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DOI:

[10.1016/j.eurpolymj.2020.109803](https://doi.org/10.1016/j.eurpolymj.2020.109803)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Yeti, F., Liu, X., Sampson, W. W., & Gong, R. H. (2020). Acetylation of lignin containing microfibrillated cellulose and its reinforcing effect for polylactic acid. *European Polymer Journal*, 134, 109803. <https://doi.org/10.1016/j.eurpolymj.2020.109803>

Published in:

European Polymer Journal

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Acetylation of Lignin Containing Microfibrillated Cellulose and Its Reinforcing Effect for Polylactic Acid

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Abstract

High hemicellulose and lignin content MFC (MFLC) was isolated from chemi-thermomechanical pulp (CTMP), and surface acetylation used to significantly decrease its polarity. This modification of MFLC provided good dispersibility in PLA when used for biocomposites fabrication via a solvent casting method. MFLC exhibited higher modification efficiency compared to lignin-free MFC. Base-catalysed surface acetylation unchanged the crystalline structure of MFLC. Detection of the hydrogen bond between acetylated MFLC (Ac-MFLC) and PLA confirmed its role in improvement of the mechanical performance, thermal properties and crystallinity of the biocomposite with Ac-MFLC acting as an effective reinforcing and nucleating agent. The approach confirms the suitability of surface functionalization of MFLC for fabrication of biocomposites for a wide range of applications such as packaging and biomedical products.

Keywords: Microfibrillated lignocellulose, Surface modification, Acetylation, Biocomposites, Polylactic acid

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1. Introduction

Awareness of environmental problems arising from petroleum-based polymers coupled with the diminishing petroleum resource and its increasing price have increased researcher's attention to biodegradable polymers. Polylactic acid (PLA) is a commercial biodegradable polymer produced from renewable sources, starch rich crops [1]. Due to its environmentally-friendly structure, low toxicity, biocompatibility and good transparency, it is attractive polymer to be

used in the fabrication of packaging materials and biomedical implants [2,3]. To improve the durability of PLA based products and hence broaden its application areas, its inherent drawbacks such as low crystallization rate and thermal stability must be addressed [4,5]. Approaches reported in the literature include modification [6], copolymerization [7] and blending with other polymers [8]. An alternative approach, and the subject of the study presented here, is the addition of natural nano fibres and their derivatives to PLA.

Microfibrillated cellulose (MFC), a precursor to nanofibrillated cellulose with some residual micron-scale fibrils isolated from wood or natural fibres using mechanical treatments, is a prominent candidate as reinforcement agent of PLA due to its unique properties such as high mechanical performance, large surface area, and biodegradability [9]. Its nanometer to submicron wide fibrils tend to form a web-like network and impart high strength to composites [10,11]. However, the strong polar nature of MFC restricts its dispersibility in non-polar media, which is the main challenge in the production of MFC reinforced composites. Abundant hydroxyl groups on the surface of MFC tend to form hydrogen bonds resulting in microfibril aggregation, which decreases the reinforcement of non-polar polymers. Surface modification increases the dispersibility of MFC in non-polar polymers by decreasing its polarity [12].

Among the various modification techniques, acetylation is a promising approach for the modification of MFC, since it is widely used for the modification of lignocellulosic sources such as wood [13], wood fibres [14] and plant fibres [15]. It effectively decreases the polarity of MFC, improving the mechanical performance [16] and thermal properties [17] by increasing interfacial adhesion between fibres and non-polar polymer matrix.

The usual approach is focused on the isolation of lignin-free MFC from delignified and bleached resources. Further, high hemicellulose and lignin containing raw materials include wood fibres [18–20], non-wood fibres [21–23], and commercial mechanical [24] and unbleached Kraft pulp fibres [25,26] could be used for the isolation of lignin containing MFC (MFLC) that has gained attention due to its high yield, low production cost and low environmental impact [27]. However, it is still difficult to obtain good interfacial adhesion

between MFLC and non-polar polymer matrix in composite applications although hemicellulose and lignin content slightly decrease the polarity of MFLC [28]. Therefore, surface treatment or modification is necessary to improve the compatibility of MFLC in non-polar polymer matrices. Moreover, MFLC could allow a high degree of modification as its surface is covered with highly accessible hemicellulose and lignin, which have highly branched semi-crystalline and totally amorphous structures, respectively.

