Microfibrillated cellulose-enabled suspension polymerisation of polystyrene

Master Thesis

submitted by
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Abstract

Micro-fibrillated lignocellulose (MFLC), micro-fibrillated cellulose (MFC) and cellulose nanocrystals were suspended in water and mixed with styrene to form oil in water (o/w) emulsions. The stabilisation behaviour was then observed over time. It was assumed that MFLC, because of its comparable high residual lignin content and its amphiphilic behaviour would have a better stabilisation mechanism. In a further step the MFLC and MFC emulsions were polymerised with the radical starter AIBN and heat of 100°C for twelve hours. The result was a cellulose-styrene composite where the MFLC-PS composite showed an even distribution of the fibrils with many polystyrene macrospheres present in the material which were covered completely by fibrils. In contrast the MFC-PS composite was not homogeneous at all and showed parts of pure PS and other parts of aggregated fibrils. No macrospheres could be found in this material. Based on the results of our work it can be concluded that MFLC shows similar emulsion stabilisation behaviour compared to MFC but when it comes to polymerisation MFLC shows superior stabilisation properties which might be due to the presence of lignin in the cellulosic material. The cellulose nanocrystals were not polymerised as no emulsion stabilisation mechanism existed.

Keywords: cellullose nanocrystals, emulsion stability, macrospheres, micro-fibrillated cellulose, micro-fibrillated lignocellulose, styrene-emulsions

Zusammenfassung

Im Zuge dieser Arbeit wurde jeweils micro-fibrillierte Lignocellulose (MFLC), micro-fibrillierte Cellulose (MFC) und Cellulose Nanocrystals (CNC) mit deionisierten Wasser suspendiert und mit Styren gemischt. Die daraus erhaltenen Styren-in-Wasser Emulsionen wurden über mehrere Stunden und Tage beobachtet. Es wurde angenommen das MFLC, das einen hohen Restligningehalt und eine Tendenz zu amphiphilen Verhalten aufweist, einen besseren Stabilisierungsmechanismus besitzt. Weiters wurden MFLC und MFC Wasser-Styren Emulsionen, mithilfe des Radikalstarters AIBN und Erhitzen auf 100°C für zwölf Stunden, polymerisiert. Das Ergebnis war ein MFLC-PS Verbundmaterial das eine gleichmäßige Verteilung der Fibrillen zeigte und sogenannte Polystyren 'Macrosspheres' aufwies die von MFLC umhüllt waren. Im Gegensatz dazu waren im MFC-PS Verbund Material Bereiche von puren Polystyren und andererseits Ansammlungen von MFC erkennbar. Die sogenannten 'Macrospheres' konnten in diesem Material nicht nachgewiesen werden. Aufgrund der Ergebnisse dieser Arbeit kann darauf geschlossen werden, dass MFLC und MFC ein ähnliches Stabilisierungsverhalten von Styrene-in-Wasser Emulsionen aufweisen. Werden diese Emulsionen allerdings unter Hitzeeinwirkung polymerisiert zeigt MFLC deutlich bessere Eigenschaften und es kommt außerdem zur Ausbildung von MFLC-PS 'Macrospheres' was darauf schließen lässt, dass, das vorhandene Lignin wesentlich zur Stabilisierung von Emulsionen beiträgt. Die CNC-Wasser-Styren Emulsion wurde nicht polymerisiert, da dieses Material keine Stabilisierungseigenschaften aufwies.

Schlagwörter: Cellulose Nanocrystals, Emulsionsstabilität, Macrospheres, Micro-fibrillierte Cellulose, Micro-fibrillierte Lignocellulose, Styren Emulsion

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1 Introduction

The polysaccharide Cellulose is the most important skeletal component in plants and an almost inexhaustible polymeric raw material. Currently science, technology, and society in general are moving towards renewable materials and more environmentally-friendly and sustainable resources, cellulose can play a major role in future developments (Klemm et al. 2005) and is therefore also in the focus of the investigation of this work.

For thousands of years cellulose was used in the form of wood or cotton, as an energy source and a material for building and clothing. (Klemm et al. 2005) Presently cellulose is the main material in writing and printing paper and in many hygiene articles such as tissues, bathroom tissues, and female hygiene products. Another product made from cellulose is synthetic fibres such as viscose or modal. Not so widely known is the fact that cellulose is also used in cosmetics and foods in various forms because of its rheological properties and its ability to stabilise emulsions (Gilbert et al. 2013) (Correa et al. 2010). Exactly this interesting behaviour of cellulosic materials is among other things studied and discussed in this paper.

Regarding the development of new materials and the utilisation of cellulose as a reinforcing material: it often fails due to the fact that cellulosic material is essentially hydrophilic and shows poor compatibility with important technical nonpolar polymers (Habibi 2014). This problem of non-compatibility of cellulose to various polymers is often bypassed by hydrophobisation of the cellulosic material. Yet in our study no hydrophobisation was applied but instead we focused on the dispersion of various cellulosic materials in emulsions.

1.1 Aim of the study

Our study was performed in order to determine how different cellulosic materials can stabilise styrene-in-water emulsions. As there is already a lot of literature about micro-fibrillated cellulose (MFC) and cellulose nano-crystals (CNC) that were used to stabilise oil-in-water emulsions the focus of our study is to compare the stabilising ability of these two forms of cellulose with that of micro-fibrillated lignocellulose (MFLC), a cellulosic material with a comparable high residual content of lignin. The motivation was also to test if it is possible to use a renewable source as a stabiliser that has the potential to substitute non-renewable stabilisers in future developments. Not only the stabilising mechanism of these materials is of interest but also the behaviour of the cellulosic material to finely disperse in the styrene-in-water emulsion and the further polymerisation of the styrene, which would then result in a new cellulose-polystyrene composite.

The thesis comprises a literature part where theoretical background is discussed and explained, an experimental part that is described in detail in the materials and methods chapter, results of the experiments, discussion, conclusion, and future prospects. Also an index of abbreviations where important terms are explained is given and shall facilitate reading and understanding the thesis.

1.2 Research Question

How is micro-fibrillated lignocellulose, compared to micro-fibrillated cellulose and cellulose nano-crystals, able to produce stable styrene-in-water emulsions in order to polymerise the styrene in a following step.

1.2.1 Hypothesis

Micro-fibrillated lignocellulose is able to form stable styrene in water (o/w) emulsion compared to other cellulosic materials such as micro-fibrillated cellulose and cellulose nanocrystals.

The underlying mechanism of this stabilisation is assumed to be on one hand a Pickering mechanism (Pickering 1907) and on the other hand a network formation mechanism. The tendency of the MFLC material towards amphiphilic behaviour, meaning that the material shows domains of higher polarity and also domains of lower polarity, found by (Gindl-Altmutter et al. 2015), is also a crucial factor in the emulsion stabilisation.

2 Literature review and theoretical background

2.1 Emulsions stabilised by cellulosic materials – State of the art

This section shall summarize the current level of knowledge concerning cellulosic material used as a stabiliser in emulsions. It shall give an overview on how cellulosic material is used as a stabiliser, how it is modified and what form of cellulose is used.

A lot of research has been done in the field of cellulose nano-crystals. Kalashnikova et al. (2011), for example, reports the successful stabilisation for several months of hexadecane-in-water emulsions with bacterial cellulose nano-crystals (BCNs). The researcher varied the concentration of the bacterial cellulose nano-crystals in the aqueous suspension from 0-5 g/L and found out that emulsions were unstable below and stable over 2g/L even after inducing stress by centrifugation. Without centrifugation emulsions were stable for several months with whatever concentration was used. In another work of Kalashnikova et al. (2013), three different sources of cellulose nanocrystals were used: namely cellulose from cotton, from bacterial cellulose and from green algae. It could be shown that the aspect ratio directly influences the coverage ratio. As the source of nano-crystals varies it could also be shown that it is possible to process partly or completely covered droplets in the range from 40 to 100% depending on the source and weight of nano-crystals.

Carrillo et al. (2015) were able to prepare multiple emulsions with cellulose nano-fibrils (CNF) consisting of water in oil (w/o) droplets dispersed in an external aqueous phase, a so-called water-in-oil-in-water (w/o/w) emulsion. The researcher prepared this emulsion in a single step in contrast to processes that involve multiple steps. Regarding modified cellulose nano-fibers, Lee et al. (2014) measured the water uptake of neat and modified bacterial cellulose nanofibers (BCNs). They found out that neat BCN exhibited the highest water and the lowest toluene uptake compared to BCN hydrophobized by esterification with organic acids. A decrease in water uptake and an increase in toluene uptake was observed with hydrophobized BCN. Another interesting work was done by Nikfarjam et al. (2015) where surfactant-free Pickering emulsions of styrene in water/oil/water were prepared and polymerized. The researcher used cellulose nano-fibrils as a stabilizer to produce VOC-free expandable polystyrene beads so that well-dispersed water microdroplets in the styrene beads could act as a blowing agent and replace the harmful volatile hydrocarbon.

The term cellulose nano-fibrils (CNF) and micro-fibrillated cellulose (MFC) are often used synonymously. Micro-fibrillated cellulose used for soybean oil-in-water emulsions was investigated by Winuprasith & Suphantharika (2015) where the scientists varied the MFC concentration in the aqueous phase from 0.05 to 0.70%. Here the mean droplet size of the emulsion increased with increasing MFC concentration. Furthermore it could be shown that the particles mainly adsorb at the oil/water interface of the emulsion. Cellulose nanofibrils hydrophobized and used as a stabiliser were investigated by Lif et al. (2010). In this study a surfactant, in combination with cellulose as the stabiliser, was used for emulsions. The MFC was used in its hydrophilic form and also hydrophobically modified. It is reported that the most stable emulsions could be achieved by using a combination of hydrophilic (untreated) and hydrophobic MFC.

Cellulose can also be used in the form of hydrophobically modified cellulose to stabilise emulsions. This subject was investigated by Sun et al. (2007). The researcher found out that the used hydrophobically modified hydroxyethyl cellulose (HMHEC) can successfully stabilise oil-in-water emulsions and also lowers the interfacial tensions at the cellulose/oil/water interface. Furthermore, they report a decrease in droplet diameter with increasing HMHEC concentration. In another study, Jia et al. (2015) stabilised oil-in-water emulsion with amorphous cellulose. It was reported that emulsions that were prepared with cellulose content of 0.07-0.56% are not stable against creaming, whereas emulsions with cellulose content above 0,83% remain stable for months. For better visualisation of the fibres a styrene-in-water emulsion stabilised by amorphous cellulose was polymerised by the oil-soluble radical initiator AIBN.

2.2 Cellulose

Cellulose is a fibrous, tough and water-insoluble substance that is found in the protective cell walls of plants. It is not only found in lower and higher plants but also in bacteria, fungi, animals as well as in some amoebas. The main function of cellulose is to give and maintain the structure of plants and other living species. Cellulose is produced everyday by these living species. A tree for example produces 10g of cellulose per day. (Dufresne 2013)

The cellulose molecule in its simplest form is composed of β-1,4 glucan chains that are interacting with each other and that can be arranged in different ways. Within the same microfibril there can be crystalline and noncrystalline forms of cellulose depending on the way the glucan chains associate. (Brown & Saxena 2007)

The chemical formula of Cellulose is $C_6H_{11}O_5$ – $(C_6H_{10}O_5)_{x-2}$ – $C_6H_{11}O_6$. It is the equivalent chemical formula to starch and callose with the difference in the above mentioned β-1,4 glucan linkage. (French & Glenn 2007)

Furthermore, cellulose has one reducing end that contains an unsubstituted hemiacetal and a non-reducing end that contains an additional hydroxyl group. The two major crystalline arrangements of cellulose are called cellulose I and II, being defined by their unit cell parameters. The most native celluloses consist of cellulose I, while celluloses that have been either dissolved and regenerated or treated with concentrated alkaline solution and then washed with water consist of cellulose II. The transformation from cellulose I to II is irreversible. (Wertz et al. 2010) The following image (Fig. 1) shows the reducing and non-reducing end of cellulose and also points out the numbering of the carbon atoms.

