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ARTICLE

Continuous process of cellulose dissolution and transesterification reaction catalysed by ionic liquid in twin screw extruder

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More energy efficient and greener processes are needed today in chemical engineering. Reactive extrusion is an example of a new innovation targeting cleaner and more sustainable processes. In this work, we first examined the solubility of microcrystalline cellulose of two concentrations (10, 20 wt%) in a mixture of 1-ethyl-3-methylimidazolium acetate (EmimOAc)/DMSO using a twin screw extruder. Also, a new method of measuring residence time distribution inside the extruder was developed and discussed. EmimOAc/DMSO mixture was recovered and reused. Next, transesterification of cellulose using long-chain acyl groups donor (vinyl laurate) was performed. The products of high degree of substitution (2.48 – 2.67) combined with great reaction efficiency (> 80%) of the process as well as low E-factor (3.5) can be obtained in a continuous way using the co-rotating twin screw extruder. Finally, the effect of cellulose concentration on crystalline structure and mechanical properties of cellulose laurate films was evaluated.

Introduction

Human progress has always been strongly related to the use of technologies and materials. Advances in these fields have considerable potential to bring about changes in society. We have also observed changes in the polymer chemistry domain. Currently, the use of renewable feedstocks for the synthesis of new materials has gained increasing attention. Cellulose is a good example of this. After its bright rise in the late 19th century (celluloid development)[1], cellulose as a functional material was replaced with inexpensive and simple-to-make fossil-based plastics. Today, our society is seeking new, sustainable materials. This is an excellent opportunity for the use of cellulose. Nevertheless, an important question "why is renewability not enough?" was discussed by *Onwukamike et al*.[2] The authors encouraged researchers working on the chemical modification of biopolymers to consider not only the renewability aspect but also the entire transformation process to promote sustainability.

Industrially employed chemical modification of cellulose (e.g., acylation) has been performed through a heterogeneous route, which generally involves several steps. First, the solid-liquid phase reaction of cellulose to an initial degree of substitution (DS) of three. Second, acid-catalysed deacylation of a highly substituted cellulose ester (DS of three) to obtain a product with the desired DS. This process is often limited to the surface of cellulose and it is impossible to control the DS. Moreover, use of harsh chemicals causes cellulose degradation during the process and produces large amounts of waste.[3] On the other hand, the homogeneous approach contributes to achieving better control of reactions with a high conversion rate. In the case of homogeneous modification, cellulose molecules are assumed to have full accessibility of all hydroxyl groups for the reaction. Recently, ionic liquids have been employed for the homogeneous acylation of cellulose in batches.[4-6] However, to achieve truly sustainable cellulose modification, the process and reaction design should be carefully considered.

The development of continuous methods for processing of chemicals helps bridge the gap between academic and industrial settings by providing more reproducible and efficient options.[7] For example, reactive extrusion (REX) uses a combination of mixing, heating, and mechanical energy to process the desired components.[8] REX showed great results when applied to the chemical modification of both synthetic and natural polymers.[9-12] However, this is a relatively new equipment for cellulose transformation.[13,14] This is due to the dense hydrogen bond network found in cellulose, which makes it difficult to process. In our previous research we studied cellulose dissolution and chemical modification in 1-ethyl-3-methylimidazolium acetate (EmimOAc)/DMSO mixture using micro compounder with volume of 5 mL. In that case, recirculation mode was used which allowed us to increase the residence time.[15]

In the present study, we report for the first time, a one step, continuous process of microcrystalline cellulose (MCC) transesterification with vinyl laurate. MCC was chosen as a model substrate to study dissolution and transesterification reaction in ionic liquid via extrusion. MCC has been previously used for reactions in batch by our group.[4] First, residence time distribution (RTD) was studied in detail by applying new method developed in our group. Next, cellulose laurate was continuously synthesized by transesterification reaction using two different MCC concentrations (10 and 20 wt%) (Scheme 1). This process leads to high DS and reaction efficiency when using equimolar amounts of reagent. It was shown that at 10 wt%, complete cellulose dissolution prior to reaction in REX provides

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products with improved properties (solubility in chloroform, elongation at break, and film transparency).

