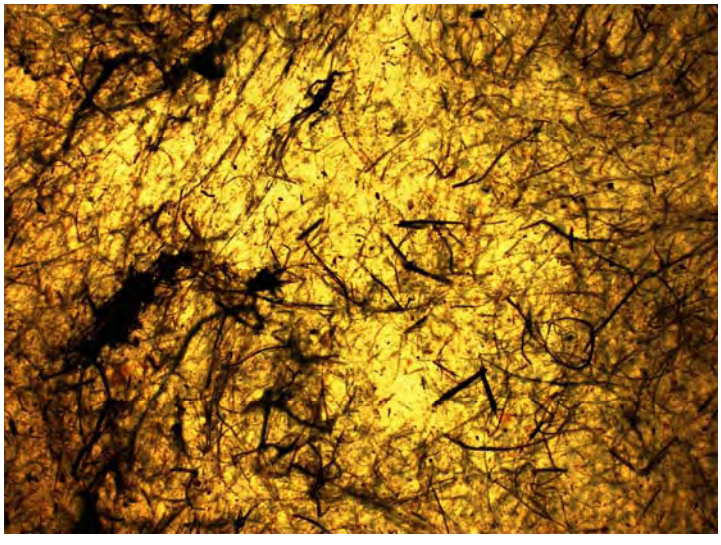
Hemp fibre and reinforcements of wheat gluten plastics



Christer Wretfors
Faculty of Landscape Planning, Horticulture and Agricultural Sciences
Alnarp

Licentiate Thesis
Swedish University of Agricultural Sciences

Alnarp

Acta Universitatis agriculturae Sueciae

ISSN 1652-6880
ISBN 978-91-85911-79-0

Tryck: SLU Repro, Alnarp 2008

Hemp fibre reinforced wheat gluten plastics

Abstract

The increasing demand for environmentally friendly materials has ushered in a new generation of bio plastics and plant fibre based composite materials. The quality of the raw components is very important when manufacturing a bio based material. For example, many plant fibres are hygroscopic, which means that moisture becomes an important quality determining factor. Therefore, a better understanding and knowledge of moisture adsorption equilibrium is of importance. The moisture adsorption equilibrium of several different plant fibres is examined in paper I. Differences in moisture adsorption equilibrium was found between unretted and retted hemp fibres, while differences between varieties were small.

An example of a renewable composite material, investigated in this thesis, is a wheat gluten plastic reinforced with hemp fibres. Paper II shows the effect of hemp fibre reinforcement on the mechanical properties of a wheat gluten based plastic film. Different fibre contents and fibre quality levels were tested. It was found that the fibres did improve the mechanical properties of the plastic and that fibre content was the most important factor in creating a stronger material. However, there were problems encountered with regards to fibre distribution in the material, poor adhesion between the fibres and plastic and a large variation in the material properties.

In paper III, we attempted to improve the fibre distribution by using a high speed grinder to mix the fibres and the plastic. Further a diamine was used as a cross linker between the fibres and the plastic to improve the bonding. It was found that the grinder did improve the fibre distribution but not sufficiently to avoid clusters of fibres. The diamine did not improve the interaction between the fibres and the plastic but it did strengthen the plastic itself to a certain degree.

It is concluded that hemp fibres can be used to improve the mechanical properties of wheat gluten plastics. However, the fibre distribution and interaction with the plastic needs to be much improved. A possible solution for the fibre distribution problem might be to decrease the viscosity of the wheat gluten dough while the fibre-plastic interaction might be improved by selecting a different cross linking substance.

Keywords: wheat gluten, plant fibre, bio plastic, hemp, renewable, composite, material, glycerol

Author's address: Christer Wretfors, Faculty of Landscape Planning, Horticulture and Agricultural Sciences, P.O. Box 104, SE-230 53 Alnarp.
E-mail: christer.wretfors@ltj.slu.se

One brief journey between Heaven and Earth.Then alas! We are the same old dust of ten thousand ages.

Li Bai 李白 (701-762), translation by Shigeyoshi Obata

Contents

List of Publications 6

Abbreviations 7

Background 8

Objectives 9

Introduction 10
Introduction to plant fibres 10
Cultivation and fibre properties 11
Introduction to bioplastics 18
Wheat gluten bioplastics 19
Composite materials 20

Materials and methods of composite materials 22
Materials 22
Compression molding 22
Quality evaluations 23
Statistical analysis 23

Results of composite materials 24
Differences of fibres of varying quality 24
Films with long versus short fibres 24
Fibre distribution in relation to grinding 24
Tensile testing 25
Fractures of hemp fibre-reinforced gluten plastics 25

Discussion 26

Conclusions 29

Suggested future research 30

References 31

Acknowledgements 37

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I Nilsson D., Svennerstedt B., Wretfors C., 2005. Adsorption equilibrium moisture contents of flax straw, hemp stalks and reed canary grass, Biosystems Engineering 91 (1), 35–43.

II Wretfors C., Cho S.-W., Hedenqvist M. S., Marttila S., Nimmermark S., Johansson E., 2008. Use of industrial hemp to reinforce wheat gluten plastics, Journal of Polymers and the Environment (submitted).

III Wretfors C., Cho S.-W., Kuktaite R., Hedenqvist M. S., Marttila S., Nimmermark S., Johansson E., 2008. Effects of fiber blending and diamines on hemp fiber reinforced wheat gluten plastics. Paper to be submitted to Journal of Biobased Materials and Bioenergy.

Paper I is reproduced with the permission of the publishers.

Abbreviations

CLSM	Confocal laser scanning microscopy
EMC	Equilibrium moisture content
HDPE	High-density polyethylene
HMW	High molecular weight
NaOH	Sodium hydroxide
Pa·s	Pascal second
PE	Polyethylene
PGA	Polyglycolic acid
PHB	Polyhydroxybuturate
PLA	Polylactic acid
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
SE-HPLC	Size-exclusion high-performance liquid chromatography
SEM	Scanning electron microscopy
WG	Wheat gluten

Background

Depletion of petroleum resources, together with increasing environmental concerns, calls for new solutions for many of our needs such as fuels, heatings, materials, technical oils etc (e.g. Winandy, 2006). Natural friendly, bio-solutions are often proposed as the most suitable ways to solve these problems. In terms of materials, plant fibres can be used for strengthening of engineering materials (e.g. Mohanty et al., 2002) and biopolymers can be used in different types of plastic materials (e.g. Jerez et al., 2005). Totally, “green” bio-materials are of extra interest. Thus strong composites containing both “green fibres” from plants and “green biopolymers” from plants would be an ideal solution. One fibre crop that is relatively easily grown in Sweden with a good yield potential is hemp fibre (Svennerstedt & Svensson, 2006). Wheat gluten has been found as a low-cost by-product from the increasing bio-fuel (ethanol) industry and as an interesting biopolymer alternative for bio-plastic production (Ullsten 2008).

Therefore, the main goal of the investigations within this thesis is to combine one of the strongest plant fibres, hemp fibre, with one of the most promising biopolymers, gluten proteins, in order to create a suitable composite material of high strength, usable for the industry for different applications.

Objectives

The main objectives of the research presented in this thesis were to:

- Investigate adsorption equilibrium moisture content in different types of fibres from various crops (paper I).
- Evaluate differences in adsorption equilibrium moisture content in hemp fibres retted and un-retted and from different varieties (paper I)
- Evaluate the possibilities of using hemp fibres to reinforce wheat gluten plastics (paper II).
- Determine the effect, if any, of fibre content on the mechanical properties of the composite material (paper II).
- Determine the effect, if any, of fibre quality on the mechanical properties of the composite material (paper II).
- Examine if a diamine could be used to increase the adhesion between fibres and plastic matrix (papper III).
- Determine if a high speed grinder could be used to improve the distribution, and decreasing the clustering, of fibres in the plastic matrix (paper III).

Introduction

Introduction to plant fibres

Plants with fibres that can be used for the manufacture of engineering materials include flax, hemp, jute, coconut and nettles. The choice of fibre type depends on the desired fibre properties and also on other factors such as price and availability.

Plant fibre properties, in turn, are influenced by a number of factors including plant variety, climate, harvest time and method, maturity, retting and method of decortication and fibre separation.

The main advantages of using plant fibre include renewability, relatively high strength and elastic modulus, low density, non-abrasiveness and biodegradability. However, one of the main drawbacks encountered by scientists trying to design new materials based on plant fibres is the large variation in fibre properties such as tensile strength and surface geometry (Kohler and Wedler, 1994). This variation exists among fibres from plants grown in the same plot, and even within groups of fibres from the same plant (Kohler and Kessler, 1999). Also, the harvesting procedure and fibre processing may further increase the variation in properties

Depending on the intended use of the fibre, the concept of quality is defined in different ways. If the fibre is used for textile or composite production, the several aspects such as strength, length, fineness, chemistry and homogeneity are important. On the other hand, if the fibre is to be used in pulp and paper production then these fibre characteristics are not as important (Mediavilla et al, 2001). There are also traditional quality

guidelines such as “a high quality fibre should be lustrous and give a decided snap when broken” (Ranalli, 1999) but they are far from adequate for advanced industrial applications.

In this thesis, the term “good quality fibres” refers to fibres with specific properties that are desired for a particular application, in our case the reinforcement of wheat gluten plastics.

Synthetic fibres, such as glass and carbon, have well defined characteristics and properties. The natural fibre alternatives show similar characteristics but exhibit a larger degree of non-uniformity. This applies to most of their characteristics: chemical composition, crystalline, surface properties, diameter, cross sectional shape, length, strength and stiffness. In addition, each step in the fibre processing chain further alters their properties (Kessler et al., 1999).

This causes problems when attempting to group fibres according to quality and when fabricating composites. To achieve strong composites, it is necessary to start with strong fibres, and also to achieve a strong bonding between the fibres and the polymer matrix (Lillholt, 2002).

According to Langenhove and Bruggeman (1992) the most important physical properties of flax fibres are fibre strength, length, fineness, cleanliness and effects of processing. This can also be said for other fibre types, such as hemp.

Cultivation and fibre properties

We know that the properties of the fibres are affected by the cultivation practise and that producing good quality natural fibre begins with the knowledge and control of the agricultural production of the raw material.

Plant growth is governed by numerous, complex processes that are not yet fully understood. These include genotype, climate, location, soil type, planting density and use of fertilizers and agrochemicals (Kessler et al, 1999). Some of these factors, such as the climate, are not under human control but can be compensated for by selecting proper genotypes and by planting the crop at the appropriate time of the year and at a suitable location etc.

The main component of plant fibres is cellulose and its molecules are held in a crystalline or para-crystalline lattice within the microfibrils, creating a structure of considerable tensile strength.

In general, the primary cell walls of a plant contain 10-20 % cellulose, the secondary walls up to 50 % and certain specialized cell walls, such as those of cotton fibres, may contain up to 98 % cellulose (Keller et al, 2001). The basic characteristics of cellulosic fibres are shown in table 1.

Table 1. Basic characteristics of cellulosic fibres (Thomsen et al., 2002).

Fibre	Cellulose (%)	Diameter (µm)	Length (mm)	Strength (MPa)
Flax	75	19	33	700
Hemp	65	25	25	600
Jute	55	20	3	350
Wood	40	33	3	150

Hemp fibres show the greatest combination of strength and stiffness of plant fibres (table 2). Plant fibres have a low density when compared to synthetic fibres glass and carbon. If the specific strength is calculated as fibre strength in relation to density, the hemp fibre (specific strength = 0.55) can be compared to glass fibre (specific strength=1.06).

Table 2. Dimensional and strength properties for flax and hemp fibres compared to synthetic fibres (Rowell et al, 1997).

Fibre	Density (kg/m3)	Strength (MPa)	Stiffness (GPa)	Elongation (%)
Flax	1 500	350	29	2.5
Hemp	1 480	820	30	3.5
Jute	1 500	580	26	1.5
Glass	2 600	2 760	73	3
Aramid	1 440	2 790	124	2.5
Carbon	1 770	3 585	235	1.5

The tissues in a mature hemp plant that make up the bark are located outside of the vascular cambium and consist of the epidermis, the cortex

and the phloem. The phloem consists of sieve tubes and phloem fibres, the later are also referred to as “bast fibres”.

The tissues located on the inside of the vascular cambium make up the wood portion of the stem and consist of the pith and the xylem. The xylem consists of vessels, ray and paratracheal parenchyma and libriform fibres, making up the “woody” portion of the stem (van der Werf, 1991).

Hemp fibres can be divided into three categories, namely primary, secondary and libriform fibres (Mediavilla et al, 2001). Secondary fibres are shorter (2 mm long) and more lignified than the primary fibres (20 mm long) and the libriform fibres are even shorter (0.5-0.6 mm long) and have the highest lignin content (van der Werf, 1991; Mediavilla et al., 2001). The length of the primary fibres is largest in the middle of the stem and decreases towards the top and bottom of the plant according to Bredemann (1927). When a cross-section of the stem is examined, it is circular at the base, semicircular at medium height and square at the top level (Heuser, 1927). Mediavilla et al. (2001) have found that 54 % of the fibres are located in the bottom part of the plant, 34 % in the middle and 12 % in the top part.

In order to maximize the stem and fibre yield, the hemp needs to be harvested at the right time. Some theories hold that the maximum yield is reached at the point of male flowering or technical maturity, others that it is reached approximately 3-4 weeks later at the beginning of seed maturity (Mediavilla et al., 2001). This later harvest does not affect the tensile strength of the bast and is advantageous for mechanical decortication of non-retted, dried hemp stems. However, a harvest time during the earlier vegetative growth stage or early flowering stage may be optimal for obtaining well-separated and smooth single hemp fibres (Keller et al 2001).

Once flowering has started, the formation of secondary fibres in the cambium between the phloem and the xylem begins and this results in an increase in stem diameter and a mismatch between the woody core and the bark. During this formation, cracks are more likely to appear in the tissue outside the cambium. The core also becomes more brittle during the progress of growth, resulting in smaller shives during the decortication process that are more easily removed from the bark (Keller et al., 2001). It has also been observed that in female plants, and probably also in

monoecious, the formation of secondary fibres starts earlier (Mediavilla et al., 2001).

The choice of growing location has a significant influence on fibre formation. If provided with an open, sunny environment, light well-drained soil and ample nutrients and water, hemp can grow to a height of 5 metres in four to six months. Exposed river banks, meadows and agricultural lands are ideal for hemp cultivation since all offer plenty of sunlight (figure 1). Hemp seeds usually germinate in 3-7 days and under favourable conditions, during the long days of summer, the plants can grow up to 10 cm per day in height. Hemp exhibits a dual response to day length. During the first 2-3 months of growth it responds to increasing day length with more vigorous vegetative growth but later in the season it requires shorter days to flower (Ranalli, 1999). Loamy soils result in more fibres forming as supportive tissue (Schäfer & Honermeier, 2000). This is interesting because it gives the farmer yet another tool for increasing the fibre content.

Figure 1. Industrial hemp field at Lönnstorp Research Station, 2003.

Another factor governing the fibre fraction proportions is the planting density. Deleuran and Flengmark (2005) recorded the highest fibre yields at a seeding density of 32-64 kg seed per hectare, while the seed yield was

highest at 8 kg seed per hectare. They also noted that while high fibre and seed yields are possible depending on the choice of cultivar and seed rate, they usually not found combined within the same cultivar.

