# The Potential of Flax Fibres as Reinforcement for Composite Materials

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# The Potential of Flax Fibres as Reinforcement for Composite Materials

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*Aan mijn moeder*

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# Nomenclature

*Symbols*

| | | |
|---|---|---|
| $a$ | width of a loop | [mm] |
| $b$ | width of a beam, tie or plate | [m] |
| $c$ | height of a loop | [mm] |
| $c_{crit}$ | critical height of a loop | [mm] |
| $C_1$ | constant depending on the load distribution | |
| $d$ | diameter of the fibre | [µm] |
| e | base of the natural logarithm | |
| $E_c$ | Young's modulus of the composite | [GPa] |
| $E_{comp}$ | compressive Young's modulus | [GPa] |
| $E_f$ | Young's modulus of the fibre | [GPa] |
| $E_{fcomp}$ | compressive modulus of the fibre | [GPa] |
| $E_m$ | Young's modulus of the matrix | [MPa] |
| $E_{tens}$ | tensile Young's modulus | [GPa] |
| $F$ | applied load | [kN] |
| $G_m$ | shear modulus of the matrix | [MPa] |
| $I$ | second moment of inertia | [$m^4$] |
| $k$ | efficiency parameter | [-] |
| $\ell$ | length of a beam, tie or plate | [m] |
| $l$ | length of a fibre fragment | [mm] |
| $L$ | length of the fibre | [mm] |
| $L_c$ | critical fibre length | [mm] |
| $L_i$ | length of fibres of sub-critical fibre length | [mm] |
| $L_j$ | length of fibres of super-critical fibre length | [mm] |
| $L_l$ | length of a fibre fragment | [mm] |

| | | |
|---|---|---|
| $m$ | Weibull modulus | [-] |
| $m_p$ | mass of a plate | [kg] |
| $M$ | material index to be optimised | |
| $R$ | radius of a loop | [mm] |
| $S$ | stiffness | [N/m] |
| $t$ | thickness of a beam, tie or plate | [m] |
| $V_f$ | volume fraction of the fibre | [-] |
| $V_l$ | volume fraction of fibres with sub-critical fibre length | [-] |
| $V_j$ | volume fraction of fibres with super-critical fibre length | [-] |
| vol% | volume percentage of fibres | [%] |
| wt% | weight percentage of fibres | [%] |
| $z$ | radius of the fibre | [µm] |
| | | |
| $\gamma_s$ | surface tension | [m $Nm^{-1}$] |
| $\Gamma$ | gamma function | |
| $\delta$ | deflection | [m] |
| $\varepsilon$ | strain | [%] |
| $\varepsilon_b$ | bundle efficiency | [-] |
| $\eta_0$ | fibre orientation factor | [-] |
| $\eta_{0,v}$ | virtual fibre orientation factor | [-] |
| $\eta_L$ | fibre length efficiency factor | [-] |
| $\nu$ | Poisson's ratio | [-] |
| $\rho$ | density | [$kg/m^3$] |
| $\sigma_c$ | strength of the composite | [MPa] |
| $\sigma_{comp}$ | compressive strength | [MPa] |
| $\sigma_{fcomp}$ | compressive strength of the fibre | [MPa} |
| $\sigma_f$ | strength of the fibre | [MPa] |
| $\sigma_l$ | strength of a fibre fragment of length $l$ | [MPa] |
| $\sigma_{lc}$ | strength of a fibre fragment at the critical fibre length | [MPa] |

| | | |
|---|---|---|
| $\sigma_m$ | strength of the matrix | [MPa] |
| $\sigma_{max}$ | strength of the material | [MPa] |
| $\sigma_{um}$ | strength of the matrix at the fibre failure strain | [MPa] |
| $\sigma_{my}$ | yield stress of the matrix | [MPa] |
| $\sigma_{tens}$ | tensile strength | [MPa] |
| $\sigma_z$ | stress on a looped fibre | [MPa] |
| $\tau$ | interfacial shear strength | [MPa] |

*Abbreviations*

| | | |
|---|---|---|
| ABS | acrylonitrile butadiene styrene copolymer | |
| CSLM | confocal scanning laser microscopy | |
| DP | degree of polymerisation | |
| EP | epoxy resin | |
| ESEM | environmental scanning electron microscopy | |
| FL | fibre length | |
| GMT | glass mat reinforced thermoplastic | |
| HDPE | high density polyethylene | |
| IFSS | interfacial shear strength | [MPa] |
| ILSS | interlaminar shear strength | [MPa] |
| MA | maleic anhydride | |
| MAPP | maleic anhydride modified PP | |
| MF | melamine formaldehyde resin | |
| NMT | natural fibre mat reinforced thermoplastic | |
| PC | polycarbonate | |
| PE | polyethylene | |
| PP | polypropylene | |
| PS | polystyrene | |
| PUR | polyurethane | |

| | | |
|---|---|---|
| PVC | polyvinylchloride | |
| PVOH | polyvinylalcohol | |
| SEBS-MA | styrene-butylene-styrene triblock copolymer | |
| SEM | scanning electron microscopy | |
| SMA | styrene maleic anhydride copolymer | |
| TEM | transmission electron microscopy | |
| $T_g$ | glass transition temperature | [°C] |
| UD | unidirectional | |
| UHMWPE | ultra high molecular weight polyethylene | |
| UP | unsaturated polyester resin | |

# Flax Related Terminology

| | |
|---|---|
| Breaking | Leading a retted flax stem between fluted rollers in order to break the woody core of the stem into shives. |
| Decortication | Extracting the fibres from the flax plant by removal of the rest of the stem. |
| Elementary fibres | Single plant cells, mostly between 10 and 25 µm thickness and between 20 and 50 mm length. |
| Fibre bundles | Coarse, ribbon-shaped fibres as they are isolated from the stem by breaking and scutching, consisting of a large number of elementary fibres in diameter. Pre-stage of technical fibres. |
| Hackling | Combing the fibre bundles to separate them into much finer technical fibres. |
| Retting | Breaking down of the pectin layer, which glues the fibre bundles to the stem, by micro-organisms. |
| Rippling | Removal of the seeds of the flax plant. |
| Scutching | Beating the fibres after breaking to remove the broken woody stem parts (shives). |
| Shives | Woody parts of the core of the stem which are formed by breaking. |
| Technical fibres | Thin long fibres consisting of 10 to 40 elementary fibres in diameter, which are the product from hackling the fibre bundles. |
| Tow | Short fibres (shorter than 30 cm), which are separated inadvertently from the fibre bundles together with the shives by the scutching process. |

# 1

# General Introduction

## 1.1 Background

Over the last decade, composites of polymers reinforced with natural fibres have received ever increasing attention, both from the academic world and from various industries. There is a wide variety of different natural fibres which can be applied as reinforcers or fillers, a diagram with a classification of the various fibres is presented in figure 1.1. All these natural fibres consist of long cells with relatively thick cell walls which make them stiff and strong. In most of the fibre plants the cells are glued together into long thin fibres, the length of which is dependent on the length of the plant. The fibres may differ in coarseness, in the length of the cells and in the strength and stiffness of the cell walls. The most important of the natural fibres used in composite materials are flax, hemp, jute, kenaf and sisal, due to their properties and availability. Flax, hemp, jute and kenaf are bast fibres, fibres which develop in the bast of the plant. Flax, hemp and jute have more or less similar morphologies and can have similar functions in the composite. These fibres are composed mainly of cellulose and some lignin and are sometimes called ligno-cellulosic fibres.
Generally four main reasons are mentioned which make the application of natural fibres

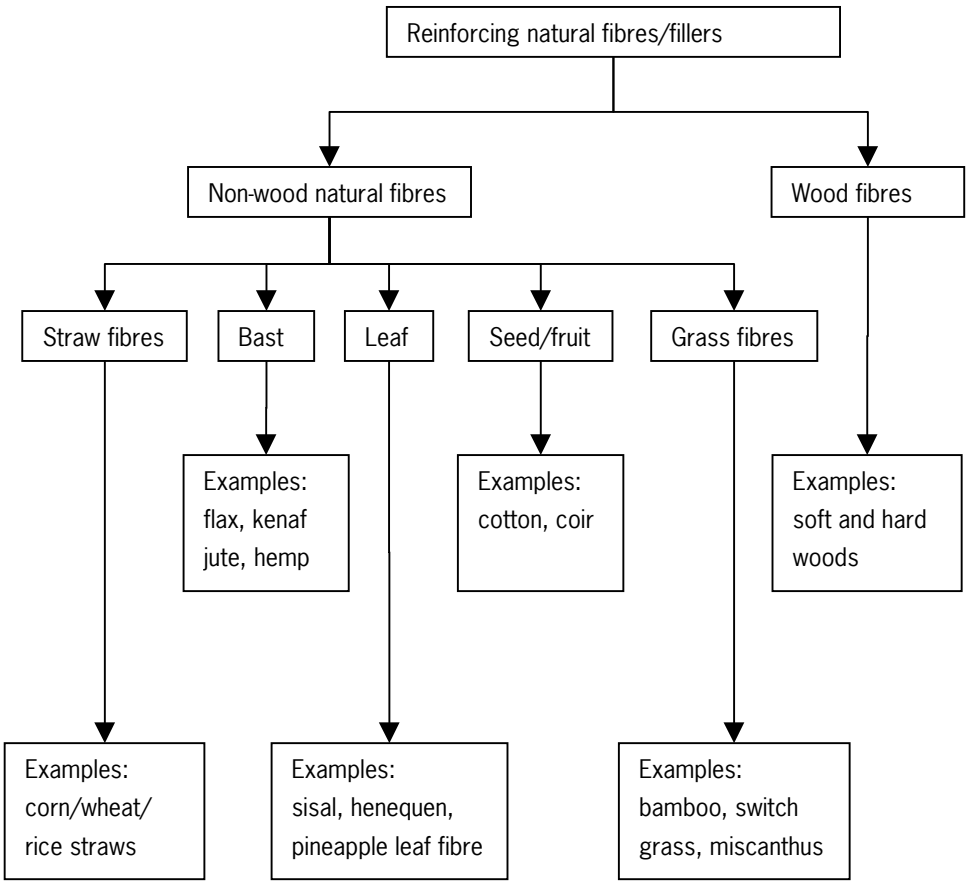


*Figure 1.1. Classification of natural fibres which can be used as fillers and reinforcers in polymers. After [1].*

attractive: (1) their specific properties, (2) their price, (3) their health advantages and (4) their recyclability. All four motives will be addressed here briefly.

Natural fibres based on cellulose have a relatively low density, and are relatively stiff and strong. Therefore their specific properties, i.e. the properties divided by the density, or the 'properties per kilo', are rather high, and actually comparable to those of glass fibres (see table 1.1). For the automotive industry, where weight reduction always is an issue, this was said to be the original reason for the development of interior parts with natural fibres as fillers. Originally, the automotive industry used wood fibres as

fillers, however, wood fibres are quite short and do have the ability to make composites stiffer, but they do not make them stronger. Therefore, later, also materials reinforced with other -longer- natural cellulose fibres, like flax, hemp and sisal were developed. Most of the interior parts in cars are still designed for stiffness and natural fibres are well suited for this application given their high specific modulus.
Natural fibre reinforced composites are originally aimed at the replacement of glass fibre reinforced composites. Depending on the exact quality of fibre needed, natural fibres are in most cases cheaper than glass fibres. Natural fibres are also expected to give less health problems for the people producing the composites. Natural fibres do not cause skin irritations and they are not suspected of causing lung cancer. This is especially an issue since the discussion on whether or not very small glass fibres can cause lung cancer, has still not ended. Although flax is known to give off a large amount of dust, this problem exists mainly in the early stages of the flax fibre isolation process and is relatively well under control in the modern flax processing industry [3].

*Table 1.1. Tensile properties and specific tensile properties of flax and glass fibres.*

| Property | E-glass [2] | Flax fibres |
|---|---|---|
| Diameter [µm] | 8-14 | 10-80 |
| Density [g/cm$^3$] | 2.56 | 1.4 |
| E-modulus [GPa] | 76 | 50-70 |
| Tensile strength [GPa] | 1.4-2.5 | 0.5-1.5 |
| Elongation to fracture [%] | 1.8-3.2 | 2-3 |
| Specific E-modulus [GPa per g/cm$^3$] | 30 | 36-50 |
| Specific tensile strength [GPa per g/cm$^3$] | 0.5-1 | 0.4-1.1 |

Natural fibre composites are also often claimed to be recyclable. There is some confusion on this issue and different sources do not agree on the feasibility of flax fibre composite recycling. For mechanical recycling -in the production process itself- natural fibres have no clear advantage over glass fibres, both fibres will suffer from a second processing step, and for flax fibres there is a chance of additional thermal degradation during this step. A definite advantage of flax fibre composites over glass fibre

composites, however, is the fact that they can be burned (euphemistically called thermal recycling) without leaving large amounts of slag.
All in all, the use of natural fibres has a definite 'green image'. For the automotive industry, for instance, this has been a serious driving force for the development of natural fibre reinforced materials and it has also induced companies like DaimlerChrysler AG to try to develop high performance materials on the basis of renewable resources [4].

## 1.2 The application of natural fibres in the automotive industry

As mentioned in the previous section it is especially the automotive industry which has in the last years developed various new components based on natural fibre composites. Whereas in 1996 the total reported use of natural fibres did not exceed 4.0 kton, by 1999 this had increased to more than 21 kton as reported by the suppliers to the European automotive industry [5]. This figure includes next to flax fibres also hemp, jute, sisal and kenaf, which all are used in composite production [6]. The use of flax was reported by the suppliers to be circa 1.6 kton in 1999, and expected to rise to 15 to 20 kton in the near future. The German and Austrian car industry alone employed 8.5 to 9 kton flax fibres in the years 2000 and 2001 [7]. The introduction of every new car model increases the demand –depending on the model- by 0.5 to 3 kton per year [8].
The automotive industry gives a long list of presumed benefits of natural fibre composites, which includes the general reasons for the application of natural fibres as discussed briefly in the previous section [5,8]:

- Low density: which may lead to a weight reduction of 10 to 30%.
- Acceptable mechanical properties, good acoustic properties.
- Favourable processing properties, for instance low wear on tools.
- Options for new production technologies and materials.
- Favourable accident performance, high stability, less splintering.
- Favourable ecobalance for part production.
- Favourable ecobalance during vehicle operation due to weight savings.
- Occupational health benefits compared to glass fibres during production.
- No off-gassing of toxic compounds (in contrast to phenol resin bonded wood and recycled cotton fibre parts).
- Reduced fogging behaviour.

- Relatively easy recycling (it is not clear whether they mean thermal recycling here).
- Price advantages both for the fibres and the applied technologies.

Obviously the production and application of natural fibre reinforced parts also brings along some difficulties [8]:

- For the production of non-wovens: presence of shives, dust, very short fibres.
- Uneven length distribution and uneven decortication of the fibres (especially for non-wovens).
- Irreproducible fibre quality combined with availability.
- Variations in non-woven quality and uniformity due to fibre quality variation.
- Moisture sensitivity, both during processing and during application.
- Limited heat resistance of the fibres.
- Specific smell of the parts.
- Limited fire retardancy.
- Variations in quality and uniformity of produced parts.
- Possible moulding and rotting.

Apparently the total balance of properties comes out positive since in ever more new models natural fibre reinforced composite parts are applied (see table 1.2).

A number of technologies and material combinations are used by the different producers. The major part of the technologies is based on the application of the natural fibres as a, usually needle punched, non-woven. The non-wovens can be impregnated or sprayed with a thermosetting synthetic binder, for instance polyester or polyurethane, and then compression moulded in a hot press into the desired shape [8]. The non-wovens can also be impregnated with polypropylene (PP) by means of a travelling extruder, after which they are covered with a second non-woven and compression moulded in a belt press. The final product is then produced by stamping [7,9]. A third commercially used option is the application of a hybrid non-woven consisting of flax fibres mixed with PP fibres, which can be moulded directly into shape in a hot press [8]. There is a clear trend towards diminishing use of thermoset and increased use of thermoplastic binders. In Germany and Austria in 2000 circa 45% of the produced natural fibre composites [7] were still produced with a thermoset binder, in 2001 and 2002 this figure had diminished to only 22 to 24% [11]. The increasing use in thermoplastic binders is driven by their easier processing characteristics as well as the existence of fogging problems caused by some of the thermoset binders. Another

trend that has come up since 2001 is the increased use of injection moulding technology for the production of natural fibre reinforced parts, although up till now this technology is not yet used for flax [12,13]. The expectation is that once injection

*Table 1.2. Application of natural fibres in automotive parts [10].*

| Manufacturer | Model<br>*Application* (dependent on model) |
|---|---|
| Audi | A3, A4, A4 Avant, A6, A8, Roadster, Coupe<br>*Seat back, side and back door panel, boot lining, hat rack, spare tire lining* |
| BMW | 3, 5 and 7 Series and others<br>*Door panels, headliner panel, boot lining, seat back* |
| Daimler/ Chrysler | *A-Series, C-Series, E-Series, S-Series*<br>*Door panels, windshields/dashboard, business table, pillar cover panel* |
| Fiat | Punto, Brava, Marea, Alfa Romeo 146, 156 |
| Ford | Mondeo CD 162, Focus<br>*Door panels, B-pillar, boot liner* |
| Opel | Astra, Vectra, Zafira<br>*Headliner panel, door panels, pillar cover panel, instrument panel* |
| Peugeot | New model 406 |
| Renault | Clio |
| Rover | Rover 2000 and others<br>*Insulation, rear storage shelf/panel* |
| Saab | *Door panels* |
| SEAT | *Door panels, seat back* |
| Volkswagen | Golf A4, Passat Variant, Bora<br>*Door panel, seat back, boot lid finish panel, boot liner* |
| Volvo | C70, V70 |

moulding of other natural fibres than wood fibres comes up, the market potential for the use of natural fibres in cars will be doubled compared to the present situation.
Although the flax fibre reinforced composites are often quoted to be developed originally to replace glass fibre reinforced materials, it turns out that -at least in the German and Austrian car industry- the thermoplastic natural fibre reinforced compression moulded parts mainly replace woodfibre filled thermoset systems. The use of woodfibre filled composites by the German and Austrian car industry has decreased from circa 60 kton per year in 1996 to circa 35 kton per year in 2001 [7]. The advantage of the use of longer natural fibres instead of woodfibres are found in the achievement of significant weight reduction (20% for the door panels of the Mercedes-Benz E-Class), and the improvement of the mechanical properties, important for passenger protection in the event of an accident [14]. Furthermore, the flax-sisal mat used by Mercedes [14] can be moulded in complicated 3-dimensional shapes, thus making it more suitable for door trim panels than the previously used materials.
In cars in which natural fibres are employed, presently 5 to 10 kilo natural fibres (flax, hemp, jute, etc.) per car are used. If the total European car industry would employ natural fibres, this would mean a market potential for circa 80 to 160 kton per year of natural fibres for compression moulded parts in cars.

## 1.3 Research on natural fibre composites

The development of natural fibre composites has profited from the policy of a number of (European) governments to support the development of technical applications for renewable resources. In Germany the 'Fachagentur für Nachwachsende Rohstoffe' has, together with the German industry, financed the development of a completely new industry for the processing of hemp fibres (a fibre similar to flax but with higher yield per hectare) and of flax fibres, which industries both had disappeared in Germany. These hemp and flax fibres are especially aimed for the use in technical applications, mainly in the automotive industry.
In the Netherlands the development of new technical applications for both flax and hemp fibres has benefited in the nineties from the policy of the Ministry of Agriculture, Fishery and Nature Management (LNV) to develop a 'fourth crop' to be cultivated in rotation with the existing three main crops (potatoes, beetroot and grains). This fourth crop was to be especially cultivated for technical use. The policy was called

'agrification', but it has not survived the turn of the millennium, although the interest in the use of renewable resources as alternative for oil based resources still exists on a smaller scale.
The nova Institut in Germany has calculated [5] that in the period between 1982 and 2002 the European Union has spent more than 50 Million Euro on subsidies directed towards the development of new flax and hemp applications and towards harvesting and fibre processing technologies. In addition to this, national projects were funded by various European countries. In Germany more than 90 Million Euro was invested on the subject. In the Netherlands the investment was considerably less, and does probably not exceed ten to twenty Million Euro. In the Netherlands, however, the application of natural fibres in composite products has hardly taken off and various initiatives to develop new applications have faltered [15], whereas in Germany, especially in the car industry, the application of natural fibres seems to take a high flight as reported in the previous paragraph. The Dutch flax producing industry is increasingly selling their products to other buyers than the traditional linen producing companies [5], and the fibres are thus increasingly used for technical applications.

## 1.4 Research program and objectives

The work described in this thesis has been performed at ATO bv (currently Agrotechnology and Food Innovations (A&F), Wageningen UR) from roughly 1995 to 2003. The thesis is a compilation of results from a number of different research and development projects, the most important of which are:

- Bladeco (1996-2002), the development of wind turbine blades from ecological materials, funded by EET. Partners in this project were, besides ATO bv, ECN, KEMA, TUD and Aerpac.
- AFPP, Agrofibre reinForced PolyPropylene (1995-1998), the development of injection moulded parts for automotive applications, funded by the EU. Partners in this project were, besides ATO bv, ECIA (now Faurecia), Solvay and Celesa SA.
- A number of smaller strategic projects performed under the successive innovation programs from the Ministry of Agriculture, Fishery and Nature Management, program 268, 'Verwerking agromaterialen' (1995-1998), program 345, 'Verwerking duurzame agromaterialen' (1999-2002), and program 412 'Groene Grondstoffen', (2003-2006)

In this thesis the relations between the structure and the mechanical properties of flax fibres are investigated. Furthermore, the effects that the specific structure and properties of the fibres have on the properties of different flax reinforced composites are investigated. The technical potential of the application of various products from the flax fibre isolation process in different polymers is described. Furthermore the question is addressed whether, from an environmental point of view, it is justifiable to use natural fibres, in particular flax fibres, as reinforcement in polymer materials for technical applications.

## 1.5 Survey of the thesis

Different aspects of the potential of flax as a reinforcement for polymer matrix composites are presented in this thesis. In Chapter 2 a survey is given of flax, its history and the isolation methods formerly and presently applied. Chapter 3 contains a literature survey on the morphology of flax fibres and describes a study on the mechanical properties and deformation behaviour of the fibres in relation to their morphology. In Chapter 4, 5 and 6 the properties of a variety of possible flax fibre composites are studied. Chapter 4 describes the properties of long unidirectional flax fibres in epoxy resin, with special focus on the compressive properties of the composites as well as the fibres. Chapter 5 describes the properties of flax fibres in natural mat reinforced thermoplastic (NMT) materials, attention is paid to the effect of two different fibre isolation stages on the properties of the composites. Chapter 6 is devoted to flax fibre compounds, either produced in a kneader or in an extruder. A comparison is also made between the theoretically expected properties of the compounds and the NMT materials. Furthermore, some attention is paid to the effect of heat on the properties of the fibres. In Chapter 7 a study is presented on the environmental impact of the various types of flax fibre reinforced materials. In Chapter 8 the market potential for this new class of materials is discussed taking into account the structure of the flax producing industry and an outlook to the future of flax fibre reinforced composites is given.

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10. Reprinted from [5] with kind permission from Dipl.-Phys. Michael Karus, nova Institut, Hürth, Germany
11. Woodfibre based parts are not taken into account in this listing.
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13. Natural fibres comprise in this case flax, hemp, jute etc. and also wood and cellulose fibres.
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15. Ceres, the producer of Duralin, has stopped development and production in the summer of 2002. Also most of the research projects on flax and hemp composites at ATO have stopped, some work is still performed on jute composites, together with partners from India and Bangladesh. Recent developments however point to a renewed interest for these materials.

# 2

# Flax, a Prehistoric Crop with Modern Applications

## 2.1 Flax, an ancient industrial fibre

Flax (*Linum usitatissimum* L.) is probably the oldest textile fibre known to mankind. It has been used since ancient times for the production of linen cloth. The first well documented application is the use of the linen fabric by the Egyptians to wrap their mummies. Linen fabric was found in graves in Egypt dating from before 5000 B.C. [1]. At that time the Egyptians were able to produce yarns and fabrics of a fineness that is nowadays unobtainable [1]. But even long before that time flax was used for various applications. At excavation sites of Stone Age dwellings in Switserland, dated at approximately 7000 B.C., flax seeds, twines and fishing nets were found [2]. The flax plant is thought to have arrived in Europe with the first farmers, and in the stone age people were usually dressed in linen clothes. In the Netherlands the cultivation of flax presumably has existed continuously ever since 2500 B.C..

Over the millennia flax has always been used as the basis for fabric, not only for clothing but also for sails and tents [4], and it was the all important fibre used for war outfit until circa 1950, after which synthetic fibres took over [1]. The flax industry has been declining ever since circa 1955, after which the competition of synthetic fibres

became stronger and stronger in different application areas. Only quite recently flax is blended with synthetic fibres to combine the advantages of both different materials, and the apparel market has once more become a large buyer for the flax industry. However, flax and especially the production of long fibres, has in this way become very dependent on the fashion industry. Consequently the flax industry has become a very cyclical business, and the industry is searching for new, preferably high value, steady markets [5].

*Table 2.1. Mechanical properties of various textile fibres [3,4].*

| Fibre | Modulus [g/den] | Elongation at break [%] |
|---|---|---|
| Wool | 9-17 | 7-15 |
| Cotton | 44-82 | 5-10 |
| Polyester | 30-60 | 7-13 |
| Linen | 204 | 2-3 |

Although the waste streams of the flax production -like the woody shives- have since long been used in for instance chipboards for building applications, only in the last decennia a renewed interest to use also the bast fibres as reinforcement in plastic matrix composites has risen. The low elasticity of the flax fibres compared to other fibres like wool and cotton (see table 2.1) -which is a disadvantage during the spinning process- is for the use in composites a prerequisite. One of the first uses in this field was linen fabric as reinforcement for phenol resin for the construction of a Spitfire aircraft during World War-II. More recent applications are found in modern cars like for instance several Mercedes models and other European cars, where non-woven fibre mats are used commercially for interior panels [9], sometimes in combination with other agrofibres [8].

Presently two types of flax are grown, fibre flax and seed flax. Fibre flax is optimised for the production of thin strong fibres. Seed flax gives coarser fibres, but far more linseed, since this plant does not have one straight stem, but the stem divides towards various flower heads. Flax grows in moderate climates and is presently cultivated among others in large parts of Western and Eastern Europe, in Canada and the USA

and in Russia. World-wide approximately 5 million hectare flax is grown [8]. Circa 3.8 million hectare is used for the production of linseed only, 0.2 hectare for fibres only, and approximately 1 million hectare for both linseed and fibres.

In the traditional flax countries like the Netherlands, Belgium and France, the main focus of the flax production lies still on the apparel and home textile market. The main output from this production chain are the long fibres for spinning yarn. For this purpose flax fibres are isolated from the plant via processes known as retting, breaking, scutching and hackling. Short fibres are produced as an inevitable by-product. In the new flax (and hemp) countries processing of the fibres is almost entirely done by the 'lin-total' concept, in which long and short fibres are not separated. The output of this process are short fibres [9]. In 1999 in the EU approximately 60 to 70 kton of short fibres was produced [9], these found their application in specialty pulps (45%) in the apparel and home textiles (20%) in composites for the automotive industry (6%, 4 kton) and in various other applications, of which especially the thermal insulation materials were expected to grow significantly. The expectation was in 1999 that the application of European flax in composites for automotive would grow quickly to 5.5 kton, in 2000 [9].

*Table 2.2. Prices, ktons sold and stock for flax fibres for the Netherlands, Belgium and France together [10]. The cleaned short fibres can be applied in composites.*

| | 98/99 | 99/00 | 00/01 | 01/02 | 02/03 |
|---|---|---|---|---|---|
| *Long fibre* | | | | | |
| Price (€/kg) | 1.26 | 1.81 | 2.33 | 2.27 | 1.95 |
| Sold (ktons) | 72.1 | 98.1 | 87.7 | 58.3 | 95.7 |
| Stock (ktons) | 20.5 | 6.5 | 13.3 | 6.8 | 10.7 |
| *Cleaned short fibre* | | | | | |
| Price (€/kg) | 0.28 | 0.31 | 0.52 | 0.57 | 0.43 |
| Sold (ktons) | 22.9 | 35.5 | 33.5 | 23.9 | 27.1 |
| Stock (ktons) | 25.3 | 18.0 | 13.7 | 12.1 | 9.5 |
| *Uncleaned short fibre* | | | | | |
| Price (€/kg) | 0.07 | 0.17 | 0.19 | 0.24 | 0.15 |

Prices for the short fibres are obviously lower than for the long fibres. Prices for the fibres sold by the scutchers in the Netherlands, Belgium and France over the last years are shown in table 2.2 [10]. The prices of the long fibres as well as the short fibres have gone up due to increasing demand from the apparel market and the bad harvest from 2001. It is clear that the price of the short fibres fluctuates together with the price for the long fibres. The stocks are presently very low, which is thought to be due partly to the demand for short fibres from the automotive industry [9].
It is obvious that at this price level long flax fibres will not be an interesting replacement for glass fibres, which would cost around € 1.75 per kilogram, whereas short flax fibres can compete with glass, even if some extra treatment would be necessary to improve processability or adhesion.

## 2.2 Flax fibre isolation methods

Figure 2.1 shows a cross section of the flax stem. The fibre bundles, which are the fibres used for textile and technical applications are located just under the skin and

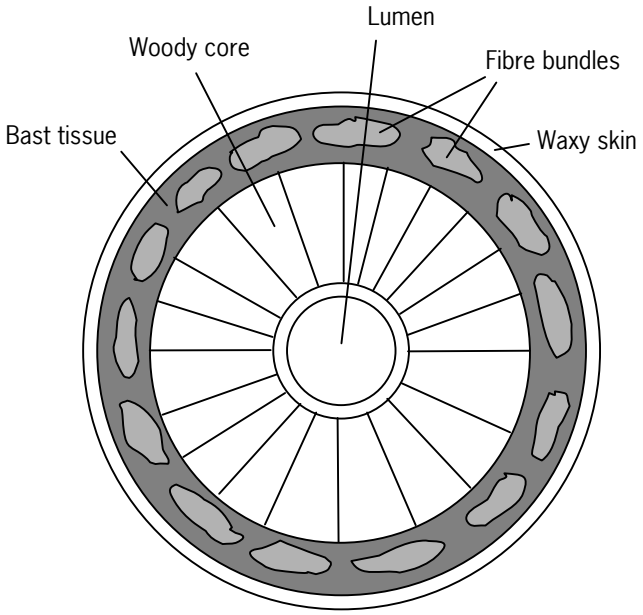


*Figure 2.1. Schematic representation of a cross section of the stem of the flax plant. See also figure 3.3.*

embedded in bast tissue. In figure 2.2 an overview is given of the retting, breaking, scutching and hackling cycle and its respective products. To harvest flax the plants are pulled out of the ground in order to retain the longest fibre length, and the flower heads are removed by rippling. Next the plants are spread over the ground for retting. During retting the pectin layer that binds the fibres to the bast tissue and the flax stem is

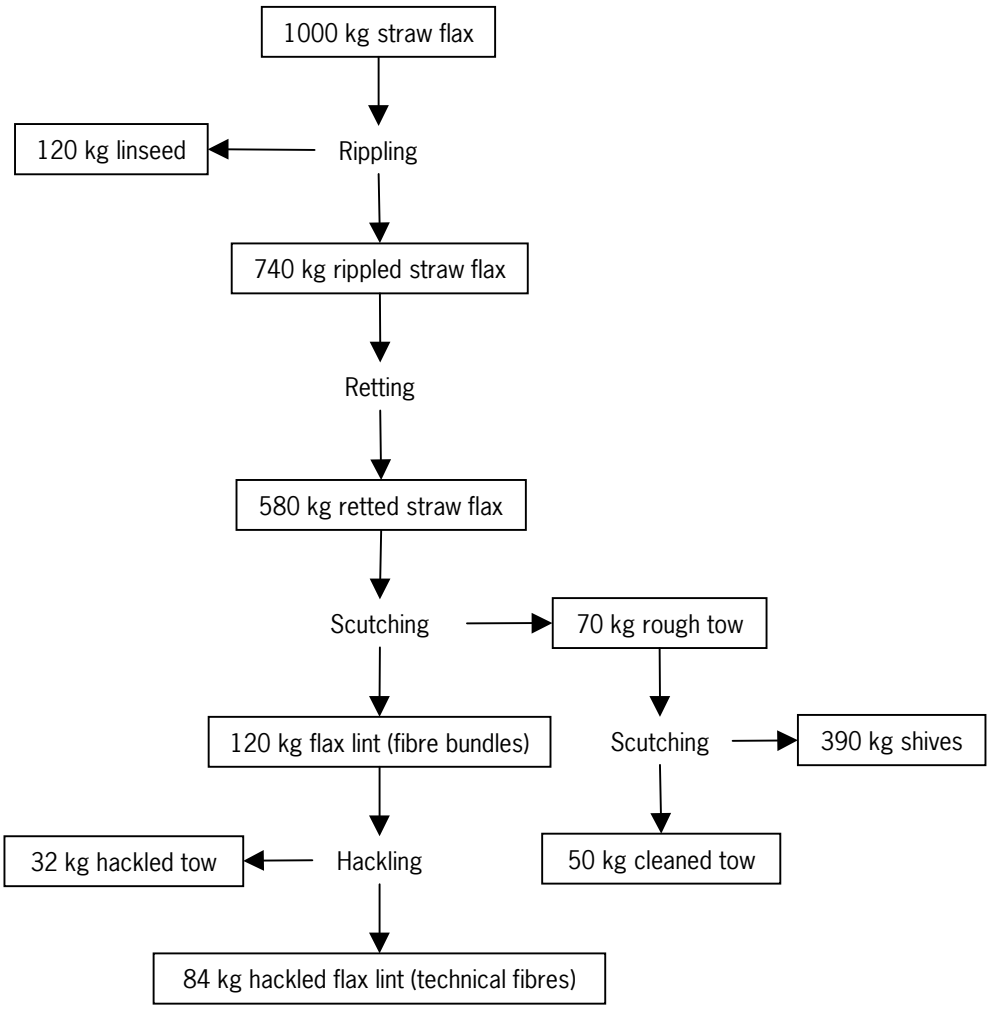


*Figure 2.2. Traditional flax fibre isolation methods and their respective products (after [11]), side products of the rippling process are chaff and ripple waste (240 kg), the weight loss during retting is due to the loss of water soluble components, the rest of the weight loss is due to the loss of dust.*

broken down [11]. Until some decades ago retting (water retting) was usually performed by immersing bundles of flax stem into running water (for which the river de Leie in Belgium was famous) or in standing water in ponds or specially prepared pits. Fermentation -by anaerobic bacteria in this case- degrades the pectins and other substances that bind the fibres to the stem. The fermentation products, however, form a serious environmental problem, so that this type of retting is no longer employed in Western Europe. Retting can also be done by simply spreading the fibres over the field (dew retting) in which case indigenous aerobic fungi partly degrade the stem. In the last century also rather sophisticated retting methods, using for instance warm water and enzymes, were developed for the production of very fine yarns [1]. However, the market for (very expensive) very fine flax yarns has disappeared, and warm water retting is a rather laborious process, so, even though warm water retting is obviously preferable from the point of process control, in practice these days almost always dew retting is chosen for economic reasons [5]. Dew retting takes, depending on the weather, three to seven weeks, after which the flax bundles are taken up and put in gaits in order to dry.

After the fibres have been loosened from the stem, the stem is broken on a brake by leading it between fluted rollers (see figure 2.3). The broken stem parts are then

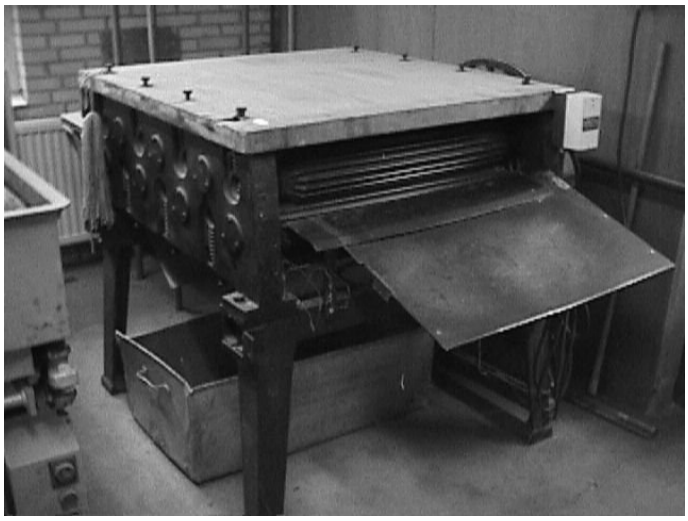

*Figure 2.3. Example of a brake, the flax stems are led between the fluted rollers.*

removed from the fibre bundles in the scutching turbine, which basically scrapes the fibres, thereby removing the broken woody stem parts, the shives. The scutching turbine exists of two interpenetrating rollers equipped with three or more knives (see figure 2.4). The knives scrape along the fibre, but since the knives are relatively sharp, they also bend the fibres just below the point of contact, introducing microstructural defects in the form of kink bands over the entire fibre length (figure 2.5). The total process to remove the wooden stem from the fibres is also called decortication.

The scutched fibres are called fibre bundles, and are still relatively coarse and thick, ribbon-shaped, like their morphology in the plant (see figure 2.1 and also figure 3.3). The coarse fibre bundles are then combed in the hackling process, during which the

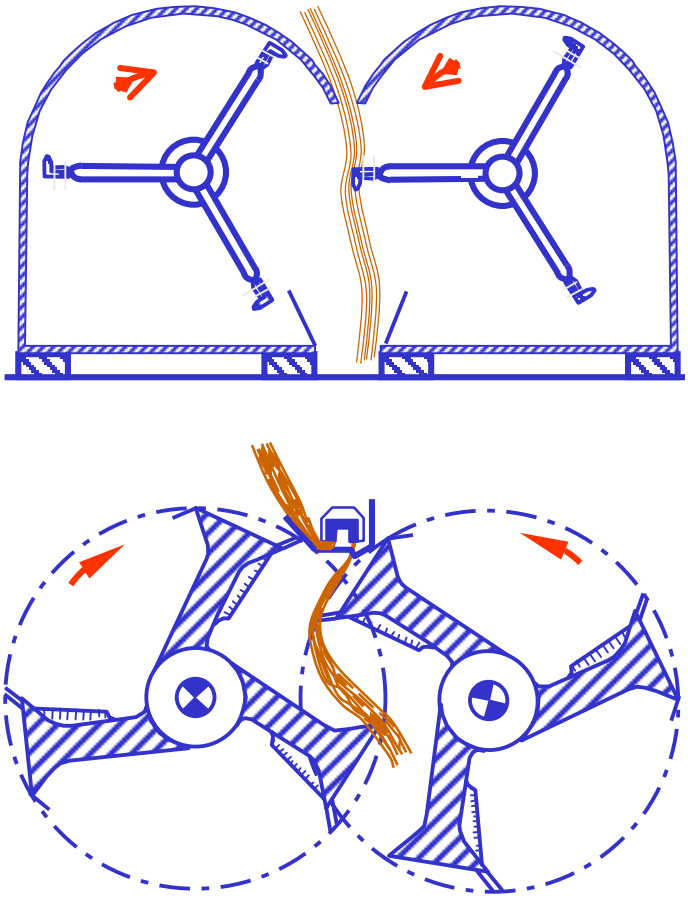

*Figure 2.4. Examples of scutching turbines (after [1]).*

ribbon-shaped fibre structure is refined towards a more or less circular fibre structure, the technical fibres. The technical fibres consequently are thinner than the fibre bundles. Similar to the scutching turbine, also the hackling combs introduce local bending in the fibres and are thus partly responsible for the kink bands in the fibres. Figure 2.1 gives also an estimate of the amount of short fibre waste, scutching and hackling tow, that is produced during the process. Scutching tow can be cleaned, i.e. the shives removed. Hackling tow does not contain shives any more. Both types of tow are sold for a wide range of applications including the production of composites, since this is a relatively cheap source of fibres with good mechanical properties.

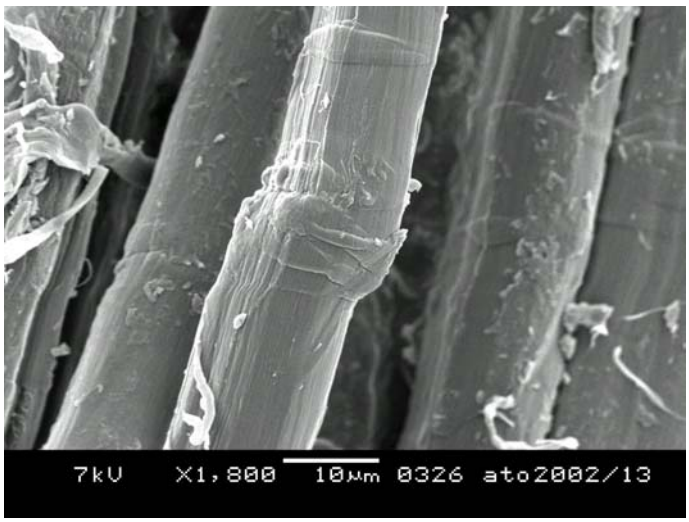


*Figure 2.5. Kink band in an elementary flax fibre.*

Apart from dew retting, recently a few new fibre isolation methods have come up, especially in view of the intended use of the fibres in composites. Green flax, which is employed by Daimler AG [9] is isolated in a slightly different way. These fibres are only lightly retted after which they are coarsely decorticated (i.e. having the woody particles removed). Subsequently, just before processing into a non-woven they are finely decorticated. These green flax fibres are coarser than dew retted fibres and Schlösser and Fölster [9] claim that they possess better mechanical properties than the retted fibres. Furthermore, since the non-wovens produced from these fibres are coarser, they are more easily impregnated with polymer. Hobson et al. [12] have studied the

quality of fibres from unretted hemp. They also find that the fibres are coarser than retted fibres, but also contain a lower amount of micro-organisms on the fibres, which they claim is another advantage at further processing.

The group of Akin at the USDA studies enzyme retting. They focus among others on the effects of various mechanical, physical and chemical pretreatments [13-15], and different enzyme mixtures [16-18] on the quality of the fibres of fibre flax and seed flax [19]. Generally they find that enzyme retting improves the fibre fineness, but decreases the fibre strength. Enzyme retting is not really new, already around 1916 experiments were done to ret flax in water to which a yeast was added [1]. In 1982 a company was set up in the Netherlands that applied enzyme retting on flax, the resulting fibres, however, were found to be unfit for the production of yarn [8]. Also various attempts in other European countries to develop enzyme retting have not led to a large scale production of enzyme retted flax [1]. A definite advantage of enzyme retting, however, is the fact that the retting process takes place under well controlled circumstances. Presently the Finnish company FinFlax Oy Ltd markets a fine, light coloured type of flax that is produced via enzyme retting. Vilppunen et al. [20] report for fibres from this process a tensile strength of 800 to 1000 MPa, which is higher than usually found for dew retted fibres, indicating that this enzymatic process is well-optimised.

Tavisto et al. [21] report on the use of frost retting to isolate flax and hemp fibres, which can be applied in the Nordic countries, where the climate does not allow dew retting.

Kessler et al. [22,23] study the influence of steam explosion on the structure and properties of the bast fibres. They find however that the tensile strength of the steam exploded fibres is significantly lower than the strength of scutched fibres.

Hornsby et al. [24] employ a pulping process in a twin screw extruder, which is commonly used for paper manufacturing, on flax straw to obtain elementary fibres. The tensile strength of the pulped fibres is, however, reduced by more than 70% due to the hydroxide, high temperature and mechanical treatments that are applied in this process.

In a comparative study between flax isolated in various different ways, Sharma et al. [25] conclude that water retted fibres have the highest quality, regarding fibre fineness, fibre strength and the absence of non-cellulosic compounds. They find that the quality of dew retted fibres varies strongly, due to the uncontrollable retting circumstances, and their strength is approximately 70% of the strength of water retted fibres. Enzyme

retted fibres have fibre fineness almost comparable to water retted fibres but a low strength, approximately 55% of the strength of water retted fibres. Furthermore they find that unretted (green) flax fibres are very coarse, and difficult to handle and have a strength of approximately 80% of the strength of water retted fibres, but somewhat higher than the strength of dew retted fibres. Van de Velde and Baetens [26] find in a comparative study that the strength of scutched and hackled green fibres is comparable to the strength of scutched and hackled dew retted fibres, they only find a slightly higher modulus for the dew-retted fibres.

## 2.3 The influence of fibre morphology on composite properties

As discussed in Chapter 1 the objective of this work is to study the relations between the morphology of the flax fibres and the mechanical properties of their composites. The fibres used in this study are either dew retted or warm water retted on lab scale and subsequently decorticated by the processes applied for the production of long flax. It turns out that one of the most important factors influencing the properties of the fibres and their composites is the damage in the form of kink bands (see figure 2.5) induced in the fibres by the decortication processes. Since all decortication processes -including both the 'lin-total' process for the production of short fibres, and the production process for green flax- induce similar damage in the fibres, the results presented in this thesis in Chapters 3, 4, and 6 are relevant for all flax reinforced composites, irrespective of the decortication process that the fibres have undergone. The study presented in Chapter 5 focuses especially on the influence of the stage of refining of the fibre (either scutched or scutched and subsequently hackled fibres) on the mechanical properties of the produced composites. Also this study has a wider applicability, since it is the morphology of the fibres that mainly influences the composite properties, irrespective of the exact mechanical process used to refine the fibres.

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# 3

# Fibre Properties and Deformation Behaviour

## 3.1 Introduction*

As opposed to man-made fibres the -technical- flax fibre is not a continuous fibre but is in fact a composite by itself. A schematic structure of the flax fibre, from stem to microfibril, is given in figure 3.1 and figure 3.2. The coarse bast fibre bundles are isolated from the stem by breaking and scutching and further refined towards technical fibres by hackling (see also Chapter 2 for more detail). The location and typical cross sections of the bast fibre bundles in the flax stem are also shown in figure 3.3, it can clearly be seen here that the fibre bundles are packed together in a tape-like morphology. They are composed of a few technical fibres, bonded together by a

*This chapter is based on the papers:

- Tensile and compressive properties of flax fibres for natural fibre reinforced composites; H.L. Bos, M.J.A. van den Oever and O.C.J.J. Peters, *J. Mater. Sci.* **37** (2002) 1683
- In situ ESEM study of the deformation of elementary flax fibres; H.L. Bos and A.M. Donald, *J. Mater. Sci.* **34** (1999) 3029

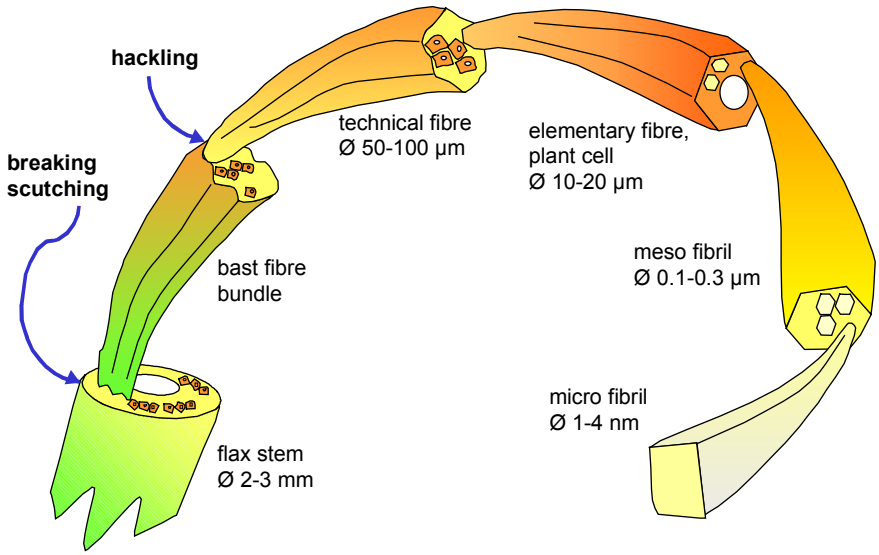



*Figure 3.1. Schematic representation of a flax fibre from stem to microfibril.*

relatively weak interphase, mainly consisting of pectins, which is at some places along the fibres as good as absent. In figure 3.3 typical spots are marked where the technical fibres in the bundle have virtually no bonding whereas they do have bonding at other positions further along the fibre. Consequently, the technical fibres are in the plant not well defined and ready separated from the root till the tip, but are more like an arbitrary bundle of elementary fibres, separated at some points and glued together at other positions. During hackling the fibre bundles are separated by the hackling combs into the technical fibres. In the technical fibres the spots with little interfibre bonding have largely disappeared, since the hackling combs are expected to preferably run through these weak spots.

In figure 3.3 it can also be seen how the technical fibres consist of elementary fibres. The elementary fibres have lengths between 2 and 5 cm, and diameters between 5 and 35 µm. The technical fibre consists of about 10-40 elementary fibres in cross section. The elementary fibres overlap over a considerable length and are glued together by an interphase mainly consisting of pectin and hemicellulose, which is a mixture of different lower molecular weight branched polysaccharides. They are not circular but a polyhedron with usually 5, 6 or 7 angles to improve the packing in the technical fibre.

