Facile Method to Obtain Low DS β-ketoesters and Esters of Microfibrillated Cellulose

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Abstract: Herein we report a facile approach to prepare low DS microfibrillated cellulose acetoacetates and esters. All the reactions were performed directly in cellulose slurries without the need of solvent evaporation, which can cause hornification, and without damaging the fibres. The products obtained display the inserted functionalities while retaining the main features and morphology of the unmodified cellulose fibres. In comparison to previously reported synthetic routes, this method is cost-effective, more environmentally friendly through omission of extra solvents and the possibility of reusing the dispersing agents, which can be recovered by distillation.

Keywords: Microfibrillated cellulose, Nanocellulose, Hydrogels, β-ketoesters

Introduction

Cellulose is a renewable, cost-effective, biocompatible and biodegradable material that has recently gained attention due to the wide range of applications in which it can be employed [1-3]. It is a polysaccharide composed of β(1→4) linked D-glucopyranose units and it can be obtained from plants or bacteria as the main sources [4]. Processed materials or cellulosic extracts which are composed of structures in the nanometer range are defined as nanocellulosic materials. These include microfibrillated cellulose (MFC, also known as nanofibrillated cellulose), cellulose nanocrystals and bacterial cellulose [5]. Cellulose nanofibrils are long chains forming a strong, complex network, which contain both amorphous and crystalline regions. Appealing properties of MFC include strength, stiffness and high aspect-ratio, which make them particularly interesting as polymer reinforcement materials [6].

The properties of cellulose fibres can be modified by chemical functionalization, allowing for tailoring of the material for specific applications. Cellulose esters, for instance, have a long history for use in coatings as they can improve important features such as flow, dry time, polishability, sprayability, viscosity and pigment dispersion [7,8]. Recent examples of cellulose esters for coating applications have been described by Aulin *et al.*, who reported the oxygen and oil barrier properties of carboxymethylated microfibrillated cellulose films for packaging materials and bioplastics [9]. The group of Ropponen demonstrated the enhancement in smoothness of MFC films after being coated with cellulose esters. The resulting derivatives showed good water vapour barrier properties and improved elastic modulus, tensile strength and elongation at break [10,11].

Cellulose β-ketoesters are also employed in coatings and plastics. The presence of the acetoacetate group offers several advantages (*e.g.* modification of viscosity and hydrophobicity) and provides a route for further chemical modifications or cross-linking [12]. The synthesis of cellulose acetoacetates has been described in literature [12-18]. One of the reported methods uses *tert*-butyl acetoacetate (t-BAA) as a starting material. Liu *et al.*, for example, reported the synthesis of cellulose acetoacetates in the presence of t-BAA after dissolving cellulose in the ionic liquid 1-allyl-3-methylimidazolium chloride (AMIMCl) [14]. In this synthetic route, several cellulose acetoacetates were obtained having a degree of substitution (DS) between 0.34 and 1.35, depending on the molar ratio of the starting materials and the reaction time. The resulting products were further reacted with chitosan to form transparent, self-healing hydrogels with improved mechanical properties. This method was subsequently applied to obtain cellulose acetoacetates, which were reacted with four amino derivatives (hexylamine, L-glutamic acid, L-cysteine and tyramine) to give the corresponding enamines [13]. This synthetic route offers several advantages, including simplicity of reaction steps and the fact that different DS values can be obtained. However, it requires the use of ionic liquids to dissolve cellulose, which are very expensive, especially in the case of large-scale reactions.

