



Development of bioplastics from oil plant by-products

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Sammanfattning

I detta examensarbete studerades möjligheten att göra bioplast av oljekaka från *Crambe Abyssinica*, *Brassica Carinata* och *Brassica Napus* (raps) för att på detta sätt skapa ett mervärde för dessa restprodukter. Materialen varmpressades och extruderades vid 100 °C med glycerol som mjukgörare. Material som pressades utan mjukgörare blev spröda. De varmpressade plattorna analyserades med avseende på mekaniska egenskaper, fukthalt, vatten- samt oljeabsorption.

Malning av oljekakan med kulkvarn resulterade inte i förbättrade egenskaper hos de varmpressade plattorna. Eftersom alla tre oljeväxter har halvtorkande oljor tillsattes ett sickativ i olika koncentrationer för att tvärbinda oljan och på så sätt addera till bioplastens matris. Plattor pressades efter förvärmning av materialen i 0 h, 2 h eller 6 h. Plattor pressades även av granulerat extrudat som förvärmts 0 h eller 2 h. Mekaniska egenskaper, fukthalt, vatten- samt oljeabsorption utvärderades för de pressade plattorna.

Hos crambe- och carinataplattorna påverkade förvärmning innan pressning egenskaperna mer än sickativkoncentration gjorde. Däremot hade koncentrationen av sickativ större inverkan på rapskakeplattornas egenskaper. Carinata och rapskaka var lättare att processa än crambe eftersom de flöt bättre. Plattor och extrudat av carinata var mer flexibla än plattor och extrudat av crambe och rapskaka. Ett tråg kunde varmpressas utav en blandning av crambe och rapskaka. Alla tre material visar potential att kunna användas som bioplaster i styva applikationer, kanske inom förpackningsindustrin.

Abstract

The feasibility of making bioplastics out of oil cake from *Crambe Abyssinica*, *Brassica Carinata* and *Brassica Napus* (Rapeseed) was studied in order to produce added value for these by-products. The materials were hot pressed and extruded at 100 °C using glycerol as a plasticizer. Pressing without plasticizer produced brittle materials. Tensile properties, moisture content, water and oil absorption were determined for the hot pressed sheets.

Ball milling of the oil cake did not result in improved properties of the pressed sheets. As the three plants all have semi-drying oils, a siccative was added in different concentrations to crosslink the oil and add to the matrix of the bioplastic. Sheets were pressed after pre-heating the materials 0h, 2 h or 6 h. Sheets were also pressed from granulated extrudate with different concentrations of siccative after pre-heating for 0 h or 2 h. Tensile properties, moisture content, water and oil absorption were determined for the pressed sheets.

Pre-heating before pressing had a larger impact than siccative concentration on the properties of crambe and carinata sheets. Siccative concentration had larger influences on the properties of rapeseed cake sheets. Carinata and rapeseed cake were easier to process than crambe as they flowed better. Carinata sheets and extrudates were more flexible than crambe and rapeseed cake sheets and extrudates. A tray could be pressed from a mixture of crambe and rapeseed cake. All three materials show potential to be used as bioplastics for rigid items, perhaps in packaging applications.

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1 Introduction

1.1 Purpose

The purpose of this study was to develop bioplastics, from oil plant by-products, for future usage in e.g. the packaging industry. This is a part of ICON, *Industrial Crops producing added value Oils for Novel chemicals*, an EU-project. Some seed oils have qualities that can be used as chemical feedstock. ICON aims to develop such high quality oils in certain industrial oil crops. The oil crops included in this project all belong to the *Brassicaceae* family, they are rapeseed (*Brassica napus*), Ethiopian mustard (*Brassica carinata*) and crambe (*Crambe abyssinica*).

In order to make plant oils a competitive alternative to petroleum based chemical feedstock, added value must be given to the by-products generated by the industry. One added value could be making bioplastics from the by-products. There are advantages with using agricultural by-products, not only are the bioplastics renewable, but they are also of low cost, which is a must if the products are to be competitive with petroleum based plastics.

Another requirement to keep bioplastics competitive is that they can be processed with customary methods for petroleum based plastics, such as compression moulding and extrusion. The aim of this thesis project was to examine the feasibility of making bioplastics from oil plant by-products, and if possible create process demonstrators and a prototype, e.g. a tray or an extrudate.

1.2 Strategy

The idea with this work was to produce bioplastics using as simple means as possible, meaning there should be few processing steps. To process the material compression moulding and extrusion were the processing choices. Parallel work was performed where pressing temperature and plasticizer content was varied and different additives were examined. Two hypotheses were the base of this project;

- milling of the material could possibly increase the interaction of the proteins leading to a stronger material
- crosslinking the oil in the material could add strength to the matrix.

A visual and sensory evaluation was made of the sheets. Tensile properties, moisture content, water and oil absorption and oxygen transmission rate were analyzed to characterize the bioplastics. Before the experimental part is described, a background with information regarding protein-based bioplastics, oil plants and crosslinking of vegetable oils can be read in the sections that follow.

1.3 Background

Steps towards replacing petroleum resources have already been taken with the development of renewable materials and fuels made from renewable products. In recent years the prefix “bio-“ has come to be frequently used when describing these new materials. Other terms frequently used are “eco-friendly” and “sustainable”. Mohanty et al. define a sustainable bio-based product as “a product derived from renewable resources having recycling capability and triggered biodegradability with commercial viability and environmental acceptability”.¹

The agricultural industry is currently a provider of renewable resources. One area of interest in terms of chemical feedstock is oil plants.² High-yielding oil crops can, with perhaps tailor-made oil quality, provide the industry with large quantities of raw material.³

The by-products from the oil plant industry contain a large quantity of proteins and sometimes residual oils, among other things.^{4,5,6,7} If bio-plastics can be made from these by-products, added value will be given to the oil plants, and cheap and abundant raw materials for bio-plastics have been found. The following sections explain more about bioplastics made from proteins and the oil plants used in this project.

1.3.1 Bioplastics

The term “bioplastics” refers to a broad concept with different explanations and definitions belonging to the word. Included in the concept can be attributes such as renewability, biodegradability, edibility and compostability among others. A bio-based product does not necessarily have to possess all the above mentioned properties. Different applications require different properties. The key-word is perhaps “bio-based”, which can be applied when the product is made from renewable raw material. If a product is made from renewable resources it is, according to Mohanty et al, carbon dioxide neutral.¹ However, more aspects need to be taken into account when determining this property, one example is the process of choice.

To describe bio-based plastics, a categorization based on production and origin is often made.⁸ The resulting categories are sometimes referred to as biosynthetic, semi-biosynthetic and chemosynthetic.⁹ A biosynthetic polymer is polymerized in a plant or a living organism, naturally or through genetic modification. The polymer is then extracted or removed from the biomass. Typical examples are cellulose, starch or proteins.^{10,11} A semi-biosynthetic polymer is polymerized in a fermentation process, e.g. by microorganisms or genetically transformed bacteria. Polyhydroxyalkanoates are examples belonging to this category.^{8,9} Finally, a chemosynthetic polymer is chemically synthesized from renewable monomers, e.g. polylactide polymerized from lactic acid monomers.^{8,9} Many of the bio-based materials are biodegradable, but as earlier mentioned, they do not all have to be.^{1,8,9}

There are several ways of producing plastic materials. Two general ways are physico-chemical or mechanical (thermoplastic) processing.¹² The former method includes the use of chemical reactants or solvents. The polymer is dissolved or dispersed and later dried.¹³ The

thermoplastic processing includes fewer steps, and it is a common method used to process plastics for e.g. packaging purposes. To be able to use conventional methods for producing bio-based plastics is a criterion for commercial viability of these materials.¹⁴ Examples of mechanical processing are compression moulding, extrusion or injection moulding.

1.3.2 Agro-materials

As mentioned above, much of the raw materials used for bio-plastics consist of polymers from nature. Many proteins, lipids and polysaccharides are agricultural biopolymers, referred to as agro-materials, which have been used for years to manufacture bioplastics.¹² The agricultural industry also produces a lot of by-products. When these by-products are rich in any of the biopolymers mentioned above, they might be useful as raw material for the chemical industry. Gluten, for instance, is a by-product from the agro ethanol industry.¹⁵ And glycerol, often used as a plasticizer, is a by-product from the biodiesel industry.¹⁶

1.3.3 Protein-based bioplastics

Proteins are biopolymers commonly consisting of 20 different types of amino acids.^{17,18} The primary structure of proteins, the order of which the amino acids are linked together, determine the interactions between the side groups of the amino acids, thus determining the structure of different sections of the chain, the secondary structure.^{17,18} The interactions can be of different character, van der Waal's interactions, hydrogen bonds, electrostatic interactions and disulfide bridges among others.^{17,18} These interactions also continue to work among the chain segments thus creating the tertiary structure of the proteins, e.g. globular, fibrous or random structure.¹⁸ The quaternary structure is reached when proteins interact together, at times with other components such as metal ions, to give the final function of the protein.¹⁹

The secondary to quaternary structure of a protein can be altered or even destroyed by outer influences such as heat, mechanical impact, chemistry etc.¹⁰ These alterations can be reversible or non-reversible.¹⁰ When processing proteins to form bioplastics, the original protein denatures to a certain amount as intermolecular bonds are ruptured and new interactions between the proteins are formed creating a macromolecular network.²⁰ Between these two steps, the polymers are arranged to the desired shape.²¹ The processing choice can be either a wet process including solubilisation, dispersion and drying of the protein plastic or a dry process where the thermoplastic properties of proteins are used to create the new macromolecular network.^{21,22} The properties of protein-based bioplastics can also be tailored as the side chains of the proteins can be chemically modified or additives can be added.⁸

Bioplastics made from proteins are generally good barriers to unpolar matters, which is very interesting for food packaging purposes.^{23,24} Due to the hygroscopic nature of proteins however, the water vapour barrier properties are not as good as for petrochemically derived polymers and the mechanical properties are strongly affected by relative humidity.⁸ Further

properties of protein-based bioplastics include biodegradability and sometimes edibility, depending on additives and/or process conditions.¹

Much work has been done on protein-based bioplastics, often as films or coatings due to many of the above mentioned properties but further interest in the non-food area has also been evoked, see Table 1 for a few examples.²⁵⁻³⁴

Table 1: Examples of protein-based bioplastics. Table adapted from A. Gennadios in "Edible films and coatings from proteins"²⁴

Application (Plastic)	Proteinaceous material	Reference
Edible films and coatings	whey protein isolate	Kokoszka et al 2010 ²⁵ Kim et al 2001 ²⁶
	wheat gluten	Gontard et al 1996 ²⁷ Gennadios et al 1993 ²⁸
	zein	Bai et al 2003 ²⁹
	gelatine	Andreuccetti et al 2009 ³⁰ Kokoszka et al 2010 ³¹
	soy protein isolate	Gennadios et al 1996 ³²
	egg albumen	
Controlled release devices	whey protein	Lee and Rosenberg 2000 ³³
"Green" composites	Soy protein and flax yarn	Chabba et al 2005 ³⁴

1.3.4 Thermoforming of proteins

Thermoforming of a material includes melting or softening of the material and then shaping it to the desired form before letting it cool. This requires process temperatures above the softening point of the protein, T_g .²⁰ As agro-materials and proteins often have a high T_g , sometimes above the decomposition temperature, the processing window can be quite narrow. A plasticizer lowers the T_g , so plasticizer content can affect the processing window.²⁰

Thermoforming of proteins can be more difficult than thermoforming of starch as the soft phase is not as fluid as that of thermoplastic starch (TPS).¹⁰ Elevated temperatures can also induce crosslinking reactions or other chemical reactions that may influence the properties of the proteinaceous materials.³⁵

Thermoforming include compression moulding, injection moulding and extrusion. Gluten has successfully been both compression moulded and extruded.¹⁵ The same has been reported for soy protein³⁶ and fish myofibrillar protein³⁷, to mention a few examples.

1.3.5 Oil cake products

Oil cake is the residual of oil plant processing after the oil has been pressed or extracted. Because of its high protein content, oil cakes from different plants have been of interest as a protein source in food or feed.^{4,5} Some crops contain anti-nutritional substances such as glucosinolates or phytic acids which make them unsuitable for food or feed, these oil cakes can be used as fertilizers instead.⁴ Other contents of the oil cakes include fibres, starch and ash for example.⁴⁻⁷

When oil cake has been subject to research, the most common subject has been that of the potential of the proteins in the cake.⁴⁻⁷ The use of oil cake as a raw material for bioplastics processing has not been extensively researched at all but two materials of interest for composite materials are sunflower cake and rapeseed cake.³⁸⁻⁴⁰

Geneau-Sbartai et al concluded that sunflower cake can be seen as a natural composite after examining the plastic properties of the components in this oil cake. The proteins could be seen as the matrix and components from the husk of the seeds as fillers in the composite.³⁸ Rouilly et al produced objects such as flower pots and tea candle holders through injection moulding. The sunflower cake was compounded with water using a twin screw extruder and after equilibration injection moulded. With thermo-mechanical and chemical treatment the proteins were denatured and crosslinked and the fibres defibrilled which enabled the processing of the composite materials.³⁹

Rapeseed cake was injection moulded by Baganz et al. They used different pre-treatments such as pulverization, hydrothermal treatment and alkaline treatment to try to improve the properties resulting in higher strength of the materials. However a binding agent was needed to injection mould these materials.⁴⁰ A master thesis performed at Innventia also used rapeseed cake and rapeseed flour as raw material for bioplastics. Chemical additives were used with some positive results regarding the properties of the materials, however all materials made were brittle.⁴¹

1.4 Oil Plants used in this project

1.4.1 Brassicaceae family

The Brassicaceae family is also called the mustard family or the cabbage family. It contains more than 3000 species belonging to about 350 genera.⁴² The former name of this family was Cruciferae, a name derived from the four pedals of the flower, shaped similar to a cross.⁴² A trait for the members of the family is their production of glucosinolates.⁴² Plants of economic value include many common crops, including broccoli, brussel sprouts, cabbage, mustard and rapeseed.⁴²

1.4.2 Rapeseed

Rapeseed (*Brassica Napus*) is one of the most common oil plants cultivated in the world, with China and Canada as the top producers.⁴³ In Europe 23 Mton were produced in 2008 with the top three countries being Germany, France and the Ukraine. Sweden was the 14th largest producer of rapeseed in 2008.⁴³

Rapeseed is cultivated for its oil content; the seeds contain 30-40% oil.⁴⁴ The fatty acid composition of the rapeseed oil determines the use of the oil. Much work has been done in developing rapeseed with tailored fatty acid composition for the end use.⁴⁵ Examples are the "double 0" (00) or canola quality of the oil, where the levels of the anti-nutritional substances erucic acid (C22:1) and glucosinolates are low or the High Erucic Acid Rapeseed, HEAR, which has a high content of erucic acid. The former variant is cultivated for food and the latter for use of the oil as chemical feedstock.⁴⁵ The main fatty acid component in the oil of the 00-variant is oleic acid (C18:1) but it also contains linoleic (C18:2) and linolenic acid (C18:3).⁴⁶ The iodine number is a way to describe the level of unsaturation and oils are divided into three categories, drying, semi-drying and non-drying oils.¹⁶ Rapeseed oil belongs to the category semi-drying oils, the iodine value is between 100 and 170 g I₂/100 g¹⁶, namely 100,4 g I₂/100 g.⁴⁶ An example of the fatty acid composition can be seen in Table 2.

The protein rich oil cake can contain approx. 50 % protein,⁴ up to 50% of these proteins are water soluble albumins, and globulins represent 25%.⁴⁷ The 00-variant is reported to have a high content of the amino acids methionine and cystine, which contain sulphur.⁴⁸ The amino acid content is reported to be well balanced and it contains high levels of essential amino acids for humans.⁴⁹ The amino acid composition can be seen in Table 3.

1.4.3 Brassica Carinata

The common name for *Brassica Carinata* is Ethiopian mustard.⁵⁰ It is derived from a cross between the species *Brassica oleracea* and *Brassica nigra*.⁵⁰ It has high glucosinolate content and high erucic acid content.⁵⁰ In dry climates, it has better agricultural performance than rapeseed.² The plant is eaten in Ethiopia, but the non-nutritional substances make the oil cake less suitable for these purposes.⁵

As mentioned above, the oil contains high levels of erucic acid, but other types with different fatty acid compositions have been developed as well.⁵⁰ The seeds can contain up to 42 % oil.² The oil is often considered as raw material for the production of bio-diesel.^{51,52} In terms of drying classification, carinata oil is a semi-drying oil with an iodine value of 109,4 g I₂/100 g.⁵² The fatty acid composition can be seen in Table 2.

Proteins were found to be the main constituent of the oil cake, approx. 40 %, with a balanced content of the essential amino acids,⁵ see Table 3 for amino acid content. The oil cake further contained 32 % fibres, 9 % moisture, 6 % soluble sugars, 5 % glucosinolates and some other minor components.⁵

Table 2: Fatty acid composition for crambe, rapeseed (00) and carinata oil.

Fatty acid	Chain length	Double bonds	Crambe oil (%) ⁵³	Rapeseed oil (%) ⁴⁶	Carinata oil (%) ⁵¹
Myristic acid	C14	0	0.1		
Palmitic acid	C16	0	2.0	4	3.1
Palmitoleic	C16	1	0.2		
Stearic acid	C18	0	0.7	2	1.0
Oleic acid	C18	1	18.0	56	9.7
Linoleic acid	C18	2	9.4	26	16.8
Linolenic acid	C18	3	6.5	10	16.6
Arachidic acid	C20	0	0.8		0.7
Gadoleic acid	C20	1	2.0		
Behenic acid	C22	0	1.8		
Erucic acid	C22	1	55.9		42.5
Others			2.6	2	Rest to 100

1.4.4 Crambe abyssinica

Crambe abyssinica is considered a non-food oil crop due to its very high content of erucic acid.² It does not cross with other *brassica* used for food, such as rapeseed,⁵⁴ and it is quite adaptable and can grow in quite many climates.⁵³ These facts make crambe interesting as industrial feedstock.² There has been research regarding the proteins in the oil seed, both isolation procedure⁷ and biochemical and functional properties of the proteins have been of interest, as a first step towards finding non-food applications for crambe meal.⁵⁵ The seeds were found to contain ca 35 % oil and the protein content of the oil cake was around 26 %.⁵³ The fibre content is also high, around 18 %.⁵³

The amino acid composition is reported to be well balanced, however the glucosinolate content in the meal makes the cake less suitable for feed.⁵⁶ Table 3 shows the amino acid composition.

Erucic acid content of the oil is very high, reports tell of 56 %, it also contains oleic, linoleic and linolenic acid, but in much smaller quantities,⁵⁶ see table 2. The iodine value of crambe oil is 110 g I₂/100 g,⁵³ which puts the oil in the semi-drying category.

Table 3: Composition of the main amino acids in the three oil crops. (g/16 g N)

Amino acid	Rapeseed defatted meal ⁴⁷	Crambe ⁵⁶	Carinata ⁶
Aspartic acid	7.0	6.9	6.5
Glutamic acid	18.7	14.8	17.1
Serine	4.4	4.2	3.6
Histidine	2.7	3.2	2.4
Glycine	5.1	4.7	4.1
Threonine	4.4	4.6	3.6
Arginine	5.6	5.5	7.0
Alanine	4.4	3.9	3.6
Proline	6.1	5.2	5.6
Tyrosine	2.3	3.0	2.4
Valine	4.9	5.8	4.3
Methionine	1.9	2.2	1.5
Cystine	1.2	2.0	2.2
Isoleucine	3.8	3.7	3.4
Leucine	7.0	5.8	5.9
Phenylalanine	3.8	4.7	3.4
Lysine	5.9	4.7	4.7
Tryptophan	1.2	1-2	0.6

1.5 Crosslinking vegetable oils

1.5.1 Oxidation of unsaturated/vegetable oils

The autoxidation of unsaturated lipids includes a series of reactions and it can be divided into different stages.^{57,58} The first step includes the formation of a free radical, reaction (1) in the scheme below. The free radical reacts with oxygen and a peroxy radical is formed, (2). The peroxy radical can abstract hydrogen from another compound and a hydroperoxide and a new radical is formed, (3). Hydroperoxide formation is followed by decomposition, in the presence of a metal catalyst the decomposition products can be alkoxy or peroxy radicals, (4), (5).⁵⁸ The radicals formed from this step can combine with other radicals leading to crosslinking and polymerization, (6). The hydroperoxides can however also decompose into different volatile or non-volatile compounds (6).⁵⁷ Figure 1 shows a simplified scheme of radical autoxidation.

