

A Closed-Loop Process from Microwave-Assisted Hydrothermal Degradation of Starch to Utilization of the Obtained Degradation Products as Starch Plasticizers

Duo Wu and Minna Hakkarainen*

Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

S Supporting Information

ABSTRACT: A green closed-loop water-based process for chemical recycling of starch was demonstrated. The process starts from microwave-assisted controllable starch degradation to functional chemicals and continues to utilization of the formed degradation products, glucose and levulinic acid (LA), as starch plasticizers. The degradation process and the effect of process parameters on the formed degradation products and residues were carefully fingerprinted by multiple techniques, e.g., NMR, ESI-MS, FTIR imaging, UV-vis, and SEM. The degradation process took place in three steps, proceeding from rupture of starch granules and oligosaccharide formation to further hydrolysis to glucose. Finally, at well-defined time point rapid degradation of glucose to LA and formic acid (FA) was initiated through a 5-hydroxymethyl furfural (5-HMF) intermediate. 5-HMF also participated in carbonization reactions leading to formation of solid carbon spheres. Through selection of processing parameters, LA could be produced in high yield with 95% selectivity. The results demonstrated that microwave-assisted degradation of starch leads to well-defined controllable degradation products. These products are directly reusable as plasticizers for new starch products, which suggest great opportunities for biomass and starch recycling, opening the door toward potential industrial applications.

KEYWORDS: Starch, Microwave, Levulinic acid, Plasticizer, Recycling, Hydrothermal degradation



INTRODUCTION

Energy crisis and climate change are among the major problems facing our society. The need to reduce CO₂ emissions has fostered great research efforts to develop alternative strategies for supplying sustainable fuels,^{1–4} platform chemicals, and renewable materials.^{5–7} Through valorization of biomass, it is possible to transform abundant, widely available, and renewable resources into functional chemicals. This is a delicate strategy for building a sustainable or closed-loop society.⁸

Starch represents one of the most abundant natural plant biomasses. As a bioplastic, it shows distinct advantages such as low cost, wide availability, and total compatibility with the environment and humans without toxic residues. It can be processed to biologically degradable materials⁹ and desirably converted into value-added chemical products such as fuels¹⁰ and platform molecules.¹¹ Starch is composed of linear amylose and branched amylopectin. These two polydisperse high molecular weight polymers consisting of D-glucose units are organized at the native state in semicrystalline granules.⁹ An unique characteristic of starch-based polymers is their thermal processing property. Multiple chemical and physical reactions may occur during processing, such as gelatinization, decomposition, melting, and crystallization. Extrusion, injection molding, compression molding, and casting are all conventional

techniques employed to process starch-based materials.¹² Besides that, starch can also be used as a granular bioadditive in thermoplastic products.¹³ However, despite the many available commercial products, the fundamental properties such as mechanical properties and moisture sensitivity still have to be enhanced to make starch-based products truly competitive with traditional petroleum-based plastics for a wider range of application. Normally, plasticizers need to be added to improve the flexibility of starch. Polyols, especially glycerol, but also ethylene glycol, sorbitol, and other sugars are the most commonly used plasticizers for thermoplastic starch. These plasticizers can form hydrogen bonds with starch to replace the strong interactions between the hydroxyl groups in starch molecules, which will allow freer movement of starch segments, resulting in starch plasticization.

Starch packaging can be biologically recycled. However, in many cases, it would be better to retain the value of starch-based packaging by material recycling, as well as to utilize waste products from agriculture that are not suitable for food production. Starch can be chemically recycled and decomposed

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to small organic molecules by acid-catalyzed hydrolysis. This reaction is of great interest for production of biofuels and biobased chemicals. Hydrothermal processing offers a route to hydrolyze carbohydrate biomass into simple compounds under elevated pressure and temperature. Combining this technique with microwave heating makes the thermal treatment greener, faster, and more efficient.^{14,15} Microwave heating is particularly efficient for chemical transformations in water as water can be superheated in sealed vessels.¹⁵ Water is clean, noncorrosive, nonflammable, renewable, readily available, and a cheap green solvent. Also, it is an effective microwave energy absorber, making water a preferable choice for microwave-assisted liquefaction of biomass. Recently, the microwave-assisted conversion of carbohydrate biomass to green chemicals has thus appeared as an attractive alternative to conventional approaches.¹⁶ The yield of reaction products is influenced by parameters such as biomass type, temperature, concentration of catalyst, and reaction time under microwave irradiation.^{17–19} The majority of the previous work concentrated on liquefaction of lignocellulosic biomass; however, the degradation of starch using microwave irradiation under aqueous conditions was also reported.^{20,21} The results showed that under acidic conditions reducing sugars (mainly glucose) were achieved in high yield within 1 h of microwave irradiation.

Levulinic acid (LA) is one of the most important green platform chemicals. Derivatives of LA can serve as feedstock for organic synthesis, polymer synthesis, and the fuel industry.^{22,23} The synthesis of LA from sucrose was first reported by Mulder²⁴ in which the hydrolysis of the glycosidic bond and subsequently two consecutive dehydration steps were combined to form equimolar amounts of LA and formic acid. Later, a large wealth of experimental exploration demonstrated that LA could be generated from cellulose,^{5,25} fructose,^{26,27} sucrose,²⁸ xylose,²⁹ and glucose,^{30,31} involving the exploitation of 5-hydroxymethylfurfural (5-HMF) as the intermediate.

In the present work, we aimed at high-yield hydrothermal degradation of starch through utilization of microwave-assisted degradation to provide a gateway toward viable manufacture of green platform chemicals. Second, to enhance the understanding over the process and parameters governing it, we applied multiple techniques to fingerprint the degradation process and degradation products at molecular level. Last but not least, we also hypothesized that the obtained starch degradation products could be directly recycled as plasticizers for new starch-based materials to obtain an efficient, green, closed-loop, water-based process, which would save resources and energy and make the recycling process much simpler, reflecting immense practical significance for commercial applications.

■ EXPERIMENTAL SECTION

Materials. Tapioca starch was received from Ibu Tani, cap anak no.1 (Bogor, Indonesia). Sulfuric acid, water (HPLC grade), sodium hydroxide, α -D-glucose (anhydrous, 96%), and levulinic acid ($\geq 97\%$) were all obtained from Sigma-Aldrich Chemie GmbH (Steinheim, Germany) and used without further purification. 2,5-Dihydroxybenzoic acid (DHB) was purchased from Fluka (Buchs, Switzerland). Glycerol was supplied by VWR International (Leuven, Belgium).

