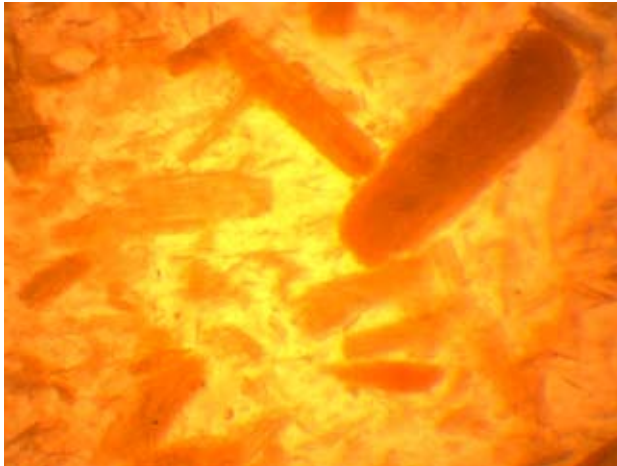


# Natural Fiber Composites

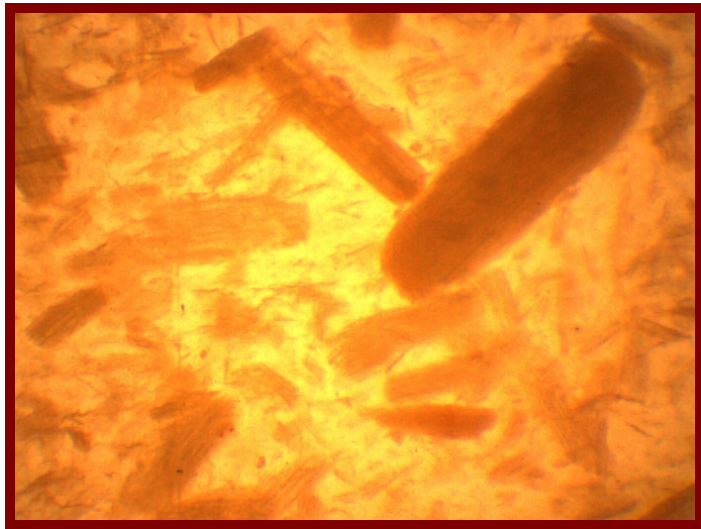
*Optimization of Microstructure and Processing Parameters*



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# Natural Fiber Composites: Optimization of Microstructure and Processing Parameters



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*“The world is not ours; we borrow it from our children”*



## **PREFACE**

The work presented in this thesis has been carried out at SICOMP and at Luleå University of Technology. It concerns compounded and injection molded natural fiber composites.

I would like to thank my supervisors: Dr. Roberts Joffe and Prof. Janis Varna and my colleagues at SICOMP, especially Runar Långström who performed much of the experimental work. I would also like to acknowledge the EU projects BIOCOMPAC and Fibernätverket and Forskarskola för kvinnor III for funding this research.

Last but not least I want to thank my family for their patience with a wife, a mother and a daughter who never seems to be willing to end her search. I love you all!



## SUMMARY

The focus of this thesis is natural fiber composites (NFC) processed by compounding and injection molding.

In paper one, wood powder polypropylene composites containing fillers with very low length to diameter ratio (average  $<3$ ) are studied using micromechanics for short fiber composites. Maximum achievable strength for this type of composites are calculated. A parametric study on strength dependence of the parameters: i) interfacial shear stress, ii) stress in matrix, iii) fiber strength and iv) fiber aspect ratio is performed. The parametric study gives guidelines on how to improve strength of short fiber composites. The conclusions of this analysis are verified by trials on composites with flax, pulp and glass fibers. However the expected strength increase is shown to be strongly limited by the manufacturing processes, which have large influence on the microstructure of the composites.

In paper two and three, full factorial trial designs are created at two levels for optimization of the compounding and the injection molding processes. Composites with flax fibers are considered for these investigations. The selected parameters in compounding are i) screw speed, ii) mass flow, iii) number of dispersing elements and iv) granule length. The parameters selected in the injection molding are i) cylinder temperature, ii) back pressure, iii) injection speed and iv) screw speed. The effects are evaluated by statistical analysis of the resulting mechanical and microstructural properties. In this study screw speed had the strongest effect in the compounding trials, while cylinder temperature had the strongest effect in the injection molding trials.

A rather simple but useful methodology for prediction of the maximum achievable strength of NFC is demonstrated in this work. Several ways to increase strength of NFC are suggested based on the results of a parametric study. However lot of work still remains before compounding and injection molding is optimized for production of NFC with better preserved fiber length, which will result in improved mechanical performance.





## **LIST OF PAPERS**

This thesis comprises the following papers:

### **Paper A**

Nyström B, Joffe R. and Långström R, Microstructure and Strength of Injection Molded Natural Fiber Composites, Journal of reinforced plastics and composites, Accepted for publication 2007

### **Paper B**

Nyström B, Joffe R. and Långström R, Processing effect on Flax Fiber Composite properties Part I: Parametric study of Compounding, submitted for publication to Composites Part A 2007

### **Paper C**

Nyström B, Joffe R. and Långström R, Processing effect on Flax Fiber Composite properties Part II: Parametric study of Injection molding, submitted for publication to Composites Part A 2007

Parts of the papers have been presented at the following conferences:

I Nyström B, Massafiber som armering i kompositer, Ekmandagarna, Stockholm, Februari 2005, Invited speaker

II Nyström B, Tailored products using natural fibers, 1st Nordic Workshop on Future Trends in Wood and Bio-composites Products, (Dept. of Engineering Design and Materials & Pulp and Fiber Research Institute), Trondheim, Norway, 10th of December 2004

III Nyström B, Joffe R, Långström R, Natural Fiber Composites: Optimization of Microstructure and Processing Parameters, Fourth Conference on Research in the European School of Materials Science and Engineering, June 7-8, 2007, ETSEIB (UPC), Barcelona, Spain



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## 1. INTRODUCTION

In the UN millennium development goals from 2000, we have agreed to work for eradication of extreme poverty and hunger and to ensure environmental sustainability [1]. These two goals are not easily met simultaneously. The fast economical growth in some developing countries that we have seen lately will hopefully continue and spread. But there are some quite alarming obstacles for this positive development to persist: i) the demand for all kinds of products increases when economical welfare is increased but the world's resources remain limited, ii) world population is growing rapidly thus demand will continue to raise in all kinds of sectors and iii) this is all happening in a time when we experience climate changes which most likely are triggered by human activities, mainly the use of fossil resources, which will escalate due to the increased consumption, if we don't act. Mankind has a large challenge to deal with. Parts of the solution are a major redirection of our consumption habits in the Western world and an alteration from using fossil to renewable resources for energy production as well as in our products.

The work presented here is not an attempt to solve these problems but this effort is to my understanding in accordance with the environmental sustainability goal. It is also in accordance with one of my most important life mottos *"the world is not ours; we borrow it from our children"*.

This thesis concerns natural fiber composites, NFC a group of composite materials where at least the reinforcing fibers originate from renewable and CO<sub>2</sub> neutral resources either wood or plants. NFC can be produced with many of the manufacturing methods that are traditionally used for conventional composites and thermoplastics such as resin transfer molding, vacuum infusion, compression molding, direct extrusion and compounding and injection molding. Different manufacturing techniques as well as different constituents result in composite materials with diverse properties. Thus the properties of NFC can be tailored for various types of applications by a proper selection of fibers, matrix, additives and manufacturing method.

Injection molded thermoplastics with and without fillers have been developed and used for many decades [2-12]. The application areas range from small door knobs and gaskets to furniture and high performance car parts. Natural fiber compounds offer numerous advantages over other injection molding compounds, for instance, low wear of manufacturing tools, often reduced cycle time and ease of recycling. One large advantage compared to thermoplastics filled with mineral fillers is that energy can be recovered by incineration with hardly any ash residue [13].

The biggest disadvantages of NFC concern their outdoor durability, effects of humidity, temperature, UV etc. Different routes to improve these properties are proposed and implemented continuously [14-15]. The problems can be handled but may affect the cost of the NFC compounds negatively. Still there are many applications which are not subjected to high moisture levels, UV or temperature changes i.e. indoor applications, where less expensive formulations of NFC can be used and reduce material costs compared to most thermoplastic compounds.

However the major driving force behind a switch from fossil based to renewable reinforcement and/or fillers would most likely be sustainability. The total consumption of thermoplastics in Western Europe alone was approximately 38 million tons in 2003 [16]. Even if only some percentages of the thermoplastics can be replaced by renewable fibers it would be a significant reduction of the use of fossil resources.

Conventional high performance composites contain long, mostly continuous filaments such as glass or carbon fibers. Although there have been attempts to develop natural fiber fabrics for technical applications [17], the main part of the NFC out on the market contain short fibers. In some types of synthetic short fiber composites (SMC, BMC, GMT) the fiber length remains the same throughout the processing stages. But for some processes, like compounding and injection molding, the fiber length is process-dependent i.e. the initial fiber length will not be preserved in the final product. Since fiber length is one of the most important parameters in terms of mechanical performance of short fiber composites [18], degradation of fiber length during processing has been extensively studied [2, 20-21].

Although extensive research has been done on injection molded NFC, this is still one area where the natural fibers have not made a market breakthrough. The focus of this work is on the compounding and injection molding techniques. I believe that the reason for the limited use of natural fiber compound in injection molded products is partly due to uncertainties about the influence of constituents on properties and lack of defined framework for product design and manufacturing in order to optimize the material and assure consistent quality. Thus, in order to make natural fiber compounds an attractive alternative for the injection molding industry, limitations on important properties and general guidelines for material optimization and processing should be established. As a result, the application areas where these materials are beneficial (in terms of performance, environment and cost) would be more easily found.

## **2. OBJECTIVES**

The hypothesis for this work was that significant improvements of the mechanical performance of compounded and injection molded NFC should be possible to achieve using micromechanical analysis and tailoring the microstructure accordingly by optimizing the manufacturing processes. The overall goals have been to find limits, regarding the material constituents and the processes, and explore ways to overcome these boundaries.

NFC materials processed by compounding and injection molding have by default limitations regarding mechanical performance (limited fiber length, degradation at high temperatures). On the other hand NFC comprises a large variety of properties since fibers, matrices and additives can be combined in so many ways and be tailored for specific applications if a basic understanding of the micromechanical mechanisms is developed. With these manufacturing methods a tremendous variation of products can be made. There are many products where NFC offers extremely attractive features such as large design freedom, low material cost, short cycle time, low machine wear and easy end of life handling. The market for injection molded products is huge and the environmental benefits of NFC materials over petroleum based thermoplastics are obvious.



Therefore my work has been focused on i) finding limits of the mechanical properties of compounded and injection molded NFC ii) defining rules of thumb for how to improve them [18], iii) optimizing the processes and iv) identify limitations in processing [21-22].

Three Papers are comprised in this thesis. The papers will not be separately discussed here but continuously referred to [18,21,22].

### **3. COMPOSITE MATERIALS**

By definition composites are engineered materials made from two or more constituents with different physical or chemical properties, which remain separate and distinct within the finished structure. The composite should also have properties which surpass the properties of the individual constituents. Composites of various kinds surround us in everyday life, natural and manmade. Examples of natural composites (not manmade) are the human bones and wood. Nature is brilliant in its construction of materials suitable for different purposes. Humans have used the idea of composite materials for ages in various applications such as building blocks from straw and clay, concrete reinforced with steel and polymers reinforced by various kinds of fibers and so on. In this study only polymer matrices with renewable natural fibers are considered.

#### **3.1. Fibers**

Polymer composites can contain fibers of different origin with diverse properties. The fiber selection is normally based on the requirements of the final product. Mineral fibers are often used in applications like electrical insulators and boat hulls. Carbon fibers, which most often are produced from PAN fibers, are used in aerospace applications, sports goods and so forth. Glass-, carbon and other conventional reinforcement materials are available as continuous fibers in roving or fabrics of various types or chopped in mats. The properties of these reinforcements are well defined and documented systematically.

Natural fibers, here defined as fibers from a natural regenerating resource (i.e. a plant or a tree), are not used for load bearing structures to any large extent today. The fibers are usually only a few millimeters up to couple of centimeters long. But these can be spun

to roving and weaved to fabrics which can be used for structural applications. Their properties are comparable to synthetic fibers in some regard, especially if specific properties are considered, see Table 1.

However these fibers have their limitations and drawbacks and it is important to be aware of them in order to use the fibers for the right applications [24,27]:

- The fibers are hydrophilic
- The compatibility between hydrophilic fibers and hydrophobic matrices is low
- The fibers are not resistant to high temperatures ( $>200\text{ }^{\circ}\text{C}$ )
- The fibers are short
- The quality and consistency of properties is affected by factors which are hard to control such as climate during growth and harvesting

The main advantage for these fibers over all other types of fibers is their origin. Plants and trees regenerate and they are  $\text{CO}_2$  neutral.

The fibers that have been studied are wood powder (WP) WPU 2-4 from Scandinavian Woodfiber, chemi-thermomechanical pulp (CTMP) from Stora Enso and spun enzymatically retted flax fiber roving (FF) from Finflax. E-glass fiber (GF) roving P192 from Vetrotrex with Tex number of 2400 has also been used for comparison (Table 1).

*Table 1. Properties of the studied fibers*

Fiber	$\rho$ ( $\text{g}/\text{cm}^3$ )	$d_f$ ( $\mu\text{m}$ )	$l_f$ (mm)	$\sigma_{tu}$ (MPa)	Specific strength ( $\text{MPa cm}^3/\text{g}$ )	$E_r$ (GPa)	Specific stiffness ( $\text{MPa cm}^3/\text{g}$ )
Wood	$\sim 1.5$	38	3	300-1000	200-670	10-80	7-53
Flax	$\sim 1.5$	19	30	500-1500	330-1000	62-69	41-46
E-Glass	2.54	24	$\sim \infty$	3400	1340	73	29

[23-26]

### **3.2. Matrix**

Polymer composites can have either thermoplastic or thermoset matrices. Both matrix types exhibit their own pros and cons.

Thermosets can not be melted once they are cured since they are chemically cross-linked. But these matrices generally have quite good mechanical properties. Creep for example is very low compared to thermoplastics.

The transition temperature,  $T_g$ , for some of the most common thermoplastics is low, giving them quite low stiffness at room temperature and above. The low  $T_g$  also makes them very brittle at low temperatures. The lack of cross-linking is one of the big advantages of thermoplastics since it makes them re-shapeable and re-meltable.

In this study one of the most frequently used thermoplastic matrices is considered, namely polypropylene, PP. Natta and Ziegler shared the Nobel price in 1963 after a patent fight over the discovery of how to synthesize polypropylene. Polypropylene is derived from propylene which is found in coal gas and can be cracked from petroleum. From the environmental point of view it would seem more advisable to use a thermoplastic originating from renewable feedstock. However such thermoplastics like cellulose esters and polylactic acids have until now been very expensive and gained quite low interest from the injection molding industry. Furthermore switching from PP to a thermoplastic from renewable feedstock with similar properties is not expected to introduce a great deal of problems, therefore the results presented here should be applicable to other matrices as well. The polypropylene that has been used is a homopolymeric PP, Adstif 770 ADXP from Montell with a high melt flow index of 45g/10min. Epolene E-43 maleic anhydride modified PP (abbreviated as MAPP or M further in the text) from Eastman Chemicals was used as adhesion promoter.

## **4. PREDICTION OF MECHANICAL PROPERTIES OF NATURAL FIBER COMPOSITES**

The rule of mixture predicts the properties of long fiber composites quite accurately. For a short fiber composite more factors have to be considered in order to get reliable predictions. When the short fiber is a renewable fiber even more obstacles are involved:

- The scatter of fiber properties is usually high and difficult to get control of since circumstances like climate during growth and harvesting plays an important role for the final properties
- The mechanical properties of the fibers as well as the fiber/matrix interface are very difficult to characterize since the fibers are so very short
- The fiber orientation and dispersion can not be studied by common methods (for example, by burning off the matrix)
- The fiber length in the final product is affected by processing. Measurement of fiber length distribution after processing involves extraction and handling of large numbers of fiber
- Measurement of correct values of the aspect ratio (length /diameter,  $l/d_f$ ) involves even more difficulties since the fibers are not always circular and furthermore the cross-section varies along the length of the fiber

Therefore the stress state also becomes more complex. Figure 1 illustrates the stress states in different types of composites.

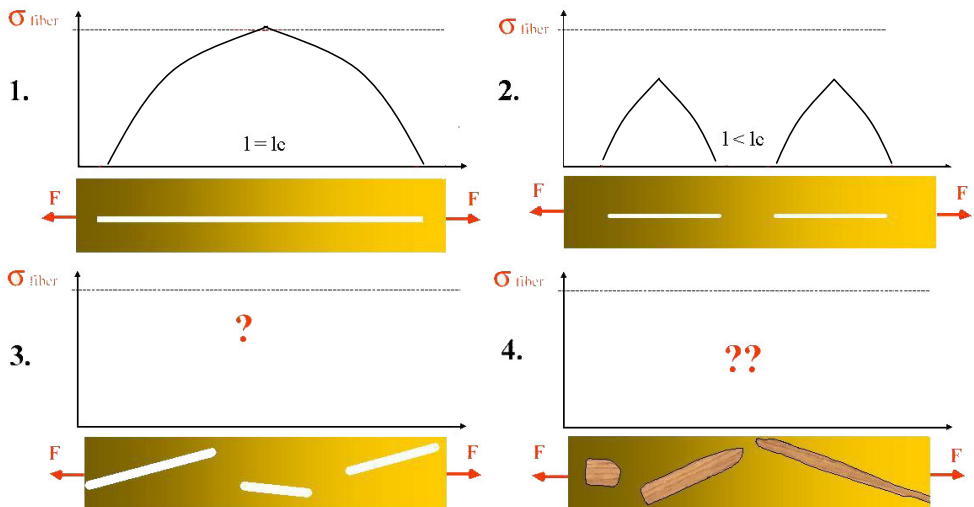


Figure 1. Stress state in long fiber, aligned short fiber, misaligned short fiber and typical short natural fiber composites

Obviously single failure mode will seldom occur in compounded and injection molded NFC. Four different damage modes have been identified during the failure of short fiber composites as described in [28]: yielding of matrix, fiber de-bonding, fiber pull-out and fiber fracture and in these composites all these modes will most likely occur (see Paper A).

It was expected that NFC would behave in a similar way as any other short fiber composite, even if these fibers aren't completely cylindrical and don't have constant diameter along their length. It has been shown earlier that rule of mixture type of models developed for synthetic short fiber composites can be applied to predict the mechanical properties of NFC with acceptable accuracy [29-30].

My work has been focused mainly on strength. The reason for this is that strength is often used as an indirect measure of increased adhesion in injection molded NFC but this is not the only parameter affecting strength of short fiber composites. The theories considered here suggest that microstructure (fiber length to diameter ratio and fiber orientation), fiber strength and matrix strength also limit the composite strength. Therefore it is not meaningful to increase adhesion beyond a certain limit. Thus it is important to find this limit.

Maleic anhydride grafted polypropylene is a frequently used coupling agent for WPC, and its effects are well documented [31-33]. This is the only adhesion promoter that has been used through out this work.

The short fiber composite strength has been calculated from Equ 1. [34-35]:

$$\sigma_{cu} = \sigma_{fu} \cdot V_f \cdot \eta_{ls} \cdot \eta_{ts} + \sigma'_{mu} \cdot (1 - V_f) \quad [\text{Equation 1}]$$

Where  $\eta_{ls}$  is the fiber length efficiency factor defined as:

$$\eta_{ls} = l / 2l_c \quad \text{for } l \leq l_c \quad [\text{Equation 2}]$$

$$\eta_{ls} = 1 - l_c / 2l \quad \text{for } l \geq l_c$$

$\sigma_{cu}$  is the composite strength,  $\sigma_{fu}$  is the fiber strength,  $\sigma'_{mu}$  is the stress in the matrix at the failure strain of the composite,  $V_f$  is the fiber volume fraction and  $l$  is the fiber

length. The factor  $\eta_{OS}$  is the orientation factor which is equal to 1 for perfectly aligned fibers.

The meaning of critical length might need some further explanation: the critical length is not a fiber property, it depends on fiber diameter, fiber strength and interfacial shear strength. The smaller  $l_c$  is the better for short fiber composites, because also very short fibers can carry load if they are longer than  $l_c$ . The critical length can be decreased by improving the interfacial shear strength, by using smaller reinforcement diameter (which can be achieved for example by better dispersion of the fibers or simply by using another thinner fiber) or by decreasing fiber strength. Not all of these actions would give a stronger composite though.

A more detailed presentation of the theoretical framework is given in Paper A.

#### 4.1. Theory versus reality

##### 4.1.1 Initial trials

In Paper A, 20-60 wt% WP/PP composites with and without MAPP were produced. A reinforcing effect was seen for all fiber fractions compared to pure PP when adhesion promoter was used while strength decreased with increasing fiber content without adhesion promoter. The effects from adhesion promoter on stiffness and strain were almost negligible. With and without adhesion promoter stiffness increased and strain decreased with increased fiber content Figure 2.

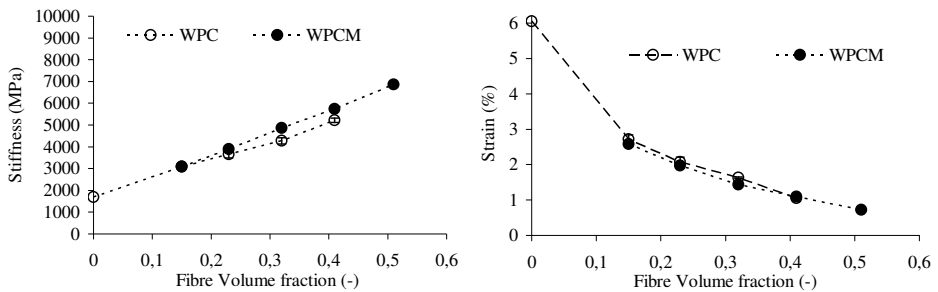


Figure 2. Composite Stiffness and strain vs  $V_f$  of wood powder with and without MAPP

The resulting strength was analyzed using the presented models (Equ 1-3 Paper A). The influence of the parameters: i) interfacial shear stress, ISS, ii) fiber length to diameter

ratio,  $l/d_f$ , iii) matrix stress and iv) fiber strength were studied. The result is shown in Figure 3a-d.

