



Maleimide grafting onto polysaccharides via mild condition esterification and its impact on their structure

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ABSTRACT

This study proposes an innovative approach to tailor the properties of two polysaccharides, microcrystalline cellulose (MCC) and potato starch, through chemical modification in dispersion. The methodology involves the grafting of 6-Maleimidohexanoic acid (6-MHA) moieties onto hydroxyl groups of the polysaccharides without dissolving them in order to keep their native structure preserved. To overcome the slow and inefficient reaction between carboxylic acids of 6-MHA and hydroxyl groups of the polysaccharides, a vinyl ester of 6-MHA was synthesized through the transvinilation of 6-MHA acid with vinyl acetate. The resulting 6-MHA ester was employed to introduce a new functionality to polysaccharides' hydroxyl groups via transesterification, catalyzed by potassium carbonate. To enhance the reactivity, the polysaccharides were mercerized prior to modification process. The efficiency of the transesterification reaction between the vinyl ester of 6-MHA and the hydroxyl groups of the polysaccharides was confirmed using Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR). Thermal behavior analysis was carried out using thermogravimetric analysis (TGA), while changes in crystallinity resulting from the modification were assessed through X-ray diffraction analysis (XRD). Finally, the impact of the modification on the morphology of polysaccharides was examined with environmental scanning electron microscopy (ESEM). Despite changes in microstructure, MCC kept its macrostructure remained morphologically unchanged while the granular structure of starch was damaged. Maleimide grafting onto MCC and starch has the potential to turn them into thermally reversible materials for various applications such as debondable adhesive or coating.

1. Introduction

Polysaccharides, as a class of natural biopolymers, have attracted considerable attention across various scientific disciplines due to their abundance, availability, biodegradability, and versatile properties [1]. Among them, starch and cellulose have emerged as promising materials, with numerous applications spanning from food [2] and pharmaceuticals [1] to materials science [3,4] and biotechnology [1]. However, despite their inherent advantages, both starch and cellulose often require tailored modifications to meet the specific properties for the intended applications.

One class of modification that has gained attention in recent years is the grafting of maleimide groups [5,6] into the polysaccharides' backbones. Maleimide functionalization offers a versatile platform for the attachment of various biomolecules, drugs, or other compounds to polysaccharides. These modifications can impart new functionalities,

such as improved drug delivery [7], enhanced adhesion properties [8], or the introduction of responsive elements, thereby expanding the applications of starch and cellulose in diverse fields.

Starch or cellulose grafted with 6-Maleimidohexanoic acid (6-MHA) will enable click chemistry between maleimide and other alkene or furan-grafted molecules through a Diels-Alder reaction. The Diels-Alder reaction stands as a cornerstone in organic chemistry, recognized for its efficiency and versatility in forming carbon-carbon bonds. It belongs to the category of cycloaddition reactions, specifically classified as a [4 + 2] cycloaddition. In this reaction, a conjugated diene reacts with a dienophile to form a new six-membered ring structure. The reaction proceeds through a concerted mechanism, where the π electrons of the diene and dienophile interact to form two new σ bonds, resulting in the formation of a cyclic product known as a cycloadduct. Click chemistry is an approach of chemical synthesis that focuses on developing efficient and selective chemical reactions that can be used to quickly and easily

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join two molecular building blocks together. This approach was first introduced by K. Barry Sharpless and his colleagues in 2001 as a way to accelerate drug delivery and material science research [9]. Click chemistry has gained significance due its efficiency and versatility [10, 11]. Click reactions are specifically designed to occur under mild, non-toxic conditions, enduring high efficiency and selectivity. This allows for rapid synthesis of complex molecules with fewer synthetic steps, minimizing waste and reducing environmental impact. The grafting of maleimide moieties onto polysaccharides subsequently unlocks a range of applications [12,13] such as debondable adhesive or coating which would further enable recycling of bonded and coated materials.

Among the various reactions available for grafting new functionalities onto polysaccharides such as starch and cellulose, esterification stands out as one of the most common utilized chemical reactions [14–20]. Esterification involves the introduction of ester functional groups into the polymer structure by reacting carboxylic acid derivatives with hydroxyl groups, typically abundant in polysaccharides. This reaction results in the formation of ester bonds, thereby altering the physicochemical properties of the polysaccharides. Esterification can be tailored to achieve specific modifications, such as enhanced solubility, hydrophobicity, improved film-forming capabilities, and biocompatibility [21]. Nonetheless, this functionalization has its limits, as it may lead to the degradation of the microstructure of polysaccharides. The microstructure is crucial in determining the inherent characteristics of starch and cellulose, such as mechanical strength, solubility, rheological behavior, and crystallinity [22]. Therefore, it is desirable to develop modification techniques that minimize the damage on the microstructure.

To effectively utilize polysaccharides as advanced materials, a high degree of substitution is required [19]. The esterification of polysaccharides can be performed in aqueous or non-aqueous media [21]. Despite being cost-effective, safe, and environmentally friendly, the method suffers from low reaction efficiency and degree of substitution (DS). In the case of starch, this is attributed to its crystalline structure and extensive intra- and intermolecular hydrogen bonding, rendering it nearly insoluble in cold water. Even for small-molecules, it is difficult to penetrate into the interior of starch granules [21]. The limited modification capabilities of starch in an aqueous environment can be remedied through the application of metal catalysts, which however are associated with health issues.

In order to achieve higher DS, starch can be esterified in a non-aqueous environment [23]. In this case, starch in its dry form undergoes modification using a solvent or the reagent as the medium, typically at elevated temperatures (≥ 100 °C). Liquid acid anhydride is often utilized in excessive quantities, serving both as the reactive agent and as a reaction solvent alongside acidic or alkaline catalysts. The esterification of polysaccharides is traditionally achieved through acyl chlorides or anhydrides reactions [4,24–27] owing to the limited reactivity between carboxylic acid groups and hydroxyl groups present in polysaccharides. Unfortunately, these reactions generate hydrochloric acid or acids as a byproduct, leading to hydrolysis of glycosidic bonds. The consequence of hydrolysis on polysaccharides structure is characterized by a transformation in the macromolecular architecture and properties of these carbohydrate polymers. Indeed, starch or cellulose are both organized in semi crystalline and amorphous areas, and their amorphous area is more prone to degradation. In an attempt to mitigate this acid-induced degradation in polysaccharides, base such as pyridine are frequently employed to neutralize the generated acid [28]. Although the use of a nitrogen stream can help in eliminating gaseous hydrogen chloride as it forms, it is important to note that even brief exposure to localized acid conditions may result structural damage to cellulose or starch. Continuous development in researching new solvent systems for non-water soluble polysaccharides, such as cellulose or certain type of starch is important for performing modification with high degree of substitution. In recent years, lithium chloride/*N,N*-dimethylacetamide

(LiCl/DMAc) has gained widespread popularity. Initially, it has been recognized for its ability to dissolve polyamides and chitin while its application expanded rapidly, with McCormick [29] and Turbak [30] independently demonstrating its capability to dissolve cellulose. The challenge of finding suitable solvents to perform the reaction is to avoid the dissolution of polysaccharides but at the same time swell them to increase their reactivity.

This article explores the feasibility of grafting maleimide groups onto starch and cellulose while preserving their microstructure intact. The study employs an innovative esterification procedure [31] that has proven to be successful in producing long chain fatty acid cellulose esters, with a high degree of substitution. This new process is based on the transesterification reaction between the hydroxyl groups present at the surface of polysaccharides and the vinyl ester of a carboxylic acid. In contrast to conventional esterification methods using acyl chlorides or anhydrides, the novel transesterification approach employing vinyl esters represents a potential mild acylation technique. Moreover, this method generates acetaldehyde as a byproduct that can be easily removed from the reaction medium due to its low boiling point (21 °C). To our knowledge, this process has not been used to graft maleimide moieties onto polysaccharides.