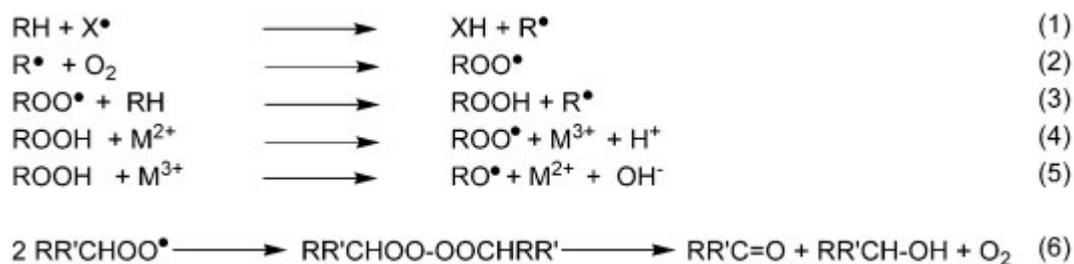


Figure 1: Scheme of radical oxidation with molecular oxygen.⁵⁸

In the third step above, a hydroperoxide is formed. How fast this procedure is, depends to a large extent on the strength of the bond that is broken between hydrogen and carbon.⁵⁷ Hydrogen on a carbon next to a carbon-carbon double bond is not as strongly bound as hydrogen can be to carbon, it can thus be removed in the autoxidation process.⁵⁷ The higher the degree of unsaturation in the vegetable oil, the more susceptible it is to autoxidation.⁵⁷

Many parameters can influence the autoxidation of unsaturated lipids.^{57,58} Temperature and oxygen availability are two things, but UV radiation can also strongly influence the autoxidation.⁵⁷ If the lipids are part of a compound, then other substances can influence the autoxidation as well. There can be pro-oxidants speeding the procedure up, or anti-oxidants, which are oxidized instead of the lipids.⁵⁷

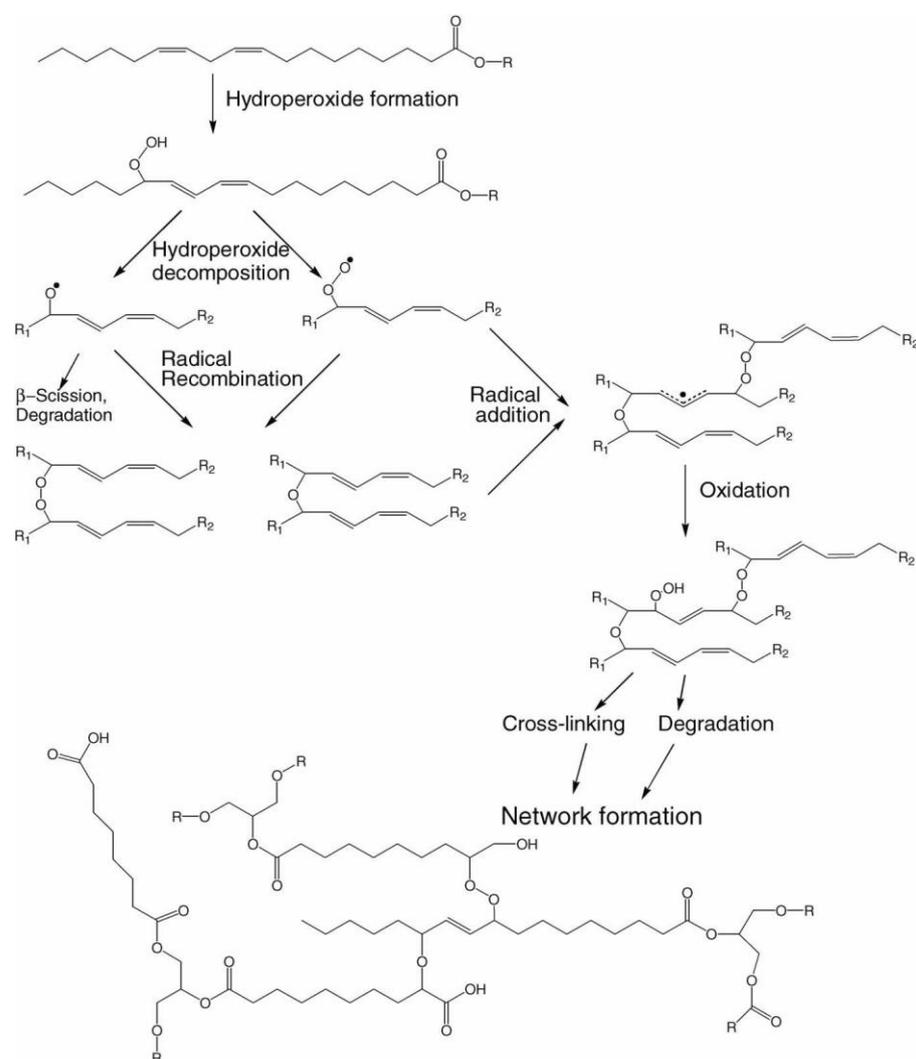


Figure 2: Scheme of network formation of oxidised oils or crosslinked alkyd paints. Secondary oxidation products are shown as well.⁵⁹

In alkyd-based paints the use of driers is common.⁶⁰ Driers are usually metal soaps, which catalyze the autoxidation process.⁶⁰ The prime role of the drying agent is to aid the decomposition of hydroperoxides, which is a relatively stable species.⁶⁰

Different metals are used in driers. Cobalt compounds are the most common driers,⁵⁹ but in the last years attempts have been made to replace it, as reports have told of cobalt as a carcinogenic substance.⁵⁸ However, cobalt driers still remain as they show very good properties.⁵⁸ The driers can be divided into three categories, primary, secondary or auxiliary driers.⁵⁹ The autoxidation catalysts are the primary driers, whereas secondary driers contribute more to the crosslinking. Secondary driers are therefore also called through driers.⁵⁹ The function of the auxiliary driers is not really clearly known, but they improve the function of primary driers.⁶⁰ Commercially a combination of metals is usually used as driers.⁵⁹

1.5.2 Manganese (III) acetylacetonate

Common metals researched to replace cobalt as a drier are manganese, lead or zirconium.⁵⁷ There are also commercial driers based on these metal soaps available.⁵⁹ To increase the activity of these driers different ligands have been of interest. Amine ligands contribute to enhanced activity of manganese driers and 2,2-bipyridyl is said to do the same.^{60, 61}

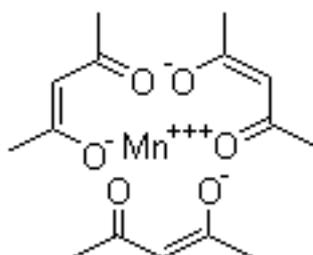


Figure 3: Manganese (III) acetylacetonate⁶²

Manganese (III) acetylacetonate ($\text{Mn}(\text{acac})_3$) was able to initiate radical autoxidation of ethyl linoleate at room temperature with more oligomerization formation and less volatile secondary oxidation product formation in comparison with other catalysts.^{60,61} It was also shown that $\text{Mn}(\text{acac})_3$ works well as a drier in real alkyd systems.⁶⁰ In radical polymerization of different compounds $\text{Mn}(\text{acac})_3$ is also used as a radical initiator, e.g. with styrene.⁶³

2 Experimental

2.1 Material

Crambe (CR), carinata (CA) and rapeseed cake (RC) were supplied by the Swedish University of Agricultural Sciences. All materials were ground 2 x 10 seconds (stirring with a spoon in between to avoid unground spots) in a Krups 75 coffee grinder, Groupe SEB, Germany, before being used. Glycerol (99,5%) was supplied from Karlshamns Tefac AB, Karlshamn, Sweden and $Mn(acac)_3$ was purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany.

2.2 Compression moulding

100 g CR meal was ball milled using a Pascal Engineering rotary ball mill, England, for 48 h with small samples collected from the ball mill every hour up until 8 h, then after 24 h and 48 h. The mill house had a volume of 5 l, 80 balls with a diameter of 25 mm were used and the jar revolution was 53 rpm. The small samples collected from the ball mill were hot pressed to a thin film between two press plates at 100°C and 220 bar for 5 minutes using a Polystat 200T, Servitec Maschinenservice GmbH, Germany.

To compare properties of the materials related to milling time, sheets were compression moulded. Unmilled meal, meal milled 24 h and meal milled 48 h, using the above mentioned ball mill with the parameters set accordingly, were pressed both pure (CR and CA) and with 15 wt% glycerol (CR, CA and RC). Before pressing, the meal and glycerol was mixed for 10 minutes using a Krups 3 Mix 5000 electric hand mixer equipped with dough hooks from Groupe SEB, manufactured in Spain, and a Bosch universal bakery machine, model MUM6650SK, Bosch GmbH, Germany. A plastic jar was placed in the middle of the bakery machine and the speed was set to “1”. The electric hand mixer was put into the jar and put on speed “M”. The mixers were stopped every 2,5 minutes to scrape the walls and bottom of the jar and the dough hooks from glycerol and dough. Figure 4 shows the mixer setting.



Figure 4: Setting for mixing the materials before pressing.

Two different moulds were used for pressing of the sheets, 60*60*0,5 mm and 100*100*0,5 mm. The pressure gauge was set to 220 bar and the temperature 100°C, pressing time was 12 min. About 8-12 g material was used for the big mould and 5,5-7 g were used for the smaller sheets.

All materials, unmilled, were pressed with 15 wt% glycerol and 0,01 wt%, 0,05 wt%, 0,1 wt% and 5 wt% Mn(acac)₃ respectively. After mixing the materials, they were filled in the form, pressed directly or heated in an Electrolux oven (model 350-970 80 11) with a temperature of 60°C for two hours or six hours respectively, then pressed as mentioned above. Early results indicated that RC properties improved when pre-heating the material. As the RC raw material available did not suffice for all of the above mentioned experiments, sheets were only pressed out of pre-heated material.

2.3 Extrusion

The materials were extruded using a Haake Rheomex twin screw extruder from Thermo Fischer Scientific GmbH, Germany. The temperature was set to 100°C and screw speed was 35 rpm. 10 g total was used for every extrusion with material without siccative, the glycerol content used was 15 wt%. After the glycerol was added to the meal the mixture was quickly manually stirred to distribute the glycerol somewhat evenly. The mixture was then manually fed to the extruder.

When preparing extrudate to be granulated and pressed, 20 g or more were fed to the extruder. The meal was continuously (although manually) fed through the extruder. The siccative concentrations used were 0,01 wt%, 0,05 wt%, 0,1 wt% Mn(acac)₃. RC was only extruded with 0 wt% and 0,1 wt% siccative as enough material for all experiments was not available.

2.4 Microscopy

The first thin films made of crambe were analysed with Scanning electron microscopy to look for homogeneity and possible pores in the film, in order to determine milling time to use. Samples were examined in a Hitachi S-4800 field-emission scanning electron microscope (FE-SEM), using a voltage of 1,0 kV. The films were cryo fractured and one cross sectional area was examined for each sample. Before insertion in the microscope, the fracture surfaces were coated with gold to a thickness of ca. 6nm using an Agar High Resolution Sputter Coater (model 208RH), equipped with a gold target/Agar thickness monitor controller.

2.5 Differential scanning calorimetry

Differential scanning calorimetry using a Q1000 auto MDSC, TA instruments, USA, were performed on pure RC, RC with glycerol, RC with glycerol and $\text{Mn}(\text{acac})_3$ (0,01 wt%, 0,05 wt% and 0,1 wt% respectively) and pure $\text{Mn}(\text{acac})_3$. Temperature ramping runs from 25°C to 200°C were performed in air and in nitrogen atmosphere for all concentrations. For pure RC, RC with glycerol and RC with glycerol and 0,05 wt% $\text{Mn}(\text{acac})_3$, runs at 60°C and 100°C were performed. Samples were stored in ambient laboratory conditions prior to testing.

2.6 Tensile testing

Tensile testing to determine mechanical properties was performed at 23°C and 50 % RH according to ASTM D882-02⁶⁴ but with dumbbell shaped specimens using a Zwick Z010 tensile tester from Zwick GmbH & Co, Germany, controlled by testXpert 7.1.

Dumbbell shaped specimens were punched from the sheets using a Elastocon EP04 cutter press, Elastocon, Sweden, with a ISO 37-type 3 cutter die. The length of the narrow part was 16 mm and the width 4 mm, total length of the specimen was 64 mm. A load cell of 200 N was used for the materials without siccative and a load cell of 10 kN was used for materials with siccative. Cross-head speed was set to 10 mm/min and initial grip separation was 40 mm. Maximum stress and strain at break was measured and Young's modulus was calculated from the initial slope of the stress-strain curve, not including the initial scatter using Matlab 2008, see Appendix 1 for an example of the program used. The thickness of the samples was determined as the mean thickness measured at five points using a thickness tester, Lorentzon and Wettre's type 21 from Lorentzon and Wettre, Sweden. Samples were conditioned at 23°C and 50 % RH for three days prior to testing. At least 10 specimen of each sheet were tested. Mean value and confidence interval of 95% confidence level was calculated.

2.7 Water absorption

The water absorption of the compression moulded sheets was determined using a method adapted from SCAN-P 12:64.⁶⁵ Absorption tests were carried out at 23°C and 50 % RH.

Four samples of size 25x25 mm were cut from each sheet. The thickness of the samples was determined as the mean thickness measured at two points using a thickness tester, Lorentzon and Wettre's type 21 from Lorentzon and Wettre, Sweden. The samples were weighed using a Sartorius AC210S, Sartorius GmbH, Germany, immersed in distilled water (100 ml in a petri dish) for 20 s and after an additional 10 s put between blotting papers where excessive water was removed by pressing the sample between the papers. The sample was once again weighed and the water absorption was calculated as

$$WA = \frac{w_a - w_b}{A} \left[g/m^2 \right]$$

where w_b and w_a are the weight of the samples in g before and after water immersion respectively, and A the total surface area in m^2 of the sample. The mean value and confidence interval of 95 % confidence level was calculated.

2.8 Oil absorption

The oil absorption was determined in the same manner as the water absorption however the samples were immersed in refined olive oil from Henry Lamotte Oils GmbH, Bremen, Germany, for 10 min, after an additional 30 s they were put between blotting papers where excessive oil was pressed from the samples. The oil absorption was calculated as

$$OA = \frac{w_a - w_b}{A} [g/m^2]$$

where w_b and w_a are the weight of the samples in g before and after oil immersion respectively, and A the total surface area in m^2 of the sample. The mean value and confidence interval of 95 % confidence level was calculated.

2.9 Moisture content

The moisture content of the sheets was determined according to ASTM D 664-94.⁶⁶ Pieces from the tensile testing were used and “half a dumbbell”-specimens were put in small glass bottles. The samples were conditioned for 48 h at 23°C and 50 % RH, weighed using a Mettler AE 163, Mettler Instrumente AG, Switzerland, then stored for 24 h at 105°C in an Electrolux oven (model 350-970 80 11) and finally cooled in a desiccator for 1 h. The moisture content in wt% was determined as the weight loss of the samples after drying and cooling. Five replicates of each sheet were analysed. The mean value and confidence interval of 95 % confidence level was calculated.

2.10 Bending resistance

The bending resistance in [mN] was assessed for the extrudates using a Lorentzon and Wettre Stiffness Tester, Lorentzon and Wettre, Sweden, according to SCAN-P 29:95.⁶⁷ A 55 mm long piece of the extrudate (width: 4 mm) was horizontally fixed in a clamp, with the part outside the clamp just in front of a blunt edge, placed approximately 5 mm from the edge of the extrudate. The force in [mN] acting on the blunt edge as the extrudate was bent 15° was measured. The test was performed at 50% RH and 23°C, samples were stored in this climate at least 48 h prior to testing. To compare properties with pressed sheets, strips of sheets from material without siccativ were tested as well. Strips 55 mm long and 4 mm wide were cut using a scalpel. At least five replicates of each sample were tested, when enough material held together, ten replicates were tested. The mean value and confidence interval of 95 % confidence level was calculated.

2.11 Oxygen transmission rate

The oxygen transmission rate in [$\text{cm}^3 \cdot \text{mm} / (\text{m}^2 \cdot \text{day} \cdot \text{atm})$] was determined using a Mocon Ox-Tran Twin apparatus, according to ASTM D 3985-95⁶⁸ at 0% RH and 23°C. The samples were masked with aluminum to an exposure area of 5 cm². The specimens were mounted in isolated diffusion cells and purged with nitrogen gas to measure the background oxygen leakage of the instrument. After the background measurements one side of the sample was exposed to flowing oxygen (99,95%) at atmospheric pressure. The oxygen transmission rate was normalized with respect to oxygen pressure and sheet thickness to yield the oxygen permeability (OP). Sheets from CR, CA and RC ball milled for 48 h and CA milled 24 h (with plasticizer) were tested.

2.12 Prototype

As a final step at the end of the thesis work a tray was pressed using the above mentioned Polystat 200T, Servitec Maschinenservice GmbH, Germany. 80 g material in total, consisting of 42,5 wt% CR, 42,5 wt% RC and 15 wt% glycerol, were put in a tray mould and pressed for 12 minutes with the pressure gauge set to 300 bar.

3 Results and discussion

3.1 Microscopy

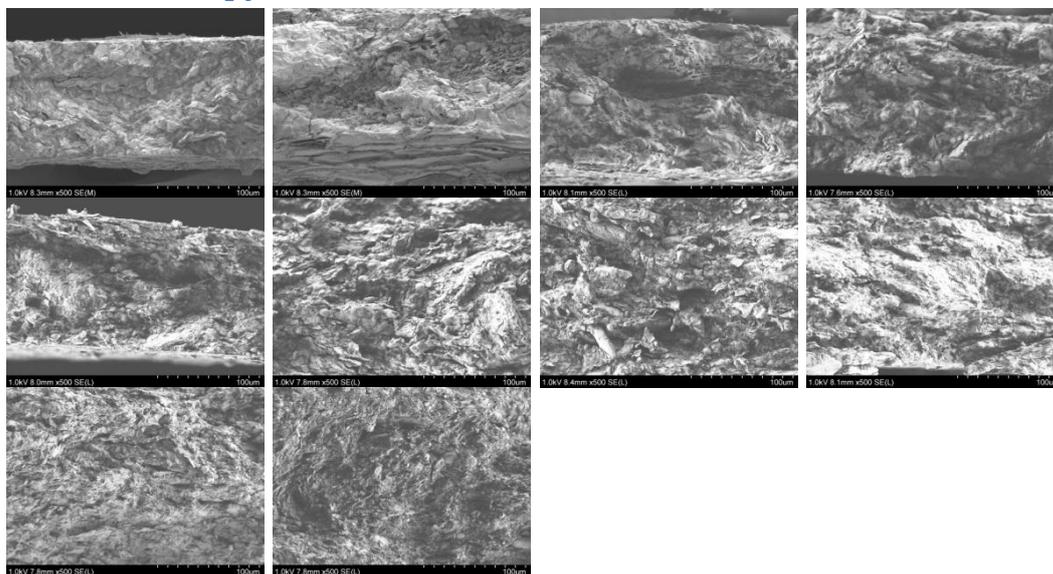


Figure 5: Scanning electron micrographs from films pressed from material ball milled for 1-8 h (from left to right, top two rows), 24 h and 48 h respectively (from left to right, bottom row).

Scanning electron micrographs were taken of milled CR to evaluate milling times to use in the study. With longer milling time the cross section seems to become more even, however the difference is not very large. There does not seem to be many large pores in the films pressed from material milled for a short time, opposed to what was anticipated. There was however a difference in the “feel” of the meal, with “softer” meal the longer the milling time, which is why longer milling times were chosen in the study.

3.2 Compression moulding

Compression moulding of the sheets was generally quite difficult, as the materials did not flow well. The samples without plasticizer were especially difficult to make. When the mould was not filled evenly enough, some parts did not harden and stayed as compressed powder. With plasticizer it was significantly easier to produce sheets, however the samples continued to be partly inhomogeneous. CA and RC were easier to press than CR due to better flow. These materials had a fat, somewhat “sticky” surface and quite a lot of oil was pressed out of the RC sheets. CR turned out to be a dry material and these sheets were not sticky.

Pre-heating before pressing of the sheets rendered uneven sheets. Although the same amount (weight) as before of material was put in the moulds, it did not seem to fill them after heating. Perhaps the hardening process started, which made the materials flow less. Another reason could be water loss due to drying, thereby losing some plasticizing effect. Sheets with siccativ pressed without pre-heating all seemed to process quite well. Despite addition of siccativ, much oil was still pressed out of the RC sheets.

Pressing sheets from granulated extrudate worked better with CA and RC than with CR. Out of the pre-heated samples, only CA processed well, the CR and RC sheets had large spots where the material had not hardened. The granulate size is a parameter that needs optimization: The size was everything from powder, using a pestle and mortar, to granulate pieces approx. 5 mm in diameter. Powder did not work well as the sheet seemed to get too densely packed and it did not flow well so sheets were uneven. Large granulate pieces rendered uneven sheets where the granulate borders were still visible. The granulate size used in the end was pieces approx 1-2 mm in diameter.

3.2.1 Crambe sheets



Figure 6: Sheets from crambe meal with 15 wt% glycerol. From left to right, unmilled, milled for 24 h and milled for 48 h.

Crambe sheets were difficult to make. Without plasticizer the form was difficult to fill evenly. Where the material had hardened, the colour was dark brown. Some bubbles formed at places indicating volatile substances in the material, such as water. With ball milled material it was as difficult, if not more so, as the powder seemed to be more densely pressed with less flow in the mould. Samples with plasticizer turned a darker beige with unmilled material and beige to dark brown at places when using milled material.