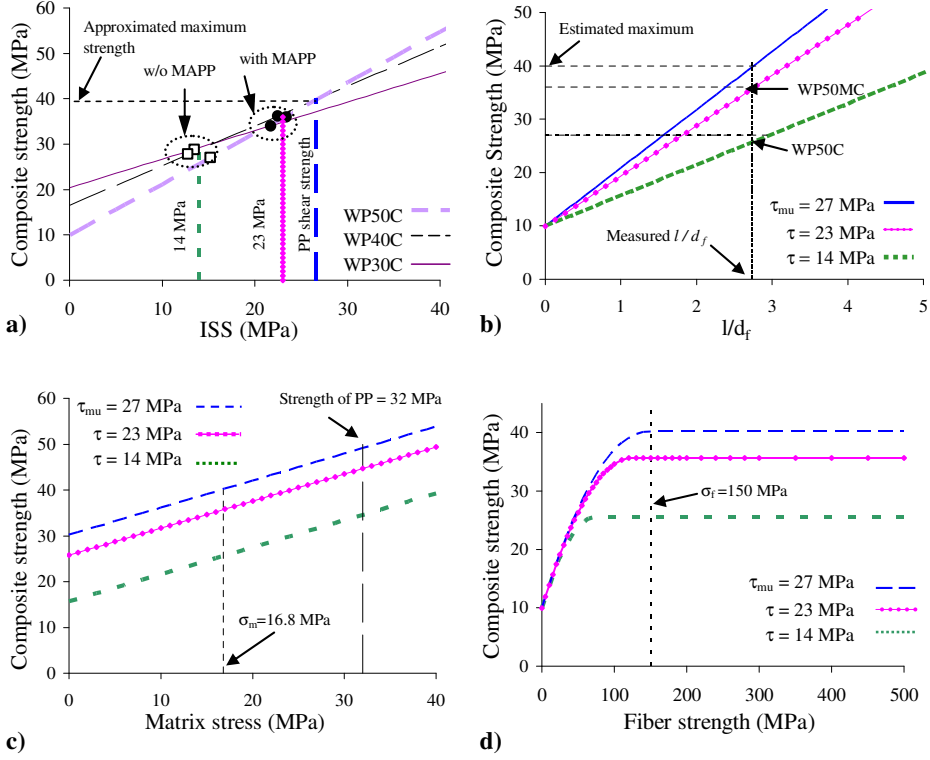


Figure 3. Theoretical parametric study of short fiber composite strength

In Figure 3 a) the calculated composite strength is compared with the experimental values for WP composites with 30-50 wt-% fibers. ISS of WP composites with and without MAPP can be estimated from the curve. Here we can see that the increase in fiber load is not positive for composite strength unless ISS is above a certain level. From this plot also a rough estimation of the maximum achievable strength in WP composites with this particular  $l/d_f$  can be done. If ISS would reach 27 MPa, which is the matrix shear yield stress, the composite would fail due to matrix shear failure, the composite strength being approximately 40 MPa.

In Figure 3 b) the importance of  $l/d_f$  is demonstrated. With a higher  $l/d_f$  much higher composite strength levels should be possible to achieve according to the theory. Even

with the lowest ISS, a reinforcing effect ( $\sigma_{cu} > \sigma_{mu}$ ) would be achieved if  $l/d_f$  was higher than 5.

In Figure 3 c) the effect of matrix stress on composite strength is illustrated. It shows how a misjudgment of the matrix stress at break affects the estimation of maximum composite strength. It also shows that for these composites the strength of the matrix plays a significant role since the fibers are too short for their full strength to be utilized.

The influence of fiber strength on composite strength is shown in Figure 3 d). Here we can see that for these composites with low  $l/d_f$  not more than 150 MPa of the fiber strength is utilized regardless of ISS. This means that even if the fiber is stronger than 150 MPa, the composite strength won't be affected, if all other parameters remain unchanged.

The main conclusions from the study presented in Paper A are:

- The maximum achievable strength of these WP/PP composites with as low  $l/d_f$  as 3 is approximately 40 MPa
- High enough adhesion must exist if higher fiber volume fractions shall be advantageous for the composite strength
- Matrix selection is really important for these composites
- Fiber strength above 150 MPa is difficult to utilize using fibers with  $l/d_f$  smaller than 3
- Fibers with higher  $l/d_f$  must be used in order to produce significantly stronger NFC

#### 4.1.2. Verifying trials

Additional composites with CTMP-, flax fiber- and glass fiber composites were produced by compounding and injection molding, in order to verify the parametric study. The strengths of these materials are shown in Figure 4. All composites have the same matrix (PP) but fibers with different properties and some contain MAPP to increase adhesion.



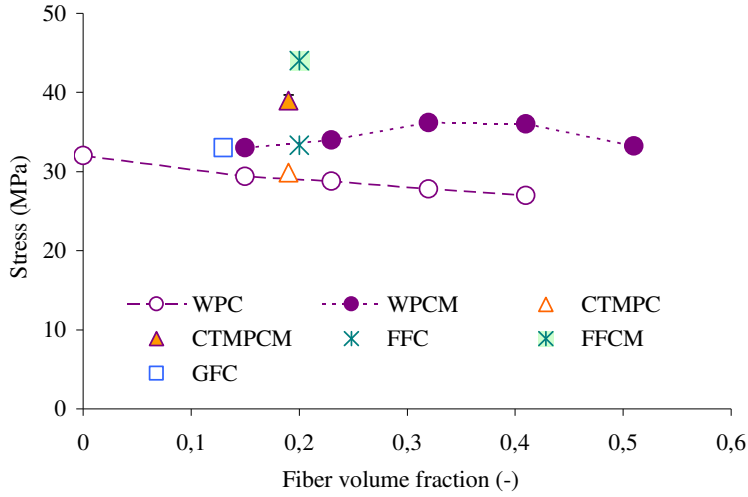


Figure 4. The tensile strength of the short fiber composites studied in Paper A

It can be seen that for the WP composites without MAPP, strength decreases with increased fiber content and the opposite (up to  $V_f \approx 0.4$ ) when MAPP is present.

When there is no MAPP added none of the fibers reinforce PP more than marginally, not even glass fiber which is by far the strongest fiber. This can be related to the critical fiber length which increases by decreased adhesion. Here all fibers are below critical length when no MAPP is used.

Flax and CTMP both give a significant reinforcing effect when MAPP is added, much better than for WP with MAPP and at quite low fiber volume fractions.

The differences in properties can all be related to the theoretical parametric study i.e. the relative differences agree quite well with the theories but the expected strength increase is higher than what has actually been achieved using pulp and flax fibers and MAPP. The explanation is to be found in the processing.

The fiber  $l/d_f$  is many times higher in both the pulp- and flax composites than in the wood powder composites. However the fiber lengths of pulp and flax fibers are severely degraded, first by the compounding and then again further decreased by the injection molding. In the final material the wood powder still has much lower  $l/d_f$  but the

difference is reduced considerably. Pulp had a final  $l/d_f$  of 12, flax 14 while the WP  $l/d_f$  was only 3 in the injection molded material, see Figure 5.

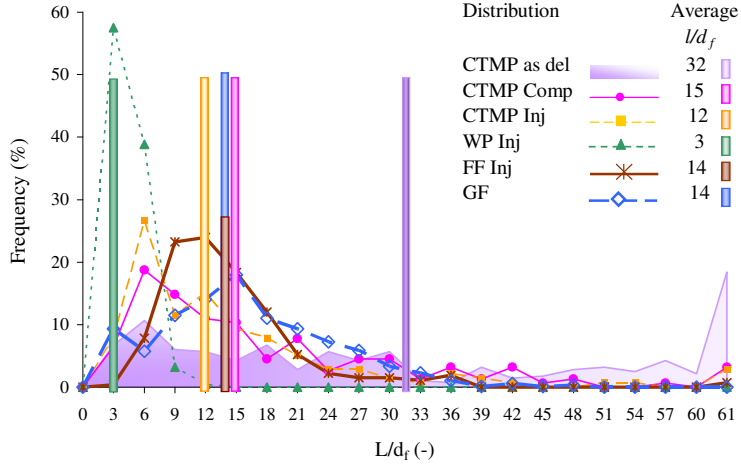


Figure 5. Average and distribution of  $l/d_f$  of different fibers at different stages of the process, CTMP as delivered, CTMP extracted from compound and CTMP, WP, flax fibers and finally glass fibers extracted from injection molded pieces

Figure 5 shows that, at least for the CTMP fibers, the compounding step is responsible for most of the fiber breakage. Fiber distribution measurements performed after the compounding trials (Paper B and C) showed a somewhat different picture for the flax fibers. For these composites both processes seem to decrease the fiber length equally.

It was also found that the fibers were less oriented using the longer fibers (FF and CTMP), which also influence the mechanical properties in the tensile direction negatively. This would result in a reduction of anisotropy of the mechanical properties of the composites but this has not been examined.

In Figure 6 the measured average  $l/d_f$  of flax fibers, CTMP and WP in the composites are used to estimate the fiber orientation and to compare it with the results from image analysis of composite specimens (Paper A).

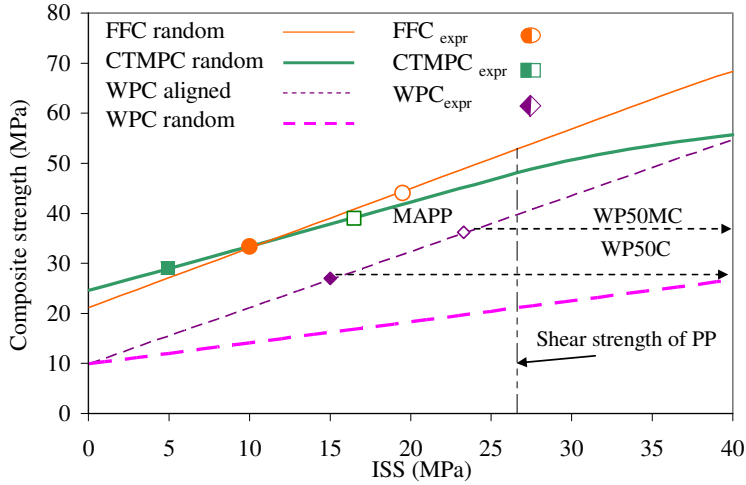


Figure 6. Tensile strength of FF30C, CTMP25C and WP20C as a function of ISS using orientation factor 3/8 for randomly distributed fibers and for WP50C also orientation factor 1 (from the parametric study)

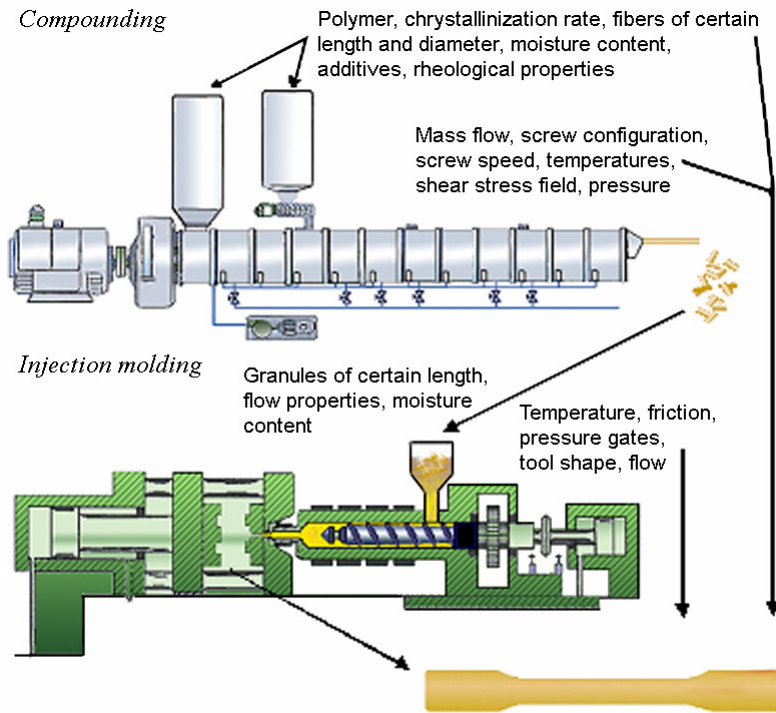
Here we can see that random orientation factor of 3/8 gives reasonable values on ISS for the CTMP and flax composites. For the WP composites random orientation gives an ISS value much higher than the shear strength of the matrix which is not realistic. This supports the findings from the image analysis that the longer fibers are less oriented than the short.

The fiber degradation during processing is severe. It is possible that there are ways to make the fibers more resistant to the shear forces in the machinery used for processing but a first logical step when trying to improve the properties further is to optimize the processes.

## 5. PROCESSING

As mentioned earlier it is generally more complicated to characterize a short fiber composite than a long fiber composite and processing is to a great extent responsible for the difficulties. In some short fiber composite processes fiber length is well preserved. However fiber orientation distribution needs to be characterized in order to be able to predict the mechanical properties of the product (SMC, BMC and GMT). For the short

fiber composites that have been studied here, it is even more difficult since the final microstructure is affected by the processes in numerous ways and many steps are involved. The mechanical properties are not only defined by fiber length and orientation. Voids, residual stresses, degradation of the matrix, degree of crystallization are some of the matrix/processing related features, which also influence the final composite properties. In Figure 7 the used processing method is described.



*Figure 7. The processing of compounded and injection molded short fiber composites, with some of the parameters affecting the final material properties described*

The materials in this study are produced by two main steps: polymer, additives and fibers are first compounded to a homogenous compound in an extruder and cut into granules which are injection molded into the final shape.

As can be seen from Figure 7 there are many parameters that affect the final material properties. Some of these parameters can be easily controlled. The selection of material

constituents obviously affects the composite properties but the processing will affect some of the constituents. For example the fiber length will decrease to some extent, due to the high shear stresses and the high pressure in all the narrow paths in these types of equipment.

The moisture content of the fibers is reduced in this process by drying in oven at 103°C for 4 hours. Normally the moisture content is around 1-3%. Dry air could be used to decrease the moisture content further but the benefit of it is questionable since the fibers have to be subjected to the humidity in the room during processing and since the extruder is equipped with exhaust outlets.

The rheological properties of the matrix will affect the fiber breakage since a more viscous polymer will lead to higher friction. Thus it is possible that some of the differences between composites with and without MAPP (see Figure 4) are due to the reduced viscosity of the polymer. It was found that the CTMP composites containing MAPP had a lower level of agglomerated fibers showing that MAPP works as a lubricant increasing the dispersion of these fibers.

## **5.1 Compounding**

There are many types of equipments available for compounding. There are plain mixers like Brabender and many types of extruders. Extruders can be equipped with a single screw or twin screws. In the case of twin screws they can co-rotate or counter rotate. The screws can be shaped just for transportation like an Archimedes screw, it can be conical to build up pressure or they can be of even thickness equipped with kneading and dispersing elements to improve blending. The length to diameter ratio of the screw as well as the free space for the material differs between screws also giving different residence time.

For these trials a co-rotating twin screw extruder from Krupp Werner&Pfleiderer ZSK 25 WLE with l/d of 44. The screws are parallel and equipped with kneading, dispersing and transporting elements. The machine is developed to give good dispersion at quite low pressure. The fibers are fed into the molten polymer which should be more

advantageous from a fiber degradation point of view. When the extrudate leaves the die it is cooled in a water-bath and cut into granules.

## **5.2. Injection molding**

The injection molding machine is defined and characterized by its clamp size and its injection capacity. Clamp force ranges from a couple of tons to several thousands of tons. The most frequently used machines lie around 300 tons [36]. Injection capacity ranges from a few grams to hundreds of kilograms.

Most of the heat that is used for melting granules evolves from friction between granules, and between the barrel and the screw. The size of the screw often gradually increases.

Two injection molding machines have been used in this work, both from Engel. Engel ES75 CC80 machine with maximum clamp force of 75 tons and shot size of 125cm<sup>3</sup>, 115g (polystyrene at 1000 bars) was used in Papers A and B. Polymertekniskt center in Färgelanda, Sweden was hired to perform the injection molding for Paper C, these were done in an Engel ES 200/50 machine with a clamp force of 50 tons and a shot size of 88g (PS).

## **6. SUMMARY OF THE PROCESSING TRIALS**

The processing is responsible for the final microstructure of these NFC. It was shown in Paper A that the strength of these composites can not be increased very much unless the microstructure is more favorable i.e. fiber length has to be better preserved. Therefore parametric studies for both processes involved in the manufacturing of these NFC were performed in order to improve the mechanical performance by achieving a lower degree of fiber length reduction.

When a manufacturing method involves two different processes each with many variables, trying to optimize this processing route by one-factor-at-the-time trials is not a very practical solution. Factorial designed trials are a more effective way of dealing with it [37]. The full factorial design was created at 2 levels. The design comprises all the possible combinations of the factor levels. For  $p$  factors at 2 levels  $N = 2^p$  runs are needed. Thus  $2 \times 2^4$  runs were needed in the present study since 4 factors were selected in

each process. Full factorial designs are orthogonal (balanced) designs. This means that the estimated effect of a factor is independent of the effects of all other factors. The factorial trials were evaluated using the statistical analysis software MODDE from Umetrics. The software calculates a model for each output response by projection to latent structures, PLS. PLS has been extensively described in the literature [38] and also both Paper B and C contain more detailed descriptions.

In total 35 flax fiber/PP composite materials were produced with different processing setups. Paper B handles the first 18 trials with different compounding setup. In Paper C the 17 remaining trials where the injection molding setup was studied, are reported.

### **6.1. Compounding trials**

NFC containing 30 weight percentages of flax, PP as matrix and MAPP as adhesion promoter were studied in the compounding trials. Screw speed, number of dispersing elements, mass flow and granule length were selected as input factors. Strength, stiffness, strain, un-notched charpy impact strength, average and maximum fiber length were selected as responses.

The mechanical properties of these flax fiber composites, produced with different compounding process setup vary as follows: strength 43 - 47 MPa, stiffness 5.3 - 6.3 GPa, strain 2.3 - 3 % and impact strength 11-14 kJ/m<sup>2</sup>. These variations are larger than the standard deviations within each material group (test specimens produced with the same setup) but the differences are still rather small. The effect of processing parameters is very low compared to the influence of adhesion: removing MAPP results in a composite with much lower strength (33MPa very close to the strength of pure PP) than any of the composites in the parameter study.

The importance of the compounding setup variations depends on what kind of product requirements the materials will have to meet.

The best setup from a microstructural point of view might not be the best from an economical point of view, especially if the gain in mechanical performance is quite low.

The study indicates that the processing parameters in the compounding step have influence on fiber length distribution. The differences in fiber length distributions do

reflect on the final microstructure and the mechanical properties of the composites but not to as great extent as expected from a theoretical point of view. A brief investigation indicated that the longer the fibers were in the granules, the larger the length reduction during injection molding. Injection molding seemed to level out the differences introduced by compounding. Therefore the logical continuation of this work was to perform a parametric study for the injection molding process.

## **6.2. Injection molding trials**

The compound with the best mechanical properties from the compounding trials was produced for the injection molding trials. Cylinder temperature, screw speed, injection speed and backpressure were varied in the injection molding process. Strength, stiffness and strain were output responses. In addition fiber length distributions and fiber orientations were studied and DSC scans were done for selected materials.

The mechanical properties of the composites, produced with different injection molding process setup but the same fiber loading and constituents (30%flax fibers and 70% PP of which 2% is MAPP), vary as follows: strength. 45-51 MPa, stiffness 6.0 – 7.4 GPa, strain 2.5 - 3 %. As in the compounding trials the variations are larger than the standard deviation within each material group (test specimens produced with the same setup) but still not dramatic. Furthermore the fit of the models was low both for stiffness and strain but for strength the predictive power of the PLS model was rather high.

The studied injection molding process parameters affect the microstructure of the composites marginally. The only clearly significant effect was that high cylinder temperature which has negative effect on strength if injection speed is low. The reason for the differences in mechanical properties are more likely a result of different crystal formations in the materials produced with high and low temperatures or a result of thermal degradation of the fibers at the higher temperature and not differences in microstructure (Paper C).

It is a positive result that the material quality is very even for most of the processing setups that were tested. However, it also indicates that more drastic actions such as optimization of runners, inlets and screw shape have to be done in order to reduce fiber cutting in the injection molding process.



## **7. FINAL REMARKS**

The fiber length to diameter ratio plays an important role for the strength of short fiber composites.

The micromechanical analysis indicates that the full potential of compounded and injection molded natural fiber composites is not reached in conventional injection molding equipment.

It is most likely that a lower degree of fiber length reduction can be achieved with more drastic measures in the processing setups or with some modification of the fibers (this has not been the scope of this study).

Much work remains before compounding and injection molding is optimized for production of NFC with better preserved fiber length which will give higher strengths. However this work shows that the material quality is rather consistent even if the processing parameters are changed within the range that has been tested. This can be regarded both as negative and positive results depending on the application.

This work shows that compounded and injection molded NFC materials with this (or similar) matrix can be used for applications with strength demands ranging from 30 MPa to almost 50 MPa simply by proper selection of fibers and adhesion promoter.

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## *Paper A*



# Microstructure and Strength of Injection Molded Natural Fiber Composites

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## Abstract

Injection molded short Natural Fiber Composites (NFC) are studied in this article. Micromechanical models are employed to investigate effects of fiber length distribution, fiber orientation, and fiber/matrix adhesion on mechanical performance of NFCs.

A parametric study showed that length/diameter ratio strongly affects the composite strength, whereas fiber strength has very little influence on strength of the composites when fiber/matrix adhesion is poor. In order to verify conclusions based on theoretical predictions, modeling results are compared with experimental results of wood powder-, flax-, pulp- and glass fiber composites.

Recommendations on improvement of strength of NFC through change of the internal structure of the materials are formulated based on results of this investigation.

**Key words:** *microstructure, composite, wood, flax, pulp, strength, injection molded, recommendation, improvement*





## INTRODUCTION

The use of natural fibers as reinforcement in composites has considerably increased during the last decades. Even though there is very large variety of fibers, matrices and manufacturing techniques used to produce natural fiber composites (NFC) these materials are often separated into their own material class. However, the variety of constituents and processing methods result in completely different materials with very diverse properties. Therefore, NFC are suitable for an extremely wide area of applications.

NFC can be produced with many of the manufacturing methods that are traditionally used for conventional composites and thermoplastics. Compression molding and direct extrusion are the most common of the processes. In USA alone approximately 300 000 tons of wood fiber composites are direct extruded annually [1]. In Germany the automotive industry uses almost 50 000 tons of NFC and 99% is produced by compression molding [2]. A number of studies concerning research and development of NFC have shown that these materials also can be produced with infusion techniques [3-5] and by injection molding [6-10].

The focus of this article is on the compounding and injection molding techniques. Although extensive research has been done on injection molded NFC, this is one area where the natural fibers still have not made a market breakthrough. For example, only 1% of the 50 000 t/a of NFC material is produced by injection molding within the automotive industry in Germany [2].

Injection molded thermoplastics with and without fillers have been developed and used for many decades [11-19]. The application areas range from small door knobs and gaskets to furniture and high performance car parts. Natural fiber compounds offer numerous advantages over other injection molding compounds, for instance, low wear of manufacturing tools, often reduced cycle time and ease of recycling. One large advantage compared to thermoplastics filled with mineral fillers is that energy can be recovered by incineration with hardly any ash residue [20]. The biggest disadvantages are connected to outdoor durability. Different routes to improve these properties are

tested continuously [21,22]. The problems can be handled but may affect the cost of the NFC compounds negatively. Still there are many applications which are not subjected to high moisture levels, UV or temperature changes i.e. indoor applications, where less expensive formulations of NFC can be used and reduce material costs compared to most thermoplastic compounds. The major driving force for governmental funding of research in the NFC area is the striving for environmental sustainable development world wide. The advantages offered by these materials in this regard are highly appealing. The total consumption of thermoplastics in Western Europe was approximately 38 million tons in 2003 [23] and in the USA the injection molding industry is growing and is expected to produce 7.5 million tons by 2008 [24]. Even if only small percentages of the thermoplastics can be replaced by renewable fibers it would make a significant positive environmental impact, since the natural fibers are CO<sub>2</sub> neutral materials opposed to the majority of the thermoplastics.

