Mechanical properties of natural-fibre-mat-reinforced thermoplastics based on flax fibres and polypropylene.

Applied Composite Materials **7:** 351–372, 2000.

Mechanical Properties of Natural-Fibre-Mat-Reinforced Thermoplastics based on Flax Fibres and Polypropylene

S. K. GARKHAIL[1], R. W. H. HEIJENRATH[1] and T. PEIJS[2,⋆]
[1]*Dutch Polymer Institute, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[2]*Department of Materials, Queen Mary and Westfield College, University of London, Mile End Road, London E1 4NS, U.K.*

Abstract. Thermoplastic composites based on flax fibres and a polypropylene (PP) matrix were manufactured using (i) a film-stacking method based on random fibre mats and (ii) a paper making process based on chopped fibres. The influence of fibre length and fibre content on stiffness, strength and impact strength of these so-called natural-fibre-mat-reinforced thermoplastics (NMTs) is reported and compared with data for glass-mat-reinforced thermoplastics (GMTs), including the influence of the use of maleic-anhydride grafted PP for improved interfacial adhesion. In addition some preliminary data on the influence of fibre diameter on composite stiffness and strength is reported. The data is compared with the existing micro-mechanical models for strength and stiffness. A good agreement was found between theory and experiment in case of stiffness whereas in the case of strength the experimental values fall well below the theoretical predictions. Results indicated that NMTs are of interest for low-cost engineering applications and can compete with commercial GMTs when a high stiffness per unit weight is desirable. Results also indicated that future research towards significant improvements in tensile and impact strength of these types of composites should focus on the optimisation of fibre strength rather than interfacial bond strength.

Key words: thermoplastic composites, NMT, GMT, natural fibre, flax fibre, polypropylene, adhesion, mechanical properties.

1. Introduction

In the last decade, research activities in the area of thermoplastic composites have shifted from 'high-performance' advanced composites towards the development of 'cost-performance' engineering composites. Especially, glass-mat-reinforced thermoplastic (GMT) materials [1], being stampable sheet products based on commodity resins such as polypropylene (PP) and moderate loadings of relatively long glass fibres in random array have proven to be very successful in high-volume markets, notably the automotive industry. Because of their excellent price-performance ratio, E-glass fibres are by far the most important fibres for these types of composites. However, these fibres do have some disadvantages. Glass fibres are non-renewable

⋆ To whom correspondence should be addressed.

and give problems with respect to ultimate disposal at the end of a materials lifetime since they can not be thermally recycled by incineration and are left behind as a residue that can damage a furnace. They are also very abrasive which leads to an increased wear of processing equipment such as extruders and moulds. Next to some ecological disadvantages, glass fibres can cause problems with respect to health and safety. For example, they give skin irritations during handling of fibre products, and processing and cutting of fibre-reinforced parts.

Nowadays, ecological concern has resulted in a renewed interest in natural materials and issues such as recyclability and environmental safety are becoming increasingly important for the introduction of new materials and products. Environmental legislation as well as consumer pressure are all increasing the pressure on manufacturers of materials and end-products to consider the environmental impact of their products at all stages of their life cycle, including ultimate disposal, viz. a 'from cradle to grave' approach. At this moment 'eco-design' is becoming a philosophy that is applied to more and more materials and products. In view of all this an interesting environmentally friendly alternative for the use of glass fibres as reinforcement in engineering composites are natural fibres based on ligno-cellulose such as flax, hemp, sisal and jute [2]. These vegetable fibres are renewable, nonabrasive and can be incinerated for energy recovery since they posses a good calorific value. Moreover, they give less concern with safety and health during handling of fibre products. In addition, they exhibit excellent mechanical properties, especially when their low price and density (1.4 g/cm^3) in comparison to E-glass fibres (2.5 g/cm^3) is taken into account. Although these fibres are abundantly available, especially in developing countries such as Bangladesh and India, most applications are still rather conventional, i.e. ropes, matting, carpet backing and packaging materials. Moreover, in the last few decades the uses of natural fibres for these type of applications has been declined due to the introduction of synthetic fibres, such as nylon and polypropylene. Hence, also in the economic interests of developing countries, there is an urgent need for new application areas for these natural fibres.

The first natural-fibre-reinforced composites were based on thermoset matrices, such as unsaturated polyester or phenolic resins, together with sisal and jute [3, 4]. More recently, developments shifted to thermoplastic matrix composites [5–11]. This paper focuses on the development of natural-fibre-mat-reinforced thermoplastics (NMTs), being GMT-like materials based on natural fibres [12]. In this study flax fibres are used as reinforcements, mainly because of their good mechanical properties when compared with other natural fibres and also because of their availability in different forms in Western Europe. PP is used for a number of reasons. First, it is easy to process and one of the cheapest polymers on the market which is of eminent importance in the 'cost-performance' sector. Secondly, it has a low processing temperature, which is essential because of the relatively low thermal stability of natural fibres (200–250°C). Finally, it has the perfect ability to protect the hydrophilic natural fibre because of its strong hydrophobic and apolar

character. A clear disadvantage of this apolar character for composite applications is its limited wettability as well as poor interfacial bonding with reinforcing fibres. This disadvantage can, however, be overcome by functionalization of the polymer, which has proven to be very effective in enhancing fibre/matrix adhesion in composite systems based on polyolefins [13–19]. In order to be able to compete with glass-fibre-reinforced composites it is expected that both flax content and the flax fibre length should be as high as possible. However, high fibre loadings and high fibre lengths will also affect the rheology and limit the processability of such composites, and therefore, a balance between mechanical performance and processability should be found.

In this research the influence of fibre length and fibre volume fraction is investigated on random flax-mat-reinforced PP composites, which were manufactured using a film-stacking method and a suspension impregnation or so-called 'paper making' method, respectively. The latter method allows for a systematic variation of the fibre length, since no fibre break-up occurs during processing. The use of conventional melt-processing methods for the production of short-fibre-reinforced compounds such as extruders will degrade the fibre length and are therefore not suitable for such a systematic study. In addition, the influence of maleic-anhydride grafted PP (MA-PP) on the mechanical performance of PP/flax composites was also studied. Flax fibre contains functional hydroxyl groups that are able to interact chemically with the MA-PP. From this an improved interfacial bond strength between the flax fibre and the modified PP is expected. In order to get a better insight in the importance of all these different parameters the experimental results were compared with model predictions using relatively simplistic micro-mechanical models for random short-fibre-reinforced composites [20–24]. Some preliminary results on the influence of fibre processing on the mechanical performance of flax-fibre-reinforced composites are also reported.

2. Experimental

2.1. MATERIALS

In this study random non-woven flax fibre mats in combination with an isotactic-polypropylene (PP) matrix of Shell (XY6500T) with a melt flow index of 35 were used. The Young's modulus of the neat PP matrix was approximately 1.6 GPa and the yield stress about 32 MPa. In this study dew-retted flax fibres were used. The fibres were converted into a non-woven mat (725 g/m^2) by Eco Fibre Products BV (The Netherlands) via a conventional punch-needling process. In order to study the effect of improved fibre/matrix adhesion on composite performance, 5 wt.% of a maleic-anhydride-grafted polypropylene (MA-PP) (Polybond® 3002, BP Chemicals Ltd.) was added to the PP homopolymer. This blend composition with a PP/Polybond® ratio of 95/5 will simply be designated as MA-PP. Compounding of this blend was carried out in a co-rotating twin-screw extruder (Werner and Pfleiderer ZSK 25), with a standard screw geometry, at 200°C. Extruded strands

were palletised to be used for film blowing subsequently. NMT composite plates with different fibre contents were manufactured using the film-stacking method. In this film-stacking method, pre-dried (24 h at 60°C) non-woven flax mats in combination with PP or MA-PP films were stacked alternately. PP films as well as the MA-PP films based on the PP/Polybond® blend were made using film-blowing equipment (Collin 30-25D/400). Impregnation of the non-woven mats was achieved by applying heat (200°C) and pressure (25 bar) in a hot-press for 15 min. The obtained composite plates were cut into dog-bone shaped tensile specimens according to ASTM D638-91 specifications.