Microwave-Assisted Degradation. Hydrothermal degradation of starch was performed in a CEM MES-1000 device. This is a multimode-type microwave solvent extraction system with a rotating turntable having a maximum effect of 950 W. Starch powder weighing 0.5 g was put into the MAE device's Teflon vessels. Thereafter, 20 mL of sulfuric acid solution (0.01 g/mL in water) was added, and the

vessels were closed gas tight. The vessels including one with a temperature probe were heated in the MAE device. Temperature was increased to 140 °C within 20 min RAMP time and maintained under constant heating at 140 °C for different time periods from 0 to 180 min. To evaluate the influence of constant and sequential microwave irradiation on starch degradation, some starch samples were also treated by sequential microwave treatment (group a). This meant a 1 min interruption in the middle of RAMP time (the heating time from room temperature to the desired temperature) and 1 min interruption every 20 min during their holding time, whereas the other group (group b) was heated constantly without interruption. The door of the microwave oven was opened during the interruption time to ensure effective cooling of the reaction mixture. Each vessel was cooled quickly in an ice bath after the predetermined heating time. Thereafter, they were opened, and the reaction products were filtered through filter paper. The residues were weighed after drying to a constant weight in a 40 °C oven, and the hydrothermal degradation efficiency was calculated from the mass of the solid degradation residue and the original starch (0.5 g). The liquid phase was then filtered through a 45 μ m nylon membrane filter to obtain a clear solution. Sodium hydroxide (1 M) solution was added until pH reached 7.0. The solutions were freeze-dried before later analysis. In addition, to evaluate the influence of catalyst concentration, a third degradation series was run under continuous microwave irradiation (at 140 °C) for 120 min with different sulfuric acid concentrations (0.01, 0.05, 0.1, and 0.2 g/mL).

Preparation of Starch Films. Plasticizer/starch and pure starch films were prepared by solution casting. The mass ratio between starch and plasticizer was 7/3 except for the pure starch film. Five plasticizer/starch films were prepared including a film with pure glucose (30 wt %), pure LA (30 wt %), glucose–LA (15/15 wt %), water-soluble compounds after 60 min of hydrothermal degradation of starch with constant microwave irradiation (holding time 60 min from group b, 30 wt %). For comparison, a fifth plasticized film was prepared with 30 wt % glycerol, as glycerol is known to be an effective starch plasticizer. The plasticizers and starch were dissolved in 100 mL distilled water at 80 °C. After 30 min gelatinization, the paste was cast on a clean Petri dish and dried at room temperature for 7 days and then another 2 days in a vacuum oven.

Product Analysis. Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra of starch powder, water-soluble degradation products, and residues were recorded by a PerkinElmer Spectrum 2000 FTIR spectrometer (Nowalk, CT) equipped with a single reflection attenuated total reflectance (ATR) accessory (golden gate) from Graseby Specac (Kent, U.K.). Spectra were scanned at 2 cm^{-1} resolution in a 4000–600 cm^{-1} interval.

Nuclear Magnetic Resonance (NMR). Soluble products after all hydrothermal degradation treatments were analyzed by a Bruker Avance 400 Fourier transform nuclear magnetic resonance spectrometer (FT NMR) operating at 400 MHz (^1H NMR and ^{13}C NMR). The temperature was 25 °C, and deuterium water (D_2O) was used as the solvent. Ten to 20 mg of each sample was dissolved in 0.5 mL of solvent.

Electrospray Ionization-Mass Spectrometry (ESI-MS). Sample filtrate was analyzed with a Finnigan LCQ ion trap mass spectrometer (Finnigan, San Jose, CA) after 100 times dilution. The solution was continuously infused into the ESI source by a syringe pump at a rate of 5 $\mu\text{L}/\text{min}$. All the samples were run with a positive mode. The LCQ ion source was operating at 5 kV, and the capillary heat was set to 175 °C. Nitrogen was employed as the nebulizing gas, and helium was used as the damping and collision gas in the mass analyzer.

Matrix-Assisted Laser Desorption Ionization-Mass Spectrometry (MALDI-MS). The DHB matrix in water (10 g/L) was mixed with sample filtrate at a volume ratio of 1:1. One microliter of that solution was spotted on the target plate. All experiments were performed using a Bruker UltraFlex time-of-flight (TOF) mass spectrometer (Bruker Daltonics, Bremen, Germany) in a positive mode. The mass-to-charge (m/z) ratio range was 200–2000 with a reflector voltage of 26.3 kV and an accelerated voltage of 25 kV.

UV–Vis Spectra. Sample filtrate solutions as well as glucose and LA water solutions (1 mg/mL) were all monitored on a UV–vis spectrophotometer (UV-2401) within wavelengths from 200 to 600 nm.

Scanning Electron Microscopy (SEM). Ultra-high resolution FE-SEM (Hitachi S-4800) was used to obtain morphological information on the spherical solid residues. Filter papers with residues on them were cut into small pieces and treated by 3 nm thick gold layers before analysis. The cross sections of the six starch films were also monitored by SEM. Film samples were covered by 3 nm thick gold layers before analysis.

FTIR Imaging. FT-IR spectra and single-peak absorbance images of the films were recorded by using a PerkinElmer Spotlight 400 system equipped with an optical microscope (Bucks, U.K.). The absorbance images of hydroxyl bonding of water at 1637 cm^{-1} were used to evaluate the water distribution. Also, absorbance images that are corresponding to the carbonyl peak of LA and hydroxyl peak of starch were both obtained and used to evaluate miscibility and distribution of plasticizers in the films.

Differential Scanning Calorimetry (DSC). DSC analysis was performed on a Mettler-Toledo DSC 820 to examine the glass transition and effect between additives and starch. Around 5 mg of each sample was enclosed into aluminum cups. The temperature was raised first from room temperature to 100 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$, then cooled to -100 $^{\circ}\text{C}$, and raised again from -100 to 200 $^{\circ}\text{C}$ with the same rate.

Thermogravimetric Analysis (TGA). A Mettler-Toledo TGA/SDTA 851e was used to evaluate the thermal stability of the films. They were heated at 10 $^{\circ}\text{C}/\text{min}$ from 30 to 700 $^{\circ}\text{C}$ with nitrogen flow in the furnace.

RESULTS AND DISCUSSION

A microwave-assisted process was developed for conversion of starch to green functional chemicals. The influences of reaction time and catalyst concentration on the process and resulting water-soluble degradation products were examined as well as the possibility to utilize the degradation products as starch plasticizers.

Identification of Degradation Products and Residues.