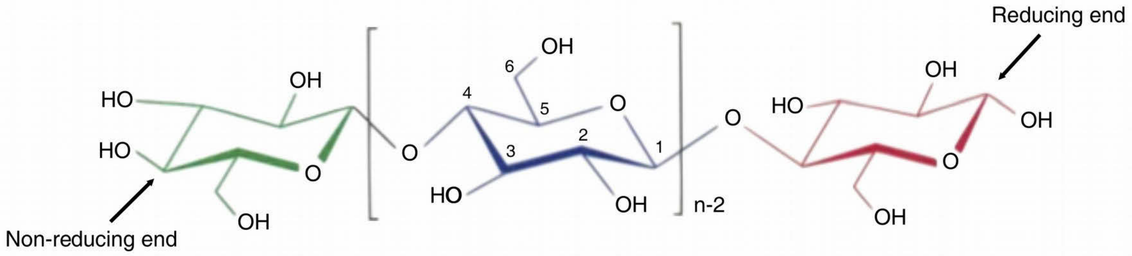

Fig. 1: Molecular structure of cellulose showing the numbering of the carbon atoms and the reducing and non-reducing ends. (After Wertz et al. 2010)

Each monomer of cellulose bears three hydroxyl groups, which is one of the most specific characteristics of cellulose. For the physical properties of cellulose and also for the crystalline packing, these hydroxyl groups and their bonding ability play a major role. (Dufresne 2013)

2.3 Emulsions

Mollet et al. (2008) define an emulsion as a thermodynamically unstable dispersion of two insoluble liquids, such as water and oil. In an emulsion, one of the components is present in the form of finely distributed spherical droplets in the second phase, called the continuous phase. If the oil is dispersed in water the emulsion is termed as an oil-in-water (o/w) emulsion. If water is dispersed in oil the emulsion is referred to as a water-in-oil (w/o) emulsion.

Emulsion stability can be weakened or destabilised by different mechanisms such as creaming, sedimentation, flocculation, and coalescence. Creaming is the separation process due to an upward motion of emulsion droplet with lower density than the continuous phase. If droplets, with higher density than the continuous phase, descend to the ground, sedimentation occurs. Flocculation is the process when droplets aggregate into flocks, which can happen when droplets collide and adhere due to long-range van der Waal's attraction. The process when droplets merge and form bigger droplets is called coalescence. Another destabilisation mechanism is Ostwald ripening, which occurs when the dispersed phase is somewhat soluble in the continuous phase. (Karlberg et al. 2005)

2.3.1 Surface activity and Surfactants

Short-chain fatty acids and alcohols are substances that are soluble in both water and oil and are therefore referred to as amphiphilic. The hydrocarbon part of a molecule is responsible for its oil solubility, while the polar carboxy or hydroxy group shows affinity for water. Present at an oil-water interface, the hydrophilic head will be buried in the water and the lipophilic hydrocarbon chain will be stretched out into the oil phase. (Mollet et al. 2008) An example for such an amphiphilic molecule is stearic acid shown in the following image (Fig. 2).

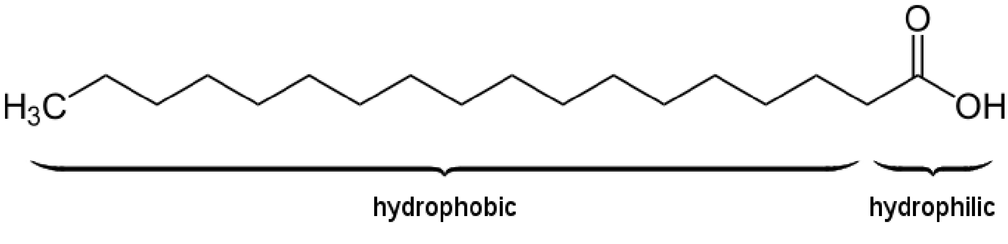

Fig. 2: Typical amphiphilic molecule: stearic acid. Showing the hydrophobic and the hydrophilic part of the molecule

The term surfactant stands for <u>sur</u>face <u>act</u>ive <u>a</u>gen<u>t</u> and is a substance that lowers the surface tensions of a medium in which it is dissolved or the interfacial tension with other phases. A surfactant which, when present in small amounts, can facilitate the formation of an emulsion is called an emulsifier. It can also enhance its colloidal stability by reducing either or both the rates of the aggregation and coalescence. (IUPAC 2001)

2.3.2 Emulsion Stabilisation

One way to produce long-lived emulsions is with the help of a third component, the above-mentioned emulsifier. The emulsifier accumulates at the interface and forms a protective layer in the form of a tough and elastic film that is not broken when droplets collide. Often a tenside can act as an emulsifier. An emulsifier must show good surface activity and must create low surface tension. (Mollet et al. 2008)

Another way to stabilize emulsions can be achieved with the help of solid particles. For example, finely divided particles that are smaller than the droplets in the emulsion and that are well wetted by the water or the oil phase can be used to stabilise emulsions. These particles accumulate at the water/oil phase boundary in the form of a solid layer preventing coalescence. (Mollet et al. 2008) This stabilisation by adsorption of solid particles onto the droplet surface is referred to as 'Pickering stabilisation'. (Pickering 1907) (Slomkowski et al. 2011)

2.3.3 Differences and similarities of solid particles and surfactants

As we have now heard that solid particles can also stabilise emulsions in a similar way as surfactants do, details of these two substance classes shall be presented here.

Regarding surfactants and their outcome of an emulsion (o/w or w/o), the size of the head group (HLB – hydrophile-lipophile Balance) is the most important factor. For a hydrophilic surfactant the area per head group is larger than that of the chain resulting in oil-in-water (o/w) emulsions. Lipophilic surfactants, where the area per chain exceeds that of the head group, will result in a water-in-oil (w/o) emulsion. For spherical particles which adsorb to the interface, the relevant parameter is the contact angle θ between the particle and the interface. Regarding hydrophilic particles, the measured contact angle θ into the aqueous phase is usually below 90° where a larger fraction of the particle resides in the water. Hydrophobic particles have, in general, a contact angle θ of higher than 90°. Here the particles reside more in oil than in water. The emulsion will result in oil-in-water when $\theta<90°$ and water-in-oil when $\theta>90°$. (Binks 2002)

Because of the high energy of attachment of particles to interfaces, the particles are thought of as being effectively irreversibly adsorbed once the attachment happens. In sharp contrast to this it should be mentioned that surfactant molecules adsorb and desorb on a relatively fast timescale. (Binks 2002)

Another difference between particles and surfactants that Binks (2002) mentions is the fact that particles do not aggregate in the same way that surfactant molecules form micelles, which results in an absence of solubilisation phenomena in the particle case.

2.4 Polystyrene

For polystyrene (PS) and general purpose polystyrene (GPPS) the chemical structure is a polyethylene backbone with laterally attached phenyl rings (Fig. 3). Those phenyl rings are responsible for the high glass transition temperature T_g of 100°C and high refractive index. Main characteristics of GPPS are high stiffness, brilliance, gloss, and hardness. It is used as transparent food packaging, beakers, shower cabinets, lamp covers, and many more applications. (Niessner & Wagner 2013)

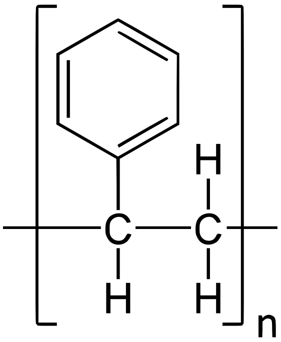

Fig. 3: Chemical formula of polystyrene. It consists of a polyethylene backbone with laterally attached phenyl rings.

For the production of polystyrene, continuous solution polymerisation is the most important method, although suspension polymerisation is also used. Because of its bulky rigid chains, polystyrene has good strength and high-dimensional stability. Typical elongation is in the range of 1-3%. (Su 2013)

To get from general purpose polystyrene to high-impact polystyrene (HIPS) and overcome the brittleness of GPPS, the material is modified by the incorporation of butadiene-based rubber. HIPS is opaque, due to light scattering at rubber particles with different refractive indexes. It is possible to create a translucent and in thin layers a near-transparent material when the particle size is reduced. (Niessner & Wagner 2013)

2.4.1 Suspension polymerisation

The process of suspension polymerisation involves mechanically dispersing a monomer in an incompatible liquid, which is usually water. The resulting monomer droplets are polymerised by use of a monomer-soluble initiator. By continuous agitation and the use of stabilisers, the monomer is kept in suspension. Such stabilisers can be polyvinyl alcohol or methyl cellulose (ether). The obtained granular beads are easy to handle and can be isolated by filtration. Polystyrene, poly(vinyl chloride), and poly(methyl methacrylate) are examples that have been prepared by this method. (Su 2013)

The advantages of suspension polymerisation are that the heat can be readily dispersed, the low viscosity, and that the polymer obtained in granular form may be used directly. On the other hand, the disadvantages are that washing and/or drying is required, that agglomeration may occur, and that a contamination by the stabilizer may occur. (Su 2013)

3 Materials and methods

The study in this paper roughly consists of three parts:

In the first part (**Part A**), three different cellulosic materials were mixed with deionized water and these three cellulose-water suspensions were then mixed with 10% of styrene to observe the emulsion behaviour over time. In addition to that, fluorescent dyes were added to each of the cellulose-water-styrene emulsions in a later step, and observed under a fluorescent microscope.

In the second part (**Part B**), only two of the previous cellulosic materials (MFLC and MFC) were again mixed with water and styrene. This time reactive styrene was used. With the help of a radical starter and heat, these cellulose-water-styrene emulsions were polymerised. Furthermore, a reference sample of pure styrene was polymerised.

In **Part C**, MFC and MFLC were characterised by AFM topography method. In addition to that, the polymerised materials (MFLC-PS, MFC-PS and pure polystyrene) were analysed using electron scanning microscopy (SEM).

In the following part the preparation of the cellulosic material, the used materials in general, the concentration used, and the mixing will be described in detail.

3.1 Part A

For the first part, three different cellulosic materials, already in an aqueous suspension, namely micro-fibrillated cellulose (MFC), micro-fibrillated lignocellulose (MFLC), and cellulose nano-crystals (CNC) were mixed with deionized water with three different concentrations each. The concentrations used for every cellulosic material were 0.1, 0.5, and 0.7% dry mass in the aqueous suspension. In the next step the aqueous suspensions were mixed, using an UltraTurrax Mixer, with styrene in a ratio of 9:1 (90% aqueous suspension and 10% styrene). These emulsions were then filled into glass tubes and observed after one, three, four hours, and after several days.

For the fluorescent microscopy small amounts of the above mentioned suspensions were produced and mixed with fluorescent dyes, namely Calcofluor White stain, Nile Red, and Nile Blue. Calcofluor is a chemical substance that bonds to cellulosic material, whereas NileRed bonds to nonpolar substances, and NileBlue bonds to polar substances like water. With all these dyes combined it is possible to distinguish the main substances of the emulsion (cellulose, water, and styrene) using the fluorescent microscope.

3.2 Part B

For the polymerisation of styrene in the emulsions (Part B) the inhibited styrene had to be distilled to produce reactive styrene in a first step. See 'Distillation of styrene' for further information. In the next step an aqueous suspension with 0.5% (w/w) dry mass of micro-fibrillated lignocellulose was mixed with 10% of reactive styrene. In total, 450g of aqueous suspension was mixed with 50g of reactive styrene. To this 1570mg of the radical starter AIBN was added. The emulsion was then put into a round-bottomed flask and heated up to 100°C for 12 hours. With the help of a magnetic stir bar the emulsion was stirred, which became more and more difficult the higher the viscosity became. This process was repeated for the aqueous MFC-styrene emulsion with the same amount of radical initiator. So again 450g of MFC-water suspension and 50g of styrene was used.

For the polymerisation of pure styrene, 42g of reactive styrene mixed with 1320mg of AIBN were put into a round bottomed flask and heated up to 100°C for 12 hours. Again the liquid was stirred with a magnetic stir bar.