For the suspension impregnation or paper making process a dispersion of flax fibres and i-PP-fibres (Young's modulus = 1.6 GPa and yield stress = 29 MPa) was made in an ethanol/water (1:1) mixture. In separate production runs, three different flax fibre lengths were used (3, 6 and 25 mm). Significantly differing fibre lengths were removed before use. After drying the materials at room temperature for 24 hours and at 60°C for one hour, the lofted mixture of flax fibres and PP fibres was consolidated in a hot-press. In the case of the paper making process interface modification through the use of MA-PP was done in a different way than in the case of film-stacked composites. In the case of the suspension impregnation route the fibres were pre-treated (coated) with pure MA-PP (Hostaprime® HC5, Hoechst). Degreasing of the flax fibres was executed via extraction of the flax fibres with an ethanol/toluene (2:1) mixture, refluxed for three hours. The extraction fluid was replaced by a new fresh fluid, which was refluxed for another hour. The fibres were subsequently washed for approximately 30 minutes with cold ethanol, followed by 6 litres of cold water over a Büchner-funnel. The extracted fibres were dried at 60°C in an oven with circulating air for 24 hours. Afterwards they were immersed in a solution of MA-PP copolymer in hot toluene (100°C) for 10 minutes. The concentration of copolymer in solution was approximately 2 wt.% on the fibres. After treatment, the fibres were extracted with toluene for one hour and a half to remove all components not chemically bonded to the flax fibres. Finally, the fibres were dried at 60°C for 24 hours. These treated flax fibres were used in the suspension impregnation process, yielding a composite plate using the compression moulding method described above.

2.2. TEST METHODS

Uniaxial tensile tests on random flax composites were performed on a universal tensile testing machine. Specimens were in accordance with ASTM D638-91 and had a dog-bone shape with an overall length of 200 mm, a width of 12.5 mm and a thickness of 2 mm. An extensometer was used to monitor the elongation of the tested specimen. High-speed dart and notched Charpy impact testing were performed on a Zwick Rel servo-hydraulic testing machine. Charpy impact tests were carried out on notched samples with a width of 12.7 mm and a thickness of 4 mm. The samples were loaded over a span of 44 mm at a speed of 3.5 m/s using the

servo-hydraulic testing machine equipped with a Charpy impact test fixture. The impact energy was calculated by dividing the total absorbed energy by the cross-sectional area of the sample behind the notch. It may be worth mentioning here that the impact energy measured is only for relative comparison and does not give the accurate toughness of the material. For accurate measurement of toughness, various correction factors like geometrical and kinetic energy correction factors are to be considered [25]. Next to Charpy impact tests, high-speed dart impact tests were performed for the determination of the penetration resistance of the composite plates. Full-penetrating dart impacts were conducted utilising the servo-hydraulic testing instrument equipped with a dart impact test fixture. Impacts were performed using a hemispherical dart of 10 mm at a test speed of 4 m/s. The laminates, having dimensions of 70 mm $\times$ 70 mm $\times$ 4 mm, were clamped between two plates with a cylindrical opening in the centre with a diameter of 20 mm. Load values during penetration were recorded using a piezo electrical transducer and impact energies were calculated from the recorded load-time curves. Some single fibre tensile tests were performed on a Zwick tensile testing machine at a test speed of 3 mm/min and gauge length of 5 mm. The fibres were mounted on cardboard frames to facilitate proper handling during the tests. Fibre diameters were measured using an optical microscope. However, these values are only rough estimates as the fibres are not circular. To rule out these effects an average diameter of about 5 readings per fibre was used for the calculation of stress values.

3. Micromechanical Models for Short Fibre Composites

3.1. COMPOSITE STIFFNESS

For the modelling of the stiffness of a short-fibre-reinforced composite, Cox [20] introduced a fibre length efficiency factor into the 'rule-of-mixtures' equation for the composite stiffness E_c. In this way the 'ineffective' loading of fibres over their stress transfer length can be taken into account. Since the fibre is only partly utilised in the case of a short fibre composite, these effects have to be taken into account when modelling the mechanical performance of such composites. The expression used by Cox yields:

$$E_c = \eta_{\mathrm{LE}} V_{\mathrm{f}} E_{\mathrm{f}} + (1 - V_{\mathrm{f}}) E_{\mathrm{m}}. \tag{1}$$

In the case of stiffness related problems, Cox's 'shear lag' model is used for the calculation of the fibre efficiency factor η_{LE} [26–31] under the assumption of elastic fibres in an elastic matrix, leading to:

$$\eta_{\mathrm{LE}} = \left[1 - \frac{\tanh(\beta L/2)}{\beta L/2}\right], \tag{2}$$

where

$$\beta = \frac{2}{D}\left[\frac{2G_{\mathrm{m}}}{E_{\mathrm{f}} \ln(R/r)}\right]^{1/2}. \tag{3}$$

The R/r factor can be related to the fibre volume fraction V_f by:

$$\ln(R/r) = \ln(\sqrt{\pi/\chi_i V_f}), \tag{4}$$

so that Equation (3) can be rewritten as

$$\beta = \frac{2}{D}\left[\frac{2G_m}{E_f \ln(\sqrt{\pi}/\chi_i V_f)}\right]^{1/2}, \tag{5}$$

where G_m is the shear modulus of the matrix, χ_i depends on the geometrical packing arrangement of the fibres, r is the fibre radius and R is related to the mean spacing of the fibres. In this study a square packed fibre arrangement is assumed, following Thomason *et al.* [28], where similar equations were used for the modelling of glass/PP composites. The inter-fibre spacing in the composite is $2R$ and χ_i equals 4. Besides ineffective fibre length, fibres are also only partially utilised due to fibre (mis)orientation. In order to take this into account, the theory of Cox was extended by Krenchel [21], who took fibre orientation into account by adding a fibre orientation factor η_0 into the 'rule-of-mixtures' equation.

$$E_c = \eta_0 \eta_{LE} V_f E_f + (1 - V_f) E_m. \tag{6}$$

The Krenchel orientation factor η_0 allows for the introduction of a fibre orientation distribution. If transverse deformations are neglected, η_0 is given by:

$$\eta_0 = \sum_n a_n \cos^4 \phi_n, \tag{7}$$

where a_n is the fraction of fibres with orientation angle ϕ_n with respect to the loading axis. For a two-dimensional (in-plane) random orientation of the fibres it can be shown that $\eta_0 = 3/8$. In a three-dimensional random fibre orientation the fibre orientation factor yields the value of 1/5. For thin section laminates with fibre lengths greater than the thickness of the sample, fibres are expected to be oriented mainly in two directions, although deviations may occur due to out-of-plane oriented fibres or bend fibres. Especially in the case of fairly flexible fibres like flax this bending action is likely to occur.