Sheets pressed from extrudate turned dark brown for CR, similar to sheets pressed from ball milled material. The extrusion step seemed to replace the ball mill. However the granulate did not flow well at all during pressing.

The sheets had a distinct smell, not necessarily a bad smell, but a well noticed smell. The surface of the sheets felt smoother at the darker parts where the material had hardened but the general impression was not that of complete smoothness. Sheets from ball milled raw material were smoother than sheets from unmilled raw material. The surface of the extrudate felt quite smooth, more even than the sheets. The surfaces were all dry.

3.2.2 Carinata sheets



Figure 7: Sheets from carinata meal with 15 wt% glycerol. From left to right, unmilled, milled for 24 h and milled for 48 h.

Carinata samples with plasticizer processed quite well. Sheets turned reddish brown and were slightly transparent. Small particles were visible in the sheets with unmilled material, with increased milling time the homogeneity was better. However some small spots stayed beige and looked like unreacted powder. There were more spots on the sheets pressed from material milled for 48 h than for the ones made from 24 h-material, whether it has to do with the milling or other circumstances regarding the mixing and compression moulding is however difficult to say as the sheets were only made at one time. The CA sheets without plasticizer became uneven and inhomogeneous. The colours were beige to reddish brown and no transparency tendencies were visible. Bubbles formed in sheets without plasticizer. Pre-heated sheets felt stiffer after pressing than sheets pressed directly after mixing. The stiff sheets were also brittle. Sheets heated for 6 hours were not as reddish brown as the other sheets; they were rather yellow-brown instead.

Carinata sheets pressed from extrudate were reddish brown, perhaps a little bit darker red than the sheets pressed from the meal. The sheets were transparent, but particles were still visible, as the sheets would be anticipated to look after being ball milled for a few hours. There was not enough material to press as many sheets as from the meal so less material was used for the smaller “extruded” sheets. Whereas CR did not flow and turned into a sheet 75% the size of the mould, CA extrudate flowed and filled the form rendering a sheet thinner than the others.

The carinata sheets had a distinct smell as well, perhaps a little touch of pungent smell, but not too unpleasant. The surfaces of the sheets were fat and somewhat sticky. Overseeing the fatty surface, these sheets had the most “plastic like” feel. Especially sheets from ball milled raw material were smooth and felt like plastic. Sheets from unmilled material had more of a rough surface. The extrudates were smooth and felt like plastic, they were not as fat and sticky as the sheets.

3.2.3 Rapeseed cake sheets



Figure 8: Sheets from rapeseed cake meal with 15 wt% glycerol. From left to right, unmilled, milled for 24 h and milled for 48 h.

Rapeseed cake sheets behaved in a similar way as CA sheets, flowing better than CR sheets. The colour was black with indications of yellow for the unmilled material. Although the material seemed to flow rather well, an occasional hole could be found in the sheet.

During pressing of RC sheets from extrudate, the material did not flow as well as during pressing of the meal. As sheets were only pressed from pre-heated material, the sheets did not turn out well due to lack of flow. Oil was pressed from the extrudate sheets as well.

Since oil was pressed from the material the sheets had fatty surfaces. They had a distinct smell, the least favourable smell of the three materials but not too unpleasant. The surfaces of these materials felt slightly porous, they were not as smooth as sheets and extrudates from CR or CA.

3.3 Extrusion

All three materials were quite easy to mix with 15 wt% glycerol; they did not turn into a dough, which was positive when feeding the material to the extruder. CA softened in the extruder feeding tube, becoming more of a dough, RC a little bit less so and CR did not soften at all in the feeding tube. CR was perceived as a dry material, drier than the other two materials. Ball milled material seemed to soften faster than unmilled material.

The fact that CR was quite dry facilitated feeding the extruder evenly. CA and RC seemed to exit the extruder at different speed during the extrusion, as the pressure from the material inside was different. Since these materials stuck to the screws, the pressure seemed to build up when the material was fed and it exited the extruder when enough material was in the barrel.

3.3.1 Crambe extrudate

The CR extrudate had a beige colour, similar to the meal. It was brittle and did not look like it had reacted during the extrusion, but rather looked like powder pressed together thoroughly. When flexed too much, the extrudate broke easily. Precaution, such as keeping the extrudate straight when collecting it, had to be taken to keep the extrudate in one piece. Looking at the screws after extrusion, CR seemed to have melted in the front regions of the screws, as shown by the darker material in figure 9.



Figure 9: Extrusion of Crambe ball milled for 48 hours. Crambe is a dry material that seemed to have melted slightly around the top of the screws.

3.3.2 Carinata extrudate

The CA extrudate turned reddish brown much as the sheets did, however spots or stripes of beige powder occurred occasionally. The extrudate was softer than and not as brittle as CR and RC extrudates, especially when still warm. As the extrudate cooled, it turned more brittle. With the addition of $\text{Mn}(\text{acac})_3$, the extrudate did not seem to have as many “powdery” parts.



Figure 10: Extrusion of unmilled carinata with 15 wt% glycerol.

3.3.3 Rapeseed cake extrudate

Rapeseed cake extrudate was the most brittle; it was difficult to keep in one piece. As with CR, the extrudate seemed to be powder pressed together thoroughly and not mixed. The extrudate was a mixed colour of yellow, brown and black. It did not seem to have reacted as much as when pressed. Oil was pressed from the material during extrusion as can be seen in figure 11 below. More oil was pressed from the material when extruding the ball milled material.



Figure 11: Extrusion of rapeseed cake ball milled for 24 h with 15 wt% glycerol. Oil was pressed from the material during extrusion.

3.4 Differential scanning calorimetry

The results from the DSC scans were difficult to interpret. The samples used were of the mixed meal, which might have influenced the result slightly as the meal might have had large pieces and all material might not have been completely in contact with the DSC pan. Perhaps results would have been better if the meal had been pressed to a pellet, however the material contains so many different constituents that it might not have helped anyway.

It can be concluded that RC contains water, bound loose and hard. All DSC graphs show a large endothermic “valley” around 100°C, see figure 11 below, which indicates the loss of water.

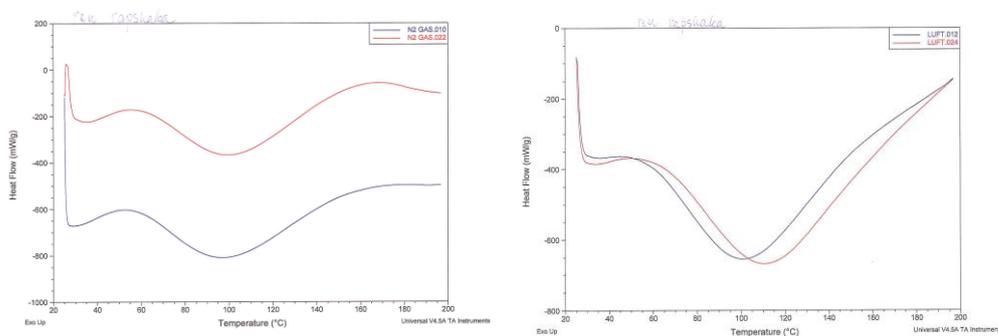


Figure 12: DSC scans of pure rapeseed cake, temperature runs from 25°C to 200°C in nitrogen (left) and air (right). Red and blue indicate double samples.

Depending on how the water is bound the “valley” can shift from 100°C to lower temperature if the water is loosely bound and in the other direction if it is more tightly bound.⁶⁹ The width of the valley in the DSC results indicates that water of both kinds is present. There is a difference between the samples run in air and the samples run in nitrogen. After the loss of water the curves seem to stabilise in nitrogen atmosphere, whereas more happens in air. Because the RC contains so many different constituents, there can be reactions occurring but not much can be said about this as they may cancel each other out or overlap to a great extent. The addition of glycerol or of a siccativ did not result in large differences of the graphs, they all look similar. All results can be seen in appendix 2.

With the runs at a set temperature, there does not seem to be much happening. All scans show a quick endothermic dip at the beginning of the scan but it seems to be related to when the machine reaches the set temperature. Other than that, nothing seems to happen with the material, see figure 13.

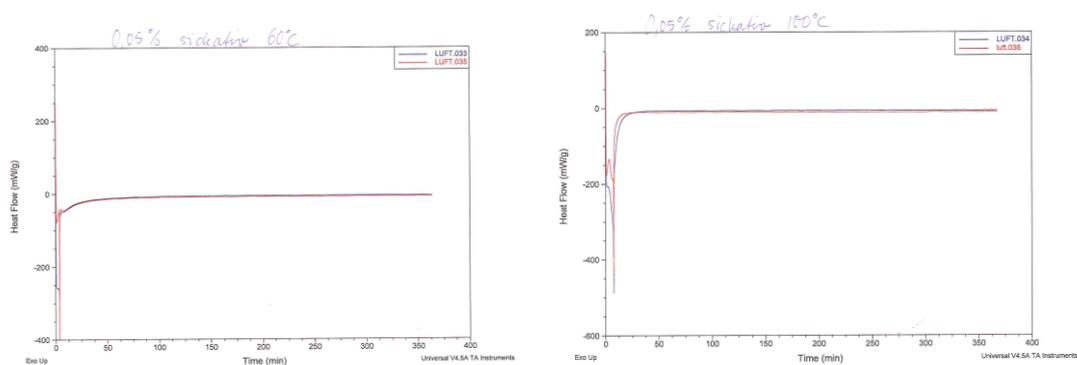


Figure 13: DSC runs of rapeseed cake with glycerol and 0,05 wt% siccativ in 60 °C (left) and 100°C (right).

3.5 Tensile testing

3.5.1 Ball milled material

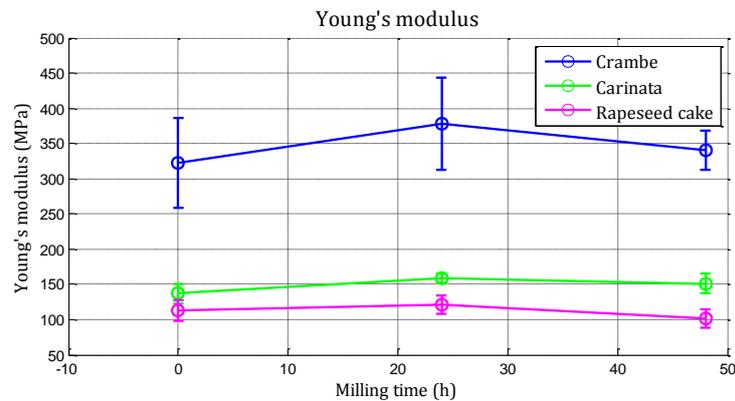


Figure 14: Young's modulus as a function of milling time for the three materials.

The tensile testing showed that CR was the material with the highest Young's modulus. CA and RC have similar Young's modulus, which is about half the value of CR. There does not seem to be a statistically significant difference in property regarding milling time. The ball milled raw material produced more homogenous final material, which can be seen in the smaller confidence intervals in fig. 14. CA and RC were more homogenous than CR, which was visible on the sheets after pressing. The CR sheets did not seem to flow well at all and the sheets were quite inhomogeneous in colour and distribution.

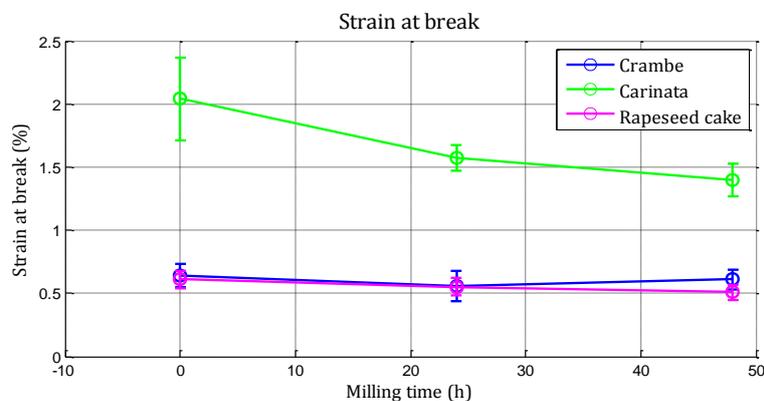


Figure 15: Strain at break as a function of milling time for the three materials.

The strain at break was very low for CR and RC sheets. CA sheets had about three times higher strain at break, but the value is still quite low. The ball milling did not seem to have an effect on the fracture strain for CR and RC, if it had an effect for the CA material, the fracture strain decreased after milling the material, see fig. 15.

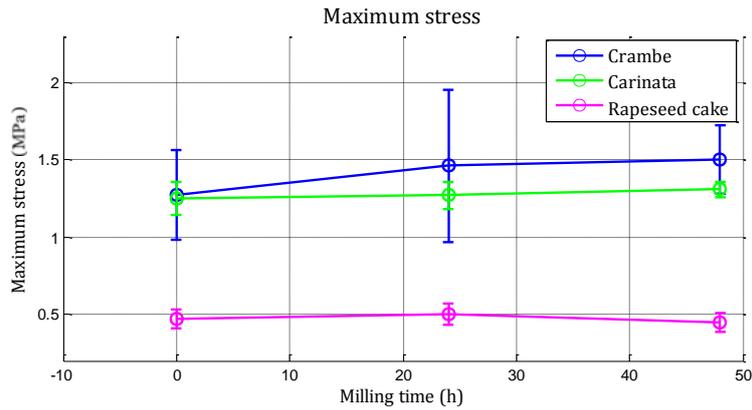


Figure 16: Maximum stress as a function of milling time for the three materials.

The maximum stress values for the materials are comparable for CA and CR, whereas RC sheets withstood significantly lower maximum stress. Ball milling did not seem to have an effect on maximum stress for the materials, see fig. 16.

Sheets without plasticizer could not be tested as they broke when clamping the specimen.

3.5.2 Crambe with added siccativ

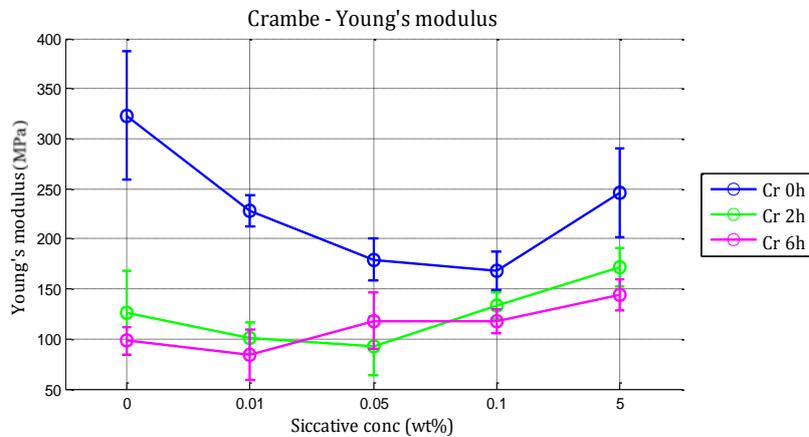


Figure 17: Young's modulus as a function of siccativ concentration for Crambe materials pre-heated 0h, 2h and 6h respectively. Note that the differences in concentration are not equal between each step at the x-axis.

Pre-heating before pressing the material without added siccativ lowered the Young's modulus to about half the value but the strain at break doubled, see fig. 17. Maximum stress was not affected, see fig 19. Water has a plasticizing effect and with pre-heating before pressing, some water should have evaporated from the sheets, thereby losing some

plasticizing effect. This would then have been noticeable as a higher Young's modulus than before. This is not the case here. Perhaps some crosslinking occurred when pre-heating. If the crosslink density is low enough, the lower Young's modulus and higher strain at break would perhaps be explained. However the strain at break is still low so the crosslinks there are perhaps not very strong.

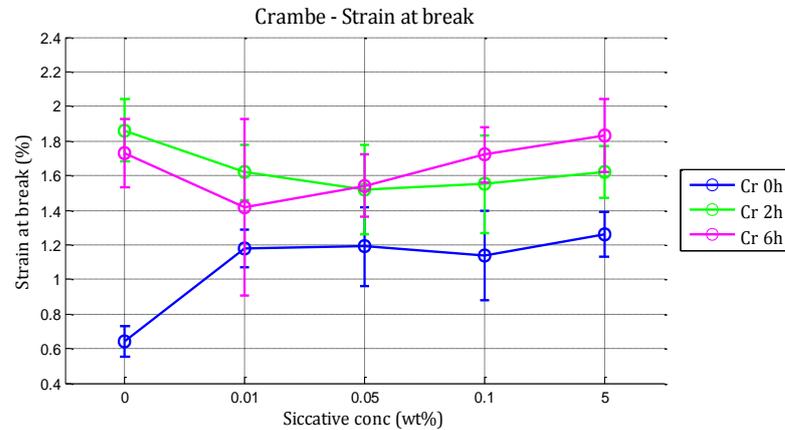


Figure 18: Strain at break as a function of siccative concentration for Crambe materials pre-heated 0h, 2h and 6h respectively. Note that the differences in concentration are not equal between each step at the x-axis.

Sheets pressed after pre-heating felt stiffer to handle but this was not reflected by the tensile testing results. It could be that there are crosslinks of different nature in the material but when exposed to moisture hydrogen bonds occur that work against the other crosslinks, making the material more sensitive.

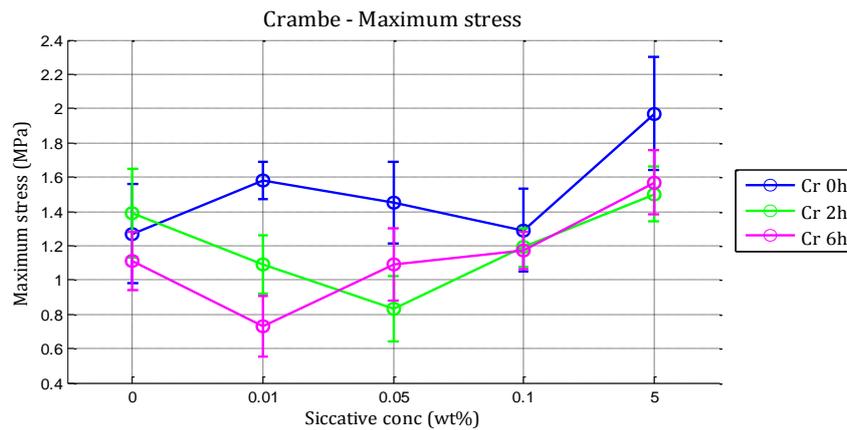


Figure 19: Maximum stress as a function of siccative concentration for crambe materials pre-heated 0h, 2h and 6h respectively. Note that the differences in concentration are not equal between each step at the x-axis.

Properties changed slightly with the addition of $\text{Mn}(\text{acac})_3$. When comparing pre-heated sheets with non pre-heated sheets, Young's modulus was higher and strain of break lower for the non pre-heated sheets. Pre-heating 2 or 6 hours did not seem to have an influence on Young's modulus or strain at break. Properties are similar for CR with 0,01 wt% $\text{Mn}(\text{acac})_3$ and 0,05 wt% respectively, but Young's modulus is higher for CR with higher content of siccative. This could have to do with the addition of $\text{Mn}(\text{acac})_3$ in itself, meaning that some crosslinking might have occurred, or maybe CR functions better when other material is added to the matrix.

Sheets made from granulated extrudate could not be tested as they were too brittle. They broke when clamping the specimen.

3.5.3 Carinata with added siccative

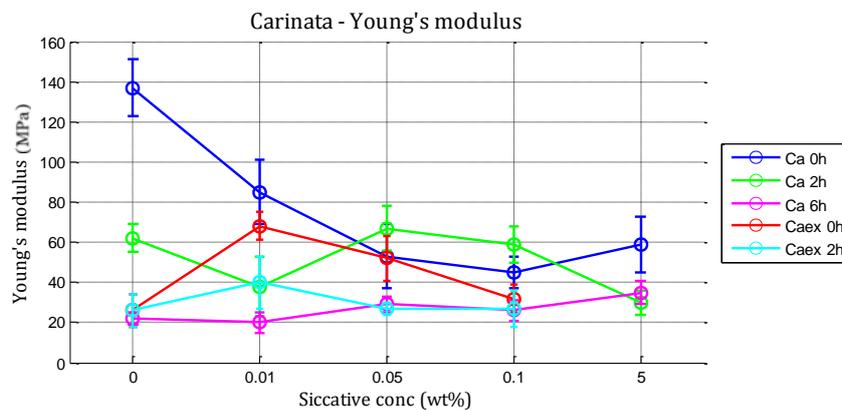


Figure 20: Young's modulus as a function of siccative concentration for carinata materials pre-heated 0h, 2h and 6h and materials pressed from extrudate pre-heated 0h and 2h respectively. Note that the differences in concentration are not equal between each step at the x-axis.

In general, the addition of $\text{Mn}(\text{acac})_3$ does not seem to have a large influence on Young's modulus, see fig. 20. Pre-heating on the other hand influences Young's modulus. Pre-heating for 6 h renders a material with lower Young's modulus than materials pre-heated for two hours or not pre-heated at all. The only value that seems to stand out is that of the non pre-heated CA sheet without siccative, a reason for this deviation is probably slightly due to the change of load-cell when tensile testing the materials. Disregarding that value, the highest Young's modulus is reached with 0,01 wt% $\text{Mn}(\text{acac})_3$ or 5 wt% $\text{Mn}(\text{acac})_3$ without pre-heating the material.