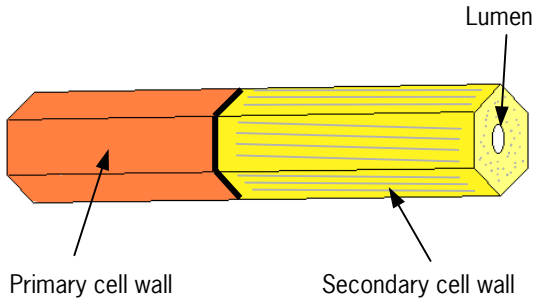
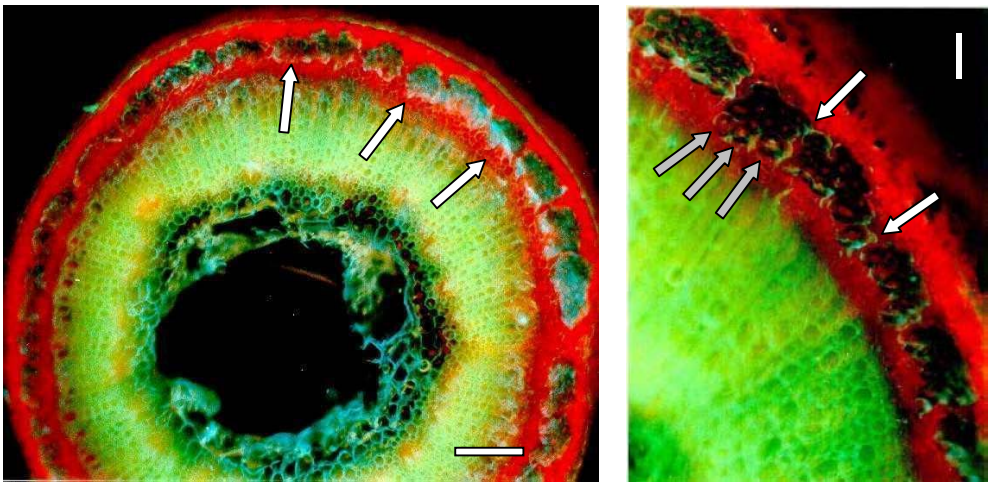



*Figure 3.2. Schematic representation of a section of the elementary fibre or plant cell. Shown is also the fibrillar structure in the secondary cell wall.*

The elementary fibres are the single plant cells (see figure 3.2). They consist of a primary cell wall, a secondary cell wall and a lumen, which is an open channel in the centre of the fibre. The lumen can be as small as 1.5% of the cross section [2].
Elementary fibres contain 65-75% cellulose, approximately 15% hemicellulose (mostly



a b

*Figure 3.3. Photographs of a cross section of a flax stem. (a) The white markers show the bast fibres. Clearly deducible is the ribbon-shaped morphology of the fibre bundles. The scale bar represents 0.1 mm. (b) Magnification of a, the white markers show spots where the interfibre bonding within the fibre bundle is virtually absent, the grey markers show the individual elementary fibres. The scale bar represents 50 µm [1].*

xylan) and 10-15% pectin [3,4]. The pectin is mainly situated in the primary cell wall [5-7], which further contains some lignin and (hemi)cellulose [6,7]. The primary cell wall is relatively thin, in the order of 0.2 µm [8]. The fibres also contain 2-5% of waxes [9], part of which can be found on the surface of the primary cell wall. The waxes might originate from the plant cuticle, which is made up of cutin, an aliphatic polyester, embedded in soluble waxes, mainly palmitic acid [10-12]. Van de Velde and Kiekens [13] find a contact angle of scutched dew retted flax fibres in water of approximately 70-80°, indicating that the fibres are partly wetted out by water, and consequently that the fibre surface is rather hydrophilic. Van Hazendonk et al. [14] on the other hand studied the surface tension of flax fibres which have undergone various surface treatments to remove the subsequent outer layers. They find that the surface tension of retted flax fibres is very low, ($\gamma_s$ = 28.5-34.2 $mNm^{-1}$) comparable to waxes. Extraction of the fatty substances makes the fibre more hydrophilic and increases the surface tension ($\gamma_s$ = 40.3-43.1 $mNm^{-1}$). Additional extraction of pectins and hemicelluloses further raises the surface tension to a value comparable to that of highly crystalline cellulose ($\gamma_s$ = 60.5-66.1 $mNm^{-1}$).

The secondary cell wall makes up most of the fibre diameter, and is made mainly from cellulose and hemicelluloses [9]. Cellulose, which is built up from the monosaccharide D-glucose, is known to form strong intra- and intermolecular hydrogen bonds [15]. These hydrogen bonds strongly determine both the physical and chemical properties of cellulose. The intramolecular hydrogen bonds give a significant stiffness to the cellulose molecules. The chief portion of the cellulose molecules are arranged in crystallites, with interspersed amorphous regions. Native cellulose has a monoclinic unit cell and is called cellulose I. Upon swelling in strong alkali the crystal structure can be disrupted and converts to the thermodynamically more stable cellulose II. The degree of polymerisation (DP) of cellulose in flax is rather high and lies for dew-retted fibres of the variety Belinka around 5000 [16].

The cellulose crystallites in the secondary cell wall are laid down in oriented, highly crystalline microfibrils which are glued together by the amorphous hemicellulose phase. The hemicellulose is known to contribute significantly to the strength of the fibre, removal of the hemicellulose results in dramatically reduced tensile strength, and causes the fibre bundles to completely disintegrate into microfibrils [5,17]. Astley and Donald [18] studied the flax cell wall with small-angle X-ray scattering (SAXS) and derived from the data analysis that the cross section of the cellulose microfibrils is

approximately 1x5 $nm^2$. Näslund et al. [19] report a microfibril diameter between 1 and 4 nm, as measured by diffraction contrast transmission electron microscopy. Astley and Donald [18] also find evidence for a crystalline/non-crystalline repeat distance of 6 to 7 nm. The microfibrils -or maybe we should say nanofibrils- are packed together in a fibrillar structure, the meso fibrils, with a fibril size in the order of 0.1 µm. The fibrils are oriented spirally at approximately +10° compared to the fibre axis [20]. The meso structure is clearly visible in the scanning electron microscope (SEM) (see figure 3.4).

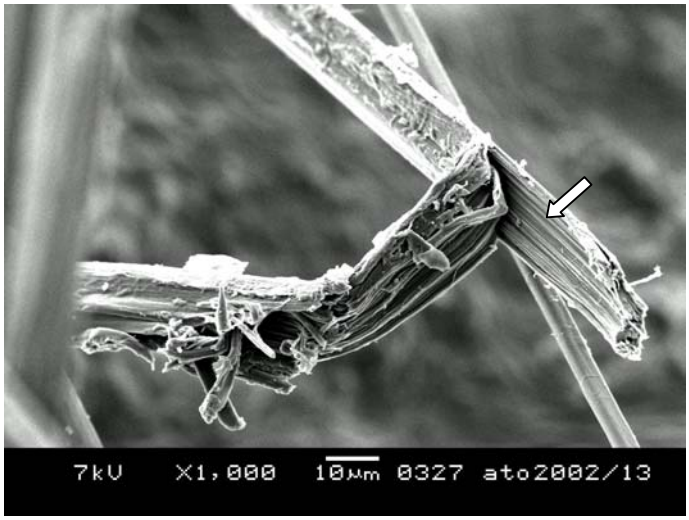



*Figure 3.4. SEM micrograph of a split elementary fibre, the marker showing the meso structure in the secondary cell wall.*

Compared to other natural fibres, flax fibres are relatively strong. Data for the tensile strength of various natural and glass fibres as presented by different authors are given in table 3.1. For flax the highest tensile strength is reported. This is thought to be due to the fact that flax has the longest elementary fibres and the smallest microfibril orientation. It is also obvious that there is a large variation in the data presented.
The modulus of flax fibres is investigated thoroughly by Baley [25] and Lamy and Baley [26]. They find that the modulus of the elementary fibres is dependent on the fibre diameter, and ranges between 39 GPa for fibres of approximately 35 µm diameter and 78 GPa for fibres around 5 µm diameter. This variation is probably related to the variation in lumen size between fibres of different diameter. Baley [25] reports an

*Table 3.1. Tensile strength, expressed in MPa, of different natural fibres and of glass fibres, presented by a number of authors.*

| | Kessler et al. [21] | nova et al. [22] | Morton et al. [23] | Satyanarayana et al. [24] |
|---|---|---|---|---|
| Flax | 400 - 1500 | 800 - 930 | 756 | |
| Hemp | | 600 - 1100 | 658 | |
| Kenaf | | 930 | | |
| Jute | | 540 | 434 | 533 |
| Sisal | | 855 | | 641 |
| Ramie | | 585 | 826 | |
| Glass | 900 - 3500 | 1625 | 1913 | |

average Young's modulus of 54 GPa resulting from numerous tensile tests on single flax fibres. This is also well within the range of moduli measured at ATO on technical fibres, which range approximately between 30 and 70 GPa. For this study a tensile modulus of 50 GPa is taken for elementary fibres as well as technical fibres.
The highly crystalline structure of the secondary cell wall makes the fibres stiff and strong in the length direction. However, due to the orientation of the crystallites and the presence of amorphous regions between the crystallites, the cell wall properties in lateral direction -both stiffness and strength- are expected to differ greatly from the properties in length direction. This anisotropy is also expected to make the fibres very sensitive towards the formation of kink bands under bending or compression (see also figure 2.5). It has long been known [27] that during washing of linen the kink bands are the spots were the fibres start to break and fibrillate, leading to deterioration of the linen texture. Also for the application in composites the fibre anisotropy, and thus the presence of kink bands and a low lateral cell wall strength, can be responsible for composite properties which are not as good as might be expected on the basis of the high fibre tensile strength.

This chapter describes the tensile and compressive strength properties of flax fibres. Furthermore, the deformation of flax fibres is investigated in situ in an Environmental

Scanning Electron Microscopy (ESEM). The ESEM allows the compressive failure of the fibres to be examined closely. Contrary to the ordinary Scanning Electron Microscope (SEM), the ESEM minimises charging of the samples due to the electron beam, and thus the surface of the samples can be studied directly without the need for coating. Since the ESEM is a surface characteristic technique, obviously only the features appearing at the fibre surface can be examined. However, eventual failure of the primary cell wall also allows a view deeper into the secondary cell wall.

## 3.2 Experimental

### *3.2.1 Materials*

Flax (variety Belinka) was warm water retted on lab scale. Part of the fibres was decorticated using pilot scale breaking, scutching and hackling procedures, part of the fibres was isolated from the plant by hand, taking special care not to damage the fibres unnecessarily.

### *3.2.2 Tensile tests*

Tensile strength of the technical fibres at span lengths of 10, 25, 50 and 100 mm was measured on a BAC tensile machine, at a strain rate of 0.005 $s^{-1}$. Fibre tensile strength at 3 mm span length of both the technical and the elementary fibres was measured on a Rheometrics RSA II in tensile mode, using a static strain sweep programme. Individual fibres were glued onto small paper frames with epoxy glue. Specially developed clamps were used to clamp the frames, and prior to the measurement the sides of the frames were cut to allow free straining of the fibre. The strain rate was 0.005 $s^{-1}$. Diameter of the fibres was determined by investigating the fibre diameter in two perpendicular directions over the fibre length and taking the smallest diameter as a rectangle. Care was taken to select fibres for the test with a relatively homogeneous diameter. All strength measurements have been performed in 25-fold.

### *3.2.3 Compression tests*

The compressive strength of the fibres was measured using an elastica loop test as developed by Sinclair [28]. Elementary fibres were placed in a loop (see figure 3.10) under an optical microscope (with magnification 200x) and their ends were strained slowly. The creation and growth of kink bands was monitored and the dimensions of the

loop during straining were measured. The elastica loop test was performed on 14 elementary fibres containing small kink bands induced by the decortication process and 8 elementary fibres free of kink bands.

### *3.2.4 Microscopy*

Scanning electron microscopy (SEM) was performed on a Philips 515 SEM and on a JEOL JSM-5600LV SEM. Environmental scanning electron microscopy (ESEM) was performed on an Electroscan ESEM 2010 at the Cavendish Laboratory, University of Cambridge, UK. Confocal scanning laser microscopy (CSLM) was performed using a Biorad MRC600 microscope from the University of Wageningen, NL.

### *3.2.5 In situ ESEM deformation study*

Elementary fibres were isolated by hand from the technical bast fibres and glued with one end onto a small cardboard frame. At the free fibre end a single knot subsequently was made, leaving a loose loop of approximately 1.5 mm radius. The free fibre end was then glued onto the other end of the cardboard frame. The cardboard frame was mounted on the tensile stage of the ESEM, and the edges of the cardboard frame were cut, allowing the fibre to be strained freely. The microscope was pumped down to vacuum and flooded with water vapour up to 4 Torr pressure (this improves imaging), leaving the fibres relatively dry, indicative of their state in a composite material or for instance during extrusion compounding together with a thermoplastic polymer. The beam voltage was kept as low as 12 keV in order to avoid beam damage to the fibres. No evidence of beam damage was found at this level. The experiments were performed at room temperature.

## 3.3 Results and discussion

### *3.3.1 Tensile properties*

Figure 3.5 shows two typical stress-strain curves, for technical fibres clamped at 100 mm and 3 mm respectively. It is apparent that there is no great difference in stress-strain behaviour between both fibres. There occurs no large scale plastic deformation in the fibres upon straining. Astley and Donald [29] attribute this to the fact that the amorphous regions between the cellulose microfibrils are already oriented, and therefore not capable to deform plastically.

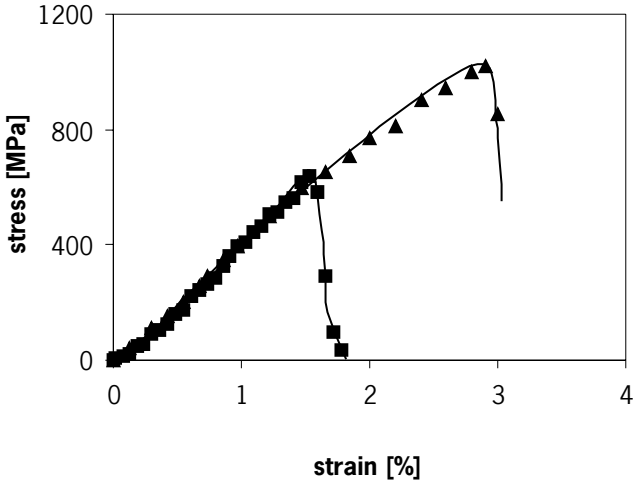



*Figure 3.5. Typical stress strain curves for technical flax fibres. ▲ 3 mm clamping length, ■ 100 mm clamping length.*

There is, however, a large difference in fibre strength between the fibres clamped at different length. Figure 3.6 shows the fibre strength as a function of clamping length. The technical fibre strength is constant, approximately 500 MPa, down to a clamping length of 25 mm. Below 25 mm the fibre strength begins to increase towards a value of about 850 MPa at a clamping length of 3 mm. This shape of the tensile strength curve as function of the clamping length was also found by Kohler and Wedler [30] for scutched flax.

Even though it is known that the strength of fibres generally increases with decreasing fibre length due to the reducing chance of the presence of critical flaws, it is unlikely that the specific dependency of strength on clamping length found in this case is caused by just this effect. Since the technical flax fibres are composed of shorter elementary fibres, it is likely that at large clamping lengths fibre failure takes place through the relatively weak pectin interphase that bonds the elementary fibres together. This gives rise to the plateau value in tensile strength of 500 MPa found for larger clamping lengths. Since the pectin interphase is oriented predominantly in the length direction of the fibre, it must break by shear failure. From the sharp fall in the curve in figure 3.5, it can be concluded that the failure in the pectin interphase is not a process involving large scale plastic flow, but happens rather instantaneously. The rise in tensile

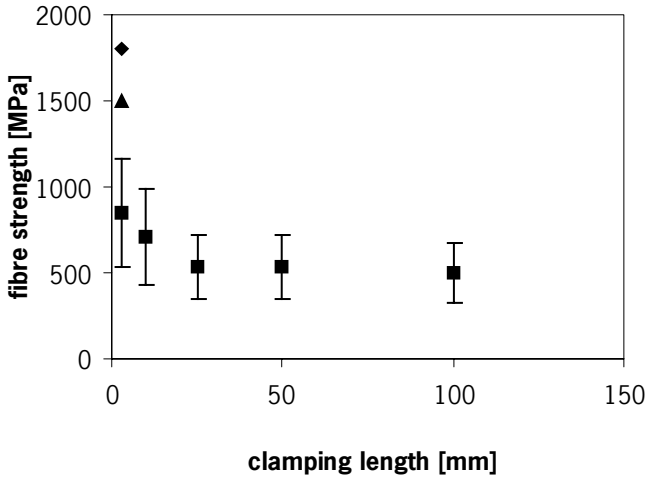



*Figure 3.6. Fibre tensile strength versus clamping length. ■ Technical fibres, ▲ elementary fibres, standard decortication, ◆ elementary fibres, hand decortication.*

strength of the technical fibres at shorter clamping lengths is caused by a change in failure mechanism. At clamping lengths below the elementary fibre length, failure can no longer take place through the pectin interphase, but the crack must now run through the, stronger, cellulosic cell wall of the elementary fibres. This is also depicted schematically in figure 3.7. The increase in strength is obviously gradual, due to the distribution in elementary fibre lengths and to the decreasing influence of critical flaws.

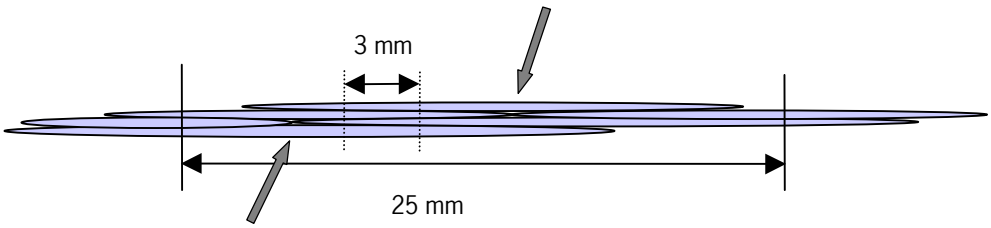



*Figure 3.7. Schematic representation of the way the fibres break. At 25 mm clamping length the elementary fibres slip apart, the points of separation are marked by the grey arrows. At 3 mm clamping length the crack has to run through the cell walls.*

The fact that the increase in strength starts around a clamping length of 25 mm supports this picture: elementary fibre lengths of flax fibres are usually quoted to lie between 20 and 50 mm, with the mean value around 30 mm.

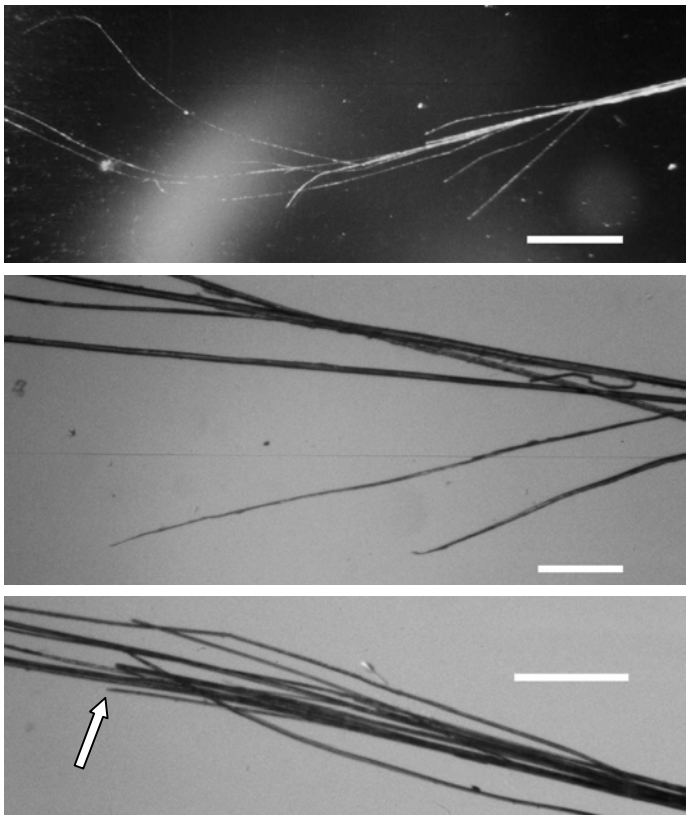



*Figure 3.8. Flax fibre tested at 50 mm clamping length. (a) Overview, scale bar is 2.5 mm. (b) Elementary fibres separated through the pectin interphase, scale bar is 0.25 mm. (c) Elementary fibres separated through the pectin interphase and broken halfway (arrow), scale bar is 0.5 mm.*

Also a closer look at the failed fibres as shown in figure 3.8 partly supports this view. Figure 3.8 shows the point of failure of a fibre tested at 50 mm clamping length. The fibre has split into elementary fibres and bundles of a few elementary fibres. Figure 3.8b shows that indeed part of the elementary fibres is intact over the entire length up to the pointed fibre ends, and have separated completely through the pectin interphase.

Some of the other elementary fibres, however, have broken halfway as can be concluded from the blunt elementary fibre ends visible in figure 3.8c. It is remarkable that approximately 6 elementary fibres have broken at the same spot. Probably at this spot a kinkband was present over a large part of the technical fibre diameter.
The length over which the fibre splitting can take place is depending on the clamping length. For fibres which are tested at long clamping length the splitting usually is visible over a length up to approximately 25 millimetres, similar to the length of the elementary fibres, giving the fibre the possibility to fail fully through the pectin interphase.

The triangular point in figure 3.6 gives the average tensile strength as measured on single elementary fibres, 1522 ± 400 MPa. This value is similar to the upper limit in tensile strength as reported by Kessler et al. [21] for the tensile strength of steam exploded flax. Van de Velde and Baetens [31] report a tensile strength of 925 MPa for elementary flax fibres. These fibres were isolated by a chemical extraction method, and it is quite possible that they lost some strength due to the influence of the chemicals. Garkhail [32] finds a tensile strength of 1200 MPa for elementary fibres.
The strength values reported above were all measured on scutched and subsequently hackled fibres. To investigate the influence of the presence of kinkbands on the fibre strength, the strength of elementary fibres isolated by hand was determined as well. These fibres were found to be virtually free of kink bands. The mean fibre strength of the hand decorticated fibres is higher, 1834 ± 900 MPa, as compared to the value of 1522 ± 400 MPa found for standard decorticated fibres (figure 3.6), but also has a considerably higher scatter on the data.
The tensile strength of single elementary fibres is clearly substantially higher than the tensile strength of technical fibres at the same clamping length; the technical fibre strength is found to be 57% of the elementary fibre strength. This strength difference is most likely due to the bundle effect. Van der Zwaag [33] gives a method to derive the strength of a bundle consisting of a large number of filaments from a Weibull plot. A Weibull plot [34] of the fibre strength data, measured both on standard decorticated and hand isolated elementary fibres, is given in figure 3.9 (each point represents a single measurement). The Weibull modulus, $m$, is the slope of the line and a measure for the scatter on the strength data. For standard decorticated flax fibres a Weibull modulus of 4.0 is found and for hand decorticated fibres a Weibull modulus of 2.2 is found. Following van der Zwaag [33] the bundle efficiency, $\varepsilon$, can now be calculated as:

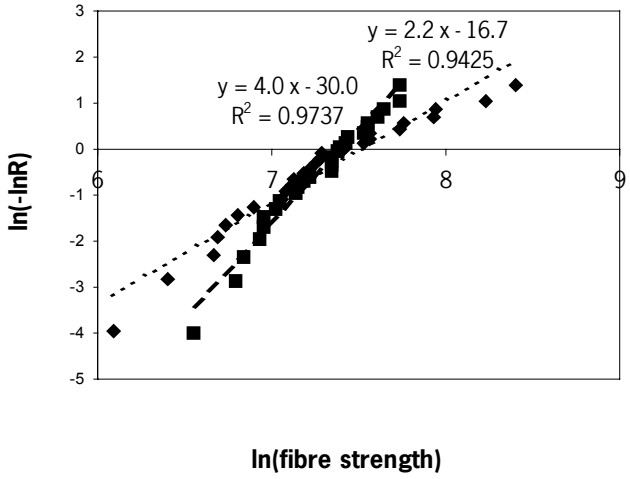



*Figure 3.9. Weibull plot of elementary fibre strengths.* ◆ *Hand isolated fibres,* ■ *standard decorticated fibres.*

$$\varepsilon = (\mathrm{e}\,m)^{-1/m} / \Gamma(1+1/m) \tag{3.1}$$

with e the base of the natural logarithm, $\Gamma$ the gamma function and $m$ the Weibull modulus. For the kinked, standard decorticated fibres with a Weibull modulus of 4.0 this leads to a bundle efficiency of 61%. Even though in principle equation 3.1 is only valid when there is no filament interaction in the bundle and when the bundle contains over 100 filaments -generally a technical fibre encloses up to 40 elementary fibres in its cross section-, the result is remarkably close to the efficiency of 57% found experimentally. For a hand decorticated bundle with a Weibull modulus of 2.2, the calculated bundle efficiency is 50%. Given a mean elementary fibre strength of hand decorticated fibres of approximately 1800 MPa, the bundle strength would be approximately 900 MPa, similar as for standard decorticated fibres. This indicates that although the standard decortication process reduces the strength of individual elementary fibres, the strength of the technical fibre is hardly affected. It can now be understood why, for the linen industry, where the strength, fineness and homogeneity of the technical fibre are the major quality parameters, the fact that the standard decortication process damages the elementary fibres is of minor importance. For

applications of the fibres in composites, however, the strength of the elementary fibre can be an extremely important parameter.
Various authors have determined the Weibull modulus of man-made fibres. Baillie and Bader [35] report for carbon fibres a Weibull modulus between 4.0 and 7.8. Wagner [36] found for UHMWPE a Weibull modulus between 5.6 and 7.7 and for aramid fibres a Weibull modulus of 7.3. A Weibull modulus between 5.1 and 5.5 is found for single glass fibres in a single fibre tension test by Andersons et al. [37]. Comparing these data with the values measured on flax it is clear that flax fibres show a higher scatter in tensile strength than man made fibres.
The scatter in strength is also much larger for the hand decorticated elementary fibres than for the standard decorticated elementary fibres. Apart from lowering the mean fibre strength, due to the kink bands it induces, the standard decortication process also breaks the fibres at some of the weakest spots, thereby reducing the scatter in fibre strength. It is interesting to note that nearly 50% of the fibres comes off as short fibre waste, during the standard production process of long fibre yarns (see figure 2.2). One could further assume that the standard decortication process especially reduces the strength of the strongest fibres, since, when there is already a flaw in the fibre present, the introduction of extra kink bands will probably only lead to a limited extra drop in strength. When there is no weak spot present, any kink band that is introduced in the fibre will lead to a serious drop in strength. Worth mentioning in this respect is the fact that from the hand isolated fibres, some were found to be stronger than 2500 MPa with one measured value of even 4200 MPa.
The presence of the kink bands, however, poses a serious problem for the use of these fibres in composite materials. Eichhorn and Young [38] and Hughes et al. [39] report in this respect that the defects in the fibres lead to local stress concentrations within the fibres, giving rise to the formation of cracks in composite materials. With the development of alternative decortication processes, especially aimed at producing fibres for the composite industry, care should be taken that the weakest fibres are removed during the process, without damaging the stronger ones.

### *3.3.2 Compressive properties*

Measuring compressive strength of fibres is not a trivial problem. A possible approach is the use of the elastica loop test. The elastica loop test was originally developed by Sinclair [28], to measure the tensile strength of glass fibres. Greenwood and Rose [40]

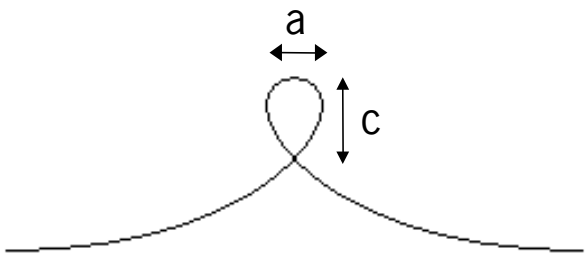



*Figure 3.10. The geometry of the loop test, at the point of failure the ratio c/a changes.*

and Peijs et al. [41] used the test to measure the compressive strength of man made polymeric fibres, like aramid, UHMWPE and PVOH, which fail in compression rather than tension. In the loop test, due to the geometry of the loop (see figure 3.10) the highest stress is found in the top of the loop. Flax fibres, as other highly oriented polymeric fibres, show compression failure in the top of the loop. Upon tightening the loop, the relative dimensions of the loop (*c/a*) will remain constant, around 1.34, until a non-linear deformation takes place in the top of the loop. The loop test subsequently takes the point of non-linear deformation as the point of failure. At that point *c/a* will increase and

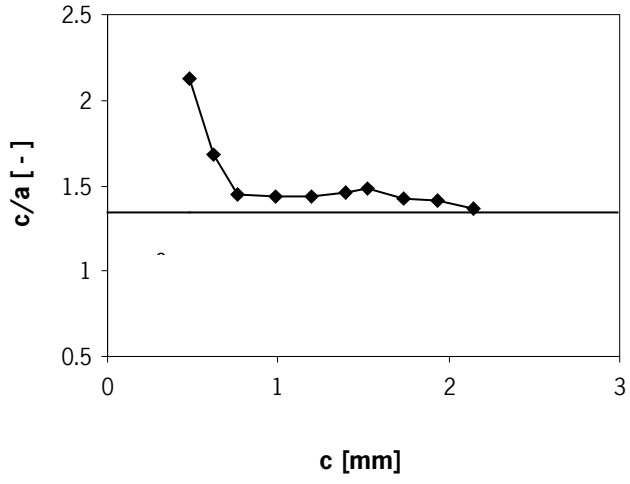



*Figure 3.11. A typical plot of c/a versus c of an elastica loop test; $c_{crit}$ is the c at which c/a starts to rise.*

from plotting $c/a$ against $c$ (see figure 3.11), the point of failure $c_{crit}$ can be determined. The stress at the moment of failure, which is then taken to be the compressive strength of the fibre, $\sigma_{fcomp}$, can then be calculated as [28]:

$$\sigma_{fcomp} = \frac{1.34\, E_{fcomp}\, d}{c_{crit}} \tag{3.2}$$

with $E_{fcomp}$ the compressive modulus of the fibre, usually assumed to be equal to the tensile modulus, and again taken as 50 GPa, and with $d$ the fibre diameter.

A problem with standard decorticated flax fibres, as mentioned before, is the large number of existing kink bands, distributed more or less evenly over the fibre length (figure 3.12a). Hand isolated fibres, on the other hand, are virtually free of kink bands (figure 3.12b), indicating that kink bands are not caused during growing, but are a result of the isolation process. A test on fourteen different single fibres led to nine fibres failing in the top of the loop giving a value for the compressive strength of 1200 ± 370 MPa. Five fibres failed at arbitrary points along the loop at lower stresses. Since all fourteen fibres are damaged by the decortication process, the compressive strength values measured on these fibres can be assumed to form a lower limit.

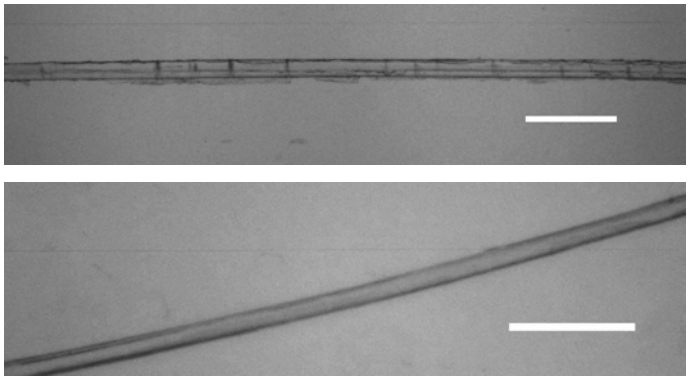



*Figure 3.12. Optical micrographs of elementary flax fibres. Scale bars indicate 100 µm. (a) Fibre containing kink bands. (b) Fibre without kink bands.*

In the loop test, irrespective of the presence of the kink bands, the loop often has the expected shape with ($c/a$) about 1.34 at the start of the test. The point at which in the loop test failure is determined corresponds to the point at which one of the kink bands in the top of the loop has grown so far that it extends over the whole fibre diameter.

In order to more closely examine the fibre deformation under compression, a few hand isolated fibres, without pre-induced kink bands, were tested in the loop test as well. The first deformation during the test which is visible in the optical microscope, are small black dots in the centre of the fibre axis in the top of the loop, starting at rather low stresses. Using equation 3.2 and substituting $c_{crit}$ by $c$, it can be calculated that these dots become visible at around 300 MPa. The black dots gradually grow in the direction of the compressive side of the fibre until around 600 MPa local thickening on the compressive side begins to occur (figure 3.13). Further tightening of the loop causes

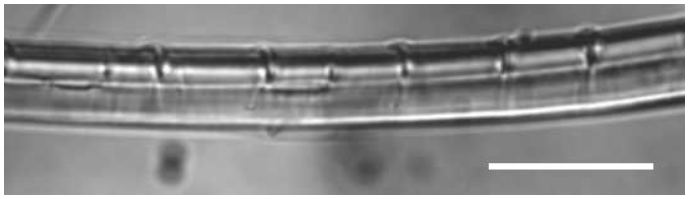


*Figure 3.13. Optical micrograph of an elementary flax fibre in a loop with local fibre thickening at the compression side of the fibre. Scale bar indicates 50 µm.*

the fibre to undergo compressive failure, similar to the standard decorticated fibres and at similar $c_{crit}$. These results give a rough indication of the initiation stress of the compressive failure. Since the first visible deformation of the primary cell wall starts to appear around 300 MPa, it is possible that at this point some larger scale deformation is also taking place in the secondary cell wall. The value of 300 MPa can then be considered as the compressive failure initiation stress.

The few tests performed on hand isolated fibres do not indicate that there is a difference in ultimate compressive failure strength between standard decorticated fibres that fail in the top of the loop and hand isolated fibres. This can be expected when it is assumed that the process of kink band formation is similar during both the decortication process and the loop test, and the point of failure is determined as merely the point at which the kinking process has occurred over the full diameter of the fibre. It does, however, pose a question to the validity of the loop test for determining the compressive strength of flax fibres, since small scale failure probably already occurs from 300 MPa on, long before the loop shows large scale non-linear deformation. The small scale deformations are distributed over the fibre and not just

located in the top of the loop, indicating that there is localised damage over the entire fibre length, and the compressive failure process is not just centered in the top of the loop. The roughly determined compressive failure initiation stress may therefore give a better indication of the fibre in compressive loading, than the loop test does.
It is, however, interesting to look at the deformation process that takes place in the kink bands. An Environmental Scanning Electron Microscopy (ESEM) micrograph of an area which has just developed a full kink band in bending is shown in figure 3.14. The primary cell wall is still intact, although it has buckled outwards. The deformation in the primary cell wall has grown over the entire fibre diameter. The damage in the secondary cell wall obviously is not visible in this micrograph. A view of what happens in the secondary cell wall during compressive failure, is shown in a Confocal Scanning Laser Microscopy (CSLM) micrograph in figure 3.15. The CSLM micrograph shows a section of the secondary cell wall of a hand isolated fibre, underneath the primary cell wall, which has deformed in a loop test and was subsequently re-straightened. The

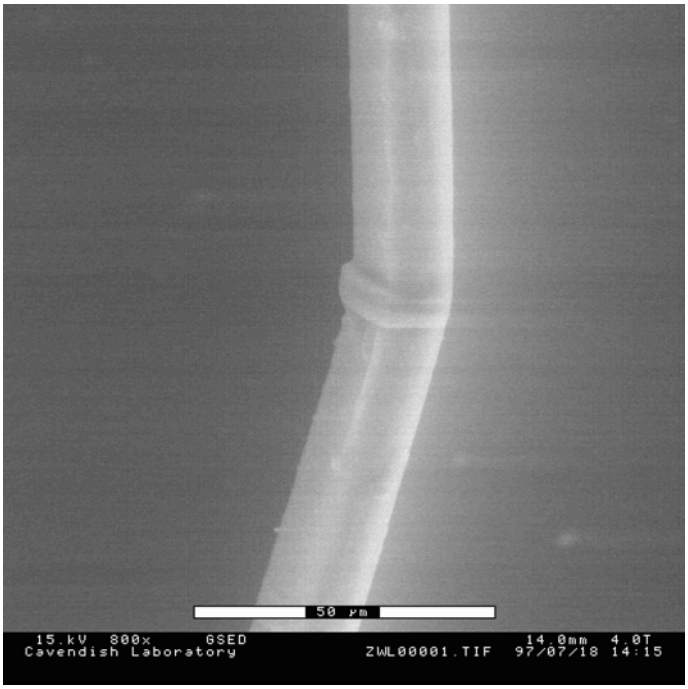



*Figure 3.14. ESEM micrograph of a flax fibre which has just developed a full kink band.*

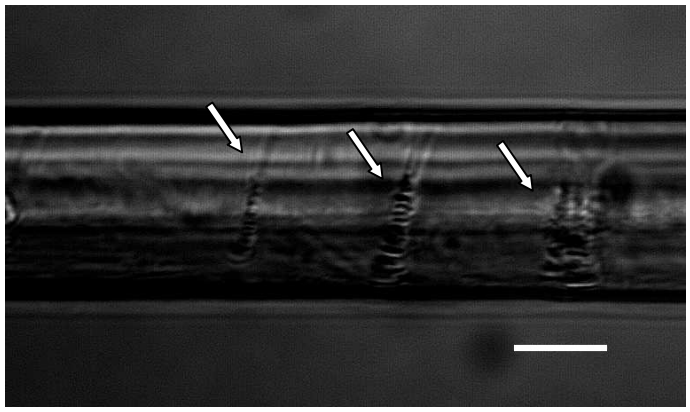


*Figure 3.15. CSLM micrograph of kink bands formed during a loop test after re-straightening of the fibre. The arrows mark the deformation bands. Scale bar indicates 10 µm.*

deformation in the fibre is localised in a number of narrow bands, shown by the arrows. The deformation bands form an angle of approximately 80° with the fibre axis, i.e. they are perpendicular to the direction of the fibrils in the secondary cell wall. Furthermore,

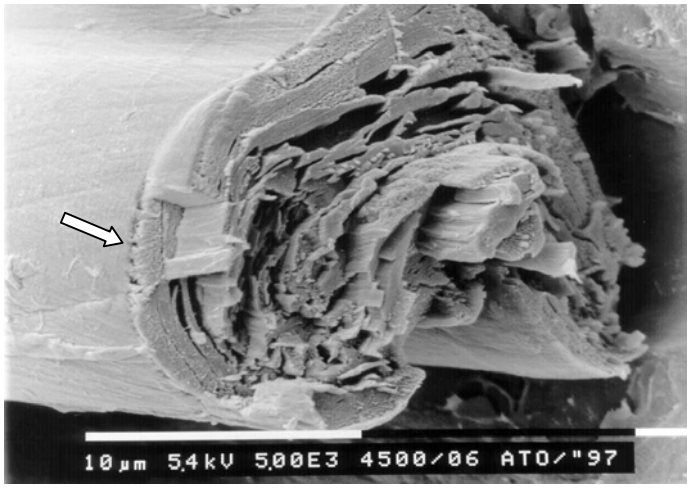



*Figure 3.16. SEM micrograph of a flax fibre fracture surface, showing the concentric layer-like structure in the secondary cell wall. Clearly visible is also the primary cell wall, marked by the arrow. The thickness of the primary cell wall at this location is approximately 0.3 µm .*

interfibrillar failure clearly has taken place within these deformed bands, the bands resemble a crack bridged by fibrils. The thickness of the bridging fibrils is approximately 0.1-0.3 µm. It is interesting to note in this respect that Eichhorn and Young [38] report an increased fibre strain in a fibre under tensile loading at the spot of a kink band.

As discussed, the secondary cell wall of elementary flax fibres has a composite-like structure. The SEM micrograph in figure 3.16 shows the cross section of a broken elementary fibre. It can be seen that the fibre has a more or less concentric layer-like structure. Furthermore, the thin primary cell wall -being the outer skin of the fibre- can be seen in this picture. The dimensions of the fibril conglomerates, which can be considered as the meso fibrils, is typically in between 0.2 and 1 µm.

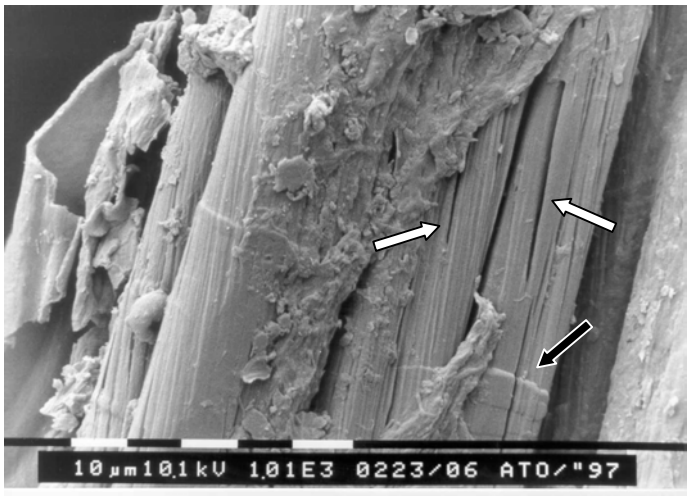



*Figure 3.17. SEM micrograph of a technical fibre after removal of the outer primary cell wall during a short soil burial period. Clearly visible is the fibrillar structure of the secondary cell wall. The white markers show the cracks running between the fibrils, the black marker shows a small kink band.*

Figure 3.17 shows a SEM micrograph from a technical fibre which has been buried in the soil during a number of days. The primary cell wall of this fibre has disappeared and the secondary cell wall of the elementary fibres with the fibrillar structure can be seen. The fibrils have the expected angle of 10° with the main fibre axis. Some longitudinal cracks are running between the fibrils (which are probably induced by fungi, during the

burial period [45]). The fibril thickness seen in the secondary cell wall is approximately 0.5 to 1 μm, somewhat larger than the thickness of the fibrils bridging the crack-like area in the CSLM micrograph (figure 3.15) and similar to the size of the meso fibrils in figure 3.16.

Williams et al. [46] give a model for the compressive failure of carbon fibres which also seems applicable to a first approximation to the mechanism of flax fibre failure under compressive loading. They depict the fibre as a stranded wire, in which the strands are slightly twisted. Since the wires have little lateral connection they buckle outwards under compressive strain. In flax fibres, the hemicelluloses that keep the fibrillar structure of the secondary cell wall together form relatively weak interphases. Under compressive loading the fibrillar structure of the secondary cell wall starts to buckle outwards, eventually causing the hemicellulose interphase to split. Apparently this is a very locally occurring process, the split zones appear to be restricted to small bands. Furthermore, the primary cell wall is not broken by this process.

For aramid (Kevlar) fibres -a rigid rod polymer fibre with a build that slightly resembles flax fibres- a similar phenomenon is reported by Dobb et al. [47]. They find microcracks aligned parallel to the polymer chain direction within the kink band after compression. They observe in the Transmission Electron Microscope (TEM) discrete shear band in which the chain direction changes abruptly compared to the adjacent fibre segments. Within each band the chains appear to be deformed through a constant angle. Since aramid polymers can be regarded as essentially rigid molecular chain polymers, compressive deformation cannot be accommodated by a gradual change in chain direction, but is expected to lead to permanent deformation. Consequently all chains within the kink band will be sheared with respect to each other. Since the TEM revealed microcracks aligned parallel to the chain direction within the kink band, they believe that the degree of shearing is non-uniform, leading to the complete separation of blocks of chains within the kink bands. Dobb et al. also investigated the effect of a tensile test on previously compressed fibres. They find two main features: firstly it appears that the displaced segments are capable of realignment along the direction of the applied force and secondly, that the fracture face is of limited axial extent and occurs within the kink band region. They find that the fracture face consists of parallel rows of lamellae, the length of which is defined by the boundaries of the kink bands. They believe the spacing of the lamellae to be associated with the presence of the microcracks in the kink bands. The fracture surface they show is very comparable to the fracture surface of the

flax fibre shown in figure 3.16. Also here a lamellar, layer-like, structure is found and the fracture face in flax fibres is always of limited extent, even though the microfibrillar structure within the secondary cell wall can be expected to be much longer. Dobb et al. find that for aramid the lamellar structure is parallel over the whole fracture face, for flax fibres the layer-like structure obviously is concentric, maybe caused by the specific built of the fibres or by the twist in the fibrillar structure. The similarity between the mechanism in aramid and flax fibres is furthermore supported by the fact that the dimensions of the fibrillar structure found in the CSLM, figure 3.15, are similar to the dimensions of the layer-like structure of figure 3.16

A closer look at figure 3.15 gives more insight in the way the kink bands grow. It is clearly visible that the crack-like areas are wider at the compression side of the sample and slowly diminish in width towards the tensile side. During bending of the fibre, all kink bands slowly grow penetrating into the width of the fibre. Once one of the kink band has grown over the full width of the fibre, the stiffness of the fibre locally drops to a large extent, leading to the non-linear deformation in the loop test.

McGarry and Moalli [48] have also investigated the compressive behaviour of Kevlar. They find that under axial compressive loading Kevlar fibres fail by buckling of fibrils located just beneath the outer surface where lateral constraint is minimal. They also find that a high modulus ceramic coating around the fibre can increase its compressive strength. It is likely that in flax fibres fracture is initiated in a similar way. The primary cell wall, however, will not have a very high modulus, and even though it does not fracture during the first stages of compressive deformation, it is not expected to contribute significantly to the compressive strength of the flax fibres.

It can be expected that in flax which has undergone the standard decortication, kink bands in a wide range of growth stage are present. It is possible that, although there are many kink bands present, none of them have grown over the full width of the fibre. This could explain why these fibres in the loop test have the expected shape with ($c/a$) of 1.34 and why the loop test gives little difference in the compressive strength for standard and hand decorticated fibres. It does, however, pose the question how standard decorticated fibres are going to behave in pure uniaxial compression, probably the fibres will have little resistance against uniaxial compressive deformation due to the damage they contain.

Even though the results of the loop test may not give a good indication of the behaviour of the fibres under uniaxial compression, the value of ca. 1200 MPa for compressive strength as obtained can be compared with data from other authors using the same test for other fibres. Peijs et al. [41] have measured compressive strength values with the loop test on various highly oriented crystalline polymers. They find a compressive strength of 180 MPa for gel-spun polyvinylalcohol, which is ca. 10% of the fibre´s tensile strength. For high-performance polyethylene fibres they quote a value for the compressive strength of ca. 60 MPa, which is only 2% of the fibre´s tensile strength. And finally, for aramid fibre (Twaron HM, Akzo) they find a compressive strength of 600 MPa, which is about 20% of the fibre´s tensile strength.
It is clear that compared to these oriented highly anisotropic polymer fibres the compressive strength of 1200 MPa measured in the loop test is unrealistically high. Furthermore, the ratio between tensile and compressive strength for flax -80% for the standard decorticated fibres- is much higher than for the high performance polymer fibres. However, the compressive failure initiation stress of 300 MPa is approximately 20% of the fibre's tensile strength and lies in the same range as the values found for the other anisotropic fibres. It is shown by DeTeresa et al. [42,43], amongst others, that the compressive strength of an anisotropic fibre is proportional to its shear modulus. The shear modulus of jute is estimated by Cichocki and Thomason [44] to be circa 3.5 GPa at room temperature, which is very low compared to the tensile modulus of the fibres, indicating a high fibre anisotropy. The low shear modulus consequently leads to a low compressive strength. If one now assumes the value of 300 MPa to be the true compressive strength, the question remains why the behaviour of the flax fibres in the loop test is different from that of the other polymeric fibres.

