



Functionalization of polycaprolactone in supercritical carbon dioxide

M.Sc Thesis



PCL-g-GMA

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 September 2009-December 2010



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1. Abstract

The oil reserves depletion and the growing concerns about plastic waste accumulation in the environment has led to the investigation of substitutes for plastic material. Polycaprolactone (PCL) and starch can be used in the blend as such a substitute. Phase separation occurs when these two polymers are mixed, so a compatibilizer must be added. In this research this compatibilizer is made by functionalization of high molecular weight polycaprolactone in supercritical carbon dioxide.

The goal of this research is to develop compatibilizer precursors using high molecular weight PCL and supercritical carbon dioxide. The functionalization degree of the compatibilizer precursors as function of the monomer and initiator intake is investigated and used in developing a mathematical model. The R^2 -value of our model is 0,967; this implies that the model has a good fit with the experimental data. GPC analysis showed that no degradation/cross linking occurred during the reactions due to the use of supercritical carbon dioxide as the solvent in the reaction. The advantage of using supercritical carbon dioxide as an environmental benign solvent is that milder reaction conditions can be used.

The compatibilizer precursors are tested for their performance in starch-PCL blends. These blends are made in the melt using a brabender. Different compatibilizers are used in different amounts to investigate changes in mechanical properties of the blends. In addition, the ratio of PCL and starch is changed. From the results can be concluded that the compatibilizer improves the mechanical properties. The amount and functionalization degree of the compatibilizer precursor have no influence on the mechanical properties. In addition, a compatibilizer made with normal melt processing is used in the blends to look to the difference with the compatibilizers made in supercritical carbon dioxide. The results show that the blends with a compatibilizer precursor made in supercritical carbon dioxide have better mechanical properties.



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4. Introduction

Plastics, with a global consumption of more than 250 million tons annual and an annual growth of approximately 5%, represents the largest field of application for crude oil outside the energy and transport sectors [1]. The plastic industry is so dependent on oil that if the price of crude oil increases, a negative effect on the plastic market follows as consequence. Another important issue with conventional plastics is that it is not easily degraded. This will result in an accumulation of plastic in the environment that is a threat to the planet. To overcome these problems, a lot of research has been done in this field; one of the most interesting is bioplastic researches. Bioplastics are plastics derived (or partly derived) from renewable biomass sources, such as vegetable oil, cellulose, starch etc. that are biodegradable and nontoxic.

Many biodegradable polymers have some limitation in their mechanical properties and cost. Starch is one of the most promising materials for bioplastics. However, starch-based plastics have poor mechanical properties and have some drawbacks in their process ability. To solve these problems, starch could be mixed with synthetic polymers. One good candidate for this mixing is polycaprolactone because the latter have good mechanical properties and is fully biodegradable.

The use of bioplastic is expected to reduce the plastic pollution rate to this planet. A good biodegradable plastic is obtained from a mixture of polycaprolactone and starch. To make this product more sustainable, the production process of this plastic also must be environmental friendly. Instead of using organic solvents in the chemical reactions, a more sustainable solvent such as supercritical carbon dioxide can be used.

4.1 Polycaprolactone

Polycaprolactone (PCL) is a biodegradable thermoplastic polymer obtained by chemical synthesis from crude oil. The primary worldwide producers of PCL are Dow Chemical (formerly Union Carbide) in the US, Solvay in Europe, and Daicel Chemical Industries in Japan. PCL is prepared by a ring opening polymerization of ϵ -caprolactone. PCL polymers can be divided in two groups according their molecular weight (MW). Polymers with a MW up to several thousand are a waxy solid or viscous liquid. These PCL are used as polyurethane intermediates, reactive diluents for high solids coatings, and plasticizers for vinyl resins. The other type of PCL has a MW greater than 20.000 and is a material with good mechanical strength. Further advantages are its good water, oil, and solvent resistance and the fully biodegradability. PCL has been shown to be degraded by the action of aerobic and anaerobic microorganisms that are widely distributed in various ecosystems. The degradation of high molecular weight PCL can be done in 12 days using *Penicillium* [2].

PCL has a low melting point (60°C) and a glass transition temperature of -60°C. Its relative high cost prohibits a direct use of this polymer and suggests the possibility of using it in the blend with less expensive natural materials (e.g. starch and proteins) in order to produce a bioplastics [3, 4]. The structure of PCL is shown in figure 1.

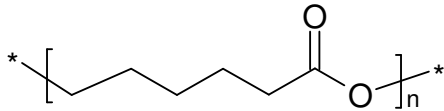


Figure 1 Structure of polycaprolactone.

4.2 Starch

Starch is one of the renewable biomass sources used in bioplastics. Starch is a major plant storage form of glucose. It consists of two components: amylose and amylopectin, the molecular structure can be found in figure 2. In amylose the glucose units are 1,4- α -D-linked together in straight chains, where in amylopectin the glucose units are 1,6- α -D-linked in a branched form. The advantages of starch are that it is relative cheap and available year round. A disadvantage is that it does not have good physical properties and therefore starch is mostly used as filler in bioplastics. There are in generally 3 ways of using starch in bioplastics. In the first way a low amount (10-20%) of starch is mixed with a traditional oil based polymer, this enhances the biodegradability and reduces the cost of the polymer. The second mode of starch application is the preparation of starch composites with a starch content more than the half by mass. This material is called a plastified starch and can exhibit mechanical properties similar to conventional plastics. In the third mode the bioplastic has a high amount (~90%) of starch, and is referred as thermoplastic starch. These plastics can vary from stable to unstable but are fully biodegradable [5]. In this research only low amounts of starch will be used in the composites.

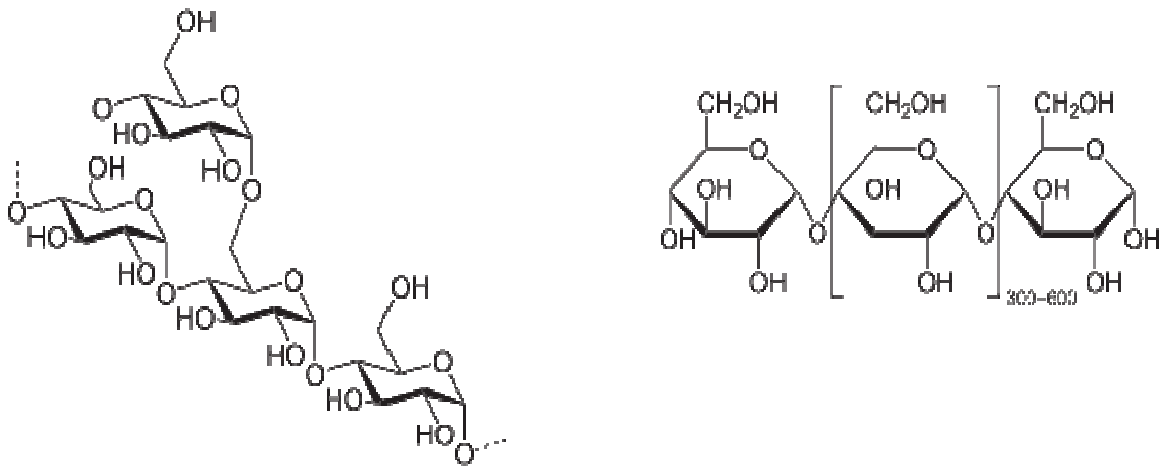


Figure 2 Structure of amylopectin (left) and amylose (right).



4.3 Compatibilizer

Blending two polymers is often performed in the melt with mechanical stirring. When two polymers are miscible, a homogeneous blend will be formed. However, from thermodynamic view-point, miscibility is rarely achieved owing to high degree of polymerization, which results to a small entropy change [6]. When immiscible polymers are mixed, phase separation will occur. One polymer will be in the dispersed phase and the other in the matrix. This phase separation often leads to a reduction in the mechanical properties [7]. Starch and PCL are also two polymers that are not miscible. When these polymers are mixed, phase separation is observed and the mechanical properties are reduced compared to pure PCL [8]. To reduce the tendency for phase separation, a compatibilizer (interfacial agent) can be added to improve the interfacial association between the two phases. The basic roles of a compatibilizer are the reduction of interfacial tension, the enhancement of interfacial adhesion, finer dispersion, and the improvement of morphological stability [7]. In this research the used starch contained a low amount of water so probably the starch will not melt at the used temperature. After processing, the starch is just dispersed as a solid. In this case the role of the compatibilizer is most probably the enhancement of interfacial adhesion between PCL and starch.

A compatibilizer is a block or graft copolymer where each block or graft has a chemical structure that is (almost) similar to the polymers to be mixed. This compatibilizer can be premade or generated in situ through covalent or ionic bonding during the reactive blending process [7]. The ideal compatibilizer would be a block-copolymer of PCL and starch which unfortunately is hard to achieve. The difficulty in the graft polymerization of PCL to starch is the existence of water in starch, because all catalysts for CL copolymerization are sensitive for moisture [9]. An alternative and easier way to synthesize this compatibilizer is the use of functionalized PCL. In a reactive blending process the functionalized PCL can react with the starch. This in situ generation is very effective because the compatibilizers are formed at the site where they are required [7]. The functionalized PCL (the compatibilizer precursor) can be synthesized by reacting a difunctional monomer with the PCL in a radical polymerization reaction. Monomers that are used in literature are maleic anhydride (MAH) [10, 11], glycidyl methacrylate (GMA) [12, 8], and diethyl maleate (DEM) [8]. The molecular structure of these monomers can be found in figure 3. Major difference between these monomers is their ability for homopolymerization. Mani et al. [13] showed that MAH, which has almost the same structure as DEM, will react as a single moiety to the PCL backbone whereas longer grafts are possible for GMA. This will result in a higher functionalization degree (FD) for GMA grafted PCL, compared to DEM and MAH. Sugih et al. [8] showed already that this is true for GMA compared to DEM. The reaction scheme of the compatibilizer precursor and the starch is shown in figure 4. The functional group of the functionalized PCL, in this case the epoxy group of the GMA, will react with the hydroxyl group of the starch, resulting in the formation of the ether linkage [14]. The real compatibilizer, PCL-g-starch is formed after the compatibilizer precursor has reacted with the starch.

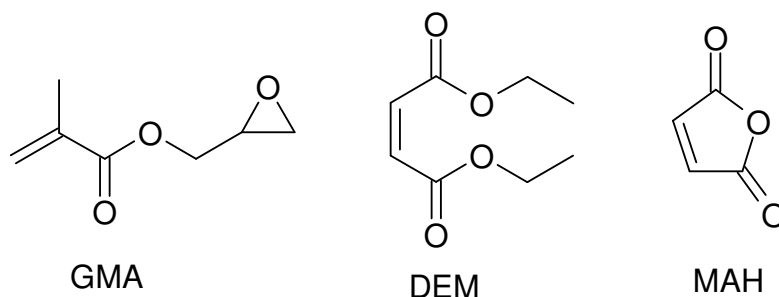


Figure 3 Used monomers in this research.

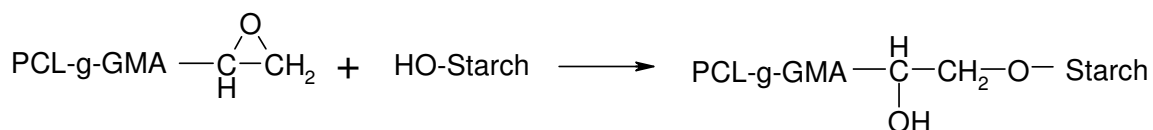


Figure 4 Reaction scheme of the compatibilizer precursor and starch.

4.4 Radical polymerization

A radical grafting reaction is used to graft the difunctional monomer to the PCL backbone. The first step in this reaction is the decomposition of an initiator. Initiator is a molecule that decomposes under heat or light and produces free radicals. In our reaction we need an initiator that decomposes when heated, this occurs often with organic peroxides and azo compounds. The most important characteristic of a polymerization initiator is its rate of decomposition expressed by its half-life ($t_{1/2}$). The half life is the time required to reduce the original initiator content at a given temperature by 50%. The half-life can be calculated from the Arrhenius equation:

$$k_d = A \cdot e^{-E_a/RT} \quad \text{and} \quad t_{1/2} = \frac{\ln(2)}{k_d}$$

Where k_d = rate constant for the initiator dissociation in s^{-1}

A = Arrhenius frequency factor in s^{-1}

E_a = Activation energy for the initiator dissociation in J/mole

R = Gas constant, 8,3142 J/mole·K

T = Temperature in K

$t_{1/2}$ = Half-life in s

For the reaction time we take four times the half-life of the initiator, which results in 10 % residual initiator. The remaining amount initiator is in this way significantly reduced that it minimizes complications during the working-up step. In our case, we are searching for an initiator that decomposes at low temperature (below 100°C) in a reasonable reaction time (below 1 hour). Low temperature condition is chosen to prevent degradation of the polycaprolactone. In appendix 1 an overview is given of the half-life of some initiators at different temperatures. Calculation of the reaction time of an initiator is also shown in this appendix. From the appendix can be concluded that several initiators meet the requirements. After looking to the costs of these initiators, azobisisobutyronitrile (AIBN) turned out to be the best initiator for

this polymerization reaction. The molecular structure and decomposition mechanism of AIBN is shown in figure 5. When AIBN is heated it decomposes in two 2-cyanoprop-2-yl radicals and a molecule of nitrogen gas. The calculation in appendix 1 shows that the half-life at 100°C is ~7 minutes, which results in a reaction time of 28 minutes (4*7). In this research, we use a temperature of 97 °C, to make a better comparison with a previous research, which results in a reaction time of 40 minutes (4*10).

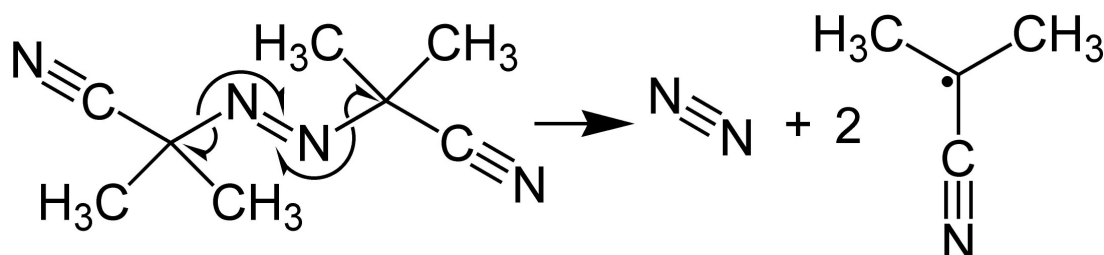


Figure 5 Radical formation of AIBN.

The second step in a radical grafting polymerization is the propagation step. In this step the radical can add to the monomer by opening the π - bond to form a new radical, in this way a polymer from the monomer is formed. The second option is that the radical abstracts a hydrogen atom from the polycaprolactone, which leads to a polycaprolactone macroradical, which can react with the monomers. The latter is the desired one. The last step is the termination step. In this step the reaction is terminated, mostly due a combination or disproportionation reaction [15, 16].

4.5 Supercritical carbon dioxide as solvent

Many chemical reactions occur in organic solvents, such as chloroform, THF and benzene. Those solvents are environmental unfriendly. Supercritical carbon dioxide (sCO₂) in other hand can be used as environmentally benign solvent in chemical reactions. A supercritical fluid is a substance at a temperature and pressure above its critical point. At this point, it can effuse through solids like a gas and dissolve materials like a liquid, which makes it very suitable as a substitute for organic solvents. From the phase diagram of carbon dioxide, figure 6, can be observed that the critical temperature and pressure is relative low, 304 K (31°C) and 7,38 MPa respectively. Water for example has a critical temperature of 647K (374°C) and a critical pressure of 22,06 MPa. The latter makes supercritical carbon dioxide suitable in the chemical industry.

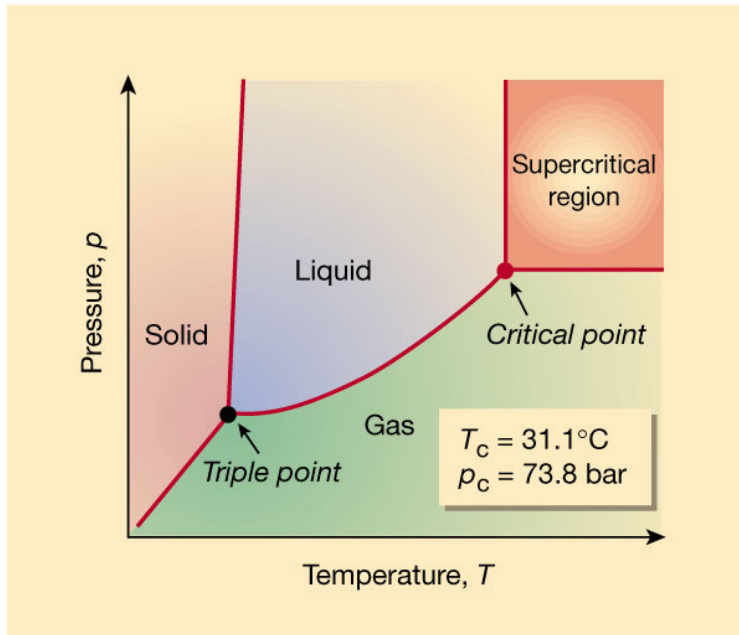


Figure 6 Phase diagram of CO₂ [17].

