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Chemical Modification of Microcrystalline Cellulose for use in Biocomposites with Polylactic acid

Bachelor of Science Thesis

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Abstract

In this study biocomposites consisting of polylactic acid (PLA) and chemically modified microcrystalline cellulose (MCC) were manufactured. The MCC was modified with three different UV-reactive monomers in order to make the MCC more hydrophobic and increase the miscibility between PLA and MCC. The modification was executed using UV-light and a photo initiator to initiate photo-grafting polymerization of the monomers. Analysis methods used were tensile test, Fourier- transform infrared, water retention value, differential scanning calorimeter and scanning electron microscope. Analysis showed that the modification made the MCC more hydrophobic, and that the miscibility between PLA and MCC increased with the modification. Tensile tests showed that the stiffness increased in all biocomposites compared to neat PLA. The modification with N-(Hydroxymethyl)acrylamide was the superior composite regarding tensile strain and stress. Even though PLA is a thermoplastic, results in this study showed that a composite consisting of modified MCC (TMPTA) and PLA is not suitable for applications where the product has to be able to withstand being heated several times, without any further alterations.

Sammanfattning

I den här studien har biokompositer innehållandes polylactic acid (PLA) och kemiskt modifierad mikrokristallin cellulosa (MCC) framställts. MCC modifierades med tre olika UV-reaktiva monomerer för att göra MCC mer hydrofob och därmed öka blandbarheten mellan PLA och MCC. Modifikationen utfördes med hjälp av UV-ljus och en fotoinitiator för att initiera en polymerisationsreaktion mellan monomererna. Analysmetoder som användes i studien var dragtest, Fourier- transform infrared, water retention value, differential scanning calorimeter, och scanning electron microscope. Analyser visade att modifieringen gjorde MCC mer hydrofob samt att blandbarheten mellan PLA och MCC ökade med modifieringen. Dragtest visade att styvheten i samtliga biokompositer ökade i jämförelse med ren PLA. Modifikationen med N-(Hydroxymethyl)acrylamide visade sig vara den överlägsna kompositen med avseende på dragstyrka och dragspänning. Trots att PLA är en termoplast påvisar resultat från denna studie att kompositer innehållande modifierad MCC (TMPTA) och PLA inte är lämpliga för applikationer där produkten ska kunna värmas om ett flertal gånger utan ytterligare modifikationer.

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1 Introduction

1.1 Background

Composites are very useful materials and play an important role in many different industries, such as the automotive. Composites are materials, which consists of two or more different raw materials with different chemical or physical properties. When combining the start materials into a composite the materials will not merge completely. When combined, the weaker material will function as a matrix for the stronger material, the reinforcement, which will be embedded in the matrix. The purpose of the production of a composite is to produce a material with different properties then the ones of the individual materials [3]. Composites are not only widely used due to their properties; such as lightweight and strength, they can also often be an economically favorable choice [1]. The plastic material in a composite is usually the costly one. Reducing the amount of plastic in the material and replacing it with a cheap material such as cellulose makes it an economical choice [1, 2]. Common types of composite are those consisting of a petroleum polymer and a natural fiber [4]. The world is now striving towards a more sustainable future, which involves finding new renewable and environmental friendly materials, which can replace materials based on non-renewable sources. In order to be able to use a material in a sustainable way, it is also important to be able to dispose of the expended product in an efficient and environmental friendly way [5]. Therefore, biocomposites are a very interesting and a useful field of study due to the fact that they consist of renewable raw material and can be biodegradable [6].

1.2 Purpose

The purpose of this study was to manufacture biocomposites consisting of microcrystalline cellulose (*MCC*) and polylactic acid (*PLA*) in different ratios. The MCC was modified with three different UV-reactive monomers, which are shown in section 2.1, table 1. The biocomposites mechanical properties, such as the tensile strength were tested in order to determine which effects the different modifications of the MCC had on the end product.

1.3 Theory

1.3.1 Cellulose and microcrystalline cellulose, *MCC*

Cellulose is a common polysaccharide found in nature, and is the key-building block in all plants. The polysaccharide is a linear molecule consisting of repeating glucose molecules bound together by 1,4- β -glycosidic bonds [7]. Cellulose consists of microfibrils, which contain both amorphous and crystalline regions. Due to its large amount of hydrogen bonds and that it has many crystalline regions the polymer is insoluble in water. MCC is extracted from cellulose through acid hydrolysis, which removes amorphous regions in the polymer. MCC consists of approximately 70 % crystalline regions, and 30 % amorphous [8]. MCC can be obtained in different forms; the one used in this study was a powder, which has an average particle size of 20 – 90 μm [9]. MCC is commonly used as reinforcement in different kind of materials and in the food- and pharmaceutical industry.

1.3.2 Polylactic acid, *PLA*

PLA is a transparent polyester recovered from glucose, and has many application areas, from food packaging to biomedical applications [10]. PLA has become a widely used polymer due to that its properties are similar to conventional petroleum plastics such as polyethylene [6]. The thermoplastic polyester has good stiffness and strength, but is inferior when it comes to impact resistance and thermal stability [4]. Common sources of the glucose used in the production process are for example rice and corn [10]. There are two mainly utilized production processes for PLA, one containing fermentation of glucose and catalytic processes and the other, more efficient way containing ring-opening polymerization of lactide [11]. PLA is a hydrophobic polymer and consists of two different isomers, D and L-isomers, depending on if the PLA derives from L-lactide or D-lactide. Depending on what ratios of the different isomers the PLA consists of it will have different thermal and physical properties [2, 12]. This knowledge about the stereo chemical structure of PLA can be used in order to produce PLA with specific properties. For example, PLA can be produced as a semi crystalline or amorphous substance [13]. The amount of crystallization can be calculated by using the heat of fusion for the substance and the heat of fusion for the substance if it would be 100 % crystalline [14]. The crystallinity of PLA will not be further investigated in this report, and data regarding the isomeric distribution in the PLA used in this study was not investigated.

1.4 Methodology

In order to make it possible for the hydrophilic MCC and the hydrophobic PLA to blend properly the properties of the MCC were altered by chemical modification. The modification was executed using UV reactive monomers such as HMAA (N-(Hydroxymethyl)acrylamide), HDODA (1,6-Hexanediol diacrylate) and TMPTA (Trimethylolpropane triacrylate), which were supposed to react with the MCC fibers and create a hydrophobic layer around them. This alteration in the physical properties of MCC was supposed to lead to that the MCC and PLA would blend better. In order to determine if the modification was successful a Fourier transform infrared (FTIR) analysis was performed. The FTIR analysis can give indications about whether or not the modification was successful, but it does not show how much of the cellulose that was modified. To get a better understanding of the degree of successfulness of the modification the water retention value (WRV) was tested. The analysis provides a value of how much water the cellulose holds, which can be compared between the modified and unmodified MCC. The purpose of the modification was to make the MCC hydrophobic, which in terms of WRV translates to a lower WRV. By comparing the WRV of the modified and the unmodified MCC a conclusion about the successfulness of the modification could be drawn. The modification process contains broadly: photo initiation and polymerization.

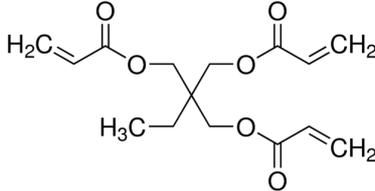
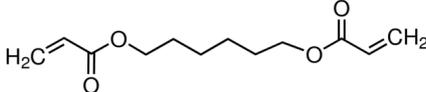
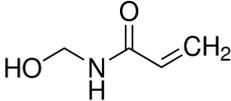
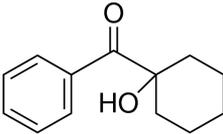
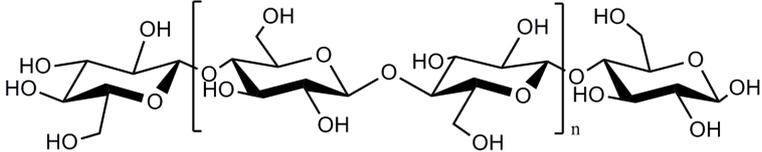
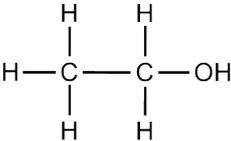
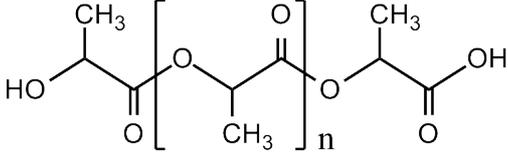
The UV light and the photo initiator are part of an initiation step, and enable the monomer to bind to the cellulose and polymerize, a suggested mechanism for the process can be seen in figure 2. In figure 1, a clarification of which hydrogen of the MCC is illustrated in figure 2 can be seen. In figure 1 the two hydrogen atoms marked with a red rectangle bonded to the aliphatic carbon atom are the two possible hydrogens, which the photo initiator could react with. Due to that the mechanism in figure 2 is a suggested mechanism, one of the hydrogens is displayed, and which is not considered relative. The reaction in figure 2 can be applied to HMAA and TMPTA as well. To clean the modified MCC from non-reacted chemicals, such as the photo initiator, monomers and rests of ethanol the MCC was refluxed with chloroform.

2 Experimental

2.1 Materials

Microcrystalline cellulose, *MCC*, PH-102 purchased from FMC biopolymer was used in this study. The *MCC* that was used in the composites containing unmodified *MCC* was used without any alterations. Poly lactic acid, *PLA*, Ingeo 3051 D from Nature Works was provided by Södra cell AB as a gift. The melting temperature (T_m) and glass transition temperature (T_g) were determined by using a METTLER DSC programmed to heat the sample from 30 – 200 °C [15]. T_g and T_m were measured to 60 °C and 150 °C respectively. The density was provided by Södra cell AB, and was 1.24 g/cm³. The UV reactive monomers HDODA, TMPTA and HMAA as well as the photo initiator, HCHPK were purchased from Sigma-Aldrich and used without any alterations. HCHPK has an absorption span between 220 – 260 nm. Ethanol, 95 % was used as a medium to enable the reaction of the other chemicals; ethanol did not take part in any chemical reaction. All mentioned chemicals are displayed in table 1 together with their full name and molecular structures.

Table 1. Molecular structures and names of the three UV-reactive monomers, the photo initiator, microcrystalline cellulose, ethanol and PLA

Name	Molecular structure
Trimethylolpropane triacrylate, (<i>TMPTA</i>)	
1,6-Hexanediol diacrylate, (<i>HDODA</i>)	
N-(Hydroxymethyl)acrylamide. (<i>HMAA</i>)	
Hydroxycyclohexyl phenyl ketone (<i>HCHPK</i> , <i>Photo initiator</i>)	
Microcrystalline cellulose, (<i>MCC</i>)	
Ethanol	
Polylactic acid, (<i>PLA</i>)	

2.2 Analysis techniques

2.2.1 Fourier transform infrared spectroscopy, FTIR

For the FTIR analysis a Perkin Elmer spectrum one was used. The wavelength interval was set to be between 400 – 4000 cm⁻¹, and performed 16 scans per sample. The tablets were prepared using 2 mg of the test substance and 300 mg of potassium bromide, (KBr).

2.2.2 Differential scanning calorimeter, DSC

A DSC measures the heat flow required to heat an empty reference pan compared to the amount needed to heat a pan with sample in it at an set heat rate [17]. In this study a Mettler DSC 820 was used to compare the thermal transition states between the composites. All samples were heated from 30 to 200 °C. The glass temperature, melting temperature and crystalline temperature were measured.

2.2.3 Water retention value, WRV

The water retention value is a method used to measure how much water the MCC holds after centrifugation under standard conditions compared to a dry sample. 4 mg of MCC was placed in a vivaspin tube and soaked with distilled water. The suspension was left for approximately 3 h and shaken once every hour. The MCC was then centrifuged at 4000 rpm for 10 minutes. The MCC was weighed and then put in an oven to dry over night by 100 °C and weighed again in dry condition. To calculate the WRV equation 1 was used, where $m(wet)$ stands for the mass of the wet MCC, measured after centrifugation and the $m(dry)$ is the mass of the MCC measured when dry.

$$WRV = \frac{m(wet)}{m(dry)} - 1$$

Equation 1.

The percentage of water held in the sample was calculated by multiplying the WRV with 100 [18].

2.2.4 Scanning electron microscope, SEM

A scanning electron microscope was used to picture the structure of the composites. The SEM operates with an electron beam; therefore the scanned sample has to be able to conduct electrical charge in order for the technique to work. Therefore the sample was sputter-coated with gold before conducting the scan. The sputter coating was executed using a JOEL, JFC-1100E at 10 mA for 80 seconds, which corresponds to a layer of approximately 100 Å.