### *3.3.3. ESEM study on compressive behaviour*

In order to further investigate the behaviour of the fibres under loading, a study was performed in the environmental SEM. The deformation behaviour of the fibres was investigated in situ by straining a fibre containing a free loop closed with a single knot (see figure 3.18). Straining of both fibre ends causes the loop to tighten slowly, thereby inducing compressive deformation on the inner side and tensile deformation on the outer side of the fibre. Since the loop is closed with a single knot, it is a nearly perfect circle, indicating that the stresses on the fibre along the loop are constant. The

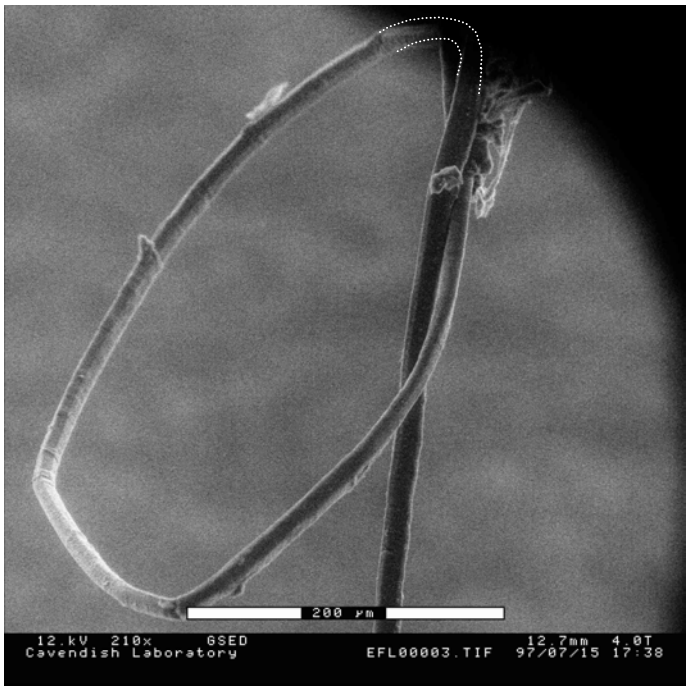



*Figure 3.18. ESEM micrograph of the geometry of the modified loop test.*

compressive stress on the inner side of the loop is approximately equal to the tensile stress on the outer side of the loop and can be written as:

$$\sigma_z = (\frac{E}{R}) z \tag{3.3}$$

with $\sigma_z$ representing both the compressive and tensile stresses on the inner and outer side of the looped fibre, $E$ the fibre modulus, which can again be taken as 50 GPa, $R$ the radius of the loop and $z$ the radius of the fibre. A fibre of a radius of 10 µm reaches its compressive yield stress of 1200 MPa at a loop radius of approximately 0.4 mm, which is exactly within the accessible range of the experiment.

Figure 3.19 shows a fibre which has just started to develop a kink band. From the curvature of the upper halve of the fibre, it can be estimated that the radius of this fibre loop is approximately 430 µm. This would correspond to a compressive strength of the fibre of approximately 1300 MPa, which is remarkably close to the value of 1200 MPa. Although this is of course a very rough estimate, it indicates that during the experiment

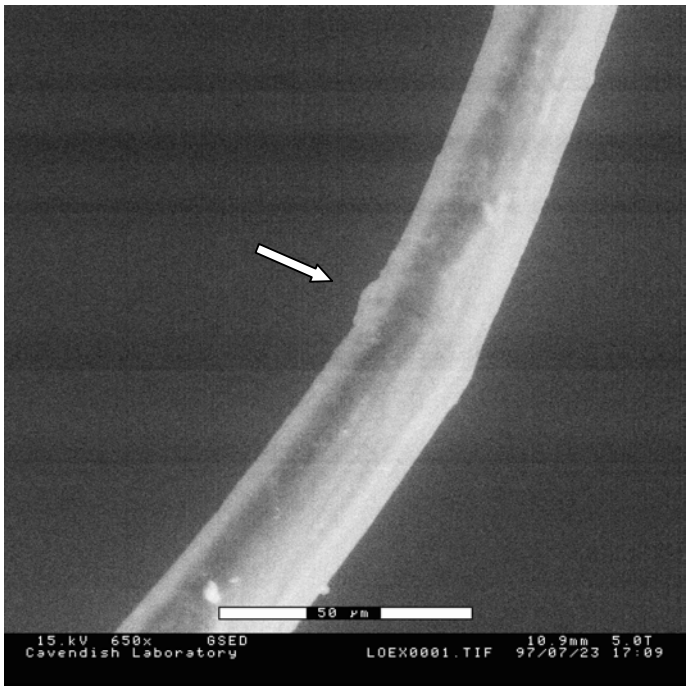



*Figure 3.19. ESEM micrograph of an elementary flax fibre which has just started to developed a kink band, marked by the arrow. Scale bar indicates 50 µm.*

in the ESEM the compressive behaviour of the fibre is expected to be comparable to its behaviour under experimental conditions outside the microscope.

Upon further straining the loop beyond the radius where the first kink band appears, the number of kink bands along the loop increases (as also shown in figure 3.15). The kink bands simultaneously become more pronounced (see also figure 3.14), up to the point where they show a strong outward buckling of the primary cell wall. However, the primary cell wall never shows actual fracture on the compression side, the deformation is of a plastic, and irreversible, nature. The deformation possibly taking place in the secondary cell wall is of course not visible in the ESEM, since it will occur beneath the visible surface.

Fracture of the primary cell wall is observed on the tensile side of a deforming kink band. Figures 3.20a to 3.20d clearly show the initiation and development of fracture of the fibre from figure 3.19 under progressive closing of the knotted loop. Just before

the primary cell wall of the fibre begins to tear, the curvature of the fibre on the tensile side is strongly increased, presumably due to failure in the secondary cell wall (not shown). A sharp crack then occurs perpendicular to the fibre axis (figure 3.20a). In figure 3.20b clearly both the primary and the secondary cell wall can be seen. At the

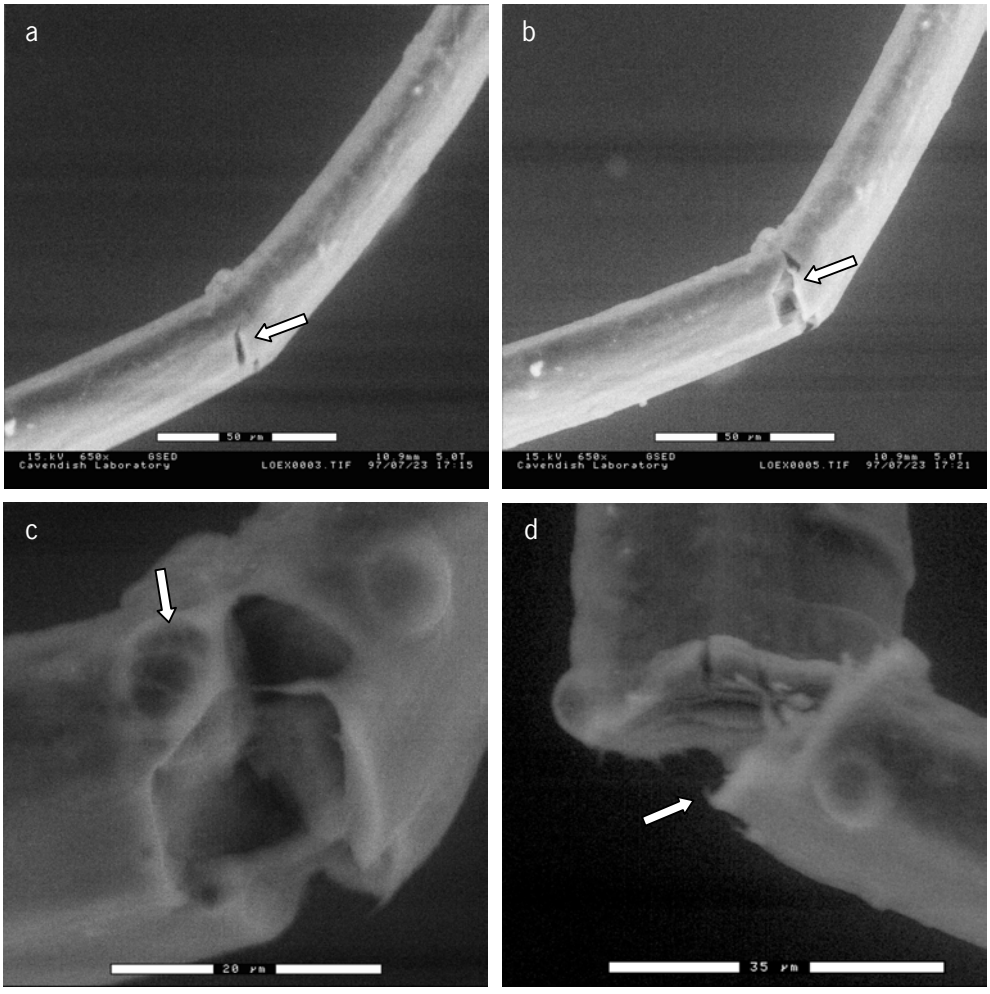



*Figure 3.20. Initiation and development of fracture in an elementary flax fibre. (a) Fracture initiates on the tensile side of the fibre. (b) Primary and secondary cell wall have separated. (c) Extended plastic deformation of the fibrils in the secondary cell wall (arrow). (d) The fibre just before complete failure, with some fibrils sticking out of the fracture surface (arrow).*

point where fracture has taken place, the primary cell wall appears to have separated from the secondary cell wall (indicated by the arrow).

Figure 3.20c gives a view inside the fibre in the deformed secondary cell wall. A fibrillated structure in the secondary cell wall is visible. The failure in the secondary cell wall bears little resemblance to the sharp crack which runs in the primary cell wall. The crack in the secondary cell wall is bridged by relatively thick fibrils. Further straining of the loop causes the primary cell wall to tear further, and the fibrils bridging the crack in the secondary cell wall show plastic drawing or fibre pull-out up to failure. Figure 3.20d is a micrograph taken just before the fibre failed. On the fracture surface some fibrils can be seen sticking out.

From this series of micrographs it is clear that the primary and the secondary cell wall show different mechanical behaviour, presumably as a consequence of the different chemical composition and morphology of both cell walls. The primary cell wall is mainly made up of amorphous pectins, which become brittle under dry conditions [49]. It is therefore not surprising that the crack growth in the primary cell wall is of a rather brittle nature.

The secondary cell wall however consists of circa 70% of crystalline cellulose. The fibrillar nature of the secondary cell wall has a large influence on its mechanical behaviour. As discussed in the previous section small cracks between the fibrils are expected to be formed due to the deformation process during kink band formation. It is likely that the holes which are visible in figure 3.20c originate from these cracks, which have widened during increased bending of the fibre. There is of course interaction between the fibrils in the secondary cell wall: the amorphous hemicelluloses form the glue that keeps the fibrils together. However, the hemicelluloses, like the pectins are expected to become brittle under dry conditions [49]. The hemicelluloses will fail due to the shear stresses induced by the kink band formation under compressive strain. Since the fibrils themselves will not fail under compression, the resulting structure will be a crack bridged by coarse fibrils, as seen in figure 3.20c and similar to the structure found with the CSLM (figure 3.15).

For the fibres studied here it is again likely that part of the damage in the secondary cell wall already exists at the beginning of the test. Moreover, the fact that figure 3.20a shows an increased curvature on the tensile side, which develops rather early during the deformation of the fibre, indicates that the secondary cell wall structure of the fibre at this spot was already damaged before the test. Since no damage was seen in the

primary cell wall, it can then be concluded that the primary cell wall could serve to keep the fibre together, even though the secondary cell wall might already be badly damaged. It is therefore also likely that the secondary cell wall of finely hackled flax fibres, which have undergone a rather severe mechanical decortication and combing procedure, is actually full of damaged zones like these. A more careful way of isolating the fibres might then improve both the tensile and the compressive strength of the elementary flax fibre, which would be of interest for the potential use of these fibres in structural composite materials.

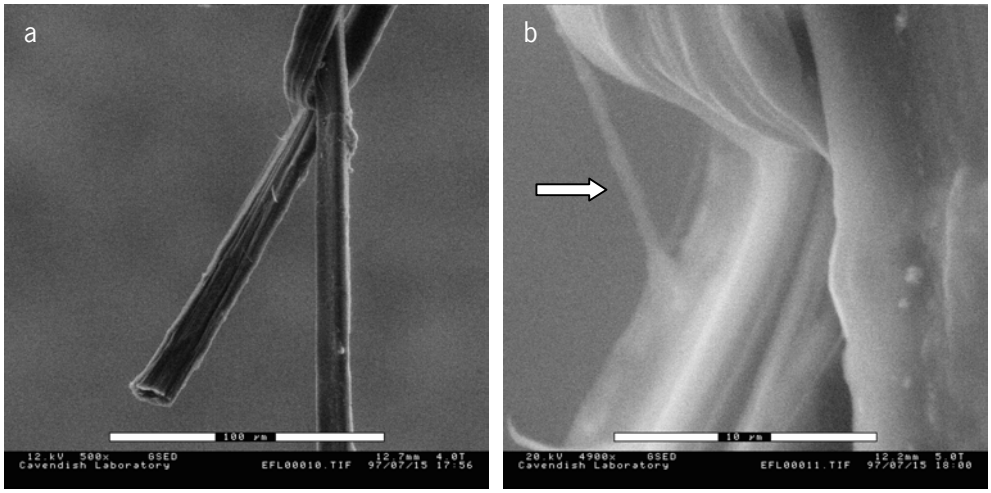



*Figure 3.21. Fibre separating in the secondary cell wall due to tightening of the loop. (a) Overview, the loop is visible in the upper right of the micrograph. (b) Magnification of the crack front, with one fibril bridging the crack (marker).*

The anisotropy of the fibre is nicely illustrated in figures 3.21a and 3.21b. This fibre has failed on the tension side as in the previous example. However, further tightening of the loop has at some point caused the crack to deviate along the direction of the fibre axis, splitting the fibre in two halves. Clearly visible on the fracture surface now is the fibrillar structure of the secondary cell wall, with the fibrils at a slight positive angle to the fibre axis. The apparent ease at which part of the fibre is stripped off over a large length indicates again that the lateral strength of the fibre is lower than the tensile strength in the length direction. McGarry and Moalli [50] find similar behaviour in Kevlar and other rigid rod fibres. They also find that these fibres have a low transverse

strength, compared with their tensile strength. The lower transverse strength is also indicated by the fact that the crack stays within the same layer; it does not cross the fibrils. The crack front in figure 3.21b shows that there is little tendency to micro fibril bridging once the direction of crack growth has changed to the length direction of the fibre. These results indicate that once a crack is running in the length direction of the fibre it will easily split the fibre over its entire length. In flax reinforced composites this could lead to a preferred direction of crack growth. Furthermore, in a composite with optimised fibre/matrix bonding, splitting of the fibre over its length might prove to be the dominant failure mechanism. Further composite strength optimisation can then only be reached by improving the strength of the hemicellulose bonding between the microfibrils in the secondary cell wall.

Apart from the difference between longitudinal and transverse strength, also the other mechanical properties of the fibres are expected to differ strongly between the longitudinal and the transverse direction. For flax fibres, to the best of the author's knowledge, no data are available, but Cichocki and Thomason [44] have investigated these differences for jute fibres. They find, among other things, a difference in longitudinal and transverse Young's modulus at 25 °C of a factor of 7, and consequently also a very low shear modulus. Also, as expected, the thermal expansion coefficients are found to be very different in longitudinal and transverse direction. Since the build of jute fibres is similar to the build of flax fibres, it is not unlikely that for flax the differences in properties in longitudinal and transverse direction will be of a similar magnitude. The low compressive strength of the fibres is obviously related to the fibre's anisotropy and the low shear modulus [42,43]. Under compressive loading, the fibre will deform more easily in lateral direction than in length direction, leading to the formation of kink bands and thus premature failure, not only during the decortication process, but also when the fibre is applied in a composite as described in Chapter 4.

The fracture surfaces in figure 3.21 show that at this depth in the fibre all fibrils are oriented in the same direction, the angle is approximately 10° off the fibre long axis. In the literature there is still some confusion regarding the actual structure of the secondary cell wall of flax. Herzog [2] has described the secondary cell wall as at least a two layered fibrillated structure with a change in fibril direction from +10° to –5° relatively close to the fibre surface. Mark [51] describes the cell wall as a three layered structure with winding angles of –30°, 6.5° and –30° for three fibril layers with

thicknesses of respectively 1.2, 5 and 0.5 μm. Davies and Bruce [52] use the same fibre model in their calculation of the mechanical response of flax fibres. The micrographs shown here, however, indicate no change in fibril direction close to the surface and a main fibril direction of 10° down to a depth of approximately 4.5 μm into the secondary cell wall. The descriptions of the secondary cell wall of flax of both Herzog [2] and Mark [51] therefore seem to be incorrect. On the basis of the micrographs of figure 3.21 no conclusions can be drawn with respect to any change in fibril direction deeper into the secondary cell wall.

## 3.4 Conclusions

Tensile properties of flax fibres depend bi-linearly on the clamping length, due to the composite-like structure of technical flax fibres. This could be one of the underlying reasons for the enormous scatter in flax fibre tensile strengths reported in literature. Single elementary flax fibres have considerably higher strengths than technical fibres. The elementary fibre strength was found to depend also on the defects introduced into the fibre through the decortication method. Compressive strength of elementary flax fibres as measured in the loop test is approximately 80% of their tensile strength, this ratio is very high compared to other anisotropic fibres. Due to the fibrillar structure of the secondary cell wall of the elementary fibres they fail in compression due to kink band formation. Since the primary cell wall of the fibres is only slightly affected by the kink band formation, it is difficult to predict the extent of fibre damage by just examining the fibre surface.

The compressive behaviour of a lignocellulosic fibre like flax can very well be studied in situ in an Environmental SEM. The modified loop test, in which the loop is closed with a single knot, allows the study of compressive and tensile deformation on respectively the inner and outer side of the loop. The difference in chemical composition and morphology of the two cell walls that form the flax fibre gives rise to differences in deformation behaviour. Failure of the primary cell wall is brittle and takes place on the tension rather than the compression side of the fibre loop. Failure of the secondary cell wall under compressive loading takes place in the lateral direction due to its highly oriented crystalline nature. Cracks bridged by coarse fibrils are formed in the secondary cell wall before the primary cell wall fails. The strength of elementary flax fibres in the lateral direction is lower than in the fibre direction. For application of flax

fibres in structural composites this is a fact which should be taken into account, as this may initiate premature failure.

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# 4

# UD Flax Epoxy Composites

## 4.1 Introduction*

Unidirectional glass fibre reinforced composites are often used in high load bearing constructions, like wind turbine blades and foot bridges. However, due to the high price of unidirectional (UD) flax fibres and flax fibre wovens not much research is done on the optimisation of UD flax fibre reinforced materials. As a model system, however, they are sometimes investigated for comparison with other data.
Composite tensile strength, $\sigma_c$, of UD materials often follows the rule of mixtures:

$$\sigma_c = V_f \, \sigma_f + (1 - V_f) \, \sigma_{um} \tag{4.1}$$

where $\sigma_f$ is the fibre tensile strength, $\sigma_{um}$ is the matrix strength at the fibre failure strain, assumed to be equal to $E_m * \sigma_f / E_f$ -with $E_m$ the matrix modulus and $E_f$ the fibre

*This chapter is based on the paper:

- Compressive behaviour of unidirectional flax fibre reinforced composites; H.L. Bos, K. Molenveld, W. Teunissen, A.M. van Wingerde and D.R.V. van Delft, *J. Mater. Sci.* **38** (2004) 2159

modulus- and $V_f$ is the fibre volume fraction. Figure 4.1 gives the tensile strength of pultruded UD flax/unsaturated polyester (UP) composites as measured at ATO bv [53]. The line represents the rule of mixtures, assuming $\sigma_f$ = 810 MPa, $E_f$ = 50 GPa and $E_m$ = 3.5 GPa. Heijenrath et al. [54] report a tensile strength of a 50 vol% flax/epoxy UD composite of 325 MPa, which is still reasonably good but lower than the value of 433 MPa which can be extrapolated for 50 vol% flax/UP composites from the data in figure 4.1. Van de Weyenberg et al. [55] find a tensile strength for 40 vol% UD carded scutched tow in epoxy of circa 150 MPa, which is relatively low. However, they prepare the composites from epoxy films and not by pultrusion. Furthermore, they also find an effect of the various decortication methods on the longitudinal strength of the composites. Similarly, the tensile modulus also usually follows the rule of mixtures.

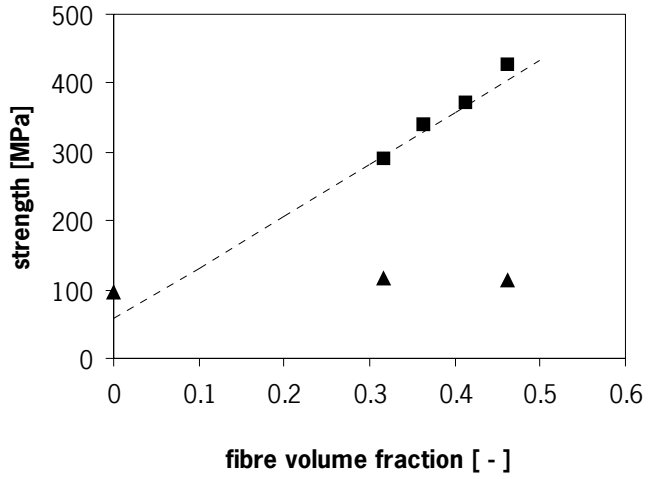



*Figure 4.1. Strength of UD flax/UP composites. ■ Tensile strength, ▲ compressive strength [53]. The line gives the rule of mixtures, for fibre strength 810 MPa, fibre modulus 50 GPa and matrix modulus 3.5 GPa.*

Given the sensitivity of the flax fibres towards kink band formation (see also Chapter 3), the compressive properties of UD composites are expected to be rather poor. This can be seen from figure 4.1 which also shows the compressive strength of the UD flax/UP composites, the compressive strength is unchanged by the addition of the fibres. Also Heijenrath et al. [54] report a very low compressive strength of 92 MPa for the 50 vol% flax/epoxy composite.

Whereas for unsaturated polyester good adhesion between the fibre and the matrix may not be automatically achieved, it is often assumed that epoxy resins would adhere well to ligno-cellulosic fibres. George et al. [56], however, report a slight increase in mechanical properties of random flax/epoxy composites by the use of a variety of treatments, a fibre treatment with 3-aminopropyltriethoxysilane resulting in an increase of the tensile strength from 53 MPa to 63 MPa and an increase in tensile modulus from 7.9 GPa to 9.8 GPa. This indicates that a good bonding between flax and epoxy is maybe not so straightforward after all.

As discussed in Chapter 3 the surface of flax fibres is by nature covered with a thin layer of waxes, which strongly reduces the accessibility of the reactive hydroxyl groups of the pectin and cellulose components on the fibre surface. Removing the wax layer changes the hydrophilicity of the surface [57] and will increase the reactivity of the fibre surface towards various substances by making the hydroxyl groups of the pectins and celluloses on the surface accessible.

Epoxies can normally easily react with hydroxyl groups. However, reaction of the hydroxyl groups on the fibre surface with the epoxy resin might be hampered by their spatial positions. Many of the hydroxyl groups in the cellulose crystals are known to form inter- and intracrystalline hydrogen bridges [58] which reduces their reactivity. Furthermore, a large part of the accessible hydroxyl groups are probably located on the pectins and hemicelluloses, and the strength of the adhesion between the pectins and hemicelluloses and the cellulose crystals is unknown. To improve the reactivity of the fibres towards the resin a modification step with maleic anhydride (MA) can be carried out. Maleic anhydride is known to be reactive towards the surface of cellulose fibres [59]. This fact is frequently used in the compatibilisation of flax/PP composites, where maleic anhydride modified PP (MAPP) can be very effective to improve composite strength [59,60]. At elevated temperatures maleic anhydride can form an ester bond with a hydroxyl group of the fibre surface [61], creating a free hydroxyl group protruding from the surface which is better accessible than the surface hydroxyl groups and which can subsequently react with the epoxy resin. Therefore, maleic anhydride is expected to increase the adhesion between fibres and matrix, but it is not expected to stabilise the kink bands present in the flax fibre structure.

In order to stabilise the kink bands which are present in the fibres as a result of the decortication process, a component would be needed that is actually able to penetrate into the fibre and fill the gaps between the fibrils in the kink band (see also Chapter 3).

It is known from work done by Rapp et al. [62] that modified melamine formaldehyde resin is able to penetrate into the cell wall of a number of wood species. It is therefore not unlikely that melamine formaldehyde (MF) resin is also able to penetrate into the cell wall of flax fibres. Rapp et al. [62] show that concentration of melamine resin in the cell wall of *Picea abies* sapwood can become as high as 20 to 30% after soaking in a dilute resin solution in water. High values like these would in the case of flax fibres certainly be sufficient to fill the hole-like defects in the kink bands and stabilise the fibres under compression. Furthermore it is possible that the melamine resin not only fills the holes in the cell wall but also diffuses in between and into the cellulose fibrils in the secondary cell wall and so internally crosslinks the fibre, forming covalent bonds in and between the fibrils.

This chapter investigates options for the optimisation of the compressive properties of UD reinforced flax fibre/epoxy composites. In order to improve the compressive properties of UD flax fibre reinforced epoxy composites, both the adhesion between fibre and matrix and the stabilisation of the kink bands are addressed.

## 4.2 Experimental

### *4.2.1 Materials*

Flax (JS-33-1995, Cebeco, NL) was warm water retted on pilot scale and decorticated via breaking, scutching and hackling. Standard E-glass roving with epoxy sizing was kindly supplied by Aerpac. Standard viscose 'Cudenka 700 yarn' was kindly supplied by AKZO-NOBEL. This yarn contains a twist. Epoxy Ampreg 20 from SP Systems with ultraslow harder, 100:30 (w/w) was kindly supplied by Aerpac. Maleic anhydride (MA) was purchased from Merck. MF resin Madurit MW909 was kindly supplied by DSM.

### *4.2.2 Methods*

Dewaxing was performed via an extraction in duplo using boiling ethanol during 3 hours, a method which is known to remove the waxy substances but not the pectins from the surface [57].

Modification with MA was performed in the gas phase. MA was heated up to 100 °C and flax fibres were held in the MA vapour during one hour. During this process the MA sublimates on the fibre and reacts with the available hydroxyl groups. The modified

fibres were dried during 2 days at 50 °C during which the non-reacted MA evaporates [63]. The percentage of MA on the fibres was determined by saponification and subsequent HPLC and was found to be 0.29 wt% of the total fibre weight.
Treatment of the fibres with epoxy resin or MF was standard performed according to the following procedure: epoxy resin was dissolved in methanol, MF was dissolved in water. The flax bundles were soaked in the solution during 10 minutes at room temperature and dried overnight at 70 °C. The percentage resin on and in the fibres was determined by weighing.
To investigate the influence of the MF treatment procedure the standard treatment was adjusted: the time of soaking the fibres in the MF solution was varied to 5 minutes and to 1 hour; the temperature at which the fibres were impregnated was increased to 70 °C; some of the fibres were pre-swelled in water during 3 hours to make them more accessible to the MF solution.

### *4.2.3 Sample preparation*

UD composite samples were prepared at room temperature via pultrusion on a lab scale set-up. The fibres were combed and cut to the appropriate length and bundles of the desired weight were prepared. The bundles were dried, soaked in the epoxy resin and pulled into the pultrusion mould by hand. A cylindrical mould of 6 mm diameter and two different rectangular moulds of 10 by 4 $mm^2$ and 10 by 2 $mm^2$ were used. The samples were precured overnight at 35 °C in a vacuum oven and subsequently cured overnight at 70 °C. Due to the nature of the flax fibres, not all fibres in a sample lie fully in the length direction of the sample, some of the fibres show a deviation from the length axis of a few degrees.
Samples for interlaminar shear strength (ILSS) and compression tests contain 50 wt% of fibre, samples for tensile tests contain 30 wt% of fibre.
Samples for the determination of the compressive strength of the pure epoxy resin were made by pouring the fluid resin in the pultrusion mould which was closed on the bottom by a rubber stopper. The same curing cycle was used as for the pultruded composites.

### *4.2.4 Materials testing*

Compression strength tests were performed on cylindrical samples with a length of 25 mm and a diameter of 6 mm, following ISO 3597-3: 1993(E) at a testing speed of

1 mm/min. At least four samples were tested per material. The fibres were oriented in the length direction. The tests were performed on a Zwick 1445 universal tester.
The modulus in compression was measured on samples of length 30 mm and diameter 6 mm, using three strain gauges for each sample all applied in length direction at 0°, 120° and 240° around the fibre. The modulus values are only indicative since only one sample per material was tested with strain gauges. The tests were performed on a 100 kN Schenk universal testing machine. The samples are longer than the compressive strength samples in order to fit with the strain gauges in the testing machine.
ILSS values were determined on samples with dimensions 25*10*4 $mm^3$ following ISO 4585:1989(E), at a span length of 20 mm and a testing speed of 1 mm/min on a Zwick 1445 universal tester. At least three samples were tested.
Fibre bundle strength was measured in tenfold using a stelometer (Spinlab AG) following ISO 3060:1974 with a clamp length of 3.2 mm, a clamp length which yields data relevant to the fracture behaviour of flax fibres in composite materials (see also Chapters 3 and 6). Bundle strength of the MF impregnated fibres was measured in fivefold following the same procedure.
Tensile tests were performed in fivefold on samples of 150*10*2 $mm^3$ at a testing speed of 1 mm/min (Young's modulus) and 10 mm/min (tensile strength) following ISO R527-3:1994. To prevent failure in the clamps, aluminium tabs were glued onto the samples with epoxy glue (Araldite SW404).
SEM micrographs were made on a JEOL JSM-5600LV scanning electron microscope. EDAX measurements were performed on a Cambridge Instruments Stereoscan 240 with a digital detector from Princeton Gamma-Tech with EDX. The materials were coated with carbon. Measurements were performed at 20 kV at approximately 10.000 counts per second. The total chemical composition was determined.

## 4.3 Results and discussion

### *4.3.1 The effect of improved adhesion*

Table 4.1 lists the tensile strength, $\sigma_{tens}$, and modulus, $E_{tens}$, of the fibres and the compressive strength, $\sigma_{comp}$, and modulus, $E_{comp}$, and the ILSS of samples containing 50 wt% of fibres, which have not undergone any surface modification. Apart from glass fibres also viscose yarn is taken as a reference material, since viscose consists almost completely of cellulose and therefore is expected to have similar reactive surface

*Table 4.1. Fibre and epoxy resin tensile strength and tensile modulus, and ILSS and compressive strength and modulus of unmodified composites.*

| | $\sigma_{tens}$ [MPa] | $E_{tens}$ [GPa] | ILSS [MPa] | $\sigma_{comp}$ [MPa] | $E_{comp}$ [GPa] |
|---|---|---|---|---|---|
| Flax | 911 ± 192 | 50† | | | |
| Viscose | 770* | | | | |
| Glass | 2600* | 73* | | | |
| Epoxy | 14.5 ± 0.6 | 2727 ± 238 | | 82 ± 7 | |
| Flax/Epoxy | | | 15.4 ± 0.4 | 119 ± 2 | 30‡ |
| Viscose/Epoxy | | | 39.6 ± 0.6 | | |
| Glass/Epoxy | | | 65.4 ± 2.2 | 595 ± 81 | 33‡ |

*Values according to the specifications of the producer. † See Chapter 3. ‡ Indicative value since only one sample was measured with strain gauges.

groups as flax fibres. The ILSS is taken as a measure for the adhesion between fibres and matrix.

It is clear that the compressive strength of the flax samples is rather low, only slightly higher than the compressive strength of the epoxy resin itself, which was found to be 82 ± 7 MPa. The compressive strength of the flax filled composites is only 20% of that of the glass filled materials. On the other hand, it can be seen that the compressive stiffness of both the glass filled and the flax filled epoxy is similar and moreover, is approximately what can be expected on the basis of the rule of mixtures [64]. The ILSS of the flax composite is only 25% of that of the glass composite whereas the ILSS of the viscose composite is circa 2.5 times as high as the ILSS of the flax composite.

The good compressive modulus of the flax/epoxy composites indicates that at small strains the presence of the kink bands from the decortication process does not yet interfere strongly with the deformation process. The flax composites show a compressive stiffness which is in accordance with the rule of mixtures. These results are in contrast to the results of Lamy and Pomel [65], who find a very low modulus in bending for UD flax/epoxy composites and who show that this is due to the presence of kink bands and other fibre defects.

Comparison of the ILSS of the viscose and the flax composite supports the assumption that without removal of the wax layer, adhesion between the flax fibres and epoxy is not

*Table 4.2. ILSS and compressive strength of flax/epoxy and viscose/epoxy composites with different surface modifications.*

| Modification | ILSS [MPa] | | $\sigma_{comp}$ [MPa] | |
|---|---|---|---|---|
| | Flax | Viscose | Flax | Viscose |
| None | 15.4 ± 0.4 | 39.6 ± 0.6 | 119 ± 2 | |
| Dewaxing | 25.4 ± 0.5 | 37.8 ± 0.9 | 137 ± 13 | 151 ± 5 |
| MA | 16.7 ± 1.0 | | 141 ± 13 | 142 ± 8 |
| Dewaxing + MA | 26.7 ± 0.5 | 42.1 ± 2.2 | 133 ± 13 | |
| Epoxy | 13.6 ± 0.7 | 40.8 ± 1.6 | | |

automatically achieved, and thus that flax fibres might not readily react with the epoxy resin.

Table 4.2 shows the effect of various fibre modifications on the ILSS and compressive strength of flax- and viscose/epoxy composites. Removal of the wax layer by ethanol extraction leads for flax composites to a significant increase in the ILSS from 15.4 MPa to 25.4 MPa. As expected ethanol extraction has no significant effect on the ILSS of the viscose composite. Modification of the surface of flax with MA without removal of the wax layer does not significantly increase the ILSS of the flax composite (table 4.2). The wax layer apparently also prevents reaction of the hydroxyl groups on the fibre surface with a small molecule like MA, possibly the MA molecules are adhered to a layer of non-cellulosic material (maybe the waxes) that is not bonded strongly to the rest of the fibre. Also pretreating the fibres with a solution of epoxy does not lead to additional adhesion as long as the wax layer is present. Removal of the wax layer and subsequent modification of the surface with MA leads to an ILSS value of 26.7 MPa, which is similar to the ILSS value found for flax composites which have only the wax layer removed and are reacted directly with the epoxy resin. Apparently, contrary to the assumption, once the wax layer is removed the surface of the flax fibres is sufficiently reactive towards the epoxy resin and does not benefit additionally by the introduction of a reactive group like MA. The same effect is seen for the viscose composite, modification with MA does not lead to a significant increase in the ILSS.

These results are similar to the results of van de Velde and Kiekens [66], who report an increase of the ILSS in a UD flax/PP system from circa 10 MPa to circa 24 MPa upon

the addition of a compatibiliser, in this case MAPP. Also van de Weyenberg et al. [55] investigated the effect of various treatments on the properties of flax/epoxy composites. They find that a treatment with acetone, which removes waxes and pectins, an alkali treatment, which removes pectins, and also impregnation with epoxy increase the longitudinal strength and stiffness. Similar to our results they find the best effect when these treatments are combined. Apart from the longitudinal properties they also report a strong increase in the transverse strength for any treatment, indicating that all these treatments improve the adhesion between the fibres and the resin.

The influence of the surface modifications on the compressive strength of flax composites does not follow the same trends as the ILSS (table 4.2). All three treatments dewaxing, MA modification and dewaxing combined with MA modification, lead to a small increase in compressive strength of the composite. It is not clear why the MA modification, which does not influence the ILSS, does result in a composite with a higher compressive strength. It is, however, obvious that the increase acquired in adhesion between the flax fibres and the matrix with the three treatments, has only a limited effect on the strength of the composite in compression. For the viscose composite, as with the flax composites, both dewaxing and modification with MA leads to a similar compressive strength.

Madhukar and Drzal [67] found for carbon fibre/epoxy composites that their compressive strength is very sensitive to the interfacial shear strength between fibres and matrix. They find an increase in compressive strength from 707 MPa to 1196 MPa, a jump of 70%, going from a system with poor adhesion (interfacial shear strength $\tau$ = 37.2 MPa) to a system with good adhesion ($\tau$ = 81.4 MPa). For the flax reinforced composites, the relation between interfacial adhesion and compressive strength is apparently weaker. This difference could be caused by the kink bands in the flax fibres, which make the fibres themselves very sensitive to compressive failure, in a way they already have failed. The pre-existing kink bands in the fibres will simply collapse under compressive loading and better adhesion between fibre and matrix cannot stop this process. The only way to overcome this is by stabilising the kinkbands, for instance by the impregnation with MF resin.

### *4.3.2. Stabilisation of the kink bands*

Table 4.3 shows the effect of the modification of the fibres with MF resin on the ILSS and the compressive stiffness of flax- and viscose/epoxy composites. Also the

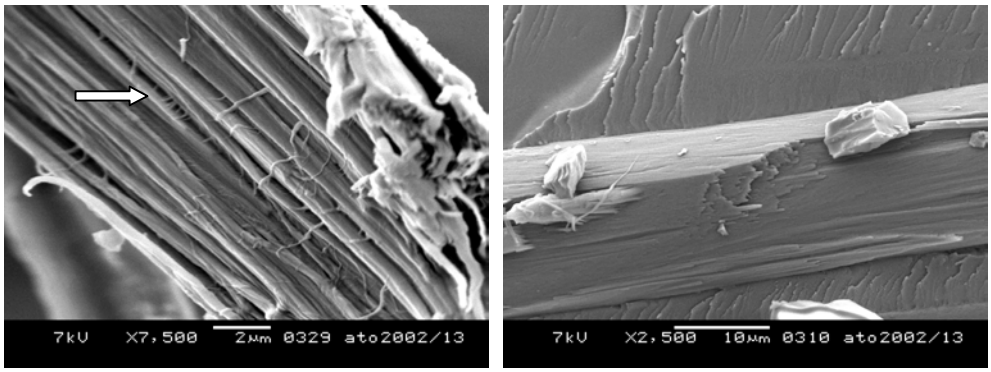
*Table 4.3. ILSS and compressive strength for composites treated with different MF concentrations.*

| Fibre | Concentration MF solution [%] | ILSS [MPa] | $\sigma_{comp}$ [MPa] |
|---|---|---|---|
| Flax | 10 | 19.7 ± 0.8 | |
| Dewaxed flax | 10 | 30.5 ± 0.7 | 250 ± 13 |
| | 20 | 27.9 ± 0.7 | 307 ± 21 |
| Viscose | 10 | 39.5 ± 1.6 | 220 ± 14 |
| | 20 | 33.7 ± 0.4 | 289 ± 9 |

influence of the concentration of the MF resin used for the impregnation is shown.
It is clear that application of MF resin (10% solution) on the flax fibres slightly increases the ILSS from 15.4 MPa to 19.7 MPa, even though the wax layer has not been removed. The combination of dewaxing and MF application leads to an increase of the ILSS to 30.5 MPa, which is double the value found for uncompatibilised systems. Obviously, MF increases the adhesion in flax epoxy composites to a large extent. Again, the modification has no effect on the ILSS in the viscose composites.
Applying MF resin to dewaxed flax fibres more than doubles the compressive strength of the flax composite towards a value of 250 MPa. It is interesting to note that the compressive strength of the flax fibre reinforced composites is now higher than that of the viscose reinforced composite even though the viscose composite shows a higher ILSS value.
The compressive strength of the composite, $\sigma_{comp}$, in the case of fibre crushing or fibre yielding is, in first approximation, governed by the rule of mixtures and can thus be written as:

$$\sigma_{comp} = V_f \, \sigma_{fcomp} + (1 - V_f) \, \sigma_{my} \tag{4.2}$$

with $V_f$ the fibre volume fraction, $\sigma_{fcomp}$ the compressive strength of the fibre and $\sigma_{my}$ the yield strength of the matrix. Assuming $\sigma_{fcomp}$ is 300 MPa -the stress at which in the loop test the first deformation is visible (Chapter 3)-, and $\sigma_{my}$ is 82 MPa, the measured compressive strength of the matrix, a compressive strength of the composite of 191 MPa can be calculated. This is higher than the compressive strength of the composite with improved adhesion, but lower than the composite system with MF resin.




a b

*Figure 4.2. SEM micrographs of flax fibres split in length direction. (a) Secondary cell wall of untreated fibre. (b) Flax fibre impregnated with MF.*

It is clear from these results that application of the MF resin leads to an additional effect above just the improvement of adhesion.

The effect that the MF impregnation has on the internal structure of the fibres is shown in figure 4.2. Both figure 4.2a and figure 4.2b show a fibre which is split in length direction. The fibre in figure 4.2b is impregnated with MF and the fibre in figure 4.2a is standard flax. Even though the micrographs have a different scale it is clearly visible that in non-impregnated flax a lot of damage along the fibrils in the secondary cell wall is present, the fibrils are at some places separated over considerable lengths (arrow). In impregnated flax the fibrils seem to have been glued together quite effectively and the fracture surface is rather smooth, even though the underlying fibrillar structure can still be made out. It can therefore be concluded that MF resin indeed fully diffuses into the fibres and is able to form bonds between the fibrils in the secondary cell wall. Additional support for this view can be found in figure 4.3, which shows two SEM-EDAX plots taken carefully inside a fibre in two different flax filled epoxy composites, one with untreated flax fibres (Figure 4.3a) and one with MF treated flax fibres (Figure 4.3b). It is expected that the nitrogen which is present in the MF resin (the chemical composition of melamine is $C_3N_6H_6$) and not in the flax fibres, will give a peak in the EDAX plot. Even though the plots are taken too close to the limit of the detector, and in spite of the abundant carbon signal, there is evidence of the presence of nitrogen in the EDAX plot of the treated fibre, indicating that the melamine resin has penetrated into the fibre.

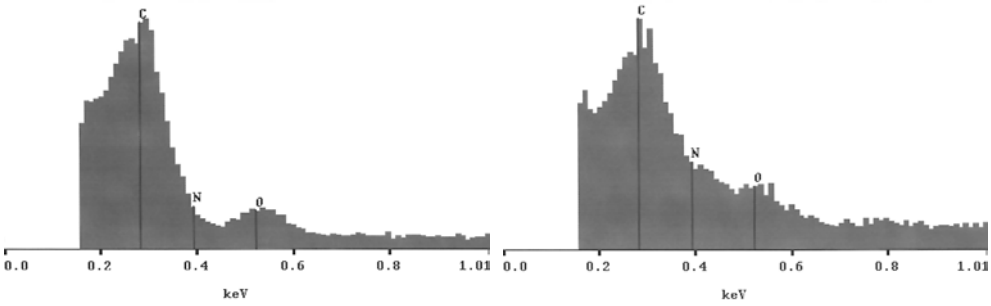



*Figure 4.3. SEM-EDAX spectrum taken inside a fibre in an epoxy matrix. (a) Non-treated fibre. (b) MF-treated fibre. The vertical axis gives the number of counts.*

Another micrograph is shown in figure 4.4. This fibre is impregnated with MF and subsequently broken in tension. Nicely visible is the internal structure of the fibre with a size of circa 0.2 µm (figure 4.4b). An interesting feature is pointed at by the arrow (figure 4.4a and 4.4c). This lump of material does not have the fine structure that the rest of the fibre has, indicating that it might be the MF resin. Moreover the shape of this lump is similar to the shape of the kink bands as reported in Chapter 3, a crack bridged by fibrils, with the exception that this is a 'negative' picture of the kink band. It might be that this is actually the MF resin that has filled the holes in a kink band in the fibre, and has cured in this shape.

Based on these results, it can be concluded that the resin inside the fibre is able to stabilise the flax fibrils under compressive loading. The fact that MF also appears to be able to stabilise the viscose composite might be caused by the twist present in the viscose yarn. Supposing that MF also penetrates into the viscose, internal cross-linking of the viscose yarn will stabilise the twist and also protect this fibre against too readily deforming in compression.

The treatments also strongly influence the failure mechanisms occurring during the ILSS and compression tests. Generally, it can be stated that with increasing ILSS, and therefore increasing adhesion, the failure mechanism gradually changes from multiple shear to single shear. Samples with a low compressive strength show progressive development of failure, whereas the samples with a high compressive strength break

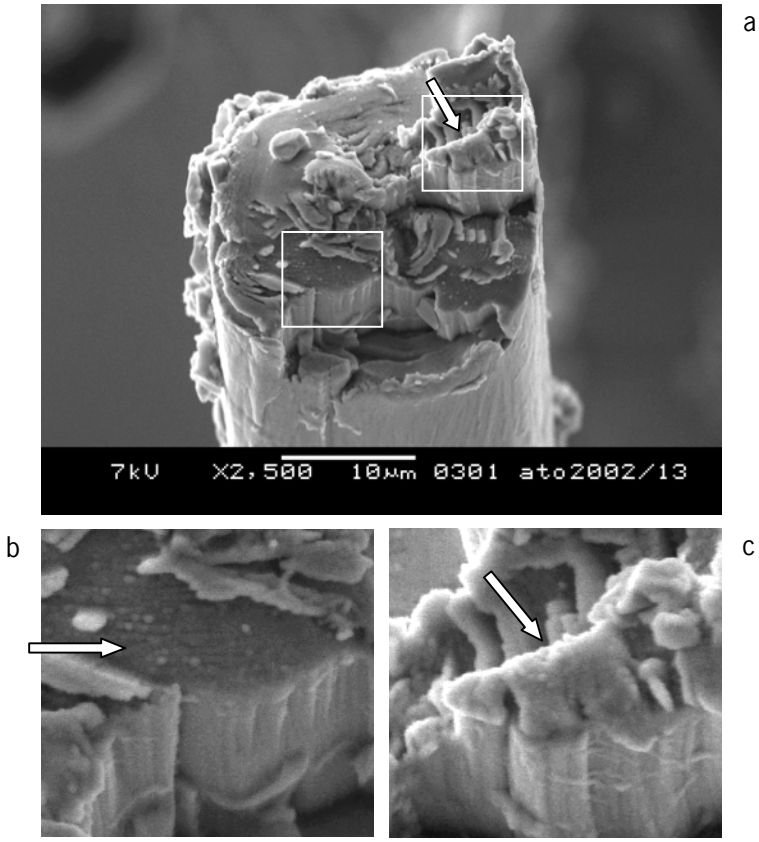



*Figure 4.4. SEM micrograph of a fibre impregnated with MF, fractured in tension. (a) The arrow points at the structure that may be the remains of a kink band. (b and c) Magnification (150%) of the areas in the white boxes in the upper micropraph. (b) Arrow points at the fine structure in the material. (c) Arrow points at the lump without the fine structure.*

instantaneously in the ILSS test as well as in the compression test. This effect is not only brought about by the impregnation with MF but also by the increase in adhesion due to the MA treatment, so it appears to be governed by the increase in adhesion rather than the increase in internal fibre stability due to the MF impregnation step. Delamination in combination with fibre kinking could well be responsible for the progressive failure observed by the materials with low compressive strength. Bazhenov et al. [68] amongst others showed that in aramid fibre composites compressive failure is caused by compressive failure of the fibres themselves. Since the highly oriented

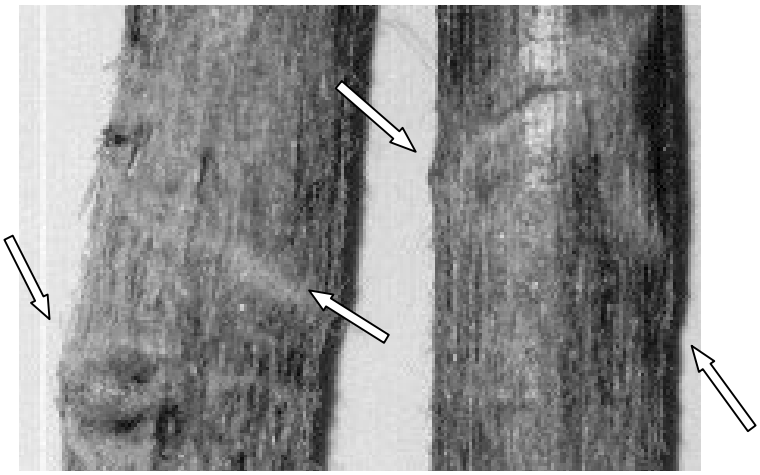


*Figure 4.5. Compression tested bars (6 mm diameter) of untreated flax epoxy composites. The thickening on both sides of the bars (arrows) points at the appearance of large scale delamination during the test.*

morphology of aramid is more or less comparable with flax fibres, it can be expected that flax composites also fail due to failure of the fibres. Bazhenov et al. furthermore find that the rule of mixtures indeed correctly describes the failure strength of aramid composites. In figure 4.5 test bars of untreated flax epoxy composites are shown. In these bars there is no sideways shift of the material above and below the deformation band, but rather a symmetric thickening at the point of deformation. This points at fibre failure, probably by kink band formation, and subsequent delamination as the mechanism of failure.