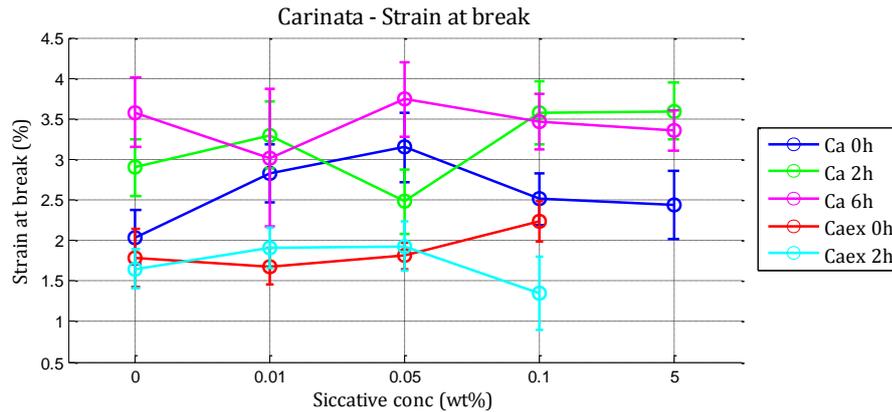


Figure 21: Strain at break as a function of siccative concentration for carinata materials pre-heated 0h, 2h and 6h and materials pressed from extrudate pre-heated 0h and 2h respectively. Note that the differences in concentration are not equal between each step at the x-axis.

When extruding CA before pressing, the addition of $Mn(acac)_3$ has an influence. The highest Young's modulus is reached with 0,01 wt% $Mn(acac)_3$, the same could be with 0,05 wt% $Mn(acac)_3$ but it cannot be stated with statistical significance.

Pre-heating for 6 h or extruding, granulating then pre-heating for 2 hours produces sheets with largely the same Young's modulus, however the strain at break is lower for the extruded material, see fig. 21.

Extruding CA, granulating it then pre-heating for 2 h renders a material with the lowest Young's modulus, lowest strain at break and lowest maximum stress. If the pre-heating step is lost, the strain at break is still relatively low but maximum stress and Young's modulus is comparable with the values of the non-extruded materials. Pre-heating for 6 h produces a material with relatively low Young's modulus and maximum stress and relatively high strain at break.

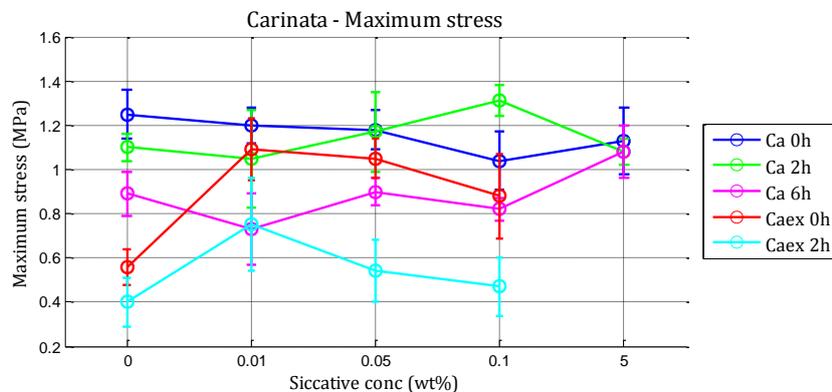


Figure 22: Maximum stress as a function of siccative concentration for carinata materials pre-heated 0h, 2h and 6h and materials pressed from extrudate pre-heated 0h and 2h respectively. Note that the differences in concentration are not equal between each step at the x-axis.

As with CR, pre-heating CA sheets without siccativ before pressing decreased Young's modulus and increased strain of break. Maximum stress was not largely influenced when pre-heating for 2 hours, but decreased slightly when sheets were heated for 6 hours, see fig. 22. This might have to with the pre-heated sheets not being processed properly, that water was dried from the material, thereby losing plasticizing effect or that too many crosslinks were formed rendering the material brittle. However the latter theory should have had an impact on Young's modulus or maximum stress, allowing them to be higher.

Sheets pressed from granulated extrudate generally had slightly lower strain at break values than materials pressed without pre-treatment.

3.5.4 Rapeseed cake with added siccativ

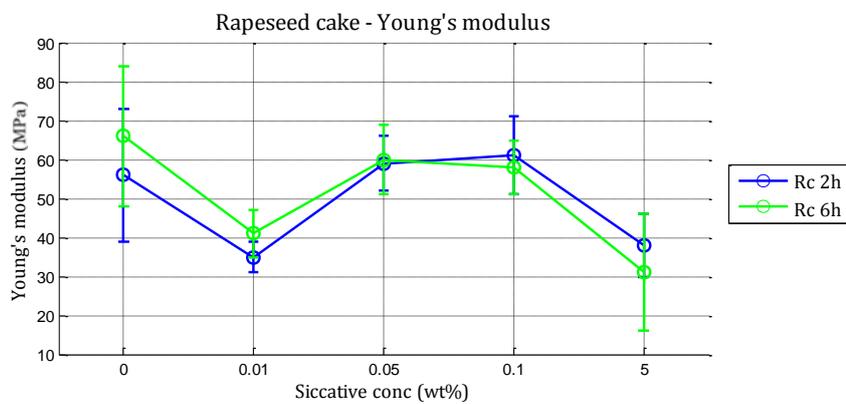


Figure 23: Young's modulus as a function of siccativ concentration for rapeseed cake materials pre-heated 2h and 6h respectively. Note that the differences in concentration are not equal between each step at the x-axis.

Comparisons of pre-heated RC materials and RC sheets without heat treatment could not be done as there was not enough material for this. Since the properties of RC sheets without heat treatment were not very good, the decision was made to compare heat treated materials.

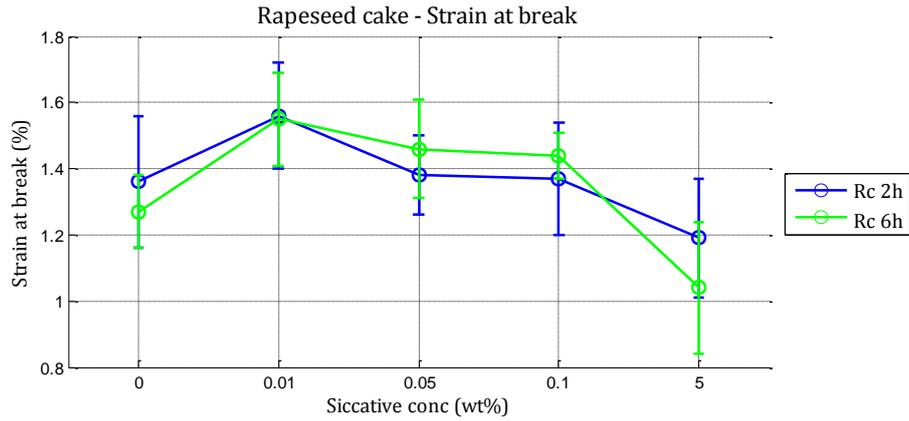


Figure 24: Strain at break as a function of siccative concentration for rapeseed cake materials pre-heated 2h and 6h respectively. Note that the differences in concentration are not equal between each step at the x-axis.

The duration of the heat treatment does not seem to influence tensile properties. However, the concentration of $Mn(acac)_3$ seems to have an influence. 5 wt% $Mn(acac)_3$ seems to be too much siccative as the materials became brittle. Out of the RC sheets, these were the sheets with lowest Young's modulus, lowest strain at break and lowest maximum stress. Adding 0,05 wt% or 0,1 wt% $Mn(acac)_3$ did not make a difference. Tensile properties of these sheets are comparable with those of the pre-heated sheets without siccative. Properties of the sheets with 0,01 wt% and 5 wt% respectively are also comparable, but strain at break is lower for sheets with 5 wt% $Mn(acac)_3$, see fig. 24.

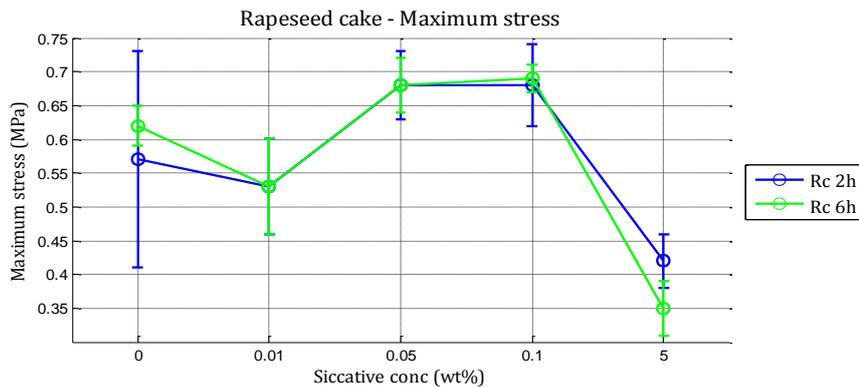


Figure 25: Maximum stress as a function of siccative concentration for rapeseed cake materials pre-heated 2h and 6h respectively. Note that the differences in concentration are not equal between each step at the x-axis.

3.5.5 Final remark tensile testing

None of the materials are very elastic and they break quite easily. CA sheets were significantly stretched before break compared to the CR and RC sheets. Addition of $\text{Mn}(\text{acac})_3$ did not seem to improve the properties significantly, it did not seem to work as a chemical additive but it might have had some plasticizing effect at times. It is probable that all materials consist of large particles that are held together by interactions between the particles. Once subjected to mechanical force these interactions are broken and the materials break. It is likely that the materials do not have any elastic deformation, but that the deformation is plastic and what is interpreted as Young's modulus is actually a measure of the plastic deformation rate.

3.6 Bending resistance

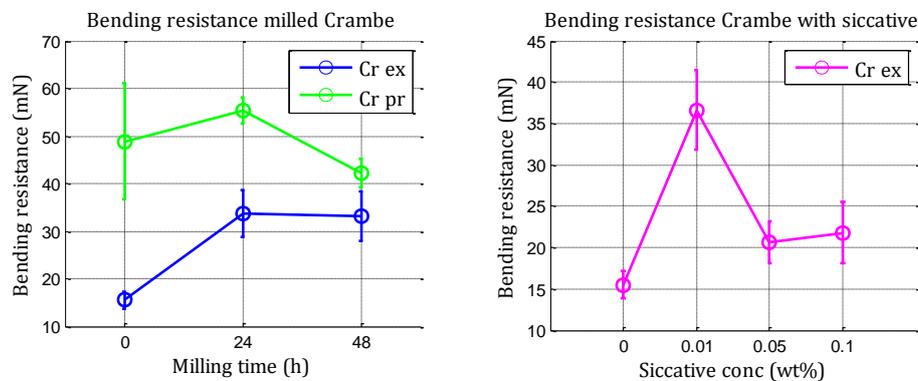


Figure 26: Bending resistance for crambe extrudate and pressed sheet as a function of milling time to the left and bending stiffness for crambe extrudate as a function siccative concentration to the right. Note that the steps in the x-axis in the right graph do not correspond to equal changes in siccative concentration.

For CR materials the moulded sheet is the stiffest material. For the sheet where the meal was milled 48 hours the bending resistance seems to be the lowest. The unmilled sample, however, has a wide confidence interval and there is a possibility of a trend with lower bending resistance for materials milled for a longer period of time. The extrudate with 15 wt% glycerol turns stiffer when the meal has been milled, regardless of milling time. Adding a siccative to the meal does not seem to have influenced the properties greatly, an exception is when 0,01 wt% $\text{Mn}(\text{acac})_3$ is added. Why this is the case is difficult to say, perhaps some reactions occurred during the extrusion.

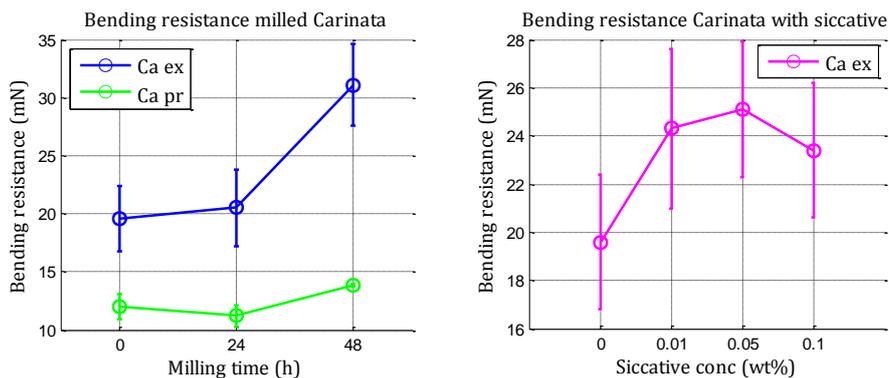


Figure 27: Bending resistance for carinata extrudate and pressed sheet as a function of milling time to the left and bending stiffness for carinata extrudate as a function siccative concentration to the right. Note that the steps in the x-axis in the right graph do not correspond to equal changes in siccative concentration.

The extrudate with 15 wt% glycerol turned out to be the stiffest material of the CA materials. There is a significant increase of the value of the bending resistance when the milling time was 48 hours. However the confidence intervals are quite wide. Here the intervals seem to widen with milling time. The moulded sheet is not as stiff as the extrudate. They also seem to be more homogenous as a material, having less wide confidence intervals than the extrudate. Adding $Mn(acac)_3$ to the meal produced extrudates with varying bending resistance. That it had an influence on the extrudate properties cannot be stated with significance.

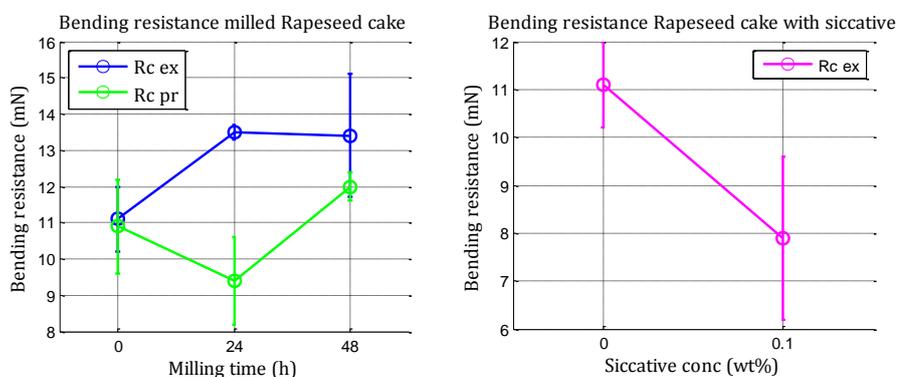


Figure 28: Bending resistance for rapeseed cake extrudate and pressed sheet as a function of milling time to the left and bending stiffness for rapeseed cake extrudate as a function siccative concentration to the right. Note that the steps in the x-axis in the right graph do not correspond to equal changes in siccative concentration.

As for CA materials, the extrudate is the stiffest RC material. The moulded sheet lies close in value when unmilled and milled for 48 hours. The milling time does not seem to affect this property significantly for any of the materials. When $Mn(acac)_3$ was added, it might have acted as a plasticizer.

3.7 Absorption tests

3.7.1 Water absorption

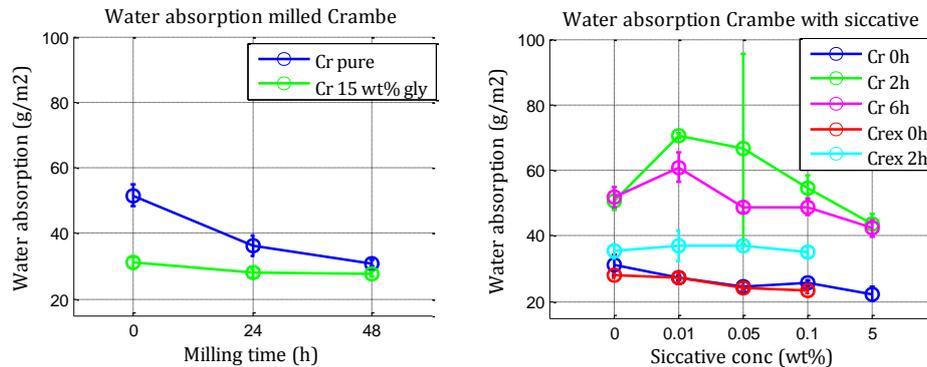


Figure 29: Water absorption for crambe pressed sheets as a function of milling time to the left and as a function of siccative concentration to the right. Note the differences in concentration for each step of the x-axis in the right graph.

The water absorption decreases slightly with milling time for CR and RC materials, whereas CA materials seem to increase water absorption ability slightly with milling time. When adding plasticizer to the CA sheets, however, milling time does not seem to influence the water absorption. The RC pressed sheets absorb slightly more than the CR sheets with plasticizer. There is not a big difference between the materials when comparing unmilled sheets. Only CR without plasticizer deviates readily, perhaps parts were badly processed in the sheet. Although the material holds together, a difference in processed and unprocessed parts is visible on the sheet. When milled 24 hours the CA and unplasticized CR sheets absorb approximately as much water per m². When milled 48 h, the CA samples absorb the most water.

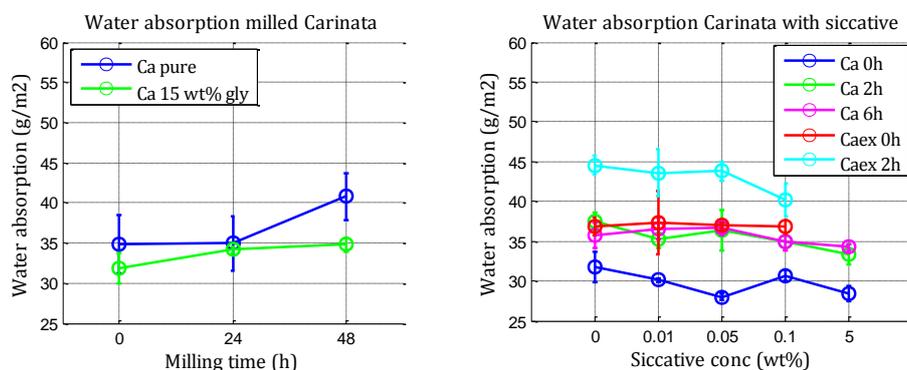


Figure 30: Water absorption for carinata pressed sheets as a function of milling time to the left and as a function of siccative concentration to the right. Note the differences in concentration for each step of the x-axis in the right graph.

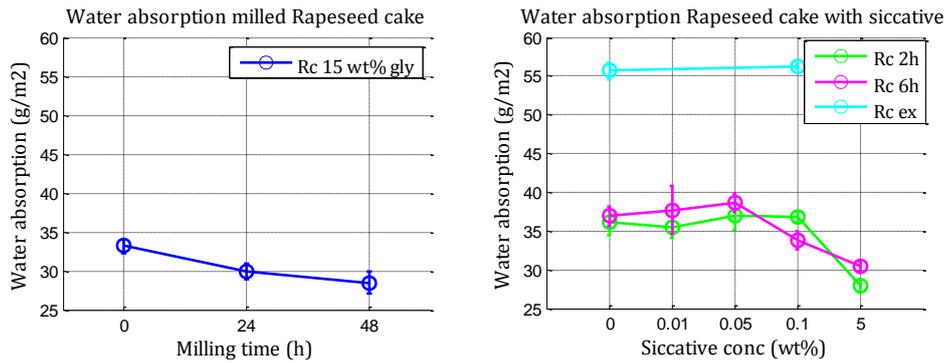


Figure 31: Water absorption for rapeseed cake pressed sheets as a function of milling time to the left and as a function of siccative concentration to the right. Note the differences in concentration for each step of the x-axis in the right graph.

After immersion the samples became slightly sticky, the CA samples became much stickier than the others and when pressed too hard, pieces from the blotting paper adhered to the test samples. The other materials were also quite sensitive but not as sensitive as the CA samples.

There is a big difference in water absorbing property for pre-heated CR sheets and sheets pressed directly. It could be that pre-heated samples were not processed properly as materials might have lost a plasticizing effect during heating. The same trend can be seen for CA sheets, however the difference is not as big. CA sheets pressed directly absorb more water than CR sheets pressed directly, but pre-heated CR sheets absorb more water than pre-heated CA sheets.