In this study, we investigated the modification of microcrystalline cellulose (MCC) and potato starch (hereafter referred as starch) using the vinyl ester of 6-MHA under mild conditions. The adjusted reaction parameter previously reported by Ref. [31], which resulted in the highest degree of substitution, were used to graft 6-MHA moieties onto cellulose and starch. Our goal was to graft 6-maleimidohexanoic acid moieties onto starch and MCC, enhancing their functionalities without compromising the integrity of these polysaccharides.

The initial step consists in the synthesis of vinyl ester through the transvinylation of 6-MHA with vinyl acetate. The synthesized ester was then used to functionalize MCC and starch through a transesterification reaction, using potassium carbonate (K_2CO_3) as mild catalyst and a mixture of dimethylformamide (DMF) and dimethylacetamide (DMAc) as solvent. This solvent mixture was chosen for its inability to dissolve starch or MCC, and its capacity to swell polysaccharide structures, thereby increasing the degree of substitution. The esterification of MCC and starch was investigated by Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. Thermal characteristics of modified MCC and starch were determined by thermogravimetric analysis (TGA). The impact of the reaction on the macromolecular chains and microstructure of MCC and starch was studied by X-ray diffraction (XRD). Finally, scanning electron microscopy (SEM) was employed to investigate the morphology of the functionalized polysaccharides.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose (MCC, powder 20 μm), potato starch, 6-maleimidohexanoic acid, chloro(1,5-cyclooctadiene) iridium-(I) dimer (Ir 57.2 %) ($[\text{Ir}(\text{cod})\text{Cl}]_2$, HS157), potassium carbonate, sodium acetate, vinyl acetate, acetonitrile, chloroform, dichloromethane, dimethylacetamide (DMAc), and dimethylformamide (DMF), Deuterated DMSO ($\text{DMSO-}d_6$, 99.80 % atom D), deuterated trifluoroacetic acid (d_1 -TFA, 99.5 % atom D), were purchased from Sigma-Aldrich (Stockholm, Sweden). All other solvents were American Chemical Society (ACS) grade and used as received.

2.2. Instrumentation

2.2.1. FTIR spectroscopy

A Fourier-transform infrared (FTIR) spectrophotometer FTIR (Spectrum Two, PerkinElmer, Llantrisant, UK) was equipped with a Universal Attenuated Total Reflectance (UATR) diamond accessory, which allows

collection of spectroscopy FTIR spectra directly on a sample without any special preparation. The “pressure arm” of the instrument was used to apply a constant pressure (monitored by software) to the sample positioned on top of the diamond crystal to ensure a good contact between the sample and the incident IR beam. All FTIR spectra were collected at a spectrum resolution of 4 cm^{-1} , with 32 scans over the range from 4000 to 500 cm^{-1} .

2.2.2. Nuclear magnetic resonance (NMR) spectroscopy

2.2.2.1. Liquid state NMR.

^1H and ^{13}C NMR spectra of starch samples in dimethyl sulfoxide- d_6 (DMSO- d_6) and ^1H and ^{13}C NMR spectra of 6-MHA samples in chloroform- d (CDCl_3) were recorded in a Bruker Avance III 600 MHz CCD (Bruker, Billerica, USA) using TMS as reference. Multiplicities were abbreviated as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, and m = multiplet.

The degree of substitution (DS) of starch 6-MHA was measured using ^1H -NMR spectroscopy, following a procedure similar to that commonly reported in the literature [32]. The DS was determined as the ratio between the integrated areas of the peaks assigned to the grafted 6-MHA and those of the starch backbone. The addition of deuterated trifluoroacetic acid (d-TFA) facilitated the exchange of labile protons from hydroxyl groups, leaving each α -D-glucopyranose unit with only seven protons. However, since starch inherently contains traces of water that d-TFA cannot completely deuterate, only the peak corresponding to the anomeric proton of starch, located around 5.20 ppm, was used for the calculation. The DS was then determined using the following equation

$$\text{DS} = \frac{\text{I}_{\text{grated 6-MHA}}}{2\text{I}_{\text{starch}}}$$

2.2.2.2. Solid state NMR.

The ^{13}C CP-MAS NMR spectra of modified and unmodified MCC samples were recorded at room temperature using a Bruker Avance III 600 MHz CCD (Bruker, Billerica, USA) equipped with a 4-mm $^1\text{H}/^{13}\text{C}$ high-resolution magic angle spinning (HR-MAS) probe. The samples were packed into 4 mm zirconia rotors. The sample spinning speed was set to 12.0 MHz, with a contact time of 1 msec, and a relaxation delay of 5 s between acquisitions.

2.2.3. Thermogravimetric analysis (TGA)

TGA plots were acquired using a Mettler-Toledo TGA2 (Mettler Toledo, Greifensee, Switzerland), under nitrogen with a flow rate of 40 mL min^{-1} , using alumina pans. For each TGA run, a sample of weight in the range 5–10 mg was introduced in a standard TGA alumina crucible pan and heated from $30\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

2.2.4. X-ray diffraction (XRD) analysis

XRD patterns were recorded on a Bruker D8 CCD (Bruker, Billerica, USA) powder diffractometer with Mo K α radiation in the angular range of $2\theta = 5\text{--}70^\circ$ at $25\text{ }^\circ\text{C}$.

2.2.5. Environmental scanning electron microscopy (ESEM)

After coating MCC and starch samples with gold using sputter coater (Emitech k550X, Quorum Emitech, England), images were taken using a PhilipsXL-30 ESEM (HITACHI, Chiyoda, Japan) at an accelerative voltage of 10 KV, with a spot size of 4.3 using the secondary electrons detector for a magnification of $\times 200$ and $\times 1000$.

2.3. Synthetic strategies

2.3.1. Hydroxyl numbers by titration

In order to calculate the necessary amount of 6-MHA required for maximum degree of substitution, the hydroxyl numbers of polysaccharides was measured using the titration method described in the standard ASTM D 4274 [33]. In this standard test method, the hydroxyl (OH) content of polyurethane raw materials, specifically polyols, is

determined. Starch samples were acetylated by reacting them with a solution of acetic anhydride in pyridine inside a pressure bottle at $98\text{ }^\circ\text{C}$. After the reaction, any excess reagent was hydrolyzed with water, and the resulting acetic acid was titrated with a standard sodium hydroxide solution. The hydroxyl content was calculated based on the difference in titration volumes between the blank and the sample solutions.

2.3.2. Synthesis of vinyl ester of 6-MHA

Vinyl ester of 6-MHA was synthesized by mixing 37.40 mmol 6-MHA in 20 mL DMF with a 10 equivalent excess of vinyl acetate in a three-necked round-bottomed glass flask equipped with a reflux condenser and thermometer, and thereafter degassed with argon for 15 min prior to reaction. The catalyst HS157 (0.01 equiv.), along with sodium acetate (0.03 equiv.), was then added, and the reaction mixture was kept under magnetic stirring in a dry argon atmosphere at $110\text{ }^\circ\text{C}$ for 24 h. After reaction, the mixture was poured in water and extracted with dichloromethane, and then the organic fraction was concentrated by a rotary evaporation. The obtained viscous sample was dissolved in a mixture of chloroform/acetonitrile (4:1, v:v), and purified using silica-gel column chromatography. After purification, the solvent was removed by rotary evaporation. The obtained vinyl ester of 6-MHA was characterized by FTIR and NMR spectroscopy.

FTIR (cm^{-1}) 3095 (vinyl C–H stretching), 3006 (chain unsaturation C–H stretching), 2938 and 2863 (saturated CH_2 stretching modes), 1750 ($\text{C}=\text{O}$ stretching of vinyl ester), 1644 (non-conjugated $\text{C}=\text{C}$ stretching), 1464 (H bending of CH_2 groups), 1135 (ester C–O stretching), 949 (CH out of plane deformation of $\text{CH}=\text{CH}_2$), 948 (CH_2 out-of-plane deformation of $-\text{CH}=\text{CH}_2$).