Starch, freeze-dried water-soluble degradation products, and dried residues were all examined by FTIR (Figure 1). The FTIR spectrum of the water-soluble degradation products

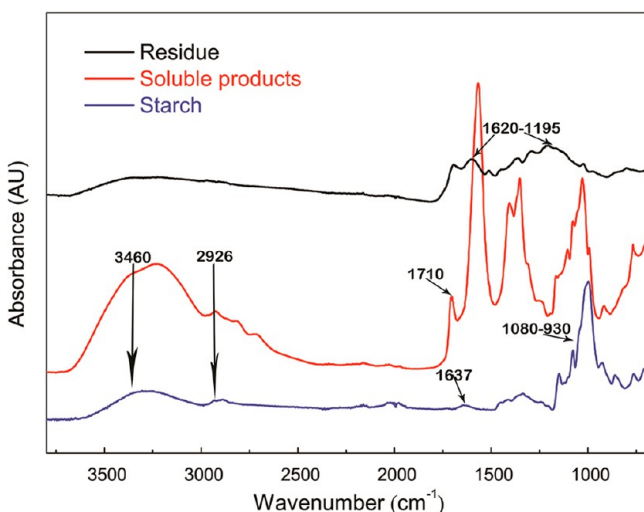


Figure 1. FTIR spectra of tapioca starch, water-soluble degradation products, and solid degradation residue. The spectra of water-soluble degradation products and degradation residue were taken after 60 min of continuous microwave irradiation.

shows the product mixture after 60 min of continuous microwave irradiation in 0.01 g/mL H_2SO_4 solution. In the FTIR spectra of the starch, the sharp band at 2926 cm^{-1} is indicative of the $-\text{CH}_2-$ stretching vibration. There are several discernible absorbencies between 1080 and 930 cm^{-1} that were attributed to C–O bond stretching. An intense band at 1637 cm^{-1} was assigned to deformation vibration of the water hydroxyl group,³² showing the inevitable water absorption of starch materials. The hydroxyl group absorbance at 3460 cm^{-1} and $-\text{CH}-$ at 2926 cm^{-1} from the starch spectrum were also present in the spectra of soluble products. However, a new absorbance band at 1710 cm^{-1} relating to the carboxyl group appeared in the spectra of soluble products. In the spectra of solid degradation residues, a furan structure was detected. The bands between 1620 and 1400 cm^{-1} can be attributed to the stretching vibration of C=C double bands in the furan rings, while the bonds at 1278 and 1195 cm^{-1} can be attributed to harmonic rocking vibrations of two hydrogen atoms in the furan rings.³³ Also, 1515–1380 and 1430–1330 cm^{-1} are the feature peaks of the furan ring.³⁴ This could indicate polymerization and carbonization of 5-HMF to form a new solid product.

The identification of water-soluble degradation products is further supported by ^{13}C NMR spectra (Figure 2a), which demonstrates glucose and/or oligosaccharides or LA and FA as the main water-soluble products. A comparison with the spectra of standard glucose (Figure 2c) and LA (Figure 2b) confirms the identification. The characteristic peaks of glucose (60.7 (C6), 69.6–75.9 (C2–C5), and 92.0 and 95.9 (α , β C1)) as well as LA (29.2 (C1), 31.3 (C2), 39.5 (C3), 181.6 (C4), 215.2 (C5)) were all observed in the spectra of the products in the aqueous phase after microwave irradiation. Comparison with the standard LA (27.5 (C1), 28.9 (C2), 37.4 (C3), 176.6 (C4), 212.6 (C5)) shows slight shifting in these peaks due to the formation of sodium levulinate during the neutralization process. The ^1H and ^{13}C NMR spectra of standard FA are shown in Figure S3 of the Supporting Information, where 7.04 in ^1H NMR is due to the proton in CH and 164.51 in ^{13}C NMR is due to the carbon. After neutralization of the liquefaction solutions, formic acid is also detected as sodium formate, and the peaks in ^1H NMR and ^{13}C NMR are shifted to 8.46 (Figure 3) and 171.05 (Figure 2), respectively. According to FTIR and ^{13}C NMR analysis, 1 h continuous microwave irradiation of starch in 0.01 g/mL H_2SO_4 solution could convert starch into glucose and/or LA and FA. Meanwhile, furan-kind solid structures were produced on the surface of the residues.

Analysis of the Degradation Process. The water-soluble degradation products from groups a and b were monitored by ^1H NMR at 20 min intervals up to 180 min of microwave-assisted reaction. The heating of samples in group a was interrupted for 1 min after every 20 min, while samples in group b were heated continuously, to explore the influence of continuous and discontinuous microwave treatment. ^1H NMR of the water-soluble degradation products and their molar ratio after different degradation times are shown in Figure 3. According to ^1H NMR, oligosaccharides, glucose, and/or LA and FA are the main water-soluble degradation products throughout the 180 min of microwave heating. In addition, a small amount of 5-HMF was detected by ^1H NMR in both groups a and b samples (small peaks at 6.59 ppm, 2H, furan ring H). 5-HMF is a known degradation intermediate between glucose and its subsequent decomposition to LA and FA.³⁵ The

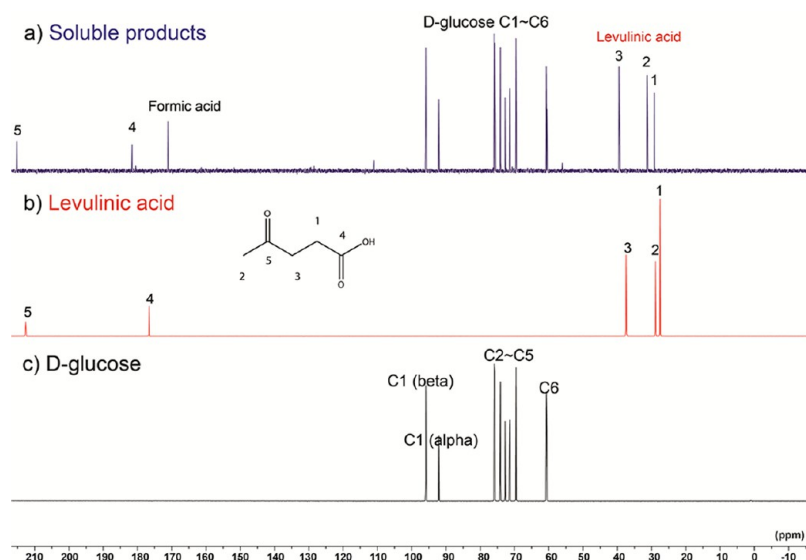


Figure 2. ^{13}C NMR spectra of (a) water-soluble degradation products from starch degradation after 60 min of continuous microwave irradiation, (b) standard levulinic acid, and (c) standard D-glucose.

signals of 5-HMF were shown weakly in the ^1H NMR, but the content was so low that no typical signals of 5-HMF were detected in the ^{13}C NMR of the soluble phase (Figures S1 and S2, Supporting Information). This indicates rapid further degradation of 5-HMF to LA and FA. Besides, after 20 min irradiation, spherical carbon residues precipitated from the degradation solution. These carbon spheres from biomass are expected to be valuable products for a number of applications.^{36,37} In our work, 5-HMF participates in the carbonization process forming solid spherical degradation residues.

The molar ratio of produced LA and FA was close to 1:1 according to ^1H NMR in Figure 3. This is in agreement with the reported dehydration process of 5-HMF forming equimolar amounts of LA and FA.^{32,33} The molar proportions of glucose (and oligosaccharides), 5-HMF, and LA were calculated and are indicated in Figure 3 (bar). The molar ratio of LA toward glucose and 5-HMF is expressed as LA selectivity (red bar), which could reach as high as 95% under 160 min continuous irradiation. In the later stage, the LA selectivity fluctuated within a small range, and a small amount of glucose always remained, indicating that the yield of LA reached an equilibrium value.