Another method described in literature uses alkylketene dimers (AKDs) in the presence of LiCl/1,3-dimethyl-2-imidazolidinone (LiCl/DMI) as a solvent. Yoshida and Isogai employed this strategy to synthesize cellulose β-ketoesters with DS values of 1.9-2.9 [15-17]. Yan *et al.* also

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used AKD in the presence of 1-methylimidazole as a catalyst to functionalise microfibrillated cellulose slurries after solvent exchange by ethanol and ethyl acetate [18]. The obtained DS values in this case were very low (<0.02). Nevertheless, to our knowledge this is the only synthetic strategy to obtain cellulose acetoacetates that has been directly applied to MFC slurries. One of the obstacles when working with such materials is that they cannot be dried from aqueous suspensions. This is due to the fact that water removal results in a reduction of external surface area, shrinkage and the formation of hydrogen bonds amongst cellulose fibres, leading to irreversible agglomeration [19, 20]. This process is known as hornification and it dramatically and irreversibly affects the size and geometry of the nanofibres and, consequently, their properties and performance in formulations. For this reason, a synthetic route that allows fibre functionalization directly in MFC slurries without the need of solvent evaporation and without damaging the fibre features is of great interest.

Herein, we report a facile, no-extra-added-solvent approach to functionalise MFC slurries with acetoacetate and ester groups with low DS. To our knowledge this is the first time that this transesterification reaction is applied for the functionalization of cellulose fibres. The MFC slurries are pre-treated by solvent exchange with the esterification reagent (*i.e.* an ethyl ester), which is then used as the dispersing agent. Therefore, the reactions could be performed without the need of extra organic solvents or of expensive ionic liquids. In comparison to previously reported methods, this strategy is extremely cost-effective and the esters employed as dispersing agents can be easily recovered by distillation. The resulting cellulose acetoacetates were further reacted with chitosan and L-lysine to form the corresponding enamine derivatives. The obtained products contained the inserted functional groups but kept the main features of the unmodified MFC slurries such as fibre morphology, dimensions and thermal degradation profile.

Experimental

Materials

Microfibrillated cellulose (dry content 3.00-3.20 wt. %) was provided by Borregaard as aqueous slurry and used as supplied. All the other commercial reagents and solvents were purchased from Aldrich, VWR, Fisher, and Alfa Aesar.

General Method for the Synthesis of MFC Acetoacetates and Esters

The reported general method applies to the majority of the performed reactions (1.00 g of dry cellulose content).

MFC Slurry Preparation by Solvent Exchange

MFC slurry (1.00 g dry content) was diluted with water (100 m*l*) and stirred for 5 mins. After 5 mins the slurry was filtered on a sinter glass funnel and washed with ethanol (2×50 m*l*). The obtained residue was then transferred into a beaker and stirred twice with ethanol for 5 mins (2×50 m*l*) and filtered each time. This same procedure was repeated three times using the ester selected for the transesterification reaction as a dispersing agent (3×50 m*l*).

Transesterification Reaction

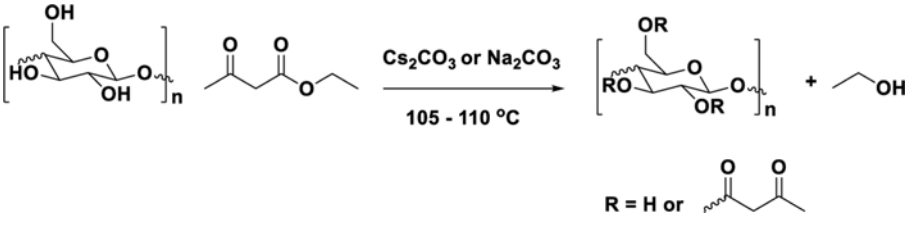
The MFC slurry suspended in the ester was collected by vacuum filtration and diluted with further dispersing agent (50 m*l*). The base (Na_2CO_3 or Cs_2CO_3) was then added and the reaction was carried out at 105-110 °C for 1 hour.

Isolation and Purification

After 1 hour, the reaction was stopped and ethanol (50 m*l*) was added. The MFC slurry was collected by vacuum filtration and washed with further ethanol (50 m*l*). The obtained substrate was then transferred into a beaker and stirred twice with ethanol for 5 mins (2×50 m*l*) and filtered each time. This same procedure was repeated for three times in the presence of water as the dispersing agent (3×50 m*l*). The final products were homogenized using an Ultra-Turrax for 5 mins (21000 rpm). The formation of the ester bond and the absence of starting material were confirmed by IR spectroscopy.