3.7.2 Oil absorption

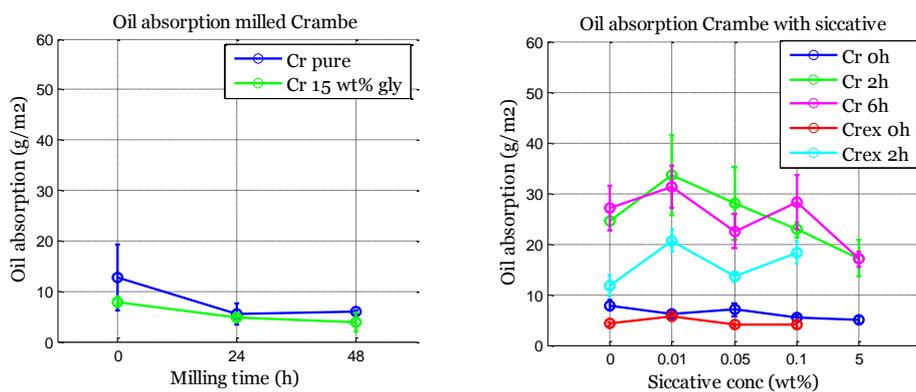


Figure 32: Oil absorption for crambe pressed sheets as a function of milling time to the left and as a function of siccative concentration to the right. Note the differences in concentration for each step of the x-axis in the right graph.

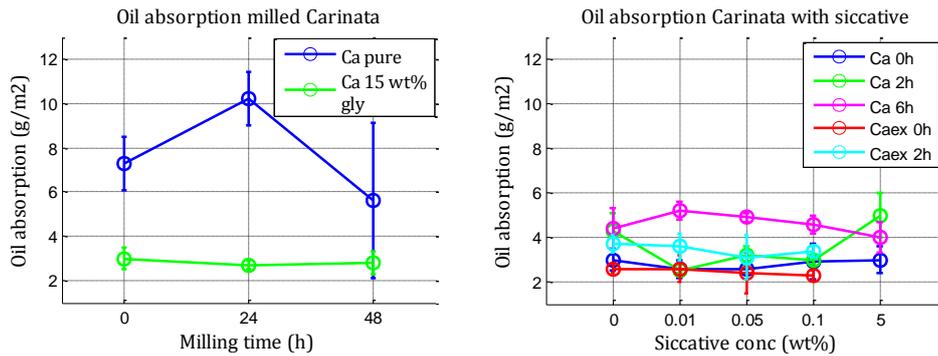


Figure 33: Oil absorption for carinata pressed sheets as a function of milling time to the left and as a function of siccative concentration to the right. Note the differences in concentration for each step of the x-axis in the right graph.

The RC and CR materials seem to show the same kind of trend as with the water absorption whereas the CA materials behave differently. The plasticized CA sheet absorbs little oil regardless of milling time. The CA sheet without plasticizer absorbs almost four times as much when milled 24 hours.

Crambe materials absorbed the most oil. However the CR sheets were also the ones to process the worst. In case of unhardened parts, they would presumably absorb more fluid. There is a large difference in absorption capability of pre-heated sheets and sheets pressed directly with the pre-heated sheets absorbing three-four times as much oil as the other sheets.

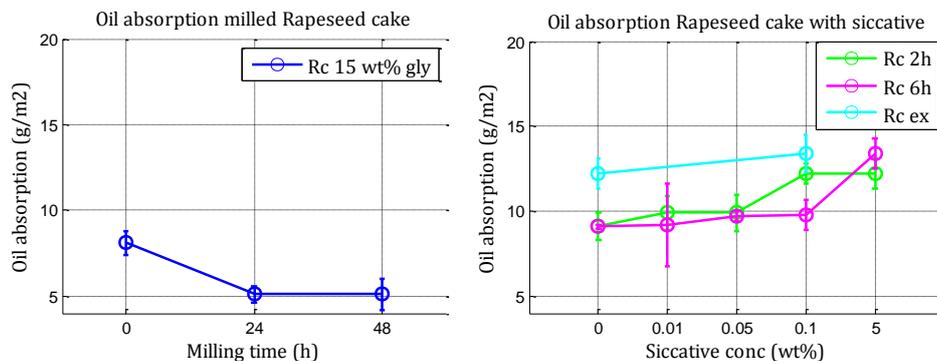


Figure 34: Oil absorption for rapeseed cake pressed sheets as a function of milling time to the left and as a function of siccative concentration to the right. Note the differences in concentration for each step of the x-axis in the right graph.

Carinata materials absorb less than CR materials. Sheets without plasticizer absorb more than sheets with glycerol. There is not a big difference between sheets pressed from meal or sheets pressed from extrudate. For sheets pressed from extrudate, pre-heated sheets

absorb more oil. For sheets pressed from meal, sheets pre-heated for 6 hours absorb more than the other sheets.

Here the samples were not as affected as with water and did not seem to dissolve. However the unplasticized samples were not very homogenous and although the most similar-looking samples were taken the properties differed quite much. This is very apparent with the unplasticized, unmilled Crambe sample where the confidence interval is very large, see fig. 33.

3.8 Moisture content

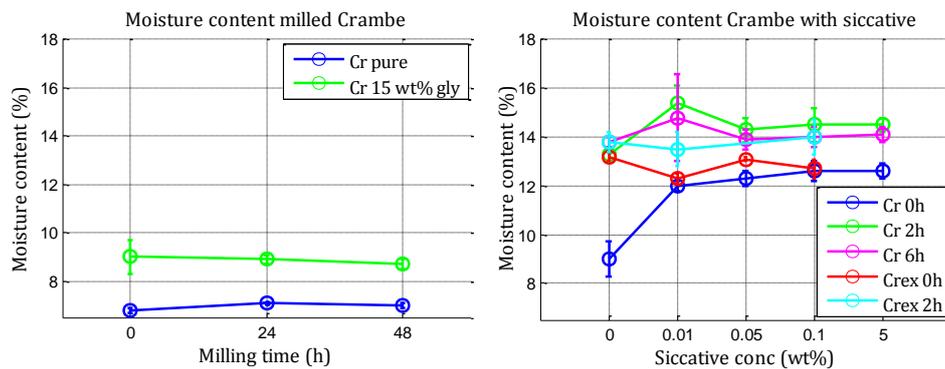


Figure 35: Moisture content for crambe pressed sheets as a function of milling time to the left and as a function of siccative concentration to the right. Note the differences in concentration for each step of the x-axis in the right graph.

The moisture content is not really influenced by the milling time of the materials, except for the RC materials. The milled RC materials contained more moisture than the unmilled samples. The CR samples contained slightly more moisture than the CA samples and plasticized materials contained approximately two per cent more moisture than the samples without plasticizer.

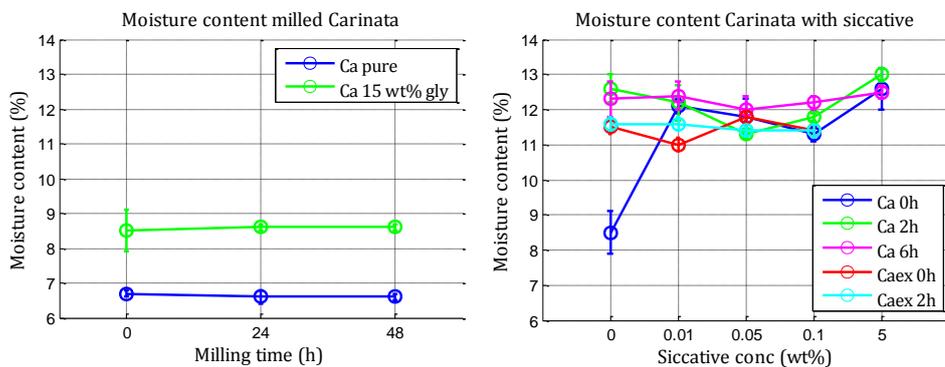


Figure 36: Moisture content for carinata pressed sheets as a function of milling time to the right and as a function of siccative concentration to the left. Note the differences in concentration for each step of the x-axis in the right graph.

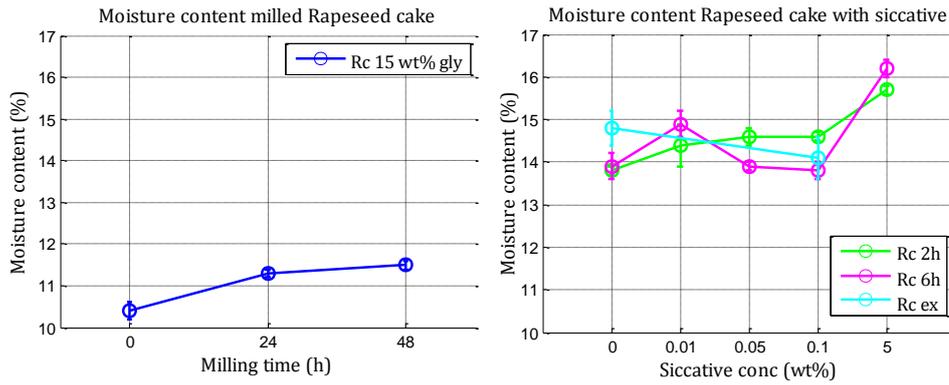


Figure 37: Moisture content for rapeseed cake pressed sheets as a function of milling time to the left and as a function of siccative concentration to the right. Note the differences in concentration for each step of the x-axis in the right graph.

There is a difference in moisture content between the first set of sheets made from milled meal and from the second set where siccative was added. Although the samples were conditioned for the same amount of time there might have been a difference in treatment of the materials. More time passed between manufacture and moisture content analysis for the first set than for the second set. This seems to have influenced the materials, even though they were kept in sealed plastic bags when not conditioned.

3.9 Oxygen transmission rate

All samples that were tested did not manage to pass the correction of the instrument, which means that the oxygen transmission rate is more than 2000 [cm³·mm/(m²·day·atm)] for each of the samples tested.

3.10 Prototype

A tray was successfully pressed from CR and RC. The use of the material combination emanated from the above reported results and “gut feeling” built up from experience of working with the materials. The tray was quite stiff and therefore easy to loosen from the mould. The tray felt more rigid than the sheets previously made and it did not break when filled with fresh fruit. Evaluation of properties of the tray were however not included in the scope of this thesis.



Figure 38: Tray pressed from crambe and rapeseed cake, to the right filled with fruit.

Compared to other trays made from different materials this tray has something of an odd smell and it is also quite heavy. There are different obstacles to overcome before this material could be used commercially but to be able to press a tray shows that the material has some potential to be used as a bioplastic.

4 Conclusions

Crambe, carinata and rapeseed oil cake can be pressed into sheets and be extruded with 15 wt% glycerol as plasticizer, carinata can also be pressed into a sheet after extrusion and granulation. Ball milling the raw material provides optical difference but tensile properties are not influenced.

Sheets of all three materials are brittle. Pre-heating before pressing generally increases strain at break and lowers Young's modulus, however the differences are not large. The materials are not very flexible and they are sensitive to moisture. The materials all show potential to be used as bioplastics for rigid items, such as trays, however more work is needed to improve properties.

5 Suggested further work

It is the author's impression that a better formulation for the three materials needs to be found. They should be individually optimized. CA is a flexible material and with an efficient crosslinker the properties could perhaps improve significantly. RC behaves similarly but might need more work to improve the flow and proper mixing of all components. CR is a dry material, which is difficult to process without further work. Perhaps a different plasticizer could be of interest, or maybe water could be mixed with CR in the extruder to compound the material better and get more of a dough-like mixture. Another approach could maybe be to add a drying oil to the mixture to crosslink and thereby add to the matrix of the bioplastics, using CR as filler. The same could be done for RC and CA. One attempt could also be to mix CR with one of the other meals used in this work as was done with the prototype. This route could maybe be further investigated in future work.

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Appendix 1: Matlab code for tensile testing

```
%Carinata ball milled for 24 h, 15wt% glycerol
%import excel file car_2415 before running file, create vectors from each
%column
measure=[176 183 214 203 220 219 233 231 219 182 221 223]; %amount of
%datapoints per test sample in the series
tjocklekca=[0.5450 0.6296 0.5800 0.6082 0.6004 0.5970 0.6156 0.6182 0.6182
0.6074 0.6158 0.6158 0.6234]; %sample thickness (mm)
bredd=4; %sample width (mm)
le=40; %grip separation (mm)

%data imported from excel file: force in (N) and strain in (mm)

%stress calculation stress=force/sample area (N/mm2)
stressca241=forceca241(1:measure(1,1))/(tjocklekca(1,1)*bredd);
stressca242=forceca242(1:measure(1,2))/(tjocklekca(1,2)*bredd);
stressca243=forceca243(1:measure(1,3))/(tjocklekca(1,3)*bredd);
stressca244=forceca244(1:measure(1,4))/(tjocklekca(1,4)*bredd);
stressca245=forceca245(1:measure(1,5))/(tjocklekca(1,5)*bredd);
stressca246=forceca246(1:measure(1,6))/(tjocklekca(1,6)*bredd);
stressca247=forceca247(1:measure(1,7))/(tjocklekca(1,7)*bredd);
stressca248=forceca248(1:measure(1,8))/(tjocklekca(1,8)*bredd);
stressca249=forceca249(1:measure(1,9))/(tjocklekca(1,9)*bredd);
stressca2410=forceca2410(1:measure(1,10))/(tjocklekca(1,10)*bredd);
stressca2411=forceca2411(1:measure(1,11))/(tjocklekca(1,11)*bredd);
stressca2412=forceca2412(1:measure(1,12))/(tjocklekca(1,12)*bredd);

%strain calculation; strain=length/initial length
strainca241=strain_mmca241(1:measure(1,1))/le;
strainca242=strain_mmca242(1:measure(1,2))/le;
strainca243=strain_mmca243(1:measure(1,3))/le;
strainca244=strain_mmca244(1:measure(1,4))/le;
strainca245=strain_mmca245(1:measure(1,5))/le;
strainca246=strain_mmca246(1:measure(1,6))/le;
strainca247=strain_mmca247(1:measure(1,7))/le;
strainca248=strain_mmca248(1:measure(1,8))/le;
strainca249=strain_mmca249(1:measure(1,9))/le;
strainca2410=strain_mmca2410(1:measure(1,10))/le;
strainca2411=strain_mmca2411(1:measure(1,11))/le;
strainca2412=strain_mmca2412(1:measure(1,12))/le;

%creating X- and Y-vectors for each sample for the initial slope of the
%test curve. X-vectors for strain and Y-vectors for stress
j=[1:length(strainca241)];
Xi1=[];Xi2=[];Xi3=[];Xi4=[];Xi5=[];Xi6=[];Xi7=[];Xi8=[];Xi9=[];Xi10=[];Xi11
=[];Xi12=[];
Yi1=[];Yi2=[];Yi3=[];Yi4=[];Yi5=[];Yi6=[];Yi7=[];Yi8=[];Yi9=[];Yi10=[];Yi11
=[];Yi12=[];
Xii1=[];Xii2=[];Xii3=[];Xii4=[];Xii5=[];Xii6=[];Xii7=[];Xii8=[];Xii9=[];Xii
10=[];Xii11=[];Xii12=[];
i=1;
for j=1:length(strainca241);
Xi1(j)=strainca241(j);
if Xi1(j) >= 0.0001;
Yi1(i)=stressca241(j);
Xii1(i)=strainca241(j);
i=i+1;
if Xi1(j) >= 0.0025;
```

```

        break
    end
end
end
i=1;
for j=1:length(strainca242);
Xi2(j)=strainca242(j);
if Xi2(j) >= 0.0001;
    Yi2(i)=stressca242(j);
    Xii2(i)=strainca242(j);
    i=i+1;
if Xi2(j) >= 0.0025;
    break
end
end
end
i=1;
for j=1:length(strainca243);
Xi3(j)=strainca243(j);
if Xi3(j) >= 0.0001;
    Yi3(i)=stressca243(j);
    Xii3(i)=strainca243(j);
    i=i+1;
if Xi3(j) >= 0.0025;
    break
end
end
end
i=1;
for j=1:length(strainca244);
Xi4(j)=strainca244(j);
if Xi4(j) >= 0.0001;
    Yi4(i)=stressca244(j);
    Xii4(i)=strainca244(j);
    i=i+1;
if Xi4(j) >= 0.0025;
    break
end
end
end
i=1;
for j=1:length(strainca245);
Xi5(j)=strainca245(j);
if Xi5(j) >= 0.0001;
    Yi5(i)=stressca245(j);
    Xii5(i)=strainca245(j);
    i=i+1;
if Xi5(j) >= 0.0025;
    break
end
end
end
i=1;
for j=1:length(strainca246);
Xi6(j)=strainca246(j);
if Xi6(j) >= 0.0001;
    Yi6(i)=stressca246(j);
    Xii6(i)=strainca246(j);
    i=i+1;
if Xi6(j) >= 0.0025;
    break
end
end
end

```

```

end
end
end
i=1;
for j=1:length(strainca247);
Xi7(j)=strainca247(j);
if Xi7(j) >= 0.0001;
    Yi7(i)=stressca247(j);
    Xii7(i)=strainca247(j);
    i=i+1;
if Xi7(j) >= 0.0025;
    break
end
end
end
i=1;
for j=1:length(strainca248);
Xi8(j)=strainca248(j);
if Xi8(j) >= 0.0001;
    Yi8(i)=stressca248(j);
    Xii8(i)=strainca248(j);
    i=i+1;
if Xi8(j) >= 0.0025;
    break
end
end
end
i=1;
for j=1:length(strainca249);
Xi9(j)=strainca249(j);
if Xi9(j) >= 0.0001;
    Yi9(i)=stressca249(j);
    Xii9(i)=strainca249(j);
    i=i+1;
if Xi9(j) >= 0.0025;
    break
end
end
end
i=1;
for j=1:length(strainca2410);
Xi10(j)=strainca2410(j);
if Xi10(j) >= 0.0001;
    Yi10(i)=stressca2410(j);
    Xii10(i)=strainca2410(j);
    i=i+1;
if Xi10(j) >= 0.0025;
    break
end
end
end
i=1;
for j=1:length(strainca2411);
Xi11(j)=strainca2411(j);
if Xi11(j) >= 0.0001;
    Yi11(i)=stressca2411(j);
    Xii11(i)=strainca2411(j);
    i=i+1;
if Xi11(j) >= 0.0025;
    break
end
end

```

```

end
end
i=1;
for j=1:length(strainca2412);
Xi12(j)=strainca2412(j);
if Xi12(j) >= 0.0001;
    Yi12(i)=stressca2412(j);
    Xii12(i)=strainca2412(j);
    i=i+1;
if Xi12(j) >= 0.0025;
    break
end
end
end

%Polynomial fitting (y=kx+m) of the initial slope to calculate Young's
%modulus as the gradient of the fitted line; E-mod=stress/strain
Emod1=polyfit(Xii1,Yi1,1);Emod2=polyfit(Xii2,Yi2,1);
Emod3=polyfit(Xii3,Yi3,1);Emod4=polyfit(Xii4,Yi4,1);
Emod5=polyfit(Xii5,Yi5,1);Emod6=polyfit(Xii6,Yi6,1);
Emod7=polyfit(Xii7,Yi7,1);Emod8=polyfit(Xii8,Yi8,1);
Emod9=polyfit(Xii9,Yi9,1);Emod10=polyfit(Xii10,Yi10,1);
Emod11=polyfit(Xii11,Yi11,1);Emod12=polyfit(Xii12,Yi12,1);
Emod=[Emod1(1,1) Emod2(1,1) Emod3(1,1) Emod4(1,1) Emod5(1,1) Emod6(1,1)
Emod7(1,1) Emod8(1,1) Emod9(1,1) Emod10(1,1) Emod11(1,1) Emod12(1,1)];
%statistical evaluation of Young's modulus (N/mm2) of the samples in the
%series calculating the average, standard deviation and confidence interval
%of 95% confidence level, based on Gaussian distribution
[medEmod,stadavEmod,konfmEmod,konfsEmod]=normfit(Emod)

%"control" Young's modulus calculated as the gradient of the line using
%k=(x2-x1)/(y2-y1)
Emodk1=(max(Yi1)-min(Yi1))/(max(Xii1)-min(Xii1));
Emodk2=(max(Yi2)-min(Yi2))/(max(Xii2)-min(Xii2));
Emodk3=(max(Yi3)-min(Yi3))/(max(Xii3)-min(Xii3));
Emodk4=(max(Yi4)-min(Yi4))/(max(Xii4)-min(Xii4));
Emodk5=(max(Yi5)-min(Yi5))/(max(Xii5)-min(Xii5));
Emodk6=(max(Yi6)-min(Yi6))/(max(Xii6)-min(Xii6));
Emodk7=(max(Yi7)-min(Yi7))/(max(Xii7)-min(Xii7));
Emodk8=(max(Yi8)-min(Yi8))/(max(Xii8)-min(Xii8));
Emodk9=(max(Yi9)-min(Yi9))/(max(Xii9)-min(Xii9));
Emodk10=(max(Yi10)-min(Yi10))/(max(Xii10)-min(Xii10));
Emodk11=(max(Yi11)-min(Yi11))/(max(Xii11)-min(Xii11));
Emodk12=(max(Yi12)-min(Yi12))/(max(Xii12)-min(Xii12));
%statistical evaluation of Young's modulus (N/mm2) of the samples in the
%series calculating the average, standard deviation and confidence interval
%of 95% confidence level, based on Gaussian distribution
Emodk=[Emodk1 Emodk2 Emodk3 Emodk4 Emodk5 Emodk6 Emodk7 Emodk8 Emodk9
Emodk10 Emodk11 Emodk12];
[medEmodk,stadavEmodk,konfmEmodk,konfsEmodk]=normfit(Emodk)

%statistical evaluation of strain at break (%) of the samples in the series
%calculating the average, standard deviation and confidence interval of
%95% confidence level, based on Gaussian distribution
strainb=[max(strainca241) max(strainca242) max(strainca243)
max(strainca244) max(strainca245) max(strainca246) max(strainca247)
max(strainca248) max(strainca249) max(strainca2410) max(strainca2411)
max(strainca2412)]*100;
[medstrainb,stadavstrainb,konfmstrainb,konfsstrainb]=normfit(strainb)