Supercritical carbon dioxide can also be used in the functionalization of polymers. sCO₂ is a poor solvent for many polymers, but it can be used as carrier of active chemical species as well as a swelling agent for the polymer [22-24]. In this way the sCO₂ facilitates the diffusion of the monomers and initiators within the polymer matrix. The swelling process is completely reversible. When the pressure is released, the polymer goes back to their original state. Another advantage of using sCO₂ for grafting reactions on polymers is the total control of the grafting degree by changing the temperature and pressure of the system. Because all these advantages of sCO₂ a lot of research is done on grafting different monomers on polymers. In all these cases the presence of sCO₂ does not modify the radical grafting mechanism but facilitates the diffusion of the reactive species in the polymer matrix [16-25]. Milder reaction condition can also be used in comparison with normal melt processing. This leads to less polymer degradation and bulk strength deterioration. In addition, a modification in the thermal properties can be observed, not only attributed to the grafting reaction but also to the plasticizing effect of sCO₂. The most important effect is the reduction of the glass transition temperature (T_g). This has a positive impact on many polymer-processing operations, this include the viscosity reduction for polymer extrusion or blending.



5. State of the art

A lot of research is already done in the field of bioplastics and especially in bioplastics with starch and PCL. Already at the beginning, researchers came to the conclusion that phase separation occurred when mixing these two polymers [26,27]. To overcome this problem a lot of research is done in finding a good compatibilizer [28-33]. Some research groups [8, 10-14, 28-30, 34, 35] have developed compatibilizers by functionalize PCL with a functional group. Others tried to graft PCL to starch by in situ ring-opening polymerization of ϵ -caprolactone in the presence of starch particles and using a catalyst [31-33]. The latter is more complex than the functionalization of PCL. The functionalization of PCL is done with different monomers. The used monomers are GMA [8, 12, 14, 29, 34, 35], MAH [10, 11, 13, 29, 30], Pyromellitic anhydride [28], DEM [8, 34] and acrylic acid (AA) [30]. From these researches can be concluded that functionalization with GMA results in the highest grafting percentage. In addition, also a higher molecular weight PCL is preferred to synthesize the compatibilizers. From the researches that used PCL-g-GMA as compatibilizer can be concluded that this compatibilizer increases the compatibility of the PCL/starch blend.

5.1 University of Groningen

The University of Groningen is already doing research in the field of bioplastics for years. A lot of research is done on starch and PCL separately. In addition, blends between PCL and starch are already investigated but still lot things have to be done. In this paragraph, an overview is given about researches on functionalization of PCL done at the University of Groningen. In Figure 7 a schematic representation of the research is given.

J.P. Drijfhout [34] used a 3000 Mw PCL to make compatibilizers with GMA and DEM in a brabender. He concluded that GMA compatibilizers have higher grafting percentages compared to DEM compatibilizers. The reason for this is that DEM is less reactive with itself, after addition of a DEM monomer the reaction is terminated. After addition of a GMA monomer, homopolymerization will occur. The main conclusions for GMA compatibilizers are increasing amounts of monomer results in more grafting. The influence of initiator increases when the amount of initiator increases. The thermal properties enhanced when the amount or length of grafted groups increases. For DEM compatibilizers can be concluded that: The grafting of DEM on PCL is much lower compared to GMA, because of the reasons mentioned before. The functionalization of PCL with DEM monomers does not influence significantly the thermal properties.

In the second part of the research, J.P. Drijfhout used the compatibilizers to make blends with starch in a brabender. When DEM compatibilizer is added to blends of PCL and starch, no change in properties is observed. The same applies, in general, for the blends with GMA compatibilizer. Small changes are observed, the properties enhances. The increase in mechanical properties of the GMA compatibilizer containing blends is the result of increased compatibility, which is because an alcohol group of starch can form a covalent bond with an epoxide of GMA.



The mechanical properties of blends do not enhance significantly, because the blends still contain starch particles and, therefore, the blends are not homogeneous. Addition of compatibilizer to blends of PCL and starch really improve the morphology, this is concluded from the fact that the interface becomes smoother. Therefore, only at the interface the compatibility between the PCL and the starch particle improves. To enhance the properties significantly, first a homogeneous blend of PCL and starch should be prepared. To prepare a homogeneous blend the starch can be gelatinized with glycerol before blending with PCL.

In the third part of the research of J.P. Drijfhout, he used supercritical carbon dioxide to mix PCL and gluten. The main conclusions are enhanced properties of the blends prepared with sCO₂ compared to blends prepared in the melt.

Another way of improving the effect of the compatibilizer is to increase the Mw of the used PCL. However, a higher Mw could not be used since the grafting reaction (carried out in the melt) would be then affected by degradation of PCL. S.G.J. Neijenhuis [35] solved this problem by using sCO₂ to graft 50.000 Mw PCL with GMA. He has made two compatibilizers, with 16 wt% and 25 wt% GMA, and found a FD of 2,3 and 3,2 respectively. In the second part of his research, he blended the compatibilizer with PCL and gluten and concluded that the thermal properties did not change when adding the compatibilizer. The tensile test showed that only the modulus decreases when adding the compatibilizer.

R.P. Roepers [20] continued the work of Neijenhuis and concluded that the functionalization degree of PCL-g-GMA is dependent on the initiator and monomer intake. He could not make a statistical model because the lack of precise data.

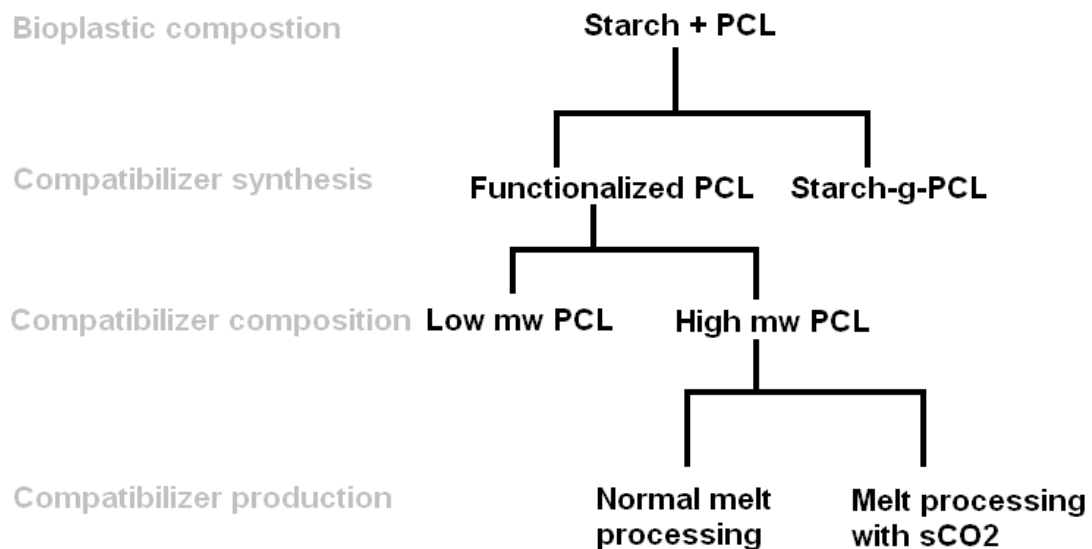


Figure 7 Overview of the different steps in the research of starch-pcl bioplastics



6. Goals

The general goal of this research is to develop compatibilizer precursors from high molecular weight PCL using supercritical carbon dioxide. The compatibilizer precursors can be used to develop bioplastics from PCL and starch with mechanical properties comparable to those from pure PCL. Literature showed that a compatibilizer is needed to mix those polymers. This compatibilizer will be synthesized by functionalization of PCL. From the literature can be concluded that a high molecular weight PCL is preferable. In this research supercritical carbon dioxide will be used in the reaction between PCL and functional monomers. A lot of research is already done in the field of such compatibilizers but the use of $s\text{CO}_2$ in the functionalization reaction of PCL is a novelty in this research. This use of $s\text{CO}_2$ is already proven by Neijenhuis [35] and Roepers [20]. In this research the advantages of using $s\text{CO}_2$ as an environmental benign solvent and swelling agent for carrying out the grafting process will be investigated. This research is divided in two parts. In the first part of this research the compatibilizer precursor is studied. In this part a mathematic model to predict the functionalization degree will be developed. In the second part, the compatibilizer is tested on performance in blends with PCL and starch. The effect of composition on the mechanical properties will be investigated. At the end of the research a comparison will be made between the compatibilizer made with supercritical carbon dioxide and one with normal melt processing.

Part 1. The study of the compatibilizer precursor.

- Effect of monomer and initiator intake on the functionalization degree (FD).
- Effect of different monomers, e.g. GMA, DEM, and MAH.
- Effect of co monomers, e.g. styrene
- Mathematical modeling to predict the FD.
- Degradation during compatibilizer precursor synthesis.

Part 2. The study of PCL and starch blends

- Effect of starch content on the mechanical properties.
- Effect of compatibilizer content on the mechanical properties.
- Effect of the functionalization degree of the compatibilizer precursor.
- Amount of compatibilizer precursor reacting with the starch.
- Comparison of compatibilizer precursor made in $s\text{CO}_2$ with the one that is made in the melt.



7. Experimental

7.1 Materials

Polycaprolactone (PCL, CAPA 6503, M_w of 50.000 g/mol and M_p of 58-60°C) from Solvay caprolactones, UK was used for the compatibilizers without further purification or drying. Monomers grafted to the PCL were glycidyl methacrylate (GMA, purity of 97%, $C_7H_{10}O_3$, M_w of 142,15 g/mol, bp of 169°C, density of 1,042 g/ml at 25°C, Sigma Aldrich), diethyl maleate (DEM, purity of >97%, $C_8H_{12}O_4$, M_w of 172,18 g/mol, bp of 225°C, density of 1,064 g/ml, Fluka), and maleic anhydride (MAH, purity of >99.0%, $C_4H_2O_3$, M_w of 98,06 g/mol, bp of 200°C, mp of 52-54°C, Fluka). Styrene was used as comonomer (ST, purity of >99%, C_8H_8 , M_w of 104,15 g/mol, bp of 145-146°C and a density of 0,909 g/ml at 25°C) was obtained from Sigma Aldrich as well. They were used without further purification. To initiate the reaction the following initiator was used: azobisisobutyronitrile (AIBN, purity of 98%, $C_8H_{12}N_4$, M_w of 164,21 g/mol, bp of 99-102°C and a density of 1,11 g/ml), obtained from Acros Organics. Besides this feedstock, other chemicals were also used to make the compatibilizer, such as carbon dioxide (Linde Schiedam, CO_2) and nitrogen (Linde Schiedam, N_2).

Following chemicals were used to perform extraction of the grafted PCL from the obtained samples: tetrahydrofuran (THF, purity of >99%, stabilized with BHT, C_4H_8O , M_w of 72,11 g/mol, bp of 66°C and a density of 0,88 g/ml) obtained from Acros Organics.

Methanol (purity of 99,8%, CH_3OH , M_w of 32,04 g/mol, bp of 64,5°C and a density of 0,791 g/ml) obtained from Lab-scan Analytical Sciences, Dublin, Ireland. Xylene (purity of >99%, C_8H_{10} , M_w of 106,17 g/mol, bp of 137-143°C and a density of 0,86 g/ml) obtained from Merck. Chloroform (purity of 99,5%, $CHCl_3$, M_w of 119,38 g/mol, bp of 61,2°C and a density of 1,492 g/ml) obtained from Lab-scan Analytical Sciences, Dublin, Ireland.

To make the blends, potato starch (with ~ 75% amylopectin and ~25% amylose) from Avebe was used. The starch was dried for at least 24 hr at 50°C under vacuum prior to use.

Table 1 summarizes the used chemicals in this research.

Table 1 Chemicals used in this research

Materials	Function	Materials	Function
Polycaprolactone	Polymer	N_2	Inert gas
Diethyl maleate	Monomer	THF	Solvent
Glycidyl methacrylate	Monomer	Methanol	Solvent
Maleic anhydride	Monomer	Xylene	Solvent
Styrene	Co-monomer	Chloroform	Solvent
AIBN	Initiator	Potato starch	Polymer
CO_2	Reaction medium		

7.2 Apparatus and procedures

7.2.1 Compatibilizer synthesis

The compatibilizers were prepared in a Parr instruments reactor (chamber volume 100 cm³) with heating mantle and turbine impeller (Figure 8). A compressor (LEWA) was used to bring the reactor to the desired pressure, a scheme of the experimental set-up is shown in Figure 9. PCL, initiator, monomer and comonomer were weighted and placed in the reactor. Intakes for each experiment are given in table 2, 3 and 4. In these tables the intakes are given in mol-% with respect to the caprolactone repeating units in PCL. The reactor was closed and flushed with nitrogen (10-30 bar) for 10 minutes to remove oxygen. After that, the nitrogen was released and the CO₂ valve was opened to pressurize the reactor to approximately 50 bars. The heating mantle was set to the desired temperature and when this temperature was reached the reactor was pressurized to the desired pressure. A stirrer (with 900rpm) was used to achieve better mixing. The reaction started when the desired temperature and pressure were reached. After certain time of reaction, the stirrer and the heating mantle were turned off and the valve was opened to depressurize the reactor. The reactor was opened to collect the samples [20].



Figure 8 Reactor

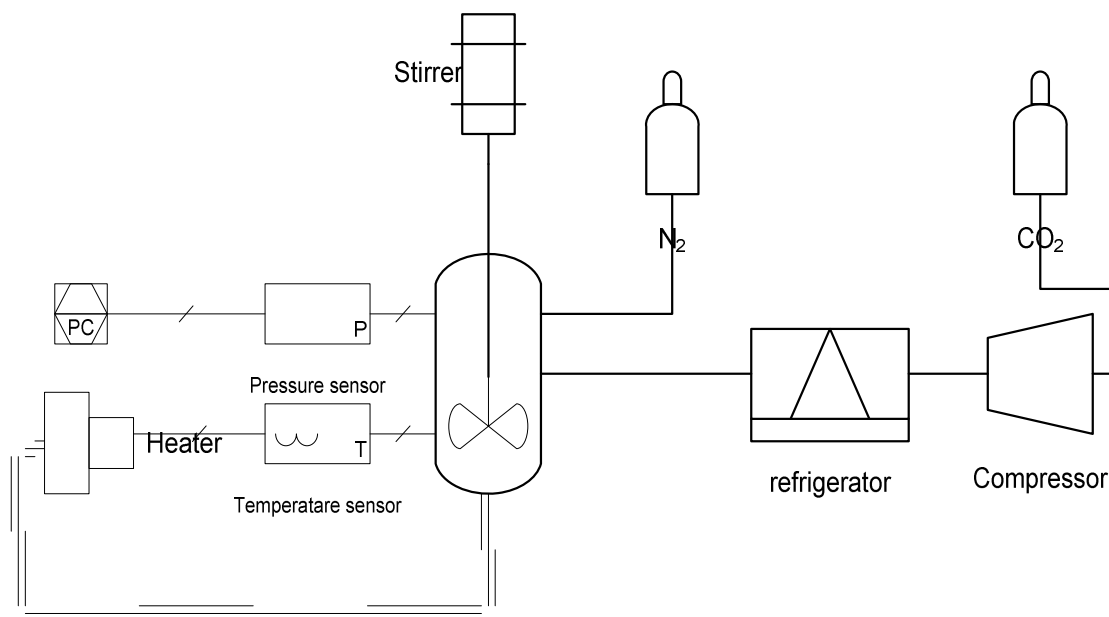


Figure 9 Scheme of the experimental set-up



Table 2 Overview of the experiments for the PCL-g-DEM compatibilizers

Sample	DEM (%-mol) ^a	AIBN(%-mol) ^a	T (°C)	P (bar)	t _{reaction} (min)
PCL-g-DEM 1	15	0,3	97	90	40
PCL-g-DEM 2	15	1,1	97	90	40
PCL-g-DEM 3	60	0,3	97	90	40
PCL-g-DEM 4	60	1,1	97	90	40
PCL-g-DEM 5 ^b	60	1,1	97	90	40
PCL-g-DEM 6	60	1,1	97	90	80
PCL-g-DEM 7	60	1,5	97	90	40
PCL-g-DEM 8	45	0,6	97	90	40
PCL-g-DEM 9 ^c	60	1,1	97	90	90
PCL-g-DEM 10 ^d	60	1.1	97	90	40

^a Mol % with respect to the CL repeating units in PCL.

^b Soaking time of 4 hr.

^c Benzoyl peroxide instead of AIBN.

^d PCL with a M_w of 3000 used instead of 50.000

Table 3 Overview of the experiments for the PCL-g-MAH compatibilizers

Sample	MAH (%-mol) ^a	AIBN(%-mol) ^a	T (°C)	P (bar)	T _{reaction} (min)
PCL-g-MAH 1	15	0,3	97	90	40
PCL-g-MAH 2	15	1,1	97	90	40
PCL-g-MAH 3	60	1,1	97	90	40

^a Mol % with respect to the CL repeating units in PCL.