3.2. COMPOSITE STRENGTH

For the modelling of the strength of discontinuous fibre composites, Kelly and Tyson [23] extended the 'rule-of-mixtures' equation for composite strength in a way similar to Cox's 'rule-of-mixtures' for composite stiffness:

$$\sigma_{uc} = \eta_0 \eta_{LS} V_f \sigma_f + (1 - V_f)\sigma_m, \tag{8}$$

where η_{LS} is the fibre length efficiency factor and η_0 is the fibre orientation factor, similar to the Cox–Krenchel model, to take off-axis fibre orientation into account. For the fibre length efficiency factor Kelly and Tyson used [23]:

$$\eta_{LS} = \frac{1}{V_f}\left(\sum_i \left[\frac{L_i V_i}{2L_c}\right] + \sum_j \left[V_j\left(1 - \frac{L_c}{2L_j}\right)\right]\right). \tag{9}$$

The first summation term in Equation (9) accounts for the contribution of all fibres of sub-critical lengths ($L < L_c$). The second summation term incorporates the strength contribution from fibres whose lengths are super-critical ($L > L_c$). A combination of Equation (8) and (9) results in the Kelly–Tyson model [23, 24] for the prediction of the strength (σ_{uc}) of a polymer composite reinforced with short off-axis fibres:

$$\sigma_{uc} = \eta_0 \left(\sum_i \left[\frac{\tau L_i V_i}{D} \right] + \sum_j \left[\sigma_j V_j \left(1 - \frac{L_c}{2L_j} \right) \right] \right) + (1 - V_f)\sigma_m. \qquad (10)$$

In the case of stiffness, the related Cox–Krenchel model, including a theoretical orientation parameter for in-plane random fibre orientations ($\eta_0 = 3/8$) [30], can be used quite effectively for the prediction of the stiffness of random fibre composites. However, previous studies have shown that the Kelly–Tyson model yields far too high values for strength of random fibre composites. Shao-Yun *et al.* [32] have modified the model further by considering the distribution function for the fibre length and the fibre orientation in the fibre efficiency factor for the strength of the composites ($\eta_0 * \eta_{LS}$). Therefore an additional (in)efficiency factor (k), which basically becomes a fitting parameter, can be included in Equation (10) to account for the fibre length, strength and orientation distribution in the random short-fibre composites:

$$\sigma_{uc} = k\eta_0 \left(\sum_i \left[\frac{\tau L_i V_i}{D} \right] + \sum_j \left[\sigma_j V_j \left(1 - \frac{L_c}{2L_j} \right) \right] \right) + (1 - V_f)\sigma_m. \qquad (11)$$

Thomason *et al.* [30] used a value of 0.2 for η_0 in the Kelly–Tyson model for predicting the tensile strength of GMT materials which was obtained by fitting this η_0 factor to the experimental data. In this case the orientation parameter η_0 has however no longer any physical meaning and becomes a fitting parameter. If we, however, translate their fitting parameter $\eta_0 = 0.2$ into a case using the more realistic orientation parameter of $\eta_0 = 3/8$, in combination with an additional (fitted) efficiency factor k this yields an efficiency factor for glass/polypropylene composites of $k = 0.53$. Although these simplistic micromechanical models are to a certain extent based on fitting, they do provide insight into the mechanical behaviour of the composite. For example, comparing the k-values of composites manufactured by different processing methods and/or containing different types of reinforcements gives some insight into the efficiency of those processing methods and reinforcements.

3.3. IMPACT STRENGTH

Various energy dissipation mechanisms may operate when a discontinuous fibre-reinforced composite fractures from an existing notch [33–36], viz. matrix fracture and deformation, fibre-matrix debonding, fibre pull-out and fibre fracture. Based

on these mechanisms various models have been proposed to predict the impact strength of a composite. According to Wells and Beaumont [36] a composite containing randomly dispersed and aligned short fibres of uniform strength will always exhibit fibre pull-out preceding fast fracture. Thomason *et al.* [33] showed that for randomly oriented short-glass-fibre/PP composites fibre fracture is a dominant energy dissipation mechanism. The problem of identifying the dominant mechanism of fracture can be tackled in two complimentary ways; either the dominance of more easily recognisable mechanisms like fibre pull-out are determined by optical or electron microscopy, or a correlation is made between these mechanism and theoretical models [36]. Cottrell [37] developed a model for unidirectional reinforcement, which includes all the above mentioned energy-dissipation mechanisms i.e. matrix fracture, fibre fracture, debonding and pull-out. As for the model predictions, it follows that the impact energy is expected to increase with increasing fibre length, up to fibre lengths equal to the critical fibre length. At fibre lengths above the critical length the impact energy is expected to decrease again [37]. This occurrence of a maximum in impact strength can be attributed to the predicted change in failure mode from fibre pull-out at short (subcritical) fibre lengths to fibre breakage at high (supercritical) fibre lengths. According to the model, the toughness of the composite can be equated to the fracture energy of the matrix, or some fraction of it, in the absence of pull-out or any other toughening mechanism [36]. This means the work of fibre pull-out tends to zero as the length, '*l*', of a fibre with uniform strength increases to infinity. Therefore this theory seems only applicable for systems where pull-out is the major fracture mechanism. Cooper [38] has shown, that the Cottrell model holds good for an epoxy/phosphor-bronze model system with uniform, discontinuous and unidirectional reinforcements with the controlled amount and size of the flaws. However, in thermoplastic composites generally no maximum in toughness is observed but a plateau value is reached with increasing fibre length [33, 34, 36, 39, 40]. Wells and Beaumont [36] have shown that in the case of the brittle reinforcements with the distribution of flaws and their size along the fibre length, the average pull-out length increases to a constant value with increasing fibre lengths. Also in the case of fibres with uniform strength they have shown a peak in the average pull-out length. Thomason *et al.* [33] found a direct relationship between tensile strength and Charpy impact strength of random in-plane glass fibre-reinforced PP laminates. Based on their observations they developed a fibre strain energy model, similar to the rule-of-mixture equation for strength and modulus of the composites:

$$U_c = U_x V_f + (1 - V_f) U_m, \tag{12}$$

where U_x is the energy factor covering all the fibre-related energy absorption mechanisms. Through experimental data and assuming the fibre fracture as a dominant energy absorption mechanism they found that:

$$U_x = U_f[L/(L + L_c)], \tag{13}$$

where U_f is the total energy involved in the fracture of the single fibres and is given by:

$$U_f = \sigma_f^2 y/2E_f, \tag{14}$$

where 'y' is the length of the fibre debonding prior to fibre fracture in a composite containing continuous fibres. Therefore Equation (12) can be modified, by substituting Equation (13) and (14) as:

$$U_c = V_f(\sigma_f^2 y/2E_f)[L/(L + L_c)] + (1 - V_f)U_m. \tag{15}$$

However, the equation above was developed for unidirectional continuous-fibre-reinforced composites and the effect of fibre orientation is not taken into account. Again, also here the model was fitted on the experimental data, in this case using debond length y as a fitting parameter. For the PP/glass composites studied a value of 12 mm for debond length was found to give good agreement between the above mentioned fibre strain energy model and experimental data. However, because of this fitting procedure the debond length lost its physical meaning. In fact for some composites the fitted debond length y was higher than the actual fibre length, meaning that also here we have to interpret the results only in a qualitative manner.