3.3 Part C

In this part AFM topography images were made of MFC and MFLC to characterize the size and diameter of the fibrils of these two cellulosic materials. For this purpose the cellulosic material was diluted to 0.001% dry mass in an aqueous suspension and two drops were then put onto a mica slide and dried in an oven for 10 minutes at 103°C.

To view the fibres in the MFLC-PS and MFC-PS composite after polymerisation Scanning electron microscopy (SEM) was used. Images of MFLC-PS, MFC-PS and pure polystyrene were taken.

3.4 Distillation of styrene

The distillation of unreactive styrene was done to remove the inhibitor and therefore obtain pure reactive styrene.

For the distillation the styrene was put into a round-bottomed flask which was then put into a bowl filled with oil to heat the round-bottomed flask evenly. The round-bottomed flask was connected to the receiver flask over the water-cooled condenser. Furthermore, the receiver flask was cooled with icewater and to the flask itself vacuum was applied.

The oil was heated up to 66-67 °C and after a while the styrene started to evaporate and the vapour slowly condensed in the condenser. The drops of the reactive styrene were then collected in the cooled receiver flask. The whole distillation process took several hours for small amounts of reactive styrene.

3.5 Preparation of micro-fibrillated cellulose

The cellulose used was obtained from the University of Maine. In order to produce micro-fibrils the cellulose was further diluted with deionized water to a dry mass content of 1% cellulose and was then processed in an APV high-pressure homogeniser. It was processed for 15 passes at a pressure that was continuously increased up to 650 bar.

3.6 Preparation of micro-fibrillated lignocellulose

For the production of micro-fibrillated lignocellulose (MFLC) solid beech chips that had been applied to an organosolv treatment were used as the starting material. These small wood chips were mixed with deionized water and added to a grinder, where the cellulosic material was processed between two grinding discs using a Masuko Supermasscolloider at 1500 rpm and a gap clearance of up to 50µm. The material was still very coarse after the first passes and became fine after several passes as the distance between the grinding discs was reduced.

After the grinding, the concentration of the material was reduced to 1% dry mass in the aqueous suspension and was further processed in an APV high-pressure homogeniser. The lignocellulosic material was processed for 15 passes at a pressure that was continuously increased up to 600 bar.

3.7 Cellulose nano-crystals

The CNC used were obtained from University Maine and diluted to the desired concentration. Cellulose nanocrystals are cellulosic nanoparticles that are prepared by using a chemical acid hydrolysis process which dissolve amorphous chains from the cellulose fibres and therefore release crystal domains. They have a more defined geometry of rod-like nanoparticles compared to micro-fibrillated cellulose. (Dufresne 2013)

3.8 Styrene

The used Styrene was obtained from SIGMA-ALDRICH. It had a molecular weight of 104.15 g/mol and contained 4-tert-butylcatechol as a stabiliser.

3.9 The radical starter – AIBN

For the polymerisation process the radical starter alpha,alpha-Azoisobutyronitrile (AIBN) obtained from MOLEKULA with a molecular weight of 164.21g was used.

3.10 Fluorescent dyes

As fluorescent dyes: Nile red and Nile blue, both obtained from ROTH, were used. Calcofluor White Stain in a liquid form was obtained from Fluka. Molecular weight is 318,38 g/mol for Nile red and 732,84 g/mol for Nile blue. Nile red and Nile blue had to be dissolved in styrene as they were purchased as a powder. For this reason Nile red and Nile blue were dissolved to 0.25% (w/w) in inhibited styrene. As Calcofluor White Stain was already available in its liquid form it could be used as obtained.

3.11 High Shear Mixer

Throughout the study a 'T10 basic ULTRA-TURRAX®' from IKA was used to mix the cellulose-water-styrene emulsions. This mixer has a speed range of 8000 to 30000 rpm. When used for mixing, the speed was increased continuously up to 30000 rpm. Emulsions were mixed for one to three minutes until a homogeneous emulsion was achieved.

3.12 Supermasscolloider

For the grinding of the wood chips, that had been applied to an organosolv treatment, a 'Supermasscolloider MKCA6-2J CE' from MASUKU SANGYO CO was used. It has a speed of 800 to 3000 rpm at 50 Hz. When processing the wood chips, a gap clearance of 50µm was set.

3.13 High pressure homogeniser

With the laboratory homogeniser 'APV-1000' from SPX Flow Technology the cellulosic material was fibrillated and homogeneously processed. The homogeniser is able to produce a maximum pressure of 1000 bar and has a throughput rate of 22 liters per hour.

4 Results and discussion

In the following section the results will be shown and discussed. The results will be listed according to the order mentioned in the Materials and Methods Chapter.

4.1 Results of Part A

The first picture (Fig. 4) shows the three different emulsions after mixing, after one, three, and four hours and shall give a quick overview on how the emulsions change in the first few hours.

The three brown glass tubes on the left are MFLC-water-styrene emulsions with MFLC concentration of 0.1, 0.5 and 0.7% (w/w) in the aqueous suspension. The next three glass tubes are emulsions of styrene in CNC-water. The concentrations of CNC in water are again 0.1, 0.5 and 0.7% (w/w). The last three glass tubes on the right are MFC-water-styrene emulsions with the same concentrations as mentioned before.

Fig. 4: Water-styrene emulsions after mixing (a), after one(b), three(c) and four(d) hours. From left to right: MFLC, CNC and MFC with concentrations of 0.1, 0.5 and 0.7% (w/w) each.

The picture on the top shows the emulsions immediately after mixing and also if and how well the cellulosic material was able to stabilise the emulsions. It can be seen that the 0.5% and 0.7% MFLC emulsions could be stabilised quite well whereas the emulsion with 0.1% MFLC was only able to stabilise about half of the dispersion. As water has a higher density than the emulsion, the emulsion part has risen to the top. The effects of aggregation or coalescence cannot be seen, however.

If we observe the MFLC emulsions after some hours, the effect of the already mentioned water separation can also be seen for the 0.5% and 0.7% emulsions. The lower the concentration, the bigger the water part that separates.

Immediately after mixing the CNC-water-styrene emulsions have a white foggy colour and it can be seen that some phase separation has already occured.

Furthermore, the styrene drops aggregate on top in the glass tube and obviously some coalescence has happened as the drops are large in size. Observing the behaviour over time of the CNC emulsion, it can be seen that the colour of the emulsions is getting brighter and clearer. It can be seen that phase separation has happened but the styrene is, even after some hours, still aggregated in drops on top in the glass tubes.

When observing the MFC-water-styrene emulsion the good stabilisation mechanism of the MFC can be seen. Only the 0.1% MFC emulsion shows some separation of water, while the other concentrations are completely stable immediately after mixing and also after 4 hours. Compared to the lignocellulosic material, no water separation occurs at a concentration of 0.5 and 0.7% for the MFC stabilised emulsions. This effect could be attributed to the partial hydrophobicity of the MFLC and the high hydrophilicity of the MFC. The MFLC contains a high residual lignin content which shows hydrophobic behaviour and therefore might repel water to some degree. The MFC on the other hand does not contain lignin at all and therefore links well with water.

4.1.1 Emulsions stabilised by MFLC

The following picture(Fig. 5) shows the emulsions stabilised by MFLC before mixing (a), after mixing (b), after one(c), three(d), four(e) hours and after one(f), eight(g) and twelve(h) days. Concentrations are 0.1, 0.5 and 0.7% (w/w) in the aqueous suspensions from left to right in each picture.

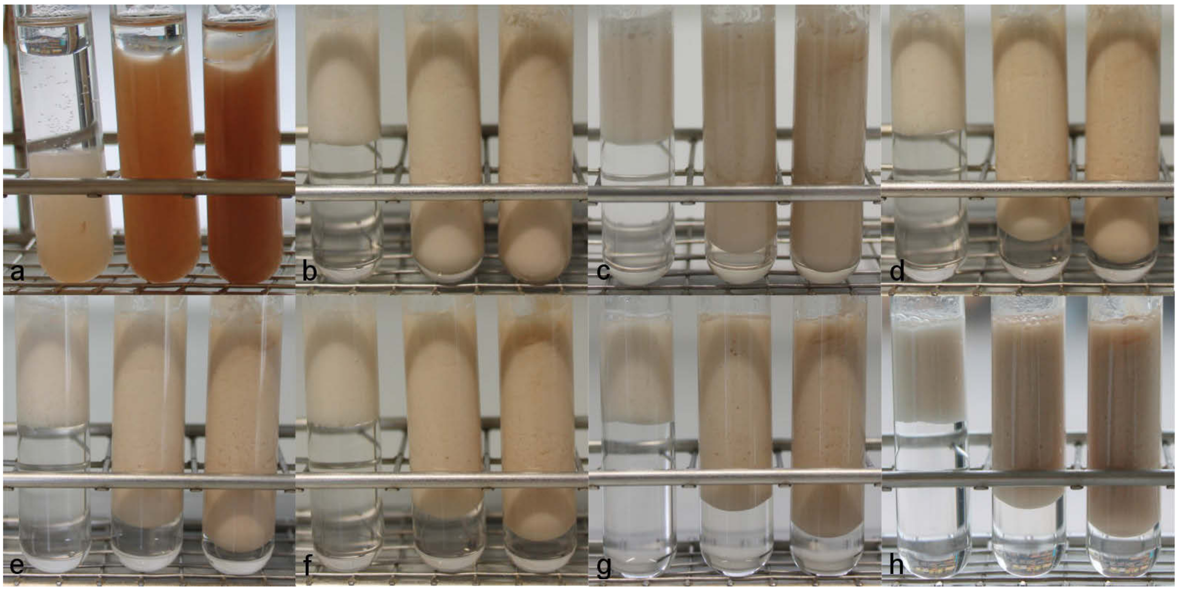

Fig. 5: Emulsions stabilised by MFLC before mixing(a), after mixing(b), after one(c), three(d), four(e) hours, after one(f), eight(g) and twelve(h) days. Concentrations are 0.1, 0.5 and 0.7% from left to right in each picture.

In image (a) the emulsion is not yet mixed and the styrene is located on top as it has a lower density than water. The first glass tube has the lowest concentration of 0.1% and shows separation of water before mixing. That could be attributed to the fact that MFLC is partly hydrophobic and does not bond so well to the water molecules. The very low concentration could also be a reason for the partial water separation. The higher concentrated emulsions in picture (a) do not show any phase separation nor any sedimentation, and it can be seen that the concentration also affects the colour of the aqueous suspension. It gets darker with a higher concentration.

The following pictures (b to h) show the emulsions after several hours and days. It can be seen that the lower the MFLC concentration, the bigger the water part that separates. In all pictures, the 0.7% emulsion has the lowest and the 0.1% emulsion has the highest water separation. Nevertheless all emulsions can be stabilised by the fibrous material and no sedimentation or coalescence of the styrene phase occurs.