Table 4 Overview of the experiments for the PCL-g-GMA compatibilizers

Sample	GMA (%-mol) ^a	AIBN (%-mol) ^a	ST (mol ratio) ^b	Temp (C)	Pressure (bar)	t _{reaction} (min)
PCL-g-GMA 1	5	0,6		97	90	40
PCL-g-GMA 2	5	1,2		97	90	40
PCL-g-GMA 3	5	1,8		97	90	40
PCL-g-GMA 4	10	0,6		97	90	40
PCL-g-GMA 5	10	1,2		97	90	40
PCL-g-GMA 6	10	1,8		97	90	40
PCL-g-GMA 7	15	0,6		97	90	40
PCL-g-GMA 8	15	1,2		97	90	40
PCL-g-GMA 9	15	1,8		97	90	40
PCL-g-GMA 10	5	2,4		97	90	40
PCL-g-GMA 11	10	2,4		97	90	40
PCL-g-GMA 12	15	2,4		97	90	40
PCL-g-GMA 13	5	3		97	90	40
PCL-g-GMA 14	10	3		97	90	40
PCL-g-GMA 15	15	3		97	90	40
PCL-g-GMA 16	8	1,2		97	90	40
PCL-g-GMA 17	10	1,2	0,5	97	90	40
PCL-g-GMA 18	10	1,2	1	97	90	40

^a Mol % with respect to the CL repeating unit in PCL.

^b Mol ratio with respect to the GMA intake

7.2.2 Work up of PCL-g-GMA products

To extract grafted PCL from the obtained sample, the sample (~10 g) was dissolved in 100 ml THF, stirred for 1,5 h and then filtered. Methanol (400 mL) was added to the filtrate to precipitate the grafted PCL. The reaction was stabilized by storing it overnight in a fridge. The solvent was decanted and the solid product was dried in a vacuum oven (40°C, 3 hr) [8].

7.2.3 Work up of PCL-g-DEM and PCL-g-MAH products

The sample (5 g) was dissolved in xylene (50ml) and refluxed at 160°C for 2 hr. The resulting suspension was filtered and precipitated with methanol (200 mL). The reaction was stabilized by storing the mixture overnight in a fridge. The solvent was decanted and the solid product was dried in a vacuum oven (40°C, 3 hr) [8].

7.2.4 Preparation of PCL–starch blends with the compatibilizers

The PCL-starch blends were prepared in a Brabender Plasticorder PL2000 batch-kneader (chamber volume 35 cm³). The intake of reagents was set around 2/3 of the chamber volume to ensure proper mixing. The operation temperature was 170°C and the rotation speed was 80 rpm. PCL, starch and compatibilizer were weighted and added to the chamber. The content was blended for 15 minutes then the product was collected. Intake for each sample can be found in table 5. In this table the intakes are given in mol-% with respect to the total moles of starch and PCL and in wt% with respect to the total mass of starch and PCL. The used compatibilizer in sample 1-6 is PCL-g-GMA 16, with a functionalization degree of 6%. In sample 9 and 10 the compatibilizers PCL-g-GMA 3, with a FD of 2 %, and PCL-g-GMA 9, with a FD of 12%, are used respectively. In samples 11-13 a compatibilizer made in the brabender, also with a FD of 6%, is used [8].

Table 5 Overview of experiments for the PCL-starch blends.

Sample	PCL-g-GMA (wt%) ^a	Starch (%-mol) ^b	PCL (%-mol) ^b	Starch (wt%) ^a	PCL (wt%) ^a
PCL/Starch 1	0	10	90	14	86
PCL/Starch 2	1	10	90	14	86
PCL/Starch 3	5	10	90	14	86
PCL/Starch 4	10	10	90	14	86
PCL/Starch 5	5	20	80	26	74
PCL/Starch 6	5	30	70	38	62
PCL/Starch 7	0	20	80	26	74
PCL/Starch 8	0	30	70	38	62
PCL/Starch 9 ^c	5	20	80	26	74
PCL/Starch 10 ^d	5	20	80	26	74
PCL/Starch 11 ^e	5	10	90	14	86
PCL/Starch 12 ^e	5	20	80	26	74
PCL/Starch 13 ^e	5	30	70	38	62

^a Wt% with respect to the mass of starch + PCL

^b Mol% with respect to the total moles of starch + PCL

^c PCL-g-GMA 3 used with a FD of 2%

^d PCL-g-GMA 9 used with a FD of 12%

^e PCL-g-GMA made in the melt used with a FD of 6%



7.2.5 Chloroform extraction of the PCL-starch blends.

To show that the compatibilizer used in the PCL-starch blends is reacted with the starch, an extraction with chloroform is performed. PCL-starch blend with compatibilizer (3 grams) is dissolved in 300 grams of chloroform by stirring it for 48 hours. From simple experiments with PCL and chloroform, starch and chloroform and compatibilizer and chloroform can be concluded that PCL and compatibilizer will dissolve in chloroform and the starch will not. After the 48 hours the starch is collected from the blend by filtering the solution. PCL is collected by using a rotary evaporator to evaporate the chloroform. PCL and starch are dried in a vacuum oven and weighted to make a mass balance. With this mass balance the amount of compatibilizer that is reacted with the starch could be calculated. The samples are also characterized with infrared spectroscopy and $^1\text{H-NMR}$.

7.3 Analysis

In this research, several analytical methods have been used. $^1\text{H-NMR}$ is used to determine the amount of grafted groups and GPC is used to determine the degradation of the compatibilizers. Tensile tests are used to determine the mechanical properties of the blends and infrared spectroscopy is used to determine the amount of compatibilizer reacted with the starch.

7.3.1 $^1\text{H-NMR}$

To calculate the functionalization degree (FD) of the compatibilizers, $^1\text{H-NMR}$ measurements were performed using a 400 MHz NMR apparatus with CDCl_3 as solvent. The FD could be calculated from the ratio between peak area of a monomer proton and peak area of a proton from the PCL backbone.

$$FD = \frac{A_{\text{monomer}}}{A_{\text{polymer}}} \cdot 100\%$$

To calculate the FD for PCL-g-GMA the area of proton at 3,2 ppm (GMA proton) is divided by the two characteristic protons resonance of the PCL backbone at 4,0 ppm. For PCL-g-DEM the characteristic proton of the DEM is at 4,2 ppm (four protons). A 5% relative error was assumed on the peak area of the NMR spectrum, leading in a 10% relative error in the FD values. Typical spectrums of PCL-g-GMA and PCL-g-DEM including the FD calculation can be found in appendix 2.

To make a $^1\text{H-NMR}$ spectrum of a starch sample, the sample is first stirred for two hours in DMSO at a temperature of 60°C. This is done because it is hard to dissolve the starch. A typical spectrum of starch can be found in appendix 2.

7.3.2 GPC

Gel permeation chromatography was used to measure the molecular size and the polydispersity (PDI) of the PCL and the grafted products. The samples were dissolved in THF (10mg/ml). The eluent, THF, was used with a flow rate of 1,0 ml/min. The average molecular weight was calculated using a calibration curve from two known PCL samples. A 10% relative error was assumed in the M_n and M_w values. The PDI can be calculated with:



$$PDI = \frac{M_w}{M_n}$$

7.3.3 Tensile tests

Tensile tests were performed to determine the strength of the blends. A Fontijne Holland (Model TH400) press is used to prepare the T-bones. This press consists of two plates that could be adjusted on different temperatures. The maximum temperature and pressure, which can be applied, is 300°C and 400 kN respectively.

T-bones were obtained from a 2 mm thick mould. The mould consisted of eight holes, so eight T-bones for each sample were prepared. First the plates were heated to 150°C. Every hole of the mould was filled with 1 gram of sample. The mould was placed between two aluminium sheets and four metal plates. The whole package was placed between the plates of the press. Before the maximum force of 150 kN was applied, first 10 times an increasing force was applied to melt the material and make sure that all air is removed. Finally, a force of 150 kN is applied and maintained for three minutes. After three minutes the temperature of the plates is set to room temperature and a water flow of 30% is used to cool the plates to 30°C, during cooling the pressure is maintained but will decrease some because of the temperature decrease. After cooling, the mould is removed from the press and the T-bones are collected.

Tensile properties of the T-bones are measured with an Instron 4301 (HO135) material testing machine with a 5 kN static load cell. Dimensions of the T-bones are measured before placing them inside the machine. The used crosshead speed was 50 mm/min. After inserting the T-bone and typing-in the dimensions, the software calculated the stress, strain and modulus of tested sample. For every sample the best 6 T-bones are tested. Data from these tensile tests are filtered in order to get a higher reliability of the data. For every sample two values, that were too high or low compared to the average, were removed. If however less than 6 t-bones are tested for one sample, then at least 4 values are kept to calculate the average and standard deviation. A typical stress-strain curve of a blend from PCL and starch, including an explanation of this curve, can be found in appendix 3.

7.3.4 Infrared spectroscopy

Infrared spectroscopy is used to check if the compatibilizer is reacted with the starch. The infrared spectrum is recorded on a Spectrum 2000 FT-IR spectrometer (Perkin Elmer), ATR mode, spectrum range of 500.0000-4000.0000. Typical infrared spectrums of PCL and starch can be found in appendix 4.



8. Results and Discussion

8.1 Functionalization degree of the compatibilizer precursors

8.1.1 PCL-g-DEM compatibilizers.

Nine samples were prepared with DEM as monomer. Monomer and initiator concentration, reaction-time and initiator were varied but analysis using $^1\text{H-NMR}$ showed no grafting. It was known from literature [36, 37] that MAH, which has a similar structure as DEM (see figure 3), has a double bond that has a lower reactivity than that of GMA. This is due to the two adjacent electron-attractive carbonyl groups of MAH and DEM. However Sugih et al. [8] showed that it is possible to react DEM with PCL. They used benzoylperoxide as initiator and 3000 M_w PCL and a brabender at 130°C to graft DEM. The major differences between their research and this research are the molecular weight of the PCL and the use of $s\text{CO}_2$. To investigate which one of the latter is responsible for the failed reactions an extra experiment is done (PCL-g-DEM 10). Instead of using the 50000 M_w PCL, the 3000 M_w is used. With the 3000 M_w PCL grafting occurred (3,2%), although this is less than Sugih obtained in the brabender a conclusion can be made that the molecular weight of our PCL is one of the reasons for the failed reactions. In addition can be concluded that $s\text{CO}_2$ can be used to graft DEM to low molecular weight PCL. From the fact that the obtained grafting percentage is lower than the one from Sugih et al. can be concluded that also other factors than de molecular weight have influence on the grafting percentage. Other factors that are different between this research and the one from Sugih et al. are the temperature, pressure, geometry of the reactor, initiator and the use of $s\text{CO}_2$. Al these factors can influence the functionalization degree.

8.1.2 PCL-g-MAH compatibilizers.

Three samples were prepared with MAH as monomer. As expected from previous experiments with DEM, no grafting occurred. The reason for this is already mentioned before: the double bond in this monomer is not reactive enough due to the two adjacent electron-attractive carbonyl groups in this monomer. This is already confirmed by John et al. [10]. They used a MAH intake of 8% to graft to high molecular weight PCL in a brabender. The maximal grafting degree after optimizing the composition, temperature and reaction time was 0,9%. From these results, little can be said about the influence of $s\text{CO}_2$ to the grafting procedure of MAH to high molecular weight PCL.

8.1.2 PCL-g-GMA compatibilizers.

Sixteen reactive compatibilizers were prepared with GMA as monomer. With $^1\text{H-NMR}$ the FD values were calculated and are graphically provided in figure 8. This figure shows the effect of the GMA intake on the FD. Five different AIBN intakes were explored. It is clear from Figure 10 that higher GMA intakes lead to higher FD values. This is independent of the AIBN intake. The explanation for this is that the GMA is able to propagate to longer grafted chains [12]. Therefore, an increase in GMA intake leads to longer GMA grafted chains and so to higher FD values. A representation of the proposed grafting reaction for GMA to PCL is given in Figure 11[12]. After the hydrogen abstraction from the PCL backbone, a PCL macroradical is formed. This macroradical has four opportunities: it can couple with another radical,

it can react in a recombination reaction with another PCL macroradical or with a GMA homopolymer or it can react with a GMA monomer. The latter is the desired reaction, this reaction is shown in Figure 12. The free radical attacks the double bond of the GMA monomer and a free radical on the tertiary carbon is formed. When the macroradical is reacted with the monomer still two things can happen. The reaction can be terminated with a radical or homopolymerization can occur with GMA monomers. Literature [8,13] says that when using GMA as monomer, this homopolymerization will occur. There is always a change that degradation occurs. The change of degradation increases with increasing the processing temperature.

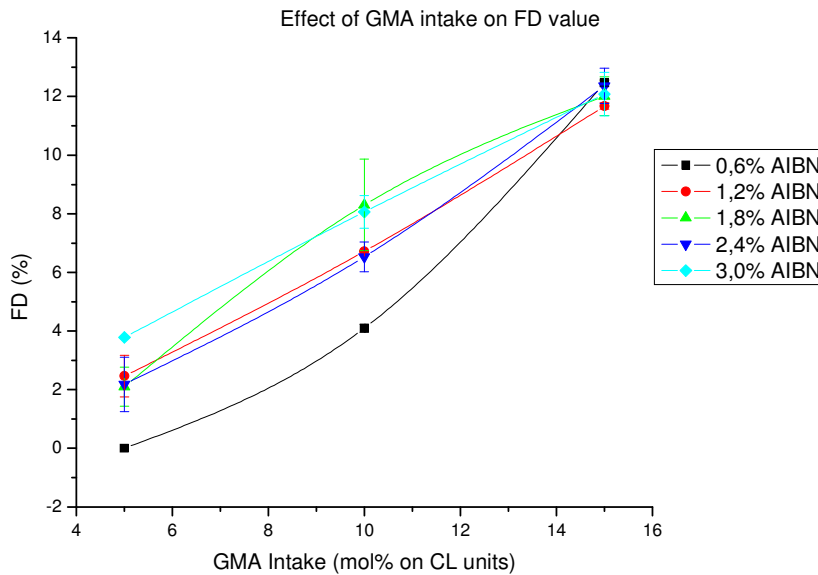


Figure 10 Effect of the GMA intake on the functionalization degree.

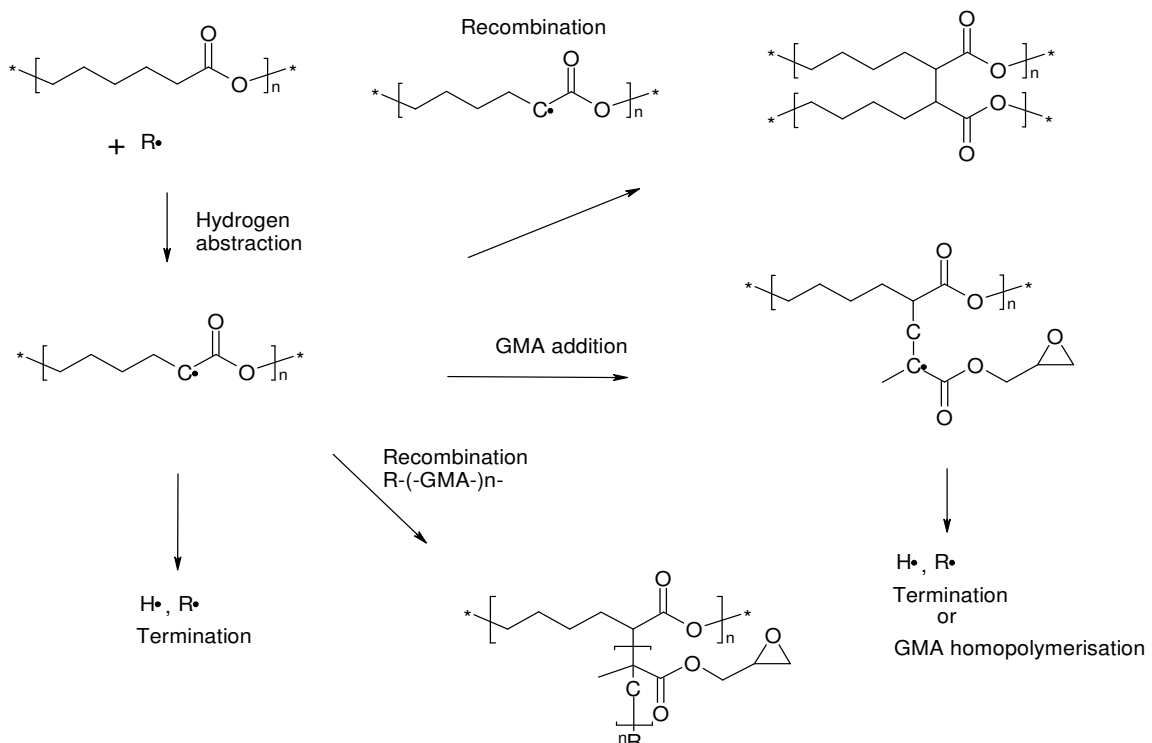


Figure 11 Proposed reaction pathways for the grafting of GMA to PCL.