2.2.5 Tensile test

Tensile tests were conducted using a Instron 5565 A loaded with a 5 kN loading cell, and the program used with the device was Bluehill 2.0. Tensile parameters described in this report are elongation, tensile strength and stiffness. The samples were fastened between two clamps, which closed using compressed air. It was important to fasten the samples straight between the claps for credible results.

2.3 Modification of MCC

During the experimental process, two batches of modified MCC were made. The modification process was executed following the same procedure; only tensile results from composites consisting of modified MCC from batch two are displayed in this report. The modification was performed by mixing approximately 3g MCC with 3 wt% photo initiator (*PI*), 10 wt% monomer and approximately 10 ml of ethanol [16]. The monomer solution was added to the PI, when the PI was dissolved, ethanol was added. MCC was added last and the solution was stirred until all MCC was homogenously incorporated into the solution. The mixture was placed in a petri dish in order to get a large surface for the ethanol to evaporate from. The petri dish was placed in room temperature in a fume hood. The ethanol was added to enable an even mix of the other components and did not take part in any chemical reaction.

The MCC mixture was exposed to UV-light treatment for 30 minutes at a distance of 770 mm and a wavelength of 254 nm. The MCC was stirred once during the treatment. After the exposure a small amount of MCC was taken for FTIR analysis. The rest of the MCC was refluxed with chloroform for 24 h, and then filtered by suction with a glass filter with a pore size of 3. The modified MCC was then dried in an oven over night at 100 °C. The modification

process was performed in the same way with the three different monomers and 2 batches were made.

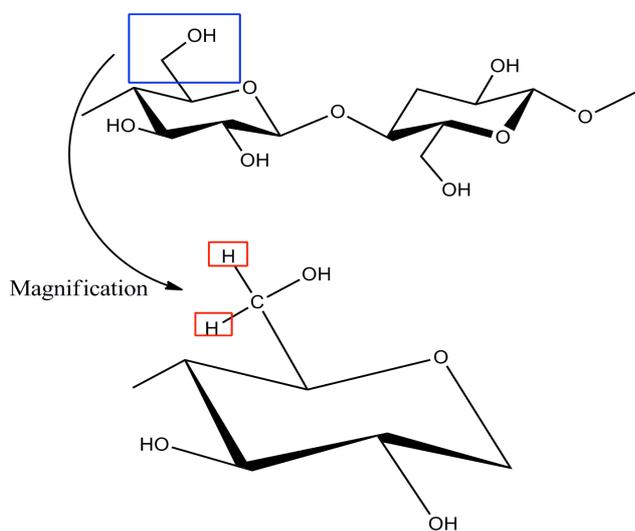


Figure 1. Showing a clarification of which hydrogen is illustrated in figure 2

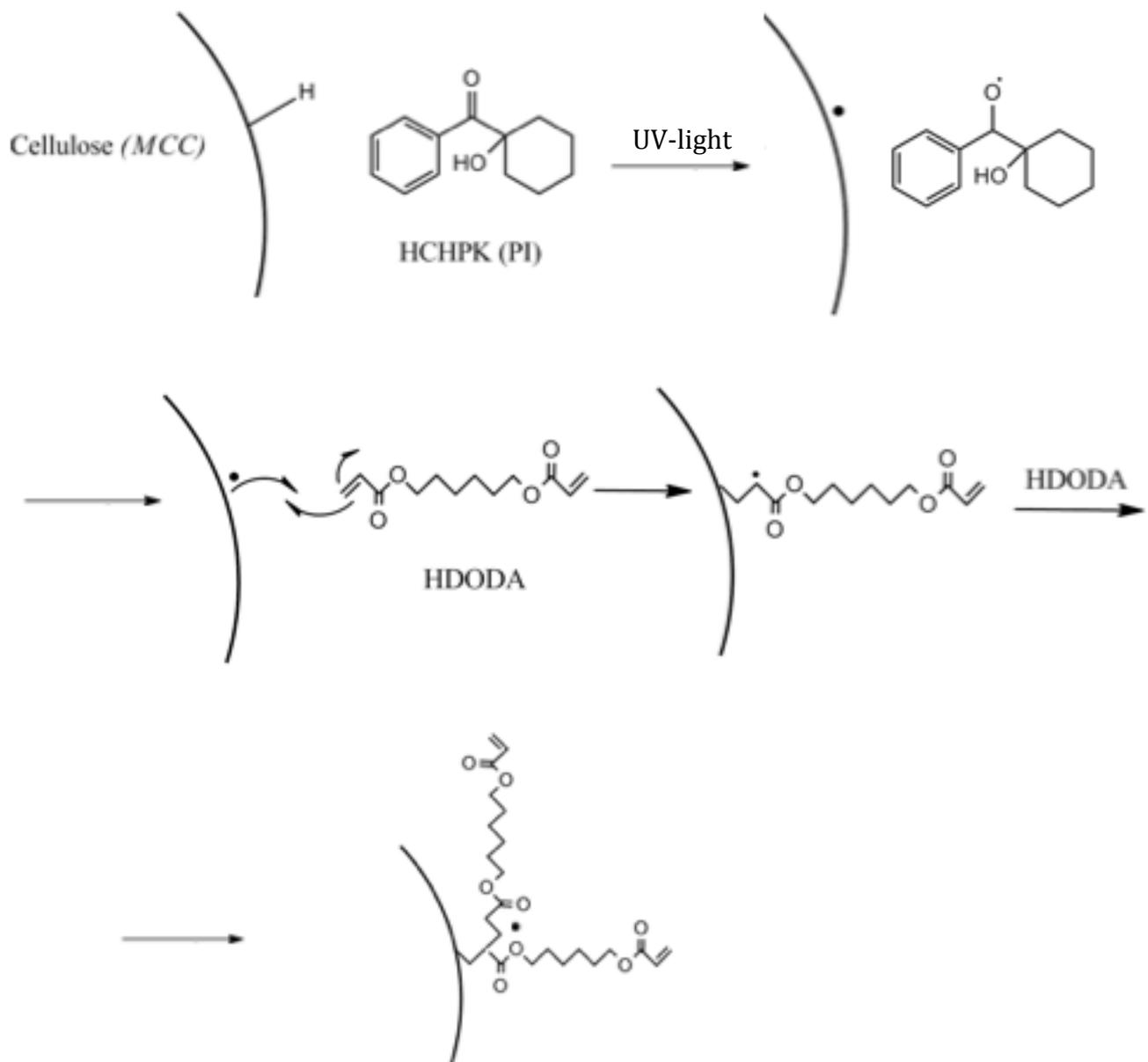


Figure 2. Showing a suggested mechanism for the modification of MCC, including polymerization of the UV-reactive monomer HDODA

2.4 Extrusion of MCC and PLA

To mix the MCC and PLA into a composite a Haake Minilab twin-screw extruder was used. The extruder was set to 190 °C and 100 rpm for 10 minutes. The components were mixed in the ratios seen in table 2.

Table 2. Showing the amount of MCC, expressed in wt % in the biocomposites. The remaining wt % corresponds to PLA

Sample description	Modification agent (<i>UV-reactive monomer</i>)
10 wt % Modified MCC	HDODA
10 wt % Modified MCC	HMAA
10 wt % Modified MCC	TMPTA
20 wt % Modified MCC	TMPTA
10 wt % Unmodified MCC	-----
20 wt % Unmodified MCC	-----

2.5 Hot-pressing

The extruded material was hot pressed into 0.5 mm thick films in 160 °C for 5 minutes at a pressure of 5 ton. The pure PLA, which was used as a reference was not extruded before hot pressed. When pressed the films were allowed to cool in room temperature with weights placed on top of them. When the films were cool they were cut into dog bone shapes in preparation for the tensile strength test. In order to get trust worthy results the dog bones middle part, where the width was 4 mm had to be free of bubbles and other impurities, which could compromise the reliability of the tensile strength test results. In order to get bubble-free films the films were broken into smaller pieces and hot pressed again. The procedure sometimes had to be repeated a few times.

2.6 Tensile test

The tensile properties of the biocomposites were tested using an Instron 5565A programmed to hold a crosshead speed of 3.6 mm/minute corresponding to a strain rate of 0.002 s⁻¹. The dog bone shaped composites were 86 mm long and had a maximal width of 13 mm and a minimum width of 4 mm. Before the test, the composite samples were incubated at 23 °C and 50 % RH for approximately 24 h. Only composites containing the modified MCC from batch two were displayed in this study due to that the first batch resulted in too few dog bones in order for the results to have any credibility.

3 Results and discussion

3.1 Modification of MCC

In this study two batches of modified MCC were made. To determine whether or not the modifications were successful, FTIR and WRV analysis were made.

3.1.1 FTIR spectrum

To determine if the modification of the MCC was successful the FTIR-spectrums from before and after reflux were compared. Figure 3 shows the FTIR spectrum for neat MCC and was used as a reference. In figure 4 and 5 the FTIR spectrums of MCC modified with TMPTA and HDODA are displayed. Both TMPTA and HDODA are esters, the band around 1750 - 1735 is typical for saturated ester groups, and 1725 - 1715 for unsaturated [16]. The increased peak after reflux, which can be seen in both figure 4 and 5 indicates that the content of saturated esters has increased, which can be an indicator for that the polymerization of the UV-reactive monomers TMPTA and HDODA has succeeded.

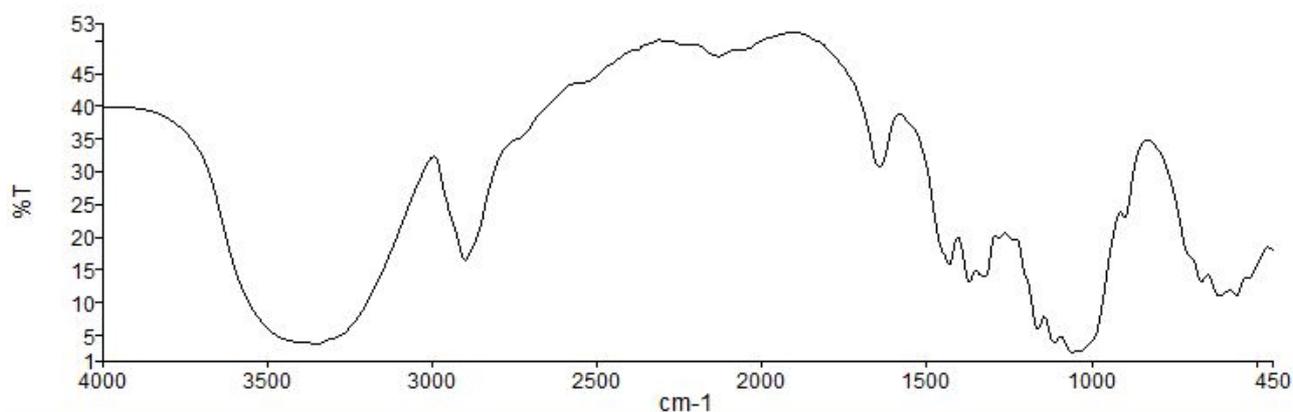


Figure 3. FTIR- spectrum for neat MCC

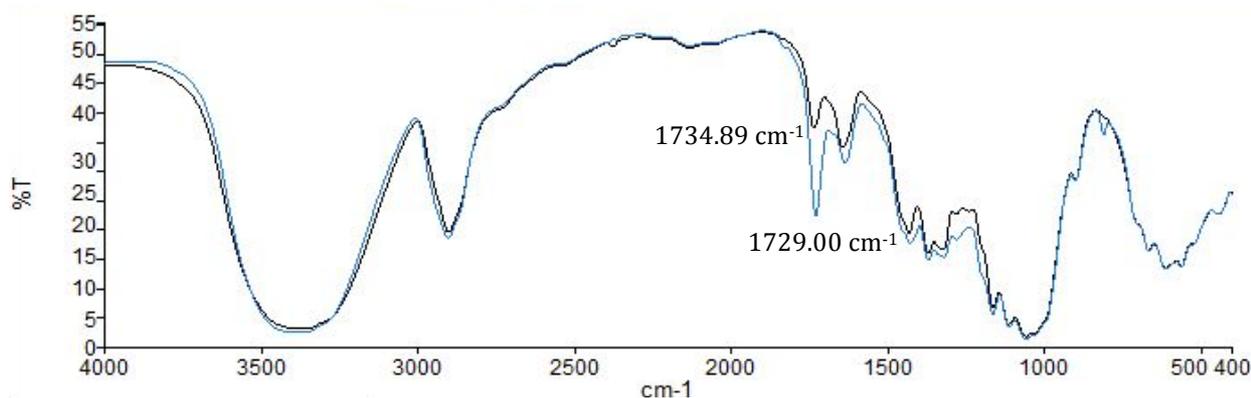


Figure 4. FTIR-spectrum for MCC modified with TMPTA before and after reflux, batch two. The green curve is from after reflux

