 230 °C, 22 N	26 (yield)	1.55 (bend)
Fusabond MD 353 D	MAPP	Du Pont	450 at 190 °C, 22 N	–	–

containing 3 wt% of coupling agent MAPP. The maximum temperature of the extruder and the die were 200 °C and 195 °C, respectively. The coated yarns were cooled with water and cut into pellets of about 4 mm length. Then the pellets were dried overnight at 110 °C. In a second step, the pellets were extruded with the same extruder under the same conditions to homogenise the fibre–matrix mixture. The screw configuration was chosen such that appropriate mixing elements were included to guarantee the dispersion of the fibres in the matrix. After cooling the thread was cut into final pellets of defined length of 4 mm. All composites used in this study had a nominal fibre content of 30% by weight. Apparent pellet densities (bulk densities) are above 300 g/L in all cases.

Injection moulding

Standard test specimens were prepared according to DIN EN ISO 527-2 (for tensile test) and DIN EN ISO 179 (for bending and Charpy impact test) using an injection moulding machine (Allrounder 270 M 500-90, Arburg, Germany) with a ram pressure of 30 kN and a feed rate of 50 cm^3/s. Zone temperatures were set to 170 °C, 180 °C, 190 °C and 200 °C from feed to nozzle and the nozzle temperature was 200 °C, while the injection pressure was in the range from 400 to 700 bar. The tool was designed for moulding two small standard test bars (Charpy and bending) and one dog bone shaped bar (tensile) at a time, each with an edge gate.

Composite mechanical testing

Tensile strength and modulus of the composites were measured according to DIN EN ISO 527 and 178, respectively, with a universal testing machine (Zwick 020) using the injection moulded standard test specimen. However, the tensile modulus was measured with a testing speed of 50 mm/min and determined as the maximum derivative at the beginning of the stress–strain curve, i.e. between 0.05% and 0.25% strain. Charpy impact strengths of the composites were determined with an impact tester (PSW 4J) according to DIN EN ISO 179 standard in the flatwise, unnoched, or the edgewise notched (notch type A) modes. The test samples were conditioned at 23 °C and 50% relative humidity for several days before testing and all the tests were performed under the same conditions.

Results and discussion

Fibre strength distribution and Weibull fit

In order to establish fibre–composite correlations, fibre properties have to be determined under experimental conditions relevant for composite applications. First of all the strength values must be determined on the relevant length scale, i.e. in the region of the critical fibre length (Bader and Hill 1993). From earlier work it is concluded, that the critical length in the present case is in the range of 0.5 mm. Such a testing length is hard to realise in practice and therefore an extrapolation of results from test spans more readily accessible (5 mm to 50 mm in our case) seems advisable. Applying the concept of a weak link chain, a Weibull distribution (Phani 1988) should give a reasonable extrapolation scheme.

Results of single fibre strength measurements for Cordenka RT700 at various clamp separations l_0 at 23 °C and 50% relative humidity are shown in Fig. 1 in terms of cumulative failure probability P. As to be expected from considerations along the line of a weakest link theory for fracture, the strength distribution shifts to higher values for shorter clamp separations. All the curves can be fitted to a Weibull distribution (Phani 1988)

$$P = 1 - \exp\{-l_0(\sigma/\sigma_0)^m\},$$

where m is the Weibull exponent and σ_0 the second fit parameter. Results for m and l_0 are given in Table 3 and an example of the fit is shown for

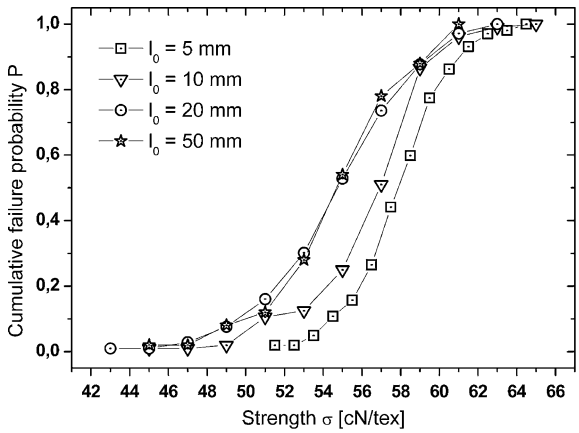

Fig. 1 Cordenka RT700 cumulative failure probability P for single fibre strength σ at various testing lenghts l_0