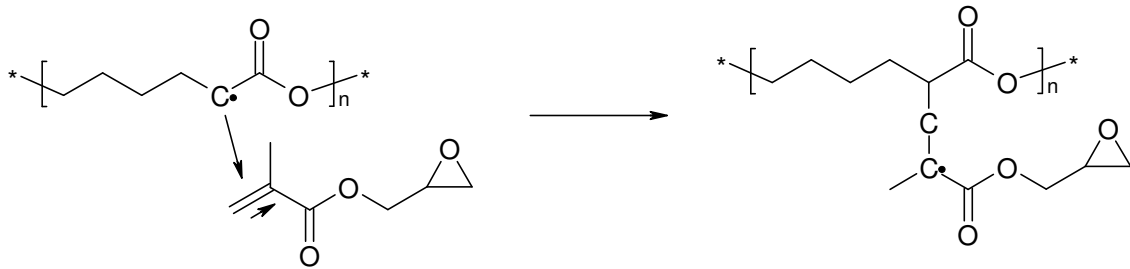


Figure 12 Reaction mechanism of GMA addition

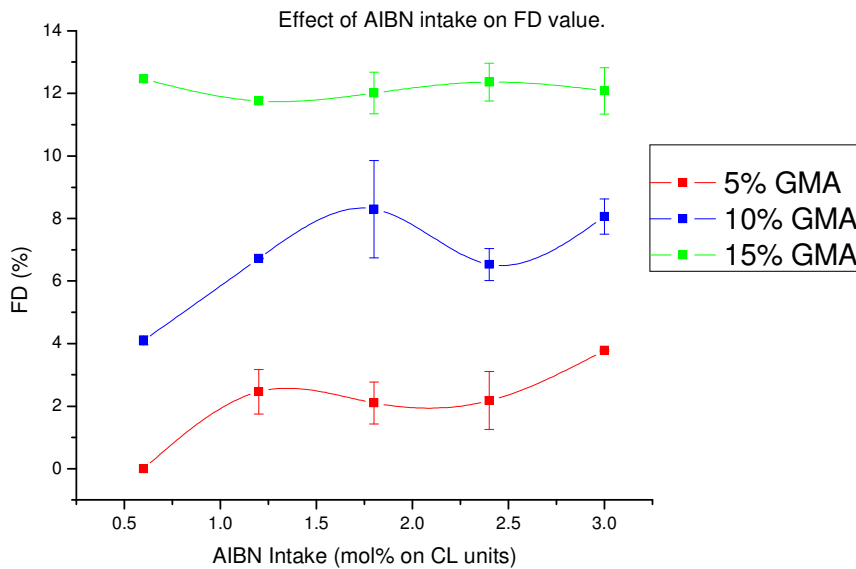


Figure 13 Effect of the AIBN intake on the functionalization degree.

Figure 13 shows the effect of the initiator intake on the FD. Three different monomer intakes were explored. With the low monomer intake (5 and 10%), it is clear that the FD degree increases with increasing initiator intake and eventually becomes almost constant. With the high monomer intake (15%), it is clear that the FD is constant and is independent of initiator intake. The explanation of the increase in FD when increasing the initiator intake is that more radicals will be formed when increasing the initiator concentration. These radicals can react with the PCL backbone, which gives PCL radicals, which can react with the monomers, leading to higher FD values. At relative more initiator intake, the FD becomes constant, this is because the possibility of side reactions will become significant. Especially the occurrence of ‘cage effects’ is the reason for the observed trend [38]. The cage is thought of as the nearest environment of the initiator molecule and the radical pair. It is assumed that it is precisely the exit of a radical from the cage that is responsible for initiation of the polymerization, whereas recombination of primary radicals, a process that competes with radical exit, deteriorates the efficiency of this stage of polymerization [39].

8.1.3 PCL-g-ST-GMA compatibilizers

Two samples were prepared with GMA as monomer and styrene (ST) as comonomer. The results were not as expected. Indeed, literature (also with $s\text{CO}_2$) [40-42] showed that styrene has a positive effect on the rate and yield of monomer grafting on polypropylene. In our case it is the opposite, adding styrene results in less grafting of GMA to PCL. Cartier et al. [40] described the mechanism of the reaction as follows: the styrene reacts with the PP macroradical, resulting in stable styryl macroradicals who can react with the GMA monomers. In our case no styrene is grafted to the PCL. To explain the latter, an extra experiment was done without GMA. In this experiment, we tried to graft styrene to PCL, but no grafting occurred. Only a little bit of polystyrene is observed. The remainder of the styrene monomers is disappeared. An explanation for the disappearance of styrene is that the unreacted styrene together with the CO_2 is vented from the reactor. Because the high vapor pressure and low boiling point, 700 Pa and 145°C respectively, the styrene evaporates easily at the used temperature. The reason that the styrene monomers do not react with the polymer could be that the reaction time is too low. In literature [41,42], they are using a reaction time of respectively 4 and 5 hours instead of our 40 minutes. The major difference between this research and those found in the articles is that they used PP instead of PCL. The exact reasons for the failed reaction must be investigated in a further research. Table 6 shows the FD of the PCL with GMA as function of the ST intake.

Table 6 Results of experiments with styrene as comonomer

Sample	GMA(%-mol) ^a	AIBN (%-mol) ^a	ST(molar ratio) ^b	FD
PCL-g-GMA 5	10	1,2	0	6,72
PCL-g-GMA 17	10	1,2	0,5	3,66
PCL-g-GMA 18	10	1,2	1	0

^a Mol % with respect to the CL repeating unit in PCL.

^b Molar ratio with the GMA intake.

8.2 Statistical model of the effect of GMA and AIBN intakes on the FD

Influence of the monomer and initiator intake on the FD values has been determined by using a multivariable regression procedure. As a result, a model is obtained for the prediction of the FD values. The model is validated with different validation methods. The first validation method was the calculation of the residuals and check if these are randomly distributed as function of the basic variables. The second validation method was the normal probabilities plot. The points should be distributed randomly along the line of this plot. The third validation method is to check if the model is significant, this is done by performing an analysis of variance (ANOVA) [43]. This procedure consists of calculating the sum of squares (SS) for the model and the error. When the relative degree of freedom (DF) is known, it is possible to calculate the mean square (MS) for the model and error. With the latter value, the F-value and the P-value can be determined for the model. The latter is a measure of the statistical significance of the model. The values for the ANOVA can be found in table 7. The very low P-value implies that the model is statistically significant. The fourth measure for how well the data fits is the calculation of the R^2 . This value tells us how good the model fits the



data. Because the R^2 value always increases as we add terms to the model, also the adjusted R^2 is calculated. The two values of R^2 must be close to each other to be sure that all important variables have been included in the model. The R^2 value for our model is 0,967 and 0,952 for the adjusted R^2 , so no important variables have been forgotten. The last validation method is the calculation of the $R^2_{\text{prediction}}$. This statistic gives some indication of the predictive capability of the regression model. The $R^2_{\text{prediction}}$ for our model is 0,896, this value is high so the overall predictive capability of the model is satisfactory.

The model provided in equation 1 gives the best description of the experimental data:

$$FD = -6,406 + 0,92[GMA] + 3,39[AIBN] + 0,015[GMA]^2 - 0,375[AIBN]^2 - 0,121[GMA][AIBN] \quad (1)$$

Where FD is the functionalization degree of PCL with GMA units and [GMA] and [AIBN] the intake of respectively GMA and AIBN in mol% with respect to the caprolactone repeating unit in PCL.

Figure 14 shows a 3D plot of this model. This 3D plot gives the functionalization degree as function of the intake of GMA and AIBN. From this plot can be concluded that the FD increases when increasing the GMA content. The amount of AIBN has almost no influence on the FD.

Table 7 ANOVA results

	SS	DF	MS	F	P-value
Model	234,202	5	46,84	52,631	2,3E-06
Error	8,01	9	0,89		
Total	242,212	14			

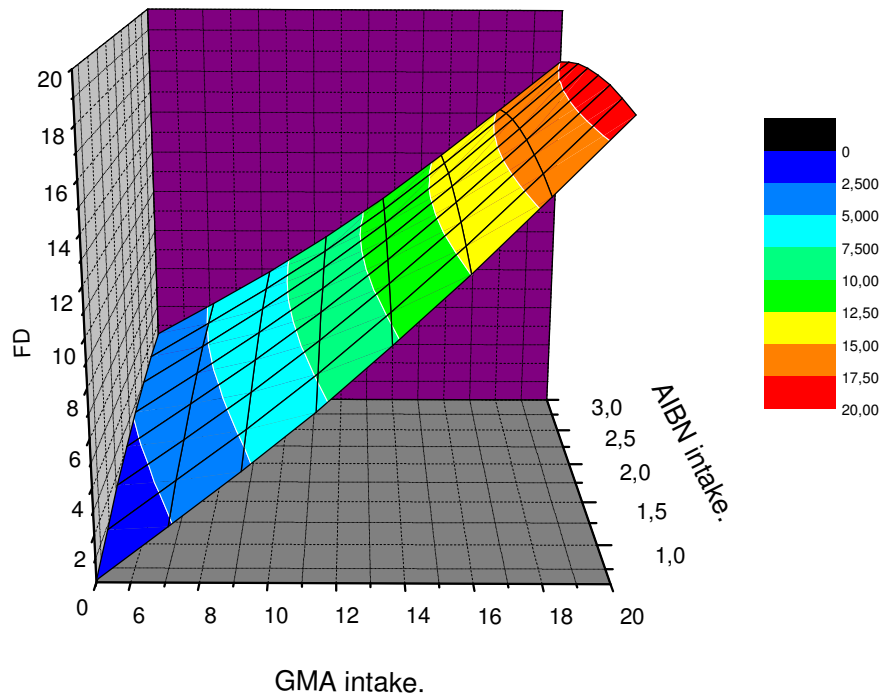


Figure 14 3D plot of the model.

8.3 Degradation

GPC analysis is performed to investigate the effect of the functionalization degree on the M_n and M_w values. An overview of the results from the GPC analysis is given in table 8. The M_w as function of the FD is plotted in Figure 15 and stays almost constant. A slight decrease of the M_n values is observed in Figure 16. From these two observations can be concluded that no chain extension has taken place. A constant M_w and a slight decrease of M_n suggest that a few low molecular weight molecules are formed. This is not observed by C-H. Kim et al. [12], they observed an increase of the molecular weight which can be related to chain extension. In our case no chain extension or degradation has occurred because the molecular weight stayed almost the same and the polydispersity was low. The reason for this difference can be related to the used temperature in the reaction, which was lower in our case. A higher temperature can cause byproducts to form, such as crosslinking products. A slight increase of the polydispersity index is observed in Figure 17, as function of the functionalization degree. This can be explained by the decreasing of the M_n while the M_w stayed constant. Furthermore can be concluded that a lot of degradation has occurred in sample 11. A reason for this is not found.

Table 8 GPC results.

Sample	GMA (%-mol)	AIBN (%-mol)	FD (%)	Mn (g/mol)	Mw (g/mol)	D (-)	Mz (g/mol)	Mp (g/mol)
PCL 50K	0	0	0	3,46E+04	4,27E+04	1,23	4,71E+04	5,02E+04
PCL- <i>g</i> -GMA 1	5	0,6	0	3,50E+04	4,27E+04	1,22	4,71E+04	5,05E+04
PCL- <i>g</i> -GMA 2	5	1,2	2,46	3,41E+04	4,24E+04	1,25	4,70E+04	4,99E+04
PCL- <i>g</i> -GMA 3	5	1,8	2,1	3,50E+04	4,25E+04	1,22	4,68E+04	4,96E+04
PCL- <i>g</i> -GMA 4	10	0,6	4,1	3,41E+04	4,23E+04	1,24	4,69E+04	4,98E+04
PCL- <i>g</i> -GMA 5	10	1,2	6,72	3,13E+04	4,12E+04	1,32	4,62E+04	4,96E+04
PCL- <i>g</i> -GMA 6	10	1,8	8,3	3,27E+04	4,22E+04	1,29	4,70E+04	5,00E+04
PCL- <i>g</i> -GMA 7	15	0,6	12,46	2,98E+04	4,14E+04	1,39	4,67E+04	5,02E+04
PCL- <i>g</i> -GMA 8	15	1,2	11,67	3,03E+04	4,11E+04	1,36	4,65E+04	4,96E+04
PCL- <i>g</i> -GMA 9	15	1,8	12,01	3,02E+04	4,13E+04	1,37	4,67E+04	4,99E+04
PCL- <i>g</i> -GMA 10	5	2,4	2,18	3,43E+04	4,25E+04	1,24	4,69E+04	5,01E+04
PCL- <i>g</i> -GMA 11	10	2,4	6,53	2,06E+04	2,54E+04	1,24	2,82E+04	3,01E+04
PCL- <i>g</i> -GMA 12	15	2,4	12,36	2,29E+04	3,98E+04	1,74	4,64E+04	5,01E+04
PCL- <i>g</i> -GMA 13	5	3	3,78	3,25E+04	4,22E+04	1,30	4,69E+04	5,01E+04
PCL- <i>g</i> -GMA 14	10	3	8,06	3,17E+04	4,15E+04	1,31	4,65E+04	4,96E+04
PCL- <i>g</i> -GMA 15	15	3	12,08	2,43E+04	4,01E+04	1,65	4,63E+04	5,01E+04
PCL- <i>g</i> -GMA 16	8	1,2	6	3,03E+04	4,14E+04	1,37	4,63E+04	4,90E+04

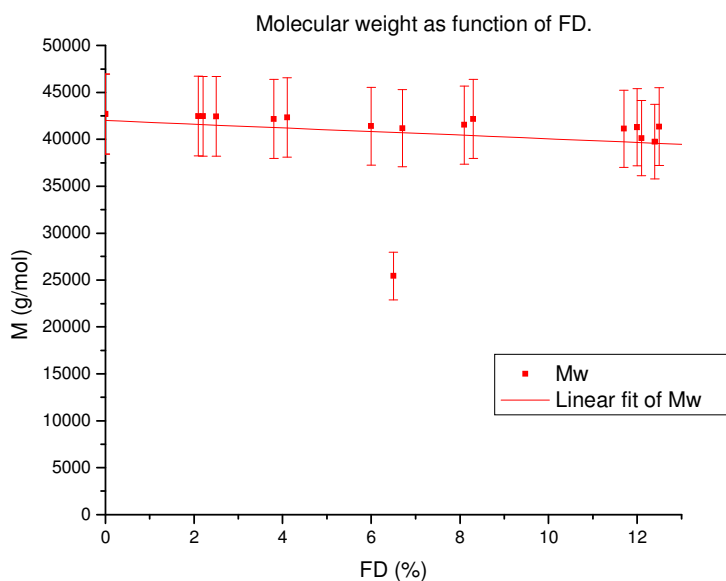


Figure 15 Mw as function of the functionalization degree.

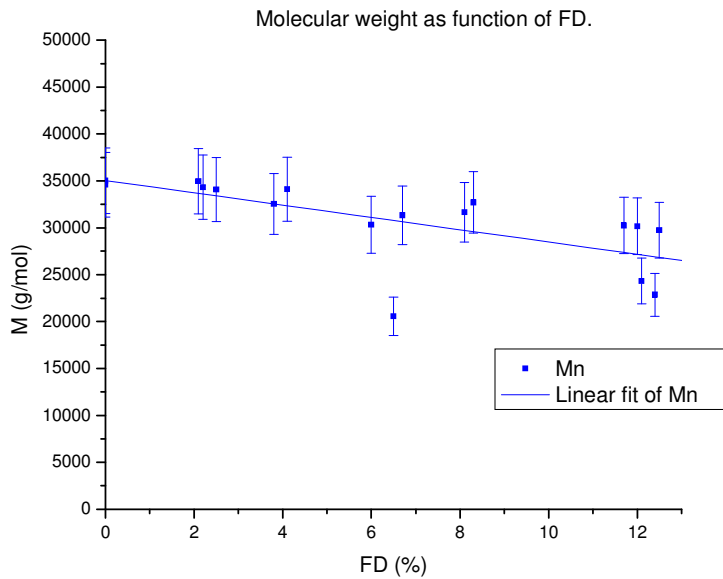


Figure 16 Mn as function of the functionalization degree.

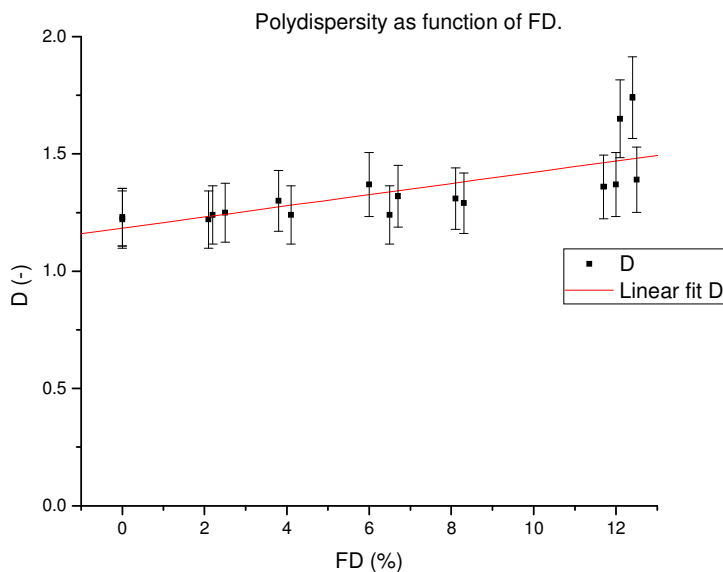


Figure 17 Polydispersity index as function of FD.