We believe that the reason for the limited use of natural fiber compound in injection molded products is partly due to uncertainties about the influence of constituents on properties and lack of defined framework for product design and manufacturing in order to optimize the material and assure consistent quality. Although deep knowledge about these materials have been accumulated among producers and researchers in this area, guidelines or simple rules of thumb for NFC development and processing are quite hard to find in the literature. Thus, in order to make natural fiber compounds an attractive alternative for the injection molding industry, limitations on important properties and general guidelines for material optimization and processing should be established. As a result, the application areas where these materials are beneficial (in terms of performance, environment and cost) would be more easily found.

The objectives of this paper is i) to verify existing models for prediction of mechanical properties of short fiber composites on injection molded NFC, ii) to carry out a parametric study in order to formulate recommendations on improvement of performance of NFC through tailoring of the internal structure of the materials and iii) to find limits on the studied mechanical properties for NFC.

## THEORY

There are numbers of factors to consider when dealing with analysis and prediction of mechanical properties of injection molded NFC:

The fiber orientation and dispersion can not be studied by common methods (for example, such as burning off the matrix). The fiber length in the final product is affected by processing. Measurement of fiber length distribution after processing involves extraction and handling of large numbers of fiber. Measurement of correct values of the aspect ratio (length /diameter,  $l/d_f$ ) involves even more difficulties since the fibers are not always circular and furthermore the cross-section varies along the length of the fiber. The mechanical properties of the fibers as well as the fiber/matrix interface are very difficult to characterize since the fibers are very short.

### **Strength of short fiber composites**

One of the ways to increase strength of NFC is to improve adhesion between the hydrophilic natural fibers and the hydrophobic thermoplastic matrix, this subject has been the focus in many studies. Oksman studied the effect of several additives on mechanical properties of WPC and on adhesion between wood particles and thermoplastics in WPC starting in 1995 [6]. In a review from 2001 on interface modifications for NFC George et al summarize different physical and chemical methods for improved adhesion [25]. In a work performed at Eastman Chemical Company (Specialty Polymers Development and Technical Service) in 2004 new grades of maleic anhydride grafted polyolefins were studied and substantial increase of strength of NFCs was achieved [26].

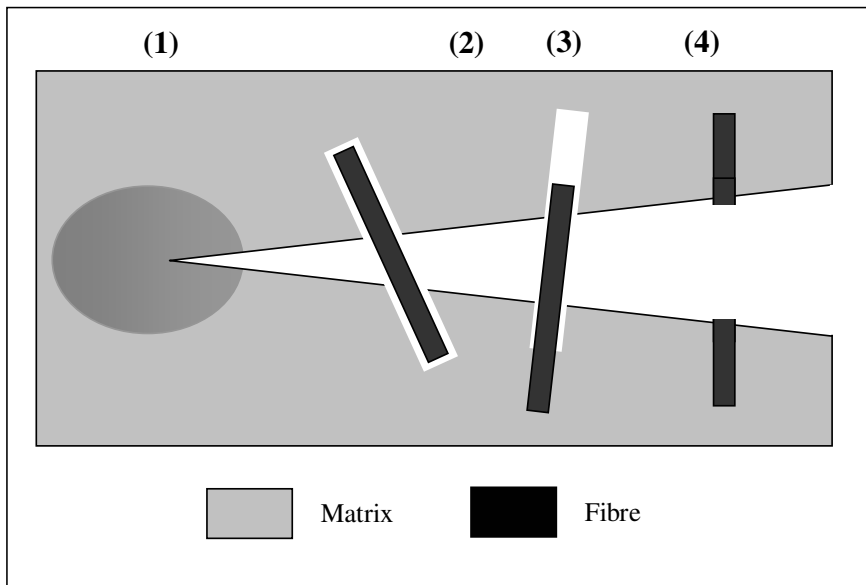
However, not only fiber/matrix interfacial strength is limiting strength of well aligned short fiber composites, the shear yield stress of the matrix is also a key property that may lead to failure of these materials. Therefore, it is not very practical to achieve “perfect” bonding between fiber and matrix if yield stress of the matrix is low.

On the other hand, it is sensible to assume that the local shear stress distribution depends on fiber  $l/d_f$  and on fiber strength. Usually fibers are not well oriented in short fiber composites and therefore, not single failure mode will occur in the material but

rather a combination of all possible modes. Four different damage modes can be identified during the failure of short fiber composites as described in [27]: yielding of matrix, fiber debonding, fiber pull-out and fiber fracture (see Figure 1).

It is expected that NFC will behave in the same way as any other short fiber composite. It has also been shown [28] that rule-of mixture type of models developed for synthetic short fiber composites can be applied to predict mechanical properties of NFC with acceptable accuracy. In this work a similar but somewhat simplified approach is used due to lack of some of the input parameters used in the models. This is due to difficulties of measurements of those parameters associated with certain properties of the constituents of NFC (namely reinforcement fibers):

- fiber/matrix interfacial shear strength between wood particles and PP is not easy to measure since these fibers are very short;
- for the same reason as above, direct measurements of fiber strength are also rather complicated;
- fiber orientation measurements are not the simplest task either.



*Figure 1. Damage modes observed in short fiber composites during failure: yielding of matrix (1), fiber debonding (2), fiber debonding and pull-out (3), fiber fracture (4)*

For a short fiber composite with well aligned fibers a critical length,  $l_c$  of the fiber is needed in order to build up the ultimate stress (strength) level  $\sigma_{fu}$  in the fiber. If the fiber is shorter than  $l_c$  then the failure will occur on the fiber/matrix interface rather than in the fiber [ 27].

Kelly and Tyson [29] proposed a linear transfer of stress from the tip of a fiber to the maximum value, when the strain in the fiber is equal to that in the matrix. By assuming constant interfacial shear stresses the fiber critical length,  $l_c$  can be derived by considering the balance of tensile and shear stresses, Eq. 1:

$$\frac{l_c}{d_f} = \frac{\sigma_{fu}}{2 \cdot \tau} \quad [\text{Equation 1}]$$

where  $\tau$  is the shear strength of either the matrix or the interface which ever is smallest,  $d_f$  is the fiber diameter and  $\sigma_{fu}$  is the strength of the fiber.

The critical length is not necessarily equal to the fiber length (most often it isn't). As it is apparent from the Equ. 1  $l_c$  can be decreased by improved interfacial shear strength, by using smaller reinforcement diameter (which can be achieved for example by better dispersion of fibers) or by decreasing fiber strength. Not all of these actions would give a stronger composite though. Assuming constant interfacial shear strength the short fiber composite strength can be calculated from Equ. 2 [29-31]:

$$\sigma_{cu} = \sigma_{fu} \cdot V_f \cdot \eta_{os} \cdot \eta_{ls} + \sigma'_{mu} \cdot (1 - V_f) \quad [\text{Equation 2}]$$

Where  $\eta_{ls}$  is the fiber length efficiency factor defined as Equ. 3:

$$\begin{aligned} \eta_{ls} &= l / 2l_c & \text{for } l \leq l_c \\ \eta_{ls} &= 1 - l_c / 2l & \text{for } l \geq l_c \end{aligned} \quad [\text{Equation 3}]$$

$\sigma_{cu}$  is the composite strength,  $\sigma'_{mu}$  is the stress in the matrix at the failure strain of the composite,  $V_f$  is the fiber volume fraction and  $l$  is the fiber length. The factor  $\eta_{os}$  is the orientation factor which is equal to 1 for perfectly aligned fibers.

Table 1. Fiber properties

Fiber	$d_f$ ( $\mu\text{m}$ )	$\sigma_{fu}$ (MPa)	$E_f$ (GPa)
Wood	38 [32]	300-1000 [8],	10-80 [8]
Flax fiber	19 [33,34]	500-1500 [35,36]	62-69 [35,37]
Glass fiber	24 [38]	3400 [38]	73 [38]

## EXPERIMENTAL

### Materials

A homopolymeric polypropylene (PP), Adstif 770 ADXP from Montell with a high melt flow index of 45g/10min was used as matrix. Epolene E-43 maleic anhydride modified PP (abbreviated as MAPP or M further in the text) from Eastman Chemicals was used as adhesion promoter. Wood powder (WP) WPU 2-4 from Scandinavian Woodfiber, chemi-thermomechanical pulp (CTMP) from Stora Enso and spun enzymatically retted flax fiber (FF) roving from Finflax were used as reinforcement. E-glass fiber (GF) roving P192 from Vetrotrex with tex number of 2400 was also used for comparison, see fiber properties in Table 1. Since all composites have the same matrix, from here on materials are abbreviated as follows: fiber/fiber weight fraction/coupling agent/composites for example WP50MC (wood powder composite with 50 weight percentage fibers and maleic anhydride added to polypropylene).

### Processing

Prior to compounding all natural fibers were dried in an oven at 105 °C for at least 4 hours. The constituents were compounded in a Krupp Werner & Pfleiderer ZSK 25 WLE co-rotating twin screw extruder with l:d of 44. Two individually controlled gravimetric K-tron feeders from Christian Berner were used for fiber weight fraction control in the case of WPC and CTMPC compounding. In the case of GFC and FFC compounding the fiber weight fraction was controlled by the speed and ascent/revolution on the side screw. The compound was pulled through a water bath and cut to 4 mm long and approximately 5 mm in diameter granules using an SF Sheer granulator. The granules were oven dried at 105 °C for at least 4 hours prior to injection

molding. Test specimens were injection molded in an Engel ES 75 CC 80 injection-molding unit. The injection molded specimens were dog bone shaped and had a total length of 218 mm with a centre cross section area of  $12 \times 4 \text{ mm}^2$ .

### **Characterization of microstructure by image analysis**

#### Fiber orientation and dispersion

The following procedures were employed to characterize orientation and dispersion of fibers:

- 1) In order to study presence of agglomerates of fibers in the composites, 5g pieces were cut out of injection molded specimens after mechanical tests and pressed into thinner samples. Pressing was carried out in a cold press as follows: The composite material was placed between steel plates in an oven and heated at  $200^\circ\text{C}$  for 15 minutes. Immediately after removal from the oven they were pressed to  $300 \mu\text{m}$  thick sheets. Thin specimens of WPC, CTMPC and CTMPMC were studied using stereo microscope.
- 2) Composite surfaces of injection molded WPC and FFC specimens of size  $12 \times 20 \text{ mm}^2$  were embedded in a polyester resin and polished. Images obtained from Olympus BH-2 microscope were analyzed using the software Analysis distributed by SIS (Soft Imaging Systems).
- 3) Pieces were cut from injection molded test specimens and images were taken in the flow and perpendicular to the flow directions using a polarized light microscope Leitz Laborlux 12 Pol S and Leica DC 300 digital camera, at Stora Enso, Imatra. Only CTMPC was studied.
- 4) Composite pieces of  $10 \times 5 \times 5 \text{ mm}^3$  size were cut from the centre of injection molded specimens and 3-D mapping was performed using an X-Ray Microtomograph (Skyscan 1072 100 kV) at Stora Enso, Imatra. In order to obtain good images by this technique it is advantageous to have materials (in this case matrix and fiber) with sufficiently different densities. Since density difference between the cellulose based fibers and the PP matrix is rather small, GFC produced under the same



conditions as corresponding NFC were used instead to produce high quality 3-D images.

#### Fiber length measurements

Fiber length measurements were done using an optical microscope Olympus BH-2 and the software Analysis distributed by SIS (Soft imaging systems). Fiber length measurements were performed on CTMP fibers and WP as delivered. CTMP, FF and GF were also extracted from injection molded specimens by Soxhlet extraction using xylene.

#### **Mechanical testing**

Mechanical testing was carried out on an Instron 8501 testing machine. Tensile tests were done according to ISO 527-2 standard. Displacement controlled test with cross head speed of 2 mm /minute and distance between clamps of 124 mm was carried out. At least five specimens of each material composition were tested.

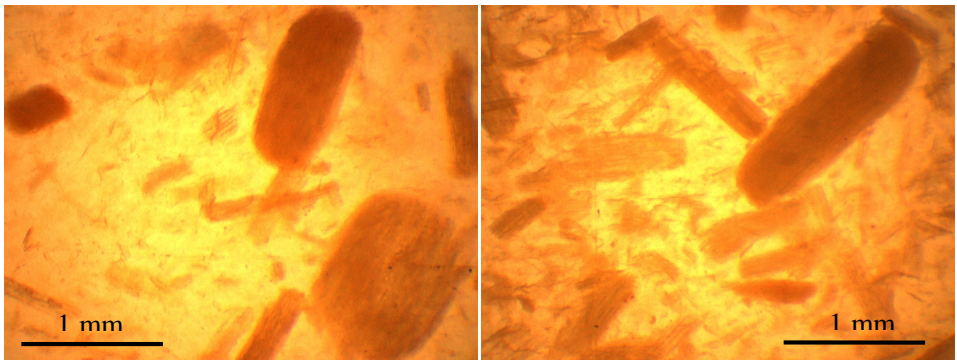
For determination of the shear strength of PP shear punch test was used. The method is a slightly modified version of ASTM D732. A sample of thermoplastic material of width 19 mm and thickness 4 mm was mounted in the sample holder and placed in the testing machine. The upper punch tool was pushed down through the cylindrical centre hole at a speed of 2 mm/min. The force needed to shear the centre cylinder out of the thermoplastic material was plotted together with the displacement of the tool. The shear strength of the material is calculated as the force divided by the surface area (thickness of the specimen multiplied by the circumference of the punch tool). Six samples were tested. The measured shear strength for the PP used in this study is  $26.6 \pm 0.6$  MPa.

## RESULTS

### Results from characterization of microstructure

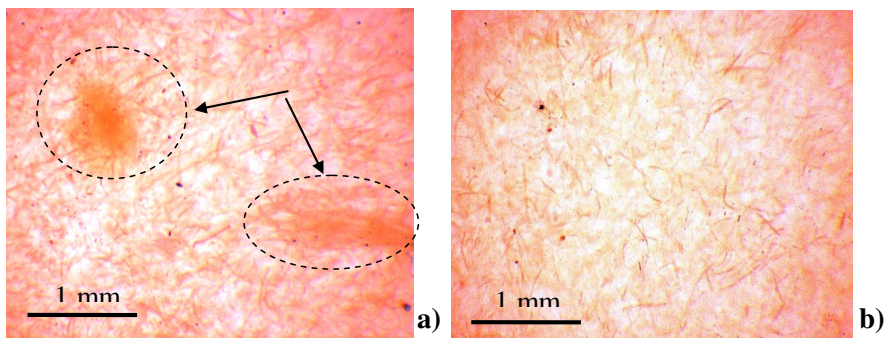
#### Dispersion of fibers and presence of agglomerates in composites

The images in Figure 2 show that both fiber length and diameter varies a lot in the WPC. Even though the extruder screws are equipped with several elements for kneading and dispersion of fibers it seems as the wood powder particles remain as bundles in the compound.



*Figure 2. Pressed pieces of injection molded WPC specimen*

Microscopy images of the pressed CTMPC samples are shown in Figure 3a and b.



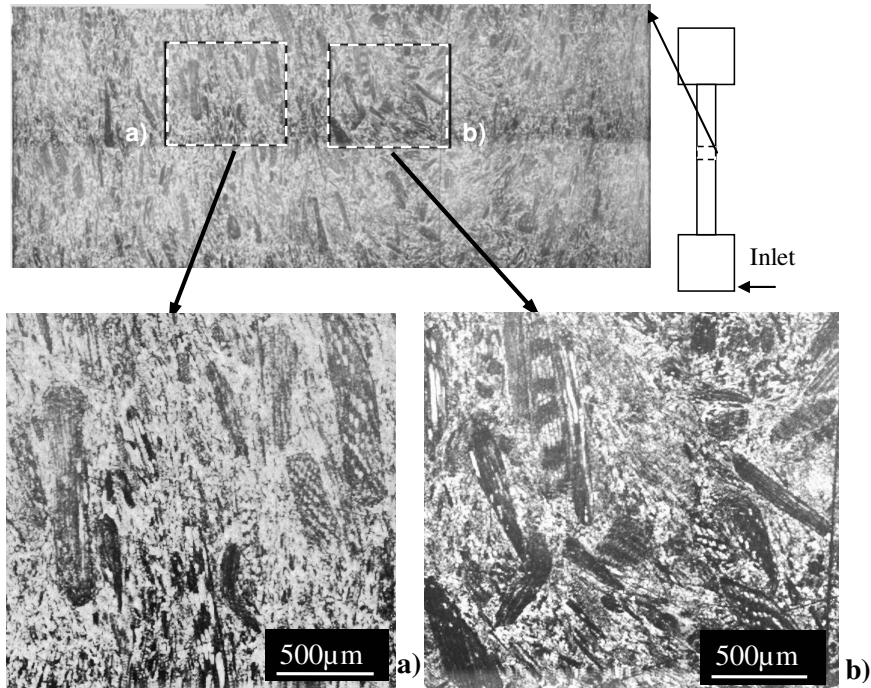
*Figure 3. Pressed pieces of injection molded a) CTMPC and b) CTMPMC specimen*

Fibers are dispersed quite well in the CTMPC, although some rather large agglomerates were found in the composites without MAPP (Figure 3a) and hardly any in the

composite containing MAPP (Figure 3b). MAPP is known to work as a lubricant as well as an adhesion promoter which obviously leads to better fiber dispersion as shown here.

#### Fiber orientation

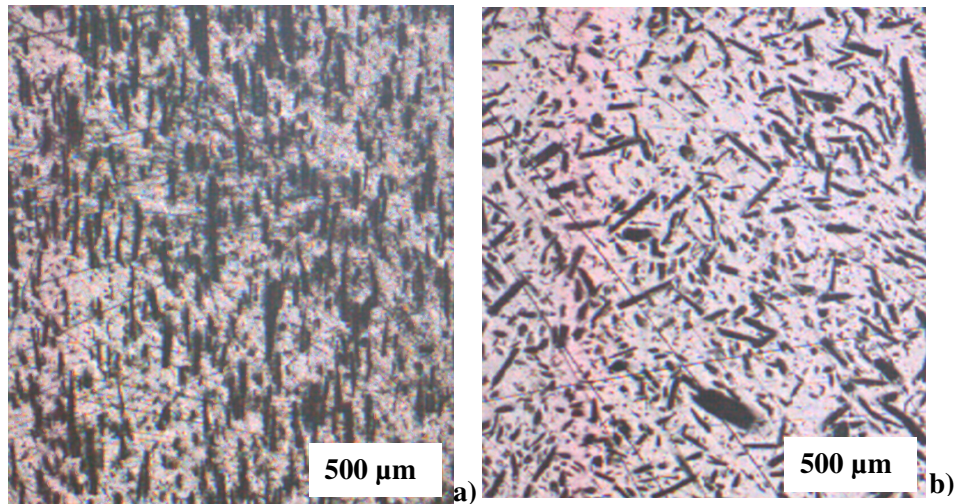
Microscopy images of a WPC surface are shown in Figure 4.



*Figure 4. Microscopy image of the surface of WP50C*

The images in Figure 4 demonstrate that most of the WP particles are rather well aligned and dispersed. It can also be seen from this figure that there is a large variation of length and diameter of these particles. There is a narrow area close to the centre line of the composite where the fibers are more misaligned (see Figure 4b).

Images taken from different sides of the FFC (the same locations as Figure 4) are shown in Figure 5.

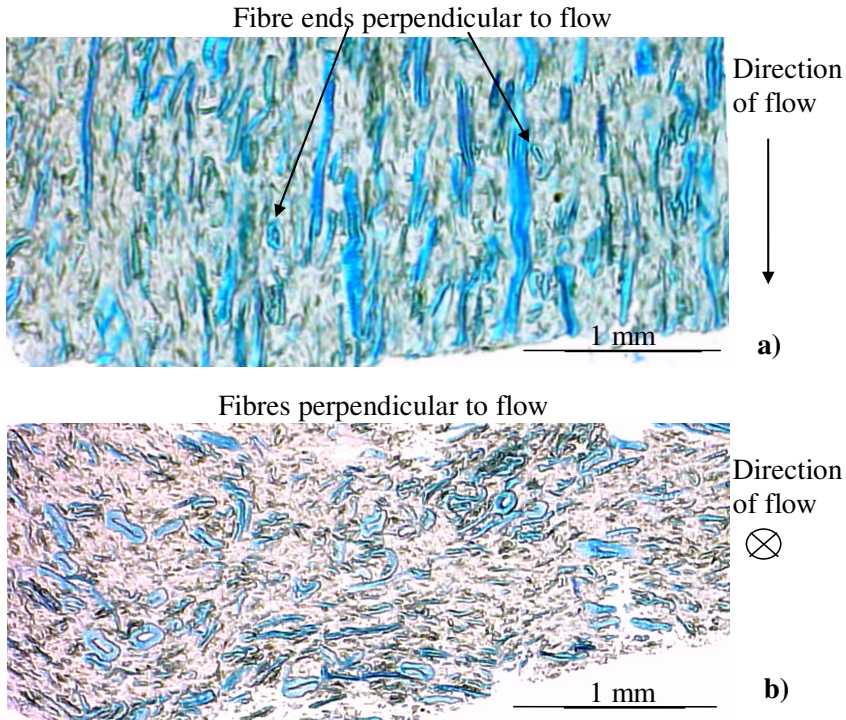


*Figure 5. Microscopy image of the surface of FFC*

Figure 5 shows that flax fibers are well distributed. It also shows that the flow pattern is not identical to the flow pattern in the WPC. Orientation varies considerably across the cross section. The lower volume fraction along with much thinner fibers compared to WP composites most likely contributes to the difference. In Figure 5a a representative image from the specimen side opposite to the inlet is shown (see Figure 4 for location of the images in relation to the inlet). Here the fibers are very well aligned. Figure 5b is a representative image of the specimen part on the same side as the inlet. Here the fibers are almost randomly distributed. This is not in line with the assumption that fibers are perfectly aligned across the whole material.

It is possible that fiber orientation varies through the thickness of these samples. This has been observed in [18]. Due to difficulties with grinding and polishing of thermoplastic composites to a viewable surface at defined depths of the specimen, the images have only been taken at one position as close to the midplane of the specimen as possible.

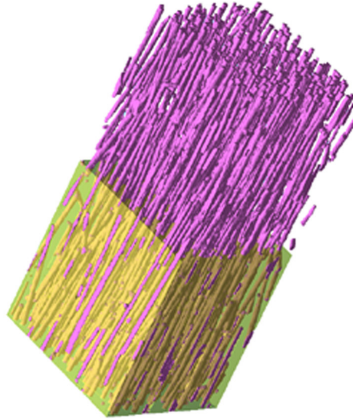
The image of cross-sections of CTMPC is presented in Figure 6.