Enamine Formation by Reaction with Chitosan

Chitosan (0.402 g, 2.5 mmoles) was dissolved in a 1 % aqueous solution of acetic acid (40 m*l*) and a gel was instantly formed. MFC acetoacetate slurry (DS=0.47-0.500 g, 2.5 mmoles) was then added. The mixture was diluted with water (60 m*l*) to facilitate mixing. The reaction was left to stir for 3 hours and product formation was monitored every hour by IR spectroscopy. After 3 hours, the reaction was stopped and the product was purified by multiple washings with water (4×50 m*l*). The final product was homogenized using an Ultra-Turrax for 5 mins (21000 rpm). The



Scheme 1. Synthesis of cellulose β-ketoesters **1**-**5**.

Table 1. Outcomes of the transesterification reactions to synthesize the MFC β-ketoesters **1-5**

Base	Compound	EQ.	EC %	DS	% Funct.
Cs_2CO_3	**1**	0.030	20 %	0.47	16 %
	2	0.020	5 %	0.10	3.3 %
Na_2CO_3	**3**	0.045	21 %	0.51	17 %
	4	0.030	10 %	0.22	7 %
	5	0.020	1.5 %	0.03	1 %

EQ.: equivalents, EC %: ester content %, DS: degree of substitution, % Funct.: % functionalization.

formation of the enamine bond was confirmed by IR spectroscopy.

Enamine Formation by Reaction with L-lysine

L-lysine (0.451 g, 3.08 mmoles) was dissolved in water (25 m*l*). MFC acetoacetate slurry (DS=0.47-0.500 g, 2.5 mmoles) was then added and the reaction was left to stir undisturbed at RT. After 24 hours, the reaction was stopped and the product was purified by multiple washings in water (4×50 m*l*). The final product was homogenized using an Ultra-Turrax for 5 mins (21000 rpm). The formation of the enamine bond was confirmed by IR spectroscopy.

General Method to Determine the Ester Content (EC %) and the Degree of Substitution (DS)

The ester content and the degree of substitution of each product were determined by titration. The samples (0.0600-0.0800 g dry content) were firstly dried and then stirred in a solution of aqueous ethanol (70 %-20 m*l*) for 30 mins. After 30 mins, NaOH 0.5 M (20 m*l*) was added and the reaction was left to stir undisturbed for 48 or 72 hrs. After this time, the excess of NaOH was back titrated with HCl 0.5 M in the presence of phenolphthalein as an indicator. A blank measurement was performed each time.

The ester content was obtained by applying the following equation:

$$EC\ \% = [(A \times B)/C] \times 100\ \%$$

A: molar variation before and after saponification
B: molecular weight of the grafted acyl residue
C: weight of the dry sample.

The degree of substitution was obtained from the following equation:

$$DS = M_{AGU} \times EC / [M \times 100 - EC \times (M - 1)]$$

M_{AGU}: molecular weight of the anhydroglucose unit
EC: ester content
M: molecular weight of the grafted acyl residue

The resulting value was then used to determine the % of functionalization.

For all of the acetoacetate derivatives, the titrations were performed in triplicates.

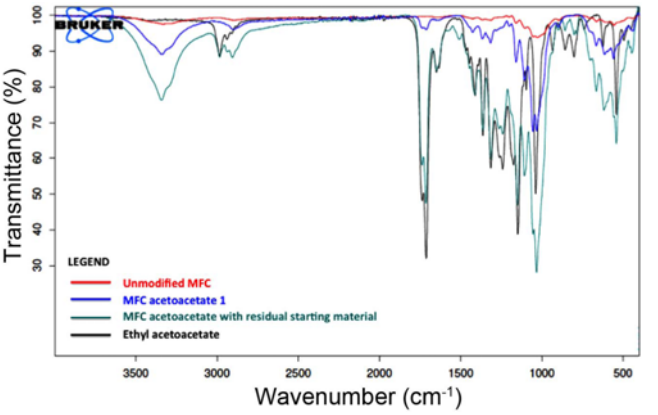


Figure 1. IR spectra of unmodified MFC, MFC acetoacetate **1**, MFC acetoacetate with residual ethyl acetoacetate and ethyl acetoacetate.