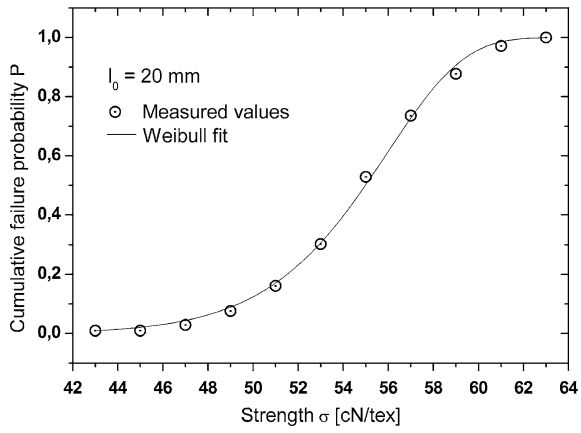

Fig. 2 Weibull fit for data at 20 mm testing length from Fig. 1

Table 3 Weibull distribution fit parameters m (exponent) and σ_0 as a function of testing length l_0

l_0 (mm)	m	σ_0 (cN/tex)
5	28	62
10	25	63
20	17	67
50	17	70

$l_0 = 20$ mm in Fig. 2. All fits have a quality of fit parameter R^2 above 0.99. However, for different testing lengths the fit parameters vary and an extrapolation to even shorter lengths becomes questionable. Nonetheless, extrapolating the shortest experimental available 5 mm Weibull function to 0.5 mm test length gives a value of 63 cN/tex instead of 58 cN/tex as the average, i.e. a 9% increase, while extrapolating the 20 mm function yields 68 cN/tex demonstrating again the change in failure mode. Moreover, it must be kept in mind that the experiments were carried out at 50% relative humidity, whereas the fibre water content is close to zero in the composites due to the severe drying (110 °C overnight). Therefore a still higher value for fibre strength in the composite is to be expected.

An important difference to the glass fibre data from the literature (Phani 1988) is shown in Fig. 3 for the width of the distribution at 20 mm (Cordenka) and 15 mm (glass, no 20 mm available). The abscissa is chosen as the relative deviation of strength σ from the average value $<\sigma>$. Here the number of glass measurements has been scaled from 50 (real measurements) to 106 (value for Cordenka) in order to have equal areas below the curves. Obviously, the glass distribution is appreciably broader than the Cordenka curve indicating the large scatter for glass fibres. Taking into account that composite failure can be caused by a single fibre failure event, the effective glass strength is reduced from the average $<\sigma>$ of 2 GPa to 1.17 GPa (values calculated from Phani 1988, his Fig. 7) while for Cordenka the reduction is only from 825 MPa to 735 MPa (cellulose density 1.5 g/cm^3). This reduces the ratio of effective glass fibre to Cordenka strength from 2.4 to 1.6 and might be a possible reason for the surprisingly good performance of Cordenka composites as compared to glass (Ganster et al. 2006, Table 5).

Single fibre measurements

In the preceding section it was shown that one simple Weibull fit does not represent all the experimental data as a function of testing length and thus a justified extrapolation to relevant testing lengths in a composite is not feasible. Therefore, for the remainder of the fibres no detailed Weibull analysis was performed. Instead, conventional single fibre testing at 23 °C and 50% relative humidity with a convenient clamp separation of 20 mm was performed with results shown in Table 4.

All the fibres have values far beyond textile viscose (see, e.g., Eichhorn et al. 2001 for Enka Viscose and other types of cellulose man-made fibres including Cordenka). The highest differences are found for S2 and T9 in elongation and, compared to the others, for S1 and S2 in strength and modulus, respectively.