```

```

%statistical evaluation of maximum stress (N/mm2) of the samples in the
%series calculating the average, standard deviation and confidence interval
%of 95% confidence level, based on Gaussian distribution
stressmax=[max(stressca241) max(stressca242) max(stressca243)
max(stressca244) max(stressca245) max(stressca246) max(stressca247)
max(stressca248) max(stressca249) max(stressca2410) max(stressca2411)
max(stressca2412)];
[medstressmax,stadavstressmax,konfmstressmax,konfsstressmax]=normfit(stress
max)

```

```

%plotting of test curves and polynomially fitted line

```

```

figure (1)
subplot (2,3,1)
plot (strainca241*100, stressca241, 'b.', Xii1*100, Yi1, 'rd')
title ('Carinata 2415-1')
xlabel ('Strain (%)')
ylabel ('Stress (N/mm2)')
subplot (2,3,2)
plot (strainca242*100, stressca242, 'b.', Xii2*100, Yi2, 'rd')
title ('Carinata 2415-2')
xlabel ('Strain (%)')
ylabel ('Stress (N/mm2)')
subplot (2,3,3)
plot (strainca243*100, stressca243, 'b.', Xii3*100, Yi3, 'rd')
title ('Carinata 2415-3')
xlabel ('Strain (%)')
ylabel ('Stress (N/mm2)')
subplot (2,3,4)
plot (strainca244*100, stressca244, 'b.', Xii4*100, Yi4, 'rd')
title ('Carinata 2415-4')
xlabel ('Strain (%)')
ylabel ('Stress (N/mm2)')
subplot (2,3,5)
plot (strainca245*100, stressca245, 'b.', Xii5*100, Yi5, 'rd')
title ('Carinata 2415-5')
xlabel ('Strain (%)')
ylabel ('Stress (N/mm2)')
subplot (2,3,6)
plot (strainca246*100, stressca246, 'b.', Xii6*100, Yi6, 'rd')
title ('Carinata 2415-6')
xlabel ('Strain (%)')
ylabel ('Stress (N/mm2)')

figure (2)
subplot (2,3,1)
plot (strainca247*100, stressca247, 'b.', Xii7*100, Yi7, 'rd')
title ('Carinata 2415-7')
xlabel ('Strain (%)')
ylabel ('Stress (N/mm2)')
subplot (2,3,2)
plot (strainca248*100, stressca248, 'b.', Xii8*100, Yi8, 'rd')
title ('Carinata 2415-8')
xlabel ('Strain (%)')
ylabel ('Stress (N/mm2)')
subplot (2,3,3)
plot (strainca249*100, stressca249, 'b.', Xii9*100, Yi9, 'rd')
title ('Carinata 2415-9')
xlabel ('Strain (%)')
ylabel ('Stress (N/mm2)')
subplot (2,3,4)
plot (strainca2410*100, stressca2410, 'b.', Xii10*100, Yi10, 'rd')

```

```
title ('Carinata 2415-10')
xlabel ('Strain (%)')
ylabel ('Stress (N/mm2)')
subplot (2,3,5)
plot(strainca2411*100, stressca2411, 'b.', Xii11*100, Yi11, 'rd')
title ('Carinata 2415-11')
xlabel ('Strain (%)')
ylabel ('Stress (N/mm2)')
subplot (2,3,6)
plot(strainca2412*100, stressca2412, 'b.', Xii12*100, Yi12, 'rd')
title ('Carinata 2415-12')
xlabel ('Strain (%)')
ylabel ('Stress (N/mm2)')
```

Appendix 2: DSC Scans

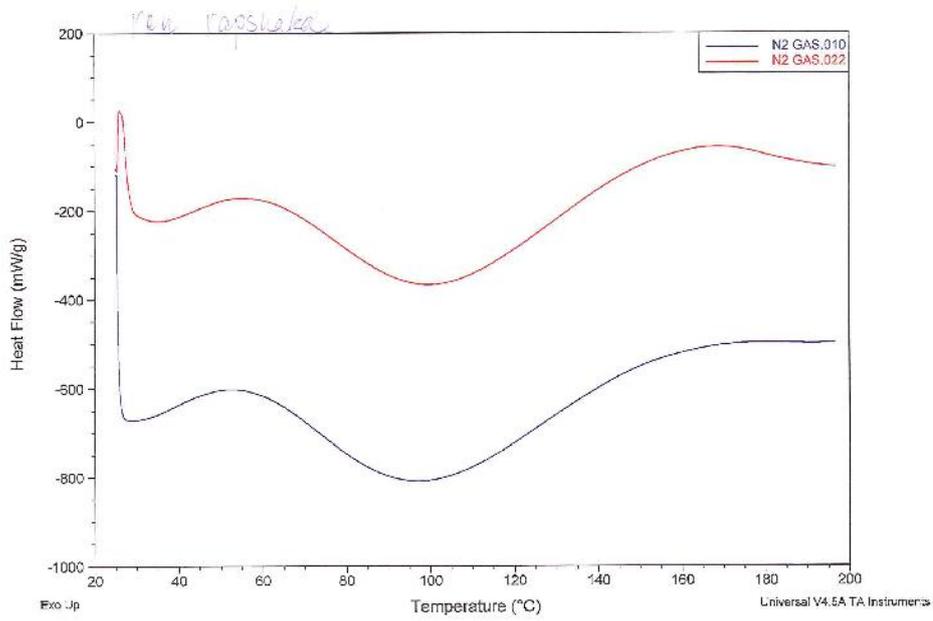


Figure 1: DSC scan of pure rapeseed cake in nitrogen atmosphere.

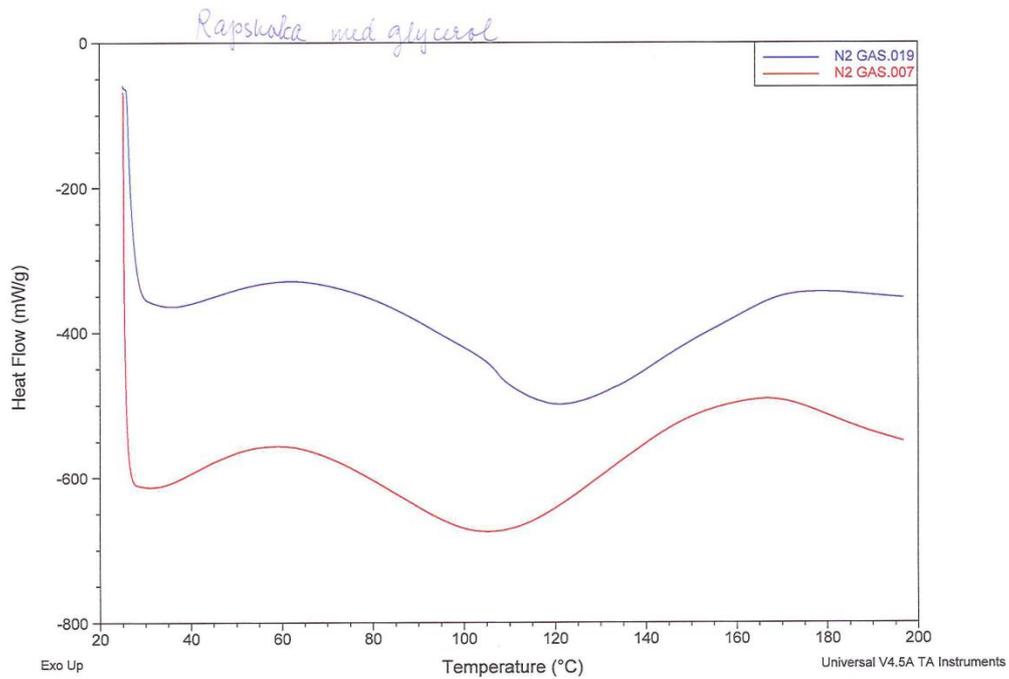


Figure 2: DSC scan of rapeseed cake with 15 wt% glycerol in nitrogen atmosphere.

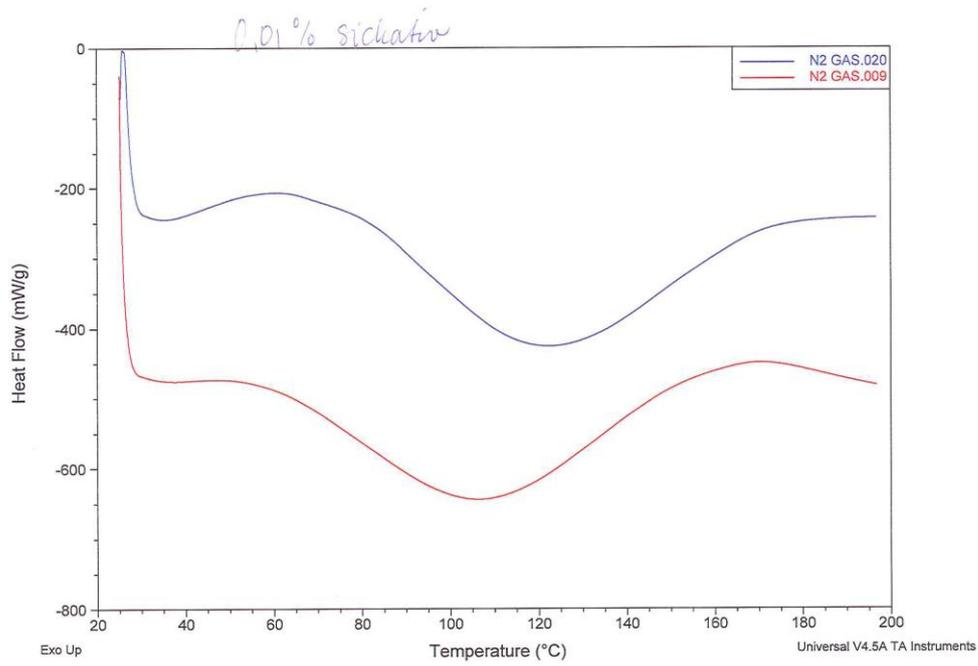


Figure 3: DSC scan of rapeseed cake with 15 wt% glycerol and 0,01 wt% $\text{Mn}(\text{acac})_3$ in nitrogen atmosphere.

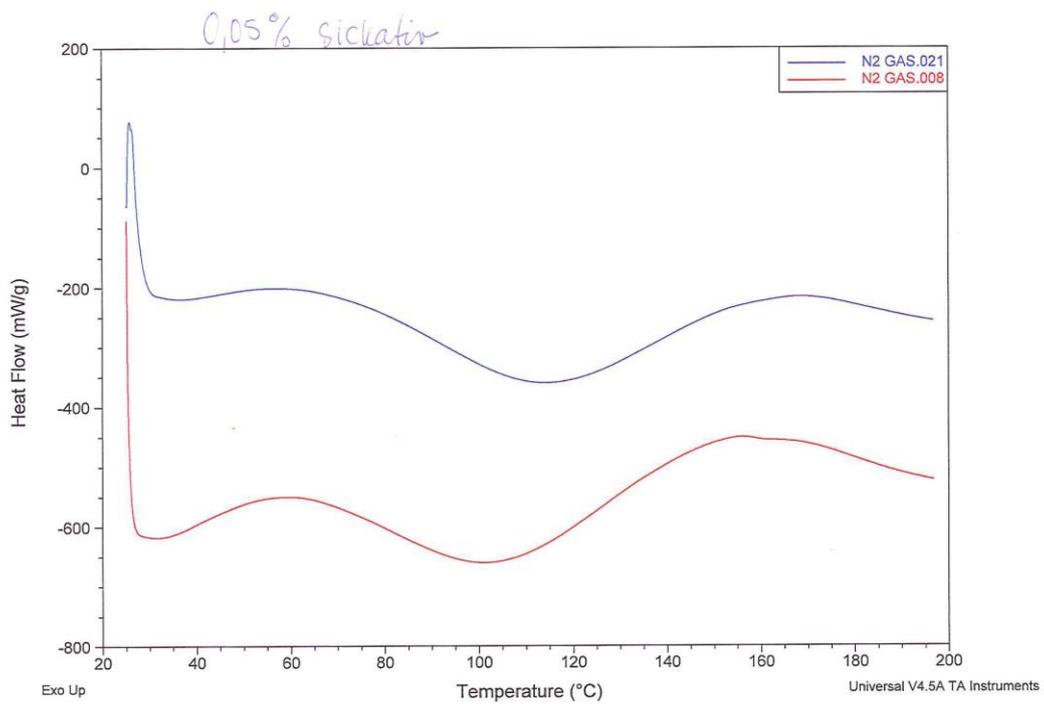


Figure 4: DSC scan of rapeseed cake with 15 wt% glycerol and 0,05 wt% $\text{Mn}(\text{acac})_3$ in nitrogen atmosphere.

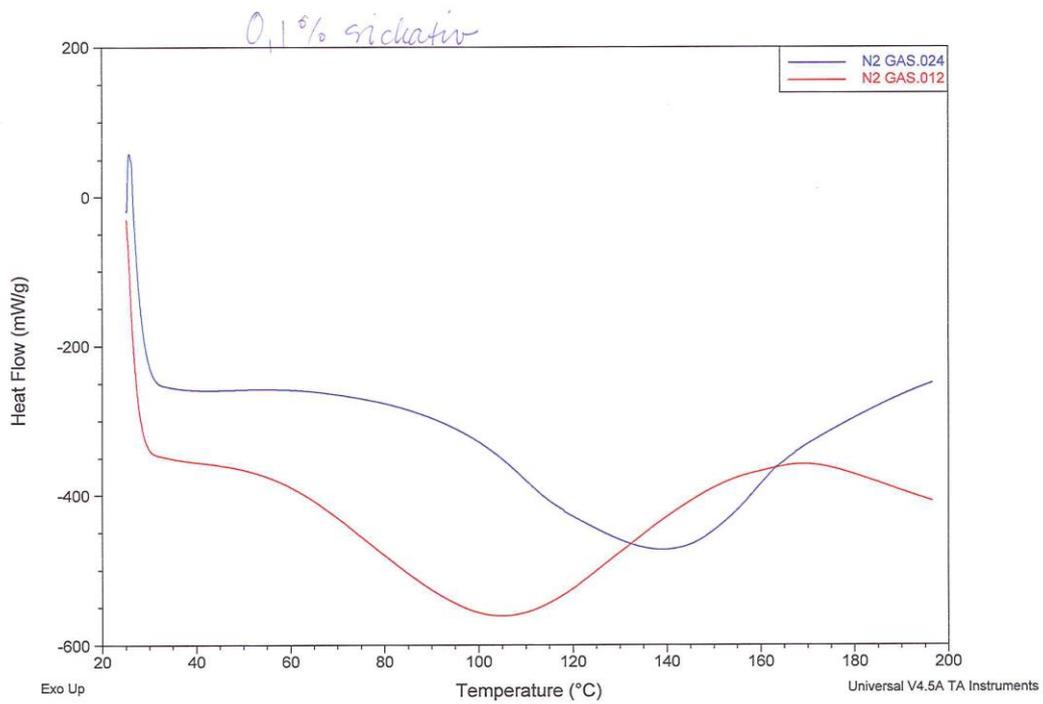


Figure 5: DSC scan of rapeseed cake with 15 wt% glycerol and 0,1 wt% $\text{Mn}(\text{acac})_3$ in nitrogen atmosphere.

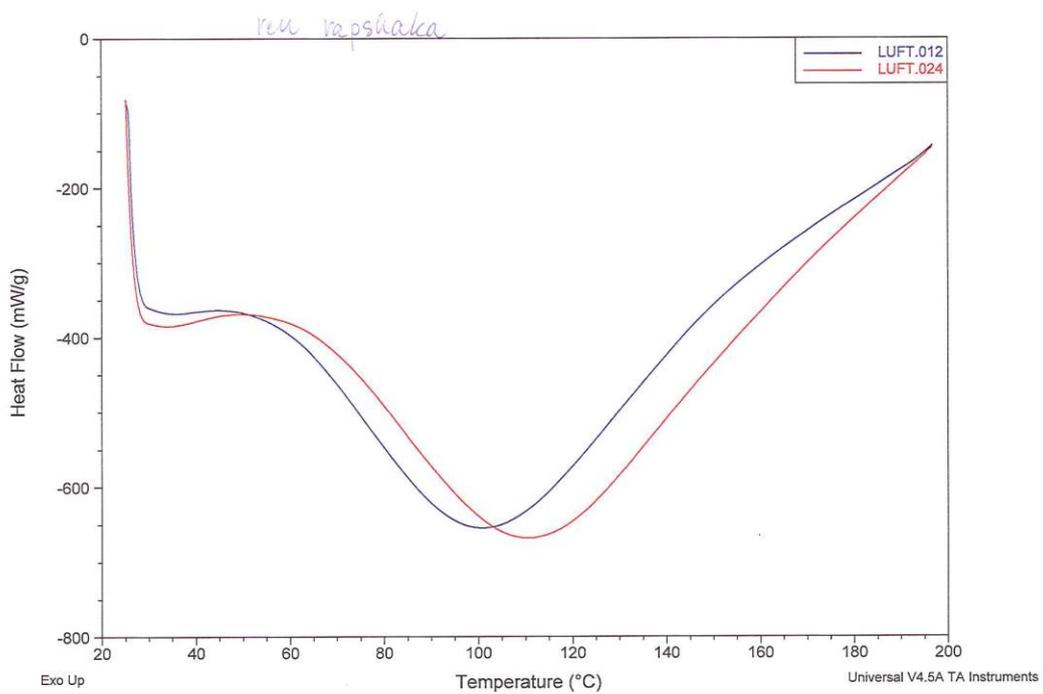


Figure 6: DSC scan of pure rapeseed cake in air atmosphere.

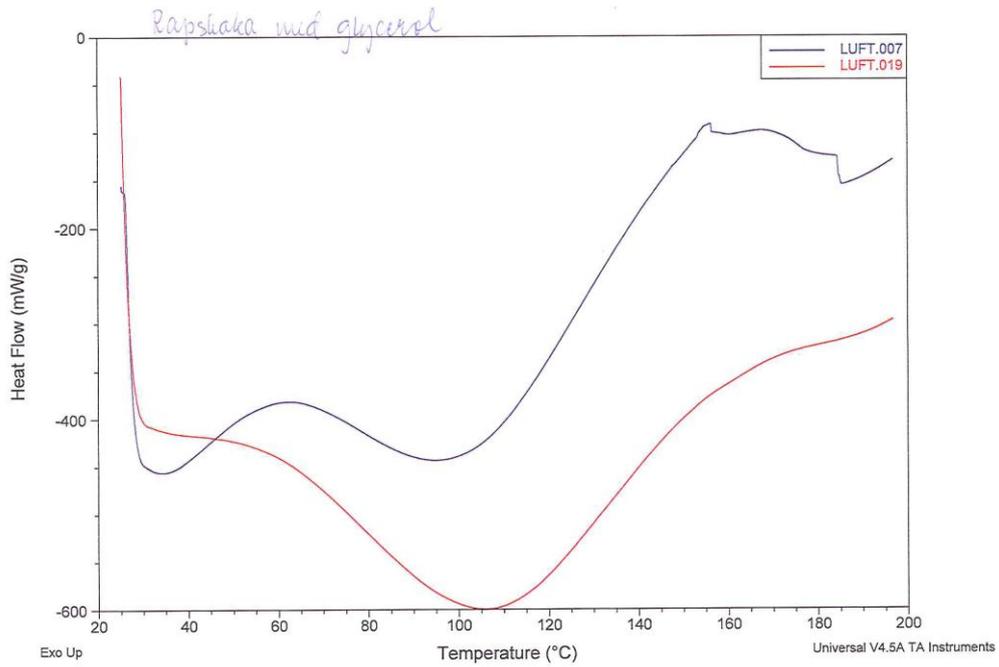


Figure 7: DSC scan of rapeseed cake with 15 wt% glycerol in air atmosphere.