During the sequential discontinuous heating, the time point for the main transformation of glucose to LA occurred later than during the continuous microwave irradiation (after 120 and 60 min, respectively). This means that the short 1 min sequential interruption during microwave irradiation can profoundly affect the transformation of glucose to LA. This is highly significant for maximization of the glucose production, when glucose is the desired end product.

The liquefaction efficiency of both processes (groups a and b samples) is depicted in Figure 4. The liquefaction efficiency for group b was always lower than the one for group a. This suggests that the continuous treatment is less effective or it favors the carbonization process leading to spherical residues. Two significant transformation time points, 120 min for group a and 60 min for group b, were observed. After these time points, the yield of LA increased rapidly (Figure 3), and the liquefied efficiency as calculated from the amount of solid

residue of the two groups seemingly declined sharply. This is most likely connected to the degradation of glucose to 5-HMF, which participates in the carbonization process leading to the formation of solid spherical carbon spheres, i.e., humins. This in turn increases the solid fraction. In summary, Figures 3 and 4 suggest that glucose is transformed to LA and its coproduct FA with high selectivity under microwave irradiation, as a side product solid of carbonized humin residue is formed.

It is of great interest to find out that the liquefaction efficiency actually decreases slightly when the sulfuric acid concentration is increased (Figure 5). The same trend was earlier found during microwave-assisted degradation of cellulose.³⁸ According to the ^{13}C NMR spectra of soluble products (Figure S4, Supporting Information), LA was produced in a larger amount when the concentration of sulfuric acid was low. A higher concentration of H_2SO_4 results in a larger amount of solid spherical residue. A possible explanation is that the higher concentration H_2SO_4 rapidly oxidizes glucose to HMF, which then reacts further to form solid carbon spheres.

ESI was employed to examine the soluble products after three microwave irradiation times (Figure 6a,b,c). At the beginning, just after the 20 min RAMP time (Figure 6a, holding time is 0 min), peaks appear at m/z $180n - 18(n - 1) + 23$, showing that starch granules had ruptured into oligosaccharides and already a small amount of glucose had been formed. Then, on prolonged microwave heating, all glycosidic bonds are hydrolyzed, resulting in the formation of glucose as the main degradation product (Figure 6b, m/z 203). Later, glucose dehydrates into 5-HMF and rapidly further transforms to LA (m/z $116 - 1 + 23)n + 23$) and FA (Figure 6c) or participates in the carbonization process. LA displays interesting complex-forming behavior in the sodium rich solution. H^+ in the carboxylic acid group of LA is replaced by Na^+ , and this carboxylate (LA-COONa) tends to gather into clusters, which contained up to seven LA-COONa units. m/z 164.9 Da corresponds to sodium sulfate (Na_2SO_4 (142) + Na (23)), which is produced by neutralizing H_2SO_4 with the NaOH solution. The observed 142 Da intervals in Figure 6b result from aggregation of Na_2SO_4 salt attached onto glucose.

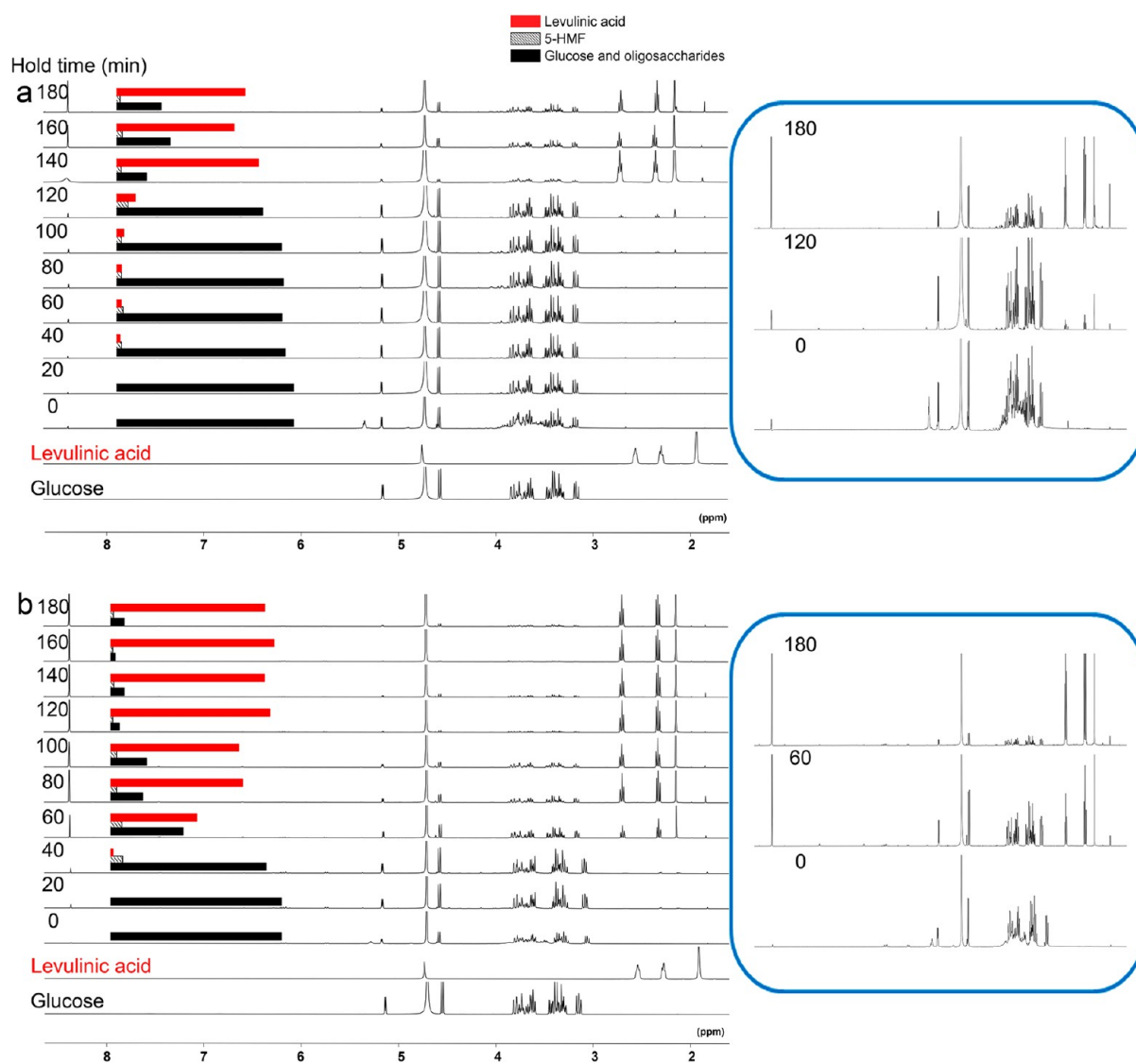


Figure 3. ^1H NMR spectra and molar ratio of formed glucose and levulinic acid after 0–180 min microwave irradiation. Samples in group a are treated with sequential microwave irradiation; samples in group b are treated with continuous microwave irradiation.