^1H NMR (600 MHz, CDCl_3): δ (ppm) = 7.18 (H_i , t, 1H, $(\text{C}=\text{O})\text{OCH}$), 6.62 (H_a , s, 2H, $\text{CH}=\text{CH}$), 4.8 (H_j , d, 1H, $\text{CH}=\text{C}$), 4.8 (H_k , d, 1H, $\text{CH}=\text{CH}$), 3.5 (H_b , t, 2H, $\text{N}-\text{CH}_2-\text{CH}_2$), 2.3 (H_f , q, 2H, $\text{CH}_2-(\text{C}=\text{O})\text{O}$), 1.61 (H_c , q, 2H, $\text{CH}_2-\text{CH}_2-\text{CH}_2$), 1.54 (H_e , q, 2H, $\text{CH}_2-\text{CH}_2-\text{CH}_2$), 1.54 (H_d , q, 2H, $\text{CH}_2-\text{CH}_2-\text{CH}_2$). ^{13}C NMR (600 MHz, CDCl_3): δ (ppm): 171.1 ($\text{C}=\text{O}$ ester), 170.4 ($\text{C}=\text{O}$ maleimide), 141.4 ($\text{O}-\text{CH}=\text{C}$), 134.4 ($\text{C}=\text{C}$ maleimide), 97.8 ($\text{CH}=\text{CH}_2$ vinyl), 37.8–24.3 (aliphatic CH_2).

2.3.3. Polysaccharides activation

MCC and starch were activated by mercerization. 20 g of the polysaccharides were placed in a beaker containing 1 L of sodium hydroxide solution (4 M). The mixture was stirred for 1 h and then filtered and washed by a series of dehydrating solvents, methanol, acetone and hexane. The samples were freeze-dried and kept under vacuum in a desiccator.

2.3.4. Grafting maleimide moieties onto polysaccharides

The activated polysaccharides (1 g) were placed in a 100 mL round-bottomed flask, containing a solution of vinyl ester (1 equivalent of polysaccharides hydroxyl groups), 0.15 g potassium carbonate (catalyst), and 15 mL of DMF and 5 mL of DMAc. After degassing with argon, the mixture was then heated under reflux with vigorous magnetic stirring for 24 h at $110\text{ }^\circ\text{C}$. At the end of reaction, the flask content was cooled down to room temperature and filtered, and excessively washed with water to remove the catalyst and then with ethanol to remove residual reagent and solvents. The obtained maleimide grafted polysaccharides were characterized by FTIR and NMR spectroscopy, XRD, TGA, and ESEM.

MCC 6-MHA: FTIR (cm^{-1}): 2929 and 2860 (saturated CH_2 stretching modes), 1770 ($\text{C}=\text{O}$ stretching of vinyl ester), 1692 ($\text{C}=\text{O}$ stretching of maleimide), 1618 (non conjugated $\text{C}=\text{C}$ stretching), 1438 (H bending of CH_2 groups), 1141 (ester C–O stretching), 783 ($\text{C}=\text{C}$ bending), and 740 (CH_2 bending).

^{13}C CP MAS NMR (600 MHz): δ (ppm): 182.9 (C_n , C_b , $\text{C}=\text{O}$), 110.0 ($\text{C}=\text{C}$), 42.2–24.6 (aliphatic CH_2).

Starch 6-MHA: FTIR (cm^{-1}): 2929 and 2857 (saturated CH_2 stretching modes), 1766 ($\text{C}=\text{O}$ stretching of vinyl ester), 1690 ($\text{C}=\text{O}$ stretching of maleimide), 1563 (non-conjugated $\text{C}=\text{C}$ stretching), 1435

(H bending of CH₂ groups), 1100 (ester C–O stretching), 800 (C=C bending), and 707 (CH₂ bending). ¹H NMR (600 MHz, (CD₃)₂SO): δ(ppm): 5.5–4.5 (m, 6, glucose unit), 1.1 (m, alkyl chain), 4.38 (m, alkyl chain).

3. Results and discussion

3.1. Chemical synthesis and spectroscopic characterization of precursor

The commercially available 6-MHA underwent functionalization through transvinylation with vinyl acetate, resulting in the formation of a new vinyl ester: vinyl 6-maleimidohexanoate denoted as MHA ester, following the procedure outlined in Fig. 1. The confirmation of the structure of the synthesized vinyl ester was achieved through a combination of spectroscopic analyses, as described earlier.

Comparing the FTIR spectra of the starting 6-MHA with the spectra of the synthesized corresponding vinyl ester revealed the appearance of new characteristic absorption bands (Fig. 2). These newly emerged absorption bands attributed to the vinyl group were situated around 3095 cm⁻¹ representing vinyl C–H stretching, 2938 and 2863 cm⁻¹ indicating saturated CH₂ stretching modes, 1644 cm⁻¹ associated with non-conjugated C=C stretching, and 948 cm⁻¹ corresponding to C–H out-of-plane deformation of CH=CH₂. The presence of a new ester bond was shown with new bands at 1750 cm⁻¹ indicative of C=O stretching in the vinyl ester and 1135 cm⁻¹ related to ester C–O stretching. The disappearance of C=O stretching band at 1680 cm⁻¹ was also observed and related to carbonyl groups of the acid, confirming the successful transformation of 6-MHA into its corresponding vinyl ester (MHA ester).

The transvinylation reaction between 6-MHA and vinyl acetate was further confirmed by ¹H NMR and ¹³C NMR. The ¹H NMR spectra of the synthesized vinyl ester displayed new resonances characteristic of the vinyl ester protons (δ 4.5, 4.8, and 7.2 ppm) in addition to those of the starting fatty acid precursor (Fig. 3).

The ¹³C NMR analysis of the synthesized vinyl ester (Fig. 4) verified the findings from the ¹H NMR (Fig. 3). Alongside the unchanged resonances related to the fatty acid carbons, the spectra of the synthesized vinyl ester exhibited a new group of signals resonating at δ 97.0 and 141.0 ppm, corresponding to the methylenic and methinic carbons of the vinyl ester group. This was consistent with results reported by Ref. [31].

3.2. Esterification of MCC and starch by MHA ester

6-MHA has been chosen as a diene for further Diels Alder reactions for both its reactivity and selectivity [5,34]. The maleimide group is an electron-deficient diene. It consists of a double bond conjugated with an imide functional group. This conjugation increases its reactivity as a diene in Diels-Alder reactions. The imide functionality is electron-withdrawing, making the diene electron-poor. This electron deficiency facilitates its reaction with electron-rich dienophiles in Diels-Alder reactions, where the diene and the dienophile undergo a cycloaddition reaction to form a cyclic compound. Maleimide-based dienes often lead to high stereoselectivity in the Diels-Alder reaction. The reaction typically proceeds through a concerted mechanism, and the electron-withdrawing nature of the maleimide helps control the stereochemistry of the newly formed cyclohexene ring. The maleimide

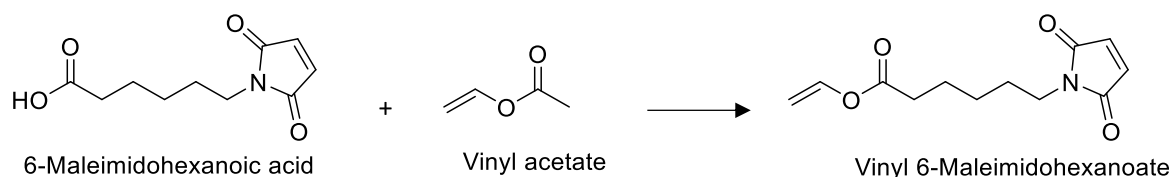


Fig. 1. Synthesis of MHA ester.