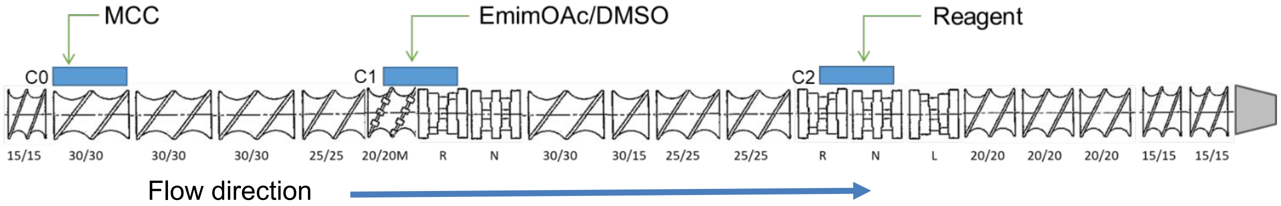


Fig. 1 Extrusion equipment and screw geometry used in this study (flight length: 435 mm, screw diameter = 20 mm). For each screw element first number signifies pitch length (mm) and the second number is element length (mm). Element 20/20m is a fibre cutting disk.

Experimental

Materials

Microcrystalline cellulose (MCC) (Avicel® PH-101, ~50 µm particle size) and anhydrous dimethyl sulfoxide (DMSO) were obtained from Sigma-Aldrich Co., LLC. (St. Louis, MO, USA). EmimOAc, with a moisture content of 0.25%, was purchased from Nippon Nyukazai Co., Ltd. (Tokyo, Japan). Vinyl laurate (VL) and all other chemicals were provided by Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). All chemicals were used as received without further purification.

Equipment used in this study

In this study, a ULTnano20TW-20MG-NH(-600) co-rotating twin-screw extruder (Technovel, Japan) with a specific geometry was used (Fig. 1). The screw configuration consists of conveying elements and kneading blocks (R, L, and N elements). Element “R” is right-handed kneading element (stagger angle 45°) with forward conveying functionality. Element “L” is left-handed kneading element (stagger angle - 45°) with reverse conveying functionality. Element “N” is neutral kneading element (stagger angle 90°). The product was extruded through a round die. The varied parameters during extrusion were cellulose concentration (Conc. = 10 and 20 wt%), screw speed (N = 60, 120, and 180 rpm), feed rate of the MCC + solvent mixture (Q = 6 and 30 g/min), and temperature (T = 60-100 °C).

MCC dissolution and RTD measurements

Prior to extrusion, MCC was dried at 70 °C for at least 12 h in a vacuum oven. The EmimOAc/DMSO mixture was prepared by mixing the two solvents in a specific ratio 1 g of EmimOAc and 3 g of DMSO. MCC and the solvent were mixed using an extruder at different ratios, as shown in Table ES1. For the cellulose dissolution experiment, powdered MCC was introduced through port C0 under a constant feed rate using a volumetric screw feeder. Since MCC is a fine powder its feed in the extruder can be held continuously. Which is a more difficult task in the case of pulp or cotton. Simultaneously, the EmimOAc/DMSO (1/3 g/g) mixture was pumped into the extruder through port C1 under a constant flow rate using a volumetric pump. The total feed rate was determined by collecting samples at the end of the extruder every 2 minutes and weighing them.

For the RTD measurements, iron oxide (Fe_3O_4) was used as a tracer. Iron oxide was selected because of its strong colour strength (black pigment), high thermal stability, and low reactivity. During the extrusion process, a small amount of Fe_3O_4 (≈ 0.02 g) was introduced through port C0. Simultaneously, sampling of the extrusion material during a stated time interval (1 min, 30 s or 10 s) was started. After extrusion, the obtained samples containing the MCC solution in EmimOAc/DMSO (1/3 g/g) and the tracer were first diluted. For example, 1 g of extruded sample was mixed with 9 g of EmimOAc/DMSO (1/3 g/g). After complete dissolution, turbidity was measured using a 2100Q Portable Turbidimeter (Hach, USA). An example of the MCC/Fe_3O_4 sample is shown in Fig. ES1. Therefore, it is important to avoid bubbles during turbidity measurements. The turbidimeter was calibrated using STABLCAL® Formazin turbidity standards (10 NTU, 20 NTU, 100 NTU, and 800 NTU). The turbidity was measured three times, and the average value was used to build the RTD curves.