4.1.2 Emulsions stabilised by CNC

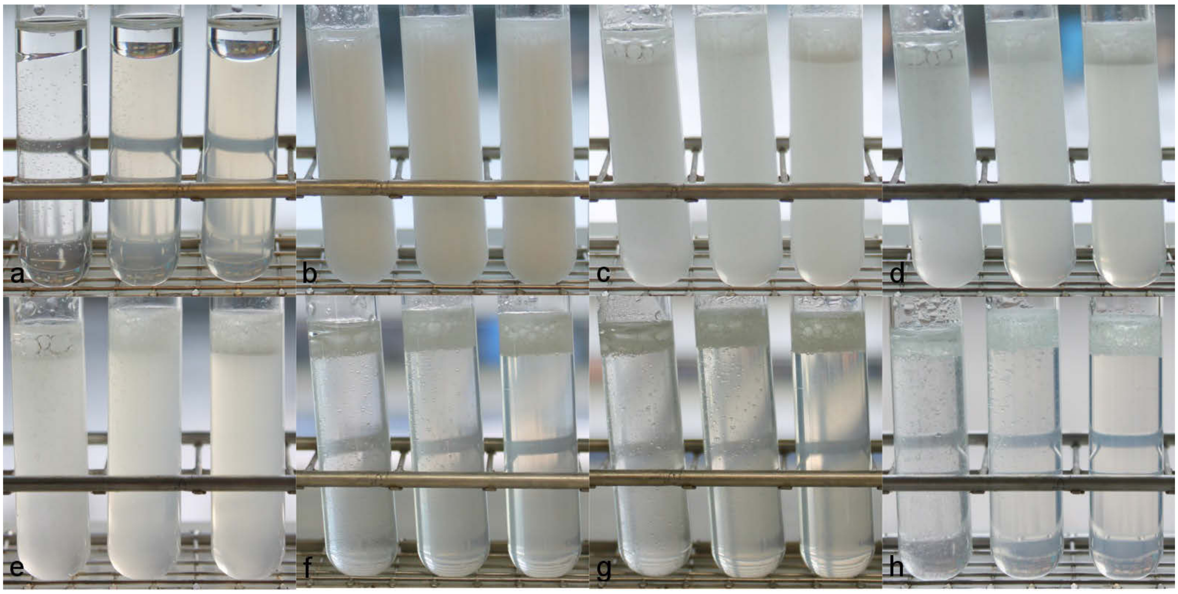

Fig. 6: Emulsions stabilised by CNC before mixing(a), after mixing(b), after one(c), three(d), four(e) hours, after one(f), eight(g) and twelve(h) days. Concentrations are 0.1, 0.5 and 0.7% from left to right in each picture.

In Fig. 6 the emulsions stabilised by the CNC are illustrated. Again the emulsions are shown before mixing (a), after mixing (b), after one(c), three(d), four(e) hours and after one(f), eight(g) and twelve(h) days.

In the first picture (a) the aqueous suspension and the separated styrene part can be seen located on top. Due to the lower density of styrene it is located above the CNC-water suspension. After mixing (b) the colour of the emulsions change and already aggregation and creaming of the styrene has occurred. When observing the emulsions over time, a colour change can be seen again. The emulsions are quite opaque in the beginning (b and c) and become more and more transparent after some hours and days (d to h). It seems that in all pictures styrene has aggregated to drops on the top of the glass tubes and that the drops are smaller in size the higher the CNC concentration is. A stabilisation mechanism of the CNC cannot be seen in whatever concentration is used. This can have several reasons and does not mean that CNC cannot stabilise emulsions in general. One reason could be the absence of network formation and the resulting low viscosity of the liquid.

4.1.3 Emulsions stabilised by MFC

Fig. 7 illustrates emulsions stabilised by MFC before mixing (a), after mixing (b), after one(c), three(d), four(e) hours and after one(f), eight(g) and twelve(h) days.

Fig. 7: Emulsions stabilised by MFC before mixing(a), after mixing(b), after one(c), three(d), four(e) hours, after one(f), eight(g) and twelve(h) days. Concentrations are 0.1, 0.5 and 0.7% from left to right in each picture.

Picture (a) shows the styrene above the MFC-water suspensions before mixing, where the lower density of the styrene can be noted. After mixing the two emulsions with higher concentrations (0.5 and 0.7%) they can be stabilised completely while the 0.1% emulsion shows water separation, which increases after one, three and four hours and stays constant after one, eight and twelve days.

The emulsions stabilised with higher concentrations don't show any water separation nor any creaming or sedimentation. The good stabilising effect could be attributed to the hydrophilicity and possible hydrophobicity of the fibres and also to the network formation that results in high viscosity and prevents styrene droplets to coalesce or to cream.

4.1.4 Fluorescence microscopy images of MFLC and MFC-water-styrene emulsions

The first Illustration (Fig. 8) shall give an overview of fluorescent microscopy images of the emulsions stabilised by MFLC and MFC with the used fibre concentrations. On the left side, the MFLC emulsions, and on the right side the MFC emulsions can be seen. As the images are fluorescent microscopy images the red colour indicates nonpolar substances (styrene), the bright blue colour indicates cellulosic material (fibrils, cell wall parts) and the black colour shows polar substances (water).

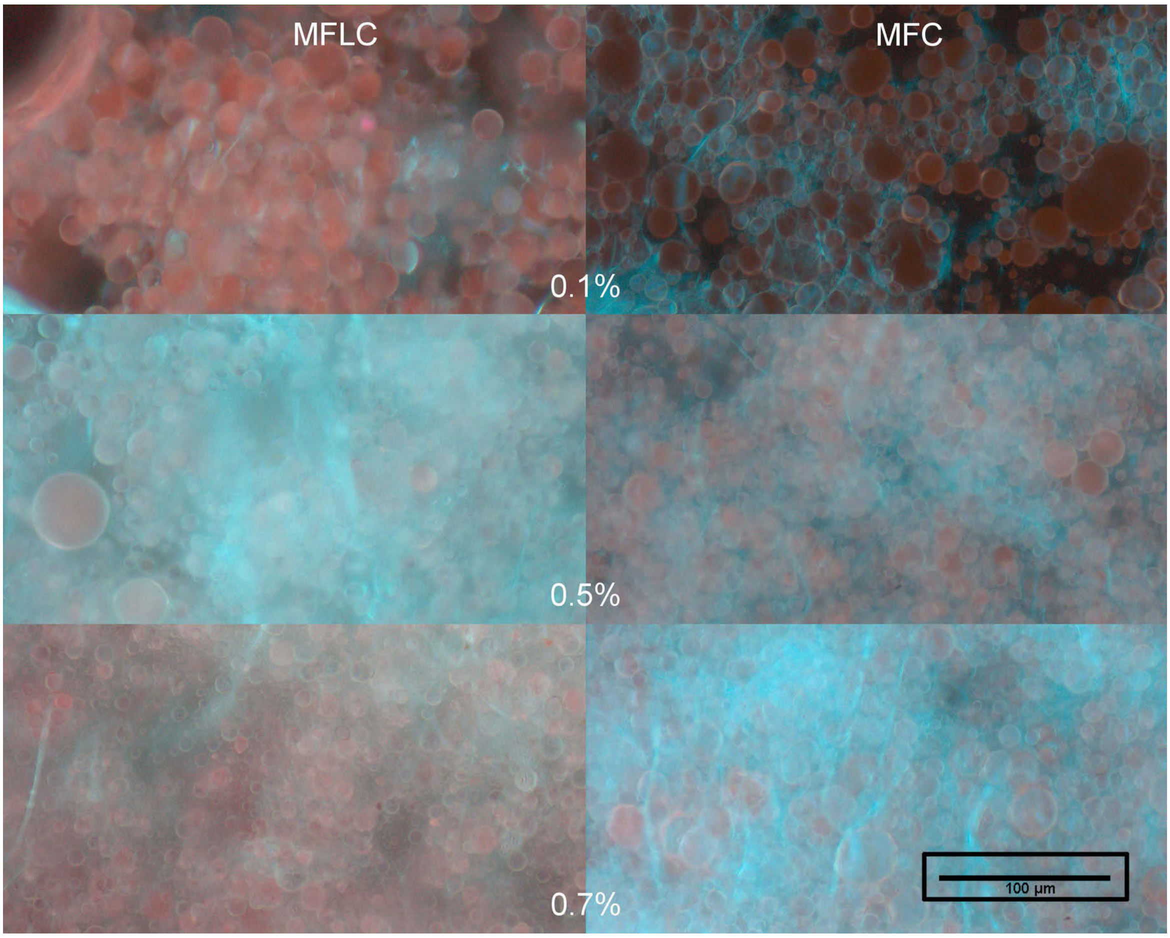

Fig. 8: Fluorescence microscopy images of emulsions stabilised by MFLC and MFC with 0.1, 0.5 and 0.7% cellulosic material (w/w) in the aqueous dispersion.

The emulsions with lowest used fibre concentration (0.1%) can be seen in the first row. It seems as if the MFLC 0.1% styrene droplets are slightly bigger in size compared to the 0.1% MFC emulsion droplets and also compared to other concentrations where on average droplets are smaller in size.

The MFC but also the MFLC achieves stable emulsions with small droplet sizes. Increasing the cellulose concentration (from 0,1 to 0,7%) causes, in general, better stabilisation of the emulsion with reduced droplet size. In all images, fibrils, indicated by the blue or white colour that can be seen and it is assumed that even smaller fibrils are attached to the droplets which can be noted as bright edges around the styrene drops.

The next image (Fig. 9) shows two styrene droplets with fibrils wrapped around the droplet surface. The left picture shows an MFLC-water-styrene emulsion, while the right picture shows a MFC-water-styrene-emulsion The droplets, ranging from 50 to over 200µm in diameter, are big in size as they have been mixed by hand and have not been prepared using an UltraTurrax high shear mixer.

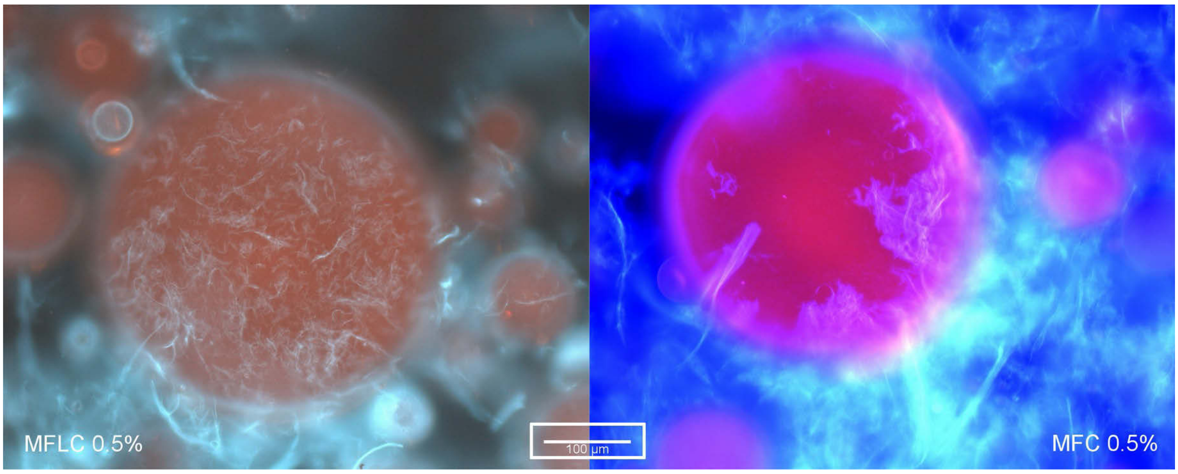

Fig. 9: MFLC and MFC water-styrene emulsion with fibrils attached to the styrene droplets. Emulsion was mixed by hand.

The image shows very well that fibrils are attached to the surface of the styrene and therefore it can be concluded that the same thing happens when mixed by an UltraTurrax high shear Mixer using different cellulose concentrations. Again the bright edge around some droplets, indicating fibrous material, can be noted. This obvious attachment of the fibres is often not visible in the other fluorescence microscopy images as the styrene droplets are much smaller and the resolution of the microscopy images is low.

4.1.5 Comparison of MFLC emulsions with different fibre concentrations

In order to view differences caused by fibre concentration in MFLC emulsions Figure 10 is given. On the left side you can see emulsions with the three different concentrations, while the right side only shows the nonpolar styrene droplets. The small droplet size in the 0.5 and 0.7% emulsions can be seen clearly. In all emulsions the droplets are packed quite densely, where the packing density increases with fibre concentration in the emulsion.