*Figure 6. Cross sections of CTMPC using a polarized light microscope*

The image in Figure 6a, shows that most of the CTMP fibers are aligned in the direction of the flow but some fibers are oriented perpendicular to the flow. It also shows that some of the pulp fibers are kinked. Those kinks might indicate that fibers are damaged or there are simply geometrical imperfections (fibers are twisted, curled etc), in either case these defects would diminish efficiency of reinforcement. It should also be noted from Figure 6 b that the shapes of the CTMP fibers are elliptical and some of the fibers are almost flattened while the hollow lumen can be seen in other fibers.

A 3-D image of GFC is shown in Figure 7.



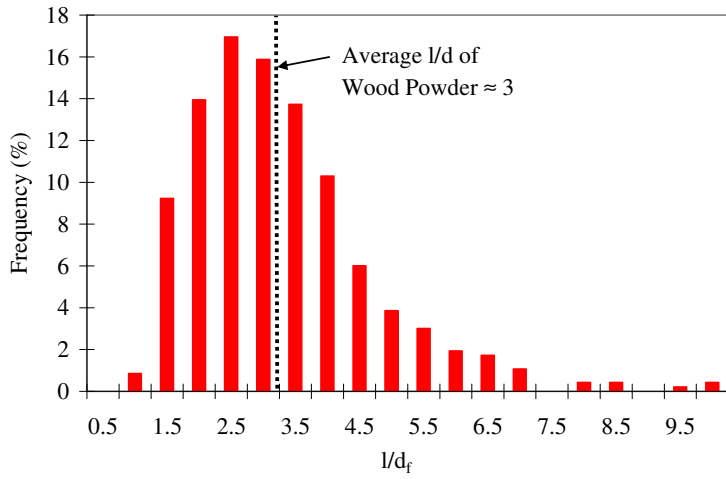
*Figure 7. Study in 3-d of the fiber direction in an injection molded GFC*

The 3-d image (Figure 7) shows that the glass fibers are quite well aligned and well distributed in the injection molded specimen. Although this analysis is not performed on actual WPC specimens due to technical difficulties mentioned earlier, this is still a good argument in support of the assumption that fibers are quite well aligned in the injection molded WPC samples as well.

### **Results from fiber length measurements**

The results from measurements of fiber length and diameter are shown in Figure 8 to Figure 10. The distribution of fiber  $l/d_f$  (length/diameter) ratio of WP is presented in Figure 8.





*Figure 8. The distribution of  $l/d_f$  ratio for WP*

Since there is such a large variation of diameter for the WP particles, in order to obtain statistically significant data both length and diameter has been measured on a large number of fibers (>500 measurements in total). The diagram shows that the  $l/d_f$  ratio is very low in these composites: the mean value is below 3.

The fiber length distribution of CTMP fibers as delivered and of CTMP fibers extracted from compound and injection molded specimens are shown in Figure 9.

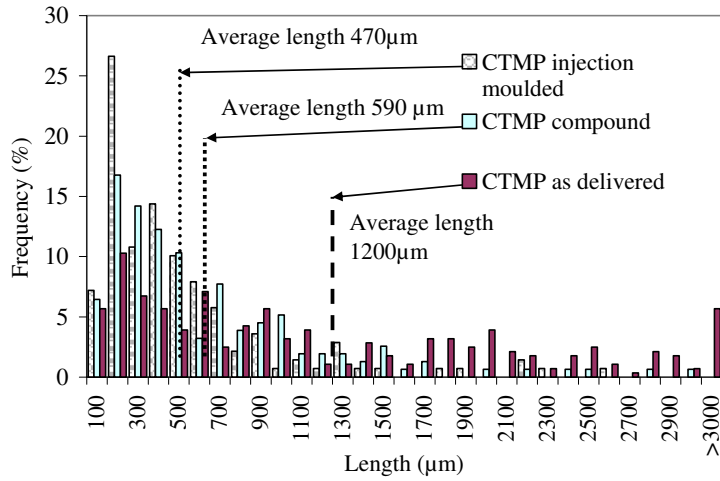


Figure 9. Fiber length distribution of fresh CTMP (as delivered) and CTMP extracted from compounded granules and injection molded test specimens

These results show that the CTMP fibers before processing (as delivered) have an average length of a few millimeters, whereas after compounding the fibers are dramatically shortened and most of the fibers are well below 1 mm. After injection molding the main part of the CTMP fibers are shorter than ½ mm.

The processing reduces the initially high  $l/d_f$  of CTMP fibers of ~32 (as delivered) to ~15 after compounding and to ~12 after the final shaping of the composite in the injection molding step. This is still 4 times higher than  $l/d_f$  of WP.

Figure 10 shows the fiber length distribution of FF and GF extracted from an injection molded specimen.



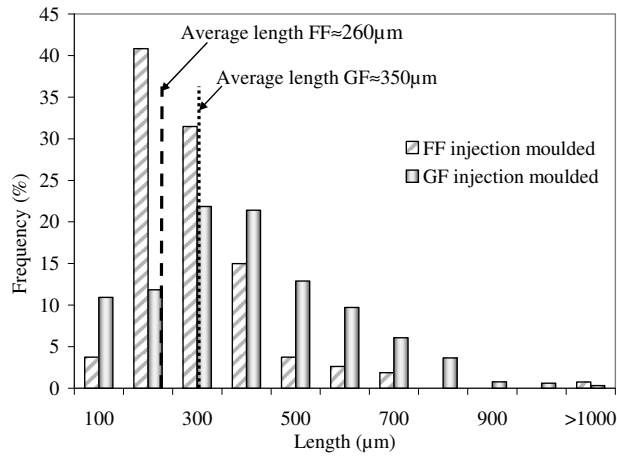


Figure 10. Fiber length measurement of FF and GF extracted from injection molded composite specimen

Although flax fibers are added in the compounding step as continuous spun roving, these fibers are shorter than the CTMP fibers after compounding and injection molding. The processing steps reduce the fiber length significantly: the average flax fiber length is less than 300  $\mu\text{m}$ . These flax fibers have an average diameter of 19  $\mu\text{m}$  which results in an average  $l/d_f$  ratio in the FFC of 14. It should be noted that there are small percentages of fibers longer than 1 mm present in the flax composite, actually some fibers are well over 4 mm.

In the GFC the fibers have an average length of approximately 350  $\mu\text{m}$ . The diameter of the glass filaments is 24  $\mu\text{m}$  resulting in the same average  $l/d_f$  as for the flax fibers. Even though these fibers also are fed into the extruder as continuous roving the longest fibers found are below 1.1 mm. It should also be noted that very small, edgy glass fiber fragments have not been taken into account here, since neither length nor diameter can be distinguished properly. These fragments of course influence composite strength negatively.

## Results of mechanical testing

The results from mechanical testing on WPC are summarized in Table 2 and relative difference of mechanical properties compared to neat PP are plotted in Figure 11 ( $K_{\text{Composite}}/K_{\text{PP}}-1$ ).

*Table 2. Summary of the mechanical test results on WPC*

<b>Composite composition</b>	<b>W<sub>f</sub> (wt %)</b>	<b>Strain at break (%)</b>	<b>Std dev (%)</b>	<b>Ultimate Stress (MPa)</b>	<b>Std dev (MPa)</b>	<b>Young's modulus (MPa)</b>	<b>Std dev (MPa)</b>
PP	0	6.1		32.0		1700	
WP20C	20	2.7	0.12	29.4	0.6	3090	47.7
WP30C	30	2.1	0.13	28.8	0.5	3662	176
WP40C	40	1.6	0.02	27.8	0.5	4275	143
WP50C	50	1.1	0.09	27.0	0.0	5218	102
WP20MC	20	2.6	0.06	33.0	0.0	3093	91.0
WP30MC	30	2.0	0.04	34.0	0.0	3889	51.0
WP40MC	40	1.4	0.08	36.2	0.5	4874	164
WP50MC	50	1.1	0.02	36.0	0.0	5732	174
WP60MC	60	0.7	0.04	33.2	0.5	6858	93.0

The results in Figure 11 show that the strength of WPC without adhesion promoter is decreasing with increasing filler weight fraction by 8-16% compared to unreinforced PP. Whereas the strength of WPC with adhesion promoter (MAPP) is 3-13% higher than for PP, having the highest value for composite with 40% and 50% weight content of wood powder and lowest for 20% and 60%.

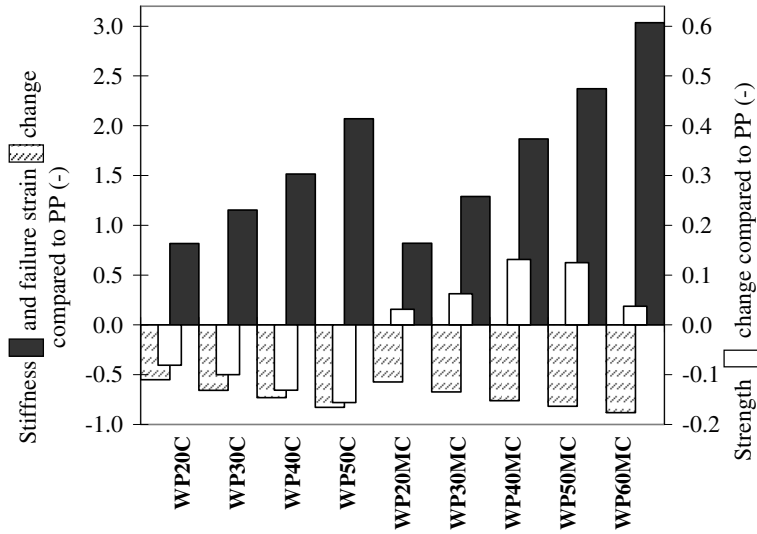


Figure 11. Summary of the mechanical tests on WPC,  $\left( \frac{K_{Comp}}{K_{PP}} - 1 \right)$

Addition of WP to PP has similar effect on stiffness for both composites, with and without MAPP. Elastic modulus is steadily increasing with increasing content of filler. Composites with MAPP have slightly higher elastic modulus (by 1-9 %) than materials without it, and the difference is highest for 40% weight content of wood powder. Increase of elastic modulus with addition of filler is very significant: by 82% for 20 wt% of wood powder and by 300% for 60 wt%.

The strain at failure is decreased quite dramatically (by 55%) already at addition of 20 wt% fibers and it continues to decrease rather linearly with increasing weight fraction of WP reaching level of only 12% of that of PP for composites with 60% wt of fillers. There is only marginal difference (within 1-2 %) of strain at failure between composites with and without MAPP.

The results of the mechanical tests on GFC, CTMPC and FFC are summarized in Table 3 and relative difference of mechanical properties compared to neat PP are plotted in Figure 12 ( $K_{Composite}/K_{PP}-1$ ).

Table 3. Summary of the mechanical test results on CTMPC, FFC and GFC

Composite composition	V <sub>f</sub> (-)	W <sub>f</sub> (%)	Strain at break (%)	Std dev (%)	Ultimate Stress (MPa)	Std dev (MPa)	Young's modulus (MPa)	Std dev (MPa)
GF30C	0.13	30	1.5	0.13	33	0.0	8919	243
CTMP25C	0.19	25	3.1	0.18	29.9	0.32	3123	115
CTMP25MC	0.19	25	2.6	0.27	39.0	0.67	3749	62
FF30C	0.23	30	2.7	0.08	33.4	0.58	5631	216
F30MC	0.23	30	2.8	0.06	44.0	0.09	5441	145

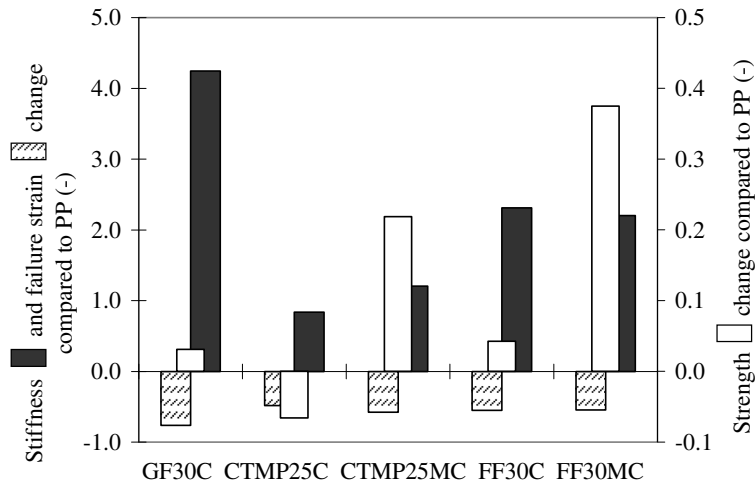


Figure 12. Summary of the mechanical tests on PP composites containing fibers with higher  $l/d$

$f$  than WP i.e. GF, CTMP and FF,  $\left( \frac{K_{Comp}}{K_{PP}} - 1 \right)$

Similarly as in the case of WPC, addition of GF, CTMP and FF leads to increase of the composite stiffness: addition of 25% of CTMP increases modulus 2 times and addition of 30% FF and GF gives 3 and 5 times higher modulus respectively than for neat PP. Addition of MAPP leads to even higher modulus in the case of CTMP but does not influence stiffness of FFC.

However, material strength is not affected by addition of fibers unless MAPP is added too. Not even GF with high strength and high  $l/d_f$  gives any reinforcing effect. Addition of MAPP actually improves strength of the PP composites by approximately 22% for CTMP and by 38% for FFC.

Strain at failure is reduced for all materials with reinforcement by approximately 50-80%.

Comparison between WPC and GFC, CTMPC and FFC and more detailed analysis will be given further in the paper.

### Parametric analysis of strength of short fiber composites

Parametric analysis is performed in order to evaluate influence of morphology of the NFC on strength and estimate ultimate limits for strength in the best case scenario by assuming optimized (idealized) condition for microstructure of the material.

Properties of the constituents used in the parametric analysis are given in Table 4. These values are used in all calculations unless otherwise is stated.

Table 4. Summary of the data used in the calculations

$W_f$	$V_f$	$\rho_f$	$\epsilon_{cu}$	$\sigma_{mu}^*$	$\sigma_{fu}$	$\tau_{mu}^{**}$	$\bar{l} / \bar{d}$	$\bar{l}^{***}$	$\bar{d}^{***}$
(%)	(%)	(g/cm <sup>3</sup> )	(%)	(MPa)	(MPa)	(MPa)	(-)	( $\mu m$ )	( $\mu m$ )
0.3	0.24	1.3	2.1	26.5	500	26.6	2.7	410	150
0.4	0.31	1.3	1.6	24.3	500	26.6	2.7	410	150
0.5	0.4	1.3	1.1	16.8	500	26.6	2.7	410	150

\* $\sigma_{mu}$  was obtained from tensile tests of the neat polymer, this is the stress in the matrix corresponding to the strain at failure of the composite,  $\epsilon_{cu}$  average of five measurements. \*\* $\tau_{mu}$ , is matrix shear strength. \*\*\* $\bar{l}$  and  $\bar{d}$  are the average fiber lengths and diameters respectively

Measurements of the adhesion between fibers and matrix as well as fiber properties are very challenging tasks because the WP particles are so short. Due to the wide spread in fiber aspect ratio ( $l/d_f$ ) average length and diameter values are used for simplicity. It has further been assumed that the fibers are well aligned. Although image analysis did not

give quantitative characteristics of the fiber orientation, qualitatively it shows that this assumption is reasonable for the WPC.

Calculated strength for WPC with 30, 40 and 50 wt-% WP is plotted in Figure 13 as a function of interfacial shear strength (ISS). The composite tensile strength is calculated from Eq. 2. Critical fiber length is changing depending on the ISS (see Eq. 1) and length efficiency factor is calculated depending on relationship between average fiber length and  $l_c$  (see Eq. 3).

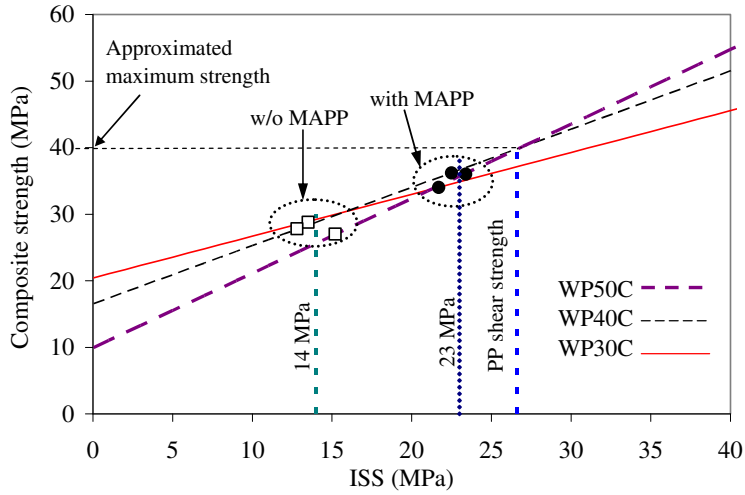


Figure 13. Tensile strength of WPC as a function of interfacial shear strength

It can be seen from Figure 13 that for low ISS the strength of the composites is increasing if the fiber content is decreased. This is in agreement with experimental results for WPC without coupling agent (see Figure 11). However, at higher ISS the strength of the material can be improved by adding more filler. This diagram also shows that if adhesion between fiber and matrix is good and ISS exceeds (or is equal to) matrix shear strength then the ultimate strength of these composites is approximately 40 MPa. Experimental values of strength also were plotted in the same figure for comparison. Since actual ISS for this material system is not known, in order to plot test results in Figure 13 experimental values of strength were used as Y-coordinate and X-coordinate was obtained by crossing calculated curve for the composite with corresponding fiber

content. The result of this exercise is very interesting: independently of fiber volume content values of ISS which are read from the calculated curves are almost the same for all materials. Thus, it is rather reasonable to assume that the values of ISS obtained by comparing experimental values of composite strength and calculated strength are actually quantitative characteristics of these material systems. Composites without MAPP indicated ISS of approximately 14 MPa and composites with MAPP show ISS of 23 MPa, which means that addition of coupling agent improved adhesion between fiber and matrix by almost 65%. These values of ISS are used further in the analysis where properties of interface are required to predict WPC strength.

It has already been mentioned before that the fiber length is of great importance for improving the composite strength. However, not only length alone but rather fiber aspect ratio ( $l/d_f$ ) has to be considered. Results of the parametric analysis with respect to the fiber length-to-diameter ratio are presented in Figure 14.

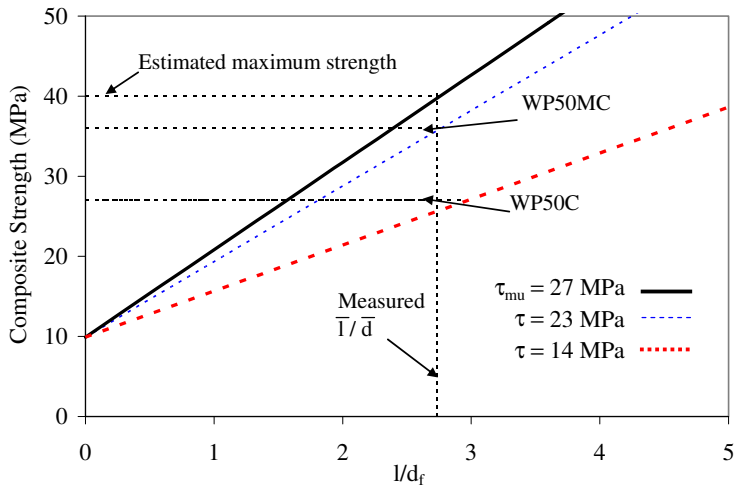


Figure 14. Tensile strength of WPC with 50 wt-% fibers as a function of fiber aspect ratio

From Figure 14 it can be seen that the  $l/d_f$  ratio has a large influence on the result. A smaller diameter leads to smaller critical fiber length and therefore, stress transfer and utilization of fiber properties are significantly improved. If the  $l/d_f$  has been underestimated the upper limit for the WPC strength is higher than 40 MPa. It is

unlikely that  $l/d_f$  has been greatly overestimated since strength values of 36 MPa have been reached. Nevertheless, it should be noted that  $l/d_f$  ratio is not actually a constant and calculations based on distribution of  $l/d_f$  would be more appropriate than use of average value as has been done in this case.

Another factor to consider in regard to geometrical properties of the fillers is fiber shape. For example, image analysis showed that there are numbers of fibers in the material that have been crashed and squeezed thus  $l/d_f$  ratio is also affected and as it has been shown, particles with low  $l/d_f$  has a deteriorating effect on the composite strength.

Naturally, mechanical properties of the fillers must greatly influence mechanical performance of the composite. In order to estimate this influence, parametric study with respect to the fiber strength is performed and these results are presented in Figure 15. It has been reported in literature [33] that wood fiber strength can vary from 300 to 1000 MPa, interval of strength up to 500 MPa is used here for calculations. Three values for ISS are used in the analysis: 14 MPa (WPC), 23 MPa (WPMC) and 26.6 MPa (shear strength of the matrix). Composite with 50 wt% of wood powder is modelled.

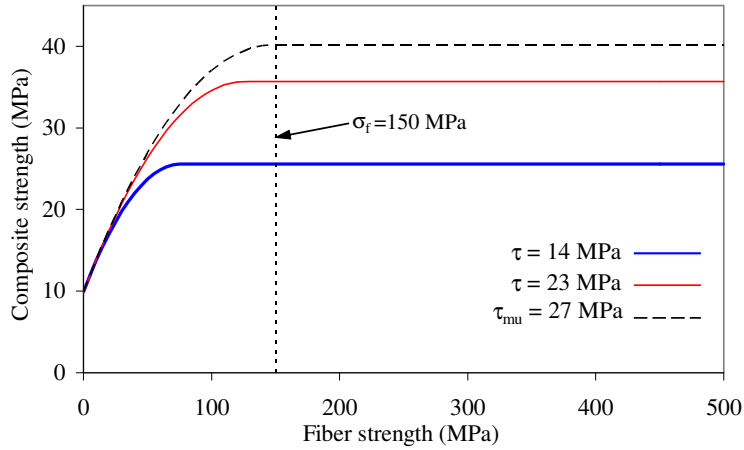


Figure 15. Tensile strength of WPC with 50 wt-% fibers as a function of fiber strength

The results presented in Figure 15 show that apparently fiber strength is not a critical parameter which defines composite strength. As a matter of fact, in this material system with very low  $l/d_f$  fibers, fibers with strength higher than 150 MPa can not be fully



utilized. This is evident from the analysis of the curve for the “best case scenario”, where ISS is equal to the matrix shear strength: strength of the composite is not affected by fiber strength over 150 MPa. It also should be noted that highest composite strength achieved in this case is approximately 40 MPa.

This analysis leads to the somewhat peculiar conclusion: there is no need whatsoever to develop fibers with very good mechanical properties, namely strength, unless fiber geometry, interface strength and matrix properties are optimized.

The next series of calculations show how the matrix properties affect strength of the composite, Figure 16. The analysis is done with respect to the matrix stress at failure strain of the composite. This stress is of course directly related to mechanical properties of the polymer. The calculation is performed for the same set of data (fiber content and ISS) as the previous one (strength of composite vs. strength of fibers).