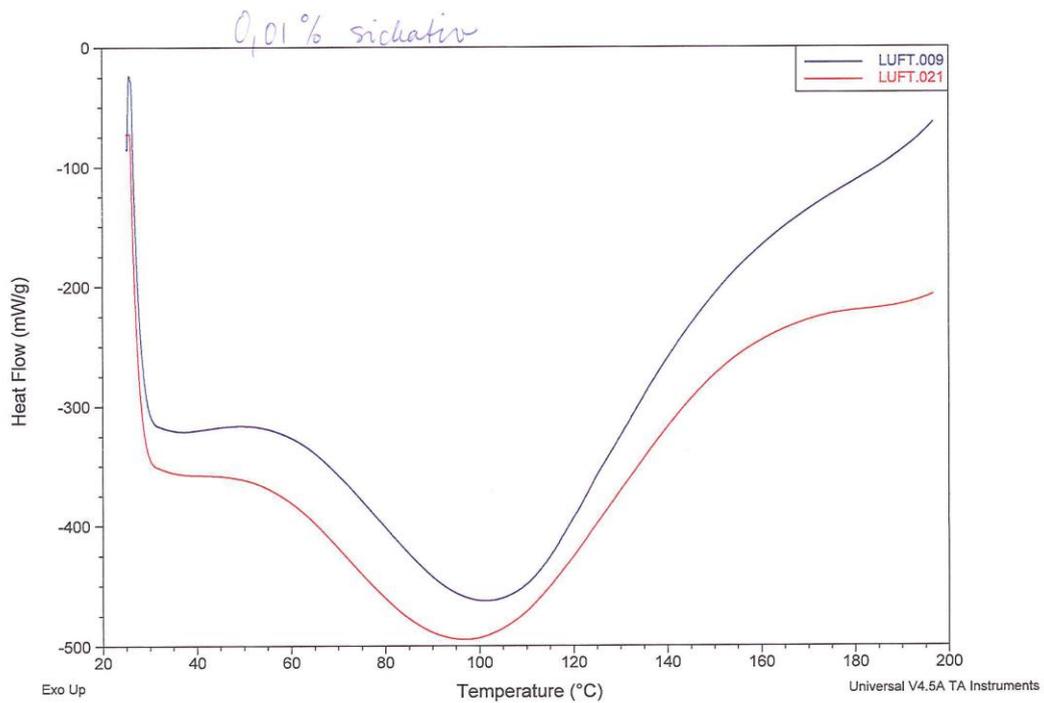


Figure 8: DSC scan of rapeseed cake with 15 wt% glycerol and 0,01 wt% $\text{Mn}(\text{acac})_3$ in air atmosphere.

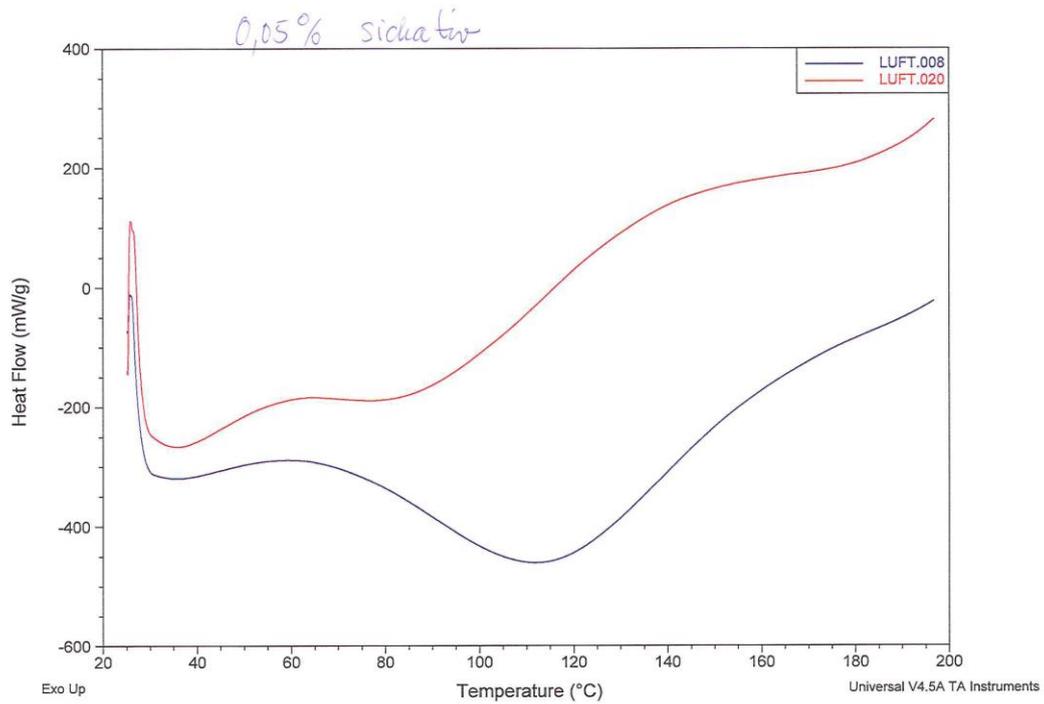


Figure 9: DSC scan of rapeseed cake with 15 wt% glycerol and 0,05 wt% $Mn(acac)_3$ in air atmosphere.

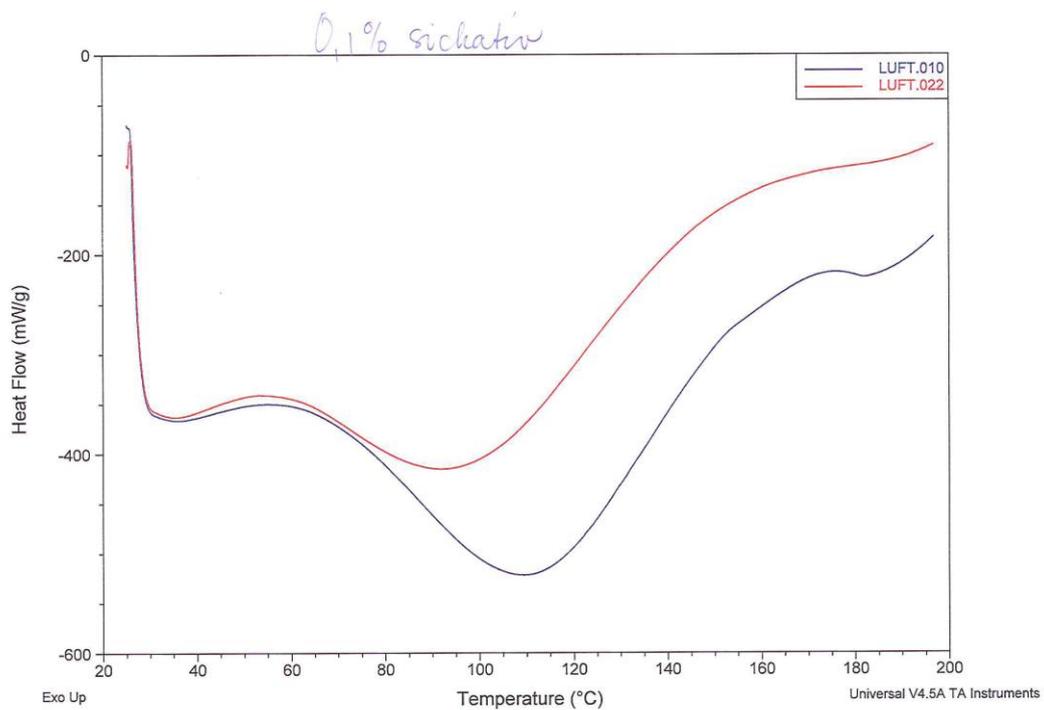


Figure 10: DSC scan of rapeseed cake with 15 wt% glycerol and 0,1 wt% $Mn(acac)_3$ in air atmosphere.

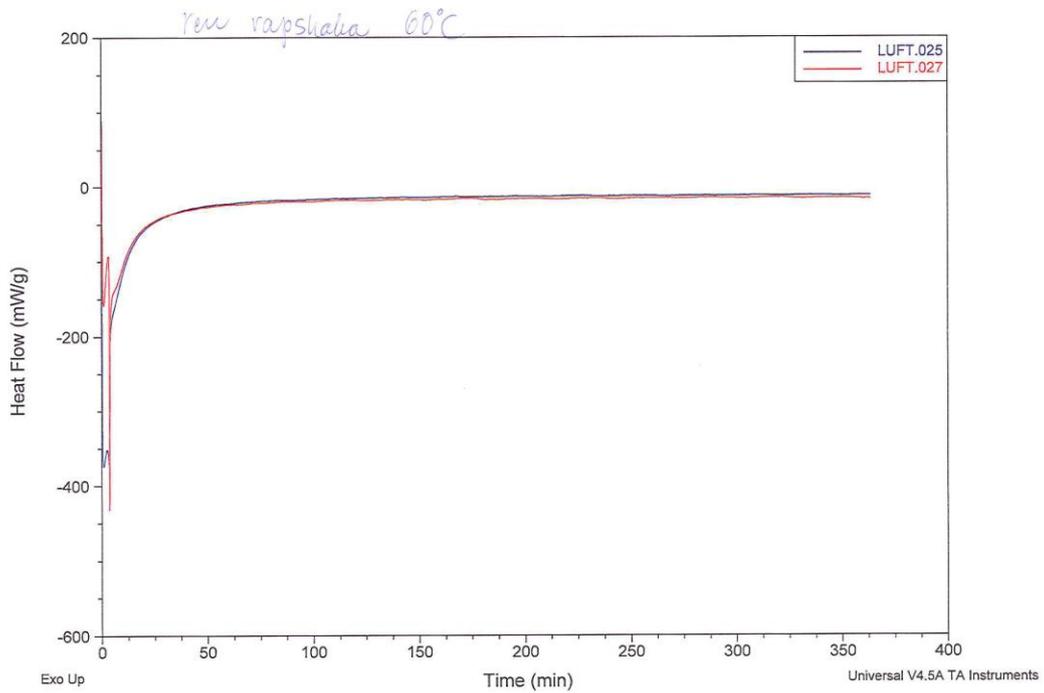


Figure 11: DSC scan of pure rapeseed cake at 60°C in air atmosphere.

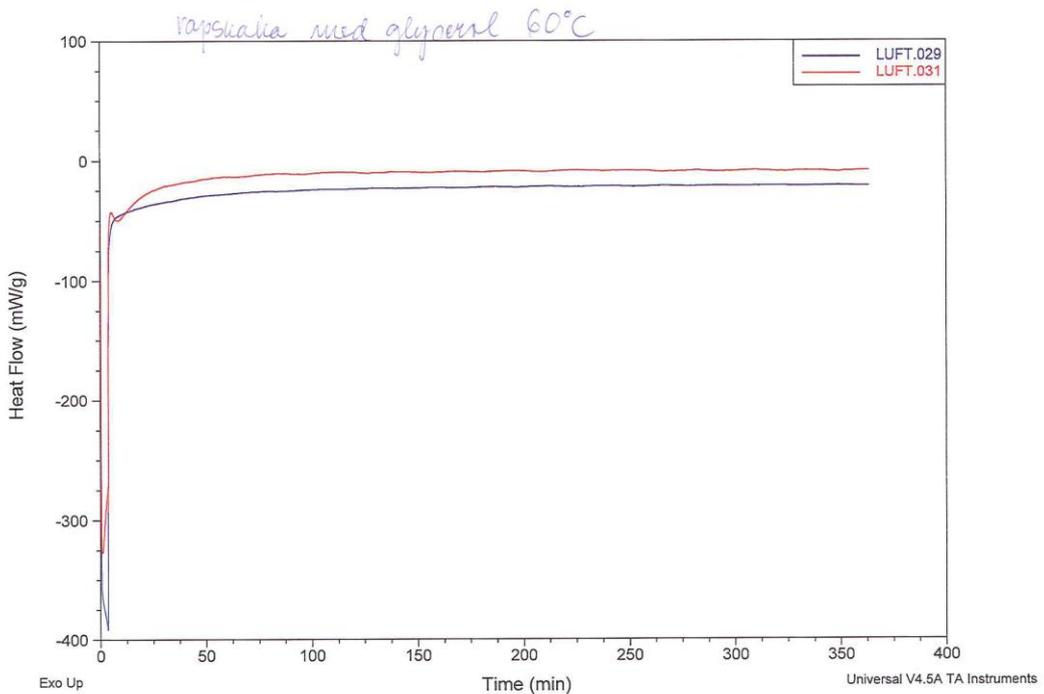


Figure 12: DSC scan of rapeseed cake with 15 wt% glycerol at 60°C in air atmosphere.

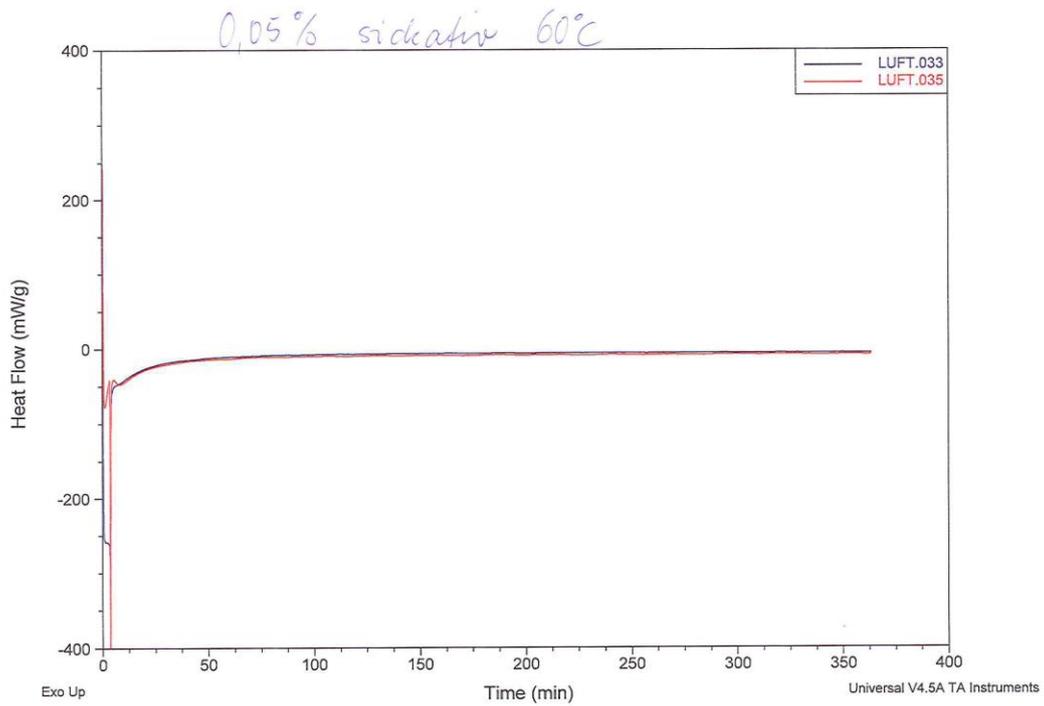


Figure 13: DSC scan of rapeseed cake with 15 wt% glycerol and 0,05 wt% $\text{Mn}(\text{acac})_3$ at 60°C in air atmosphere.

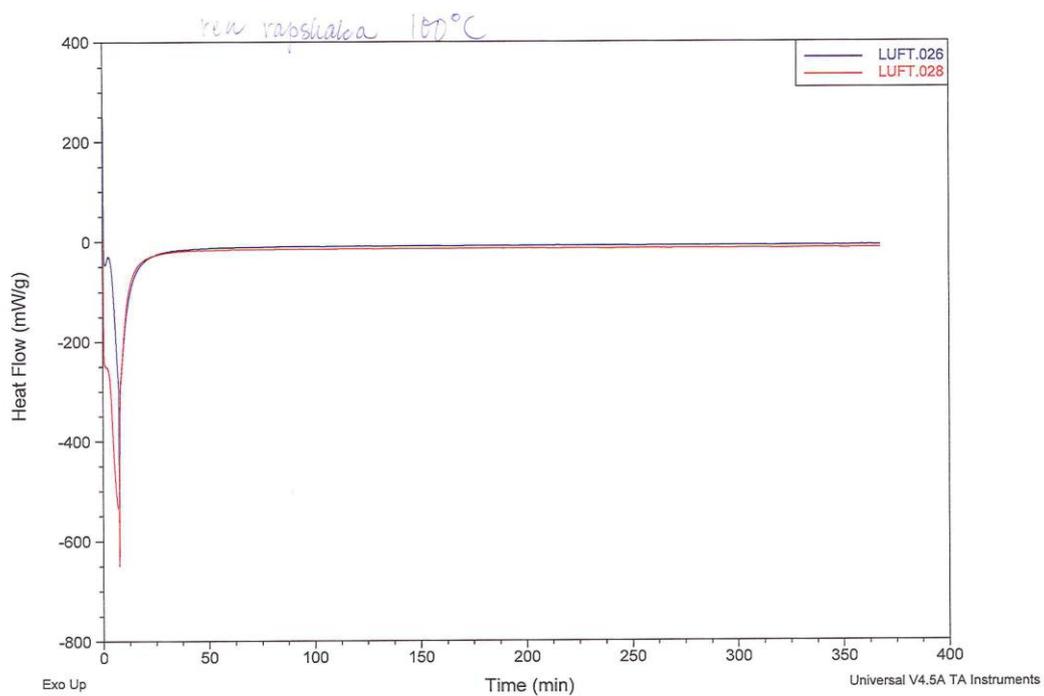


Figure 14: DSC scan of pure rapeseed cake at 100°C in air atmosphere.

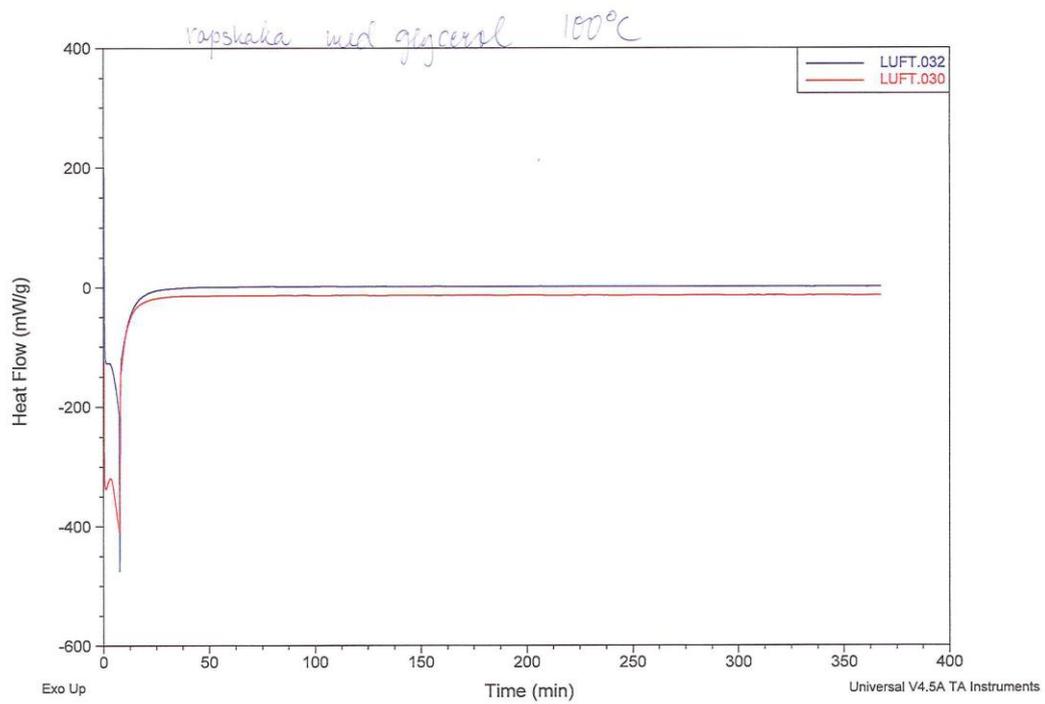


Figure 15: DSC scan of rapeseed cake with 15 wt% glycerol at 100°C in air atmosphere.

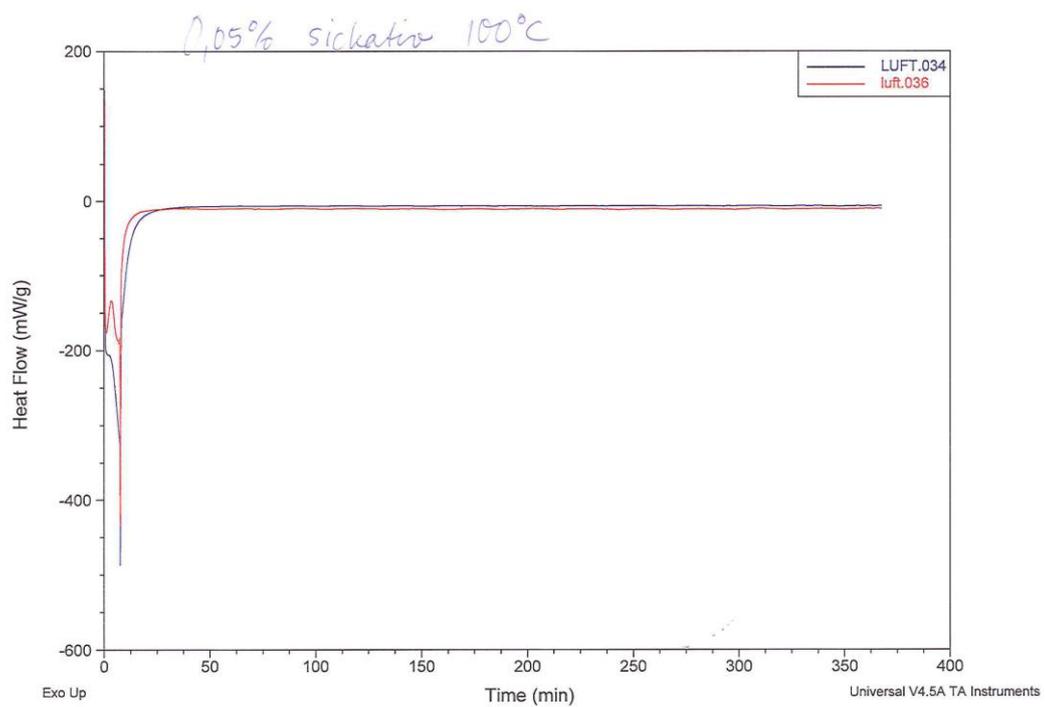


Figure 16: DSC scan of rapeseed cake with 15 wt% glycerol and 0,05 wt% $\text{Mn}(\text{acac})_3$ at 100°C in air atmosphere.