Figure 4.6 shows two SEM micrographs of a deformation band in a sample of MF treated flax epoxy. This is the surface of the sample, so these fibres were deformed with little lateral constraint. Nevertheless it can be concluded from figure 4.6a that indeed in this system delamination between the fibres and matrix makes an important contribution to the failure process of the composite. It can furthermore be seen that within the deformation band various fibres show kinks themselves. There seems to be a preferred direction of the fibres within the deformation band, but the fibres have separated sideways, due to the absence of lateral constraint. Striking is, however, that the fibres have not broken, the fibres can accommodate the compressive strain by the formation of kink bands, and again, as seen in Chapter 3, the primary cell wall serves

to prevent the fibres from fracturing completely. In figure 4.6b, which is taken from the same specimen as figure 4.6a, it can be deducted from the fibrous structures that the fibres have delaminated internally as well, in spite of the MF treatment. This suggests that, even in the MF treated materials, internal failure of the fibres by kinking is one of

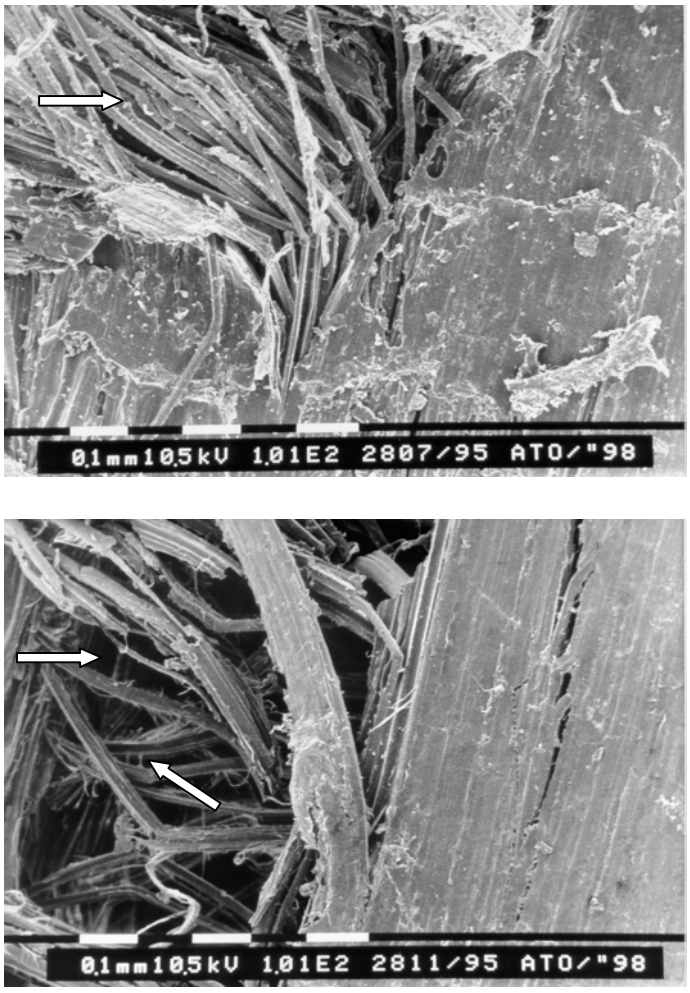



*Figure 4.6. Compressive failure of an MF treated flax epoxy composite, seen from the surface of the specimen. (a) The fibres have delaminated from the resin. The arrow points at a spot where the fibres also show microkinking. (b) The fibrillar structures (arrows) suggest that the fibres suffered also internal delamination.*

the important -if not the determining- failure mechanisms under compressive loading. Attempts to make polished surfaces from the inside of the samples, in order to have a better look at the failure mechanism occurring, have failed due to the fact that the fibres seem to smear out during the polishing process.

Table 4.3 further shows the effect that changing the MF concentration in the solution in which the fibres are soaked has on the ILSS and the compressive strength of the composites. Increasing the MF concentration in the soaking solution, and therefore increasing the amount of resin on and in the fibres, decreases the ILSS for both the viscose and flax fibre reinforced composites. However, it increases to a significant extent the compressive strength of the composites. Premature failure of the brittle MF could account for the fact that the ILSS decreases with increasing MF amount. The fact that the compressive strength increases with increasing MF content is now clearly not caused by increased adhesion. Two effects might be present:

- the MF layer around the fibre is thicker at higher MF contents and thus the resin phase of the composite contains a higher amount of MF resin compared to the amount of epoxy. This will lead to higher compressive strength of the composite since MF resin is known to have a higher compressive strength than epoxy resin. McGarry and Moalli [47] report in this respect a linear increase in compressive strength of rigid rod polymeric fibres with coating thickness of a stiff ceramic coating, an effect that might also play a role in the flax MF system,
- the fibres might contain internally a higher amount of MF resin and have therefore become stronger in compression.

Probably both effects play a role, but it is striking that the fibres are now able to withstand a much higher compressive loading.

### *4.3.3 The effect of MF modification on the tensile strength*

Now it is clear that the compressive strength is increased by the modification of the fibres by MF resin. However, the effect of MF modification on the tensile strength shows a quite different trend. Tensile strength and tensile modulus of both flax and viscose fibres and composites without and with MF treatment are given in table 4.4. The composites show a straight stress-strain curve and break without prior yielding. It is clear that whereas dewaxing has no influence on the strength of flax fibres the impregnation with MF resin seriously decreases the fibre strength. The same effect is

*Table 4.4. Fibre tensile strength and composite tensile strength and modulus without and with MF treatment. Composites contain 30 wt% fibre.*

| Fibre type | Fibre | Composite | |
|---|---|---|---|
| | $\sigma_{tens}$ [MPa] | $\sigma_{tens}$ [MPa] | $E_{tens}$ [GPa] |
| Flax | 750 ± 131 | 249 ± 25 | 23.3 ± 3.3 |
| Flax dewaxed | 820 ± 52 | 242 ± 28 | 18.5 ± 1.0 |
| Flax dewaxed+ MF* | 441 ± 44† | 147 ± 8 | 23.9 ± 0.8 |
| Viscose | 510 ± 19 | 203 ± 5 | 8.9 ± 0.06 |
| Viscose dewaxed + MF* | 336 ± 34‡ | 256 ± 7 | 11.0 ± 0.4 |

*Concentration MF in solution 20%. † This sample contains 26 % MF. ‡ This sample contains 42% MF.

seen in the composite, the tensile strength of the flax reinforced composite with MF treatment is lowered dramatically compared to the tensile strength of the unmodified composite. The modulus of the composite seems uninfluenced by the impregnation step. On the other hand, the tensile strength of the viscose composite is increased by 25% due to the addition of MF.

Possibly, whereas in the viscose fibres the MF resin is expected to be distributed evenly through the fibres, in flax there are regions in the fibre which consist completely of MF resin (in the areas of the kink bands). Under tension the excess of brittle resin in the fibres could lead to early crack formation, reducing the strength of the composite. Another explanation might be that the fibrils in the cell wall and the interfaces between the elementary fibres are now connected so strongly that the fibre looses its ability to redistribute stress concentrations, occurring under tension, and that consequently its toughness is lowered.

It is interesting to compare these results with experiments performed by Hepworth et al. [70], who were able to let epoxy resin penetrate into the flax cell wall after an urea treatment. They find that UD-composites made with these fibres have a 30% higher stiffness but similar strength compared to UD-composites from untreated fibres. They do not report any data on the compressive properties of their materials. The fact that epoxy resin is by itself far stronger than MF resin could account for the fact that in their materials the tensile strength of the composites with untreated fibres is similar to the

tensile strength of the composites with epoxy treated fibres. The increase in modulus is less easily explained. It is furthermore of interest to note that epoxy is not by itself able to penetrate into the flax cell wall [70].

*4.3.4 The effect of MF modification on the compressive strength*

It can now be expected that the better the MF resin is diffused into the fibres, the higher the compressive strength of the composite will become. Figure 4.7 shows compressive strength data of composites containing fibres which were impregnated via different routes, against the total amount of MF present in the composite. Both the time and the temperature of the impregnation step were varied and also two batches of fibres were allowed to pre-swell in water during three hours in order to make them more accessible to the resin. The differences in MF content were reached by changing the concentration of the MF solution.

The MF amount does not seem to be governed by the method of application.

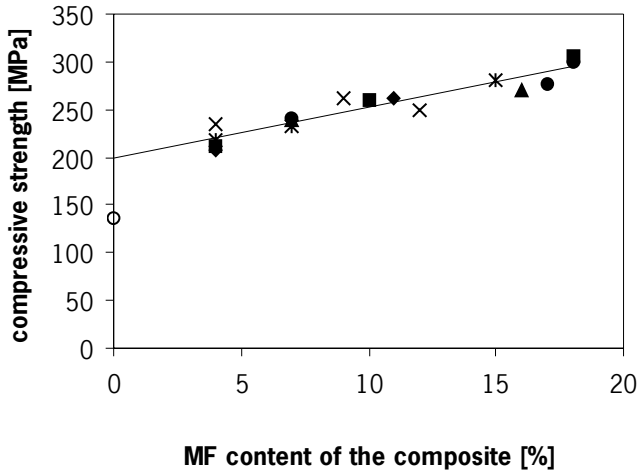



*Figure 4.7. Compressive strength versus MF content in the composite, influence of the impregnation method. ◆ 20 °C, no pre-swell, 5 min in MF. ■ 20 °C, 3 hours pre-swell in water, 5 min in MF. ▲ 20 °C, no pre-swell, 1 hour in MF. × 70 °C, no pre-swell, 5 min in MF. ✻ 70 °C, 3 hours pre-swell in water, 5 min in MF. ● 70 °C, no pre-swell, 1 hour in MF. O no MF treatment. The solid line gives the trend taking all data but the blank. Standard deviations fall approximately within the size of the markers.*

Furthermore there is no drop or jump in the compressive strength with changing MF content or with changing method of application, as might be expected when the fibres are not fully filled with resin by some of the application methods. It is therefore clear that the method of resin application does not have any influence on the compressive strength of the composites, the only governing factor seems to be the total amount of MF resin present in the composite.

It might be that since the fibres are rather thin, the penetration of resin into the fibres is so fast that 5 minutes in a 20 °C solution is enough to ensure effective impregnation of the fibres. The fact that kink bands often end just under the very thin primary cell wall which forms the fibre surface, might indeed make the fibres and especially the kink bands very easily accessible for the resin.

If it is assumed that all fibres in figure 4.7 are equally impregnated, the values can be compared. The solid line gives the mean trend of the compressive strength with the amount of MF in the composite. As mentioned before, MF resin is expected to have a higher compressive strength than epoxy resin (roughly ca. 275 MPa vs. ca. 82 MPa). The rise in compressive strength is found to be ca. 5.3 MPa per percent MF resin. From the rule of mixtures given in equation 4.2 it can be calculated that the effect of the addition of MF would lead to an increase of circa 2 MPa per percent MF resin given the compressive resin strength stated above. This again indicates that the addition of MF resin has an additional effect on the compressive strength of the fibres. Moreover, there is a sharp rise in the compressive strength going from 137 MPa for the composite without MF to over 200 MPa for the composites with MF, which can be expected when the kink bands are filled with resin and will thus not immediately collapse under the first deformation. Following the rule of mixtures and assuming that the MF resin itself gives an increase in compressive strength of 2 MPa per percent resin added, it can be concluded that every percent of MF added to the fibre increases the compressive strength of the fibres with 10 MPa, leading to a compressive fibre strength of circa 450 MPa at an MF content of 18%. This is obviously higher than the value of 300 MPa at which first deformation is visible in the loop test, but still much lower than the compressive strength of 1200 MPa that follows from the loop test as reported in Chapter 3. However, it indicates that the mechanism by which the fibres fail in compression can be changed by the impregnation with MF. This again supports our view that the MF resin actually is able to fill the hole-like defects that are present in the

fibres due to the decortication process and also cross-link the fibres internally and thus stabilise the fibres under compression.

## 4.4 Conclusions

The wax layer that is normally present around flax fibres prohibits the reaction of the fibres with a resin like epoxy or a reactive molecule like MA. Only after the wax layer is removed it is possible to form a proper bond between fibres and matrix.
Compressive strength of unidirectional composites of flax is low due to the presence of kink bands in the fibres, which are formed during the isolation steps, by which the fibres are separated from the plant. Merely improving the adhesion between flax fibres and the matrix is not sufficient to improve the compressive strength.
It is possible to stabilise the fibres in compression by impregnating them with an MF resin. The resin diffuses into the fibre, filling the holes that are present in the kink bands and also cross-linking the elementary fibre internally and thus stabilising the fibres under compressive loading. Impregnation of the fibres with the resin is a fast process, probably due to the small dimensions and relatively open structure of the flax fibres. Unfortunately the impregnation with MF resin leads to serious embrittlement of the fibres, thus reducing the tensile strength of the fibres and the resulting composite, making this route as yet unsuitable for the production of structural composites from flax fibres.

## 4.5 References

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# 5

# Natural Mat Thermoplastics

## 5.1 Introduction*

Over the last years, much research has been dedicated to natural fibre mat reinforced polypropylene composites (NMT) as a possible replacing material for GMT (glass mat thermoplastics) [1-6]. Especially the automotive industry, with Daimler-Benz AG as one

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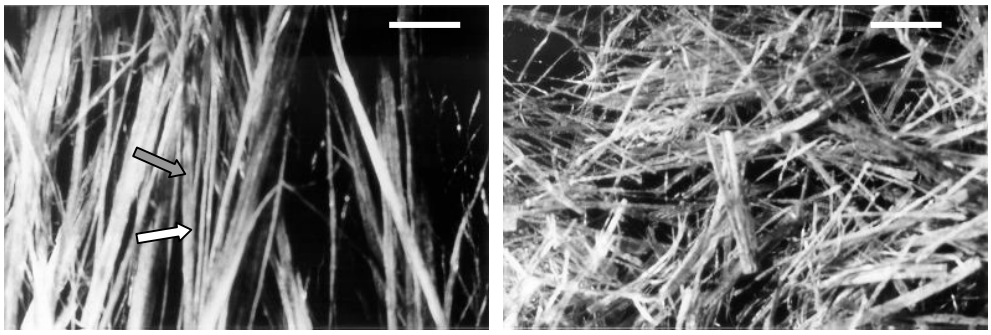
*This chapter is based on the papers:

- Influence of the physical structure of flax fibres on the mechanical properties of flax fibre reinforced polypropylene composites; M.J.A. van den Oever, H.L. Bos and M.J.J.M. van Kemenade, *Applied Composite Materials* **7** (2000) 387
- Flax fibre physical structure and its effect on the mechanical properties of flax fibre reinforced polypropylene composites; M.J.A. van den Oever, H.L. Bos and K. Molenveld, *Die Angewandte Makromolekulare Chemie* **272** (1999) 71
- Thermoplastic composites based on flax fibres and polypropylene: Influence of fibre length and fibre volume fraction on mechanical properties; T. Peijs, S. Garkhail, R. Heijenrath, M. van den Oever and H. Bos, *Macromol. Symp.* **127** (1998) 193

of the leading firms, have developed materials which have found their way into commercial applications [7]. The fibres in these NMTs are generally present in the form of a needle punched non-woven mat. To ensure good penetration of the polymer into the mat, a relatively low density fibre mat is preferable [1]. Generally, for pricing reasons, the fibres in the mat are either green decorticated fibres or dew retted scutched fibres. The disadvantage of green decorticated fibres is that they are relatively water sensitive, whereas the disadvantage of long scutched fibres is that they contain a large amount of weak intrafibre bonds.



a b

*Figure 5.1. Photograph of cut scutched flax fibres with different cutting length. (a) 25 mm, clearly visible is that at some points along the bundle the fibres have split (white arrow), whereas at other points along the same bundle they are glued together (grey arrow). (b) 6 mm, the bundles have separated in transverse direction due to the cutting. Scale bars correspond to 3 mm.*

This is illustrated in figure 5.1. Figure 5.1a shows scutched fibres cut at a length of 25 mm, while figure 5.1b shows at the same magnification the same scutched fibres, but now cut at a length of 6 mm. Clearly visible is that at a cutting length of 25 mm the fibres are still present in relatively thick bundles (in which, however, the weak intrafibre bonds are apparent), whereas at a cutting length of 6 mm the bundles have separated. This clearly indicates the weakness, or indeed absence, of intrafibre bondings over a significant length of the scutched fibre bundles. Obviously, the lateral strength of the scutched fibre bundles is determined by the bond strength between the technical fibres. Since in NMTs fibres are randomly oriented, the weak lateral bonds will introduce weak links in a flax fibre bundle reinforced composite. Failure of the

composite is therefore expected to not only initiate at the fibre-matrix interface but also within the fibre bundles. Furthermore, cracks will run or initiate not only through the fibre-matrix interface, but also through the interface between the elementary fibres within the bundles. This is displayed schematically in figure 5.2.

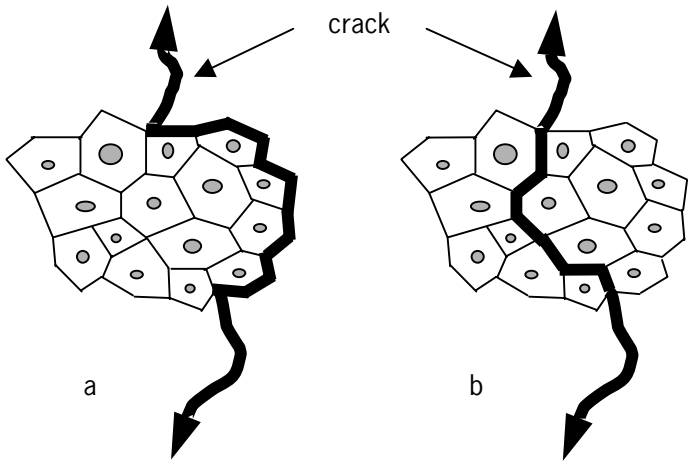



*Figure 5.2. Schematic view in cross section of a fibre bundle in a matrix containing a crack. (a) The crack runs through the fibre-matrix interface. (b) The crack runs through the interfaces between the elementary fibres. If weak spots are present at these interfaces (see figure 5.1a) the crack can also initiate here. Further optimisation of the fibre-matrix interface will in this case have limited effect on composite strength.*

For stiffness, the presence of weak lateral bonds presumably poses less of a problem. In various studies the very high specific stiffness of agrofibres could be effectively used in polypropylene (PP) composites, both in melt impregnated long technical fibre and injection moulded short elementary fibre reinforced composites and in NMTs [1-6].
For strength however, an effective use of the intrinsic fibre strength, is only reported by Mieck et al. in a study on green flax fibre reinforced PP composites [6]. Whereas for extruded and injection moulded composites the ineffective use of the intrinsic strength of the reinforcing fibre might be due to the sub-critical length of the fibres after processing, as described in Chapter 6 and Appendix A, this cannot be the cause in melt impregnated NMT materials. However, in the NMTs the strength of the technical fibres,

which is lower than the strength of elementary fibres (see Chapter 3), is not used effectively in most published data [4,4,5]. This might in a number of cases be partly due to non-optimal fibre-matrix interaction for the technical flax fibre in the PP matrix. But also the weak lateral bonds in the fibres -i.e. the bonds between the elementary fibres- will play a significant role in lowering the composite properties. As a consequence, improved bonding between fibre and matrix -which has proved to enhance the properties of all kind of glass/PP composites [10], extrusion and injection moulding flax/PP compounds (Chapter 6) and unidirectional flax/PP composites [11]- will not necessarily improve the properties of randomly oriented flax fibre composites up to a level that is in line with the average tensile strength of technical flax fibres.

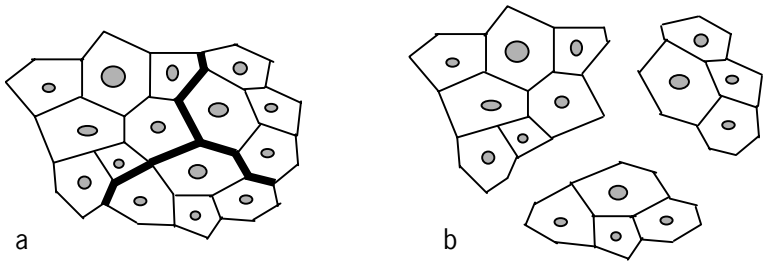



*Figure 5.3. Schematic view of a cross section of (a) scutched and (b) hackled fibres. The fat lines represent the weak intrafibre bonds in the scutched fibres. After hackling the fibres have separated through these weak interfaces. Hackled fibres consequently consist of less cells in the bundle and are thinner than scutched fibres.*

In this chapter this hypothesis is tested by comparing NMTs from scutched flax fibre bundles with NMTs from hackled technical fibres with the same fibre length. The hackled technical fibres are expected to give a better performance in NMTs, since they contain fewer weak interfibre bonds and less cells in the bundle due to the action of the hackling combs (see also Chapter 2), this is shown schematically in figure 5.3. The influence of improved fibre–matrix adhesion on the mechanical properties of both the scutched and hackled flax fibre reinforced composites is studied by using maleic anhydride modified PP (MAPP) as a compatibiliser. The improved bonding is expected to have a stronger effect in the hackled fibre composites than in the scutched fibre composites (see figures 5.2 and 5.3).

The random flax fibre reinforced PP composites were manufactured using a wet laid process. This method allows for controlling the length of the fibre, which is desired in order to compare the different data using the Cox-Krenchel model for the Young's modulus [12,13] and the Kelly-Tyson model for the tensile strength of the composites [14]. Futhermore, the wet laid process ensures an optimal mixing between the flax fibres and the polymer, which consequently only requires localised flow of the polymer upon heating to obtain excellent impregnation. This in contrast to the large scale impregnation of dense fibre mats by the polymer melt, the method described by Schlösser and Knothe [7]. For glass/PP GMT materials it is known that for the melt impregnation method the level of impregnation and the void content are very dependent on the melt viscosity of the PP [15], for GMT therefore often a low molecular weight PP is used, leading to a compromise in properties. It is likely that for flax/PP this will be similar. The wet laid composites used for this study will in this respect more closely resemble the commercial NMTs made from comingled flax/PP fibres non-wovens, since also in these materials better impregnation can be expected.

## 5.2 Experimental

### *5.2.1 Materials*

Scutched dew retted and hackled warm water retted flax (Belinka) and polypropylene (PP) fibres of Retiflex (Retiflex Fibra Corta; fibre diameter around 20 µm; fibre length 12 mm; melt flow index 35, kindly supplied by Brands Text bv, Tilburg) were used. The long scutched and hackled fibres were cut on a guillotine chopper at a length of 6 mm. In order to study the effect of improved fibre-matrix adhesion on composite performance, 3.5 wt% maleic-anhydride grafted polypropylene (MAPP) (Hostaprime® HC5, kindly supplied by Hoechst Benelux Industrie nv, Amsterdam) was used.

### *5.2.2 Composite production*

Random flax/PP composites were made via a wet laid process using lab scale paper making equipment. Flax and PP fibres were stirred together in a water/ethanol (1:1) mixture. In pure water the PP fibres rose very quickly to the liquid surface, thus hindering a good distribution of the flax fibres in the PP fibres. Therefore, a mixture of water and ethanol with a density of about 0.9 g/cm$^3$ was used. This density allows the formation of a stable dispersion of flax and PP fibres. For the compatibilised materials

the compatibiliser was added as a powder during the wet mixing process [16]. After drying the flax/PP fibre sheet at 60 °C for 24 hours the fluffy mat of flax and PP fibres was consolidated in a hot-press at 200 °C and 40 bar pressure during 15 minutes. Composites with fibre fractions of 20 and 40 vol% were made, assuming a fibre density of 1.4 g/cm$^3$.

### *5.2.3 Mechanical testing*

Specimens were cut with dimensions 100*15*2, 40*15*2 and 50*15*2 mm$^3$. The composites were conditioned for 2 weeks at 23 °C and 50% RH prior to mechanical testing. Uniaxial tensile tests were performed in 5-fold on the 100*15*2 mm$^3$ specimens, using a Zwick universal tester, type Z010. The grip to grip separation was 65 mm and the extensometer gauge length was 50 mm. The crosshead speed was 1 mm/min. Flexural tests on the 40*15*2 mm$^3$ specimens were performed in 5-fold on a Zwick universal tester, type 1445 at a span length of 32 mm and a crosshead speed of 1 mm/min. The unnotched Charpy impact tests were performed at least in 7-fold on a Ceast pendulum impact tester according to ISO 179, using a 4J hammer at an impact velocity of 2.9 m/s. The support length was 40 mm and the specimens were impacted flat-wise.

## 5.3 Results and discussion

### *5.3.1 Tensile stiffness*

In literature often modelling is used in order to predict composite mechanical properties. In this study models are used to compare the actual measured performance of the NMTs with the intrinsically possible performance as expected by the model. The composites in this study, obtained via a wet laid process with fibres longer than the composite thickness, show random in-plane fibre orientation. One of the most widely used theories to model random in-plane fibre reinforced composite stiffness was developed by Cox and Krenchel. Starting with the 'rule-of-mixtures', Cox [12] added a factor to account for the limited efficiency of stress transfer from the matrix to the fibres due to finite fibre length, $\eta_L$. Krenchel [13] added a factor to account for fibre orientation, $\eta_0$. The Cox-Krenchel theory can be written as given in equation 5.1:

$$E_c = \eta_0 \eta_L V_f E_f + (1 - V_f) E_m \tag{5.1}$$

where $E_f$, $E_m$ and $V_f$ are the fibre and matrix stiffness and the fibre volume fraction, respectively. From the 'shear lag' theory developed by Cox an expression for $\eta_L$ is found:

$$\eta_L = \left(1 - \frac{tanh(\beta L/2)}{\beta L/2}\right) \tag{5.2}$$

where:

$$\beta = \frac{2}{d}\left(\frac{2\,G_m}{E_f\,ln\left(\sqrt{\pi / X_i V_f}\right)}\right)^{\frac{1}{2}} \tag{5.3}$$

and where $d$, $L$ and $G_m$ are the fibre diameter, the fibre length and the shear modulus of the matrix, respectively. Thomason and Vlug [18] state that there is some confusion on the interpretation of the 'shear lag' theory that was developed by Cox. In this thesis the calculation of Thomason and Vlug [18] is followed, using the value $X_i$ = 4.0 for square packing of the fibres. For random in-plane fibre reinforced composites a fibre orientation factor $\eta_0$ = 0.375 can be derived [13]. Furthermore, the following input parameters were been used in the model: $E_f$ = 50 GPa, $E_m$ = 1.6 GPa, $L$ = 6.25 mm, $G_m = E_m/2(1+\nu)$, with $\nu$, Poisson's ratio, taken as 0.4. The flax fibres do not have a circular cross-section, especially the scutched fibres have different ribbon-like physical structures as was shown in figure 3.3. When translated to circular cross-sections, however, the average fibre diameter $d$, determined on a large number of fibres used in this study [17], was found to be 80 µm and 50 µm for scutched and hackled fibres, respectively. The $L/d$ values of the scutched and hackled fibres are thus 78 and 125, respectively. Since mainly elastic properties are involved in the Cox-Krenchel model, the fibre diameter in itself has no significant effect on the predicted modulus data.

In figure 5.4 the Young's modulus of flax/PP and flax/PP/MAPP composites based on 20 and 40 vol% of both scutched and hackled flax fibres is given, both as a function of fibre volume fraction and of fibre weight fraction. For presentation reasons the data are plotted over a small range of fibre volume fractions, the modulus data should be read, however, at fibre fractions of 20 and 40 vol% exactly. Besides the experimental data, the tensile Young's modulus of commercial GMT [19] and the Cox-Krenchel prediction is also plotted. The Cox-Krenchel prediction is about the same for scutched and hackled fibre composites, the slight difference being caused by the different $L/d$ ratios of the fibres. Based on these data, it can be concluded that the stiffness of both scutched and

hackled flax fibre reinforced PP comes close to the stiffness of commercial GMT based on volume fraction and exceeds the stiffness of commercial GMT based on weight

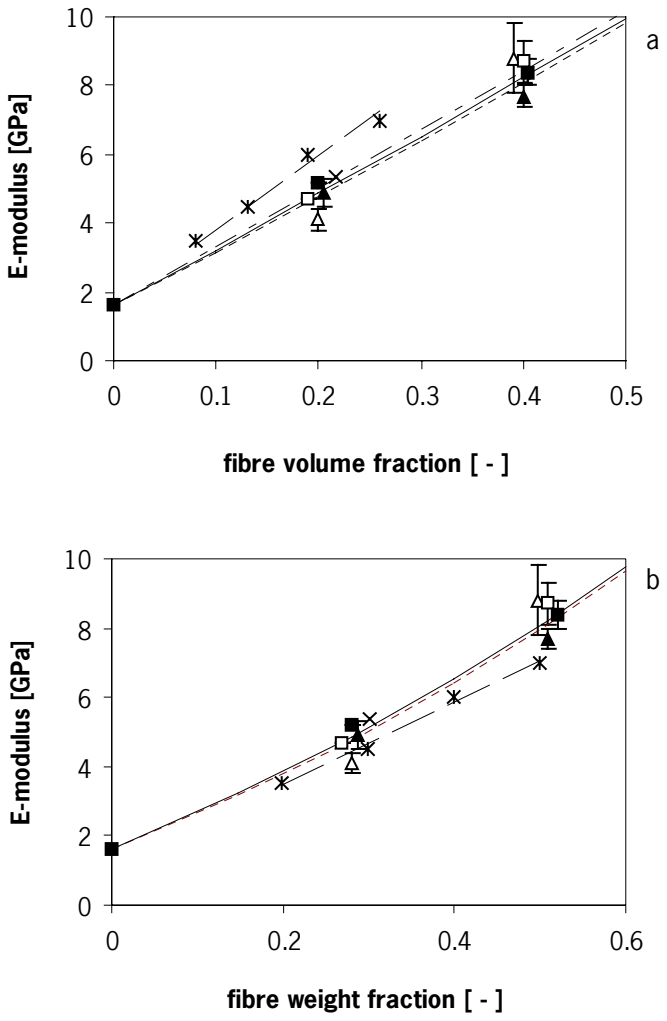



*Figure 5.4. Tensile modulus of* ∆ *scutched flax/PP and* □ *hackled flax/PP and* ▲ *scutched flax/PP/MAPP and* ■ *hackled flax/PP/MAPP composites versus (a) fibre volume and (b) fibre weight fraction.* x *is greenflax mat/PP/MAPP [7].* –✱––✱– *are E-modulus values of commercial GMT [19]. The lines represent the Cox-Krenchel prediction:* ———— *for 6 mm long hackled fibres,* ····· *for 6 mm long scutched fibres,* — - — - — *for 100 mm long hackled fibres. Error bars falling within the markers are left out.*

fraction, i.e. for materials of the same weight. The Cox-Krenchel prediction seems to give a rather accurate description of the composite stiffness. As expected, addition of MAPP has no significant effect on composite stiffness. Data from Schlösser and Knothe [7] are also presented. The point gives the mean value of the stiffness in length and in transverse direction of a greenflax mat/PP/MAPP composite. Despite the fact that in this material the fibres are much longer, the stiffness of the resulting composite is similar. The dashed/dotted line gives the Cox-Krenchel prediction of long fibres (100 mm). The data from Schlösser and Knothe fit nicely on this line. The results indicate that also for flax reinforced composites, as in glass reinforced composites [18], a good composite modulus is obtained at relatively low $L/d$ values. Also, greenflax composites apparently have similar stiffness as the retted/scutched/hackled flax composites. When the low price of scutched fibres compared to E-glass fibres is taken into account, these materials are particularly of interest from a cost-performance point of view, giving relatively light and cheap materials at a certain stiffness. As other studies already have shown, it can thus be concluded that flax/PP composites can compete with GMT materials in stiffness critical applications [4].

### *5.3.2 Tensile strength*

Kelly and Tyson [14] extended the 'rule-of-mixtures' for strength prediction of composites reinforced with fibres aligned in loading direction:

$$\sigma_c = \eta_L V_f \sigma_f + (1 - V_f)\sigma_{um} \tag{5.4}$$

where $\sigma_f$ is the fibre tensile strength, $\sigma_{um}$ is the matrix strength at the fibre failure strain, assumed to be equal to $E_m * \sigma_f / E_f$ and $V_f$ is the fibre volume fraction. Following Kelly-Tyson, the fibre length efficiency factor, $\eta_L$, is:

$$\eta_L = \frac{1}{V_f}\left[ \Sigma \frac{L_i V_i}{2 L_c} + \Sigma V_j \left(1 - \frac{L_c}{2 L_j}\right)\right] \tag{5.5}$$

where $L_c$ is the critical fibre length according to Kelly and Tyson:

$$L_c = \frac{\sigma_f d}{2\tau} \tag{5.6}$$

Furthermore, $V_i$ is the fibre volume fraction of fibres of length $L_i$ shorter than the critical fibre length, $V_j$ is the fibre volume fraction of fibres of length $L_j$ longer than the critical fibre length, $d$ is the fibre diameter and $\tau$ is the fibre-matrix interfacial shear strength.

The two summation terms in equation 5.5 account for the fibres of sub-critical length ($L < L_c$) and super-critical length ($L > L_c$) respectively.

Equation 5.4 is valid for discrete, aligned fibres only and cannot be integrated to give a simple numerical orientation factor to account for random fibre orientation as in the case of the description of composite stiffness. Whereas the modulus can be estimated from the summation of the contributions of the fibres and the matrix, this is not valid for composite strength, since failure of a composite is not only dependent on bulk material properties but on defects as well. However, equation 5.4 can be extended for random composites as [20]:

$$\sigma_c = k\,\eta_0\,\eta_L V_f\ \sigma_f + (1 - V_f)\,\sigma_{um} \tag{5.7}$$

where $\eta_0$ is the orientation factor, accounting for the random orientation of the fibres and $k$ is the fibre efficiency factor, accounting for the extent to which the properties of the fibre are expressed in the properties of the composite. Thomason et al. [21] use a virtual orientation factor, $\eta_{0,v}$, which equals $k * \eta_0$, and found a value of 0.2 to fit for commercial GMT, for wet laid glass/PP composites and for extruded glass/PP compounds, covering a fibre length range of 0.1-50 mm and a fibre concentration range of 10-60 wt%. In this study the value of 0.2 for $k * \eta_0$ is used in the Kelly-Tyson

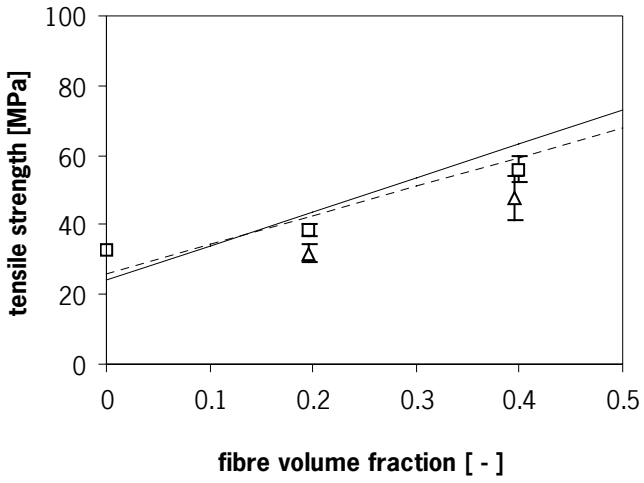



*Figure 5.5. Tensile strength of Δ scutched flax/PP and □ hackled flax/PP composites versus fibre volume fraction. The lines represent the Kelly-Tyson prediction for the uncompatibilised system: ———— for hackled fibres, ····· for scutched fibres.*

model to get a first approximation of the flax/PP composite strength. In the model furthermore the following input parameters were used: $\sigma_f$ = 810 and 750 MPa for scutched and hackled fibres, respectively, as measured at 3 mm spanlength, which is about the critical fibre length (see Chapter 3 and 6); $L$ = 6.25 mm; the average diameter $d$ = 80 µm and 50 µm for scutched and hackled fibres, respectively. The hackled fibre strength is somewhat lower than the scutched fibre strength due to extra damage introduced during the hackling process. The interfacial shear strength (IFSS) between the fibre and the matrix, $\tau$, is taken to be 8 MPa for flax/PP and 12 MPa for flax/PP/MAPP, for both scutched and hackled fibres (see Appendix A).

In figure 5.5 the tensile strength of PP composites with 20 and 40 vol% of scutched and hackled flax fibres is given. Besides, the Kelly-Tyson predictions (using $k * \eta_0 = 0.2$) for scutched and hackled fibre reinforced PP composites are plotted. Contrary to the modulus data, the strength of both scutched and hackled fibre based composites does not reach the predicted values. Addition of MAPP, which increases the IFSS, does result

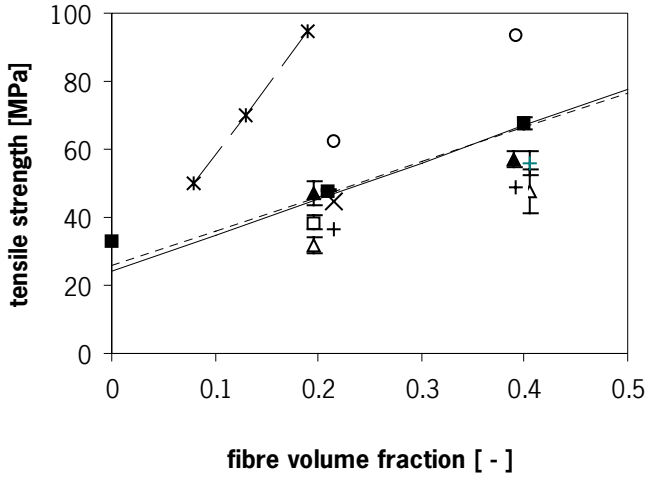



*Figure 5.6. Tensile strength of* Δ *scutched flax/PP and* □ *hackled flax/PP and* ▲ *scutched flax/PP/MAPP and* ■ *hackled flax/PP/MAPP composites versus fibre volume fraction.* x *is greenflax mat/PP/MAPP [7], + is retted flax mat/PP/MAPP [6],* O *is greenflax mat/PP/MAPP [6] and –*✳*––*✳*– the tensile strength values of commercial GMT [19]. The lines represent the Kelly-Tyson prediction for compatibilised systems: ———— for hackled fibres, ····· for scutched fibres. Error bars falling within the markers are left out.*

in improved composite strength (figure 5.6). The 20 vol% hackled and scutched fibre composites now give similar values. The 40 vol% hackled fibre/PP/MAPP composite strength equals the Kelly-Tyson prediction, the 40 vol% scutched fibre/PP/MAPP composite strength, however, is lower than the prediction.

*Table 5.1. The value of k, the efficiency parameter, with $\eta_0$ = 0.2, for composites without and with compatibiliser, fitted from figures 5.5 and 5.6.*

| | *k* flax/PP | flax/PP/MAPP |
|---|---|---|
| Scutched fibres | 0.77 | 0.93 |
| Hackled fibres | 0.89 | 1.03 |
| Glass fibres | 1 | 1 |

Table 5.1 lists the efficiency factor, *k*, values obtained from fitting the measured data in figures 5.5 and 5.6, assuming now that $\eta_0$ equals 0.2. In this way a measure for the efficiency of the various flax fibres compared to glass fibres is obtained. It is clear from this table that the fibre efficiency of scutched fibres is lower than of glass fibres. For hackled fibres, the addition of the compatibiliser leads to a fibre efficiency which is similar as the efficiency Thomason et al. found for glass fibres [21]. The difference between scutched and hackled fibres could be due to the presence of more weak interfibre bonds in the scutched fibres. The effect of the weak lateral bonds in retted scutched flax fibre reinforced PP can also be seen from the SEM micrographs in figure 5.7. The first conclusion from these micrographs is that addition of MAPP improves the fibre matrix adhesion, both for scutched and hackled fibre composites. This can be concluded from the shorter pull out length for both scutched and hackled fibre composites with MAPP added. The scutched fibres, however, show also a lot of fibre splitting besides fibre-matrix debonding, whereas the hackled fibres do not. In figure 5.7c the arrow indicates a point where part of the fibre bundle seems to have been pulled out of the opposite matrix. Furthermore, the debonding surfaces in figures 5.7c and 5.7d are relatively smooth (compare with figure 6.10), indicating that the compatibiliser, even though it considerably improves the tensile properties, still only introduces limited chemical bonding between the fibres and the matrix.

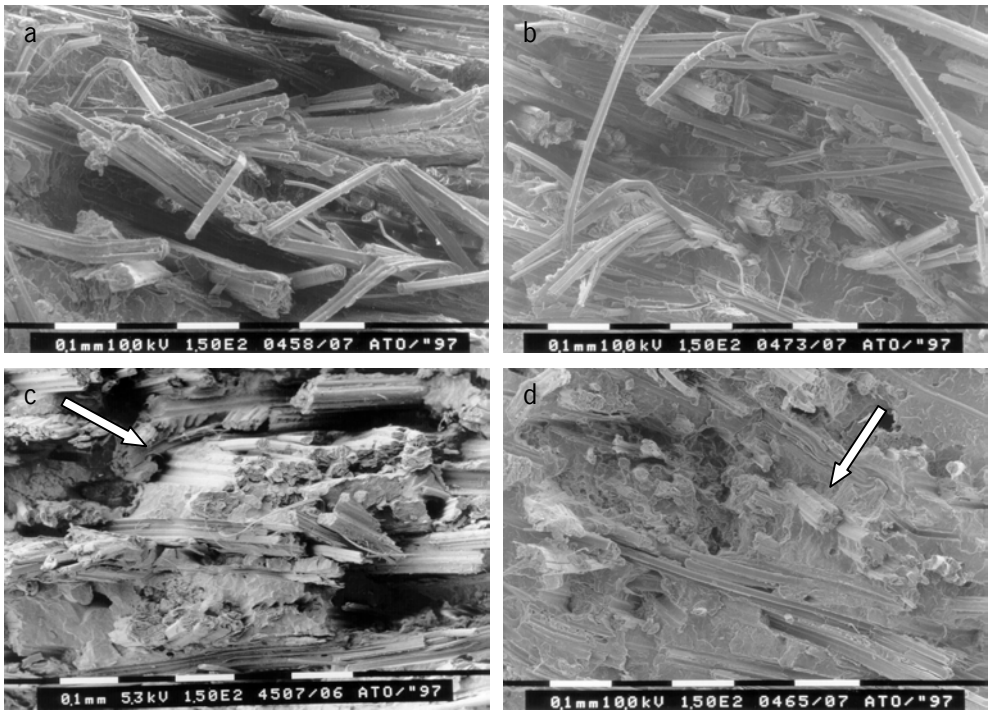



*Figure 5.7. SEM micrographs of cryo fracture surfaces. (a) Scutched flax/PP. (b) Hackled flax/PP, note the long pull out length in these two samples. (c) Scutched flax/PP/MAPP, the arrow indicates where part of the bundle is pulled out of the matrix at the opposite side. (d) Hackled flax/PP/MAPP, note the relatively clean fracture surface, indicated by the arrow.*

Data from Schlösser and Knothe [7] and Mieck et al. [6] are also presented in figure 5.6. The points give the mean value of the strength in longitudinal and in transverse direction of green flax mat/PP/MAPP composite. Apparently, Mieck et al. have been able to effectively use the tensile strength of the green flax fibres in the resulting composites [6]. Values as high as this have, however, afterwards not been reported again. Thomason et al. [21] have found that for glass fibre GMTs the molecular weight of the PP has no significant influence on the tensile properties of the composite, this suggests that also for NMTs this probably is not the case and consequently that the high values found by Mieck et al. are not caused by differences in molecular weight of the matrix. Since Mieck et al. are using green flax, the interfaces between the elementary fibres will not be weakened due to the retting process, leading to a higher

fibre efficiency. This could account for the high values they find. Since the tensile strength of green flax usually lies in the same order as the tensile strength of dew retted flax (see Chapter 2), this points to the conclusion that failure in the composites is initiated by transverse cracks.
From figure 5.6 it is furthermore apparent that the actual values and the prediction of flax fibre reinforced composite strength lie significantly below GMT [19] values, which is mainly due to the lower technical flax fibre strength as compared to the glass fibre strength (see table 1.1). From a plot of the composite strength versus fibre weight fraction (not shown here) it can be concluded that the hackled flax fibre reinforced composites show a strength that is about 60% of the GMT composite strength over the range up to 40 wt% of fibres. It might be possible to bridge the gap with GMT strength when elementary fibres are used in composites.

Elementary fibres suitable for use in NMTs are not (yet) available. The steam explosion approach by Kessler et al. [22] and Kohler and Wedler [23] resulted in fairly elementary flax fibres, however, the strength of the elementary fibres was not maintained (see also Chapter 2). As reported in Chapter 3 dew retted elementary fibres have a strength of over 1500 MPa compared to about 800 MPa for technical fibres. Furthermore, the elementary fibres have clearly a higher transverse strength than the technical fibre bundles, this counts for both the scutched and the hackled fibre bundles. Another advantage of using elementary fibres may be that they show better interaction with MAPP/PP matrices than technical fibres do (Appendix A). Using well isolated elementary fibres could theoretically lead to a composite strength of 130 MPa at a fibre volume fraction of 0.4. This is shown in figure 5.8a and 5.8b, where the Kelly-Tyson predictions for hackled flax/PP, hackled flax/PP/MAPP and elementary flax/PP/MAPP are plotted together with the experimental GMT data [19] versus volume and weight fractions. Thus, on basis of fibre weight fractions, for elementary flax/PP/MAPP composites a higher tensile strength than for GMT is predicted for all fibre fractions. This is a reason to further study the isolation of flax fibres.

Another option to optimise composite properties is obviously the use of green flax, which has undergone only a very short retting period and is then directly decorticated. When the data of Mieck et al. [6] on green flax fibre reinforced composites are analysed with the Kelly-Tyson model and the above mentioned parameters for fibre length and

diameter and fibre-matrix interaction, a fibre strength of 1000 MPa is found, which is, to the best of the author's knowledge, an upper bound for technical flax fibres. This indicates, as also mentioned on the previous page, that green flax, which is only partly retted, has a higher tensile strength at long clamping length than the fully retted fibres and thus that the interface between the elementary fibres is stronger, since it will be

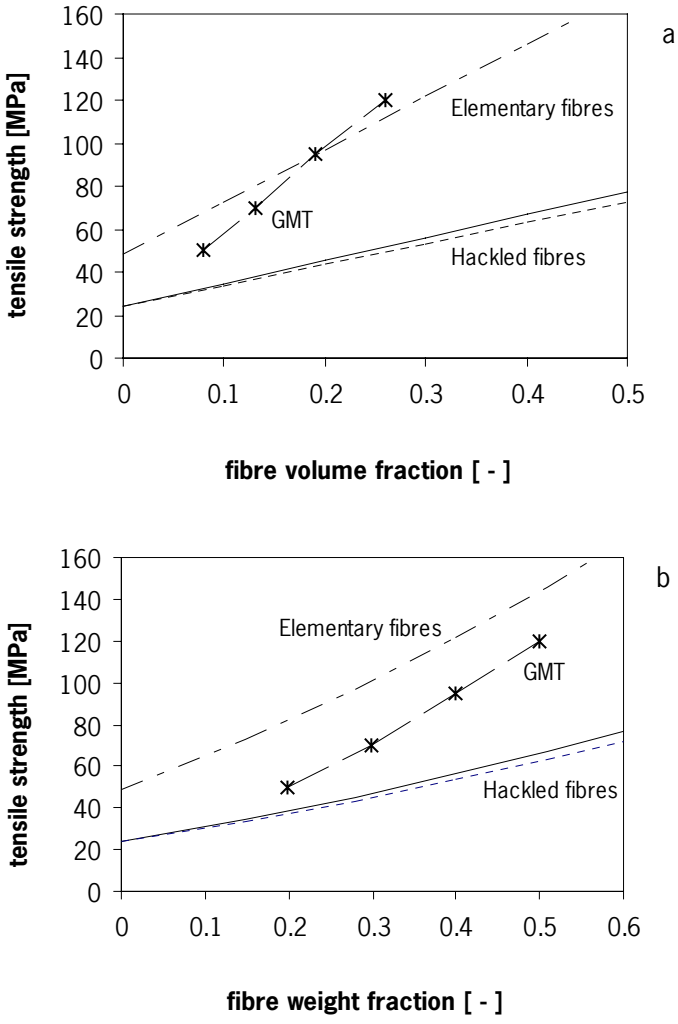



*Figure 5.7. Kelly-Tyson predictions of the tensile strength of: ——— hackled flax/PP/MAPP, - - - - - -hackled flax/PP, ·–·–·– elementary flax fibre/PP/MAPP, compared with –*–*– commercial GMT values [19], versus (a) fibre volume fraction and (b) fibre weight fraction.*

especially this interface which is responsible for fibre failure (see also Chapter 3). This automatically implies that the green fibres have a higher transverse strengh. However, given the data of Schlösser and Knothe [7] they have not yet succeeded in effectively translating this high fibre strength into commercial composites. The reason that retted fibres are still studied is that green flax fibres still contain the major part of the low molecular weight components, which are present in the fibres after growing. These low molecular weight components are particularly responsible for water absorption which makes the fibres dimensionally unstable when they come into contact with water or at higher relative humidities. Furthermore, the low molecular weight components make the fibres more sensitive for elevated temperatures, which limits the processing temperature range. During retting the low molecular weight components are partly removed. Further discussion on the effect of temperature on the fibre properties is presented in Chapter 6.