Higher seeding rates can have a positive effect on crop biomass and stem production during periods of reduced rainfall and draught (Gorchs & Lloveras, 1999). The bast fibre content increases with planting density, probably due to less secondary growth (van der Werf, 1991). Also, too much rainfall will result in lower stem and fibre yield due to oxygen deficiency in the soil (Isolahti & Sankari, 2003).

Nitrogen fertilization increases plant height and stem diameter but only up to 100 kg N ha-1 (Gorchs & Lloveras, 1999). If the amount of available nitrogen is too high, the result is lower stem quality due to an increase in the stem diameter (Ranalli, 1999). Rates between 50 and 100 kg N ha-1 seem most appropriate when hemp is grown for fibre production. Higher nitrogen rates should only be used when the crop is grown for both seed and fibre. If only seed production is desired, a rate of 30 kg N ha-1 is enough (Gorchs & Lloveras, 1999). Along the same lines, a nitrogen supply of 175 kg ha-1 minus the reserve of soil mineral nitrogen would allow optimal crop growth and yields of up to 15 t ha-1 of above ground dry matter (Ranalli, 1999).

For applications where long fibres are required, the proportion of bast fibres is most important. It is known that a high bark yield and bast fibre content, combined with low secondary fibre content, is advantageous. Fibre yield is highly correlated with stem and bark development and reach maximum at the same time (Mediavilla et al, 2001). A cellulose content of 79 % at harvest has been reported by Keller et al (2001) and it has been shown that the content increases continuously with time independent of the growth stages. This seems to indicate that a longer growth period is desirable for fibre production. In Scotland, hemp has been reported to benefit from longer summer days when compared to the same varieties grown under more southern conditions. While the total yield is not as high, it is believed that the quality might be superior (Morrison & Stewart, 1997).

It is generally assumed that for a crop to reach its full potential it must not be affected by shortage of water and nutrients or other stress factors, such as pests and diseases. Under such ideal conditions, the production of dry

matter is approximately proportional to the amount of photo synthetically active radiation intercepted by the crop canopy (van der Werf et al, 1991).

The fibres themselves can be viewed as very complex natural composites, where the properties are determined by the degree of polymerisation of cellulose and the arrangement of the fibrils and the related crystalline. The amount of hemi-cellulose, pectin and lignin is also important. The lignin makes the stem rigid and the pectin glues the fibre bundles together. Retting is a common method for preparing the harvested fibres for decortication. The degree of retting greatly affects the end quality of the fibres and is in turn partly controlled by the moisture content of the straw (Nilsson, 2002). During the primary process of retting, pectic polysaccharides in the phloem are degraded and the bast fibre bundles are liberated from the cortex and xylem (van Dam, 1999). Figure 2 shows a SEM image of a retted hemp fibre bundle. The pectins associated with the middle lamella are removed, allowing the fibre bundles to separate from the surrounding cells of the stem. Hemicellulose is only partly removed by the retting process (van Hazendonk et al., 1996). The first processing step is the extraction of the fibres from the plant stem and the separation from the wood shives. Decortication of well-retted stems needs much less mechanical energy and gives a higher yield of fine fibres. Also a lower mechanical impact decreases the damage to the fibres (Kessler et al, 1999).

The natural and processing induced defects in the fibre wall structure have an effect on the tensile properties of the fibre. Longer fibres have been proven to have lower tensile strength because they have a greater chance of containing defects. Natural fibres can therefore not be treated as homogenous structures but contain local defects resulting in heterogeneous stress and strain distributions throughout the fibre (Mott et al., 1996).

The large natural variation in plant fibres poses a challenge when fibres are used as components in construction materials. For example, the author was involved in field trials conducted at SLU in Alnarp during the years 2004-2006, where different hemp and flax varieties were grown in order to test the impact of cultivation factors on fibre tensile properties. Different varieties, nitrogen fertilization and seeding rates were examined and then the tensile strength of the fibre bundles was tested (Svennerstedt, 2008). Further statistical analysis (ANOVA) was carried out on the material using 240 tensile tests done on hemp fibres from these trials. No significant differences caused by nitrogen and seeding rates with regards to fibre

tensile strength were revealed. The tested hemp fibres had also a large standard deviation of approximately 27 percent (results not shown). This indicates that the large natural variation may have “overshadowed” the effect of the different treatments.

A well-defined separation of single fibres by a subsequent degumming process might also be required, especially if the fibres are to be used by the industry. There are several chemical and physical degumming processes that dissolve and remove the gum substances between the fibres. The efficiency of these methods can be further increased by the addition of technologies such as steam explosion and ultrasound. However, they are very energy demanding and therefore expensive. Another method is controlled biological degumming using a bioreactor with adapted micro organisms and their enzymes. The preferred starting material for this method is green, non-retted decorticated bark. This is one way of dealing with the inhomogeneous nature of the starting material, since it is caused to a large degree by the retting process (Keller et al., 2001).

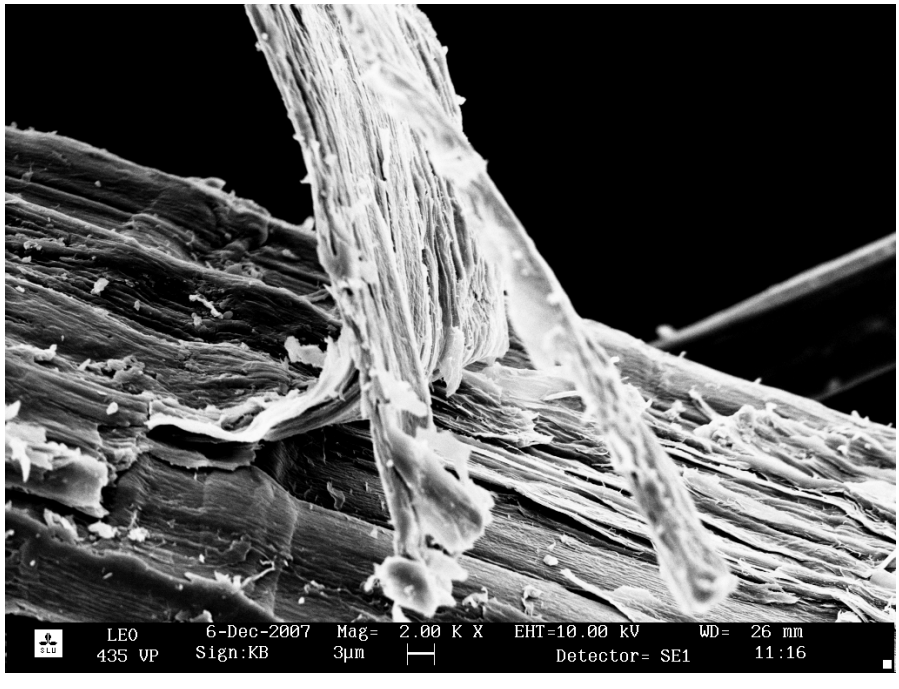


Figure 2. SEM image of a hemp fibre bundle, with peeled back outer layer. Image courtesy of Kerstin Brismar, SLU Alnarp.

The post harvest treatment and storage is also of outmost importance for maintaining the fibre quality. A high quality fibre will be quickly destroyed if stored under poor conditions. Since many plant fibres, such as hemp and flax, are hygroscopic and retain moisture, humidity is of particular importance. Fibres can be stored for several years if the moisture content is below 15 % (wet basis). If the moisture content is above 16 %, there is a risk that the retting process will continue and deteriorate the fibres. The fibres will adsorb moisture when the internal vapour pressure is lower than that of the surrounding air. When the internal and external vapour pressures are equal, the moisture content of the fibres are said to represent the equilibrium moisture content (EMC). The EMC is defined as the moisture content of a biological material after it has been subjected to a constant temperature and relative humidity for an infinitely long period of time. The EMC of hemp, flax and reed canary grass is investigated in paper I. The plant material was subject to several temperature and humidity intervals and weighed at each specific temperature and humidity value until the point of EMC was reached. When equilibrium was reached at the highest humidity level, the specimens were oven dried to determine the moisture contents and then the intermediate moisture contents where back-calculated. Several different isotherm models for predicting the EMC were then evaluated with different models providing the best goodness of fit depending on the type of fibre. This is important, because by using the correct model to understand fibre moisture adsorption; we can improve on the post harvest storage and handling procedures. If fibres are to be used commercially for production of materials in the future, most likely the most optimal fibre quality for certain application is needed and then knowledge about moisture and influences of storage conditions are of highest importance.

Introduction to bioplastics

Similar to plant fibre based materials, there is also an increasing worldwide interest in high performance bio-based plastics due to increasing demands for environmentally friendly materials and to the depletion of petroleum resources (Winandy, 2006). The main advantage of bio-based plastics is their expected properties of being bio-degradable and/or compostable.

Bio-based plastic materials is no novelty, they have been known and used since long. Before the development of petroleum based plastics, renewable materials based on polymers were dominating. By the start of the petroleum

period, petroleum plastics were introduced and dominating due to their many possible applications and the low price of the petroleum. With the increased price of petroleum and the many environmental problems caused by petroleum based plastics, high performance plastic materials of renewable origin has increased in interest again (Ullsten, 2008). However, today, only 1% of the total plastic market is bio-based plastics.

A range of biopolymers have been tested and evaluated for usefulness as bio-based plastic materials; e.g. cellulose, starch, collagen, casein, plant proteins and polyester (e.g. Jerez et al., 2005). Of those different polymers, wheat gluten is one of the most interesting ones due to its low cost, low oxygen permeability of films at dry conditions and the high content of hydrogen bonds in the films (Ullsten, 2008).

Wheat gluten bioplastics

Wheat gluten-based polymers are a new and interesting alternative to traditional synthetic plastics due to their combination of mechanical, oxygen barrier and film-forming properties (Cuq et al., 1998; Gennadios, 2002; Olabarrieta et al., 2006).

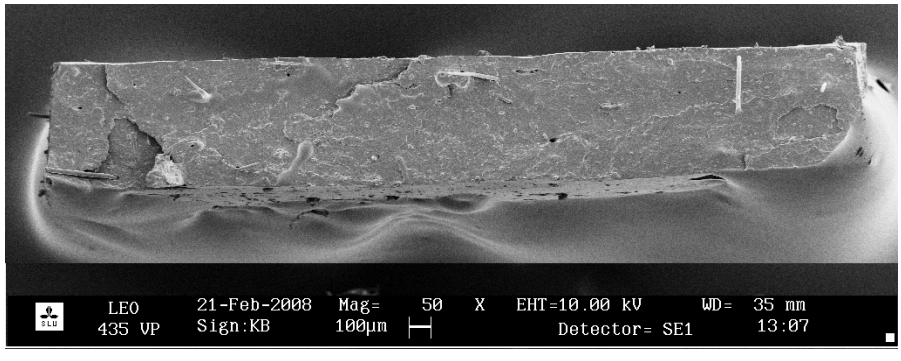


Figure 3. SEM image of a wheat gluten plastic fracture surface. Image courtesy of Kerstin Brismar, SLU Alnarp.

Wheat gluten (WG) films (figure 3) have a high content of hydrogen bonds and therefore low oxygen permeability under dry conditions. However, the high content of hydrogen bonds might also be negative, making the film brittle. Therefore, it is important to use a polar plasticizer that breaks the polypeptides bonds. Such a plasticizer increases the toughness of the plastic film although, simultaneously it decreases the barrier properties. Glycerol is

the most commonly used plasticizer. The advantage of glycerol is that it is highly polar and easy to disperse in the protein matrix. The plasticizing effect is increased by the hygroscopic and water absorbing character of glycerol. Other possible plasticizers to use is e.g. triethanolamine. Due to plasticizer migration and oxidation of free thiol groups over time, bittleness might develop in gluten plastic films at storage (Gällstedt et al, 2004).

Wheat gluten polymer materials can be manufactured using several processing methods, including extrusion, compression molding and solution casting (Ullsten et al., 2006). Compression molding and extrusion are commercially more interesting due to faster processing times. During compression molding, high temperature, plasticizer content and type, pH, processing time and shear rate all influence the mechanical properties due to their importance for protein polymerisation (Roy et al., 1999; Redl et al., 1999). Sulphydryl from the amino acid cysteine is responsible for creating disulphide cross-links during oxidation. The reorganization of the intramolecular disulphide bonds into intermolecular disulphide bonds is an important part of the aggregation process (Morel et al., 2002; Domenec et al., 2002). The upper temperature limit of the processing window is determined by depolymerization together with over extensive aggregation (Gällstedt et al., 2004).

Composite materials

When using a plastic in a composite material, it functions as a binder for the fibre reinforcement material and gives protection against moisture and ultra violet light that can otherwise break down the fibre.

Synthetic polymers are the most commonly used binders today, owing to the fact that early research was focused on replacing the synthetic fibres only and not the binders. The more commonly used synthetic polymers in biocomposites are polypropylene, HDPE, PVC, PS, epoxies and polyesters. Also the thermal stability, as the plant fibres start to degrade at around 220 °C, restricts the choice of matrix polymers to conventional thermoplastics, such as PE, PP, PVC and PS. Another important factor is the viscosity of the polymer. For good impregnation of the fibre, the viscosity of the polymer melt should not exceed 100 Pa·s in case film stacking is chosen or 1000 Pa·s for co-mingled technique (Kandachar &Brouwer, 2002).

The main advantage of using synthetic polymers as binders is that they are cheaper than other alternatives. However, they are not environmentally friendly and as such they undermine, to a certain degree, the use of the natural fibres themselves.
Because of this, there is now a trend to replace the synthetic polymers with renewable and biodegradable alternatives (figure 4). Examples of biodegradable polymers are Polylactic acid (PLA), Polyglycolic acid (PGA), Polyhydroxybuturate (PHB) and wheat gluten based polymers. When judging these biopolymers as suitable matrixes for bio fibre composites, the density and the temperature related properties seem to be the limiting criteria for the choice of suitable polymers. For instance, PLA has a low density and its melting temperature (150-162 °C) is well suited for manufacturing bio fibre composites.

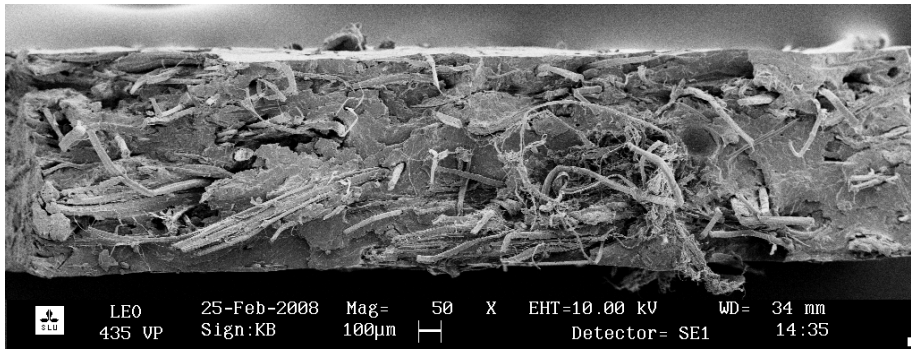


Figure 4. SEM image of a hemp fibre reinforced wheat gluten plastic fracture surface. Image courtesy of Kerstin Brismar, SLU Alnarp.