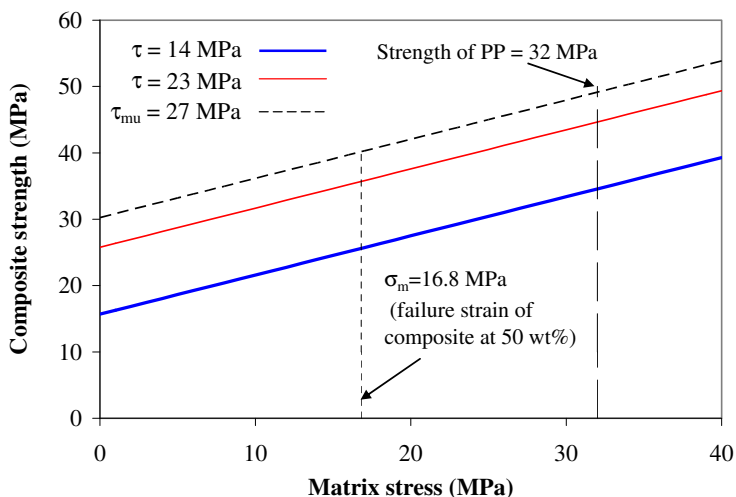


Figure 16. Tensile strength of WPC with 50 wt-% fibers as a function of stress in matrix at failure strain of composite

The diagram in Figure 16 shows that the matrix stress has rather strong influence on the ultimate strength of the composite. Stress in matrix used for the previous calculations is estimated from five separate tests on unreinforced polymer (see Table 4). It should be noted that this stress might be wrongly estimated because stress state in the composite is

more complex than in neat polymer. If the matrix stress at failure has been overestimated the ultimate composite strength is lower than was stated earlier and the other way around if the matrix stress has been underestimated.

The upper limit of WPC strength is given by the “best-best case scenario”: if the ISS is equal or higher than the shear strength of the matrix and the stress in the matrix at the failure of the composite is equal to the tensile strength of the polymer. In this case the upper limit for the composite strength is approximately 49 MPa. However, the assumption of this kind of “best case scenario” is very unlikely to be fulfilled.

### **Comparison between WPC and composites with large fiber aspect ratio**

GFC, CTMPC and FFC strength can be compared to strength of WPC in terms of the parameters influencing strength which were identified in the previous section. This comparison will help to re-evaluate conclusions made from the parametric study on strength of WPC.

The main difference between these composites is fiber aspect ratio: GF and FF have almost 5 while CTMP has approximately 4 times higher  $l/d_f$  than WP. All results discussed below are presented in Table 2, Table 3, Figure 11 and Figure 12.

The strengths of all GF-, FF- and CTMP composites are higher than the strengths of WPC without coupling agent. The fibers in FFC and CTMPC seem to be less aligned than in WPC, and GFC has lower fiber volume fraction than WPC but still these composites are stronger than WPC. Apparently the higher  $l/d_f$  fibers in these composites outweigh the effects from orientation and volume fraction.

The CTMP25MC has significantly higher strength than the WPC (with and without MAPP) presented in this study. Even if the high  $l/d_f$  ratio measured on virgin pulp is not retained after processing the  $l/d_f$  of the CTMP fibers is still much higher than for the WP. Aspect ratio of the fibers is high enough to ensure reasonable stress transfer and therefore there is a fair increase of strength with addition of CTMP fibers into polymer combined with MAPP, the strength increases by 22 % compared to pure matrix.

The FF30MC has highest strength of all the studied composites. The strength is increased by 38% compared to the PP matrix. For WP30MC strength is increased by

only 6% compared to PP. Even if FF are less aligned in the composite the higher  $l/d_f$  results in a stronger composite than in the case of WPC.

Qualitatively the experimental values and the parametric study are in quite good agreement. However, it should be noted that quantitatively the predicted values for composites with higher  $l/d_f$  fibers (GF, FF and CTMP) are much higher than experimental using the same models and assumptions (the same ISS and the same orientation factor) that were used in the case of WPC. It is known that the orientation factor and fiber aspect ratio are not independent variables. Many studies have shown that longer fibers in compounded materials lead to a more random orientation and therefore a lower orientation factor [18,39,40], GFC were studied. In our study WP has considerably lower  $l/d_f$  than CTMP and FF but are similar with respect to density (which might be a factor influencing flow) and therefore, random in-plane orientation for these composites is assumed and orientation factor is set to 3/8 [28]. The tensile strength as a function of ISS for FF30C, CTMP25C and WP50C has been plotted in Figure 17. The WP50C curve with orientation factor 1 has been added for comparison in the same graph.

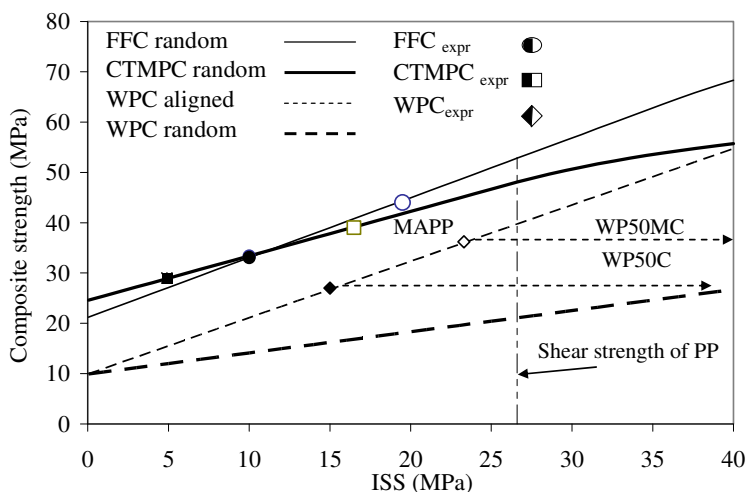


Figure 17. Tensile strength of FF30C, CTMP25C and WP20C as a function of ISS using orientation factor 3/8 for randomly distributed fibers and for WP50C also orientation factor 1(as in the parametric study)

From Figure 17 it is clear that the theoretical ISS for WP50MC exceeds the matrix shear strength if orientation factor  $3/8$  for randomly in-plane oriented fibers is used in the calculations. For The FF30C and CTMP25C on the other hand ISS values of 20 and 17 are obtained respectively for randomly distributed fibers. These values are reasonable and agree rather well with earlier results [35]. Without MAPP, ISS is only 4.5 for the CTMP25C while it is approximately 10 for FFC. This is also reasonable; since CTMP25C contains quite large bundles (Figure 3) which affect the strength of the composite negatively, i.e. it decreases the average  $l/d_f$ .

## CONCLUSIONS

Experimental results along with theoretical predictions of tensile strength of short natural fiber composites manufactured by compounding and injection molding have been presented using stress transfer model with constant interfacial shear stress. Predictions are based on rule-of-mixture type of expressions developed for short fiber composites using stress transfer model with constant interfacial shear stress. Parametric analysis has been performed in order to find the limitations of strength properties of these materials and to define reliable and simple recommendations for how to improve mechanical performance of NFC.

In order to model mechanical properties of the composites extensive characterization of microstructure of these materials was performed since models require geometrical properties of fibers as input. Distributions of fiber length (fiber aspect ratio) for different materials were obtained by image analysis. These results indicated that, first of all, there is large scatter in experimental results: very short fibers along with rather long ones are present in the material. Second, and more important; this investigation showed that fiber length is dramatically reduced during processing. Based on analysis of micrographs of material cross-sections it was concluded that wood fibers in these composite materials have strong preferential orientation caused by the flow of the compound during manufacturing. Therefore, for simplification purposes and due to lack of quantitative data it was assumed that all WPC are unidirectional in the theoretical analysis. Image analysis also suggested that addition of coupling agent leads to better dispersion of fibers in CTMPC.

The parametric study indicated that the strength of short natural fiber composites is mostly limited by fiber aspect ratio and interfacial shear strength. The results showed that strength of the fibers can not be fully utilized in the case of very low  $l/d_f$  fibers and for material systems with poor adhesion between fibers and matrix. As a matter of fact it has been shown that in PP composites with average aspect ratio of  $l/d_f = 3$ , effective fiber strength that can be utilized is only 150 MPa. It also has been concluded that even in the best-case scenario when ISS is higher than shear strength of the matrix, the maximum composite strength that can be achieved in the studied material system (WPC) is limited by approximately 40 MPa. Comparisons of results for WPC with CTMPC, FFC and GFC, which all have higher aspect ratio, are used to support the results obtained from the parametric study. Improved strength but lower improvement of strength than expected for the higher  $l/d_f$  fiber composites can be explained in terms of variations in orientation and in difficulties in determination of correct  $l/d_f$ .

Therefore, it is clear that higher tensile strength of the short NFC can be achieved by increasing  $l/d_f$  of the fibers and improving interfacial strength. An upper limit for the achievable strength of compounded and injection molded NFC can be approximated if the micro structure is known.

Finally, processing also has large effect on composite strength: i) fiber length is extensively reduced for many types of fibers both by compounding and injection molding, improvements can probably be done in order to reduce fiber cutting in both processes, ii) dispersion of fibers is needed but a balance between good dispersion and fiber cutting for different fibers should be possible to find and iii) different processing parameters as well as the rheological properties of the material influence the final orientation of fibers in the composite, which should be taken into account already during design of injection molding tools.

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## ***Paper B***



# **Processing effect on Flax Fiber Composite properties**

## **Part I: Parametric study of Compounding**

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**Key words:** microstructure, composite, flax, strength, stiffness, compounding, injection molding

### **Abstract**

Natural fiber composites based on flax and polypropylene prepared by compounding and injection molding are studied in this work. Factorial trials and statistical analysis is employed to investigate effects of processing parameters on microstructure and on mechanical performance. The tested parameters in the compounding step are screw speed, mass flow, number of dispersing elements and granule length. These parameters all influence the final structure and the mechanical properties of the composites although the differences in the material properties are rather small. The most important parameters turned out to be screw speed and granule length.



## INTRODUCTION

Consumption increases world wide in a way that has never been seen before. This development is positive yet unsustainable. We experience climate changes which most likely are at least partly triggered by human activity such as use of fossil resources, releasing substances to the atmosphere that has been bound in the depths of the planet for hundreds of thousands of years. The need for a holistic and more sustainable use of resources is needed. This is one of the reasons why the use of environmentally friendly materials becomes very important. One such material is natural fiber composites which are increasingly used. The natural fibers are a CO<sub>2</sub> neutral renewable material which can provide reinforcing properties in composites and/or act as filler to reduce consumption of petrochemical material in commodity plastics. To achieve truly sustainable development optimized processing is of high importance. A robust process that generates low amounts of scrap and consumes less energy is desirable.

The material group natural fiber composites (NFC) include various types of matrices, fibers and additives. It is the fibers that normally constitute the mechanical properties of a fiber composite. Conventional high performance composites contain long, mostly continuous fibers such as glass or carbon fibers. Although there have been attempts to develop natural fiber fabrics for technical applications [1], the main part of the NFC out on the market contain short fibers. The achievable mechanical properties of short fiber composites are limited by many factors. For some types of short fiber composites (SMC, BMC, GMT) fiber length remains the same during the processing stage. But for some processes like compounding and injection molding the fiber length is process-dependent i.e. the initial fiber length will not be preserved in the final product. Since fiber length is one of the most important parameters in terms of mechanical performance of short fiber composites [2], degradation of fiber length during processing has been extensively studied. The degradation of different non renewable fibers during compounding before injection molding was studied in [3]. The influence of fiber properties on the performance of glass-fiber-reinforced polymers were studied in [4]. In [5] the influence of fiber length, fiber loading and fiber orientation on the mechanical properties of PP/sisal composites was evaluated. The mechanical properties of

flax/polypropylene compounds, manufactured both with a batch kneading and an extrusion process was compared with properties of Natural Fiber Mat Thermoplastic composites in [6]. Bledzki et al studied the structure–properties relationship between different wood fibers/polypropylene composites and different compounding techniques; they found that the twin screw extruder had many advantages compared to other compounding techniques [7]. In a recent work, we studied the relationship between microstructure and macroscopic mechanical properties of compounded and injection molded natural fiber composites [2]. This study indicated a quite strong influence from processing on the final microstructure of the composites containing flax fibers as well as wood fibers. The study indicated that the achievable strength is quite limited if the fiber length can not be preserved. However, the processing parameters that are responsible for fiber length degradation have not been identified in this two-step process. One reason is that it is difficult to relate forces needed to break fibers to the shear field developed in these types of machinery according. Franzén et al [3] identified three different mechanisms responsible for fiber fracture and the resulting fiber length distribution in the compounding process, these were: i) fiber/fiber interaction, ii) fiber machinery interaction and fiber polymer interaction. All of these mechanisms are influenced by the processing setup to some extent. This study is an attempt to optimize the compounding and injection molding of flax fiber composites in order to achieve the optimal microstructure and as a result improved mechanical performance of this material. Four important processing parameters in each processing step have been evaluated by studying the resulting microstructure and the mechanical properties of the composites.

Due to the large amount of data the authors decided to split the paper in two parts: this paper, Part I, deals only with the compounding process. In part II the injection molding process will be addressed. The main objectives of this work are i) to evaluate the influence of the processing conditions are on the final material properties, ii) to find the best possible processing conditions that gives material with best mechanical properties and iii) to identify processing parameters that can be further improved.

## **EXPERIMENTAL**

### **Materials**

A homopolymeric polypropylene (PP), Adstif 770 ADXP from Montell with a high melt flow index of 45g/10min was used as matrix. Epolene E-43 maleic anhydride modified PP (abbreviated as MAPP or M further in the text) from Eastman Chemicals was used as adhesion promoter. Spun enzymatically retted flax fiber (FF) roving from Finflax Oy (Finland) was used as reinforcement. All composites consist of 30 weight-% fibers and 70 weight-% matrix. Except one of the composites contains pure PP in all other materials 2% MAPP is added to the PP.

### **Processing**

Prior to compounding the fibers were dried in an oven at 105 °C for at least 4 hours. The constituents were compounded in a Krupp Werner & Pfleiderer ZSK 25 WLE co-rotating twin screw extruder with l/d of 44. Fibers were fed into the molten polymer on the screws. The fiber weight fraction was controlled by the speed and ascent/revolution on the side screw. The compound was pulled through a cooling water bath and cut to 4 and 10mm long and approximately 5 mm in diameter granules using an SF Sheer granulator. The granules were oven dried at 105 °C for at least 4 hours prior to injection molding. Test specimens were injection molded in an Engel ES75 CC80 machine with maximum clamp force of 75 ton and shot size of 125cm<sup>3</sup>/115g (based on polystyrene at 1000 bars). The injection molded specimens were dog bone shaped. The specimens had a total length of 218 mm and a centre cross section area of 12 x 4 mm<sup>2</sup>. Processing parameters are shown in Table 1.



*Table 1. The setups for the compounding trials*

Temperature		Target
Zone 2	(°C)	180
Zone 4	(°C)	180
Zone 5	(°C)	170
Zone 6	(°C)	175
Zone 7	(°C)	175
Zone 9	(°C)	185
Zone 10	(°C)	190
Dye	(°C)	200
Type and size	(mm)	Circular, diameter 4
Pressure	(bar)	Varies
Vacuum		Yes
Main screw		
Speed	(rpm)	250 / 325 / 500
Torque	(%)	Varies
Side screw		
Speed	(rpm)	595 / 446 / 595
Roving	Nr of	2 / 4 / 4
Mass flow	(kg/h)	2.14 / 3.21 / 4.28
Main feeder		
Mass flow	(kg/h)	7. 15 / 10.7/ 14.3
Dispersing elements	Nr of	2 / 4 / 6
Granule length	(mm)	4 / 10 / 10
Fiber weight fraction	(%)	30

All parameters where 3 different values are given are connected to the selected parameters in the factorial trials. Values are given as they are adjusted when the factor is tested on: low /midpoint/ high level.

The setup for the injection molding machine was the same during production of all test specimens from all the different compounds. The injection molding parameters are shown in Table 2.

Table 2. The setup for the injection molding unit during all compounding trials

		Set.	Actual
Packing pressure	(bar)	1	45-49
Hold pressure	(bar)	1	45-49
Mold temperature	(°C)	40	40
Temperature profile	(°C)		
	Nozzle	190	
	Zone 1	185	
	Zone 2	180	
	Zone 3	175	
Shot size	(mm)	75	
Packing time	(sec.)	20	
Hold time	(sec.)	2.5	
Cooling time	(sec.)	50	
Injection speed	(mm/sec)	45	

### Definition of processing parameters

The experimental design used for optimization of processing parameters is  $2^4$  full factorial trials [8]. Four factors (input parameters or independent variables) are investigated in the compounding process.

The selected factors are tested on high and low level and one midpoint where all parameter are supposed to take the intermediate value. The trial setup is best described with cubes where the trials are indicated by node points an  $x_i$  [ $i=1..4$ ] are the four parameters:

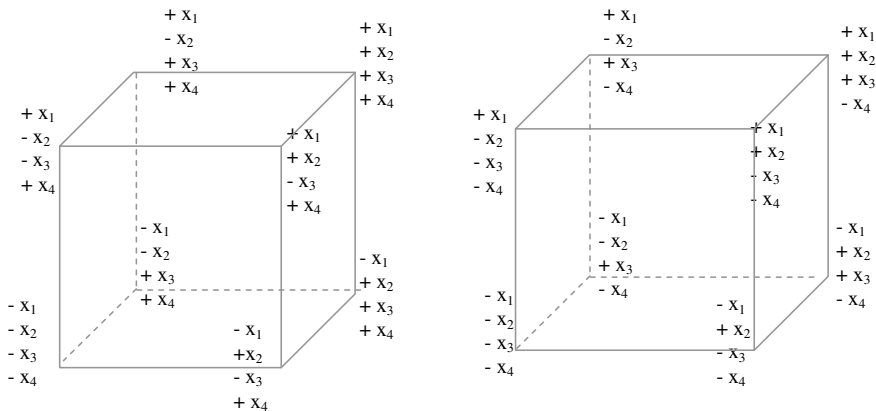


Figure 1. Schematic description of parameter trials

The midpoint trial is performed in order to detect nonlinear behavior. In our study it is not possible to use intermediate granule length since we only have access to two cutting lengths thus this parameter is held only on high level during the midpoint trial. The parameters and the tested levels are the following: The mass flow (7.2 - 14.3 kg/h), the screw speed (200 - 500 rpm), number of dispersing elements (12 - 6) and granule length (4 - 10mm). In total 17 materials with different compounding setups all injection molded with the same setup and one material which is not part of the factorial design but is used for comparison as reference material. In this case the parameters are set on the intermediate values and the material is produced without adhesion promoter. This is done in order to evaluate the importance of fiber/matrix interaction compared to the four selected parameters.

This experimental design allows evaluation of the individual parameters and gives also indications about parameter interaction.

The studied output responses (or dependent variables) were: fiber length, tensile strength, stiffness, elongation at maximum stress.

It should be noted that it is not obvious which parameters that have to be selected and at what level they have to be fixed in order to get the best response. There is a possibility that some of the significant parameters have not been considered. It is possible that larger differences between low and high level would show more clear results. However, the selected levels are within the normal ranges for this type of processing and equipment and not just arbitrary chosen to scale up the experimental response.

In Table 3 all 18 experiments are summarized. The abbreviations used from now on for each parameter and for each experiment are also included in the table. The +, 0 and – means that the parameter is held on high, midpoint or low level.

Table 3. Experimental set-up, abbreviations of parameters in brackets

	Screw speed (Rev)	Number of Dispersing elements (Dis)	Mass flow (Mas)	Granule length (Gra)
1 Rev- Dis+ Mas+ Gra+	-	+	+	+
2 Rev- Dis+ Mas- Gra+	-	+	-	+
3 Rev+ Dis+ Mas+ Gra+	+	+	+	+
4 Rev+ Dis+ Mas- Gra+	+	+	-	+
5 Rev- Dis+ Mas+ Gra-	-	+	+	-
6 Rev- Dis+ Mas- Gra-	-	+	-	-
7 Rev+ Dis+ Mas+Gra-	+	+	+	-
8 Rev+ Dis+ Mas- Gra-	+	+	-	-
9 Rev- Dis- Mas+ Gra+	-	-	+	+
10 Rev- Dis- Mas- Gra+	-	-	-	+
11 Rev+ Dis- Mas+ Gra+	+	-	+	+
12 Rev+ Dis- Mas- Gra+	+	-	-	+
13 Rev- Dis- Mas+ Gre-	-	-	+	-
14 Rev- Dis- Mas- Gra-	-	-	-	-
15 Rev+ Dis- Mas+ Gra-	+	-	+	-
16 Rev+ Dis- Mas- Gra-	+	-	-	-
17 Rev0 Dis0 Mas0 Gra+	0	0	0	+
18 Rev0 Dis0 Mas0 Gra+ No MA	0	0	0	+

### Characterization of microstructure

Fiber length measurements were performed manually, using an optical microscope Olympus BH-2 and the software Analysis distributed by SIS (Soft imaging systems). Fibers were extracted from granules by Soxhlet extraction using xylene.

### Mechanical testing

Mechanical testing was carried out on an Instron 8501 testing machine. Tensile tests were done according to ISO 527-2 standard. Displacement controlled test with cross head speed of 2 mm /minute and distance between clamps of 124 mm was carried out. At least five specimens of each material composition were tested. Impact tests were done on a Charpy testing machine on un-notched specimens according to ISO 178 standard.

## RESULTS

A  $2^4$  full factorial trial generates a very large amount of data. The data is presented as condensed as possible in a way which gives insight in what effect the four parameters have on microstructure and on the mechanical performance of the flax fiber composites.

### Statistical evaluation of parameter importance

The factorial trials were evaluated using the statistical analysis software MODDE from Umetrics [9]. The software calculates a multiple linear model for each output response by projection to latent structures, (PLS) on the form:

$$y = a_0 + a_1 \cdot x_1 + a_2 \cdot x_1^2 + a_3 \cdot x_1 \cdot x_2 \dots + a_n \cdot x_n$$

where  $y$  is a respons,  $a_i$  the approximation coefficients,  $x_i$ - the  $i$ -th parameter. The PLS regression coefficients are identical to those obtained by multiple regression but PLS can deal with many responses simultaneously, taking their covariance's into account. This provides us with an overview of how all the factors affect all the responses. PLS also calculates all interaction effects.

The goodness of fit is expressed as Correlation coefficient  $R^2$ ,  $R^2_{adjusted}$  and the Cross-validity correlation coefficient,  $Q^2$  for each model. These coefficients will take values between 0 and 1: if these coefficients are close to 0 there is no linear relationship between  $x$  and  $y$ , if they equal 1, the model explains the studied output response.  $R^2$  and  $Q^2$  should deviate as little as possible. A high  $R^2$  while  $Q^2$  is low indicates that there are many insignificant factors in the model, many interaction terms and so on added. The PLS has been extensively described in the literature and only this brief description will be given here [9]. In Table 4 the calculated coefficients,  $a_i$  for each factor, for each PLS model is presented.