8.4 Mechanical properties of the PCL-starch blends.

Sample PCL-g-GMA 16 is evaluated as interfacial agent in PCL-starch blends. PCL-g-GMA 16 is chosen because it has an FD of 6% which is the average of all the samples. A total of eight blends were prepared, which consist of 3 binary blends not containing any compatibilizer (as reference) and 5 tertiary mixtures with compatibilizer. The latter consist of two series, one with a fixed PCL to starch ratio and one with a fixed compatibilizer intake at three different starch to PCL ratios. An overview of the tensile test results can be found in appendix 3. The stress and strain at break decreases as starch content increases (Figure 18 and Figure 19). This is in

agreement with previous data on starch-PCL blends [11, 44-47] and is related to the lack of interfacial adhesion between the starch particles and the PCL matrix. The modulus, Figure 20, showed a different trend than reported in most literature [11, 44-46]. The modulus increased when the starch content is 10% and then decreases when the starch concentration is increased until 20 and 30%. In literature, the modulus will continuously increase when increasing the starch content. There is a difference between the observed trend and those found in these literature papers, which can be explained by the type of starch and PCL used. The articles found in literature all uses maize starch instead of potato starch. Maize starch contains more amylose and because of that it has a higher modulus [48]. The only paper that shows the same trend that is observed in our research is from Li and Favis [47]. They used the same polycaprolactone and used the same deformation rate as in our research. So probably, the combination of the used PCL and starch and the used deformation rate influences the modulus. Another important trend is that the compatibilized blends showed higher stress, strain and modulus than their uncompatibilized ones. This is in agreement with literature [10, 29-31] and can be correlated to a better interfacial adhesion between the two phases.

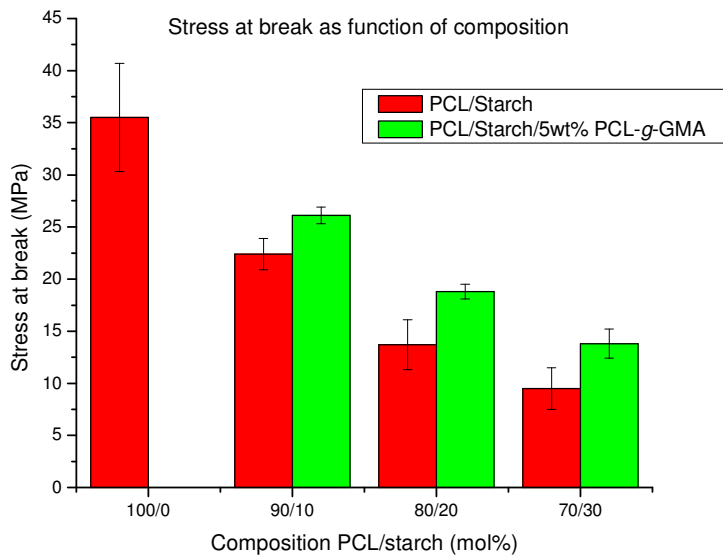


Figure 18 Stress at break as function of starch content.

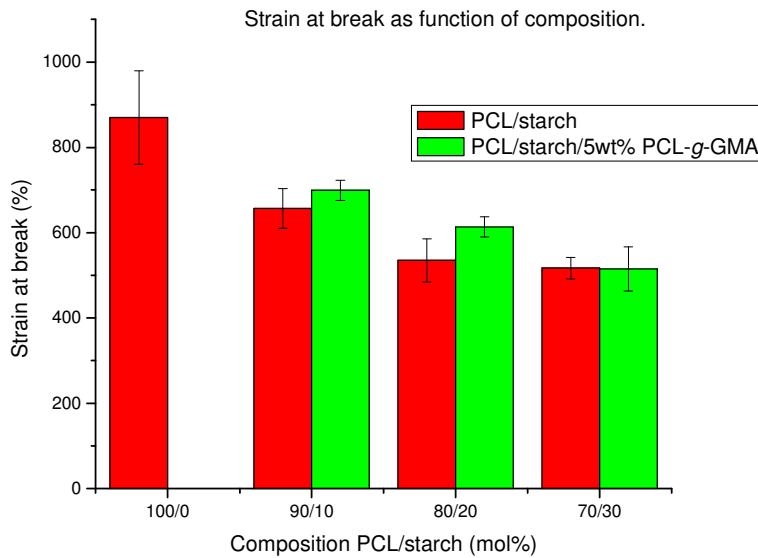


Figure 19 Strain at break as function of starch content.

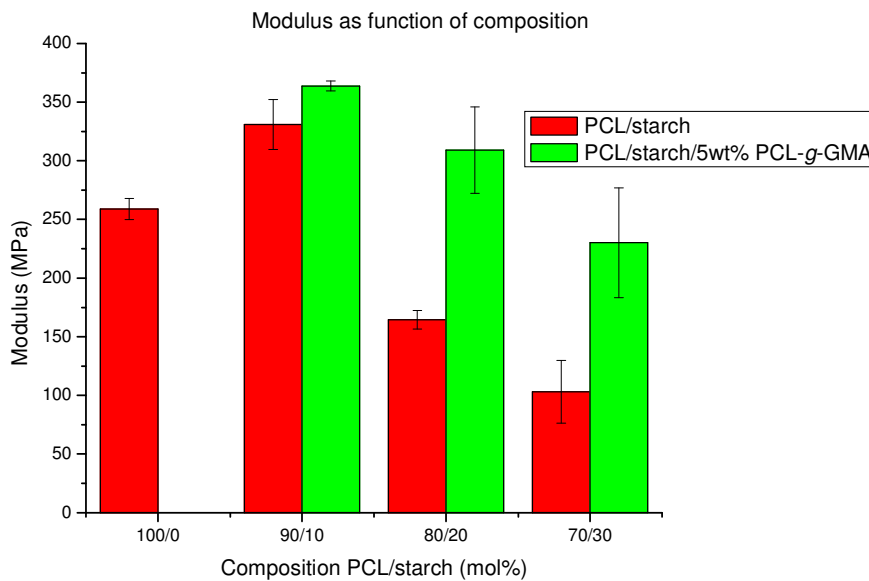


Figure 20 Modulus as function of starch content

From the series with a fixed PCL to starch ratio and an increasing amount of compatibilizer can be concluded that the amount of compatibilizer has no significant influence on the stress, strain and modulus (Figure 21, Figure 22 and Figure 23 respectively). This is in agreement with Sugih et al. [8], which also concluded that there is not a function between the mechanical properties and the compatibilizer intake. However M. Avella et al. [44] observed a trend when changing the compatibilizer intake with a fixed PCL to starch ratio. The reason for these different observations is probably due to the particle size of the starch. If the particle size of the starch is smaller, the total interfacial surface will be bigger and more compatibilizer is needed to cover this interface. From the calculation in appendix 5 can be assumed that

in our case less than $2 \cdot 10^{-6}$ wt% compatibilizer is needed to cover the interface of the starch particles. In this calculation an assumption is made that every GMA group reacts with one $-OH$ group of a starch particle. Sugih [8] showed already that this is not true so the calculated value gives only a rough estimation. From this rough calculation a conclusion can be made that, in our experiments, the compatibilizer is used in excess.

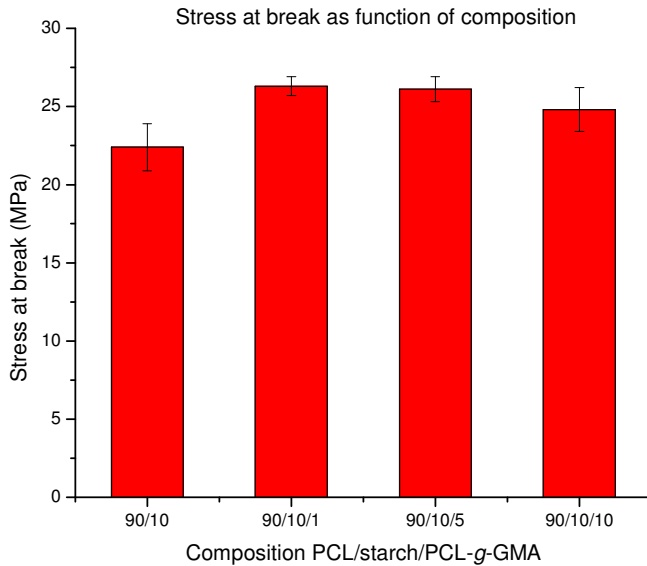


Figure 21 Stress at break as function of compatibilizer intake.

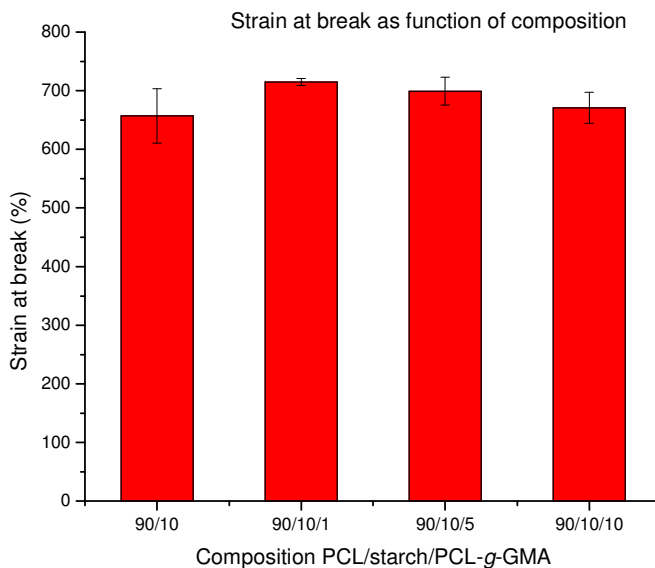


Figure 22 Strain at break as function of compatibilizer intake.

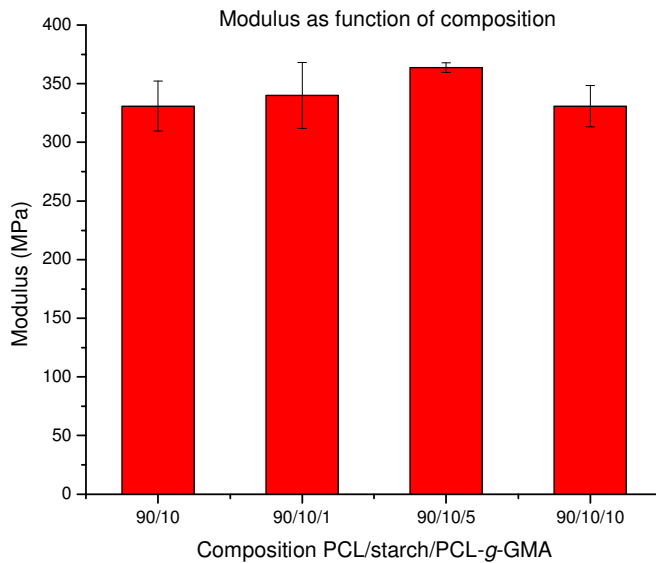


Figure 23 Modulus as function of compatibilizer intake.

To investigate the effect of the functionalization degree of the used compatibilizer on the mechanical properties, two extra blends are prepared with two different compatibilizers. The used compatibilizers have a functionalization degree of 2% and 12% respectively. A higher functionalization degree means more epoxy groups that can react with the hydroxyl groups of the starch. The results of the experiment can be found in Figure 24, Figure 25 and Figure 26. These results show that there is not a significant effect of a higher FD on the mechanical properties. This observation is also made by Sugih [8]. He showed that PCL-g-DEM with a FD of 1,7% has to same compatibilizing effect as PCL-g-GMA with a FD of 9,6%. Probably if one GMA group in a graft reacts with one of the -OH groups on the surface of the starch particles will render the remaining GMA groups less accessible for further reaction with other starch -OH groups.

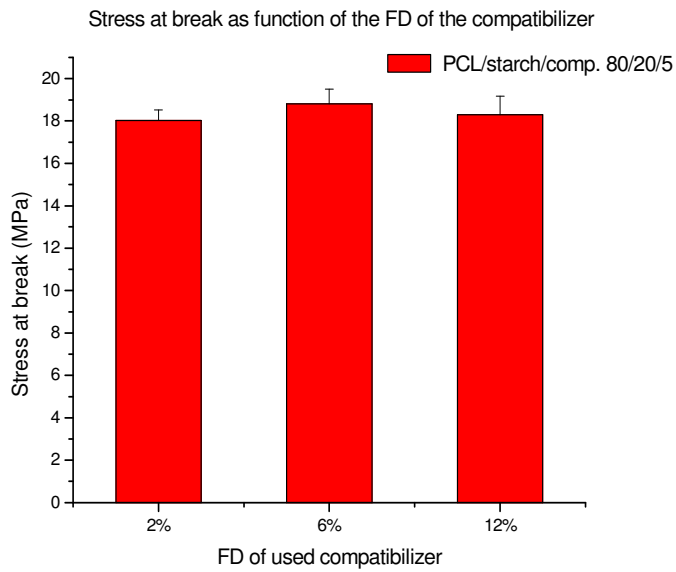


Figure 24 Stress at break as function of the FD of the used compatibilizer

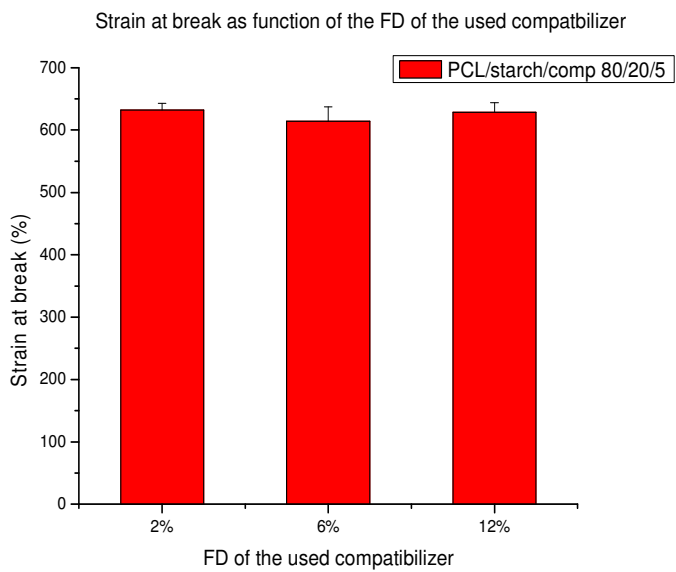


Figure 25 Strain at break as function of the FD of the used compatibilizer

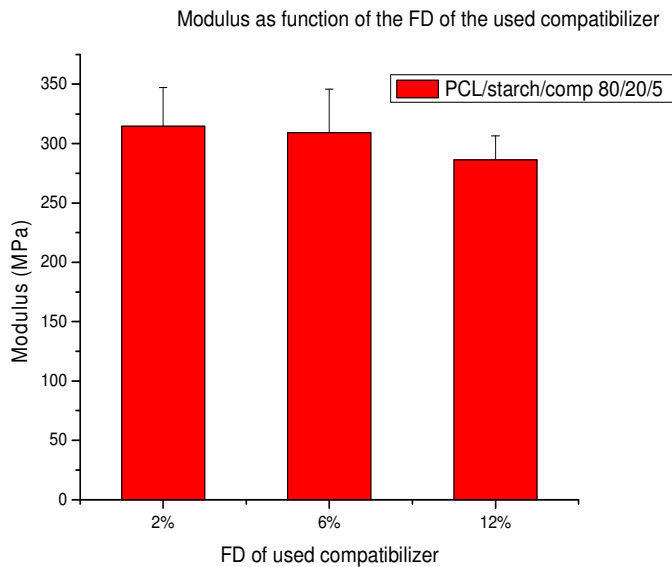


Figure 26 Modulus as function of the FD of the used compatibilizer

8.6 Chloroform extraction of the PCL-starch blends

The samples PCL-starch 5 and PCL-starch 6 with a starch content of respectively 20 and 30 percent are used in the extraction. After the extraction, the PCL and starch phase are weighted to make a mass balance. Unfortunately, our mass balance was not accurate enough to calculate the percentage of the compatibilizer that is reacted. NMR and infrared spectroscopy also did not show indication that the compatibilizer is reacted with the starch. A reason for this is that a very low amount of compatibilizer is used in these blends, so the intensity of these peaks are very low compared with the PCL and starch peaks.

To show that a reaction will occur between the epoxy group of the GMA and the hydroxyl groups of the starch an extra experiment is done. A blend is made by mixing the compatibilizer with starch in the ratio of 70/30. The same procedure is followed as the one with the PCL-starch blends. The mass balance of the extraction can be found in Table 9, for the accuracy the experiment is done in duplicate. From this table can be concluded that the starch phase increases in weight, this means that the compatibilizer reacts with the starch and becomes insoluble in chloroform. From these data the percentage of epoxy groups that is reacted with the hydroxyl groups of the starch can be calculated. Knowing that the functionalization degree of the compatibilizer is 6%, the percentage can be calculated by dividing the amount of reacted compatibilizer (0,041 for sample 1) by the known amount of epoxy groups (this is 6% of 2,1 for sample 1). When this is done a percentage of 33% and 36% for respectively samples one and two are found.

Table 9 Mass balance of the extraction.