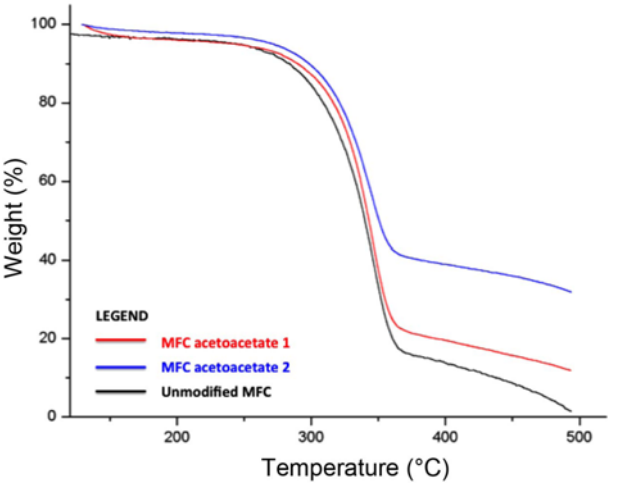


Figure 2. TGA thermograms for MFC acetoacetate **1**, MFC acetoacetate **2** and unmodified MFC.

ATR-IR Spectroscopy

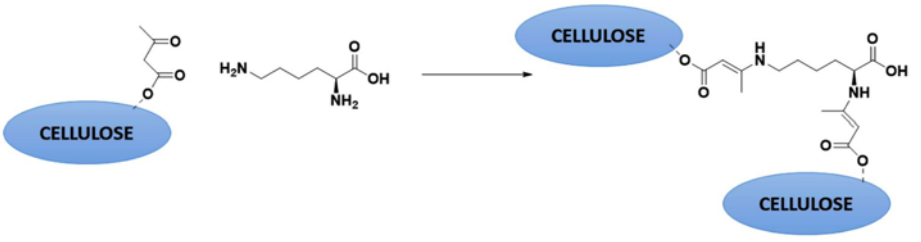
IR spectra of the dry products were recorded in the range of 4000-550 cm^{-1} by attenuated total reflectance (ATR) on an Alpha Bruker Spectrometer.

Microscopy

Atomic force microscopy measurements were completed using a Park Systems XE7 AFM. Samples were prepared by diluting as prepared samples to 0.01 % and drop casting on mica plates in ambient conditions. Images were taken using tapping mode with CONTSCR 10M tips and image processing completed using Gwyddion Pro software.

TGA

TGA measurements were taken on a TA Instruments



Scheme 2. Scheme of the reaction of cellulose acetoacetate with L-lysine.

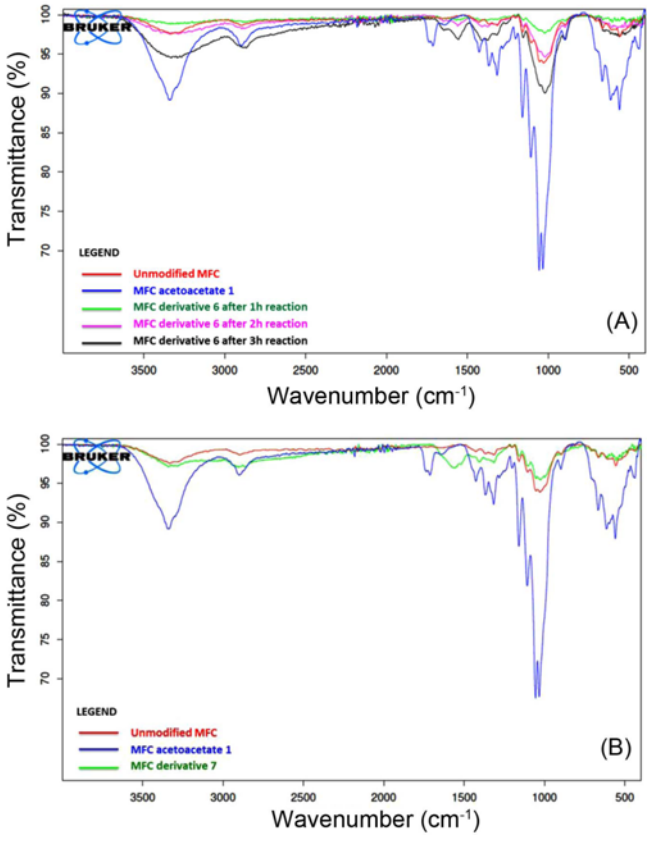
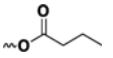
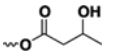
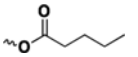
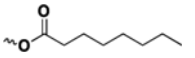