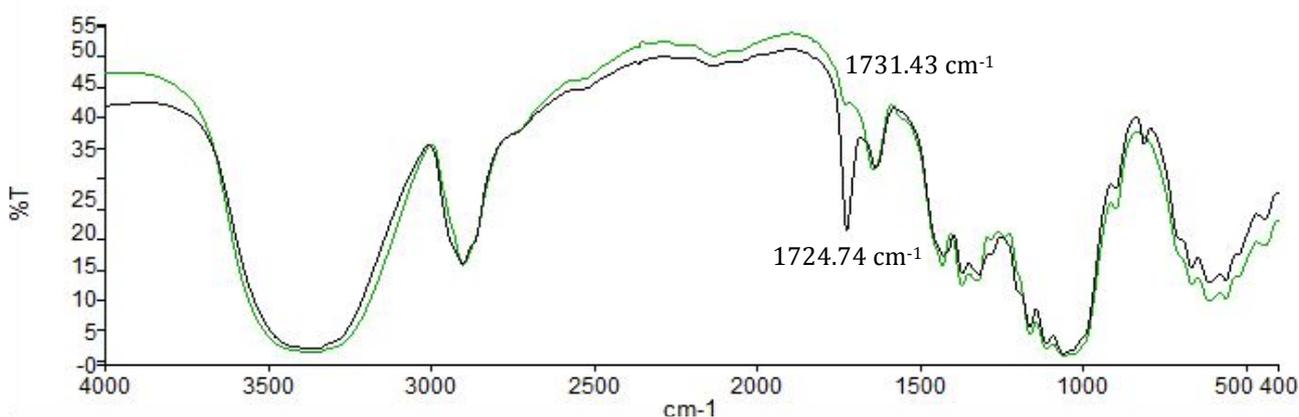


Figure 5. FTIR-spectrum for MCC modified with HDODA before and after reflux, batch two. The green curve is from after reflux

HMAA is unlike TMPTA and HDODA not an ester, but an amide. Therefore not the same absorption band can be regarded. When analyzing the modification with HMAA, the alkene (C=C)-stretch, which has an absorption band between 1680 – 1620 was analyzed [19]. When HMAA polymerizes the double bond between the carbon atoms is going to transform into a single bond. The polymerization brings with other words a decrease of alkenes in the sample. The FTIR spectrums of the MCC modified with HMAA did not show any distinct changes from before to after reflux, therefore the spectrums from batch one are displayed. As can be seen in figure 6, the peak around 1650 – 1660 is decreased from before to after reflux. The peak fits in to the absorption band of alkenes, and was therefore regarded. The decrease of the peak from before to after reflux indicates that something has happened with the alkene bonds in the

sample. If this change depends on a decrease of double bonds could not be distinguished from the FTIR results alone.

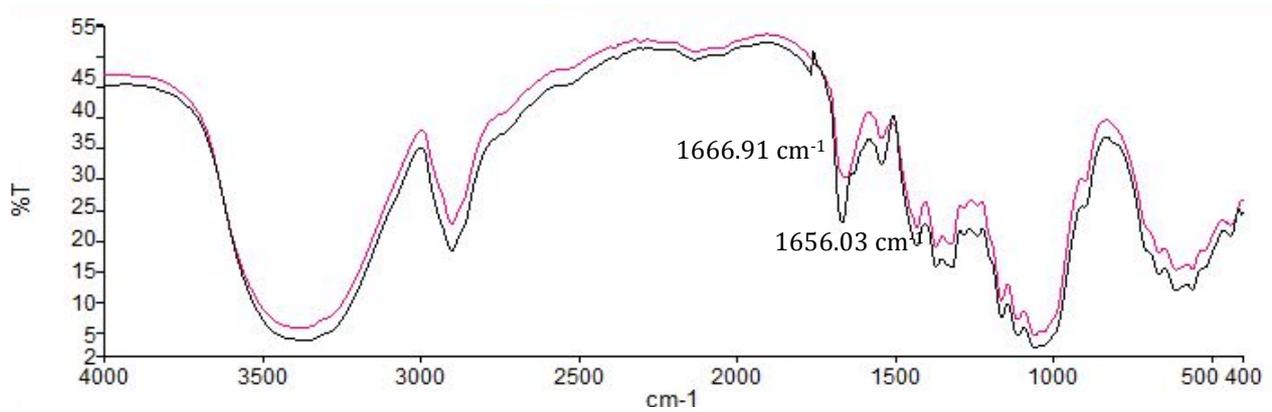


Figure 6. FTIR-spectrum for MCC modified with HMAA before reflux and after reflux, batch one

FTIR-spectrum for all samples can be found in appendix (I).

3.1.2 Water retention value

In order to confirm, or clarify the results from the FTIR the water retention values of the modified MCC were measured and compared to unmodified MCC. The values were calculated using equation 1, and can be seen in table 3, where the results are displayed.

Table 3. Showing the different water retention values and percentage of water in the sample for each modification type. Two replicates were performed; standard deviations are shown in the brackets

Batch No.	Modification type	WRV	Water in sample (%)
----	Unmodified MCC	0.726 (0.0043)	72.6
1	TMPTA	0.512 (0.2)	51.2
1	HDODA	0.488 (0.045)	48.8
1	HMAA	0.468 (0.104)	46.8
2	TMPTA	0.377 (0.189)	37.7
2	HDODA	0.53 (0.125)	53
2	HMAA	0.372 (0.15)	37.2

Table 3 shows that all modified MCC samples had a decreased WRV compared neat MCC. The decreased WRV values for the modifications with HDODA and TMPTA from batch two together with the FTIR results; seen in section 3.1.1, figure 4 and 5 for the specimens leads to the conclusion that the modifications were successful.

The WRV showed that the hydrophobic properties of the MCC modified with HMAA increased, in both batch one and two. Though inconclusive FTIR results were obtained; seen in section 3.1.1 figure 6, the decreased WRV concludes that the modification was successful. The amount of successfulness was however not investigated.

The modification processes were carried out following the same routine, but as the results in table 3 are showing, the WRV differs between both the replicates and batches. The differences of the values between the batches could indicate that the modification process has optimization potential. The deviations for the modified samples are higher than for the neat

MCC. This could indicate that the WRV of the neat MCC is more trustworthy than the ones of the modified samples. In order to retrieve more trustworthy WRVs for the modified samples, more replicates could be made. This study did not focus on the optimization of the modification of MCC through the UV curing reaction. The amount of monomer used in the reaction has been optimized and determined to 10 wt% [16]. Other parameters such as the time exposed to UV-radiation, wavelength and other factors have not yet been optimized. Therefore that would be an area of this study for future development.

3.2 Tensile tests

Tensile tests were conducted on more than five replicates; the data displayed in this report only comprises the samples, which underwent breakage in the middle of the tested area, other tested specimens were dismissed. The composites, as well as the neat PLA did not undergo a necking procedure during the break. The materials seem to lack in elasticity in order for necking to occur, instead they underwent a stiff break in the middle of the tested area. In figure 7 all specimens are displayed where the difference in color is prominent comparing the different composites. The composites containing unmodified MCC seem to have a more yellow color than the ones containing modified MCC according to figure 7. In table 4 information regarding what contents the different dog bones in figure 7 have is displayed.

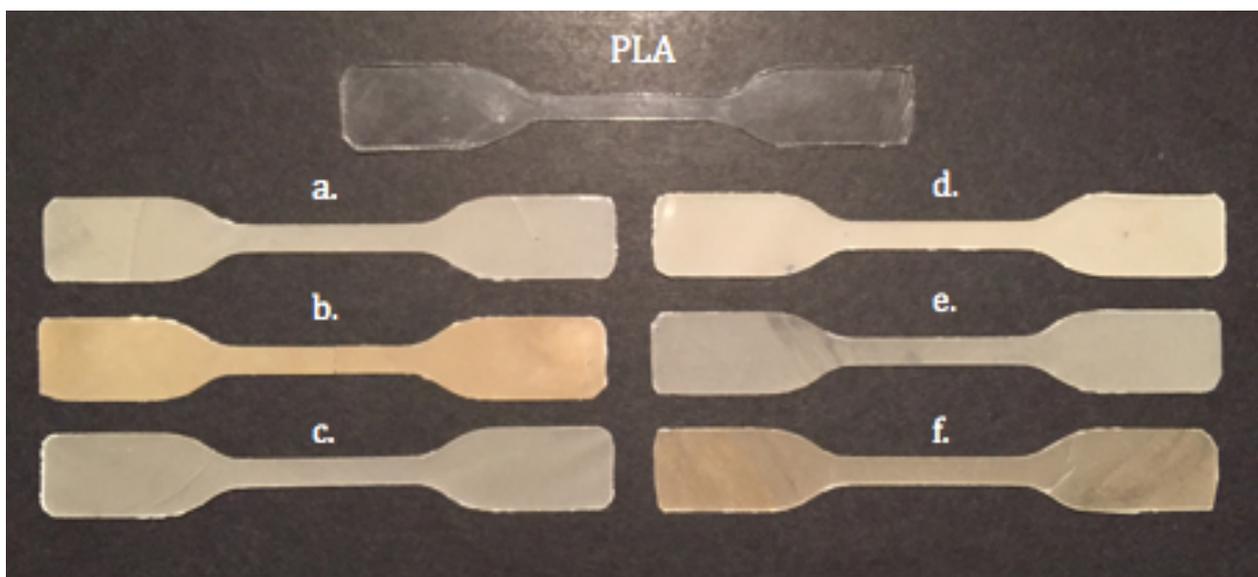


Figure 7. Showing the different dog bone shaped composites in comparison to each other and neat PLA

Table 4. *Displaying the contents of the composites in figure 7*

Letter	Sample description
(a)	10 wt % MCC modified with HDODA
(b)	20 wt % Unmodified MCC
(c)	10 wt % MCC modified with TMPTA
(d)	20 wt % Modified MCC TMPTA
(e)	10 wt % MCC modified with HMAA
(f)	10 wt % Unmodified MCC

The tensile strength curves for all composites containing 10 wt% MCC are displayed in figure 8. Figure 9 shows the two composites containing 20 wt% MCC. The tensile strength curve for neat PLA is displayed in both figure 8 and 9. All specimens can be compared in figure 10. When regarding the curves, three parameters can easily be analyzed: The tensile stress, tensile strain and Young's modulus. The tensile stress corresponds to the tensile strength of the material, tensile strain the elongation and Young's modulus the stiffness. Each curve represents an average of five replicates.

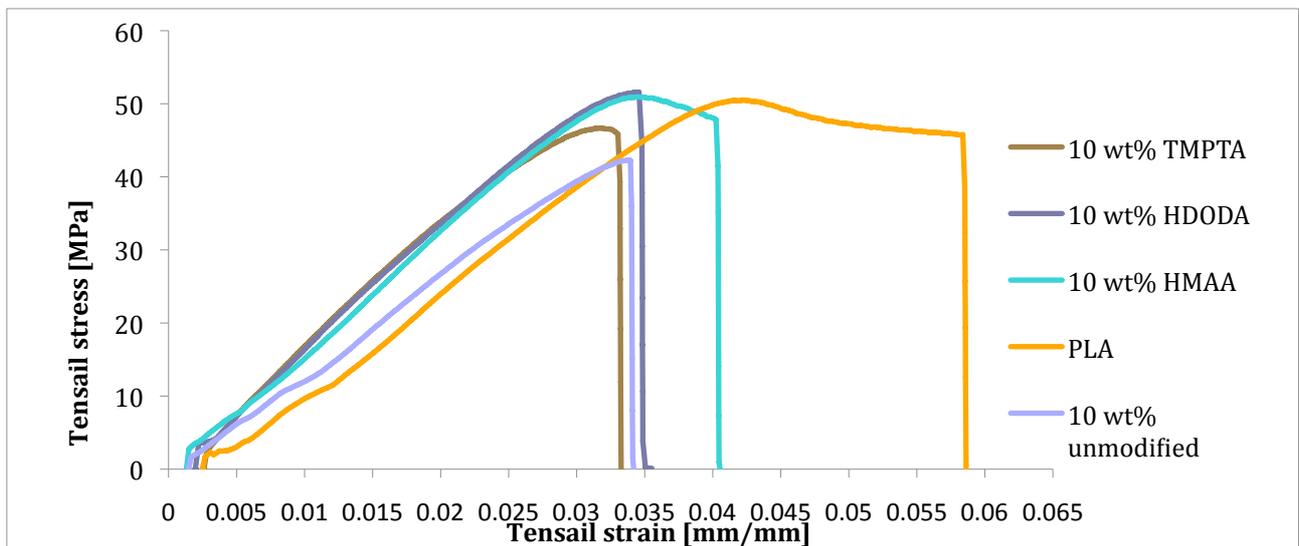


Figure 8. *Showing the tensile strength curves of the biocomposites containing 10 wt% MCC and neat PLA.*