To recover the EmimOAc/DMSO mixture, MCC/Fe_3O_4 samples were first precipitated in an excess of methanol (50 mL per gram of MCC) and further vacuum filtered. The EmimOAc/DMSO mixture was separated from methanol by simple rotary evaporation of methanol. Proton NMR was measured in order to determine the purity of recovered EmimOAc/DMSO mixture.

Cellulose laurate synthesis

The experimental protocol for the reaction using a twin-screw extruder was similar to that used for cellulose dissolution. Two different concentrations of MCC (10 and 20 wt%) were chosen while keeping the other parameters fixed (Q = 30 g/min, N = 60 rpm, T = 80 °C). However, vinyl laurate (3 eq./ anhydroglucose unit (AGU)) was added through C2 port under a constant flow rate (12.57 g/min and 25.15 g/min for 10 and 20 wt% MCC, respectively) using volumetric pump (Fig. 1, Reagent). Note that although the reaction system is open to air, EmimOAc has a negligible vapour pressure and DMSO has a high boiling point enabling operation without solvent vaporization issues.

The extruded cellulose laurate (CL) samples were firstly dispersed in an excess of methanol (50 mL/g of CL), followed by vacuum filtration and washing with methanol. The samples were air-dried at room temperature and in a vacuum oven at 70 °C for 24 h.

Characterization

ATR-FTIR spectroscopy. Samples were analysed using a Thermo Fisher Scientific Nicolet iS10 spectrophotometer (Thermo Fisher Scientific, Inc., Tokyo, Japan) equipped with an attenuated total reflection (ATR) unit. The number of accumulated scans was set as 64.

NMR spectroscopy. ^{1}H NMR spectra of fresh and recovered EmimOAc/DMSO (1/3 g/g) mixture were recorded in $CDCl_3$. ^{1}H NMR spectra of the cellulose laurate samples were obtained at room temperature using a JNM-ECA 600 spectrometer (JEOL Ltd., Tokyo, Japan) in deuterated chloroform solvent ($CDCl_3$) at Advanced Research Center, Kanazawa University. A drop of concentrated trifluoroacetic acid (TFA) was added to the samples to shift the residual water signals and the remaining hydroxyl protons of cellulose from the region of AGU signals into a region of non-interest. The DS_{main} of cellulose laurate samples was calculated from the integral of the terminal CH_3 group (I_{CH3}) of laurate chain at 0.8 ppm and the area of the AGU signals (I_{AGU}) at 3.2–5.2 ppm using the following equation:

$$DS_{main} = \frac{7 \times I_{CH_3}}{3 \times I_{AGU}} \qquad (1)$$

To study the possible side reaction of acetylation during cellulose laurate synthesis[16], the DS_{side} (acetylation) was calculated using the area of the acetyl group (I_{acetyl}) at 2.0–2.2 ppm and the area of the AGU signals (I_{AGU}) at 3.2–5.2 ppm by applying the following equation:

$$DS_{side} = \frac{7 \times I_{acetyl}}{3 \times I_{AGU}} \qquad (2)$$

The reaction efficiency (RE) of the cellulose laurate synthesis process was calculated using the following equation:

$$RE\ (\%) = \frac{DS_{main}}{DS_{th}} \times 100\% \qquad (3)$$

Where DS_{main} is the obtained DS and DS_{th} is a theoretical DS that is equal to the vinyl laurate/cellulose molar ratio.

E-factor was used to evaluate the sustainability of the described process. The E-factor is the actual amount of waste produced in the process[17], and is defined as the mass ratio of waste to the obtained product:

$$E-factor = \frac{Weight\ of\ raw\ materials\ -\ Weight\ of\ product}{Weight\ of\ product} \qquad (4)$$

X-ray diffraction analysis (XRD). XRD measurements were conducted using a Rigaku Miniflex X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu Kα radiation (λ = 0.1542 nm). The X-ray generator was operated at a current of 2 mA and voltage of 20 kV. Diffraction patterns were recorded in the range of 10-50° (2θ) using a scanning rate of 5° min^{-1}.