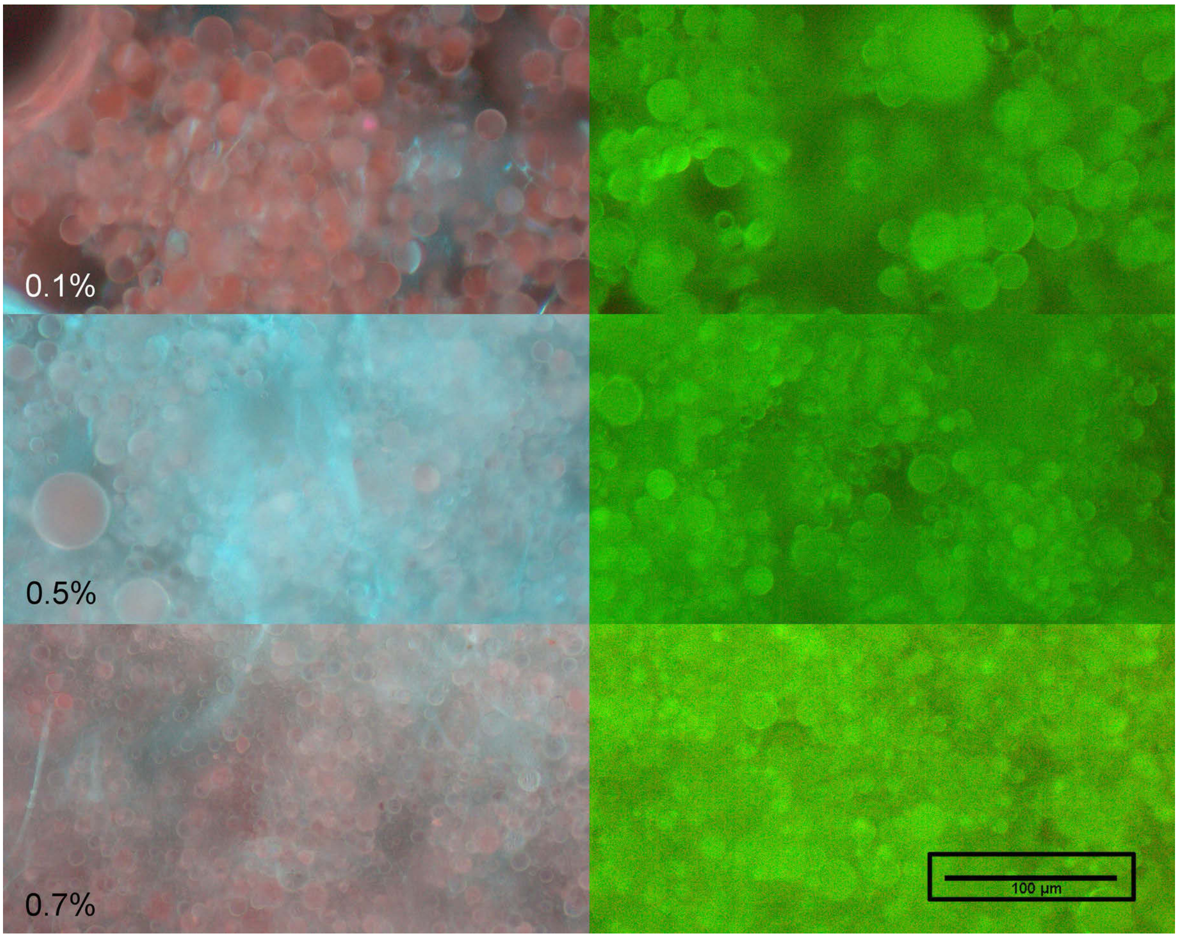

Fig. 10: Fluorescence microscopy images of MFLC water-styrene emulsions with different concentrations. The right side shows only nonpolar substances (styrene) in the emulsion.

4.1.6 Comparison of MFC emulsions with different fibre concentrations

Figure 11 compares the three different concentrations of the MFC emulsions. The image shows the emulsions with all their components on the left, while the right side only displays nonpolar substances. The emulsions with the 0.5 and 0.7% MFC concentration seem to have the smallest styrene droplets in comparison to the 0.1% emulsion. As already observed at the MFLC emulsion, that the drops are packed quite densely in higher fibre concentrated emulsions, this is also the case for MFC water-styrene emulsions.

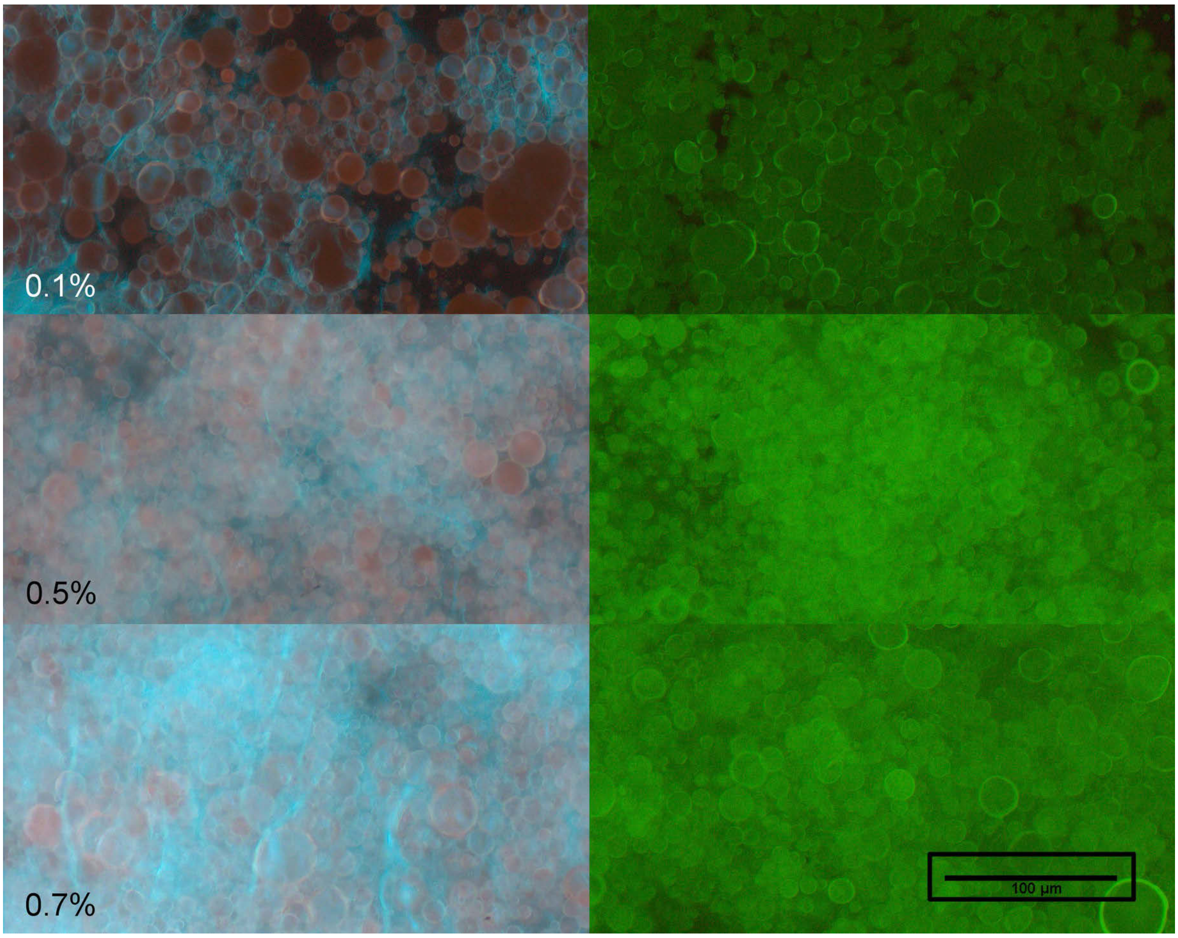

Fig. 11: Fluorescence microscopy images of MFC water-styrene emulsions with different concentrations. The right side shows only nonpolar substances (styrene) in the emulsion.

4.1.7 Droplet diameter distribution of MFLC and MFC water-styrene emulsions

In the next image (Fig. 12) droplet diameter distribution of MFLC and MFC stabilised emulsions are given. The droplet diameter distribution is given in a box plot chart where the droplet diameter is shown on the ordinate and each fibre concentration of MFC and MFLC is given on the abscissa.

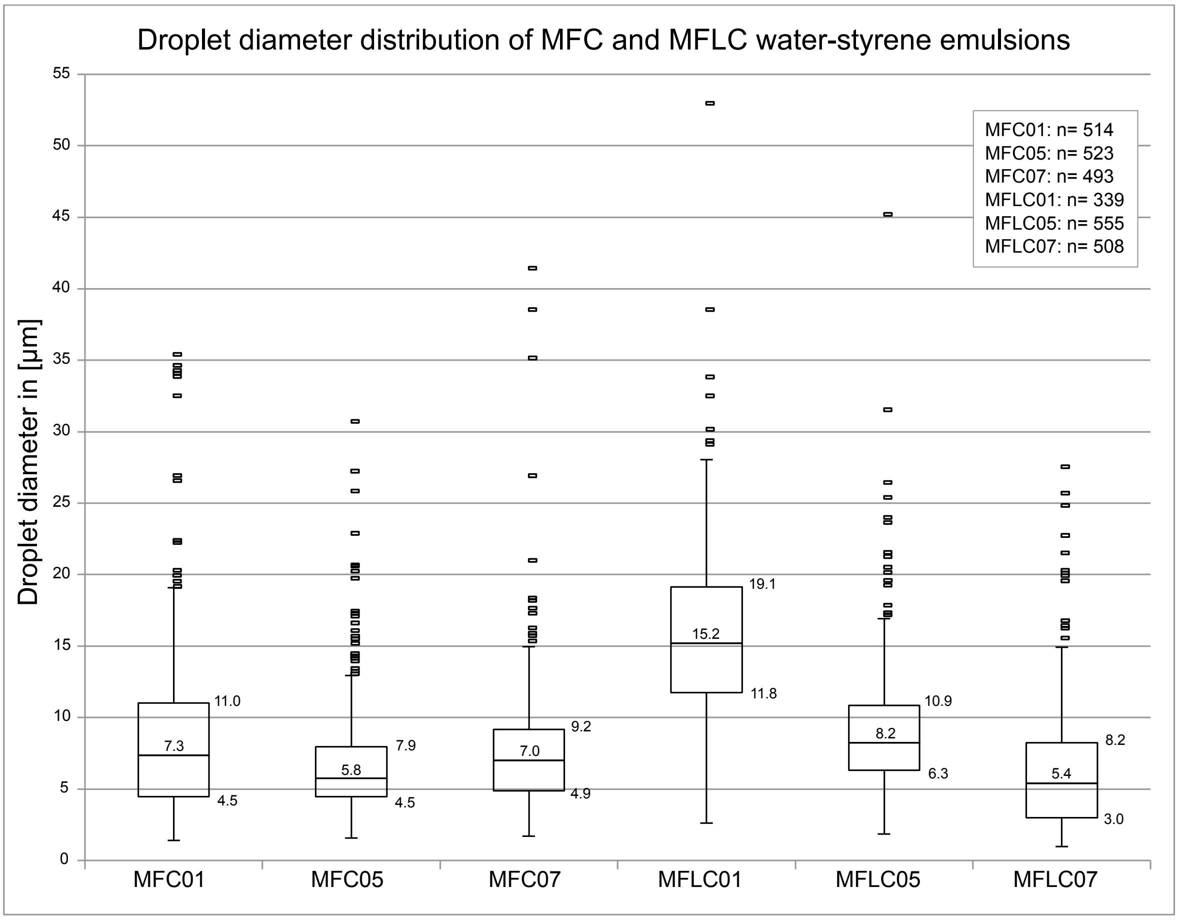

Fig. 12: Droplet diameter distribution of MFC and MFLC water-styrene emulsions. Number of samples is shown in the top right corner.

Regarding the MFC emulsions, it can be seen that all of them have, in general, a similar droplet diameter distribution. For the 0.1% MFC emulsion, 50% of the droplets are in the range of 4.5 to 11µm. 25% are smaller than 4.5µm and 25% are bigger than 11µm. Some outliers can also be seen in the box plot chart that have droplet diameters in the range of 20 to 36µm.