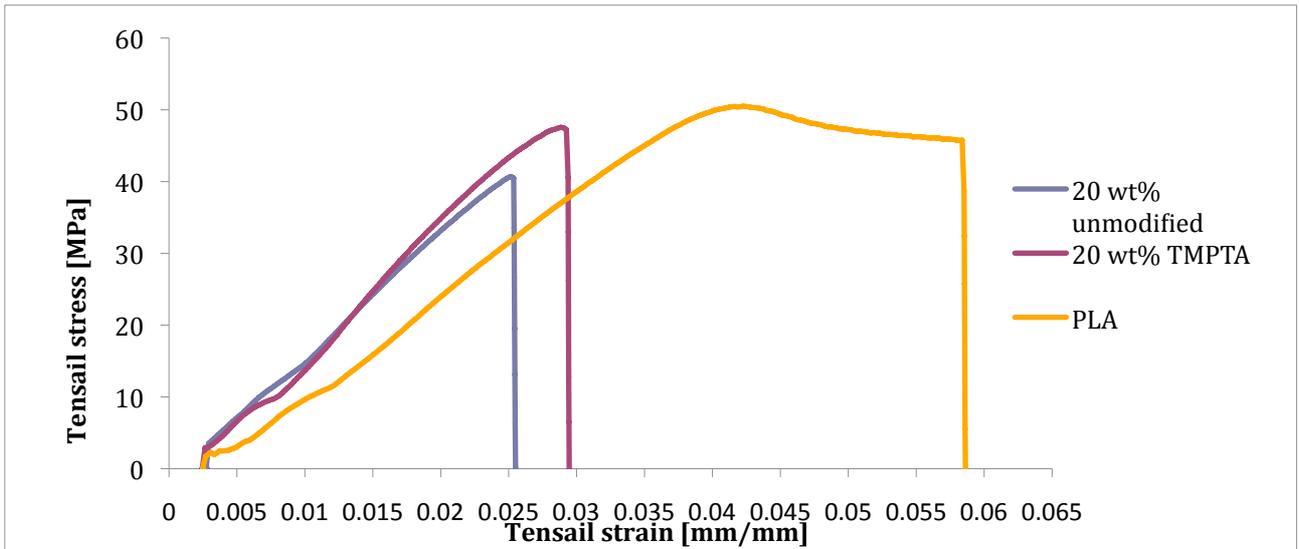


Figure 9. Showing the tensile strength curves of the two biocomposites containing 20 wt% MCC and neat PLA.

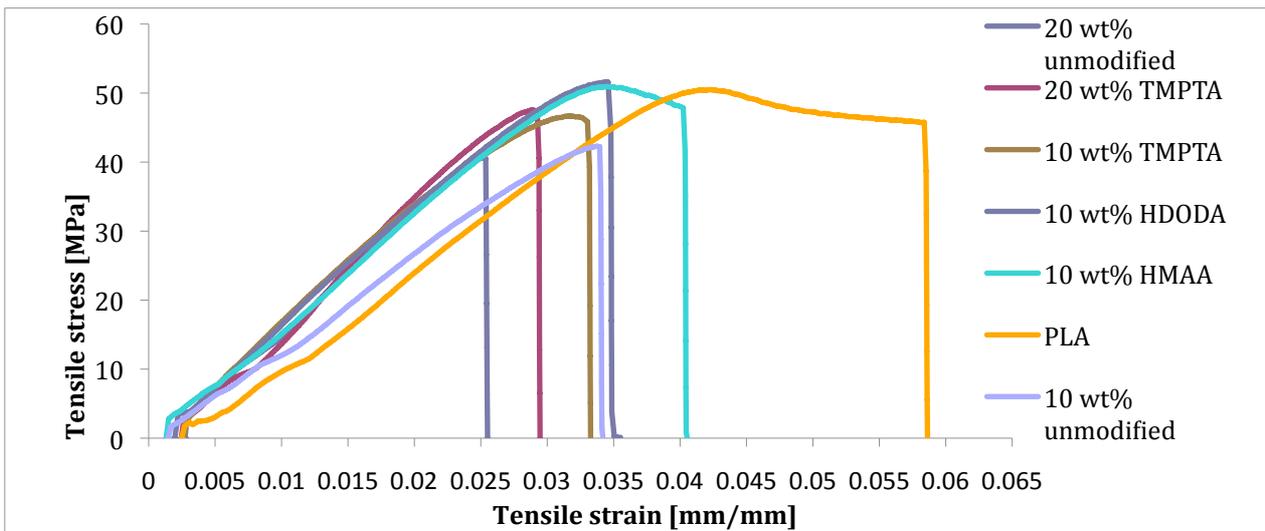


Figure 10. Showing the tensile strength curves of the different biocomposites and neat PLA.

Table 4. Results from tensile tests for each composite and pure PLA as a reference. The displayed results are average sums of the five specimens regarded. Standard deviations are shown in the brackets

Sample description	Tensile strain at maximum load [mm/ mm]	Tensile stress at maximum load [MPa]	Young's modulus [MPa]
10 % Modified MCC, TMPTA	0.031 (0.003)	43.81 (2.97)	1811.5 (56.9)
20 % Modified MCC, TMPTA	0.027 (0.003)	44.27 (5.55)	2134.6 (145.8)
10 % Modified MCC, HMAA	0.036 (0.002)	51.31 (2.14)	1829.3 (48.8)
10 % Modified MCC, HDODA	0.035 (0.002)	50.53 (1.93)	1838.8 (94.0)
10 % Unmodified MCC	0.030 (0.0006)	42.28 (8.42)	1723.5 (116.2)
20 % Unmodified MCC	0.025 (0.003)	41.17 (6.06)	2016.0 (154.2)
100 % PLA	0.043 (0.0007)	52.26 (2.3)	1712.3 (77.4)

The results in table 4 are showing that the composites are superior to neat PLA regarding their young's modulus, the stiffness. The biocomposite containing 20 wt% MCC modified with TMPTA seems to be the stiffest of them. With the increase of the content of MCC in the composite the materials stiffness is clearly increased. Recording to the results of the tensile strain at maximal load, PLA is the most elastic material from the tested ones. PLA also seems to be superior in tensile strength, which the tensile stress shows. The samples containing MCC modified with HMAA and HDODA are showing the most elasticity as well as most tensile strength of the composites. HMAA and HDODA modifications seem to have resembling effects on the composites mechanical properties.

3.3 DSC

DSC tests were made on all composites, neat PLA, neat MCC and the modified MCC from batch one and two. In figure 11 the DSC curves for neat PLA and all composites except the one containing 20 wt% MCC modified with TMPTA which can be seen in figure 12 are displayed. As can be seen in figure 11 the specimens exhibit relatively similar thermal properties, which may also be seen in table 5. All specimens show a glass temperature and a melting temperature. The composite containing 10 wt% MCC modified with TMPTA and the one containing 20 wt% unmodified MCC are showing a slight peak around 125 °C which could

indicate some crystallinity. When regarding the curve of the composite containing 10 wt% MCC modified with TMPTA in figure 11 it can be seen that the exothermic peak around 125 °C may not be a peak but rather appeared due to an offset baseline. Therefore the peak was not regarded as an indication for crystallinity and the value was written in brackets in table 5. The curve named 20 wt% unmodified in figure 11 does not seem to have an offset baseline. Therefore the exothermic peak could indicate some crystallinity. The increase of crystallinity from 10 wt% unmodified MCC to 20 wt% could devolve upon that MCC it self is semi crystalline, and an increased ratio of MCC could therefore also increase the crystallinity of the material.

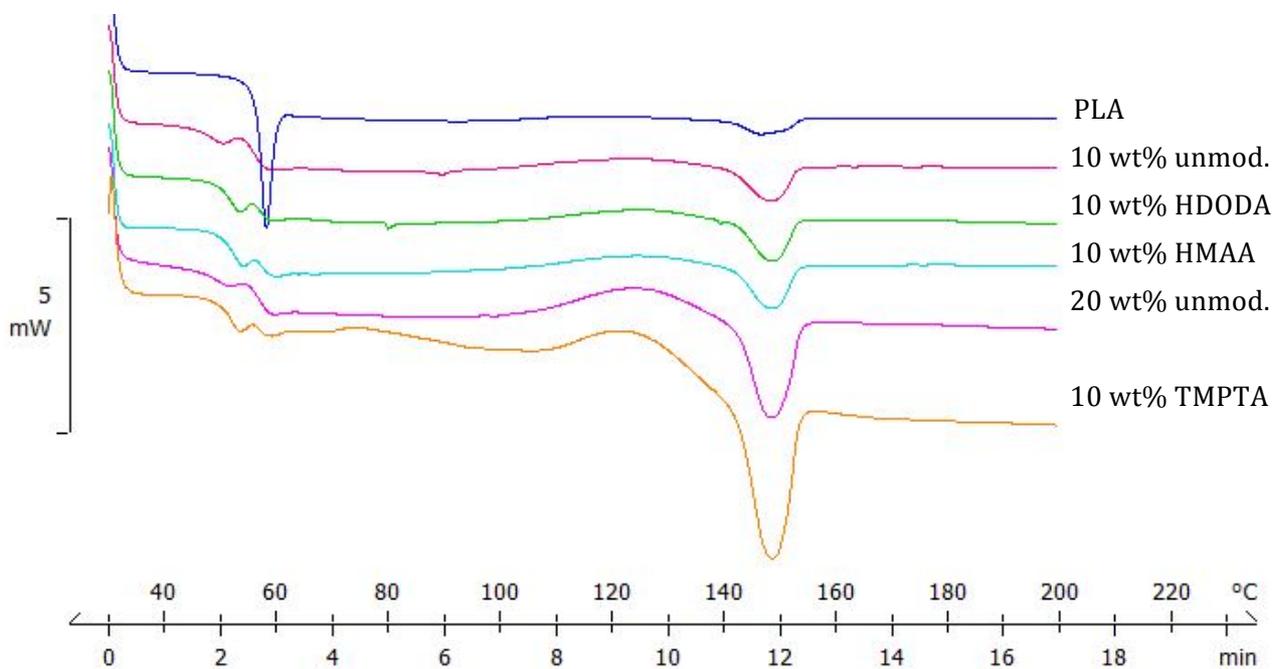


Figure 11. Showing the DSC curves of the different composites and neat PLA.

Table 5. Showing the crystalline temperature (T_c), glass temperature (T_g) and melting temperature (T_m) for the different composites. The ones missing a T_c did not show any crystallinity during the DSC. B1 and B2 stands fore batch one and batch two respectively. No replicates were made

Sample description	T_g [°C]	T_c [°C]	T_m [°C]
10 wt % Modified MCC, TMPTA	52.57	(123.06)	148.18
10 wt % Modified MCC, HMAA	53.44	-----	148.30
10 wt % Modified MCC, HDODA	54.99	-----	148.46
10 wt % Unmodified MCC	58.10	-----	148.32
20 wt % Unmodified MCC	57.72	123.69	148.23
100 % PLA	55.52	-----	146.85
			(1): 134.57
10 wt % Modified MCC, TMPTA	48.73	105.55	(2): 144.70
			(1): 142.07
20 wt % Modified MCC, TMPTA	51.44	107.57	(2): 149.56
			(1): 138.92
24 wt % Modified MCC, TMPTA	51.43	111.52	(2): 147.10
Unmodified MCC	-----	-----	153.68
B1: MCC modified with TMPTA	-----	-----	154.74
B1: MCC modified with HMAA	-----	-----	153.58
B1: MCC modified with HDODA	-----	-----	169.07
B2: MCC modified with TMPTA	-----	-----	161.61
B2: MCC modified with HMAA	125.77	-----	162.83
B2: MCC modified with HDODA	-----	-----	158.29

Results in table 5 are showing that the composites melting temperature is relatively constant around 148 °C. This means a slight improvement of the melting temperature in the composites compared to neat PLA. The slight increase could be explained by that neat MCC has a higher melting temperature than neat PLA, when combined the melting temperature should increase. The amount of MCC, as well as the modification type seems not to have made

any difference recording to the results in table 5. The three composites written in cursive style in table 5 are samples, which became brittle after several hot pressing procedures and had two melting peaks, and therefore two melting temperatures. The three specimens all got a more yellow color as they became brittle. The MCC from batch two modified with HMAA showed a glass temperature, written in cursive in table 5, this result do not seem likely due to that none of the other modified MCC, as well as the neat MCC showed any trends of a glass temperature. Therefore the glass temperature written in cursive style in table 5 was not considered as an accurate result.