4. Results and Discussion

4.1. INFLUENCE OF FIBRE LENGTH

4.1.1. *Composite Stiffness*

The results of the tensile tests on the flax-fibre-reinforced PP composites, with varying fibre lengths as manufactured using the papermaking process, are given in Figures 1 and 2. Figure 1 shows the Young's modulus for the systems based on PP and MA-PP together with the Cox–Krenchel model predictions. In the model a modulus of 50 GPa for the flax fibre and a modulus of 1.6 GPa for the PP matrix is used, both values were obtained from tensile tests on the single fibres and the bulk matrix. A rather good agreement is found between the model predictions and experimental data. No effect of improved adhesion on the modulus of PP/flax composites is observed indicating good wetting of the fibres. Only the data for a fibre length of 3 mm shows a somewhat increased composite stiffness with the use of MA-PP. Presumably, the higher interfacial bond strength in case of MA-PP/flax leads to a slight decrease of the critical fibre length and consequently a small improvement in composite stiffness might occur for this type of composite. At fibre lengths of 6 and 25 mm this improvement is not observed since in both cases the fibre length is well above the critical fibre length. No fibre length dependence is observed for the developed MA-PP/flax as the fibre lengths are higher than critical lengths thus showing a plateau zone in the curve.

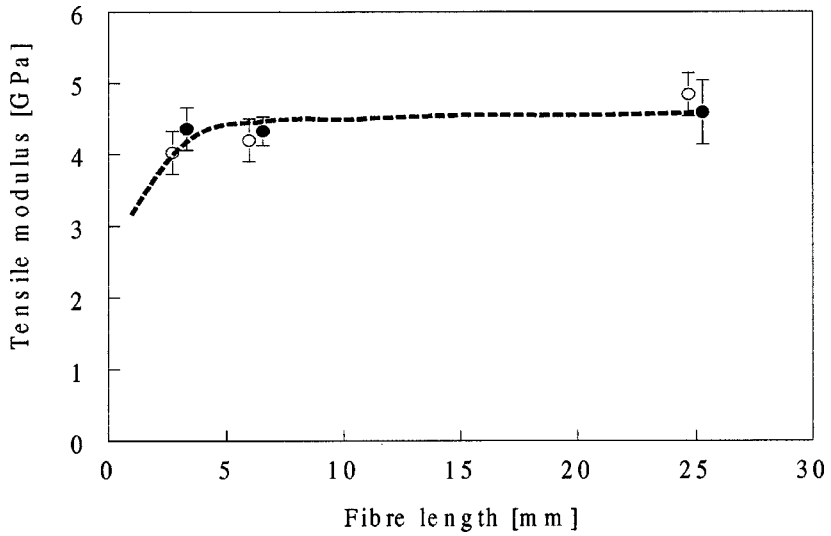

Figure 1. Tensile modulus of the flax/PP composites (○) and the flax/MAPP composites (●) as a function of the flax fibre length. The dashed line represents the Cox–Krenchel prediction for both the PP/flax and MA-PP/flax composite systems.

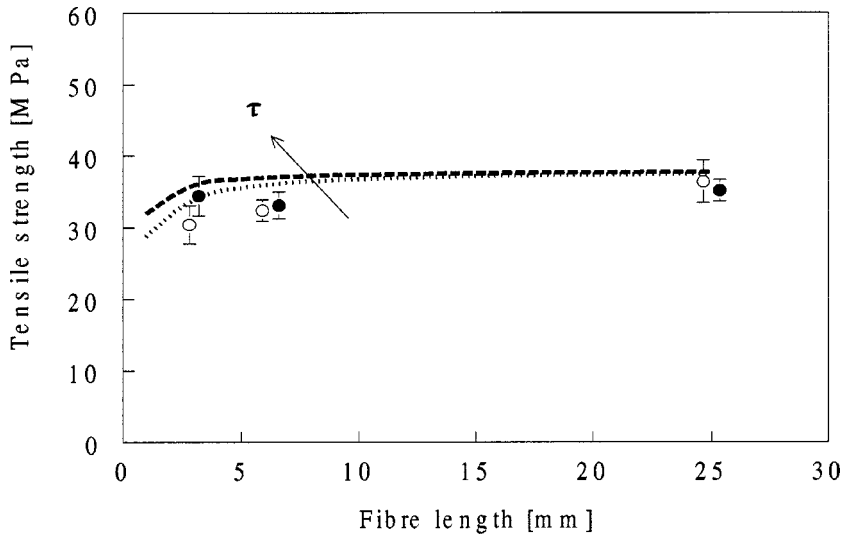

Figure 2. Tensile strength of the PP/flax composites (○) and the MA-PP/flax composites (●) as a function of the flax fibre length. The dotted line and the dashed line represent the Kelly–Tyson prediction for the PP/flax and the MA-PP/flax composites, respectively.

4.1.2. *Composite Strength*

For the model predictions using the Kelly–Tyson equation a and fibre strength of 620 MPa, as obtained from the single fibre tensile test, is used together with an interfacial bond strength (τ) of 8 MPa for PP/flax [41] and 16 MPa for MA-PP/flax. As a matrix strength a value of 32 MPa is used. The interfacial shear strength value of 16 MPa for the MA-PP/flax system is taken similar to the shear yield stress of the pure PP matrix as calculated from the von Mises yield criterion ($29/\sqrt{3}$ MPa). This means that for this composite system perfect adhesion, i.e. a matrix dominated rather than an interface dominated shear failure mode is assumed. Hence, this will give some insight into the importance of interface modifications for maximising composite strength.

In Figure 2 both the results of the tensile strength measurements as well as the model predictions for PP/flax and MA-PP/flax as a function of the fibre length are plotted using the fibre orientation factor η_0 of 3/8 and a fitted efficiency parameter k of 0.2. Comparing now this efficiency parameter with that for a PP/glass system ($k = 0.53$) as recalculated from the data reported by Thomason *et al.* [30], it becomes clear that the reinforcing efficiency of flax fibre is less than those of glass fibres. One reason for this could be the fairly large scatter in the strength values of natural fibres, which are not taken into account in the current model. In the case of a fairly brittle failure mode weak fibres may trigger catastrophic fracture of the composite material, leading to an overall low value for strength. Another, probably more important and most likely related effect is the poor lateral strength of the natural fibres as they are used today. Unlike isotropic glass fibres, natural fibres exhibit like most biological materials a hierarchical composite-like structure. They consist of cellulose microfibrils with diameters in the order of a couple of nanometers, which form together so-called elementary fibres of 10–20 μm in diameter. The elementary fibres or fibre cells are bond together by pectin, forming the next hierarchical microstructure; a technical fibre with a diameter of around 50–100 μm. These technical fibres are subsequently arranged in the form of bundles in the stem of the plant and are bond together by a weak pectin and lignin matrix. Depending on the effectiveness of the fibre opening process one can go down in microstructure, hence removing weak spots in the composite-like structure and obtaining reinforcing elements of higher strength. Unfortunately, however, despite attempts like steam explosion where one tries to separate the elementary fibres from the technical fibres, most of today's fibres used in composite application are fibre bundles and/or technical fibres. They are produced using mechanical fibre opening processes like breaking of the flax stem and scutching and have a fairly poor strength (600–800 MPa) compared to glass fibres. Elementary fibres or cells, however, have much higher strengths (1200–1500 MPa) and could on a weight bases compete with glass fibres (2400 MPa). Even higher strengths are foreseen when microfibrils could be used as reinforcing elements in nanocomposites. Clearly, future developments in this area should therefore focus on further optimisation of the fibre opening process.