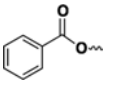
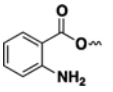
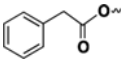
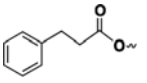
Figure 3. IR spectra of MFC acetoacetate derivatives **6** and **7**, respectively reacted with chitosan (3A) and L-lysine (3B).

Table 2. Outcomes of the transesterification reactions to synthesize the MFC alkyl esters **8-11** (2A) and the MFC aromatic esters **12-15** (2B)

(A) Alkyl esters

Functionality	Compound	EC %	DS	% Funct.
	**8**	4 %	0.087	3 %
	**9**	18 %	0.41	14 %
	**10**	3.5 %	0.1	3 %
	**11**	7 %	0.1	3 %

(B) Aromatic esters

Functionality	Compound	EC %	DS	% Funct.
	**12**	9 %	0.16	5 %
	**13**	23 %	0.40	13 %
	**14**	28 %	0.53	18 %
	**15**	5 %	0.06	2 %

EQ.: equivalents, EC %: ester content %, DS: degree of substitution, % Funct.: % functionalization.

model SDT Q600. Dry samples were heated from 30 to 550 °C under a constant nitrogen stream at 100 ml/min and heating rate of 10 °C/min.

Results and Discussion

Synthesis of MFC Acetoacetates

MFC acetoacetes were synthesized by a transesterification reaction in the presence of Na_2CO_3 or Cs_2CO_3 as a base (Scheme 1). Similar reactions were previously reported by the Wetzel's group, who employed this synthetic strategy to obtain fatty acid starch esters from starch and fatty acid vinyl esters [21]. In their research they explored the influence of the carbonate catalyst (Na_2CO_3 and Cs_2CO_3) on the reaction outcome and the DS of the isolated products. The best results were obtained in the presence of Cs_2CO_3 as a catalyst (3 mol %) at 110 °C, whereas Na_2CO_3 caused a deceleration of the reaction rate.

The use of Cs_2CO_3 for the transesterification of β-ketoesters with a wide range of alcohols was also described by Krishnaiah *et al.*, who demonstrated the applicability of this reaction using twenty different alcohols under conventional and unconventional conditions (*i.e.* in the presence of

ultrasound or microwave irradiation) [21].

We therefore decided to exploit this synthetic approach to functionalise MFC slurries with acetoacetate groups in the presence of a sodium or cesium carbonate catalyst at 105-110 °C. The amount of catalyst was varied as reported in Table 1. The highest DS value was obtained using 0.045 eq. of Na_2CO_3, which led to a 0.51 DS (17 % functionalization).

Before every reaction, the MFC slurry was pre-treated by solvent exchange with ethanol and then ethyl acetoacetate. This β-ketoester is liquid at room temperature, therefore it could be used as a dispersion medium during the solvent exchange and easily recovered after the process by distillation. This avoids the use of less environmentally friendly organic solvents. Furthermore, since it is an ethyl ester, the only by-product formed during the reaction is ethanol, which was also used for the solvent exchange.