Materials and methods of composite materials

Materials

In our investigations, evaluating possibilities to reinforce wheat gluten plastics by the use of hemp fibres, the following materials were used;

- Wheat gluten (WG) powder was used, supplied by Reppe AB, Lidköping, Sweden (paper II and III).
- Glycerol supplied by Karlshamns Tefac AB, Karlshamn, Sweden (paper II and III).
- The diamine, Jeffamine® EDR-176, was provided by Huntsman Holland BV, Holland (paper III).
- Three different types of industrial hemp fibres in order to provide three distinct quality levels; poor, standard and good quality (paper II and III). Also hemp fibres of different length were tested (paper II).

Compression molding

Plastic dough was prepared by mixing gluten and glycerol to a content of 30 wt%. Long (paper II) and short (paper III) hemp fibres of different qualities were added in different quantities (5, 10 and 15%; paper II and III). Dough and fibre was transferred either to an electrical blender (paper II and III), or to a high speed grinder (paper III) for mixing. For samples containing diamine, Jeffamine® EDR-176 was added to the fibre-dough samples prior to mixing (paper III).

Compression moulded films were manufactured using a PHI press; moulding temperature 130 °C, applied pressure 1600 bar, and moulding time 5 min. By using Mylar foils, square films were obtained with sides of 100 mm length and 0.5 mm thickness (paper II and III).

Quality evaluations

Tensile strength was tested on dumbbell-shaped specimens of the reinforced plastics (paper II and III).

In order to study the fibre distribution in the plastics, samples from each treatment were studied by stereo light microscopy with a digital camera (paper II).

To further study the fibre raw material and the finished plastic material structure, scanning electron microscopy (SEM) was used (paper II and III). The same method was used to investigate fracture surface of the samples (paper II and III).

For further evaluation of bondings between the protein matrix and polymerization structures of the proteins confocal laser scanning microscopy (CLSM) was used (paper III).

Protein polymerization behaviour was evaluated using size-exclusion high-performance liquid chromatography (SE-HPLC; paper III).

Statistical analysis

Statistical analyses were carried out using the SAS software package for Microsoft Windows (SAS Institute Inc, NC, USA; paper II and III).

Results of composite materials

Differences of fibres of varying quality

SEM showed that good quality fibres consisted of thick fibre bundles with relatively clean and only mildly damaged fibre surfaces. The poor quality fibres showed clear surface damage and fibre degradation, as well as thinner fibre bundles. The standard quality fibres were in between as related to appearance (paper II).

Films with long versus short fibres

Compression moulded films containing long fibres were generally non-homogeneous, regardless of amount and quality of fibre. Also, the fibres were very unevenly distributed within the material with fibres lumped together in bundles. The short fibres were better, although still unevenly distributed in the gluten matrix and clustered together in bundles. No clear difference in the behaviour of the different fibre qualities, in the gluten film, was seen (paper II).

Fibre distribution in relation to grinding

Fibre distribution throughout the plastic material was somewhat improved by the use of a high speed grinder instead of an electrical blender (paper III). However, the use of the high speed grinder also led to a decrease in tensile strength properties of the plastic in comparison to the use of the electrical blender. Despite the fact that fibre distribution was improved by the use of a high speed grinder, standard deviations for measured

parameters were still large, indicating uneven distribution of the fibres (paper III).

Tensile testing

Tensile strength of the hemp fibre-reinforced gluten plastic varied in relation to hemp fibre content and quality (paper II and III). With increasing fibre content, tensile strength and E modulus were found to increase, while strain decreased. No significant influences of fibre quality on tensile strength or stress were found. However, E modulus was found to increase with improved fibre quality (paper II and III). Also the grinding was found to play a minor role in determination of the tensile strength parameters (paper III). The most important factor of those investigated for variation in tensile strength parameters was hemp fibre content (paper III). Also, addition of Jeffamine® was found to significantly influence tensile strength parameter (paper III). Findings suggest that the increased tensile properties by the addition of Jeffamine® was mainly due to an increased protein polymerization leading to a noticeable change in the structure of the plastic itself, i.e. the crack formations decreased and the appearance became more “plastic” (paper III).

Fractures of hemp fibre-reinforced gluten plastics

Gluten film without fibre reinforcement showed a uniform fracture surface and the break was in a sheet-like manner. For films with fibre reinforcement, the fracture surfaces were uneven independent of if the films were reinforced with good or poor quality fibres. Fracturing generally seemed to have started around areas where the fibres were clustered and where air pockets had started to form (paper II).

Fibres were found to have been pulled out of the gluten plastic matrix, rather than breaking during tensile testing (paper II). The addition of the diamine Jeffamine® to hemp fibre reinforced gluten plastic films was not observed to lead to a better bonding between the hemp fibres and the protein matrix (paper III). Still the “pull-out” effect of the fibres was seen as a result of insufficient binding (paper III). A gathering of high molecular weight (HMW) glutenin subunits were found along the border of the fibres independent if Jeffamine® was added or not (paper III).

Discussion

The present investigations clearly showed the possibilities to reinforce wheat gluten plastics with industrial hemp fibres (paper II and III). Only one previous investigation has studied possibilities to use industrial hemp fibres to reinforce wheat gluten plastics, and within that study only long hemp fibres were tested (Kunanopparat et al., 2008). Our study clearly showed the advantages of using short industrial hemp fibres instead of long ones in reinforcing the wheat gluten plastics (paper II). Also, other studies have shown the advantage of using short industrial hemp fibres instead of long ones, although the purpose was to reinforce soy protein plastics (Mohanty et al., 2005).

Despite the better distribution of the short industrial hemp fibres in the gluten matrix as compared to the long ones, still the fibres showed a tendency to cluster together during the mixing process (paper II). Uneven distribution of fibres in plastic matrices is a general problem as it leads to weaker unreinforced zones in the materials in which cracks and brakes are starting (e.g. Liu et al., 2004; 2005). One possibility to improve the distribution of fibres in the gluten plastic matrix could be to improve the blending of fibres and gluten before compression molding. In paper II an electric blender was used to mix the fibres with the gluten powder. The use of this blender caused part of the plastic mix to stick to the walls of the glass container while the hemp fibres tended to collect at the bottom of the container (paper II). Therefore, a high speed grinder was instead used in paper III. The use of the high speed grinder improved the distribution of fibres in the matrix, although, still the distribution was not acceptable (paper III). One reason for the still uneven distribution might be the small volume capacity of the grinder itself. Larger material samples had to be prepared in smaller batches. Thereafter the batches were combined before

pressing (paper III). However, the fibres themselves are also known to exhibit a high variation in tensile properties resulting from a range of factors such as plant variety, climate variations, harvest times, moisture content, maturity, retting, methods of decortication and other technical processes (paper I; Kessler et al., 1999). In conclusion, the grinder itself seemed to play a minor role for the result of distribution of fibres in the protein matrix. Other solutions have to be search for in order to improve the fibre distribution in the matrix (paper III). Such solutions might for example be additions of SDS to the sample to reduce the protein polymerization behaviour, or additions of alkali solutions to decrease interfibrillar regions in the fibres (Liu et al., 2004).

It is a well known fact that tensile strength parameters are influenced by additions of fibres to plastic materials, and similar findings have also been reported in several studies relating to natural fibres and bio-plastics. Addition of natural fibres has been found to increase the tensile properties of a range of materials (e.g. Mohanty et al., 2002; 2005; Liu et al., 2004; 2005; Kunanopparat et al., 2008). In similarity with these previous findings, the present investigation also showed an increase in tensile strength by additions of fibres to the gluten plastics (paper II and III). Our results showed a correlation between amount of fibres added and tensile strength (paper II and III), which is in contrary to the findings in another study (Liu et al., 2005). However, the previous study (Liu et al., 2005) did not investigate either the same type of fibre or the same type of protein matrix. Regarding fibre content intervals used in the present study, the amount of hemp fibres added to wheat gluten plastics seems to be important for increasing the tensile strength in the films.

Fibre quality was not found to influence tensile strength properties in our investigations (paper II and III). To our knowledge no previous study has investigated the relationships between the quality of natural fibers added to bio-plastics and the influences on tensile strength parameters. One might, however, expect that there should be a positive relationship between quality and tensile strength parameters. The major explanation for the limited relationship between fibre quality and tensile strength properties found in our investigations seems to be a poor bonding between the fibres and protein matrix (paper II and III). Pull-out of fibres could be seen in the experiments (paper II and III) instead of breakage of the fibres at tensile tests, indicating poor bonding. Also, when using other types of natural fibres in other types of plastic materials, poor bonding has been reported

(Liu et al., 2004; 2005). Suggestions of solutions for the poor bonding between fibres and plastic materials have mainly been additions of different additives to the reinforced plastics (Liu et al., 2004; 2005). In our studies, we tried to add a diamine, Jeffamine®, known to have cross-linking properties (paper III). However, the results showed no increased bonding between the fibre and the gluten matrix with the addition of the diamine (paper III). When solutions for better bonding between the fibre and the protein matrix have been found, quality of the fibre will most likely play a role. The most suitable quality of the fibre than has to be evaluated and determinations of parameters such as adsorption equilibrium moisture contents of the fibres, as investigated in paper I, might be one determinant of the most suitable quality of the fibre.

Increased tensile strength of the reinforced plastics was obtained after additions of Jeffamine® (paper III). Also in earlier investigations, increased tensile strength has been obtained after additions of different types of additives, e.g. compatibilizers (Liu et al., 2005). Actually, in the present investigation (paper III), a combination of additions of Jeffamine® and a high amount of fibre gave the highest increase in tensile strength. However, the main reason for the improved tensile properties by the addition of Jeffamine® was due to an increased polymerization of the proteins in the gluten plastic matrix (paper III). An increased polymerization of the proteins is known to increase the tensile strength of bio-plastic materials (Gällstedt et al., 2004; Ullsten et al., 2006; Olabarrieta et al., 2006). Increased protein polymerization might also be the reason for increased tensile strength in other materials with additions. Such investigations have mainly not been carried out.

If an increased protein polymerization in the gluten matrix is the main aim, then there might be better additives to use than Jeffamine®, e.g. NaOH (Ullsten et al., 2008). For better bonding of the fibres to the gluten matrix, additional studies have to be carried out in order to find an additive leading to improved bonding between the fibres and the matrix.

Conclusions

Short industrial hemp fibres are a good solution for reinforcement of gluten plastics, creating a strong, stiff and sustainable eco-efficient material for the automotive and building product industry. The fibre content has a significant effect on the mechanical properties of the composite material.

Before the material can be used, problems with uneven distribution of hemp fibres and poor adhesion between fibres and the matrix in the material have to be resolved.

Also, the most suitable fibre quality to be used in the materials have to be determined as this was not possible in the present investigations due to poor bonding between the fibres and the plastic material.

Use of a high speed grinder to blend fibres and plastic dough lead to better fibre distribution compared to the use of an electrical blender. However, there is room for further improvement as the fibres still exhibited tendencies to bundle together.

Addition of the diamine to the material did not improve bonding between fibres and plastic but improved the mechanical properties of the wheat gluten plastic itself by an increased polymerisation of the proteins in the gluten matrix. Further studies are required to find a way of improving the interaction between fibres and gluten plastic.

Suggested future research

There are a number of research tasks that need to be undertaken if hemp fibre reinforced wheat gluten plastic is to become a viable commercial alternative to traditional composite materials.

The fibre distribution needs to be improved and a possible solution might be a better mixing procedure using a high capacity grinder. Another possibility could be to decrease the viscosity of the plastic dough to facilitate the fibre dispersion in the dough. Further decreasing the length of the fibres is yet another possibility that needs to be examined.

The interaction between the fibres and the plastic also needs to be improved in order to take advantage of the inherent strength of the fibres. The inherent problem of combining hydrophilic fibres with a hydrophobic plastic material must be taken into account. The solution could possibly be the addition of a powerful cross-linking substance.

When the problem with improved bonding between the fibres and the gluten matrix has been solved, the most suitable quality of fibres to add to the gluten has to be evaluated.

Another interesting question is the long term behavior of the fibres in the plastic, in particular if they will start to deteriorate due to possible moisture adsorption.

Also it is important that an analysis be performed to determine the actual environmental value and/or impact of the composite material once the above problems have been satisfactorily solved.

References

Bredemann G., 1927, Beitrage zur Hanfzüchtung, Weitere Versuche zur Züchtung auf Fasergehalt, Zeitschrift für Pflanzenzüchtung 12: 259-268.

Cuq B., Gontard N., Guibert S., 1998, Proteins as agricultural polymers for packaging production. Cereal Chem 75:1-9.

Deleuran L.C., Flengmark P., 2005, Yield Potential of Hemp (Cannabis sativa L.) Cultivars in Denmark, Journal of Industrial Hemp 10(2): 19-31, The Haworth Press Inc., Binghamton, NY 13904, USA.

Domenek S., Morel M-H., Bonicel J., Guilbert S J., 2002, Polymerization kinetics of wheat gluten upon thermosetting, A mechanistic model, Agric Food Chem 50:5947-5954.

Gennadios A., 2002, Protein-based films and coating, CRC Press LLC, Boca Raton, Fl.

Gorchs G. & Lloveras J., 1999, Crop yield and fiber production of hemp cultivars from Spain grown in the humid cool areas of southern pyrenees (northest Spain), Proceedings of the

workshop on alternative crops for sustainable agriculture (COST WG 814-II), June 13-15, 1999, Turku, Finland.

Gällstedt M., Matozzi A., Johansson E., Hedenqvist M.S., 2004, Transport and tensile properties of compression-molded wheat gluten films, Biomacromolecules 5:2020-2028.

Heuser O., 1927, Die Hanfpflanze, Hanf- und Hartfaser, Julius Springer Verlag, Berlin, Germany.

Isolahti M.J. & Sankari H.S., 2003, article handout, Agricultural Research Center (MTT), North Ostrobothnia Research Station, FIN-92400 Ruukki, Finland.

Jerez A., Partal P., Martinez I., Gallego C., Guerrero A., 2005, Rheology and processing of gluten based bioplastics, Biochemical Engineering Journal, 26(2-3): 131-138.

Kandachar P., Brouwer R., 2002, Applications of bio-composites in industrial products, In: Materials Research Society Symposium – Proceedings vol 702:101.

Keller A., Leupin M., Mediavilla V., Wintermantel E., 2001, Influence of the growth stage of industrial hemp on chemical and physical properties of the fibres, Industrial crops and products 13:35-48.

Kessler R.W., Kohler R., Tubach M., 1999, Strategy for a sustainable future of fibre crops, Proceedings of the international conference on natural fibres performance, 27-28 May, 1999, Copenhagen, Denmark.

Kohler R. & Kessler R.W., 1999, Designing natural fibres for advanced materials, Proceedings of the 5th International conference on woodfibre–plastic composites, 25-26 May, Madison, USA.

Kohler R. & Wedler M., 1994, Non-textile applications of flax fibres, Vortrags-nr 331, Proceedings of the Techtextil-symposium, 1994, Frankfurt, Germany.

Kunanopparat T., Menut P., Morel M-H., Guilbert S., 2008, Reinforcement of plasticized wheat gluten with natural fibers: from mechanical improvement to deplasticizing effect, Composites part A: Applied science and manufacturing 39:777-785.

Langenhove L. & Bruggeman J.P., 1992, Methods of fibre analysis, The biology and processing of flax: 545-572, Eds. Sharma H.S.S. and Van Sumere C.F., M Publications, Belfast, ISBN 0 9519963 0 4.

Lillholt H., 2002, Strength of cellulose and fibres, Proceedings of the 23rd Risö International Symposium on Materials Science, 2-5 September, 2002, Risö National Laboratory, Denmark.