With respect to the effect of enhanced interfacial bonding as a route to improve composite strength it becomes clear from the model predictions that, at least compared to routes that focus on the optimisation of fibre strength, no major effects can be envisaged. Only in the case of relatively short fibres interface modification may have a significant effect on composite strength. Still, interface optimisation is a topic of concern and will definitely affect the durability of the composite in a positive way [14]. However, for strength optimisation its effect will be too small to bridge the gap with glass fibre systems. Regarding the effect of fibre length, similar to the stiffness there appears to be no significant influence on the measured composite strength. Due to the easier way of mixing and consequently better impregnation, the composite with 3 mm long fibres may have a higher quality than the 6 and 25 mm ones. Moreover, during the chopping of the fibres into the desired length the weak internal interactions between the elementary fibres results in extensive fibrillation or splitting of these short fibres and a decrease of the flax fibre diameter and consequently, an increase in fibre aspect ratio. As a result, the stress transfer becomes more effective which may yield a composite with relatively better properties.

4.1.3. *Impact Strength*

The results from the notched Charpy impact tests are plotted in Figure 3 as a function of fibre length. It can be seen that in the case of PP/flax the impact energy increases with increasing fibre length until a plateau level is reached, whereas in the case of MA-PP/flax the impact energy increases and then drops of at the highest fibre length. At relatively low fibre lengths the impact strength for MA-PP composites is higher than that of PP composites, whereas at fibre lengths of 25 mm the impact energy decreases in the case of MA-PP and is lower than that of PP /flax. This behaviour can be explained by the decrease in critical fibre length with the addition of MA-PP, thus leading to additional energy contributions by fibre fracture for the shorter fibre system. Whereas at higher fibre lengths ($L \gg L_c$) the improved adhesion leads to a decrease in energy dissipation because of limited fibre debonding and pull-out mechanisms. This was also observed through scanning electron microscopy (SEM) as shown in Figures 4 and 5, where the PP/flax composites show longer fibre pull-out lengths as compared to the MA-PP/flax composites with fibre lengths of 25 mm. In case of PP/flax composites the trend in impact strength versus fibre length is similar to the experimental trend observed by various workers in the area of thermoplastic based composites [33, 34, 36, 39, 40] and is in agreement with the strain energy model predictions (Equation (15)) for PP/glass systems. The model, using 'debond length' (y) as a fitting parameter, is plotted with the experimental data in Figure 3. In the case of PP/flax system we found a fitted 'debond length' of 12 mm, which is similar to the value reported by Thomason et al. for a PP/glass system. As mentioned earlier the effect of fibre orientation is not taken into account in the strain energy model and the 'debond length' may not be considered as a real measure for actual debonding. However, from this analysis

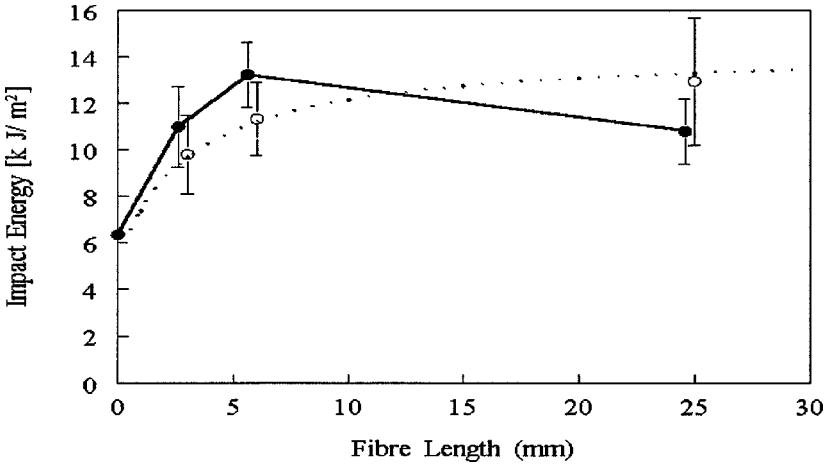

Figure 3. Notched Charpy impact strength of the PP/flax composites (○) and the MA-PP/flax (●) a function of the flax fibre length. The dotted line represents the fibre strain energy model predictions for PP/flax.

it can be concluded that to improve the impact strength of PP/flax composites the fibre strength is to be further improved to obtain debonding and pull-out at higher fibre lengths and higher fibre strain energies at shorter fibre lengths. For the model predictions (Equation (15)) the fibre strength (σ_f) of 620 MPa, fibre modulus (E_f) of 50 GPa, fibre volume fraction (V_f) of 0.2, matrix fracture energy (U_m) of 6.34 kJ/m^2 which was calculated by Charpy impact testing, critical fibre length (L_c) of 3 mm and debond length parameter (y) of 12 mm is used. The trend in impact strength as observed for the MA-PP based system seems to be in agreement with the Cottrell model, which also shows an optimum in the impact energy versus fibre length curve. In the Cottrell model this optimum is calculated, for aligned short fibre composite systems with fibres of uniform strength, at a fibre length equal to the critical fibre length, being approximately 3 mm for our composite systems. Clearly, in a system based on randomly oriented flax fibres with a high variation in strength, length and diameter such model can only be used in a qualitative manner. Still, the trend observed indicates that for the unmodified PP/flax composite energy absorption is to some extend governed by pull-out and debonding. Although the optimum in impact energy as a function of fibre length can be explained on the bases of fibre pull-out mechanisms as the principal mechanism of energy absorption, this trend is rarely observed in real composites. As mentioned earlier, most thermoplastic composites show a maximum plateau value for impact energy rather than a drop at high fibre length. Although the drop observed here is only minor it is still an indication for the importance of fibre pull-out as an energy absorption mechanism in this composite system.

Figure 4. Scanning electron micrograph of fracture surface of PP/flax composite ($V_f = 0.2$ and fibre length = 25 mm).

Figure 5. Scanning electron micrograph of fracture surface of flax/MA-PP composite ($V_f = 0.2$ and fibre length = 25 mm).

4.2. INFLUENCE OF FIBRE VOLUME FRACTION

4.2.1. *Composite Stiffness*

The influence of fibre volume fraction was investigated on composites based on non-woven fibre mats, which were manufactured using the film-stacking technique. Figure 6 shows the tensile modulus of the MA-PP/flax composites together with the Cox–Krenchel prediction and data of commercially available glass-mat-reinforced thermoplastic (GMT) materials [1], as a function of fibre volume fraction. Based on the data obtained, it can be concluded that the stiffness of flax-fibre-reinforced PP is comparable to E-glass-fibre-reinforced PP composites. Especially, when the relatively low density of the flax fibre (1.4 g/cm^3 for flax compared to 2.5 g/cm^3

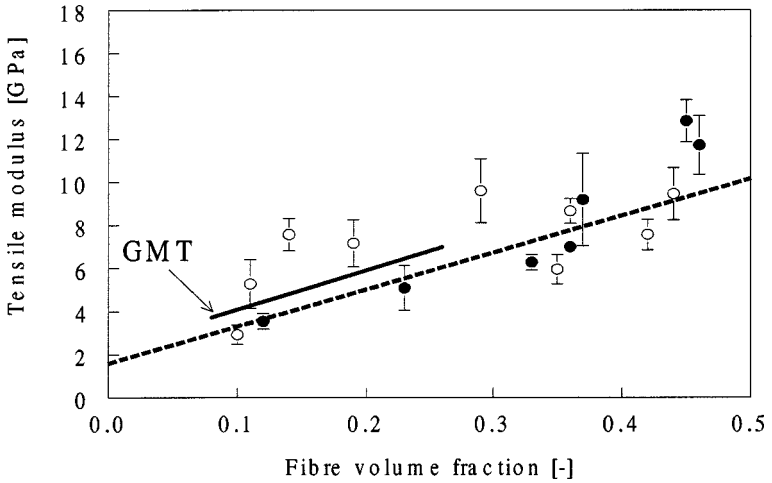

Figure 6. Tensile modulus of the PP/flax composites (○) and the MA-PP/flax composites (●) as a function of fibre volume fraction. The dashed line represents the Cox–Krenchel prediction for both PP/flax and MA-PP/flax. The solid line represents the data for commercially available GMT.