Here, we isolated MFLC from chemi-thermomechanical pulp (CTMP) fibres, and modified its surface using simple base-catalysed transesterification method to increase its dispersibility and interfacial adhesion with PLA for fabrication of biocomposite films with high mechanical and thermal properties. We also modified the surface of lignin-free MFC to compare the modification efficiency with MFLC. It is expected that the highly reactive hydroxyl groups in the chemical structure of MFLC will lead to an increase in the modification efficiency, improving the properties of the final biocomposite products to be used in various industrial applications.

2. Experimental Section

2.1. Materials

PLA (IngeoTM Biopolymer 4043D) was supplied by NatureWorks LLC (USA). PLA has a density of 1.24 g cm⁻³ and average molecular weight of 1.3×10^5 g mol⁻¹. CTMP with 27 % lignin (Table S1) was supplied by SCA (Sweden). Acetic anhydride and dimethylformamide (DMF) were purchased from Acros Organics (UK). Anhydrous potassium carbonate, chloroform, acetone and ethanol were purchased from Fischer Scientific (UK). All chemicals were reagent grade and used without any further purification.

2.2. MFLC Preparation

CTMP was soaked into water overnight before refining, carried out using a Medway beater (Reed Paper, UK) for 30 min. The refined pulp was screened using a Sommerville Fractionator

fitted with a 200 mesh, corresponding to approximately 76 μm hole size. The fine material passing through the mesh was collected on a muslin cloth and then further fibrillated using a homogenizer (IKA T18) at 20000 rpm for 1 h.

2.3. MFLC Acetylation

Acetylation was carried out following procedure described by Çetin et al. [29]. The reaction was carried out in a three-necked round-bottomed flask equipped with condenser under nitrogen flow. Fig. 1 shows the schematic representation of the acetylation process. 2 g freeze-dried MFLC was homogenized in DMF (100 ml) for 2 min, and then transferred into a three-necked round-bottomed flask containing K_2CO_3 (0.3 g) and acetic anhydride (6 ml). The suspension was mixed and heated at 90 °C for 1 h. The reaction was terminated by adding 5 ml deionized water. After cooling for 20 min, the suspension was centrifuged to remove excess chemicals, and rinsed first with deionized water (200 ml) at 60 °C for 2 h, and then with ethanol/acetone (50/50) mixture (200 ml) at 60 °C for 2 h. After rinsing with solvent, samples were solvent exchanged with water, and freeze-dried.

Fig. 1. Schematic illustration of MFLC, its surface modification with acetic anhydride and Ac-MFLC biocomposites fabricated using solvent casting method.

2.4. PLA Biocomposite Preparation

PLA biocomposite films containing 0.5, 1, 1.5, 2.5 and 5 % acetylated MFLC (Ac-MFLC) were prepared using a solvent casting method. PLA granules were firstly mixed with chloroform (CHCl_3) at room temperature until fully dissolved. The Ac-MFLC suspension in CHCl_3 was sonicated (Qsonica-700) for 2 min and transferred into PLA solution. This Ac-MFLC/PLA suspension was mixed, sonicated, and then poured slowly into Petri dishes, taking care to avoid bubbles. The CHCl_3 was evaporated off at room temperature overnight. Finally, biocomposite films were dried by vacuum oven at 40 °C for 48 h to eliminate the residual solvent. The thickness of biocomposites was around 50 μm , as measured with a digital platen micrometer (Messmer Instruments, UK).

2.5. Characterization

The morphology of the MFLC and Ac-MFLC was observed using scanning electron microscopy (SEM – Zeiss Ultra-55), operated at 1.5 kV acceleration voltage and 5 mm working distance. MFLC in deionized water (0.03 %) and Ac-MFLC in CHCl_3 (0.03 %) were sonicated for 1 min, and a droplet was deposited onto mica disc, and then with thin layer of gold. FTIR spectra of the MFLC and Ac-MFLC were determined by using Thermo Nicolet 5700 spectrometer in ATR mode, equipped with 1.5 mm contact area in diameter. The spectrum was recorded in the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} for 32 scans per sample. X-ray diffraction (XRD) patterns of MFLC and Ac-MFLC were collected by ProtoXRD (USA) diffractometer using $\text{Cu } K\alpha$ (40kV/40mA) radiation ($\lambda=1.54060$) between $2\theta=0^\circ$ and 60° with step size $2\theta=0.02^\circ$.