Table 4. Summary of coefficient for the PLS models

	Tensile strength (MPa)	Tensile stiffness (MPa)	Strain at max stress (%)	Impact strength (kJ/m <sup>2</sup> )	Fiber max length (μm)	Fiber average length (μm)
<b>Constants</b>						
	44.73	5770	2.71	12.9	3008	328.7
<b>Main factors</b>						
Rev	-0.80	- 207.3	+0.12	+0.033	-988	-76.2
Dis	-0.06	+ 56.6	+0.05	+0.32	-768	- 33.2
Mas	+0.11	+91.4	- 0.06	-0.02	-170	+ 25.7
Gra	+0.27	+170.8	-0.08	-0.41	+278	
<b>Interaction effects</b>						
Rev x Dis			-0.03	+0.13	+519	+18.3
Rev x Mas	+0.09		0.02	+0.38		
Rev x Gra			-0.03	+0.34	-515	
Dis x Mas			0.04		+410	+13.7
Dis x Gra				-0.23		
Mas x Gra	-0.29			+0.16	+292	
<b>Model predictive power</b>						
<b>R<sup>2</sup></b>	0.700	0.550	0.704	0.174	0.906	0.649
<b>Q<sup>2</sup></b>	0.680	0.507	0.662	0.077	0.691	0.421

In these models each main factors has some influence for all the responses except for fiber average length where granule length does not matter (see Table 3). The  $R^2$  and  $Q^2$  values are above 0.6 for most models. These results confirm that the selected parameters are relevant but the parameters can not fully describe the real system.

In Fig. 2 to Fig. 5 the coefficients for each response are presented, error bars showing the significance of each coefficient. In the models the values of the factors,  $x_i$  only takes values -1 (when the factor is on low level), 0 (factor in midpoint) and 1 (factor on high level) thus for the low level to have positive influence the coefficient has to be negative.

Below each plot you will find  $N$  the total number of experiments,  $DF$  the number of experiments minus missing values,  $R^2$  and  $Q^2$ ,  $R^2$  adjusted the fraction of variation of the response explained by the model adjusted for degrees of freedom,  $RSD$  the residual standard deviation which is used in the computation of confidence interval for coefficients and finally the Confidence level.

### Strength model

In the discussion concerning the strength model it is considered advantageous to keep the parameters on the level that results in a material with higher strength.

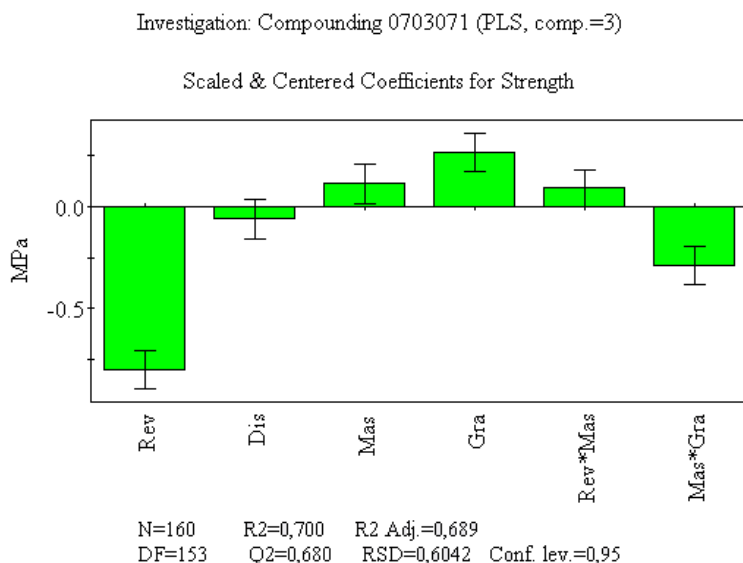


Figure 2. Coefficients for strength model

The most important factor for strength is screw speed (Rev). Keeping Rev on low level is advantageous. Long granules (Gra) are better than short and high mass flow (Mas) has a slightly positive influence on strength. Quite surprising is that the number of dispersing elements (Dis) does not give larger effect, the significance of Dis is low, which is seen by the error bar which is outside the range of the coefficient (Fig. 2). The interaction effect from Mas and Gra is significant according to this model. This might be an effect from the granulator speed which presently is not adjustable. We have noted that for some setups granules are more torn apart than cut because of the

unsynchronized speeds of extrudate and granulator. This problem can be overcome by using a granulator with adjustable speed. The other interaction effects have low significance; yet removing these parameters reduces the significance of the model slightly.

### Stiffness model

In the discussion regarding stiffness it is considered advantageous to keep the parameters on the level that results in a material with higher stiffness.

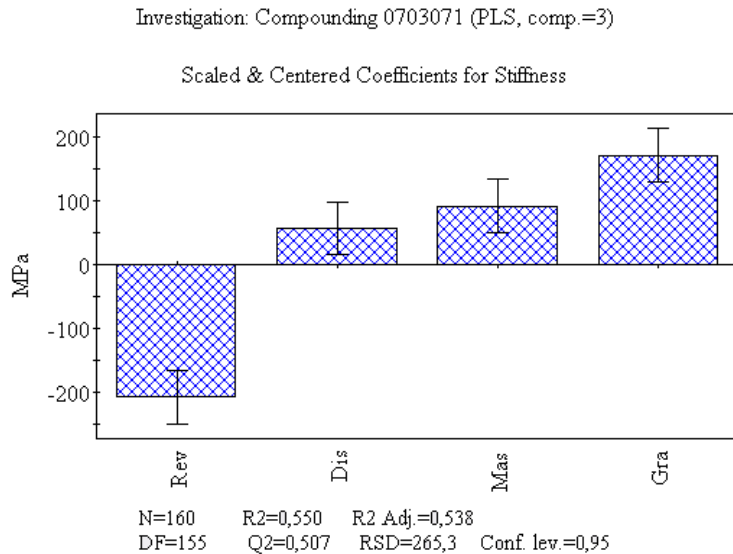


Figure 3. Coefficients for stiffness model

High screw speed is negative while many dispersing elements, high mass flow and long granules all are positive for stiffness. The  $R^2$  and  $Q^2$  values are lower for the stiffness model than for the strength model i.e. the parameters does not describe the stiffness changes as well as they describe strength changes. The interaction effects between parameters have low significance and are therefore all excluded from the model (Fig.3).

High screw speed, long granules and high mass flow influences are positive for both strength and stiffness.

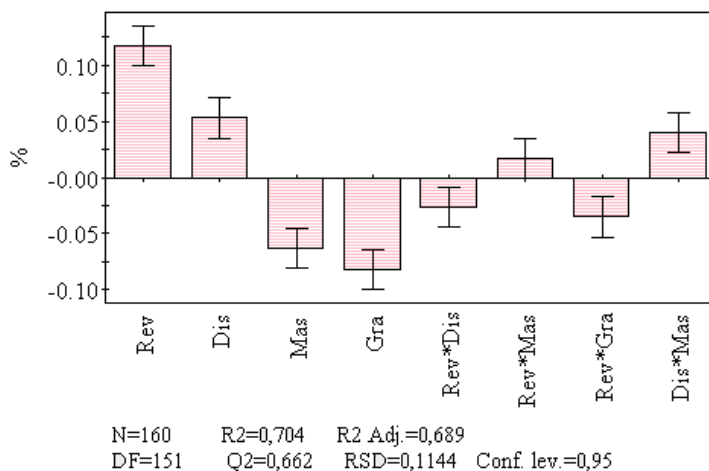


### Strain model

In the following discussion regarding strain it is considered advantageous to keep the parameters on the level that results in a material with higher strain, although this is not necessarily a requirement for good mechanical performance.

Investigation: Compounding 0703071 (PLS, comp.=3)

Scaled & Centered Coefficients for Strain

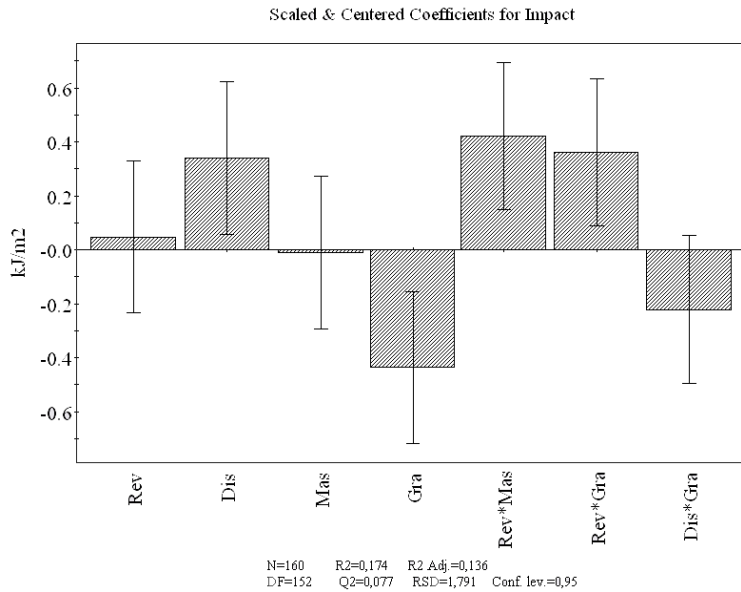


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Figure 4. Coefficients for the Strain model

For strain contrary to strength and stiffness high screw speed is positive if high strength is wanted. Many dispersing elements, low mass flow and short granules are also preferable to achieve high strain. In this model significant interaction between many of the parameters is observed. The largest interaction effect is between number of dispersing elements and mass flow, keeping both these parameters on the same level is positive for strain (Fig. 4).

## Impact strength model



*Figure 5. Coefficient for Impact strength*

It can be seen from fig. 5 that the predictive power is low for the Impact strength model. The most important parameters are the dispersing elements and the granule length. Since the fit is so low the impact strength results are not considered for further evaluation.

## Fiber Length models

For the following models only one output result is considered in each case. One set of approximately 400 fibers has been measured in each case. The maximum and the average length for each group of fibers have been used in the analysis (Fig.6 and Fig 7).

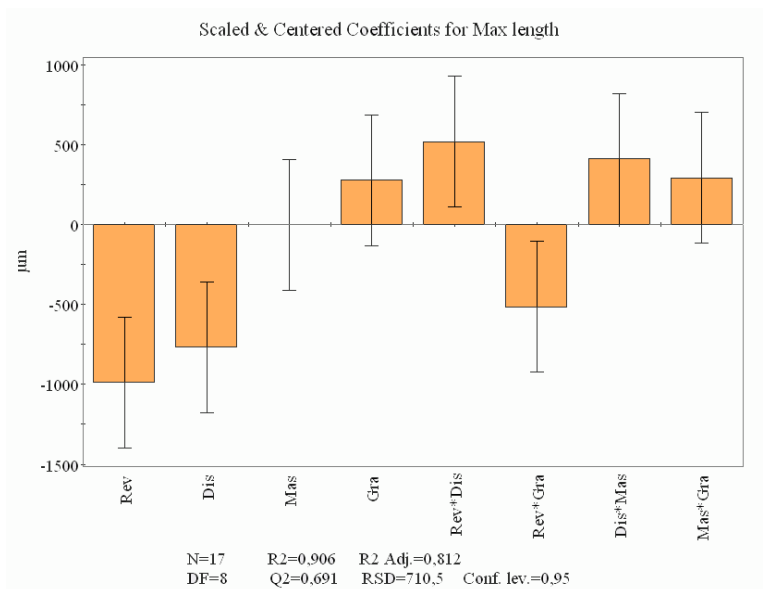
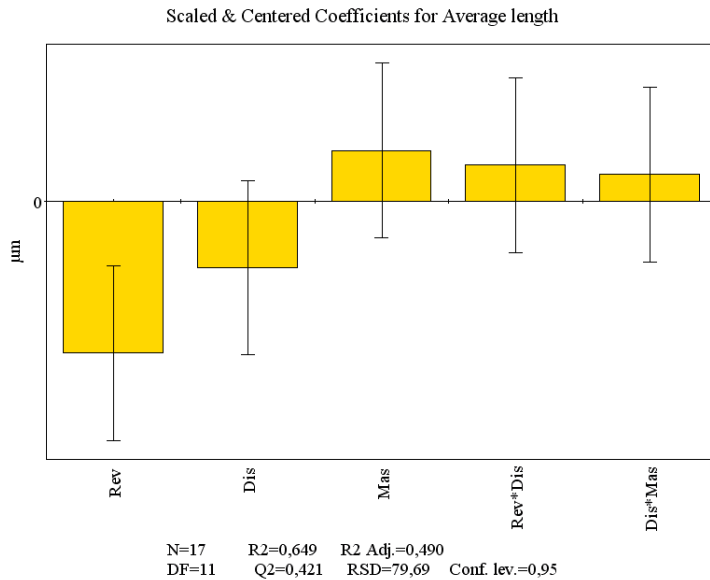


Figure 6. Coefficients for the maximum length

It could be expected that the longest fibers should be found in materials produced with long granules; this model indicates that granule length has significance only as an interaction coefficient with screw speed. High screw speed and many dispersing elements are negative for maximum length and mass flow has no significant effect. Since the model is based on one single measurement (the longest fiber in one set of ca. 400 fibers for each experimental setup) the importance of this model should not be overestimated (Fig. 6). However this model indicates that the best setup for achieving long granules is the setup that also gives highest strength and stiffness; therefore it still has some relevance. The fiber length distributions give further information about how the processing parameters affect the microstructure.



*Figure 7. Coefficients for the Average length model*

To get a high average length low screw speed is the main factor. The rest of the factors have very low significance (Fig. 7). It is obvious that fiber length can not be represented by only one value (average or maximum length). Therefore it is important to look at the fiber length distributions as well. But both these models indicate the importance of low screw speed which is in agreement with the models for strength and stiffness. This is in accordance with the theory. The setup that gives the most advantageous fiber lengths should give the best mechanical performance.

### **Fiber length distributions, the effect of processing parameters**

In Fig.8 fiber length distributions in the granules used for injection molding of the different specimens are shown. In a) all long granules produced with few dispersing elements, b) all short granules produced with few dispersing elements, c) all long granules produced with many dispersing elements and in d) all short granules produced with many dispersing elements are shown.

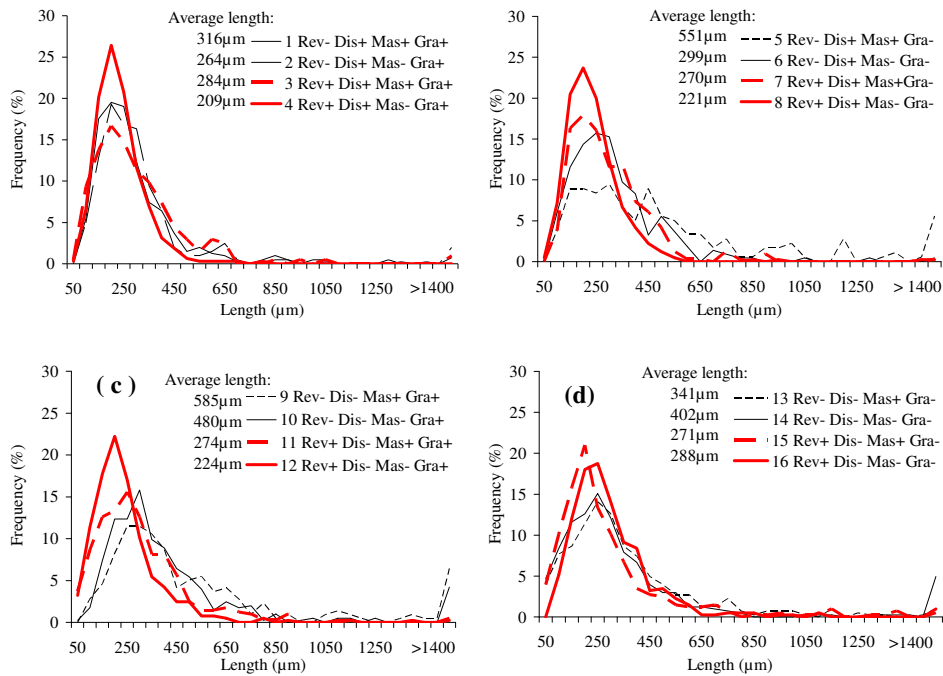


Figure 8. Fiber length distribution in materials produced with a) many dispersing elements and long granule, b) many dispersing elements and short granules. c) few dispersing elements and long granules and d) few dispersing elements and short granules

Some quite large differences can be found in the fiber length distributions. In Table 5 the change going from high to low for each parameter is presented as key values calculated from the corresponding fiber distributions.

The influence of screw speed on fiber length distribution, Table 5 Rev+→Rev- and Fig.8:

When all other parameters are held constant going from high to low screw speed gives higher average length in all cases, the change is larger than 100% in the two cases with few dispersing elements and long granules and also in the case with many dispersing elements, high mass flow and short granules. The maximum frequency peak is decreased in all cases but one, when all other parameters are on high level. For 5 of the material- couples fiber length of the frequency peak is increased while for the remaining three couples it is unaffected.

The influence of number of dispersing elements on fiber length distribution, Table 5 Dis+ →Dis- and Fig. 8:

When all other parameters are held constant going from high to low number of dispersing elements result in higher average length in 5 cases. The frequency peak is decreased in 6 cases but all changes are smaller than 10%. Fiber length of the frequency peak is increased in 4 cases, unaffected in 3 and decreases in one.

The influence of mass flow on fiber length distributions, Table 5 Mas+ →Mas- and Fig.8:

When all other parameters are held constant, going from high to low mass flow result in lower average length in 6 cases. The change is smaller than 20 % in all cases but two. The frequency peak is increased in the case when all other parameters are on high level otherwise the changes are small. Fiber length of the frequency peak is increased in 1 case, unaffected in 5 and decreases in 2.

The influence of granule length on fiber length distributions, Table 5 Gra+ →Gra- and Fig. 8:

Going from high to low granule length gives lower average length in 5 cases when all other parameters are held constant. The change is smaller than 20 % in all cases but two. The frequency peak is decreased in 1 case, increased in 6 and unaffected in 1. Fiber length of the frequency peak is increased in 1 case, unaffected in 5 and decreases in 2.

Table 5. Summary of the influence of each parameter on key properties of the fiber length distributions

	<b>Rev+ →Rev-</b>	<b>Change of Average fiber length (%)</b>	<b>Change of frequency in Maximum peak (%)</b>	<b>Change of Length in maximum frequency peak (%)</b>
3-1	Dis+ Mas+ Gra+	11	16	0
4-2	Dis+ Mas- Gra+	26	-7	0
7-5	Dis+ Mas+ Gra-	104	-8	50
8-6	Dis+ Mas- Gra-	35	-8	25
12-10	Dis- Mas- Gra+	115	-6	50
11-9	Dis- Mas+ Gra+	113	-4	20
16-14	Dis- Mas- Gra-	39	-4	0
15-13	Dis- Mas+ Gra-	26	-7	25
<b>Dis+ →Dis-</b>				
3-11	Rev+ Mas+Gra+	-4	-7	25
4-12	Rev+ Mas- Gra+	7	-4	0
2-10	Rev- Mas- Gra+	82	-4	50
1-9	Rev- Mas+ Gra+	85	-8	50
8-16	Rev+ Mas- Gra-	30	-5	25
7-15	Rev+ Mas+ Gra-	0	3	0
6-14	Rev- Mas- Gra-	35	-1	0
5-13	Rev- Mas+ Gra-	-38	5	-17
<b>Mas+ →Mas-</b>				
3 -4	Rev+ Dis+ Gra+	-26	58	0
1 -2	Rev- Dis+ Gra+	-17	0	0
7-8	Rev+ Dis+ Gra-	-18	6	0
5 -6	Rev- Dis+ Gra-	-46	6	-17
9-10	Rev- Dis- Gra+	-18	4	0
11 -12	Rev+ Dis- Gra+	-18	7	-20
13 -14	Rev- Dis- Gra-	18	1	0
15 -16	Rev+ Dis- Gra-	7	-2	25
<b>Gra+ →Gra-</b>				
1-5	Rev- Dis+ Mas+	74	-51	50
2-6	Rev- Dis+ Mas-	13	-4	25
3-7	Rev+ Dis+ Mas+	-5	1	0
4-8	Rev+ Dis+ Mas-	6	-3	0
12-16	Rev+ Dis- Mas-	29	-3	25
11-15	Rev+ Dis- Mas+	-1	5	-20
10-14	Rev- Dis- Mas-	-16	-1	-17
9-13	Rev- Dis- Mas+	-42	3	-17

To summarize the effect of the parameters on fiber length distributions:

- Lower screw speed has a clear positive influence on fiber length distribution. In all cases average length is higher and the frequency peak is moved towards longer lengths.
- Fewer dispersing elements has similar effect as low screw speed but the effects are not as strong and clear-cut.
- Low mass flow has the strongest negative effect. In most cases average length decreases and more short fibers are produced.
- Short granules do not have as negative effect as expected. Even though the long granules are more than twice as long as the short the effect is not very consistent.

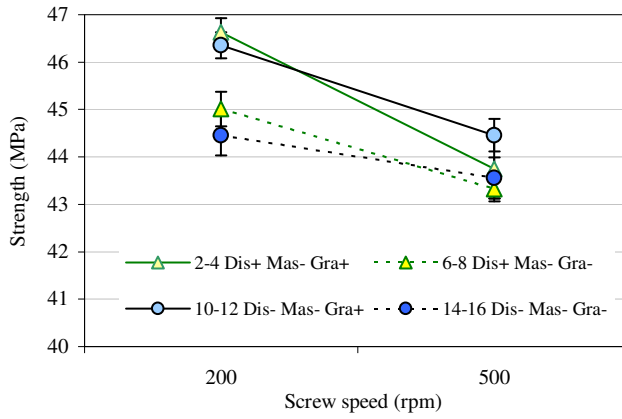
### **The effect of processing setup on mechanical properties**

In Fig. 9 to Fig. 11 the effect of the processing parameters on strength, stiffness and strain are shown. All materials produced with low massflow are found in diagrams (a) and materials produced with high massflow are shown in diagrams (b).