*5.3.3 Flexural properties*

The flexural strength of scutched and hackled flax fibre reinforced PP and PP/MAPP composites is given in figure 5.9. The scatter in the obtained strength data is quite

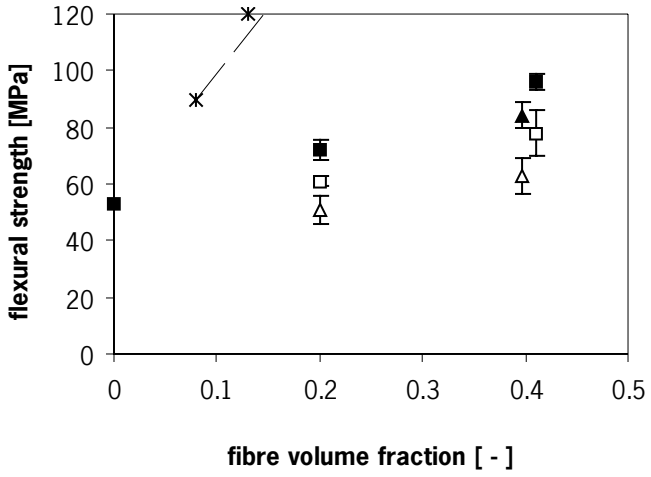



*Figure 5.9. Flexural strength of* ∆ *scutched flax/PP and* □ *hackled flax/PP and* ▲ *scutched flax/PP/MAPP and* ■ *hackled flax/PP/MAPP composites versus fibre volume fraction. –*∗*–––*∗*– represents the flexural strength values for commercial GMT [19].*

large, but nevertheless the differences in flexural strength between scutched and hackled fibre reinforced composites are similar to the differences in tensile strength. It appears that the composites fail at the tension side before the upper yield strength is reached. Similar to tensile data, the flexural strength of scutched and hackled flax/PP composites cannot compete with that of GMT. Again this is mainly due to the lower technical fibre strength of flax fibres compared to glass fibres. When the specific densities of the fibres are taken into account (plot flexural strength versus versus fibre weight fraction, not shown here), the hackled flax fibre composite strength is 65% of the glass composite strength, fairly similar to the tensile data. This indicates further that the weak compressive properties of the flax fibre do not play a significant role in the flexural failure behaviour of the composites.

The tensile modulus is mainly dependent on fibre volume fraction and not on the physical structure of flax fibres, nor on the adhesion between fibres and matrix (as was shown in figure 5.4). The flexural modulus of both scutched and hackled flax fibre composites, presented in figure 5.10, however, shows a different trend. The scutched

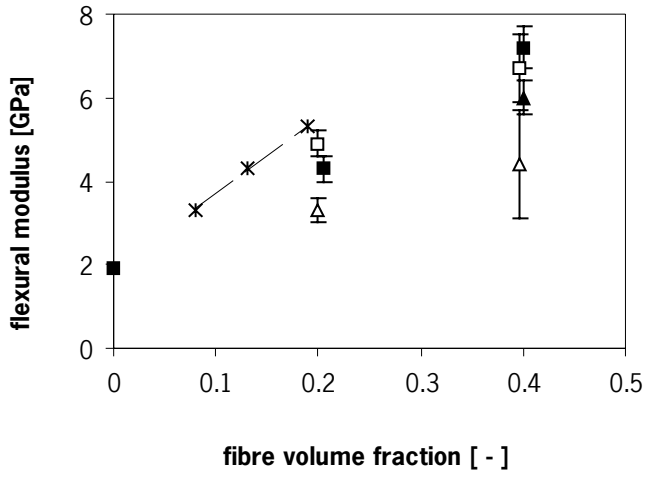



*Figure 5.10. Flexural modulus of* ∆ *scutched flax/PP and* □ *hackled flax/PP and* ▲ *scutched flax/PP/MAPP and* ■ *hackled flax/PP/MAPP composites versus fibre volume fraction. –*✱*––*✱*–– represents the flexural modulus values for commercial GMT [19].*

fibre composites show significantly lower flexural stiffness than the hackled fibre composites and adhesion improvement significantly increases the flexural modulus at 40 vol% fibres whereas it seems to slightly decrease the stiffness at 20 vol% fibres. Piggott [24] suggests that especially at higher volume fractions packing problems can decrease the flexural modulus of a composite, due to out-of-plane orientation of part of the fibres. This would mean that especially the hackled fibres, of which -at the same fibre fractions- more separate fibres will be present would suffer from this effect. However, especially the scutched fibres appear to have an exceptionally low flexural stiffness at high volume fractions. Furthermore, also at 20 vol% the modulus of the uncompatibilised scutched fibre composites is significantly lower than for the hackled fibre composites. This suggests that the weak lateral bonds in the scutched fibres might have a significant effect on the flexural modulus and possibly the scatter of the flexural modulus. Possibly the weak bonds inside the scutched fibres themselves, introduce localised shear at very low deformations. This localised shear, which will be more severe for scutched than for hackled fibres and which will be more severe without than with improved fibre-matrix interaction, can cause the lower flexural modulus data compared to tensile data and compared to what might be expected. The results indicate that both the adhesion between the fibre and the matrix as well as the bonding within the fibres themselves is more important in flexural than in tensile loading.

### *5.3.4 Impact strength*

The unnotched Charpy impact strength of PP and PP/MAPP composites based on 20 and 40 vol% of both scutched and hackled flax fibres is shown in figure 5.11. The impact strength decreases compared to pure PP, but then increases slightly with increasing fibre loading, with decreasing fibre-matrix adhesion and with decreasing lateral fibre strength. The scatter in data within each composite is, however, quite large. It should be noted here that the scutched and hackled fibres have similar lengths but different average diameters and therefore different aspect ratios.

Impact strength of fibre reinforced materials is determined for the larger part by the energy dissipated during fibre pull-out. Fibre pull-out is governed by a competition between fibre breakage and interface failure and is thus determined both by the fibre tensile strength and by the interfacial shear strength. The adhesion between the fibres and the matrix in the NMTs with compatibiliser is expected to be good, given the tensile strength of the NMTs and the high interfacial shear strength for fibre bundles in PP

presented in appendix A. Therefore, it is mainly the fibre strength that will determine the impact properties of the NMTs. Compared to glass fibres, the flax fibres have a much lower tensile strength (circa 800 MPa versus 2000 MPa), which implies that the pull-out length of flax fibres will be much lower than of glass fibres. Therefore it is not surprising that the impact strength of NMTs is much lower than the impact strength of GMTs, even lower than the impact strength of pure PP. The scutched fibres show a slightly higher impact strength than the hackled fibres, which could be due to the fact that they also have a slightly higher tensile strength.

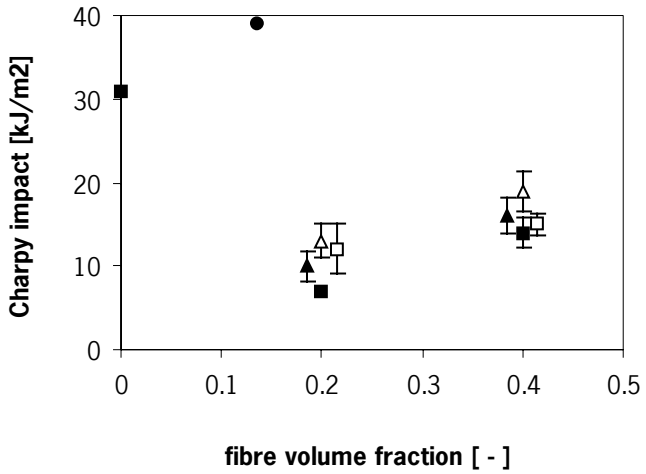



*Figure 5.11. Unnotched Charpy impact strength of ∆ scutched flax/PP, □ hackled flax/PP, ▲ scutched flax/PP/MAPP and ■ hackled flax/PP/MAPP composites versus fibre volume fraction; ● represents an average GMT value [27].*

A higher fibre-matrix adhesion results in shorter average pull-out lengths and therefore causes lower impact strengths. This explains why the materials without compatibiliser have a slightly higher impact strength than the materials with compatibiliser. A precondition for this explanation is that the fibres are longer than the critical fibre length. The fibre length in the tested NMT materials is 6 mm. In appendix A the critical fibre length was found to be circa 2.8 mm for scutched fibres with improved fibre-matrix adhesion and approximately 3.8 mm for scutched fibres without improved fibre-matrix adhesion, the critical fibre length for hackled fibres is lower than for scutched

fibres. In the tested NMT materials the mentioned precondition is therefore expected to be fulfilled. Figure 5.12 shows that indeed the pull-out lengths of flax fibres in the flax/PP specimens are longer than in the flax/PP/MAPP composites. Besides, the pull-out lengths of flax fibres are longer in the scutched than in the hackled fibre composites which indicates that the fibre lateral strength has a similar effect on fibre pull-out length as fibre-matrix adhesion has. Possibly part of the fibre is pulled out here

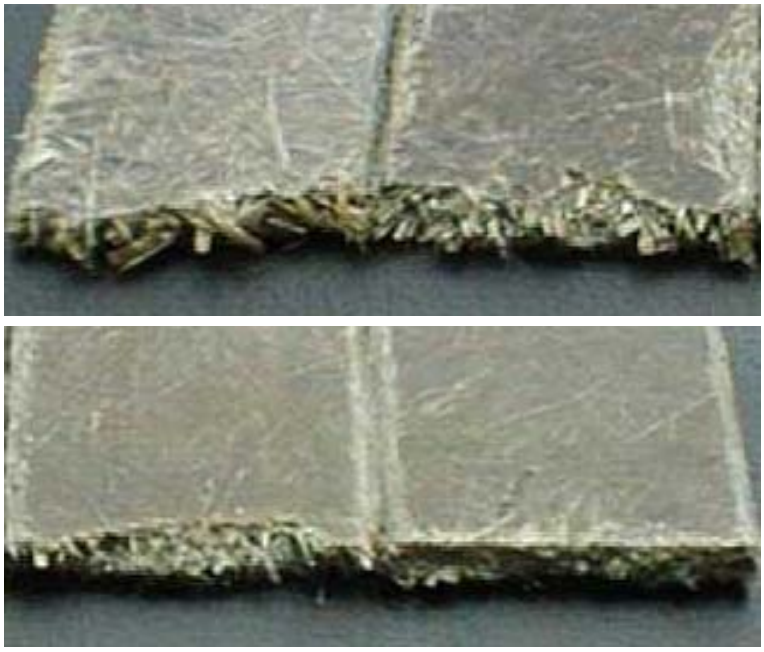



*Figure 5.12. Photographs of fibre pull-out of Charpy impact NMT bars; from left to right: (a) scutched flax/PP, scutched flax/PP/MAPP, (b) hackled flax/PP and hackled flax/PP/MAPP. Width of the samples is 15 mm.*

while the rest of the fibre remains within the matrix (as was also indicated in figure 5.7c), which indicates that also internal fibre pull-out can be one of the energy absorbing processes. This could also add to the slightly higher values found for the scutched fibre composites, since the scutched fibres will have more posibilities for internal pull-out than the hackled fibres. Another effect that plays a role here is the fibre diameter. Since scutched fibres are thicker than hackled fibres they have a more favourable surface to diameter ratio which results in a longer pull-out length. Next to the

longer pull-out length, the scutched flax reinforced composites show a larger damaged area than the hackled flax reinforced composites. This can be seen from figure 5.13 where the flax fibres even buckle out of the scutched flax/PP composite surface over a band of circa 2 mm width.

*Figure 5.13. Photograph of the blow side of Charpy impacted flax/PP composites; from left to right: scutched flax/PP, scutched flax/PP/MAPP, hackled flax/PP and hackled flax/PP/MAPP. The arrow indicates where the scutched fibres buckle out in the scutched flax/PP composite.*

Next to the difference in pull-out length and damage area, generally it might be said that improving the fibre-matrix adhesion and the internal fibre lateral strength results in a shift from a plane stress state towards a plane strain state and therefore makes the material more brittle. The behaviour of the flax reinforced NMT materials differs from the conclusions Thomason and Vlug [25] draw for the notched Charpy impact behaviour of wet laid glass/PP composites. They find that for these materials it is not so much the friction energy during pull-out that affects the impact strength but the elastic energy stored in the glass fibres and the matrix prior to fibre fracture. This is also shown in figure 5.14, where the Charpy impact strength is plotted versus the composite tensile strength. Whereas Thomason and Vlug [25] and Thomason [26] find for glass fibre GMT a strong correlation between tensile strength and both the unnotched [26] and notched [25] Charpy impact strength, for the flax reinforced materials there does not seem to

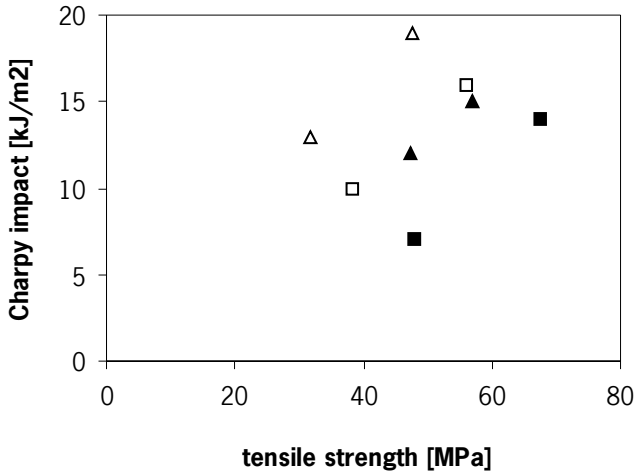



*Figure 5.14. Unnotched Charpy impact strength versus tensile strength for* Δ *scutched flax/PP,* □ *hackled flax/PP,* ▲ *scutched flax/PP/MAPP and* ■ *hackled flax/PP/MAPP composites.*

be a correlation at all. Since there is no correlation between the impact with the elastic energy stored in the fibres, one could assume that very little elastic energy is stored at all. A possibility could be that the damaged zones in the fibres -the kink band- initiate early failure, at many spots along the fibre, during impact loading, preventing the fibre to take up elastic energy. This could account for the fact that the scutched fibres give slightly better results in impact testing, these fibres contain fewer kink bands, because they have not undergone the hackling process, and consequently show longer fibre pull-out. Futhermore, in the scutched fibres more intrafibre pull-out seems to take place, which is an extra energy consuming mechanism during the fracture process. The absence of a relation between the tensile strength and the impact strength indicates that, whereas at quasi-static testing, during the normal tensile tests, the kink bands are still able to support a substantial load, during impact loading they fail early in the process, preventing the fibres to take up a substantial amount of elastic energy. This will further lower the impact strength of NMTs compared to GMTs.

Wald [27] found for GMT material with 30 wt% glass fibre and similar composite thickness an impact strength of 40 kJ/m$^2$ on average. The impact strength of this GMT material, which has a fibre volume fraction of 0.135, is plotted in figure 5.11 as well.

As mentioned above, the lower Charpy impact strength for the NMTs compared to the glass fibre composites can be partly attributed to the shorter pull-out length of the flax fibres compared to glass fibres, due to the lower fibre strength. The impact strength of the NMTs might further be influenced negatively by premature failure of the kink bands. Furthermore, as a consequence of the shorter pull-out length of the flax fibres, the matrix deformation zone in the flax reinforced composites will be smaller than in the glass fibre composites, which further limits energy uptake during the impact test.

The impact strength of a composite is a complex resultant of fibre fracture, matrix deformation and fracture, fibre-matrix debonding and fibre pull-out. Therefore in this study only a qualitative and no quantitative evaluation can be performed. The impact strength of flax fibre reinforced composites, however, can most probably be enhanced when instead of the flax fibre bundle properties the properties of the stronger elementary fibres can be utilised. Extruded and injection moulded flax/PP/MAPP materials contain elementary fibres. The properties of these materials will be discussed in the next chapter

## 5.4 Conclusions

The composite-like structure of flax fibres has no influence on the tensile modulus of flax fibre reinforced composites, neither has improved fibre-matrix interaction. The tensile modulus of scutched and hackled fibre reinforced NMTs is comparable to that of commercial GMT on basis of fibre volume fractions, on basis of fibre weight fractions the flax fibre reinforced composites perform better.
The tensile and flexural strength of flax fibre reinforced composites is determined both by the tensile strength of the fibre and by the presence of weak lateral fibre bonds. Consequently hackled fibres give stronger composites than scutched fibres. Addition of MAPP increases the tensile and flexural strength of hackled flax/PP composites more than of scutched flax/PP presumably due to the presence of less weak lateral bonds in hackled fibres. Both the tensile and flexural strength of hackled fibre composites is about 60-65% of GMT strength compared on the basis of fibre weight fraction.
The flexural modulus is dependent on the physical structure of flax fibres and on fibre-matrix adhesion as well. The mechanism behind this result is not very clear at the moment. The flexural modulus of hackled fibre reinforced composites is somewhat

lower than of GMT on basis of fibre volume fractions, on basis of fibre weight fractions the flexural modulus is comparable for both types of composites.
The unnotched Charpy impact strength of flax NMT composites decreases with increasing internal fibre bonding and enhanced fibre-matrix adhesion for the two volume fractions investigated. The unnotched Charpy impact strength increases with rising fibre fraction. The impact strength of the flax NMT composites is much lower than generally reported for GMT materials. The mechanism of energy uptake during fracture seems to be different in flax NMT composites compared with GMT materials.

## 5.5 References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the MAPP. In this study 3.5 wt% MAPP is used in order to study the influence of improved fibre-matrix adhesion for both 20 and 40 vol% flax composites.

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# 6

# Short Flax Fibre Reinforced Compounds

## 6.1 Introduction

Short flax fibre reinforced compounds can be made by mixing flax fibres with a thermoplastic matrix at elevated temperature in an extruder or a kneader. The advantage of these materials compared to the compression moulded NMTs described in the previous chapter is that they can be injection moulded into complex three dimensional shapes. Furthermore, the production time for injection moulded products is usually much shorter than for products made via compression moulding. For large production volumes and smaller product size, the injection moulding technology can therefore be considerably cheaper.

Most work on the extrusion compounding of cellulosic fibres is performed with short wood fibres. Only few groups are working on the compounding and injection moulding of bast fibres. Most of this work is done with polypropylene (PP) as the matrix material, but very little work is done with flax as the reinforcing fibre. Karmaker and Youngquist [1] report the properties of injection moulded 50 wt% PP/50 wt% jute compounds, without and with maleic anhydride modified PP (MAPP) as compatibiliser. They produce the composites by melt blending PP with the fibres in a K-mixer (a thermokinetic mixer),

which is a batch process. The median fibre length in their compounds lies at 350 and 390 µm for compounds without and with compatibiliser respectively. They find a tensile modulus of circa 7.5 GPa, and a flexural modulus of circa 10 GPa, both of which are not affected by the addition of compatibiliser. The strength of the materials on the other hand is strongly affected by the addition of the compatibiliser. The addition of only the jute fibres increases the tensile strength from 27 MPa for pure PP to 30 MPa for the compound and the flexural strength from 31 MPa to 50 MPa. Addition of the compatibiliser further raises the tensile strength to 59 MPa and the flexural strength to 88 MPa. Rana et al. [2] find similar results on a PP compound with jute and they show with SEM micrographs the adhesion between the fibres and the matrix. They also report an increased Charpy impact strength upon the addition of MAPP. Thomason et al. [3] produce jute filled 'long fibre' injection mouldable PP via a special process. They report a modulus of 4.1 to 4.4 GPa and a tensile strength of 35 to 45 MPa for a 30 wt% filled material. Sanadi et al. [4] produce kenaf fibre reinforced compounds in the same K-mixer. They also find a huge influence of the addition of a compatibiliser on the tensile and flexural strength. Furthermore, they also find an increase in the unnotched Charpy impact strength upon the addition of the compatibiliser. In another paper Sanadi et al. [5] show that, contrary to what is usually the case for glass fibre reinforced materials, the MAPP with a low MA content and the highest molecular weight proves not to be the most effective compatibiliser. Sanadi et al. blame this on the fact that with a high molecular weight MAPP, the few MA molecules grafted on the chain might have difficulty 'finding' the reactive hydroxyl groups on the fibre surface. Caulfield et al. [6] point out that during processing of a PP/kenaf compound, material from the outer fibre surface -for instance the waxes- is sheared off from the fibres and blends in with the matrix. This causes the matrix to achieve the characteristic brown colour, but may at the same time also influence the properties of the matrix material. Caulfield et al. suggest it may, among other things, lead to a reduction in the $T_g$ of the matrix.

Snijder et al. [7] show that, also for polystyrene (PS) reinforced with flax fibres, addition of a compatibiliser (Styrene Maleic Anhydride (SMA) copolymer in this case) the flexural strength increases, but the increase here is much smaller, from 58 MPa to circa 66 MPa.

Hornsby et al. [8] study the properties of PP compounds reinforced with linseed flax straw, which is pulped on a pulping extruder before it is mixed with PP. These fibres, however, have suffered so severely from the pulping process [9], that little reinforcing

action is preserved, and they find an increase in tensile strength from 33 MPa to 39 MPa upon the addition of 25 wt% flax straw and MAPP as a compatibiliser.
A lot of work is done on the modification of PP with wood fibres or wood flour. Oksman and Clemons [10] published a study on the optimisation of the mechanical properties of PP/wood flour composites by means of the addition of various compatibilisers. They study especially the impact behaviour of the composites. They succeed in doubling the unnotched (from 86 to 167 J/m) and the notched (from 26 to 54 J/m) Izod impact strength while retaining a tensile strength of 30 MPa and a modulus of 1.9 GPa, by adding a maleated styrene-ethylene/butylene-styrene triblock copolymer (SEBS-MA). Oksman et al. [11] also studied the location of this compatibiliser and they found part of it to be located at the interface between the wood particles and the matrix. Also in this case the maleic anhydride part of the molecule reacts with the surface of the wood particles. It is clear, however, from the reported numbers that wood flour is by no means as effective in increasing the properties of PP compounds, as longer natural fibres like flax, kenaf and jute are.
The increase in Charpy impact strength by the application of a rubbery interphase between the fibres and the matrix is also found by Gassan and Bledzki [12] for a flax fibre mat/PUR composite. They find a correlation between the thickness of the rubbery interphase and the increase in Charpy impact strength, together with a decrease in flexural strength.

The production of natural fibre reinforced compounds on an industrial scale is by no means trivial. At ATO bv a process is developed for the continuous production of natural fibre reinforced compounds on a twin screw extruder [13]. The bottleneck of this process is the feeding of the fibres to the extruder, especially for fibres like flax which are not available as sliver for an acceptable price. A prototype feeder has been patented by ATO bv [14] but has up till now not been further developed. Schäfer [15], from DaimlerChrysler AG, describes a procedure to produce granulate from a thermoplastic polymer and a natural fibre via a 'ring mould press', in which the granulate and the fibres are mixed after which they are granulated and can be injection moulded into the desired shape. It is not clear whether this process is already commercially used. Garkhail [20] uses an Amandus Kahl peletising press to produce fibre pills which can be fed into the extruder.
It is obvious that during the melt blending step, whether it is performed in a kneader or

in an extruder, the fibres are broken into smaller fragments. Von Turkovich and Erwin [17], among others, investigated the fibre break-up of glass fibres on a single screw extruder. They find that fibre volume fraction, initial length and initial state of dispersion have little influence on the final fibre length. In dilute suspension the fibre break-up seems to be governed by the shear flow stresses, which bend and eventually curl up the fibre. Model studies performed at ATO bv [18] on flax fibres in a viscous medium subjected to a Couette flow field, confirm that break-up of flax fibres in shear flow is caused by bending. In some cases, after fracture has taken place, the fibres are found to be still bound together by a very thin long fibril. The mechanism is similar as the mechanism described in the in-situ ESEM study presented in Chapter 3. It can, however, also be expected that, when the fibres become small enough to travel between the flight of the extruder screw and the barrel, they will be more or less ground to particles which are smaller than can be produced via the bending process. Apart from breaking the fibres into small pieces, both the kneader and the extruder also separate the technical fibres into elementary fibres [13].

A number of authors investigated the thermal degradation of flax fibres at temperatures around 200 °C [20,19-21], they find that generally thermal degradation is not really significant in the first few minutes and at lower temperatures. Gassan and Bledzki [19] show that untreated flax retains its strength during an exposure of 120 minutes at 170 °C, whereas the strength decreases with roughly 50% when the fibre is exposed to 210 °C during the same time span. Generally, the conclusion is drawn that when the processing parameters, and especially the temperature and the residence time, are well under control, the production of flax fibre compounds should be possible without significant loss of stiffness and strength. Figure 6.1 shows the residual tensile strength of fibres that were subjected to a heat treatment during 5 minutes in a tin bath [22] under ambient atmosphere. The triangles represent untreated fibres, the squares represent fibres that were subjected to a light alkali treatment with 0.3 wt% alkali, in order to remove the pectins and hemicelluloses which were suspected to be the thermolabile components. It is obvious from this figure that already an exposure to 200 °C during 5 minutes leads to a drop in tensile strength of circa 25%. At higher temperatures the drop in strength becomes dramatic. The strength loss of flax fibres at higher temperatures is probably caused by two effects:

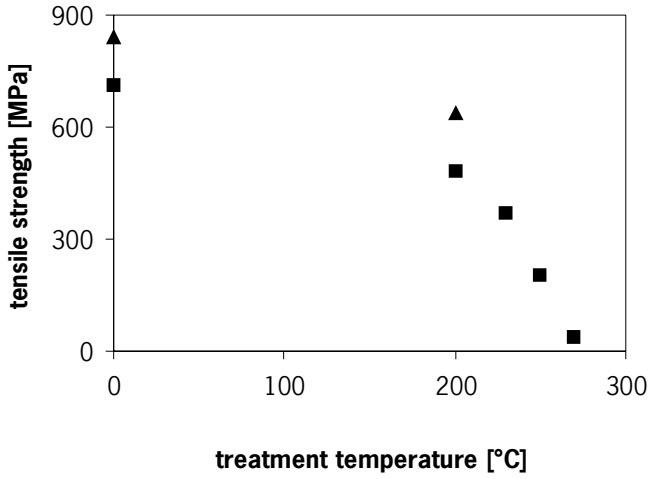


*Figure 6.1. Residual strength of technical flax fibre bundles after heat treatment during 5 minutes in a tin bath, giving an instant temperature rise. ▲ untreated fibres, ■ alkali treated fibres [22].*

- The first is the decrease in the molecular weight of the cellulose chains in the cell wall. Van Hazendonk et al [23] investigated the effect of steam and alkali treatment on the degree of polymerisation (DP) and the tensile strength of flax. They find a fairly linear relation between the DP and the fibre strength. The drop in fibre strength between the untreated blank and the alkali treated blank (in figure 6.1) can be attributed to this effect [23]. Van Hazendonk et al. report furthermore a decrease in DP during a steam treatment of the fibres, obviously brought about by hydrolysis of the cellulose chains under wet conditions. Gassan and Bledzki [19] find that also a heat treatment at ambient humidity lowers the DP of the cellulose.
- The second factor influencing the strength of the fibres is the presence of water and the drying history of the fibres. Stone and Scallan [24] describe a phenomenon generally found in cellulosic fibres which is known as hornification: once the fibres have been dried to below a certain water content, their properties change irreversibly. The higher the temperatures at which the drying is performed, the stronger this effect becomes. Stone and Scallan attribute this to irreversible closure of certain very small pores in the cellulosic structure. Scallan [25] suggests that the closing up of the cell wall structure results in an increased internal

bonding. This would result in less plastically deformable fibres, which are more brittle. This effect of embrittlement is well known for wood fibres and is found also in other cellulosic fibres, like flax [24,26]. Predrying the fibres before compounding might thus have an additional negative effect on the properties of the fibres.

It is quite possible that in all the compounds and NMTs these phenomena have taken place but to what extent is unknown. To the best of the autor's knowledge no data are available on the actual residual fibre strength of natural fibres after processing with a polymer. Snijder et al. [27] showed that processing of flax fibre compounds is possible to temperatures of at least 260 °C for 5 minutes, without a significant loss in properties of the resulting compound. Care needs to be taken, however, in commercial-scale processing, where the residence time distribution can be broad and the temperature control is limited and hot spots can occur in the melt. These factors will inevitably lead to weak products. Some interest is presently shown by extruder manufacturers towards the production of natural fibre compounds. Hanawalt [28] from ENTEK extruders describes how to design the extruder to produce a compound from a thermoplastic with natural fibres. Large commercial scale production of thermoplastic extrusion compounds with (long) natural fibres, seems presently not to take place. Wood fibre compounds, however, are made commercially in, for instance, the USA. Much effort has been put into the optimisation of the compounding process, which has, amongst others, led to the development of the Woodtruder [29], in which the wood fibres are fed to the extruder and subsequently dried before the polymer is fed to the extruder.

This chapter investigates the properties of short flax fibre/PP compounds. A comparison is made between materials produced in a batch kneader and materials made via a twin-screw extrusion process. Tensile and flexural properties are also compared with the properties of the NMT materials presented in Chapter 5. Furthermore, the impact behaviour of the materials is investigated in more depth.

## 6.2 Experimental

### *6.2.1 Materials*

Flax bast fibres were produced from scutched, dew retted flax (variety Belinka). The fibres were chopped to 6 mm prior to compounding. The fibres were not dried before compounding; they contained about 10 wt% moisture. In all the experiments reported

here the fibre content (weight fraction) refers to the undried fibres. Isotactic polypropylene (PP) (homopolymer, pellets, MFI = 12 g/10 min., for most experiments a Stamylan P grade from DSM) was used as the matrix material. The MAPP compatibiliser was Epolene™ G-3015 and was kindly supplied by Eastman Chemical Company.

### *6.2.2 Compound production*

Kneaded compounds were prepared in a Haake Rheomix 3000 batch kneader, equipped with roller rotors at a set temperature of 185 °C. The polymer and compatibiliser (3 wt%) were added to the kneader first and kneaded for circa 2 minutes to obtain a constant torque. Next the fibres were added and the resulting mixture was kneaded, making sure that after the last fibres were added, kneading was continued for 4 minutes. This leads for the 28 wt% filled compounds to a total kneading time of 10 minutes and for the 51 wt% compounds to a total kneading time of 11.5 minutes. For the 28 wt% filled material the temperature increased to maximum 205 °C during kneading, for the 51 wt% compounds the material temperature was 209 °C maximum. The material was subsequently cooled and converted into granules using a pelletiser from KT Handling Ltd.

Extruded compounds were produced via a patented process [13] on a Berstorf ZE 40 co-rotating twin screw extruder at a screw speed of 200 rpm and a melt temperature of 200 °C. PP or a mixture of PP and MAPP, was fed upstream, the fibres were fed downstream in the molten polymer. The screw built-up of the extruder during this process is such that the fibres are separated optimally into elementary fibres, while retaining a fibre length as high as possible. The extruded strands were quench-cooled by immersion in a water bath and granulated using a pelletiser from C.F. Scheer & Cie.

Next, both the kneaded and the compounded materials were injection moulded on a Demag Ergotech 25-80 compact. The temperature profile of the screw was 35/150/190/190/190, the temperature of the melt was thus kept below 200 °C. The mould temperature was 30 °C and the samples were cooled during 12 seconds.

### *6.2.3 Mechanical testing*

Tensile and flexural test bars were injection moulded from the granulated compounds. The test specimens were conditioned for at least 7 days at 50% RH and 23 °C. Tensile properties were measured on a Zwick Z010, following ISO R527, using dogbone samples of 2*5 $mm^2$ diameter and a gauge length of 25 mm. Flexural properties were

measured using samples of dimensions 4*10*80 $mm^3$ on a Zwick 1445 according to ISO 178. Charpy impact (unnotched and notched with notch type A) was measured using the same samples on a Ceast pendulum impact tester following ISO 179.

### *6.2.4 Fibre length measurement*

Measurement of the fibre length and thickness distribution of the compounded and kneaded materials was done by preparing the fibres between two glass slides for colour positives. The slides were scanned on a Minolta Dimage Scan MultiPro at 4800 dpi. Scanner software Dimage scan 1.0 out of Photoshop 5.0 LE was used to process the data. Fibres longer than 1500 µm were not measured.

## 6.3 Results and discussion

### *6.3.1 Stiffness and strength of kneaded and extruded compounds*

Flexural stiffness of the kneaded and extruded compounds is presented in figure 6.2 together with the data from the hackled NMTs presented in Chapter 5. The flexural

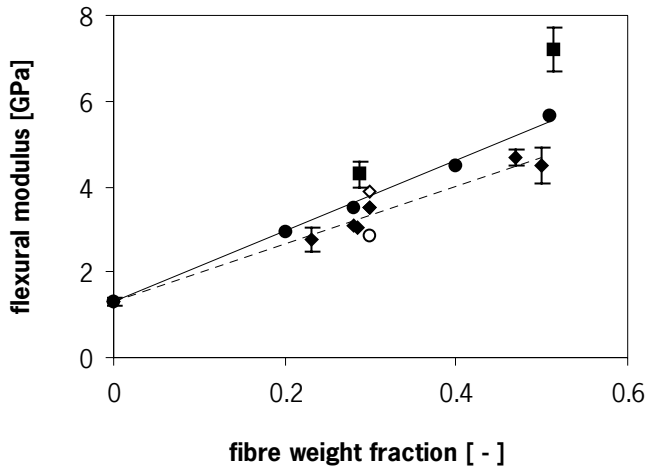


*Figure 6.2. Flexural modulus of ● kneaded flax/PP/MAPP and O kneaded flax/PP, and ◆ extruded flax/PP/MAPP and ◇ extruded flax/PP compounds, compared with ■ hackled flax/PP/MAPP NMTs, versus fibre weight fraction. The fitted lines are: ———— kneaded and – – – – – extruded flax/PP/MAPP. Error bars smaller than the marker size are not shown.*

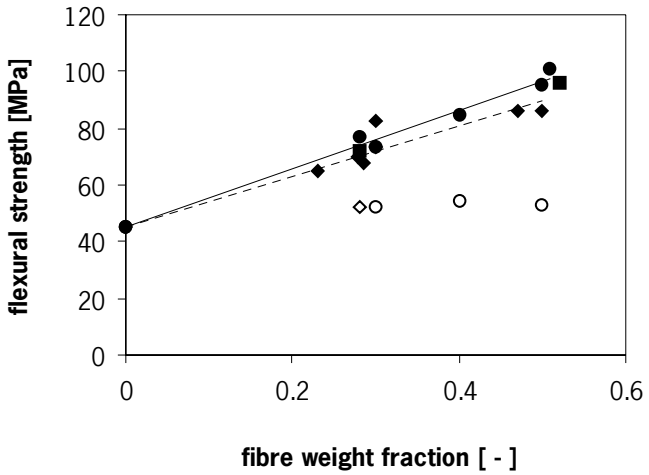


*Figure 6.3. Flexural strength of ● kneaded flax/PP/MAPP and O kneaded flax/PP, ◆ extruded flax/PP/MAPP and ◇ extruded flax/PP compounds, compared with ■ hackled flax/PP/MAPP NMTs, versus fibre weight fraction. The fitted lines are: ———— kneaded and – – – – – extruded flax/PP/MAPP. Error bars falling within the size of the marker are not shown.*

strength of the materials is presented in figure 6.3. It is obvious that the flexural stiffness of the hackled NMT materials is significantly higher than of the compounds, especially at 51 wt% fibre loading. The flexural strength of the compounds, however, is very similar to the strength of the hackled NMT materials, even though there is a large difference in fibre length, and roughly a factor 10 difference in the aspect ratio between the two fibre types. The strength data for especially the kneaded compounds lie at the upper limits of the NMT data (compare also figure 5.9). The drawn lines show a straight fit for the kneaded compounds, the dotted lines give a fit for the extruded compounds. It is clear that the kneading process gives materials with slightly better properties at the same weight fraction than the extrusion process. Furthermore, it is apparent that whereas the addition of fibres without a compatibiliser leads always to an increase in modulus, the flexural strength of the materials is unaffected by the fibres, as long as the adhesion between fibres and matrix is not optimised.

In figures 6.4a and 6.4b the tensile modulus and tensile strength of the materials are shown, respectively. The tensile modulus of the kneaded compounds lies well within the

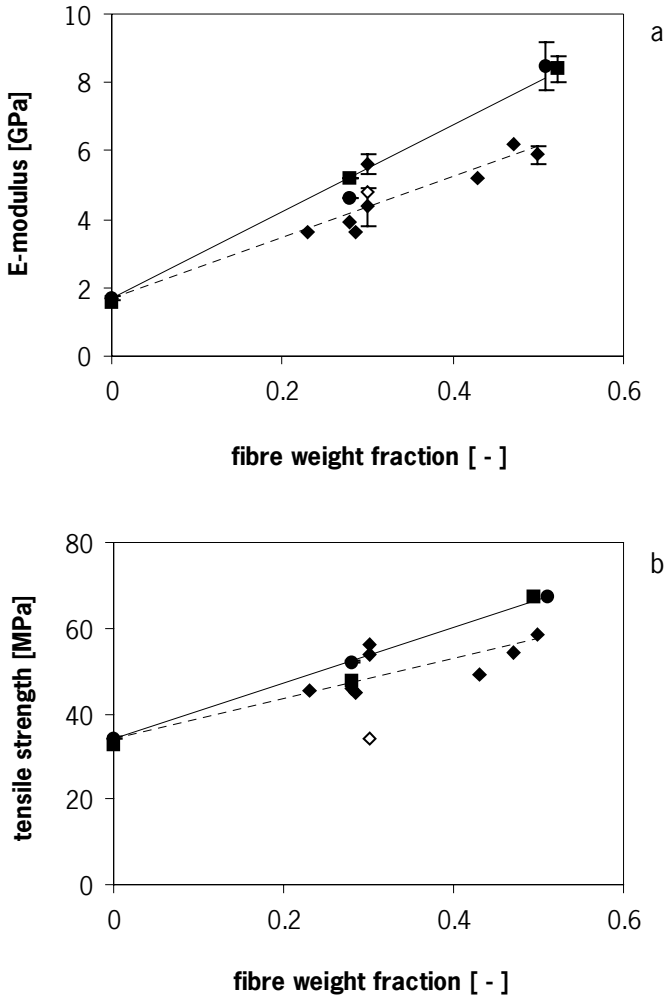


*Figure 6.4. (a) Tensile modulus and (b) tensile strength of ● kneaded flax/PP/MAPP, ◆ extruded flax/PP/MAPP and ◇ extruded flax/PP compounds, compared with ■ hackled flax/PP/MAPP NMT, versus fibre weight fraction. The fitted lines are: ——— kneaded and – – – – – extruded flax/PP/MAPP. Error bars falling within the marker size are not shown.*

same range as the tensile modulus of the NMT materials. Again the strength of the kneaded compounds lies at the upper limit of the strength of the NMT materials (see also figure 5.6). The materials produced in the extruder again show somewhat lower

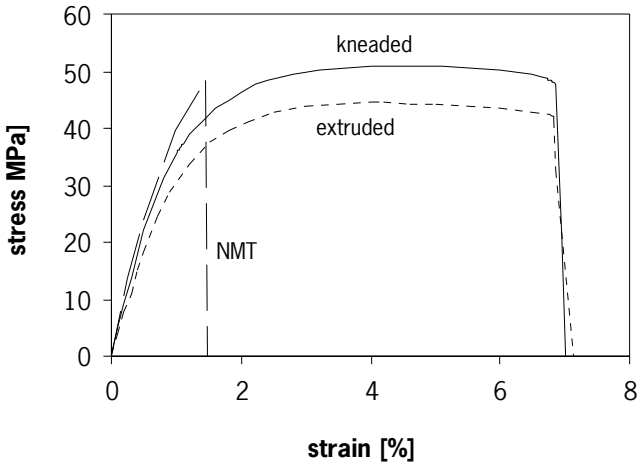


*Figure 6.5. Typical stress-strain curves of the 28 wt% ———— kneaded and – – – – – extruded materials, compared with —— —— —— 28 wt% NMT.*

stiffness and strength than the kneaded compounds, the difference between the kneaded and extruded compounds is larger than in the case of the flexural properties.
It is at first sight unexpected that both the bending and the tensile properties of the flax/PP compounds show so little difference with the properties of the NMT materials, given the large difference in fibre length of the fibres. However, the orientation of the fibres in the compounds and the NMTs is also very different, and this could counteract the effect of the difference in fibre length on the properties. Apart from this, the strain at break of the NMTs is much smaller than of the compounds, as is shown in figure 6.5, which shows the stress strain curves of the different materials with 28 wt% fibre loading. The compounded materials -both the kneaded and the extruded- are far more ductile than the NMTs. The higher ductility of the compounds is obviously caused by the shorter fibre length.
Figure 6.6 shows the fibre length for kneaded and extruded materials after injection moulding. The kneaded material shows a somewhat shorter fibre length than the extruded material, and, as can be expected, the fibre length is lower in compounds with a higher fibre loading. The fibre length distribution of the extruded material is also somewhat broader than of the kneaded material. The mean fibre length of the materials is calculated from these plots and shown in table 6.1. There is a slight difference in the

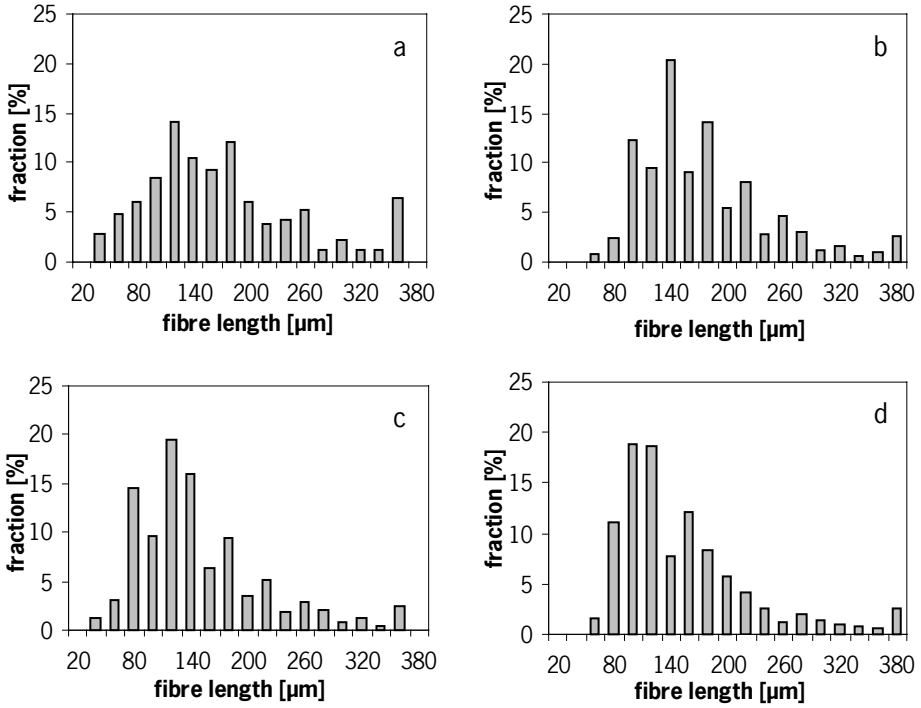


*Figure 6.6. Fibre length distribution of the compounds after injection moulding into a tensile test bar. (a) 28 wt% extruded, (b) 51 wt% extruded, (c) 28 wt% kneaded, (d) 51 wt% kneaded.*

mean fibre length for the different materials. The critical fibre length $L_c$ of these materials can be calculated following Kelly-Tyson [30]:

$$L_c = \frac{\sigma_f \; d}{2\,\tau} \tag{6.1}$$

Using a fibre strength $\sigma_f$ of 1500 MPa as determined in Chapter 3 for elementary

*Table 6.1. Mean fibre length of the kneaded and extruded materials.*

| Material | 20 vol% (28 wt%) | 40 vol% (51 wt%) |
|---|---|---|
| Kneaded | 160 µm | 140 µm |
| Extruded | 190 µm | 170 µm |

fibres, a fibre diameter $d$ of 15 µm (see table 6.3) and an interfacial shear strength $\tau$ of 28 MPa as found in Appendix A, a critical fibre length of 400 µm can be calculated. It is clear that the majority of the fibres in the compounds are shorter than the critical fibre length, which indicates that they probably are not loaded up to their failure stress within the compound.

As discussed in Chapter 5 the tensile strength of a composite can be modelled via the Kelly-Tyson approach [30,31] as:

$$\sigma_c = k\,\eta_0\,\eta_L\,V_f\,\sigma_f + (1 - V_f)\,\sigma_{um} \tag{6.2}$$

where $\eta_0$ is the orientation factor and $k$ is the efficiency factor, $\sigma_{um}$ is the matrix strength at the fibre failure strain, assumed to be equal to $E_m * \sigma_f / E_f$ and $V_f$ is the fibre volume fraction. Following Kelly-Tyson, the fibre length efficiency factor, $\eta_L$, is:

$$\eta_L = \frac{1}{V_f}\left[\Sigma\frac{L_i V_i}{2 L_c} + \Sigma V_j\left(1 - \frac{L_c}{2 L_j}\right)\right] \tag{6.3}$$

where $V_i$ is the fibre volume fraction of fibres of length $L_i$, shorter than the critical fibre length and $V_j$ is the fibre volume fraction of fibres of length $L_j$, longer than the critical fibre length. The two summation terms in equation 6.3 account for the fibres of sub-critical length ($L < L_c$) and super-critical length ($L > L_c$) respectively. In Chapter 5 a virtual orientation factor ($\eta_{0,v} = k * \eta_0$) of 0.206 is found for NMT materials with hackled fibres, which will also be used here for the kneaded and extruded compounds.
From the length distribution of the kneaded and extruded samples a fibre length efficiency factor, $\eta_L$, can be calculated from equation 6.3: $\eta_L$ equals 0.17 for the 28 wt% kneaded compounds and $\eta_L$ equals 0.20 for the 28 wt% extruded compounds. This leads, using $E_f$ = 50 GPa, $E_m$ = 1.6 GPa and $\sigma_f$ = 1500 MPa, at a fibre loading of 28 wt% to a predicted tensile strength of 49 MPa for the kneaded material and 50 MPa for the extruded material. The measured values are 52 MPa for the kneaded material and 45 MPa for the extruded material, respectively, which is very close to the prediction. However, in spite of the more profitable length distribution of the extruded materials, they show properties which are somewhat lower than expected. It is possible that during extrusion the materials have undergone a more severe heat exposure than during kneading and that the strength of the extruded fibres has decreased more during processing than the strength of the kneaded fibres. The fact that also the modulus of the extruded materials is lower than of the kneaded materials points to this

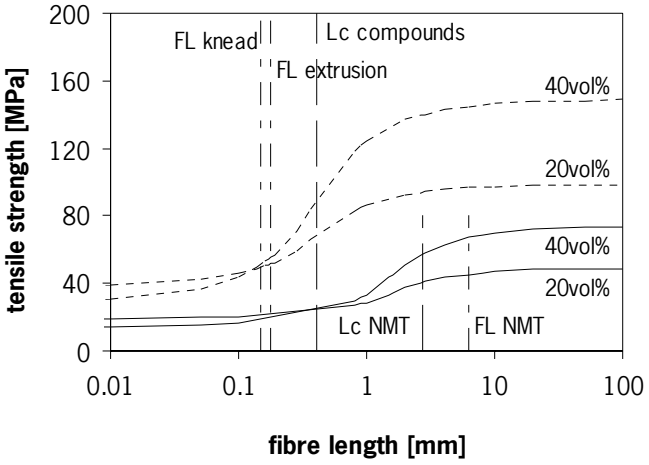


*Figure 6.7. Tensile strength as a function of fibre length for 20 vol% and 40 vol% materials, following Kelly-Tyson. ——— NMTs, – – – – – compounds, — — — — Lc of the compounds and NMTs, –·–·–·–·– actual mean fibre length (FL) in kneaded and extruded compounds and NMTs.*

conclusion, since it is usually found that the modulus of natural fibre filled materials is mainly depending on the fibre loading.

Following Thomason et al. [31] the strength prediction from the Kelly-Tyson model can be plotted against the fibre length. In figure 6.7 this plot is shown for both the NMT materials and the compounds. For each material the strength versus fibre length is shown for a 20 fibre volume percent material (= 28 wt%) and for a 40 fibre volume percent material (= 51 wt%). The predicted tensile strength of the compounds at higher fibre length is obviously much higher than that of the NMTs due to the assumed higher fibre strength of the elementary fibres in the compounds. Both the critical fibre length and the actual (mean) fibre length of the NMT materials as well as the compounds are indicated in the plot. The tensile strengths predicted for the 20 and 40 vol% NMTs and compounds (assuming that all fibres in the material have a length equal to the mean fibre length given in table 6.1) are shown in table 6.2 and compared with the measured values. As can be seen the predicted values for the NMTs and most of the compounds lie very close together, just as the actually measured values. However, this seems to be completely coincidental, since the values lie on a very different curve. The aspect

*Table 6.2. Tensile strength of NMTs and compounds as measured and calculated following Kelly-Tyson.*

| | | Tensile strength [MPa] | |
|---|---|---|---|
| Fibre fraction | Material | Calculated | Experimental |
| 20 vol% | Kneaded | 50 | 52 ± 0.2 |
| (28 wt%) | Extruded | 53 | 45 ± 0.2 |
| | NMT | 45 | 48 ± 0.5 |
| 40 vol% | Kneaded | 50 | 67 ± 0.3 |
| (51 wt%) | Extruded | 54 | 58 ± 0.4 |
| | NMT | 67 | 68 ± 1.8 |

ratio of the fibres obviously has a large influence here. The aspect ratio of the hackled fibres lies around 120, whereas the aspect ratio of the compounds is approximately 10, thus making the hackled fibres much more effective than the compounded fibres. The model becomes somewhat inaccurate at shorter fibre length (especially apparent at the 51 wt% (40 vol%) kneaded material), due to the fact that not the actual strength of the matrix is taken into account, but the stress in the matrix at the point where the fibres break, because the matrix is expected to fail at this point as well. At low fibre content or with very short fibres this assumption no longer holds. Nevertheless, it can be concluded that the kneaded and extruded compounds have the potential to form much stronger materials, if it were only possible to retain the fibre length during compounding, while separating the fibre bundles into elementary fibres. On the other hand, as can be concluded from the fact that the extruded materials usually show somewhat inferior properties compared to the kneaded materials, it is of the utmost importance to carefully control the temperature of the melt during extrusion and further processing steps. Obviously, the more sophisticated the materials become, the more important this aspect will be.