Capillary rheometer measurements. The softening temperature (T_s), flow-beginning temperature (T_{fb}) and offset temperature (T_{off}) were determined using a Flow Tester (Shimadzu Flow tester CFT-500EX) (Fig. ES2). Constant Heating Rate Method was applied starting from 50°C at a heating rate of 3 °C min^{-1} with a constant load of 50 N. The diameter and length of the die were 1 and 10 mm, respectively. The amount of sample used for each experiment was 0.8 – 1.0 g.

Cross-polarizing optical microscopy. Measurements were performed using an MT9430L microscope (Meiji Techno Co., Ltd.). The samples were placed between two microscope glass slides prior to observation. When cellulose was completely dissolved, only a black image was obtained.

Measurement of mechanical properties. To prepare the films, cellulose laurate was compounded at T_{off} + 10 °C in an Xplore MC5 microcompounder equipped with a short co-rotating twin-screw (Xplore Instruments BV, Sittard, The Netherlands). The obtained extrudate (3 g) was cut into small pieces and pressed using hot plates coupled to a pressing machine. The samples were initially heated between hot plates for 5 min at T_{off} + 10 °C followed by pressing (30 kN) for 5 min.

Tensile tests were conducted in accordance with JIS K7139 A12. An EZ-SX (Shimadzu, Tokyo, Japan) equipped with a load cell of 200 N at a crosshead speed of 5 mm min^{-1} was used for this test.

Results and discussion

Cellulose dissolution with twin screw extruder

It was previously reported that up to 20 wt% of MCC can be dissolved using EmimOAc and EmimOAc/DMSO mixture in batch[18] and in the loop mode extruder.[15] The main drawback of this direct extrusion process is the limited length of the extruder and, as a result reduced residence time of the mixture inside the machine. In the first part of our work, we examined the dissolution abilities of two different concentrations of MCC (10 and 20 wt%) in an EmimOAc/DMSO (1/3 g/g) mixture by varying the other extrusion parameters. The specific ratio of EmimOAc/DMSO was chosen based on previous results.[15] Cellulose concentration plays an important role for MCC complete dissolution inside the extruder.[19] Complete cellulose dissolution prior to reaction is required for homogenous esterification which influences the final properties of cellulose esters. In our experiment, 20 wt% MCC did not completely dissolve despite varying the conditions (temperature, screw speed, feed rate). Even at 100 °C the small particles were observed in the extruded samples (Fig. ES2a). In contrast, 10 wt% MCC showed complete dissolution at all studied temperatures (Fig. ES2b,c,d). In conclusion, the cellulose concentration is an important parameter to consider for a homogenous process.

Residence time measurements

To understand cellulose dissolution process in the twin screw extruder, the residence time distribution was studied by non-reactive tracer method using a turbidity test. First, the total feed rate increased during extrusion from 6 g/min to 30 g/min, as shown in Fig. 2, and the residence time of extrusion can be significantly decreased while ensuring the complete dissolution of MCC at low screw speeds (Fig. ES4). When the feed rate increased, the residence time distribution shifted towards lower times, with a significant decrease in the distribution peak broadness. This is qualitatively in good agreement with previously published data.[20] For further experiments, we chose a higher feed rate (30 g/min). A high feed rate allows the synthesis of more materials per unit of time. Furthermore, the RTD distribution could potentially affect the DS distribution. In this case, a narrower RTD results in a more uniform distribution of DS in the synthesised cellulose laurate samples.

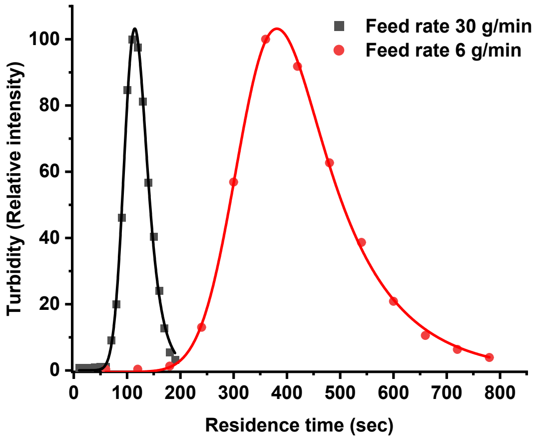


Fig. 2 Influence of feed rate on residence time distribution (Conc = 10 wt%, T = 80 °C, N = 60 rpm).