Table 4 Mechanical properties of spun cellulose fibres (single fibre measurements) used in this study (20 mm testing length)

Material	Strength			Elongation		Modulus		
	cN/tex Average	cN/tex s.d.[a]	MPa Average	% Average	% s.d.	cN/tex Average	cN/tex s.d.	GPa Average
Std	55	3	825	13	1.5	1,300	100	19.5
T34	52	3	780	14.5	1.5	1,340	80	20.1
T18	52	3	780	13	1.5	1,320	100	19.8
T9	51	2	765	10	1	1,270	80	19.1
S2	52	3	780	17	2	1,160	60	17.4
S1	44	2	660	10	1.5	1,270	120	19.1

[a] Standard deviation

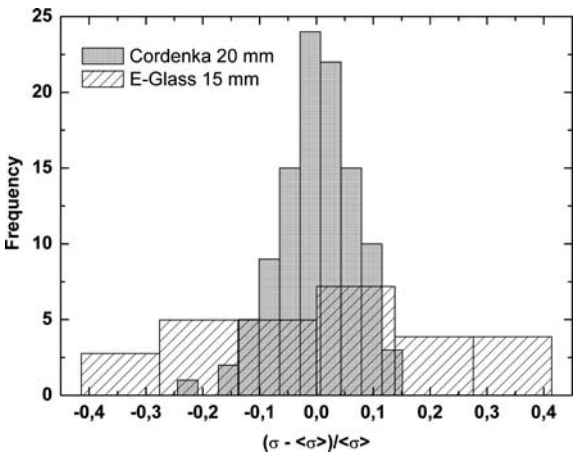

Fig. 3 Probability density distribution of the relative deviation of strength σ from the average value $<\sigma>$ for Cordenka RT700 (grey) and E-glass (hatched)

Correlations between fibre and composite properties

For correlating fibre and composite properties, ideally the fibre properties should be determined under conditions prevailing in the composite. Due to the severe drying step in the compounding process after the coating, the fibres are likely to be close to completely dry in the composite, as also shown by the little to none steam generation at the degassing in the second compounding step. At the testing conditions of 50% relative humidity, however, the fibres have an equilibrium water content of approximately 10.5% (gravimetric determination). As it is well known (e.g. Krässig and Kitchen 1961) water acts as a plastisizer, i.e. it reduces strength and modulus and increases elongation, thus in the composite the fibres are stiffer and stronger than tested. However, due to the similarity of the fibres the property shift is likely to be maintaining the order of the fibres in terms of their mechanical behaviour and thus correlations to composite properties should be possible.

In order to give a general comparison of the mechanical behaviour of the components and the composite, tensile stress–strain curves for the composite, the Cordenka RT 700 fibre and the polypropylene matrix are shown in Fig. 4. Fibre and matrix curves are scaled with the volume fractions of the respective phases in the composite. As expected, no simple superposition scheme can be postulated and composite elongation is lower than fibre or even matrix elongation.

Strength

The comparison of single fibre and composite strength data is depicted in Fig. 5. Obviously, no clear correlation can be seen. The linear correlation

Table 5 Property profile of composites with moist fibre

Strength (Mpa)		Modulus (Gpa)		Elongation (%)		Charpy (kJ/m^2)		Notched Charpy (kJ/m^2)	
Average	s.d.[a]	Average	s.d.	Average	s.d.	Average	s.d.	Average	s.d.
73	1	2.88	0.03	10.7	0.7	80	5	16	1