Bowyer and Bader [32,33] presented in the early seventies a method for deriving values for the interfacial shear stress $\tau$ and the virtual fibre orientation factor $\eta_{0,v}$ (which equals $k * \eta_0$) from a simple combination of the tensile stress-strain curve and the composite fibre length distribution. Thomason [34] recently reviewed and extended this

method. Bowyer and Bader extended the original Kelly-Tyson concept to model the stress strain curve of a composite prior to failure. The Kelly-Tyson model can be simplified to $\sigma_{uc} = \eta_{0,v}(X+Y)+Z$ where $Z$ is the matrix contribution, $X$ is the sub-critical fibre contribution and $Y$ is the super-critical fibre contribution, in reference to the critical fibre length from equation 6.1. Bowyer and Bader argued that at any value of composite strain, $\varepsilon_c$, there exists a critical fibre length $L_\varepsilon$, which is equal to:

$$L_\varepsilon = E_f \varepsilon_c d / 2\tau \tag{6.4}$$

Fibres shorter than $L_\varepsilon$ carry an average stress equal to $L\tau/d$ and fibres longer than $L_\varepsilon$ carry an average stress equal to $E_f\varepsilon_c(1-(E_f\varepsilon_c d/4L\tau))$. The composite stress at any strain level is then given by:

$$\sigma_c = \eta_{0,v}\left(\sum_i\left[\frac{\tau L_i V_i}{d}\right]+\sum_j\left[E_f\varepsilon_c V_j\left(1-\frac{E_f\varepsilon_c d}{4\tau L_j}\right)\right]\right)+(1-V_f)E_m\varepsilon_c \tag{6.5}$$

Bowyer and Bader then showed that, although $\eta_{0,v}$ and $\tau$ are not generally known, values for these parameters can be obtained if the composite stress ($\sigma_1$ and $\sigma_2$) at two strain values ($\varepsilon_1$ and $\varepsilon_2$) is known. The matrix contribution $Z$ at these two strains can be determined from a tensile test on the pure matrix material [34] and used to calculate the ratio $R$ of the fibre contributions at the two strains:

$$R = \frac{\sigma_1 - Z_1}{\sigma_2 - Z_2} \qquad R' = \frac{X_1 + Y_1}{X_2 + Y_2} \tag{6.6}$$

Equation 6.5 can then be used with an assumed value of $\tau$ to calculate the ratio $R'$, the theoretical value of $R$. At this point the calculation is independent of $\eta_{0,v}$. The value of $\tau$ is then adjusted until $R' = R$, and that value of $\tau$ is then used in equation 6.5 to obtain a value for $\eta_{0,v}$ (which is assumed to be the same at both strain levels). This analysis method can be further extended to derive a value for $\sigma_{uf}$, the fibre stress at composite failure.

Using the fibre length distributions given in figure 6.6, and following the above analysis at two strains, $\varepsilon_1$ = 0.5% and $\varepsilon_2$ = 2%, the interfacial shear strength $\tau$ and virtual orientation factor $\eta_{0,v}$ were calculated for all the different compounds. For the NMT materials the fibre length was assumed to be monodisperse at 6.25 mm, and the two strain values were taken as 0.5 and 1%. The calculation is rather dependent of the diameter of the fibres. In table 6.3 the measured fibre diameters of the compounded materials are given, it is clear that the kneaded materials have a lower mean fibre

*Table 6.3. Interfacial shear strength $\tau$ and virtual orientation factor $\eta_{0,v}$ calculated from the stress-strain curves, the mean fibre thickness d, and the fibre length distribution, following the method of Bowyer and Bader [32].*

| Fibre fraction | Material | d [µm] | $\tau$ [MPa] | $\eta_{0,v}$ |
|---|---|---|---|---|
| 20 vol% | Kneaded | 13.3 ± 4.7 | 28.7 | 0.085 |
| (28 wt%) | Extruded | 16.2 ± 6.1 | 27.8 | 0.073 |
| | NMT | 50 | 6.5 | 0.010 |
| 40 vol% | Kneaded | 12.8 ± 4.7 | 15.3 | 0.234 |
| (51 wt%) | Extruded | 15.7 ± 5.4 | 23.0 | 0.145 |
| | NMT | 50 | 2.9 | 0.177 |

diameter than the extruded material, indicating that they have separated further into elementary fibres than the extruded materials have. The calculated values for $\tau$ and $\eta_{0,v}$ are also shown in table 6.3. It is clear that the values for the interfacial shear stress lie in the same order as the values measured using the single-fibre-fragmentation test reported in Appendix A: 28 MPa for elementary fibres in a PP/MAPP matrix and 12 MPa for scutched fibres in a PP/MAPP matrix. Only the 51 wt% NMT gives a much lower value for $\tau$, this might be due to the fact that in the calculation a monodisperse fibre length distribution is assumed for these materials. The values found for $\eta_{0,v}$ for the 28 wt% materials are all rather low. Also, contrary to the assumption, $\eta_{0,v}$ is not completely independent of the strains used in the calculation, there is usually a difference of about 0.02 between the $\eta_{0,v}$ values calculated at the two strains used in the analysis (in the table the mean of these values is given). The values of $\eta_{0,v}$ for the 51 wt% materials, however, come quite close to the value of 0.206 that was found for the NMTs in Chapter 5. The virtual orientation factor, $\eta_{0,v}$, equals $k * \eta_0$ and thus accounts for both the fact that the fibres are not all oriented in the length direction of the sample (if they were, $\eta_0$ would be 1), and for the inefficiency of the fibres due to limited adhesion and other factors (in the case of no adhesion $k$ would be 0). The adhesion between fibres and matrix is rather good in the compounded materials. Therefore, possibly, in the case of the 28 wt% materials the fibres are oriented less favourably in the tensile bars, than in the higher filled materials, due to the difference in flow properties of the materials, leading to a lower $\eta_{0,v}$.

Also for the modulus a plot as a function of fibre length can be made, following the Cox-Krenchel approach as described in Chapter 5 [18-37]:

$$E_c = \eta_0 \eta_L V_f E_f + (1 - V_f) E_m \tag{6.7}$$

with:

$$\eta_L = \left( 1 - \frac{tanh(\beta L/2)}{\beta L/2} \right) \tag{6.8}$$

where:

$$\beta = \frac{2}{d} \left( \frac{2 G_m}{E_f \ln(\sqrt{\pi / X_i V_f})} \right)^{\frac{1}{2}} \tag{6.9}$$

A plot of the predicted Young's modulus versus fibre length is shown in figure 6.8, using $E_f$ = 50 GPa, $E_m$ = 1.6 GPa, $X_i$ = 4, and $G_m = E_m/2(1+\nu)$ with $\nu$, Poisson's ratio, taken as 0.4. Also the fibre lengths in the extruded and kneaded compounds and the NMTs are given. Contrary to the plot for the tensile strength, in this case the prediction

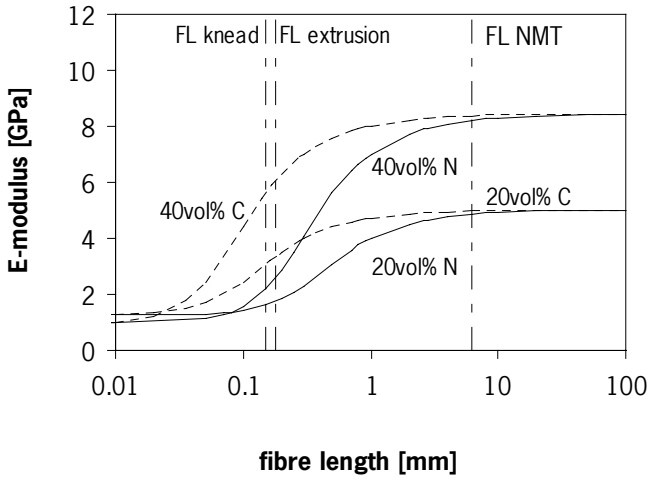


*Figure 6.8. Young's modulus as a function of fibre length for 20 vol% and 40 vol% materials, following Cox-Krenchel, ———— NMTs (N), – – – – – compounds (C), –·–·–·–·– actual mean fibre length (FL) in the kneaded and extruded compounds and the NMTs. The E-modulus of both elementary and hackled fibres is taken as 50 GPa.*

is not correct. The measured values of the modulus at similar fibre volume fraction lie very close to each other, whereas the model now predicts a much lower modulus for the kneaded and extruded compounds (see also table 6.4). The only difference between the NMTs and the compounds in the model lies in the difference in fibre thickness. For the compounds a fibre thickness of 15 µm is assumed, whereas for the NMTs the fibre thickness of the hackled fibres, 50 µm is taken. This difference accounts for the shift of the compound curves to the left.

A number of reasons could account for the misfit between the model and the data:

- As in the rest of this work, the Young's modulus of the hackled fibres and the elementary fibres both is assumed to be 50 GPa. As discussed in Chapter 3 the modulus of the fibres is difficult to measure, and it is quite possible that the value of 50 GPa for the elementary fibres is an underestimation. If a modulus of 80 GPa is assumed for the elementary fibres and a modulus of 50 GPa for the hackled fibres the plot of figure 6.8 changes into the plot of figure 6.9a. The predicted values for the modulus at 20 and 40 vol% for the compounds and the NMTs are given in table 6.4. They now lie much closer together, and also lie closer to the measured values, although they are still lower than the measured values.

*Table 6.4. Young's modulus of NMTs and compounds as measured and calculated following Cox-Krenchel, for a fibre modulus $E_f$ of 50 GPa for hackled fibres and 50 GPa and 80 GPa for elementary fibres, and for two different orientation factors $\eta_0$.*

| | | Young's modulus [GPa] | | | |
|---|---|---|---|---|---|
| | | Calculated | | | Experimental |
| Fibre fraction | Material | $E_f$=50 GPa $\eta_0$=0.375 | $E_f$=80 GPa $\eta_0$=0.375 | $E_f$=50 GPa $\eta_0$=0.63 | |
| 20 vol% | Kneaded | 3.2 | 3.7 | 4.4 | 4.6 ± 0.2 |
| (28 wt%) | Extruded | 3.4 | 4.2 | 4.9 | 5.6 ± 0.3 |
| | NMT | 4.9 | | | 5.2 ± 0.0 |
| 40 vol% | Kneaded | 5.4 | 7.0 | 8.5 | 8.5 ± 0.7 |
| (51 wt%) | Extruded | 5.9 | 7.9 | 9.3 | 6.2 ± 0.2 |
| | NMT | 8.2 | | | 8.4 ± 0.4 |

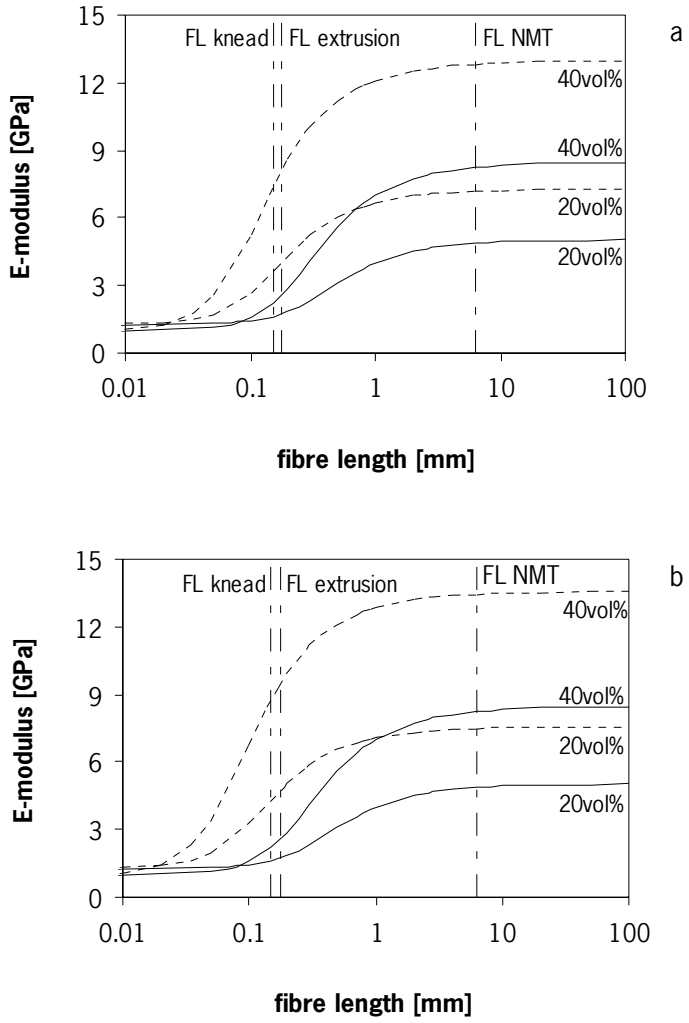


*Figure 6.9. Young's modulus as a function of fibre length for 20 vol% and 40 vol% materials, following Cox-Krenchel, ——— NMTs , – – – – – compounds, –·–·–·–·– actual mean fibre length (FL) in the kneaded and extruded compounds and the NMTs. (a) The Young's modulus of the hackled fibres is taken as 50 GPa, of the elementary fibres as 80 GPa. (b) The orientation factor $\eta_0$ is taken as 0.375 for the NMTs and as 0.63 for the compounds.*

- Another reason why the Cox-Krenchel prediction for the compounded materials is too low might be the orientation factor $\eta_0$. For a 2-D random composite, like the NMTs are, the orientation factor can be calculated to be 0.375, but in the injection moulded compound bars it is likely that the orientation factor will not be the same. Thomason [38] fits for a short glass fibre reinforced injection moulded PP an orientation factor of 0.69. Inserting this value in the Cox-Krenchel equation gives for our flax composites a somewhat high result. However, there are two reasons why for the flax compounds the orientation factor might be lower: (1) the test bars used in this work have smaller dimensions than the ones Thomason used, and (2) the flax fibres are found to be rather bent or even curled after the extrusion and injection moulding process, unlike glass fibres. Using an orientation factor of 0.63 and a fibre modulus $E_f$ = 50 GPa, predicts for the 51 wt% kneaded compound a modulus of 8.5 GPa and for the 28 wt% compound of 4.4 GPa (see table 6.2) which is also a satisfactory result. The resulting plot is presented in figure 6.9b.

From both explanations it follows that, if it were possible to produce compounds with a longer fibre length, the resulting stiffness might increase significantly. Furthermore, the fact that especially at high fibre loadings the extruded compounds show relatively low moduli again could point at the temperature sensitivity of the materials.

### *6.3.2 The effect of compatibilisation*

Another difference between the NMTs and the compounds is the kind of compatibiliser used and the way it is applied. In both cases a maleic anhydride modified PP (MAPP) is used, but from a different producer. For the NMTs the compatibiliser used is Hostaprime® HC5 (Hoechst), and it is added as a powder to the fibre mixture, during the wet mixing step in the paper making equipment. The used amount (3.5 wt%) was determined during a short optimisation study [39]. For the compounds the compatibiliser applied is Epolene™ G-3015, and the compatibiliser is fed to the kneader or extruder together with the polymer. The optimisation of the compatibiliser for the compounds has yielded this as the best combination found so far [40,41]. Whereas for the tensile strength it is possible that the NMT data are on the low side due to suboptimal fibre matrix adhesion, for the Young's modulus the difference in compatibiliser would make no difference since the modulus usually does not depend on the adhesion between fibres and matrix.

The effect of the compatibiliser is shown in figure 6.10 and 6.11. Without

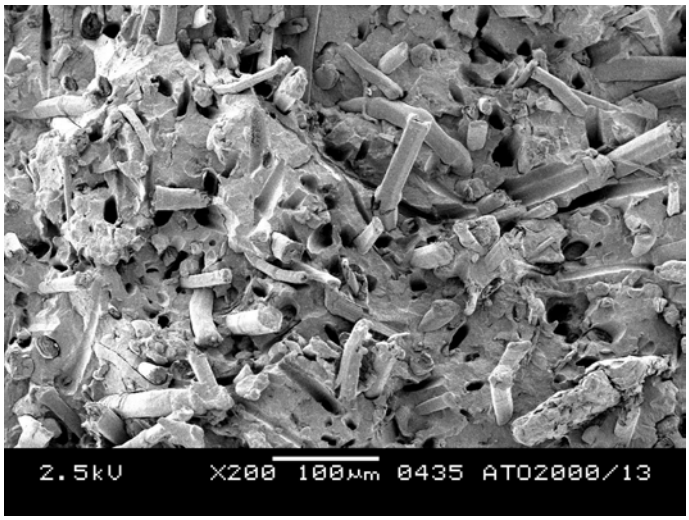


*Figure 6.10. SEM micrograph of an uncompatibilised extrusion compound of 30 wt% flax/PP. Note the many deep holes where fibres have been pulled out.*

compatibiliser (6.10) the fibres are clearly loose in their sockets, whereas with compatibiliser (6.11a and 6.11b) the fibres are fully coated and embedded within the PP. Figure 6.11b shows clearly how well the compatibiliser is adhered to the primary cell wall. It should be noted that the adhesion is reached within the time frame of the extrusion step (a few minutes), and that the fibres are not treated before extrusion. Given the fact that the fibres are opened-up during extrusion, and that a lot of new surface is created during this process, the effect of a fibre surface treatment before extrusion would be minimal.

Another interesting effect is shown in figures 6.12a and 6.12b. The crack has in these cases not run through the fibre/matrix interphase, or perpendicular through the fibre, but it has fully split the fibre over its length. Part of the secondary cell wall of the fibre in figure 6.12b seems to have been pulled out, whereas the primary cell wall -with maybe a small part of the secondary cell wall- is still adhered to the PP matrix (see the arrow). A small fibril bundle has come out of the secondary cell wall that was left at the bottom. The grey arrow points at a fibril that has separated from the small fibril bundle. The thickness of this fibril is roughly 0.25 µm, again similar to the meso structure found before (Chapter 3) in the secondary cell wall.

As is discussed in Chapter 3 the lateral strength and thus the shear strength within the

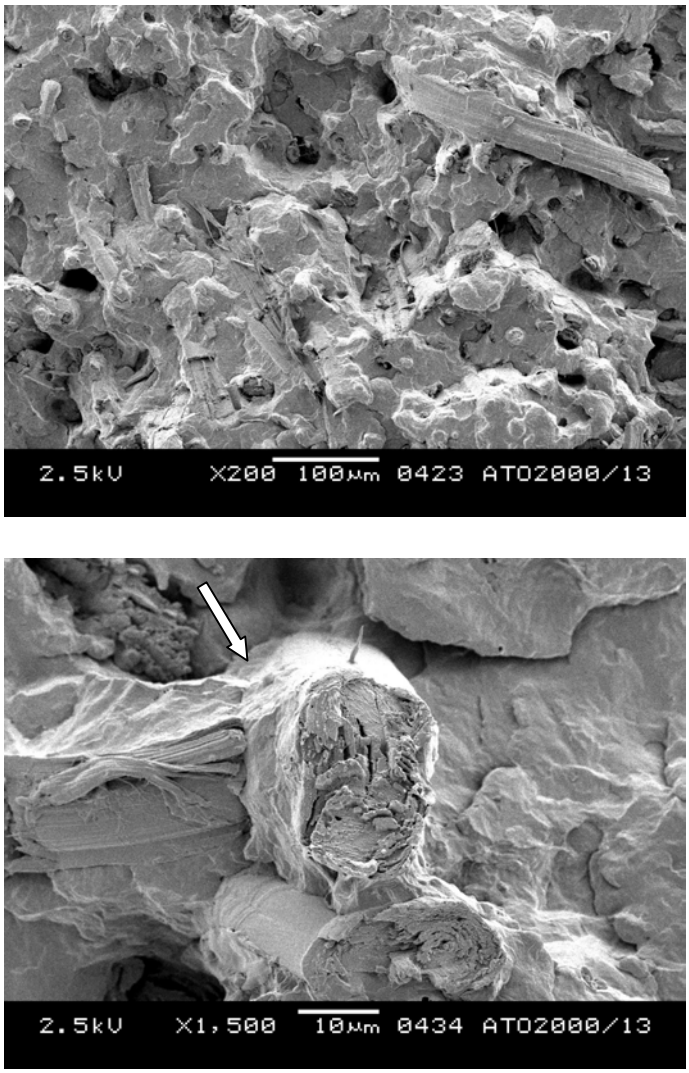


*Figure 6.11. SEM micrograph of 30 wt% flax/PP/MAPP extrusion compound. (a) Note the undeep holes and the short fibre pull out length. (b) The matrix is adhered very well to the primary cell wall (arrow). Note also that the lumen is closed, due to the extrusion and/or injection moulding process.*

fibre cell wall is lower than the strength of the fibre in length direction. This fact poses a limit on the strength increase that can be reached by the addition of a compatibiliser. Once the fibre matrix adhesion has become stronger than the lateral or shear strength

of the secondary cell wall, this last figure has become the limiting factor, and composite strength cannot be further increased by optimisation of the compatibiliser. The only option to further increase the strength, once this point is reached, is to try to

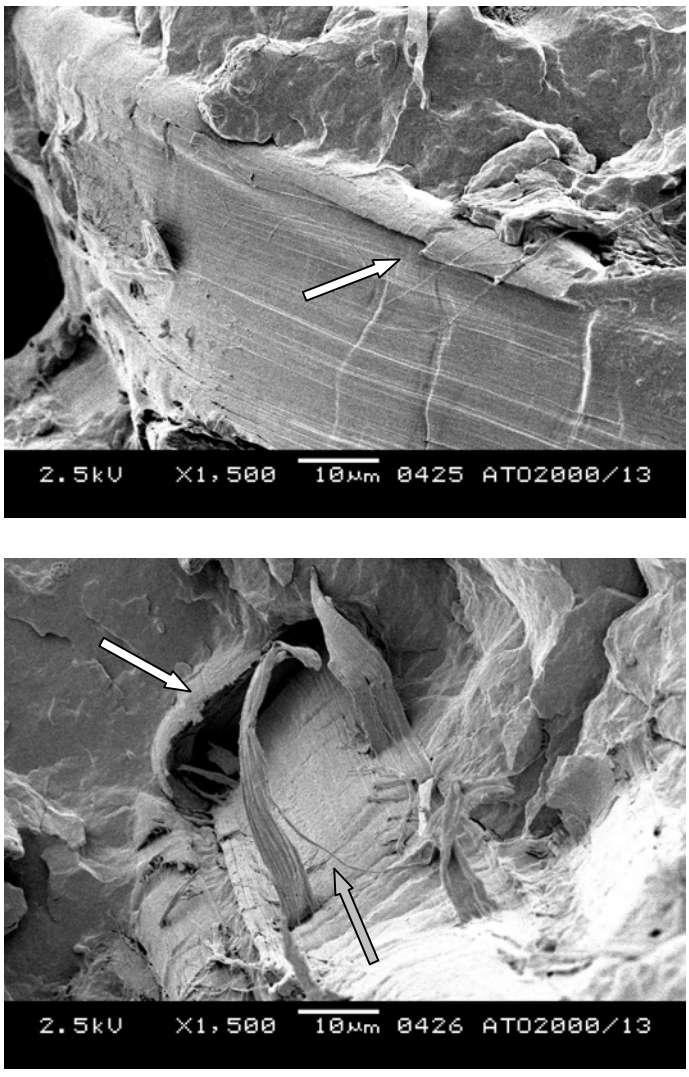


*Figure 6.12. SEM micrographs of fracture surfaces of flax/PP/MAPP extrusion compounds, the crack has run in length direction through the secondary cell wall. (a) The arrow points at the sharp edges of the primary cell wall. (b) The white arrow indicates the remains of the primary cell wall, the grey arrow indicates a thin fibril pulled out of the secondary cell wall.*

further increase the lateral strength of the secondary cell wall, and thus increase the adhesion between the meso fibrils within the secondary cell wall. One of the ways open to do this is by breeding new varieties of the flax plant [42]. Another way might be the chemical cross-linking of the internal fibre structure, as was presented in Chapter 4. In that case care should be taken not to embrittle the fibres, as happens when melamine resins are used for the fibril cross-linking (see Chapter 4).

### *6.3.3 Impact properties*

The unnotched Charpy impact properties of the materials are presented in figure 6.13. It is clear that the short fibre compounds perform better in impact than the NMT materials, which is presumably due to their greater ductility (see also figure 6.5). Also in this case the kneaded materials are better than the extruded materials. Contrary to the NMTs, the impact strength is going down at higher fibre content, both for the compatibilised and for the uncompatibilised systems. The absolute values of the impact

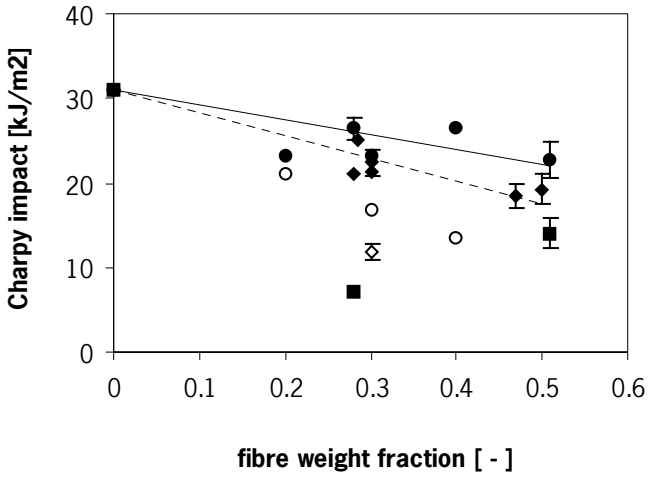


*Figure 6.13. Unnotched Charpy impact of ● kneaded flax/PP/MAPP and ○ kneaded flax/PP, ◆ extruded flax/PP/MAPP and ◇ extruded flax/PP compounds, compared with ■ hackled flax/PP/MAPP NMTs, versus fibre weight fraction. The fitted lines are: ——— kneaded and – – – – – extruded flax/PP/MAPP. The PP value is for Retiflex PP used in Chapter 5, the PP used for the compounded materials did not break during the test. Error bars falling within the markers are not shown.*

strength, however are low compared to glass fibre data, which are usually found to be higher than 40 kJ/m$^2$. The notched Charpy impact for the kneaded materials is 4.9 ± 0.5 kJ/m$^2$ for the 28 wt% kJ/m$^2$ material and 4.8 ± 0.1 for the 51 wt% material, exactly the same as the value found for pure PP 4.7 ± 0.4 kJ/m$^2$. This is also in contrast to the behaviour found with short glass fibre reinforced PP, where a strong increase of the notched impact is found with increasing fibre content [38], to values around 10 kJ/m$^2$ or higher.

Contrary to the NMT materials, the length of the fibres in the compounds is lower than their critical length. This means that fibre pull-out can only have a limited contribution to the energy uptake during impact. The fact that the impact strength increases with the addition of a compatibiliser supports this view: at subcritical fibre length addition of the compatibiliser will help to increase the debonding and frictional force between fibres and matrix and thus the energy dissipated during the fracture process. Nevertheless, even though the fibres are rather short, they are separated into elementary fibres and thus much stronger than the fibres in the NMTs (see also Chapters 3 and 5). The fibre strength of the elementary fibres, 1500 MPa, lies much closer to the fibre strength of glass fibres, 2000 MPa, so one might expect a better impact strength than is actually achieved.

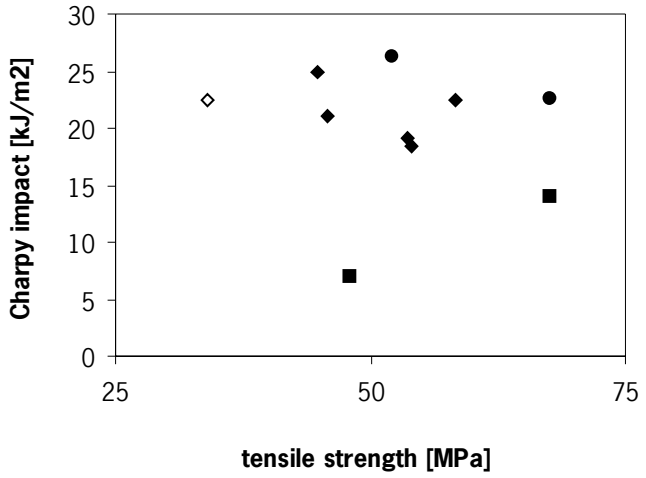


*Figure 6.14. Charpy versus tensile strength of ● kneaded flax/PP/MAPP, ◆ extruded flax/PP/MAPP and ◇ extruded flax/PP compounds, and ■ hackled flax/PP/MAPP NMTs.*

Thomason and Vlug [43] and Thomason [38] find a strong correlation between the tensile strength of a composite and its Charpy impact strength (both for notched and unnotched Charpy data). This leads them to conclude that the elastic strain, which is stored in the fibres prior to fracture, and which is released after fracture and dissipated into heat and kinetic energy, is a major contributor to the impact strength of glass fibre reinforced materials.

Figure 6.14 gives the unnotched Charpy data versus the tensile strength for flax fibre reinforced compounds and NMTs. The unnotched Charpy impact of the compounds show a slight reverse dependency on the tensile strength, higher strength gives a lower impact, this contrary to the dependence found in the NMT materials. A correlation, as found by Thomason and Vlug, however, is fully absent, indicating that stored strain energy is no major contributor to the impact strength. For the NMT materials a correlation exists between the impact strength and the fibre pull-out length (Chapter 5). In the NMTs in some cases fibres were seen to be internally split, in which case the friction in the fibre contributed probably to the energy absorption process. For the compounds the pull-out length is very short, but the impact strength is higher than for NMTs. This, together with the micrograph shown in figure 6.12b, could give a clue of the process occurring. It is quite possible that in the case of a compatibilised matrix the fibre does not debond on the fibre matrix interface, but somewhat deeper in the fibre, maybe between the primary and secondary cell wall, or within the secondary cell wall. Friction between the split cell walls could then be responsible for part of the energy absorption. The fact that the extrusion compounded materials show a slightly lower Charpy impact strength than the kneaded materials could then be explained by the fact that in the extrusion compounded materials the separation of the fibre bundles into elementary fibres is never as perfect as in the kneaded materials (see also table 6.3), so that in this case the –lower energy consuming– friction between elementary fibres does also contribute to the fracture process. Also the presumably more severe thermal history of the extruded materials could influence the impact properties in a negative way. Both the hackled and the compounded fibres apparently do not have the potential to store elastic strain energy during the fracture process, presumably due to the intricate internal structure which gives rise to a lot of stress concentrations and premature failure during high rate deformation.

It appears that the material has now found a 'new' weakest link, the lateral strength or shear strength of the fibre cell walls. This would at the same time implicate that further

optimisation of the impact properties of flax fibre reinforced materials, will be an extremely tedious job, since it is the fibre cell wall that would need to be modified.

## 6.4 Conclusions

The fibre length of both extruded and kneaded flax filled PP materials after injection moulding is significantly reduced. The extruded samples show, as expected, a slightly higher fibre length and broader length distribution and a slightly higher fibre thickness. Modulus and tensile strength of both extruded and kneaded flax fibre reinforced compounds lie in the same range as of NMT materials, despite the fact that these last materials have a much longer fibre length and a higher aspect ratio. It can be assumed, however, that especially the strong fibre length reduction that takes place during the compounding process is causing a severe reduction in compound stiffness and strength, and that stiffness and strength of the compounded materials might increase if the fibre length was retained better.

Optimisation of the fibre/matrix interaction by the use of a very effective compatibiliser seems to have led to a new failure mechanism occurring in the materials, the splitting of the fibre within the secondary cell wall. It appears that especially the impact properties of the material suffer from this phenomenon, but it might also limit the tensile and bending strength of the materials.

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# 7

# The Environmental Impact of Flax Reinforced Composites

## 7.1 Introduction

The main reason for choosing a natural fibre reinforced composite lies -for many potential users- in the assumed environmental benefits that these materials can provide. This chapter therefore focuses on the environmental considerations of the use of flax fibres, especially in construction materials. A short literature survey is presented on health and environmental issues. Next a short introduction to Life Cycle Analysis (LCA) is given. Following, an analysis of the environmental impact of the production of theoretically optimal flax versus glass reinforced construction beams is presented. The beams are designed to withstand a certain load, using either a strength or a deformation criterion. The numbers used in this chapter are based partially on the results of an extended LCA study on wind turbine blades performed by four partners in the Bladeco project: ECN, KEMA, TUD Stevin Laboratory (currently the knowledge centre WMC) and ATO bv (currently Wageningen UR, A&F). Next, the results of this theoretical study are compared with the environmental impact of the NMTs and the compounded materials presented in the previous chapters and with GMTs and short glass fibre reinforced compounds. Finally attention is given to potential sources of

environmental gain during service and end-of-life of flax fibre filled materials compared with glass fibre filled materials.

## 7.2 Health concerns for natural fibre processors

The general feeling of many people on materials like flax fibres is that they will be more friendly for employees in the processing industry, giving for instance less skin irritation than glass fibres. Still, also natural materials can pose health problems for workers. In a comparative study on the handling of various types of agricultural materials Dutkiewicz et al. [1] show that during threshing of flax in a barn relatively high concentrations of dust and endotoxins in the air are found. Buick and Magee [2] investigated the microbial contamination of local flax dust. They find that flax dust is contaminated by both gram positive and gram negative bacteria and by fungi, and they also demonstrate the presence of significant levels of endotoxins. It has long been known that the inhalation of organic vegetable fibres can cause occupational lung disease. In fact, Buick and Magee [2] state that the first ever definitive statement on health problems during flax processing is attributed to Ramazzini [3] as early as 1705. Ramazzini wrote: *"Those who card flax and hemp so that it can be spun and given to the weaver to make the fabric find it very irksome. For a foul and poisonous dust flies out from these materials, enters the mouth, then the throat and lungs, makes the workmen cough incessantly, and by degrees brings on asthmatic troubles"* and *"these people complain that they suffer more in the hackling of flax than in hemp"*. Modern flax companies have diminished these problems by using closed processing systems and adequate exhaust hoods [4], but in older processing facilities also nowadays large amounts of airborne dust can be found. This is an aspect that should definitively be taken into account when processing facilities for natural fibre/polymer composites are set up.

## 7.3 A short introduction on Life Cycle Assessment (LCA)

The environmental impact of a product can be investigated using a Life Cycle Assessment (LCA) method. The LCA method focuses on the entire life cycle of a product from raw material acquisition to final product disposal. An LCA can be performed in various ways. One of the well known methods was developed by the

Centrum of Milieukunde (CML) in Leiden [5]. This method was further extended in the Eco-indicator 95 method [6], which was developed by a consortium of Dutch companies. The Eco-indicator 95 method weighs environmental effects that damage ecosystems or human health on a European scale. The method is valued for its good transparency and handling [7]. It expresses the ecological effects of products and processes in one single number, with the dimension milliPoints [mPt].

The LCA following this method is structured in five parts:

- The goal definition, during which the aim and scope of the study as well as the function and the functional unit of the studied product are defined.
- The inventory, during which all polluting emissions and consumption of resources (and energy) per functional unit are listed (the environmental impact table).
- The classification, during which all environmental impacts are grouped under certain environmental effects (see below), aggregated within these environmental effects (using a classification factor, which reflects the degree to which they contribute to an effect), and normalised (see below). The result of this phase is an environmental profile, listing for each environmental effect one numerical value.
- The evaluation, during which the effects are weighed among each other to integrate the environmental profile into one environmental impact number.
- The analysis, during which the results are interpreted and the uncertainties in the results are estimated.

The environmental effects taken into account in the Eco-indicator 95 method are:

- Greenhouse effect (reference is carbon dioxide, $CO_2$).
- Ozone layer depletion (reference is CFK-11).
- Acidification (reference is sulphate, $SO_4^{2-}$).
- Eutrophication (the ability to form biomass, reference is phosphate, $PO_4^{3-}$).
- Heavy metals (reference is lead, Pb).
- Carcinogenics (probability of the occurrence of cancer, reference is polyaromatic hydrocarbons).
- Winter smog (dust and soot particles, reference is $SO_2$).
- Summer smog (photochemical oxydant formation, reference is ethene, $CH_4$).
- Pesticides (reference is amount of active ingredient).

According to Heijungs et al. [5], a normalised environmental effect can be calculated by relating the environmental effect to the total effect of a society to the environmental

category affected, over a certain period of time. For the normalisation of the Eco-indicator 95 method (in the classification phase) a scale factor was developed which considers the environmental influences per inhabitant of Europe during one year.
The significance of each environmental effect is classified (during the evaluation phase) by using a weighing factor (see table 7.1), with which it is multiplied. In this way a small effect can still have a significant influence. The weighing factors are determined via the distance-to-target method, the difference between the present values and the target values of an environmental effect. The greater this distance, the more serious the effect is rated and the higher the weighing factor is. The weighing factors could thus change over time when new viewpoints emerge. Further developments are still being undertaken in order to further develop, improve and refine the LCA methods [8,9].
The simplicity of the Eco-indicator 95 method is at the same time its weakness. The fact that the environmental impact of a product is expressed in a single number implies a significance that does by no means exist. Whereas the analysis of the Eco-indicator 95 method is rather refined, the quality of the input data may be questioned. The data collection during the Bladeco project [10] showed that sometimes producers are very willing to provide figures needed as input for the calculations, but if they are not, the quality of the input diminishes rapidly. This might obviously have a very significant influence on the Eco-indicator, and might even lead to wrong conclusions. Also difficulties in defining the system limits, for instance when comparing very different materials or products, could lead to inaccuracy in the data. Especially in a general study as was performed within the Bladeco project it is unavoidable that the quality of the input differs between the different materials.

## 7.4 Environmental impact of flax fibre reinforced materials versus glass fibre reinforced materials

The work presented in this chapter is partly based on an LCA performed by ECN and KEMA on wind-turbine blades in the Bladeco project [10], following ISO 14040 and ISO/DIS 14041 (1997), the guidelines of CML [5], the Eco-indicator 95 method [6] and using the software of SimaPro [11]. The data used for the LCA were collected by ECN, KEMA, TU Delft, ATO bv and Aerpac, by means of a questionnaire sent to various producing companies and a literature study. In this project an approach to determine the environmental impact of a construction based on its performance -a performance-

*Table 7.1. Weighing factors used in the Eco-indicator 95 method [6].*

| Environmental effect | Weighing factor | Criteria |
|---|---|---|
| Greenhouse effect | 2.5 | 0.1 °C per 10 years, 5% ecosystem damage |
| Ozone layer depletion | 100 | Chance on 1 death per year per 1 million people |
| Acidification | 10 | 5% ecosystem damage |
| Eutrophication | 5 | Rivers and lakes, damage to unknown number of aquatic systems (5%) |
| Summer smog | 2.5 | Occurrence of smog periods, health complaints esp. asthma patients and elderly, occurrence of agricultural damage |
| Winter smog | 5 | Occurrence of smog periods, health complaints esp. asthma patients and elderly |
| Pesticides | 25 | 5% ecosystem damage |
| Heavy metals | 5 | Lead content in blood of children, limited life expectancy and learning performance of unknown number of people |
| Heavy metals | 5 | Cadmium content in rivers, eventually also influencing humans |
| Carcinogenics | 10 | Chance on 1 death per year per 1 million people |

specific environmental impact- was developed, and published by Bulder et al. [12].
The complete LCA study that underlies the analysis presented in this chapter can be found in the report “Levenscyclus analyse van windturbine materialen II” [13]. The

*Table 7.2. Environmental impact of the various materials [13].*

| Materials category | Material | Eco-indicator [mPt/kg] | Remarks |
|---|---|---|---|
| Fibres | Flax | 0.34 | Hackled long fibres, value might be too low, since production of used pesticides is not taken into account |
| | Glass | 2.31 | Including extraction of raw materials, transport and production |
| Matrix materials | EP resin | 10.2 | Including extraction of raw materials, transport and production, mean European data |
| | UP resin | 9.45[1] | Value might be too low, because production of energy carriers is not taken into account |
| | PP | 2.99 | Including extraction of raw materials, transport and production, mean European data |

[1]This value is for hand lay-up, for closed mould processing the Eco-indicator would be 3.08 mPt/kg.

weighing factors used are given in table 7.1.

The environmental score for a number of materials, expressed in milliPoints per kilogram material [mPt/kg], as determined in the Bladeco project are presented in table 7.2. The materials are epoxy (EP) resin (standard resin, mean data of 4 European producers [14]), unsaturated polyester (UP) resin (laminating resin, based on data from DSM-BASF Structural Resins [15], RIVM/LAE [16], Brydson [17], Austin [18] and ECN [19]), polypropylene (PP) (mean European data [20]), E-glass (production at PPG in

Hoogezand, the Netherlands [21]) and flax (hackled long fibres grown in Zeeuws-Vlaanderen in the Netherlands [22]).

For the analysis presented in this paragraph, six hypothetical unidirectional (UD) composites are assembled from the three matrices, EP, UP and PP, combined with either glass fibres or flax fibres. For these hypothetical composites the properties as a function of fibre fraction is calculated. Next, from each of these composites a structural element is designed, either a tie, for a tensile load, or a beam, for a bending load. From the functional requirements -the element should either have a certain strength or a certain stiffness- the dimensions of the element can be determined. Finally from the dimensions of the element the environmental impact can be calculated.
First the analysis for a tension tie, both for a strength and for a stiffness limited application is presented. Next the analysis for a beam in bending for a stiffness limited application is given.

### *7.4.1. The properties of the hypothetical composite materials.*

The mechanical properties assumed for this study are shown in table 7.3. For a UD fibre reinforced composite made from these materials the modulus, $E_c$, can be calculated for different fibre volume fractions, $V_f$, using a simple rule of mixtures:

$$E_c = V_f E_f + (1 - V_f) E_m \tag{7.1}$$

*Table 7.3. Tensile strength, Young's modulus and density of the fibres and matrices.*

| Material | Tensile strength [MPa] | Young's Modulus [GPa] | Density [kg/m$^3$] |
|---|---|---|---|
| Flax hackled long | 750 | 50 | 1400 |
| E-glass | 2000 | 76 | 2560 |
| EP resin | 100 | 3 | 1200 |
| UP resin | 90 | 2 | 1100 |
| PP | 38 | 1.4 | 900 |

with $E_f$ the modulus of the fibre and $E_m$ the modulus of the matrix. Similarly, the strength, $\sigma_c$, of the UD composite can be calculated as:

$$\sigma_c = V_f \, \sigma_f + (1 - V_f) \, \sigma_{um} \tag{7.2}$$

with $\sigma_f$ the fibre strength and $\sigma_{um}$ the matrix stress at the fibre failure strain, assumed

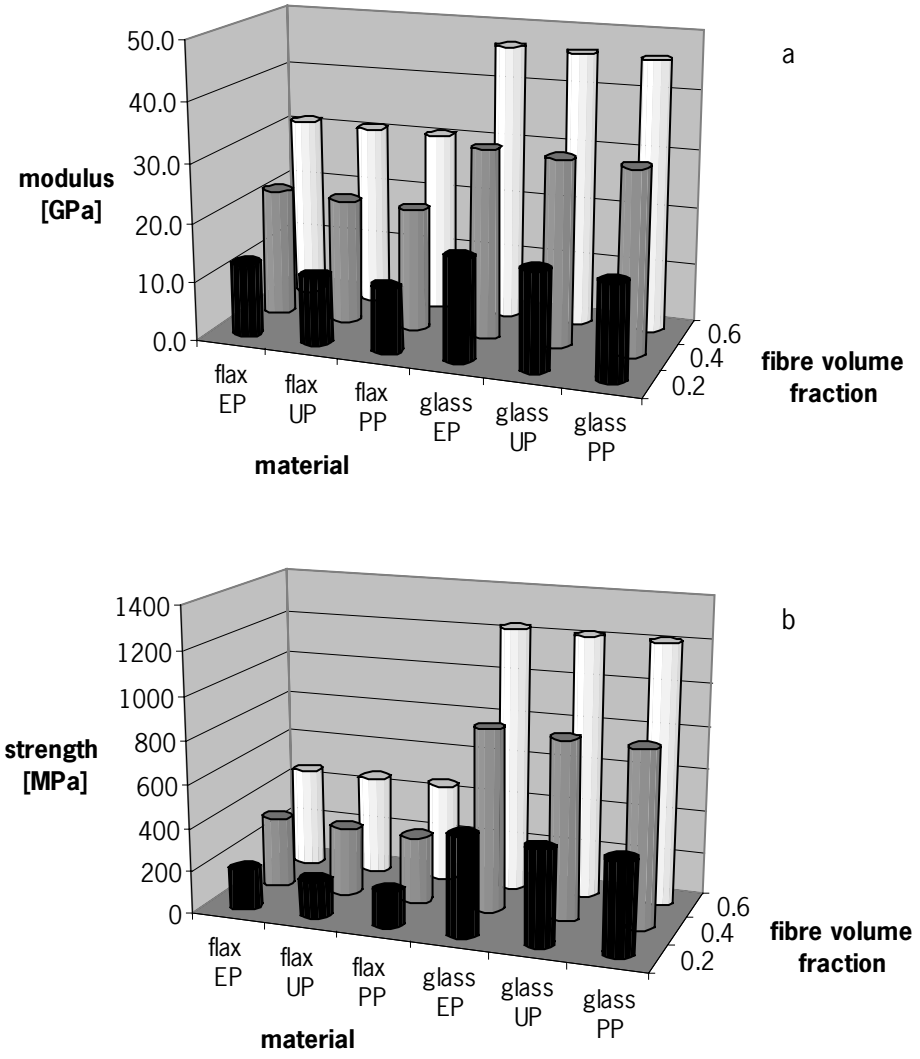


*Figure 7.1. Properties of the six different composites. (a) Young's modulus. (b) Tensile strength.*

to be equal to $E_m * \sigma_f / E_f$. The adhesion between the fibres and the matrix is assumed to be perfect. The modulus and strength of flax and glass fibre composites with the three different matrices, EP resin, UP resin and PP, and with three different fibre volume

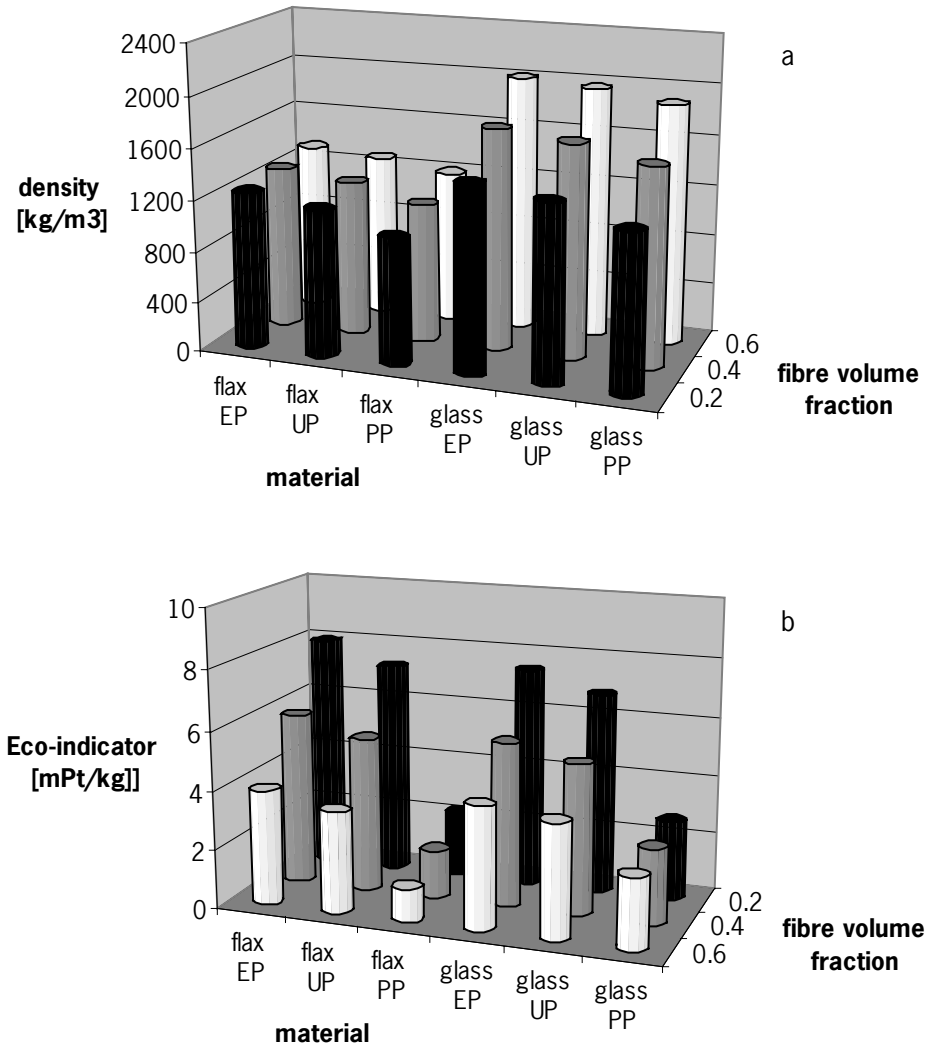


*Figure 7.2. Material properties of the six different composites. (a) Density. (b) Eco-indicator, note that in this graph the order of the volume fractions is reversed for the sake of clarity.*

fractions, 20%, 40% and 60% are given in figure 7.1. It is obvious that the properties are mainly determined by the fibres. Furthermore the density and the Eco-indicator of the various material combinations are given in figure 7.2. From figure 7.2b it can be concluded that the environmental impact of the composites is determined for the largest part by the matrix and consequently that especially at higher fibre volume fractions the flax fibre composites have a lower environmental impact than the glass fibre composites.