Liu W., Mohanty A.K., Askeland P., Drzal L.T., Misra M (2004) Influence of fiber surface treatment on properties of Indian grass fiber reinforced soy protein based biocomposites, Polymer 45:7589-7596.

Liu W., Misra M., Askeland P., Drzal L.T., Mohanty A.K., 2005, 'Green' composites from soy based plastic and pineapple leaf fiber: fabrication and properties evaluation. Polymer 46:2710-2721.

Mediavilla V., Leupin M., Keller A., 2001, Influence of the growth stage of industrial hemp on the yield formation in relation to certain fibre quality traits, Industrial Crops and Products 13:49-56.

Mohanty A.K, Misra M., Drzal L.T., 2002, Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world, J Polymers Environm 10:19-26.

Mohanty A.K., Misra M., Drzal L.T., 2005, Injection molded biocomposites from soy protein based bioplastic and short industrial hemp fiber, J Polymer Environm 13:279-285.

Morel M-H., Redl A., Guilbert S., 2002, Mechanism of heat and shear mediated aggregation of wheat gluten protein upon mixing, Biomacromolecules 3:488-497.

Mott L., Shaler S.M, Groom L.H., 1996, Experimental Micromechanics: Quantifying fiber cell wall deformation and fracture, University of Main, USA.

Morrison I.M., Stewart D., 1997, Alternative fibre crops grown under Scottish conditions, Scottish Crop Research Institute, Dundee, UK.

Nilsson D., 2002, A model for the drying and rewetting processes of flax straw, Proceedings of the symposium on Production, processing and use of natural fibres, 10-11 September, 2002, Potsdam, Germany.

Olabarrieta I., Cho S-W., Gällstedt M., Sarasua J.R., Johansson E., Hedenqvist M.S., 2006, Aging properties of films of plasticized vital wheat gluten cast from acidic and basic solutions, Biomacromolecules 7:1657-1664.

Ranalli, P. (editor), 1999, Advances in hemp research, The Haworth Press, Binghamton, NY 13904-1580, USA.

Roy S., Weller C.L., Gennadios A., Zeece M.G., Testin R.F., 1999, Physical and molecular properties of wheat gluten films cast from heated film forming solutions, J Food Sci 64:57-60.

Redl A., Morel M-H., Bonicel J., Guilbert S., Vergnes B., 1999, Rheological properties of gluten plasticized with glycerol: dependence on temperature, glycerol content and mixing conditions, Rheol Acta 38:311-320.

Schäfer T. & Honermeier B., 2000, Investigations to optimise the cultivation technique of fibre hemp in Germany, Institute of Agronomy and Plant Breeding I, Justus.Liebig University, Giessen, Germany.

Svennerstedt B., 2008, Hemp fibre strength and thickness – a study of plant development of swedish grown industrial hemp, Journal of Industrial Hemp, Manuscript, Haworth Press Inc. USA.

Svennerstedt B., & Svensson G., 2006, Hemp (Cannabis Sativa L.) Trials in Southern Sweden 1999-2001, Journal of Industrial Hemp, Volume 11 (1), pg 17-25, Haworth Press Inc. USA.

Thomsen A.B., Klinke H.B., Hoffmeyer P., Lilholt H., 2002, Materials derived from biomass – concepts and examples, Proceedings of the 23rd Risö International Symposium on Materials Science, 2-5 September, 2002, Roskilde, Denmark.

Ullsten N H., Gällstedt M., Johansson E., Gräslund A., Hedenqvist M S., 2006, Enlarged processing window of plasticized wheat gluten using salisylic acid. Biomacromolecules 7:771-776.

Ullsten H., 2008, Processing and development of wheat gluten plastics, Doctoral thesis, Polymer Technology, KTH, Stockholm, Sweden.

Ullsten N.H., Cho S-W., Spencer G.M., Gällstedt M., Johansson E., Hedenqvist M., 2008, Properties of plasticized vital wheat gluten wheets with sodium hydroxide and/or salicylic acid (submitted).

Van Hazendonk J.M., Reinerink E.J.M., de Waard P., van Dam J.E.G., 1996, Structural analysis of hemicellulose components of flax bast fibres (Linum usitatissimum L.), Carbohydrate Research 291, 141-154.

Van Dam J.E.G., 1999, Optimization of methods of fibre production from agricultural raw materials, Proceedings of the international conference on natural fibre performance, 27th-28th May 1999, Copenhagen, Denmark.

Van der Werf H.M.G., 1991, Agronomy and crop physiology of fibre hemp – a literature review, Center for Agrobiological Research, CABO Report 142, Wageningen, The Netherlands.

Winandy J.E., 2006, Advanced wood- and bio-composites: Enhanced performance and sustainability, Proc. of 4th International Conference on Advanced Materials and Processes, University of Waikato, Hamilton, New Zealand.

Acknowledgements

There are a number of people who I would like to thank for helping me out in various ways during my time in Alnarp.

Eva Johansson, my main supervisor, who introduced me to the world of wheat gluten plastics. You have been a tremendous support and source of inspiration Thank you!

Sven Nimmermark, my assistant supervisor and most excellent friend. I am going to miss our many discussions and terrific pizza lunches.

Gwen Spencer, for all her help and wickedly dark sense of humor.

Salla Marttila, Master of the Microscope, for all her help and useful input.

Kerstin Brismar, many, many thanks for helping me get those great SEM images.

Maria Luisa Prieto-Linde, we'd all be really lost without you!

Sung-Wo Cho, who went above and beyond the call of duty to help me out during my times in Stockholm.Your hard work and dedication is an inspiration to us all.

Mikael Hedenqvist, for his valuable advice and help during my visits to Stockholm.

Ramune Kuktaite, those CLSM images look great! Many thanks!

Anders Prahl, my great creative friend and coffee break buddy.

Ingmar Sjölin, my pal and lunchtime sparring partner.

Torulf Nilsson, former fibre colleague, friend and brother-in-arms.

Christina Kolstrup, for being a great friend and for keeping me sane during those on-the-edge moments.

All my other friends and colleagues in Alnarp, I could not have done it without you!

Sifu Garry Hearfield, my very best friend, martial arts master and spiritual brother.

My parents and my sister for always being there for me.

And most importantly, I want to thank my true love and beautiful wife Lina. I don’t know how or why you put up with me but you give my life real meaning.

To anyone and everyone I have forgotten to mention above, you have my sincere gratitude and appreciation.

I

Biosystems Engineering (2005) **91** (1), 35–43
doi:10.1016/j.biosystemseng.2005.02.010
PH—Postharvest Technology

Adsorption Equilibrium Moisture Contents of Flax Straw, Hemp Stalks and Reed Canary Grass

D. Nilsson[1]; B. Svennerstedt[2]; C. Wretfors[2]

[1]Department of Biometry and Engineering, Swedish University of Agricultural Sciences, P.O. Box 7032, SE-750 07 Uppsala, Sweden; e-mail of corresponding author: daniel.nilsson@bt.slu.se
[2]Department of Agricultural Biosystems and Technology, Swedish University of Agricultural Sciences, P.O. Box 43, SE-230 53 Alnarp, Sweden; e-mail: bengt.svennerstedt@jbt.slu.se

(Received 28 May 2004; received in revised form 22 February 2005; published online 15 April 2005)

The quality of fibres obtained from flax, hemp and reed canary grass is dependent on the moisture characteristics of the crops. In this study, the adsorption equilibrium moisture contents of un-retted and dew-retted flax straw, un-retted and frost-retted hemp stalks and spring-harvested reed canary grass were determined using the dynamic gravimetric method at different temperatures (5, 15, 25 °C) for relative humidities in the range 35–95%. Non-linear regression was used to fit five commonly used three-parameter isotherm models [the modified Henderson model, the modified Chung–Pfost model, the modified Halsey model, the modified Oswin model and the modified Guggenheim–Anderson–de Boer (GAB) model] to the data obtained. The goodness-of-fit of the models was compared using the mean relative percentage deviation, the standard error of estimate and residual plots. The modified Halsey model was considered the best for predicting the equilibrium moisture content of un-retted flax and spring-harvested reed canary grass, and the modified Oswin model for predicting the equilibrium moisture content of dew-retted flax and un-retted hemp, while the Chung-Pfost model was the best for predicting the equilibrium moisture content of frost-retted hemp. For flax and hemp, there were statistically significant differences between un-retted and retted plant materials, whereas the differences between varieties were small.

1. Introduction

1.1. *Background*

The increased awareness of sustainable production in recent decades has led to the search for new environmentally friendly products. Natural fibres from flax (*Linum usitatissimum* L.), hemp (*Cannabis sativa* L.) and reed canary grass (*Phalaris arundinacea* L.) are alternatives that can replace synthetic fibres (*e.g.* carbon, glass and polyester fibres) in many industrial applications. For example, hemp fibres have a lower density than carbon fibres, and are among the strongest of the natural fibres (Rowell *et al*., 1997). Flax and hemp fibres can be used as reinforcement material in composites, rubber and concrete, in non-woven products, and as insulation material (Smeder & Liljedahl, 1996; Svennerstedt, 2003), whereas fibres from reed canary grass can be used for making paper (Finell, 2003). The important advantages of natural fibres are that these are produced from renewable materials and can be degraded biologically after use.

The bast fibres from flax and hemp are released from the core and epidermis by retting. In the dew-retting process, in which the crop is exposed to dew, rain, wind and sunlight in the fields, the pectic substances attaching the fibres to the stem are degraded by microorganisms (Van Sumere, 1992). An alternative option is to harvest the crop in the following spring (Landström *et al*., 1996; Pasila, 1998). The microbiological degradation, the changes in morphological structure and the loss of leaves of frost-retted plants facilitate the drying process in the spring and the subsequent fibre separation.

In the Nordic countries, the harvest season in the autumn is often rainy and the air humidity often high. This can cause problems for the harvesting, storage and

Notation

A, B, C	constants	Q_A, Q_B, Q_C	constants
D	dummy variable	T	temperature, °C
d_f	degrees of freedom of regression model	Y	measured equilibrium moisture content, % (db)
E_S	standard error of estimate	$\hat{Y}$	predicted equilibrium moisture content, % (db)
H_R	relative humidity, decimal		
M_D	equilibrium moisture content, % (db)		
N	number of data points		
P	mean relative percentage deviation, %		

processing of crops. Fibre quality may, for example, be low in some years as a result of in-field over-retting if the crop cannot be harvested at an optimum point in time due to poor weather conditions. Furthermore, retted flax straw can be preserved for several years if the moisture content is below 15% (wb). However, if the moisture content is above 16%, there is a risk that the retting process will continue during storage, resulting in fibre quality deterioration (Sultana, 1992). Damp fibre crop stems are also more difficult to process due to their higher friction coefficient (Pasila, 1998).

Hygroscopic materials, such as flax, hemp and reed canary grass, adsorb moisture when the vapour pressure within the material is lower than the vapour pressure of the surrounding air. When the internal vapour pressure is equal to the vapour pressure of the surrounding air, the moisture content of the material represents the equilibrium moisture content (EMC). The internal vapour pressure is dependent on the surrounding environment, *i.e.* the temperature and relative humidity, as well as on the characteristics of the plant material. The EMC of a biological material is therefore defined as the moisture content of the material after it has been exposed to a particular environment with a constant temperature and relative humidity for an infinitely long period of time (Brooker *et al.*, 1992).

There are a number of different methods for determining the EMC. The most commonly used are the static and the dynamic gravimetric methods (Speiss & Wolf, 1987). In the static method, the sample reaches the EMC in still air moistened by various salt solutions; whereas in the dynamic method the air is mechanically moved and often moistened by air conditioning units (Brooker *et al.*, 1992; Viswanathan *et al.*, 2003). However, the main advantage of the dynamic method is that the sample reaches equilibrium more rapidly than with the static method.

The resulting EMC (expressed on a dry weight basis) at different relative humidities for given temperatures can be described by sorption isotherms. The isotherms usually have a sigmoid shape and can be divided into three different regions (Van den Berg & Bruin, 1981; Rahman, 1995). In the first region, *i.e.* at low relative humidities, there is monolayer adsorption of water molecules strongly bound by van der Waal forces. In the second region of the isotherm, there is multi-layer adsorption; and the enthalpy of vaporisation in this region is less than in the first region. In the third region, the isotherm rises steeply as practically free water becomes mechanically entrapped in the void spaces of the material, mainly as a result of capillary condensation (Van den Berg & Bruin, 1981; Nevander & Elmarsson, 1994; Rahman, 1995). The enthalpy of vaporisation is lowest in this region.

Several isotherm models have been proposed to fit EMC data from agricultural products (Van den Berg & Bruin, 1981). The most commonly used models are the modified Henderson model, the modified Chung–Pfost model, the modified Halsey model, the modified Oswin model and the modified Guggenheim–Anderson–de Boer (GAB) model (Jayas & Mazza, 1993; ASAE, 2000; Aviara *et al.*, 2004). These models are presented in Table 1. The modified Henderson model (Thompson *et al.*, 1968) and the modified Chung–Pfost model (Pfost *et al.*, 1976) are good models for starchy grains and fibrous materials (Chen & Morey, 1989). The modified Henderson model seems, for example, to be best for the prediction of EMC for wheat straw, according to Duggal and Muir (1981). The modified Halsey model (Iglesias & Chirife, 1976) is appropriate for high oil and protein products (Chen & Morey, 1989). The modified Oswin model (Chen & Morey, 1989) is suitable for, *e.g.* safflower seeds (Jayas & Mazza, 1991) and corn and corncobs (Chen & Morey, 1989). The GAB model (Van den Berg, 1984), which was modified by Jayas and Mazza (1993) to a three-parameter model in order to include the effects of temperature, has been recommended as a standard model for food (Lomauro *et al.*, 1985). However, Chen and Jayas (1998) showed that the GAB model is inadequate for many starchy products.

A deeper knowledge of the adsorption EMC characteristics of flax straw, hemp stalks and reed canary

Table 1
The five most commonly used three-parameter isotherm equations for calculation of the equilibrium moisture content (EMC) of agricultural products (Jayas & Mazza, 1993)

Name	*Equation*
Modified Henderson	$M_D = (\ln(1-H_R)/(-A(T+C))^{1/B}$
Modified Chung–Pfost	$M_D = \ln(-(T+C)\ln(H_R)/A)/(-B)$
Modified Halsey	$M_D = (-e^{(A+BT)}/\ln H_R)^{1/C}$
Modified Oswin	$M_D = (A+BT)/(1/H_R-1)^{1/C}$
Modified GAB	$M_D = (ABH_R(C/T))/((1-BH_R)(1-BH_R+BH_R(C/T)))$

M_D, moisture content, % (db); H_R, relative humidity (decimal); T, temperature, °C; A, B, and C constants specific to each equation.

grass is useful for proper management of harvest and post-harvest operations, as well as for improving quality control during storage. The kinetics of water sorption on flax fibres have been studied by Kohler *et al*. (2003), and the EMC and capillarity properties of fibre and shive fractions of flax and hemp by Kymäläinen and Pasila (2000) and Kymäläinen *et al*. (2001). However, no studies were found in the literature in which the EMC of whole flax straw, hemp stalk or reed canary grass straw had been investigated. The ASAE publishes data and constants for isotherm EMC equations for agricultural products (ASAE, 2000), but no data for these fibre crops were found.