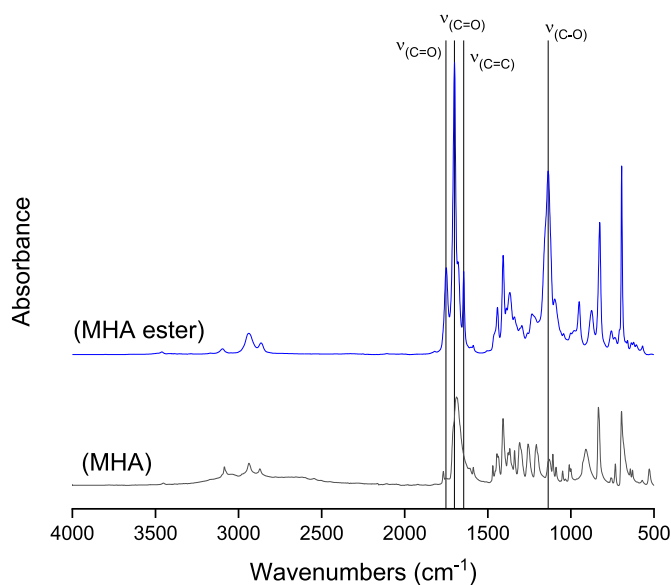


Fig. 2. FTIR absorbance spectra of unmodified and modified 6-MHA (MHA ester).

group can undergo a Diels-Alder reaction at both the 1,2- and 1,4-positions of the double bond. However, in many cases, the 1,4-addition (ortho-addition) is favored due to steric hindrance and the possibility of forming a more stable product [5].

The reactions were conducted following the procedure outlined in Fig. 5, using potassium carbonate as a mild catalyst. In previous research [31], the degree of grafting of fatty chains onto MCC's hydroxyl groups was measured as a function of reaction time and temperature. The results in that work revealed that increasing both reaction time and temperature led to a higher level of esterification in the MCC. Notably, the effect of reaction temperature was more significant than that of reaction time. In other words, raising the reaction temperature favored the diffusion of the vinyl ester into the MCC hydroxyl groups to a greater extent.

This disparity in the effects of temperature and time could be attributed to the diffusion mechanism governing the accessibility of hydroxyl groups and the size of the reagent. Specifically, the three hydroxyl groups present in an anhydroglucose unit of MCC are not equally accessible. Without using specific conditions [35], the primary hydroxyl group can be more reactive compared to the two secondary hydroxyl groups, primarily due to stereochemical hindrance factors.

The result of the previous research lead us to choose the optimum reaction condition as 24 h duration and temperature 110 °C. The reaction temperature was chosen considering the anticipated polymerization of maleimide, which is known to occur at temperatures above 120 °C [36].

3.2.1. Spectroscopic characterization of the synthesized MCC and starch esters

Figs. 6 and 7 show the FTIR spectra of unmodified and esterified MCC and starch. The MCC polymer modified through transesterification

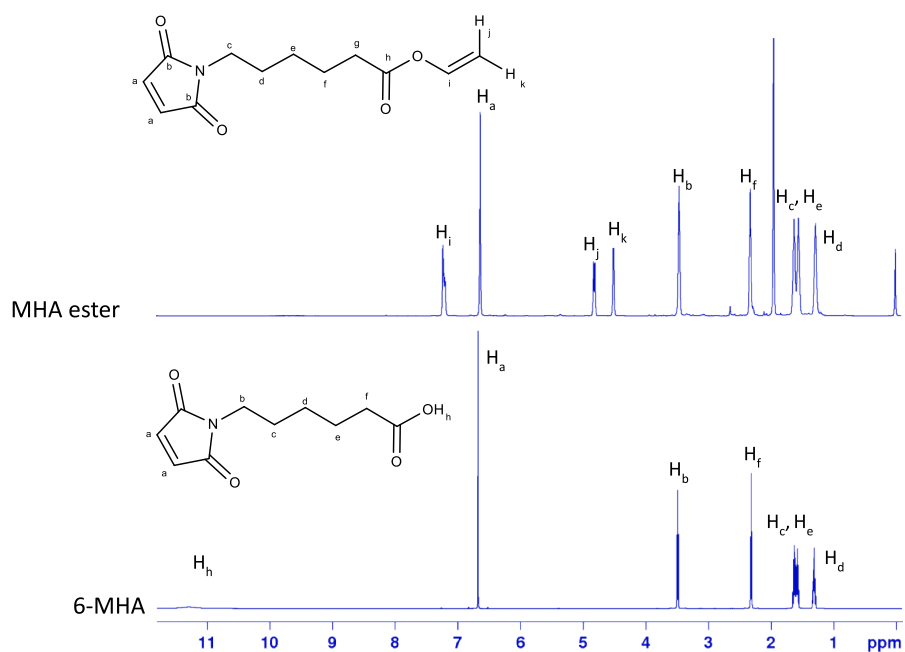


Fig. 3. ^1H NMR spectra of unmodified and modified 6-MHA (6-MHA ester).

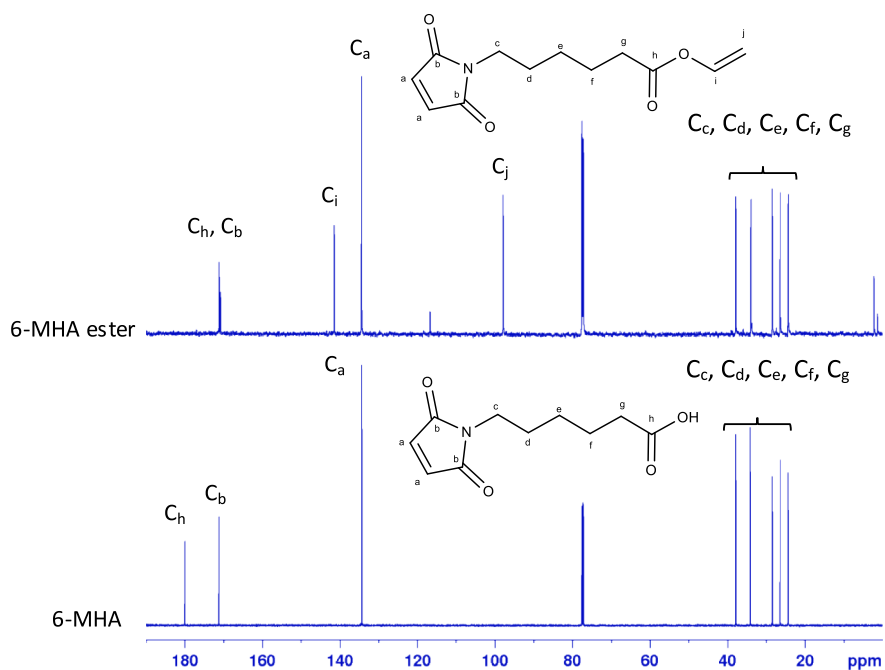


Fig. 4. ^{13}C NMR spectra of unmodified and modified 6-MHA (6-MHA ester).

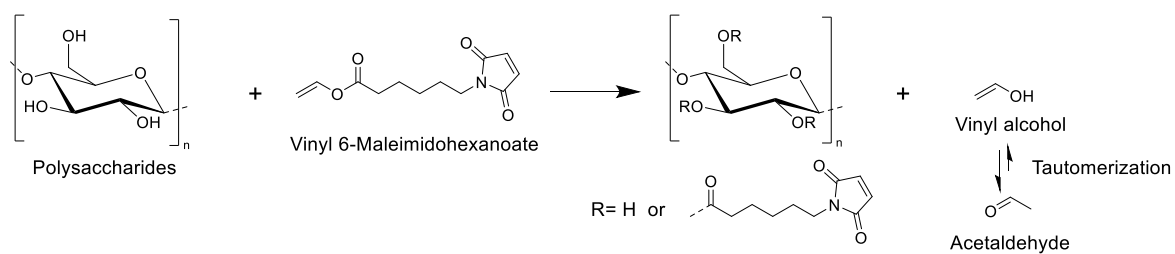


Fig. 5. Synthesis of esterified polysaccharides.