2.6. The X-ray photoelectron Spectroscopy (XPS)

XPS of the MFLC and Ac-MFLC were conducted using a Kratos Axis Ultra Hybrid. X-ray source run at 15 mA, emission at 225 W. The pass energies of low and high resolution were 80 eV and 20 eV, respectively. The quantification of carbon bonds of MFLC and Ac-MFLC was carried out by fitting the C1s high resolution spectra. The binding energy scale of (C-C) was

shifted to 284.8 eV. The degree of surface substitution (DSS) was calculated from the peak areas using Equation (1): [30]

$$DSS = \frac{C_{acetyl}}{C_{cell}/6} \quad (1)$$

where C_{acetyl} is the atomic concentration of acetyl groups (O-C=O) after acetylation, and C_{cell} is the atomic concentration of (C-O + O-C-O) group in cellulose or lignocellulose for MFC and MFLC, respectively.

Characterization of Biocomposites

The biocomposite films were cut into rectangles (100 mm × 10 mm × 50 μm) and their tensile properties determined using an Instron 5544 Universal Testing Machine equipped with a 100 N load cell; the jaw separation was 50 mm and the rate of displacement was 5 mm s⁻¹. Thermal behaviours of PLA and Ac-MFLC biocomposites were investigated using Differential Scanning Calorimeter (DSC Q100, TA Instruments) in N₂ atmosphere. A heating/cooling/heating cycle was carried out for characterizations. Approximately 3 mg of samples were heated between 0 and 250 °C at 10 °C min⁻¹ heating and cooling rate. The crystallinity of the biocomposites was calculated using Equation (2): [31]

$$X_c = \frac{\Delta H_m}{\Delta H_m^o \omega} \times 100 \quad (2)$$

where X_c is the crystallinity (%), ΔH_m is the melting enthalpy, ΔH_m^o is the melting enthalpy of 100 % crystalline PLA sample (assumed to be 93.7 J g⁻¹) and ω is the weight fraction of PLA in the composite.

3. Results

3.1. Morphology and Dispersibility

The initial diameter of CTMP fibres was 27 μm (Table S2). After fibrillation process, the diameter of isolated individual cellulose microfibrils (MFLC) were measured from image analysis of scanning electron micrographs as being in the range 40 nm to 400 nm, indicating

successful fibrillation of the CTMP fibres during the homogenization process (Fig. 2a). Red arrows numbered 1 and 2 show the MFLC with nanometer and submicron sizes, respectively. In addition to MFLC, globular-shaped particles were observed on microfibrils, which are marked by red arrows numbered 3, which are likely to be lignin particles; similar morphological structures were reported in previous studies [27,32,33]. This fibrillation technique was successfully used for the isolation of MFC with a narrow distribution of diameters from lyocell fibres in the literature [34,35]; we note that these fibres consist of pure reconstituted cellulose. Here, we observed rather broad distribution of microfibril diameters, which can be attributed to our source fibres being natural and to their appreciable hemicellulose and lignin content. Heating the materials above the glass transition temperature of lignin softens the hemicellulose/lignin matrix, facilitating the fibrillation of cellulose microfibrils [36]. However, fibrillation was carried out without any heat or chemical pre-treatment in our study, perhaps favouring the non-uniform morphology and cross-linked MFLC/lignin complex structures observed. The SEM image of Ac-MFLC (Fig. 2b) shows that there was no significant change on the morphology of microfibrils after acetylation. MFLC protected its highly fibrillated structure; however, increasing the hydrophobicity caused the agglomeration of MFLC when it deposited onto the hydrophilic mica disk [37].

The dispersibility of freeze-dried MFLC and Ac-MFLC was observed in water and three different solvents, namely dimethylformamide (DMF), tetrahydrofuran (THF) and chloroform with different polarities and dielectric constants (Fig. 2d). MFLC could be homogeneously dispersed in water; however, it quickly precipitated at the bottom of solution in all organic solvents. After introducing the acetyl groups, and decreasing the polarity of microfibrils, Ac-MFLC sedimented in water, whereas good dispersion of Ac-MFLC occurred in all organic solvents without any observable sedimentation. Ac-MFLC formed a clear and transparent suspension in all organic solvents, especially in DMF and chloroform, as the result of acetylated surface of MFLC, which enables the dispersion of microfibrils in organic solvents by preventing the possible hydrogen bonding between adjacent microfibrils [37].