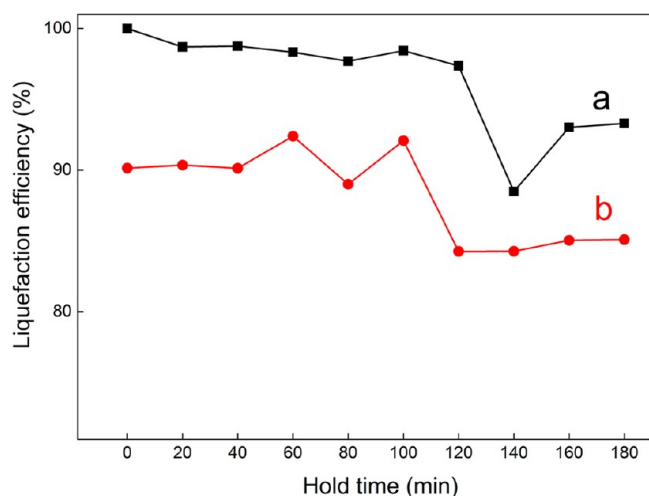


Figure 4. Liquefaction efficiency after sequential (group a) and continuous (group b) microwave heating.

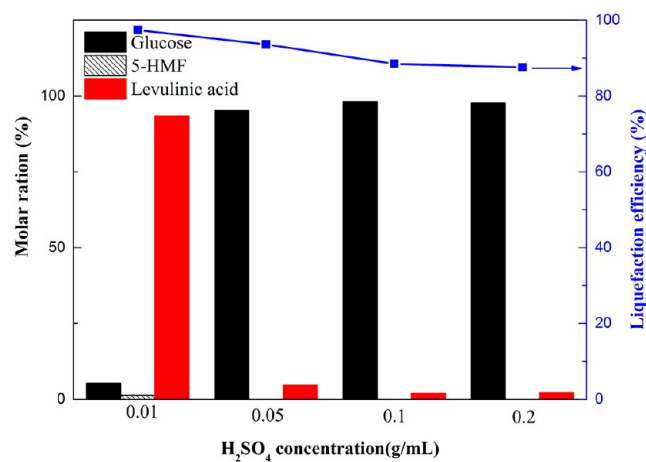


Figure 5. Liquefaction efficiency and molar ratio of soluble products after microwave-assisted degradation of starch with different H_2SO_4 concentrations.

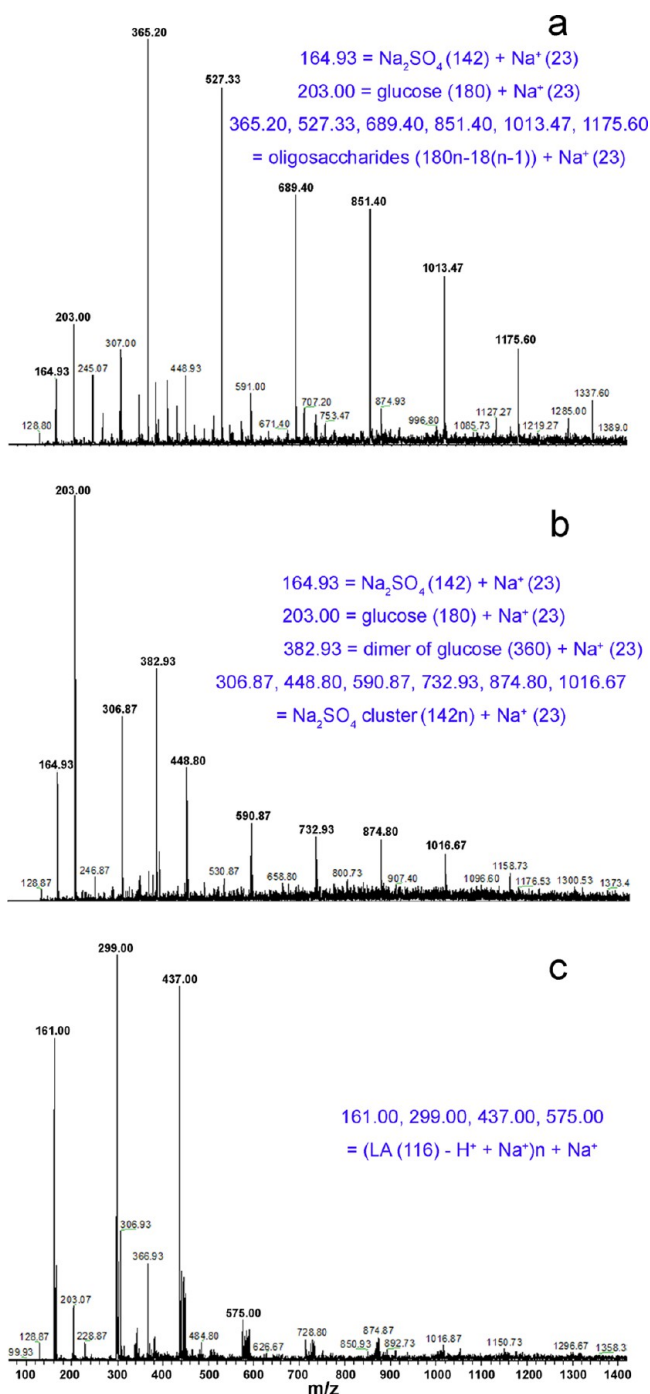


Figure 6. ESI-MS spectra of the water-soluble products after microwave-assisted hydrothermal degradation of starch. Continuous microwave heating times (holding times) were (a) 0, (b) 40, and (c) 180 min.

Furthermore, the MALDI-MS spectra (Figure S5, Supporting Information) as parallel evidence certify the three main degradation stages under microwave irradiation described above. ESI-MS in the MS/MS mode can exert electron power to a molecule with a specific m/z value, which results in fragmentation of the molecule enabling further structural evaluation. Figure S6 of the Supporting Information shows the ESI-MS spectra of the standard glucose solution, and the inset illustrates the MS/MS spectra when power is exerted on m/z 203.00. ESI-MS offers the possibility to differentiate

between glucose (m/z 203 = 180 + 23) and the dimer of glucose (m/z 383 = 180 + 180 + 23). According to the proposed reaction pathway of glucose decomposition, glucose can be cleaved to erythrose and glycolaldehyde in supercritical water.³⁹ These two products are produced by C–C cleavage of glucose via retro-aldol condensation. Under MS/MS (Figure S6, inset, Supporting Information), the glycolaldehyde (60 Da) fragmentation was released from glucose, and the remaining erythrose fragment (143 Da = 120 + $\text{Na}^+(23)$) was detected. The presence of glycolaldehyde can also be observed in MALDI-MS at m/z 104.9 Da (glycolaldehyde (60) – H^+ (1) + $\text{Na}^+(23)$ + $\text{Na}^+(23)$). The MS/MS of LA did not result in fragmentation to smaller molecules (data not shown). However, as stated above, the LA formed dimer, trimer, and even higher complexes in water according to Figure S7 of the Supporting Information.