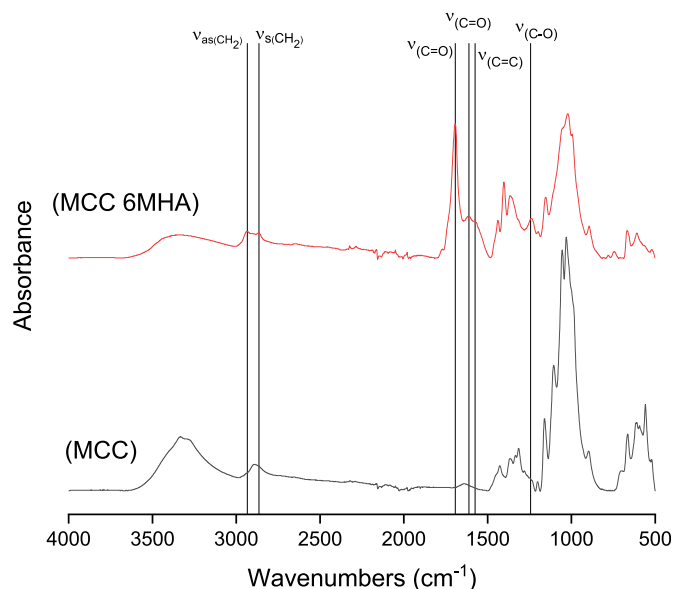


Fig. 6. FTIR absorbance spectra of MCC and esterified MCC (MCC 6-MHA).

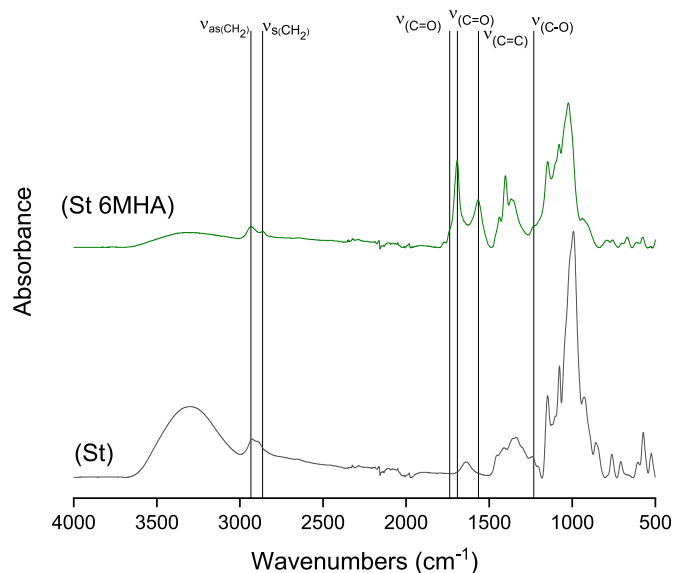


Fig. 7. FTIR absorbance spectra of starch (St) and esterified starch (St 6-MHA).

reaction showed new absorption bands at 1741 cm^{-1} that is attributed to the stretching of the ester carbonyl group ($\text{C}=\text{O}$), the band at 1695 cm^{-1} is assigned to the stretching of the carbonyl group in the maleimide group, while the band around $1560\text{--}1600\text{ cm}^{-1}$ is attributed to $\text{C}=\text{C}$ stretching. The band at 1236 cm^{-1} is attributed to the $\text{C}-\text{O}$ stretching associate to new formed ester groups. Some new bands were identified as characteristics for the 6-MHA such as: $\text{C}-\text{H}$ bonding absorption bands at 1440 cm^{-1} and $1400\text{--}1410\text{ cm}^{-1}$ and the $\text{C}-\text{N}$ stretching absorption bands at 1360 cm^{-1} . These results were found to be in accordance with previous studies [31,37]. The appearance of new absorption bands in the region between 2800 and 3000 cm^{-1} corresponds to the stretching vibrations of the $\text{C}-\text{H}$ bonds in the acyl groups. This indicates the presence of acyl substituents in the modified MCC. The spectra of starch samples displayed the same absorption bands with a notable difference in the carbonyl stretching vibrations at 1740 cm^{-1} and the $\text{C}=\text{O}$ stretching at $1690\text{--}1700\text{ cm}^{-1}$ assigned to the maleimide group [38]. Additionally, on both MCC and starch spectra, one of the most significant changes is the decrease in the intensity of the hydroxyl groups

absorption bands. This is indicative of successful transesterification, where 6-MHA moieties have been grafted into the polysaccharides backbone, thus reducing the available hydroxyl groups. The observed vibrations related to unchanged hydroxyl groups in the spectra can be explained as the reaction is performed in dispersion. MCC and starch were not dissolved, this type of chemical modification would not affect the hydroxyl OH groups protected inside their respective fibrous or granule structure. These hydroxyl groups are important as they maintain the internal organization of the polysaccharides, if affected, the disruption of hydrogen bond between chains or between traces of water would not enable the fibrous or granular structure to maintain.

The modified MCC samples underwent additional characterization using ^{13}C CP-MAS NMR spectroscopy (Fig. 8). Apart from the primary pattern corresponding to cellulose carbons, distinct signals corresponding to the newly introduced 6-MHA moieties were visible in the spectra of modified MCC. These signals were directly assigned on the modified MCC spectra based on the nomenclature provided in the associated structure. These signals were in accordance with studies made by others [31,39]. The new signals corresponding to the alkyl chains were located in the region of $20\text{--}50\text{ ppm}$ while a weak signal was observed around 180 ppm assigned to carbonyl groups.

The NMR spectroscopic analysis of the modified starch samples (Fig. 9) showed relatively low intensity of the different peaks associated to starch due to the challenging issue of their low solubility in various deuterated solvents. It should also be noted that while the reaction may modify a significant portion of the accessible hydroxyl groups on the starch surface, it represents only a small fraction of the total hydroxyl groups present in the starch. As a result, the ratio between the remaining and modified hydroxyl groups tends to make the intensity of the new peaks relatively low. Consequently, alternative strategies or solvents that enhance solubility may be necessary to more effectively interrogate the structural alterations and characteristics of these modified starch samples using NMR techniques. It should be noted that the peaks corresponding to the protons of the hydroxyl groups attached to carbon C6 (H9) and C3 (H8) are significantly decreased. This is expected, as the primary alcohol linked to carbon C6 is generally more reactive than the secondary alcohol at carbon C3, unless under specific conditions. ^{13}C NMR showed no signal of starch neither and trials of ^{13}C CP MAS NMR were made but unsuccessful. Despite the low intensity of the peaks observed, the spectra showed the apparition of two new peaks at 1.1 ppm and 4.38 ppm that can be respectively attributed to alkyl group and methoxy group that tends to confirm the modification according to literature [32,40].