In the subsequent experiment, the cellulose weight ratio was varied from 10 to 20 wt%. As shown in Fig. 3, the residence time of 10 wt% MCC solution was slightly shorter than that of the 20 wt% MCC solution. General observation: All RTD curves have a classical shape, highlighting a delay time and a pronounced tail.

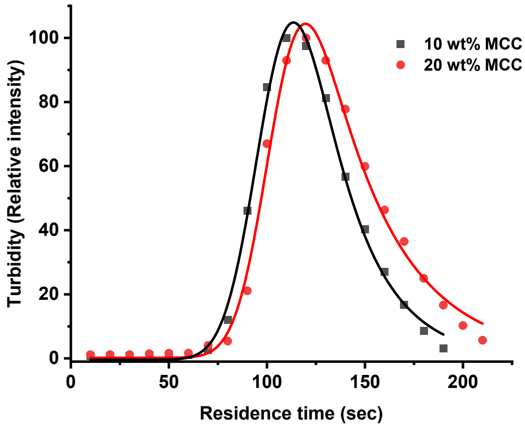


Fig. 3 Influence of cellulose concentration on residence time distribution (T = 80 °C, N = 60 rpm, Q = 30 g/min).

An increase in the screw speed decreased the average residence time inside the extruder (Fig. 4). Interestingly, changes in screw speed did not affect the shape of the RTD curves. In contrast, for higher screw speeds (120-180 rpm), small undissolved MCC particles were observed, which can be explained by shorter residence time inside the extruder (Fig. ES5).

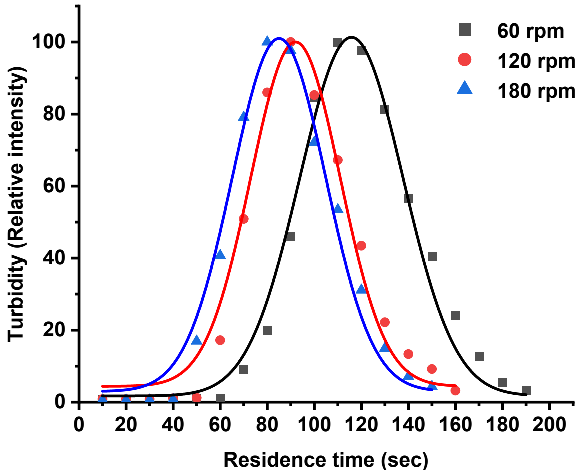
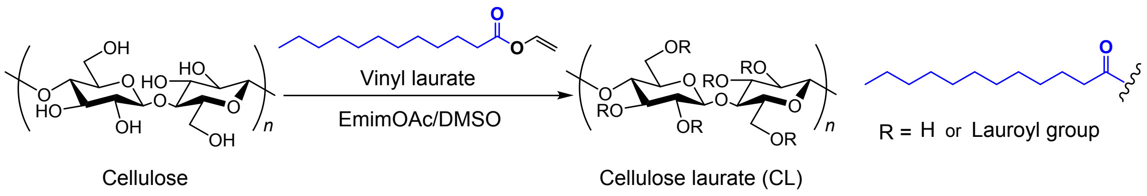


Fig. 4 Influence of screw speed on residence time distribution (Conc = 10wt%, T = 80 °C, Q = 30 g/min).

MCC chemical modification reaction with vinyl laurate

In our previous study, we showed that cellulose laurate can be synthesised with a wide range of DSs (0.53-2.73) and with high reaction efficiency (RE: > 86 %) using the micro compounder Xplore MC5.[15] However, in that case, it was impossible to synthesise the product in a continuous manner. Moreover, because the micro compounder volume was low, only small amounts (3-5 g per extrusion) of the mixture were extruded. Therefore, we were interested in investigating large-scale continuous reactions. The kneading blocks constitute the dominant dispersive mixing unit of the extrusion system. Unlike the conveying element, the mixing element generally operates when fully filled with material.[21]