for E-glass) is taken into account, the stiffness per unit weight may even surpass that of GMT materials. Moreover, as a result of the price competitiveness of flax fibres compared to E-glass fibres these materials are particularly of interest from a cost-performance point of view. A rather good agreement is found between the experimental data and the predictions using the Cox–Krenchel model (Equation (6)). Again, in the model a modulus of 50 GPa for the flax fibre and a modulus of 1.6 GPa for the PP matrix is used, together with an effective fibre length of 25 mm for the random flax mat material along with the orientation factor η_0 of 3/8.

4.2.2. *Composite Strength*

Figure 7 shows the tensile strength of the manufactured PP/flax and MA-PP/flax composites, together with the Kelly–Tyson predictions for PP/flax and MA-PP/flax as well as data of commercial glass fibre based GMT materials [1]. In the model the same material parameters are used as in the Cox–Krenchel model for the prediction of composite stiffness as a function of the fibre volume fraction. Again, a fibre strength of 620 MPa is used. These micromechanical calculations also clearly indicate that differences in interfacial shear strength of the order of 5–15 MPa, as can be expected for PP based composites have no significant influence on the predicted composite strength in the case of these long fibre composite systems (Figure 7). Clearly, GMT materials show superior strengths compared to the manufactured NMTs for all volume fractions. With respect to the effect of improved interfacial bonding in the case of MA-PP/flax composites, similar to the model predictions, no significant effects on tensile strength was found. Moreover, based on micromechanical calculations no major further improvements can be envisaged in the case

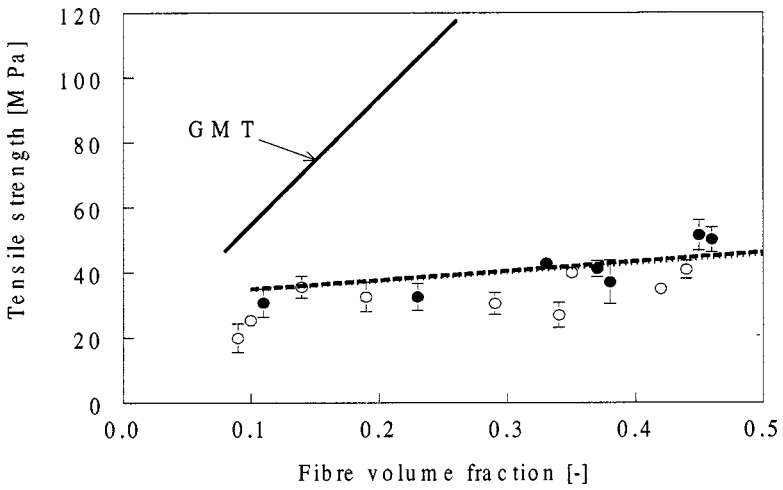

Figure 7. Tensile strength of the PP/flax composites (○) and the MA-PP/flax composites (●) as a function of fibre volume fraction. The dashed line represents the Kelly–Tyson predictions for PP/flax and MA-PP/flax composites. The solid line represents the data for commercially available GMT.

of NMTs based on relatively long fibres, since already an 'upper adhesion limit' of matrix dominated shear failure is used for the calculation of the theoretical strength of MA-PP/flax. Obviously, the strength of the flax fibre composites is intrinsically limited by the relatively weak flax fibre bundles. These results indicate that, for the development of a strength competitive NMT, future research should focus on the optimisation of fibre strength rather than interface strength. The key area for the improvement of the tensile strength of the PP/flax composites lies clearly not only in the interface modifications for improved adhesion but mainly in modifications in the fibre opening process leading to improved fibre strength.

4.2.3. *Impact Strength*

Figure 8 shows the influence of fibre content on the notched Charpy impact energy of PP/flax composites. The absorbed impact energy increases with increasing flax fibre content up to 25% volume fraction beyond which no further improvement in impact energy was measured. At high fibre lengths the impact energy absorbed by natural fibre composites can be mainly attributed to fibre fracture. The fairly good wet-out of the fibres in combination with the relatively low strength of flax fibres yields composites that fail in fairly brittle manner. Due to the relatively low fibre strength the contribution in energy dissipation by fibre debonding and pull-out mechanisms is expected to be relatively low. It is expected that this brittle failure mode, which increases with increasing fibre volume fraction, leads to the plateau zone at higher fibre volume fractions. For comparison again data for a commercial GMT is plotted. Clearly NMT is inferior to GMT when it comes down to impact strength. Compared to PP/glass, PP/flax composites absorb less energy by mech-

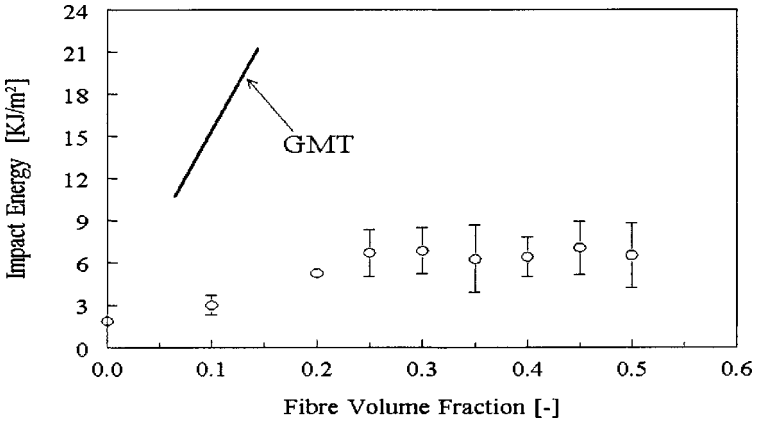

Figure 8. Notched Charpy impact strength of the PP/flax composites (○) as a function of fibre volume fraction. The solid line represents data for GMT.