1.2. *Objectives*

The objectives of this study were to obtain EMC data for three Swedish fibre crops (flax, hemp and reed canary grass) at different temperatures (5, 15, 25 °C) for relative humidities in the range 35–95%, and to evaluate the suitability of applying five commonly used isotherm EMC equations (*i.e*. the modified Henderson, the modified Chung–Pfost, the modified Halsey, the modified Oswin and the modified GAB equations) to predict the EMC of these crops.

2. Materials and methods

2.1. *Plant material*

The flax varieties Viola and Elise were investigated in this study. These varieties were grown at Uppsala in central Sweden and cut on 29 July 2002 at early yellow ripeness. Sheaves were taken from windrows with unretted straw on 29 July; from windrows with (almost) normally dew-retted straw on 28 August; and from windrows with over-retted straw on 21 September. The sheaves were air-dried indoors to a moisture content of about 10% (wb) and then stored in un-heated storehouses.

The hemp varieties studied were Felina and Futura. The crop was grown at Alnarp in southern Sweden, and stalks were taken randomly from un-retted hemp harvested on 3 October 2001, and from frost-retted hemp harvested in the following spring on 22 March 2002. The stalks were dried and stored in un-heated storehouses.

The reed canary grass used was grown at Umeå in northern Sweden. It was harvested around 20 May 2002, and the Palaton variety was used. The reed canary grass was harvested as soon as the moisture content was lower than about 16% (wb), and then stored in un-heated storehouses.

2.2. *Experimental procedure*

The plant material was cut in lengths of about 20 cm and placed on perforated trays. Then, the samples were dried in an oven at 50 °C to an initial moisture content of about 5–7% (db) to ensure adsorption conditions. The flax samples had an average dry matter weight of about 30 g, the hemp samples of about 40 g, and the reed canary grass samples of about 20 g. Each experimental treatment was in triplicate.

The trays were then placed in climate chambers with temperatures of 5, 15 and 25 °C. At 5 °C, the relative humidity was increased step by step from 53 to 72% and finally to 95%. For the temperatures 15 and 25 °C, the relative humidity was increased from 35 to 53% to 72% and finally to 90%. The climate chambers were connected to air conditioning units (*e.g.* JUMO type D 95·820), in which the temperature and relative humidity were controlled to accuracies of $\pm 0{\cdot}5$ °C and $\pm 2{\cdot}0$%, respectively. The units were regularly calibrated. The air velocity in the climate chambers was 0·3 m/s at maximum.

At each specific value of temperature and relative humidity, the samples were weighed using a Mettler PM4800 electronic balance with a precision of 0·01 g. The samples were weighed every second or third day until the change in sample mass between two successive readings was about 0·01 g or less. When equilibrium was reached at the highest value of the relative humidity (90 or 95%), the samples were oven-dried at 105 °C for 24 h in order to determine the moisture contents. Then, the intermediate moisture contents were back-calculated.

2.3. *Analysis of data and model fitting*

The average EMC value of the three replicates was calculated, and the constants A, B and C in the five isotherm equations (Table 1) determined using the non-linear regression procedure NLIN in the SAS statistical package (SAS Institute Inc., Cary, NC, USA). This procedure minimises the sum of residual squares in an iterative process.

The goodness of fit of each model was assessed by calculation of the mean relative percentage deviation P and the root mean square of the residuals or the standard error of estimate E_S

$$P = \frac{100}{N} \sum \frac{|Y - \hat{Y}|}{Y} \quad (1)$$

$$E_S = \sqrt{\frac{\Sigma (Y - \hat{Y})^2}{d_f}} \quad (2)$$

where: Y and $\hat{Y}$ are the measured and predicted equilibrium moisture contents in % (db); N is the number of data points; and d_f the degrees of freedom. Lower values of P and E_S indicate better model fits.

Chen and Morey (1989) showed that low values of P and E_S were not sufficient criteria for evaluating the goodness of fit of isotherm equations, and recommended the use of residual plots in addition. Therefore, the residuals were plotted against measured EMC values and evaluated visually for randomness or pattern. If the plots have a clear pattern, the model was not be accepted (Chen & Morey, 1989).

To evaluate if there were any significant differences in the parameter estimations between varieties and between degrees of retting for flax and hemp, three further parameters Q_A, Q_B and Q_C and a control variable D were introduced into the regression model that was considered to predict the EMC best. For the parameters A, B and C, the terms Q_AD, Q_BD and Q_CD were added, where D was set to 1 for all observations belonging to one variety or degree of retting, and to 0 for all observations belonging to another variety or degree of retting. If the approximate 95% confidence intervals in the estimations of Q_A, Q_B or Q_C did not contain zero, it was assumed that there was a significant difference in the estimations of A, B or C.

3. Results

3.1. *Flax*

The values of the parameters A, B, C and the corresponding values of P and E_S when EMC data for un-retted and dew-retted flax straw of the variety Viola were fitted to the five isotherm equations (Table 1) are shown in Table 2. For un-retted flax, the modified Halsey equation was considered the best at predicting the EMC because it produced the lowest values of P and E_S; 1·28% and 0·27, respectively, and no clear systematic pattern in the residual plot (*Fig. 1*). For dew-retted flax, the values of P (2·65%) and E_S (0·42) were lowest with the modified Oswin equation. The observed EMC data and the predicted EMC with these equations for un-retted and dew-retted flax are shown in *Figs 2* and *3*, respectively. The EMC values were somewhat higher for un-retted flax, especially at higher values of the relative humidity. The EMC values for un-retted flax also had less variation when the temperature was varied.

Table 2
Parameters and goodness of fit measures for the isotherm models describing the equilibrium moisture content (EMC) of un-retted and dew-retted flax of the Viola variety

	Constants			*Mean relative deviation (P), %*	*Standard error of estimate (E_S)*
	A	*B*	*C*		
Un-retted flax:					
Mod. Henderson	$3{\cdot}38 \times 10^{-4}$	84·8	1·31	8·67	1·54
Mod. Chung–Pfost	230	$1{\cdot}27 \times 10^{-1}$	71·3	9·55	1·90
Mod. Halsey	5·11	$-8{\cdot}46 \times 10^{-3}$	2·26	1·28	0·27
Mod. Oswin	11·3	$-4{\cdot}91 \times 10^{-2}$	2·57	3·15	0·54
Mod. GAB	5·35	$8{\cdot}82 \times 10^{-1}$	−656	6·04	1·47
Dew-retted flax:					
Mod. Henderson	$2{\cdot}09 \times 10^{-4}$	56·4	1·65	4·62	0·87
Mod. Chung–Pfost	207	$1{\cdot}74 \times 10^{-1}$	33·5	4·54	0·85
Mod. Halsey	6·50	$-1{\cdot}68 \times 10^{-2}$	2·81	2·92	0·56
Mod. Oswin	11·5	$-6{\cdot}84 \times 10^{-2}$	3·20	2·65	0·42
Mod. GAB	7·01	$7{\cdot}69 \times 10^{-1}$	170	6·60	1·29

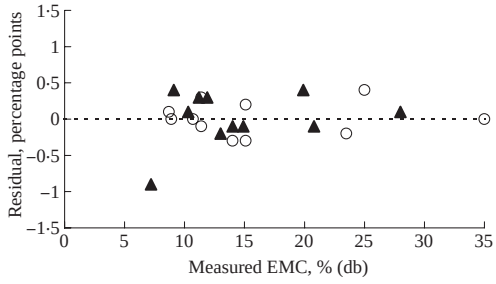


Fig. 1. Residual plots for un-retted flax (Viola) evaluated by the modified Halsey model (◦) and for dew-retted flax (Viola) evaluated by the modified Oswin model (▲): EMC, equilibrium moisture content

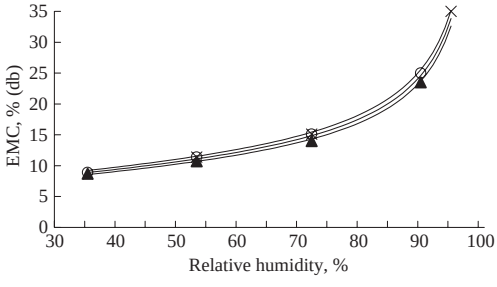


Fig. 2. Adsorption isotherms predicted with the modified Halsey equation (solid lines) for un-retted flax straw (Viola) and measured data at 5°C (×), 15°C (◦) and 25°C (▲): EMC, equilibrium moisture content

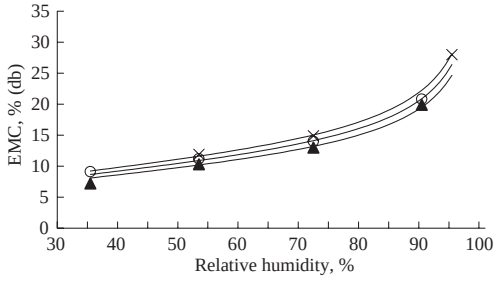


Fig. 3. Adsorption isotherms predicted with the modified Oswin equation (solid lines) for dew-retted flax straw (Viola) and measured data at 5°C (×), 15°C (◦) and 25°C (▲): EMC, equilibrium moisture content

When observed EMC data from the Viola and Elise varieties were fitted to the Halsey equation, there were no significant differences in the parameters at a confidence level of 0·95. This result was valid for both un-retted and dew-retted flax, indicating that the differences between the varieties were small.

When un-retted Viola flax was compared to retted and over-retted Viola flax with the Halsey equation, there were statistically significant increases in the value of A to 6·50 and the value of C to 2·81 in the former case, and a statistically significant increase in the value of C to 2·41 in the latter case.

3.2. *Hemp*

The values of the parameters A, B and C for hemp (Felina) harvested in the autumn (un-retted) and in the following spring (frost-retted) are presented in Table 3. The modified Oswin equation predicted the EMC for un-retted hemp with the lowest values of P (2·57%) and E_S (0·44), whereas the modified Chung–Pfost equation predicted the EMC for frost-retted hemp with the lowest values of P (2·79%) and E_S (0·54). These equations showed no clear systematic pattern in the residual plots (*Fig. 4*). The resulting isotherm curves of these equations, together with measured data, are shown in *Figs 5* and *6*. Similar to flax, the EMC varied less for un-retted hemp than for frost-retted hemp when the temperature was changed.

When the Felina and Futura varieties were compared using the modified Oswin equation, there was a statistically significant increase in the value of B to $2{\cdot}12 \times 10^{-2}$ for Futura for un-retted hemp stalks, whereas there were no significant differences between the varieties for frost-retted hemp stalks. A statistically significant increase in the value of C to 3·37 was observed when un-retted and frost-retted hemp (Felina) were compared.

3.3. *Reed canary grass*

The results from the parameter estimations for spring-harvested reed canary grass are shown in Table 4. The values of P and E_S for the modified Halsey equation were 3·66% and 0·63, respectively, which were somewhat lower than the values for the modified Oswin equation. The residual plot is shown in *Fig. 7* and predicted EMC curves and the measured data in *Fig. 8*.

4. Discussion

The best model for each treatment had an acceptably close agreement with the measured data, and the highest values of P and E_S were 3·66% and 0·63, respectively, for spring-harvested reed canary grass with the modified

Table 3
Parameters and goodness of fit measures for the isotherm models describing the equilibrium moisture content (EMC) of un-retted and frost-retted hemp of the Felina variety

	Constants			*Mean relative deviation (P), %*	*Standard error of estimate (E_S)*
	A	*B*	*C*		
Un-retted hemp:					
Mod. Henderson	$1{\cdot}44 \times 10^{-4}$	130	1·52	5·24	0·91
Mod. Chung-Pfost	433	$1{\cdot}61 \times 10^{-1}$	108	4·87	0·89
Mod. Halsey	5·74	$-4{\cdot}09 \times 10^{-3}$	2·59	3·72	0·61
Mod. Oswin	10·6	$-2{\cdot}29 \times 10^{-2}$	2·96	2·57	0·44
Mod. GAB	6·01	$8{\cdot}16 \times 10^{-1}$	571	4·59	0·98
Frost-retted hemp:					
Mod. Henderson	$1{\cdot}40 \times 10^{-4}$	78·8	1·73	3·02	0·60
Mod. Chung–Pfost	293	$1{\cdot}92 \times 10^{-1}$	47·1	2·79	0·54
Mod. Halsey	6·67	$-1{\cdot}21 \times 10^{-2}$	2·95	6·03	0·92
Mod. Oswin	10·8	$-4{\cdot}64 \times 10^{-2}$	3·37	4·19	0·68
Mod. GAB	7·04	$7{\cdot}41 \times 10^{-1}$	171	4·02	0·86

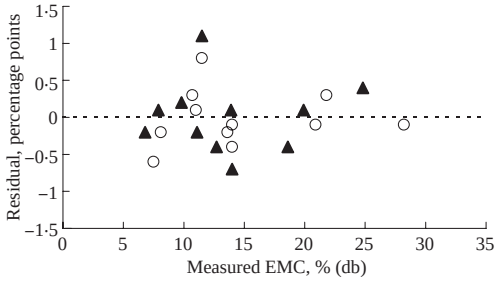


Fig. 4. Residual plots for un-retted hemp (Felina) evaluated by the modified Oswin model (◦) and for frost-retted hemp (Felina) evaluated by the modified Chung–Pfost model (▲): EMC, equilibrium moisture content

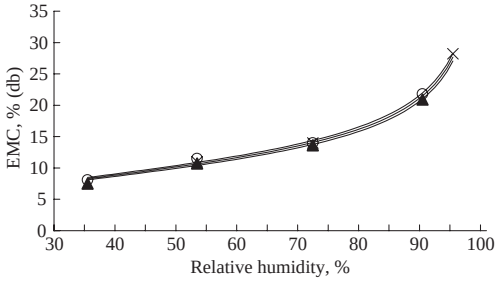


Fig. 5. Adsorption isotherms predicted with the modified Oswin equation (solid lines) for un-retted hemp stalks (Felina) and observed data at 5 °C (×), 15 °C (◦) and 25 °C (▲): EMC, equilibrium moisture content

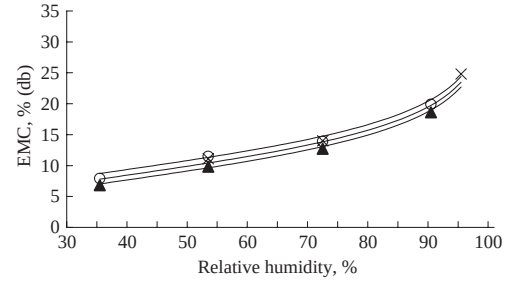


Fig. 6. Adsorption isotherms predicted with the modified Chung–Pfost equation (solid lines) for frost-retted hemp stalks (Felina) and observed data at 5 °C (×), 15 °C (◦) and 25 °C (▲): EMC, equilibrium moisture content

Halsey equation. The residual plots indicated that there were no clear systematic patterns, although the relatively few data made it difficult to draw certain conclusions. The discrepancies between the varieties were small, and no statistically significant differences in the parameter estimations were found, except for a difference in the constant *B* in Oswin's equation between the varieties Felina and Futura for un-retted hemp stalks. Although the choice of model in these comparisons may have an impact on the results, it can be concluded that the varieties studied had very similar EMC characteristics.