The emulsions of MFC 0.5 and 0.7% are very similar in droplet diameter distribution where the median of MFC 0.5% emulsion is slightly lower than the median of the MFC 0.7% emulsion. Both emulsion have outliers that go up to about 31µm (MFC 0.5%) and 42µm for the MFC 0.7% emulsion. It is also interesting that there is a big difference between the MFC 0.1% and the MFLC 0.1% emulsion in droplet diameter. A significant difference in droplet diameter between the other concentration of MFC and MFLC is not visible.

When observing the MFLC emulsions the MFLC 0.1% emulsion has a very noticeable droplet diameter distribution. Droplet diameter ranges from about 2.5 to

28µm with outliers going up to about 53µm. When comparing the MFLC 0.1% emulsion with the higher MFLC concentrations a decreasing median can be seen. The median of the MFLC 0.5% emulsion has a value of about 8.2 while the median of MFLC 0.7% emulsion is 5.4.

It can be concluded that the droplet diameter of the MFLC emulsions decreases with increasing fibre concentration in the aqueous suspension. This decrease in droplet diameter with increasing concentration was also found by (Sun et al. 2007) where HMHEC was used as the stabiliser. A trend for the MFC stabilised emulsions, however, cannot be recognised. In a study of (Winuprasith & Suphantharika 2015), an increase in droplet size with increasing MFC concentration could be shown where the concentration in the aqueous suspension have been varied between 0.05 and 0.7% (w/w).

4.2 Results of Part B

In Figure 13 the results of the polymerisation of the emulsions are given. Picture (a) shows the polymerised styrene from the MFLC water-styrene emulsion. In picture (b) the polymerised styrene from the MFC water-styrene emulsion is given and picture (c) shows pure polymerised styrene.

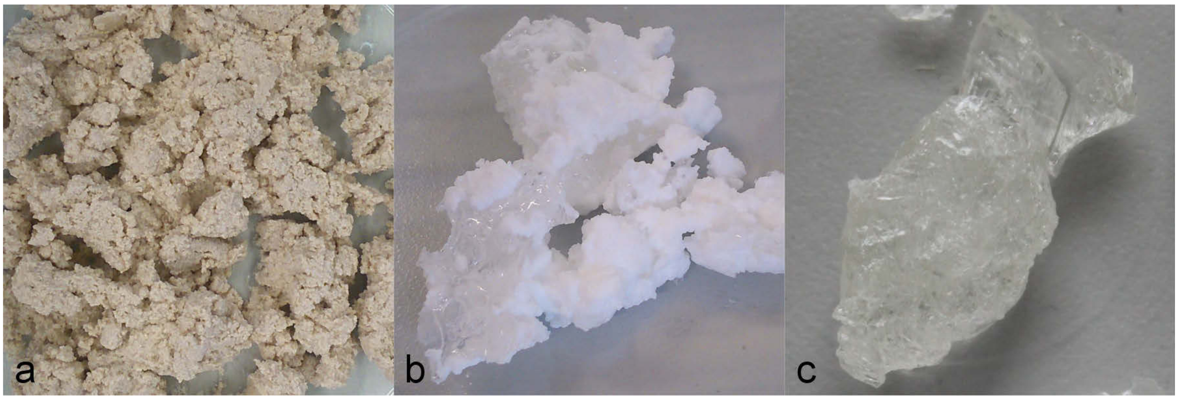

Fig. 13: Images of the results of the polymerisation process. MFLC-styrene composite (a), MFC-styrene composite (b) and pure polystyrene (c)

The MFLC-polystyrene composite (a) has a bright brown colour and the fibers are distributed well in the polystyrene. It seems as if the composite consists of very small particles that are attached to each other. Possibly fibers are wrapped around small styrene droplets. The composite has a partially crumbly consistency.

Comparing the MFC- to the MFLC-styrene composite it can be seen that this material is not at all homogeneous. The MFC-styrene-composite (b) shows on one hand parts of pure polystyrene and on the other hand parts of aggregated fibres.

An explanation for this could be phase separation that happened during the harsh polymerisation process.

The last picture (c) shows pure polystyrene. The material is quite brittle and fairly transparent.

4.3 Results of Part C

4.3.1 AFM topography images of MFLC

In the following several AFM topography images of micro-fibrillated lignocellulose are given.

Figure 14 presents AFM topography images in different zoom levels (a to c) and profiles of three small fibrils (d). The arrow highlights the area that has been zoomed into and that is shown in the subsequent image.

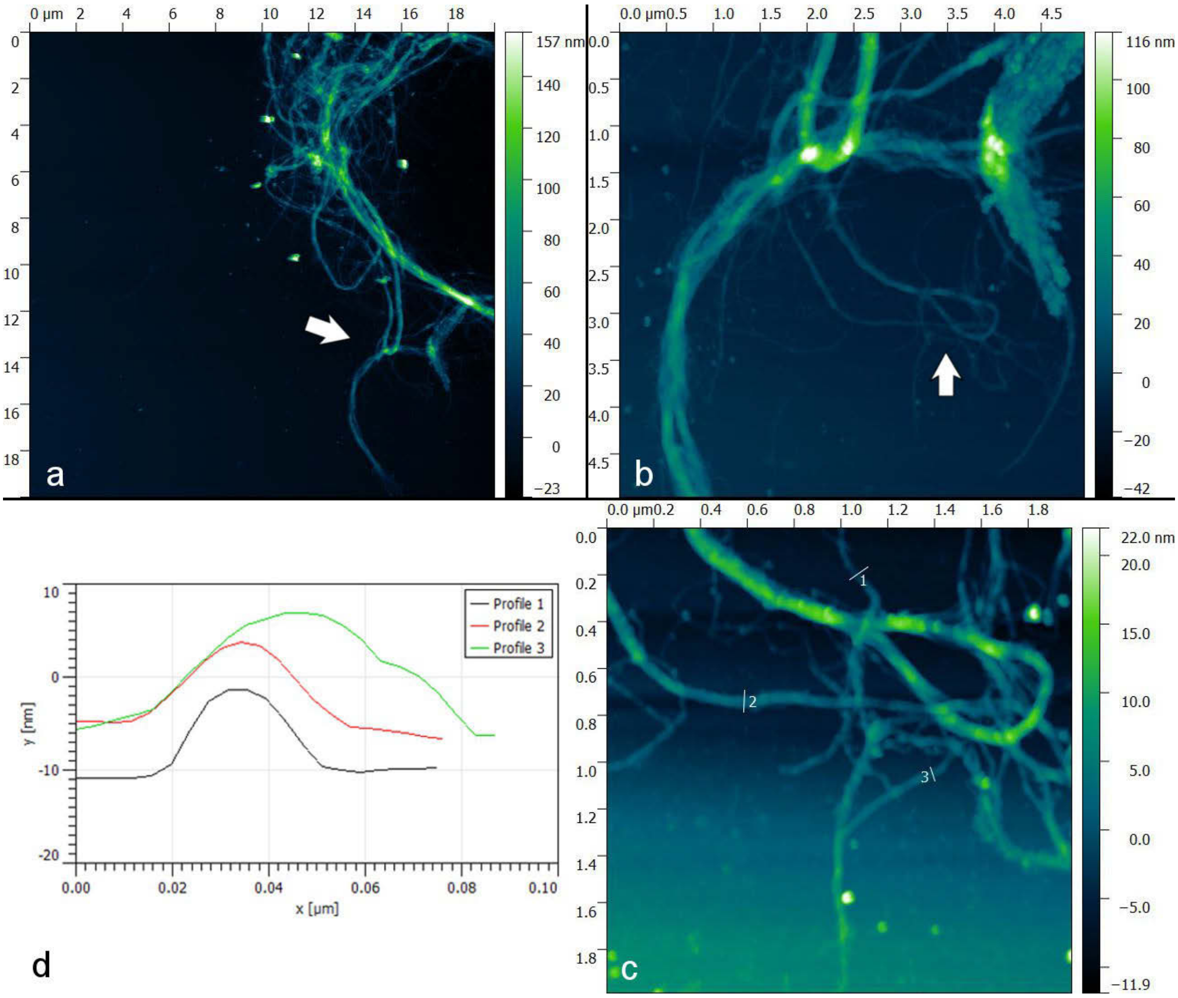

Fig. 14: AFM topography images of micro-fibrillated lignocellulose (a-c). Profile of three fibrils (d).

From image (a) and (b) it can be concluded that the ligno-cellulosic material consists of several bigger fibrils but also of a lot of very small fibrils that are aggregated and attached to each other. In image (c) the fibrils can be seen: a profile was taken of them and that is displayed in (d). The fibril profile presented in (d) reveals that the smallest fibrils can have diameters in the range of several nanometres. Profile 1 and 2 for example have fibril diameters of about 10 nm and profile 3 is also only slightly higher with approximately 14 nm. Of course in the entire cellulosic material there is a large amount of fibrils with increased diameters but this measurement shall just give an example of how small fibril diameter can get. The high aspect ratio, that means the ratio of fibril length to diameter, can also be seen here.

4.3.2 AFM topography images of MFC

Figure 15 presents several images of AFM topography of micro-fibrillated cellulose. Pictures (a) to (c) show different zoom levels of the cellulosic material while picture (d) shows profiles of three fibrils from picture (c). The arrows highlight the area that was zoomed into and that is shown in the following picture.

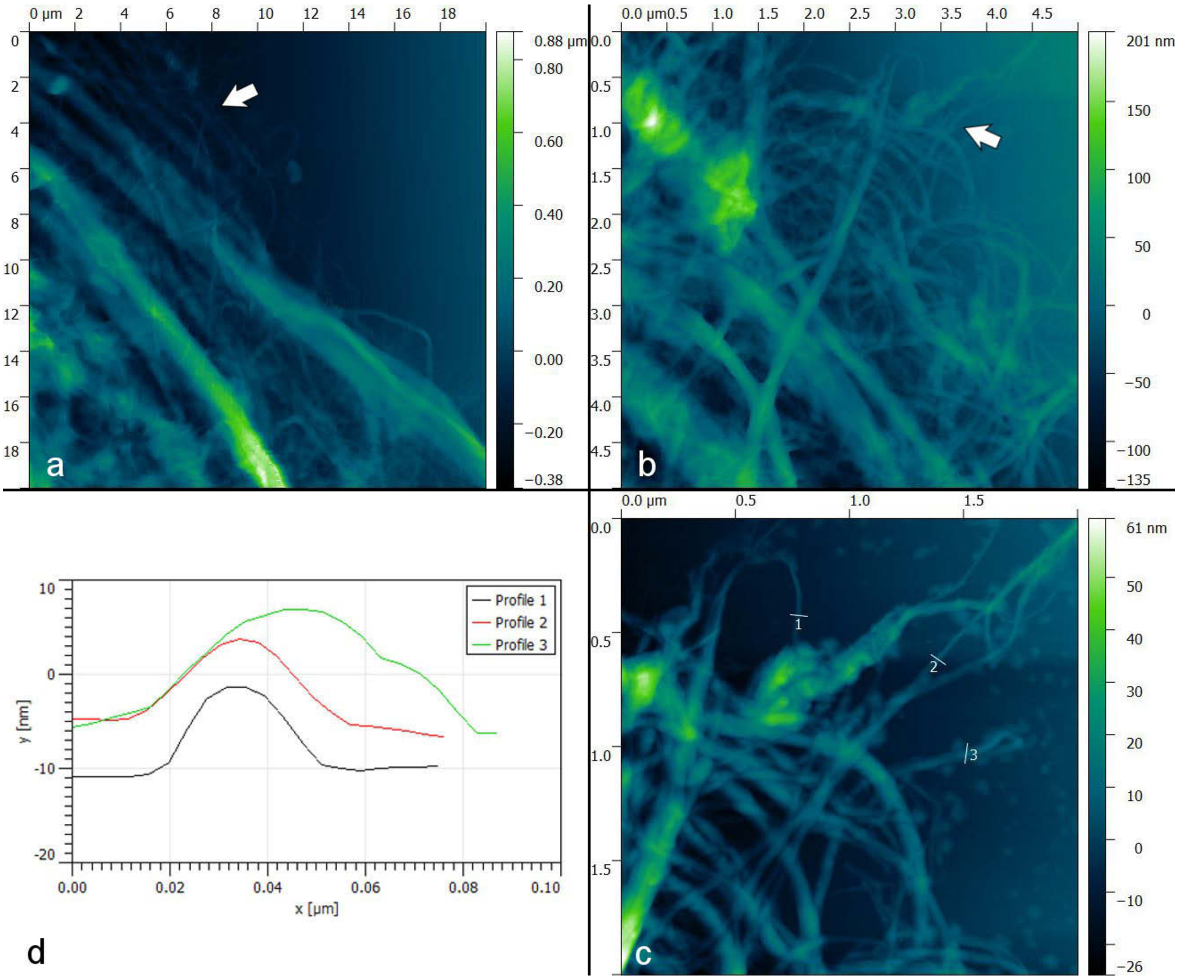

Fig. 15: AFM topography images of micro-fibrillated cellulose (a-c). Profile of three fibrils (d)

Regarding image (a) it can be seen that there are a couple of bigger and a lot of very thin fibrils. This becomes even clearer when observing picture (b), where fibrils are distributed in a random way and are still quite close to each other.