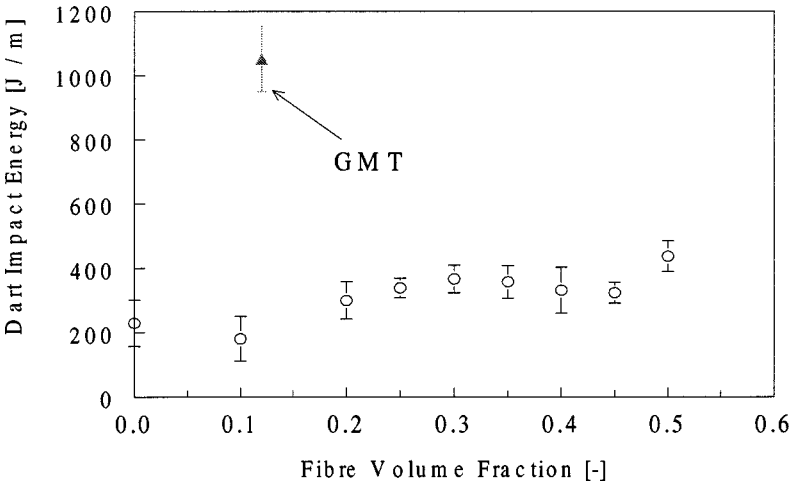

Figure 9. Dart impact energy of the PP/flax composites (○) as a function of fibre volume fraction, together with experimentally obtained data for a commercial GMT-grade.

anisms like fibre pull-out as well as fibre strain energy. Since PP/flax composites exhibit comparable interfacial properties to PP/glass composites but much lower fibre strengths these composites are likely to fail in a rather brittle failure mode with fibre fracture at relatively low strain levels likely to be favoured over fibre pull-out. However, in the case of glass fibres the fibre strength over interface strength ratio is much higher, which means that in these composites more pull-out will take place in combination with fibre fracture at much higher strain (energy) levels. Figure 9 shows the results obtained from the high-speed dart impact testing of the same PP/flax composite system. Clearly the trend is quite similar to that of the Charpy impact testing. Further improvement of the impact performance of NMT is key for a successful large scale introduction in applications where currently GMT mate-

rials are used since many of today's applications where GMT has replaced sheet moulding compounds (SMCs) are driven by the excellent impact performance of GMT.

4.3. INFLUENCE OF FIBRE DIAMETER ON COMPOSITE STRENGTH

As mentioned earlier, future developments towards improved strength and impact properties of NMT should focus on further optimisation of fibre processing. Depending on the effectiveness of the fibre opening process one can go further down in microstructure, hence obtaining reinforcing elements of higher strength. Most of today's fibres used for composite application are either fibre bundles and/or technical fibres. They are produced using mechanical fibre opening processes like breaking of the flax stem and scutching and have a fairly poor strength. A preliminary study was therefore carried out to see if an additional hackling operation, where the fibre tows are combed to remove impurities like woody parts and to obtain a larger quantity of thinner technical fibres rather than coarse fibre bundles, may lead to fibres of higher strength. Two types of flax fibres, both of equal length (6 mm), however, processed in different ways, were used: (i) scutched flax fibres and (ii) hackled flax fibres, where the fibre bundles are combed to separate the fibre bundles into individual technical fibres. Next to effects directly related to fibre processing, another reason for these additional experiments using hackled fibres is related to the influence of a decrease in fibre diameter on the improvement of fibre strength. As discussed earlier, a small improvement in tensile strength with interface modification was observed only for composites based on flax fibre lengths of 3 mm. For the composite systems based on 3 mm flax fibres the experimental data (see Figure 2) is also in better agreement with the model predictions than in the case of high fibre lengths. It was argued that these relatively high strength values in the case of 3 mm fibres were due to a decrease in fibre diameter as a result of fibre splitting of the technical flax fibre when cut into 3 mm fibre lengths. In order to justify this reasoning, additional experiments using hackled fibres were performed to investigate the effect of different fibre diameters on the tensile strength values of the composites. The fibre diameter distribution of these fibres is plotted in Figure 10. Next to these 6 mm fibres also the fibre diameter distribution of a 25 mm scutched fibre was measured to show the effect of fibre length on the average fibre diameter. Clearly, the 25 mm long scutched flax fibre exhibits the highest mean fibre diameter since less splitting occurs during cutting of these long fibres. In order to take these differences in fibre diameter into account, the flax fibre diameter distribution of Figure 10 was incorporated in the Kelly–Tyson model. For experimental validation, composites based on the two types of 6 mm long flax fibres and an unmodified PP matrix were prepared using the suspension impregnation process. Figure 11 shows the tensile strength of both types of composites for two fibre volume fractions. The fibre strength for both types of flax fibres is assumed to be comparable ($\sim$620 MPa). Also the other applied material parameters, including the efficiency

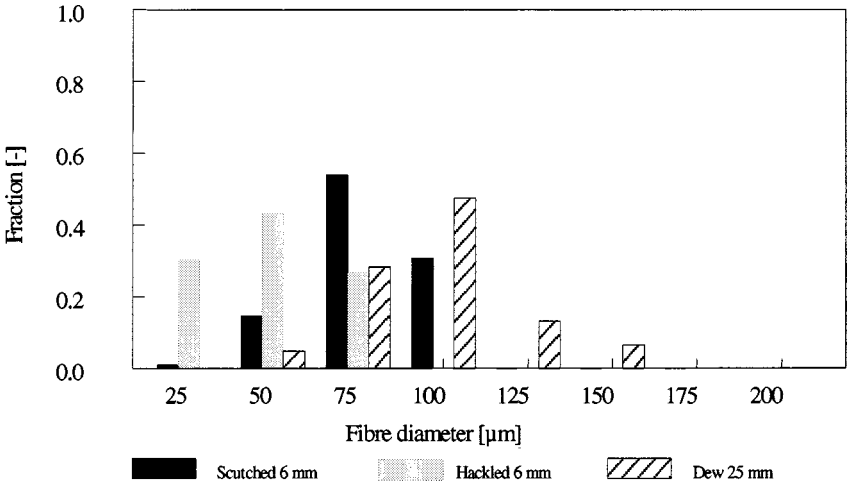

Figure 10. Fibre diameter distribution of three types of flax fibres: (i) scutched (dew retted) 6 mm long flax, (ii) hackled (warm water retted) 6 mm long flax and (iii) dew retted 25 mm long flax.

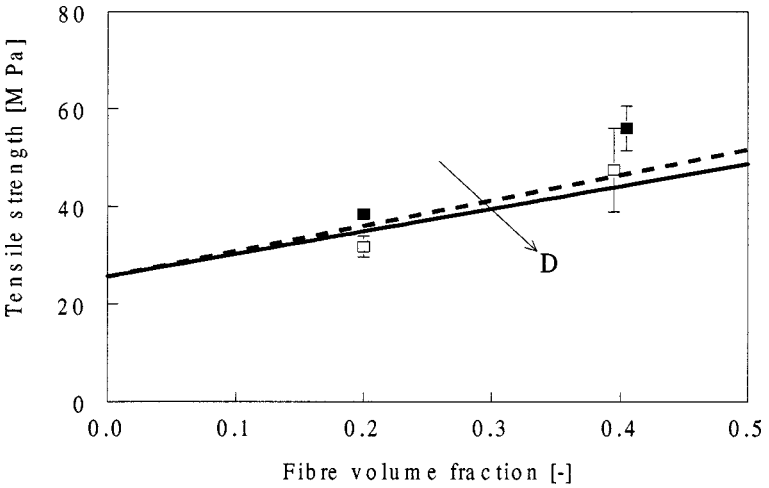

Figure 11. Tensile strength of scutched (dew retted) 6 mm (□) and hackled (warm water retted) 6 mm (■) PP/flax composites as a function of fibre volume fraction. The dashed line and the solid line represent Kelly–Tyson predictions for the PP/flax composites using warm water retted hackled (small fibre diameter) and the dew retted (large fibre diameter) flax fibres, respectively.

parameter in the model are the same as before, viz. an interfacial bond strength of 8 MPa for PP/flax composites and the fibre diameter distribution of Figure 10. From the strength data it can be seen that the scutched fibre composite shows inferior properties compared to the hackled and combed flax fibre composites. Similarly, the Kelly–Tyson model predicts a higher composite strength for hackled flax fibre reinforced composites than for scutched flax fibre composites, especially at higher

volume fractions. The improvement obtained using an additional scutching step are not that dramatic. However, more significant improvements are foreseen if further optimisations in the area of fibre opening could lead to the use of elementary fibre cells or even microfibrils.