The degree of substitution (DS) of starch was determined using ^1H NMR (see Fig. S1) and was estimated to be 0.27. While this represents a relatively low DS, it corresponds to a modification of 47 % of the

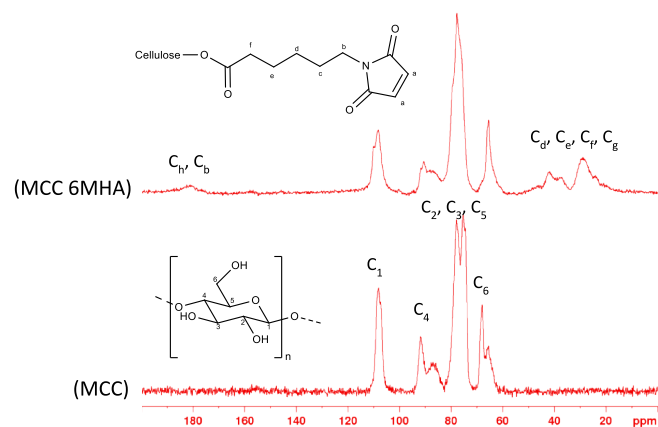


Fig. 8. ^{13}C CP-MAS NMR spectra of unmodified and modified MCC with 6-MHA ester for 24h at $110\text{ }^\circ\text{C}$.

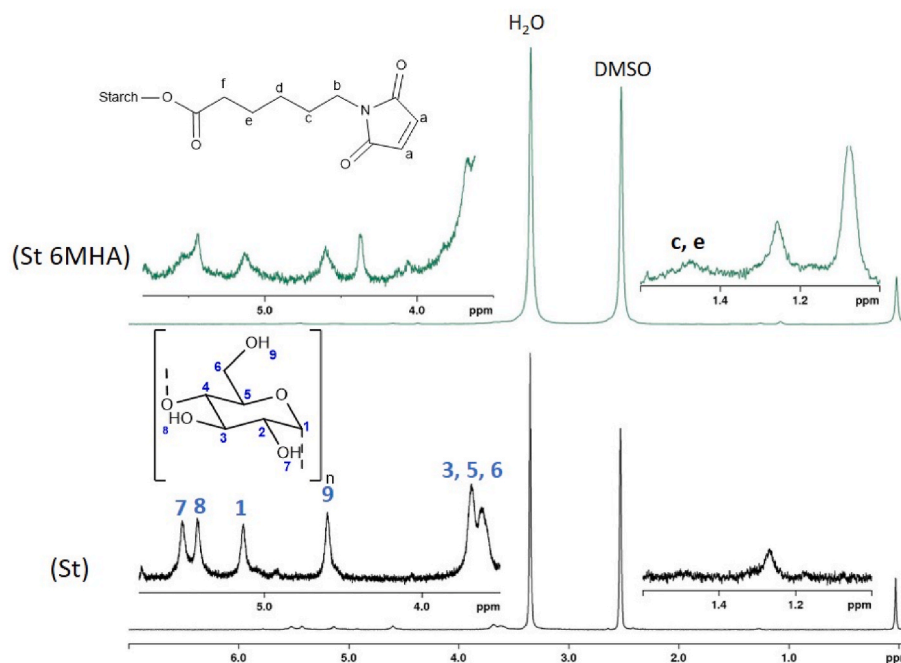


Fig. 9. ^1H NMR spectra of unmodified (St 6MHA) and modified starch (St) with 6-MHA ester for 24 h at 110 °C.

available hydroxyl groups when considering the 3.56 mmol/g hydroxyl content of starch, as determined by titration in dispersion. It is worth noting that the calculated DS may underestimate the actual value due to the limited solubility of the modified starch in $\text{DMSO}-d_6$.

3.2.2. Thermal properties of the synthesized MCC and starch esters

Figs. 10 and 11 present the TGA and DTG thermograms of both starch and MCC before and after modification. Continuous nitrogen was used to study the decomposition properties of the MCC samples by performing TGA at optimum reaction time and temperature according to previous study (Jebrane et al., 2017). The weight loss reported was normalized against the initial weight of the samples analyzed (Fig. 10). The results indicated that the thermal degradation of native MCC began at 295 °C and showed a single weight-loss step. In contrast, modified MCC was less stable and began to decompose at relatively lower temperatures than unmodified MCC. This was expected because the grafting acyl groups into MCC's hydroxyl groups affect its crystallinity contributing to its thermal instability [31]. Additionally, modified MCC

displayed two distinct degradation steps visible on the DTG thermogram, attributed at 159 °C to the degradation of the grafted 6-MHA and a second peak attributed to degradation of the MCC backbone starting at 230 °C reaching a maximum at 322 °C (Fig. 11a). Similar results have been reported in the literature [31].

The thermal stability of esterified starch was significantly improved in comparison to unmodified starch. For native starch, a two step degradation pattern was observed (Fig. 10b). It can be interpreted as a first step linked to the water evaporation that was trapped into starch structure, and a second step related to the starch backbone degradation at 300 °C. Modified starch initiated its decomposition at around 230 °C but at a significantly lower rate than native starch since the degradation of starch is not complete at 630 °C. Although the thermal stability of esterified starch outperformed that of native starch, modified samples exhibited a similar decomposition process with the initial stage starting at a lower temperature compared to unmodified starch. The thermal stability behavior of starch can be explained in two different ways. A first explanation is that starch can perform retrogradation [41]. This

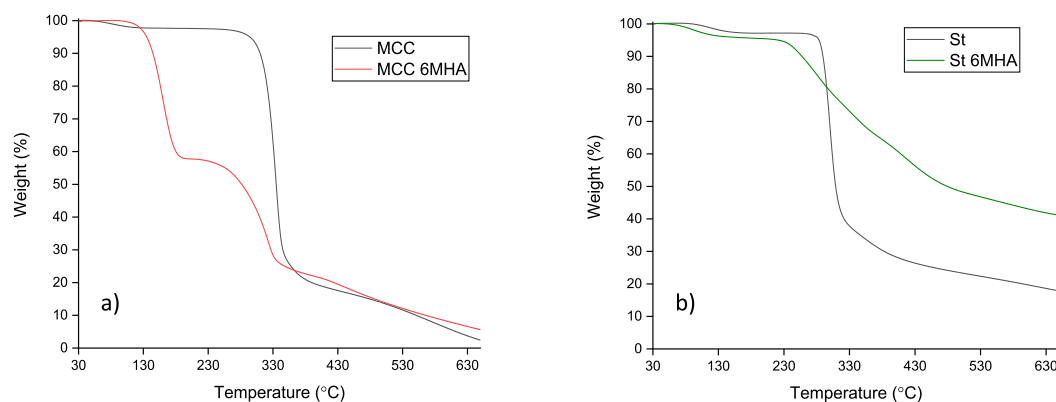


Fig. 10. TGA thermograms of (a) unmodified and modified (MCC 6-MHA) MCC and (b) unmodified and modified (St 6-MHA) starch (St) with 6-MHA ester for 24 h at 110 °C.

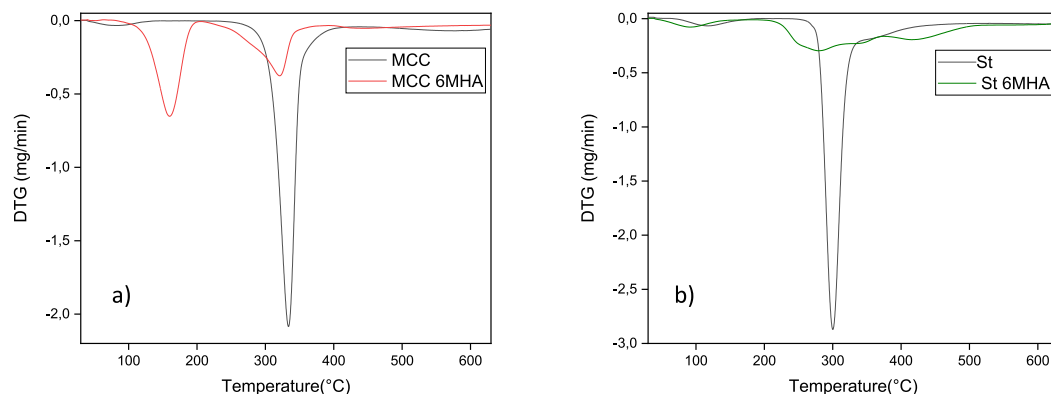


Fig. 11. DTG thermograms of (a) unmodified and modified (MCC 6-MHA) MCC and (b) unmodified and modified (St 6-MHA) starch with 6-MHA ester for 24 h at 110 °C.

complex phenomenon occurs when a starch gel, formed after gelatinization, undergoes structural changes upon cooling and aging. During retrogradation, amylose and amylopectin molecules re-associate and form ordered structures. When starch retrogrades, the reformation of crystalline structures occurs, resulting in a more ordered and stable structure, resistant to heat [42]. This phenomenon might have happened during the first step of the chemical process, when mercerized starch gelatinized in contact with sodium hydroxide solution, and after precipitation and filtration the gel like material was freeze-dried. A second explanation for the observed enhanced thermal stability, consists in supposing that it was achieved a relatively high degree of substitution, meaning a significant reduction of hydroxyl number within the starch molecules after esterification. Given that the primary decomposition mechanism of starch relies on inter- or intra-molecular dehydration reactions involving water as a primary decomposition product, the reduction in the number of remaining hydroxyl groups resulted in an improvement of thermal stability at lower temperatures. Similar observations have been done by Ref. [43].