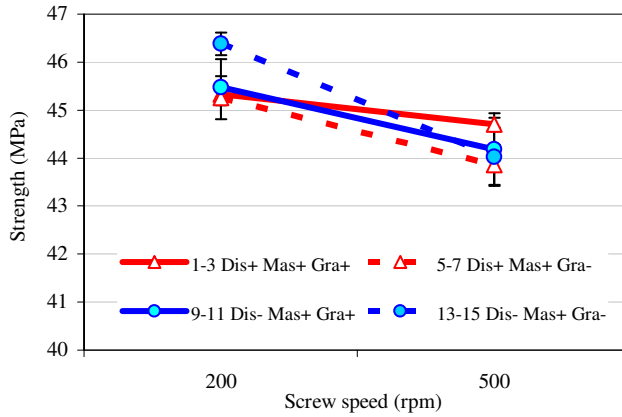
#### Strength, the effect of processing parameters

In Fig. 9 a) the largest effect on composite strength can be seen. It is achieved when the specimens are produced with low mass flow, many dispersing elements, long granules and screw speed is changed from 200 to 500 rpm. All materials produced with low screw speed are better than the ones produced with high screw speed (the other parameters kept constant), but the differences are quite small and in some cases not significant. The statistical analysis indicated that many parameters interact. The long granules seem to be beneficial only when mass flow is low. The effect of dispersing elements is not easy to interpret. It seems to be slightly advantageous to use many dispersing elements when screw speed is low and mass flow is low.





a)



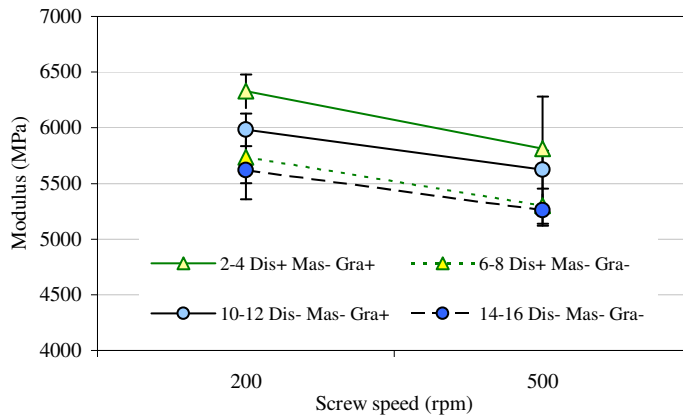
b)

Figure 9. Strength of materials produced with fixed a) low mass flow and b) high mass flow

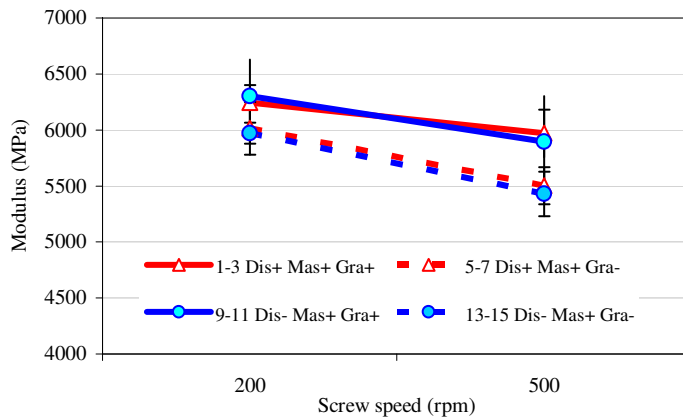
The difference between the worst and the best material is only 3MPa. This can be compared to the case where no adhesion promoter was used. The strength for this material was 13 MPa lower than the best material from the factorial trials and 10 MPa lower than the worst thus improvement of adhesion has much more significant effect on strength than any of the processing parameters.

### Stiffness, the effect of processing parameters

Decreasing screw speed has similar effect on stiffness as on strength (Fig. 10). Here the effect of the long granules can be seen. The modulus is almost 0.5 GPa which is 8% lower when short granules are used compared to long granules. The modulus is slightly higher when high mass flow has been used. Number of dispersing elements is slightly better only when mass flow is low. With high mass flow the effect from dispersing elements is negligible.



a)



b)

Figure 10. Stiffness of materials produced with constant a) low mass flow and b) high mass flow

The material with the lowest stiffness had a Young's modulus of 5.3GPa while the stiffest material had 6.3GPa. The midpoint with and without MAPP had no significant difference in modulus (the average values of 5.4 GPa and 5.6 GPa) thus increased adhesion does not have significant effect on stiffness.

#### Strain, the effect of processing parameters

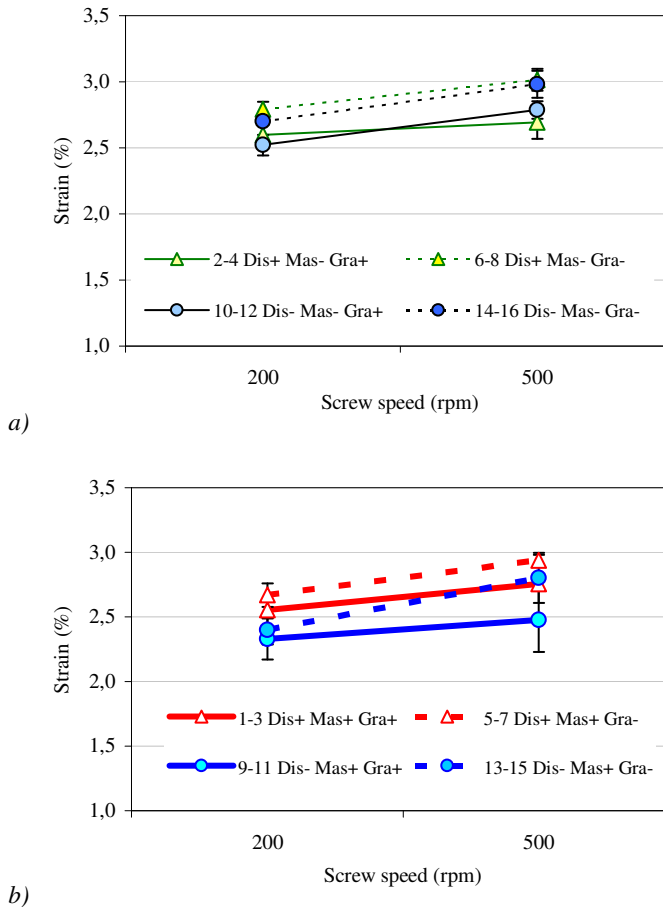


Figure 11. Strain of materials produced with constant a) low mass flow and b) high mass flow

Decreasing screw speed has the opposite effect on strain compared to stiffness and strength. Strain is reduced when screw speed is decreased. This effect is larger for materials produced with short granules.

Strain varies between 2.3% and 3%. The midpoint with and without MAPP had strains of 2.7-2.8% i.e. no significant difference.

## **SUMMARY**

### **Statistical analysis**

Regression models have been applied based on  $2^4$  factorial designed processing trials where four factors in the compounding process have been tested on two levels. Screw speed, number of dispersing elements, mass flow and granule length were selected as input factors. Strength, stiffness, strain, un-notched charpy impact strength, average and maximum fiber length were selected as responses.

The model for impact strength had low fit and very low predictive power. For the rest of the measured responses models with high predictive power and good fit have been achieved.

The most important factor for all models was screw speed. Only screw speed has significant influence on average fiber length. This parameter is also important for other output responses, such as stiffness and strength. This conclusion is well in agreement with the fact that fiber length has large influence on mechanical properties.

### **Mechanical properties**

The regression analysis implies that the level on the tested processing factors have significant influence on the mechanical properties.

Lower screw speed gives a material with higher strength and stiffness. Strain on the contrary, decreases when low screw speed is used.

Higher mass flow is positive for strength and stiffness but leads to reduced composite strain.

The number of dispersing elements had lower significance than expected. Significance for this factor is very low for strength. For stiffness the larger number of dispersing elements is positive but the influence is quite small. For strain, the use of many dispersing elements leads to higher strain. For strain the number of dispersing elements

also interacts with mass flow-if both these factors are either high or low simultaneously, the effect is positive.

Granule length had quite high influence on all mechanical properties. It is the second most important factor except for impact strength where it is the most important factor. The longer granules are positive for strength, stiffness and impact strength and negative for strain.

### **Microstructure**

In this study we have focused on the compounding process. Therefore the microstructure study was limited to measurements of the fiber length distributions in granules, i.e. excluding possible further fiber cutting in the injection molding process.

The study indicates that low screw speed preserves fiber length better but this effect is more pronounced when the extrudate is cut into longer granules.

Using many dispersing elements makes the fiber length more homogenous but the average length becomes shorter. However, if the screw speed is high this effect is not as pronounced.

The effect of mass flow on fiber average and maximum length seems to be negligible.

We can conclude that even if we can see that all the studied parameters affect fiber length and the differences are quite large, the effect on the mechanical properties is quite low. It is evident that average fiber length is decreased by increasing the rotation speed of the screw (while other parameters are fixed). Changes of fiber length causes changes of strength and stiffness: better mechanical performance is obtained for composites with longer fibers. However these changes are much lower than what could be expected from a micromechanical point of view. Since the differences in fiber length distribution in the granules (prior to injection molding) do not reflect fully on the mechanical properties it is reasonable to believe that the fiber cutting in the injection molding levels out the differences achieved in the compounding step to some extent. This statement is supported by measurements of fiber length distribution on 2 materials, produced with different amount of dispersing elements, in the uncut extrudate, granules and the injection molded testbar. The results are shown in Table 7.

Table 6. Fiber average length in extruded rod, granule and piece of testbar from material 1 and 9

Material	Type	Average length ( $\mu\text{m}$ )	Length loss compared to previous processing step (%)
1 Rev- Dis+ Mas+ Gra+	Extrudate	467	
1 Rev- Dis+ Mas+ Gra+	Granule	336	27
1 Rev- Dis+ Mas+ Gra+	Testbar	241	27
9 Rev- Dis- Mas+ Gra+	Extrudate	1047	
9 Rev- Dis- Mas+ Gra+	Granule	572	45
9 Rev- Dis- Mas+ Gra+	Testbar	292	49

From Table 6 one can conclude that for the material that initially contains longest fibers the cutting into granules reduces average length more in relative number than for the material containing quite short fibers. This relation is also true for the injection molding process. The relative fiber length decrease is higher for granules with longer fibers. Similar results have been reported in the literature for various types of fibers by Franzén et al [3]. They found that lower force was needed for breaking a long fiber than a short. Already in 1959 Forgas and Mason studied the flow of Rayon and Dacron fibers in sheared suspension and found that longer fibers were more bent than short [10].

### Final remarks

In this study the mechanical properties of composites, produced with different processing setup but the same fiber loading and constituents (30%flax fibers and 70% PP of which 2% is MAPP), vary as follows: strength. 43 - 47 MPa, stiffness 5.3 - 6.3 GPa, strain 2.3 - 3 % and impact strength 11-14 kJ/m<sup>2</sup>. These variations are larger than the standard deviation within each material group (test specimens produced with the same setup) but the differences are still rather small. The effect of processing parameters is very low compared to the influence of adhesion promoter: removing the MAPP results in a composite with much lower strength (33MPa very close to the strength of pure PP) than any of the composites in the parameter study.

The importance of the processing setup related variations depends on what kind of product requirements the materials will have to meet.

The best setup from a microstructural point of view might not be the best from an economical point of view, especially if the gain in mechanical performance is negligible.

This work shows that the studied processing parameters in the compounding step have influence on fiber length distribution. The differences in fiber length distributions do reflect on the final microstructure and the mechanical properties of the composites but not to as large extent as expected from a theoretical point of view. A brief investigation indicated that the longer the fibers were in granules, the larger the length reduction during injection molding of the fibers. Injection molding seems to level out the differences achieved in the compounding process. It seems to be important to adjust the injection molding process to further improve this type of materials.

## ACKNOWLEDGMENTS

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## *Paper C*



# **Processing effect on Flax Fiber Composite properties**

## **Part II: Parametric study of Injection molding**

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**Key words:** microstructure, composite, flax, strength, stiffness, compounding, injection molding

### **Abstract**

The influence of injection molding on mechanical properties of short Natural Fiber Composites is studied in this work. A recent work, where the compounding process was studied demonstrated that the step when the product takes the final shape, during the injection molding process has a major effect on the microstructure and on the resulting material properties.

Factorial trials and statistical analysis is employed to investigate effects of processing parameters on microstructure and on mechanical performance. The tested parameters in the injection molding step are screw speed, cylinder temperature, injection speed and back pressure. These parameters all influence the final structure and the mechanical properties of the composites, although the differences in the material properties are rather small. The most important parameters seem to be cylinder temperature and injection speed.



## INTRODUCTION

The natural resources are limited and the world population is growing rapidly. Eventually our consumption patterns need to be readjusted. The most logical solution is to switch from using limited to renewable resources where it is possible. This is also one of the reasons why the use of natural fibers as reinforcement in composites is increasing in many parts of the world. Even if it is easy to find advantages for the renewable materials from the sustainability point of view the introduction of these in different products should be made in a conscious way. Material and process development for these materials is still needed in order to use them where their properties are advantageous.

Much work has been done to develop composites from renewable fibers i.e. natural fiber composites, NFC and also from bio-based polymers in the last decades. Compounding and injection molding is a manufacturing route that has been studied extensively [1-5]. Even though it has been shown that this process is suitable [6] and that the properties of NFC can be tailored for many applications by a proper selection of fibers, matrix and additives, a real break through in the use of this material group in the injection molding industry has not been seen yet. We believe that there is a need to find the limitations of the materials and to optimize processing accordingly. The microstructure of the materials defines the mechanical properties of the product and the processing strongly affects the final microstructure. In [7] the microstructure and strength relation was studied and it was found that processing is the main obstacle for producing strong NFC by compounding and injection molding. Much work remains before the processing is adapted and tuned for production of natural fiber composites with optimal properties. As it seems the main challenge is to preserve the fiber length throughout the processing cycle.

In a recent work the influence of different processing parameters in the compounding step was examined (Part I) [8]. It was found that even if the process parameters could be optimized to increase the fiber length in the compound the mechanical properties did not improve as much as expected. This indicated that the injection molding process is responsible for the most severe degradation of fiber length. This paper, part II is focused

on the injection molding (using equipment developed mainly for glass fiber composites) and combinations of polypropylene (PP), maleic anhydride grafted PP (MA) and flax fibers (FF). The objectives are i) to evaluate to what extent the processing conditions affect the final material properties, ii) to find the best processing setup and iii) to identify processing parameters that can be further optimized.

## **EXPERIMENTAL**

### **Materials**

A homopolymeric polypropylene (PP), Adstif 770 ADXP from Montell with a high melt flow index of 45g/10min was used as matrix. Epolene E-43 maleic anhydride modified PP (abbreviated as MAPP or M further in the text) from Eastman Chemicals was used as adhesion promoter. Spun enzymatically retted flax fiber (FF) roving from Finflax was used as reinforcement. All materials have the same amount of fibers, matrix and MAPP except one where MAPP is replaced with PP.

### **Processing**

Prior to compounding the fibers were dried in an oven at 105 °C for at least 4 hours. The constituents were compounded in a Krupp Werner & Pfleiderer ZSK 25 WLE co-rotating twin screw extruder with l/d of 44. The fiber weight fraction was controlled by the speed and ascent/revolution on the side screw. The compound was pulled through a water bath and cut to 10mm long and approximately 5 mm in diameter granules using an SF Sheer granulator. The granules were oven dried at 105 °C for at least 4 hours prior to injection molding. Test specimens were injection molded at Polymertekniskt centrum in Färgelanda, Sweden on an Engel ES 200/50 machine with maximum clampforce of 50 ton and shot size of 88g (polystyrene at 1000 bars). The injection molded specimens were dogbone shaped and had a total length of 175 mm with a centre cross section area of 10x2.2 mm<sup>2</sup>.

### **Full factorial trials**

The experimental design used here is full factorial trials. Four factors (parameters) are varied in the injection molding process. From the previous compounding trials the best process setup was selected [8] (resulting in the strongest and stiffest composites) to produce granules for the 17 different injection molding trials. Four processing parameters are tested on high and low level and one midpoint as follows: the injection speed (low 15

- mid 35 - high 70 mm/s), the screw speed (low 94 - mid 150 - high 360 rpm), the back pressure (low 1- mid 5- high 15bar) and the cylinder temperature (low 170 - mid 190 - high 210°C) in the injection molding step.

These are all parameters that can easily be adjusted in the machine control system. It should be mentioned that there are many more parameters that most likely influence the microstructure of the composite for example inlet dimensions, dimension changes and shape of the runners, the shape of the screw etc. But rebuilding of the equipment was not in the scope of this study.

The studied output responses were: fiber length, fiber orientation, tensile strength, tensile stiffness and strain at maximum stress. The process setup for each trial and the abbreviations used from now on are listed in Table 1.

*Table 1. Processing setup for materials produced with different injection molding setups*

<b>Material abbreviation</b>	<b>Injection speed (Inj)</b>	<b>Screw speed (Scr)</b>	<b>Back pressure (Bac)</b>	<b>Cylinder temperature (Cyl)</b>
1 Inj+ Scr+ Bac+ Cyl+	+	+	+	+
2 Inj+ Scr- Bac+ Cyl+	+	-	+	+
3 Inj+ Scr+ Bac- Cyl+	+	+	-	+
4 Inj+ Scr+ Bac+ Cyl-	+	+	+	-
5 Inj+ Scr- Bac- Cyl+	+	-	-	+
6 Inj+ Scr- Bac+ Cyl-	+	-	+	-
7 Inj+ Scr+ Bac- Cyl-	+	+	-	-
8 Inj+ Scr- Bac- Cyl-	+	-	-	-
9 Inj- Scr+ Bac+ Cyl+	-	+	+	+
10 Inj- Scr- Bac+ Cyl+	-	-	+	+
11 Inj- Scr+ Bac- Cyl+	-	+	-	+
12 Inj- Scr+ Bac+ Cyl-	-	+	+	-
13 Inj- Scr- Bac- Cyl+	-	-	-	+
14 Inj- Scr- Bac+ Cyl-	-	-	+	-
15 Inj- Scr+ Bac- Cyl-	-	+	-	-
16 Inj- Scr- Bac- Cyl-	-	-	-	-
17 Inj0 Scr0 Bac0 Cyl0	0	0	0	0



## **Characterization of microstructure by image analysis**

### **Fiber orientation and dispersion**

Composite surfaces of injection molded FFC specimens of size 10x30 mm<sup>2</sup> were polished on a Struers Rotopol-1 grinding machine. Images obtained from Olympus BH-2 microscope were analyzed using the software Analysis distributed by SIS (Soft imaging systems).

### **Fiber length measurements**

Fibers were extracted from injection molded composite pieces by Soxhlet extraction using xylene. Fiber length measurements were done using an optical microscope Olympus BH-2 and the software Analysis distributed by SIS (Soft imaging systems).

### **Mechanical testing**

Mechanical testing was carried out on an Instron 8501 testing machine. Tensile tests were done according to ISO 527-2 standard. Displacement controlled test with cross head speed of 2 mm/min and distance between clamps of 124 mm was carried out. At least five specimens of each material composition were tested.

### **DSC analysis**

Differential scanning calorimetry using a Perkin Elmer TGA 7 with nitrogen (flow rate 20 ml/min) was applied. The samples were encapsulated in aluminium pans with two holes in the top. Specimens of 15-20 mg were tested at 10°C/min heating rate within - 50°C – +220°C temperature interval.

## **RESULTS AND DISCUSSION**

A 2<sup>4</sup> full factorial trial generates a very large amount of data. The data is presented as condensed as possible in a way which gives insight in what effect the four parameters have on microstructure and on the mechanical performance of the flax fiber composites.

### **Statistical evaluation of parameter importance**

The factorial trials were evaluated using the statistical analysis software MODDE from Umetrics [9]. The software calculates a multiple linear model for each output response by projection to latent structures, (PLS) on the form:

$$y = a_0 + a_1 x_1 + a_2 x_1^2 + a_3 x_1 \cdot x_2 \dots + a_n x_n$$

where  $y$  is a response,  $a_i$  the approximation coefficients,  $x_i$  the  $i$ -th parameter. The PLS regression coefficients are identical to those obtained by multiple regression but PLS can deal with many responses simultaneously, taking their covariance's into account. This provides us with an overview of how all the factors affect all the responses. PLS also calculates all interaction effects.

The goodness of fit is expressed as Correlation Coefficient  $R^2$ ,  $R^2_{adjusted}$  and the Cross-Validity Correlation Coefficient,  $Q^2$  for each model. These coefficients will take values between 0 and 1: if these coefficients are close to 0 there is no linear relationship between  $x$  and  $y$ , if they equal 1, the model explains the studied output response.  $R^2$  and  $Q^2$  should deviate as little as possible. A high  $R^2$  while  $Q^2$  is low indicates that there are many insignificant factors in the model, many interaction terms and so on added. From [9] a deeper insight in PLS can be gained.

The calculated coefficients,  $a_i$  for each factor, for each PLS model are presented in Table 2.

Table 2. Coefficients for the PLS models

	Tensile strength (MPa)	Tensile stiffness (MPa)	Strain at max stress (%)
<b>Constant</b>			
	46.7	6504	2.66
<b>Main factors</b>			
Injection Speed	- 0.63	-205	-0.016
Screw Speed	-0.24	-75.6	0.003
Back Pressure	-0.50	-50.1	0.063
Cylinder Temperature	-1.26	-256	0.053
<b>Interaction effects</b>			
Inj x Scr	0.20		-
Inj x Bac	-	55.7	-
Inj x Cyl	1.04	191	-0.050
Scr x Bac	-0.25	-73.9	0.009
Scr x Cyl	0.19		-0.024
Bac x Cyl	0.21	74.1	-0.024
<b>Model fit and predictive power</b>			
$R^2$	0.83	0.48	0.19
$Q^2$	0.80	0.42	0.10

In these models each main factors has some influence for all the responses (see Table 2). The  $R^2$  and  $Q^2$  values are close to 0.8 for the strength model while quite low values for the stiffness- and strain models. The low values for these models indicate that these parameters do not correlate with the measured differences in stiffness and strain very well.

In Figure 1 to 3 the coefficients for each response are presented, error bars showing the significance of each coefficient. In the models the values of the factors,  $x_i$  only takes values -1 (when the factor is on low level), 0 (factor in midpoint) and 1 (factor on high level) thus for the low level to have positive influence the coefficient has to be negative.

Below each plot you will find  $N$  the total number of experiments,  $DF$  the number of experiments minus missing values,  $R^2$  and  $Q^2$ ,  $R^2_{adjusted}$  the fraction of variation of the

response explained by the model adjusted for degrees of freedom, *RSD* the residual standard deviation which is used in the computation of confidence interval for coefficients and the Confidence level.

### Strength model

Figure 1 shows that the predictive power of the strength model is quite high, both  $R^2$  and  $Q^2$  are close to 0.8. The most important parameter is cylinder temperature. Low temperature gives higher strength. All the main parameters give higher strength if they are held on the low level. There is also a rather strong interaction effect between cylinder temperature and injection speed. The other interaction effects are of minor importance according to this model.

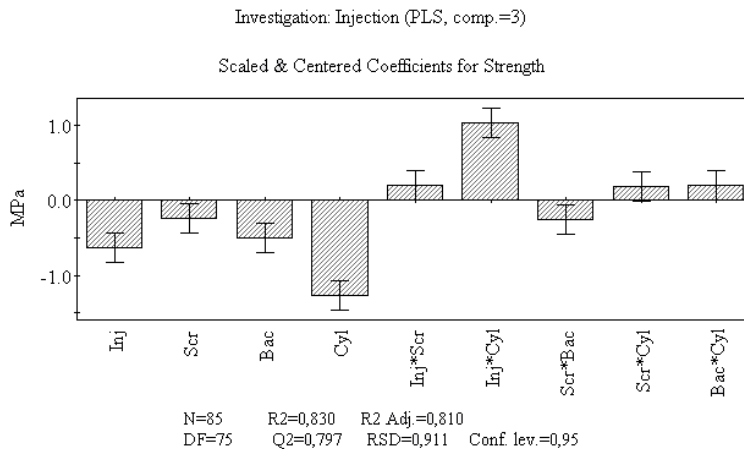


Figure 1. Coefficients for the Strength model

### Stiffness model

Figure 2 shows that the stiffness model has quite low predictive power, both  $R^2$  and  $Q^2$  are below 0.5. The most important parameter is again cylinder temperature but injection speed is almost as important. All the main parameters give higher stiffness if they are held on the low level. There is also rather strong interaction effect between cylinder temperature and injection speed.