[a] Standard deviation

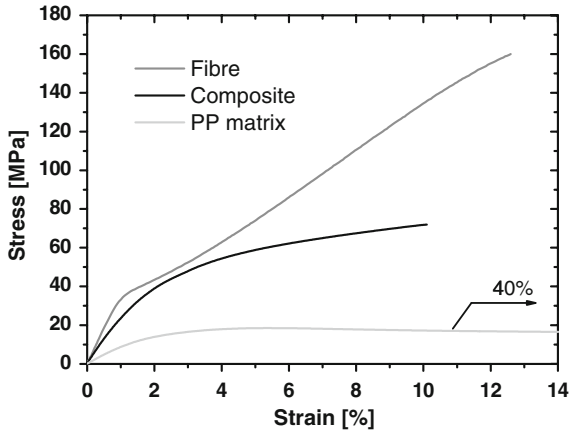

Fig. 4 Stress–strain curve for composite compared with stress–strain curves for fibre and matrix scaled with their volume fractions in composite

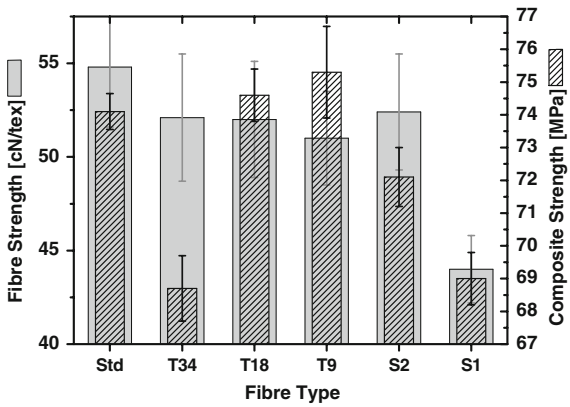

Fig. 5 Correlation between single fibre strength (left) and composite strength (right)

coefficient (Press et al. 1992) is 0.53. The point most out of range is the composite strength for T34, the thickest fibre in the series. Possibly the reduced interface between fibre and matrix due to increase in fibre diameter can be a cause for this behaviour (comp. also the calculation in the "Modulus" paragraph).

Elongation and impact strength

Different from the strength behaviour, a good correlation is seen for fibre and composite elongation, as depicted in Fig. 6. Here the variation of fibre elongation is closely followed by the variation in composite elongation, i.e. a highly extendable fibre will result in a composite with high elongation at break and the correlation coefficient is 0.93. This can be explained by assuming the composite failure caused by the failure of

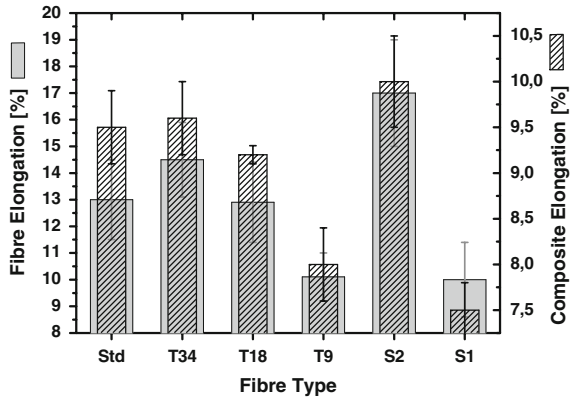

Fig. 6 Correlation between single fibre elongation (left) and composite elongation at break (right)

the reinforcing fibre or by the failure of the fibre–matrix interface when the full fibre extension is reached. In view of the good coupling found in these kind of composites (Ganster et al. 2006) the former interpretation seems more likely. In the cited reference as well as in Ganster and Fink (2006), SEM pictures of cryo fractured surfaces show the adherence of matrix material to the fibre even after composite failure allowing to rule out fibre pull out as the energy absorbing process and hinting at a complex failure process combining matrix shear and fibre break.

More important for practical applications than composite elongation is composite impact strength. Both unnoched and notched Charpy impact strength correlate quite satisfactorily with the elongation of the reinforcing fibre, as shown in Figs. 7 and 8 with correlation coefficients of 0.97 and 0.82, respectively. This correlation is not improved by using the fibre work of fracture (area under the stress–strain curve) instead of fibre elongation, as could be conjectured from a simple composite work of fracture model. Fibre elongation, as shown in Fig. 6, is correlated to the composite elongation. I.e. a composite (of the given materials combination Cordenka plus PP) with high elongation displays a high impact strength. Both properties are characteristics for failure processes, however, they are tested at very different testing speeds. Composite elongation is determined with speeds of 50 mm/min, while Charpy impact is tested with 2.9 m/s, i.e. a factor of 3600 faster. Nonetheless, as the above correlation has been established, the composite elongation via the fibre elongation can be used as a design parameter for high impact composites.