The formation of the MFC β-ketoesters **1-5**, was confirmed by IR spectroscopy (Figure 1). The IR spectra of the synthesized acetoacetates displayed the peaks of the stretching band of the acetoacetyl carbonyls (1739 and 1708 cm^{-1}). The other characteristic bands for cellulose derivatives appeared at 3300 cm^{-1} (-OH vibration) and 2890-2910 cm^{-1} (-CH stretching). The $-CH_2$ and $-CH_3$ vibration signals and the -C-O-C- stretching bands were also visible in the region between 1000 and 1500 cm^{-1}.

By comparing the IR spectral profile of the functionalised polymers with that of ethyl acetoacetate it was possible to confirm the absence of residual starting material after purification (Figure 1). This was supported by a significant decrease in intensity of the carbonyl groups bands (1739 and 1708 cm^{-1}) and the disappearance of the bands at 2984 cm^{-1} and 1640-1650 cm^{-1}, which can be respectively attributed to the $-CH_2$ stretching of ethyl acetoacetate and to hydrogen bonding of the β-ketoester in the enolic form. These observations, together with the fact that extensive purification by multiple washings was undertaken and that, when the reaction did not work, cellulose slurry could be isolated without traces of residual ethyl acetoacetate, were considered enough to validate the purification method and confirm the absence of starting materials.

This was further supported by TGA, which showed no evidence of remaining ethyl acetoacetate (Figure 2).

Enamine Formation by Reaction with Chitosan and L-lysine

MFC acetoacetate **1** (DS=0.47) was selected as the precursor to obtain the corresponding enamine derivatives by reaction with chitosan (enamine derivative **6**) and L-lysine (enamine derivative **7**, Scheme 2). These experiments were performed to confirm that the isolated products could also be used for further reactions in water, without need of tedious solvent exchange steps.

Both reactions were carried out in water by mixing MFC acetoacetate slurry (**1**) with the two starting materials. Since chitosan is not water soluble, but it can be dissolved in a 1 % acetic acid solution, the reaction with this polysaccharide was performed in a slightly acidic environment. The enamine bond formation was monitored by IR spectroscopy every hour for three hours, which showed that the conversion was already complete after one hour. By contrast, the reaction with L-lysine was conducted for 24 hours according to the method described by Liu *et al*., who observed the highest conversion rates after this time [13].

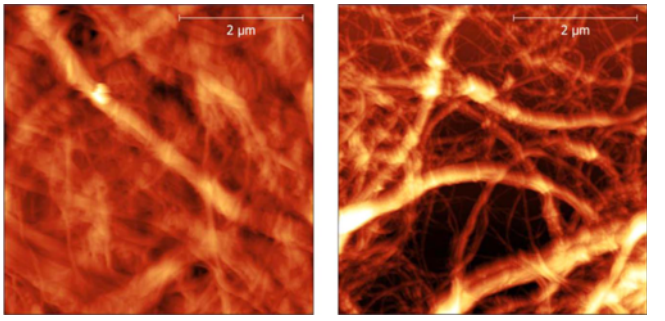


Figure 4. AFM images of the fibre network present in untreated MFC (left) and cellulose acetoacetate **1** (right), both samples dried from aqueous dispersion.

In both cases, IR spectroscopy displayed the enamine bond formation (1650 and 1605 cm^{-1}) and the disappearance of the β-ketoester band at 1738 cm^{-1} (Figures 3A and 3B).

Synthesis of MFC Alkyl and Aromatic Esters

To verify if this synthetic method could also be employed in the presence of other esters, further alkyl and aromatic MFC esters were synthesized (Tables 2A and B). The starting materials were carefully selected, as their use in the solvent exchange and then in the transesterification required them be in a liquid state at room temperature and have a high boiling point (since the reactions were carried out at 105-110 °C). All the reactions were performed for 1 hour using of Na_2CO_3 as a catalyst (0.045 eq.). The applied conditions were chosen on the basis that they gave the best results for MFC acetoacetate.