Figure S8 of the Supporting Information manifests the aggregation behavior of LA in aqueous phase by MS/MS on 437 and 299 Da (Figure S8, inset, Supporting Information). The peak at 437 Da can be easily striked to 299 Da and further to 161 Da, which means the LA carboxylate (LA–COONa) is detached from its trimer and dimer clusters one by one.

When starch was discontinuously degraded in 20 min intervals (group a), the starch degradation solution changed color from clear to light yellow in 40 min and then to brown after 120 min (Figure 7). The color change starts at the same

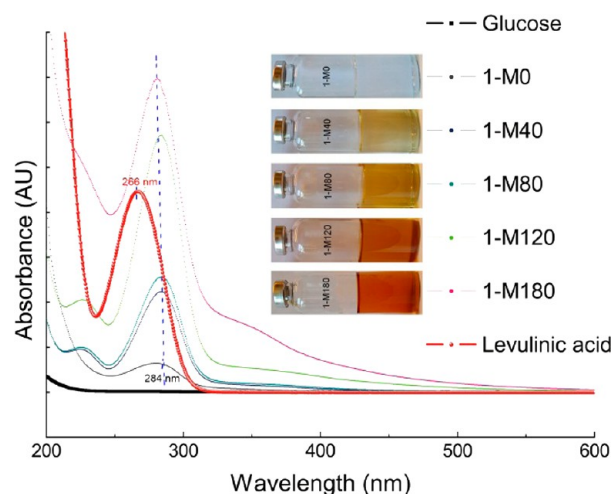


Figure 7. UV-vis absorbance spectra of water-soluble degradation product mixtures after different holding times (1-M0, 1-M40, 1-M80, 1-M120, and 1-M180). Samples are from group a.

time when the decomposition of glucose is initiated (40 min) and turns even deeper when the amount of LA increases (120 min). We measured UV-vis absorbance spectra of the degradation solutions (Figure 7). All five samples were from group a (noted as 1-M system) and were treated with discontinuous microwave heating. Glucose shows no characteristic absorbance peak. It is reported that LA and HMF have strong absorption in the UV range below 330 nm, and their characteristic absorption is at wavelength of 266 and 284 nm.⁴⁰ In Figure 7, there is a slight blue shift from 284 to 266 nm when increasing microwave treatment time. This suggests that soluble 5-HMF transfers to LA during microwave treatment. Absorbance was also observed to increase with prolonged time, indicating that more LA was accumulated. According to the previous production molar ratio presented in Figure 3a, the

amount of LA is much higher than the amount of 5-HMF. However, the ring structure in 5-HMF has strong UV absorbance and imposes a predominant effect in the recorded UV–vis spectra, where a strong absorbance is observed close to the characteristic absorption maximum reported for 5-HMF. The color is produced during the hydrothermal degradation of starch under microwave heating. It is a common phenomenon during polysaccharides transformation, but there is no clear explanation for this complex process now. This significant feature offers a chance to monitor or control the soluble degradation products and their distributions.

Regarding the residues that were produced during microwave degradation, Figure 4a shows that the amount of residue increases dramatically just after 120 min. This coincides with the time when glucose starts to transfer to LA (Figure 3a). 5-HMF is a well-known degradation intermediate during this transformation. The turning points at 120 min in Figures 3a and 4a strongly indicate that glucose transformation and 5-HMF play important roles in the production of the residue.^{34,41} The formation of spherical humin residues can thus be connected to further reactions or polymerization of 5-HMF.

Residues of samples from group a (1-M0, 1-M40, 1-M80, 1-M120, and 1-M180) collected on filter paper were dried at 40 °C and investigated with SEM (Figure 8). The original starch

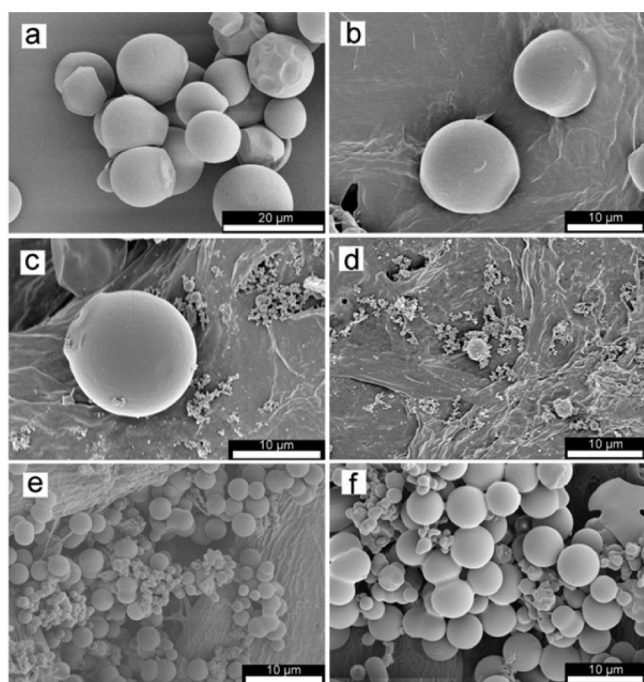


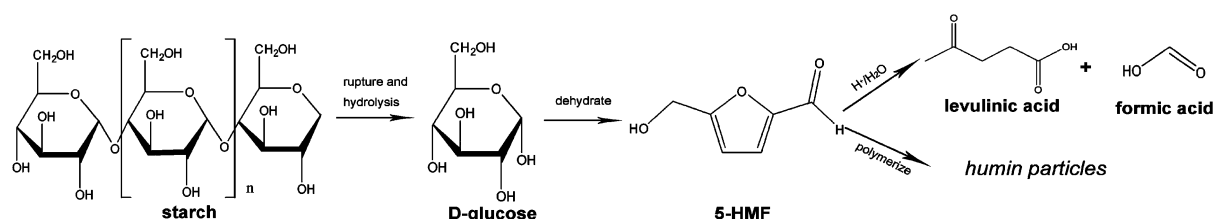
Figure 8. SEM images of (a) tapioca starch and solid residues from starch degradation after microwave holding times of (b) 0, (c) 40, (d) 80, (e) 120, and (f) 180 min. Samples are from group a with continuous microwave heating.