Figure 12 is displaying the DSC curve for one of the three specimens, which became brittle after reheating with the hot press approximately four times. As can be seen in figure 12, the specimen shows an exothermic peak around 110 °C, which can indicate crystallinity. The brittleness of the sample also contributes to the conclusion of that the crystallinity in the material has increased. The double melting peaks in figure 12 are indications of that there are two materials present in the sample. This could mean that the PLA and MCC somehow have separated during the repeated melting procedures. The melting temperatures of the specimen in figure 11 do not match the ones of neat PLA or MCC, which makes it harder to draw a distinct conclusion regarding what happened with the sample.

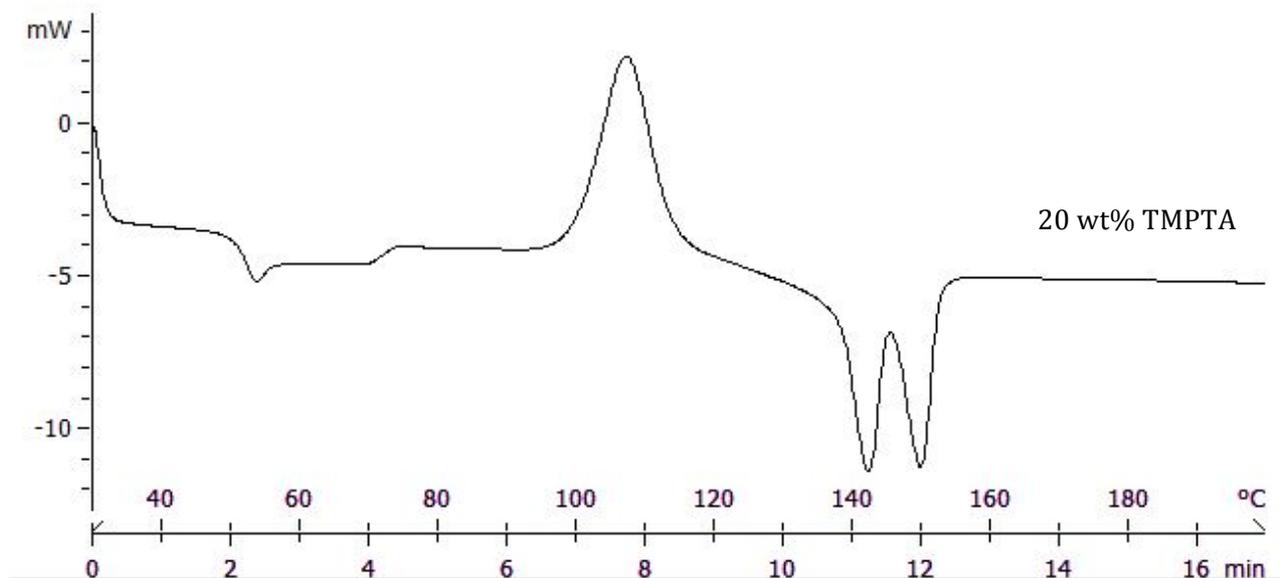


Figure 12. Showing the DSC curve for one of the specimens, which became brittle after hot pressing. Specimen displayed is the one containing 20 wt% MCC modified with TMPTA

DSC curves for all specimens in table 5 are found in the appendix (II).

3.4 Scanning electron microscope images

SEM images of neat PLA, the composites containing 10 wt% unmodified MCC, 10 wt% MCC modified with TMPTA and 20 wt% MCC modified with TMPTA are displayed. Pictures of a region of break as well as a region where the specimens had been cut were taken. The images are showing significant differences between figure 13, 14 and 15. When regarding neat PLA, displayed in figure 10, one can see a homogeneous, relatively even surface. In figure 14 and 15 more rough surfaces can be seen. Comparing the latter two, one can see darker parts in figure 14, which are not present in figure 15. The darker parts are likely to be the MCC due to that they are not present in either figure 13, neat PLA or in the other images displaying composites containing modified MCC. The differences in figure 14 and 15 can confirm that the modification of MCC increased the miscibility between MCC and PLA. Therefore the SEM images confirm the results from the FTIR and WRV, that the modification of the MCC was successful.

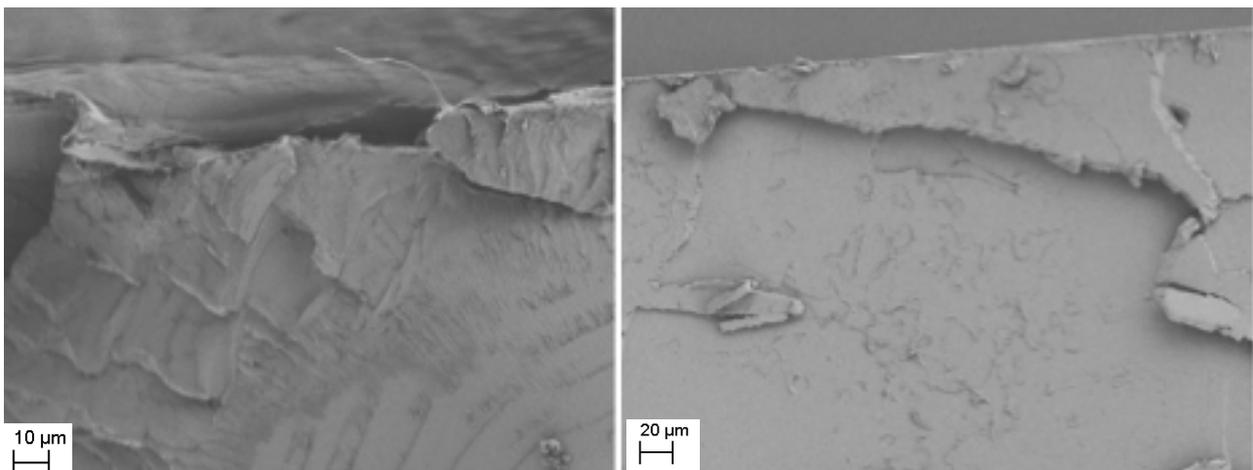


Figure 13. SEM images of neat PLA. The image at the left shows a region after break from tensile test, and the left an after cutting the material

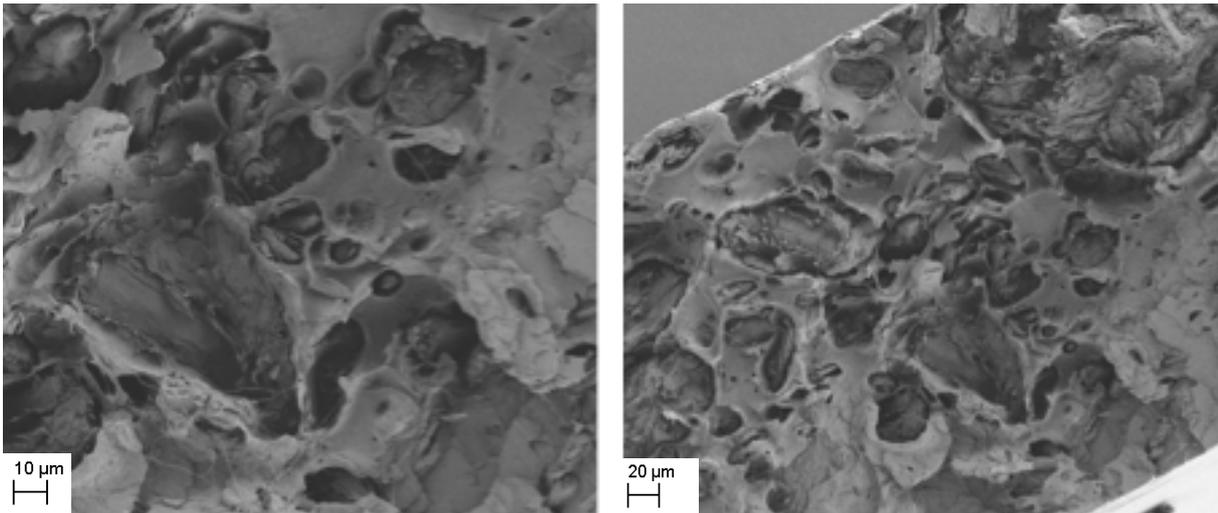


Figure 14. SEM images of composite containing 10 wt% unmodified MCC. Both images are showing a region after break from tensile test

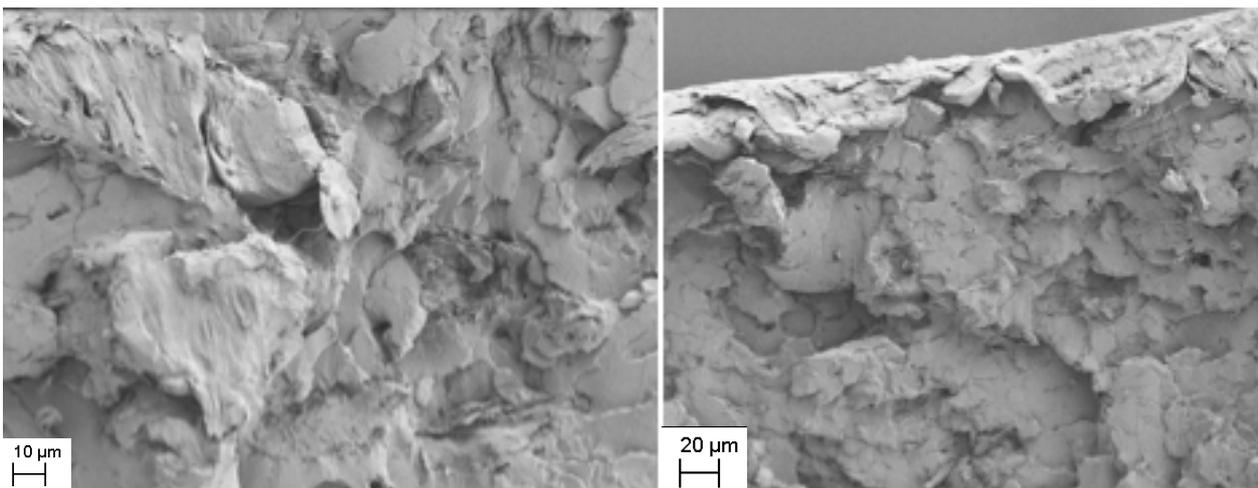


Figure 15. SEM images of composite containing 10 wt% MCC modified with TMPTA. Both images are showing a region after break from tensile test

In figure 13 the composite containing 20 wt% MCC modified with TMPTA is displayed. The sample is from after the composite became brittle, possibly due to degradation of MCC as discussed in section 3.3. The left image displaying a cut region shows that the composite crumbled along the cut. In figure 13, no MCC can be distinguished, which could be an indication for that the MCC has been degraded. Regarding figure 12 no MCC is distinguished either, but no previous results are indicating degradation of MCC in the sample. Therefore the SEM image, seen in figure 13 did not give any more clarification to what happened when the composite became brittle.

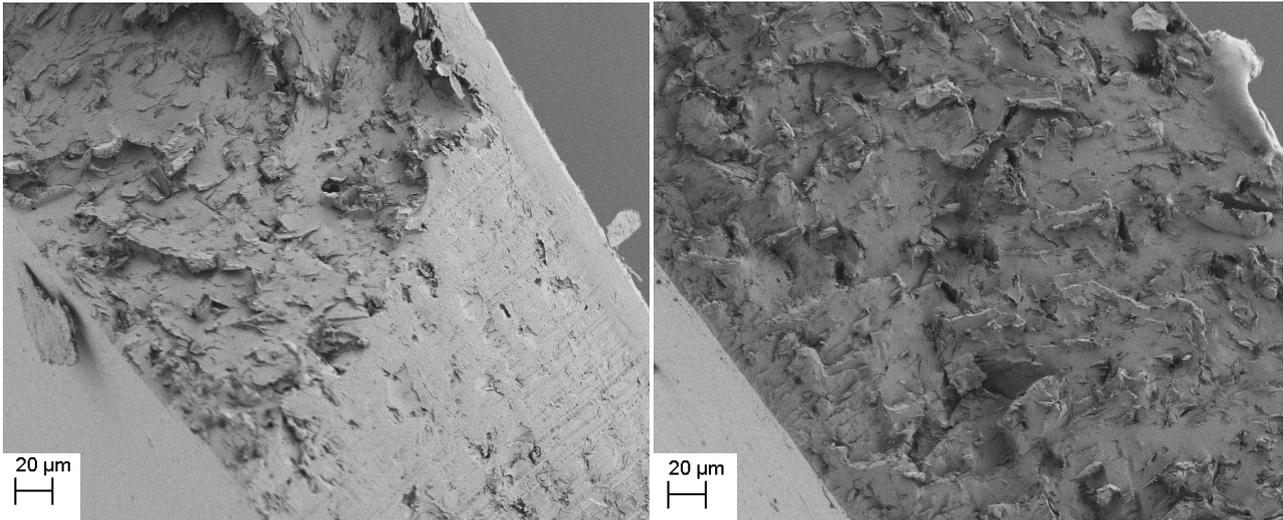


Figure 16. SEM images of the composite containing 20 wt% MCC modified with TMPTA.