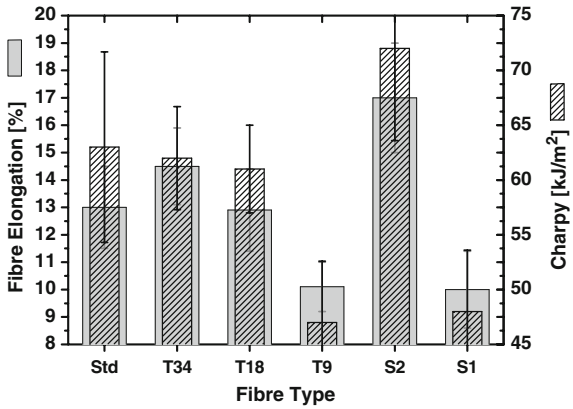

Fig. 7 Correlation between single fibre elongation (left) and composite Charpy impact strength (right)

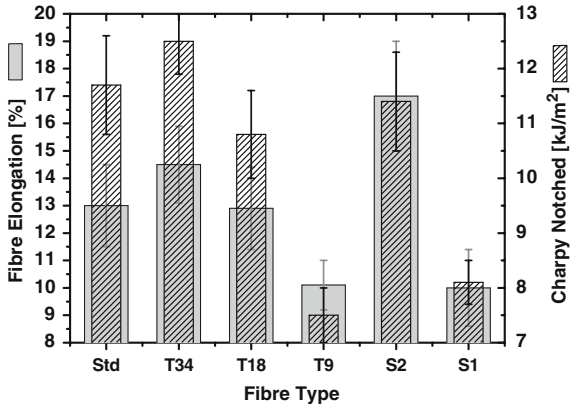

Fig. 8 Correlation between single fibre elongation (left) and composite Charpy notched impact strength (right)

This is corroborated in the following way for the standard fibre RT 700. Instead of drying the pellets from the first compounding step overnight at 110 °C, pellets were dried for 3 h at 60 °C to remove only surface water and keeping a certain amount of water (3.5%) in the fibres as a platisizer. The resulting composites had a property profile as shown in Table 5. Obviously, elongation and impact were substantially increased without much change in strength or modulus (see below).

Modulus

The comparison of single fibre and composite modulus data is depicted in Fig. 9. Similarly to the strength case, no clear correlation can be seen and a negative correlation coefficient is found. In particular

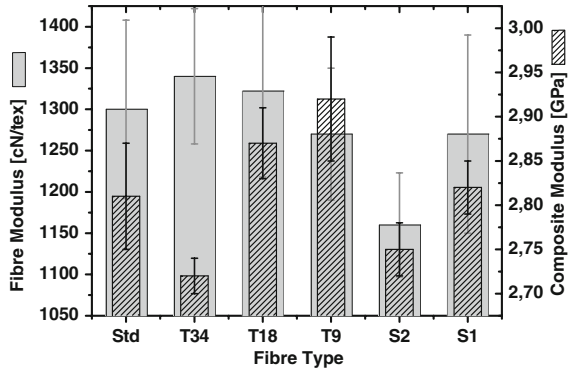

Fig. 9 Single fibre modulus (left) and composite tensile modulus as a function of fibre type

for the fibres with varying titre, fibre modulus decreases with decreasing titre while composite modulus increases. However, in contrast to strength, for the composite modulus E_c a modified rule of mixture can be applied with some justification combining fibre modulus E_f and matrix modulus E_m as follows (see, e.g., Thomason and Vlug 1996):