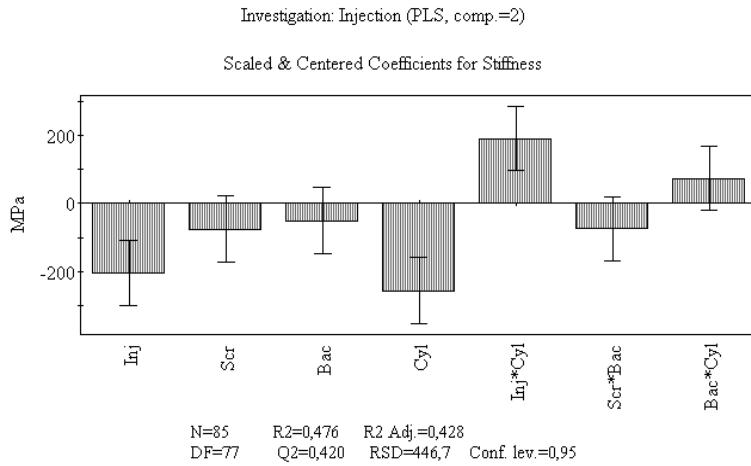


Figure 2. Coefficients for the Stiffness model

### Strain model

Figure 3 shows that the predictive power of the strain model is quite low,  $R^2$  is 0.189 and  $Q^2$  is below 0.1. Cylinder temperature and backpressure and the interaction effect between cylinder temperature and injection speed are the only significant parameters.

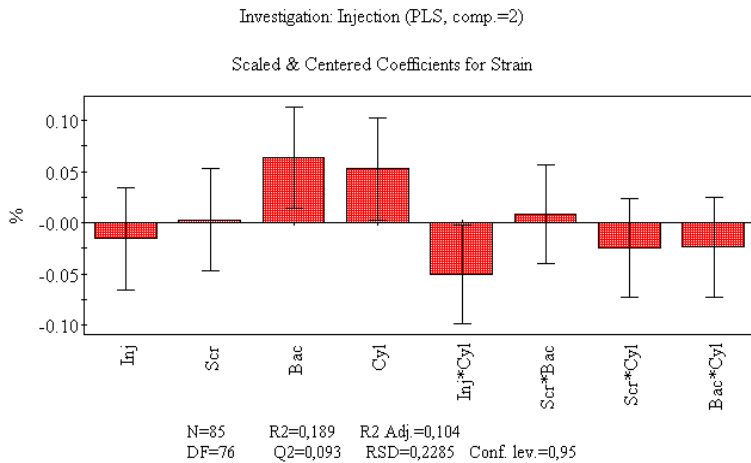


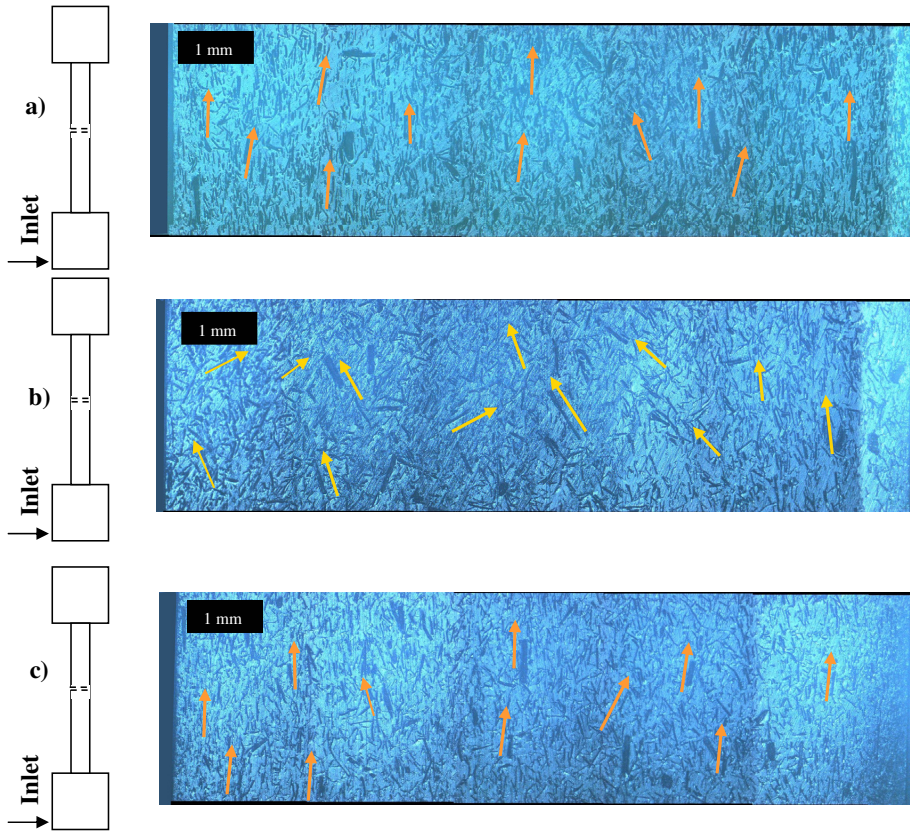
Figure 3. Coefficients for the Strain model

## **Results from characterization of microstructure**

The differences between the mechanical properties of these 17 materials were expected to be reflected in their microstructure.

### Fiber orientation

Two materials with high (14 and 15) and two materials with low (10 and 1) strength produced under the same conditions except high and low cylinder temperature, were studied by image analysis. Images taken from two of the specimens, material 14 and 10 are shown in Figure 4 a) to c). For material 14 two depths were studied just below the surface (Fig. 4 a) and closer to the midplane (Fig. 4 b) of the material. Material 10 was studied only close to the surface. All images are taken at the same position on the specimens (see Figure 4).



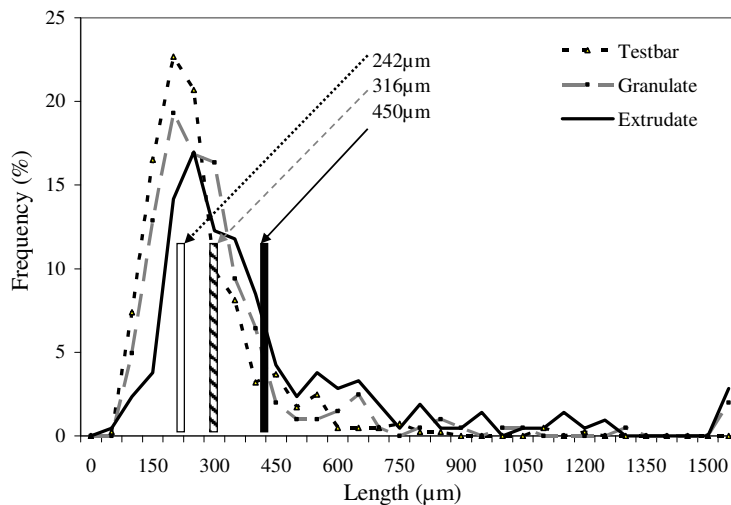
*Figure 4. Cross-section of the specimens a) material 14 close to surface, b) material 14 close to the middle with respect to the thickness c) material 10 close to the surface*

It is clear that fiber orientation in specimen 14 varies through the thickness (see Fig. 4 a and b). Close to the surface (Fig. 4a) the fibers seem to be quite well aligned, especially along the sides of the specimen while closer to the midplane (Fig. 4b) the fibers are quite randomly distributed. The difference within one specimen at different depths is larger than the difference between two specimens produced with different injection molding set up (compare Fig. 4 a and b with Fig. 4 a and c). Sample 14 seems to have a bit more pronounced fiber orientation than sample 10 but the depths might differ slightly between these two samples, thus no distinct conclusions can be drawn. No distinct differences could be found between material 15 and 1 either; therefore no images are shown from these measurements. According to these results, the factors considered for this analysis do

not affect fiber orientation in any way. This implies that fiber orientation is not responsible for the differences in the composites mechanical properties, at least not to any large extent. This type of layered structure in injection molded PP has been documented by others [10].

#### Fiber length distribution before and after injection molding

The fiber distributions in i) an extruded uncut rod, ii) from 10 mm granules and iii) from an injection molded specimen were measured in order to compare how compounding and injection molding influences the fiber length degradation. The result is shown in Figure 5.



*Figure 5. Fiber length distribution in the uncut extruded rod, in 10 mm granules and in a testbar from the same material and processing setup*

Figure 5 shows that very few fibers are longer than 1 mm: in the uncut compound 7%, in the granules 3% and in the testbar less than 1 %. However the number of very small fibers is very significant: 20% of the fibers in the uncut compound, almost 40% of the fibers in the granules and finally almost 50% of the fibers in the testbar are smaller than 200μm. The average length is reduced by almost a factor 2 going from uncut compound to testbar resulting in an average fiber length in the testbar of approximately 240μm compared to 450μm in the uncut compound. These results indicate that the injection molding process indeed must be optimized in order to prevent dramatic degradation of the average fiber length.



### Process parameters influence on final fiber lengths

To study the effect of the process parameters on fiber length, fibers were extracted from material 14, 10 and 2 and the fiber length distributions were analyzed. One material was produced with low cylinder temperature, and one with high injection speed, all with low screw speed and high backpressure. The results are shown in Figure 6.

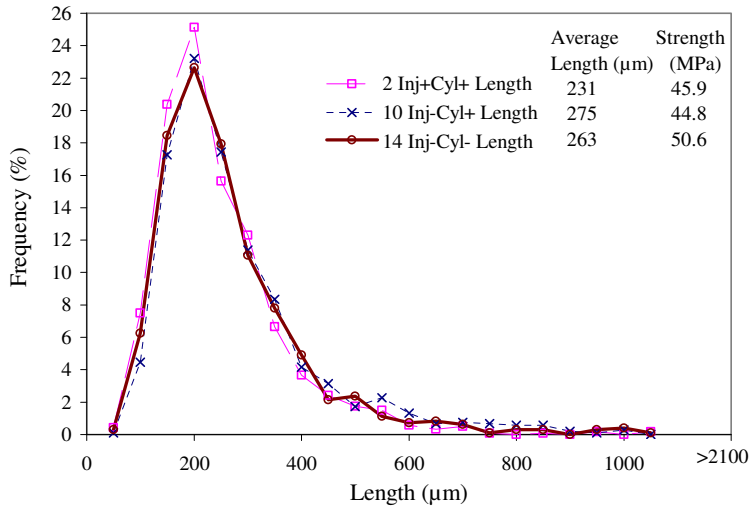


Figure 6. Fiber length distribution in material 2, 10 and 14

The fiber length distributions are very similar in these three materials (Figure 6). The material produced at high injection speed (material 2) has slightly higher amount of short fibers than the ones (10 and 14) produced at low injection speed. Different cylinder temperature does not seem to have any influence on fiber length distribution if all other parameters are constant (material 10 compared to 14). It seems as the differences in strength can not be explained from the fiber length distributions.

### **Analysis of mechanical testing**

The mechanical properties are presented as a function of the main factor Cylinder Temperature in Figure 7 to Figure 9.

### Strength, the effect of processing parameters

The effect from cylinder temperature change is only significant when injection speed is low (see Fig. 7 a: 15-11, 16-13 and Fig. 7 b: 14-10, 12-9). In the case when back pressure and screw speed are high this effect is small (12-9). The biggest effect from changing the cylinder temperature is achieved when injection- and screw speed are low and back-pressure is high (14-10), the strength difference in this case is almost 12%.

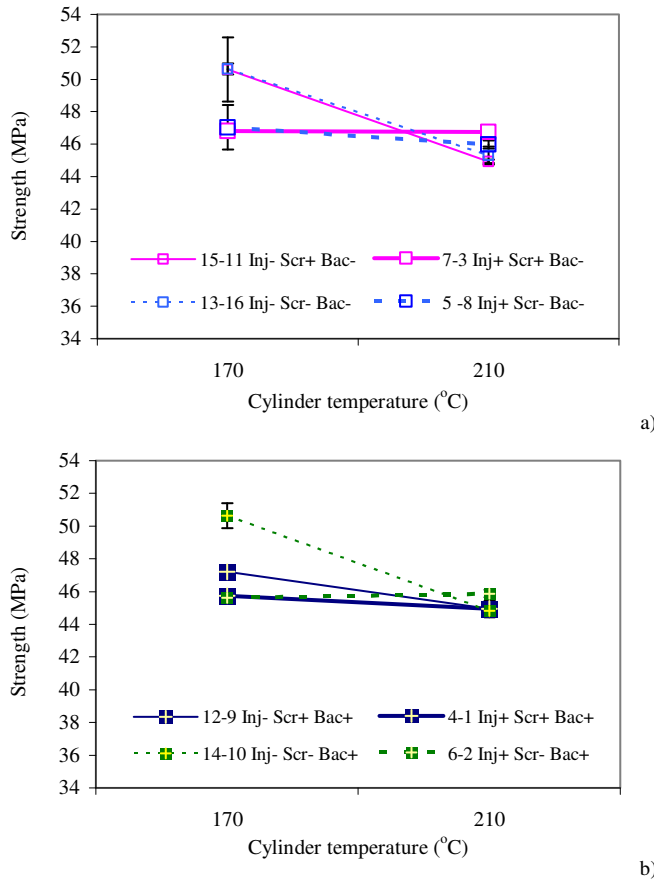


Figure 7. The strength of materials when cylinder temperature is changed from high to low at a) low back pressure and b) high backpressure

### Stiffness, the effect of processing parameters

The effect of the process parameters on stiffness is more complex and the differences are smaller. There is an indication of increase of stiffness for materials produced at low back

pressure when cylinder temperature is decreased (see Fig. 8a). The effect is similar when backpressure is high and injection- and screw speed are low (see Fig. 8 b:14-10).

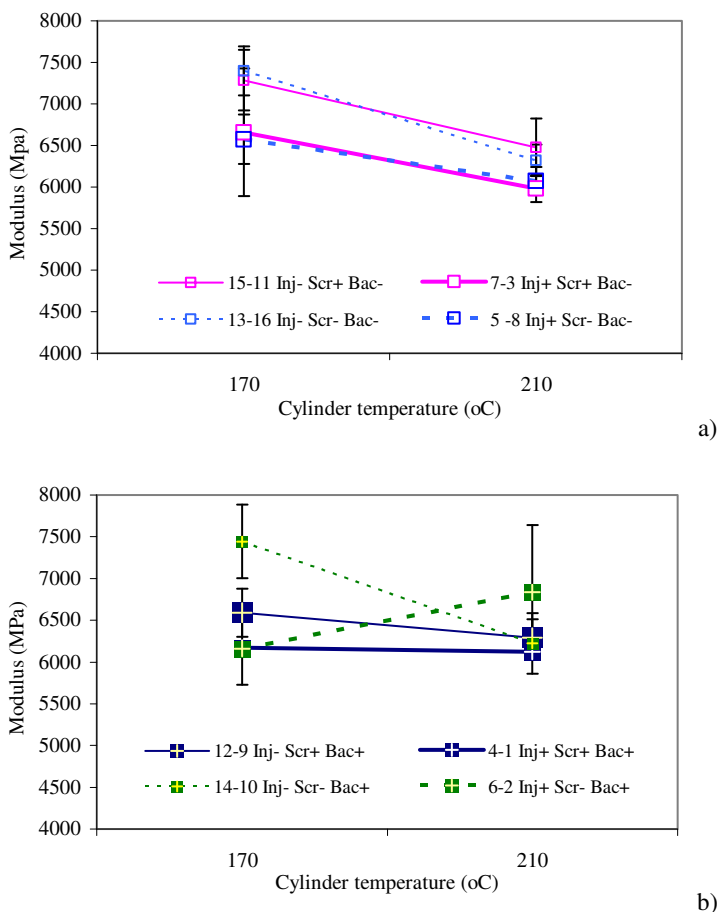
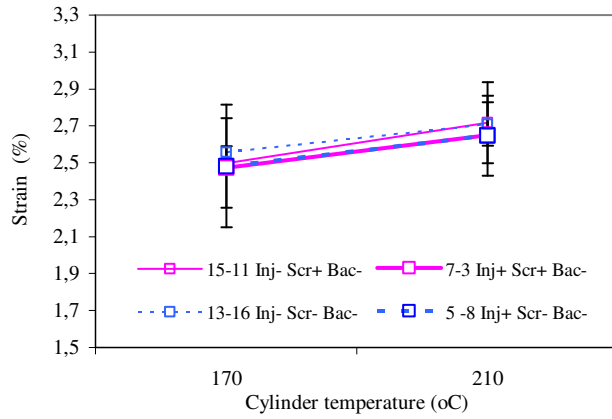


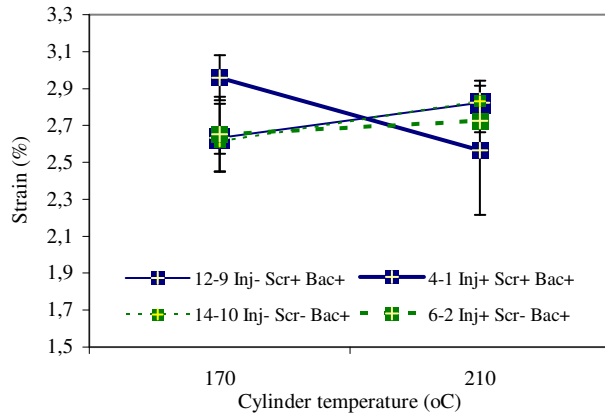
Figure 8. The stiffness of materials when cylinder temperature is changed from high to low temperature with a) low back pressure and b) high backpressure

### Strain, the effect of processing parameters

The effect from the different parameters on strain is very small. Most of the data points overlap (see Fig. 9). This explains the very low significance of the PLS model which indicates that these parameters do not affect the strain properties of these composites significantly.



a)



b)

Figure 9. The strain of materials when cylinder temperature is changed from high to low temperature with a) low back pressure and b) high backpressure

### DSC analysis

Since the quite large differences in strength properties can't be explained from the measured microstructure parameters (orientation and fiber length), DSC scans were performed to gain further information about the materials morphology i.e. crystallinity of the matrix. DSC scans on the matrix material, the reinforcing fibers and composite material 14 and 10 are plotted in Figure 10. For material 10 a rerun was also performed.

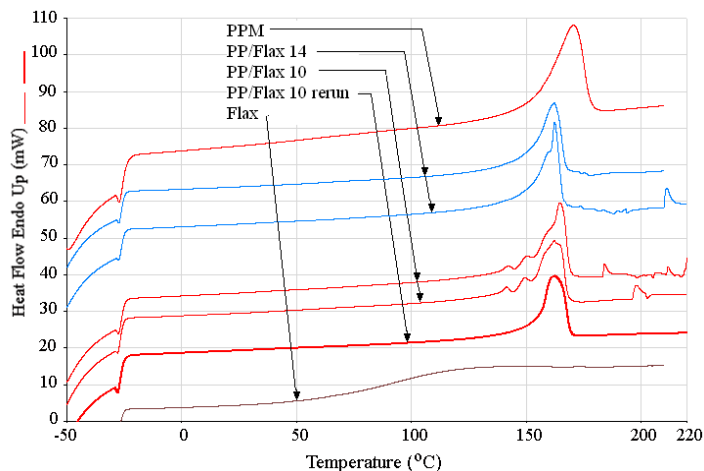


Figure 10. DSC temperature scan for PPM and flax, two runs of composite material 14 and 10 respectively and a rerun on material 10 (the curves are shifted on the y-axes)

The melt peak temperature is slightly lower in all the composite materials compared to the PPM, 170°C compared to 162°C-164°C. Material 10 has a broader melting peak area with one large and two small peaks. After cooling and a second run the smaller peaks disappear. This indicates that the higher processing temperature affects the matrix crystallization, which might explain the differences in the mechanical properties (see Fig. 10).

The formation of different crystallographic forms has been extensively investigated [11-15]. Stress-induced nucleation in reinforced PP depends on the cooling rate, fiber length, position along the fiber and viscoelastic properties of the PP melt according to [11]. Formation of  $\beta$ -spherulites is preferred in a temperature gradient according to [13]. The temperatures at which the peaks occur for material 10 relates rather well with melting temperatures of different types of crystals reported in [14]. The influence of degree of crystallinity on the mechanical properties of a PP matrix is significant according to [15]. However there might also be other mechanisms involved; in [16] isothermal TGA analysis of retted flax fibers showed around 5% mass loss after 20 minutes exposure time at 220 °C. The strength reduction was slightly above 10% after subjection to 220°C for only five minutes. The highest temperature used in the present study is 210°C and the residence time is short. The DSC scan of flax fibers shows a  $T_g$  at around 88°C but no

other effects are visible (Fig. 10) however a degradation of the fiber properties can not be completely excluded.

## **SUMMARY**

Factorial trials have been performed on the injection molding process setup for NFC containing 30 weight percentages of flax. Cylinder temperature, screw speed, injection speed and backpressure have been varied on two levels. Output parameters were the mechanical properties of the 17 batches NFC injection molded under different conditions. A regression model with quite high predictive power for strength was achieved. The regression models for stiffness and strain had lower predictive power. For selected materials also fiber orientation and fiber length distribution measurements as well as DSC analysis were performed.

The mechanical properties of the composites, produced with different injection molding process setup but the same fiber loading and constituents (30% flax fibers and 70% PP of which 2% is MAPP), vary as follows: strength. 45-51 MPa, stiffness 6.0 – 7.4 GPa, strain 2.5 - 3 %. These variations are larger than the standard deviation within each material group (test specimens produced with the same setup).

Cylinder temperature was the most important factor for all the measured mechanical properties, strength, stiffness and strain. It is possible that the fibers degrade since the high-level cylinder temperature is 210 °C. However it is possible that the differences in mechanical properties mainly originate from dissimilarity in crystal formation due to temperature variation. Initial DSC scans supports this hypothesis.

Fiber orientation was found to vary through the thickness of the test bars, having quite well aligned fibers close to the surface and almost randomly distributed fibers at the mid-plane of the same sample. The differences of fiber orientation within one specimen are larger than the differences obtained from materials produced at different processing conditions.

The degradation of fiber length in the injection molding process is quite high. A comparison between the fiber distributions in granules (after compounding) and in injection molded specimens showed that the injection molding is responsible for the most

severe fiber length degradation. This result is in agreement with results obtained after the compounding trials in [8].

Fiber length distributions in materials produced with different injection molding setup showed very small differences.

## **CONCLUSIONS**

The studied process parameters affect the microstructure of the composites marginally. The only clearly significant effect was high cylinder temperature which has negative effect on strength and only indications on that the effect is the same on stiffness. The reason for the difference in mechanical properties is ascribed either to differences in crystal formation or to thermal degradation of the fibers.

A cylinder temperature of 210 °C should probably be avoided to preserve the fibers mechanical properties.

It is a positive result that the material quality is very even for most of the processing setups that have been tested here. However, other means such as optimization of runners and inlets have to be used in order to reduce fiber cutting in the injection molding process.

## **ACKNOWLEDGMENTS**

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