Fig. 2. SEM images of MFLC (a) and Ac-MFLC (b). Scale bar is 1 μ m. FTIR absorbance of MFLC and Ac-MFLC (c), dispersibility of MFLC (upper image) and Ac-MFLC (lower image) (d) in water (1), N,N-dimethyl formamide (2), chloroform (3) and tetrahydrofuran (4).

3.2. Chemical Analysis

The chemical structure of MFLC and Ac-MFLC was investigated by FTIR, XPS and XRD in order to determine the efficiency of the acetylation and the crystalline structure of MFLC. The FTIR spectra of MFLC and Ac-MFLC are shown in Fig. 2c. MFLC exhibited characteristic cellulose-I spectra possessing strong peaks at around 3340 cm⁻¹ and 1035 cm⁻¹, which are attributed to the (–OH) and (C–O) stretching, respectively. However, two additional peaks which are absent in the cellulose-I spectra were observed at 1508 cm⁻¹ and 1592 cm⁻¹ indicating (C=C) and (C–H) skeletal vibrations in phenyl groups of the characteristic aromatic lignin [38,39]. The structural change of MFLC was verified by appearance of three new peaks

referring to attached acetyl group onto cellulose after acetylation. Those three new peaks appeared at 1738 cm^{-1} , 1369 cm^{-1} and 1232 cm^{-1} which are associated with carbonyl esters ($-\text{COO}-$), ($-\text{CH}$) and (C-O) stretching of acetyl group, respectively. The hydroxyl stretching vibration at 3340 cm^{-1} decreased after acetylation confirming the successful esterification of MFLC.

The surface chemical compositions and the quantitative evaluation of DSS of Ac-MFLC were determined using XPS. The survey spectra (Fig. S1) showed only C1 and O1 peaks at 285 eV and 533 eV, respectively. It reveals that no potassium peak observed on the spectra, confirming that the unreacted catalyst was removed completely during the rinsing and washing stages after acetylation. Fig. 3 shows the high resolution C1s spectra giving information about carbon chemistry of microfibrils. MFLC exhibited characteristic carbon peaks at 285, 286.5 and 288 eV, which are attributed to (C-C), (C-O) and (O-C-O) bonds, respectively (Fig. 3a) [40]. Furthermore, it exhibited a small peak at 289 eV associated with the (O-C=O) bond characteristic of the hemicellulose, xylan [41]. The intensity of this peak increased due to the introduction of ester groups after acetylation of MFLC (Fig. 3b) [42]. The relative peak areas of MFLC and Ac-MFLC are listed in Table S3. The peak area of (C-C) increased with the acetylation; however, the peaks area of (C-O) and (O-C-O) decreased due to acetyl substitution of ($-\text{OH}$) groups with (O-C=O) groups. The degree of surface substitution (DSS) was calculated as 1.02 from the XPS peaks area, showing the rapid acetylation mechanism of MFLC.

Fig. 3. XPS analysis of MFLC (a) and Ac-MFLC (b). XRD spectra of MFLC and Ac-MFLC (c).

We carried out the surface acetylation of MFC isolated from bleached softwood pulp also, using the same mechanical treatments as for MFLC. The same acetylation technique was performed to compare the efficiency of the acetylation reaction between acetylated MFC (Ac-MFC) and Ac-MFLC. High-resolution C1s spectra of MFC and Ac-MFC and its relative peaks area are shown in Fig. S2 and Table S3, respectively. The acetylation results showed that MFLC exhibited 27 % higher DSS than MFC. This shows clearly that the high lignin and hemicellulose content of MFLC (Table S1) increased the acetylation efficiency due to the different reactivities of cell wall polymers [43]. Lignin and hemicellulose exhibit higher reactivity than cellulose during the modification with acetic anhydride, since cellulose has fewer accessible hydroxyl groups than lignin and hemicellulose due to its high crystallinity [44,45]. Therefore, MFLC exhibited higher