Cellulose laurate was successfully obtained under continuous-flow conditions. The stability of the flow during the reaction was confirmed by collecting and weighing the samples in vials every 2 min. In addition, for this reaction system an equimolar amount of vinyl laurate (3 mol per AGU) was employed. The CL structures were confirmed using ATR-FTIR spectroscopy (Fig. ES6) and ^{1}H-NMR (Fig. ES7). A precise structural analysis of CL was reported in our previous article.[15] It is important to mention that bands of hydroxyl groups in the crystalline regions (3350 cm^{-1}) can be seen in the FTIR spectrum of CL20 (Fig. ES6b) but were absent for sample CL10 (Fig. ES6a). In addition, the CL20 sample did not completely dissolve in $CHCl_3$ (Fig. ES8). From Table 1 it can be seen that the DS for both synthesised CL samples is high (2.48-2.67). The reaction time (from the introduction of the reagent through the C2 port until the recovery of CL from the round die) in both cases is short; however, in the case of 20 wt% MCC, the residence time is slightly longer (Fig. 3), which can explain the difference in the DS. In addition, because the 20 wt% MCC sample contained undissolved cellulose, the equivalent amount of vinyl laurate relative to the dissolved MCC increased, providing a slight excess of reagent and, as a result, a higher DS. It has to be mentioned that it is difficult to obtain the DS of 3 when using equimolar amounts of long alkyl chain acyl donor due to steric hindrance of the aliphatic chains in cellulose esters.[22] At the same time, reaction efficiencies for both the synthesised samples were high (> 80%). It was previously reported, that undesirable side reaction between EmimOAc-derived anion and acyl donor can occur, resulting in cellulose acetylation.[23] As can be seen from Table 1, the side reaction is minimal for both samples (DS_{side} < 0.1). Cellulose acylation with vinyl esters is faster than the side reaction of acetyl introduction by a mixed acid anhydride generated from the reaction between vinyl laurate and EmimOAc.[16] Short reaction time and low amounts of EmimOAc based on the high cellulose concentration conditions (10-20 wt%) could possibly suppress the side reaction. Furthermore, acetaldehyde, the by-product of this reaction, can be easily removed from the reaction system due to its low boiling point. Finally, considering the total feed rate (for the production of CL10: 42 g/min) and reaction yield (83%) it would be possible to obtain 13.5 kg/day of CL.

Table 1 Influence of cellulose wt% on transesterification reaction with vinyl laurate.

Sample	MCC [wt%]	DS_{main}	RE [%]	DS_{side}
CL10	10	2.48 ± 0.05	83	0.07 ± 0.02
CL20	20	2.67 ± 0.04	89	0.09 ± 0.02

Reaction conditions: T = 80 °C, Q = 30 g/min, n = 60 rpm, in EmimOAc/DMSO (1/3 g/g); vinyl laurate 3 eq./[AGU]

Product characterization

XRD analysis

In its native state, microcrystalline cellulose highlights the cellulose I crystal structure.[24] Three peaks were detected in the diffraction patterns. The broad peak at ~15.5°, consists of two peaks (14.8° and 16.7° for Iβ). The peak at 22.4° is characteristic of the distance between hydrogen-bonded sheets in cellulose I. The peak at 34.4° is assigned to the ordering along the cellulose fibre direction (Fig. 5 black line). In the pretreated cellulose pattern shown in (Fig. 5 red and blue lines), the characteristic peaks of cellulose I reduce. In contrast, peaks at 20.8° appear, indicating cellulose II, which is more thermodynamically stable than cellulose I.[25] The shift of the main peak of cellulose I from 22.4° to 20.8° indicates an expansion of the lattice, and the reduction of the peaks at 14.8° and 16.4° suggests a disturbance in the arrangement of cellulose chains within the hydrogen-bonded sheets.[18] Both samples (10 and 20 wt%) consist of coexisting cellulose I and II allomorphs with a higher amount of amorphous phase. The fact that 20 wt% MCC sample highlights remaining Cellulose I peak at 22.5°, is in good agreement with the poor cellulose solubility in this case, as revealed by optical microscopy (Fig. ES3).