	Sample	Total weight (grams)	PCL- <i>g</i> -GMA (grams)	Starch (grams)	PCL- <i>g</i> -GMA (moles)	Starch (moles)
Input	1	3,000	2,100	0,900	0,01602	0,00556
	2	3,050	2,135	0,915	0,01629	0,00565
Output	1	2,989	2,059	0,930	0,01571	0,00574
	2	3,059	2,089	0,970	0,01594	0,00599
Difference	1	-0,011	-0,041	0,030	-0,00031	0,00019
	2	0,009	-0,046	0,055	-0,00035	0,00034

8.7 Advantages of supercritical carbon dioxide

In this paragraph will be investigated whether the use of $s\text{CO}_2$ really has advantages, as stated in literature [18-25], above normal melt processing. The mechanical properties of a starch-PCL blend with a compatibilizer which is processed in both ways are compared. The compatibilizer made with normal melt processing in the brabender is made by my colleague Sunny Qian [49]. The compatibilizer has an identical functionalization degree as the one from the supercritical carbon dioxide reactor. It can be possible that the two compatibilizers differ in their topology or in their molecular weight, which can influence the mechanical properties of the final blend. In the brabender the temperature is much higher, because the lack of the advantages from supercritical carbon dioxide, which will probably lead to more degradation and a higher polydispersity. The results of the tensile test are shown in Figure 27, Figure 28 and Figure 29. From Figure 27 and Figure 28 can be seen that the stress- and strain at break slightly decreases when using the compatibilizer made in the brabender compared to the one from the carbon dioxide reactor, especially the one at starch intake of 30%. The effect of the two compatibilizers on the modulus is shown in Figure 29. Here can be seen that the modulus slightly decreases when using the compatibilizer made in the brabender, the modulus stays constant at a starch intake of 30%. Although the differences are not that big, one can say that the compatibilizers made in the reactor with supercritical carbon dioxide have a better influence on the mechanical properties of the blends than the ones from the brabender, especially when the starch intake is higher. To explain the latter one should look to the molecular weight and topology of the compatibilizers made in the brabender and compare this with the compatibilizers made with the supercritical carbon dioxide reactor. All the compatibilizers made in the melt with the brabender are made by Sunny Qian [49]. The GPC results of compatibilizers made with and without $s\text{CO}_2$ are graphically shown in Figure 30, Figure 31 and Figure 32.

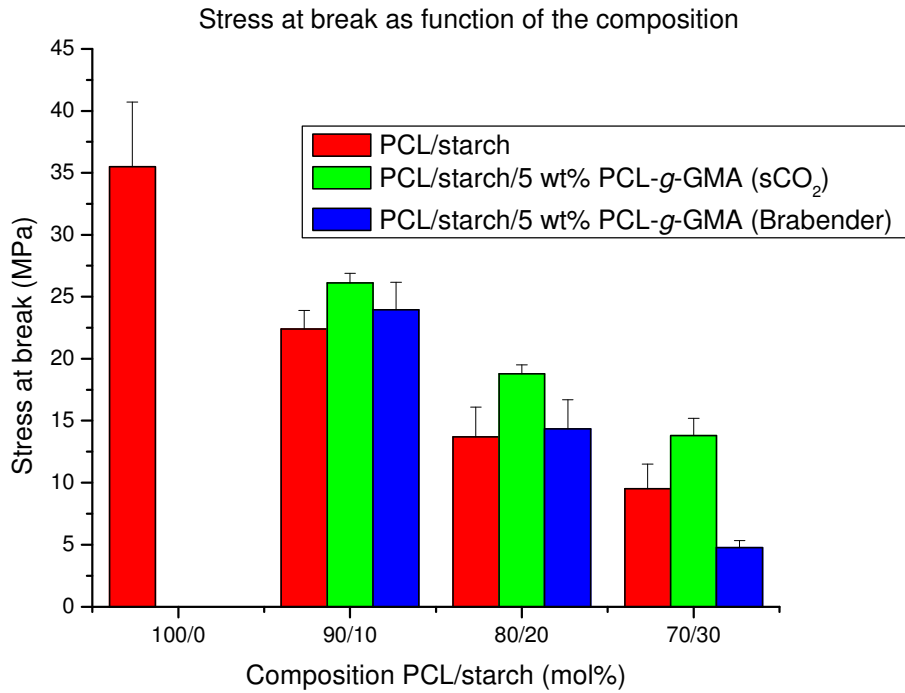


Figure 27 Stress at break as function of the composition

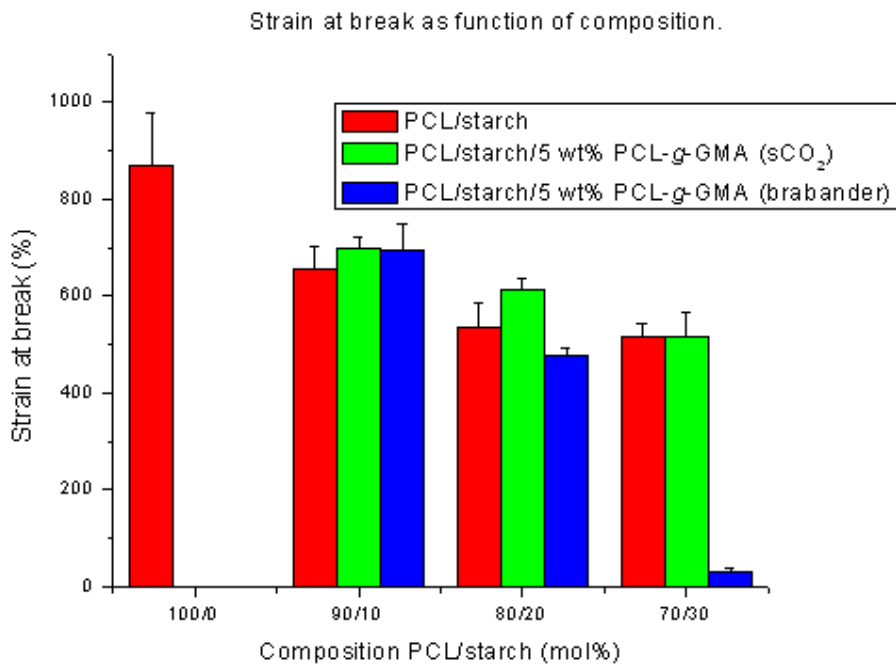


Figure 28 Strain at break as function of the composition

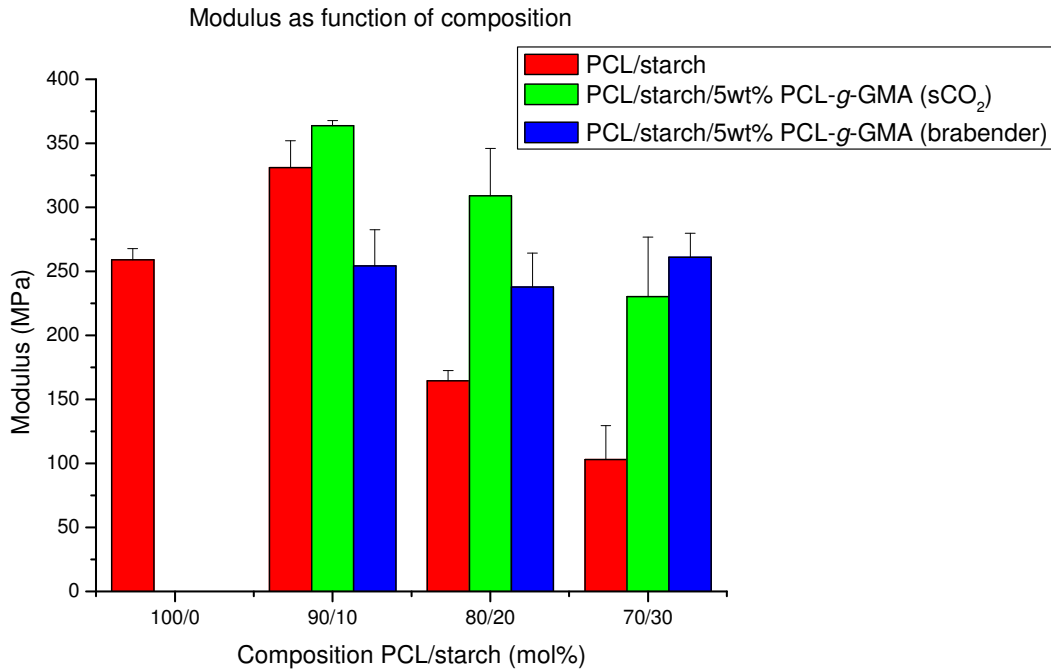


Figure 29 Modulus as function of the composition

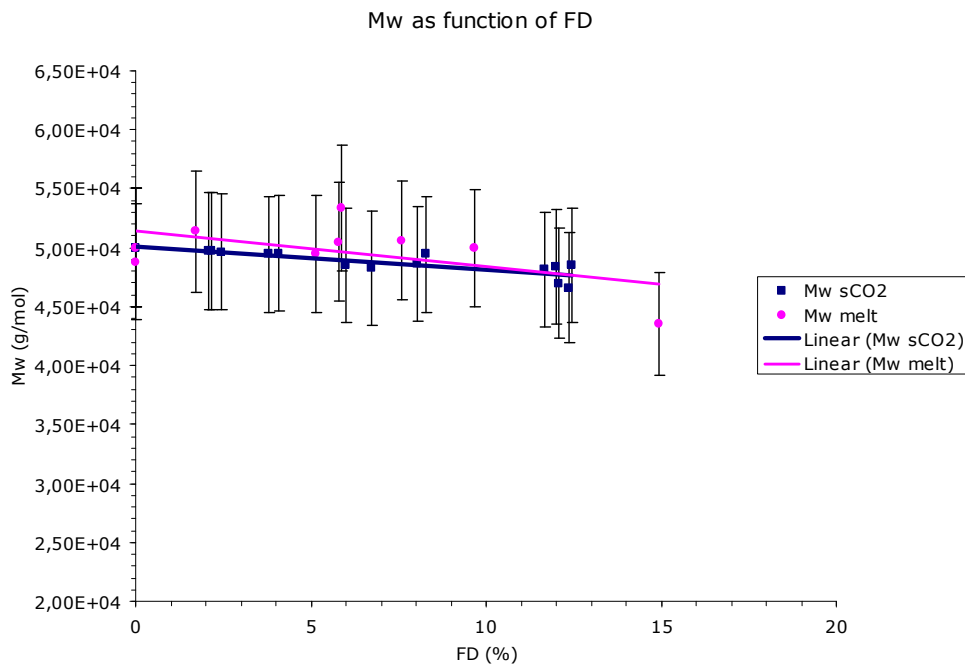


Figure 30 Mw as function of FD for compatibilizers made with and without sCO₂

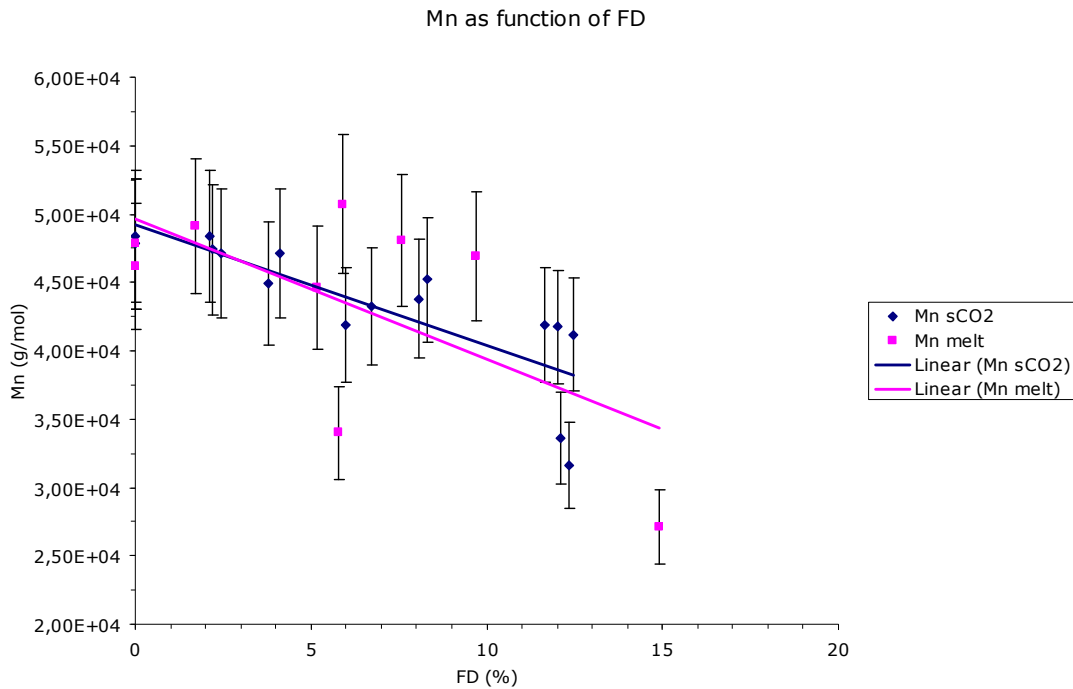


Figure 31 Mn as function of FD for compatibilizers made with and without sCO₂

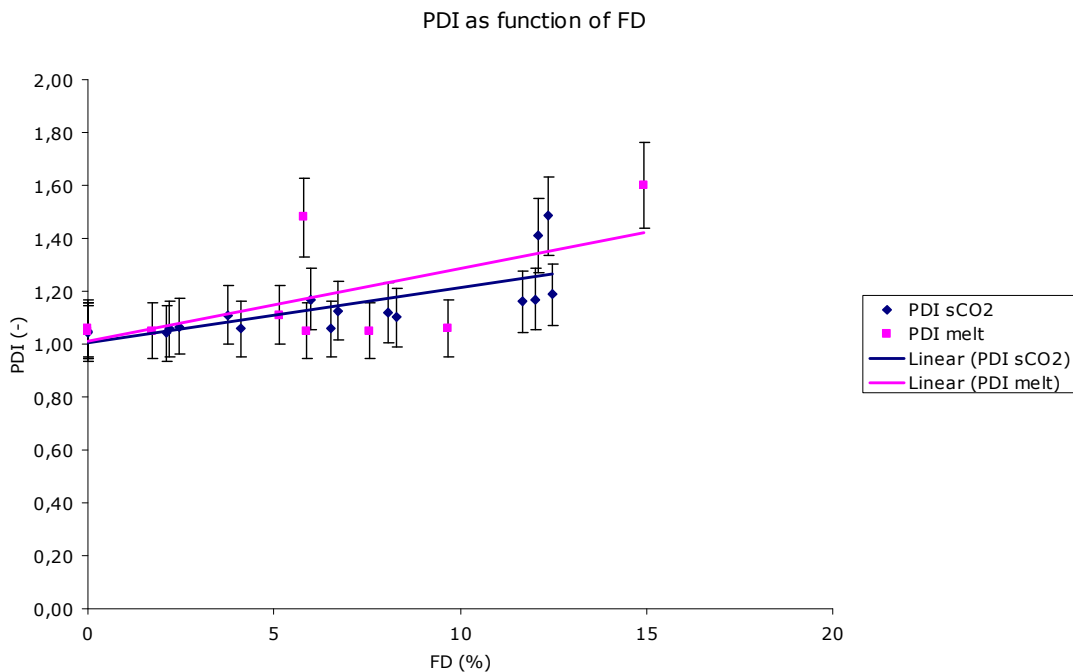


Figure 32 PDI as function of FD for compatibilizers made with and without sCO₂

The GPC result of the compatibilizers with and without sCO₂ are both made with a different calibration curve. To compare both, the results of the ones made with sCO₂ are recalculated in the way that the pure PCL has the same value as the one made in the melt with the brabender. From Figure 30, Figure 31 and Figure 32 can be concluded that the Mw, Mn and PDI respectively do not differ much if they are made with or without sCO₂ as function of the FD. One thing that can be said is that the

values from the compatibilizer made in the melt with the brabender have a larger variance. From these result a conclusion can be made that the molecular weight is probably not responsible for the higher mechanical properties of the blends with the compatibilizer made with $s\text{CO}_2$. The difference between the two compatibilizers would probably be a different topology. Sugih [8] already proved that for blends with a low amount of starch not the amount of functional groups is important but how they are divided along the PCL backbone. The expectation is that the $s\text{CO}_2$ facilitates the diffusion of monomers and initiator within the polymer matrix. As a result that the GMA groups are more homogeneous divided along the PCL backbone. This hypothesis is not proven yet.