In picture (c) some very thin fibrils can be seen from which three profiles were measured. Profile 1 and 2 show a diameter of approximately 9-10nm. The third fibril that was measured has a slightly bigger diameter of approximately 12-13nm. As already mentioned for the micro-fibrillated ligno-cellulose these measurements shall give an idea of the diameter range of the micro-fibrillated cellulose that was used.

4.3.3 SEM images of MFLC-polystyrene composite

As scanning electron microscopy gives high resolution images of extremely small substances, it was used to observe how the lignocellulosic material interacts with the polystyrene after the polymerisation process.

Three SEM images of MFLC-polystyrene composite in three zoom levels are pictured in Figure 16.

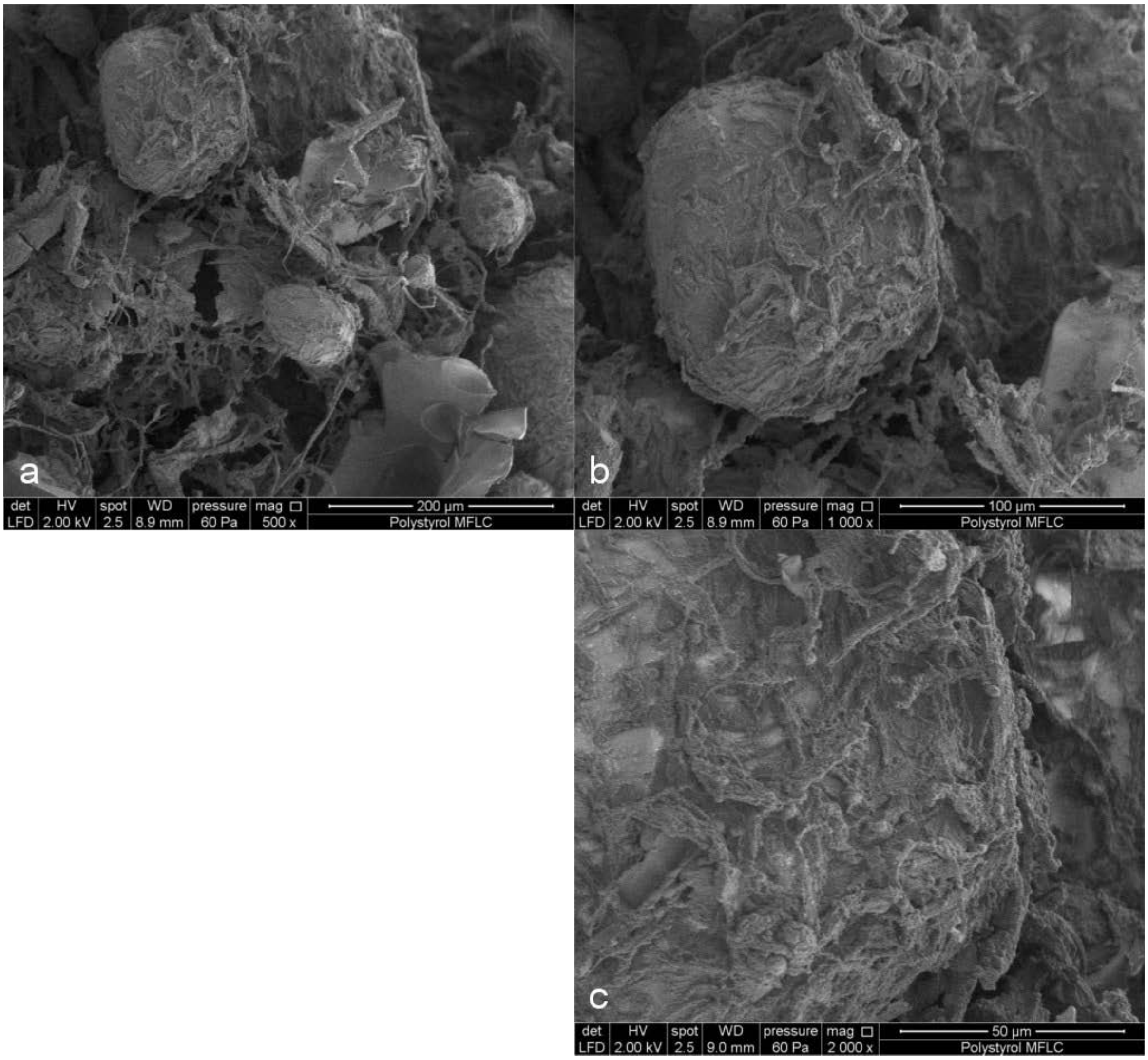

Fig. 16: Scanning electron microscopy (SEM) images of MFLC-polystyrene composites. 500x, 1000x and 2000x magnification in image a,b and c.

Picture (a) shows the composite material with a 500x magnification. It can be seen that there is a lot of lignocellulosic material that covers the polystyrene surface. This coverage of the fibrils is in some parts of the image very randomly but in some cases very directed where fibrils cover spheres of polystyrene almost completely. In this image three of these spheres can be seen. The picture also reveals very few parts of polystyrene that are not covered with any fibrils at all. The diameter of these spheres is in the range of about 40 to 120µm.

Image (b) presents a magnification of image (a) where one of the spheres can be seen. The fibrils are attached very firmly to the polystyrene surface forming a network that is wrapped around the polystyrene spheres. Observing the sphere and the fibrils around it, it can be seen that the lignocellulosic material consists partly of very thin and long fibrils (high aspect ratio), of short fibrils (low aspect ratio) and of other cell wall parts. As already mentioned the fibrils are attached very closely to the polystyrene surface, where they are not simply lying there but somehow bonded to the polystyrene. In addition, some longer fibrils also follow the radius of the sphere.

An even more detailed image of the sphere can be seen in (c) where magnification is 2000x. Here the different fibril diameters are visible. If the sphere is not covered by coarse fibrils it is covered by very thin ones. On the top left corner, a few uncovered parts can be observed.

The next image (Fig. 17) shall once again show these macrospheres in the MFLC-polystyrene composite. Microspheres range in diameter of about 40 to 170 µm and higher, visible in image (a). When comparing this to the styrene droplets of the 0.5% MFLC emulsions (3 to 18 µm) the polymerised droplets are many times bigger in diameter.

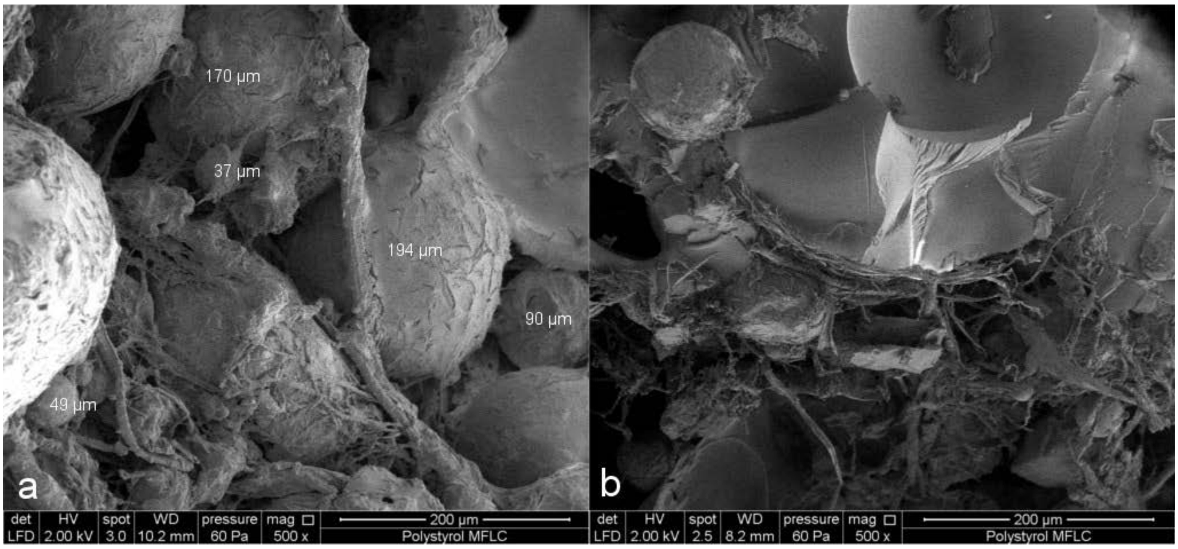

Fig. 17: Scanning electron microscopy (SEM) images of MFLC-polystyrene composite showing microspheres and their diameters.

Picture (b) displays parts of the MFLC-polystyrene composite that are not covered by fibrils. Only some microspheres can be seen.

From the SEM images we have now seen, it can be concluded that a large number of MFLC-polystyrene macrospheres exist in the composite material. These macrospheres have diameters of about 40 to 170 µm and up, and the ligno-cellulosic material is bonded firmly to the polystyrene surface. Compared to the styrene droplets in the emulsion before the polymerisation process the polymerised styrene droplets (macrospheres) are many times bigger in size. Although there is a large number of MFLC-polystyrene macrospheres, there are also parts of polystyrene that are not covered by fibrils present in the composite.

4.3.4 SEM images of MFC-polystyrene composites

Figure 18 presents the results of the SEM of the MFC-polystyrene composite. Image (a) to (c) are SEM images in different zoom levels.