5. Conclusions

For the production of random PP/flax composites two production methods similar to the commercially known methods for glass/PP composites were used. First, the so-called film-stacking method based on flax non-woven fibre mats and secondly, a suspension impregnation or so-called paper making process using short flax fibres. Material parameters that were studied for the optimisation of the mechanical performance of such composites were: fibre length, fibre volume fraction and interface modification through the use of a maleic-anhydride grafted PP grade. In order to get a better insight in the importance of these different parameters for the optimisation of composite performance, the experimental results were compared with model predictions using micromechanical models for random short-fibre-reinforced composites. As expected, there is a significant effect of fibre volume fraction on mechanical properties, whereas, no real experimental evidence for the anticipated increase in mechanical performance with increasing fibre length was found.

Based on the experimental results it can be concluded that the stiffness of the flax based NMTs is comparable to E-glass based GMTs composites. Especially, when focusing on the specific composite properties as a result of the low density of flax. In combination with the price-competitive character of flax fibres these materials might especially be of interest from a ‘cost-performance’ point of view. However, due to the relatively low tensile strength of the flax fibre bundles and technical fibres compared to E-glass fibres, the tensile strength of flax based NMTs is significantly lower than that of their glass fibre counterparts. In short, it can be concluded that NMTs based on a PP matrix and flax fibres can compete with E-glass based GMT materials in stiffness critical structures, whereas for strength and impact critical applications these materials still need to be optimised further. To close the gap with GMT these optimisations should mainly focus on fibre strength through new developments in the fibre opening process, rather than on the optimisation of the interfacial bond strength.

Acknowledgements

The authors would like to thank Dr. Gerard Pott of Ceres B.V. for supplying the flax fibre mats. Part of this research has been carried out at ATO-DLO, Wageningen, The Netherlands. We would like to thank Harriëtte Bos for allowing us to use the suspension impregnation equipment at ATO-DLO. The help and assistance in the preparation of the composites using the suspension impregnation technique, as well

as, the stimulating discussions with Martien van den Oever of ATO-DLO are also gratefully acknowledged.

References

1. Berglund, L. A. and Ericson, M. L., In J. Karger-Kocsis (ed.), *Polypropylene: Structure, Blends and Composites*, Vol. 3, Chapman & Hall, London, 1995, p. 202.
2. Morton, W. E. and Hearle, J. W. S., *Physical Properties of Textile Fibres*, 2nd edn, Wiley, New York, 1975.
3. Satyanarayana, K. G. et al., In I. H. Marshall (ed.), *Composite Structures*, Vol. 1, Elsevier Appl. Sci., London, 1981, p. 618.
4. Chawla, K. K. and Bastos, A. C., In *Proc. 3rd. Int. Conf. Mech. Behaviour of Materials*, Vol. 3, Pergamon Press, Toronto, 1979, p. 191.
5. Kuruvila, J., Thomas, S., Pavithran, C., and Brahmakumar, M., *J. Appl. Polymer Sci.* **47**, 1993, 1731.
6. Selzer, R., *Advanced Composite Letters* **4**(3), 1995, 87.
7. Sanadi, A. R., Caulfield, D. F., Jacobson, R. E., and Rowell, R. M., *Ind. Eng. Chem. Res.* **34**, 1995, 1889.
8. Mieck, K. P., Nechwatal, A., and Knobelsdorf, C., *Die Angewandte Makromolekulare Chemie* **224**, 1995, 73.
9. Park Buyng-Dae and Balatinecz, J. J, *Polymer Composites* **18**(1), 1997, 79.
10. Herrera-Franco, P. J. and De Aguilar-Vega, J., *J. Applied Polymer Sci.* **65**, 1997, 197.
11. Clemons, C. M., Giacomin, A. J., and Koutsky, J. A., *Polymer Eng. and Sci.* **37**(6), 1997.
12. Heijenrath, R. and Peijs, T., *Advanced Composite Letters* **5**(3), 1996, 81.
13. Rijsdijk, H. A., Contant, M., and Peijs, T., *Composites Science & Technology* **48**, 1993, 161.
14. Van den Oever, M. and Peijs, T., *Composites Part A* **29A**, 1998, 227.
15. Felix, J., Enhancing Interactions Between Cellulose Fibres and Synthetic Polymers, Ph.D. Thesis, Chalmers University of Technology, Goteborg, Sweden, 1993.
16. Felix, J. M. and Gatenholm, P., *J. Applied Polymer Sci.* **42**, 1991, 609.
17. Sain, M. M. and Kokta, B. V., *J. Applied Polymer Sci.* **54**, 1994, 1545.
18. Karmaker, A. C. and Youngquist, J. A., *J. Applied Polymer Sci.* **62**, 1996, 1147.
19. Hornsby, P. R., Hinrichsen, E., and Tarverdi, K., *J. Material Sci.* **32**, 1997, 1009.
20. Cox, H. L., *Brit. J. Appl. Phys.* **3**, 1952, 72.
21. Krenchel, H., In *Fibre Reinforcement*, Akademisk Forlag, Copenhagen, 1964.
22. Folkes, M. J., In *Short Fibre Reinforced Thermoplastics*, Research Studies Press, Chichester, 1985, p. 16.
23. Kelly, A. and Tyson, W. R., *J. Mech. Phys. Solids* **13**, 1965, 329.
24. Kelly, A. and Macmillan, N. H., In *Strong Solids*, Clarendon Press, Oxford, 1986, 269.
25. Plati, E. and Williams, J. G., *Polymer Engg. and Sci.* **15**(6), 1975, 470–477.
26. Ericson, M. and Berglund, L., *Composite Science and Technology* **43**, 1992, 269.
27. Ericson, M. and Berglund, L., *Composite Science and Technology* **49**, 1993, 121.
28. Thomason, J. L. and Vlug, M. A., *Composites Part A* **27A**, 1996, 477.
29. Rosenthal, J., *Polymer Composites* **13**, 1992, 462.
30. Thomason, J. L., Vlug, M. A., Schipper, G., and Krikor, H. G. L. T, *Composites Part A* **27**, 1996, 1075.
31. Pan, N., *Polymer Composites* **14**, 1993, 85.
32. Fu Shao-Yun and Lauke Bernd, *Composite Science and Technology* **56**, 1996, 1179.
33. Thomason, J. L. and Vlug, M. A., *Composites Part A* **28A**, 1997, 277.
34. Wells, J. K. and Beaumont, P. W. R., *J. Material Sci.* **20**, 1985, 1275.
35. Wells, J. K. and Beaumont, P. W. R., *J. Material Sci.* **20**, 1985, 2735.

36. Wells, J. K. and Beaumont, P. W. R., *J. Material Sci.* **23**, 1988, 1274.
37. Cottrell, A. H., *Proceedings Royal Society A* **282**, 1964, 2.
38. Cooper, G. A., *J. Material Sci.* **5**, 1970, 645.
39. Bijsterbosch, H., 'Long Fiber Reinforced Polyamides', Ph.D. Thesis, Twente University, Twente, The Netherlands, 1992.
40. Gupta, V. B., Mittal, R. K., and Sharma, P. K., *Polymer Composites* **10**(1), 1989, 16.
41. Mieck, K. P., Nechwatal, A., and Knobelsdorf, C., *Die Angewandte Makromolekulare Chemie* **225**, 1995, 37.