The sample is taken from after it became brittle. At the left can a cut version be seen, and at the left a broken.

4 Summary of results

When hot pressing the composites into films, the procedure sometimes had to be repeated in order to get films with as little bubbles as possible. During this procedure an occurrence was observed. Three films became very brittle after hot pressing several times; due to the brittleness it was not possible to cut any dog bones out of the samples. As shown in table 5 MCC, modified and unmodified have approximately the same melting temperature, therefore the conclusion can be made that it is not the modification itself that protects the MCC during the extrusion, but rather the interaction between the MCC and the PLA. Worth noticing is also that the three regarded specimens all contained MCC modified with TMPTA. If a modification with TMPTA leads to a composite that is more thermal instable than the other modifications is not a conclusion that could be drawn at the moment. Regarding the DSC curve in figure 12, some distinct differences between it and the other composites in figure 11 can be observed. The curve in figure 12 is showing a crystalline peak, as well as a double melting peak. The double melting peak indicates that there are two different materials present. There are many possible explanations for this phenomenon; one being that the components MCC and PLA separated in some way during the melting process (hot pressing). The composites color change can indicate degradation of MCC, which in turn could explain the crystalline peak in the DSC curve. During degradation of the MCC the amorphous parts would have been degraded first, which would result in a more crystalline MCC. Which material actually caused the crystalline peak was not further investigated in this study.

The miscibility between modified MCC and PLA compared to unmodified MCC seems to be improving with the modification. When examining the samples in figure 7, a distinct difference in color can be observed when comparing the composites containing unmodified and modified MCC. The ones containing unmodified MCC have a yellow color compared to a more light grey color in the ones with modified MCC. As mentioned before, the yellow color could be an indicator of that the MCC has been degraded. The possible degradation would have had to occur during the extrusion, due to that the samples had a yellow color from thereon. A possible, but not further investigated explanation for why this occurred for the unmodified and not for the ones containing modified MCC could be that the modified MCC blends in to the PLA matrix better than the unmodified, and therefore the modified MCC is more protected during the extrusion. The difference in melting temperature between the modified and unmodified MCC is not likely to have been the reason for the degradation

differences, due to that the differences are too small when regarding that the extrusion occurred at 190 °C. How well the modification of the MCC went did not seem to influence the thermal properties of the MCC, the melting temperatures did not differ that much comparing the two batches. When comparing the SEM images of the composites containing 10 wt% unmodified and 10wt % modified MCC, figure 14 and 15, it is conspicuous that the material in figure 15 seems to look more homogenous than the one in figure 14. If this occurred due to the modification or not would be a very interesting factor to investigate further in future studies.

It could have been interesting to investigate the differences between the tensile properties of the composites made from batch one and two due to the different successful modifications of MCC. Unfortunately there were not enough specimens that reached the requirements for obtaining valid results from batch one. The FTIR results for the composite containing MCC modified with HMAA from batch two showed no distinct differences in the regarded area from before and after reflux, which could mean that the modification failed. WRV analysis of the sample showed though that the modified MCC had a lowered water retention value; therefore the modification must have been successful even though FTIR did not show distinct results.

5 Conclusion

The modification that showed the most promise for a biocomposite was the one where HMAA was used, though no transcendent properties compared to neat PLA were obtained. All biocomposites showed an increase of Young's modulus, or with other words, stiffness, compared to neat PLA. None of the modifications seemed to have any affect on the thermal properties of the biocomposites. The varying results of the modification process are showing optimization potential. The miscibility between PLA and MCC was found to increase with the modification of MCC.

Even though PLA is a thermoplastic, results in this study showed that a composite consisting of modified MCC (TMPTA) and PLA is not suitable for applications where the product has to be able to withstand being heated several times, without any further alterations.

6 Acknowledgements

The author would like to thank Södra Cell AB for the gift of the PLA used in this study. The division of organic chemistry, as well as the division of polymer technology at Chalmers University of Technology are gratefully acknowledged for the use of their equipment, recourses and support.

The following people deserve special thanks for their contributions to this thesis:

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My friend and fellow student, Jonathan Carbol for helping me through tough struggles with my computer.

Last, but not least, I would like to thank my classmates who worked on their bachelor thesis at the department of organic chemistry for helpful discussions and many laughs.