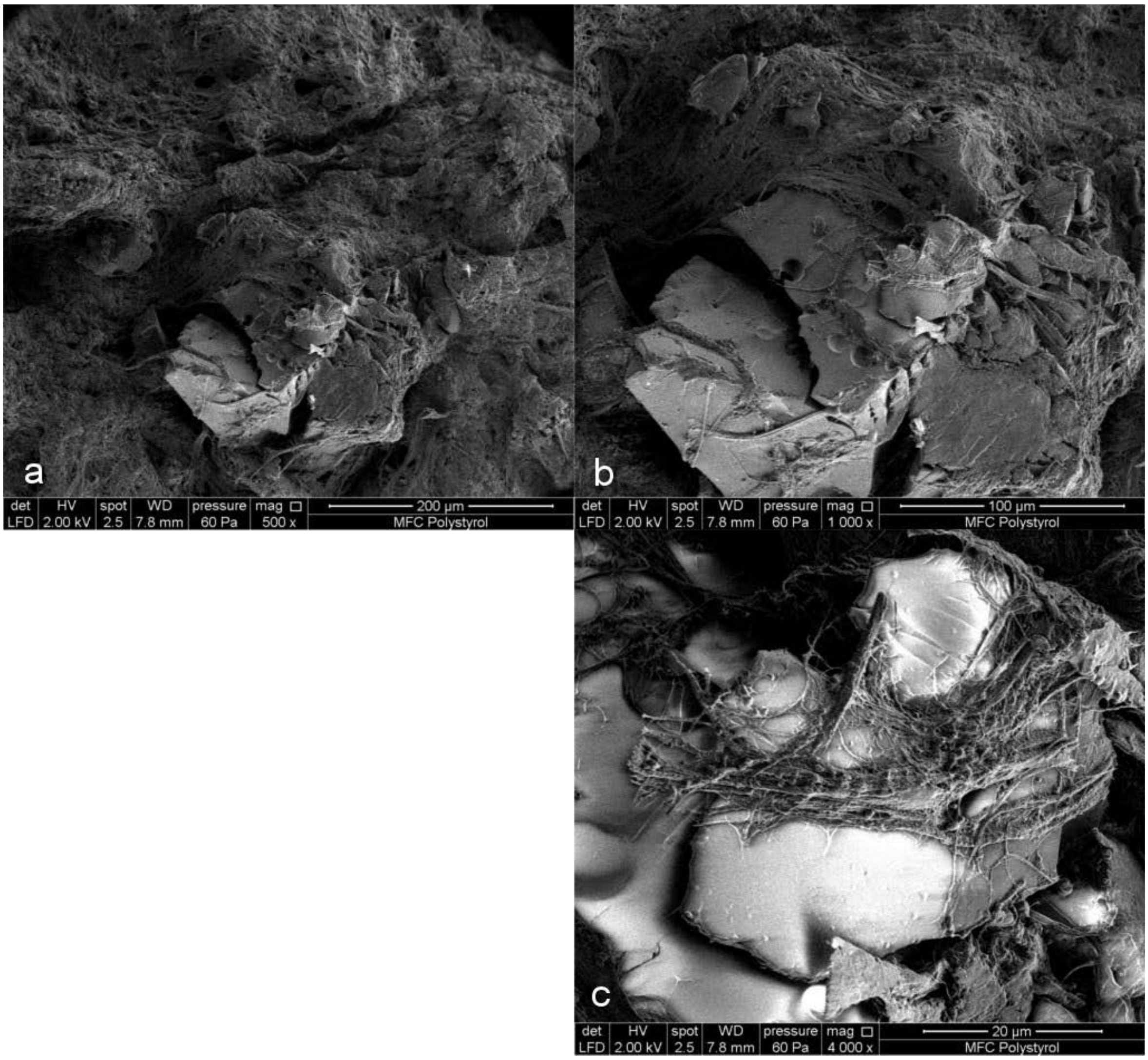

Fig. 18: Scanning electron microscopy (SEM) images of MFC-polystyrene composite.

The first image shows the composite material with a magnification of 500x, where a lot of cellulosic material and only few areas of polystyrene can be seen. The fibrils are attached to the polystyrene surface but no spheres, as is the case for the MFLC-polystyrene composite, exist. This could be explained by a phase separation process in the emulsion during the polymerisation process. Already the macroscopic observation has revealed on one hand parts of pure polystyrene and on the other hand parts of MFC on the polystyrene surface.

Images (b) and (c) illustrate a magnification of the previous SEM image where parts of pure polystyrene can be noticed. In image (c) fibrils are attached to the polystyrene surface. The even distribution of very small but also bigger fibrils as observed on the MFLC-polystyrene composite, cannot be seen here.

5 Conclusion

A major objective of this work was to find out how different cellulosic materials can stabilise styrene-in-water emulsions. From the research that has been carried out it is possible to conclude that MFLC and MFC both are able to stabilise emulsions for several days and weeks, although some minor creaming occurs. This creaming, however, is more distinct for the MFLC-water-styrene emulsion and may be attributed to the comparable high residual lignin content. Furthermore, creaming is increased with decreased fibril concentration which is in good agreement with a work of (Winuprasith & Suphantharika 2015). Cellulose nanocrystals were also tested for its stabilisation behaviour of an emulsion, but for this material the stabilisation mechanism was almost non-existing. Big styrene droplets could be shown to rise to the surface almost immediately after mixing, which still exist after several days and weeks.

The fluorescent microscopy images revealed that both cellulousic materials (MFLC and MFC) show excellent stabilisation behaviour. The styrene droplets are distributed evenly throughout the emulsions and no coalescence of styrene droplets can be noted. A fine edge around the styrene droplets can be seen in both the MFLC and the MFC stabilised emulsions and implies that fibrils are attached to the droplets which help to avoid coalescence of the droplets and at the same time produce stable emulsions. This steric hindrance of particles to stabilise emulsions and the absorption of these particles at the oil-water interface is widely known and was also found by (Winuprasith & Suphantharika 2015) and (Kruglyakov & Nushtayeva 2004). With higher concentrations of either MFLC or MFC, the viscosity increases. This network formation, due to the fibrous material, is also thought to be the reason for the stabilisation mechanism and supported by (Xhanari et al. 2011) and (Tadros 1987). Differences in the fibre concentration result in slightly different droplet size. Analysing the fluorescence images revealed that MFLC-water-styrene droplet diameters are in the range of several micrometre (2-28µm). A decrease in droplet diameter with increasing fibre concentration was shown, which is consistent with a study of (Sun et al. 2007). A trend for styrene droplet diameters in the MFC-water-styrene emulsions, with diameters ranging from 2-18µm, however, could not be noted.

The polymerisation of the MFLC and MFC water-styrene emulsions, both

0.5% fibril concentration, yielded two cellulose-polystyrene composite materials. The MFLC-polystyrene composite had a light brown colour and showed homogeneous distribution of the fibrils. The MFC-polystyrene composite, on the other hand, showed parts of pure polystyrene and parts of aggregated fibrils and was not homogeneous at all, which could be explained by phase separation that happened during the polymerisation process.

The findings of the scanning electron microscopy concerning the two composite materials revealed the existence of macrospheres in the MFLC-polystyrene composite, which could not be found in the MFC-polystyrene composite. These macrospheres were covered almost completely by lignocellulosic fibrils and a firm attachment of these fibrils onto the polystyrene surface could be noted. Macrospheres had diameters in the range of 40 to 200 µm which is many times bigger than the styrene droplets found in the unpolymerised MFLC emulsions. Considering the circumstances of the harsh polymerisation process, coalescence may have happened resulting in bigger droplets. The amphiphilic behaviour of the MFLC material is also assumed to have supported the stabilisation mechanism during the polymerisation process what has obviously succeeded to stabilise the styrene droplets.

From the AFM topography images that have been carried out it is possible to conclude that both the MFLC and the MFC have fibril diameters as small as 10nm. Of course many fibrils with higher diameters are present in both materials and also a high aspect ratio of the fibrils was found.

6 Retrospect and future prospects

In this work basic research about cellulosic material used as an emulsion stabiliser was carried out that generated interesting findings. It has been demonstrated that MFLC and MFC are similar when stabilising styrene-in-water emulsions. When regarding the polymerisation process of these two stabilisers, MFLC yielded a homogeneous material with well-distributed fibrils which in contrast was not the case for the MFC stabilised water-styrene emulsion.

The findings suggest that this approach of first producing MFLC-water-styrene emulsion and the further polymerisation could be useful in future developments of a new lignocellulosic biocomposite with improved properties and new applications. Future work could involve the testing of different fibril concentrations and also different styrene concentrations in the emulsions.

The macrospheres that have been found in the MFLC-water-styrene emulsions after polymerisation will also need further research. Especially, work on how to control the macrospheres' size, as the polymerised macrospheres are many times bigger in size than the unpolymerised droplets, will be of interest. It is suggested to use a different polymerisation process that does not need high temperatures as was the case in our study. Eventually, using a different polymerisation technique would allow use of MFC as a stabiliser for emulsions which would then also result in MFC-polystyrene macrospheres.

Future research questions could address the field of the polymerisation processes and how to improve and facilitate this process. Furthermore, other polymers used in a similar polymerisation process and also stabilised by cellulosic materials would be of interest.

The present work showed that micro-fibrillated cellulose and micro-fibrillated lignocellulose is a fantastic material with many interesting properties that could have many possible applications for instance as a new partly bio-based material. Further work concerning this cellulosic material will be needed to better understand it and to use it appropriately in many applications.

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Index of abbreviations

Aggregation: is the process or the result of the formation of aggregates.

CNC: cellulose nanocrystals

Coalescence: is the disappearance of the boundary between two particles, which are usually droplets or bubbles, in contact.

Creaming: is separation due to upward motions of emulsion droplets with lower density than the continuous phase. (Karlberg et al. 2005)

Dispersion: is a material comprising more than one phase where at least one of the phases consists of finely divided phase domains dispersed throughout a continuous phase. (Slomkowski et al. 2011)

Emulsifier: is a surfactant which when present in small amounts facilitates the formation of an emulsion. (IUPAC 2001)

Emulsion: is a fluid system in which liquid droplets are dispersed in a liquid. (Slomkowski et al. 2011)

Flocculation: is aggregation of droplets into flocks, which can happen when droplets collide and adhere due to long-range van der Waal's attraction. (Karlberg et al. 2005)

MFC: micro-fibrillated cellulose

MFLC: micro-fibrillated lignocellulose

Sedimentation: is the settling of suspended particles under the action of gravity or a centrifugal field. (Slomkowski et al. 2011)

Surfactant: means **surf**ace **act**ive **a**gen**t**. Are compounds that lower the surface tension between two liquids or between a liquid and a solid. Surfactants may act as wetting agents and emulsifiers.(IUPAC 2001)

Suspension: Dispersion of solid particles in a liquid. (Slomkowski et al. 2011)

Suspension polymerization: Is a polymerization in which polymer is formed in monomer, or monomer-solvent droplets in a continuous phase that is a non-solvent for both the monomer and the formed polymer. (Slomkowski et al. 2011) the components is present in the form of finely distributed spherical droplets in the second phase, called the continuous phase. If the oil is dispersed in water the emulsion is termed as an oil-in-water (o/w) emulsion. If water is dispersed in oil the emulsion is referred to as a water-in-oil (w/o) emulsion.

Emulsion stability can be weakened or destabilised by different mechanisms such as creaming, sedimentation, flocculation, and coalescence. Creaming is the separation process due to an upward motion of emulsion droplet with lower density than the continuous phase. If droplets, with higher density than the continuous phase, descend to the ground, sedimentation occurs. Flocculation is the process when droplets aggregate into flocks, which can happen when droplets collide and adhere due to long-range van der Waal's attraction. The process when droplets merge and form bigger droplets is called coalescence. Another destabilisation mechanism is Ostwald ripening, which occurs when the dispersed phase is somewhat soluble in the continuous phase. (Karlberg et al. 2005)

2.3.1 Surface activity and Surfactants

Short-chain fatty acids and alcohols are substances that are soluble in both water and oil and are therefore referred to as amphiphilic. The hydrocarbon part of a molecule is responsible for its oil solubility, while the polar carboxy or hydroxy group shows affinity for water. Present at an oil-water interface, the hydrophilic head will be buried in the water and the lipophilic hydrocarbon chain will be stretched out into the oil phase. (Mollet et al. 2008) An example for such an amphiphilic molecule is stearic acid shown in the following image (Fig. 2).

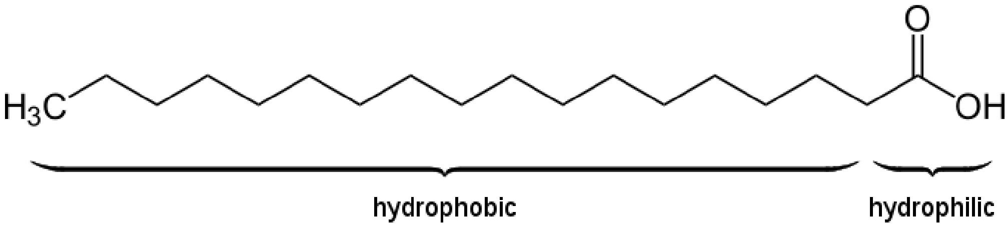

Fig. 2: Typical amphiphilic molecule: stearic acid. Showing the hydrophobic and the hydrophilic part of the molecule

The term surfactant stands for <u>sur</u>face <u>act</u>ive <u>a</u>gen<u>t</u> and is a substance that lowers the surface tensions of a medium in which it is dissolved or the interfacial tension with other phases. A surfactant which, when present in small amounts, can facilitate the formation of an emulsion is called an emulsifier. It can also enhance