In contrast to the variety comparisons, there were clear differences between un-retted and retted materials, especially regarding EMC levels at high relative humidities, and regarding the influence of temperature on the EMC. These differences were also confirmed with statistically significant differences in the constant *C* for

Table 4
Parameters and goodness of fit measures for the isotherm models describing the equilibrium moisture content (EMC) of spring-harvested reed canary grass of the Palaton variety

	Constants			*Mean relative deviation (P), %*	*Standard error of estimate (E_S)*
	A	*B*	*C*		
Mod. Henderson	$3{\cdot}73 \times 10^{-4}$	28·9	1·59	6·37	1·27
Mod. Chung–Pfost	122	$1{\cdot}61 \times 10^{-1}$	15·9	8·01	1·62
Mod. Halsey	6·63	$-3{\cdot}21 \times 10^{-2}$	2·72	3·66	0·63
Mod. Oswin	12·9	$-1{\cdot}33 \times 10^{-1}$	3·09	4·08	0·68
Mod. GAB	8·50	$7{\cdot}44 \times 10^{-1}$	75·3	11·08	2·28

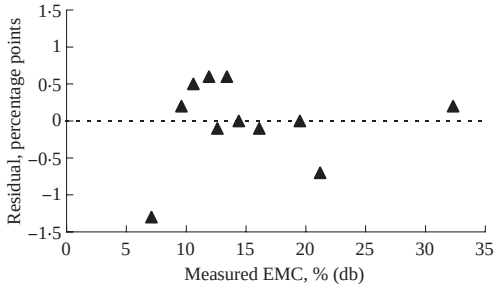


Fig. 7. Residual plots for spring-harvested reed canary grass (Palaton) evaluated by the modified Halsey model: EMC, equilibrium moisture content

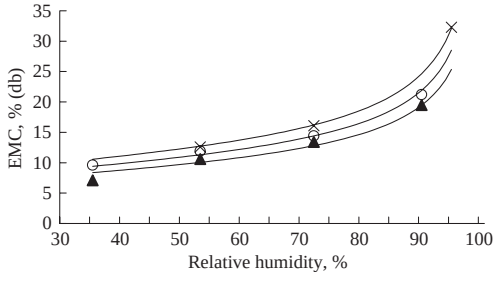


Fig. 8. Adsorption isotherms predicted with the modified Halsey equation (solid lines) for spring-harvested reed canary grass (Palaton) and observed data at 5 °C (×), 15 °C (○) and 25 °C (▲): EMC, equilibrium moisture content

all tests between un-retted and retted materials. The difference between un-retted and retted material is most likely a result of changes in plant structure and chemical composition during the retting process. For example, the contents of pectins and water-soluble substances are reduced during retting of flax, whereas the (relative) content of cellulose is increased (Sharma *et al*., 1999).

Results from sorption isotherm studies of well-defined biological materials presented in the literature may differ considerably due to variations in substrate, equipment design (choice of salt solutions or air conditioning units and uniformity of air conditions, layer thickness, *etc*.) and handling procedures (Wolf *et al*., 1985). For a comparison, however, it can be noted that the EMCs in this study were similar to those obtained by Kymäläinen and Pasila (2000) when they determined the EMC for flax and hemp fractions (fibres, fine shives and coarse shives) at a temperature of 20 °C and relative humidities of 15, 76 and 97%. For the air condition 20 °C/76%, for example, they found that the average EMCs for fibres, fine shives and coarse shives from un-retted flax were 20·2, 16·1 and 14·6% (db), respectively, while the corresponding value in this study for whole stems from the Viola variety was 15·8% (db) (calculated with the Halsey equation).

Kymäläinen and Pasila (2000) also found that the EMC for flax and hemp fractions at relative humidities of 15 and 76% were similar or slightly higher for crops harvested in the autumn in comparison to crops harvested in the following spring. At a relative humidity of 97%, however, they found that the EMC was clearly higher for un-retted plant material than for frost-retted, and that the un-retted samples began to lose weight earlier due to mould growth. These differences in EMC and the tendency to develop moulds at high values of relative humidity were also observed in the present study.

Regarding spring-harvested reed canary grass, the EMC data obtained in the present study were generally lower in comparison to the adsorption data for wheat straw obtained by Duggal and Muir (1981), particularly at a relative humidity around 90%. The results were, however, similar to those for alfalfa hay (ASAE, 2000). The modified Halsey equation was the best at predicting the EMC of reed canary grass, followed by the modified Oswin equation. This was in accordance with the EMC data published by ASAE (2000), in which these equations often have good fit to measured data for fibrous and graminaceous materials.

Generally it took less than 10 days to reach equilibrium as it was defined in Section 2.2. As pointed out by Banaszek and Siebenmorgen (1990a), the adsorption rate is dependent on both the temperature and the relative humidity. For rough rice, the adsorption rate was found to be higher for higher temperatures, at least in the earlier stages, and was twice as high at 90% relative humidity than at 70% relative humidity. In this study, 60–90% of the increase in weight of the samples occurred during the two first days when the air conditions were 5 °C/53%. The lowest values in the interval were valid for un-retted plant material, and the highest for retted material. When the air conditions were 25 °C/53%, 90–100% of the increase in weight occurred during the first two days.

The samples in this study were dried before they were placed in the climate chamber in order to ensure adsorption conditions also for the lowest EMCs at 25 °C/35%. There is a risk, however, for drying to low moisture contents to cause irreversible changes in the material. For rough rice, Banaszek and Siebenmorgen (1990a and 1990b) showed that the adsorption EMC was dependent on not only the temperature and the relative humidity, but also on the initial moisture content. Lower initial moisture contents resulted in lower EMCs, and this relative change in EMC with respect to a change in the initial moisture content seemed to be independent of the temperature and relative humidity combinations used in their study. Yang and Cenkowski (1993) also showed that successive adsorption–desorption cycles at a temperature of, *e.g.* 25 °C shift the isotherms downward for canola. A downward shift of the isotherm means that the relative humidity is increased for the same EMC, which may result in a higher susceptibility to microbial growth. Such adsorption–desorption effects may also be valid for the fibre crops investigated in this study when they are exposed to multiple drying and rewetting cycles in the swathes before harvest.

5. Conclusions

The equilibrium moisture contents (EMCs) of un-retted and dew-retted flax straw, un-retted and frost-retted hemp stalks and spring-harvested reed canary grass were determined and fitted to five commonly used three-parameter EMC equations. The modified Halsey equation was the best for predicting the EMC for un-retted flax straw and for spring-harvested reed canary grass, and the modified Oswin equation for dew-retted flax straw and for un-retted hemp stalks, while the modified Chung–Pfost equation was best suited for frost-retted hemp. For flax and hemp, there were statistically significant differences between un-retted and retted plant material, whereas the differences between varieties were small.

References

ASAE (2000). Moisture relationships of plant-based agricultural products. ASAE D245.5 Oct95. ASAE Standards 2000. American Society of Agricultural Engineers

Aviara N A; Ajibola O O; Oni S A (2004). Sorption equilibrium and thermodynamic characteristics of soya bean. Biosystems Engineering, **87**(2), 179–190

Banaszek M M; Siebenmorgen T J (1990a). Moisture adsorption rates of rough rice. Transactions of the ASAE, **33**(4), 1257–1262

Banaszek M M; Siebenmorgen T J (1990b). Adsorption equilibrium moisture contents of long-grain rough rice. Transactions of the ASAE, **33**(1), 247–252

Brooker D B; Bakker-Arkema F W; Hall C W (1992). Drying and Storage of Grains and Oilseeds. Avi, van Nostrand Reinhold, New York

Chen C; Morey R V (1989). Comparison of four EMC/ERH equations. Transactions of the ASAE, **32**(3), 983–990

Chen C; Jayas D S (1998). Evaluation of the GAB equation for the isotherms of agricultural products. Transactions of the ASAE, **41**(6), 1755–1760

Duggal A K; Muir W E (1981). Adsorption equilibrium moisture content of wheat straw. Journal of Agricultural Engineering Research, **26**(4), 315–320

Finell M (2003). The use of reed canary-grass (*Phalaris arundinacea*) as a short fibre raw material for the pulp and paper industry. Doctoral Thesis, Agraria 424, Swedish University of Agricultural Sciences, Umeå, Sweden

Iglesias H A; Chirife J (1976). Prediction of effect of temperature on water sorption isotherms of food materials. Journal of Food Technology, **11,** 109–116

Jayas D S; Mazza G (1991). Equilibrium moisture characteristics of safflower seeds. Transactions of the ASAE, **34**(5), 2099–2103

Jayas D S; Mazza G (1993). Comparison of five, three-parameter equations for the description of adsorption data of oats. Transactions of the ASAE, **36**(1), 119–125

Kohler R; Dück R; Ausperger B; Alex R (2003). A numeric model for the kinetics of water vapor sorption on cellulosic reinforcement fibers. Composite Interfaces, **10**(2–3), 255–276

Kymäläinen H-R; Pasila A (2000). Equilibrium moisture content of flax/linseed and fibre hemp straw fractions. Agricultural and Food Science in Finland, **9,** 259–268

Kymäläinen H-R; Hautala M; Kuisma R; Pasila A (2001). Capillarity of flax/linseed (*Linum usitatissimum* L.) and fibre hemp (*Cannabis sativa* L.) straw fractions. Industrial Crops and Products, **14,** 41–50

Landström S; Lomakka L; Andersson S (1996). Harvest in spring improves yield and quality of reed canary grass as a bioenergy crop. Biomass and Bioenergy, **11**(4), 333–341

Lomauro C J; Bakshi A S; Labuza T P (1985). Evaluation of food moisture sorption isotherm equations—part I and part II. Lebensmittel–Wissenshaft und Technologie, **18,** 111–124

Nevander L E; Elmarsson B (1994). Fukthandbok, praktik och teori. [Moisture handbook, practice and theory.]. Svensk Byggtjänst och författarna, Stockholm (in Swedish)

Pasila A (1998). A new method for harvesting flax and hemp. In: The 1st Nordic Conference on Flax and Hemp Processing, 10–12 August 1998, Tampere, Finland (Talvenmaa P; Salonen R; Mäkininen M, eds)

Pfost H B; Maurer S G; Chung D S; Milliken G A (1976). Summarizing and reporting equilibrium moisture data for grains. ASAE Paper No. 76-3520. St. Joseph, Michigan

Rahman S (1995). Food Properties Handbook. CRC Press, New York

Rowell R M; Young R A; Rowell J K (1997). Paper and Composites from Agro-based Resources. Lewis Publishers, New York

Sharma H S S; Faughey G; Lyons G (1999). Comparison of physical, chemical and thermal characteristics of water-, dew- and enzyme-retted flax fibers. Journal of Applied Polymer Science, **74,** 139–143

Smeder B; Liljedahl S (1996). Market oriented identification of important properties in developing flax fibres for technical use. Industrial Crops and Products, **5,** 149–162

Speiss W; Wolf W (1987). Critical evaluation of methods to determine moisture sorption isotherms. In: Water Activity: Theory and Applications to Food (Rockland L B; Beuchat L R, eds). Marcel Dekker, New York

Sultana C (1992). Growing and harvesting of flax. In: The Biology and Processing of Flax (Sharma H S S; van Sumere C F, eds). M Publications, Belfast

Svennerstedt B (2003). Plant fibres in sustainable constructions. Special Report 243. Department of Agricultural Biosystems and Technology, Swedish University of Agricultural Sciences, Alnarp, Sweden

Thompson T L; Peart R M; Foster G H (1968). Mathematical simulation of corn drying. A new model. Transactions of the ASAE, **11**(4), 582–586

Van den Berg C; Bruin S (1981). Water activity and its estimation in food systems: theoretical aspects. In: Water Activity: Influences on Food Quality (Rockland L B; Stewart G, eds), pp 1–61. Academic Press Inc., New York

Van den Berg C (1984). Description of water activity of foods for engineering purposes by means of the GAB model of sorption. In: Engineering and Foods (McKenna B M, ed), pp 119–131. Elsevier Science Publishers, New York

Van Sumere C F (1992). Retting of flax with special reference to enzyme-retting. In: The Biology and Processing of Flax (Sharma H S S; van Sumere C F, eds). M Publications, Belfast

Viswanathan R; Jayas D S; Hulasare R B (2003). Sorption isotherms of tomato slices and onion shreds. Biosystems Engineering, **86**(4), 465–472

Wolf W; Speiss W E L; Jung G (1985). Standardisation of isotherm measurements (cost-project 90 and 90 bis). In: Properties of Water in Foods in Relation to Quality and Stability (Simatos D; Multon J L, eds), pp 661–679. Martinus Nijhoff Publishers, Dordrecht, The Netherlands

Yang W H; Cenkowski S (1993). Effect of successive adsorption–desorption cycles and drying temperature on hygroscopic equilibrium of canola. Canadian Agricultural Engineering, **35**(2), 119–126

II

To be submitted to *J Polymers Environm*

Use of industrial hemp fibers to reinforce wheat gluten plastics

C.Wretfors[1], *S.-W. Cho*[2], *M. S. Hedenqvist*[2], *S. Marttila*[1], *S. Nimmermark*[1] *E. Johansson*[1]*

[1]Faculty of Landscape Planning, Horticulture and Agricultural Sciences, Swedish University of Agricultural Sciences, P.O Box 104, SE-230 53 Alnarp, Sweden, christer.wretfors@ltj.slu.se

[2]Dept. of Fiber and Polymer Technology, Royal Institute of Technology, SE-100 44 Stockholm, Sweden.

*Corresponding author: Eva.johansson@ltj.slu.se

Running title: Hemp fibers reinforce wheat gluten plastics

Abstract

The next generation of plastics and other materials must be sustainable and industrially eco-efficient, developed through green chemistry. Some of the most promising plastic materials from the green sector are created from wheat gluten. By reinforcing these gluten plastics, mechanical properties might be improved, enabling usage in a wider range of applications. The present study investigates the possibilities of reinforcing wheat gluten plastics with hemp fibers.

Hemp fiber-reinforced gluten plastic samples were manufactured using compression moulding at a temperature of 130 °C, with an applied pressure of 1600 bar for 5 minutes. The fiber content was 5, 10, 15 and 20 weight-% and three different fiber qualities (poor, standard, good) were tested.

The effect of fiber length, content and quality on mechanical properties was examined using tensile testing, light microscopy and scanning electron microscopy.

The results showed that hemp fiber reinforcement influenced tensile strength and strain, as well as E modulus of the material. The amount of fiber included in the material showed a significant positive correlation with strength and E modulus, and a negative correlation with strain. Quality of the hemp fibers did not play any significant role for strength and strain, but the E modulus was significantly and positively correlated with hemp fiber quality. However, the reinforced gluten material generally showed very uneven tensile strength and strain characteristics within the material due to clustering of the fibers and to poor bonding between fibers and gluten material. Both these problems have to be resolved before reinforcement of gluten plastics by industrial hemp fibers is applicable on an industrial scale.

Keywords: composite materials, hemp, plastics, renewable raw materials, wheat gluten

Introduction

There is currently worldwide interest in high performance bio-based plastics and composite materials due to increasing demands for environmentally friendly materials for industrial use [19] and to the depletion of petroleum resources.

Wheat gluten-based bioplastics are an interesting alternative to traditional synthetic plastics in various applications due to their combination of mechanical, oxygen barrier and film-forming properties [1], [3], [14]. Wheat gluten plastic material can be manufactured using several processing methods, including extrusion, compression moulding and solution casting [17]. Compression moulding and extrusion are commercially more interesting due to faster processing times. During compression moulding, high temperature, plasticiser content and type, pH, processing time and shear rate all influence the mechanical properties due to their importance for protein polymerisation [16], [15]. Sulphydryl from the amino acid cysteine is responsible for creating disulphide cross-links during oxidation. The reorganisation of the intramolecular disulphide bonds into intermolecular disulphide bonds is an important part of the aggregation process [13], [2]. The upper temperature limit of the processing window is determined by depolymerisation together with overextensive aggregation [4].