7 References

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Appendix I, FTIR spectrums

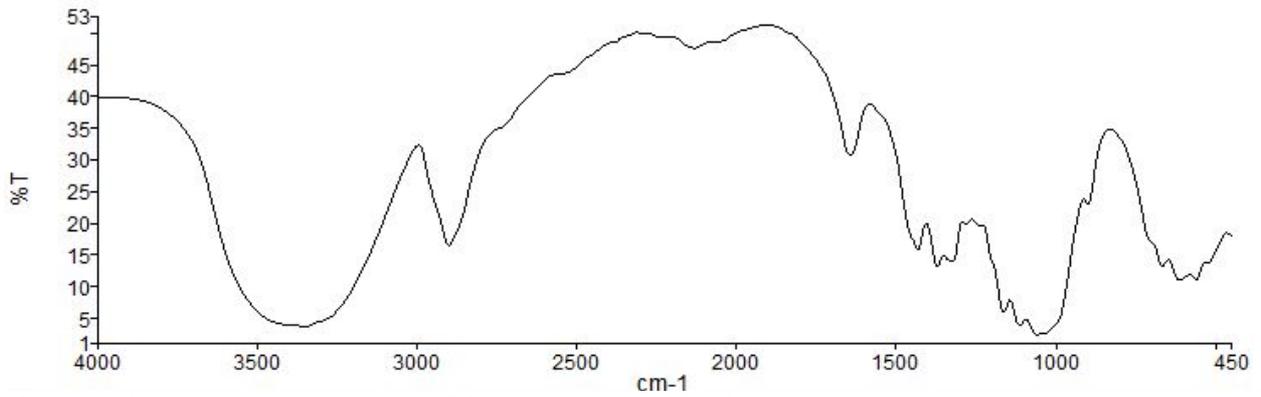


Figure I.1 . FTIR-spectrum for MCC modified with HDODA before reflux, batch 1

FTIR-spectrums from batch 1

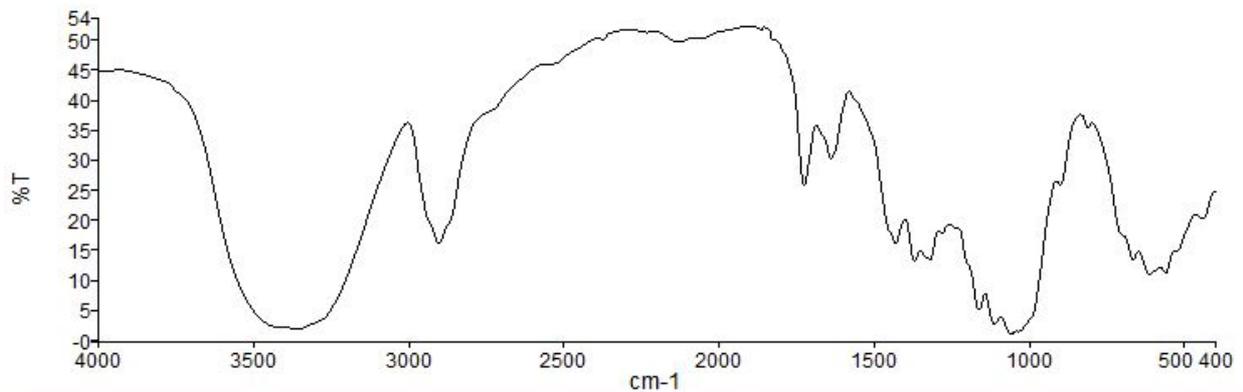


Figure I.2 . FTIR-spectrum for MCC modified with HDODA before reflux, batch 1

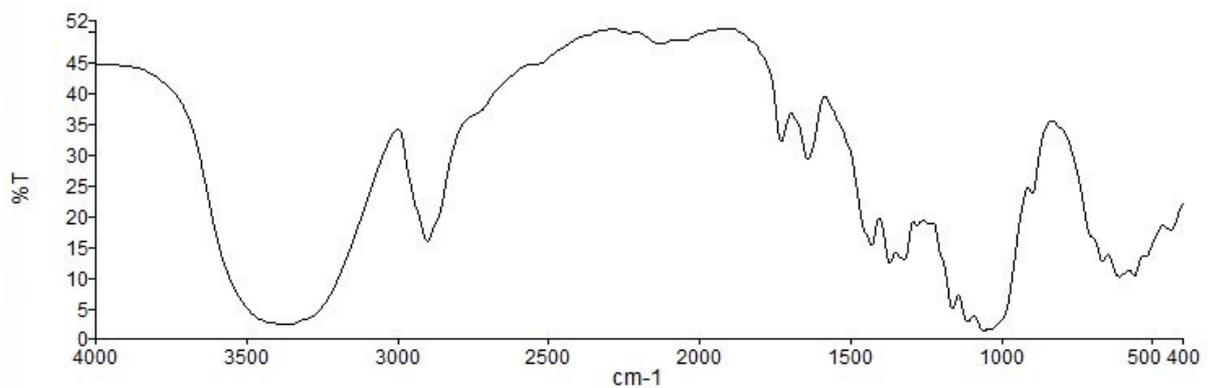


Figure I.3. FTIR-spectrum for MCC modified with HDODA after reflux, batch 1

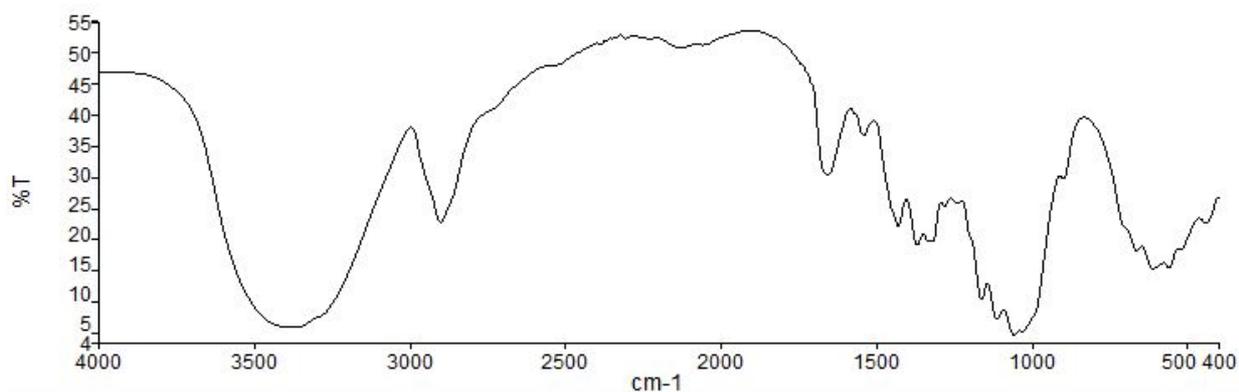


Figure I.4. FTIR-spectrum for MCC modified with HMAA before reflux, batch 1

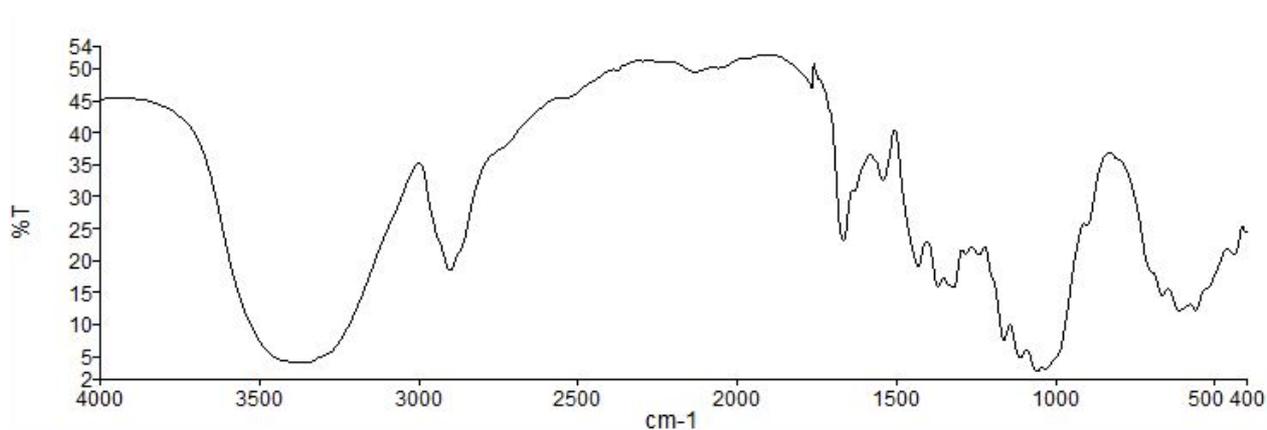


Figure I.5. FTIR-spectrum for MCC modified with HMAA after reflux, batch 1

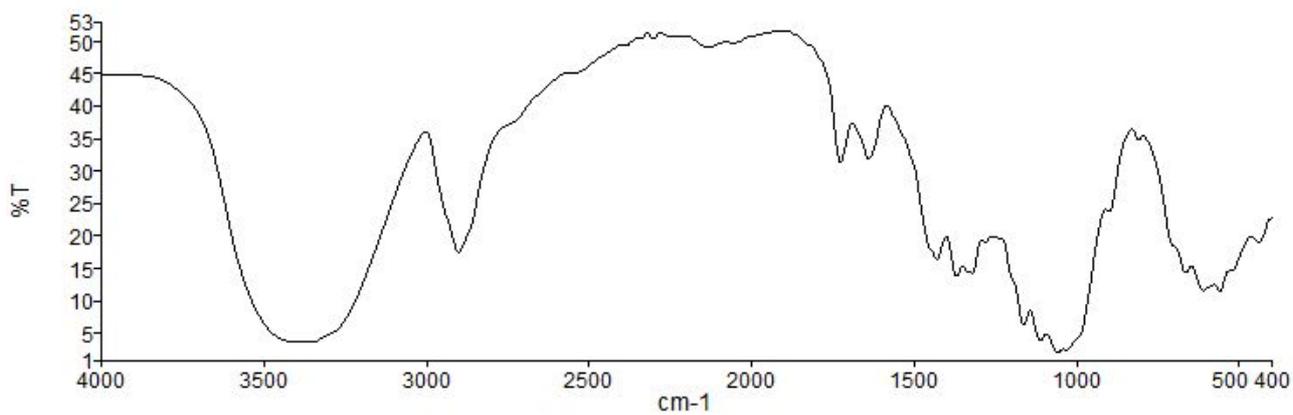


Figure I.6. FTIR-spectrum for MCC modified with TMPTA before reflux, batch 1

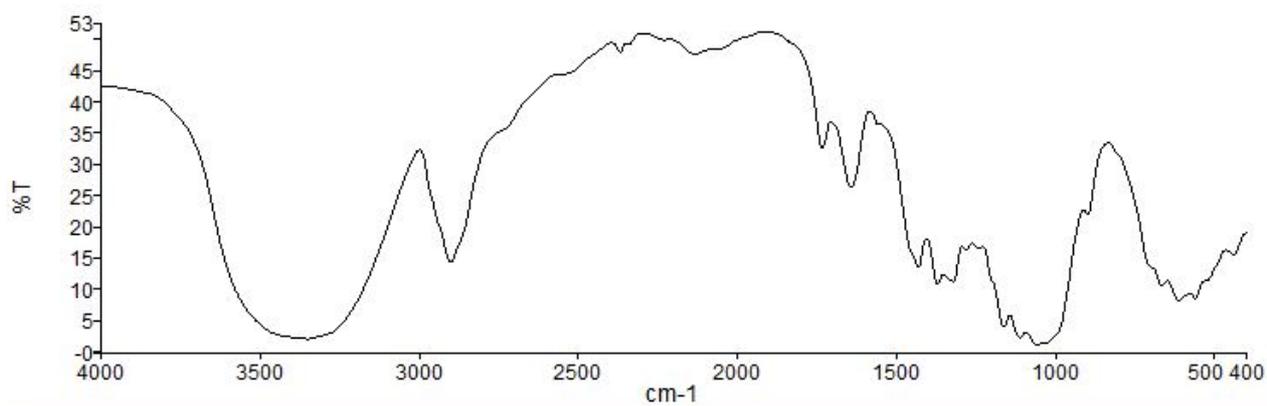


Figure I.7. FTIR-spectrum for MCC modified with TMPTA after reflux, batch 1

FTIR-spectrums from batch 2

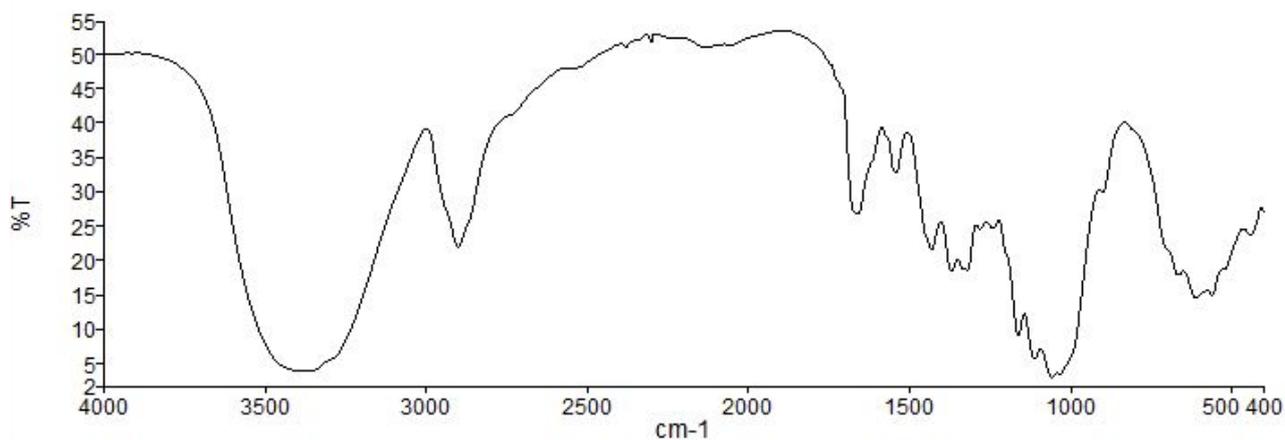


Figure I.8. FTIR-spectrum for MCC modified with HMAA before reflux, batch 2

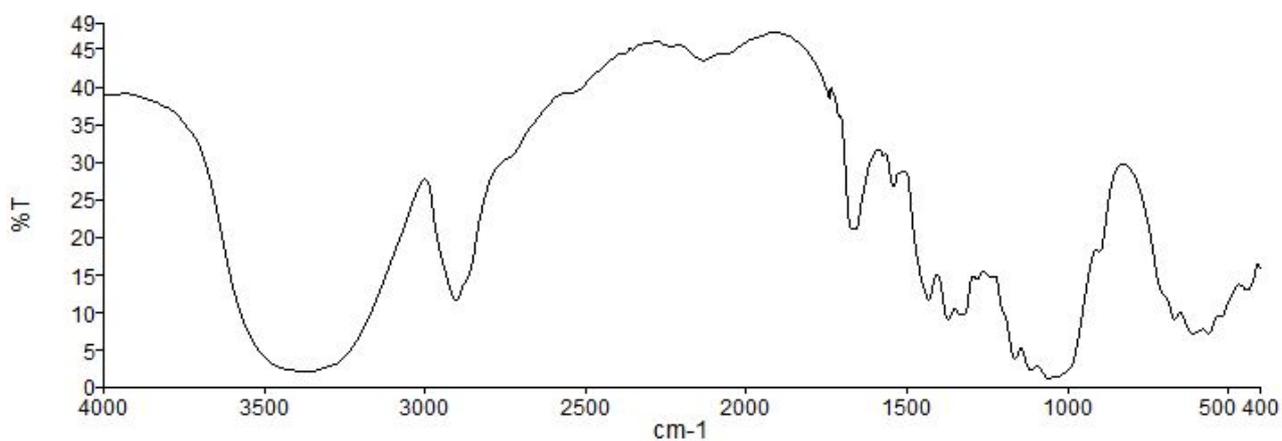