$$E_c = \eta_c * v_f * E_f + (1 - v_f) * E_m$$

where v_f is the fibre volume fraction and η_c an efficiency factor reflecting both fibre orientation and finite fibre length. Moreover, η_c is assumed to be a product of two factors η_{SL} and η_o taking into account fibre length (shear lag factor) and fibre orientation (and possible other effects), respectively. In more detail, the shear lag factor is given by

$$\eta_{SL} = 1 - \tanh(\beta L/2)/(\beta L/2)$$

where with a shear-lag parameter β given by Nairn (1997)

$$\beta^2 = \frac{2}{r_f^2 E_f E_m}\left[\frac{E_f v_f + E_m v_m}{\frac{v_m}{4G_f} + \frac{1}{2G_m}\left(\frac{1}{v_m}\ln\left(\frac{1}{v_f}\right) - 1 - \frac{v_m}{2}\right)}\right]$$

with L and r_f as average fibre length and radius, respectively, G_m as the matrix shear modulus (set here equal to $E_m/3$), and G_f as the fibre shear modulus taken as 1 GPa (Fortisan value from Meredith 1954, Table V). Assuming an equal η_o for all the fibres, which should be a reasonable assumption in view of the equal fibre fraction, with an E_m of 1.17 GPa and an L of 0.5 mm (Ganster et al 2006) results are obtained as shown in Fig. 10. Shear-lag parameters β are between 0.045 for T34 and 0.174 for T9, the highest and lowest titre, respectively.

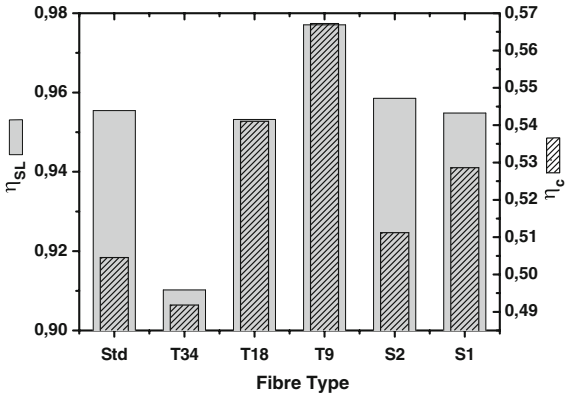

Fig. 10 Correlation between shear-lag factor η_{SL} for modulus (left) and composite efficiency factor η_c

The correlation between fibre modulus in form of shear-lag factor (including matrix and fibre shear modulus) and composite efficiency factor η_c is satisfactory giving a correlation coefficient of 0.76. In particular, the right order is established for the variation in titre: decreasing titre gives increasing shear-lag factor along with increasing experimental composite efficiency factor. The main reason for this is the fact that fibre aspect ratio L/D is taken into account in the shear-lag model reflecting the increased surface area for transmitting matrix stress to the fibre.

A similar procedure was formally applied to the case of fibre and composite strength giving again an improved correlation in particular for the fibres with varying titre. However, to the authors' knowledge, no appropriate physical model is available for this much more complex case of fracture initiation and propagation in the fibre or the fibre matrix interphase.

Conclusions

Analysing the strength distribution of the reinforcing fibres it was shown that for a given testing length, strength can be fitted to a Weibull distribution with parameters depending on testing length. An extrapolation to length scales relevant for composite applications leads to an increase in strength of 9%. The strength distribution is sharper than for E-glass fibres (literature values) resulting in an effective glass to Cordenka strength ratio of 1.6 instead of 2.4 for average values of the respective distribution.

Fibre elongation at break is clearly correlated with composite elongation at break. Composite elongation in turn correlates with both notched an unnotched Charpy impact strength of the composite. Thus fibre elongation can be used as a design tool to produce composites with favourable impact properties. Besides variations in the spinning process yielding fibres with high elongation, water can be used as an external plastisizer leading to increased fibre elongation. With an appropriate drying regime during compounding, improvements in impact properties of 37% (unnotched) and 68% (notched) can be reached without compromising composite strength and modulus.

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