Another example of solvent-free strategy to obtain alkyl esters from fatty acids and cellulose was reported by the group of Borredon, who described the mixed acylation of cellulose with fatty acids and acetic anhydride [22-24]. This method enabled achieving several cellulose esters with different DS values using an excess of fatty acid as a dispersing agent. Although this approach was found to be successful, it has the limitation that when applied to short chain fatty acids, the pungent, persistent odour of the starting material can be a major drawback, especially when high quantities are required to suspend the cellulose fibres. By contrast, our suggested method employs ethyl esters of organic acids, which quite often have a very pleasant, fruity fragrance. This allows the use of high quantities of starting

material without the issues related to the strong odour of short chain aliphatic acids.

By applying the previously described method, a number of MCF alkyl esters (**8-11**) were obtained (Table 2A). Only very low DS (< 0.41) were achieved, with the exception of the β-hydroxybutyrate derivative (**9**), which was obtained in a 0.41 DS. Compared to the other organic acid esters, which have a low reactivity, ethyl β-hydroxybutyrate is likely to react in a similar way to ethyl acetoacetate. The aromatic derivatives (**12-15**) were also achieved with low DS values (< 0.4). A higher percentage of functionalization was obtained for derivatives **13** (13 % - DS=0.40) and **14** (18 % - DS=0.53), probably due to their higher reactivity compared to the other aromatic esters used as starting materials.

For all of the synthesized alkyl and aromatic MFC esters (**8-15**), the formation of the desired products was confirmed by IR spectroscopy, which displayed the characteristic band of the ester bond in the region 1720-1750 cm^{-1}.

Morphology of Cellulose Fibres

The cellulose acetoacetate samples were imaged by AFM to compare the morphology and network arrangement of the modified cellulose to the MFC starting material (Figure 4). After modification, the fibres within the network remain relatively unchanged on the nano-scale. However, the packing arrangement appears slightly different, with the modified fibres less closely-packed. It is possible that the altered outer layer of the one-dimensional fibres affects the bundling of fibres in the microstructure, as similar effects have been observed for cellulose systems where chemical modification has been performed [25,26]. While the smaller fibre bundles in the network are the same size, the proportion of larger fibre bundles decreases, with the unmodified MFC sample exhibiting an average fibre bundle diameter of 146(±64) nm compared to 81(±33) nm for the acetoacetate cellulose. However, the overall morphology of the fibres is maintained, with no significant changes to the shape or surface features.

Conclusion

A novel, facile synthetic method to functionalise MFC slurries by transesterification was successfully used to achieve modified cellulose products. The MFC slurries were pre-treated by solvent exchange with ethanol and then with the starting material (*i.e.* an ethyl ester), which was used as a dispersing agent. This method allowed achieving MFC β-ketoesters and esters with low DS, without the need of organic solvents or costly ionic liquids. The MFC cellulose acetoacetate (DS=0.47) was further reacted with chitosan and L-lysine to form the corresponding enamine derivatives. These reactions could be conducted in water or in a 1 % acetic acid solution with no need of solvent exchange. The synthesized MFC β-ketoesters and esters contained the inserted functionalities but kept the main features of the unmodified MFC slurries such as thermal degradation profile, but showed a slight separation of the fibre network in the fibre diameter while maintaining a similar network morphology. In comparison to previously reported approaches there are several advantages, including the fact that this method is cost-effective, more environmentally friendly and the dispersing agents can be recovered by distillation. The results herein described show that this synthetic process could be very promising to modify MFC slurries. However, further studies to expand the scope of this research and its applicability to large scale reactions, are needed and will be carried out in the future.