Appendix 3: Tables of results

The tables that follow show the results from the analyses performed in the study.

The abbreviations for the different materials are composed as follows:

Oilcake/siccative concentration – milling time/wt% glycerol – pre-heating time

where Cr means Crambe, Ca - Carinata, Rc - Rapeseed cake, Crex – extruded crambe, Caex – extruded carinata and Rcex – extruded rapeseed cake.

Example 1: *Ca-2415* is to be understood as carinata ballmilled for 24 h with 15 wt% glycerol

Example 2: *Crex0,01-2h* is to be understood as extruded crambe with 0,01 wt% Mn(acac)₃ preheated for 2h.

All analyses were performed on pressed sheets with the exception of bending resistance where *ex* refers to the actual extrudates.

Tensile testing

Table 1: Tensile properties of Crambe, Carinata and Rapeseed cake materials unmilled and ball milled 24 h and 48 h respectively. Values are shown as mean value and confidence interval of 95% confidence level.

Material	Young's modulus (MPa)	Strain at break (%)	Maximum stress (MPa)
Cr-015	323 ± 64	0,64 ± 0,09	1,27 ± 0,29
Cr-2415	378 ± 65	0,56 ± 0,12	1,46 ± 0,49
Cr-4815	341 ± 28	0,61 ± 0,08	1,50 ± 0,22
Ca-015	137 ± 14	2,04 ± 0,33	1,25 ± 0,11
Ca-2415	159 ± 7	1,57 ± 0,10	1,27 ± 0,09
Ca-4815	151 ± 14	1,40 ± 0,13	1,31 ± 0,05
Rc-015	113 ± 15	0,61 ± 0,07	0,47 ± 0,06
Rc-2415	121 ± 13	0,55 ± 0,07	0,50 ± 0,07
Rc-4815	102 ± 13	0,51 ± 0,06	0,45 ± 0,06

Table 2: Tensile properties of Crambe films with added siccativ. Values are shown as mean value and confidence interval of 95% confidence level.

Material	Young's modulus (MPa)	Strain at break (%)	Maximum stress (MPa)
Cr015 - 0h	323 ± 64	0,64 ± 0,09	1,27 ± 0,29
Cr015 - 2h	126 ± 42	1,86 ± 0,18	1,39 ± 0,26
Cr015 - 6h	98 ± 14	1,73 ± 0,20	1,11 ± 0,17
Cr0,01 - 0h	228 ± 15	1,18 ± 0,11	1,58 ± 0,11
Cr0,01 - 2h	101 ± 16	1,62 ± 0,16	1,09 ± 0,17
Cr0,01 - 6h	84 ± 25	1,42 ± 0,51	0,73 ± 0,18
Cr0,05 - 0h	179 ± 21	1,19 ± 0,23	1,45 ± 0,24
Cr0,05 - 2h	93 ± 29	1,52 ± 0,26	0,83 ± 0,19
Cr0,05 - 6h	118 ± 28	1,54 ± 0,18	1,09 ± 0,21
Cr0,1 - 0h	168 ± 19	1,14 ± 0,26	1,29 ± 0,24
Cr0,1 - 2h	133 ± 13	1,55 ± 0,28	1,19 ± 0,11
Cr0,1 - 6h	118 ± 12	1,72 ± 0,16	1,17 ± 0,11
Cr5 - 0h	246 ± 44	1,26 ± 0,13	1,97 ± 0,33
Cr5 - 2h	172 ± 19	1,62 ± 0,15	1,50 ± 0,16
Cr5 - 6h	144 ± 16	1,83 ± 0,21	1,57 ± 0,19

Table 3: Tensile properties of Carinata materials with added siccativo. Values are shown as mean value and confidence interval of 95% confidence level.

Material	Young's modulus (MPa)	Strain at break (%)	Maximum stress (MPa)
Ca015 - 0h	137 ± 14	2,04 ± 0,33	1,25 ± 0,11
Ca015 - 2h	62 ± 7	2,90 ± 0,35	1,10 ± 0,06
Ca015 - 6h	22 ± 3	3,58 ± 0,43	0,89 ± 0,10
Ca0,01 - 0h	85 ± 16	2,83 ± 0,36	1,20 ± 0,08
Ca0,01 - 2h	38 ± 15	3,30 ± 0,41	1,05 ± 0,22
Ca0,01 - 6h	20 ± 5	3,02 ± 0,85	0,73 ± 0,16
Ca0,05 - 0h	53 ± 16	3,15 ± 0,43	1,18 ± 0,09
Ca0,05 - 2h	67 ± 11	2,48 ± 0,40	1,17 ± 0,18
Ca0,05 - 6h	29 ± 4	3,74 ± 0,46	0,90 ± 0,06
Ca0,1 - 0h	45 ± 8	2,51 ± 0,32	1,04 ± 0,13
Ca0,1 - 2h	59 ± 9	3,58 ± 0,39	1,31 ± 0,07
Ca0,1 - 6h	26 ± 5	3,46 ± 0,34	0,82 ± 0,05
Ca5 - 0h	59 ± 14	2,44 ± 0,42	1,13 ± 0,15
Ca5 - 2h	30 ± 6	3,59 ± 0,35	1,08 ± 0,06
Ca5 - 6h	35 ± 6	3,36 ± 0,25	1,08 ± 0,12
Caex015 - 0h	26 ± 8	1,78 ± 0,36	0,56 ± 0,08
Caex015 - 2h	26 ± 8	1,65 ± 0,24	0,40 ± 0,11
Caex0,01 - 0h	68 ± 7	1,68 ± 0,23	1,09 ± 0,14
Caex0,01 - 2h	40 ± 13	1,91 ± 0,25	0,75 ± 0,21
Caex0,05 - 0h	52 ± 11	1,81 ± 0,16	1,05 ± 0,09
Caex0,05 - 2h	27 ± 3	1,93 ± 0,30	0,54 ± 0,14
Caex0,1 - 0h	32 ± 7	2,23 ± 0,25	0,88 ± 0,19
Caex0,1 - 2h	27 ± 9	1,35 ± 0,45	0,47 ± 0,13

Table 4: Tensile properties of Rapeseed cake materials with added siccativ. Values are shown as mean value and confidence interval of 95% confidence level.

Material	Young's modulus (MPa)	Strain at break (%)	Maximum stress (MPa)
Rc015 - 0h	113 ± 15	0,61 ± 0,07	0,45 ± 0,06
Rc015 - 2h	56 ± 17	1,36 ± 0,20	0,57 ± 0,16
Rc015 - 6h	66 ± 18	1,27 ± 0,11	0,62 ± 0,03
Rc0,01 - 2h	35 ± 4	1,56 ± 0,16	0,53 ± 0,07
Rc0,01 - 6h	41 ± 6	1,55 ± 0,14	0,53 ± 0,07
Rc0,05 - 2h	59 ± 7	1,38 ± 0,12	0,68 ± 0,05
Rc0,05 - 6h	60 ± 9	1,46 ± 0,15	0,68 ± 0,04
Rc0,1 - 2h	61 ± 10	1,37 ± 0,17	0,68 ± 0,06
Rc0,1 - 6h	58 ± 7	1,44 ± 0,07	0,69 ± 0,02
Rc5 - 2h	38 ± 8	1,19 ± 0,18	0,42 ± 0,04
Rc5 - 6h	31 ± 15	1,04 ± 0,20	0,35 ± 0,04

Bending resistance

Table 5: Bending resistance for extrudates with and without siccativ, and for pressed materials without siccativ. Values are shown as mean value and confidence interval of 95% confidence level.

Material	Bending resistance (mN)	Material	Bending resistance (mN)	Material	Bending resistance (mN)
Crex015	15,5 ± 1,7	Caex015	19,6 ± 2,8	Rcex015	11,1 ± 0,9
Crex2415	33,7 ± 4,8	Caex2415	20,5 ± 3,3	Rcex2415	13,5 ± 0,2
Crex4815	33,2 ± 5,2	Caex4815	31,1 ± 3,5	Rc4815	13,4 ± 1,7
Cr015	48,9 ± 12,1	Ca015	12,0 ± 1,1	Rc015	10,9 ± 1,3
Cr2415	55,3 ± 2,8	Ca2415	11,2 ± 0,9	Rc2415	9,4 ± 1,2
Cr4815	42,2 ± 2,9	Ca4815	13,8 ± 0,1	Rc4815	12,0 ± 0,4
Crex0,01	36,6 ± 4,8	Caex0,01	24,3 ± 3,3	Rcex0,1	7,9 ± 1,7
Crex0,05	20,6 ± 2,5	Caex0,05	25,1 ± 2,8		
Crex0,1	21,8 ± 3,7	Caex0,1	23,4 ± 2,8		

Water absorption

Table 6: Water absorption for Crambe, Carinata and Rapeseed cake materials. Values are shown as mean value and confidence interval of 95% confidence level.

Material	Water absorption (g/m ²)	Material	Water absorption (g/m ²)	Material	Water absorption (g/m ²)
Cr00	51,6 ± 3,2	Ca00	34,9 ± 3,6		
Cr240	36,2 ± 3,2	Ca240	35,0 ± 3,4		
Cr480	30,9 ± 1,0	Ca480	40,8 ± 2,9		
Cr015	31,1 ± 1,7	Ca015	31,8 ± 1,9	Rc015	33,2 ± 0,9
Cr2415	27,9 ± 1,4	Ca2415	34,2 ± 0,4	Rc2415	30,0 ± 1,0
Cr4815	27,6 ± 0,8	Ca4815	34,8 ± 0,9	Rc4815	28,5 ± 1,4
Cr015 - 2h	50,8 ± 3,0	Ca015 - 2h	37,5 ± 1,1	Rc015 - 2h	36,1 ± 1,6
Cr015 - 6h	51,8 ± 3,2	Ca015 - 6h	35,7 ± 1,6	Rc015 - 6h	36,9 ± 1,2
Cr0,01 - 0h	27,4 ± 0,8	Ca0,01 - 0h	30,1 ± 0,3	Rc0,01 - 2h	35,5 ± 1,3
Cr0,01 - 2h	70,5 ± 0,8	Ca0,01 - 2h	35,3 ± 1,2	Rc0,01 - 6h	37,7 ± 3,1
Cr0,01 - 6h	61,0 ± 4,6	Ca0,01 - 6h	36,6 ± 1,4	Rc0,05 - 2h	36,9 ± 1,8
Cr0,05 - 0h	24,7 ± 1,5	Ca0,05 - 0h	28,0 ± 0,4	Rc0,05 - 6h	38,6 ± 1,2
Cr0,05 - 2h	66,6 ± 2,9	Ca0,05 - 2h	36,4 ± 2,5	Rc0,1 - 2h	36,8 ± 0,6
Cr0,05 - 6h	48,8 ± 1,8	Ca0,05 - 6h	36,7 ± 1,0	Rc0,1 - 6h	33,8 ± 1,1
Cr0,1 - 0h	25,6 ± 0,9	Ca0,1 - 0h	30,7 ± 0,7	Rc5 - 2h	27,9 ± 0,8
Cr0,1 - 2h	54,6 ± 3,9	Ca0,1 - 2h	35,0 ± 0,8	Rc5 - 6h	30,4 ± 0,7
Cr0,1 - 6h	48,8 ± 2,6	Ca0,1 - 6h	34,9 ± 1,1	Rcex015 - 2h	55,7 ± 1,1
Cr5 - 0h	22,4 ± 2,2	Ca5 - 0h	28,4 ± 1,0	Rcex0,1 - 2h	56,2 ± 0,3
Cr5 - 2h	43,8 ± 3,1	Ca5 - 2h	33,4 ± 1,3		
Cr5 - 6h	42,3 ± 2,7	Ca5 - 6h	34,3 ± 0,4		
Crex015 - 0h	27,9 ± 0,5	Caex015 - 0h	36,8 ± 1,1		
Crex015 - 2h	35,3 ± 2,2	Caex015 - 2h	44,5 ± 1,2		
Crex0,01 - 0h	27,3 ± 1,6	Caex0,01 - 0h	37,3 ± 4,0		
Crex0,01 - 2h	37,1 ± 4,8	Caex0,01 - 2h	43,6 ± 2,9		
Crex0,05 - 0h	24,0 ± 0,8	Caex0,05 - 0h	37,0 ± 0,4		
Crex0,05 - 2h	37,1 ± 0,9	Caex0,05 - 2h	43,8 ± 1,2		
Crex0,1 - 0h	23,4 ± 0,7	Caex0,1 - 0h	36,8 ± 0,9		
Crex0,1 - 2h	35,1 ± 1,5	Caex0,1 - 2h	40,2 ± 2,1		

Oil absorption

Table 7: Oil absorption for Crambe, Carinata and Rapeseed cake materials. Values are shown as mean value and confidence interval of 95% confidence level.

Material	Oil absorption (g/m ²)	Material	Oil absorption (g/m ²)	Material	Oil absorption (g/m ²)
Cr00	12,8 ± 6,5	Ca00	7,3 ± 1,2		
Cr240	5,5 ± 2,1	Ca240	10,2 ± 1,2		
Cr480	5,9 ± 0,3	Ca480	5,6 ± 3,5		
Cr015	7,9 ± 1,0	Ca015	3,0 ± 0,5	Rc015	8,1 ± 0,7
Cr2415	4,8 ± 0,8	Ca2415	2,7 ± 0,2	Rc2415	5,1 ± 0,5
Cr4815	3,9 ± 0,9	Ca4815	2,8 ± 0,5	Rc4815	5,1 ± 0,9
Cr015 - 2h	24,6 ± 1,9	Ca015 - 2h	4,3 ± 0,8	Rc015 - 2h	9,1 ± 0,8
Cr015 - 6h	27,1 ± 4,4	Ca015 - 6h	4,4 ± 0,9	Rc015 - 6h	9,1 ± 0,1
Cr0,01 - 0h	6,1 ± 0,1	Ca0,01 - 0h	2,6 ± 0,4	Rc0,01 - 2h	9,9 ± 1,0
Cr0,01 - 2h	33,5 ± 7,9	Ca0,01 - 2h	2,5 ± 0,1	Rc0,01 - 6h	9,2 ± 2,4
Cr0,01 - 6h	31,3 ± 4,2	Ca0,01 - 6h	5,2 ± 0,4	Rc0,05 - 2h	9,9 ± 1,1
Cr0,05 - 0h	7,0 ± 1,3	Ca0,05 - 0h	2,6 ± 0,2	Rc0,05 - 6h	9,7 ± 0,3
Cr0,05 - 2h	28,1 ± 7,2	Ca0,05 - 2h	3,2 ± 0,4	Rc0,1 - 2h	12,2 ± 0,6
Cr0,05 - 6h	22,5 ± 3,4	Ca0,05 - 6h	4,9 ± 0,2	Rc0,1 - 6h	9,8 ± 0,9
Cr0,1 - 0h	5,4 ± 0,6	Ca0,1 - 0h	2,9 ± 0,8	Rc5 - 2h	12,3 ± 0,9
Cr0,1 - 2h	22,8 ± 1,6	Ca0,1 - 2h	3,0 ± 0,2	Rc5 - 6h	13,4 ± 0,9
Cr0,1 - 6h	28,3 ± 5,4	Ca0,1 - 6h	4,6 ± 0,4	Rcex015 - 2h	12,2 ± 0,9
Cr5 - 0h	4,9 ± 0,7	Ca5 - 0h	3,0 ± 0,6	Rcex0,1 - 2h	13,4 ± 1,1
Cr5 - 2h	17,2 ± 3,5	Ca5 - 2h	5,0 ± 1,0		
Cr5 - 6h	17,0 ± 1,5	Ca5 - 6h	4,0 ± 0,7		
Crex015 - 0h	4,2 ± 0,3	Caex015 - 0h	2,6 ± 0,2		
Crex015 - 2h	11,7 ± 2,1	Caex015 - 2h	3,7 ± 0,4		
Crex0,01 - 0h	5,8 ± 0,2	Caex0,01 - 0h	2,3 ± 0,6		
Crex0,01 - 2h	20,6 ± 2,2	Caex0,01 - 2h	3,6 ± 0,6		
Crex0,05 - 0h	4,0 ± 0,4	Caex0,05 - 0h	2,4 ± 0,9		
Crex0,05 - 2h	13,5 ± 1,0	Caex0,05 - 2h	3,1 ± 1,0		
Crex0,1 - 0h	4,0 ± 0,7	Caex0,1 - 0h	2,3 ± 0,2		
Crex0,1 - 2h	18,3 ± 2,2	Caex0,1 - 2h	3,4 ± 0,2		

Moisture content

Table 8: Moisture content for Crambe, Carinata and Rapeseed cake materials. Values are shown as mean value and confidence interval of 95% confidence level.

Material	Moisture content (%)	Material	Moisture content (%)	Material	Moisture content (%)
Cr00	6,8 ± 0,1	Ca00	6,7 ± 0,1		
Cr240	7,1 ± 0,0	Ca240	6,6 ± 0,2		
Cr480	7,0 ± 0,1	Ca480	6,6 ± 0,1		
Cr015	9,0 ± 0,7	Ca015	8,5 ± 0,6	Rc015	10,4 ± 0,2
Cr2415	8,9 ± 0,2	Ca2415	8,6 ± 0,1	Rc2415	11,3 ± 0,1
Cr4815	8,7 ± 0,2	Ca4815	8,6 ± 0,1	Rc4815	11,5 ± 0,1
Cr015 - 2h	13,3 ± 0,3	Ca015 - 2h	12,6 ± 0,4	Rc015 - 2h	13,8 ± 0,1
Cr015 - 6h	13,8 ± 0,2	Ca015 - 6h	12,3 ± 0,5	Rc015 - 6h	13,9 ± 0,3
Cr0,01 - 0h	12,0 ± 0,2	Ca0,01 - 0h	12,1 ± 0,2	Rc0,01 - 2h	14,4 ± 0,5
Cr0,01 - 2h	15,4 ± 0,7	Ca0,01 - 2h	12,2 ± 0,5	Rc0,01 - 6h	14,9 ± 0,3
Cr0,01 - 6h	14,8 ± 1,8	Ca0,01 - 6h	12,4 ± 0,4	Rc0,05 - 2h	14,6 ± 0,2
Cr0,05 - 0h	12,3 ± 0,3	Ca0,05 - 0h	11,8 ± 0,5	Rc0,05 - 6h	13,9 ± 0,1
Cr0,05 - 2h	14,3 ± 0,5	Ca0,05 - 2h	11,3 ± 0,1	Rc0,1 - 2h	14,6 ± 0,1
Cr0,05 - 6h	13,9 ± 0,4	Ca0,05 - 6h	12,0 ± 0,4	Rc0,1 - 6h	13,8 ± 0,2
Cr0,1 - 0h	12,6 ± 0,4	Ca0,1 - 0h	11,3 ± 0,2	Rc5 - 2h	15,7 ± 0,1
Cr0,1 - 2h	14,5 ± 0,7	Ca0,1 - 2h	11,8 ± 0,1	Rc5 - 6h	16,2 ± 0,2
Cr0,1 - 6h	14,0 ± 0,4	Ca0,1 - 6h	12,2 ± 0,2	Rcex015 - 2h	14,8 ± 0,4
Cr5 - 0h	12,6 ± 0,3	Ca5 - 0h	12,6 ± 0,6	Rcex0,1 - 2h	14,1 ± 0,5
Cr5 - 2h	14,5 ± 0,3	Ca5 - 2h	13,0 ± 0,2		
Cr5 - 6h	14,1 ± 0,3	Ca5 - 6h	12,5 ± 0,2		
Crex015 - 0h	13,2 ± 0,2	Caex015 - 0h	11,5 ± 0,2		
Crex015 - 2h	13,8 ± 0,4	Caex015 - 2h	11,6 ± 0,2		
Crex0,01 - 0h	12,3 ± 0,2	Caex0,01 - 0h	11,0 ± 0,2		
Crex0,01 - 2h	13,5 ± 0,7	Caex0,01 - 2h	11,6 ± 0,2		
Crex0,05 - 0h	13,1 ± 0,1	Caex0,05 - 0h	11,8 ± 0,1		
Crex0,05 - 2h	-	Caex0,05 - 2h	11,4 ± 0,1		
Crex0,1 - 0h	12,7 ± 0,4	Caex0,1 - 0h	11,4 ± 0,2		
Crex0,1 - 2h	14,0 ± 0,7	Caex0,1 - 2h	11,4 ± 0,2		