3.2.3. XRD analysis of MCC and starch esters

Fig. 12a presents the XRD patterns of MCC before and after esterification. The XRD pattern of native MCC exhibited three main diffraction peaks at 7, 10, and 15.6°, associated respectively to the crystalline cellulose I structure 101, 10 $\bar{1}$, and 002 diffraction planes. Following the

reaction with MHA ester, the main characteristic planes of cellulose were significantly weakened or entirely disappeared. Instead, a new amorphous halo appeared between $2\theta = 7$ and 18°, which can be attributed to an increase of amorphous phase in the cellulosic backbone. These observed changes were consistent with similar findings reported in the literature for esterified cellulose, which were associated with an increasing intermolecular distance of the backbone chain due to the length of grafted entities [44]. Nonetheless, the mercerization performed to increase MCC reactivity might have affected its morphology and crystallinity. In order to investigate the morphology of MCC before and after mercerization and modification, observations were performed under an ESEM.

The main characteristic peak observed for native starch (Fig. 12b) at 7.8 and 10.5° following by overlapping peaks at 13.7, 15.5, 16.45 and 21° disappeared on the XRD pattern of modified starch. Only a broad peak centered at 9.65° and a small peak at 20° were visible. This result indicates the total loss of crystallinity of the esterified starch contradicting the idea of starch retrogradation. Indeed, previous work performed by Ref. [45] showed that freeze dried starch samples that undergo retrogradation can show a broad peak in their XRD pattern, but it will still be centered at the position of native starch peaks. The examination of XRD data from various starch acetylation methodologies [46] reveals a consistent trend. The crystalline structure of native starch is typically destroyed during esterification processes, as documented by

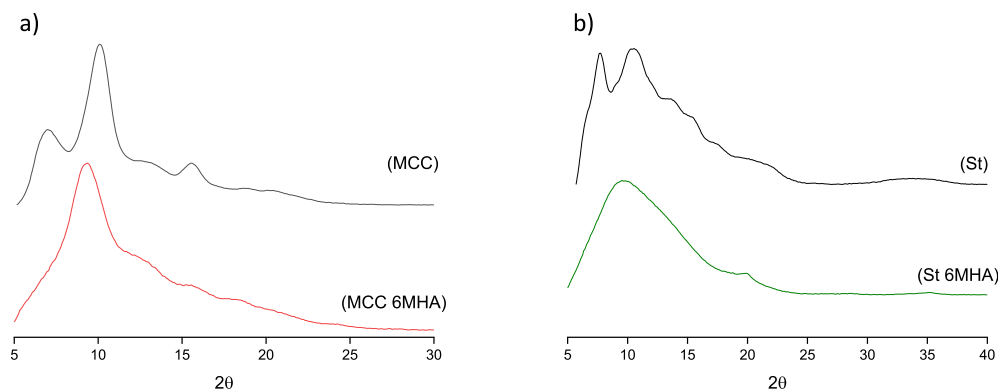


Fig. 12. XRD patterns of unmodified (MCC) and modified MCC (MCC 6-MHA) with 6-MHA ester for 24 h at 110 °C (a) and unmodified (St) and modified potato starch (St 6MHA) with 6-MHA ester for 24 h at 110 °C (b).

Ref. [18]. In starch, crystallinity is predominantly attributed to the formation of double helices facilitated by intermolecular hydrogen bonds within amylopectin chains. Consequently, the reduction in crystallinity observed during acylation is frequently attributed to the diminished formation of both inter- and intra-molecular hydrogen bonds. This decrease arises due to the partial substitution of starch hydroxyl groups with ester groups, ultimately leading to the destruction of the original ordered crystalline structure, as elucidated by Ref. [47].

The disappearance of well-defined crystalline structures was reported with a high degree of substitution. The decrease in the number of hydroxyl groups inhibited the capacity for inter-molecular hydrogen bond formation, resulting in the emergence of amorphous patterns characterized by broad peaks, as documented by Ref. [20]. Moreover, the degradation of the microstructure of both polysaccharides indicates that not only their surfaces undergo modification but also the core. This was possible due to the ability of DMAc to swell polysaccharides and open up their structures [48].

3.2.4. Morphology of MCC and starch before and after modification

The alkaline pre-treatment of starch and MCC followed by the esterification reaction might have changed the microstructure and interaction between their macromolecules as shown previously in the XRD analysis, and thus morphological changes could be expected. The morphology of MCC and starch as revealed by ESEM in their unmodified states, after mercerization, and after esterification are shown in Figs. 13 and 14.

The ESEM images of native MCC showed rough surfaces of linear micro particles of varied sizes not exceeding 100 μm . The mercerization treatment did not seem to have any particular effect on the shape or size of the MCC particles, showing a resistance of cellulose to alkaline treatment [52]. The esterified MCC particles showed similar shape with the unmodified MCC ones with an increase of the number of small particles that can be explained by the mechanical stress caused by a long time agitation at 110 $^{\circ}\text{C}$. The ESEM images of native starch granules showed oval or ellipsoidal shape particles, flattened along one axis, ranging from few μm to 100 μm in diameter. The surface of granules

appeared mostly smooth and lacked pronounced surface irregularities. The only irregularities appeared to be the result of contact from one granule onto another. Unlike MCC, mercerized starch showed a loss of organized microstructure. It seems that the gelatinization of starch due to alkaline treatment caused, after freeze-drying, a disintegration of starch microstructure [49]. The oval granules merged or melted into random shaped particles and agglomerates with rough surfaces with sizes ranging from few μm to more than 100 μm . Same observations were made for esterified starch, although the surface of particles appeared to be smoother. A similar starch morphology has been reported in studies where starch was esterified under acid conditions [19, 40].

The differential response of MCC particles and starch granules to alkaline treatment, such as mercerization, can be attributed to the differences in their chemical structure and molecular arrangement, as presented in supporting information (FS2 and FS3).

Cellulose fibers have a fibrous, thread-like structure. This structure, with its strong intermolecular interactions, contributes to the overall stability of cellulose fibers. Cellulose molecules are arranged in highly ordered, crystalline structures, held together by extensive hydrogen bonding between adjacent cellulose chains. This crystalline structure provides significant stability and resistance to chemical treatments, including alkaline solutions [52]. Cellulose is a linear polysaccharide composed of repeating glucose units linked by β -1,4-glycosidic bonds [50]. These glucose units are connected in a way that forms long, straight chains. The β -1,4-glycosidic bonds in cellulose are highly stable and resistant to hydrolysis under alkaline conditions.