One possibility for expanding the potential areas of application for bio-based plastics is to add additional mechanical properties, such as tensile and impact strength, to the material, e.g. by reinforcement with bio-fibers. Plants containing fibers of interest for the manufacture of engineering materials include flax, hemp, jute, coconut and nettles [11]. The main advantages of using plant fiber are renewability, high strength and elastic modulus, low density, non-abrasiveness and biodegradability [6]. Engineered wood and lignocellulosic composite technologies can lead to considerable addition of value to a diverse number of raw materials. The development of industrial composite processing technology will also automatically provide producers with the possibility to adapt to the constantly changing qualities of raw materials. At present, the level of performance of engineered composite products limits the application of such materials [19].

The use of plant fibers to reinforce plastics has been investigated in quite a number of studies (e.g. [11]). However, the use of plant fibers for reinforcement of bioplastics is still relatively uncommon and primarily uses different types of plant fibers in soy-based bioplastics [10], [12]. One very recent study investigated the possibilities of using natural fibers to reinforce plasticised wheat gluten [8]. The use of natural fibers for reinforcement of plastics is influenced by a number of factors including plant variety, climate variations, harvest times, maturity, retting, methods of decortication and other technical processes [5]. All these variables combine to create one of the main drawbacks encountered when trying to design new materials based on plant fibers, namely the large variation in fiber properties such as tensile strength and surface geometry [6]. This variation exists among fibers from plants grown in the same plot, and even within groups of fibers from the same plant [7]. The general advantages of using plant fiber include renewability, high strength and elastic modulus, low density, non-abrasiveness and biodegradability.

The main aim of the present study was to investigate the possibility of using industrial hemp fibers to reinforce wheat gluten plastics manufactured by compression moulding. An additional aim was to study the influence of the amount of fiber added and the quality of the fiber on tensile strength, strain and E modulus. Furthermore, fiber distribution and fracture surfaces were investigated using stereomicroscopy and scanning electron microscopy (SEM).

Materials and Methods

Materials

Wheat gluten (WG) powder was supplied by Reppe AB, Lidköping, Sweden. The powder consisted of 84.8 wt% wheat gluten proteins, 8.1 wt% wheat starch, 5 wt% water, 1.34 wt% fat and 0.76 wt% ash. Glycerol with a concentration of at least 99.5 wt% and a water content of less than 0.5 wt %, was supplied by Karlshamns Tefac AB, Karlshamn, Sweden.

Three different types of industrial hemp fibers were selected in order to provide three distinct quality levels:

- Hemp fiber type 1 – poor quality: Unretted hemp stalks, harvested by forage harvester, were partially dried in plastic tubs with fans placed underneath the hemp material. The resulting fiber was heavily retted and designated ‘poor’ quality.
- Hemp fiber type 2 – standard quality: Unretted hemp stalks, harvested by forage harvester, were processed through a hammer mill with sieve size 50 mm (Kamas Industri AB, Sweden) and then through a step cleaner (Hergeth Gmbh, Germany) to remove larger size shives. The resulting fiber type was designated ‘standard’ quality.
- Hemp fiber type 3 – good quality: Unretted hemp stalks, harvested by forage harvester, were processed through a hammer mill (Kamas Industri AB) without any sieve installed and then through a step cleaner (Hergeth Gmbh, Germany) to remove large and small shives. Because no sieve was used, the fiber passed quickly through the mill, resulting in less fiber damage. The resulting fiber type was designated ‘good’ quality.

Sample preparation for compression moulding

Dough was prepared by mixing gluten and glycerol to a content of 30 wt% (given as the mass of glycerol per total weight of glycerol and WG). Each blend was mortared for five minutes using a Mortar Agate from VWR International. When the dough was assessed as being homogeneous, hemp fiber of the desired type and amount was added.

For the initial tests, 5, 10 and 15% of poor, standard and good quality hemp fiber were added to form separate samples of hemp fiber-reinforced gluten plastics. The samples were compression moulded directly after addition of the hemp fibers, following the methodology described below. During these initial tests, it was found that the fibers were too long, resulting in poor fiber distribution throughout the plastic.

For all subsequent samples, shorter fibers were used. These were prepared by removing any woody substances manually and then processing the fibers in a high speed grinder (model A10, IKA-WERKE, Staufen, Germany) for 2 x 10 seconds, resulting in very short fibers to facilitate a more uniform distribution through the plastic material. The gluten dough together with the desired amount (5, 10, 15 and 20%) of short industrial hemp fibers were added to an electrical blender (Waring Commercial, USA) and mixed until an even blend of dough and fibers was achieved.

Compression moulding

Compression moulded films were processed using a PHI press (Pasadena Hydraulics Inc, California, USA). Portions of 10 g of dough were placed in an aluminium frame between Mylar foils, which in turn were placed between metal plates. The frame was used to obtain square films with sides of 100 mm length and a thickness of 0.5 mm. The moulding temperature was 130 °C, and the pressure was set to 100 bar, which gave an applied pressure of 1600 bar. The moulding time was 5 min. After moulding, the plates were removed from the press and the films were allowed to cool to ambient temperature. The Mylar foils were then removed and the films were separated from the frame using a scalpel.

Sample thickness measurements

The thickness of each sample was measured using a Mitutoyo IDC-112B micrometer (Mitutoyo Scandinavia AB) in accordance with SCAN-P 7:96 at 23 °C and 50% relative humidity (RH), at a static pressure of 100 kPa.

Tensile testing

A Zwick Z010 tensile strength tester (ZwickRoell) equipped with a 10 kN load cell controlled by a testXpert 7.1 (Lambda Instruments AB) was used to determine the mechanical properties of the samples. The measurements were performed according to ISO 527-3:1995(E). Dumbbell-shaped specimens were punched out with a narrow width of 4 mm and conditioned for three days at 23 °C at 50% RH before testing. A crosshead speed of 100 mm/min and an initial grip distance of 40 mm were used. Fifteen replicates of each sample were tested.

Light microscopy (LM)

Samples from each treatment were studied by stereo light microscopy with a digital camera Leica DC 300 (Leica Microscopy Systems Ltd, Cambridge, UK) in order to evaluate the fiber distribution throughout the plastic. Nine images were taken for each sample in order to cover the entire sample area.

Scanning electron microscopy (SEM)

An LEO 435VP scanning electron microscope (Cambridge, UK) with a secondary electron detector at acceleration voltage of 10 kV was used to study the fiber raw material and the finished plastic

material. The native samples were mounted on the stubs and sputtered with an Au/Pd 3:2 coating (JFC-1100, JEOL, Tokyo, Japan).

Images were taken of the fiber raw material to categorise it into one of the three quality types by observing the state of the fiber bundle surfaces.

Plastics samples of the specific treatment that showed the biggest variation in E modulus during tensile testing were chosen for further SEM analyses. The fracture surface of samples from this treatment was compared with that of another almost similar treatment that exhibited a much smaller variation in E modulus, the only difference being the fiber quality. The surface of the samples in the area of the actual fracture was observed in order to study the fiber fracture and distribution.

Statistical analysis

Statistical analyses were carried out using the SAS software package for Microsoft Windows (SAS Institute Inc, NC, USA). Analyses of variance (ANOVA) was carried out, followed by calculation of means for the different treatments with significance determined using LSD (0.05).

Results

fiber quality

The good quality fibers showed thick fiber bundles with relatively clean and only mildly damaged fiber surfaces when studied using SEM (Fig. 1a). The poor quality fibers sustained a larger degree of surface damage and fiber degradation, with thinner fiber bundles (Fig. 1b). The standard quality fibers were relatively undamaged and clean, with a mixture of thinner and thicker fiber bundles.

Films with long fibers

The compression moulded films containing the long fibers were very non-homogeneous, regardless of amount and quality of fiber, and the fibers were very unevenly distributed within the material. fibers tended to be lumped together in bundles (results not shown). As the results were not satisfactory, although promising, further work including tensile testing was carried out on samples to which short fibers were added.

Films with short fibers

When the fibers added were short instead of long, they were much better distributed throughout the gluten matrix. However, the fibers were still somewhat unevenly distributed in the gluten matrix and were clustered together in bundles (Fig. 2a and 2b). The fibers had a random orientation in the matrix. Some contaminating plant tissue was also seen. No clear difference in the behaviour of the different fibere qualities in the gluten film was seen by light microscopy.

Tensile testing of short hemp fiber-reinforced gluten plastics

Tensile strength and E modulus of the short hemp fiber-reinforced gluten plastic samples varied in relation to hemp fiber content and quality (Table 1). However, standard deviations for measured parameters were large due to the uneven distribution of fibers in the materials (Table 1).

ANOVA analysis showed significant influences of treatments (content and quality of short hemp fibers in the gluten plastics) on tensile test parameters such as stress, strain and E modulus (Table 2). Gluten plastics without any hemp fiber added were found to have low tensile strength (maximum stress and stress at fracture), while the strain (strain at maximum stress and strain at fracture) was high. The E modulus was also found to be low. With increasing content of short hemp fibers tensile strength and E modulus were found to increase, while strain decreased (Table 3). No

significant influences of fiber quality on tensile strength or stress were found. However, E modulus was found to increase with improved fiber quality (Table 4).

Fracture surfaces of short industrial hemp fiber-reinforced gluten plastics

The fracture surface of gluten film without fiber reinforcement was very uniform (Fig. 3) and the gluten film tended to break in a sheet-like manner, similarly to proteins in the starchy endosperm of dehydrated cereal grains. Samples from the treatment with 15% good quality fiber were chosen for SEM analyses as this was one of the samples with most variation in tensile strength measurements. The fracture surfaces of these samples was compared with the fracture surface of samples of the treatment with 15% poor quality fiber, which was one of the most even treatments in terms of variation in tensile testing measurements. The SEM images showed that the fibers were unevenly distributed throughout the material (Fig. 4), as was found by light microscopy (Fig. 2). Fig. 4a shows uneven fracture surfaces in films with good quality fibers, while Fig. 4b the corresponding fracture surfaces for poor quality fibers. In both cases, fracturing seemed to have started around areas where the fibers were clustered and where air pockets had started to form, and the fibers were protruding from the matrix. The more even fracture surfaces (Fig. 4b and d) show clearly that gluten film had broken in a sheet-like manner, as in Fig. 3. Fewer fibers were protruding from the matrix than in the uneven fracture surfaces, but there were still air pockets near the clustered fibers. When the protruding ends of fibers were examined more closely, it was seen that the fibers had been pulled out of the gluten plastic matrix, rather than breaking during tensile testing (Fig. 5). The typical blunt end of pulled-out fiber bundles shown in Fig. 5a suggests that this is a surface formed during milling of the fibers. For comparison, Fig. 5b shows the only fiber end we could find in the material screened where the fiber appeared to have actually broken during tensile testing, as shown by the serrated edges of the fiber bundle.

Discussion

The present study confirmed the finding by [8] that it is possible to use industrial hemp fibers to reinforce wheat gluten plastics. In contrast to [8], both long and short industrial hemp fibers were tested in the present investigation, and short ones were found to give a better distribution of fibers in the gluten matrix. The advantage of using short industrial hemp fibers instead of long has also been pointed out by other authors, e.g. [12] for reinforcing soy protein plastics.

Tensile strength and E modulus of wheat gluten plastics were increased by reinforcement with hemp fibers, as was also found by [8]. Addition of natural fibers has also been found to increase the tensile properties of a range of other materials (e.g. [12], [11]; [10], [9]). In other studies, natural fibers have been shown to compare favourably with glass fibers, and hemp fibers have been shown to out-perform e.g. kenaf fibers [18]. As in other investigations [10], fiber content in the present study had a significant effect on tensile strength, with an increase in fiber content resulting in a stronger and stiffer material. Contrary to previous results [10], our investigation did not show a negative influence of increasing fiber content on fiber dispersion. The reason might be the different plastic and fiber materials used in the studies, soy protein and pineapple leaf fibers in that by [10] compared with gluten proteins and hemp fibers in our study. If a stronger gluten protein material with higher stiffness is required, it is therefore desirable to include as much short industrial hemp fiber reinforcement as possible.

Although the short industrial hemp fibers were better distributed in the gluten matrix than the long ones, a relatively high standard deviation was still found during the tensile testing and this was most likely caused by an uneven distribution of the fibers throughout the plastic. The fibers showed a tendency to cluster together during the mixing process and this caused weaker, unreinforced zones

in the material, as could be seen clearly by both light microscopy and SEM. Uneven distribution of natural fibers in plastic matrices has also been reported in previous studies [10], [9]. Several reasons for this were identified in the present investigation. First, the blender used for this experiment caused part of the plastic mix to stick to the walls of the glass container while the hemp fibers tended to collect at the bottom of the container, where the rotating blade was located. One possible way of achieving a better distribution of fibers in the gluten matrix would therefore be to find a better method of blending the fibers together with the plastic dough, e.g. by using a high performance mixer. Another possibility is the addition of substances that increase the viscosity of the plastic dough.

The present investigation showed limited influences of fiber quality on tensile strength properties, with significant effects only being recorded for E modulus. To our knowledge, there are few previous investigations on the relationships between fiber quality and tensile strength properties of natural fibers. The only published study investigating the possibility of reinforcing gluten plastics with industrial hemp fibers does not compare quality of the hemp fibers and relationships to tensile properties [8].

The limited effect of fiber quality on tensile strength properties was probably due to the poor bonding between fibers and plastic observed in the present study. This poor bonding was visible as a pull effect, where the fibers did not fracture during tensile testing. Air pockets were also observed around clustered fibers, again suggesting poor bonding between the fibers and the matrix. Because the wheat gluten plastic itself was much weaker than even the lower quality fibers, no effects of fiber quality could be detected during tensile testing. If a stronger bonding had been achieved between the fibers and the plastic, the different fiber qualities might have had a more dramatic effect. Poor bonding between natural fibers and plastic materials has also been reported by other authors [10], [9]. Different solutions have been suggested, e.g. addition of alkali solutions to

decrease the interfibrillar region by removing the hemicellulose and lignin [9]. Other suggested solutions are additions of compatibilisers such as polyester amide grafted glycidyl methacrylate [10]. Treatment of Indian grass fibers with alkali solution has been shown to lead to a more homogeneous dispersion of fibers in plastics and also to an improvement in fiber reinforcement efficiency [9], while addition of compatibiliser to soy-based bioplastic reinforced with pineapple leaf fibers led to increased tensile and flexibility properties and impact strength, as well as better dispersion of the fibers [10]. For better and more even distribution of short industrial hemp fibers within gluten protein plastics, a method is needed in which a cross-linking agent can be added to help create hydrogen bonds to both the fibers and the plastic.

Conclusions

Short industrial hemp fibers are a good solution for reinforcement of gluten plastics, creating a strong, stiff and sustainable eco-efficient material for the automotive and building product industry. Before the material can be used, however, problems with uneven distribution of hemp fibers and poor bonding between fibers and the matrix in the material have to be resolved. Possible solutions for a better distribution of fibers in the material include use of a better mixer, increased viscosity of the plastic dough and/or additions of cross-linking substances for creating linkages between fibers and the dough.

Acknowledgements

This work was financed by Formas. The authors thank Maria Luisa Prieto-Linde for practical help in the laboratory and Kerstin Brismar for her assistance with SEM.