### *7.4.2 A strong tie for tensile loading*

Using these material properties, ties of equal load bearing capacity were designed for each material combination, where each tie can carry a tensile load, $F$, of 1000 kN, taking into account a safety factor of 2. The tie has a width, $b$, of 100 mm and a length, $\ell$, of 1 m. The necessary thickness, $t$, can then be calculated as:

$$t = F \,/\, ( \tfrac{1}{2} \sigma_{max}\, b ) \tag{7.3}$$

where $\sigma_{max}$ is the strength of the material, equal to $\sigma_c$. The minimum thickness of the ties of equal strength for each material combination is given in figure 7.3. It is obvious

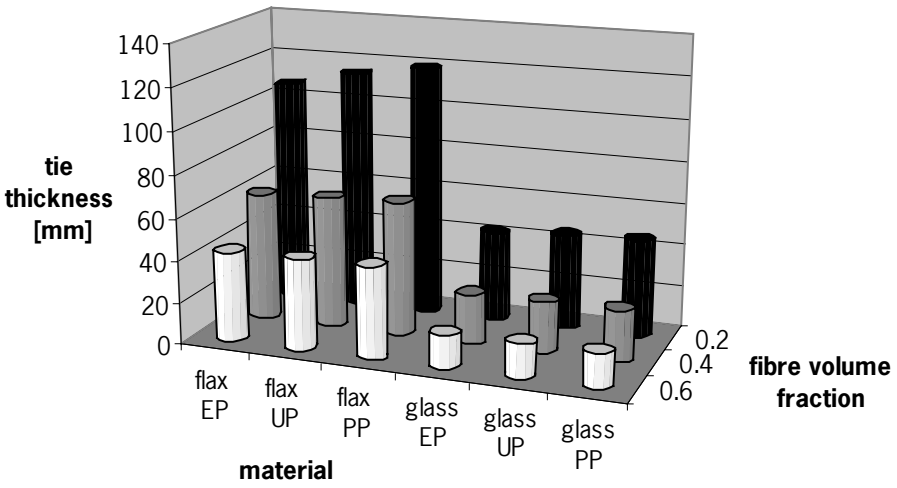


*Figure 7.3. Thickness of a tension tie, width 100 mm and length 1 m, with variable thickness, designed to withstand a load of 1000 kN with a safety factor of 2, as a function of fibre volume fraction, for the six material combinations.*

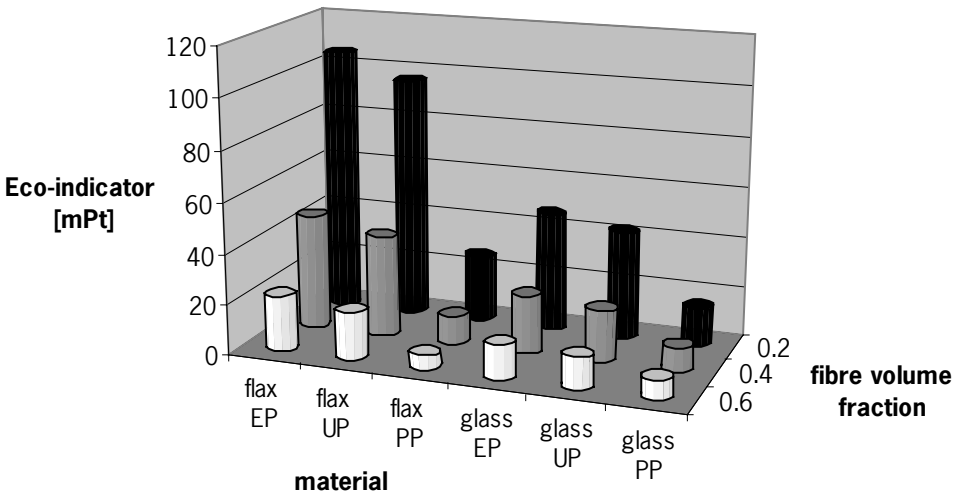


*Figure 7.4. Eco-indicator of a tension tie, width 100 mm and length 1 m, with variable thickness, designed to withstand a load of 1000 kN with a safety factor of 2, as a function of fibre volume fraction, for the six material combinations.*

that there is a huge difference in tie thickness between the flax reinforced materials and the glass reinforced materials due to the difference in fibre strength. Converting the fibre volume fraction to weight fraction, and then calculating the Eco-indicator for the fibres and the matrix and adding these values, gives the total Eco-indicator of the tie. In figure 7.4 a graph is shown of the Eco-indicator of the various materials versus the fibre volume fraction. It is clear from this graph that for the systems based on EP and UP resins, the environmental impact of the flax fibre reinforced materials is higher than that of the glass fibre reinforced materials. This is due to the lower strength of the flax fibres, resulting in a much thicker constructive element, and consequently the use of more resin. Only for the PP based systems, at higher fibre content some environmental advantage in the use of flax fibres occurs.

The difference in weight between the glass and flax fibre ties is smaller than the difference in thickness, due to the lower density of the flax fibres compared to glass. In figure 7.5 the Eco-indicator for these systems is plotted versus the fibre weight fraction. It is clear that, up to very high fibre loading, the use of flax fibres in either EP or UP resin, results in a higher environmental impact of the total tie. Only for the PP

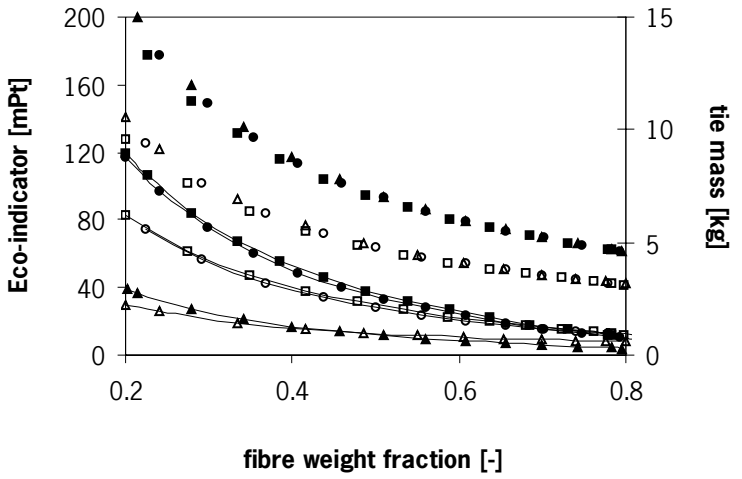


*Figure 7.5. Eco-indicator of a tension tie, width 100 mm and length 1 m, with variable thickness, designed to withstand a load of 1000 kN with a safety factor of 2, as a function of fibre weight fraction, for the six composites.*
■ *flax/EP,* □ *glass/EP,* ● *flax/UP,* O *glass/UP,* ▲ *flax/PP,* Δ *glass/PP. The lines in the bottom of the graph give the Eco-indicator, the markers in the top of the graph give the mass of the beams.*

based material, the Eco-indicator of the flax reinforced tie undercuts that of the glass reinforced tie at a fibre weight fraction higher than approximately 0.45. The mass of the various ties is also indicated in figure 7.5, and it is clear that in all cases the flax fibre reinforced ties are much heavier than the glass fibre reinforced ties.
In reality, when a construction is designed with a material as unknown as the flax fibre reinforced composites, a designer would use a considerably higher safety factor than 2, which would make the flax reinforced materials come out even worse.
The final production step to make the ties is not taken into account in these calculations. Obviously its effect depends mainly upon the temperatures at which the resin is cured, respectively the PP is processed. Generally speaking, the energy consumption of the thicker ties will be higher than that of the thinner ties, so this would only widen the gap between the glass and the flax fibre reinforced materials.

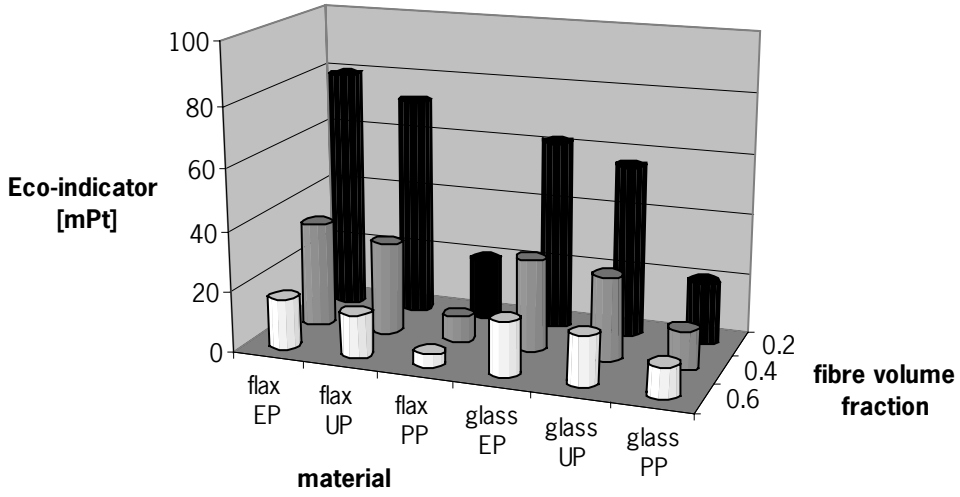


*Figure 7.6. Eco-indicator of a tension tie, width 100 mm and length 1 m, with variable thickness, designed to give a maximum strain of 1 % at a load of 1000 kN, as a function of fibre volume fraction, for the six material combinations.*

### *7.4.3. A stiff tie for tensile loading*

The same calculation can also be performed on ties designed for equal stiffness. Considering a tie of the same length and width as in the previous paragraph, the necessary thickness for a tie, which should carry a certain tensile load, can then be calculated as:

$$t = F / ( b E_c \varepsilon) \tag{7.4}$$

with $E_c$ the modulus of the material and $\varepsilon$ the strain. Suppose the tie should give a maximum strain of 1% at an applied load of 1000 kN. The Eco-indicator of these ties is shown in figure 7.6. The flax fibre reinforced EP and UP ties in this case still show a higher environmental impact. The flax/PP tie shows, depending on the fibre volume fraction, a similar or better environmental impact compared to the glass/PP tie. The Eco-indicator and the mass of this tie plotted versus the fibre weight fraction are shown in figure 7.7. Now the situation has changed. For materials with the same weight fractions and thus densities, the flax fibre reinforced materials are preferable from an environmental point of view, and the ties are lighter in weight. This is obviously due to

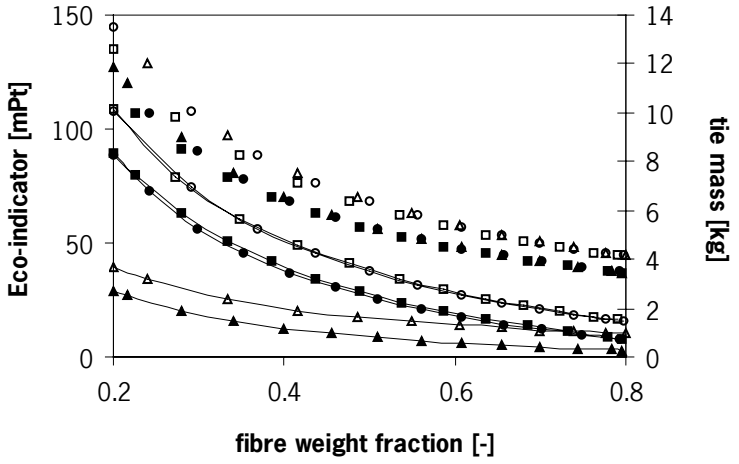


*Figure 7.7. Eco-indicator of a tension tie, width 100 mm and length 1 m, with variable thickness, designed to give a maximum strain of 1 % at a load of 1000 kN, as a function of fibre weight fraction, for the six composites.*
■ *flax/EP,* □ *glass/EP,* ● *flax/UP,* O *glass/UP,* ▲ *flax/PP,* Δ *glass/PP. The lines in the bottom of the graph give the Eco-indicator, the markers in the top of the graph give the mass of the beams.*

the relatively good specific modulus of the flax fibres. The pay-off is that for the glass fibre reinforced materials the tie is loaded up to 19% of the maximum allowable stress, whereas for the flax fibre reinforced materials the tie is loaded up to 33% of the maximum allowable stress.

### *7.4.4. A stiff beam for flexural loading*

Apart from stiffness in tension, the bending stiffness is an even more relevant parameter for many constructive parts. Consider a similar beam, but now put on two simple supports with a span $\ell$ of 1 meter and loaded at the midpoint by a load $F$ equal to 1 kN. When a maximum deflection, $\delta$, of 10 mm at the midpoint is allowed, the required thickness of this beam can be calculated as:

$$t = \left[ F\ \ell^3\ /\ (4\ b\ \delta\ E_c\ ) \right]^{1/3} \tag{7.5}$$

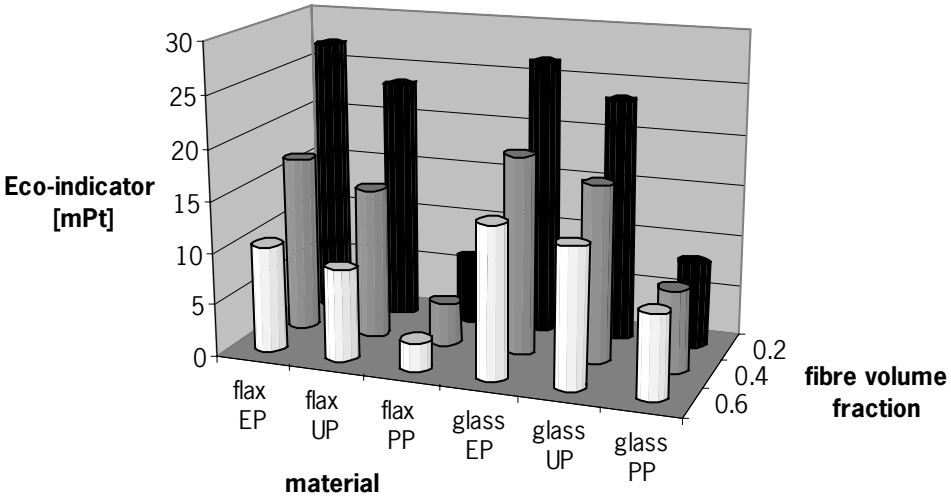


*Figure 7.8. Eco-indicator of a deflection beam, width 100 mm and length 1 m, with variable thickness, designed to give a maximum deflection of 10 mm at a load of 1000 kN, as a function of fibre volume fraction, for the six material combinations.*

Strictly speaking this equation is valid only for an isotropic material. Here, the deflection will be somewhat greater than the calculated value due to the shear contribution of the matrix phase between the fibres to the total deflection. However, since we are comparing materials with different fibres but the same matrix, and since in the case of a relatively long support distance as used here the shear contribution to the total deflection will be relatively small, this equation is a good approximation. The Eco-indicator as function of fibre volume fraction is given in figure 7.8. It is clear that for this constructive element, the use of flax fibres is preferable from an environmental point of view over the use of glass fibres, except for the flax/EP beam with a fibre volume fraction of 0.2. The Eco-indicator as a function of fibre weight fraction and the mass of the beam are shown in figure 7.9. When the materials are compared on the basis of fibre weight fraction, the difference is even larger. Also the flax fibre reinforced beams are lighter in weight than the glass fibre reinforced beams. As long as the loading is relatively moderate, a flax fibre reinforced beam thus is the better choice.
This conclusion is in good agreement with the applications for flax fibre reinforced materials known so far from the automotive industry, where mainly panels are applied

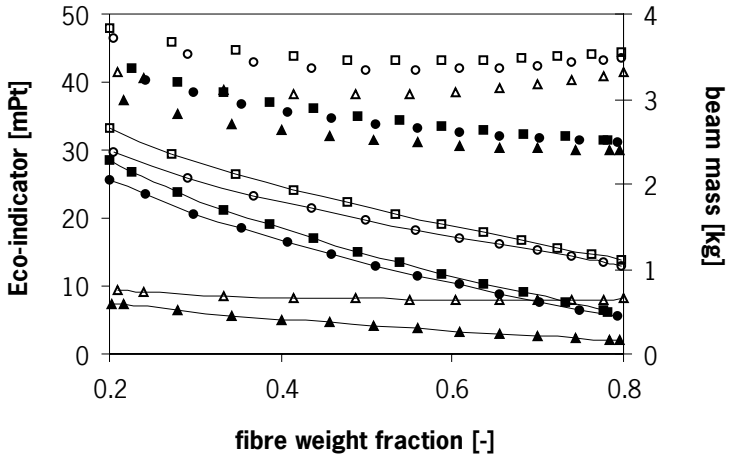


*Figure 7.9. Eco-indicator of a deflection beam, width 100 mm and length 1 m, with variable thickness, designed to give a maximum deflection of 10 mm at a load of 1000 kN, as a function of fibre weight fraction, for the six composites. ■ flax/EP, □ glass/EP, ● flax/UP, O glass/UP, ▲ flax/PP, Δ glass/PP. The lines in the bottom of the graph give the Eco-indicator, the markers in the top of the graph give the mass of the beams.*

that are designed on the basis of a stiffness criterion. Even though these materials are not produced from UD composites but from impregnated fibre mats, the arguments and outcome should be the same (see also paragraph 7.5). Desired properties coincide in this case with low weight of the constructive part and favourable environmental performance, especially when PP is used as the matrix material.

### *7.4.5 Sensitivity of the analysis*

As mentioned in the introduction on the LCA method, the single values calculated for the environmental impact of the various materials suggest a statistical significance that is unreal. Therefore, in figure 7.10a and 7.10b the influence of the Eco-indicator value of the fibres and the matrix, respectively, is displayed for a 30 wt% glass and flax fibre reinforced PP composite. In figure 7.10a the value of the Eco-indicator is varied between the value used for flax fibres and glass fibres in this study (between 0.34 mPt and 2.31 mPt). For the tension tie designed using an equal streng criterion, the glass fibre reinforced material is preferable in all cases, for the tension tie designed using an

equal strain criterion, the glass fibre reinforced material would become the better choice if the flax fibre Eco-indicator increased by a factor of 4 (the fourth data point). For the deflection beam, the flax fibre Eco-indicator would have to increase by more

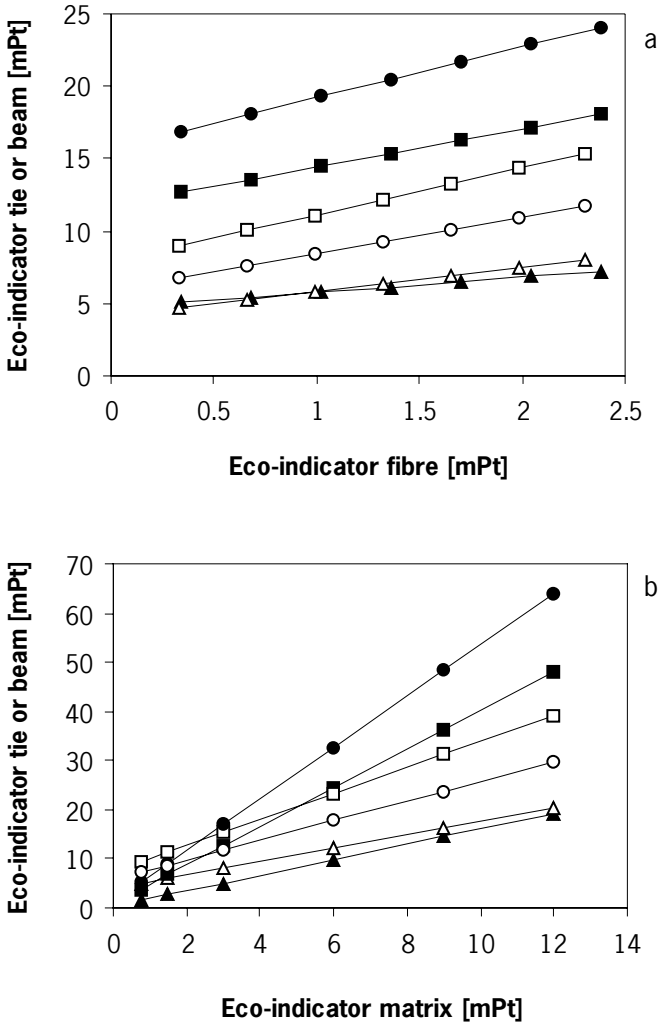


*Figure 7.10. Sensitivity of the Eco-indicator of flax and glass fibre reinforced beams for the Eco-indicator value of (a) the fibres and (b) the matrix. ● flax/PP, tension tie equal strength criterion, O glass/PP, tension tie equal strength criterion, ■ flax/PP, tension tie equal stiffness criterion, □ glass/PP tension tie equal stiffness criterion, ▲ flax/PP, deflection beam equal stiffness criterion, ∆ glass/PP, deflection beam equal stiffness criterion.*

than a factor of 6 to make the glass fibre composite the material of choice. In figure 7.10b the value of the Eco-indicator of the matrix material is varied between 0.75 mPt and 12 mPt. It is clear from this graph that the higher the Eco-indicator of the matrix the less attractive the natural fibre reinforced composite becomes. Only for the flexural beam, within this range of matrix Eco-indicator values, the flax composites are preferable in all cases.

## 7.5 Environmental impact of NMTs and compounds

It is interesting to compare the results of this theoretical study on optimal UD composites with the materials discussed in the previous chapters. Since there is little chance that the properties of the UD composites presented in Chapter 4 will, within the next couple of years, reach acceptable levels, we will focus this part of the study on the flax/PP NMT materials and compounds discussed in the Chapters 5 and 6 and compare them with literature data of GMTs taken from Berglund et al. [23] and glass fibre reinforced PP compounds taken from Thomason [38]. The Young's modulus and tensile strength used for the different materials in the calculations are given in table 7.4.

*Table 7.4. Young's modulus and tensile strength of the flax and glass filled materials at 30 and 50 wt% fibre loading.*

| | Fibre fraction [-] | Tensile modulus [GPa] | Tensile strength [MPa] |
|---|---|---|---|
| flax PP NMT | 0.3 | 5.20 | 48 |
| | 0.5 | 8.40 | 68 |
| glass PP GMT [23] | 0.3 | 4.50 | 70 |
| | 0.5 | 7.00 | 120 |
| flax PP compound | 0.3 | 4.63 | 52 |
| | 0.5 | 8.47 | 68 |
| glass PP compound [38] | 0.3 | 7.39 | 120 |
| | 0.5 | 12.00 | 133 |

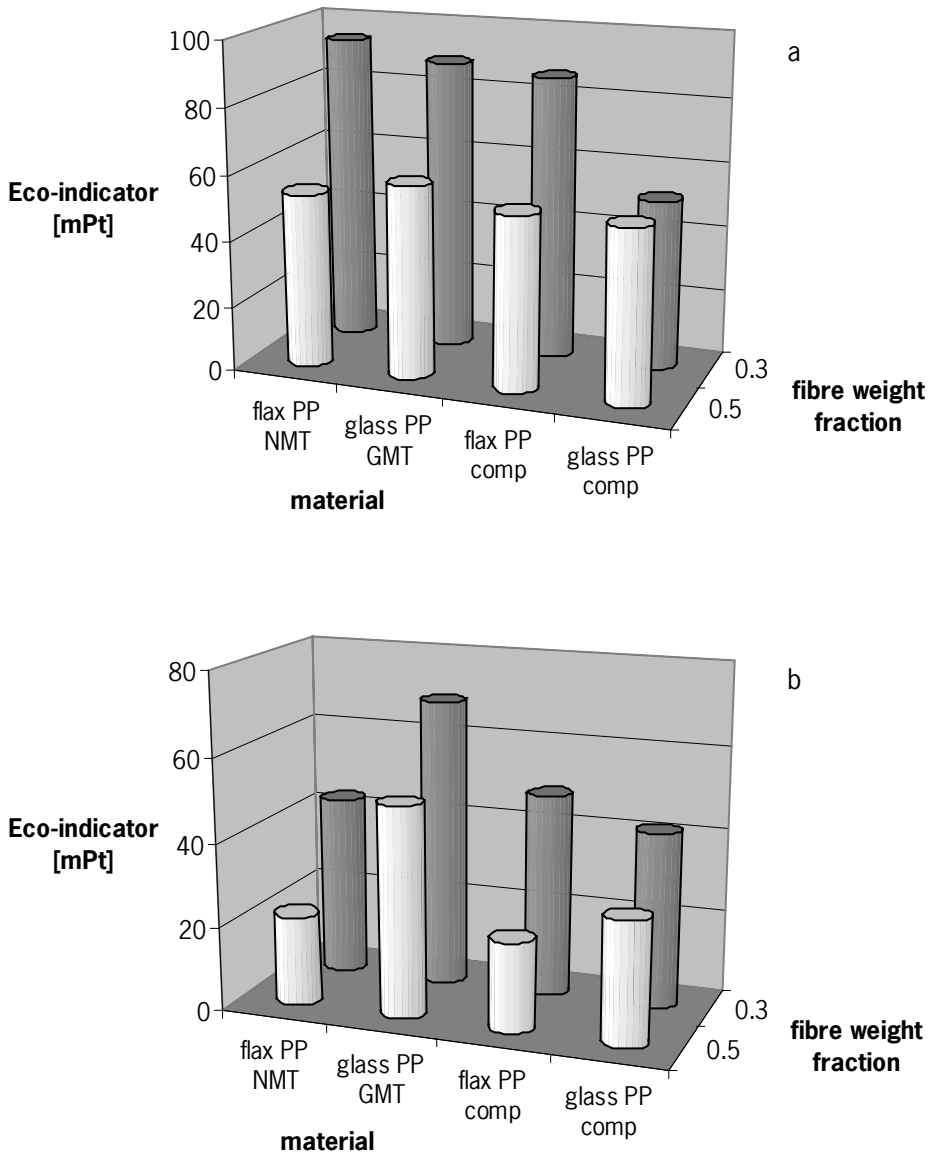


*Figure 7.11. Eco-indicator of a tension tie, based on actual material properties: (a) designed using an equal strength criterion, (b) designed using an equal stiffness criterion.*

In figure 7.11a the environmental impact of the same tension tie as used in the previous paragraph (width 100 mm, length 1 meter, load 1000 kN, and a safety factor of 2), but now designed with the NMTs, GMTs and compounds, is shown. It is clear that, apart from the glass fibre reinforced compound with 30 wt% fibres, which has a clear environmental advantage over the other materials at this weight fraction, the glass and flax fibre reinforced materials show very similar environmental impact at the same fibre weight fraction. Obviously the materials with the higher fibre loading have a lower environmental impact due to the reduced influence of the matrix.
In figure 7.11b the environmental impact of the same tie is shown, but now designed using an equal stiffness criterion, i.e. maximum 1% strain at an applied load of 1000 kN. For this constructive element, at a fibre weight fraction around 0.3, the flax fibre filled materials are similar to the short fibre reinforced glass fibre material, whereas at a fibre weight fraction around 0.5 the flax fibre filled materials are preferable from an environmental point of view.
In figure 7.12 the environmental impact of the beam designed for equal bending stiffness (maximum deflection of 10 mm at the midpoint at a load of 1 kN) is shown.

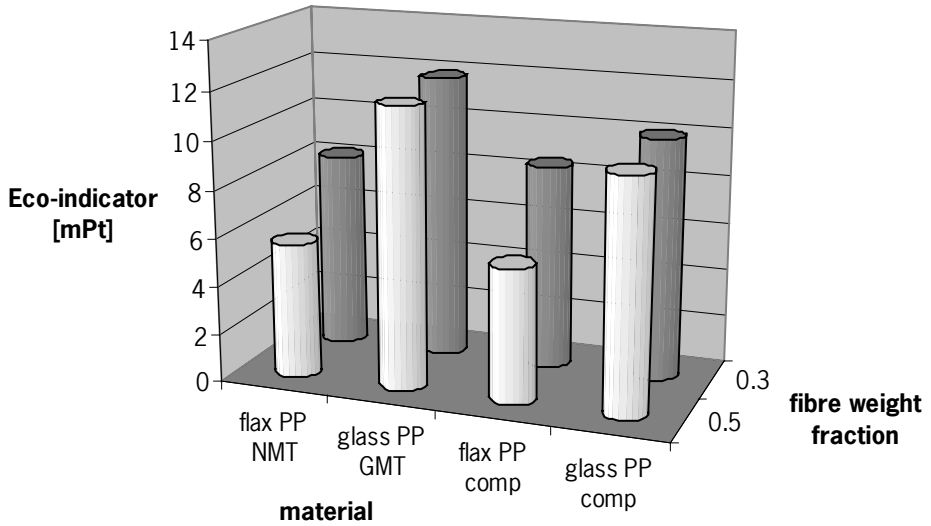


*Figure 7.12. Eco-indicator of a deflection beam, designed using an equal stiffness criterion, based on actual material properties.*

Now the flax fibre filled materials show for both fibre weight fractions a much lower environmental impact.
Although not exactly the same, these results, based on actual tensile strength and Young's modulus data, follow roughly the same patterns as the theoretical study presented in paragraph 7.4. Especially for elements designed for equal bending stiffness, the flax fibre reinforced materials are, from an environmental point of view, an interesting alternative for glass fibre filled materials.

## 7.6 Environmental benefit of flax fibre composites during service and end-of-life

Apart from the direct benefit of lower environmental impact of the constructive part which is in some cases reached, also during use the flax fibre reinforced material could contribute to a lower environmental impact, especially when the part is used in any transport application. Due to the lower weight, fuel consumption of a transporting vehicle could be lowered when any glass fibre reinforced part is replaced by a flax fibre reinforced part, as long as the part is designed for stiffness.
Various studies are presented in the literature on the environmental benefit of the application of natural fibre reinforced materials in transport. The coefficient of reduction of fuel consumption for a gasoline driven car ranges from 0.34 l/(100 kg*100 km) (for lighter cars) to 0.48 l/(100 kg*100 km) (for heavier cars), based on the New European Driving Cycle (NEDC) [25], whereas the saving on diesel is somewhat lower, ranging from 0.29 to 0.33 l/(100 kg*100 km). Wötzel et al. [7] compare a hemp reinforced side panel for the Audi A3 with one from ABS (Acrylonitril Butadiene Styrene copolymer) using the Eco-indicator 95 method. They find that not only there is a minor environmental advantage of the hemp reinforced part during the production phase (only 8%), but also the weight saving due to the application of the hemp reinforced part leads to a (limited) energy saving and thereby further environmental advantage during the use phase. Corbière-Nicollier et al. [26] studied the life cycle assessment of china reed (*Miscanthus sinensis*) fibre reinforced PP as a replacement for glass fibre reinforced PP for the production of transport pallets. They use various methods to estimate the environmental impact among which the Eco-indicator 95 method. They report an environmental advantage of about 30% due to the use of the natural fibre reinforced material. They report a significant reduction of energy consumption due to weight

saving during the use phase. Corbière-Nicollier et al. also show an interesting table of potential energy saving by various applications of china reed: substitution of a glass fibre transport pallet leads, for a total transport distance of 100 000 km, to a potential energy saving of 2500 GJ/ha, whereas using china reed for heat production as replacement for oil would result only in an energy saving of 200-240 GJ/ha. A much higher environmental gain is thus reached by applying the fibre in the transport pallets.

A final potential advantage of the use of flax instead of glass fibres is in the end-of-life phase. Similar to glass fibre reinforced materials it is impossible to produce materials from flax filled plastics with little reduction in properties by recompounding them after the use phase. In fact, natural fibres generally suffer even more from a renewed heat step than glass fibres [27]. However, incineration (euphemistically called thermal recycling) can be a desirable option. In this respect, the main advantage of the application of flax fibres can be found in thermosets, which cannot be recycled otherwise, or in recycled thermoplastics, which are closer to their end-of-life incineration than virgin thermoplastics. In the Bladeco project [28] a comparison between various end-of-life scenario's was performed and incineration was indicated as probably the most viable option. The bonus for incineration (which can be substracted from the Eco-indicator) is depending on the amount of combustible material in the final product. Corbière-Nicollier et al. [26] report a net bonus for the incineration of PP of 21.5 MJ/kg and a bonus for the incineration of a natural fibre (china reed in this case) of 8.3 MJ/kg. Glass fibres cost energy, 1.7 MJ/kg [26], during incineration and add negatively to the total Eco-indicator. For the natural fibre reinforced composite part this means that about 25% of the energy costs of the production of the part are won back by incineration. For the glass reinforced part, which costs almost twice as much energy to produce in the first place, circa 13% of the energy costs are won back by incineration.

## 7.7 Conclusions

Concluding, it can be stated that it is impossible to generally define the environmental advantage of the application of a flax fibre reinforced material. A significant environmental advantage of a product, based on these materials is typically not found during the production phase of the product, but during the use phase. The magnitude

of the environmental advantage depends obviously on the kind of application. In other words: the environmental gain is usually due to a secondary effect, such as weight saving, and is then not caused by the 'green' origin of the fibre. It is therefore not possible to give a general rule of thumb of the advantages of the use of flax fibre composites. In many cases the material may even lead to an increased environmental impact, due to the limited strength of flax fibres and consequently of flax fibre composites.

Generally speaking it is not wise to use a flax fibre reinforced material for heavily loaded parts. The advantage of the material can mostly be found in its reduced weight compared to standard materials, especially in stiffness driven applications. Hence, application of the material in a transport related product usually leads to the highest environmental gain.

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# 8

# A Future for Flax Reinforced Composites?

## 8.1 Introduction

Is there a future for flax fibre reinforced composites? To shed some light on this question, in this chapter first an analysis of the flax industry in Western Europe is made, to try to identify where the innovative strength within this branch is situated. Next two possible application areas for flax fibre composites will be presented: the application of flax fibre non-wovens in the automotive industry, and the development of an extrusion and injection moulding grade of flax fibres with a thermoplastic. The special drivers for the development of these industrial applications are identified and possible success or failure of the introduction of flax fibre composites in the market -in combination with required strategic actions for the flax industry- is discussed. In the final paragraph an outlook is given to other possible application areas of flax fibre composites.

## 8.2 The West European flax industry

The West European flax industry is a remainder of a much larger industry that has existed up till the 1950's [1]. Being an ancient industrial branch, the different

processing steps, like rippling, water retting, scutching, hackling, and spinning were all done by separate (family) firms, which together made up the complete production chain, forward or backward integration did hardly exist.

These days the flax industry in Western Europe is concentrated in the South West of the Netherlands (Zeeuws Vlaanderen), the Western part of Belgium (West Vlaanderen) and the North West of France (Normadie-Manche). Here especially the Dutch and the Belgian situation are analysed [2]. The flax industry is still characterised by the existence of many small (family) firms. In the Netherlands approximately 10 so called 'scutchers' remain [3], generally small firms with a few employees. The scutchers usually have contracts with a number of farmers growing flax for them, sometimes they also grow their own flax. The scutchers and/or farmers harvest and ripple the flax plants, dew ret the plants, and subsequently the scutchers break and scutch the flax. Products from these firms are seeds, shives, scutched flax lint and scutching tow (see also figure 2.2). Up till a few years ago, the scutched lint and tow was always delivered to the distributive traders, mostly Belgian firms, which used to form the only link between the scutchers and the spinners. The distributive traders upgrade the scutched fibres by mixing different lots to obtain a certain quality and often they also hackle the fibres. Recently, the scutchers have started to sell scutched fibres directly to the spinners. Next to this, China has come up as a new flax country, about 70% of the world wide flax production is spun and woven in China, and also Chinese distributive traders are now active on the European flax market [4]. The Belgian distributive traders, however, still play a world-wide role in the trade in flax fibres and are a powerful and regulating player in the flax market [8]. In the Netherlands only one hackler exists, a firm which is more forwards integrated in that it not only scutches but also hackles the fibres. In the Netherlands no flax spinners are left. Since the flax business is a very cyclic business, the firms usually have relatively large warehouses where they stock the processed flax until the market conditions are favourable for selling. The firm directors are usually strongly focused on the trading side of the business, hence innovations are done in small steps, often in co-operation with a company that builds processing machinery.

In Belgium the situation is comparable, but the flax industry is considerably larger than in the Netherlands, with approximately 70 scutchers, and also 4 spinners and 13 flax weavers [6]. Many of these firms are smaller family businesses, but there are also some larger companies. An example of a larger company is Procotex International SA, which has recently done a number of innovative developments [7]. In France the flax

business is also much larger than in the Netherlands. The French flax processors are generally much larger than they are in Belgium and the Netherlands, and there are also a few more innovative companies looking for new developments. Nevertheless, also for the French flax business, the Belgian distributive traders are important [8]. Most European flax firms are a member of the CELC (Confédération Européenne du Lin et du Chanvre), which is based in Paris.

The attractiveness of a branch is according to Porter [8] determined by the structure of that branch. This structure can be analysed on the basis of five competitive forces [9]:

- the intensity of rivalry among existing firms in the branch
- the threat of the entry of new competitors in the branch
- the threat of the entry of substitute products
- the bargaining power of suppliers
- the bargaining power of buyers

The model of Porter is given in figure 8.1. The factors that determine the five competitive forces are given in figure 8.2. The model is not able to give a quantitative evaluation of the attractiveness of a branch [10] (a quantitative model would require an enormous amount of data from different sources, which are not usually available), it can, however, be used for a qualitative description. All five forces jointly determine the

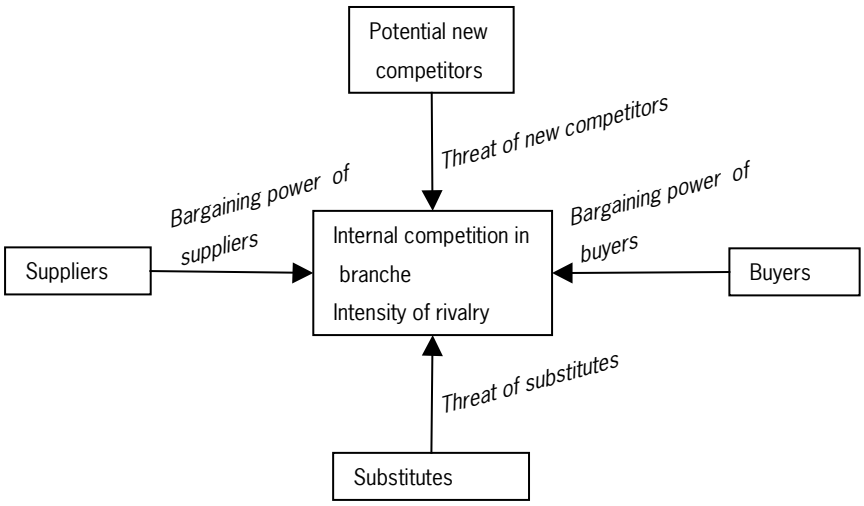


*Figure 8.1. The five competitive forces in a branch of industry as given by Porter [8].*

intensity of industry competition and the strongest force or forces are governing and are crucial to a firm from the point of strategy formulation.

A qualitative structural analysis of the West European flax industry, taking the perspective of for instance a scutcher, can be made following the method by Porter [9], taking into account the most important determinants.

| **Barriers of entry** | **Determinants of rivalry** |
|---|---|
| Economies of scale | Branch growth |
| Product differentiation | Set costs/value added |
| Brand identity | Temporary excess of capacity |
| Switching costs | Product differences |
| Capital requirements | Brand identity |
| Access to distribution channels | Switching costs |
| Cost advantages independent of scale | Concentration and equilibrium |
| - Learning or experience curve | Complexity of information |
| - Favourable access to raw materials | Diversity of competitors |
| - Proprietary product technology | Company interests |
| Government policy | Barriers of exit |
| Expected retaliation | |
| **Determinants of power of suppliers** | **Determinants of threat by substituting products** |
| s | |
| Costs of changeover suppliers | Relative price/performance of |
| Existence of substituting products | substituting products |
| Concentration of suppliers | Costs of changeover |
| Importance sales-volume for suppliers | Inclination to substitutes. |
| Relative costs of purchase | |
| Cost-reducing inputs | |
| Differentiation-increasing inputs | |
| Thread of forward inputs compared to backward integration | |
| **Determinants of power of buyers** | |
| *Negotiation power* | *Price sensitivity* |
| Concentration of buyers versus | Price/ total purchase |
| concentration of suppliers | Product differences |
| Volume of purchase | Brand identity |
| Relative costs of changeover | Quality/ performance |
| Informedness of buyers | Profit margins |
| Ability for backwards integration | Motivation decision makers |
| Substitute products | |
| Boldness | |

*Figure 8.2. The determining factors in the model of Porter.*

*The intensity of rivalry among existing competitors*

The intensity of rivalry among existing competitors is probably quite strong: the branch has been shrinking over the last decades until about five years ago, the product differences are low (at least within the Netherlands, Belgium and France), as is the brand identity, and depending on the demand from the fashion industry, the branch has an over-capacity. On the other hand, many flax producers stock their production in years with low demand until economic times have improved. Storage costs apparently are not unbearably high and price fluctuations are damped due to this practice. However, it has in the past not led to a price which is stable over the years. Prices are strongly influenced by the demand of the apparel market, and thus vary strongly with the fashion. Prices for long flax vary over the years between € 1.15 and € 2.50 per kilo and the prices for short fibres vary also with changing demand from the fashion industry from € 0.25/kg to € 0.60/kg [4,8]. The last five years, however, the branch is changing due to the rise of China [4]. China can produce linen fabric for a lower price than the West European industry can, but still buys scutched flax in Europe for its high quality. This has increased the application of linen in the apparel industry and has increased demand. Thus the last five years, the branch has been growing again and prices have stabilised at a relatively high level (see also table 2.2), but the prices have become more dependent on the exchange rate of the dollar. The intensity of rivalry has thus diminished, and many companies are earning relatively well and have intensified their innovations over the past years.

There are a fair number of competitors, but they all know each other, and they seem to be keeping a watchful eye on each other in order to retain the balance in the industry.

The barriers of exit lie mainly in the fact that the companies usually are family businesses and generally are fully concentrated in the flax industry, however, when there is no successor, the companies often cease to exist.

*The threat of entry*

Threat by new entrants comes form varying sides. The most important new entrant is China, which has over the last year strongly increased its hackling, spinning and weaving capacity for flax, however, the expectation is that the Chinese are likely to keep buying scutched flax in Europe due to its high quality and the expertise of the European flax growers and scutchers [4]. Most of the flax spinning and weaving capacity has already left Western Europe, so for the scutchers this might not make

much difference. A second threat of entry comes from Eastern Europe (some of the new EU countries) and Russia, which process and export considerable amounts of flax, although it is generally perceived to be of inferior quality. On the other hand, many West European spinners and weavers have already shifted their production to the east [12]. Third, in the late nineties it appeared that southern countries like Spain would enter the flax market, however, the growing of flax in this part of Europe appears to have been related purely to the European subsidies and has disappeared as quickly as it has come up. And last, new start-up companies, especially in Germany, the UK and Denmark, have appeared in the late nineties which produce short fibre only for technical markets, following the 'lin-total' concept [8]. Some of these companies, however, have already disappeared again.

Access to distribution channels could be an entry barrier, the traditional flax industry is relatively small and is governed for a major part by the distributive traders. It will not be easy to enter into this world as a new player. However, the new technical applications are aimed at a very different market (see below). There exists a learning curve within the industry since natural fibres are not easy to work with and experience gives existing competitors an advantage and provides a barrier of entry (as we shall see later this learning curve is also a barrier for the natural fibres to enter other application areas).

Generally it can be stated that as long as the main outlet for the flax producing industry lies in the apparel market, it will not be interesting for Western European companies to enter the business. For the newly developed technical market, however, there are a number of new entrants in Western Europe [7]. This is especially a threat for the short fibre market, which is by the traditional flax processors seen as a side market, although there are some traditional companies that only process short fibres from the traditional flax isolation process. If the flax industry would be successful in defining more new high value outlet channels for their products, more new Western European companies might enter the business.

*Pressure from substitute products*

The pressure from substitute products is very strong and is the main reason that the once very profitable flax industry has been declining so strongly since the fifties of the previous century. Cotton, as well as synthetic fibres, have taken over the majority of the flax market, and it cannot be expected that the market position of these other fibres will become weaker over the coming years, although the cheaper linen that now comes

from China seems to be able to regain some of the market share for flax.
Whereas for the apparel market other natural fibres as hemp, jute and sisal are no alternative, for the technical applications in the automotive industry it does not seem to make much difference which natural fibre is applied. This indicates that in this new market the threat from substitute products comes from other natural fibres and when flax prices are high, flax fibres in the automotive industry might be readily replaced by other natural fibres [7].

*The bargaining power of buyers*
The bargaining power of the traditional buyers, the Belgian distributive traders was very strong but has been diminishing over the last couple of years, since also the scutchers now have direct contacts with the spinners [4].
For technical applications, especially in the automotive industry, the bargaining power of the buyers is immense. For the processors larger sales and longer contracts can be gained, but especially the automotive industry is known for its sharp price negotiations with suppliers [14].

*The bargaining power of suppliers*
The bargaining power of suppliers is not very strong; the suppliers of the scutchers are farmers, who often grow the flax under contract. There is a subsidy on the growing of flax supplied by the European Union. Quality of the flax is something that changes every year and scutchers nowadays sometimes buy processed flax from other processors to supply a buyer with the desired quality [4]. Apart from the subsidy on the growing of flax there is also a subsidy on the processing of flax: for the seasons 2002-2003 until 2005-2006, the subsidy for long flax fibres is € 160/ton and for cleaned short flax (and hemp) fibres is € 90/ton. From 2006 onwards the subsidy for long flax fibres will be € 200/ton, whereas there will be no more subsidy for short fibres [15].

Adding everything up, it can be concluded that the flax processing business has been a very difficult branch to be in, but it has improved considerably over the last couple of years, due to the increasing demand from the fashion industry. Consequently, the industry and also its innovations are now very much focused on the fashion industry again and not so much on technical applications.
The long fibres are not likely to find an application as reinforcement for composite

| Product / Market | Present product | New product |
|---|---|---|
| Present market | A Market penetration | C Product development |
| New market | B Market development | D Diversification |

*Figure 8.3. Expansion vector matrix, different growth strategies according to Ansoff [16]. The risk of the strategies increases going from A to D.*

materials, not only due to their high price (similar as glass fibres), but also because long flax fibre composites suffer from inferior compressive properties, which makes them unsuitable to replace glass fibres in many technical applications, as described in Chapter 4. The short fibres are more likely to find an application in a technical market.
The smaller flax processors are not very likely to do large innovative developments on their own. The larger companies, however, have substantially more innovative strength. One of the examples of a recent innovation for the technical market is the development of the production line for comingled flax/PP by the Belgian company Procotex International SA [7]. This development took place in the nineties, the period that the flax industry was suffering from low prices. Procotex was well fit to set up this line, since they had their experience with processing both flax and other natural fibres and polymeric fibres. In terms of the expansion vector matrix of Ansoff [16] (figure 8.3) this development was a diversification step, making a formerly non-existing product for a new market, and was thus a high risk step. The PP used in the felt production line is a product from their own recycling business -for which it formerly appeared to be difficult to find a high-value application [7]- turning the company into its own customer (vertical integration) (see also figure 8.4, which shows the breakdown Ansoff [16] gives for the various possible strategies of diversification). The product from the felt line, however, was for a completely new market, notably the automotive industry, for which they also had to invest to obtain a ISO 9002 certification. The felt production itself was for Procotex also a new technology but it is tightly related to their core competence, being the processing of natural and polymeric fibres (see figure 8.4).

<table>
<tr><td></td><td colspan="3">New products</td></tr>
<tr><td rowspan="5">New Missions</td><td>Products<br><br>Markets</td><td>Related technology</td><td>Non-related technology</td></tr>
<tr><td>Same type</td><td colspan="2">Horizontal diversification</td></tr>
<tr><td>Company is its own customer</td><td colspan="2">Vertical diversification</td></tr>
<tr><td>Similar type</td><td colspan="2" rowspan="2">(1) (2)<br>Concentric<br>diversification<br>(3)</td></tr>
<tr><td>New type</td><td>Conglomerate diversification</td></tr>
</table>

(1) Marketing and technology related

(2) Marketing related

(3) Technology related

*Figure 8.4. Growth vectors in diversification according to Ansoff [16].*

## 8.3. The application of fibre mat based composites in the German automotive industry

As can be concluded from the analysis given in Chapter 7 one of the most likely applications for flax fibre composites is within the automotive industry. This was recognised relatively early by the German automotive industry, which has developed during the nineties a number of parts made out of NMTs. The automotive industry is generally known for its innovative application of new materials. On the other hand, wood fibre filled materials have always been used within the automotive industry, making the step towards the application of NMTs smaller than it might seem.