In contrast, starch granules are composed of both amorphous and semi-crystalline blocklets. The amorphous blocklets, composed of amylose, are more likely to be modified in a first place. The amorphous regions in the semi-crystalline blocklets, which contain the branching points of amylopectin, are more susceptible to hydrolysis. These amorphous regions can be more easily disrupted under alkaline conditions, leading to changes in granule crystallinity and morphology [53]. At a molecular level, starch is a mixture of two different polysaccharides, amylose and amylopectin. Amylose consists of linear chains of glucose

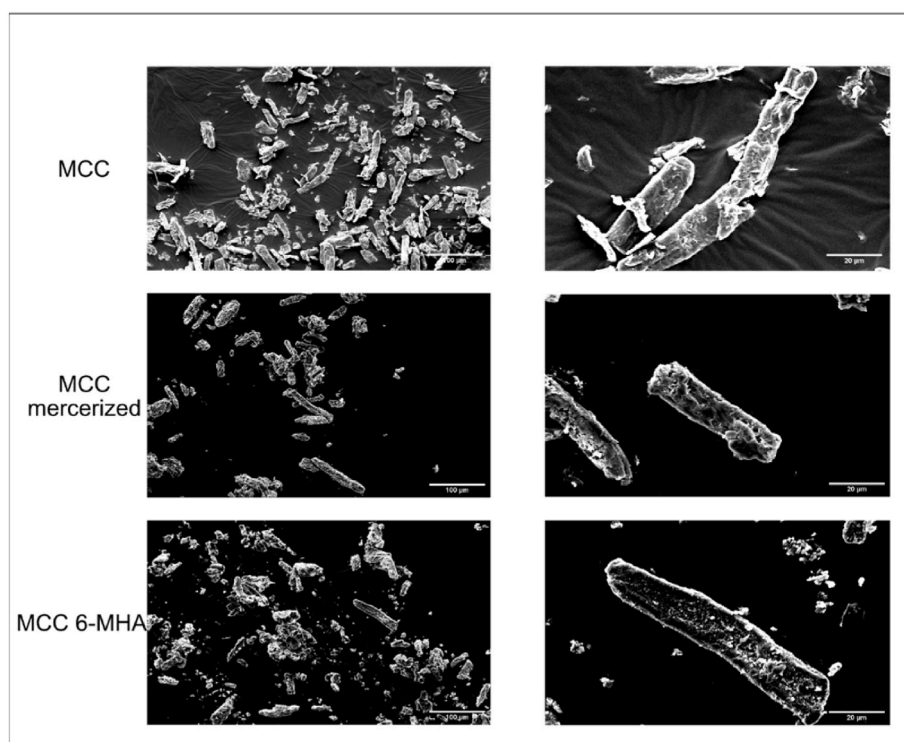


Fig. 13. ESEM images of MCC before and after modification (MCC 6-MHA).

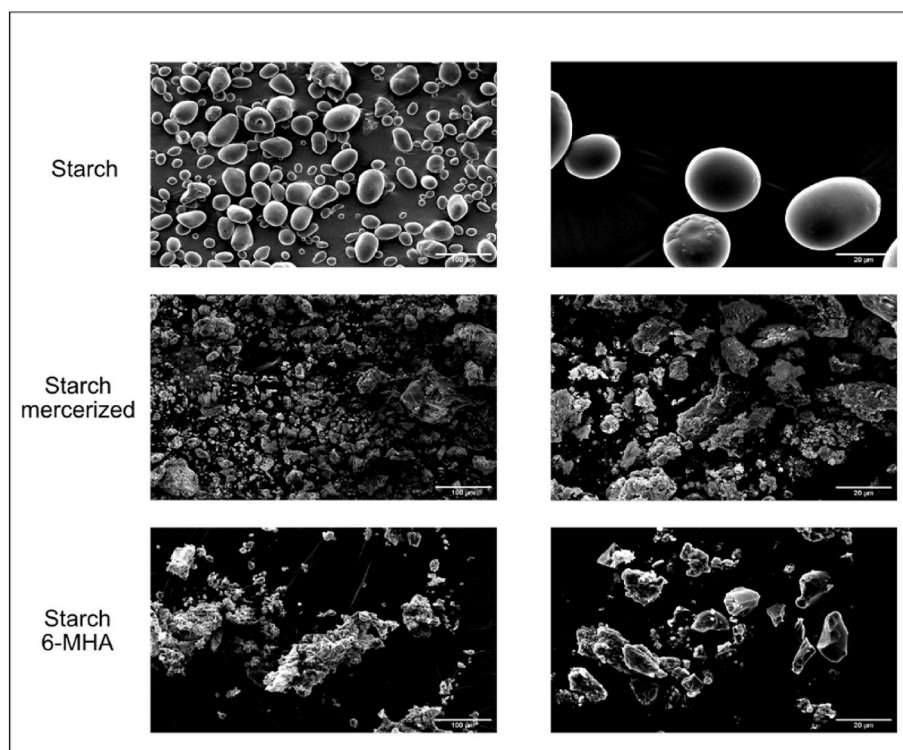


Fig. 14. ESEM images of starch before and after modification (Starch 6-MHA).

units, but amylopectin has branched structures with both α -1,4 and α -1,6-glycosidic bonds [43,51]. The presence of α -1,4-glycosidic bonds in starch makes it more susceptible to hydrolysis under alkaline conditions [53].

In summary, MCC's strong, linear, and highly crystalline structure, as well as the stability of its β -1,4-glycosidic bonds and extensive hydrogen bonding, make it more resistant to alkaline treatment. Starch, with its branched, less organized structure and α -1,4-glycosidic bonds, is more vulnerable to the effects of alkaline solutions. The differences in chemical composition and structural organization between MCC and starch may explain why cellulose fibers appear to have similar size and shape when after alkaline treatment starch granules are degraded.

Grafting maleimide into polysaccharides open a wide range of possibilities to develop new materials for various applications (coatings, paintings, adhesives, composites, ...) as it enables these latter to undergo click chemistry with furan grafted molecules or polymers. As mentioned earlier, the traditional esterification generate or occurs in presence of hydrogen chloride that can hydrolyze glycosidic bonds and thus destroy polysaccharides native structure. We believe that these organized structures have interesting mechanical properties to develop new materials. As the morphology and microstructure of MCC remains similar after modification, we believe that cellulose has mostly kept his mechanical properties and could be a good candidate to perform Diels Alder reaction to develop thermally responsive materials.

4. Conclusions

6-MHA was grafted on the surface of both MCC and starch using a mild condition transesterification reaction. The evidence of the grafting was shown by FTIR and NMR spectroscopy. The thermal analysis alongside with XRD analysis and ESEM observations brought a new understanding of the impact of this process on the stability and microstructure of the modified polysaccharides.

This modification had a significant impact on the crystallinity of the polysaccharides, which lead to different evolution of their microstructures.

Indeed, if ESEM images corroborated the alteration of starch granules after the activation of starch hydroxyl groups by mercerization, the morphology of MCC seemed relatively unchanged.

Opposite effect of modification were observed concerning thermal analysis. TGA analysis of both polysaccharides before and after modification revealed that the partial loss of crystallinity of MCC make it degrade at lower temperature when starch seemed to have gain thermal stability with its full carbon backbone degradation still not reached at 600 °C.

These findings pave the way for further research into a tailored utilization of modified starch and MCC in a variety of industrial applications such as the development of debondable adhesive or coating promoting the recyclability of bonded materials.

CRediT authorship contribution statement

Valentin Silveira: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Mohamed Jebrane:** Writing – review & editing, Validation, Methodology, Conceptualization. **Adrien Letoffe:** Writing – review & editing, Validation. **Stergios Adamopoulos:** Writing – review & editing, Validation, Resources, Conceptualization.

Informed consent statement

Not applicable.

Data availability statement

The data presented in this study are available from the corresponding author upon request.

Funding

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Not applicable.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.carres.2025.109401>.

Data availability

Data will be made available on request.

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