References

1. Cuq B, Gontard N, Guibert S (1998) Proteins as agricultural polymers for packaging

production. Cereal Chem 75:1-9

2. Domenek S, Morel M-H, Bonicel J, Guilbert S (2002) Polymerization kinetics of wheat gluten upon thermosetting. A mechanistic model. J Agric Food Chem 50:5947-5954
3. Gennadios A (2002) Protein-based films and coating. CRC Press LLC, Boca Raton, Fl
4. Gällstedt M, Matozzi A, Johansson E, Hedenqvist MS (2004) Transport and tensile properties of compression-molded wheat gluten films. Biomacromolecules 5:2020-2028
5. Kessler R.W, Kohler R, Tubach M (1999) Strategy for a sustainable future of fiber crops, Proceedings of the international conference on natural fibers performance, Copenhagen, Denmark
6. Kohler R, Wedler M (1994), Non-textile applications of flax fibers, Vortrags-nr 331, Proceedings of the Techtextil-symposium, 1994, Frankfurt, Germany.
7. Kohler R, Kessler R.W. (1999), Designing natural fibers for advanced materials, Proceedings of the 5th International conference on woodfiber–plastic composites, 25-26 May, Madison, USA.
8. Kunanopparat T, Menut P, Morel M-H, Guilbert S (2008) Reinforcement of plasticized wheat gluten with natural fibers: from mechanical improvement to deplasticizing effect. Composites part A: Applied science and manufacturing 39:777-785
9. Liu W, Mohanty AK, Askeland P, Drzal LT, Misra M (2004) Influence of fiber surface treatment on properties of Indian grass fiber reinforced soy protein based biocomposites. Polymer 45:7589-7596
10. Liu W, Misra M, Askeland P, Drzal LT, Mohanty AK (2005) 'Green' composites from soy based plastic and pineapple leaf fiber: fabrication and properties evaluation. Polymer 46:2710-2721
11. Mohanty AK, Misra M, Drzal LT (2002) Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world. J Polymers Environm 10:19-26
12. Mohanty AK, Misra M, Drzal LT (2005) Injection molded biocomposites from soy protein based bioplastic and short industrial hemp fiber. J Polymer Environm 13:279-285
13. Morel M-H, Redl A, Guilbert S (2002) Mechanism of heat and shear mediated aggregation of wheat gluten protein upon mixing. Biomacromolecules 3:488-497

14. Olabarrieta, I., Cho, S-W., Gällstedt, M., Sarasua, J.R., Johansson, E., Hedenqvist, M.S. (2006) Aging properties of films of plasticized vital wheat gluten cast from acidic and basic solutions. Biomacromolecules 7:1657-1664
15. Redl A, Morel M-H, Bonicel J, Guilbert S, Vergnes B (1999) Rheological properties of gluten plasticized with glycerol: dependence on temperature, glycerol content and mixing conditions. Rheol Acta 38:311-320
16. Roy S, Weller CL, Gennadios A, Zeece MG, Testin RF (1999) Physical and molecular properties of wheat gluten films cast from heated film forming solutions. J Food Sci 64:57-60
17. Ullsten NH, Gällstedt M, Johansson E, Gräslund A, Hedenqvist MS (2006) Enlarged processing window of plasticized wheat gluten using salicylic acid. Biomacromolecules 7:771-776.
18. Wambua P, Ivens J, Verpoest I (2003) Natural fibers: can they replace glass fiber reinforced plastics? Composites Sci Technol 63:1259-1264
19. Winandy J.E (2006) Advanced wood- and bio-composites: Enhanced performance and sustainability. Proc. of 4th International Conference on Advanced Materials and Processes. University of Waikato, Hamilton, New Zealand.

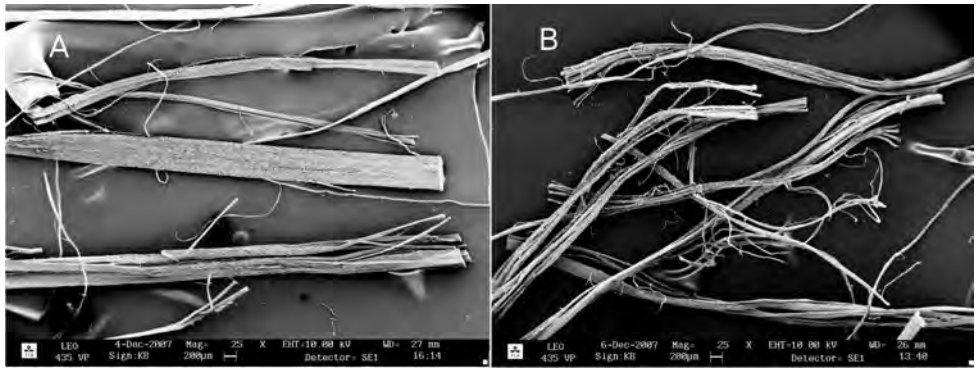


Figure 1. SEM images showing short hemp fibers of a) good and b) poor quality. Scale bar 200 μm.

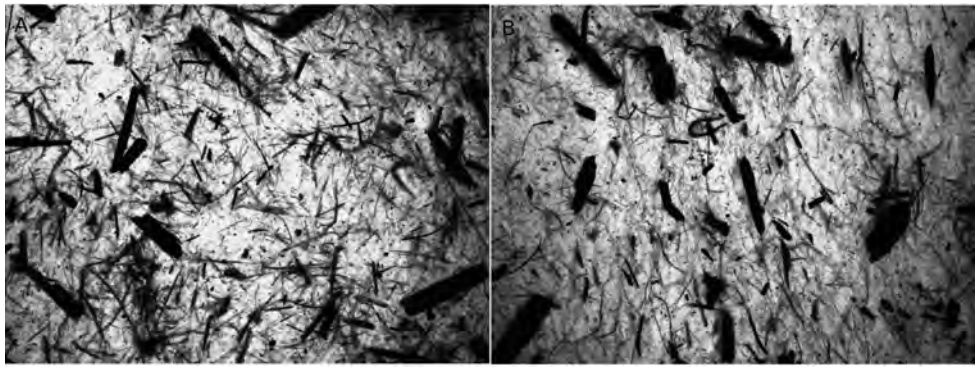


Figure 2. Light microscopy images showing gluten films reinforced with short hemp fibers of a) good and b) poor quality.

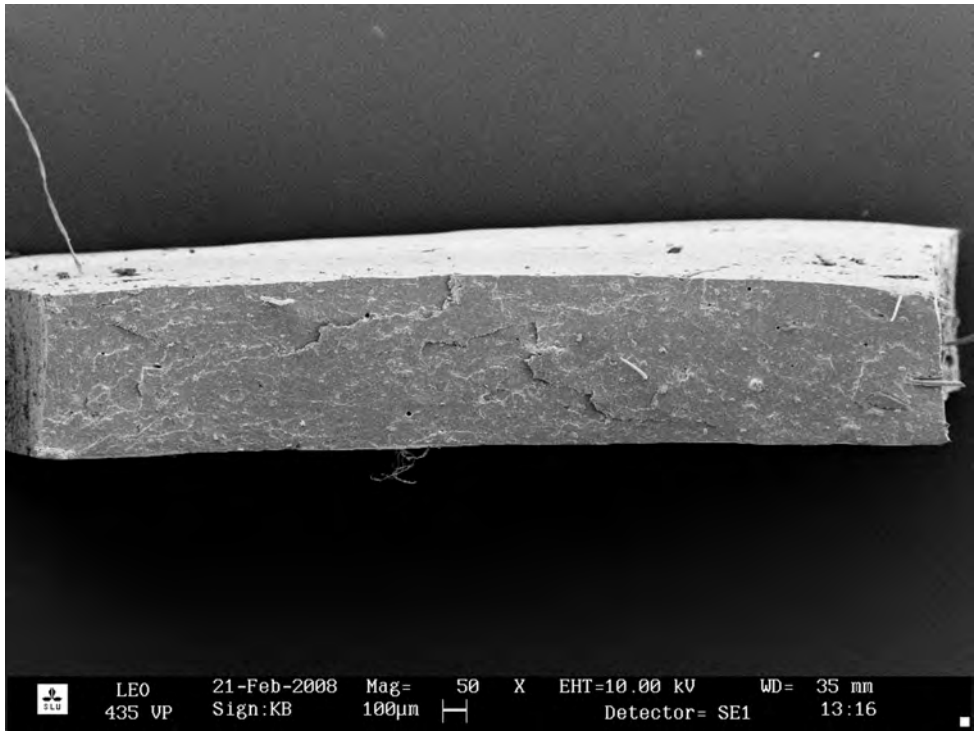


Figure 3. SEM image showing gluten plastic film without fiber reinforcement. Scale bar 100 µm.

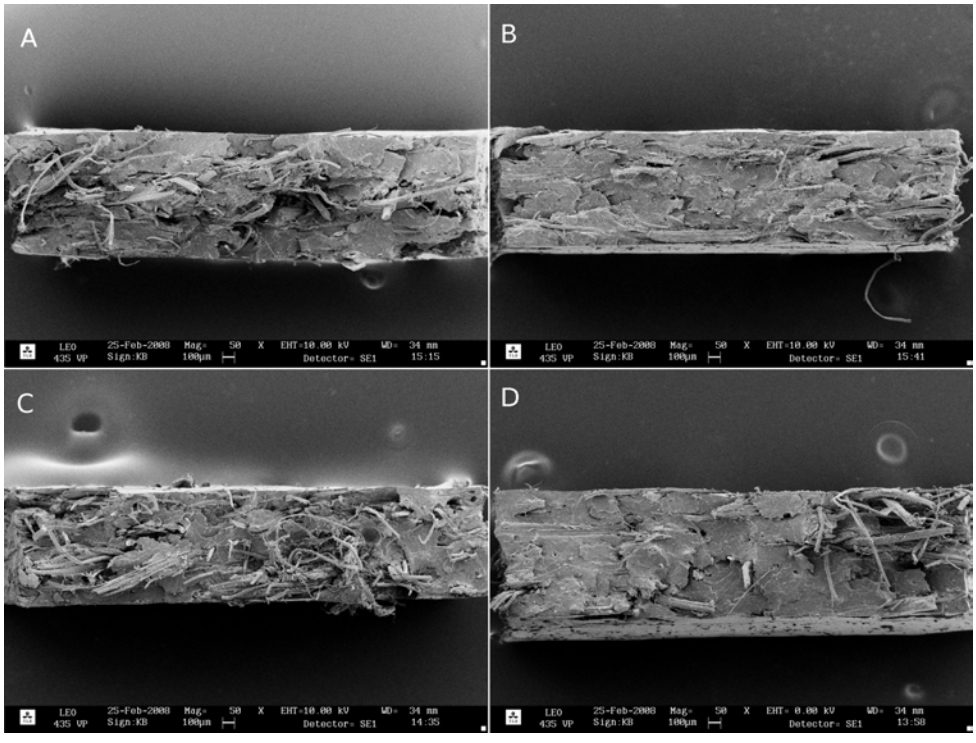


Figure 4. SEM images showing fracture surfaces of gluten film reinforced with short hemp fibers of a) good quality fibers and uneven fracture surface, b) good quality fibers and more even fracture surface, c) poor quality fibers and uneven fracture surface, and d) poor quality fibers and even surface. Scale bar 100 µm.

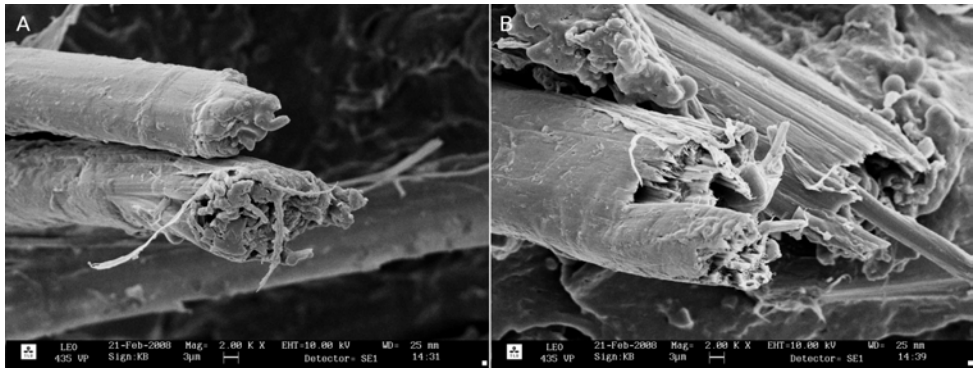


Figure 5. SEM images showing magnification of pulled-out fibers from a fracture surface, a) typical blunt-end fiber and b) more rare broken fiber with serrated edges. Scale bar 3µm.

Table 1: Mean E modulus and strain at fracture of hemp fiber reinforced gluten plastics containing different fiber amounts and qualities. N=15. Standard deviation is shown within parenthesis.

Treatment	E-modulus (MPa)	Strain at fracture (%)
Wheat gluten	23.8 (7.1)	149.2 (15.6)
5 % fiber, poor	40.6 (13.2)	42.0 (15.7)
10 % fiber, poor	84.2 (53.1)	21.6 (9.7)
15 % fiber, poor	108.9 (59.0)	12.6 (4.2)
20 % fiber, poor	141.9 (52.8)	10.2 (2.3)
5 % fiber, average	45.6 (18.5)	37.3 (14.9)
10 % fiber, average	88.1 (56.4)	18.3 (8.4)
15 % fiber, average	113.2 (65.0)	12.8 (3.9)
20 % fiber, average	228.9 (116.1)	9.2 (4.1)
5 % fiber, good	41.4 (14.3)	45.9 (17.4)
10 % fiber, good	82.0 (41.3)	21.7 (12.9)
15 % fiber, good	143.1 (145.5)	15.8 (9.1)
20 % fiber, good	227.1 (93.5)	8.6 (2.2)

Table 2: Mean squares from analyses of variance (ANOVA) of treatments (content and quality of short industrial hemp fibres in reinforced gluten plastics) on tensile test parameters

Source	DF	Maximum stress	Strain at maximum stress	Stress at fracture	Strain at fracture	E-modulus
Treatment	12	13.9***	21.7***	5.0***	21.2***	65.9***
Error	182	1.8	0.1	1.3	0.1	4.8

*** indicate significant differences were found.

Table 3: Mean values of tensile strength measurements at different fiber content.

Fiber content	Maximum stress	Strain at maximum stress	Stress at fracture	Strain at fracture	E-modulus
0%	2.6cd	147.3a	2.5bcd	149.2a	23.7d
5%	2.3d	35.9b	1.9d	41.5b	42.5d
10%	3.3c	13.8c	2.5c	20.5c	84.8c
15%	4.1b	10.0d	2.9ab	13.7d	12.8b
20%	4.7a	6.1d	3.3a	9.3e	199.3a

Means with the same letters within a column do not differ significantly (LSD 0.05).
Tensile values are given in MPa.

Table 4: Mean values of tensile strength measurements at different fiber quality.

Fiber quality	Maximum stress	Strain at maximum stress	Stress at fracture	Strain at fracture	E-modulus
Bad	3.5a	16.8a	2.6a	21.6b	94.0b
Average	3.8a	15.3a	2.9a	19.3a	118.9ab
Good	3.5a	18.0a	2.6a	22.9b	123.4a

Means with the same letters within a column do not differ significantly (LSD 0.05).
Tensile values are given in MPa.