DSS than MFC as its microfibril surface is covered with more accessible lignin and hemicellulose matrix which could be rapidly modified using AA/DMF/K₂CO₃ system. The effect of acetylation on the crystalline structure of MFLC was evaluated using X-ray diffraction (XRD) analysis. Fig. 3c shows the diffraction pattern of MFLC and Ac-MFLC. MFLC exhibited characteristic cellulose diffraction peaks 2 θ angles at 16.6°, 22.7° and 34.8° indicating 101, 002 and 004 lattice planes, respectively [46]. The diffraction pattern of Ac-MFLC did not change considerably after acetylation compared to that of un-modified MFLC. The intensity of peaks was maintained after acetylation, indicating that crystalline structure was preserved during the modification. However, Ac-MFLC exhibited slightly broader peaks than MFLC at 16.6° and 22.7°, which is consistent with the increased interlayer distance of individual crystalline cellulose resulting in acetylation of the cellulose chain [47]. The preserved cellulose crystalline structure showed that the inner crystal layers of cellulose were unmodified during acetylation. This is due to the surface modification of MFLC, especially the hemicellulose/lignin complex structure surrounding the cellulose microfibrils. Furthermore, K₂CO₃ catalyzed esterification [29,48,49] offers a more moderate condition for the modification of nanocellulose compared to pyridine [50], citric acid [51] and sulfuric acid [15] catalyzed esterifications, disrupting the crystalline interlayer of cellulose during the reaction by excessive acetylation resulted in increased accessible hydroxyl groups [52]. Taken together, the FTIR, XPS and XRD results showed that the surface of MFLC was successfully acetylated without decrystallization of cellulose microfibrils as the result of modification of more reactive hemicelluloses/lignin complex on the surface of MFLC.

3.3. Properties of Biocomposites

The reinforcing capacity of Ac-MFLC was determined by measuring the mechanical performance of biocomposites in which Ac-MFLC content was adjusted between 0.5 % and 5 %. The mechanical properties of biocomposites are shown in Fig. 4a. The error bars present 95 % confidence intervals on the data, and the maximum coefficients of variation of tensile

strength and Young's modulus across the samples were 6 % and 9 %, respectively. The addition of Ac-MFLC clearly increased the tensile strength and Young's modulus of PLA, which shows the reinforcing ability of Ac-MFLC. Low Ac-MFLC content (0.5 % and 1 %) significantly improved both tensile strength and Young's modulus, which can be attributed to good stress-transfer at the interface with Ac-MFLC, and uniform dispersion of Ac-MFLC in PLA [47]. As the hydrophobicity of MFLC improved after acetylation, its dispersion in PLA and the dissolving medium chloroform increased. The addition of 1 % Ac-MFLC increased the tensile strength and Young's modulus of PLA by 37 % and 28 %, respectively. At the higher levels of addition, both tensile strength and Young's modulus reached a plateau; the data suggest a small decrease in tensile strength with the addition of 5 % Ac-MFLC, which may be attributed to increased fibre-fibre interactions resulting in insufficient wetting and a decrease of stress-transfer efficiency between Ac-MFLC and PLA [47].

Fig. 4. The mechanical performance of biocomposites with different Ac-MFLC content (a). SEM images of the fracture surface of neat PLA (b) and 1 % Ac-MFLC reinforced biocomposite with different magnification (c-d). FTIR spectra of neat PLA and biocomposites (e). The interaction mechanism between Ac-MFLC and PLA in biocomposites (f).

The fracture surface morphologies of the PLA and biocomposites are shown in Fig. 4b-d. Neat PLA showed a smooth surface indicating the brittle fracture (Fig. 4b). Arrow number 1 shows

the white spot which could be the result of the initiation of fibril formation. However, fibrils could not propagate due to the brittleness of the PLA. Small voids were also observed (arrows numbered 2) on both neat PLA and biocomposite. After adding Ac-MFLC, the fracture surface of PLA exhibited a rough and coarse structure, suggesting a ductile fracture (Fig. 4c) [53]. Furthermore, bridging fibrils (arrow 1) were observed as the result of craze formation of PLA, due to plastic deformation prior to final fracture. High magnification SEM images (Fig. 4d) of the biocomposite show submicron sized fibrils (arrow 2) broken during the fracture without pulling out, indicates a good interfacial bonding between PLA and Ac-MFLC.