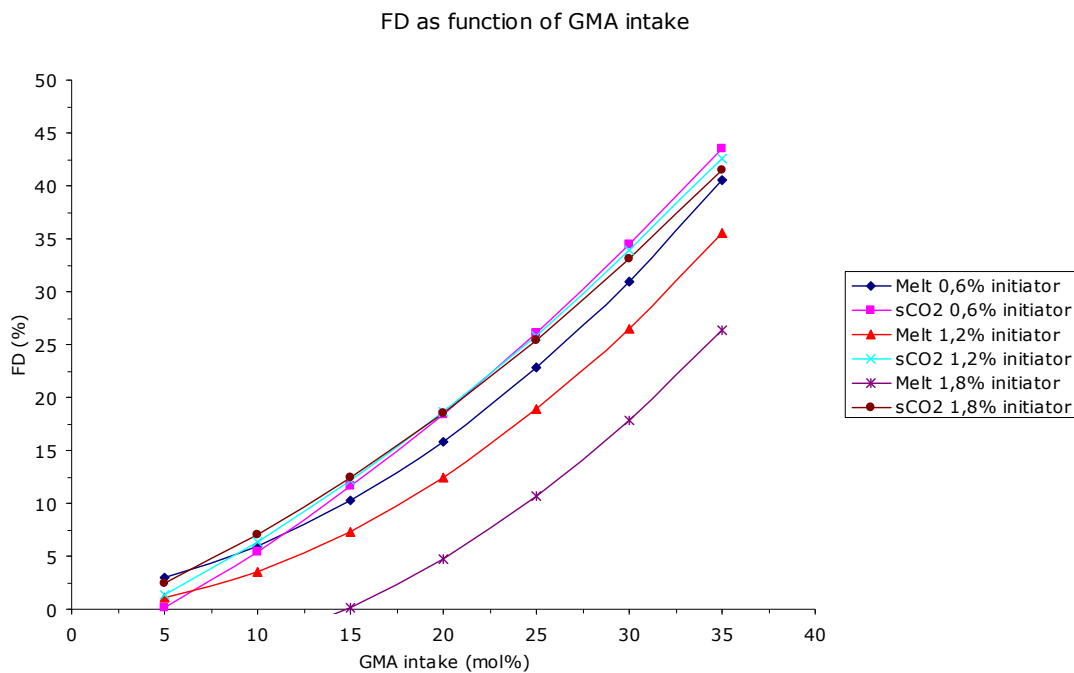


Figure 33 FD as function of the GMA intake for compatibilizers made with and without $s\text{CO}_2$.

Figure 33 shows the functionalization degree as function of the GMA intake for compatibilizers made with and without $s\text{CO}_2$ at different initiator intake. As can be seen from this graph is that the FD of the compatibilizer made with the $s\text{CO}_2$ is independent of the initiator intake. This is not the case for the ones made in the brabender. There can be concluded that the grafting efficiency for compatibilizers made in $s\text{CO}_2$ is better than for those made in the brabender.



9. Conclusion

The general goal of this research was to develop compatibilizers for PCL/starch blends using supercritical carbon dioxide. To reach this goal the research was divided into two parts. The first part consists of the preparation of compatibilizer precursors. The compatibilizer precursors were prepared by functionalization of polycaprolactone with three different monomers in supercritical carbon dioxide. The second part consists of the preparation of the PCL-starch blends with the compatibilizer precursor.

Compatibilizer precursor.

From three monomers that were tried to graft the PCL, only GMA turned out to be a good one. The other two, DEM and MAH, are not reactive enough due to the two adjacent electron-attractive carbonyl groups of these monomers. From the samples with GMA can be concluded that higher monomer intake leads to more grafting. A higher initiator intake leads in the beginning to a higher and eventually a constant functionalization degree. From the obtained data, a good insight is gained in the behavior of the functionalization degree as function of the monomer and initiator intake. With these data, a mathematical model is obtained. The R^2 -value of our model is 0,967; this implies that the model has a good fit with the experimental data. With the obtained mathematical model a comparison is made with a model obtained from literature for compatibilizers made in the melt without $s\text{CO}_2$. The major difference was that the initiator intake has a negative effect on the functionalization degree for the compatibilizers made without $s\text{CO}_2$, which is not the case for compatibilizers made with $s\text{CO}_2$. GPC result showed that no degradation or chain extension has occurred in the reactions. To increase the rate and yield of the reaction between PCL and GMA there was tried to use styrene as co-monomer but the results were not as expected. The overall conclusion of this part is that the use of supercritical carbon dioxide in the functionalization of PCL is a good alternative for normal melt processing.

PCL and starch blends

Three compatibilizer precursors were used to make blends with PCL and starch. The results were as expected because the blends with the compatibilizer showed better mechanical properties than the uncompatibilized ones. The epoxy group of the compatibilizer precursor is reacted with the hydroxyl group of the starch leading to the real compatibilizer. This compatibilizer improves the interfacial adhesion between the two phases resulting in a mixture with better mechanical properties. To prove that this reaction really took place an extraction was performed with the compatibilizer precursor and starch. The mass balance of this experiment showed that 33% of the epoxy groups are reacted with the starch. From this observation can be concluded that a reaction took place. In addition, the effect of the amount of compatibilizer precursor on the mechanical properties of the blend is investigated. It turned out that the amount has no influence on the mechanical properties of the blends because the compatibilizers precursor is used in excess. Also the functionalization degree of the compatibilizers has no influence on the mechanical properties, this because only one GMA group in a graft reacts with an $-\text{OH}$ group at the surface of a starch particle and the other GMA groups will remain less accessible. At the end of this research the effect of using $s\text{CO}_2$ in the preparation of the compatibilizers precursors on the mechanical properties of the blends is investigated. Blends with a compatibilizer



made with $s\text{CO}_2$ are compared with blends with a compatibilizer made with normal melt processing. The result was that blends with a compatibilizer made with $s\text{CO}_2$ have better mechanical properties. GPC results showed that no difference in molecular weight are present so probably the topology of the two different compatibilizers are responsible for the obtained differences. The hypothesis is that the $s\text{CO}_2$ facilitates the diffusion of monomers and initiator within the polymer matrix. As a result that the GMA groups are more homogeneous divided along the PCL backbone which will result in a better compatibilization effect.



10. Recommendations for further research

A lot have been researched but still more have to be done. In this chapter some recommendation for further research will be given.

In this thesis, a mathematical model is obtained to predict the functionalization degree from the monomer and initiator intake. However this model is only valid when using the right temperature and pressure, 97 °C and 90 bar respectively. It would be better to take into account the pressure and temperature in the model. To do this a few compatibilizers has to be made at different temperatures and pressures and investigate how this influences the functionalization degree.

Three monomers are tried to be grafted to polycaprolactone and only the GMA was reactive enough to graft to polycaprolactone. Instead of these three monomers, other monomers could be tried, such as methyl methacrylate or acrylic acid, and look how they react with the polycaprolactone.

One of the goals of this research was to use supercritical carbon dioxide in the functionalization process and show that this has advantages above the process in the brabender. The results in this thesis showed that the mechanical properties of the PCL-starch blends with the compatibilizer made under sCO₂ are the same or better than the blends with the compatibilizer from the brabender. To explain these results the differences between the two compatibilizers should be further investigated. GPC analysis showed already that the molecular weight does not differ much for both compatibilizers. In addition, the difference in topology should be investigated; there could be a difference in the length of the GMA homopolymers that is responsible for the observed differences.

To make the PCL-starch blends more sustainable they should be made under supercritical carbon dioxide instead of in the brabender. Another research has to be done on how these blends behave under supercritical carbon dioxide.

In the work-up of the compatibilizers a lot of organic solvents are used. All these solvents have a negative effect on the sustainability of the final product. One could also try to use supercritical carbon dioxide to perform the extractions.

Summarized:

- Make the mathematical model better by including the temperature and pressure.
- Look to other monomers to graft PCL and compare this with GMA.
- Gain a better understanding in the differences between the compatibilizer made in the brabender and the one made under sCO₂.
- Investigate the probability of using sCO₂ in the blending of PCL and starch.
- Investigate the probability of using sCO₂ for the extraction of the compatibilizers.



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13. Appendixes

13.1 Initiators

Table 10 shows some initiators which could be used for radical polymerizations. This table shows the activation energy and the Arrhenius frequency factor for the Arrhenius equation. The half life at different temperatures can be calculated with the Arrhenius equation and the parameters of Table 10, the results are shown in Table 11. An example of such a calculation is shown below.

Table 10 Arrhenius parameters of some initiators from Akzo Nobel [15]

Initiator	Activation energy, E_a , (J/mole)	Arrhenius frequency factor, A , (1/s)
Dilauroyl peroxide	123370	3,92E+14
Diisobutyryl peroxide	109060	3,37E+14
dibenzoyl peroxide	122350	6,94E+13
dicumyl peroxide	152670	9,24E+15
di(4-tert-butylcyclohexyl peroxydicarbonate	126390	7,44E+15
dicetyl peroxydicarbonate	124300	3,02E+15
2,2-Azodi(isobutyronitrile	130230	2,89E+15
2,2-Azodi(2-methylbutyronitrile)	128930	1,38E+15
diisopopyl peroxydicarbonate	124010	3,35E+15
didecanoyl peroxide	130480	3,64E+15
tert-Amyl peroxy-2-ethylhexanoate	132110	1,77E+15
tert-butyl peroxyneodecanoate	115470	1,52E+14
1,1,3,3 tetramethylbutyl peroxyneodecanoate	115790	3,98E+14
cumylperoxyneodecanoate	114590	3,12E+14

Table 11 Half-life of some initiators in hours.

Initiator	$t_{1/2}$ at 60°C (hr)	$t_{1/2}$ at 80°C (hr)	$t_{1/2}$ at 100°C (hr)
Dilauroyl peroxide	11,08	0,89	0,09
Diisobutyryl peroxide	0,07	0,01	0,00
dibenzoyl peroxide	43,29	3,54	0,38
dicumyl peroxide	18552,01	816,68	50,25
di(4-tert-butylcyclohexyl peroxydicarbonate	1,74	0,13	0,01
dicetyl peroxydicarbonate	2,01	0,16	0,02
2,2-Azodi(isobutyronitrile	17,90	1,25	0,12
2,2-Azodi(2-methylbutyronitrile)	23,45	1,68	0,16
diisopopyl peroxydicarbonate	1,63	0,13	0,01
didecanoyl peroxide	15,56	1,08	0,10
tert-Amyl peroxy-2-ethylhexanoate	57,65	3,86	0,35
tert-butyl peroxyneodecanoate	1,65	0,16	0,02
1,1,3,3 tetramethylbutyl peroxyneodecanoate	0,71	0,07	0,01
cumylperoxyneodecanoate	0,58	0,06	0,01



Example of a calculation to determine the reaction time

2,2-Azodi(isobutyronitrile)

$$k_d = A \cdot e^{-E_a/RT}$$

$E_a = 130230 \text{ J/mole}$ (table 9)

$A = 2,89E^{+15} \text{ s}^{-1}$ (table 9)

$R = 8,3142 \text{ J/mole}\cdot\text{K}$ (gas constant)

$T = 373 \text{ K}$ (for example)

Inserting these values in the equation gives $k_d = 0,001665 \text{ s}^{-1}$. Inserting this value in the next equation gives $t_{1/2} = 416 \text{ s}$.

$$t_{1/2} = \frac{\ln 2}{k_d}$$

Inserting the result of $t_{1/2}$ in the next equation gives $t_{\text{reaction}} = 1664 \text{ s} = 28 \text{ min}$

$$t_{\text{reaction}} = 4 \cdot t_{1/2}$$

Conclusion: if the reaction temperature is 100°C than a reaction time of 28 minutes is needed.

13.2 NMR

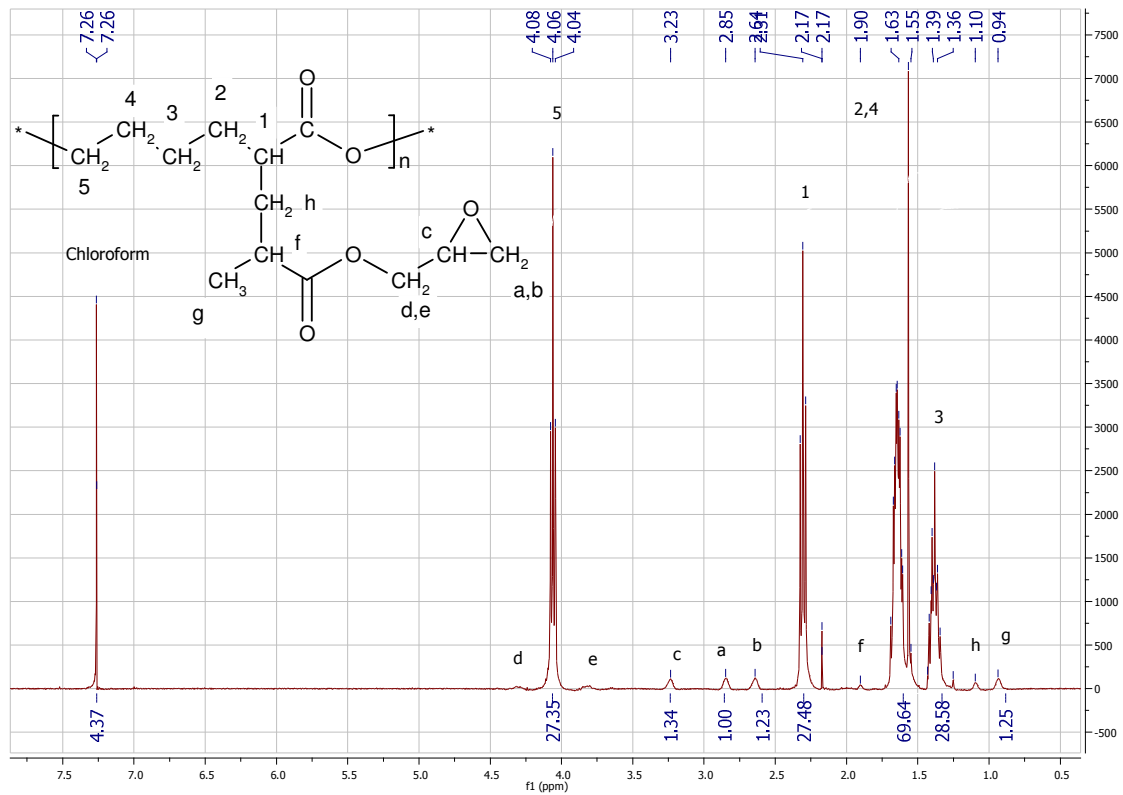


Figure 34 NMR spectrum of PCL-*g*-GMA

Figure 34 shows a typical ^1H -NMR spectrum of PCL-*g*-GMA. The next equation is used to calculate the FD of this polymer. The area of signal 5 is divided by two because signal 5 represents two protons

$$FD = \frac{A_c}{\frac{A_5}{2}} \cdot 100\%$$

$$FD = \frac{1,34}{\frac{27,35}{2}} \cdot 100\% = 9,8\%$$

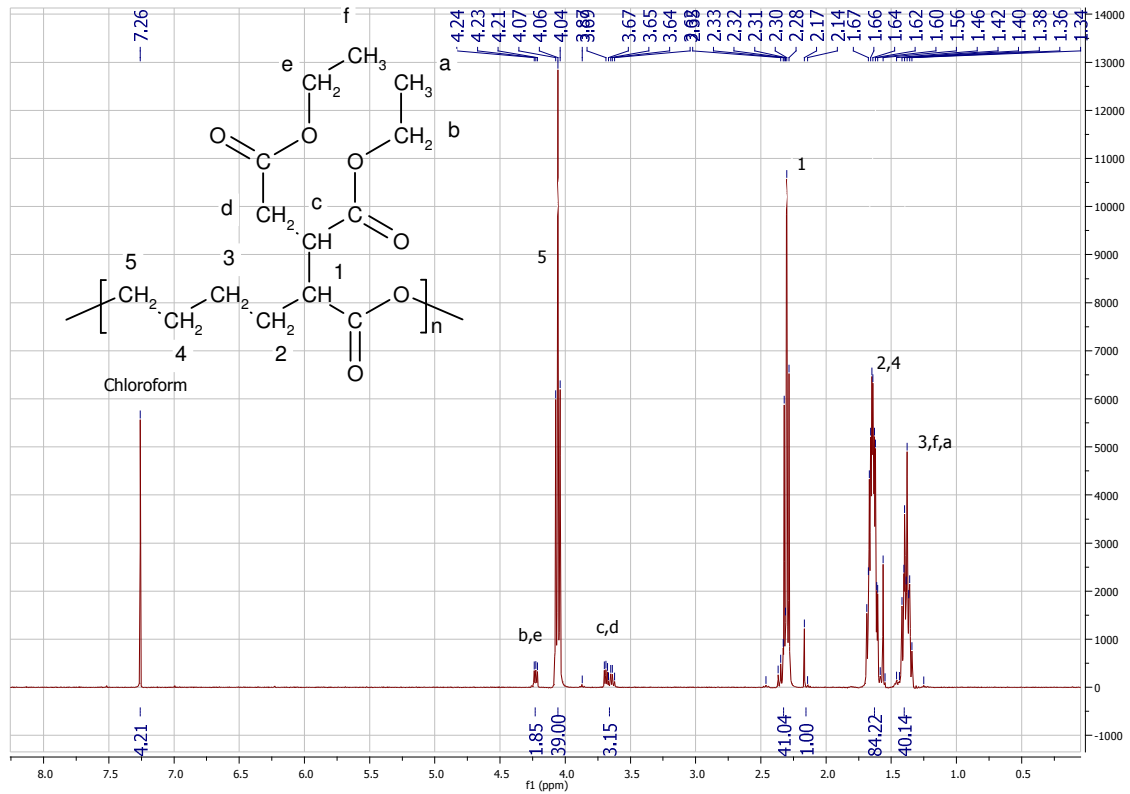


Figure 35 NMR spectrum of PCL-g-DEM

Figure 35 shows a typical spectrum of PCL-g-DEM. The calculation of the FD is shown below. The area of signal b,e is divided by 4 because it represents 4 protons, the area of signal 5 is divided by 2 because it represents 2 protons.