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References

1. A. Dufresne, *Materials Today*, **16**, 220 (2013).
2. T. Abitbol, A. Rivkin, Y. F. Cao, Y. Nevo, E. Abraham, T. Ben-Shalom, S. Lapidot, and O. Shoseyov, *Curr. Opin. Biotechnol.*, **39**, 76 (2016).
3. D. Klemm, F. Kramer, S. Moritz, T. Lindstrom, M. Ankerfors, D. Gray, and A. Dorris, *Angew. Chem. Int. Ed.*, **50**, 5438 (2011).
4. H. G. D. Barud, R. R. da Silva, H. D. Barud, A. Tercjak, J. Gutierrez, W. R. Lustri, O. B. de Oliveira, and S. J. L. Ribeiro, *Carbohydr. Polym.*, **153**, 406 (2016).
5. C. Y. Chang and L. N. Zhang, *Carbohydr. Polym.*, **84**, 40 (2011).
6. N. Lavoine, I. Desloges, A. Dufresne, and J. Bras, *Carbohydr. Polym.*, **90**, 735 (2012).
7. K. J. Edgar, C. M. Buchanan, J. S. Debenham, P. A. Rundquist, B. D. Seiler, M. C. Shelton, and D. Tindall, *Prog. Polym. Sci.*, **26**, 1605 (2001).
8. M. Edge, N. S. Allen, T. S. Jewitt, and C. V. Horie, *Polym. Degrad. Stabil.*, **26**, 221 (1989).
9. C. Aulin, M. Gallstedt, and T. Lindstrom, *Cellulose*, **17**, 559 (2010).
10. P. Willberg-Keyrilainen, J. Vartiainen, J. Pelto, and J. Ropponen, *Carbohydr. Polym.*, **170**, 160 (2017).
11. P. Willberg-Keyrilainen, J. Vartiainen, A. Harlin, and J. Ropponen, *Cellulose*, **24**, 505 (2017).
12. K. M. Arnold, W. W. Blount, J. E. Lawniczak, D. W. Lowman, and K. J. Edgar, *Abstr. Pap. Am. Chem. Soc.*, **208**, 1 (1994).
13. H. C. Liu, L. D. Rong, B. J. Wang, Z. P. Mao, R. Y. Xie, H. Xu, L. P. Zhang, Y. Zhong, and X. F. Sui, *Carbohydr. Polym.*, **170**, 117 (2017).
14. H. C. Liu, X. F. Sui, H. Xu, L. P. Zhang, Y. Zhong, and Z. P. Mao, *Macromol. Mater. Eng.*, **301**, 725 (2016).

15. Y. Yoshida and A. Isogai, *Cellulose*, **14**, 481 (2007).
16. Y. Yoshida and A. Isogai, *Cellulose*, **13**, 637 (2006).
17. Q. L. Yang, M. Takeuchi, T. Saito, and A. Isogai, *Langmuir*, **30**, 8109 (2014).
18. Y. T. Yan, H. Amer, T. Rosenau, C. Zollfrank, J. Dorrstein, C. Jobst, T. Zimmermann, J. Keckes, S. Veigel, J. Z. Li, and W. Gindl-Altmutter, *Cellulose*, **23**, 2759 (2016).
19. M. Beaumont, J. Konig, M. Opietnik, A. Potthast, and T. Rosenau, *Cellulose*, **24**, 1199 (2017).
20. C. Duan, Y. D. Long, J. G. Li, X. J. Ma, and Y. H. Ni, *Cellulose*, **22**, 2729 (2015).
21. G. Krishnaiah, K. C. Rajanna, K. R. Reddy, M. S. Kumar, P. Srinivas, and Y. R. Rao, *Res. Chem. Intermed.*, **41**, 2739 (2015).
22. J. Peydecastaing, C. Vaca-Garcia, and E. Borredon, *Cellulose*, **18**, 1015 (2011).
23. J. Peydecastaing, C. Vaca-Garcia, and E. Borredon, *Cellulose*, **18**, 1023 (2011).
24. C. Vaca-Garcia and M. E. Borredon, *Bioresour. Technol.*, **70**, 135 (1999).
25. E. Espino-Perez, S. Domenek, N. Belgacem, C. Sillard, and J. Bras, *Biomacromolecules*, **15**, 4551 (2014).
26. G. Siqueira, J. Bras, and A. Dufresne, *Langmuir*, **26**, 402 (2010).