FTIR analysis of PLA and Ac-MFLC biocomposites was used to determine the interactions between PLA and Ac-MFLC (Fig. 4e). Biocomposites exhibited similar FTIR spectra to neat PLA. However, the intensities of the peaks slightly increased at 1076, 1747, 2942 and 2994 cm^{-1} , associated with (C-O), (C=O), symmetric and asymmetric (-CH) bending, respectively [54,55]. The increased intensity of these peaks could be due to the presence of (C-O), (C=O) and (-CH) groups in the chemical structure of Ac-MFLC [56]. Similar increase in the intensity of these peaks was reported in previous studies in which PLA biocomposites reinforced with acetylated nanocellulose [50,57,58]. The interactions between cellulosic fibres and PLA matrix influence the carbonyl (C=O) bending of which peak broadening and/or location shifting indicate the interactions between carbonyl oxygen of PLA and hydroxyl hydrogen of cellulose [59,60]. No carbonyl peak shifting at 1747 cm^{-1} and unbound hydroxyl stretching at 3300 cm^{-1} were observed in the FTIR spectra of biocomposites (Fig. 4e), since the hydroxyl groups on the surface of MFLC were substituted with acetyl groups. However, a new peak was observed at 920 cm^{-1} ascribed to the out of plane aromatic (C-H) bending (Fig. 4e inner image) [61]. This could be due to the hydrogen bond between the aromatic hydrogen of lignin and the carboxyl oxygen of PLA; the mechanism is shown in Fig. 4f. This confirms the strong interactions between Ac-MFLC and PLA. As the surface of MFLC is covered with hemicellulose/lignin complex structure connected to cellulose microfibrils via hydrogen bonds, the aromatic lignin

acted as a bridge between microfibrils and PLA matrix. However, the biocomposite with 5 % Ac-MFLC content exhibited weak peak intensity at 920 cm^{-1} compared to other biocomposites. It might be due to the fibre-fibre interactions decreasing the fibre-matrix interface, and leading to the low mechanical performance.

Fig. 5. (a) DSC thermogram of PLA and biocomposites (b). Photograph of solvent-cast biocomposite films showing transparency at different addition levels of Ac-MFLC, as indicated below.

Thermal behaviour of PLA and biocomposites was investigated using DSC analysis (Fig. 5). The characteristic DSC data such as glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m), melting enthalpy (ΔH_m) and degree of crystallization, which were calculated from DSC thermogram, are reported in Table S4. The T_g of neat PLA was $55.6\text{ }^{\circ}\text{C}$, and the introduction of Ac-MFLC slightly increased the T_g by around 1 to $2\text{ }^{\circ}\text{C}$ depending on the Ac-MFLC content in the biocomposites. This is due to the restricted amorphous chain mobility, causing high energy requirement for the transformation of the biocomposites [50]. Furthermore, the T_c , T_m and X_c of PLA increased significantly with the addition of Ac-MFLC due to the nucleating effect of microfibrils. However, the 5 % Ac-MFLC added biocomposites exhibited lower X_c than other biocomposites, which might be result of microfibril aggregation resulting in decrease the number of nucleating sites [62]. Overall, the

improved Ac-MFLC dispersibility and its strong interactions with PLA increased the thermal properties of the biocomposites. [This result can be supported by the appearance of biocomposites, exhibiting high transparency with the benefit of the improved dispersion of Ac-MFLC in PLA matrix \(Fig. 5b\).](#)

Conclusions

In this study, we isolated high lignin containing MFLC, and modified its surface using acetylation. The chemical analysis of acetylated MFLC demonstrated that MFLC was successfully acetylated without damaging the crystalline structure. MFLC exhibited higher DSS compared to lignin-free MFC after acetylation. This indicates that the high lignin and hemicellulose content of MFLC promoted the acetylation reaction performed with acetic anhydride. The generated Ac-MFLC was used as a reinforcing agent in a PLA matrix to make biocomposite films using a solvent casting method. The reduced polarity of MFLC improved its dispersibility and the quality of the interface with PLA matrix. The addition of low weight percentage of Ac-MFLC improved both the mechanical performance and thermal properties of neat PLA. Moreover, Ac-MFLC significantly increased the crystallinity of PLA, which we attribute to the Ac-MFLC promoting nucleation.

[We suggest that Ac-MFLC could be used as a promising reinforcing agent in other types of polyester with the benefit of its decreased polarity which might lead to improvement of its dispersibility and interfacial bonding with polyesters.](#)

Acknowledgements

We acknowledge the valuable support of Enrique Lallana-Ozores for freeze-drying, Ben Spencer for XPS analysis, and John Warren for XRD analysis of microfibrils. We also acknowledge the scholarship provided by the Republic of Turkey - Ministry of National Education, and Turkish Forestry Service.

Appendix A. Supplementary data

The following are the supplementary are provided:

Chemical composition of CTMP, fibre dimensions of CTMP, XPS survey spectra of MFLC and Ac-MFLC, XPS relative peaks area of all microfibrils, XPS analysis of MFC and Ac-MFC, DSC data of neat PLA and biocomposites.

Notes

The authors declare no competing financial interest.

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