$$FD = \frac{A_{b,e}/4}{A_5/2} \cdot 100\%$$

$$FD = \frac{1,85/4}{39,00/2} \cdot 100\% = 2,37\%$$

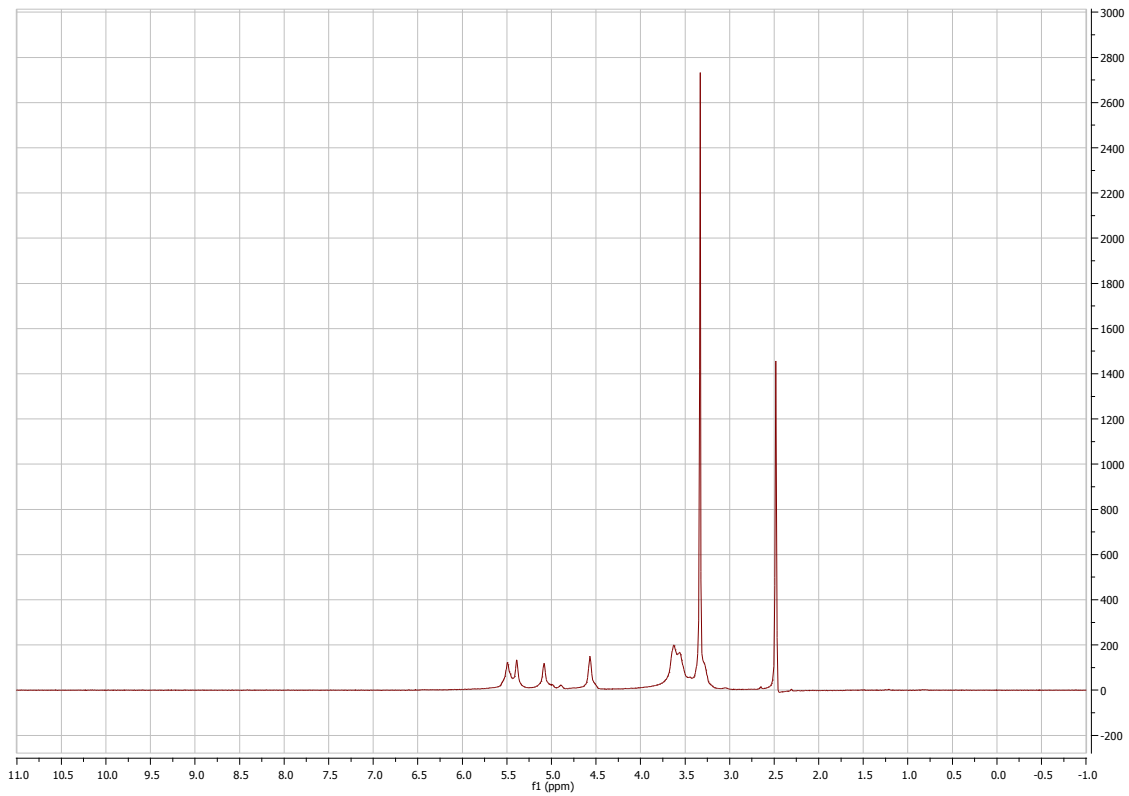


Figure 36 Typical spectrum of starch in DMSO

Figure 36 shows a typical spectrum of starch in DMSO. The typical signals of starch are at 3.6, 4.6, 5.0, 5.4 and 5.5 ppm. The other two signals, at 2.5 and 3.3 ppm, are from DMSO.



13.3 Tensile test

During testing the sample in the tensile test, a stress-strain curve is obtained. This curve is a graphical representation of the relationship between stress, derived from measuring the load applied on the sample, and strain, derived from measuring the deformation of the sample. The tensile stress can be calculated using the next formula.

$$\sigma = \frac{F}{A}$$

Where σ is the tensile stress in Pascal, F is the tensile force in Newton over the specimen and A is the cross-sectional area in cubic meters of the specimen.

For calculating the strain, the next formula can be used.

$$\varepsilon = \frac{l_1 - l_0}{l_0} \cdot 100\%$$

Where ε is the tensile strain in %, l_0 is the original length in meters of the specimen and l_1 is the final length in meters of the specimen.

Another important parameter is the modulus. The modulus says something about the stiffness of a material. A lower modulus means a more rubber-like material. The modulus is defined as the slope of the stress-strain curve in the elastic region. The modulus can be calculated with the next formula.

$$E = \frac{\sigma}{\varepsilon}$$

Where E is the modulus in Pascal, σ is the stress in Pascal and ε is the strain in %.

In Figure 37, a typical stress-strain curve of a blend of PCL and starch is shown. The linear part at the beginning of the curve is the elastic region which goes to a maximum. This maximum point is called the yield point. After the yield point there is a drop in stress, this is caused by necking of the sample. The material in the neck stretches and then new material at the neck shoulders necks down. Then the neck propagates until it spans the full gage length of the specimen, this process is called drawing. After the drawing an increase in stress is observed, this is due to straightening of the polymer chain, which eventually results in a fracture. From the point of fracture, the stress and strain at break can be calculated.

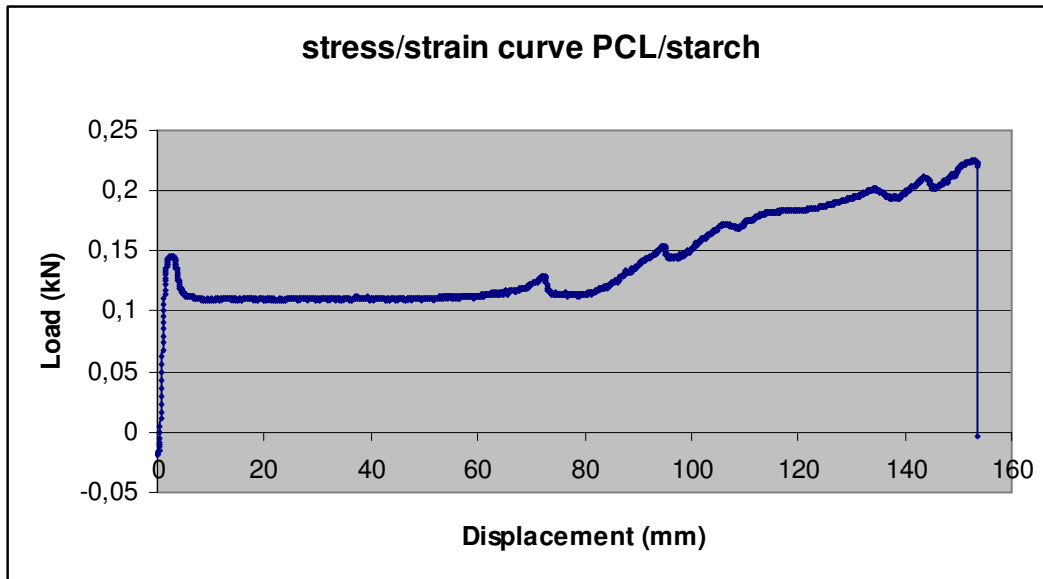


Figure 37 Typical stress-strain curve of a PCL-starch sample.

Table 12 shows the results of the tensile test of all the tested samples. The last three samples are the blends with the compatibilizer made in the brabender.



Table 12
 Results from
 the tensile
 test

	σ (Mpa)	ϵ (%)	Stress at break (Mpa)	Strain at break (%)	Auto modulus (Mpa)	Man Modulus (Mpa)
PCL	36,0	867,0	35,5	870,0	258,8	262,2
- Standard deviation	5,4	108,2	5,2	109,2	9,0	14,1
PCL/Starch 90/10	23,0	653,2	22,4	656,6	330,8	340,0
- Standard deviation	1,5	47,0	1,5	46,3	21,3	21,7
PCL/Starch/C(6%) 90/10/1	26,8	710,5	26,3	714,7	340,0	281,4
- Standard deviation	0,5	6,7	0,6	5,8	28,2	112,1
PCL/Starch/C(6%) 90/10/5	26,5	696,8	26,1	699,3	363,7	361,8
- Standard deviation	0,8	23,8	0,8	23,9	4,1	29,0
PCL/Starch/C(6%) 90/10/10	25,4	666,9	24,8	670,6	330,8	348,9
- Standard deviation	1,5	25,7	1,4	26,7	17,7	37,3
PCL/Starch 80/20	15,1	528,1	13,7	535,0	164,5	171,2
- Standard deviation	1,2	51,0	2,4	50,6	8,0	9,2
PCL/Starch/C(6%) 80/20/5	19,6	609,3	18,8	613,9	309,1	320,4
- Standard deviation	0,7	24,2	0,7	23,6	36,8	95,4
PCL/Starch 70/30	11,8	506,9	9,5	516,9	103,0	113,4
- Standard deviation	0,9	24,2	2,0	25,0	26,6	26,8
PCL/Starch/C(6%) 70/30/5	14,5	509,7	13,8	515,0	230,2	177,9
- Standard deviation	0,6	53,9	1,4	51,7	46,7	124,4
PCL/Starch/C(2%) 80/20/5	18,5	631,8	18,0	636,1	314,7	315,9
- Standard deviation	0,2	11,1	0,5	10,5	32,7	31,2
PCL/Starch/C(12%) 80/20/5	18,8	628,7	18,3	631,9	286,4	292,6
- Standard deviation	0,6	15,1	0,9	14,5	20,2	18,0
PCL/Starch/C(6%)brabender 90/10/5	24,4	689,8	23,9	695,3	254,2	262,0
- Standard deviation	2,2	53,9	2,2	53,4	28,2	33,3
PCL/Starch/C(6%)brabender 80/20/5	15,2	472,8	14,4	478,0	237,8	244,3
- Standard deviation	1,9	17,1	2,4	14,2	26,3	34,8
PCL/Starch/C(6%)brabender 70/30/5	12,2	8,8	4,8	29,9	260,9	265,7
- Standard deviation	0,3	1,0	0,6	8,3	18,9	16,8

13.4 Infrared spectroscopy

Figure 38 shows a typical spectrum of a PCL sample. The typical carbonyl bond can be found at 1720 cm^{-1} . In Figure 39, a typical spectrum is shown for a starch sample. Typical in this spectrum is the broad peak around 3320 cm^{-1} .

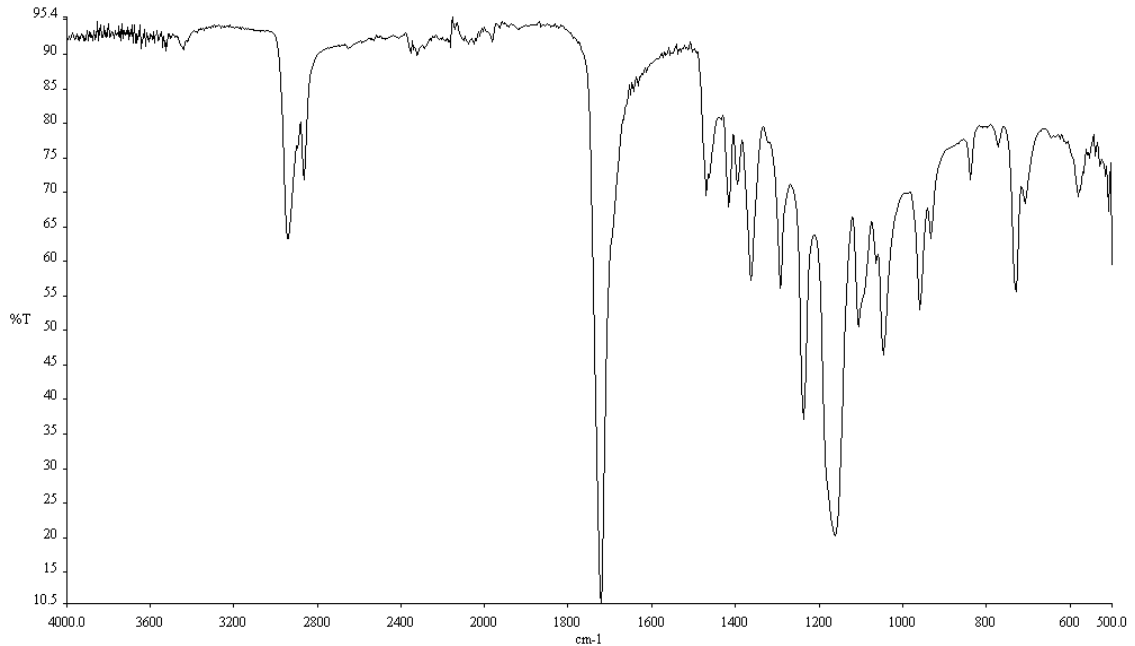


Figure 38 Typical infrared spectrum of PCL.

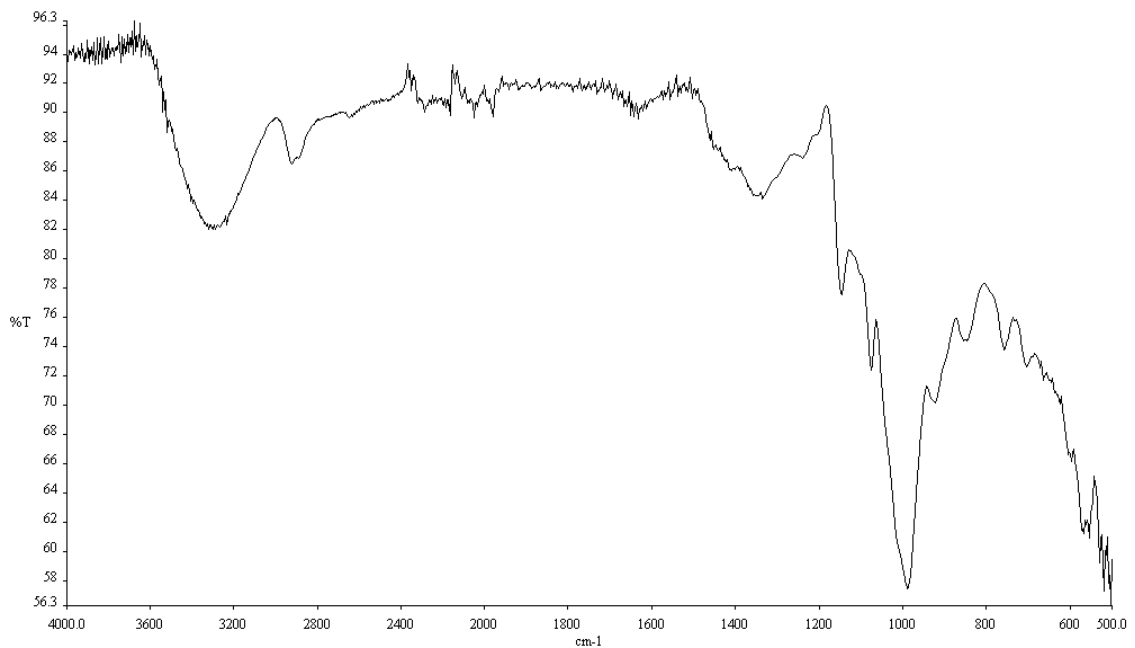


Figure 39 Typical infrared spectrum of starch.



13.5 Calculation amount of compatibilizer

In this appendix a rough calculations is made to calculate the amount of compatibilizer is needed to cover the interface between starch and PCL. From the SEM pictures of Sugih et al. [6] can be assumed that the starch particles have a diameter of 15µm. If we suppose that the particle is a sphere, then the surface can be calculated with the next formula:

$$S_{sphere} = 4\pi r^2$$

With r the radius of the sphere. Inserting the radius of the particle gives a surface of $7,18 \cdot 10^{-10} \text{ m}^2$. The radius of a hydroxyl group is supposed to be 110 pm (radius of oxygen + hydrogen). We suppose that the surface of the starch particle is covered with hydroxyl groups. Each hydroxyl group covers a square of $((2 \cdot 110 \text{ pm})^2) 4,84 \cdot 10^{-16} \text{ m}^2$. By dividing the surface of the starch particle by the surface of a hydroxyl group gives the total amount of hydroxyl groups. When doing this a value of $1,48 \cdot 10^6$ is obtained. Dividing this value with the constant of Avogadro gives the maximal moles of hydroxyl groups at the surface of a starch particle, resulting in $2,5 \cdot 10^{-18} \text{ mol}$. The total volume of a starch particle can be calculated with the next formula:

$$V_{sphere} = 4\pi r^3$$

Inserting the radius gives $5,3 \cdot 10^{-15} \text{ m}^3$. With the density (600 kg/m^3) and the molar mass (162 g/mol) the total moles of starch is obtained in one particle, resulting in $2 \cdot 10^{-11} \text{ mol}$. A ratio is obtained when dividing the moles of hydroxyl groups by the moles of starch, $1,25 \cdot 10^{-7} : 1$. If we suppose that every hydroxyl group reacts with one GMA group then $1,25 \cdot 10^{-7} \text{ mol}$ GMA is needed to cover the interface of one mol starch. The used compatibilizer has a FD of 6%, so $(100/6) \cdot 1,25 \cdot 10^{-7} = 17,9 \cdot 10^{-7} \text{ mol}$ compatibilizer is needed. When using 90 mol% PCL and 10 mol% starch then a weight percentage (wt% of total weight PCL and starch) of $2 \cdot 10^{-6} \%$ compatibilizer is needed.

Conclusion: If the surface of the starch particle consists only of hydroxyl –groups and every hydroxyl group reacts with one functional-group of the PCL then $2 \cdot 10^{-6} \text{ wt\%}$ compatibilizer is needed by a PCL/starch ratio of 90/10 mol%.