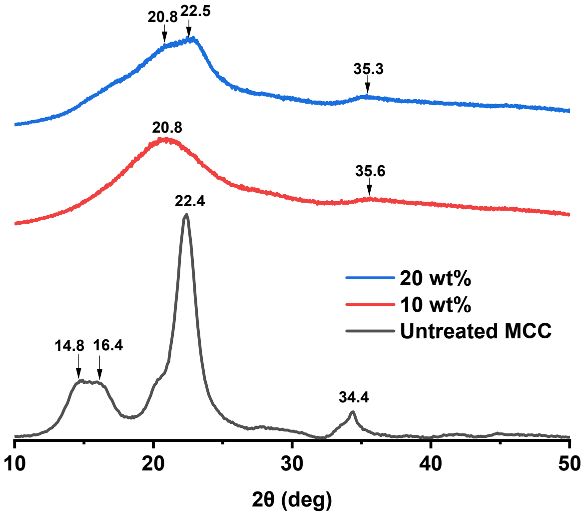


Fig. 5 Powder XRD patterns of MCC treated in EmimOAc/DMSO (1/3 g/g) mixture.

Both reacted samples (Fig. 6), showed similar patterns. An extensive decline in the crystalline order of the MCC was observed. The main peak of MCC at 22.4° decreased and shifted towards lower 2θ values. The formation of a new ordered structure corresponding to the crystallisation of long aliphatic side chains was confirmed.[26] The diffraction pattern of the CL20 sample highlights a broad shoulder at 22.8° as well as a residual peak at 34.7°, which indicates the remaining MCC crystalline structure and, as a result, lower rates of cellulose fibres swelling. This finding is in good agreement with the optical microscopy results (Fig. ES3).

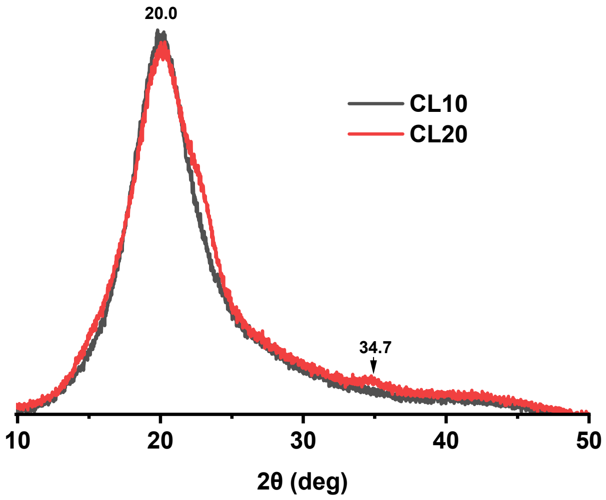


Fig. 6 Powder XRD patterns of the synthesised cellulose laurate samples.

Thermal and mechanical properties of CL samples

The design of cellulose-based materials with uniform characteristics is of great importance because of their many areas of potential applications. Therefore, it is essential to investigate the thermal and mechanical properties of cellulose esters.

In terms of thermal properties, both CL samples showed an improvement in the degradation temperature compared to unmodified cellulose. Moreover, for both samples T_{off} are low (T_{off} for CL10: 172.9 °C and CL20: 151.1 °C) and are far from their degradation temperatures (Td,10%) (Table ES2). No additional plasticizers were required for melt processing in this case.

Subsequently, cellulose laurate films were prepared. Fig. 7 shows the stress-strain curves of samples CL10 and CL20. For both samples the average elastic modulus and tensile strength are quite similar (CL10: 172.2 ± 5.1 MPa, 6.5 ± 0.4 MPa; CL20: 198.4 ± 3.5 MPa, 5.8 ± 0.4 MPa, respectively). Samples exhibit a rather ductile behaviour, as previously reported by several studies.[27,28] However, in terms of elongation, the CL sample synthesised under complete dissolution conditions (CL10) shows greater dataset value consistencies and smaller standard deviation values (CL10: 31.2 ± 0.4 %; CL20: 24.6 ± 7.3 %). It is possible that partially undissolved MCC particles affected the mechanical properties of the CL films. Moreover, there was a clear difference in the transparency between the two films (Fig. ES9). The opacity of the films made from CL20 indicates the presence of undissolved cellulose crystals. This limits the use of CL films in specific applications.