had a shape of smooth large spherical granules (Figure 8a). Twenty minutes of RAMP time did not seem to change the starch granules significantly (Figure 8b). However, judging from the small amount of remaining starch detected on the filter paper, the short heating process was enough to result in significant dissolution of starch granules. This was also shown by ESI-MS, MALDI-MS, and NMR analysis. Starch granules then turned smaller and irregular as they were disrupted under the microwave heating. Meanwhile, formation of small spherical particles started, and these were collected on the filter paper. The diameter of these particles presented a narrow distribution ranging from 0.5 to 2 μm , as shown in Figure 8c. These spherical particles had a strong tendency to aggregate and coalescence (Figure 8d). The underlying mechanism of residue formation has been proposed as the polymerization of 5-HMF under heating.³⁰ According to an intensive study on the polymer chemistry of furans by Gandini et al.,⁴² the two functional groups of 5-HMF may undergo condensation polymerization and also serve as precursors for other difunctional monomers. They also suggested a mechanism for the hydrolytic ring-opening of 5-HMF into an aliphatic open-chain product, which could further polymerize. Formation of similar humins have been observed earlier after acid-catalyzed conversion of carbohydrates such as sucrose, glucose, and fructose,^{30,43} and the chief culprit is suspected to be 5-HMF. Formation of humins includes nucleation and growth. When 5-HMF is induced to accumulate, it can form precursors to polymerization on the surface of insoluble char. The polymerization pathway is enhanced by higher concentration of 5-HMF (Figure 8e,f). The average diameter of the spheres increases continually as the 5-HMF conversion reaction progresses. Growth appears to involve both single particles increasing in size as well as coalescence of two or more particles. This mechanism is supported by the previous FTIR spectra of residue (Figure 1). The polymerization reaction of 5-HMF molecules to form humin particles allow the furan ring to exist in the residues. It also explains why little 5-HMF was observed among the water-soluble compounds and why the yield of LA remained almost constant (Figure 3) during longer reaction times.

On the basis of the above discussion, the microwave-assisted degradation process of starch was proposed to proceed according to Scheme 1. Starch first ruptured into oligosaccharides and then hydrolyzed to glucose. With high temperature, glucose dehydrate to 5-HMF, which is rapidly further converted to LA and FA in the acid solution. This transformation was accompanied by polymerization of 5-HMF as a side reaction. The products of 5-HMF polymerization were spherical humin particles.

Closed-Loop Recycling of Water-Soluble Degradation Products as Starch Plasticizers. Six starch films were prepared by solution casting, including starch, starch–glycerol,

Scheme 1. Conversion Process of Starch to LA under Microwave Irradiation



starch–glucose, starch–LA, starch–glucose–LA, and starch–M60. SEM pictures were taken from the cross section of each film (Figure 9). The plain starch film was brittle and

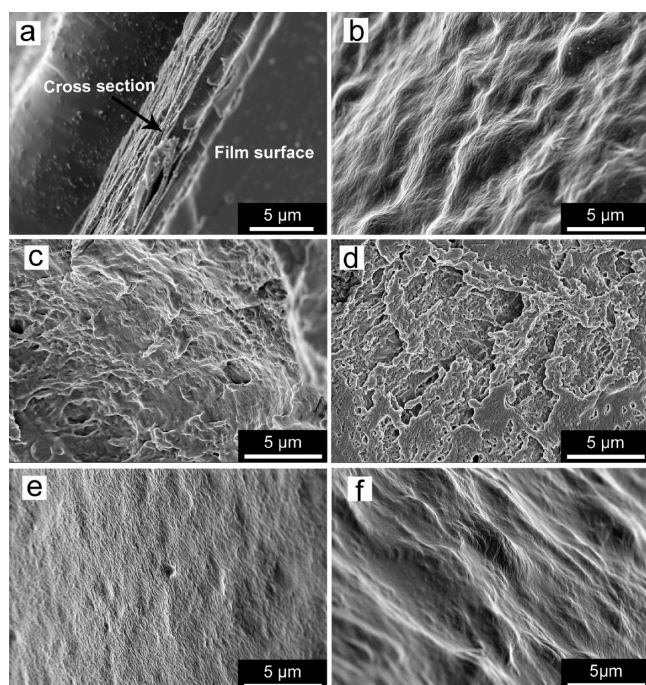


Figure 9. SEM images of the cross section of (a) starch, (b) starch–glycerol), (c) starch–glucose, (d) starch–LA, (e) starch–glucose–LA, and (f) starch–M60 films.

discontinuous, presenting a lamellae-like side view (Figure 9a). Glycerol is one of the most commonly used starch plasticizers. The quality and flexibility of the film containing starch and glycerol was high, and SEM images of the film showed a homogeneous and smooth cross section (Figure 9b). Blending starch with pure glucose or LA separately resulted in rather rough films and interspaces within the film (Figure 9c,d). The starch–LA film was fragile, and the color was white instead of transparent. However, glucose and LA together (1:1 wt %) resulted in a smooth and flexible starch film with a high quality (Figure 9e). The fibrillar structure could be observed, similar to the one observed for the model starch–glycerol films.

On the basis of these results, the water-soluble degradation products after 60 min of microwave irradiation with glucose and a LA ratio close to 1:1 (Figure 3b) were chosen to demonstrate the potential of starch hydrothermal degradation products as starch plasticizers. The starch–M60 film plasticized with water-soluble degradation products was flexible to a certain extent and of good quality (Figure 9f). Besides, it displayed topography similar to starch–glycerol film in Figure 9b. Overall, the combination of glucose and LA resulted in good and homogeneous dispersion of the plasticizers in the starch films. These results were supported by carbonyl (1740 cm^{-1}) single-peak absorbance images obtained by the IR spotlight technique, which clearly showed enhanced dispersion of LA in starch films when added together with glucose (Figure S9, Supporting Information). The hydroxyl of starch (3460 cm^{-1}) absorbance images for starch–LA and starch–M60 are also shown in Figure S9 of the Supporting Information.

The moisture absorbance of the starch films was evaluated by single-peak water absorbance (1637 cm^{-1}) images. Starch

materials always absorb water from air. The distribution and concentration of this incorporated water are indicated by colors, and the images are shown in Figure 10. The images show even distribution of water in all films, except the starch–LA film, for which a clearly more heterogeneous distribution is illustrated (Figure 10d).

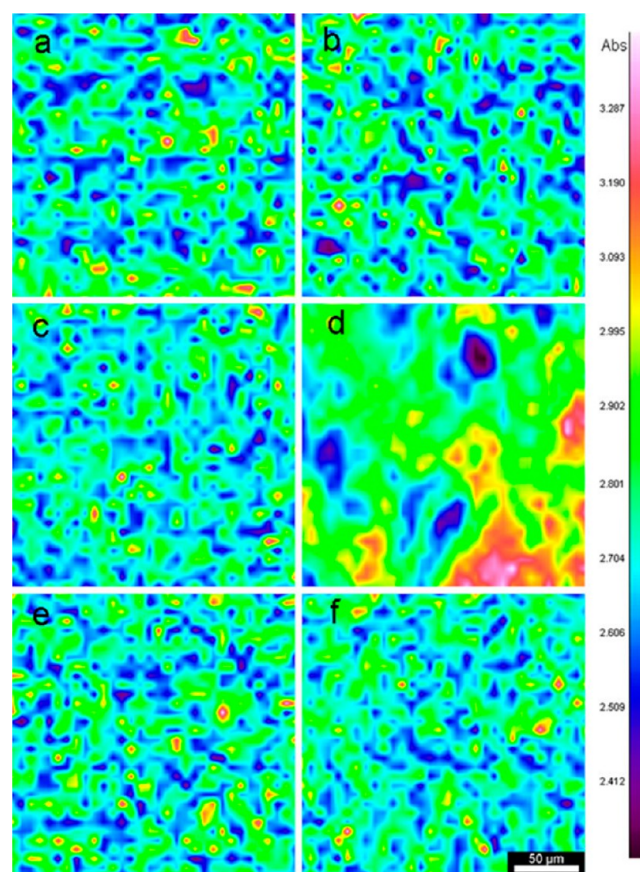


Figure 10. Hydroxyl of water signal peak absorbance images of (a) starch, (b) starch–glycerol, (c) starch–glucose, (d) starch–LA, (e) starch–glucose–LA, and (f) starch–M60 film surfaces.