Figure I.9. FTIR-spectrum for MCC modified with HMAA after reflux, batch 2

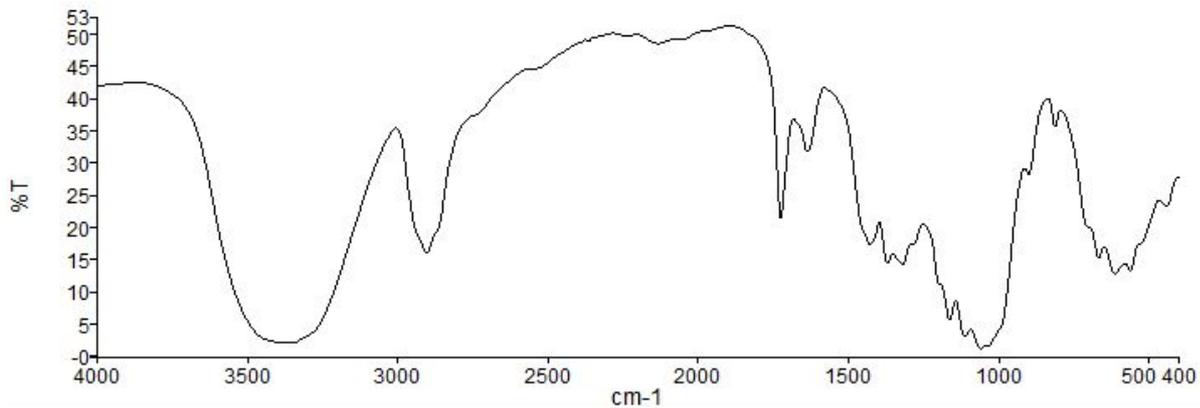


Figure I.10. FTIR-spectrum for MCC modified with HDODA before reflux, batch 2

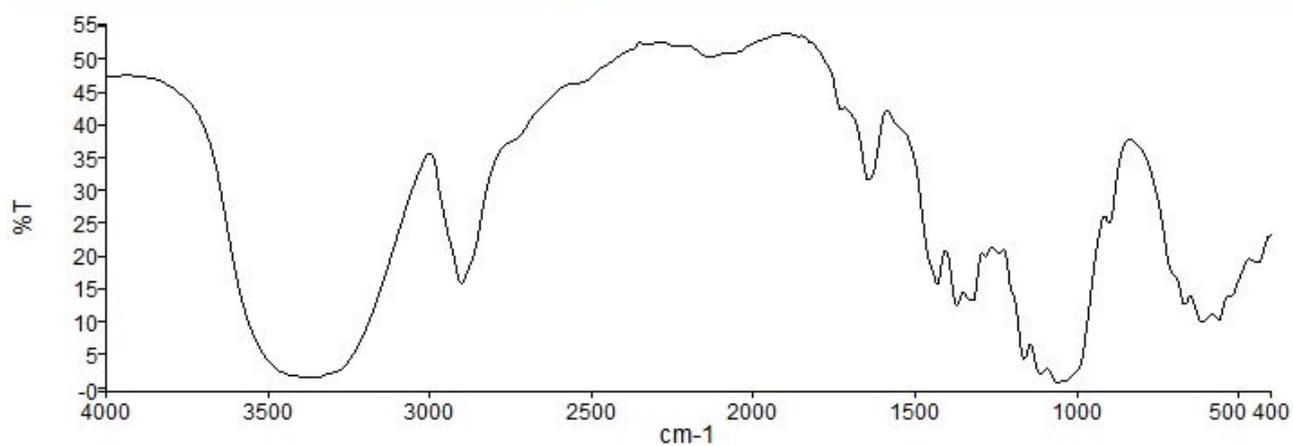


Figure I.11. FTIR-spectrum for MCC modified with HDODA after reflux, batch 2

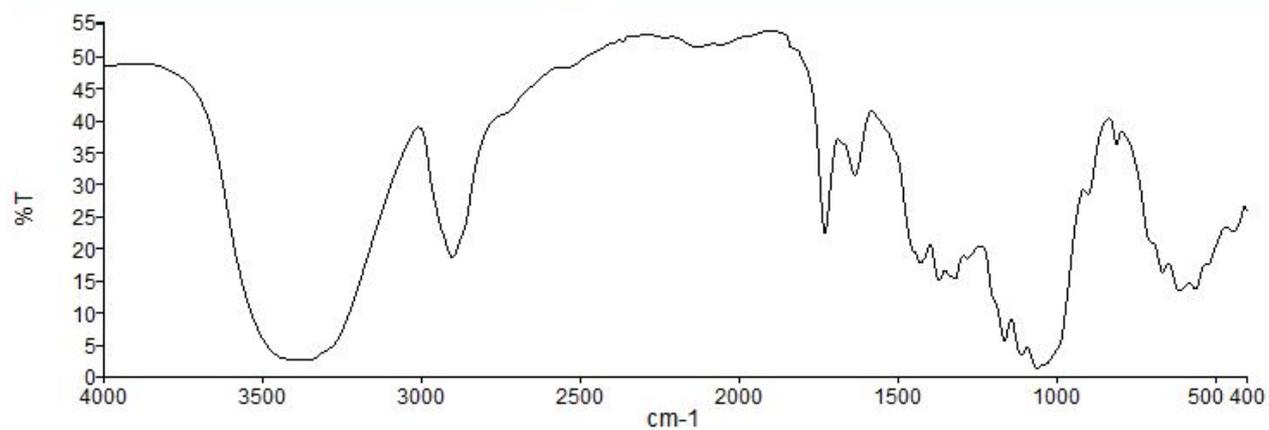


Figure I.12. FTIR-spectrum for MCC modified with TMPTA before reflux, batch 2

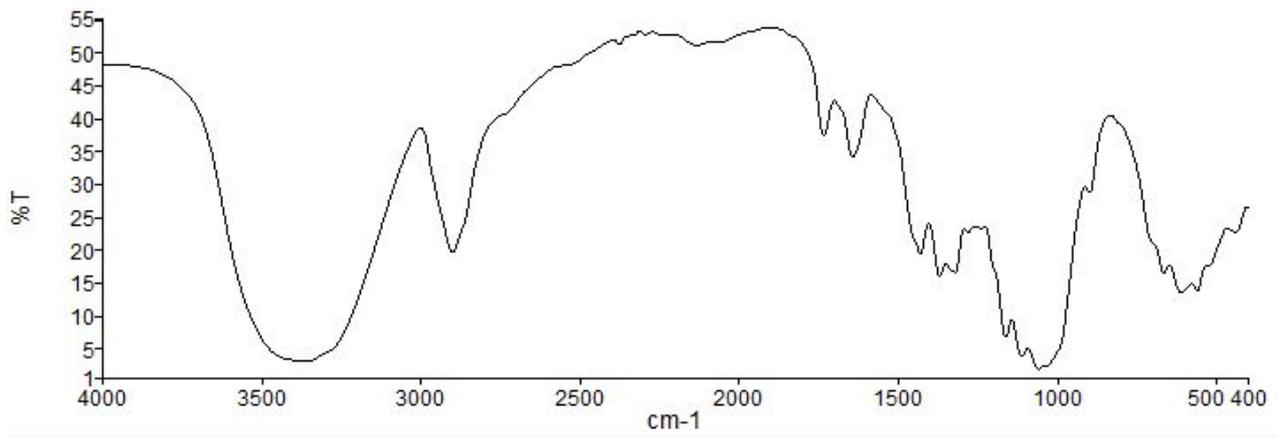


Figure I.13. FTIR-spectrum for MCC modified with TMPTA after reflux, batch 2

Appendix II, DSC curves

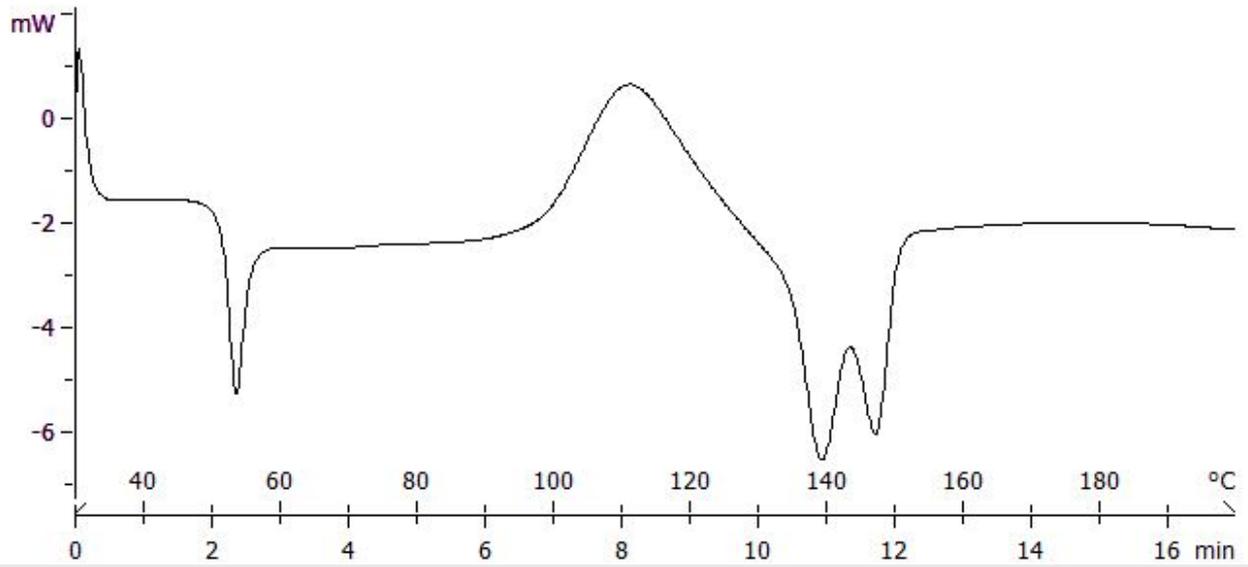


Figure II.1. DSC curve for a specimen, which became brittle, containing 24 wt % MCC modified with TMPTA

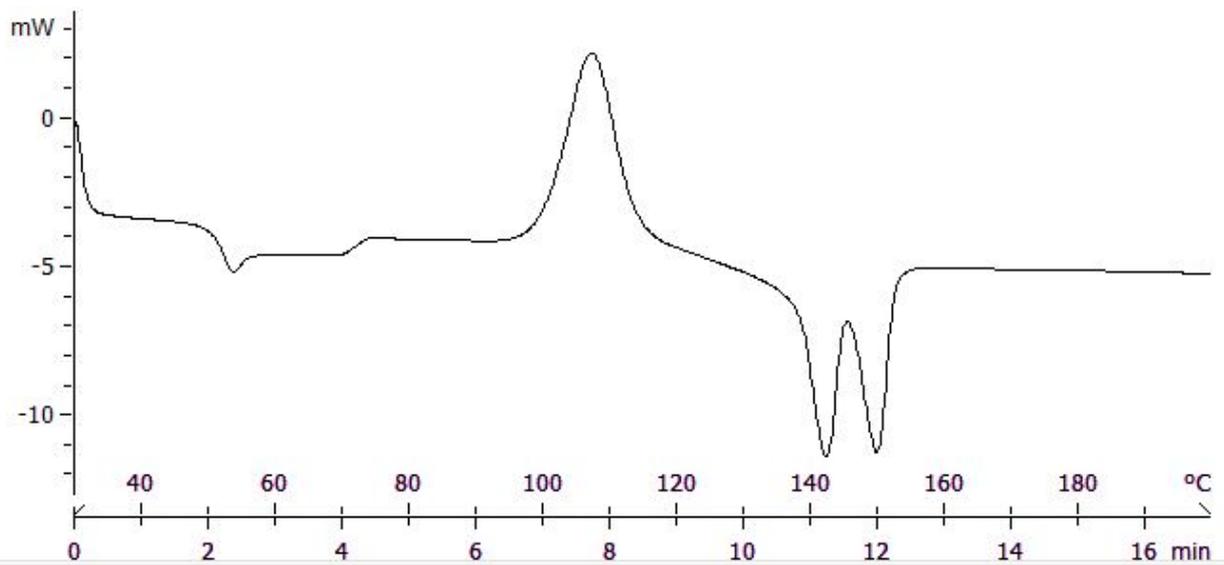


Figure II.2. DSC curve for a specimen, which became brittle, containing 20 wt % MCC modified with TMPTA

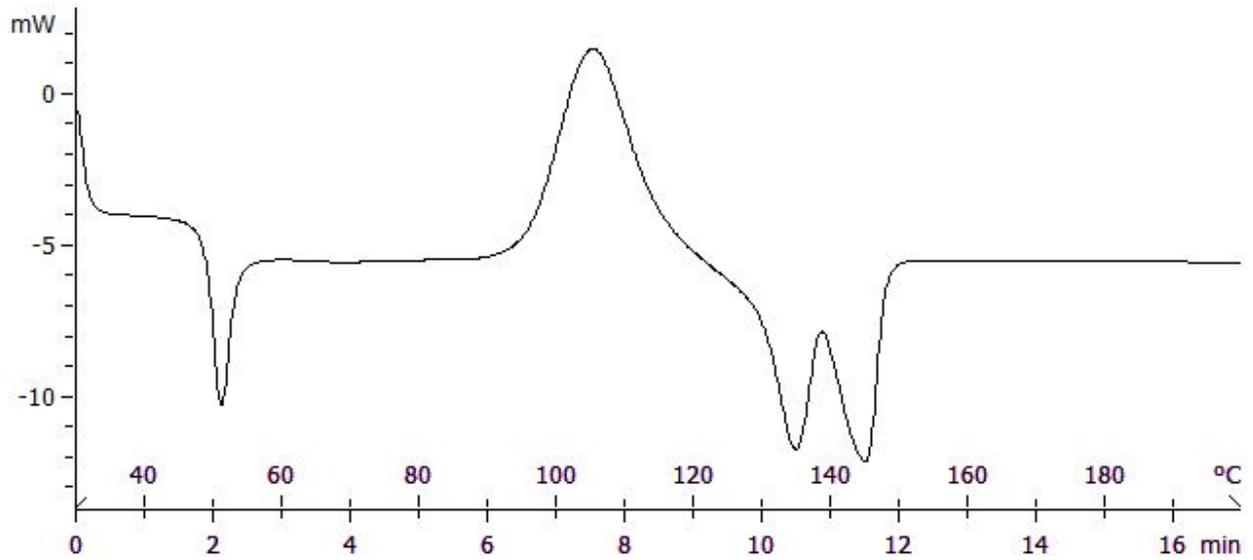


Figure II.3. DSC curve for a specimen, which became brittle, containing 20 wt % MCC modified with TMPTA

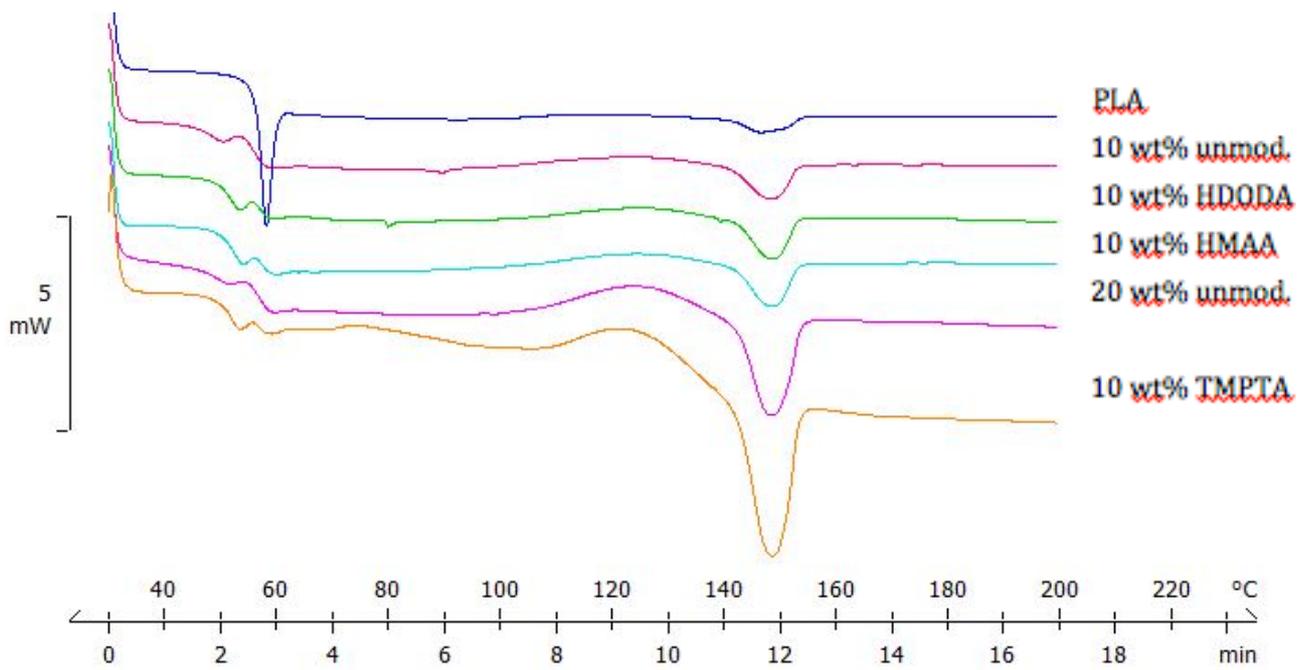


Figure II.3. DSC curves of the different composites and neat PLA.