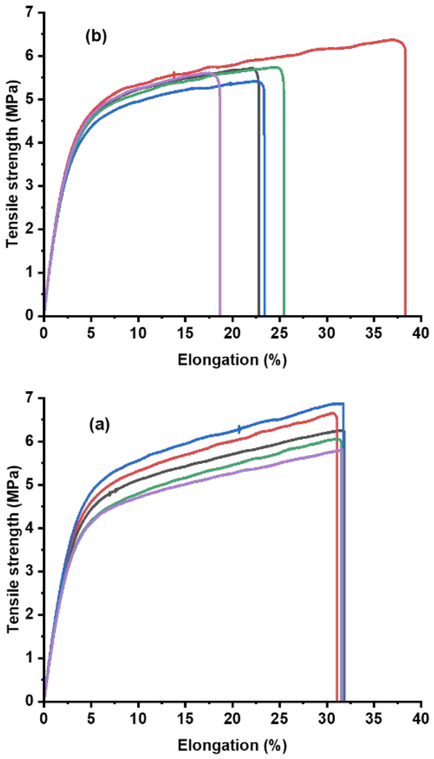


Fig. 7 Tensile strength-elongation behaviour of cellulose laurate films CL10 (a) and CL20 (b).

Process sustainability and solvent reusability

The recyclability and reuse of solvent is important for designing sustainable processes. In our previous study, we reported successful recycling and reuse of ionic liquid EmimOAc used at small extrusion scale.[15] In the current study, we describe the recycling of EmimOAc/DMSO mixture after turbidity measurements to separate MCC/Fe_3O_4 mixture from EmimOAc/DMSO (Experimental: MCC dissolution and RTD measurements). It was possible to recover up to 94 wt% of EmimOAc/DMSO mixture (Scheme ES1). Moreover, the purity of the mixture as well as the ratio between EmimOAc and DMSO were confirmed using ^{1}H-NMR (Fig. ES10 and Fig. ES11). The recovered mixture was successfully reused to prepare other samples for turbidity measurements.

E-factor was also calculated for our process. For CL10 the E-factor is 3.5 (for detailed calculation see ESI 'E-factor calculation'). The E-factor value of our process is significantly lower compared to other reported cellulose esters synthesis in batches.[2] It is important to point out that cellulose concentration and the amounts of reagents contribute most to the E-factors. The low value of E-factor in our study was achieved due to high cellulose concentrations combined with an equimolar amount of reagent. Consequently, solvent recycling and reuse can drastically decrease the E-factor making the overall process greener.[29,30]

Conclusions

Our research investigated cellulose dissolution and reaction using EmimOAc/DMSO mixture as a solvent system and co-rotating twin screw extruder as a reactor. Cellulose complete dissolution highly depends on initial cellulose concentration. It was possible to completely dissolve 10 wt% cellulose solution within a short time (less than 3 minutes) using moderate temperature (80 °C) in a continuous extrusion process. Moreover, new method for measuring RTD was described in this work. The influence of extrusion parameters (screw speed and feed rate) on RTD analysed by this method was consistent with previously reported results.

It was revealed that the reaction of cellulose laurate synthesis proceeds continuously with high RE (83-89%). Furthermore, based on applied feed rate, the estimated yield of CL product is 13.5 kg/day. It was also shown that complete cellulose dissolution has consequential influence on mechanical properties of CL films.

We believe that this research can be optimised in the future (screw configuration, feed rate, screw speed). In this case, it would be interesting to use a computer simulations of extrusion processes. We also encourage further research investigating direct agricultural biomass chemical modification using reactive extrusion. Systems containing several different constituents (ex. cellulose, hemicellulose, lignin) could be much more complex in terms of dissolution and reactivity.

Author Contributions

Conceptualization, R.M., D.H., N.W. and K.T.; methodology, R.M., D.H., N.W., T.F. and K.T.; validation, R.M., D.H., T.F., N.W. and K.T.; formal analysis, R.M.; investigation, R.M., G.S.; resources, T.F., K.T.; writing—original draft preparation, R.M.; writing—review and editing, all authors; supervision, D.H., N.W. and K.T.; project administration, N.W. and K.T.; funding acquisition, N.W. and K.T. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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