DSC and TGA analysis of the starch films was performed to evaluate the influence of plasticizers. Starch alone presented a T_g near $100\text{ }^{\circ}\text{C}$, which could be attribute to starch gelatinization. Compared with pure starch film, a lower glass transition region was shown in the DSC curve of the starch–glycerol film (Figure 11). In the temperature range from -50 to $200\text{ }^{\circ}\text{C}$, starch–glucose–LA and starch–M60 films showed the same trend as starch–glycerol film, indicating that glucose and LA together improve the mobility of the starch segments. As for the starch–LA film, LA melted at $30\text{--}35\text{ }^{\circ}\text{C}$ during the first heating, and it again crystallized in the starch film during cooling. The crystals then again melted during the second heating of DSC, which resulted in a melting peak at $16\text{ }^{\circ}\text{C}$ in the starch–LA film. LA crystals in the high carboxyl concentration and low water concentration areas also explain the phase separation in FTIR images of the starch–LA film (Figure S9 a, Supporting Information, and Figure 10d). It is interesting that crystallization of LA was prevented when glucose together with LA was blended in the starch film. The interaction of hydroxyl in glucose and carboxyl in LA thus seems to prevent LA from crystallizing.

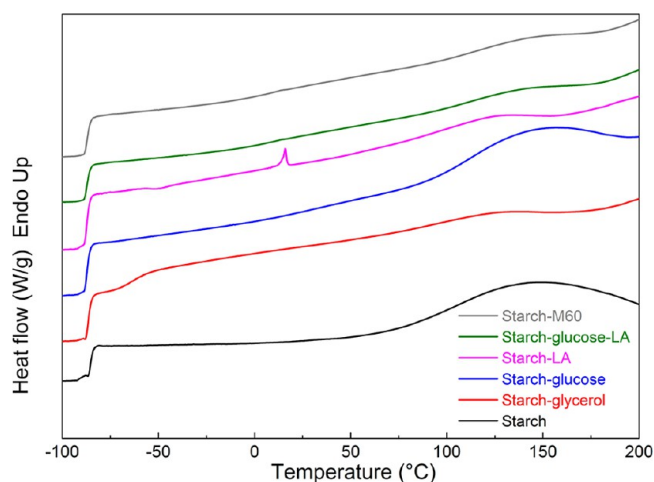


Figure 11. DSC thermograms for the starch films with different compositions.

Figure 12 shows the typical processes of weight loss during heating of the different films. It is shown that there are two

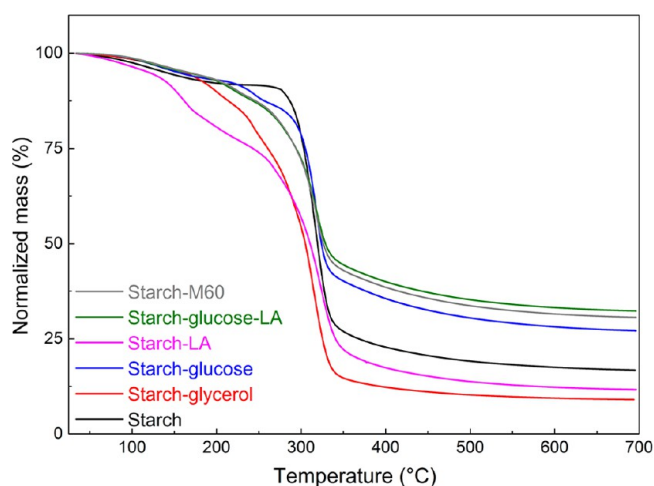


Figure 12. TGA curves for the starch films with different compositions.

major weight loss phases. The first phase represents the evaporation of water at around 100 °C. The weight loss during this phase depends on the moisture content. The second weight loss phase corresponds to thermal decomposition, which commences at around 300 °C. Glycerol could evaporate when temperature reaches around 290 °C; therefore, the starch–glycerol film started to decompose much earlier than the other films. Low thermal stability is a drawback of the starch–glycerol film. However, the starch–glucose–LA and starch–M60 films both display much better thermal stability than the starch–glycerol one. Besides, the moisture content is also proved to be lower compared to the other compositions. The starch–LA film exhibited the lowest thermal stability. LA alone did not improve the flexibility and moisture resistance of the starch film. When mixed with glucose, the combination both improved the flexibility and also kept the thermal stability of starch. On the basis of the comparison between the starch–glucose–LA and starch–M60 films, the influence of formic acid, sulfuric acid, and other minor components in the degradation mixture was not significant. The water-soluble

degradation products of starch from microwave heating containing mainly glucose and LA were compatible with starch and improved the flexibility and properties of the films.

CONCLUSIONS

Green, fast, and high-yield hydrothermal degradation of starch to functional chemicals was achieved by an acid-catalyzed microwave-assisted reaction. In addition, high selectivity toward glucose or LA and FA formation was demonstrated. The degradation process took place in three steps. First, starch granules ruptured to oligosaccharides, and then, these were further hydrolyzed to glucose. At a well-defined time point during the degradation process, fast dehydration of glucose to LA and FA was initiated through 5-HMF as an intermediate degradation product. At the same time, 5-HMF was also involved in polymerization/carbonization reactions leading to formation of insoluble humins, spherical particles. LA was produced in high yield and 95% selectivity through continuous microwave irradiation of starch. Sequential microwave irradiation, on the other hand, increased the liquefaction yield and also, interestingly, delayed the transformation of glucose to LA, indicating a promising potential for high-yield production of glucose from biomass.

The water-soluble degradation product mixtures could be directly recycled and reused as plasticizers for new starch films reducing the brittleness of the films. Utilization of less energy-consuming microwave-assisted reactions and water as a green solvent provides possibilities for up scaling the process. A green closed-loop process for reusing old starch products is thus demonstrated, opening a promising door for industrial recycling and manufacture of starch-based materials.

ASSOCIATED CONTENT

Supporting Information

NMR spectra of water-soluble starch degradation products; MALDI-MS of water-soluble degradation products, illustrating the three stages during the degradation process; ESI-MS of glucose, levulinic acid, and final soluble degradation products; and carboxyl and hydroxyl signal peak absorbance images of starch–LA film and starch–M60 film. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Phone +46-087908271. E-mail: minna@kth.se.

Notes

The authors declare no competing financial interest.

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