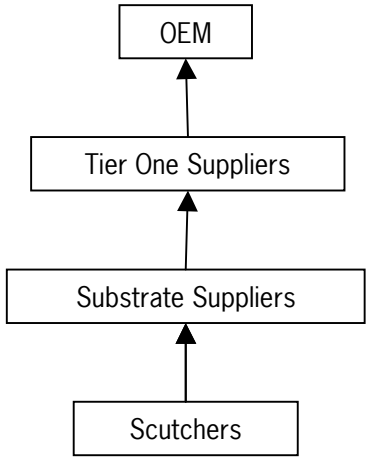


*Figure 8.5. The structure of the automotive industry insofar relevant to the natural fibre reinforced materials supply chain [14].*

The automotive industry is a highly integrated branch of industry. The structure of the automotive industry, insofar relevant for the natural fibre reinforced materials supply chain is shown in figure 8.5 [14] and exists of: (1) the OEMs (Original Equipment Manufacturers), which are the familiar car and vehicle brands, (2) TIER One Suppliers, suppliers of specialised components for assembly by the OEMs, typical examples are Johnson Controls, Visteon and Lear Corporation, (3) substrate suppliers, mainly non-woven producers in the wider textile industry, but this might also be plastics compounders in the case of natural fibre compounds, (4) natural fibre suppliers, for flax the flax processors (scutchers). In order to influence specification and usage of natural fibres, the fibre suppliers must work with all parts of the supply chain, which for a small flax processor is as good as impossible to do. The principal innovators in automotive components are the Tier One suppliers and it is believed that their research and product selection decisions will be the main determining factor in the growth of the natural fibre sector [14].

A problem for the application of natural fibre non-wovens in automotive applications is that the non-woven industry is predominantly based on synthetic fibres and there is a general reluctance to process bast fibres [14], since natural fibres are perceived as dirty and contaminant. This is an area where a flax processor has a definite advantage, being used to the processing of the dusty natural fibres. Procotex, for example, has

made use of this advantage. Also, the Tier One suppliers that presently produce components from natural fibres seem to be the ones that already had experience in the processing of wood fibres. For instance Johnson Controls has developed and produces the inner lining of doors of the Mercedes S-class from a PU sprayed natural fibre mat. They have designed the part together with Mercedes and developed the mat together with the substrate supplier [17]. The production is performed at Grefrath, at the former Fibrit plant. Fibrit used to produce parts for the automotive industry from wood fibres and a resin via a rather intricate process, indicating that the company was used to apply a natural material in their products.

In for instance Germany, the UK and Sweden, much effort has been put into improving flax processing techniques. Short fibre lines following the 'lin-total' concept, in which only short fibres and no long fibres are produced, have been set up recently [8]. Furthermore, In Germany, Belgium and France a number of companies have succeeded in setting up new lines for instance for the production of felts. Germany has increased the innovative strength of the industry by spending large amounts of subsidies on the development of technologies for processing renewable resources (see also Chapter 1). The fibres from the 'lin-total' short fibre production lines are better suited for application in non-wovens, regarding the fibre length and fibre length homogeneity, than the tow from the textile fibre isolation process. These fibres might thus prove to be a substitute product for the tow of the long fibre producers. Already in 1999 Schuh from Daimler-Chrysler reported that, whereas previously mainly by-products of the textile industry were used -mainly because of their low price-, from then on increasingly fibres were obtained from plants cultivated specifically for industrial applications [18]. Daimler-Chrysler uses in particular green decorticated flax.
A threat for the application of flax in the non-wovens is that it appears to be relatively easily substituted by other natural fibres. Despite all the arguments summed up by the automotive industry for the application of natural fibres (see also Chapter 1), cost reduction is considered as one of the major drivers for the application of natural fibres in the automotive industry [14]. The Tier One's make their choice depending on the fibre price. The increase of the flax fibre price in 2001 and 2002, due to the increasing demand from the apparel industry, has led to a stagnation in the application of flax in automotive composites, whereas the total application of natural fibres has increased further in this period [7]. It might be expected that at this moment further technology

development will focus on other fibres than flax and with the increasing performance demands on the natural fibre composites, this lost ground might not so easily be won back by flax fibres. Fact is that Lear Corporation has replaced flax fibres with kenaf, hemp and jute in their 'natural fibre polypropylene' [19]. On the other hand, when the price of flax decreases, the automotive industry might once again prove to be a buyer from the flax industry. To stabilise sales of flax to the automotive industry, development in the field of flax reinforcement could focus on the fact that flax, due to its finer fibre structure, might have specific advantages over the other fibres. This will, however, only become apparent when the technological development has gone further and the materials have become more sophisticated than they are today.

The main advantage that flax has over the other natural fibres is that there is an existing and well working supply chain, that is able to deliver fibres with the desired quality to the automotive branch. This is a fact that could be put to use by the combined flax branch in an attempt to win market share for flax fibres within the automotive industry.

## 8.4 Flax in natural fibre filled extrusion compounds

What could be the viability of the application of flax in natural fibre filled compounds? As was shown in Chapter 6 it is possible to make acceptable materials for injection moulding applications by mixing the flax fibres with a polymer on a twin screw extruder. Even though, for flax, the feeding of the fibres to the polymer melt still needs to be scaled up.
As was also concluded in the previous paragraph, it is striking that almost all attempts to develop materials on the basis of natural fibres with a plastic are done by the natural fibre producing industry and not by, for instance, the plastics processing industry. Many plastics producers have tried at small scale to mix natural fibres with their polymers, but they usually do not continue their attempts. There are a number of reasons for this fact:

- it is difficult to handle a natural fibre like flax, the fibres are not free flowing, rather voluminous and they produce a lot of dust, plastics producers are not used to this combination of properties,
- it requires some skill to make materials that do not smell and look burned, and that have acceptable properties; plastics producers often stop their attempts to

produce natural fibre compounds rather frustrated since they get pitch-black materials with bad mechanical properties [20],
- the property improvement reached with natural fibres is limited compared to, for instance, glass fibres; especially for very experienced plastics compounders this is a psychological barrier, because they usually make materials with impressive properties [21].

It can be concluded that, contrary to what might have seemed obvious, the usually highly innovative plastics industry is not the big innovator in the field of natural fibre reinforced composite materials. Innovation comes from the flax processing industry or from universities or R&D institutions. Presently, there is some starting commercial interest from end-users of plastics for the application of natural fibre compounds [22], which might prove to be the trigger that the industry has been waiting for. Again, the problem for flax in this application is the fact that jute and hemp perform equally well as flax fibres in the compounded materials [23], so that also here it will become a matter of price which fibres will be applied.

## 8.5 Strategic choices for the flax producing industry

It is obvious that on the long run the flax industry itself has the biggest economic interest in alternative applications for flax fibres. However, they have limited innovative strength and R&D capacity. So, what options are open to them?

Ansoff [16] presents a way to develop a firms strategy, by considering its product-market scope, its growth vector (expansion or diversification), the competitive advantages of certain strategic choices and the synergy that can be reached. In his perspective generally firms try to improve their product and process technology and expand their sales territory in order to increase their market share. However, when the objectives of the firm can no longer be met within the present product market scope, a firm needs to diversify.
For the flax industry the present situation in the apparel market is rather good, however, since the world wide flax production capacity is expanding significantly, it is not unlikely that prices might drop again within the near future. For a flax processor in a once more declining market, diversification might be the way forward. Ansoff gives a further development of the growth vectors in diversification as shown in figure 8.4,

divided in horizontal diversification, vertical integration, concentric diversification and conglomerate diversification. Conglomerate diversification, starting to do something completely different for a different market will not be considered here further. An important characteristic of horizontal diversification is that it consists of moves within the same economic environment of the diversifying firm. Generally, this will contribute little to the stability of the firm. For the flax industry this would mean for instance starting to process other natural fibres as well, for the same customers. Obviously, when one wants to get away from a cyclic branch like the apparel branch this would not be the way to go. Vertical integration (see figure 8.4) will offer even less assurance of stability. Basically, by for instance starting up a hackling line, a scutcher would even become more dependent on the same market segment. Even if the synergy to be gained in this step can be significant, in the long run it will not help to get a more stable basis for business.

Concentric diversification can be done aimed at a similar type of customer, with either related technology or unrelated technology or for a new type of customer, with related technology. Considering the flax processing industry and assuming that they want to keep on processing flax, one of their competitive advantages is that they are used to work with a difficult product as natural fibres. They could start for instance the production of non-wovens (like Procotex has done) or other intermediate products for the technical market. It might also be a good choice to start producing (intermediate products from) hemp and for instance jute, since in this way the expertise in handling natural fibres can be exploited, and the firm becomes less sensitive to the flax price.

Another possible concentric diversification strategy could be to set up a joint venture between a flax processor and a plastics compounder, optionally with the help of an external R&D institution, for starting up a natural fibre compounding line. The flax processor could use its experience with natural fibres by aiding the plastics processor to set up a working production line. There are two important conditions that would have to be met in order to make this work: (1) the market for the resulting material would need to be closer defined than it is today, a natural fibre compound has mechanical properties that lie in between that of very cheap chalc filled PP and that of more expensive but mechanically much better glass filled PP, making it difficult to target the right application (see also the next paragraph), (2) the flax fibre processors would need to add a quality aspect to the fibres to make them less easily replaceable. An understandable fear of the flax processors to enter in such a joint venture is that once

the technology works, the plastics producer will buy cheaper flax fibres from, for instance, Eastern Europe or might start to work with other natural fibres altogether. The way around this could be when the flax processor itself (or optionally together with other flax processors) sets up a compound processing line.
Also when a flax processor wants to diversify in the direction of the non-woven market, they would need to make their product non-interchangeable with other natural fibres. For flax fibres this could mean the use of the fact that the fibres are finer, which could provide specific mechanical properties. For instance Daimler-Chrysler uses a blend of flax and sisal for a favourable combination of material toughness and processing ease [18]. When these materials become more mature, it is quite possible that flax will have its own market niches, providing a long term stable market for the flax processors.

## 8.6 Application niches for flax fibre composites

It would be helpful to have a rough indication of the positioning of flax fibre filled materials versus other materials, to be able to identify possible niches of application. Ashby [24] describes a method to compare the performance of a variety of materials for a specific constructive element. Since from the work presented in this thesis it follows that the most obvious application for flax fibre reinforced materials lies in lightweight, stiff constructive elements, the analysis given here will be based on this kind of application. Following Ashby [24], consider the development of a stiff plate, loaded in bending, as light as possible, of thickness $t$, a set width $b$ and a length $\ell$, which must not deflect more than $\delta$ under a load $F$. Its stiffness $S$ must then be greater than:

$$S = \frac{F}{\delta} \geq \frac{C_1 E I}{\ell^3} \tag{8.1}$$

where $E$ is the Young's modulus, $C_1$ is a constant which depends on the distribution of load and $I$ is the second moment of inertia, which for a plate is:

$$I = \frac{b t^3}{12} \tag{8.2}$$

The stiffness, length and width of the plate are specified, the thickness is free. The mass of the plate can be reduced by reducing $t$ but the stiffness criterion must be met. The mass, $m_p$, of the plate is given by:

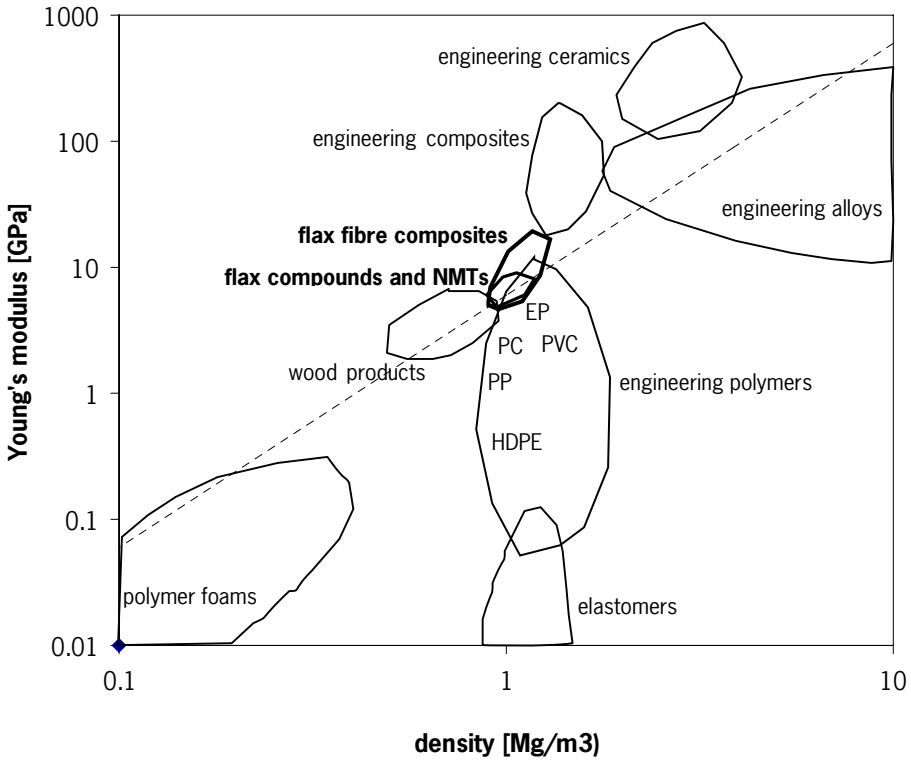


*Figure 8.6. Positioning of flax fibre composites as function of Young's modulus and density versus a variety of materials (based on [24]). The dashed line gives the design criterion for a stiff light plate, loaded in bending.*

$$m_p = b\,t\,\ell\,\rho \tag{8.3}$$

with $\rho$ the density. Using equations 8.1, 8.2 and 8.3 to eliminate *t,* and grouping the material properties gives:

$$m_p \geq \left(\frac{12\,l^6\,b^2}{C_1}\right)^{1/3} \frac{\rho}{E^{1/3}} \tag{8.4}$$

which implies that the best materials for a light stiff plate are those with the largest material index *M*:

$$M = \frac{E^{1/3}}{\rho} \tag{8.5}$$

Figure 8.6 gives a graph of the Young's modulus versus the density of a number of different material groups. The flax fibre filled materials are given by the bold lines, where the larger area represents all flax filled materials, including UD long fibre filled composites. The smaller circle in the lower half of the larger area represents the modulus versus density range of the NMTs and compounds from Chapters 5 and 6 of this thesis. The dashed line gives the design criterion '$E^{1/3}/\rho$ is constant' from equation 8.5. All materials that lie on this line would give a plate with a certain stiffness of the same mass. A plate from materials that lie towards the upper left half of the line would be lighter, materials that lie towards the lower right half would give a heavier plate. Now it is easy to compare the material groups for this specific application. The flax reinforced materials perform better than unfilled polymers, but they perform worse than most engineering composites, which indicates that for most applications that require fibre filled composites flax fibre materials are not the right choice. However, for applications where polymers are not stiff enough, and engineering composites are an overkill, flax reinforced materials might be a good choice, although they would have to compete for these kind of applications with for instance chalc filled PP which is very cheap. The advantage of a flax filled composite might then lie in processing properties, like the possibility to make large 3-D components, which is one of the reasons to apply NMTs for inner door linings. For flax fibre reinforced compounds an extra advantage might be found in combining the fibres with a biodegradable matrix, to make a fully biodegradable compound. The final decision to use a flax fibre composite is thus obviously also depending on processing properties and a number of other parameters, including price.

Given the work presented in this thesis, I now challenge you, reader, to define an application for which flax fibre reinforced composites are exactly the right material at the right place for the right price.

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# Appendix A. Adhesion in Flax Fibre Reinforced Composites

## A.1 Introduction*

Several groups have investigated methods to improve the adhesion between cellulose based fibres and a variety of matrix materials. The methods ranged from the formation of a transcrystalline morphology at the interface by slow cooling [1], plasma treatment of the fibres [2] to several different types of functionalised additives like silanes [3,4], to the use of graft copolymers. For composites with polypropylene (PP) as matrix, the most effective compatibiliser was found to be maleic anhydride grafted polypropylene (MAPP). Felix and Gatenholm have proven by using various surface techniques that the maleic anhydride is covalently bonded to the cellulose surface by esterification [5] and that the PP part of the grafted chains mixes with the PP of the matrix [6], forming an effectively bonded interphase. Although most of this work was done with wood fibres as reinforcing agent, the results appear to be transferable to flax fibre reinforced materials as well. Mieck et al. have investigated the influence of both functionalised silanes [7] and MAPP [8] on the fibre matrix adhesion of (green) flax/PP composites and found both to have similar effects. Since MAPP can simply be added to the PP matrix material before or during processing, whereas silanes have to be coupled separately to the fibre surface, the use of MAPP has taken a larger flight.

Though several authors studied the effect of improved fibre-matrix adhesion on general composite properties like stiffness, strength and impact behaviour, little is made clear about the level of effective use of the fibre strength [9]. Only few groups have tried to

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*This appendix is based on the paper:

- Critical fibre length and apparent interfacial shear strength of single flax fibre polypropylene composites; M.J.A. van den Oever and H.L. Bos, *Adv. Comp. Letters*, **7** (1998) 81

measure the strength of the interface between cellulose fibres and the polymer. Felix and Gatenholm [1] have used the single-fibre-fragmentation test to determine the interfacial shear strength (IFSS) in cotton fibre/PP composites. Sanadi et al. [10] used a pull-out test to determine the IFSS in wood/PE composites. Stamboulis et al. [11] have used the pull-out test to investigate the IFSS for (a.o.) flax/PP and flax/PP/MAPP composites. Garkhail [12] used a micro-debond test for flax/PP and flax/PP/MAPP composites.

An effective use of fibre strength, is an important parameter for optimal mechanical performance of composites, since unnecessarily large fibre lengths will limit the processability of a composite. Apart from the IFSS, the critical fibre length, therefore, is a useful parameter in the optimisation of mechanical properties versus processability.

In this study the critical fibre length of both scutched flax fibre bundles and elementary fibres in a polypropylene matrix is determined, using single-fibre-fragmentation tests. The stress transfer in both elementary and scutched single flax fibre polypropylene composites is studied by determining the critical fibre length and the apparent IFSS. Furthermore the influence of improved fibre-matrix interaction is reported. The single-fibre-fragmentation test is used since it is -from an experimental point of view- easier to perform than a pull-out test on natural fibre/thermoplastic composites.

## A.2 Experimental

Thin polypropylene (PP) sheets with thickness 0.1 mm are compression moulded from granules (HV 252, Solvay) at 200°C and 20 bar pressure, using an overhead slide with a 50*100 mm rectangle cut-out as a mandrel. Scutched fibre bundles without visual weak inter elementary fibre bondings are selected from scutched warm water retted flax fibres bundles, processed at ATO bv. Elementary fibres are peeled-off from fibre bundles of the same handful of scutched fibres. Scutched and elementary flax fibres are stuck onto a PP-sheet, covered with a second sheet and hot-pressed at 200°C and 20 bar.

The effect of improved fibre-matrix adhesion on the critical fibre length is studied using a precompounded blend of 1 wt% maleic-anhydride-modified polypropylene (MAPP) (Hostaprime® HC5, Hoechst) and 99 wt% PP as the matrix.

The single fibre composites are loaded in tension in a home built tensile rig. After the specimens show no further fibre fracture, the stress is reduced to zero again and the

length and the visual diameter (viewed from one side) of the fragmented fibres is measured using an optical microscope Olympus BH2. Photographs of tested single fibre composites are made using a Zeiss Axioplan microscope and a standard Zeiss camera.

## A.3 Results and discussion

The critical fibre length, $L_c$, of fibres in a composite is determined by fibre fracture, interfacial bond strength, interfacial debonding, interface friction and matrix plastic deformation [13] and therefore difficult to determine exactly. An estimation of the critical fibre length, however, can be obtained from the average fibre fragmentation length in a loaded single fibre composite, $L_{av}$, according to [14]:

$$L_c = \frac{4}{3} L_{av} \tag{A.1}$$

This equation supposes a constant fibre diameter, whereas the diameters of the different elementary and scutched flax fibres used are not constant. The elementary

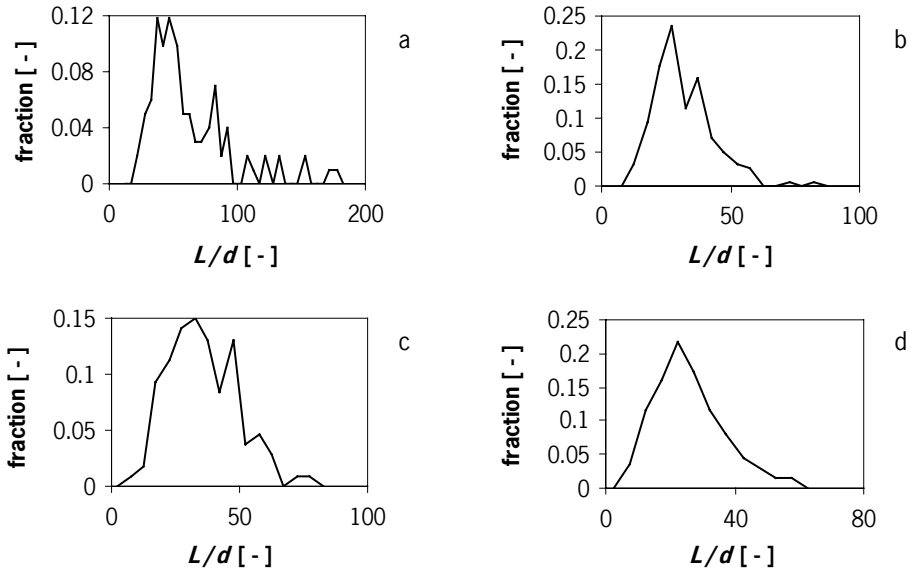


*Figure A.1. Distribution of measured L/d-values. a) Elementary fibres in PP, b) elementary fibres in PP/MAPP, c) technical fibres in PP, d) technical fibres in PP/MAPP.*

fibre diameter varied between 10 and 15 µm between different fibres, the scutched fibre diameter is not constant even over the fibre length and varied in this study between 30 and 120 µm. Therefore, in this case the fibre fragmentation length over the diameter, *L/d*, is a more useful parameter than the fibre fragmentation length, *L*.
The distributions of the measured *L/d* values for the elementary and scutched flax fibres in both PP and PP/MAPP are given in figure A.1. At least 100 fibre fragments per composite are taken into account. The *L/d* values show large scatter due to a relatively large scatter in fibre strength compared to synthetic and mineral fibres and due to locally weaker fibre-matrix interfaces as a result of contamination on the fibre surface.
An indication of the critical fibre length can be obtained by determining the average *L/d* value of the various fractured fragments in the single fibre composites. The average *L/d* values and the calculated critical fibre lengths, assuming a diameter of 12.5 µm for elementary fibres and a diameter of 80 µm for scutched fibre bundles, are given in table A.1. The calculated critical lengths for elementary fibres are larger than the elementary fibre lengths that are found in extruded and injection moulded flax/PP compounds. In extruded compounds the fibre length can be is about 1 mm [15], which is similar to the length of fibres in extruded glass/PP composites [16]. After injection moulding, however, the fibre length is significantly shorter. In Chapter 6 fibre length values are found of 0.1 to 0.2 mm, which are similar to or even shorter than the lengths of jute/PP [17] and glass/PP injection moulded compounds [18]. The fibre length in the NMT materials described in Chapter 5 is larger than the critical length of

*Table A.1. Measured average L/d-values and critical fibre length ($L_c$) calculated from equation A.1 of elementary fibres and scutched fibre bundles in PP and PP/MAPP.*

| | $(L/d)_{average}$ [-] | $L_c$ [mm] |
|---|---|---|
| elementary fibre in PP-matrix | 59 ± 25 | 0.98 |
| elementary fibre in PP/MAPP-matrix | 31 ± 11 | 0.52 |
| scutched fibre bundle in PP-matrix | 36 ± 12 | 3.8 |
| scutched fibre bundel in PP/MAPP-matrix | 26 ± 11 | 2.8 |

scutched flax fibre bundles [19], which indicates that in these materials improvement of fibre-matrix adhesion might not affect the composite properties to such a large extent. However, since optimal strength is only reached at a fibre length of approximately ten times the critical fibre length [20], optimal flax reinforcement would only be reached at a fibre length of about 10 mm in the compounds described in Chapter 6 and a length of 30 to 40 mm for the NMTs described in Chapter 5.

From the fibre fragmentation lengths in a single fibre composite an apparent interfacial shear strength (apparent IFSS), $\tau$, can be determined, using the Kelly-Tyson theory [21]:

$$\tau = \frac{\sigma_f \, d}{2 \, L_c} \tag{A.2}$$

where $\sigma_f$ is the fibre strength, which should be determined at a gauge length equal to the fragmentation length of the fibre in the single fibre composite. Using the data of Chapter 3, the average tensile strength at the critical fibre length, $\sigma_{lc}$, for both scutched fibre bundles and elementary flax fibres can be calculated from the Weibull distribution as follows [22]:

$$\frac{\sigma_l}{\sigma_{lc}} = \left( \frac{L_c}{L_l} \right)^{\frac{1}{m}} \tag{A.3}$$

where $\sigma_l$ is the measured fibre strength at fibre length, $L_l$, and $m$ is the Weibull modulus. In table A.2 the experimental data of $L_l$, $\sigma_l$ and $m$ and the calculated $\sigma_{lc}$ and $\tau$, based on the critical lengths as determined in table A.1, are given.

*Table A.2. Calculated apparent interfacial shear strength, $\tau$, of flax/PP composites, determined from single-fibre tensile tests and single-fibre-fragmentation tests.*

| | $L_l$ [mm] | $\sigma_l$ [MPa] | $m$ [-] | $L_c$ [mm] | $\sigma_{lc}$ [MPa] | $\tau$ [MPa] |
|---|---|---|---|---|---|---|
| elementary fibre in PP | 3 | 1520 ± 240 | 4.0 | 0.98 | 2011 | 13 |
| elementary fibre in PP/MAPP | 3 | 1520 ± 240 | 4.0 | 0.52 | 2356 | 28 |
| technical fibre in PP | 3 | 810 ± 240 | 2.2 | 3.8 | 727 | 8 |
| technical fibre in PP/MAPP | 3 | 810 ± 240 | 2.2 | 2.8 | 836 | 12 |

The Kelly-Tyson model only gives a rough prediction of the fibre-matrix shear strength. However, since researchers in general agree that a really accurate model is not available at the moment [20], the Kelly-Tyson model can give a first indication of the fibre-matrix adhesion. The limited validity of the model probably accounts for the apparent IFSS-value of 28 MPa for elementary fibres in a PP/MAPP-matrix, which is higher than the shear yield strength of the pure PP-matrix as calculated from the Von Mises yield criterion, being 18 MPa (the matrix yield stress divided by √3). It can, however, be concluded that the fibre-matrix adhesion improves considerably by using MAPP as a compatibiliser, especially when elementary fibres are concerned. The improved adhesion can also be derived from the matrix yielding at the broken fibre ends in both elementary and scutched fibre PP/MAPP composites (see figure A.2), whereas in PP composites no matrix yielding of this kind is observed. The results indicate that good interaction between flax fibres and the PP/MAPP-matrix is possible and that the flax fibres can be used effectively in strength applications.

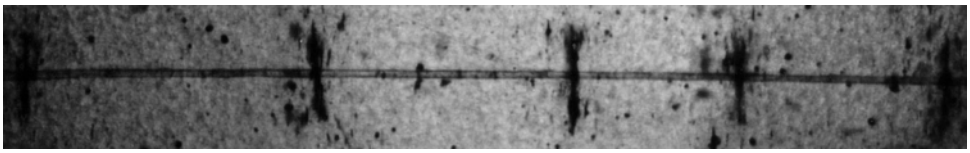

*Figure A.2. Photograph of a fragmented elementary flax fibre in PP/MAPP; the fibre diameter is about 10 µm.*

The apparent IFSS found for scutched fibre bundles is very similar to the data measured by Garkhail [12] using a micro-bond test. Garkhail finds an IFSS of 7 MPa for scutched fibres in PP, which increases to circa 10 MPa upon the addition of MAPP. The apparent IFSS for elementary fibres in PP of 13 MPa is in the same order as the IFSS of 10.6 MPa that Stamboulis et al. [11] found with a single fibre pull-out test. They find for elementary fibres embedded in MAPP, however, a value of 11.4 MPa with the single fibre pull-out test, whereas the single-fibre-fragmentation test gives 28 MPa. Stamboulis et al. suggest that the reason for the low value they find for the compatibilised system might be due to the sample preparation method: specifically the time allowed for the single fibre composites preparation is probably not enough for the maleic anhydride to agglomerate on the fibre surface. In the single-fibre fragmentation test this problem apparently does not occur. The lower IFSS-values for scutched flax fibre bundles

compared to elementary fibres is probably due to contamination on the surface of the (scutched) fibres. Both scutched fibre bundles and elementary fibres are covered with a pectin and waxy layer. However, the scutched fibre bundles are besides pectin and wax partly covered with woody bast material, which hinders optimal fibre-matrix stress transfer. The woody bast material on scutched fibre bundles can be removed by applying further textile processes like hackling.

It appeared that in all tested composites fibre fracture takes place at the kink bands, already present in the fibres before testing. This is different from the situation in carbon or glass fibre composites, which do not have pre-induced flaws to the same extent as natural fibres do. However, during the fragmentation test not all kink bands fracture during loading and therefore, the measured critical fibre length is not just the 'fibre length between kink bands'. Furthermore fibre strength value used in the calculation is extrapolated from measurements on fibres also containing kink bands. This assures that a realistic fibre strength is used in the calculations, and that the effect of the kink bands on the fibre strength is taken into account. However, as was presented in Chapter 3, there is a large scatter in the fibre strength both for elementary and for scutched flax fibre bundles. This scatter leads to a large scatter in the length of the fibre fragments found in the fragmentation test as can be seen in figure A.1, and adds thus to the scatter in the $L/d$ data and the IFSS.

## A.4 Conclusions

From the single-fibre-fragmentation tests, the critical fibre length for elementary flax fibres is found to be about 1 mm with PP and 0.5 mm with PP/MAPP as matrix, being significantly longer than the fibre lengths in extruded and injection moulded compounds. For scutched flax fibres the critical fibre length is found to be 3.8 mm and 2.8 mm with PP and PP/MAPP as matrix, respectively, which is slightly shorter than the average fibre length in an NMT material.

The high apparent interfacial shear strength for elementary flax fibres in PP/MAPP and the matrix yielding at the elementary fibre fragmentation ends indicate that adhesion between fibres and matrix will not be the limiting factor for the use of flax fibres in strength applications. However, the critical length values determined indicate that for optimal properties, the fibres need to be far longer than they are in the materials described in this thesis.

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# Summary

In the early nineties a strong interest arose towards the application of renewable resources in modern materials. This was fed both by environmental concerns and by the interest of the agricultural industry, which was looking for new outlets for its products. It was in this light that research on the application of natural fibres as reinforcement for composite materials started. Flax fibres were considered to be one of the best candidates for this application, due to their high stiffness and strength and relatively low density. However, soon it became apparent that it was far more difficult to produce good quality composites from flax fibres and a polymer matrix than was originally anticipated. Initially, most research focused on improving the interfacial bond strength between the flax fibre and the polymer matrix, in order to improve the properties of the composites. These interface modifications often followed schemes similar to the ones used in the past for glass fibre. However, unlike isotropic glass fibres, flax fibres -like most biological materials- exhibit a highly anisotropic hierarchical structure.

In this work the relation between the anisotropic structure of the flax fibre and its deformation behaviour is described and the effect of this deformation behaviour on a variety of different composites made with flax reinforcement is investigated.

The structure of the flax fibre is composite-like in itself (Chapter 3), with the long fibres (technical fibres) consisting of fibrous plant cells, called the elementary fibres. Also the cell wall of the elementary fibres is made out of a fibrillar structure. It is this repetition of fibrillar structures which strongly influences the deformation behaviour of the fibre.
Firstly, the tensile strength of the fibres is strongly dependent on the clamping length during the test. At long clamping lengths the elementary fibres simply fail within the interface between the cells, but at shorter clamping lengths the crack has to run through the cell wall of the elementary fibres, which leads to a large increase in fibre strength. The tensile strength of the elementary fibres themselves is roughly twice that of long technical fibres at short clamping length, which is due to the bundle effect.
Secondly, due to the fibrillar nature of the cell wall, the fibres are very sensitive to the

formation of kink bands under bending or compressive deformation. It appears that, due to the processes applied to isolate the fibres from the plant (breaking, scutching and hackling, (Chapter 2)) the fibres are actually full of kink bands, a fact which obviously influences both their tensile and compressive strength.

Application of technical flax fibres in unidirectional epoxy composites (Chapter 4) leads usually to composites which have an acceptable tensile strength, but a very poor compressive strength. The disappointing compressive strength is caused mainly by the kink bands present in the fibres. It was shown that it is possible to stabilise the kink bands by filling them up with melamine resin, which penetrates easily into the fibres and subsequently cross-links the fibrillar structure. The compressive strength of composites with melamine treated fibres is increased significantly, however, the treatment leads to an embrittlement of the fibres and the tensile strength of the composites is strongly reduced. Thus, the method is as yet not suitable for the production of unidirectional composites from flax fibres.

Composites of short flax fibre mats or randomly oriented non-wovens impregnated with polypropylene (PP), so-called NMTs, are increasingly used in the automotive industry. The properties of these composites depend on the degree of refining of the fibres (Chapter 5). Mats made from scutched fibres give composites with lower strength than mats made from, finer, hackled fibres. Comparison with glass fibre mat reinforced composites (GMTs) shows that in hackled fibre composites the fibres are just as effective in transferring their strength to the composite as glass fibres are. However, since the maximum tensile strength of flax is much lower than that of glass, the NMTs show lower strength than the corresponding GMTs. On the other hand, the moduli of NMTs and GMTs at the same fibre volume fraction are similar. Due to the lower density of flax fibres it is therefore possible to make lighter constructive elements from NMTs than from GMTs, as long as the design is stiffness controlled.

In compounded flax/PP composites the fibres are refined further towards elementary fibres during the melt processing step (Chapter 6). However, during this compounding step the fibres are, similar to glass fibres, also broken up into very short segments. Despite the very short fibre length, these compounds show similar mechanical properties as the NMTs, with the impact behaviour of the short fibre compounds being

even significantly better than that of the NMTs. Micromechanical analysis indicates that if a process could be developed in which the fibre length is retained better, the properties of these materials might increase significantly.

Adhesion, or rather the lack of adhesion, between flax fibres and a polymer matrix is in the literature generally perceived as a problem. Indeed, in a flax/epoxy composite adhesion is not automatically obtained (Chapter 4). To improve the adhesion between the fibres and an epoxy matrix it is necessary to first remove the waxy layer that surrounds the fibres by nature. After removal of the waxes the fibre surface reacts readily with the resin or other surface modifiers and improved adhesion between the fibres and the matrix can thus be achieved. Also flax and polypropylene do not automatically adhere, but here the addition of maleic anhydride modified PP (MAPP) leads to improved adhesion between the fibres and the matrix (Chapter 5, 6 and appendix A). In this case it is not necessary to first remove the waxy layer. Apparently, during the mixing step of the fibres with PP, which is always done at temperatures near 200 °C, the waxes diffuse into the matrix, leaving the fibre surface exposed for reaction with the compatibiliser. It is therefore also not necessary to modify the fibres before they are mixed into the matrix. The interfacial shear strength of flax/PP/MAPP composites can easily approach the yield strength of the matrix (appendix A), which indicates that adhesion between the fibres and the matrix is probably not the factor limiting the mechanical performance of flax reinforced composites. It appears that in certain cases internal failure of the fibres, due to their composite-like structure, is the factor that limits tensile and compressive strength as well as impact strength of the materials (Chapter 4, 5 and 6).

From the technical performance of flax fibre reinforced composites it follows that they are especially fit for the use in applications designed for stiffness. The environmental impact of flax fibre composite parts is also lowest when the materials are used in applications which require above all flexural stiffness at a low weight (Chapter 7). For applications where high tensile strength is required a constructive element reinforced with flax fibres needs to be designed thicker than a similar element reinforced with glass fibres, due to the lower tensile strength of flax. Such a thicker element inevitably leads to the use of more material and hence a higher environmental impact. This is especially the case when the matrix material has a high environmental impact, as many

thermoset materials have. However, due to the high specific modulus of flax it is possible to construct lighter elements for cases where bending stiffness is important. For transport applications this leads to an extra environmental gain since the lighter construction leads to the saving of petrol during service life of the vehicle.

Summarising, flax reinforcement is certainly not the panacea it was hoped to be in the early nineties. Nevertheless, for certain applications the use of flax as a reinforcement for polymers has advantages over the application of glass reinforcement. These applications are primarily to be found in parts which are designed for optimum stiffness at minimum weight. Useful applications can thus be found in the transport sector. Since the advantages of the use of flax reinforced composites are often of a secondary effect, of which not the producer but the user profits, it would be helpful to support the application of these materials with legislation or dedicated subsidies.
Flax reinforced composites have similar properties as composites reinforced with other natural fibres. Flax, however, has the advantage that in Western Europe the supply chain is relatively stable due to the existence of the linen producing industry. A limiting factor for the application of flax is that the prices of flax fibres, also of the short fibres suitable for application in composites, are strongly dependent on the apparel fashion. Recent history has shown that in years where the flax price is relatively high, flax for reinforcement of polymers is replaced by other natural fibres like hemp and jute. For the near future, development in the field of flax reinforcement should therefore be aimed at better exploiting the specific advantages of flax compared to other natural fibres, namely its fineness and its relatively high strength.

# Samenvatting

Begin negentiger jaren ontstond er een sterke interesse in de toepassing van hernieuwbare grondstoffen in moderne materialen. Deze interesse kwam voort uit zowel zorg voor het milieu, als uit een behoefte van de landbouwsector, die op zoek was naar nieuwe toepassingen voor zijn producten. In deze context begon het onderzoek naar de toepassing van natuurlijke vezels als versterkers in composietmaterialen. De verwachting was dat vlas één van de beste kandidaten voor deze toepassing zou zijn, aangezien vlas sterk, stijf en relatief licht is. Het bleek echter veel moeilijker te zijn om goede composieten te maken van vlas en een polymere matrix dan men oorspronkelijk verwachtte. De oorzaak hiervan ligt onder andere in de specifieke structuur van de vlasvezel.

Vlas heeft van zichzelf een composietachtige structuur (hoofdstuk 3), waarbij de lange vezels (technische vezels) die uit de plant worden geïsoleerd bestaan uit bundels van lange dunne cellen, die elementaire vezels worden genoemd. De celwand van deze elementaire vezels is ook weer opgebouwd uit een vezelachtige structuur, met lange dunne fibrillen van cellulose. Het is deze herhaling van fibrillaire structuren die verantwoordelijk is voor het deformatiegedrag van de vezel.

Ten eerste is de treksterkte van de technische vezels sterk afhankelijk van de inklemlengte tijdens een trekproef. Bij langere inklemlengtes bezwijken de technische vezels in het grensvlak tussen de elementaire vezels, maar bij korte inklemlengtes loopt de scheur door de celwand van de elementaire vezels. Hierdoor neemt de treksterkte van technische vezels sterk toe bij afnemende inklemlengte. De treksterkte van de elementaire vezels zelf is ongeveer twee keer zo hoog als de treksterkte van technische vezels bij vergelijkbare inklemlengte. Dit is één van de redenen waarom er in de literatuur zoveel uiteenlopende waarden voor de vezelsterkte worden genoemd.
Ten tweede zijn de vezels, door de anisotrope fibrillaire structuur van de celwand, erg gevoelig voor knikken onder buig- of drukbelasting. Het blijkt zelfs dat, door het proces waarmee de vezels uit de plant geïsoleerd worden (braken, zwingelen, hekelen (hoofdstuk 2)), de vezels al vol zitten met knikbanden, waardoor de vezelsterkte

natuurlijk vanaf het begin al negatief wordt beïnvloed. Ook de eigenschappen van de verschillende composieten die met deze vezels gemaakt kunnen worden lijden hieronder.

Toepassing van technische vlasvezels in unidirectioneel versterkte epoxycomposieten (waarin de vezels allemaal in dezelfde richting liggen) leidt tot materialen met meestal een redelijke treksterkte, maar met een slechte compressiesterkte (hoofdstuk 4). De tegenvallende compressiesterkte wordt voornamelijk veroorzaakt door de knikbanden die in de vezels zitten. Onder compressiebelasting in de vezelrichting kreukelen de vezels als het ware in elkaar, waardoor het materiaal vroegtijdig bezwijkt. Het blijkt mogelijk te zijn om de knikbanden te stabiliseren, door de vezels te impregneren met een melaminehars. De melaminehars dringt door in de vezels en verknoopt de fibrillen. Composieten gemaakt met deze behandelde vezels hebben een veel hogere compressiesterkte, echter, de behandeling leidt tot een verbrossing van de vezels en de treksterkte van de composieten wordt hierdoor sterk verlaagd. Deze methode is derhalve (nog) niet geschikt om unidirectionele composieten uit vlasvezels te maken.

Composieten gemaakt uit matten van korte vlasvezels of uit non-wovens, die worden geïmpregneerd met een polymeer zoals polypropyleen (PP), NMT's genaamd, worden in toenemende mate gebruikt in de automobielindustrie. De eigenschappen van deze composieten zijn afhankelijk van de isolatiegraad van de vezels (hoofdstuk 5). Matten gemaakt van gezwingelde vezels geven composieten met een lagere sterkte dan matten gemaakt van gehekelde vezels, die fijner zijn. Vergelijking met glasvezelmat versterkte composieten (GMT's) laat zien dat in composieten met gehekelde vezels, de vlasvezels net zo effectief zijn als glasvezels in het overbrengen van hun sterkte aan het composiet. Maar omdat de maximale sterkte van technische vlasvezels veel lager is dan van glasvezels, zijn de NMT's minder sterk dan de GMT's. Aan de andere kant is de stijfheid van NMT's en GMT's bij dezelfde vezel-volumefractie vergelijkbaar. Aangezien vlasvezels een lagere dichtheid hebben dan glasvezels, is het dus mogelijk om lichtere constructie-elementen te maken van NMT's dan van GMT's, zolang stijfheid het voornaamste ontwerpcriterium is.

In gecompoundeerde vlas-PP composieten worden de vezels verder geïsoleerd tot elementaire vezels tijdens het inmengen in de PP-smelt (hoofdstuk 6). Bij deze

verwerkingsstap worden de vezels echter ook opgebroken tot heel kleine segmentjes, net zoals dat bij glasvezels gebeurt. Ondanks de zeer geringe vezellengte hebben de gecompoundeerde materialen vergelijkbare eigenschappen als de NMT's, hun slagvastheid is zelfs beter. Micromechanische analyse toont aan dat een productieproces dat de vezellengte beter in tact laat, compounds met significant betere eigenschappen zou geven.

Hechting, of beter het gebrek aan hechting, tussen vlasvezels en de polymeermatrix wordt in de literatuur vaak als het belangrijkste probleem in vlasvezelcomposieten beschouwd. Inderdaad blijkt dat in een vlas-epoxycomposiet niet vanzelf vezel-matrixhechting optreedt (hoofdstuk 4). Om de hechting tussen vezels en matrix te verbeteren is het nodig om eerst het natuurlijke waslaagje te verwijderen dat de vezels omhult. Hierna reageert het vezeloppervlak gemakkelijk met de hars of met andere hechtverbeteraars waardoor een goede hechting bereikt kan worden. Ook PP en vlas hechten niet vanzelf, maar de toevoeging van maleïnezuur anhydride gemodificeerde PP (MAPP) leidt gemakkelijk tot verbeterde hechting tussen vezels en matrix (hoofdstukken 5, 6 en appendix A). In dit geval is het niet noodzakelijk om eerst het waslaagje te verwijderen. Tijdens het mengen van de vezels in de PP-smelt diffunderen de wassen de matrix in. Het vezeloppervlak wordt hierdoor bereikbaar voor de hechtverbeteraar. Het is daarom niet nodig om de vezels te modificeren voordat ze met de matrix worden gemengd of geïmpregneerd. De afschuifsterkte van het grensvlak tussen vezels en matrix benadert vaak de afschuifsterkte van de matrix (appendix A), wat aangeeft dat de hechting tussen vezels en matrix maximaal is en niet de factor is die de mechanische eigenschappen van vlasvezelcomposieten begrenst. Het blijkt dat in een aantal gevallen het intern falen van de celwand, veroorzaakt door zijn composiet-achtige structuur, de factor is die de trek- en compressiesterkte alsook de slagvastheid van de composietmaterialen laag houdt (hoofdstukken 4, 5 en 6).

Uit de mechanische eigenschappen van de materialen volgt dat zij vooral geschikt zijn voor toepassingen waar stijfheid vereist is. Ook de milieu-impact van voorwerpen uit vlasvezelcomposieten is het laagst, wanneer de materialen worden gebruikt in toepassingen waarbij vooral buigstijfheid bij een laag gewicht vereist is (hoofdstuk 7). Voor toepassingen waarbij een hoge treksterkte gevraagd wordt, moet een onderdeel uit vlasvezelcomposiet (door de lagere treksterkte van vlas) dikker worden

geconstrueerd dan eenzelfde onderdeel uit glasvezelcomposiet. Een dikker onderdeel leidt tot meer gebruik van materiaal en daardoor onvermijdelijk tot een hogere milieubelasting, vooral wanneer het matrixmateriaal zelf een hoge milieubelasting heeft, wat het geval is bij veel thermohardende harsen. Echter, door de hogere specifieke stijfheid, de "stijfheid per kilo", is het mogelijk om lichtere onderdelen te maken uit vlascomposiet dan uit glascomposiet wanneer de buigstijfheid belangrijk is. Voor toepassingen in de transportsector leidt dit tot een extra milieuwinst, aangezien de lichtere constructie leidt tot brandstofbesparing.

Concluderend blijkt vlas geen panacee te zijn, zoals men begin jaren negentig hoopte. Niettemin heeft het gebruik van vlasvezels voor bepaalde toepassingen voordelen boven het gebruik van glasvezels. Deze toepassingen liggen vooral in onderdelen waarbij optimale stijfheid bij minimaal gewicht gevraagd wordt. Zinvolle applicaties liggen daarom vooral in de transportsector. Aangezien de voordelen van vlasvezels vaak in een secundair effect liggen, waarvan niet zozeer de producent maar de gebruiker profiteert, is het zinvol om de toepassing van vlasvezelcomposieten te stimuleren met behulp van subsidie of wetgeving.
Vlasvezelcomposieten hebben eigenschappen die vergelijkbaar zijn met composieten, gemaakt met andere natuurvezels, zoals hennep en jute. Vlas heeft echter als voordeel dat de linnenindustrie zorgt voor een stabiele productieketen. Een beperkende factor voor het gebruik van vlas is, dat de prijzen van vlasvezels, ook van de korte vezels die geschikt zijn voor toepassing in composieten, sterk afhankelijk zijn van de mode-industrie. De recente geschiedenis laat zien dat in jaren waarin de vlasprijs relatief hoog is, vlasvezels voor de versterking van composieten worden vervangen door andere natuurlijke vezels zoals hennep en jute. In de nabije toekomst moet de ontwikkeling op het gebied van vlasversterking derhalve worden gericht op het beter uitnutten van de specifieke voordelen van vlas in vergelijking met andere natuurvezels, namelijk zijn fijnheid en de relatief hoge sterkte van de elementaire vezels.

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*Harriëtte*

# Curriculum vitae

Harriëtte Louise Bos werd geboren op 7 januari 1964 te Groningen. In 1982 behaalde zij het gymnasium β diploma aan het Praedinius Gymnasium aldaar. In datzelfde jaar begon zij met de studie Scheikunde aan de Rijksuniversiteit Groningen. In 1987 studeerde zij af binnen de vakgroep Fysische Chemie met als specialisatie laser spectroscopie. Direct daarna kwam zij in dienst van DSM Research te Geleen, waar zij een anderhalf jaar durende tweede fase opleiding voor polymeertechnoloog heeft gevolgd. In het kader van deze opleiding volgde zij cursussen aan de Universiteit Twente en de Technische Universiteit Eindhoven en deed zij een jaar lang onderzoek naar modelvorming van het extrusieproces. In 1989 begon zij als researchmedewerker in de groep Deformatie en Breuk binnen de sector Ontwikkeling Kunststoffen bij DSM Research, waar zij fundamenteel en toegepast onderzoek heeft verricht naar de mechanische eigenschappen van verscheidene polymere materialen. In 1994 trad zij in dienst bij het Instituut voor Agrotechnologisch Onderzoek, ATO-DLO, te Wageningen (thans Agrotechnology and Food Innovations, onderdeel van Wageningen UR). Hier heeft zij onder andere een aantal jaren een groep geleid die zich richtte op de ontwikkeling van agrovezel gevulde kunststoffen. Op dit moment is zij binnen Wageningen UR verantwoordelijk voor het onderzoeksprogramma Groene Grondstoffen en werkt zij één dag per week voor Wageningen UR bij het ministerie van LNV in den Haag.